UNIVERSIDAD POLITÉCNICA DE MADRID

**ESCUELA TÉCNICA SUPERIOR DE INGENIEROS DE
CAMINOS, CANALES Y PUERTOS**

**Development of multifunctional flexible and
structural supercapacitors based on
carbon nanotube fibers**

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"Distinguishing the signal from the noise requires both scientific knowledge and self-knowledge: the serenity to accept the things we cannot predict, the courage to predict the things we can, and the wisdom to know the difference."

Nathaniel Read Silver

Dedicated to my family

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Resumen

Hay un gran interés en el estudio de nuevos materiales funcionales que puedan almacenar energía y posean aumentadas propiedades mecánicas simultáneamente. Entre estos se incluyen los electrodos para supercondensadores flexibles y estructurales de alta potencia, los cuales tienen aplicación en diversos campos como el aeroespacial, vehículos eléctricos/híbridos y electrónica portátil. La fibra macroscópica de nanotubos de carbono es considerada como un potencial candidato multifuncional para el desarrollo de electrodos flexible y con una alta tenacidad para supercondensadores.

En esta tesis se investigan en detalle varias características de las fibras de nanotubos de carbono (CNTs), incluyendo su estructura, textura y sus propiedades mecánicas y electroquímicas. El estudio revela que la compleja estructura jerárquica de las fibras se caracteriza por una red de CNT altamente porosa con un área superficial de $256 \text{ m}^2 \text{ g}^{-1}$ y una amplia distribución del tamaño de poro desde meso- a macro-escala. Esto da lugar a una combinación única de propiedades mecánicas, con una tenacidad de hasta 61 J g^{-1} , y de propiedades electroquímicas. Además, la baja dimensionalidad de las fibras de CNT hace que se observe el fenómeno de capacitancia cuántica cuando se determinan sus propiedades electroquímicas en semicelda. Conviene mencionar que la capacitancia cuántica intrínseca de las fibras se refleja en el comportamiento electroquímico de los dispositivos completos. Además, las propiedades del material se pueden ajustar de manera controlada por medio de un proceso de funcionalización con ozono en fase gaseosa, el cual modifica las propiedades electroquímicas de las fibras mediante cambios en el carácter hidrofílico, la estructura electrónica y la pseudocapacitancia asociada a los grupos funcionales redox activos que se originan en la superficie de los CNTs.

Además de las propiedades fisicoquímicas y electroquímicas de las fibras de CNTs, esta tesis también describe el desarrollo de supercondensadores multifuncionales de doble capa (EDLCs) usando electrodos basados en fibras de CNTs y electrolitos poliméricos. Para este propósito se prepararon membranas de electrolito polimérico compuestas de un líquido iónico 1-butil-1-metilpirrolidinium bis(trifluorometanosulfonil)imida ($\text{Pyr}_{14}\text{TFSI}$) y un termoplástico, el poli(vinilideno fluoruro-co-hexafluoropropileno) (PVDF-co-HFP). Estos electrolitos poliméricos fueron caracterizados en base a su conductividad iónica y sus propiedades mecánicas y térmicas. El proceso de ensamblaje de los supercondensadores flexibles se basa en el uso de una membrana polimérica prefabricada que se intercala entre dos electrodos de fibra de CNT. Las fibras actúan como colector de corriente y material activo, y la membrana como separador y electrolito. Mediante este método de fabricación se ensamblaron dispositivos de hasta 100 cm^2 con una buena reproducibilidad. Estos dispositivos muestran una capacitancia específica, densidad energética y

densidad de potencia de 28 F g^{-1} , 11.4 Wh kg^{-1} y 46 kW kg^{-1} respectivamente. Además, presentan una alta estabilidad bajo deformaciones por flexión. Finalmente, se fabricó un prototipo de supercondensador compuesto por 4 celdas conectadas en serie que se ajustaba a las especificaciones requeridas por la empresa que financió parte de esta tesis doctoral. Adicionalmente, mediante la fabricación de electrodos de fibras de CNT de un solo filamento se exploró otro aspecto de la multifuncionalidad como es la transparencia.. El mismo método de fabricación de los dispositivos se utilizó para producir supercondensadores transparentes totalmente sólidos con elevada transmisión óptica del 74% y excelentes propiedades electroquímicas (densidad de potencia de 1370 kW kg^{-1}).

Finalmente, los supercondensadores flexibles mencionados anteriormente se utilizaron para producir supercondensadores estructurales en forma de laminados. Se demostró un método de fabricación simple que consistía en la inclusión de supercondensadores flexibles entre dos telas de fibra de carbono, seguido de una infusión y el curado de un polímero termoestable tipo resina. El comportamiento electroquímico de los dispositivos se evaluó durante la infusión de la resina epoxi, después del curado, y durante la deformación por flexión del dispositivo. En todos los casos se observó una alta eficiencia coulombica y estabilidad.

La utilización de supercondensadores flexibles perforados permitió mejorar las propiedades interlaminares del material compuesto, sobre todo en ensayos a cizalla. Esta estrategia ofrece una amplia gama de parámetros de diseño sobre los que se puede incidir y con los que se puede obtener el deseado rendimiento estructural del dispositivo. Un análisis preliminar de diferentes configuraciones y arquitecturas de compuestos intercalados ilustra la envolvente de las propiedades mecánicas y de almacenamiento de energía, y el factor clave para aumentar la eficiencia multifuncional y producir un ahorro de peso en relación con los sistemas monofuncionales convencionales.

Abstract

There is a great deal of interest in the study of new functional materials which can simultaneously store energy and possess augmented mechanical properties. These include electrodes for flexible and structural high power supercapacitor devices, which find application in diverse fields such as aerospace, electric/hybrid vehicles and portable electronics. Macroscopic fibers of carbon nanotubes are considered as a potential multifunctional candidate for application as flexible and tough electrodes in supercapacitors.

In this thesis, various features of CNT fibers, including their structure, textural, mechanical and electrochemical properties are investigated in detail. The study particularly reveals that the complex hierarchical structure of the fibers leading to a unique combination of high mechanical properties with toughness up to 61 J g^{-1} , highly porous CNT network with surface area of $256 \text{ m}^2 \text{ g}^{-1}$ and broad pore size distribution from meso to macroscale. Furthermore, the low dimensional nature of CNT fibers makes their quantum capacitance observable when measuring electrochemical properties of CNT fibers in half and full cell. The properties of the material can be further tuned by well-controlled gas phase functionalization, which modify electrochemical properties through changes in wetting, electronic structure and pseudocapacitance of redox active functional groups.

Besides the intrinsic physicochemical and electrochemical properties of CNT fibers, this thesis also describes the development of high-performance multifunctional flexible supercapacitor based on CNT fiber electrodes and polymer electrolytes. For this purpose, all-solid polymer electrolyte membranes based on 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($\text{Pyr}_{14}\text{TFSI}$) ionic liquid and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) thermoplastic were prepared and extensively characterized in terms of their ionic conductivity, mechanical and thermal properties. The assembly process of all-solid supercapacitor device is based on utilization of a pre-cast PE membrane sandwiched between two CNT fiber electrodes, with the CNT fibers acting as current collector and active material and the membrane as separator and electrolyte. The method can be applied to fabricate free-standing devices from 0.785 to 100 cm^2 with good reproducibility. These devices show specific capacitance, energy and power densities of 28 F g^{-1} , 11.4 Wh kg^{-1} and 46 kW kg^{-1} , respectively, and high stability under flexural deformations. Finally, a supercapacitor prototype consisted of 4 stacked cells was manufactured and shown to comply with specifications for the target application of the sponsors of a part of this work. Another aspect of multifunctionality such as transparency was explored by making single-filament CNT fiber electrodes. The same fabrication method of devices was used to produce all-solid transparent supercapacitors with high optical transmission of 74% and outstanding

electrochemical properties (power density of 1370 kW kg^{-1}).

Finally, abovementioned flexible supercapacitor devices were used to produce laminated structural supercapacitor composites. A simple fabrication method was demonstrated through embedding CNT fibers/polymer electrolyte interleaves between carbon fiber fabrics, followed by infusion and curing of a thermosetting polymer. Electrochemical behaviour of the device was evaluated during epoxy infusion, after resin curing and during flexural deformation. A high coulombic efficiency and stability were observed in all cases. Grid-shaped interleaves enable to improve interlaminar properties of the composite and offer a wide range of design parameters to obtain desired composite performance. A preliminary analysis of different configurations and architectures of interleaved composite illustrates the envelope of mechanical and energy storage properties, and the key factor to increase multifunctional efficiency and produce weight savings relative to conventional monofunctional systems.

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CHAPTER 1

Introduction

1.1 Motivation

A supercapacitor (SC), also denoted as ultracapacitor or electrochemical capacitor, is a type of electrochemical energy storage system which combines high power density, high efficiency, moderate energy density and long cycle life. Having these properties, SCs complement other energy storage systems. The Ragone plot in *Figure 1.1* introduces the most common way of comparison of different energy storage devices in terms of their energy and power densities.[1] As illustrated, batteries possess high specific energy, but low power density. They can provide a large amount of energy, but are limited by long charging and discharging times. Conventional capacitors have very high power densities, delivering energy in a short time, but the amount of energy is very low. In the middle of the Ragone plot, supercapacitors combine superior specific energy compared to conventional capacitors, and remarkable specific power, hundreds to thousands of times more than batteries. As such, supercapacitors occupy an important position between conventional capacitors and batteries in terms of energy and power of electrochemical systems.

Most of commercial supercapacitor devices are used in consumer electronics, where they serve both as a power source and energy storage element to power electronic gadgets.[2, 3] Their application has been also extended to military sector, employing supercapacitors as alternative power for electronics in black boxes on helicopters and armed vehicles. Supercapacitors are considered for implementation as a short time energy storage system in hybrid electric vehicles, fuel cell vehicles and industrial

1.1 Motivation

equipment as well as for energy recovery in public transportation.[4] However, despite their broad use supercapacitors still possess limitations mainly associated with fast self-discharge, low specific energy and high cost per watt as compared to batteries. In addition, most of commercial devices have a voltage limited to 2.5–2.7 V. It can be increased through a serial connection of individual cells, but this reduces the total capacitance, increases the internal resistance and requires voltage balancing[5].

Figure 1.1. Ragone plot representing the power and energy densities of SC and other electrochemical systems.

In recent years, there has been an interest in novel electronic devices which are flexible, bendable, stretchable and even structural. This has led to the need of corresponding energy storage systems capable to retain their primary functions but with augmented mechanical properties. The work in this thesis is set in the content of developing and studying new materials and fabrication methods for flexible and structural supercapacitors. By achieving the optimal level between electrochemical and mechanical properties, such systems could deliver high power while acting as a load bearing structural element, potentially offering a weight reduction relative to monofunctional systems used in aerospace, electric/hybrid ground transport, textile and portable electronics.

The main goal of this thesis consists in addressing materials science challenges associated with the development of high-performance multifunctional flexible and structural supercapacitors based on fabrics of carbon nanotubes (CNTs) and polymer electrolyte combining high electrochemical and mechanical properties, stability and high safety. Additionally, part of this work also targets the fabrication of a prototype and demonstration of its operation according to specifications provided by the sponsor of this project.

1.2 Thesis structure

Following a short introduction of the research background in Chapter 1, Chapter 2 reviews the previous studies on the multifunctional electrode materials, all-solid electrolytes and flexible and structural supercapacitors. It presents the current progress in development of multifunctional supercapacitor devices and discloses their working principles, fabrication methods and potential applications. The methods used for synthesis of functional materials and assembling of electrochemical devices are described in Chapter 3, as well as the details of characterization techniques utilized to analyze the properties of produced materials, composites and supercapacitors.

In Chapter 4 the features of macroscopic CNT fibers, including their structure, textural, mechanical and electrochemical properties, are studied in detail. Furthermore, gas phase functionalization as a tool to tailor the properties of CNT fibers and its impact on the structure and specific characteristics of the carbon material are introduced.

Chapter 5 presents the development of all-solid flexible supercapacitor based on CNT fiber electrodes. It explores the preparation and characterization of polymer electrolytes (PEs) with optimum combination of mechanical properties and ionic conductivity, using an ionic liquid and several polymer matrices. Different approaches for assembling of all-solid flexible supercapacitor and development of an effective method for fabrication of free-standing devices are addressed. Mechanical properties of the CNT fiber/PE membrane/CNT fiber composite and its electrochemical behaviour in the standard cell and self-standing state are evaluated. The large-area all-solid and highly-flexible supercapacitor device was produced and optimized for a specific target application in the aircraft interior. Additionally, all-solid transparent supercapacitors based on single CNT fiber sheets were produced and their electrochemical and optical properties were examined.

Chapter 6 introduces fabrication and characterization of structural supercapacitor based on all-solid thin sandwich structures of CNT fiber veils and PE embedded between carbon fiber (CF) plies and followed by infusion and curing of epoxy resin. The employment of semi structural CNT fiber/PE membrane composite as energy storage system and fiber reinforced polymer as structural composite enables creating a structural supercapacitor capable to withstand high mechanical stresses. The effect of different configurations and architectures of structural composites on their electrochemical and mechanical properties are studied. Multifunctional efficiency as a measure of potential weight reduction is analyzed for fabricated composites and expected optimized structures.

Finally, the main conclusions of the work are summarized in Chapter 7. The future prospects in the development of multifunctional materials and energy storage devices are also outlined.

CHAPTER 2

Literature review

2.1 Introduction to supercapacitors

2.1.1 Mechanism of energy storage

Supercapacitors operate by similar principles as conventional capacitors, relying on interfacial charge organization through electrostatic forces (*Figure 2.1*). However, unlike conventional capacitors, which store energy electrostatically through dielectric polarization causing charge accumulation on opposite electrode plates, as shown schematically in *Figure 2.1a*, in supercapacitors charge is stored in a thin electric double-layer (EDL) at the interface between the electrode and an electrolyte. An EDL can be defined as a structure of a charge accumulation occurring at the boundary of two phases represented as two equal but oppositely charged space charge layers. The positive and negative charges accumulated in electrodes under a voltage are compensated by anions and cations of the electrolyte, respectively (*Figure 2.1b*). In such a configuration each electrode-electrolyte interface represents a capacitor so that the complete cell can be considered as two capacitors in series. Consequently, the cell capacitance for SC can be calculated as:

$$\frac{1}{C_{cell}} = \frac{1}{C_1} + \frac{1}{C_2}, \quad (2.1)$$

where C_{cell} is the total capacitance of the full cell, and C_1 and C_2 represent the capacitances of the two electrodes, respectively.

2.1 Introduction to supercapacitors

For a conventional capacitor capacitance (C) can be represented as:

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}, \quad (2.2)$$

where ε_0 is the dielectric constant of free space and ε_r is relative permittivity of the insulating material. The equation particularly emphasizes the importance of the surface area of the electrodes (A) and the distance between them (d), directly related to electrode material and the devices construction, respectively.

The basic structure of a supercapacitor consists of porous electrodes, providing large surface for ion adsorption, an electrolyte, acting as a source of ions, and separator, allowing the transfer of ions, while preventing a direct contact between the electrodes. The spread of adsorbed ions over a wide surface of EDLC's electrodes results in a larger charge stored under a voltage supply compared to electrostatic capacitors. In EDLC d corresponds to the thickness of the double layer, which is determined by both the size and solvation of the ions in an electrolyte. It is close to atomic dimensions (<1 nm), several orders of magnitude lower than in electrostatic capacitors. Along with large surface area this gives rise to substantially higher capacitance of SCs relative to conventional capacitors.

Figure 2.1. Schematic comparison of energy storage mechanisms for a) conventional capacitors and b) electric double-layer capacitors.

Unlike electrochemical capacitors that usually show no major changes in properties of electrode materials during operation, batteries store energy through electrochemical reaction which involves the transfer of charge across the interface between the electrodes and electrolyte causing compositional and structural changes in the electrode materials. The electrostatic capacitive mechanism involved in charge-storing processes in SCs is much faster than the faradaic reactions, so although SCs have significantly lower energy density than batteries, they possess several orders of magnitude higher

2.1 Introduction to supercapacitors

power density. Moreover, chemical reactions imply changes in the molecular or crystalline structure of the electrode material, which often affects stability of batteries limited by few thousands of charge-discharge (CD) cycles. As a result, supercapacitors have longer life expectancies (millions of CD cycles) and can be charged and discharged in much shorter times (seconds).

2.1.2 Key electrochemical characteristics

As was mentioned above, the primary characteristics determining the performance of an energy storage device are energy and power densities. The maximum energy that can be stored in a SC without ionic resistance from the electrolyte is directly calculated as follows:

$$E_{max} = \frac{CV^2}{2}, \quad (2.3)$$

where V is the maximum voltage and C is the specific capacitance. Capacitance is usually determined by the following equation:

$$C = \frac{Q}{V} = \frac{It}{V}, \quad (2.4)$$

where Q , I and t correspond to the stored charge, discharge current and discharge time, respectively.

The maximum power, described as the energy expended per unit time, can be calculated by:

$$P_{max} = \frac{V^2}{4R_s}. \quad (2.5)$$

Here, R_s corresponds to the equivalent series resistance (ESR) comprising the resistance contribution of SC components, such as electrode, current collector, electrolyte and separator.. These simple equations highlight the interest in using materials with high specific capacitance and high electrical conductivity as electrodes, and with wide electrochemical stability and high ionic conductivity as electrolytes. It is important to mention here that the maximum operating voltage in a SC is limited by the electrochemical stability window of the electrolyte whereas its ionic conductivity affects the ESR.

Moreover, in order to achieve high level of multifunctionality such as in flexible and structural devices, these characteristics should be compatible with augmented mechanical properties both in electrodes and electrolyte.

2.1.3 Types of supercapacitors and associated materials

Depending on the means by which charge is stored the three main classes of supercapacitors can be distinguished: electric double-layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors. An EDLC stores energy in the double-layer by charging electrochemically inactive electrodes at the electrode/electrolyte interface as explained above.

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Carbon-based materials possess very high specific surface area (SSA), good electrical conductivity and low cost. Thus, they are of special interest for EDLCs, where the amount of charge stored on the electrode/electrolyte interface strongly depends on the effective surface area and pores availability to the electrolyte ions. In this regard, various high surface area carbons, such as activated carbon (AC), carbon aerogel, carbon nanotubes and graphene, have been widely applied as active electrode materials for high-performance EDLCs.

Pseudocapacitor is the second type of SCs which is based on pseudocapacitive processes arising due to fast and reversible surface redox reactions between the electrode and the electrolyte.[6] This leads to substantial growth of specific capacitance and energy density, but comes with the sacrifice of lower power density due to slower faradaic reactions compared to electrostatic processes. Owing to their capability to undergo reversible redox reactions, transition metal-based materials such as various metal oxides,[7] hydroxides,[8] nitrides,[9] carbides,[10] phosphides,[11] selenides,[12] sulfides,[13] and conducting polymers[14, 15] are promising active materials to improve capacitive properties of SC systems. A typical class of pseudocapacitive materials widely studied in the form of nanomaterials is transition metal oxides (e.g. ruthenium oxide (RuO_x), manganese oxide (MnO_x) etc). A growing interest in these materials is related to the ease of large-scale fabrication and the vast energy storage capabilities superior to conventional nanocarbons. Conducting polymers (CPs) (e.g., polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), etc.) are also considered as a promising category of pseudocapacitive active materials. In addition to their good electronic conductivity CPs possess inherent flexible polymeric nature suitable for application in multifunctional SCs.

The third type is hybrid battery-supercapacitors. Such systems consist of a capacitive electrode made of EDLC-like porous carbon material or pseudocapacitive elements, and a battery-type electrode such as intercalation materials or metal oxides (nickel oxide (NiO_x), cobalt oxide (CoO_x) and iron oxide (FeO_x), etc). It can have either an asymmetric configuration using one capacitive electrode against a faradaic electrode, or a composite design where both electrodes contain redox active material integrated into highly porous carbon.

Apart from electrode material, the electrolyte is another important component of SCs closely determining its performance. It is a major factor affecting the operating voltage of the system, and thus defining its maximum energy and power densities directly related to square of the cell voltage. Typically, in conventional supercapacitors electrolytes exist in a liquid state. However, the use of liquids causes a risk of leakage and require proper sealing with strong encapsulation. In this context, utilization of all-solid polymer electrolytes is of choice. They provide higher reliability, flexibility, wider range of operation temperature and usually do not need sealing. On the other, hand they suffer from reduced ionic conductivity critical for practical application in SCs.

2.1.4 Augmented mechanical properties of multifunctional SCs

Multifunctional flexible or structural SCs should be able to bear high strain (or stress) induced by external mechanical deformations, such as bending, compressing, folding, twisting or stretching, while preserving their electrochemical performance and structural integrity. Among the large number of reported supercapacitors with augmented mechanical properties, the most common type has high flexibility in bending. The flexibility of a device can be achieved by a suitable structural design or using intrinsically deformable materials. For instance, to diminish the impact of flexural stress on the brittle components of a SC in a multilayer-structured bendable device, they can be placed near the neutral plane of the multilayer, where bending strain vanishes.[16, 17] Destruction resulting from bending force can be also minimized by splitting a mechanical neutral plane[18–20] that allows avoiding a large modulus mismatch and premature failure in multilayer structures. Additionally, novel complex architectural designs, such as wire/cable patterns,[21] origami design,[22, 23] and bridge island design,[24, 25] are also considered as a promising tool for achieving high stability under extreme mechanical deformations.

For a rectangular beam with E Young's modulus, b width and h thickness, flexibility, reciprocal of the flexural rigidity, is given by[26]:

$$F \sim \frac{12}{Ebh^3}, \quad (2.6)$$

Thereby, it turns out that flexibility is inversely proportional to the thickness of the sample cubed, and thus can be enhanced simply by minimizing the thickness of the devices. However, in terms of energy storage capabilities, thin electrodes offer limited energy and power and influences the overall performance of flexible devices because of the quantity reduction of active materials.[27] Therefore, research on flexible electrochemical systems should not be blindly centered on ultrathin power source devices, while disregarding their application requirements.

Alternatively, high flexibility of electrochemical devices can be reached by selecting materials with intrinsically good flexural behaviour directly related to the properties of their building blocks. The reciprocal relationship between flexibility and dimensions of the material can be as well applied at nanoscale level, and the electrodes consisted of a network of crystalline domains with better flexural properties will result in higher flexibility of the system. For instance, the structure of a nanocarbon network (e.g. CNT or graphene) can undergo substantial rearrangement and bending of the molecules, which because of their small diameter (~ 10 nm) (*Figure 2.2a*) produce very small bulk stresses. In comparison, a powder activated carbon (AC) with covalently bonded domains cannot accommodate large deformations under bending and behaves similar to a ceramic, with the relevant thickness close to the bulk electrode thickness (~ 10 μ m) (*Figure 2.2b*).

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Figure 2.2. SEM images comparing the structures of a) a network of CNTs[28] and b) activated carbon[29].

Besides flexibility in bending, the device can be intended to operate at large strains (stretchable) or have a high tensile strength. For this purpose, various fiber-shaped devices assembled by twisting together two yarn electrodes coated with a layer of gel polymer electrolyte have been reported.[30, 31] Such structures have demonstrated great potential as flexible SCs that can be woven into various electronic textiles.

The precise mechanical requirements on supercapacitor materials are dictated by the target application and its associated mechanical deformations. But simplifying, a useful characteristic that represents an overall figure of merit for materials mechanical properties is its fracture energy (i.e. toughness). It contains indirectly a measure of both strength and strain-to-fracture and can be studied for a wide range of materials. The tensile properties of a SC sandwich structure, typically composed of two electrodes and polymer electrolyte (PE) matrix (*Figure 2.3*), can be roughly predicted using what a rule of mixture[32]:

$$\sigma_{SC} = \sigma_{el}V_{el} + \sigma_{PE}V_{PE} , \quad (2.7)$$

$$E_{SC} = E_{el}V_{el} + E_{PE}V_{PE} , \quad (2.8)$$

where σ_{SC} , σ_{el} , and σ_{PE} , and E_{SC} , E_{el} , and E_{PE} indicate the tensile strength and the elastic modulus of SC composite, electrodes and polymer electrolyte, respectively, and V_{el} and V_{PE} are the volume fractions of the electrode material and PE matrix, respectively. These expressions assume that electrodes and PE are homogeneous, stress is uniformly distributed, there are no voids, and the electrodes and the PE are completely coupled. It highlights an important feature of laminated supercapacitor: although the tensile mechanical properties (σ_{el} and E_{el}) of the electrodes normally dominate, the contribution of PE cannot be ignored, when it represents a considerable volume fraction.

Figure 2.3. Schematic representation of SC sandwich structure.

Aside from mechanical requirements in tension some electrochemical systems also target to be exposed to loading cases like compression, torsion and impact etc. In typical solid and flexible SCs, the composite comprises a soft polymer matrix with poor shear properties. This can cause delamination of the structure and, as a result, electrochemical and mechanical failure of the device. In fact, shear properties of the composites are usually dominated by polymer matrix. Consequently, high shear modulus (G_{12}) and interlaminar shear strength (ILSS), determining the ability of composite in resisting the delamination failure, are of interest in structural supercapacitors. It can be achieved by using solid polymer electrolytes exhibiting higher stiffness. However, the challenging aspect is in a strong conflict of the mechanical and electrical demands: a modification of the PE to increase mechanical behaviour leads to a significant reduction in its ionic conductivity and *vice versa* (see below in *Section 2.5*)[33]. Thus, the optimum balance between two functions should be determined depending on the final requirements of the target application.

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Broad use of carbon materials in multifunctional supercapacitors is caused by the attractive combination of their intrinsic properties, including high electrical conductivity, SSA and mechanical performance. *Table 2.1* introduces comparative properties of the most common carbon electrode materials (AC, graphene and CNT) and a typical redox active metal oxide (MnO_2). As it is seen, despite high specific capacitance MnO_2 exhibits poor conductive and mechanical behaviour, which does not allow to realize its electrochemical capabilities in self-standing shape by itself. In contrast,

carbon materials provide the optimum multifunctionality, exhibiting a good balance between the main electrode characteristics. AC with SSA of $800\text{--}3200 \text{ m}^2 \text{ g}^{-1}$ is a preferred electrode materials in commercial supercapacitors due to the high values of specific capacitance ranging from 50 to 350 F g^{-1} . [34] However, the structure of powdered AC considerably complicates the formation of free-standing electrodes that can withstand reasonable flexural deformation. On the other hand, graphitic

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nanocarbon materials, such as graphene and CNTs, demonstrate superior electrical conductivity and substantially higher fracture energy, although with lower SSA and capacitance than AC. This makes feasible assembly of nanocarbons into free-standing, highly porous and conductive electrodes, desired for flexible electrochemical energy storage systems.

With such a set of properties graphene and CNTs can play simultaneously various roles: as active material, conductive additive, current collector and optionally as a multifunctional scaffold for pseudocapacitive or battery-type materials. In particular, the use of free-standing electrodes of nanocarbon assemblies as a host for high-capacitance components, such as metal oxides or CPs, enables to enhance electrical conductivity, cyclic stability due to efficient electron transfer, improve gravimetric electrochemical properties due to better packing of the materials, and achieve good structural integrity and excellent mechanical durability.

Table 2.1. Comparison of various properties for different carbon materials and metal oxide (properties of individual building blocks in brackets).

Electrode material	Conductivity, S m ⁻¹	SSA, m ² g ⁻¹	Capacitance, F g ⁻¹	Fracture energy, J/g
AC	0.01-30[35, 36]	800-3200[37]	50-350[38, 39]	0.2[36] (1.6*10 ⁴) ^a [40]
Graphene	10-35000[41–43]	100-1500[44, 45]	20-300[46]	120[42] (3.6*10 ³) ^b
CNT	50-35000[47, 48]	100-1300[49, 50]	10-200[51]	92[52, 53] (6.56*10 ³) ^c [54]
MnO ₂	10 ⁻⁵ – 10 ⁻⁷	20-320[55–57]	60-1380[57, 58]	0.43 ^d [59]

a) Theoretical prediction of simulated molecular structure of AC, b) calculation for individual graphitic building block, c) direct measurement of the tensile properties of individual millimeter-long MWCNT, d) estimated assuming 1% of strain normal for ceramic materials.

The main challenge of materials science consists in synthesizing and assembling carbon electrodes in such a way that multiple properties of the materials are maximized. Furthermore, the method employed is also often selected considering the subsequent assembly of a full supercapacitor device.

Representative examples of different materials and architectures selected to highlight the benefits and drawbacks of each are discussed below. An important distinction is the fabrication method, amongst solvent-based (filtration, casting) and using pre-formed arrays, typically as macroscopic fibers. The fabrication route has a direct impact on the resulting properties, particularly on the balance between energy/power density and mechanical properties.

2.2.1 Carbon-based electrodes produced from dispersions

Due to their excellent mechanical properties and general multifunctionality CNTs and graphene have been widely employed in flexible SCs. The most commonly used methods to produce flexible carbon electrodes consist in deposition of a carbon dispersion onto various flexible substrates, such as

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cellulose paper,[60]–[62] plastic,[63, 64] metallic current collector[65] or carbon cloth (CC)[66, 67].

For example, flexible electrodes based on CNTs have been produced by dip-coating of a cotton sheet in CNT dispersion (*Figure 2.4a*)[61], filtration of CNT ink on a regular office paper (*Figure 2.4b*)[60] and by spray-coating of CNTs on a polyethylene-terephthalate (PET) films (*Figure 2.4c*)[63]. The resultant free-standing electrodes showed high flexibility and large SSA. All-solid SC devices fabricated by using different gel electrolytes demonstrated promising electrochemical properties, with capacitance values in the range 80-135 F g⁻¹. Recently, an alternative method based on direct ink writing has been employed for the printing of both CNT electrodes and all fully-packaged flexible supercapacitors (*Figure 2.4d*).[68] This approach enables to control spatial distribution of printed material with high accuracy and reproducibility, demonstrated by producing high-performance all-solid SC device with excellent retention of electrochemical properties under bending.

Figure 2.4. Examples of common approaches to fabricate flexible carbon-based electrodes from dispersions, including a) dip-coating,[61] b) filtration of a dispersion of nanocarbons,[62] c) spray coating[69] and d) direct ink writing[68].

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Similarly, different flexible electrodes based on graphene were developed. A simple filtering a suspension through a sheet of filter paper[62], infiltrating aerogels inside the N-doping cotton-derived carbon frameworks[70] and an electrophoretic deposition on a CC[67] were demonstrated toward fabrication of free-standing highly porous graphene-based electrodes. Corresponding all-solid flexible SCs assembled by using common poly(vinyl alcohol) (PVA)-based gel electrolytes offered good flexible and electrochemical properties comparable to CNT-based materials, with specific capacitance in the range 80-200 F g⁻¹.

Alternatively, a direct laser reduction of graphene oxide (GO) films drop-cast onto a flexible substrate from a dispersion using a standard LightScribe DVD optical drive has been applied as a strategy to produce mechanically robust carbon electrodes (*Figure 2.5*).[71] Such flexible SCs do not require any binder or current collector and achieve remarkable energy density 20 times higher than that of similar AC electrodes. Excellent stability >95% of the initial capacitance was maintained at different bending angles from 0 to 180 °C and after 10,000 cycles.

Figure 2.5. Schematic illustration of the fabrication of laser-scribed graphene-based electrodes for employment in flexible supercapacitors.[71]

Large-area hierarchical porous graphene films produced through postreduction of a blade-cast GO hydrogel, obtained from the dispersion of GO nanosheets, have been demonstrated as promising electrode materials for flexible energy storage devices.[72] High SSA of 1316 m² g⁻¹ attributed to a good exfoliation of the graphene nanosheets in the porous film and modest electrical conductivity of 112 S m⁻¹ were accompanied by moderate mechanical properties with measured strength of 2 MPa (toughness ~ 3.9 J g⁻¹). Assembled into a flexible SC reduced graphene oxide (rGO) films exhibit high areal specific capacitance (71.0 mF cm⁻² at 1 mA cm⁻²) with nearly negligible capacity losses in a highly bent state and long-term cycling stability both in initial state and under bending (>96% capacitance retention after 5000 charge/discharge cycles at 10 mA cm⁻²).

A number of studies have been devoted to development of structures combining different carbon

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materials for carbon-based flexible electrodes.[73–76] Many approaches have been attempted to prepare high quality graphene/CNT electrodes for fabrication of flexible SCs.[74, 75, 77, 78] Such architectures enable preserving high surface area of the nanocarbons by physical separation of 2D graphene sheets, while providing high electrical conductivity of CNTs networks for effective charge transport. On account of good dispersive properties of GO a popular method to fabricate hybrid graphene/CNT-based electrodes is *via* a simple liquid phase mechanical mixing of GO and CNTs with further infiltrating of flexible substrates.[74] These materials show enhanced electrochemical performance ($\sim 265 \text{ F g}^{-1}$) relative to individual electrode components but still suffer a relatively poor interconnection between graphene and CNTs.

A more complex architecture of the carbon material consisting of AC, rGO and CNTs has been recently reported.[73] An AC/CNT/rGO film was fabricated by a facile vacuum filtration on a plastic membrane from the suspension solution of all three components. Self-supporting carbon electrodes peeled from the substrate showed better capacitive behaviour than the AC, pure CNT film or rGO with specific capacitance of 101 F g^{-1} owing to synergetic effect of the components. In this structure CNTs contribute to enhanced electronic conductivity, while AC particles prevent restacking of rGO sheets and aggregation of CNTs, providing high SSA for large EDL capacitance.

These results demonstrate that it is relatively easy to produce SC device with high flexibility and stable electrochemical properties based on nanocarbon dispersions. But as a consequence of their random distribution and orientation, normally short length of their building blocks and not controlled assembly into macroscopic structure, their ability to withstand substantial deformation or stress is low. As an example, a free-standing CNT film produced by vacuum filtration, also known as buckypaper, presents a Young's modulus of 15 GPa and tensile strength of 80 MPa which leads to a specific toughness lower than 0.5 J g^{-1} . [79] Therefore, to extend mechanical stability of the electrodes, other forms of nanocarbon assemblies should be considered.

2.2.2 Carbon-based electrodes produced from pre-formed macroscopic arrays

2.2.2.1 *Electrodes based on macroscopic fibers of nanocarbons*

Supercapacitors based on graphitic fibers offer an attractive format for wearable and fiber-reinforced composites. But more importantly, the fiber architecture enables alignment and better packing of graphitic layers, leading to superior mechanical and electrical properties compared with those of films of randomly-oriented small building blocks.

Among various approaches to produce graphene-based fibers (GBFs), e.g. wet spinning, electrophoretic method and film conversion, solution spinning has become the most popular method.

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It is based on injection of GO, dispersed in various organic and aqueous media, into a coagulation bath to form a gel-state fiber, which can be further extracted and dried (and reduced if needed) (*Figure 2.6a,b*).[80] Typically, this material shows high electrical conductivity ($20\text{--}400\text{ S cm}^{-1}$) and large SSA (up to $2605\text{ m}^2\text{ g}^{-1}$) resulting in specific capacitance of $99\text{--}409\text{ F g}^{-1}$ obtained in different aqueous and organic electrolytes (*Figure 2.6c*).[80, 81] Their tensile strength is $10\text{--}502\text{ MPa}$ (*Figure 2.6d*) and toughness is around $2\text{--}20\text{ J g}^{-1}$, inferior to those of CFs, but superior than those of graphene-based membranes and aerogels.[82, 83] This combination of electrochemical and mechanical properties makes them very attractive material for flexible SC devices.[77, 84]

Figure 2.6. a) Schematic illustration of wet-spinning process of graphene fibers,[83] b) representative SEM micrograph of wet-spun rGO fiber,[85] c) CV curves obtained for heat-treated graphene fibers in 1M H₂SO₄ at 10 mV s^{-1} [85] and d) stress-strain curves of GO and rGO fibers[83].

Several attempts have been made to produce flexible AC electrodes assembled into a fiber.[86, 87] AC powders combined with GO can be processed into fiber through the wet-spinning technique, similar to the procedure for GBFs.[86] By employing GO as both dispersant and binder providing mechanical support with its further reduction, AC fibers exhibit high surface area of $1476.5\text{ m}^2\text{ g}^{-1}$, but still have modest mechanical flexibility and electrical conductivity (185 S m^{-1}). The produced fiber showed enhancement in electrochemical properties compared to AC powder (180.1 F g^{-1} at 0.4 A g^{-1}) related to presence of rGO, which increases the electrical conductivity of the material and contributes

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to formation of mesopores and macropores. The AC/rGO fibers were finally employed as free-standing electrode for all-solid flexible SCs without need of a polymer binder, conducting additive or additional current collector. However, resulting from low mechanical stability of raw powder material, AC/rGO fibers do not possess required mechanical properties for application as tough electrodes (tensile strength of 22.7 MPa and toughness $\sim 0.8 \text{ J g}^{-1}$).

CNT fibers can be produced by dry spinning from a nanotube forest (*Figure 2.7a*)[88] or a floating CVD reaction zone (*Figure 2.7b*)[89] and wet spinning from a CNT dispersion (*Figure 2.7c*)[90], as described for GBF. CNT fibers poses continuous macroscopic filaments of CNTs preferentially aligned parallel to the fiber axis (*Figure 2.8a*). The integrated features of well-stacked CNTs with long length (up to mm scale) and large aspect ratio enables the coexistence of high SSA ($100\text{--}500 \text{ m}^2 \text{ g}^{-1}$) and high mechanical properties (average tensile strength $\sim 1 \text{ GPa}$ and average Young's modulus $\sim 130 \text{ GPa}$) of CNT fibers (*Figure 2.8b*).[91] With respect to GBFs, they have similar values of electrical conductivity ($10\text{--}10^4 \text{ S cm}^{-1}$), lower surface area, but show improved mechanical capabilities in tension.[92] In addition to this, CNT fibers are attractive for multifunction SCs because of the possibility to make large device based on continuous fibers.

Figure 2.7. Different methods for spinning CNT fibers by a) drawing from a forest of aligned CNTs,[88] b) direct spinning from the gas-phase during CNT synthesis by CVD[89] and c) wet spinning of nanocarbons dispersed in liquid[90].

The high mechanical properties of CNT fibers combined with moderate SSA makes them a candidate electrode material not only in flexible but structural power composites. Their use as electrodes for

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high performance SCs has been discussed in a number of studies.[53, 93, 94] Overall, the specific capacitance of as-produced CNT fibers varies from 23 to 80 F g^{-1} , which is considerably lower relative to GBFs and AC (*Figure 2.8c*). Capabilities can be substantially enhanced by chemical functionalization[95] or introduction of pseudocapacitive active elements[96, 97], as discussed below. Large mechanical properties of CNT fibers can be also maximized by making a PVA gel composite material produced by wet spinning method.[98, 99] Such material possesses outstanding energy-to-break over 600 J g^{-1} , but demonstrate low specific capacitance (5 F g^{-1}) partially attributed to moderate mass fraction of CNTs (60 wt.%) with respect to dry-spun fibers (>95 wt.%).

Figure 2.8. a) SEM images representing CNT fiber structure produced by CVD spinning process, b) stress–strain curve of an as-spun CNT fiber yarn and c) CV curve of as-spun CNT fibers measured in NaCl aqueous electrolyte[53].

Numerous works were devoted to exploration of CNT fibers prospect in yarn-like SC devices,[100, 101] which introduce a special class of energy-storage systems with certain applications (*Figure 2.9*). Unidirectional sheets of fiber, on the other hand, exhibit more defined properties, which can be directly taken for accurate comparison with traditional planar electrodes. Notwithstanding that although separate studies of CNT fibers mechanical and electrochemical properties indicate their potentially large contribution to the field of multifunctional energy storage, still there is a lack of reports on flexible SCs based on this material. Furthermore, the targeted CNT fiber-based SC electrodes explored had a size of $<10 \text{ cm}^2$ and thickness of few μm , limited by CNT fibers availability

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and reproducibility of the material's fabrication in a continuous large-scale. Thereby, there is a lack of studies unveiling feasibility of producing large-area CNT fiber electrodes with reproducible performance for employment in multifunctional electrochemical energy storage systems. Thus, one of the main objectives of this work consists in exploring the possibility of employing large scale CNT fiber electrodes with well-controlled properties for fabrication of SC devices with total energy storage performance compatible with real application.

Figure 2.9. a) The structure (top) and optical microcopy image (bottom) of yarn-like stretchable SC based on CNT fibers[100], b) schematic illustration of the structure of the coaxial CNT fiber-based SC (top) and a SEM image of the coaxial SC made into a knot (bottom)[101].

2.2.2.2 Electrodes based on carbon fibers

Several works have focused on the development of multifunctional electrodes with mechanical performance beyond simple flexibility and instead targeting the combination of high capacity with mechanical properties in the range of structural composites. Thanks to their high-performance mechanical properties (tensile strength of 3-7 GPa and modulus 200-965 GPa), CFs have been considered as a promising candidate for structural SCs. However, their extremely low SSA ($\sim 0.1 \text{ m}^2 \text{ g}^{-1}$) leads to a very small specific capacitance ($\sim 0.06 \text{ F g}^{-1}$)[102] several orders of magnitude below values for conventional carbon materials. The challenge consists in increasing the intrinsically low surface area of CFs without compromising their mechanical performance. Several methods, such as chemical activation by acids, bases and surfactants,[102–104] growth of CNTs onto CFs or CNT sizing of the carbon fibers[105] and introduction of carbon aerogels (CAG)[106] have been explored and led to large increases in SSA ($37\text{-}163 \text{ m}^2 \text{ g}^{-1}$) as depicted in *Figure 2.10* without compromising tensile properties. Embedding structural CFs into a monolithic CAG was found to be the most promising approach, as it also leads to improved in-plane compression strength and modulus of the composite by up to 4.5-folds. However, despite substantial enhancement in surface area, specific capacitance varies between $6\text{-}14 \text{ F g}^{-1}$, which still does not approach the values for AC and nanocarbon electrodes.

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Figure 2.10. Specific surface area and specific capacitance of as-received and modified CFs.[107]

Very recently, a robust flexible film integrating CFs, graphene and hierarchical porous activated carbon was reported.[108] The electrodes were prepared by two step process including formation of thin 10 μm graphene/CF films from large graphene flakes and CF bundles by electrochemically-driven bubbling method with further activation of biomass cellulose and KOH slurry with graphene additive (*Figure 2.11a,b*). The hierarchical hybrid film showed improved tensile strength of 5.3 GPa compared to pristine CFs (4.8 GPa) (*Figure 2.11c*). This was attributed to the tight core-shell fiber structure, in

Figure 2.11. a) Schematic illustration of electrochemically-driven spreading of carbon fiber bundles, b) scanning electron micrographs of graphene/CF film, c) Stress-strain curves of single CF at various stages of fabrication and d) CD curves and specific capacitance of graphene-AC/CF electrode under different current densities.[108]

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which CFs serve as the reinforcement while graphene/AC nanosheets act as “binders” to cover and interconnect spreaded individual CF filaments through carbon π - π stacking. The fibers demonstrated good electrical conductivity (110 S cm^{-1}) combined with large SSA ($831 \text{ m}^2 \text{ g}^{-1}$) and broad size distribution in micro to macro range. Electrochemical performance of the material was evaluated in symmetric SC device using KOH electrolyte, in which the active material achieved 129 F g^{-1} of specific capacitance (*Figure 2.11d*).

2.2.3 Comparison of multifunctional carbon-based electrodes

The preceding discussion has shown the wide range of mechanical and electrochemical properties of multifunctional carbon-based electrodes. The distinction made above with respect to the synthesis method and resulting properties of various forms of carbon can be observed through a figure of merit. A convenient way to compare these materials is by plotting specific capacitance versus toughness, as shown in *Figure 2.12*. It particularly highlights that graphitic nanocarbons (e.g. CNTs) assembled into fibers possess an optimum balance between tensile properties and energy storing capabilities, taking place between buckypapers with high capacitive performance but poor mechanical properties and CFs with large values of fracture energy but relatively low capabilities to store energy. Furthermore, the plot does not consider another aspect of nanocarbon fibers: due to their pre-formed highly porous

Figure 2.12. Comparison of specific capacitance and toughness for different carbon materials (data from [94] and references within).

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structure CNT fibers is an ideal conductive and flexible scaffold for deposition of pseudocapacitive materials. Although the data is limited to electrodes comprising exclusively nanocarbons, which have limited capacitance, these differences propagate to other systems where the nanocarbons are combined with metal oxide nanoparticles and CPs. Therefore, an objective of this thesis consists in revealing the prospect of CNT fibers for application as multifunctional electrodes in flexible and structural SCs. This includes comprehensive study of textural, electrochemical and mechanical properties of the fibers and investigation of their performance in full cell multifunctional SC devices.

2.3 Hybrid composite electrodes in multifunctional SC

2.3.1 Transition metal oxides

The pseudocapacitive materials provide higher specific capacitance with respect to purely EDLC carbon materials that arises from the energy storage mechanism through fast reversible surface redox reactions, ascribed to their multiple valence state changes. However, most of the metal oxides (MeO) are semiconductors or insulators with low electrical conductivity ($10^{-5} - 10^{-7} \text{ S cm}^{-1}$). This seriously restricts their practical application in electrochemical devices due to poor electron transport kinetics. On the other hand, most of these metal oxides and related materials are mainly in powdered form. To address these limitations the commonly used approach consists in depositing them as brittle ceramics on conductive porous and often flexible substrates.[7, 109–111]

Pseudocapacitive inorganic materials can be deposited onto flexible substrates by dip coating, painting, rod coating and dispensing-writing.[112–114] Various oxide nanomaterials, such as MnO_2 , Mn_3O_4 , Fe_2O_3 , RuO_2 , V_3O_7 have been loaded on cellulose paper, metallic mesh and foam, carbon cloth, plastics and metal-coated polymers (e.g., Cu or ITO-coated polyethylenenaphthalate (PEN), polyethyleneterephthalate (PET), polyethersulfone (PES) and polyimides (PI)).[7, 111, 115–118] Although RuO_2 exhibits the best electrochemical performance (high specific capacitance, long cycle life, high conductivity, and good electrochemical reversibility), MnO_2 is more attractive from practical point of view because of its cost-effectiveness, fairly high theoretical specific capacitance ($\sim 1370 \text{ F g}^{-1}$) and ease of fabrication.[57] In this regards, numerous studies have been sought to deposition of different MnO_2 polymorphs on flexible scaffolds.[118–121] Recent works reported deposition of MnO_2 on carbon fiber cloth (CFC)[118, 120] and carbon fiber paper (CFP)[121, 122]. The growth of MnO_2 nanosheets on CFP[121] and CFC[120] was conducted *via* water-bathing precipitation method, during which the carbon substrates act both as supporting scaffolds and reducing agents. The resultant flexible electrodes deliver similar specific capacitance of $\sim 700 \text{ F g}^{-1}$ and maintain 50-65% of maximum capacitance after increasing current density 10 folds ($10\text{-}20 \text{ A g}^{-1}$).

2.3 Hybrid composite electrodes in multifunctional SC

Further improvement in specific capacitance ($650\text{--}1450\text{ F g}^{-1}$), cyclic stability and rate capability can be achieved by using electrodes with multi-component transition metals, such as $\text{MnO}_2@\text{ZnO}$, [123] $\text{Co}_3\text{O}_4@\text{NiCo}_2\text{O}_4$, [124] $\text{Zn}_2\text{SnO}_4@\text{MnO}_2$ [125] and $\text{SnO}_2@\text{MeO}$ ($\text{Me} = \text{Ni, Co, Mn}$) [126]. However, such materials often pose hybrid structures with pronounced features of faradaic battery-like electrochemical response, which cannot be treated as purely pseudocapacitive electrodes. [127] In particular, CD profile used to evaluate electrochemical performance of the material shows clear deviation from nearly linear discharge curve of capacitive electrodes, and in this instance specific capacitance cannot be obtained from the discharge slope. Nevertheless, many works disregard such distinction that gives rise to significantly overestimated values unrelated to realistic capabilities of the electrodes.

Furthermore, another critical aspect of these systems is their thickness and mass loading. The faradaic redox process substantially increase specific capacitance, but comes with the price of impeded electron and ion transport leading to reduced power. The use of thin MeO films allows to enhance power density because of the shorter transport paths for ions and electrons. Herewith, these properties may not scale up linearly and fabrication of the electrodes with practical mass loading comparable to conventional SCs can result in considerable drop of electrochemical characteristics.

2.3.2 Conducting polymers

The most common approaches to produce flexible conducting polymers electrodes are through chemical or electrochemical polymerization on different substrates. [14, 128, 129] CPs take different morphologies, such as bulk powder, nanosheets, nanorods, and nanowalls, which can strongly affect the electrochemical performance of the material.

PPy has greater mechanical flexibility than most other conducting polymers. As such, there has been extensive research on CPs electrodes for flexible SCs during last years. [14, 130–132] PPy has been deposited on cotton fabric, [133] CFC [131] and bacterial cellulose nanofibers [14], leading to specific capacitance of $150\text{--}380\text{ F g}^{-1}$ and high stability under bending conditions.

PANI has been also widely explored for application in flexible electrochemical systems due its variable oxidation state and highest doping capacitance (i.e. number of ion dopants per polymer unit). This contributes to high theoretical specific pseudocapacitance (2000 F g^{-1}) superior to PPy (620 F g^{-1}) and PEDOT (210 F g^{-1}). [134] On this basis, remarkable electrochemical properties have been obtained for flexible electrodes based on nanostructured PANI materials with different morphology. A 3D conducting net with cross-linked structure, nanotube arrays, hydrogel and PANI coated PET nanofibers were successfully synthesized on various substrates reaching specific capacitance of $430\text{--}601\text{ F g}^{-1}$, combined with excellent flexibility. [135–138]

2.3 Hybrid composite electrodes in multifunctional SC

2.3.3 Metal oxide-conducting polymer hybrids

The binary or multiple composites of transition metal-based compounds and CPs in most instances are much more competitive electrode materials to fulfill the restrictions of flexible SCs application. Incorporation of metal oxides into CPs enables a number of beneficial effects translated into improved performance of multifunctional electrochemical devices. The oxides mainly provide high pseudocapacitance resulting from their excellent redox properties, whilst CPs are responsible for mechanical flexibility and electrical conductivity allowing easier processing of each component in the composite. The hybrid electrodes usually offer increased conductivity, rate capability, lifetime and flexibility superior to those of each individual electrode components.[139–141]

During last years, several composites based on varied metal oxides and conducting polymers have been proposed as promising electrodes for flexible SCs.[142–144] Different hybrid systems such as $\text{TiO}_2@\text{PPy}$ core shell nanowires,[144] $\text{PANI}/\text{MnO}_2/\text{TiN}$ nanowire array[145] and $\text{NiCo}_2\text{O}_4@\text{PANI}$ nanorod arrays[146] have been directly grown on carbon cloth and achieved 190–900 F g^{-1} of specific capacitance at 1 A g^{-1} and more than 90% of the capacitance retention after 3000 cycles at different cycling rates. Moreover, some of these electrodes were employed for assembling an all-solid SCs which retained about 91.7% of its initial capacitance after 2000 cycles under harsh bent and twisted conditions.[144]

2.3.4 Hybrid electrodes of carbon-based and pseudocapacitive materials

Hybrid composite electrodes combine both carbon materials and pseudocapacitive elements in one structure. In such composite systems, the carbon network often serves as a scaffold, which maximizes the effective surface of redox active material, while provides the channels for fast charge transport. The carbon network also provides mechanical reinforcement and can lead to self-standing electrodes, often with high flexibility. The large electronic conductivity of many carbon structures benefits rate capability and power density of the devices, whereas pseudocapacitive components are the main sources that store the charge and contribute to high specific capacitance and high energy density of the hybrid electrodes. These hybrid composites are typically made by incorporation of nanocarbons such as CNTs or graphene with metal oxides or/and CPs.

A sequence of such materials was developed producing binary or ternary nanocomposites of graphene, CNTs with different transition metals oxides (e.g., MnO_2 , Fe_2O_3 , Fe_3O_4 , V_2O_5 , Co_3O_4 , etc.) and conducting polymers (e.g., PANI, PPy and PEDOT). Metal oxides are commonly deposited onto carbon networks through electrodeposition[147–149] or hydrothermal methods[150–152], whereas CPs electrodes are coated by electropolymerization[153, 154] or chemical polymerization[155, 156]. The choice depends on whether the nanocarbons are dispersed and mixed with MeO in particle format, or if MeO or CP is coated onto preformed nanocarbon arrays.

2.3 Hybrid composite electrodes in multifunctional SC

The ultimate multifunctional performance of hybrid electrode highly depends on the volume/weight fraction of its constituents. Low nanocarbon volume fraction (i.e. high volume fraction of MeO) leads to large capacitance, but low mechanical properties, often requiring a substrate to form a free-standing electrodes. Examples include the composites of graphene or CNTs and MnO_2 typically grown on different supporting materials, such as graphite foil[157], commercial textiles[148] and Ni foam[158]. A composite of CNTs and MnO_2 deposited on a regular office paper with high mass loading of the metal oxide exhibited 540 F g^{-1} of specific capacitance normalized by the weight of total active material[159], for example. However, although the electrodes were flexible and only slightly degraded after being rolled 100 times, after 200 bending cycles the composite material became brittle.

Producing self-standing flexible electrodes requires substantial enhancement of nanocarbons volume fraction. To overcome the need of additional substrates and maximize the efficiency of flexible SCs some efforts have been directed toward producing self-standing flexible electrode entirely consisted of active hybrid materials. However, the values of capacitance in such systems are much lower of those reported for the pristine metal oxide and rarely surpass $200\text{-}300 \text{ F g}^{-1}$. For instance, a free-standing $\text{MnO}_2\text{@CNTs/CNTs}$ paper-like film has been prepared by vacuum filtration and exhibited 141 F g^{-1} with only 4% fading for the capacitance when bended to 180° . [160] Such difference is mainly related to the contribution of nanocarbon to the weight of active material, reducing the volume fraction of MeO. In another study, graphene/ MnO_2 /CNTs flexible electrodes with significant mass loading of active material (8.80 mg cm^{-2}) exhibited 372 F g^{-1} of specific capacitance, while having distinct tensile properties with specific strength, Young's modulus and corresponding toughness of 48 MPa, 2.3 GPa and 0.75 J g^{-1} , respectively.[161]

Another strategy to fabricate flexible electrodes was *via* synthesis of the composites of metal oxides and carbon nanofibers (CNFs) or CNT fibers.[96, 162] A free-standing membrane of CNFs with embedded $\alpha\text{-MoO}_3$ nanoparticles produced by electrospinning method achieved high specific capacitance of 762 F g^{-1} at 1 mA cm^{-2} , and still retaining 403 F g^{-1} at 50 mA cm^{-2} (*Figure 13a,b*). [162] The electrode shows high flexibility and excellent cycling performance with $<1\%$ of capacitance fading after 10,000 cycles at 3 mA cm^{-2} (*Figure 13c*). It stands to mention that CD profile in *Figure 4.13b* indicates faradaic behaviour typical for battery-like materials. Thus, obtained values should be compared to pseudocapacitive hybrid systems with precaution, also considering the performance of a full SC device.

2.3 Hybrid composite electrodes in multifunctional SC

Figure 2.13. a) SEM image of the as-prepared MoO₃-CNF membrane and the photograph demonstrating its flexible nature (inset), b) CD curves under different current densities and c) long-term cycling performance of the MoO₃-CNF membrane in 2M KOH electrolyte.[162] (d) SEM morphologies of MnO₂ deposited on expanded hydrogel-like CNT film, e) CV curves measured in 1M Na₂SO₄ electrolyte and f) mechanical performance of the MnO₂/hydrogel-like CNT film.[163]

In another work, a hydrogel-like CNT film produced through electrochemical activation of CNT films was used as a substrate for deposition of MnO₂. [163] Aside from good electrochemical performance ($>300 \text{ F g}^{-1}$ at 0.1 A g^{-1}) the free-standing composite electrodes had moderate mechanical stability with the strength of 17.5 MPa and the strain of 4% (*Figure 13d-f*).

Composites of carbon fibers and metal oxides have also been recently examined in the context of structural energy storage application. CF modification by deposition of electrochemically active MeO has been shown to improve both mechanical and electrochemical properties.[164, 165] CuO nanowires grown on the surface of the CFs by hydrothermal method lead to considerable enhancement of textural properties ($\text{SSA} \sim 133 \text{ m}^2 \text{ g}^{-1}$) and electrochemical performance ($C_s \sim 2.5 \text{ F g}^{-1}$ with NaOH and $\sim 6.7 \text{ F g}^{-1}$ with EMIMBF₄/LiTFSI). Moreover, the CuO nanowire-decorated CF samples exhibited an improvement in tensile strength of the final composite by 80.6% and modulus by 77.1% compare to bare fibers. The observed increment of mechanical properties is related to facilitated load sharing resulting in a higher energy required to break the composite. A similar hybrid electrode was designed by growing ZnO nanotubes on woven CFs and exhibited $164 \text{ m}^2 \text{ g}^{-1}$ of SSA, 18.8 F g^{-1} of specific capacitance and $>93\%$ of capacitance retention over 2500 CD cycles at 1 V in EMIMBF₄/LiTFSI electrolyte.[164]

Hybrid composites of carbon materials and conducting polymers have been also extensively explored for application in flexible SC. Carbon materials can serve as percolating networks enhancing the

2.3 Hybrid composite electrodes in multifunctional SC

relatively poor mechanical stability of CPs and improving the control over the morphology and size of coated and/or encapsulated CPs. Undoubtedly, one of the most studied hybrid systems are based on PANI and CNTs or graphene.[154–156, 166] For instance, PANI nanowires arrays deposited on carbon cloth-supported SWCNTs exhibited 410 F g^{-1} and 90% of the capacitance retention after 3000 CD cycles at 3 A g^{-1} . [167]

The ternary hybrid systems of carbon materials, metal oxides and CPs have also been explored. A typical strategy to design multicomponent flexible architecture is based on layer-by-layer deposition of nanocarbons and pseudocapacitive materials on flexible substrates.[168–171] A flexible electrode of PEDOT:poly(styrenesulfonate) (PSS) wrapped MWCNT/MnO₂ composite has led to 428 F g^{-1} with 18% decay in specific capacitance after 2000 CD cycles.[168] Similarly, a CNT@PPy@MnO₂ sponge electrode with a core-double-shell structure resulted in 325 F g^{-1} at 2 mV s^{-1} . The material demonstrated good capacitance retention >90% after 1000 CD cycles at 100 mV s^{-1} under 50% compressive strain.[171]

Finally, *Table 2.2* summarizes the recent results on flexible electrodes based on various materials. At a glance, pseudocapacitive materials and specifically transition metal oxides obtain the highest values of specific capacitance ($500\text{--}1500 \text{ F g}^{-1}$) accompanied by good cyclic stability. However, note that the properties of these materials are normalized considering only the contribution of the active material and ignoring the weight of flexible and conductive substrates, which are necessary to provide sufficient mechanical stability and electronic transport. These conductive support constitutes a large mass fraction of the flexible electrodes, typically as high as 70-90%.[27] Moreover, some gravimetric electrochemical characteristics are irrelevant for real application because of extremely low thickness of electrode materials or negligible mass loading. These systems may show a very high gravimetric capacitance, but those characteristics will not scale up linearly with the thickness of the electrodes. As a result, such information provides a misleading information and introduces uncertainty in the field of multifunctional SC electrodes.

Some researchers have reported a freestanding flexible graphene foams@PPy@MnO₂ electrodes with specific capacitance of 601 F g^{-1} [174], normalized by the mass of MnO₂, which was 21 wt.% of the total composite. The PPy (6 wt.%) and graphene foam (73 wt.%) contributions were ignored due to the low mass loading of the conducting polymer and small specific capacitance of the carbon material.

However, a graphene foams@MnO₂ composite has only 337 F g^{-1} , emphasizing a significant impact of the conducting polymer. Therefore, the values of electrochemical characteristics normalized exclusively by the weight of individual pseudocapacitive components are often inaccurate and complicate comparison of the reported materials. These details should be under primary consideration particularly for representation of electrochemical results of the hybrid materials, where synergistic effect of the components cannot be neglected.

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Table 2.2. Comparison of electrochemical performance for different flexible electrode materials.

Electrode material	Substrate	Electrolyte	Capacitance, $F\ g^{-1}$	Cycle stability	Mechanical stability
CNT paper[60]	free-standing	EMIMTFSI	135 at $2\ A\ g^{-1}$	97% retention after 4000 CD cycles at $15\ A\ g^{-1}$	flexible
3D rGO aerogel on the N-doped cotton-derived carbon[70]	free-standing	6M KOH	225 at $1\ A\ g^{-1}$	98% retention after 10 000 CD cycles at $5\ A\ g^{-1}$	flexible
graphene/AC/CF[108]	free-standing	6M KOH	150 at $5\ mV\ s^{-1}$	-	flexible, semi-structural
CF+CAG[106]	free-standing	3M KCl	14.3 at $5\ mV\ s^{-1}$	-	structural
CNT fibers[53]	free-standing	NaCl	80	-	flexible, semi-structural
MnO ₂ nanosheets[121]	CFP	1M Na ₂ SO ₄	714 at $0.5\ A\ g^{-1}$	87% retention after 1200 CD cycles at $5\ A\ g^{-1}$	flexible
Ni/Co/Mn ₂ mixed oxides[172]	CC	2M KOH	1434 at $2\ mA\ cm^{-2}$	94% retention after 3000 CD cycles at $20\ mA\ cm^{-2}$	flexible
FeCo ₂ S ₄ -NiCo ₂ S ₄ [173]	silver-sputtered textile cloth	3M KOH	1519 at $5\ mA\ cm^{-2}$	92% retention after 3000 CD cycles at $10\ mA\ cm^{-2}$	flexible
PANI nets[136]	graphite paper	1M H ₂ SO ₄	601 at $0.5\ A\ g^{-1}$	72% retention after 1000 CD cycles at $5\ A\ g^{-1}$	flexible
δ -MnO ₂ @CNTs/CNTs film[160]	free-standing	1M Na ₂ SO ₄	149 at $0.2\ A\ g^{-1}$	90% retention after 5000 CV cycles at $50\ mV\ s^{-1}$	flexible
ZnO/CF[164]	free-standing	EMIMBF ₄ /LiTFSI	18.8 at $5\ mV\ s^{-1}$	93% retention after 2500 CD cycles at $1\ A\ g^{-1}$	structural
CNT-PPy[153]	CC	0.5M H ₂ SO ₄	486 at $1.25\ A\ g^{-1}$	82% retention after 10 000 CD cycles at $8\ A\ g^{-1}$	flexible
PANI-CNT fibers[93]	free-standing	1M H ₂ SO ₄	240 at $10\ mV\ s^{-1}$	100% retention after 30 000 CD cycles at $2\ mA\ cm^{-2}$	flexible, semi-structural
CNT-MnO ₂ -PPy sponge[171]	free-standing	2M KCl	325 at $2\ mV\ s^{-1}$	90% retention after 1000 CV cycles at $100\ mV\ s^{-1}$	compressible

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2.4.1 All-solid electrolytes

All-solid electrolytes based on polymer matrixes are possible alternative to liquid electrolytes, which are considered as an unfortunate drawback for flexible energy storage devices. They are easier for

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handling, lightweight, transparent, have higher reliability, flexibility, wider range of operation temperature and usually do not need sealing. However, solid-state electrolytes have lower ionic conductivity, as compared to liquid, resulting in higher resistance of SCs, and consequently reduced energy and power. In this regard, numerous research attempts have been focused on development of novel all-solid electrolytes achieving enhanced ion mobility and stability, without sacrificing their mechanical properties.[175, 176]

PEs can be divided into three main types based on their physical state and composition: gel polymer electrolytes (GPEs), solid polymer electrolytes (SPEs) and composite polymer electrolyte (CPEs). They also differ in resultant properties, and particularly in ionic conductivity and mechanical robustness. The ionic conductivity is closely related to the degree of crystallinity and the viscosity of the PEs, which also define their mechanical behaviour.[177, 178] The ions have low mobility in crystalline phase, and this leads to lower ionic conductivity. On the other hand, higher degree of crystallinity affects improved mechanical properties of the matrix. Therefore, there is a strong conflict between mechanical and electric demands of PEs, as illustrated in *Figure 2.14*.

Figure 2.14. Ion conductivity versus stiffness for solid polymer electrolytes. The highlighted area indicates desired properties of the PEs for high performance multifunctional structural SCs.[33]

The SPEs usually based on highly crystalline polymer matrices exhibit considerable values of stiffness. They are potentially capable to fulfill the requirements for structural energy storage systems, in which interlaminar mechanical properties of the composite are dominated by the polymer matrix.[179] However, their poor ionic conductivity ($10^{-8} \sim 10^{-7}$ S cm⁻¹) significantly restricts the performance of SC devices, which often cannot be charged at high currents, take long charging/discharging time and consequently results in low values of energy and power.[102] Incorporation of additives, such as plasticizers[180] or inorganic fillers[181, 182], into a polymer host enables to overcome some limitations of SPEs and attain the conductivity enhancement

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($10^{-5} \sim 10^{-6} \text{ S cm}^{-1}$). These are considered to be CPEs, with improved electrochemical properties, which still did not approach the values for conventional liquid electrolytes. GPEs can be assembled into free-standing mechanically stable membranes, but their stiffness is far beyond the SPEs performance. Nevertheless, owing to their superior ionic conductivity ($10^{-4} \sim 10^{-3} \text{ S cm}^{-1}$) compared to SPEs and CPE, GPEs remain the most commonly used solid-state electrolytes in flexible SCs, in which modest mechanical properties are sufficient.

While dry SPEs and in many cases CPEs are prepared by complexing/dissolving ionic salts into coordinating polar polymer hosts, providing mechanical stability, fabrication of most of GPEs additionally includes the use of organic/aqueous solvents.[176] This enables decreasing viscosity of the electrolyte and assisting in the dissociation of the salts. All three types of PEs can be prepared blending the components by solution or melt processes, such as casting method,[183] phase inversion,[184] in situ polymerization,[185] and extraction-activation method.[186]

The wide variety of polymeric hosts includes PVA, poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP), poly(methyl methacrylate) (PMMA) as well as a number of polymeric ionic liquids (PILs)[187]. The main criteria determining good performance of a polymer are fast segmental motion of polymer chain, presence of special groups promoting the dissolution of salts, low glass transition temperature, high molecular weight, and high electrochemical and thermal stability. PVA has been broadly utilized as a popular host polymer due to its good mechanical properties, high flexibility and high charge storage capacity. Usually, it is considered in the context of aqueous electrolytes because of its excellent hydrophilic properties arising from the presence of a large extent of the polar hydroxyl group. The ionic conductivity in such systems as PVA-KOH-H₂O is strongly dependent on the content of KOH and water in the film.[188]

Despite its low ionic conductivity at ambient temperatures PEO-hosted PEs have also received an upsurge of interest. PEO provides high capacity in salt complexation, good dimensional stability, mechanical flexibility and chemical stability. Several strategies have been utilized to improve the ionic conductivity of PEO-based electrolyte systems such as addition of organic plasticizers and fillers[189] or by blending PEO with another highly amorphous polymers.[190]

Among other promising host materials considerable efforts have been devoted to PVDF and its PVDF-co-HFP due to their good affinity to electrolyte solution, remarkable mechanical properties, high electrochemical stability and large dielectric constant. The film based on PVDF-co-HFP copolymer possesses two randomly mixed monomers resulting in higher amorphicity, and thus better ion mobility. In particular, the co-existence of crystalline PVDF and the amorphous HFP in the copolymer allows to reach a good balance between ionic conductivity and mechanical strength of the PEs. A comparative study of the PEs based on PVDF and PVDF-co-HFP host materials and PC +

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DEC + LiClO₄ has demonstrated that the membrane comprised of PVDF-co-HFP exhibits better performance over the PE with PVDF.[191]

Different organic and aqueous solvents are utilized to dissolve both the polymer hosts and electrolytic salts and consequently provide the medium for ionic conduction. The criteria for an appropriate solvent include high dielectric constant ($\epsilon > 15$), donor number for more dissociation of ion and chemical and electrochemical stability. Such organic solvents as acetone, EC, DEC, propylene carbonate (PC), dimethyl carbonate (DMC), dimethyl formamide (DMF) and tetrahydrofuran (THF) are normally used.

Depending on the type of supporting electrolytes, there are four families of PEs based on proton,[192] alkaline,[193] inorganic salts,[117] and ionic liquids (ILs)[194]. Proton conducting polymer electrolytes are typically prepared by mixing a polymer matrix with a proton donor solution (H₂SO₄, H₃PO₄, HCl, CH₃COOH) dissolved in a polar solvent. The most widely used PEs for flexible SCs are H₂SO₄-PVA[135, 195] and H₃PO₄-PVA[71], which provide excellent proton conductivity but suffer from high chemical activity and corrosiveness. Alkaline PEs (e.g., PEO-KOH, PVA-KOH, PAAK-KOH) have been also widely employed in all-solid SCs. The values of ionic conductivity for alkaline GPEs membrane usually lay in the range between 10^{-4} and 10^{-2} S cm⁻¹. Introduction of salts (K₃[Fe(CN)₆])[196] and plasticizers (PC)[197] enables further increasing ionic mobility.

The rising interest to IL as potential electrolyte for SC originates from its unique properties, including good chemical and electrochemical stability, non-flammability, negligible vapour pressure and high ionic conductivity. The combination of ILs and suitable polymers allows to form all-solid PEs retaining the main properties of ILs, while providing newly acquired mechanical robustness. Incorporation of ILs into polymer matrices not only adds the mobile conductive ions within the polymer network but also enhances the flexibility of the skeleton supporter.

A broad range of IL cations (e.g., imidazolium, pyridinium, alkylammonium, alkylphosphonium, pyrrolidinium, guanidinium, alkylpyrrolidinium, etc) and anions (e.g., Cl⁻, Br⁻, I⁻, PF₆⁻, BF₄⁻, NO₃⁻, TFSI⁻, etc) offer a variety of IL-based polymer electrolytes (*Figure 2.15a*). The fabrication methods of IL-based polymer electrolytes can be classified into three categories: doping of polymers with ILs, in situ polymerization or crosslinking of monomers in ILs, and synthesis of polymeric ionic liquids (PILs) (*Figure 2.15b*). Numerous works have reported preparation of IL-gelled polymer electrolytes using fluorinated polymers, especially polytetrafluoroethylene (PTFE), PVDF and PVDF-co-HFP, as host polymers.[198–201] Combination of good thermal, oxidative and mechanical stabilities and film formation abilities makes these polymers excellent candidates for IL-based PEs.

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Figure 2.15. a) Examples of cations and anions used in the formation of ILs, b) schematic representation of IL-based polymer electrolytes fabrication methods.

ILs have a wide electrochemical window of up to 7 V that makes them particularly promising candidates to improve energy and power densities of all-solid SCs. For instance, PE membrane based on PVDF, polyvinyl acetate (PVAc) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) has been produced *via* solution-casting method.[198] The PVDF/PVAc/IL electrolyte exhibited the maximum ionic conductivity of $2.4 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature and 50 wt.% of IL, high thermal stability ($\sim 300^\circ \text{C}$) and wide potential window $> 4 \text{ V}$. Another PE system was prepared blending a poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide PIL (pDADMATFSI), and its corresponding IL N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr₁₄TFSI).[183] The resultant all-solid PE membrane with IL:PIL weight ratio of 60:40 obtained $5 \times 10^{-4} \text{ S cm}^{-1}$ of ionic conductivity at room temperature (Figure 2.16a). Moreover, owing to exceptional electrochemical stability of Pyr₁₄TFSI, a symmetric SC assembled using produced membrane and AC electrodes could operate at 3.5V (Figure 2.16b).

Figure 2.16. a) Arrhenius plot of ionic conductivity of the PE membrane with 60% wt. of Pyr₁₄TFSI and photo of free-standing membrane (inset), b) CD profiles obtained at 1 mA cm^{-2} for all-solid SC based on the Pyr₁₄TFSI PE membrane and AC electrodes.[183]

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Structural PEs represent an individual class of solid-state polymers, which can be used as stiff multifunctional matrixes in structural power composites. Structural electrolytes are usually produced by dissolving ionic salts (e.g. LiTFSI) in organic solvents, then mixed with the crosslinking polymer such as poly(ethylene glycol) diglycidyl ether (PEGDGE) and diglycidyl ether of bisphenol-A (DGEBA).[106] These electrolytes are fairly rigid to withstand considerable mechanical loads but have very poor ionic conductivity. Therefore, additional ILs are utilized in order to produce bicontinuous networks and intensify the ion diffusion in the electrolyte (*Figure 2.17a*).[179] Such IL-epoxy resin composites demonstrate a modulus-conductivity trade-off attributed to the formation of bicontinuous structure of electrolyte and mechanical reinforcement with a uniform network of struts/channels, the dimensions of which were influenced by the composition of the formulation (*Figure 2.17b*). Further improvement both in mechanical and electrochemical properties was achieved by introduction of inorganic nanoparticles. Composite structural electrolytes based on PEGDGE epoxy resin (65 wt.%) and 1M TBAPF₆ in PC showed a substantial increase in ionic conductivity ($1.1 \times 10^{-4} \text{ S cm}^{-1}$), electrochemical window ($\sim 5 \text{ V}$) and compression strength ($\sim 5 \text{ MPa}$) after addition of 6 wt% mesoporous TiO₂. [202]

Figure 2.17. a) Schematic illustration of the preparation procedure of structural electrolytes based on IL and epoxy resin, where LiY is a lithium salt, b) multifunctional performance of IL-epoxy resin electrolytes and an electron image of their bicontinuous structure (inset).[179]

2.4.2 Multifunctional flexible and structural SCs

Although in the previous sections multifunctional characteristics of electrodes and polymer electrolytes were discussed in details, it is necessary to overview the performance of full cell SC devices comprising both electrodes with augmented mechanical properties and robust PEs. Highly flexible SC devices have been fabricated with CNTs,[60, 63] graphene[67, 70] and their composites[75, 78] and delivered moderate specific capacitance, energy and power density in the range of 80-200 F g⁻¹, 2-20 Wh kg⁻¹ and 2-23 kW kg⁻¹, respectively, using aqueous polymer electrolytes. To enhance specific energy and power several studies have employed IL-based PEs with superior electrochemical stability as compared to aqueous systems. A simple device architecture

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consisting of two azide-functionalized MWCNT thin film electrodes enclosing a PE membrane based on EMIMBF₄ IL and PVDF-co-HFP polymer has been proposed.[64] Owing to high operating potential of 3V all-solid SC achieved high energy density of 25 Wh kg⁻¹ and power density of 161 kW kg⁻¹ (Figure 2.18a,b). Despite the high voltage applied it showed excellent cycling stability with capacity retention >90% after 5000 CD cycles at 1 A g⁻¹ (Figure 2.18c).

The advantage of using ILs for flexible carbon-based SC has been also illustrated comparing electrochemical properties of the devices assembled with PVA-H₂SO₄ and EMIMTFSI-silica gel electrolyte.[60] Specific capacitance, energy and power density of flexible symmetric SC based on CNT buckypaper electrodes was found to be about 80 F g⁻¹, 2 Wh kg⁻¹ and 1.5 kW kg⁻¹, respectively, with aqueous PE (~1V) and 135 F g⁻¹, 41 Wh kg⁻¹ and 164 kW kg⁻¹, respectively, with IL-based electrolyte (Figure 2.18d). The improvement in electrochemical properties observed for EMIMTFSI-silica gel electrolyte were attributed to fast ion transport in silica channels, which is comparable to that in the liquid electrolytes. In addition, the device fabricated with EMIMTFSI-silica gel electrolyte achieved outstanding stability over 4000 CD cycles without noticeable capacitance degradation at 15 A g⁻¹ and excellent capacitance retention >96% after 100 bending cycles at 50 mV s⁻¹ (Figure 2.18e,f).

Figure 2.18. a) Charge-discharge curves at different current densities, b) Ragone plot and c) cyclability test of functionalized MWCNTs SC with EMIMBF₄ electrolyte.[64] d) Ragone plot of CNT paper all-solid SCs with aqueous and IL-based gel electrolytes, e) photograph of the CNT paper flexible SC and f) CV curves measured at 50 mV s⁻¹ before and after 100 bending cycles.[60]

The operating potential of electrochemical systems can be enhanced by implementation of alternative SC geometries and configurations. In particular, asymmetric SCs (ASCs) consisting of two different electrode materials have been used as effective strategy to extend the operating voltage window of

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flexible devices.[75, 78] All-solid ASCs have been produced utilizing CNTs@3D graphene aerogel (GA) electrodes. The asymmetric configuration was achieved by depositing MnO_2 and PPy on two separate electrodes then sandwiched together with PVA- H_2SO_4 gel electrolyte. The fabricated device could be charged to 1.8V and delivered 18.4 Wh kg^{-1} energy density and 2.3 kW kg^{-1} power density. Similar flexible ASC assembled with graphene foam/CNT/ MnO_2 and graphene foam/CNT/PPy hybrid films has showed comparable values of energy (23 Wh kg^{-1}) and power density (2.7 kW kg^{-1}) at 1.6V.[75]

As mentioned above, substantially higher specific capacitances of pseudocapacitive electrodes with respect to carbon materials enable to enlarge energy storage capabilities of flexible SCs. Metal oxides have been extensively studied for fabrication of all-solid flexible SCs. Symmetric devices have been produced using PVA-based aqueous PEs and various metal oxides (e.g. RuO_2 ,[7] Co_3O_4 ,[111] Mn_3O_4 ,[115] MnO_2 [203]) deposited on flexible substrates. The devices exhibit superior specific capacitance of $130\text{--}240 \text{ F g}^{-1}$ at 1 V that contributes to enhanced energy and power densities of SCs. Generally, conducting polymers provide lower electrochemical properties as compared to metal oxides and metal chalcogenides. Specific energy and power of flexible symmetric SCs normalized by the weight of CPs are normally ranged between $12\text{--}22 \text{ Wh kg}^{-1}$ and $1\text{--}7 \text{ kW kg}^{-1}$, respectively.[14, 204] However, such systems often have remarkable stability under highly bent, stretched or compressed conditions. The combination of metal oxides and conducting polymers have found a good perspective for utilization in all-solid ASCs extending the potential window in an aqueous electrolytes beyond the thermodynamic limit of water. Free-standing highly-bendable ASC devices fabricated with metal oxides/CPs positive electrodes deliver fairly high energy ($10\text{--}60 \text{ Wh kg}^{-1}$) and power ($1\text{--}10 \text{ kW kg}^{-1}$).[142, 143, 205]

The hybrid composites of carbon materials, transition metals oxides and conducting polymers have been extensively explored for assembling flexible SC devices.[154, 166, 169, 170] Different contributions to charge stored through EDL formation and reversible redox reactions cause diverse amount of energy ($10\text{--}60 \text{ Wh kg}^{-1}$) and power ($2\text{--}40 \text{ kW kg}^{-1}$) per unit mass of active material. On top, carbon materials provide additional mechanical robustness to the electrodes reflected in high stability of the SCs under mechanical stresses.

The creation of new multifunctional electrodes with high mechanical properties beyond simple flexibility opened a new research area of structural energy storage systems. In this regard, several studies have explored different aspects of structural SCs.[102, 103, 106, 164, 165] Generally, carbon fiber reinforced polymer (CFRP) has been employed as the main component of structural composite (Figure 2.19). Different polymer matrixes (e.g., PEGDGE, DGEBA and MVR444 epoxy) have been utilized together with ionic salts such as LiTFSI or EMIMTFSI in order to provide sufficient ionic mobility. The structural EDLC fabricated with bare CFs could attain high mechanical performance

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but extremely poor electrochemical behaviour owing to low surface area of the carbon material. In this context, various attempts have been addressed to improve capacitive capabilities of structural composites through modification of CFs with high surface area carbon materials (CNTs, CAG) or metal oxides (CuO, ZnO). One of the most pronounced enhancement both in mechanical and electrochemical properties has been obtained for CAG-modified CF.[106] Structural EDLC based on CAG-modified CF, glass fiber separator and PEGDGE with 10 wt.% EMIMTFSI exhibited around 0.1 mWh kg⁻¹ energy density, 3.8 mW kg⁻¹ power density and 71 mF g⁻¹ specific capacitance. Its interlaminar shear strength of 8.7 MPa and shear modulus of 895 MPa were also higher as compared to non-modified CF based composite.

Figure 2.19. Architecture of structural supercapacitor.[102]

Current advances in the development of multifunctional all-solid SCs are summarized in *Table 2.3*. As one can see, the general trend is oriented to the use of hybrid composite systems based on transition metals-based materials which provide high pseudocapitance directly reflected on the energy storage capabilities of SCs. Furthermore, most of the recent studies reveal the prospect of asymmetric SCs which enable enhancing the operating voltage and thus energy and power of the electrochemical devices. On the other hand, although the reported flexible systems possess excellent performance, they greatly depend on PEs and normally are assembled with the common PVA-based aqueous GPEs. The maximum MeO performance is achieved for thin films. This raises the importance of flexible substrates having a large fraction in all-solid systems and determining the overall capacitance normalized by the weight of entire SC device. On top, the synthesis of metal oxides and metal chalcogenides electrodes usually is complicated that makes it difficult to scale up their fabrication.

Flexible SCs based on carbon materials normally exhibit lower values of capacitance, but the use of PEs with wide electrochemical windows allows to increase the maximum potential of the system. Although this strategy can be effectively applied to reach high values of energy density only a few works have explored the combination of new multifunctional electrode materials and advanced polymer electrolytes. In addition, due to excellent electrical conductivity of carbon materials it is

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unnecessary to use metal foils as current collector, polymers as the binder, and complementary carbons as the conductive additive. It also affects the electrochemical properties of SC devices allowing its operation at higher current densities and resulting in improved power.

Although most of presented devices target to be operated under bending conditions, normally their tensile and shear mechanical properties are far below the values for structural composites. The employment of modified CF electrodes and epoxy-based structural electrolytes enables approaching mechanical performance of conventional composites. But still, their energy storage capabilities of such systems remain low that limits their practical application.

It must be kept in mind that despite all of the progress in development of flexible and structural SCs, still there is need for large scale controlled fabrication of the materials and devices. For this purpose, the study of new multifunctional electrodes and all-solid electrolytes should be coupled with new effective routes for their manufacture favorable toward efficiency on an industrial scale. Also, importantly, the future research on the multifunctional systems should focus on a balance between electrochemical and mechanical properties.

Table 2.3. Comparison of multifunctional SC performance with different electrode materials and all-solid electrolytes.

Electrode material	All-solid electrolyte	Operating voltage, V	Capacitance, F g ⁻¹	Energy density, Wh kg ⁻¹	Power density, kW kg ⁻¹	Mechanical properties, MPa
CNT paper[60]	PVA-H ₂ SO ₄	1	80 at 2 A g ⁻¹	2 at 2 A g ⁻¹	1.5 at 30 A g ⁻¹	N/A
CNT paper[60]	EMIMTFSI-silica	3	135 at 2 A g ⁻¹	41 at 2 A g ⁻¹	164 at 30 A g ⁻¹	N/A
3D rGO aerogel on the N-doped cotton-derived carbon[70]	PVA-KOH	1	200 at 0.1 A g ⁻¹	20 at 0.1 A g ⁻¹	4 at 5 A g ⁻¹	N/A
Mn ₃ O ₄ thin films[115]	PVA-H ₂ SO ₄	1	115 at 0.1 A g ⁻¹	18 at 10 mA cm ⁻²	6 at 50 mA cm ⁻²	N/A
PANI-PVA hydrogel [204]	PVA-H ₂ SO ₄	0.8	153 at 0.25 A g ⁻¹	13.6 at 0.25 A g ⁻¹	1 at 2.5 A g ⁻¹	N/A
ZnFe ₂ O ₄ nanoflakes@ZnFe ₂ O ₄ /C nanoparticles//rGO [206]	PVA-KOH	1.6	347 at 3 mA cm ⁻²	81 at 3 mA cm ⁻²	13 at 10 mA cm ⁻²	N/A
NiCo ₂ O ₄ @PPy nanowire arrays//AC[142]	PVA-KOH	1.6	165 at 1 mA cm ⁻²	59 at 1 mA cm ⁻²	10.2 at 30 mA cm ⁻²	N/A
MnO ₂ @PANI//graphene foam[207]	PVA-KOH	1.5	118 at 0.5 A g ⁻¹	37 at 1 A g ⁻¹	4 at 5 A g ⁻¹	N/A
Carbon fiber + CAG[106]	PEGDE + 10% IL	0.1	0.602	0.001	3.3x10 ⁻⁵	G ₁₂ = 8710 S ₁₂ = 895

2.5 Potential applications of multifunctional SCs

2.5 *Potential applications of multifunctional SCs*

Although the development of flexible supercapacitors have been extensively explored during the last decade such multifunctional systems are still fairly new to the market. Nonetheless, flexible SCs are already considered or in the process of being implemented in a number of potential applications. Currently, conventional supercapacitors found to be useful for applications that demand energy in a

short periods of time. Back up and main power sources, electrochemical actuators, renewable energy sources, electric and hybrid vehicles is an incomplete list of areas where SCs are consumed. Additional functionalities such as flexibility or mechanical robustness imply alternative ways for the use of energy storage devices. Thin and flexible SCs offer volume savings that can mitigate the problem of fitting conventional electrochemical systems in electric and hybrid ground transport or aerospace electronics. They can exploit a lot of space which is inaccessible to the current rigid and bulky energy storage devices. Similar concept can be applied for integration of energy storage devices with energy harvesting systems. Some examples are shown in *Figure 20*.

Figure 2.20. a) Schematic and the prototype of the self-charging power system composed of dye-sensitized solar cell, triboelectric nanogenerator and all-solid flexible SC; b) flexible hybrid system for effective harvesting of solar energy using all-solid SC; c) structural design of the transparent and flexible self-charging power film used to drive mobile electronics; d) the use of structural SCs as structural element and energy storage system in the body of a car.

CHAPTER 3

Experimental methods

3.1 Materials and devices preparation

3.1.1 Chemicals

Thiophene (extra purity $\geq 99\%$) and ferrocene (purity = 98%) were obtained from Acros Organics and 2-butanol (purity $>99\%$) from Sigma Aldrich and were used for synthesis of CNT fibers. Ferrocene was purified by a sublimation/recrystallization process. Acetone (purity $>99\%$) was used to densify CNT fibers and prepare PE solutions. Aluminum foil (25 μm thickness and 99% purity) received from Goodfellow was used as a current collector. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, purity $\geq 99\%$) and N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide, Pyr₁₄TFSI (high purity, $>99.5\%$) were obtained from Solvionic and stored in the glove box. Poly(diallyldimethylammonium) chloride solution (pDADMAC) (average M_w 400,000–500,000, 20 wt.% in H₂O), poly(vinylidene fluoride) (PVDF) (average M_w $\sim$ 534,000 by GPC, powder) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) (average M_w $\sim$ 400,000, average M_n $\sim$ 130,000, pellets) were purchased from Sigma Aldrich and utilized as polymer matrixes for PEs. DERA KANE 8084 epoxy vinyl ester resin available from Ashland Inc., and MEKP hardener and cobalt octoate catalyst supplied by Plastiform S.A were used as epoxy matrix mixture for infusion process.

3.1 Materials and devices preparation

3.1.2 Synthesis of CNT fibers

Macroscopic fibers of carbon nanotubes were produced by the direct spinning method, in which a CNT aerogel grown by catalyst chemical vapour deposition (CVD) is continuously drawn directly from the vertical tubular reactor as a CNT fiber. The fabrication procedure involved injection of the precursor mixture in a liquid state into the upper part of the reactor using mass flow controller to adjust the feed rate. The precursor mixture contained ferrocene as a catalyst source, thiophene as a promoter and butanol as a common carbon source. The percentage of the precursor mixture was 97.7 wt.% of C source, 0.8 wt.% of promoter and 1.5 wt.% of catalyst source. Toluene was also employed as alternative carbon source in order to produce highly aligned fibers with improved mechanical properties. CNT fibers were produced using different precursor feed rate (2 ml h^{-1} or 5 ml h^{-1}), drawing winding rates (from 3 to 40 m min^{-1}) and controlled carrier hydrogen flow allowing to tailor the degree of CNTs orientation. The typical parameters fixed to produce high-throughput material were 5 ml h^{-1} of feed rate and 5 m min^{-1} of winding rate, which produce a nearly isotropic material. This material was the main one used in this thesis. It exhibits high degree of graphitization observed by Raman spectroscopy ($I_D/I_G \sim 0.2$), have few CNT layers (3–5) and small diameters (average inner diameter of 5 nm).

CNT fibers drawn out from the reactor were continuously spun on various substrates (e.g. aluminum foil, mylar plastic etc). The mass loading of carbon material was adjusted by varying the time of fiber collection. As-spun samples were consolidated through exposure to acetone and dried under vacuum at 100°C overnight prior to further characterization. Commercial CNT fiber samples supplied by Tortechn Nano Fibers, Nanocomp Technologies and INFRA were also produced by the direct spinning method. In house samples were produced by Dr. V. Reguero (IMDEA Materials).

3.1.3 Ozone functionalization of CNT fibers

The gas phase functionalization of CNT fibers was performed through exposure to ozone using a Cleaner ProCleaner™ Plus. The instrument consists in a high energy light (i.e., $\lambda = 185 \text{ nm}$) that produces ozone from atmospheric oxygen (i.e., there is no gas flowing). Initially, as-spun CNT fiber yarns (or films) were subjected to different reaction times to follow the kinetics of the process (i.e., 5 min, 15 min, 30 min or 2 h). The samples obtained after the ozone treatment were directly used for further characterization. Ozone treatment of CNT fibers and characterization of the samples were carried out with the help of Dr. D. Iglesias (University of Trieste).

3.1.4 Fabrication of polymer electrolyte membranes

Polymer electrolytes were produced using Pyr₁₄TFSI ionic liquid and three different polymer hosts

3.1 Materials and devices preparation

including PVDF, PVDF-co-HFP and Poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl) imide (pDADMATFSI). pDADMATFSI was prepared by a simple ion exchange reaction from pDADMAC and LiTFSI. LiTFSI (1.7 g) dissolved in distilled water (2 ml) was mixed with the aqueous solution of pDADMAC (4 g of 20% salt solution in 20 ml of distilled water) with stoichiometric salt to polymer ratio of 1.7. The mixed solution was stirred for 5 minutes at room temperature and the resulting product was filtered and dried at 130 °C in vacuum overnight. The ionic liquid based polymer electrolytes were produced by first dissolving 3 g of a polymer host in 20 ml of acetone, adding Pyr₁₄TFSI ionic liquid drop by drop and stirring the mixture. Different mass ratios of IL and polymer in PE (40:60, 50:50, 60:40 and 70:30) were obtained by adjusting the volume of IL in the initial solution.

Free-standing all-solid PE membranes were prepared by casting the PE solution and doctor blading (*Figure 3.1*). The membrane thickness was varied from 35 to 160 µm by adjusting the height of the blade. Solvent was evaporated at room temperature overnight, followed by annealing at 80 °C under vacuum during 3 hours.

Figure 3.1. Experimental setup of doctor blade casting of PE membrane.

3.1.5 Fabrication of all-solid EDLCs in Swagelok cell

All-solid EDLC devices were assembled for testing in a Swagelok[®] cell by two techniques: 1) impregnation of electrodes with PE solution and 2) sandwiching a free-standing PE membrane between two carbon electrodes. Before assembling EDLC devices all electrodes of CNT fibers normally deposited on aluminum foil were dried at 100 °C under vacuum during 3 hours and cut to a coin-like shape with a projected surface area of 0.785 cm².

Electrode impregnation was performed by adding acetone solution of PE onto the CNT fiber electrodes using a micropipette. The solution was easily seeped through the porous electrodes and hence CNT fibers could be filled with the all-solid electrolyte. In order to obtain electrodes with varied

3.1 Materials and devices preparation

ratios of PE to active material different volume of PE solution was added. The impregnated electrodes were dried at 80 °C under vacuum during 5 hours. Finally, all-solid symmetric EDLCs were assembled by facing two impregnated electrodes (0.785 cm²) and pressing them in 2-electrode Swagelok cell.

All-solid EDLCs were also fabricated by alternative approach employing a free-standing PE membrane used as all-solid electrolyte and separator. The coin shaped devices were prepared by sandwiching a PE membrane (1.13 cm²) between two bare CNT fibers electrodes (0.785 cm²) and pressing the structure in 2-electrode Swagelok cell.

3.1.6 Assembly of self-standing all-solid EDLCs

Fabrication of self-standing EDLCs consisted of sandwiching a preformed PE membrane between two CNT fiber electrodes of similar weight, introducing the composite into a plastic pouch film, applying a moderate pressure of 4 tons during 10 min with an uniaxial press (CARVER model 3853-0) and laminating the device using a conventional pouch laminator. This process produced excellent sealing. Samples were characterized at room temperature at least 1 hour after lamination in order to avoid possible spurious effect arising from the lamination process.

3.1.7 Fabrication of structural power composite with embedded all-solid EDLC

The structural power composites were fabricated by vacuum assisted resin infusion using CF fabrics and a thermosetting resin. A thin self-standing EDLC based on CNT fibers and PE membrane interleaf was placed between CF layers prior to infusion of epoxy resin. The CF laminates comprised 8 layers [0]₈ of Hexcel G0926 (five 370 g m⁻² harness satin fabric with 6K fiber yarns). The epoxy matrix consisted of MEKP hardener, cobalt octoate catalyst and DERA KANE 8084 elastomer-modified bisphenol-A epoxy vinyl resin, which were mixed at the recommended ratio of 100:1.5:0.3. The infusion process involves sealing the fabric lay-up with a plastic bag and applying vacuum to infuse the fluid through the fabric as porous media. Upon opening an inlet port connected to the resin pot the resin flows through the laminate driven only by the pressure gradient between inlet and outlet. Infusion was carried out using two layers of distribution media (98 g m⁻²; Airtech Green Flow 75) which ensures appropriate through-the-thickness flow from both sides of the interleaf to avoid void generation. Polyester EconoStitch (88 g m⁻²) layers were used as peel-ply materials. To avoid direct contact between EDLC interleaf and carbon fabrics double-sided adhesives tape was attached to both sides of the EDLC interleaf. The full curing process takes 48 hours at room temperature, with the matrix reaching its gel point after 30 – 60 minutes. Fabrication of structural composites and their mechanical characterization were performed together with Y. Ou (IMDEA Materials).

3.2 Characterization of materials

3.2.1 Electron and optical microscopy

Optical microscopy

Optical micrographs were obtained in reflection mode with an optical microscope OLYMPUS BX51 equipped with a camera OLYMPUS ColorView, and were acquired using the built-in system (analySIS auto). Each series of the samples was captured at different magnifications, but constant focus and light intensity in order to minimize images variability between samples. The conventional optical system has a fundamental resolution limit of several microns due to wave nature of light.

Scanning electron microscopy

Scanning electron microscope (SEM) enables to achieve considerably higher resolution of the specimens, as compared to the optical microscope, utilizing a beam of electrons to form an image instead of light. The SEM maps scattered secondary electrons from the atoms of the sample, and thereby constructs an image which provides information about the surface morphology. Back-scattered electrons and X-rays occurring after interaction of the electron beam with the sample contain additional information about elemental composition of the material. Here, SEM was employed to determine the morphology of CNT fibers, PE membrane and their composites. SEM images were recorded using a dual beam FIB-FEGSEM microscope (Helios NanoLab 600i FEI) at 5 kV and different magnifications and a Tabletop microscope (Hitachi TM-1000) at 15 kV.

Transmission electron microscopy

Transmission electron microscopy (TEM) is usually employed to explore the atomic and molecular structure of the samples in a sub-nanometric scale. It uses electron beam with well-defined energy, which is normally two orders of magnitude above that of SEM. Unlike SEM, the pattern of the sample is replicated from transmitted electrons passed through the analyzed specimen that restricts the thickness of the sample. In the present work, TEM was used to study the structure and composition of CNT fibers. The images were acquired with a Talos F200X microscope (FEI), operating at 80-200 kV. TEM samples were prepared by dispersing a small amount of CNT fibers in absolute ethanol and sonicating it in an ultrasonic power bath for 30 minutes. After that, the dispersion was drop cast onto a copper TEM grid.

3.2 Characterization of materials

3.2.2 Raman spectroscopy

The Raman spectroscopy is a non-destructive vibrational technique which is used to qualitatively or quantitatively analyze molecular composition of the materials. Raman signal from a sample, also known as Raman scattering, occurs due to inelastic interaction of the single wavelength laser beam with the material that causes changes in polarizability of the sample's molecules in electric field. Every Raman signal corresponds to a specific vibrational frequency of a molecule bond, and it is highly sensitive to the orientation of the bonds. This makes Raman spectroscopy a very powerful method for characterization of carbon nanomaterials and, particularly, CNTs.

In this work, Raman spectra were obtained using Invia Renishaw spectrometer equipped with He-Ne laser at 532 nm in the range from 150-3200 cm^{-1} using 50x objective lens and 10s exposure time. All spectra were averaged from 10 data points acquired from different positions in the sample.

3.2.3 Synchrotron X-ray methods

Small- and wide-angle X-ray scattering

Small-angle X-ray scattering (SAXS) experiments provide structural information of large molecular assemblies like polymers or fibers, whereas Wide-angle X-ray scattering (WAXS) alike powder X-ray diffraction is used to determine atomic and molecular structure of crystals. Simultaneous SAXS and WAXS measurements enables to cover a wide angular range of scattering (up to $\sim 1^\circ$ for SAXS and from 5° for WAXS) that results in a broad length scale from a few microns to a few angstroms. Both techniques are based on detecting the intensity of X-rays elastically scattered from the samples. Due high photon flux, excellent beam collimation and photon density synchrotron radiation offers the possibility to conduct in situ characterization of different materials in dynamic experiments. The schematic of the experimental SAXS/WAXS setup is shown in *Figure 3.2*.

Figure 3.2. Schematic of experimental setup of simultaneous SAXS and WAXS measurements.

SAXS and WAXS measurements were performed at the Non Crystalline Diffraction (NCD-SWEET) beamline 11 of ALBA Synchrotron Light Facilities, which has a tunable wavelength over the range

3.2 Characterization of materials

of 0.62 - 1.90 Å and energy range of 6.5 - 20 keV. A photon counting detector Pilatus 1M (Dectris) with an active image area of 168.7 x 179.4 mm², total number of 981 x 1043 pixels and 25 frames/sec frame rate was used for collecting SAXS patterns. A CDD detector LX255-HS (Rayonix) with an active image area of 168.7 x 179.4 mm², total number of 981 x 1043 pixels and 10 - 140 frames/sec frame rate was utilized for WAXS experiments. The beam size had dimensions of 100 µm (horizontal) x 50 µm (vertical) In all experiments SAXS and WAXS data were calibrated using silver behenate (AgC₂₂H₄₃O₂) and chromium (III) oxide (Cr₂O₃), respectively.

In this work, SAXS was performed in order to study the effect of draw ratio during the spinning process on the degree of CNTs orientation in fibers. SAXS patterns were acquired with 0.5 sec exposure time for densified single filaments of CNT fibers deposited on a metallic hollow frame ($d_{\text{hole}} \sim 6$ mm) used to direct the beam through the sample. SAXS profiles of CNT fibers were averaged from 100 patterns. A pattern of the empty frame was used as a baseline.

WAXS measurements were carried out in order to study time- and temperature-resolved cold crystallization of ionic liquid in polymer electrolyte membranes. WAXS patterns were acquired with 1.5 sec exposure time every 2 °C during melting/cooling cycles using a Linkam controller. A pattern of the empty Linkam cell was collected for subtraction of the baseline. SAXS and WAXS patterns were analyzed using DAWN Science software. In situ WAXS experiment was carried out with the help of Dr. J. P. Fernandez and B. Mas (IMDEA Materials).

X-ray tomography

X-ray tomography is a method used to explore composition, size, shape, orientation distribution and connectivity between individual features/components of the sample. The technique relies on the differences between X-ray absorption coefficients of different sample phases detecting decrease of the X-ray beam's intensity (attenuation) passed through the sample. The computer-assisted reconstruction method allows to convert the X-ray radiographies taken from various viewing angles into a 3D images of analyzed samples.

This technique was utilized to analyze the morphology of structural power composites, distribution of epoxy resin and quantitative contribution of voids to the total volume of the sample. X-ray tomography of the composite samples was performed at the TOMCAT beamline of the Swiss Light Source (Paul Scherrer Institute, Villigen) using a monochromatic X-ray beam energy of 18 keV. X-ray images were acquired with the detector at 40 mm distance from the sample to allow for phase contrast effect. Four consecutive volumes were acquired and stitched together after reconstruction. For each individual volume, 1501 projections were measured with an exposure time of 100 ms per projection and a resolution of 1.625 µm/voxel. The detector system consisted of a 2560 x 2160 pixel CMOS camera coupled to an Optique Peter microscope system with a ×4 objective lens to magnify the visible light

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converted by a LuAG:Ce 20 μm scintillator. The image reconstructions were made using phase retrieval algorithm based on Paganin approach. The measurements were performed by J. J. Torres and analyzed with the help of Dr. F. Sket (IMDEA Materials).

3.2.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative surface-sensitive method used to characterize chemical composition of a material. The technique is based on photoelectric effect, measuring the kinetic energy and number of electrons emitted from the surface (1-10 nm) of the sample exposed to X-ray beam irradiation. XPS spectra are obtained by counting ejected electrons over a range of electron kinetic energies, where peaks correspond to the atoms emitting electrons of a specific characteristic energy.

XPS was utilized to analyze chemical composition of ozonized CNT fibers and quantitatively determine the contribution of different functional groups. The data were collected in a Phoibos 100 (SPECS GmbH) and SPHERA-U7 (Scienta Omicron GmbH) hemispherical energy analyzers with a monochromatic Al-K α ($h\nu = 1486.71\text{ eV}$) X-Ray source. To fit XPS spectra Gaussian/Lorentzian peak shapes and Shirley background profile subtraction were used. The results were analyzed by Dr. B. Aleman (IMDEA Materials).

3.2.5 Thermal analysis

Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a common technique for characterization of materials thermal stability and investigation of temperature and weight changes during decomposition reactions, which often allows quantitative composition analysis. TGA is performed by measuring a mass change as a function of temperature or time. Here, TGA was employed to qualitatively estimate the amount of organic and carbonaceous impurities and residual catalyst in CNT fibers. The experiments were performed with a thermogravimetric analyzer TGA Q500 (TA Instruments) with a ramp of $10\text{ }^{\circ}\text{C min}^{-1}$ under air from 25 to $900\text{ }^{\circ}\text{C}$, under a controlled air flow (90 ml min^{-1}).

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measures the heat flows relative to an inert reference when the sample is heated or cooled, providing quantitative and qualitative information about physical and chemical changes in material involving endothermic and exothermic processes, or changes in heat capacity. DSC was used to study phase changes in ionic liquid based polymer electrolytes during heating and cooling. The measurements were performed on a differential scanning calorimeter Q200

3.2 Characterization of materials

(TA Instruments) equipped with a refrigerated cooling system. Heating-cooling-heating cycles were carried out with the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in the temperature range from $-70\text{ }^{\circ}\text{C}$ to $180\text{ }^{\circ}\text{C}$ to allow complete phase transitions of the PE components and avoid any possible degradation of the material.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) is used to study viscoelastic behaviour of the polymer-based materials. In DMA test the samples are subjected to a periodic mechanical stress during heating or cooling at fixed temperature rate. It measures storage and loss modulus related to elastic and viscous response, respectively, as a function of temperature that provides information about material's stiffness, energy dissipation and mechanical damping. DMA was performed in order to analyze mechanical behaviour of PE membrane and pure PVDF-co-HFP membrane at different temperatures. The test was carried out on a Dynamic Mechanical Thermal Analyser TA Q800 (TA Instrument) in a tensile mode. Free-standing membranes were cut into rectangular shapes with dimension of $10\text{ mm} \times 5\text{ mm} \times 0.2\text{ mm}$ (length, width and thickness, respectively). The storage modulus, loss modulus and the loss tangent were obtained as function of temperature from -130 to $120\text{ }^{\circ}\text{C}$, at fixed frequencies of 1 Hz , oscillatory amplitude of $30\text{ }\mu\text{m}$, and heating rate of $3\text{ }^{\circ}\text{C/min}$. The experimental data were analyzed with a TA Universal 2000 software. All thermal analysis tests were carried out with the help of Dr. J. P. Fernandez (IMDEA Materials).

3.2.6 Gas adsorption analysis

Gas adsorption, also known as BET gas adsorption, is widely employed technique for analysis of various properties of porous solid materials. It is based on the phenomenon of physical adsorption of inert gas molecules on the surface of analyzed samples. To avoid any interactions between the adsorbate and adsorbent nitrogen gas is commonly used. The analysis of adsorption isotherms showing the change in the total volume of adsorbed molecules by measuring the change of gas pressure provides comprehensive information about materials pore structure, including specific surface area, porosity, pore volume and pore size distribution.

To calculate the surface area of analyzed sample Brunauer–Emmett–Teller (BET) theory is most commonly applied. It is based on an extension of the Langmuir monolayer model for multilayer adsorption assuming that the adsorptive molecules in the first layer act as sites for molecules in the second layer and so on for molecules in the higher layers. It presumes that the adsorbed molecules do not interact with each other and that the occupation probability of a site does not depend of the occupancy of neighboring sites. Such artificial conditions of the BET theory restricts applicability of the BET equation to a limited range of the adsorption isotherm, typically $p/p^0 \sim 0.05\text{--}0.35$. [208] For this reason, the BET monolayer capacity (n_m) should be always obtained from the best linear fit of the isotherm.

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The BET equation in the conventional linear form can be expressed as:

$$\frac{p/p^0}{n(1-p/p^0)} = \frac{1}{n_m C} + \frac{(C-1)}{n_m C} (p/p^0), \quad (3.1)$$

where n is the amount of nitrogen adsorbed at the relative pressure of p/p^0 and C is a constant associated with the isotherm shape. C values in the range of 80–150 for nitrogen at 77 K indicate the formation of well-defined monolayers on many non-porous and mesoporous adsorbents.[208, 209] The monolayer capacity n_m calculated from the linear regression of the BET plot of $(p/p^0/[n(1-p/p^0)])$ versus p/p^0 can be directly used to calculate specific surface area as follows:

$$SSA = \frac{n_m \cdot L \cdot \sigma}{m}, \quad (3.2)$$

where m is the mass of the sample, L is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$) and σ is the average area occupied by each molecule in the completed monolayer, which for nitrogen at 77K corresponds to 0.16257 nm^2 assuming that the monolayer has the liquid form of close-packed structure.[208, 209]

At the same time, it appears that BET model often becomes invalid for the characterization of microporous adsorbents.[210, 211] The specific surface area of micropores can be determined using t-plot method, which describes the statistical thickness of the film of adsorptive on a non-porous reference surface. The experimental isotherm can be transformed into a t-plot by replotting the amount adsorbed (n) against the standard multilayer thickness (t) at the corresponding p/p^0 , and according to de-Boer[212]:

$$t (\text{\AA}) = \left(\frac{13.99}{0.034 - \log(p/p_0)} \right)^{1/2}, \quad (3.3)$$

The slope of the linear section of t-plot gives the value of external surface area, and the intercept of the linear fit in the low pressure range is taken as the microporous volume.

The choice of procedure for analysis of pore sizes strongly depends on the particular features of analyzed samples. Among various classical approaches proposed for characterization of mesoporous materials, Barrett-Joyner-Halenda (BJH) method appears to remain the most popular. It describes the relationship between volume of capillary condensate and relative pressure. The model assumes applicability of the Kelvin equation, which predicts the pressure at which adsorptive will spontaneously condense in a cylindrical pore of a given size, and that all pores have a cylindrical shape. Condensation occurs in pores that already have some multilayers on the walls. Therefore, the pore size can be estimated from the Kelvin equation (relation between the pore radius and the relative pressure) and the statistical thickness equation (dependence of the statistical film thickness on the relative pressure). The distribution of pore size is represented by the derivatives $dV(\log d)$ of total pore volume, derived from the amount of adsorbed nitrogen, as a function of logarithm of pore diameter $\log d$.

3.2 Characterization of materials

In this study, gas adsorption experiments were carried out using a Gemini VII 2390 Surface Area Analyzer (Micromeritics) with N₂ at 77 K. The samples were dried first at 100 °C in air atmosphere for 24 hours and later degassed at 300 °C under vacuum for 3 hours prior to the measurements. The adsorption/desorption isotherms were obtained at 77 K by allowing 6 s for equilibration between each successive point. Specific surface area of CNT fibers was estimated applying the BET model to adsorption branch of the isotherm within the linear region of the BET plot. To estimate contribution of microporous t-plot analysis has been employed. The pore size distribution and pore volume were determined by the BJH method applied to the desorption isotherm data.

3.3 Mechanical test

3.3.1 Tensile tests of CNT fibers and PE membranes

Tensile test of CNT fibers and PE membranes were performed using a Textechno Favimat tensile tester with a 2N induction load cell. The samples were placed vertically between two pairs of grip blocks closed by an adjustable-force spring. In order to avoid a slack of samples small pretension of 0.0025 N/tex was applied. A continuous strain rate of 0.5 mm/min was used until complete failure of the sample. Densified single-filaments of CNT fibers exposed to mechanical test had a length of 20 mm. The obtained tensile properties were normalized with respect to the mass per unit length of the fibers (specific gravity, SG). The linear density of CNT fibers was obtained by weighing the sample of a known length estimated from the rate and time of the fiber spinning and confirmed by the vibroscopic method. The specimens of free-standing PE membranes had a rectangular shape with dimension of 10 mm x 5 mm (length and width, respectively). The thickness varied between 74 - 98 µm and was measured for every individual sample. The results were averaged from 3 and more than 20 experiments for PE membranes and CNT fibers, respectively. The stress-strain measurements on CNT fibers were performed by Dr. V. Reguero (IMDEA Materials).

3.3.2 Tensile test of CNT fiber/PE membrane composites

The tensile test of the EDLC sandwich structure of CNT fiber sheets and PE membrane were carried out with an INSTRON 5966 dual column tabletop universal testing system using a gauge length of 15 mm and a test speed of 0.5 mm min⁻¹. In order to ensure that the specimen is firmly gripped and is set to undergo a tensile test the samples were fixed on the edges between two rigid strips of plastic with deposited fresh epoxy on its surface and pressed until complete resin curing. The dimensions of the specimens were determined with a digital micrometer and varied in the range 1.35 – 1.60 mm (length), 1.01 – 1.14 mm (width) and 70 – 120 µm (thickness). Specific properties obtained by dividing load by sample linear density gave similar values to those based on the cross-section stress normalized by

3.3 Mechanical test

specific gravity, thus confirming that the determination of sample cross section is accurate. The mass fraction of fibers was determined by weighing CNT fiber sheets and the PE membrane before assembly for each EDLC device. Volume fraction was calculated taking densities of 1.4 and 1.78 g cm⁻³ for Pyr₁₄TFSI and PVDF-co-HFP, respectively. For CNT fibers, the density in the composite was estimated as 0.7 g cm⁻³ based on previous results infiltrating high molecular weight thermoplastics.[213] The estimation of potential improvement of the composite mechanical properties was evaluated based on experimental results, assuming that the sandwich structure of PE membrane and CNT fibers follows the rule of mixture:

$$E_c = f \cdot E_f + (1 - f) \cdot E_m, \quad (3.4)$$

where E_c , E_f and E_m are mechanical characteristics (tensile strength or modulus) of the composite, CNT fibers and PE membrane, respectively, and f is the volume fraction of the fibers in the composite ($f = V_f/(V_f + V_m)$). A rule of mixture was also used to determine composite strength.

3.3.3 Bending test of structural composites

Four-point bending test of structural composites was carried out on rectangular cross-section beams with a Universal electromechanical testing machine (INSTRON 3384), using a displacement rate of 1 mm/min. The tests were performed according to ASTM D7264/D7264M-0726 standards. The beam dimensions were 250.0 mm x 40.0 mm x 2.9 mm, for the sample length, width and thickness, respectively. The load span and the support span were set at 100 mm and 200 mm, respectively. The bending stress was calculated for every point on the load-deflection curve using the following equation:

$$\sigma = \frac{3PL}{4bh^2}, \quad (3.5)$$

where σ is the bending stress at the outer surface in the load span region (constant moment), P is the total applied force measured with the load cell, L is support span, b is width of the beam and h is thickness of the beam. The maximum bending strain at the outer surface also occurs at mid-span, and it may be calculated as follows:

$$\varepsilon = \frac{4.36\delta h}{L^2}, \quad (3.6)$$

where ε is maximum strain at the outer surface and δ is mid-span deflection obtained from the testing frame actuator displacement. Mechanical characterization of the structural composites was performed together with Y. Ou (IMDEA Materials).

3.4 Electrochemical methods

Electrochemical methods are used to characterize the response of materials to applied potential/current, which provides information about electrochemical processes occurring in the system and electrochemical behaviour of the analyzed material. Typically, electrochemical cell consists of two or three electrodes immersed into electrolytic media, which transports the electric charge generated on the electrodes through ionic conduction. In three-electrode configuration (*Figure 3.3a*) reference electrode (RE) with constant electrochemical potential measures and controls the potential on the analyzed working electrode (WE), without passing any current. Current on the WE is balanced by passing the current through counter electrode (CE), which should not participate in electrochemical processes. Thus, the potential changes of the WE are measured independent of changes that may occur at the CE, which enables to study the specific processes taking place at the WE. In order to avoid any limitations in the kinetics of the electrochemical process, CE must possess total capacitance higher than the capacitance of the WE.

In two electrode configuration (*Figure 3.3b*) CE and RE are shorted on one of the electrodes and the potential across the complete cell (WE, electrolyte and CE) is measured. Therefore, the two electrode configuration can be used whenever the precise control of the interfacial potential is not critical (e.g. characterization of SC devices). The electrochemical analysis techniques such as cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy are the most common methods employed to characterize electrochemical properties of electrode materials and devices.

Figure 3.3. Schematic representation of a) three electrode and b) two electrode configurations of electrochemical cell.

3.4 Electrochemical methods

3.4.1 Cyclic voltammetry

CV is one of the most widely used techniques for qualitative and quantitative characterization of the material's electrochemical properties and specific processes occurring at the electrodes. It provides information about the kinetics and thermodynamics of electron-transfer processes, and analysis of coupled electrochemical reactions or adsorption processes. CV is a potential controlled method measuring the current flow through the cell during sweeping the voltage applied between two potential limits. The common representation of CV results in which the current response is plotted as a function of voltage is shown in *Figure 3.4*. The potential is swept from V_1 to V_2 and back to V_1 . The rate at

Figure 3.4. Schematic showing the cyclic voltammetry curve of ideal capacitive material.

which this is achieved is the voltammetric scan rate (V/s). A purely capacitive material demonstrates rectangular CV curve, where the total area of the box in the CV corresponds to the total charge associated with both ion absorption and ion desorption. Any deviation from ideal capacitive behaviour translates into the changes of CV shape, which indicates the nature of observed alterations (e.g. presence of redox reactions, electrochemical degradation of the electrolyte, low electrical conductivity of the electrode material etc).

In this work, CV experiments were carried out in a glass cell with three-electrode configuration using platinum mesh as a counter electrode and silver wire as a pseudoreference electrode. The working electrode was made by connecting the CNT fiber sample to a platinum wire. For characterization of the ozonized CNT fibers in the aqueous electrolyte, Hg/HgO was employed as reference electrode. Scan rates applied ranged from 5 to 1500 mV s^{-1} and the voltage window varied from 2 - 3.5 V for $Pyr_{14}TFSI$ ionic liquid electrolyte and 1.2 V for 1M KOH aqueous electrolyte. All measurements were performed using a Biologic VMP multichannel potentiostatic–galvanostatic system and the data was analyzed with EC-Lab software. Specific capacitance of the analyzed sample was obtained by

integrating the area under CV curves and normalizing by mass of active material according to the equation:

$$C = \frac{\int_{E_1}^{E_2} i(E) dE}{2m\nu(E_2 - E_1)} \quad (3.7)$$

where E_1 and E_2 are cutoff potentials in CV, $i(E)$ is the instantaneous current, m is the mass of active material, ν is the potential scan rate.

3.4.2 Galvanostatic charge-discharge

Galvanostatic CD is a common technique used to evaluate the performance of electrochemical devices. CD curves represents the alteration of voltage along the time during applying a constant positive (charge) and negative (discharge) current within limited voltage range. The potential between the two electrodes is measured. *Figure 3.5* shows typical CD curve with triangular-shaped profile, characteristic of purely capacitive EDLC.

Figure 3.5. Schematic representation of CD profile for EDLC device.

In this study, CD tests of EDLC devices based on CNT fibers were performed from 0 to 3.5 V for IL-based electrolytes and from 0 to 3.5 V using varied current densities from 1 to 50 mA cm⁻². EDLCs were characterized in a conventional two-electrode Swagelok cell employing two coin-shaped electrodes (0.785 cm²) of CNT fiber film infiltrated with liquid electrolyte and separated by cellulose paper separator (130 μm). All-solid EDLCs were assembled and tested by CD both in Swagelok cell and as free-standing devices using PE membrane as electrolyte source and separator. CD was applied to estimate specific capacitance, energy density, power density, equivalent series resistance (ESR) and cycling stability of EDLCs. Specific capacitance of full devices was calculated from the slope of

3.4 Electrochemical methods

discharge curve as:

$$C_{cell} = \frac{I}{slope} \quad (3.8)$$

Specific capacitance of a single electrode in the symmetric device was obtained as:

$$C_s = 4C_{cell} \quad (3.9)$$

Values of real energy (E_{real}) and power (P_{real}) densities and were calculated by integrating discharge curves of full devices according to the equations:

$$E_{real} = I \int V dt, \quad (3.10)$$

$$P_{real} = \frac{E_{real}}{t_{dis}}, \quad (3.11)$$

where I is the constant current applied and t_{dis} is discharge time. ESR was estimated from CD data as:

$$ESR = \frac{\Delta V}{2I}, \quad (3.12)$$

3.4.3 Electrochemical impedance spectroscopy

The EIS method consists in measuring the response of an electrode to a sinusoidal potential modulation at different frequencies (ω) and small voltage amplitude of 5-10 mV, where linear dependence between potential perturbation ($V(\omega)$) and current response ($I(\omega)$) can be assumed. Therefore, impedance ($Z(\omega)$) can be described similar to Ohm's law as:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{|V_0| \sin(\omega t)}{|I_0| \sin(\omega t - \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t - \phi)}, \quad (3.13)$$

where ϕ is a phase shift of the current with respect to the potential, E_0 and I_0 are amplitudes of potential and current, respectively, and ω is the radial frequency ($\omega = 2\pi f$, where f is in Hz). Using theory of complex functions impedance can be represented as:

$$Z = |Z|(\cos\phi + i \cdot \sin\phi) = Z' + iZ'', \quad (3.14)$$

where Z' and Z'' represent real and imaginary parts of the impedance, respectively. EIS data is often shown in a Nyquist plot which consists in plotting the imaginary impedance component against the real impedance component (Z') at each frequency, as shown in *Figure 3.6*. Such a complex impedance plane plot enables to fit the experimental curve to an equivalent electrical circuit and extract the circuit components. Measuring the impedance at different frequency enables observe different process in the

studied system. The high frequency region normally corresponds to resistive behaviour of the electrode, while low frequency range describes its capacitive behaviour.

Figure 3.6. Schematic of the Nyquist plot with impedance vector.

In this thesis, EIS was employed for various purposes, including the measurement of ionic conductivity of PE membranes, differential capacitance of CNT fibers as a function of electrode potential and analysis of resistive response and complex capacitance of the EDLCs.

Ionic conductivity of PE membranes

Ionic conductivity of PE membranes at different temperatures was measured using two-electrode Swagelok cell in which a coin-shaped membranes (1.13 cm^2 area and $70 - 120 \text{ }\mu\text{m}$ thickness) were sandwiched between two stainless steel pistons. The samples were placed in the dynamic climate chamber (BINDER, Model MK 53 (E2)) and impedance spectra were obtained in the frequency range from 1 MHz to 10 mHz at the bias voltage of 0 V with a potential amplitude of 10 mV and at different temperatures each of which was stabilized for 20 minutes before the EIS measurements. Ionic conductivity was calculated as:

$$s = \frac{t}{R \cdot A}, \quad (3.15)$$

where, t is the thickness of the membrane, A is the geometrical area of the membrane and R is the resistance obtained from the intercept of the curve with the real axis on a Nyquist plot.

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Differential capacitance and conductivity of CNT fiber electrodes

Measurements of differential capacitance and electrical conductivity of CNT fiber electrodes under polarized conditions were performed in a 3-electrode configuration. *Figure 3.7* depicts the schematic of the setup used. The sample was charged by applying and holding a constant voltage for 10 min before each impedance measurement was started. The corresponding EIS was determined at the bias voltage at 10 mHz and voltage amplitude 10 mV. The experiments were carried out by starting at 0 V (against Ag reference) and sequentially increasing the voltage stepping the potential in ± 0.1 V increments. Capacitance values were calculated from experimental data according to equation:

$$C_A = -\frac{1}{2\pi f Z'' m SSA}, \quad (3.16)$$

where Z'' corresponds to the imaginary part of the impedance at 10 mHz, m is the mass of the sample and SSA is specific surface area of CNT fibers obtained from BET measurement.

The resistance measurement was performed immediately following the EIS experiment by using a multimeter connected to the CNT fiber electrode by two Pt wires after disconnecting the working electrode from the potentiostat. The sequence of impedance and resistance measurements was repeated at different bias voltages.

Figure 3.7. Schematic illustration of experimental setup for EIS measurement of differential capacitance and conductivity at polarized conditions.

EIS of the full EDLC

As illustrated in *Figure 3.8*, typical Nyquist plot of full EDLC system includes 3 regions: high-frequency region representing purely resistive behaviour, medium frequency part corresponding to diffusion limitations of the cell and low frequency pristine capacitive region. A semicircle at high frequency particularly contains information about the bulk electrolyte resistance (R_s) and ion charge

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transfer resistance between electrode and electrolyte (R_{ct}), obtained as first intercept of the plot with x axis and the diameter of the semicircle, respectively. Equivalent series resistance (ESR), which is a sum of all ohmic contributions, is found as the second intercept of the semicircle with the real Z' axis. When the frequency decreases, the semicircle is followed by a straight line whose tangent to the real axis is 45° . This region is usually called the Warburg curve (Z_w) and it is related to deeper penetration of the signal into the porous structure of the electrode accompanied by diffusion of the electrolyte ions. At low frequency, the imaginary part of the plot sharply increases and a nearly vertical line is observed, indicating a pristine capacitive behaviour. The ions have sufficient time to form double-layer, occupying most of the electrode surface area. Thereby, EDL capacitance (C_{dl}) can be estimated from the imaginary part of low frequency region.

All contributions to the complex Nyquist plot can be represented in an equivalent circuit, simulated based on experimental data. *Figure 3.8* (inset) shows a typical equivalent circuit of an EDLC consisted of bulk electrolyte resistance, charge transfer resistance, Warburg element and EDL capacitance. By fitting the experimental EIS curve with an appropriate equivalent circuit model, the realistic values of each element can be calculated.

In this work, EIS of symmetric EDLCs were obtained in the frequency range from 200 kHz to 10 mHz at a bias voltage of 0 V with a potential amplitude of 10 mV.

Figure 3.8. A typical Nyquist plot for an EDLC cell and its equivalent circuit (inset).

3.5 Other characterization techniques

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3.5.1 Optical transmittance measurement

Optical spectroscopy is a powerful technique widely used to study how a material interacts with light ranging from infrared through ultraviolet. It is particularly useful for measuring absorption/transmission of a sample at various wavelength. Absorption during light propagation happens when the light frequency is resonant with the transition frequencies of the molecules in the analyzed medium that leads to transition among the electronic energy levels of the molecule. The transmission (T) in the medium, defined as the ratio between transmitted intensity (I) and the incident intensity of the light (I_0), is clearly related to the absorption, because only unabsorbed light will be transmitted. According to the Beer-Lambert's law, the intensity of transmitted light can be obtained as:

$$I = I_0 \ln^{-\epsilon Cl}, \quad (3.17)$$

where l is the path length of the sample, C is the concentration of the adsorbing species and ϵ is the molecular extinction coefficient which depends on the frequency of the incident radiation.

The transmittance spectra were acquired using a double beam Shimadzu UV-2600 ultraviolet-visible spectrophotometer which allows to simultaneously measure a sample light beam and reference (BaSO_4) light beam. All spectra were obtained in the wavelength range 300-1000 nm with wavelength resolution of 0.95 nm and wavelength accuracy of 0.5 nm. Each experimental spectra was corrected by subtracting the background spectrum.

3.5.2 Flame retardancy testing

The UL94 vertical burning test is widely employed for characterization of flame retardant properties of materials. It measures ignitability and flame spread of vertical bulk materials exposed to 20 mm-high flame. The flame is applied to the specimen from the bottom end for 10 seconds after which the burning time is recorded. If the sample is not ignited or its burning ceases, the flame is applied for an additional 10 seconds. The classification of the flame retardancy of the material depends on the burning time and the dripping phenomena. In this work, the vertical burning test were carried out using a UL94 vertical flame chamber instrument (Fire Testing Technology, UK) according to the ASTM D3801-10 standard. The 150 mm long and 50 mm wide specimen of CNT fiber/PE membrane/CNT fiber composite with a thickness of around 300 μm was wrapped longitudinally around a 13 mm diameter mandrel before test.

To determine relative flammability of materials limiting oxygen index (LOI) test is often applied. LOI

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is the minimum amount of oxygen in oxygen/nitrogen mixture (vol.%) which is required to sustain the flaming combustion of the material. Unlike qualitative burning tests, LOI provides a numerical measure of flammability. The LOI is measured by placing the samples in a flow of oxygen/nitrogen gas and increasing the concentration of oxygen until the sample will support combustion. The LOI test of the CNT fiber/PE membrane/CNT fiber composite was performed with an oxygen index meter (Fire Testing Technology, UK) according to ASTM D2863-13 standard. The sample dimensions were 125 mm × 6.5 mm × 0.3 mm (length, width and thickness, respectively). The tests were performed with the assistance of L. Zhang (IMDEA Materials).

CHAPTER 4

Textural, mechanical and electrochemical properties of CNT fibers

In this work the study of multifunctional flexible or structural energy storage devices is focused on development of novel electrode materials combining structural and electrochemical functions. Chapter 4 discusses the properties of macroscopic CNT fibers that make them a promising material for flexible and structural supercapacitors. *Section 4.1* introduces the structure of CNT fiber and its relation to textural and mechanical properties of the material. This includes different conditions of fiber production, such as draw ratio, and their effect on mechanical properties, surface area and pore sizes. In *Section 4.2* electrochemical behaviour of CNT fibers was extensively studied in IL electrolyte. Specific character of quasi metallic fibers in electrolytic media related to finite density of states of low dimensional material and quantum capacitance contribution affecting overall electrochemical system were discussed. Energy storage capabilities of CNT fibers examined in half and full cells were revealed and compared to commercial CNT fiber sheets. Determined correlation between thickness of CNT fiber electrodes and power density of EDLCs was discussed.

Finally, *Section 4.3* is devoted to examination of structural, electronic and electrochemical changes in CNT fibers modified by gas phase functionalization. The structural changes in functionalized material were extensively studied and linked to alterations of mechanical properties and electrical conductivity. The influence of ozone treatment on electrochemical performance of functionalized fibers was studied in aqueous electrolyte and in IL media. The Section discusses diversified effect of functional groups enhancing capacitive properties of oxidized fibers through pseudocapacitive contributions of redox

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reactions, improved hydrophilicity and modified electronic structure. The newly acquired properties of functionalized CNT fibers were described both in 3-electrode system and full SC device.

4.1 Textural, structural and mechanical properties of CNT fibers

4.1.1 CNT fiber structure

High aspect ratio nanocarbons in the form of long CNTs are considered as ideal candidates for tough electronics owing to combination of their unique molecular properties with the possibility to assemble them into a network structure such as a fiber. The porosity and mechanical properties of this network should be strongly determined by inter- and intra-particle properties, and by the morphology of the network in terms of orientation and size of the nanobuilding blocks. Therefore, study of CNT fiber structure, its textural and mechanical properties is essential part on the way to understand electrochemical features of the material and employing it in multifunctional energy storage systems.

In this work, CNT fibers were synthesized by direct spinning method, whereby an aerogel of CNTs is directly drawn out of the chemical vapour deposition chamber during growth of CNTs. A schematic representation of this process is depicted in *Figure 4.1a*. A precursor mixture containing carbon source (normally butanol or toluene), catalyst (ferrocene) and promoter (thiophene) is introduced to the reactor heated up to 1250 °C, where reaction occurs. The inert atmosphere in the reactor is controlled by the hydrogen carrier gas, which also plays an active role in synthesis of CNTs. The structure and properties of CNT fibers are closely related to synthetic parameters such as concentration of the precursors and hydrogen in the reactor, precursors feed rate, gas flow rate and draw ratio. This method enables production of large-area uniform samples in semi-industrial quantities, while also offering the

Figure 4.1. a) Schematic representation of the direct spinning process of CNT fiber from the aerogel. Photographs of b) as-spun CNT fiber and c) densified unidirectional CNT fiber sheet.

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possibility to tailor their structure[214] and molecular composition[215, 216] and thus preserve some of the low-dimensional properties of the constituent CNTs on a macroscopic scale. The photograph of typical CNT fiber sample in as-spun state is presented in *Figure 4.1b*. Densification of highly porous as-spun fibers with organic solvents, e.g. acetone, enables to form thin unidirectional sheets (*Figure 4.1c*).

Figure 4.2 presents electron micrographs of CNT fibers at different magnifications, which describe the main features of the material structure. At low magnification (*Figure 4.2a*) the sample appears as a dense array of bundles of CNTs with preferential orientation along the fiber axis. At high magnification, the electron micrograph in *Figure 4.2b* shows a network structure in which CNTs are interconnected by overlapping over substantial lengths, yet they also branch out and thus form pores. The exceptionally long length of the CNTs in these fibers (up to mm scale) implies that they can efficiently transfer stress/energy/charge to adjacent elements even if they are imperfectly packed in other areas. Thus, large porosity and high-performance mechanical properties can coexist in the same material. On the building block scale, the CNTs are highly graphitised and have been appropriately synthesized to have few layers (1–5) and small diameters (average inner diameter of 4.7 nm) (*Figure 4.2c*).

Figure 4.2. Electron micrographs showing CNT fiber microstructure (a) The fiber's network structure of predominantly aligned CNTs forming part of bundles, where they can transfer stress/charge/energy, but also imperfectly packed and giving rise to a large porosity. (b) High magnification SEM micrograph showing CNT bundles branching out. (c) The CNTs of this sample are highly graphitized and have few layers.

Direct spinning process of CNT fibers enables achieving varied degree of fiber's orientation by lowering the concentration of nanotubes in the gas phase and reducing the density of entanglements in the aerogel, thus allowing alignment of fiber's building blocks.[214] Previous works have shown that the degree of CNT orientation in the fibers has a strong effect on the bulk mechanical properties[214, 217] that implies possible changes in textural properties of the material as well. With

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this evidence in mind, it is particularly important to explore the impact of alignment on textural and mechanical properties of the electrodes used in this study. Different degrees of samples orientation were achieved by varying the draw ratio of the spinning process directly related to winding rate. The carrier gas velocity roughly corresponds to 0.3 m min^{-1} , which is several times slower than the speed of fiber's spinning. Thereby, draw ratio represents the rate of aerogel drawing with respect to the gas velocity along the reactor. The degree of orientation upon faster drawing was analyzed by SAXS and quantitatively estimated by comparison of full-width at half maximum (FWHM) values of the azimuthal profile of the CNT reflection.

Figure 4.3a,b shows SAXS patterns obtained for single filaments of CNT fibers spun at 4.6 and 126 draw ratio. SAXS reflection depicts a narrower distribution of the X-ray intensity for the sample produced at higher draw ratio with the FWHM from azimuthal integration decreasing from 37 to 12 (Figure 4.3c). These results indicate clearly defined improvement in orientation of CNT bundles parallel to the fiber axis at higher draw ratio. It is worth mentioning that despite the main interest is related to CNT fiber sheets consisted of many filaments (>300) and further used as electrodes, single filament can be considered as the most accurate scenario for the study of CNTs orientation. In the case of CNT yarns or sheets composed of many filaments the orientational distribution reflected in intensity of SAXS pattern might be significantly broadened by fiber misalignment and thus give overestimates of the FWHM compared to individual CNT fiber filaments.

Figure 4.3. Influence of draw ratio on the CNT orientation along the fiber axis. (a), (b) SAXS patterns obtained for individual filament of CNT fibers produced at draw ratio of 4.7 and 126, respectively, and (c) azimuthal integration of SAXS profiles showing variation of FWHM for different draw ratio.

4.1.2 Textural properties of CNT fibers

Further insight into the pore-network structure of CNT fibers is obtained by gas adsorption/desorption analyses. Despite gas adsorption becomes a widely used technique for characterization of material's

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textural properties, it imposes certain restrictions on the measurements, which are not always considered. The major limitation of the gas adsorption measurement of CNT fibers is associated with the minimum weight of the sample caused by sensitivity of the equipment. The use of a sample with low total surface area can cause substantial deviations of values of adsorbed volume of gas and consequently result in under or overestimated textural properties of the material. Minimum surface area of a sample required to achieve reliable results is 10-15 m², which in case of CNT materials approximately corresponds to 40-60 mg. Such amount of CNT fibers produced by dry spinning process needs 1.5-2 hours of continues drawing, during which uniformity of the sample can be disrupted. Moreover, such limited amount of the material makes accuracy of mass determination and proper degassing process more important. The effect of temperature or partial gas adsorption during sample weighing needs to be totally excluded. Before and during adsorption/desorption measurements different factors should be also considered and adjusted for the type of material exposed to the test, such as necessary drying/degassing conditions, adsorption equilibration time, the number of measured points and the range of relative pressure. For instance, the value of relative pressure is a key parameter for determination of fibers properties, but it directly depends on the temperature and saturation pressure of the system, which can significantly vary during the test. Single measurement of these parameters can cause a noticeable error in obtained isotherm and low reproducibility of measured values. Therefore, the experiments were carried out with extreme caution taking into account all mentioned remarks.

The textural properties of CNT fibers drawn at different rates (i.e. draw ratios) were measured by nitrogen adsorption/desorption analysis. As an example, *Figure 4.4a* depicts the isotherm obtained for the sample produced at mid draw ratio (DR = 63). According to the Brunauer–Deming–Deming–Teller (BDDT) classification, the shape of the isotherm presents mixed features corresponding to both type II and type IV (the intermediate flat region at low P/P_0 corresponds to type II, while hysteresis loop at high P/P_0 corresponds to type IV). Type II is generally found in macroporous materials with a wide distribution of pore sizes but no presence of micropores. Indeed the presence of micropores in CNT fibers was discarded by t-plot determination. At high $P/P_0 > 0.8$ the isotherm exhibits a small hysteresis loop, typically present in type IV isotherms, that reveals capillary condensation in big mesopores and macropores attributed to the presence of big interparticle voids between CNT bundles.

Specific surface area calculated by multi-point BET approach (SSA) appears at 256 m² g⁻¹ and the total pore volume (V_{tot}) at 1.4 cm³ g⁻¹. Linear regression on the multi-point BET in the relative pressure range 0.1 to 0.3 shows the correlation coefficient R^2 of 0.9998 indicating high accuracy of obtained values (*Figure 4.4b*). It is noteworthy, that the literature values of SSA for CNT fibers are scarce, possibly due to the difficulties in producing the ~1–10 km uniform fiber required for typical BET measurement, but they range from 75 to 500 m² g⁻¹. [53, 218–222] Such variation in specific

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Figure 4.4. Textural properties of CNT fibers. (a) N₂ adsorption-desorption isotherm, (b) linear regression on the multi-point BET plot, (c) dependence of specific surface area and total pore volume on the draw ratio, (d) scanning electron micrographs (SEM) showing difference in orientation and packing of CNT bundles in fibers produced at low (4.7) and high (126) draw ratios, (e) dependence of the fiber linear and volumetric density on the draw ratio and (f) TG curves obtained for samples drawn at different draw ratios.

surface area can be attributed to several factors, including difference in intrinsic properties of fibers

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produced by different techniques and challenges associated with gas adsorption measurement of the carbon material. First, the variety of methods of CNT fiber production results in deviation of the material's purity. The utilization of wet spinning method affects the presence of many residual molecules of surfactant and coagulant in the final product. Furthermore, alteration of synthesis condition, e.g. precursor mixture, temperature, size and type of reactor, can also influence on the amount of carbonaceous impurities and residual catalyst contained in the as spun fibers, which lower surface area of the graphitic material (see below, *Figure 4.17d*).

It is especially worthy to consider the impact of draw ratio on textural properties of fibers. A faster drawing of the aerogel enables assembling CNTs in more packed structure with better alignment of CNT bundles. It implies alteration not only of fiber morphology but its porous structure. *Figure 4.4c* shows that increase of draw ratio causes drop of total pore volume in CNT fiber from $1.8 \text{ cm}^3 \text{ g}^{-1}$ (DR = 4.7) to $1.1 \text{ cm}^3 \text{ g}^{-1}$ (DR = 126). As expected higher drawing rate results in condensation of aerogel into a denser fibers with highly packed bundles, thus reducing available free space clearly observed by SEM images (*Figure 4.4d*). The improvement in fiber's packing at different draw ratios can be seen by comparison of linear and volumetric densities depicted in *Figure 4.4e*. Since the mass production of CNT fibers is constant and independent from draw ratio, linear fiber density shows a tendency to decrease with increasing winding rate following the expected inverse relation, whilst volumetric density increases at higher winding rates as the higher degree of alignment improves packing.

Although the increase in CNT alignment leads to reduction of pore volume, the surface area of CNT fibers demonstrate contrary behaviour (*Figure 4.4c*). The reduction in specific surface area of the carbon material at lower draw ratio is expected to be related mainly to increased content of carbonaceous impurities. Slower drawing of CNT fiber is accompanied by prolonged presence of the material inside of the reactor, which promotes longer exposure to low surface area side carbon materials, e.g. amorphous carbon and aromatic hydrocarbons, which are simultaneously produced during decomposition of the precursor. On the other hand, the raise of winding rate results in decrease of amount of non-graphitic impurities and increment of CNT fraction in the fibers which is observed as decline of weight loss in TG curves (*Figure 4.4f*). Therefore, despite the compaction of interbundle space and consequently decline of pore volume the enhancement of draw ratio from 4.7 to 126 affects the enhancement of fibers specific surface area from 240 to $283 \text{ m}^2 \text{ g}^{-1}$.

There is a variety of properties which can alter specific surface area of CNT fibers, such as tube/fiber diameter, bundling, purity and surface functionalization, among which bundling attracts particular attention as specific feature of CNT fibers. Theoretical predictions demonstrated that specific surface area of individual carbon nanotubes consisted of three walls, considering as average for MWCNT fibers produced in this work, with diameter from 5 to 10 nm varies from 480 to $515 \text{ m}^2 \text{ g}^{-1}$. [50]

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However, agglomeration of CNTs to bundles with 5 tubes will lead to the drop of total surface by 30%, with 7 tubes by 43%, with 10 tubes – by half. Therefore, only bundling reduces theoretical surface area of CNTs to 240-360 m² g⁻¹. This rough estimation is based on several assumptions, i.e. all CNTs in bundles are identical and arranged in a perfectly packed network, which considerably mismatches real system. Nevertheless, it gives an idea how significant is deviation of surface area caused by formation of bundles in CNT fibers and indicates how large increment in specific surface area can be reached by debundling of CNTs.

The contribution of micropores during adsorption/desorption of nitrogen molecule was estimated by t-plot method using Harkins and Jura thickness equation. *Figure 4.5a* shows typical t-plot for CNT fibers, where positive intercept of the linear extrapolation to the adsorption axes corresponds to micropore volume and the V/t slope is proportional to the area of pores capable to form multilayer, whereas micropores, which have already been filled by adsorption fluid, cannot contribute further to the adsorption process. The specific surface area of micropores derived from the slope of the t-plot is <2 m²/g indicating negligible contribution of pores with size less than 2 nm. This conclusion contains essential information. The kinetic diameter of nitrogen is 3.64 Å,[223] which means that adsorption of molecules can occur both outside and inside of CNTs, excluding the area between the layers of MWCNTs. According to the obtained results CNTs are arranged very compactly in the bundles during catalytic growth leaving no interstitial space for foreign molecules. Moreover, due to substantial length of nanotubes up to mm scale, internal volume of CNTs could give a significant rise to total surface area of the fibers. Contrariwise, the absence of micropores suggests that CNTs are principally closed during their growth on the ends by catalyst particles or carbon shell blocking the path for nitrogen intercalation as shown in *Figure 4.5c*.

Figure 4.5b confirms that the pore size distribution calculated by BJH method is broad and includes both large mesopores (>10 nm–50 nm) and macropores (>50 nm). Comparison of BJH results obtained for fibers produced at different draw ratios shows that improvement of CNTs alignment by drawing has no additional effect on distribution of pore sizes. Rough estimation by fitting experimental data using Lorentz function reveals nearly identical full width at half maximum of pore volume related to average pore diameter, which was found to be around 60 nm. This also indicates that the decrease of pore volume at higher draw ratio does not involve redistribution of pore sizes and can be related to reduction of large macropores. In summary, the isotherm results are in good agreement with electron micrographs (SEM and TEM) and SAXS data and indicate that the high specific surface area of CNT fibers can be attributed to the external surface of aligned long CNTs that through their assembly form pores in a wide range of sizes.

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Figure 4.5. (a) t-plot showing negligible contribution of micropores to total volume of CNT fibers, b) Pore size distribution calculated by BJH method for CNT fibers produced at low (4.7) and high (126) draw ratio and c) TEM images showing CNTs closed on the ends by carbon shell or catalyst particles.

4.1.3 Mechanical properties of CNT fibers

The key feature of macroscopic CNT fibers is the possibility to assemble this material into a continuous network structure such as horizontally aligned CNT sheets or CNT yarns that can thus withstand large stresses and deformations providing unique combination of mechanical robustness and porosity. The mechanical stability of the CNT fibers derives from their long length approaching the mm scale and it is strongly determined by its morphology in terms of CNTs orientation. Tailoring the degree of alignment of the CNTs in the fiber by varying the draw ratio of the CNT aerogel during spinning process enables maximizing mechanical properties of the material.[214] A higher degree of orientation leads to increase in tensile properties, as observed in the plots of specific stiffness and toughness as functions of draw ratio (*Figure 4.6a*). It shows that specific stiffness increases with draw ratio, whereas toughness (energy-to-break) remains fairly constant.

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Figure 4.6. Mechanical properties of individual filaments of CNT fibers. (a) Dependence of specific stiffness and toughness on the draw ratio. (b) Strain–stress curves for as-spun CNT fibers at a mid draw ratio of 63, showing mechanical performance of the material.

Although the increase in CNT alignment improves their packing and thus reduces some pore volume, as was showed, specific surface area is affected vice versa exhibiting small increment at higher draw ratio (see *Figure 4.4c*). This implies that the electrode material based on highly aligned CNT fibers with mechanical properties in the high performance range can be produced without sacrificing its high surface area for energy storage. Moreover, it should be remarked that orientation effect does not involve any alterations in CNT composition decoupling synthesis of building blocks from their assembly.[214] Therefore, electrochemical behaviour of CNT fibers in electrolytic media is expected to be invariable at different degree of CNTs alignment and to depend only on the small differences in surface area. Accordingly, the fibers produced at a mid draw ratio of 63, corresponding to a relatively slow winding rate of 20 m min^{-1} that facilitates electrode fabrication and its uniformity, can be considered as a sample representing average electrochemical performance of the material. *Figure 4.6b* shows stress–strain curves for this sample (the test was repeated several times). Its specific tensile strength and modulus are 0.35 GPa per SG and 20 GPa per SG , respectively, similar or above aluminum and steel. Toughness, taken here as fracture energy, is 35 J g^{-1} , comparable to aramid fiber (Kevlar) and carbon fiber (CF). It is worth mentioning that to study the effect of draw ratio on mechanical properties of CNT fibers, individual filaments were subjected to tensile test in order to avoid additional effect of fiber misalignment in multi filament CNT yarns. The presence of artefacts related to filament misalign in CNT fiber sheets or yarns can lead to noticeable lowering of mechanical properties depending on number of filaments and degree of misalignment.

Unlike conventional carbon electrode materials, performance of which is mainly determined by their textural properties, tough electrodes should be consider in context of their multifunctionality, where mechanical properties and light weight are also relevant. Depending on desired application, electrodes can be oriented on operation under flexion, at large strains or have a high tensile strength that dictates different mechanical requirements. Specific toughness, representing the energy absorbed by the

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material up to fracture, indirectly comprises a measure of both strength and strain-to fracture. The comparison of specific surface area and toughness for different carbon materials is showed in *Figure 4.7*. Activated carbon provides extremely high specific surface area up to $2000 \text{ m}^2 \text{ g}^{-1}$, [224] but very low toughness even in a mixture with polymer binder ($<0.2 \text{ J g}^{-1}$). [225] Conversely, as-produced carbon fibers achieve high toughness of 14 J g^{-1} , but negligible surface area of around $0.2 \text{ m}^2 \text{ g}^{-1}$. [102] Commercial activated carbon fibers provide substantially increased specific surface up to $1100 \text{ m}^2 \text{ g}^{-1}$, but demonstrate reduced values of toughness 8.4 J g^{-1} due to highly defective structure formed during chemical activation. [102] Buckypaper made by filtration of randomly oriented CNTs have $150\text{--}600 \text{ m}^2 \text{ g}^{-1}$, [226] corresponding to surface area range of regular CNTs, but short lengths and random distribution of nanotubes limiting specific toughness of the material typically by 0.5 J g^{-1} . [79, 227] Interestingly, CNTs assembled into continuous macroscopic fibers might present simultaneously high toughness, up to 100 J g^{-1} , [53] and specific surface area of $76\text{--}250 \text{ m}^2 \text{ g}^{-1}$. [218, 220] In addition, as discussed above most of CNT fibers exhibit high porosity with pore sizes in the meso ($10 \text{ nm}\text{--}50 \text{ nm}$) and macro scale ($>50 \text{ nm}$) suitable for adsorption of wide variety of molecules and ions that extends the materials' potential for application in energy storage systems.

Figure 4.7. Comparison of specific surface area and toughness for different carbon materials.

Apart from excellent mechanical and textural properties of CNT fibers it is necessary to highlight their high electrical conductivity. Owing to the unique structure composed of network of very long CNTs, fibers can eventually translate outstanding conductivity of individual nanotubes to macroscopic scale. However, imperfection of building blocks, non-uniformity of produced nanotubes in terms of chirality, diameter, length and number of walls, defects of constituent CNTs and impurities like amorphous carbon and aromatic hydrocarbons lower their performance. Therefore, as-produced fibers have extremely wide range of conductivities related to the quality of as-made material and presence of foreign compounds. [53, 228] Measured longitudinal electrical conductivity of as-spun CNT fibers

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at mid draw ratio consisting of multiwalled CNTs reaches up to $3.5 \times 10^5 \text{ S m}^{-1}$ and it can be tailored depending on CNT type (number of walls, diameter etc.) and purity of the material.

4.2 Electrochemical properties of CNT fibers

4.2.1 Electrochemical characterization of CNT fibers in half-cell

Planar samples of CNT fibers were characterized by cyclic voltammetry in a half-cell. Pyr₁₄TFSI ionic liquid was chosen as the electrolyte because it combines a high ionic conductivity ($2.7 \times 10^{-3} \text{ S cm}^{-1}$ at RT) and wide electrochemical stability window (up to 3.5 V).[229, 230] At the same time, evaluation of electrochemical behaviour of CNT fibers in common aqueous electrolytes is not convenient due to highly hydrophobic nature of this material coming from the conjunction of high surface roughness of fibers and high graphitization of CNTs. All CV experiments exhibited a coulombic efficiency ($\mu = Q^+/Q^-$) higher than 95%, thus considered as within the reversibility criteria even at high voltages. *Figure 4.8a* presents the specific capacitance values as a function of scan rate and potential limits (voltage window). The values of capacitance are very high at low scan rates (5 mV s^{-1}) and high voltage (3.5 V), and then decrease due to slow charging caused by localized π states and limitations in electrolyte ion diffusion.[231] At 3.5 V specific capacitance reaches a maximum of 78 F g^{-1} at 5 mV s^{-1} , comparable to the values reported for wet-spun CNT fibers (48 and 100 F g^{-1} for as-spun and annealed CNT fibers, respectively)[232], electrochemically activated CNT fibers (100 F g^{-1})[233] and graphene in Pyr₁₄TFSI ionic liquid.[234] At low voltages of 2.0 V and 2.5 V, capacitance remains close to $20\text{--}24 \text{ F g}^{-1}$, in line with literature data.[98, 219, 235]

More interestingly, *Figure 4.8b* shows that all CV curves exhibit so-called butterfly-shape, with the current changing substantially with applied voltage. Such behaviour differs from the ideal EDLC system assuming linear and constant dependence between charge and potential normally manifested in rectangular CV curves. In order to better understand the origin of observed deviation it is necessary to discuss possible reasons which can alter electrochemical performance of a supercapacitor. Deviations from rectangular CV curves can be introduced by non-Faradaic phenomena associated with poor electrical conductivity or small pore sizes of electrode material. In the first case high scan rate can affect the capacitance causing more resistive respond of the material resulting in more elongated shape of CV.[236, 237] Continuous narrowing of the cyclic voltammogram shape at high voltage can also occur due to ion sieving in electrodes with small pore sizes.[238] Exceptionally high electrical conductivity and broad pore size distribution of CNT fibers enable excluding both factors explaining alterations in electrochemical behaviour. Among Faradaic processes contributing to changes in the shape of CVs there are redox reactions, electrochemical degradation of the electrolyte and electrochemical activation of the electrode material. Characteristically, only redox reactions can

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Figure 4.8. (a) Specific capacitances (C_s) at different scan rates and voltage limits. (b) CV curves at a scan rate of 50 mV s^{-1} .

achieve fairly high reversibility showing admissible coulombic efficiency. TEM images and Raman spectra (Figure 4.2c and 4.11b) show that CNTs exhibit mostly high graphitization indicating negligible fraction of surface functional groups further confirmed by XPS (Figure 4.2I), whereas catalyst metal particles remain in inactive state being encapsulated by graphite layers. In order to confirm that and to exclude substantial effect of impurities and pseudocapacitive contribution of redox active functionalities to electrochemical performance of the material, CNT fibers were purified by an annealing pretreatment. The treatment consisting in annealing at 400°C in argon for 2 hours leads to desorption of organic impurities, confirmed by TGA (Figure 4.9a). Electrochemical test of as-spun and annealed samples does not show any significant difference in their capacitive behaviour (Figure 4.9b) discarding the contribution of Faradaic reactions from surface functional groups. Therefore, the origin of specific deviation from ideal capacitive performance presumably lies not in composition but in quasi-metallic nature of CNT assemblies in fibers.

Figure 4.9. (a) TG curves (in N_2) and (b) CV curves at scan rate of 50 mVs^{-1} obtained for as-spun and annealed CNT fiber samples

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It is worthy to highlight that distinctive electrochemical nature seen in butterfly-shape of CV curves primarily refers to electronic structure of the electrode material and is independent from features of electrolyte. *Figure 4.10* presents cyclic voltammograms obtained for CNT fibers in 1M KOH aqueous (*Figure 4.10a*) and 1M TBAPF₆ in PC (*Figure 4.10b*). Both curves demonstrate nonlinear increase of the current during charge and discharge equivalent to the one obtained in Pyr₁₄TFSI with parabolic shape of CV and its minimum near pzc. The type of electrolyte, its properties and concentration can influence the position of pzc relative to the reference or even overall shape of CV curve,[239, 240] but the strong dependence of current on applied voltage is observed irrespective of electrolytic media.

Figure 4.10. Butterfly-shaped CV curves at scan rate of 50 mVs⁻¹ obtained for CNT fibers in (a) 1M KOH aqueous electrolyte and (b) 1M TBAPF₆ in propylene carbonate.

In low dimensional systems observed deviation from ideal capacitive behaviour has another origins which arise from “chemical” or also called “quantum” capacitance.[241] To better understand the reasons for emergence of quantum capacitance, two big classes of electrically conductive materials, metals and semiconductors, should be considered. *Figure 4.11a,b* depicts the qualitative difference between them by comparison of energy diagrams. The main feature of metallic materials is large density of states (DOS) near the Fermi level, whereas semiconductors possess a relatively small bandgap. In the first case, the applied potential shifts the full band structure through electrostatic potential drop over the double layer without alteration of the Fermi level position relative to the band edges (*Figure 4.11a*). Conversely, when an electrochemical system has a lack of DOS near the Fermi level the insertion of charge carriers by applied potential at the electrode/electrolyte interface raises the Fermi level and overcomes the energy spacing to fill or deplete each subsequent state, whilst the band structure remains unchanged (*Figure 4.11b*). Thereby, a considerable part of the electrode potential goes to a change of chemical potential of the material (eV_Q) instead of contributing to electrostatic change of the double layer (eV_{EDL}). In this way, the applied potential will be split between electrostatic component corresponding to formation of electric-double layer and chemical component

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related to the change of the DOS occupation. The presence of two contributions can be represented as two capacitances in series, where the first one corresponds to EDLC (C_{EDL}) and the second one to quantum capacitance (C_Q) (Figure 4.11c).[242, 243] Thus, the total capacitance is dominated by the smaller one that explains the difference between classical metallic electrodes with extremely large DOS near the Fermi level due to the large electron density and Fermi energy (e.g. Au) and semiconducting material with a distinctive band gap.

Figure 4.11. (a) Energy diagram showing difference in behaviour of (a) metallic system ($C_Q \gg C_{EDL}$) and (b) semiconducting system with dominance of quantum capacitance ($C_Q \ll C_{EDL}$). (c) Simplified representation of total interfacial capacitance between electrode and electrolyte consisted of electrostatic double-layer capacitance and quantum capacitance connected in series.

The behaviour of semiconducting materials is also common for quasi-metallic carbons. It has been measured experimentally for highly oriented pyrolytic graphite (HOPG),[244] highly graphitic carbon fiber derived from phenolic resin,[245] some activated carbons,[246] graphene[239] and SWCNT[247–249]. The voltage dependence of capacitance in graphitic systems was initially attributed to a space charge capacitance component corresponding to the spread of charge into the bulk carbon electrode.[246] However, unlike traditional electrodes such as metals, in low dimensional systems it represents a quantum capacitance which follows the DOS near the Fermi level, closely revealing features such as the linear dispersion in graphene[239] and the band gap (if present) and van Hove singularities in CNTs.[250] A particular feature of these low dimensional nanocarbons is that DOS around the intrinsic Fermi level is very low, about $0.0022 \text{ states atom}^{-1} \text{ eV}^{-1}$ for HOPG,[251, 252] in contrast with metals such as Pt or Au, for which DOS is $0.28 \text{ states atom}^{-1} \text{ eV}^{-1}$ and fairly constant for a broad range of energies.[253] For such materials with finite density of states near the Fermi level and consequently limited density of mobile charge carriers, the charge carrier concentration starts playing a crucial role and quantum capacitance begins to dominate.

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The results of CV indicate that CNT fibers act similar to the second type of materials with significant contribution of quantum capacitance. For bulk samples of CNTs containing a distribution of diameters and chiral angles, the joint DOS resulting from superposition of individual DOS retains a low density of states near the Fermi level, although it loses single-molecule features such as van Hoff singularities and leads to a smooth almost linear lineshape.[254]

More common way to study electrochemical alterations caused by quantum capacitance is by measuring differential capacitance as a function of electrode potential by a potential scan at a fixed low frequency (herein 10 mHz) where DOS occupancy is stationary.[239, 255–257] *Figure 4.12a* shows the plots of capacitance normalized by surface area (C_A) and relative longitudinal conductivity, obtained at different applied potential. The data are directly determined by impedance measurements in the half-cell and referenced to potential at zero charge (pzc). Unlike typical electrode materials, exhibiting differential capacitance and conductivity independent on the electrode potential, CNT fiber shows characteristic V-shaped curves, attributed to quantum capacitance origin.[239, 256] There is a good correspondence between the two plots, confirming the quasimetallic nature of the CNT fiber electrodes and the relevance of the DOS for charge screening and transport.

The minimum of differential capacitance of $3.2 \mu\text{F cm}^{-2}$ at 0 pzc is in excellent agreement with values for HOPG ($3 \mu\text{F cm}^{-2}$)[244] and high quality CVD graphene samples ($2.5\text{--}3.5 \mu\text{F cm}^{-2}$)[258]. It confirms the high degree of graphitization of the CNTs produced by the direct spinning process. The precise lineshape of density of states near the Fermi level of the constituent few-layer CNTs in the fibers is beyond the scope of this study; however, it should be noted that assuming a linear dispersion relation in the range ($0 - \pm 1 \text{ V}$) the left and right slopes of C_A/pzc are $5 (\mu\text{F cm}^{-2})\text{V}^{-1}$, comparable to 3–5 layer high-quality graphene with aqueous electrolyte ($2.5\text{--}7 (\mu\text{F cm}^{-2})\text{V}^{-1}$)[258].

Figure 4.12. (a) Area normalized differential capacitance and normalized conductivity vs. potential at zero charge (pzc) calculated from electrochemical impedance at 10 mHz and different bias voltages. (b) Raman spectra of a CNT fiber sample electrode showing upshifts in the 2D and G bands as a consequence of hole doping after impregnation with IL.

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Another important observation consisted in the shift of pzc relative to the Ag reference electrode by about 0.35 V suggests electrochemical carrier doping by the ionic liquid. Raman spectroscopy measurements before and after contact with IL show an upshift of the 2D and G bands of 5 cm^{-1} (2677.5 ± 0.5 to 2682.5 ± 0.1) and 2 cm^{-1} , (1579.6 ± 0.33 to 1581.6 ± 0.11) respectively, (*Figure 4.12b*). Raman measurements confirm that indeed the IL acts as a p-dopant[259, 260] providing roughly one carrier per 150 C-atoms at 0 V (assuming 275 cm^{-1} per carrier per C-atom)[261, 262]. The general mechanism of electrochemical doping can be depicted by the following reaction: $150C + h^+ + TFSI^- = [150C]^+TFSI^-$. The results above highlight the fact that even bulk samples of CNT fiber electrodes preserve the low dimensionality of their nanobuilding blocks. While control of the type of CNT could have at first seemed only to affect textural properties of electrodes, the electronic structure of CNTs and its coupling to the electrolyte at a molecular level are clearly relevant in these systems.

The concept of coexistence of quantum and EDL capacitances for quasimetallic CNT fibers with finite DOS enables explaining some individual features in electrochemical behaviour of the material. For instance, the results of nitrogen adsorption measurements showed that increase of CNT alignment in fibers at higher draw ratio leads to small raise of specific surface area that implies an increment in the number of ions adsorbing on the CNT surface and consequently a modest growth of specific capacitance. However, CV test reveals nearly identical shape and area of CV curves (*Figure 4.13a*) indicating similar values of specific capacitance for fibers produced at different draw ratios. Despite slight increase of EDL capacitance, the total capacitance remains predominantly unaffected due to prevalence of quantum capacitance. In the same time, decoupling synthesis of fibers building blocks from their assembly during variation of drawing conditions preserves electronic structure of CNTs and thus retains quantum capacitance. *Figure 4.13b* shows plots of differential capacitance as a function of electrode potential for CNT fibers produced at draw ratios of 4.7 and 63. Both samples exhibit fairly similar symmetric V-shaped curves, but distinctively CNT fibers with lower surface area obtain higher area-normalized capacitance at pzc. This is in good agreement with CV results denoting close values of total capacitance, which are unequivocally changed after normalization by different effective area. These results particularly highlight the fact that increase of quantum capacitance by modification of CNTs electronic structure is an essential step towards further improvement of energy storage capabilities by extension of the surface area.

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Figure 4.13. (a) Butterfly-shaped CV curves and (b) V-shaped curves of area-normalized differential capacitance at different potential for CNT fibers produced at low (4.7) and medium (63) draw ratios.

4.2.2 Electrochemical characterization of CNT fibers in full-cell

To investigate how the behaviour of the electrode/electrolyte interface, discussed in previous section, affects the performance of the final devices, CNT fiber-based EDLCs were assembled and characterized. Symmetric EDLCs were built by assembling a Celgard separator between two CNT fiber coin-shaped electrodes of similar weight in a two electrode Swagelok cell using pure $\text{Pyr}_{14}\text{TFSI}$ electrolyte. The electrochemical characterization of the devices was performed using electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge. EIS measurements on CNT fiber-based EDLC give a Nyquist plot, presented in *Figure 4.14a*. EIS results disclose presence of a vertical straight line at low frequencies typical of capacitive behaviour and a semicircle at high frequency which is conditioned by many factors including the resistance of the bulk electrolyte and the interfacial

Figure 4.14 (a) Nyquist plot and (b) real (C') and imaginary (C'') parts of complex capacitance as a function of frequency obtained from EIS for CNT-fiber based EDLC.

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properties between electrolyte and CNT fiber electrode. Due to the high electrical conductivity of the fibers and the presence of accessible meso and macropores, the equivalent series resistance (ESR) extrapolated from the second intersection of the semicircle with the X axis is only around 30 Ohm, half of that in similar EDLC prepared with activated carbon electrodes.[263]

The EIS results also provide indirect information concerning the shape, size and distribution of pores. The data show the absence of the diffusion control region typically observed in impedance loci as a slope of $\pi/4$ (45°) at medium frequency. This confirms that formation of the double layer in the pores of CNT fibers is not diffusively limited owing to the features of material's textural properties. Importantly, due to the frequency dependence of the penetration depth of the AC wave given as Penetration Depth (PD) = $(Z/R)^{1/2}$, where Z is the impedance and R is the resistance per unit length down the pore, not only size but also shape of pores determines the impedance loci.[264] The decrease of frequency is accompanied by deeper penetration of the signal into porous media of the electrode and thereby the influence of textural properties on electrochemical behaviour can be distinguished through Warburg diffusion region at medium frequency with distinct straight line at 45° angle. Direct transition from pristine resistive behaviour to low frequency capacitive region and a lack of clear Warburg element indicate reasonably full accessibility of fiber pores excluding any diffusion limitations caused by pores size or shape.

To better understand the behaviour of the EDLC based on CNT fibers during ion adsorption evolution of the complex capacitance was analyzed. The complex capacitance can be described as:

$$C(\omega) = C'(\omega) - jC''(\omega), \quad (4.1)$$

where $C'(\omega)$ and $C''(\omega)$ are the real and imaginary parts of the complex capacitance, respectively. The first component calculated as $C'(\omega) = \frac{Z'}{\omega|Z|^2}$ is a characteristic feature of the electrode and electrode/electrolyte interface which represents the capacitance of the cell measured during constant-current discharge, while the second one is related to an energy dissipation by an irreversible process, including the dc-conductance and other relaxation-associated loss, and can be obtained as $C''(\omega) = \frac{Z''}{\omega|Z|^2}$. Figure 4.14b shows the real $C'(\omega)$ and imaginary $C''(\omega)$ parts of the complex capacitance plotted as a function of the ac frequency. $C'(\omega)$ sharply increases between 860 and 25 Hz and exhibits nearly full capacitance at frequency of 0.1 – 0.01 Hz. However, despite achieving high capacitance at low frequency the plot does not reach its plateau still demonstrating growing tendency. This indicates that a certain fraction of fibers' pores still remains vacant for ions and capacitance of the EDLC can be further enhanced simply by extension of the time period intended to ions adsorption.

The plot of imaginary capacitance $C''(\omega)$ obtains a peak within the given frequency range that indicates an effective pore utilization of ions. Relaxation time constant, which corresponds to a time

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required to release 50% of the total stored energy of the EDLC, calculated from the frequency of the $C''(\omega)$ maxima as $\tau_0 = \frac{1}{2\pi f_0}$ was found to be 44 ms, comparable to multilayered graphene film (13.3 ms)[265] and much shorter than for activated carbon (260-1250 ms)[266, 267]. Moreover, fairly viscous IL gives considerable rise to τ_0 , which is two orders of magnitude higher for other EDLCs based on mesoporous carbon and Pyr₁₄TFSI electrolyte ($\tau_0 = 8$ s)[268]. Small relaxation time constant is a strong factor of power features which denotes fast ion diffusion in CNT fiber electrodes derived from full accessibility of the material's pores and high electrical conductivity of the fibers.

Figure 4.15a shows the charge–discharge voltage profile of CNT fiber-based EDLC from 0 V to 3.5 V at 5 mA cm⁻². As opposed to a conventional EDLC in which the slope of the voltage profile is constant (and consequently so is capacitance), in CNT fiber-based EDLC the dependence of capacitance on bias voltage manifests as bulging of the CD profiles. Approximate contribution of quantum capacitance to the discharge curve can be estimated by plotting a straight discharge line with the slope at pzc, which represents a theoretical non low dimensional carbon material with SSA of CNT fibers (Figure 4.15a). Since quantum capacitance contribution in non low dimensional carbons is relatively negligible, total capacitance can be defined as $C_{\text{tot}} = C_0 \times \text{SSA}$, where C_0 is area-normalized capacitance of HOPG ($C_0 = 3 \mu\text{F cm}^{-2}$)[244] similar to that of CNT fibers (C_A) at pzc. The results show that the quantum capacitance of the electrodes produces substantial increase in the real energy densities of the device, obtained by the integration of the discharge curves. Figure 4.15b presents a reciprocal derivative of the discharge profiles for tested CNT fiber-based EDLC and theoretical non low dimensional carbon, which is proportional to the total capacitance of the device ($C_{\text{tot}} \sim 1/(dV/dt)$). Introduction of quantum capacitance component translates into non-linear behaviour of the capacitance of EDLC device and an increase of total capacitance by a factor of 1.5-2. This rough

Figure 4.15 (a) Galvanostatic CD profile and (b) reciprocal derivative of discharge curve at 5 mA cm⁻² comparing the behaviour of CNT fiber-based EDLC to theoretical non low dimensional carbon.

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estimation reveals that the enhancement of electrochemical properties of CNT fiber-based EDLC induced by low quantum capacitance are substantial as compared to non low dimensional carbons. Furthermore, the results suggest that energy storage capabilities of CNT fibers might be further improved by increase of C_Q through modification of electronic structure of the CNTs. This can be achieved by variety of approaches including change of CNT structure during CVD growth, chemical doping of nanotubes with heteroatoms and functionalization.

As the thickness of electrodes is known to affect electrochemical performance of supercapacitors[269, 270], it is of particular interest to consider the effect of thickness of CNT fibers on device's properties. Because there are no major changes in volumetric density as the CNT fiber is continuous laid down on the winder, electrode thickness can be taken as proportional to mass loading. Demonstrative representation of observed tendencies can be seen by comparison of charge-discharge curves obtained for symmetric EDLCs with large difference in CNT fiber mass loading. *Figure 4.16a* reveals a distinct decrease of the slope of discharge profile from 0.471 V s^{-1} to 0.121 V s^{-1} proportional to increase in mass loading of the active material from 2.12 to 0.58 mg cm^{-2} . Thereby specific capacitance normalized by mass of electrodes, which is reciprocal to the slope according to *Equation 3.8*, remains unchanged as well as ESR following identical for both devices Ohmic drop (0.1 V). Accordingly, specific capacitance, calculated from the slope of the discharge profile and normalized by mass of CNT fiber electrodes, is independent of electrode thickness in the investigated range at around 23 F g^{-1} (*Figure 4.16b*). Although equivalent series resistance (ESR) extracted from the ohmic drop exhibits some variations in the range of $30\text{-}65 \text{ } \Omega$ probably due to changes of applied pressure in the cell, approximately it is kept constant at around $45 \text{ } \Omega$ (*Figure 4.16c*). Constant specific capacitance and ESR imply invariable values of energy density corresponding to area under discharge curve normalized by mass of active material (*Figure 4.16b*). On the other hand, CD test in *Figure 4.16a* discloses that discharge time is linearly proportional to mass loading. Therefore, since energy density is independent of mass loading, specific power, estimated as $P_{real} = E_{real}/t$, is inversely proportional to mass loading.

The Ragone plot in *Figure 4.16d* clearly depicts that whereas energy density remains fairly constant at around 11 W h kg^{-1} (at 2 mA cm^{-2}), power density drops rapidly as mass loading (or electrode thickness) is increased. These results indicate that electrode thickness limits power density per electrode mass through an inverse relationship and that thicker electrodes are inherently slower to charge. Such behaviour is in contrast with many studies showing the resistance dependence of electrode thickness,[2, 271, 272] although it is predicted for a highly conductive electrode when all surface area is accessible for ions and micropore transport effects are neglected. For an ideal symmetric EDLC under a constant applied current the discharge time can be expressed as[273]: $t_D = \frac{V - V_0 - IR_\infty}{2I} \times C_s \rho_v L$, where V is the voltage applied, V_0 is the initial potential, I is the current, R_∞ is the electrode resistance, C_s is the gravimetric capacitance, ρ_v is the volumetric density, and L is the

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electrode thickness. This simple at first sight dependence has very important application for any real device of practical relevance, enabling to elucidate requisite parameters of EDLC in order to achieve desired electrochemical properties. It also helps to implement accurate comparison of power and energy densities reported in the literature, which can appear high only on account of sample dimensions or electrodes' masses.

Figure 4.16 Electrochemical properties of CNT fiber sheet electrodes as a function of electrode mass loading (i.e., thickness) obtained from charge-discharge at 2 mA cm^{-2} . a) Comparison of CD curves for EDLCs with low (0.58 mg cm^{-2}) and high (2.12 mg cm^{-2}) CNT fiber mass loadings. b) Energy density, specific capacitance, c) ESR and d) Ragone plots for EDLCs with different mass loadings of CNT fiber electrodes.

Figure 4.17a also includes results from CD of EDLC devices with commercial CNT fiber sheets. Commercial CNT fiber samples from suppliers 1 (Tortech, mass loading 2.51 mg cm^{-2}) and 2 (INFRA, mass loading 3.70 mg cm^{-2}) fall approximately on the same line as those produced in-house (IMDEA), while this particular sample from the supplier 3 (Nanocomp, mass loading 2.76 mg cm^{-2}) has a shorter CD time and thus a lower figure-of-merit of power density times mass loading. CD profiles included in Figure 4.17b are in line with measurements of CNT fiber in half-cell (Figure 4.17c). At 5 mV s^{-1} and 3.5 V , for example, materials from Tortech and INFRA suppliers and produced in-house have a specific capacitance around 31 F g^{-1} , whereas that for the Nanocomp sample

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is only 24 F g^{-1} . The observed difference in electrochemical performance is explained by difference in composition of CNT fibers. The sample from Nanocomp has a significantly higher fraction of impurities (41 wt% residual catalyst) confirmed by TG analysis and clearly detected by TEM (*Figure 4.17d*). As a consequence the reduced gravimetric surface area reflects in decrease of specific capacitance of the sample determined both by CV and CD tests.

Figure 4.17 a) Discharge time and power density obtained from charge-discharge at 2 mA cm^{-2} as a function of electrode mass loading. b) Charge-discharge profiles of EDLC containing CNT fibers at 2 mA cm^{-2} and c) cyclic voltammograms from half-cell measurements of CNT fibers produced in-house and at scale-up facilities (commercial suppliers Tortech, INFRA and Nanocomp). (d) TG curves comparing thermal behaviour of commercial CNT fibers and TEM images of S3 sample showing high content of metal particles (inset).

Finally, the conjunction of highly-porous electrodes that preserve the electronic features of their low dimensional building blocks and the high electrochemical stability of the $\text{Pyr}_{14}\text{TFSI}$, compared for example to aqueous electrolytes, results in high energy density values of EDLCs. Maximum capacitance, energy and power values obtained for the device with CNT fibers mass loading of 0.81 mg/cm^2 (thickness of 24 nm) were as high as 32 F g^{-1} and 14 Wh kg^{-1} at 1 mA cm^{-2} and 58 kW kg^{-1} at 50 mA cm^{-2} , respectively. The cycling stability of the device was also measured, by

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performing 10000 charge–discharge cycles at 3.5V and intermediate current density of 5 mA cm^{-2} . Presented in *Figure 4.18a* as changes in specific capacitance and real energy density against number of cycles, the data show very good cyclability. The capacitance retention was found to be higher than 93% while the energy density increased by 14% during the first 5000 cycles and then remained nearly constant for the next 5000 cycles. Initial increment of capacitance and energy density during first 100 cycles correspond to electrochemical activation of the material, when further growth of energy can be related to ambient temperature fluctuations which result in decrease of the ohmic drop. *Figure 4.18b* depicts comparison of CD profiles of 5 and 5000 cycles which confirms reduction of the ohmic drop giving rise to the area under discharge curve and thereby increasing energy of the EDLC.

Figure 4.18. Cycling stability test of the EDLC. (a) Capacitance and energy retention over 10 000 cycles at 5 mA cm^{-2} and (b) comparison of CD profiles at 5 and 5000 cycles.

4.3 Gas phase functionalization of CNT fibers

Although CNT fibers exhibit promising multifunctionality for employment in energy storage systems their properties can be further tailored to expand the range of application. First, macroscopic fibers of CNTs are known to be strongly hydrophobic due to conjunction of high surface roughness and low surface energy of the material. This behaviour limits the use of CNT fiber in electrochemical devices based on aqueous electrolytes, which normally achieve high power performance due to large ionic conductivity of the electrolytic media and consequently low resistance of EDLC devices. Second, specific electrochemical behaviour of the fibers caused by intrinsic electronic properties and reflected in low quantum capacitance limits overall capacitance of the system. This indicates that energy storage capabilities of the EDLC can be further enhanced by modifying electronic structure of CNTs, for example by introducing different functional groups acting as dopants and altering the DOS. Functionalization of CNT fibers with redox active groups along with using aqueous electrolytes can also give considerable rise to total capacitance through reversible Faradaic reactions increasing pseudocapacitance of the material.

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Therefore, it is of interest to study the impact of functionalization on the properties of CNT fibers, which in case of CNT fibers is particularly challenging since the macroscopic morphology of the anisotropic material must be preserved. There is clearly the need for developing protocols that accurately control the level of CNT fiber functionalization, and accordingly interfacial processes, yet preserving the morphology of the fibers.

4.3.1 The impact of functionalization on structure and physico-chemical properties

The most common route to functionalize CNTs is through wet-chemical methods which are usually accompanied by dispersion of CNTs in homogeneous system allowing tight interaction with components of different chemical nature, although it must be properly fine-tuned not to compromise excessively CNT electronic properties. This traditional approach is unsuitable in case of CNT fibers, which require preservation of macroscopic morphology. Gas-phase reactions can be considered as ideal solution for this purpose, among which the use of ozone is of particular interest since it can be conveniently generated in situ by irradiation of air with a high-energy UV lamp.

This method was explored by post-functionalization of as-spun CNT fiber samples through time-controlled exposure to ozone, which was generated in situ with the UV lamp of a UV–ozone cleaner under ambient conditions. Ozonized samples exhibit the newly acquired hydrophilicity, demonstrated by immersing the fiber in the bi-phasic system composed of toluene and water (*Figure 4.19a*). In *Figure 4.19b* it can be clearly seen that water spreads on and penetrates into the functionalized material at a significantly higher rate relative to the pristine CNT fibers. For CNT fibers exposed to ozone for

Figure 4.19. Evidence of hydrophilic nature of CNT fibers after functionalization. a) When immersed in a biphasic system composed of toluene-water, pristine CNT fibers locate in the organic phase (left), while functionalized CNT fibers locate in the aqueous phase (right). Methylene blue was added as a water-soluble dye to visualize more clearly the two phases. b) Optical micrographs monitoring the spreading of a water droplet after contact onto films of CNT fibers functionalized for 5 minutes (top) or 120 minutes (bottom). The dashed lines mark the advance of the liquid front.

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5 minutes, the water droplet preserves spherical shape upon contact with the fiber, after which it gradually infiltrates into the carbon pores and slowly spreads over it. Prolongation of ozone exposure to 2 hours results in instant wetting of CNT fibers with more uniform droplet spreading and noticeably faster water infiltration. For reference, pristine samples show no evidence of wetting by water on these time scales.

The adjustment of functionalization process enables not only altering hydrophilic behaviour of the material, but also provides a degree of surface engineering control in terms of the concentration of functional groups and subsequently electronic properties particularly interesting for electrochemical application of CNT fibers. For this purpose, samples subjected to different reaction times were analyzed in more detail. Raman spectroscopy was employed to characterize the impact of different functionalization time on structural changes of the carbon material. Raman spectra are shown in *Figure 4.20a*. Each of them consists of the three relevant signals: 1) the D-band due to out-of-plane vibrations from A_{1g} mode (c.a. 1350 cm^{-1}), 2) the G-band due to the in-plane tangential E_{2g} mode (c.a. 1580 cm^{-1}) and 3) the 2D-band (or G') corresponding to the overtone of D-band and resulting from a two-phonon lattice vibrational process (c.a. $2600\text{--}2700\text{ cm}^{-1}$).[274]

Overall, pristine CNT fibers are strongly resonant, with a very low D-band intensity and an asymmetric G-band indicative of few-layer highly graphitized CNTs. Raman spectra change rapidly upon exposure to ozone. First, D-band experiences a distinctive growth of the peak intensity, which is proportional to the level of defects and irregularities in that structure of CNTs.[275] An increase in the fraction of defective CNTs is also reflected in a raise of a weak shoulder of the G-band at 1612 cm^{-1} corresponding to D' band, which is a double resonance feature induced by disorder and defects.[276, 277] Likewise, there is a gradual enlargement of the D+G-band at 2933 cm^{-1} more pronounced for highly functionalized samples ($\geq 30\text{ min}$). It is not well elucidated what this change is attributed to, but it can be referred to disruption on stacking between CNT layers, similar to exfoliation effect, due to deeper penetration of destructive ozone molecules into inter layers of multi-walled nanotubes at longer ozone exposure. *Figure 20b* shows evolution of D, D' and G+D peak intensities normalized by intensity of G-band over increase of reaction times, ranging from 5 minutes to 2 hours. All three ratios exhibit rising tendency at longer treatment confirming clear disruptive impact of the functionalization on the π electron network of carbon nanotubes. Moreover, comparing the Raman spectra in the D-G band range (*Figure 4.20c*), it can be found an enhancement of the valley lines between the D and G bands, which is also attributed to functionalization effect.[278] *Figure 4.20d* shows that the effects of functionalization are generally stable in time, a common concern associated with low-temperature UV irradiation or similar treatments.[279, 280] The manifestation of functionalization effect is evident already after 5 minutes of exposure to ozone. Such trend continues as the treatment is prolonged up to two hours, but at that point the concentration of defects is considered excessive for practical applications.

4.3 Gas phase functionalization of CNT fibers

Figure 4.20. Raman characterization of functionalized CNT fibers. a) Normalized Raman spectra of pristine and functionalized CNT fibers, b) I_D/I_G , $I_{D'}/I_G$ and I_{D+G}/I_G ratios for different ozonation time, c) Normalized Raman spectra showing increase of intensity of the valley between D and G modes and d) evolution of the I_D/I_G ratio upon increase of reaction time and its stability over time up to 3 weeks.

To study the chemical environment of CNTs and confirm incorporation of functional groups onto CNT fibers XPS analysis was further utilized. *Figure 4.21a* presents normalized XPS survey spectra of pristine and ozone treated samples. The comparison of the oxygen to carbon relative content with increasing reaction time, obtained from the peak areas, shows a rise from 0.09 to 0.40. The detected small amount of oxygen in the pristine CNT fibers mainly originates from adsorbed molecular species. By contrast, after ozone treatment the observed increase in the O1s region corresponds to the formation of oxygen functional groups bounded to carbon (*Table 4.1*). *Figures 4.21b,c* show XPS spectra for C1s core level of pristine and 5 minute-treated CNT fibers with their corresponding fitting components. The C1s emission of pristine CNT fibers (*Figure 4.21b*) is peaked at 284.5 eV, apparently corresponding to sp^2 -hybridized graphitic carbon in the tube structure ($\text{C}=\text{C}$). Upon the deconvolution of the C1s peak three smaller components were additionally observed: the peak at 285.1 eV attributed to sp^3 carbon ($\text{C}-\text{C}$), the peak at 286.1 eV related to oxygen-containing species ($\text{C}-\text{O}$) and the peak at 290.2 eV representing $\pi-\pi^*$ transitions.[281, 282] First two intensities are associated

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with carbonaceous particulates and amorphous carbon produced as by-products of the CVD reaction, while the presence of the component at the higher binding energy range of 290 eV indicates high degree of CNT fiber graphitization. Deconvolution of the C1s peak for 5 minutes functionalized fiber depicted in *Figure 4.21c* reveals growing contribution of the components at high binding energies (from 285 eV to 290 eV) relative to sp^2 carbon and the sharp loss of the $\pi-\pi^*$ transition band at high treatment time (>30 min) (*Table 4.1*), confirming introduction of functional groups onto CNT fibers. Furthermore, the approximate assignation of oxygen-containing components of C1s peak discloses presence of C-O (at 286.0 ± 0.6 eV), C=O and O-C=O (at 289 ± 1 eV). [282–284] *Table 4.1* summarizes quantitative results of XPS and shows how the ratio of O1s peak area with respect to C1s peak ($O1s/C1s$) increases with ozone treatment exposure time.

Figure 4.21. XPS data for pristine and ozonized CNT fibers. (a) Normalized survey spectra showing the increment of O1s to C1s ratio with ozone exposure time, and normalized XPS spectra in the C1s region and their deconvolutions for (b) pristine and (c) 5 minutes functionalized CNT fibers.

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Table 4.1. Fitting details of C1s XPS spectra and the ratio between oxygen-carbon (C-O, C=O and O-C=O) and sp² carbon components of pristine and functionalized CNT fibers.

Oxidation time	C=C		C-C		C-O		C=O, O-C=O		$\pi-\pi^*$		O1s//C1s
	Peak (eV)	Area (%)	Peak (eV)	Area (%)	Peak (eV)	Area (%)	Peak (eV)	Area (%)	Peak (eV)	Area (%)	
Pristine	284.5	42	285.1	33	286.1	12	0	0	290	13	0.09
5 min	284.4	30	284.8	30	285.4	22	288	6	290	12	0.24
15 min	284.5	30	284.9	26	285.4	19	288	13	291	12	0.26
30 min	284.5	30	284.9	42	286.0	9	289	19	0	0	0.29
120 min	284.5	21	284.8	45	286.0	18	289	16	0	0	0.40

The impact of ozone treatment on mechanical properties and electrical conductivity of fibers was studied for individual filament of CNT fibers before and after 15 minutes of exposure to ozone. The results are summarized in *Table 4.2*. The short time treatment leads to reduction of toughness, but increase of modulus, while preserving the specific strength. This is a consequence of the removal of surface impurities and the introduction of surface functional groups in CNTs taking part in adjacent bundles. The presence of functional groups at the interface between two nanotubes without crystallographic registry under shear is expected to improve load transfer; the functional groups protrude normal to the CNT axis and provide corrugation[285] in the otherwise flat potential between turbostratic graphitic layers[286]. CNT fibers exposed to thermal, plasma oxygen and electron beam irradiating treatment were reported to exhibit similar behaviour.[287–289] Characterization of longitudinal electrical conductivity of functionalized fibers demonstrates the decline of properties relative to the pristine material. *Table 4.2* shows that 15 minutes of ozone exposure provokes the drop of conductivity from 11188 for pristine fibers to 5900 S m⁻¹. This is a consequence of the derivatisation of the conjugated system, with the corresponding binding of otherwise de-localized charge, and also of a reduced contribution from surface adsorbates acting as dopants.[290, 291]

Table 4.2. Longitudinal mechanical and electrical properties of pristine and functionalized CNT fibers.

CNT fibers	Tensile strength (GPa SG ⁻¹)	Tensile modulus (GPa SG ⁻¹)	Specific toughness (J g ⁻¹)	Electrical conductivity (S m ⁻¹)
Pristine	0.46 ± 0.13	21.4 ± 6.2	35.5 ± 26.4	11.2 × 10 ³
15 min functionalized	0.52 ± 0.12	43.7 ± 10.7	8.4 ± 4.4	5.9 × 10 ³

Longer functionalization times significantly reduce mechanical properties, and thus handling that considerably complicates the mechanical test. The gradual fading of mechanical properties at prolonged functionalization can be affected by sidewall damage,[292] vacancies,[293] broken layers and other defect sites along the CNT walls resulting from transformation of the sp² C=C bonds to out

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of plane sp^3 C-C bonds, which induce weakening of the fracture strain and tensile strength[294], large reduction in Young's modulus[295] and deterioration of the torsion behaviour of CNTs[296]. TEM observation (*Figure 4.22*) confirms noticeable degradation of CNTs after long exposure to ozone.

Figure 4.22 TEM images of CNT fibers a) before and b) after ozone treatment (120 minutes).

4.3.2 Electrochemical properties of functionalized CNT fibers

Modification of the properties of CNT fibers by ozone treatment assumes alteration of their electrochemical behaviour. For instance, the formation of oxygen functional groups on CNTs walls might provide a redox activity which contributes with pseudocapacitance to the overall capacitance.[297–299] Acquired hydrophilicity of functionalized samples also makes most of CNT fiber surface available for adsorption of ions dissolved in aqueous electrolytes. Furthermore, introduction of defects and functional groups implies changes in electronic structure of CNT fibers which cause alteration of DOS and consequently quantum capacitance.[300, 301]

To evaluate changes in electrochemical behaviour of CNT fibers exposed to ozone treatment the pristine and functionalized samples were first characterized in a three-electrode system using 1M KOH electrolyte. *Figure 4.23a* shows CV results obtained for CNT fibers subjected to different reaction times at a scan rate of 50 mV s^{-1} . The CV curves indicate that the pristine sample has a low capacitance, which in this case is a consequence of the electrolyte not capable to infiltrate inner pores of the electrode and instead only interacting with the outer surface of the fibers. In contrast, the functionalized samples show a considerable increase in capacitance, as well as the presence of a pair of broad Faradaic peaks at -0.37V and -0.43V , evidently indicating the coexistence of an EDL capacitance and pseudocapacitance. Longer functionalization times result in an increase of these pseudocapacitive peaks and in the overall capacitance of the sample. The observed Faradaic processes

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correspond to redox reactions of oxygen-containing functionalities, presence of which was confirmed by the above XPS data.[37, 302]

Figure 4.23. (a) CV curves obtained in 1M KOH electrolyte at a scan rate of 50 mV/s and (b) capacitance plots for CNT fibers subjected to different functionalization times.

Considering possible redox processes for different surface functional groups in aqueous KOH electrolyte the following reactions were proposed:[37]

Among them the acidic sites on carbon, namely carboxyl and phenol groups, participate only in quasireversible or irreversible processes (*Equations 4.2, 4.4*) especially in alkaline KOH electrolyte.[37, 299] In the KOH medium these groups can be diminished or neutralized transforming into basic sites, which are adverse to the pseudocapacitive reactions.[303] Thus, it can be assumed that the major contribution to pseudocapacitance of functionalized CNTs origins from carbonyl groups (*Equation 4.3*) (or quinone groups as a particular case for graphitic carbons). The crucial role of carbonyl groups in electrochemical performance of supercapacitors has been described for various types of porous carbon materials.[304, 305]

The values of specific capacitance at different scan rates calculated from the area of the CV curves are presented in *Figure 4.23b*. A comparison of pristine fibers and samples treated for 5 min shows a large increase from 14 to 23 Fg⁻¹, whereas 2 hours of exposure leads to 46 Fg⁻¹. Functionalized CNT fibers retain 90-93% of their capacitance at higher scan rates (*Figure 4.23b*), indicating good rate capability due to the combination of easily accessible electrode pores in meso and macro scale with high conductivity and small ions size of the electrolyte.

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These results denote considerable improvements of CNT fiber electrochemical performance in a symmetric SC device. *Figure 4.24* depicts results of CD and EIS obtained for pristine and functionalized samples in the full-cell. The discharge profiles in *Figure 4.24a* show an increase in capacitance and no changes in equivalent series resistance from the value for pristine CNT fibers. The impedance data (*Figure 4.24b*) are consistent with CD results indicating similar value of ESR around $3 \Omega\text{cm}^2$ and absence of noticeable difference in ion charge transfer resistance. Moreover, alike pristine sample Nyquist plot for functionalized fibers reveals direct transition from semicircle at high-frequency region to vertical straight line at low frequencies without distinctive diffusion limitations. This observation indicates that feasible increase of surface area does not involve appearance of micropores determining diffusion problems during charge of fibers. The capacitance plots in *Figure 4.24c* obtained from charge-discharge measurements reveal substantial increase of specific capacitance for CNT fibers after 2 hours of ozone treatment from 7 to 30 F g^{-1} . Consequently, the devices with functionalized CNT fibers maintain similar values of power at $20\text{--}30 \text{ kW kg}^{-1}$ while experiencing a large increase in energy density (*Figure 4.24d*) from 0.34 to 1.29 Wh kg^{-1} in comparison with pristine material.

Observed improvements in electrochemical properties are attributed to the dual effect of induced functional groups making CNT fiber more hydrophilic and thus allowing the aqueous electrolyte successfully infiltrate carbon electrodes, and contributing an additional pseudocapacitive component to the total capacitance through reversible redox reactions. Moreover, functionalization is known to enhance specific surface area SSA of CNTs to different extent by debundling, cutting and opening CNTs and introducing topological defects on carbon nanotubes surface.[306–308] Owing to mild conditions of ozone treatment the main impact of functionalization on CNT fiber surface area can be derived from introduction of morphological defects. Experimental measurement of the SSA for functionalized CNT fiber is hindered by the required minimum weight of the sample ($\sim 50 \text{ mg}$) for nitrogen sorption test. CNT fibers with desired minimum overall surface area poses either very large or very densified sample, which cannot be easily and homogeneously functionalized. Nevertheless, since contribution of Faradaic reactions to the increasing overall area of CV curves at higher functionalization times cannot be decoupled from EDL capacitance rising due to improved infiltration of the material or enhanced SSA, all three components should be considered as potential endowment to the change in electrochemical performance of functionalized CNT fibers.

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Figure 4.24. (a) Discharge profiles, (b) Nyquist plots, (c) Capacitance and (d) Ragone plots comparing electrochemical performance of pristine and 120 min-functionalized CNT fibers in symmetric SC device with 1M KOH electrolyte.

In addition to the effects mentioned above, functionalization has an impact on the electronic properties of the CNT fibers, thus on quantum capacitance and in the experimentally-determined overall capacitance of the material. These effects can be observed in an ionic liquid, which produces full wetting and does not undergo redox reactions over a wide range of potential due to high electrochemical window of Pyr₁₄TFSI and absence of water molecules (H^+/OH^- ions) required for redox processes associated to functional groups. A comparison of cyclic voltammograms, now in absence of pseudocapacitive reactions (*Figure 4.25a*), shows that functionalized samples lose the characteristic “butterfly” shape of pristine samples and have instead a profile more similar to a bulk 3D carbon. Indeed, the evolution of nonlinear dependence between current and voltage in CVs to nearly constant I-V curve can be clearly followed by the increasing reaction time. Similarly, EIS measurements give a much weaker dependence of differential capacitance against electrochemical potential (*Figure 4.25b*). This behaviour is in good agreement with DFT calculations for

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functionalized graphene[301] predicting a peak of DOS near the Fermi level which is reflected in the peak of differential capacitance at pzc.

The obtained results demonstrate that functionalization has a large electronic effect on the total capacitance. This is attributed to the introduction of oxygen-containing groups producing new energy states near the Fermi level,[300] similar to dopants[258] or charged impurities,[239] and which increase quantum capacitance and thus total EDL capacitance. Noting that these capacitive contributions are in series, the increase in C_Q makes it less accessible, making the electrostatic component corresponding to formation of electric-double layer more dominant and hence reducing the dependence of total capacitance on electrochemical potential.

Figure 4.25. (a) CV curves at 50 mV/s and (b) Differential capacitance calculated from electrochemical impedance at 10 mHz obtained for pristine and functionalized CNT fibers in IL.

Figure 4.26a represents CD profiles for symmetric EDLC devices based on pristine and functionalized CNT fibers obtained in the full-cell. Unlike pristine fibers demonstrating non-linear slope of discharge profile, functionalized material exhibits triangular shape of charge-discharge curve typical for ideal EDLC behaviour. This is in well accordance with results obtained in half-cell confirming extinction of quantum capacitance dominance and thus increases the overall capacitance. The maximum specific capacitance of CNT fibers exposed to ozone for 2 hours is increased from 29.5 to 45.4 F g⁻¹ relative to pristine material (Figure 4.26b). As a result, EDLC based on functionalized CNT fibers shows a large rise in energy density from 13.5 to 17 Wh kg⁻¹, although power values are slightly reduced by 11-13% (Figure 4.26c). Noticeably, the increment of total capacitance and energy density caused by functionalization and consequential modification of CNTs electronic structure is higher than estimated from quantum capacitance limitation in nonlinear CD (Figure 4.15). Although the approximation of quantum capacitance impact on deviation of EDLC performance is rough, the increase of energy density is considerable and cannot be explained only by prevalence of C_Q . The eventual increase of

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specific surface area implies more pronounced effect on electrochemical properties of the material, considering diminishing effect of C_Q component and enlarging contribution of C_{EDL} , directly proportional to SSA. Hereby, dual function of ozone treatment results in substantial improvement of electrochemical performance of CNT fibers and energy storage capabilities of EDLCs based on it.

Figure 4.26. (a) CD profiles, (b) Capacitance and (c) Ragone plots obtained in IL for EDLCs based on pristine and 120 min-functionalized CNT fibers. (d) Specific capacitance obtained from CV for CNT fibers subjected to different time of ozone exposure against oxygen to carbon ratio from XPS data.

Finally, the influence of oxygen concentration in the samples on electrochemical properties of functionalized fibers in aqueous and IL media can be seen in Figure 4.26d. The specific capacitance in aqueous electrolyte increases monotonically with oxygen atomic content in the samples. The contribution of pseudocapacitance, increased SSA or improved wettability cannot be distinguished but it is clear that observed growth of fibers capacitance is a consequence of all three components combined. At the same time, less pronounced enhancement of capacitance in IL media, where CNT fibers does not experience poor infiltration and redox processes, emphasizes that the main effect of

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functionalization on electrochemical behaviour in aqueous electrolyte is derived from acquired hydrophilicity and Faradaic reactions. It is worthy to remark, that the degree of fibers wettability is expected to reach maximum after 0.5-2 hours of functionalization, while further extension of ozone treatment time should lead to increase of concentration of oxygen-containing groups participating in redox reactions and enhancing pseudocapacitance of CNT fibers. This is reflected in smoothing of the dependence between oxygen content and specific capacitance which after 30 min approaches a line of lower slope. Similar fading of functional groups impact at longer treatment determined in IL shows the growth of capacitance from 33.5 F g^{-1} to 37 F g^{-1} after 5 minutes of functionalization and around 40 F g^{-1} for the sample exposed to ozone for 30 hours. The initial capacitance surge can be explained by the change in electronic structure of CNT fibers discussed above, which erases limitations induced by C_Q component of total capacitance and thus discloses potential of fibers surface area and C_{EDL} . Higher concentration of functional groups prolongs modification of CNTs electronic properties and increase of quantum capacitance although these changes do not result in corresponding considerable raise of capacitance, now basically controlled by SSA and electronic double layer capacitance. Thereby, gas phase functionalization can be considered as effective way for tuning electrochemical properties of CNT fibers by introduction of functional groups, which can alter electronic and hydrophobic properties of CNTs and undergo reversible redox reactions increasing pseudocapacitance of the fibers.

4.4 Summary

Examination of structural features of the fibers in different scales reveals a network of CNTs interconnected by overlapping over substantial lengths, which are also branch out thus forming a porous system. CNT fibers exhibit high surface area around $256 \text{ m}^2\text{g}^{-1}$ and broad pore size distribution including large mesopores ($>10 \text{ nm}$ – 50 nm) and macropores ($>50 \text{ nm}$). The textural properties of CNT fibers are closely related to conditions of fiber production and can be modified by changing the draw ratio. Increase of winding rate reflects in more packed CNT assemblies which reduce the total volume of pores, whilst the increase of CNTs alignment at higher draw ratio raises SSA of the material.

The exceptionally long length of the CNTs associated in interwoven bundles implies high mechanical stability of the fibers. Tailoring the degree of CNTs orientation enables to enhance mechanical properties achieving superior tensile strength of 1.1 GPa SG^{-1} , modulus of 62 GPa SG^{-1} and toughness up to 61 J g^{-1} . Multifunctional nature of CNT fibers combining excellent mechanical properties, high surface area and high electrical conductivity poses superb behaviour as tough electrodes of multifaceted electrochemical systems.

CNT fibers exhibit high specific capacitance in half-cell experiments (78 F g^{-1}) and full-cell EDLC devices (32 F g^{-1}) using $\text{Pyr}_{14}\text{TFSI}$ ionic liquid electrolyte. The specific electrochemical behaviour of

4.4 Summary

CNT fibers manifested in capacitance increasing substantially with applied voltage denotes the presence of quantum capacitance component, which follows the density of states near the Fermi level and dominates in low dimensional system. The deviation of CD profile from triangular shape of ideal EDLC behaviour caused by quantum capacitance limitation shows that electrochemical performance of the device based on CNT fibers is suppressed by C_Q prevalence.

The combination of high surface area of the electrodes with wide electrochemical stability of the electrolyte results in 14 Wh kg^{-1} of energy density and 58 kW kg^{-1} of specific power, although the values of power density should be taken as relative to the mass of CNT fibers per unit area. The electrode thickness proportional to mass loading limits power per electrode mass through an inverse relationship due to increasing discharge time of CNT fiber-based EDLC. The linear dependence of galvanostatic discharge time with mass loading is in line with theoretical predictions for a symmetric EDLC with highly conductive electrodes and no micropore diffusion or micropore resistance. Commercial CNT fiber sheets also follow the same trend. The cycling stability test of the device over 10000 cycles shows excellent capacitance and energy retention.

The functionalization of CNT fibers was explored by a simple method using UV-generated ozone. Gas-phase reaction conditions and the absence of purification steps permit the preservation of CNT fiber morphology at both the macro- and the micro-scale. The degree of CNT fiber functionalization can be fine-tuned by simply varying the reaction time, as confirmed by Raman and XPS analyses. The convenient UV-generated ozone-mediated oxidation of CNT fibers renders them hydrophilic and enables use of water-based electrolytes. Short exposure of CNT fibers to ozone ($\leq 15 \text{ min}$) induces changes in tensile properties and longitudinal electrical conductivity of the material reflected in increase of specific strength and modulus and reduction of electrical conductivity.

The influence of functionalization on electrochemical properties of CNT fibers was studied in 1M KOH aqueous electrolyte and Pyr₁₄TFSI ionic liquid. After 2 hours of functionalization the material experiences increase of capacitance from 14 Fg^{-1} to 46 Fg^{-1} attributed to diversified effect of oxygen-containing groups improving wettability of fibers and participating in redox reactions enhancing pseudocapacitance of the system. Unlike aqueous media CNT fibers in IL does not experience redox processes neither wetting limitations that enables decoupling pseudocapacitive effect and modification of CNTs electronic structure. The increase of ozone treatment time is followed by weakening the dependence of differential capacitance against electrode potential, which indicates fading of quantum capacitance dominance and leads to significant rise of overall capacitance.

The improvement of electrochemical performance for functionalized samples in the half-cell affects the properties of CNT fibers in 2-electrode device. Corresponding increases of specific capacitance and energy density for supercapacitor devices obtained for functionalized fibers indicate the prospect of the gas-phase functionalization method for electrochemical application.

CHAPTER 5

Fabrication, properties and application of all-solid flexible supercapacitor

Development of multifunctional energy storage systems is usually centered on discovering new electrode materials because they principally determine fundamental limits of energy storage capabilities and overall mechanical stability. However, successful fabrication of flexible devices is also dependent on the proper integration of key components such as electrodes, current collectors, solid electrolytes and packing materials.

The Chapter 5 presents the development of flexible supercapacitors based on CNT fibers following all steps of fabrication procedure. At first, *Section 5.1* discusses the preparation and characterization of polymer electrolyte (PE) based on Pyr₁₄TFSI ionic liquid. Several polymer matrixes and different concentrations of IL were tested to evaluate the optimum combination between mechanical properties and ionic conductivity of PE system. In *Section 5.2*, all-solid supercapacitors were assembled in two-electrode Swagelok cells using CNT fiber electrodes and PVDF-co-HFP /Pyr₁₄TFSI (40:60 wt.%) polymer electrolyte. The devices were produced by two distinctive approaches based on direct casting impregnation of the electrodes with PE solution or sandwiching a PE membrane between two electrodes. The fabricated all-solid devices were characterized to identify the most effective method of EDLC assembly. *Section 5.3* is devoted to exploration of a suitable and easy scalable method for producing free-standing flexible EDLC devices. The effects of applied pressure, role of the current

5.1 Preparation and characterization of ionic liquid-based polymer electrolyte

collector and size of device on the performance and reproducibility of electrochemical properties are studied. Characterization of mechanical properties of CNT fiber/PE membrane composite and stability of large-area, all-solid EDLCs under bending conditions, are discussed. Here, fire resistive properties and self-discharge behaviour of the all-solid EDLC were also explored.

Section 5.4 introduces optimization of EDLC architecture and configuration in the context of target application in the aircraft interior. Stack configuration of EDLC prototype based on individual cells connected in series is designed according to application requirements. Electrochemical characteristics of assembled prototype are evaluated through comprehensive comparison to the individual flexible EDLC. Final test of the device powering a specific mechanical component is examined.

In *Section 5.5* other aspects of multifunctionality of all-solid EDLC systems such as transparency of single-filament CNT fibers are revealed. The electrochemical and optical properties of transparent all-solid EDLCs based on CNT fiber electrodes with controlled thickness were examined. Finally, a free-standing transparent EDLC device was assembled and characterized.

5.1 Preparation and characterization of ionic liquid-based polymer electrolyte

5.1.1 Characterization and comparison of polymer electrolytes based on different polymer matrixes

An important component of flexible supercapacitors is the solid polymer electrolyte which defines rate capability, electrochemical stability and mechanical properties directly associated with overall performance of energy storage device. Importantly, it enables producing thin-film SC composites without any additional separator that is beneficial in terms of energy density and overcoming leakage problems associated to liquid electrolytes. Particularly, polymer gel electrolytes, corresponding to the concept of immobilization/solidification of liquid electrolyte using small amount of polymer material, represent a class of all-solid electrolytes, which combines high ionic mobility and suitable dimensional/mechanical stability.[309]

Among wide variety of polymer gel electrolytes, those containing ionic liquids are considered as promising candidates for developing high-performance batteries and supercapacitors.[310, 311] ILs possesses a broad diversity of unique physico-chemical properties, including wide electrochemical window and appropriate ion mobility with environmental friendly nature. Incorporation of IL into polymer matrix additionally softens the polymer chain giving rise to easier polymer segmental motion. Therefore, the presence of IL implies a growth of amorphousness of PE improving its final ion

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conducting properties. Another crucial feature of ILs is their high electrochemical stability that endows high operational voltage of EDLC, which according to equations $E_{max} = \frac{CV^2}{2}$ and $P_{real} = \frac{V^2}{4ESR}$ determines energy and power densities through quadratic dependence. This emphasizes that small extension of applied voltage within stability range of the electrolyte can entail substantial rise of EDLC electrochemical performance. In these terms, Pyr₁₄TFSI enables maximizing energy storage capabilities of electrochemical system allowing sustained operation of the supercapacitor at very high potential window of 3.5-3.7V.[263, 312, 313] Apart from electrochemical advantages, most of ILs offer the possibility to discard the use of low temperature-flammable components that additionally implies high safety level of the energy storage system.

On the other hand, physico-chemical properties of polymers determine both mechanical stability and ionic mobility of the electrolyte. Various polymer matrices have been explored as host polymers for PEs, among which semi-crystalline PVDF-based systems ($-[CH_2-CF_2]_n-$) received high attention because of their excellent mechanical strength and great compatibility with the mobile phase. Moreover, owing to the strongly electron-withdrawing CF₂ groups, PVDF-based PEs achieve high electrochemical stability. Also, high dielectric constant of PVDF ($\epsilon = 8.2-10.5$), relative to other common polymers such as PAN or PMMA, determines a high concentration of charge carriers in all-solid electrolytes. However, along with large crystalline regions, which provide sufficient mechanical integrity for the processing of free-standing films, PVDF normally consists of only 40-50% of amorphous domains capable of trapping liquid electrolytes. The use of copolymer of vinylidene fluoride with hexafluoropropylene (PVDF-co-HFP) enables significantly expanding the amorphous region by HFP units to 65-70%,[314, 315] thereby facilitating ion conduction. These properties in combination with excellent chemical and thermal stability, high hydrophobicity and good solubility in many organic solvents make PVDF-co-HFP very suitable host polymer for PEs.[316, 317]

As alternative to non-charged conventional polymers, polymeric ionic liquids (PILs) present another class of polymer matrixes contributing to facilitated ionic mobility by having polymer-bearing ILs features in their structure.[318] The structure of PILs consisted of either polycation or polyanion incorporated into the polymer backbone predetermines the nature of ionic conductivity realized through the transport of the counter-anions or counter-cations, respectively. The excellent compatibility of PILs with their ionic liquids counterparts helps to preserve some of the unique properties of ILs, while providing intrinsic polymer characteristics.[187] In particular, pyrrolidinium-based PIL (e.g. pDADMATFSI) can be easily synthesized and together with its corresponding Pyr₁₄TFSI ionic liquid it creates a stable and high performance binary PE mixture for all-solid supercapacitors.[183]

Normally, the choice of a polymer electrolyte is based on the critical application requirements, which include high-ionic conductivity, sufficient chemical, thermal and electrochemical stability and high

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mechanical strength. In this work, three PE systems based on PVDF, PVDF-co-HFP and pDADMATFSI combined with Pyr₁₄TFSI were investigated. The three polymer electrolytes exhibit excellent chemical resistance, high decomposition temperature and high potential window, so their comparison is limited to a trade-off between ionic conductivity and mechanical properties. All PEs were prepared by dissolving IL and polymeric component in acetone with the mass ratio of 60:40% and subsequent casting using doctor blade technique. The obtained free-standing, uniform and transparent films were compared in terms of their ionic conductivity and mechanical properties. It should be mentioned that interpretation of ionic conductivity of polymer electrolytes is usually complicated due to presence of more than one phase and various factors such as method of preparation, impurities and thermal history can greatly affect phase distribution of PEs. Particularly, the size and spatial distribution of nonconducting crystalline phase can significantly alter conductivity values owing to their impact on tortuosity of the ion paths. Therefore, it is very difficult to prepare directly comparable samples of PE unless they consist of only amorphous phase. To avoid any deviation of PE properties all membranes were produced and tested at the same conditions.

Ionic conductivity (σ) values of free-standing PE membranes determined by impedance spectroscopy at different temperatures are shown in *Figure 5.1a*. The observed nonlinear conductivity dependence on temperature in the Arrhenius plot can be described by the Vogel-Tammann-Fulcher (VTF) model, as $\sigma = AT^{-1/2}e^{-\frac{B}{k(T-T_0)}}$, where A is the pre-exponential factor, B is pseudo-activation energy for the charge-carriers motion, k is the Boltzmann's constant and T_0 is the idealized glass transition temperature of the polymer. Such behaviour, reflected in curved logarithm of conductivity plots, is common for polymer electrolytes in which conductance occurs in the amorphous region. The increase of conductivity upon growing temperature is in a good agreement with the facilitation of internal bond rotation of the polymer chain which rises up the segmental mobility and finally provides a route for ion transportation. The fitting of the curve with VTF model, which is commonly seen in amorphous polymer electrolytes, confirms high amorphousness of the polymer matrixes and plasticity provided by Pyr₁₄TFSI. The non-linear behaviour of the Arrhenius plots also implies that ionic motion in the PEs is well coupled to polymer segmental relaxation.[319] All three membranes exhibit σ values in nearly close range both at low (between 3×10^{-7} S cm⁻¹ and 3×10^{-6} S cm⁻¹) and high temperatures (5×10^{-3} S cm⁻¹ to 3×10^{-2} S cm⁻¹) and, noticeably, ionic conductivity reaches very similar values at room temperature (RT) (2.5×10^{-4} – 3.6×10^{-4} S cm⁻¹). Generally, ionic conductivity of PEs is directly related to the their glass transition temperature (T_g), where lower T_g provides better mobility of the polymer chain segments resulting in increased ionic mobility of the electrolyte. Although the transfer from pDADMATFSI to a polymer gel electrolyte based on IL is usually accompanied by substantial decrease in its T_g (from 310 °C to ~ -50 °C at 60 wt.% of IL)[320, 321], the glass transition temperature is still lower for PVDF-based PEs with identical polymer/IL ratio owing to low intrinsic T_g of the polymer matrix (from -36 °C for polymer matrix to ~ -80 °C for PE)[322, 323].

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Figure 5.1. a) Arrhenius plot of ionic conductivity and b) Stress–strain curves obtained for PE membranes based on PVDF, PVDF-co-HFP and pDADMATFSI coupled to Pyr₁₄TFSI ionic liquid of 60 wt.%.

The effect of lower glass transition temperature for PVDF-based electrolytes compared to pDADMATFSI becomes pronounced at low temperature $< 20\text{ }^{\circ}\text{C}$ due to restricted segmental motion of the polymers chains, leading to higher ionic conductivity of PVDF and PVDF-co-HFP polymer electrolytes. Furthermore, TFSI⁻ anions have stronger interactions with the cationic backbone of the PIL that at low temperature can considerably affect ionic conductivity of the PE by hindering the ions motion.

The RT ionic conductivity is mainly dominated by IL due to its high concentration and mitigated impact of the T_g , that agrees with previously reported results.[320, 322] At temperature $>70\text{ }^{\circ}\text{C}$ the ionic motion becomes completely decoupled from the polymer segmental relaxation, and pDADMATFSI exhibits from 2 to 6 folds higher conductivity as compared to PEs based on PVDF and PVDF-co-HFP. Such enhancement can be derived from the PIL features: 1) the presence of additional TFSI⁻ counter-anions provide higher ions content and 2) the interaction of PIL backbone with ions at high temperature facilitates ions dissociation, thus increasing the effective charge carriers' concentration.[187]

More distinctive difference between the PEs arises from results of tensile test. *Figure 5.1b* shows strain-stress curves obtained for PE membranes with 60 wt.% of IL. The curves consist of two distinct regions: the initial linear part attributed to the elastic region and nonlinear region at higher strain related to the plastic deformation. PVDF and PVDF-co-HFP demonstrate much better mechanical properties than pDADMATFSI obtaining high elongation at break ($88\pm31\%$ and $182\pm51\%$, respectively) and high tensile strength ($3.0\pm0.5\text{ MPa}$ and $2.8\pm0.8\text{ MPa}$, respectively). The use of pDADMATFSI as a polymeric host leads to substantially lower mechanical properties with maximum strain of $15\pm5\%$ and tensile strength of $0.21\pm0.06\text{ MPa}$. Such a poor mechanical stability of

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polymerized ILs based on pDADMA⁺ polycations is in good agreement with the literature results.[324] The raise of elongation at break for the co-polymer compare to neat PVDF is associated with higher degree of the polymer amorphousness, which promotes flexibility of the membrane by allowing more chain mobility. It is important to mention that the morphology, microstructure and consequently mechanical properties of the membrane can be substantially affected by conditions of membrane preparation, including the type of solvent and its evaporation rate, conditions of polymer crystallization and annealing (drying) history.[325, 326] In order to avoid any deviations caused by difference in the procedure of membrane fabrication, all conditions were accurately reproduced.

Table 5.1 summarizes the physico-chemical properties of the three PEs having 60% of Pyr₁₄TFSI. As can be seen, the membrane based on PVDF-co-HFP achieves better performance in terms of tensile properties and ionic conductivity compared to PVDF and pDADMATFSI polymer electrolytes. Moreover, the insertion of fluorinated side groups in PVDF-co-HFP, which produce disorder in macromolecules and thus reducing crystallinity,[327] enables achieving sufficient solubility in most of organic solvents, facilitating preparation of PE mixtures in solvents with low boiling point (e.g. acetone, isopropanol). On the other hand, In addition, copolymer possesses lower melting point compare to PVDF and pDADMATFSI that opens perspective of alternative approaches for creating all-solid electrode/electrolyte composites through hot-pressing at fairly low temperature. Thereby, according to the high conductivity, mechanical properties and processability, PVDF-co-HFP presents the highest perspective among considered compounds as a host polymer for mechanically stable IL-based polymer electrolytes.

Table 5.1. Comparison of physico-chemical properties of PEs containing PVDF, PVDF-co-HFP or pDADMATFSI blended with 60 wt.% of Pyr₁₄TFSI.

Polymer electrolyte (60% IL content)	σ at 20 °C. S cm ⁻¹	Tensile strength, MPa	Elongation at break, %	T _m of pure polymer, °C	Solubility of pure polymer		
					acetone	water	DMSO
PVDF/Pyr ₁₄ TFSI	2.5*10 ⁻⁴	3.0±0.5	88±31	177*	+	-	+++
PVDF-co-HFP/Pyr ₁₄ TFSI	3.6*10 ⁻⁴	2.8±0.8	182±51	143*	++	-	+++
pDADMATFSI/Pyr ₁₄ TFSI	2.9*10 ⁻⁴	0.21±0.06	15±5	N.D.*	+++	-	+++

* Obtained from DSC analysis; N.D. refers to a not determined value

5.1.2 Effect of IL content on the properties of PE membrane

5.1.2.1 Thermal analysis

In order to correlate changes in physico-chemical properties of polymer electrolytes with the content of IL, thermal behaviour of PEs with different polymer/IL ratios was explored by means of DSC. DSC curves of pure polymer and PVDF-co-HFP/Pyr₁₄TFSI membranes with IL content varied from 40 to

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70% are showed in *Figure 5.2*. Pure PVDF-co-HFP exhibits an endothermic peak during heating at 144.5 °C, corresponding to melting of crystalline form, and an exothermic peak during cooling at 113.6 °C, attributed to reverse crystallization of the polymer. Introduction of Pyr₁₄TFSI reflects in a gradual reduction of melting and crystallization temperatures (T_m and T_c , respectively), with increasing content of IL (*Table 5.2*). This behaviour is arisen from interaction between the polymer matrix and the IL affecting the kinetics of melting and crystallization processes. Furthermore, both peaks become broader and less intense with additional content of IL indicating a decrease of the crystal size.[328]

Figure 5.2. DSC thermograms of pure PVDF-co-HFP copolymer and polymer electrolytes with different content of Pyr₁₄TFSI during a) heating and b) cooling.

The values of enthalpy (ΔH_m) calculated from the area of melting peaks and normalized by the total weight of PE show clear tendency to decrease with higher content of IL, confirming lowering crystallinity of PE membranes (*Table 5.2*). The percentages of crystallinity (χ_c) of the copolymer were evaluated according to the equation $\chi_c = \Delta H'_m / \Delta H_m^0$, where $\Delta H'_m$ is a value of enthalpy obtained from the DSC curves and normalized by the weight of copolymer, and ΔH_m^0 is the standard fusion enthalpy of 100% crystalline PVDF measured at the equilibrium melting point and corresponds to 104.7 J g⁻¹. [329, 330] *Table 5.2* shows that the values of χ_c for different compositions of PE are

Table 5.2. DSC data of pure PVDF-co-HFP copolymer and polymer electrolytes with different content of Pyr₁₄TFSI.

Polymer electrolytes	T_m (polymer), °C	T_c (polymer), °C	ΔH_m , J/g	χ_c (polymer), %	T_{cc} (IL), °C	T_m (IL), °C
Pure PVDF-co-HFP	144.5	113.6	36.8	35	-	-
40 wt.% of IL	131.0	76.4	19.2	31	-	-
50 wt.% of IL	126.9	67.0	16.1	32	-35.0	-7.4
60 wt.% of IL	122.5	54.5	12.4	30	-40.4	-7.4
70 wt.% of IL	117.0	36.5	10.0	32	-41.4	-8.1
Pure Pyr ₁₄ TFSI	-	-	-	-	-51.1	-18.4

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fairly similar (30-32%) but slightly lower than χ_c of the pure copolymer ($\chi_c = 35\%$) indicating that crystallinity of samples is slightly reduced with introduction of IL plasticizer although further increase of IL content does not suppress the crystalline part of the copolymer.

Noticeably, DSC curves in *Figure 5.3a* obtained during heating from -60 °C reveal presence of several peaks in the range of temperature from -55 °C to 0 °C for most PEs and pure IL. The exothermic peak observed at -51.1 °C for pure IL is attributed to cold crystallization (T_{cc}) of Pyr₁₄TFSI,[331, 332] which is arisen from rearrangement of the large ions into an ordered structure due to the thermal energy supplied during heating, which is not available at $T < -55$ °C. On further heating, the formed crystals start to partially melt at -26.6 °C, followed by instant complete melting manifested in strong and sharp endothermic peak at -18.3 °C (T_m).

Figure 5.3. a) DSC thermograms of pure copolymer, pure IL and PEs with different content of IL during heating and b) WAXS curves in the waterfall representation obtained for PE (60 wt.% IL) during heating (acquisition rate of 1 frame/4°C).

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Alike pure IL, the PEs with different content of IL demonstrate several phase transition processes upon heating. All peaks associated to crystallization and melting of IL in polymer electrolytes shift to higher temperatures. As it is indicated in *Table 5.2*, the decrease of IL content from 70% to 50% in PE results in higher values of T_{cc} and T_m . The observed phenomenon indicates the presence of an excess of “free” IL in PE with $IL \geq 50\%$ associated with self-aggregation of IL into small domains that reveals micro-phase separation in the membranes. It stands to mention that phase separation in this context reflects only partial formation of small IL domains enclosed in amorphous phase of PVDF-co-HFP, which however, does not imply the liquid leakage appearance onto the membrane surface. The sample with 40% IL content behaves similar to pure copolymer and cold crystallization of Pyr₁₄TFSI cannot be detected. This indicates that reduction of IL concentration to 40 wt.% enables to avoid self-aggregation of IL. As a general trend, the reduction of IL concentration in the PE leads to several changes in *Figure 5.3a*: 1) the area of all peaks is significantly decreased and the temperature of crystallization-melting processes is higher, 2) the first melting peak becomes less intense and much broader. The distinctive reduction of peaks area implies gradual decrease in the total volume of IL domains. Furthermore, considerable shift and broadening of the peaks for PEs compared to pure IL infer that the ions of Pyr₁₄TFSI interact with the polymer that inhibits crystallization and subsequent melting of the IL domains.

The phase transitions observed at low temperatures for most polymer electrolytes were studied in detail by in situ WAXS during heating. *Figure 5.3b* shows waterfall of WAXS curves obtained for PE membrane containing 60 wt.% of IL in the temperature range from -80 °C to +160 °C. Upon initial heating from -80 °C to -40 °C the curves reveal presence of two characteristic X-ray scattering peaks at $2\theta = 12.2^\circ$ and 18.7° assigned to amorphous Pyr₁₄TFSI[333, 334] and crystalline PVDF-co-HFP[199], respectively. Another sharp signal at 20.2° corresponding to crystalline PVDF-co-HFP[199], which is overlapped with another broad amorphous peak of the IL at $20.0\text{-}20.9^\circ$ [333, 334] is also visible.

In good agreement with DSC results ($T_{cc} = -40.4^\circ\text{C}$), IL begins to crystallize above -40 °C and a series of sharp peaks with different intensity appear at 10.6° , 12.2° , 12.5° , 13.4° , 17.8° . These peaks are related to IL domains organized in different crystal structures. The most intense peak of the crystalline Pyr₁₄TFSI appears at 20.0° , which despite overlapping with the signal of the copolymer (20.2°) is manifested in a distinct increase of its intensity. Further heating to -20 °C leads to melting of least stable crystals of IL, reflected in extinction of some signals ($2\theta = 12.2^\circ$, 12.8° , 19° , 20°) and emergence of a new peak ($2\theta = 12.5^\circ$). This denotes that IL domains can partially recrystallize into a more thermodynamically stable Pyr₁₄TFSI polymorphs derived from excess IL suppressing interfacial interactions between Pyr₁₄TFSI and copolymer. Complete melting of IL at -12 °C is manifested in disappearance of all sharp peaks ($2\theta = 10.6^\circ$, 12.5° , 13.4° , 17.8°) related to crystalline IL. Finally, melting of PVDF-co-HFP completed at 130 °C causes transformation of two intensive crystalline

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peaks ($2\theta = 18.7$ and 20.2°) to one broad peak of amorphous polymer ($2\theta = 17.8$). All these results are in good agreement with the DSC analysis corroborating the self-aggregation of IL into small domains.

The presence of “free” liquid in polymer electrolyte can be crucial for mechanical stability of the membrane. To investigate the plasticizing effect of IL incorporated into polymer matrix and the impact of IL self-aggregation on mechanical properties of the PE membrane, DMA test was performed. *Figure 5.4* depicts tan delta ($\tan \delta$) and storage modulus (E') obtained from DMA test during heating from -130°C to 120°C for pure PVDF-co-HFP and PE (60 wt.% IL) membrane. The tan delta curve obtained for pure PVDF-co-HFP shows a single relaxation process centered at -38°C (*Figure 5.4a*), which indicates the transition from elastic to viscous behaviour and it is directly associated to glass transition. A much broader and more intense relaxation process appears at lower temperature for PE membrane (-58°C) that is in good accordance with expected decrease of T_g . In fact, PE membrane reveals more complex behaviour with distinctive asymmetry of the relaxation related to overlapping of several processes. First, at lower temperature relaxation exhibits sharp rise, attributed to T_g of the IL[331, 332] merging into the glass transition of the polymer and the cold crystallization/melting processes of IL, which cannot be clearly distinguished. Unlike pure copolymer exhibiting fairly symmetric peak, declinations of the major peak for the PE in the temperature range from -45°C to -5°C reflected in asymmetry of the curve indicate presence of the crystallization/melt transitions of IL determined by DSC and WAXS.

Figure 5.4. DMA results showing a) tan delta and b) storage modulus as a function of temperature for pure PVDF-co-HFP and PE (60 wt.% IL).

As expected, storage modulus of the membranes obtained from DMA test decreases with addition of IL (*Figure 5.4b*) owing to its plasticizing effect. Although the drop of the modulus at low temperature ($-120^\circ\text{C} - -90^\circ\text{C}$) is only 20% due to the glassy state of IL, the difference becomes more drastic at 25°C (1735%). However, even at that temperature the polymer electrolyte membrane still maintains a storage modulus of about 23 MPa. In fact, even above 100°C the PE membrane does not collapse

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retaining a storage modulus of 0.4-1.8 MPa. This behaviour is much better than for other swelled PE films reported in literature which collapse at temperature lower than 100 °C.[335] These results confirm that cast PE membranes based on PVDF-co-HFP and Pyr₁₄TFSI behave as solid systems and despite observed phase separation remain mechanically stable up to high temperatures.

5.1.2.2 Ionic conductivity and mechanical stability

Ionic conductivities as a function of temperature of PE membranes based on PVDF-co-HFP with varied concentration of IL are depicted in *Figure 5.5a*. The observed conductivity dependence on temperature again fits with VTF model typical for amorphous polymers. As expected, polymer electrolytes exhibit lower ionic conductivity than the pure Pyr₁₄TFSI, because the ionic motion of the PE is limited by the local segmental motions of the polymer chain matrix. It is also observed that the increase of IL concentration from 50% to 60% leads to a considerable improvement of ionic conductivity, especially at low temperatures. Further increment of IL content to 70 wt.% causes less pronounced increase of ionic conductivity. The observed enhancement of ionic conductivity with IL content is closely linked to increase in a total number of mobile charge carriers progressively forming more IL pathways through the polymer.

Tensile test of free-standing membranes also discloses considerable variation of mechanical properties depending on the composition (*Figure 5.5b*). The increase of IL content from 50% to 70% causes drastic decline in the Young's modulus from 22±6 MPa to 5±1 MPa, elongation at break from 193±62% to 125±25% and decrease in tensile strength from 4.3±1.0 MPa to 1.9±0.5 MPa. Such a gradual degradation of mechanical properties is attributed to reduction in the degree of PE global crystallinity at higher concentration of amorphous IL.

Figure 5.5. a) Arrhenius plot of ionic conductivity measured for PE membranes with different IL content (ionic conductivity of pure IL at 25°C was added for comparison) and photo of transparent freestanding PE membrane (inset). b) Stress–strain curves obtained for PE membranes with different IL content.

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Table 5.3 summarizes ionic conductivity and mechanical properties of PVDF-co-HFP/Pyr₁₄TFSI membranes. At 60 wt.% of IL the membrane was found to have the optimum balance of mechanical robustness and ionic conductivity. Its RT conductivity is around $3.6 \times 10^{-4} \text{ S cm}^{-1}$, compared to $2.7 \times 10^{-3} \text{ S cm}^{-1}$ for the pure IL, when its mechanical stability is only slightly lower than 50 wt.% IL membrane, showing $14 \pm 4 \text{ MPa}$ of modulus, $3.4 \pm 0.8 \text{ MPa}$ of tensile strength and maximum strain of $177 \pm 40\%$. Therefore, the polymer electrolyte composed of 40 wt.% of PVDF-co-HFP and 60 wt.% of Pyr₁₄TFSI was selected for employment as all-solid PE in multifunctional supercapacitors.

Table 5.3. Mechanical properties and ionic conductivity obtained for PVDF-co-HFP/Pyr₁₄TFSI polymer electrolyte membranes with different IL content.

Polymer electrolyte	σ at 20 °C. S cm^{-1}	Young's modulus, MPa	Tensile strength, MPa	Elongation at break, %
50 wt.% of IL	1.0×10^{-4}	22 ± 6	4.3 ± 1.0	193 ± 62
60 wt.% of IL	3.6×10^{-4}	14 ± 4	3.4 ± 0.8	177 ± 40
70 wt.% of IL	5.7×10^{-4}	5 ± 1	1.9 ± 0.5	125 ± 25

5.2 Fabrication of all-solid EDLC based on PVDF-co-HFP/Pyr₁₄TFSI polymer electrolyte

The assembling process of all-solid supercapacitors normally consists of many intermediate steps as shown in Figure 5.6. The first step consists in deposition of electrode material on highly conductive current collector or creating stable self-standing electrodes, for instance by vacuum filtration of carbon material through porous membranes. Direct spinning of CNT fibers on desired substrate considerably facilitates the fabrication of electrodes, which essentially can be employed in entirely free-standing state without using a current collector owing to high electric conductivity of the fibers. The next challenge is achieving a proper impregnation of the CNT fibers with the PE to maximize the electrode-electrolyte contact surface that finally determines the electrochemical performance of the EDLC. In order to reveal more appropriate method for assembling all-solid devices, two approaches have been explored in this work: i) the direct impregnation of a polymer electrolyte solution on top of the electrode by drop casting, and ii) the use of a pre-cast PE membrane that was sandwiched between two electrodes (see Figure 5.6). To evaluate the efficacy of these two methods, both of them were systematically applied to assemble EDLCs that were electrochemically characterized by galvanostatic CD, as detailed below.

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Figure 5.6. Schematic illustration of the fabrication process of all-solid supercapacitor.

5.2.1 Direct casting impregnation method

First, the CNT fiber electrodes were produced by direct spinning onto aluminum current collector. The direct impregnation method was implemented by spreading an acetone solution of ionic liquid (Pyr₁₄TFSI) and polymer matrix (PVDF-co-HFP) on top of the coin-shape CNT fiber electrodes (0.78 cm²). After complete evaporation of the solvent two impregnated all-solid electrodes were faced together and pressed in Swagelok cell forming a symmetric EDLC. By varying the amount of electrolyte solution different weight ratios between PE and CNT fibers were obtained (PE/CNT fiber = 2.2/1 – 63/1).

The CD profiles of the different devices at 5 mA cm⁻² and the corresponding plots of specific capacitance at different current densities are shown in *Figure 5.7a-b*. It can be observed that the three EDLCs assembled with high and similar PE/CNT fiber ratio (63/1, 57/1 and 53/1) exhibit very different CD curves that demonstrate diversified electrochemical properties. In particular, ESR calculated from ohmic drop ($ESR = V_{\text{drop}}/2I$) are very high (70 to 170 Ω cm²) probably due to the large amount of PE, whereas specific capacitance obtained at 1 mA cm⁻² ranges from very low (8.5 F g⁻¹) to extremely high (75 F g⁻¹) values. Therefore, direct casting impregnation method does not lead to reproducible results probably due to non-homogeneous distribution of the electrolyte within CNT fibers pores.

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Figure 5.7. a) Charge-discharge profiles at 5 mA cm^{-2} and b) Capacitance plots obtained for EDLCs assembled in Swagelok cell using CNT fiber electrodes impregnated with different amount of PE; c) SEM images of impregnated CNT fiber electrodes indicating homogeneous distribution of PE at high impregnation ratio (>50) and appearance of regions not covered with PE at low impregnation ratio (<2.8), d) cross-sectional SEM images of CNT fiber electrodes before (top) and after (bottom) PE impregnations showing formation of PE isolating layer between Al current collector and CNT fibers.

The use of lower impregnation ratio (2.2/1, 2.8/1 and 4/1) should allow to form a thinner interfacial layer minimizing the separation between electrodes and reducing the ESR of the devices. However, *Figure 5.7a* shows that only one of the three SCs (with 2.8/1 PE/CNT fiber ratio) achieves a CD curve with the triangular shape typical for supercapacitors with good coulombic efficiency. The other two devices (with 4/1 and 2.2/1 PE/CNT fiber ratio) exhibit distinctive short-circuit which is caused by non-homogeneous distribution of the PE mixture in the electrodes resulting in appearance of regions on the surface of CNT fibers not covered with PE (*Figure 5.7c*). Thus, reducing the impregnation ratio does not improve the reproducibility of the fabrication method. It is worth mentioning that the ESR of this device is still high ($65 \Omega \text{ cm}^2$) and not very different from the values obtained for higher impregnation ratios indicating that the origin of the high resistance might not be exclusively attributed

5.2 Fabrication of all-solid EDLC based on PVDF-co-HFP/Pyr14TFSI polymer electrolyte

to the thick layer of PE separating the two electrodes. In fact, SEM image in *Figure 5.7d* (top) depicts a local spacing between current collector (aluminum foil) and CNT fibers before impregnation of PE suggesting a deficient contact between current collector and electrode material. Once the PE is impregnated it penetrates to those gaps (*Figure 5.7d* bottom) forming an isolating layer which enhances the resistance of EDLCs. The formation of this isolating layer together with the non-uniform distribution of the PE among electrode's pores demonstrate that direct casting impregnation method is not appropriate for assembling all-solid EDLC.

5.2.2 Utilization of a pre-cast PE membrane

An alternative way to control separation thickness, avoid formation of additional isolation layer between current collector and carbon electrodes and, importantly, achieve more homogeneous distribution of polymer electrolyte within CNT fibers, consists in using a self-standing PE membrane prepared in a previous step. Symmetric EDLCs were assembled by sandwiching the PE membrane (with controlled composition and thickness) between two unidirectional sheets of CNT fibers deposited onto Al foil in a Swagelok cell. *Figure 5.8* shows the results of EIS and CD obtained for 6 individual EDLCs with PVDF-co-HFP/Pyr₁₄TFSI (60 wt.% of IL) PE membranes of similar thickness (~100-140 μm). A reference EDLC was additionally fabricated using pure Pyr₁₄TFSI embedded in a cellulose separator (130 μm) for comparison purposes. Very similar Nyquist plots with narrow distribution of ESR were obtained for the 6 devices demonstrating high reproducibility of the fabrication method (see *Figure 5.8a*). Excellent reproducibility of the EDLCs fabricated using PE membranes is also discernible from galvanostatic tests revealing fairly similar triangular CD profiles (see *Figure 5.8b*). Similar values of specific capacitance, energy and power densities in all solid devices indicate well controlled and homogeneous infiltration of the electrolyte into CNT fiber pores in Swagelok cell and demonstrate good reliability of the fabrication method.

Moreover, adequate impregnation of the membrane into the nanostructured electrodes was confirmed by comparison of EIS and CD measurements on EDLC devices assembled with pure liquid. Nyquist plots in *Figure 5.8a* exhibit similar behaviour for pure IL and all-solid EDLCs with distinctive semicircle at high frequency directly passing into vertical straight line at low frequency attributed to a capacitive behaviour. As expected, the lower ionic conductivity of the polymer electrolyte compared to pure Pyr₁₄TFSI results in higher bulk electrolyte resistance (R_b), obtained from the first intersection of the semicircle on real axis at higher frequencies. However, the replacement of liquid electrolyte by PE in EDLC does not lead automatically to a rise of ESR (obtained from the second intersection of the semicircle on real axis). In fact, the value of ESR for liquid-based device (51 $\Omega\cdot\text{cm}^2$) is in the range of values for all-solid EDLCs (47-56 $\Omega\cdot\text{cm}^2$). This is probably due to small variation in conditions of Swagelok cell assembly (ambient temperature and applied pressure in the cell) and slightly lower thickness of the PE layer between electrodes than the cellulosic separator in pure IL

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device. Charge-discharge profiles of all-solid devices at 3.5V exhibit equilateral triangular shape alike pure IL-based EDLC indicating high coulombic efficiency ($\mu > 90\%$ at 1 mA cm^{-2}) and high reversibility of the all-solid electrochemical system during charge/discharge process. Comparison of specific capacitance for liquid based and all-solid EDLCs in *Figure 5.8c* reveals similar performance with maximum values of 29 F g^{-1} and 27 F g^{-1} , respectively. Ragone plot in *Figure 5.8d* demonstrates similar electrochemical properties for all-solid EDLC reaching $10\text{--}11 \text{ Wh kg}^{-1}$ of energy density and $11\text{--}13 \text{ kW kg}^{-1}$ of specific power compare to 12 Wh kg^{-1} and 12 kW kg^{-1} for liquid-state EDLC.

Figure 5.8. a) Nyquist plots, b) CD profiles obtained at 5 mA cm^{-2} , c) Capacitance and d) Ragone plots comparing performance of all-solid EDLCs assembled using pre-cast PE membranes and pure IL-based device in Swagelok cell.

The results of electrochemical tests comparing all-solid EDLCs assembled by casting impregnation technique and employing a PE membrane are summarized in *Table 5.4*. Electrochemical parameters of EDLC assembled with pure IL are also included in the table. As was mentioned before, direct casting infiltration method achieves low reproducibility of electrochemical properties due to non-uniform distribution of the polymer electrolyte and to the formation of an isolating layer between the

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current collector and the CNT fibers. Unlike direct casting technique, the utilization of pre-cast PE membrane enables reaching reproducible capacitive behaviour. Furthermore, the devices exhibit similar electrochemical performance to liquid devices assuming complete and homogeneous penetration of the electrolyte into meso and macropores of CNT fibers, which thus confirms the adequate filling of CNT fiber voids with the PE and its uniform distribution through the thickness of the electrodes.

Table 5.4. Electrochemical characteristics obtained for liquid-based and all-solid EDLCs assembled by casting impregnation method and employing PE membrane.

Electrolyte/Fabrication method	ESR, $\Omega\cdot\text{cm}^2$	Capacitance, F/g	Energy, Wh/kg	Power, kW/kg	Coulombic efficiency, %
Pure Pyr ₁₄ TFSI	51	29.5	12.3	12.3	90-99
Casting impregnation of PE	70-170	8.5-75	2.5-21	3.2-18	64-92
Utilization of PE membrane	47-56	27.0-27.5	10.5-10.9	11-13	89-98

In summary, the 60 wt.% Pyr₁₄TFSI and 40 wt.% PVDF-co-HFP polymer electrolyte achieves superb affinity of polymer matrix and ionic liquid resulting in high ionic conductivity, reasonable mechanical strength and robust IL retention ability at the solid state. Observed properties of the full devices enable considering the selected PE membrane (60 wt.% Pyr₁₄TFSI and 40 wt.% PVDF-co-HFP polymer) as promising solid-state electrolyte to be employed for fabrication of high-performance flexible SC device using a casting impregnation technique.

5.3 Assembling and electrochemical characterization of free-standing flexible all-solid EDLC

5.3.1 Impact of pressure on electrochemical behaviour of EDLC system

Common procedure of conventional EDLC fabrication is based on sandwiching a cellulosic or polymeric separator between two electrodes inside a metallic casing or in a pouch cell and filling with liquid electrolyte before hermetic sealing. Widely known relevancy of compaction pressure during assembling of electrochemical cells was explained by necessity to minimize the gap between the electrodes and to improve the contact of the active material with the metallic current collector.[336] Although applied pressure plays a crucial role in all-solid supercapacitors, the impact of compression force on the electrode/electrolyte interfacial properties of devices still remains unexplored and a better understanding is essential for the development of a reliable fabrication method.

Most of the EDLC prototypes prepared at lab-scale are based on coin cells or Swagelok cells in which

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the applied pressure during assembling is very high endowing proper electrochemical behaviour. In fact, the EDLCs explored in previous section were assembled using Swagelok cell in which all the components are properly compressed. However, the main purpose of this section is to fabricate a self-standing device able to function without any external applied pressure. This means that homogeneous impregnation of the polymer electrolyte and appropriate electrical contact between electrode and current collector should be accomplished when assembling the device by applying certain pressure and should be maintained after pressure release.

To evaluate the influence of applied pressure during assembling on the electrochemical performance of all-solid EDLC, a 4 cm² free-standing prototype was fabricated by sandwiching a pre-cast PVDF-co-HFP/Pyr₁₄TFSI membrane (IL 60 wt.%) between two rectangular CNT fiber electrodes (*Figure 5.9b*, inset) and galvanostatic charge-discharge measurements were carried out under varied compression conditions. *Figure 5.9* shows that before applying pressure to the device its electrochemical performance was insignificant, with capacitance and energy density close to 0 due to poor impregnation of PE membrane. The infiltration of polymer electrolyte into porous CNT fibers begins at around 0.3-0.4 MPa where a triangular-shaped CD profile is visible (*Figure 5.9a*). It is demonstrated that further increase of applied pressure initially provokes a sharp and linear enhancement of electrochemical properties (see energy density and capacitance in *Figure 5.9b*). This might be attributed to the better impregnation of the membrane into the carbon material reflected in higher effective surface area occupied by electrolyte and to the drastic decrease of ESR as observed in CD curves (*Figure 5.9a*). This significant drop of ESR is associated with the improved electric contact between current collector and electrode and with the reduction of the separation between the CNT fiber films (i.e. membrane thickness) due to the viscoelastic nature of the membrane. Noteworthy is that despite improving performance of the device, CD curves in the pressure range of 0.38-0.68 MPa still demonstrate distinctive deviation from ideal triangular shape at high voltage. This phenomenon might be related to misbalance in effective surface area of not proportionally impregnated electrodes at not optimal pressure resulting in overcharge of one of electrodes, and high resistance of the EDLC device. Beyond an intermediated pressure of around 1.0 MPa, CD profiles manifest triangular shape obtaining 99% of coulombic efficiency, corresponding to nearly ideal EDLC behaviour. The device achieves the maximum performance at 2.2 MPa exhibiting 23 F g⁻¹ of specific capacitance and 6.6 Wh kg⁻¹ of energy density. These values are similar to those obtained in Swagelok cell representing optimal pressure conditions and close to ultimate degree of electrode impregnation. High pressure of >1 MPa enables more complete impregnation of electrodes with the membrane and better uniformity of PE through the thickness of CNT fiber films reflected in nearly ideal electrochemical behaviour of the EDLC. Moreover, high pressure allows further reducing the interfacial resistance between the electrode and the current collector, thus reducing the ESR of the supercapacitor clearly seen from decreased ohmic drop of CD curve.

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Figure 5.9. a) CD profiles at 5 mA cm⁻² and b) Energy density and specific capacitance obtained from CD tests showing electrochemical performance of 4 cm² all-solid EDLC (inset) under different pressure conditions.

To be considered as a “self-standing device”, the supercapacitor should function properly without any additional pressure applied after fabrication. Noticeably, *Figure 5.9a* shows that relieving of pressure (dotted line) only causes a small decline of EDLC performance because of partial withdrawal of PE membrane from CNT fibers and consequently larger distance between electrodes which causes a slight enhancement of ohmic drop. All these issues provoke a small drop of specific capacitance and energy density of about 2%. Such behaviour denotes minor limitations of using the EDLC device in a free-standing state and defines the requirement of compression force to achieve high performing solid supercapacitors. From all this, it is seen that applying high pressure during fabrication can be considered as a key step to promote the suitable impregnation of electrode pores with polymer electrolyte endowing an effective utilization of the surface area of CNT fibers in all-solid electrochemical systems.

5.3.2 Fabrication and scaling-up of free-standing all-solid EDLC devices

Practical application of flexible EDLCs is impeded by the necessity to translate the performance of small devices achieved in lab scale (1 - 4 cm²) to larger prototypes close to large-scale production (100 cm²). Even more so, the all-solid electrochemical system should be implemented in a free-standing state to make use of the EDLC’s flexibility. To address these issues, a simple assembly process based on room-temperature pressing of a polymer electrolyte membrane between two CNT fiber sheets, and a further step of lamination in plastic using a conventional laminating machine was employed. Besides providing desired compression, the laminating pouch shell ensures optimal encapsulation of the EDLC device and its protection from exposure to air or humidity. This is particularly necessary for long-term use of devices because ingress of water in ionic liquid-based electrolytes might cause a significant reduction of their electrochemical stability window and degradation of device properties.[337] Additionally, this approach expedites the process to fabricate free-standing EDLCs compare to conventional methods of supercapacitor assembling, which

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normally involve over 15 stages, including forming a slurry of carbon in powder, coating it on a current collector, assembling into a cell, injection of liquid electrolyte, vacuum standing, sealing, etc.

A scheme of the assembly of the flexible all-solid EDLC is presented in *Figure 5.10a*. After deposition of CNT fibers on aluminum foil, the polymer electrolyte membrane is consolidated between the two electrodes by simply applying desired pressure of 2.5 MPa during 15 minutes, selected according to the results discussed in previous section. Following step includes the device lamination which helps to keep the structure under a small compressive stress normal to the EDLC layers and accordingly maintain good impregnation of the soft PE membrane into the porous CNT fiber structure. *Figure 5.10b* presents SEM image of the cross section of a CNT fiber sheet/PE membrane/CNT fiber sheet composite structure extracted from fully operational devices. SEM observations reveal penetration of polymer matrix into electrode pores and presence of PE surrounding CNT fibers. The interfacial regions show extensive infiltration of the polymeric phase into the fiber structure and no evidence of large gaps or delaminated areas. The thickness of the used membranes (38 μm) is significantly reduced compare to the one employed in Swagelok cells, but still it is substantially thicker than the CNT fiber sheets (7 μm). Although this ensures reproducibility in the fabrication of large-area devices, the electrochemical performance of devices can be further optimized by reducing the PE thickness.

Figure 5.10. Assembly of all-solid EDLC. a) Scheme of the fabrication of devices by pressing a polymer electrolyte membrane between two CNT fiber sheet electrodes and laminating and b) cross-section SEM images of CNT/PE/CNT composite in a solid EDLC.

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The efficiency of proposed fabrication method was explored by electrochemical characterization of the devices before and after lamination step. It should be noticed that the electrochemical characterization was performed in a free-standing state without applying any external pressure. *Figure 5.11a,b* presents the results obtained from CD of all-solid EDLC of 4.5 cm^2 and a mass loading of 1.15 mg cm^{-2} (electrode's thickness of around $14 \text{ }\mu\text{m}$) before and 90 hours after lamination. *Figure 5.11a,b* demonstrates that the small compressive stress applied during lamination step has a

Figure 5.11. Electrochemical properties of all-solid EDLC in freestanding state before and after lamination. a) Capacitance, b) Ragone plot, and c) capacitance retention when cycled at 5 mA cm^{-2} and 3.5 V . d) Image of free-standing laminated all-solid EDLCs of different size, e) capacitance and f) Ragone plots of 4.5 , 25 , and 100 cm^2 laminated devices and photo of freestanding all-solid EDLC of 100 cm^2 lighting a blue LED (inset).

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positive effect on capacitance and energy density of the devices, as previously observed in similar systems discussed in the literature.[336, 338] In fact, the laminating rollers provide high temperature of around 80-90 °C, at which PE does not melt but decreases its elasticity that facilitates impregnation and allows more uniform distribution of the PE into CNT fibers. The data show that capacitance reaches 28 F g⁻¹ at 1 mA cm⁻², nearly similar to the results obtained in Swagelok cell and close to the value for pure IL EDLCs. This leads to power and energy densities as high as 46 kW kg⁻¹ and 11.4 W h kg⁻¹, respectively, together with a coulombic efficiency >97% at 1 mA cm⁻². This behaviour confirms the efficient exploitation of electrode properties using the simple fabrication method discussed above.

As it was mentioned above, alongside of maintaining EDLC under compression state, the laminated configuration protects the device from humidity absorption preserving electrochemical stability of the electrolyte and consequently lifetime of electrochemical device. Long-term stability of assembled devices (both before and after lamination) was investigated by conducting 10 000 charge–discharge cycles from 0 to 3.5 V at 5 mA cm⁻². *Figure 5.11c* shows that capacitance retention after cycling was higher than 96% demonstrating excellent stability of the EDLC to extensive cycling. It is important to note that despite excellent cyclability of the all-solid device before lamination, similar to the one demonstrated for laminated free-standing EDLC, long-term stability and lifetime of non-encapsulated electrochemical system might be perceptibly faded beyond the timeframe analyzed in the lab (*vide infra*). The sealing of SCs based on IL electrolyte by enclosing plastic shell prevents ongoing exposure of the system to harmful humidity and degradation of electrochemical stability even under not operating conditions that can discernibly prolong utilization time of fabricated devices critical for target applications.

The practical advantage of considering assembly process using CNT fiber electrodes and PE membrane consists in easy scalability of EDLC fabrication and capability of employing commercial CNT fiber sheets. To confirm the scalability of the fabrication method, all-solid free-standing EDLC devices with the size from 0.78 cm² to 100 cm² were produced by lamination method (see photograph in *Figure 5.11d*). The capacitance and Ragone plots for EDLCs of different sizes in *Figure 5.11e,f* indicate small reduction in specific capacitance and consequently energy density for large area devices accounted for less than 10%. The major difference was found in the power density of the devices. However, as discussed in previous chapter, power density demonstrates reciprocal dependence on electrode mass loading, so the difference in the electrochemical properties can be attributed to a variation in electrode thickness/mass loading. This means that the scaling-up process is adequate and does not have a significant impact on the electrochemical properties of produced EDLC. Nonetheless, fabrication of more uniform electrodes and achieving better control of thickness and homogeneity of cast membrane can further improve the performance of large area devices.

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In order to investigate the reproducibility of the fabrication process for large devices, six rectangular 100 cm² all-solid EDLCs (inset *Figure 5.11f*) were produced and characterized. The scaled-up 100 cm² devices showed good reproducibility with deviation of energy and power values within 10% (*Figure 5.12*) and similar electrochemical properties compare to EDLCs of smaller size. For 100 cm² devices, capacitance was around 22 F g⁻¹, with energy density reaching 8.8 W h kg⁻¹ and power density 4 kW kg⁻¹ for a mass loading of 2.4 mg cm⁻². A narrow range of values of electrochemical characteristics indicates feasibility to produce fairly equivalent large-area EDLCs following the proposed fabrication procedure. This conveys essential information that the simple lamination technique can be implemented for assembling reproducible electrochemical devices for the purposes of certain application. Facile scalability along with good control of electrochemical performance enable to apply this approach for further conventional manufacture of all-solid devices.

Figure 5.12. Histograms showing reproducibility of a) Energy density and b) Power density of 100 cm² free-standing all-solid EDLCs.

5.3.3 Flexibility and mechanical stability of free-standing EDLCs

In order to evaluate electrochemical capabilities of free-standing all-solid EDLCs under flexural conditions galvanostatic charge-discharge measurements were performed on 100 cm² samples at different deflection angles from 45° to 180°. To ensure that electrochemical measurements did not correspond to a transient state associated with the viscoelasticity of the PE, all measurements were carried out one hour after bending/releasing. The results presented in *Figure 5.13a,b* demonstrate that all produced EDLC devices show a high flexibility, without deterioration of electrochemical properties after several bending cycles. Galvanostatic CD curves show that bending the devices slightly decreases the ohmic drop (decreasing ESR) while keeping appropriate coulombic efficiency. Very importantly, after unloading the device to the unstrained state, even after being fully folded, it recovered its initial properties. Power density was approximately constant throughout the bending cycles, whereas energy density increased substantially in the bent state, but then went back to its original value after unloading (*Figure 5.13b*). This is most likely a consequence of the bending stress locally improving polymer infiltration as schematically represented in *Figure 5.13c*.

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Figure 5.13c shows the scheme describing compression impact on PE infiltration, which denotes that under bending, the laminar structure experiences a compressive stress normal to the plane. Because of the viscoelastic nature of the polymer electrolyte, this stress can induce additional infiltration into the porous CNT fiber structure. This is in agreement with presence of few available pores not occupied by PE for large scale devices caused by alteration of CNT fiber thickness along the area of electrodes. Bending of EDLCs, which already undergo certain compression in laminated pouch, provides additional tension which enables filling some free pores by solid electrolyte. The formation of new PE/CNT fiber interface implies that a larger charge can be stored and thus energy density increases. However, power density remains unchanged, since the increase in energy comes with a proportional increase in charge/discharge time ($P_{\text{real}} = E_{\text{real}}/t_{\text{dis}}$). Outstanding flexibility of assembled devices was also confirmed by connecting a LED to the EDLC and observing its behaviour under folding conditions. Figure 5.14 shows that the device was capable to power blue LED after folding it on itself twice. Such extreme stability of the composite under flexural deformations can be ascribed to low out-of-plane stiffness of its components. The flexibility of a material is defined as:

$$f = \frac{1}{k} = \frac{\delta}{P}, \quad (5.1)$$

where f is flexibility, k is stiffness, δ is displacement and P is applied force.

Figure 5.13. Operation of devices under flexural deformation. a) Charge–discharge profiles of EDLC and b) calculated energy density obtained at 2 mA cm^{-2} for different bending angles from 0° to 180° . c) Scheme of laminated EDLC's cross-section demonstrating changes in a degree of PE membrane impregnation before and after bending the device.

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Reciprocal relation between flexibility and stiffness indicates that CNT fiber sheet and PE membrane should provide high stability to the composite exposed to bending forces owing to their low out-of-plane stiffness, which can be illustrated as negligible force required to provoke significant out-of-plane displacement.

A unique feature of CNT fiber-based electrodes is their combination of high surface area and high mechanical properties, which could be exploited to produce devices which are not only flexible but also have structural properties. In fact, the further goal implemented in the next chapter is to produce structural composites with energy storing capabilities that thus combine two functions and can lead to a weight reduction, for example, in components used in electric transport. As the first step in this direction, CNT fiber electrodes were produced at high draw ratio. This enables achieving a high degree of CNT alignment parallel to each other and to the fiber axis, which thus leads to higher strength and stiffness than high-throughput grade CNT fibers obtained at low draw ratio.

Figure 5.14. Photographs and schematic of a 100 cm² laminated EDLC device powering a blue LED after multiple folding.

To demonstrate contribution of CNT fibers to high mechanical stability of the EDLCs, the composites of highly-oriented fibers and PE membrane were subjected to mechanical testing. The CNT fiber sheet/PE membrane/CNT fiber sheet EDLC structure was removed from the plastic laminate and current collectors and tested in tension. *Figure 5.15a* shows a photograph of a typical device as well as examples of the stress–strain curves. The maximum tensile strength and modulus measured were 53 MPa and 790 MPa, compared to 3.4 MPa and 14 MPa for the polymer electrolyte membrane. In specific units these composite values correspond to 39 and 577 MPa SG⁻¹, while specific toughness calculated from the area of stress–strain curve reaching 3.7 J g⁻¹. The value of specific strength is, for example, higher than that of a 102 copper alloy (22–36 MPa SG⁻¹). But ultimately, these results should be taken as a starting point for further improvements on mechanical properties.

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It is worthy to note that the fiber volume fraction in these composites is below 14 vol.%, whereas traditional fiber-reinforced polymer composites have typically volume fractions above 50%. Furthermore, these electrodes have not been optimized for cooperative load bearing between individual CNT fiber filaments. If the tensile properties of an individual filament can be realized in an electrode and the membrane thickness reduced by a forth, according to the rule of mixtures (Equation 3.4) the resulting composite would have specific modulus and strength of approximately 18 and 0.37 GPa SG⁻¹, respectively.

Figure 5.15. a) Stress–strain curves obtained for PE membrane and CNT fibers/PE composites with different mass fraction (MF) of highly-oriented CNT fibers, previously used as EDLCs and b) Ragone plot comparing electrochemical properties of freestanding EDLCs based on highly oriented (structural EDLC_1, 2, and 3) and high-throughput CNT fibers produced in-house.

The employment of highly-oriented CNT fibers does not necessarily require a sacrifice of EDLC's electrochemical performance. The similar capacitive behaviour in a half-cell of CNT fibers obtained at different draw ratios reported in Chapter 4 suggests no significant alteration in the performance of all-solid EDLCs based on highly-oriented and high-throughput grade CNT fibers. To confirm this, three free-standing all-solid EDLC devices based on highly-oriented fibers (“*Structural EDLC*” in the legend) were assembled and tested by charge-discharge measurements. Ragone plot in Figure 5.15b demonstrates similar electrochemical performance of EDLCs fabricated with highly-oriented fibers and those produced with high-throughput grade CNT fibers. The all-solid devices possess an energy density in the range of 9.7–10.1 W h kg⁻¹ and a power density of 8.7–18.3 kW kg⁻¹ for a CNT fiber mass loading of around 1.2–1.7 mg cm⁻².

Finally, Table 5.5 presents a summary of electrochemical and mechanical properties of reported flexible all-solid EDLC, for reference. The comparison highlights the fact that most literature reports are on very small samples compared with real conventional devices. It stands to mention, that unlike most of reported systems composed of high SSA carbon materials (e.g. AC, graphene, CNTs) EDLC

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Table 5.5. Comparison of this work with flexible all-solid EDLCs reported in literature.

Electrode material	Electrolyte	Capacitance of the device, F g ⁻¹ [mF cm ⁻²]	Energy, Wh kg ⁻¹ [μWh cm ⁻²]	Power, kW kg ⁻¹ [mW cm ⁻²]	Strength of SC composite, MPa g ⁻¹ cm ³	Modulus of SC composite, MPa g ⁻¹ cm ³	Size of device cm ²
CNT fibers (this work)	Pyr ₁₄ FSI-(PVDF-HFP)	28	11.4	46	53 (tensile)	790 (tensile)	100
Activated carbon/CNTs[339]	[BMIM][BF ₄] - (ETPTA)	N/A [100]	10.3	3	N/A	N/A	micro SC
CNTs[340]	[EMIM][TFSI]-(PS/PEO/PS)	57 [0.34]	17.5 [0.42]	1.7 [35]	N/A	N/A	1
Reduced graphene oxide (RGO)/ Polyaniline (PANI)/MWCNT[341]	[EMIM][BF ₄]	154	12	17.2	N/A	N/A	0.3
Graphene hydrogel[195]	H ₂ SO ₄ -PVA	186 [372]	6.5	5	N/A	N/A	1.75
RGO-poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT/PSS)[342]	H ₃ PO ₄ -PVA	52.7	2.83	3.59	N/A	N/A	1.6 (30)
Celulose nanofiber/RGO aerogel[343]	H ₂ SO ₄ -PVA	207	6	4.65 [15.5]	N/A	N/A	2
CNTs/bacterial nanocellulose[344]	[EMIM][TFSI]-(PS-PEO-PS)	50.5	15.5	14	N/A	N/A	1
CNT/paper[60]	[EMIM][TFSI]-silica	134.6	41	40	N/A	N/A	1
RGO films[72]	H ₂ SO ₄ -Polyimide	53.2 [71]	7.35 [9.8]	30 [40]	N/A	N/A	1.5
CNT/Carbon cloth[66]	H ₃ PO ₄ -PVA	106.1 [38.75]	6.6 [2.4]	52 [19]	N/A	N/A	1
3D N-doped activated CNF/bacterial cellulose[345]	H ₂ SO ₄ -PVA	175	6.1	50	N/A	N/A	2.4
Highly aligned CNTs[346]	H ₃ PO ₄ -PVA	29.2	2.4	0.9	N/A	N/A	1.2 - 3
Carbon aerogel modified CF fabrics[106]	[EMIM][TFSI]-PEGDGE	0.6	8.4×10 ⁻⁴	3.3×10 ⁻⁵	5 (shear)	519 (shear)	59.5
Activated CF[102]	LiTFSI + [EMIM][TFSI]-PEGDGE	0.052	1.4×10 ⁻³	2.7×10 ⁻³	4.58 (compressive)	11000 (tensile)	25 (323)
Polyacrylonitrile (PAN) -based CF[347]	LiTFSI-(25% SR494+75% CD552)	0.093	0.021	1.5×10 ⁻⁴	485 (tensile)	12000 (tensile), 310 (shear)	25

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device based on CNT fibers beyond excellent flexibility provides high mechanical stability, owing to superb mechanical properties of the electrode material. On the other hand, its electrochemical properties are orders of magnitude higher than those of EDLCs based on carbon fibers. Such multifunctional composite combining energy storage capabilities and structural properties poses a great prospect for further extension of promising application in fully structural EDLCs.

5.3.4 Other aspects of all-solid EDLCs

5.3.4.1 Current collector-free EDLC devices

In conventional energy storage systems[348, 349], and even in case of flexible devices,[350–352] the use of a conductive substrate is indispensable owing to its primary function as current collector and capability to keep the mechanical integrity of the electrode. Such architecture often affects nonuniform and sluggish transport of electrons and ions, especially in through-thickness direction of electrodes, and contributes to redundant volume/weight of total devices.

In contrast, CNT fiber sheet provides high electrical conductivity that might exclude the need of conductive substrate. However, despite being not essential, the use of aluminum current collector still remains important for assembly of all-solid EDLC devices because it acts as a flat substrate which promotes uniform distribution of applied pressure and homogeneous impregnation of the electrolyte. Moreover, it preserves carbon material from infiltration of plastic pouch during lamination process. Therefore, aluminum foil might be further replaced by a thinner and lighter flat substrate, which does not need to be necessarily conductive.

Figure 5.16. a) Images of free-standing EDLC devices assembled by using CNT fiber electrodes deposited on mylar plastic (top) and aluminum (bottom) substrate. b) CD curves obtained at 5 mA cm^{-2} for two devices based on mylar and aluminum substrates.

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To confirm this, two different EDLCs of 4 cm² with similar mass-loading were assembled by employing CNT fiber electrodes deposited either on transparent electrical insulating mylar plastic or in aluminum foil (see *Figure 5.16a*). Electrochemical performance of the two self-standing devices was explored by charge-discharge experiments. As it can be noticed in *Figure 5.16b*, the two devices show very similar electrochemical properties with close values of specific capacitances (26 and 27 F g⁻¹) and energy densities (10 and 10.2 Wh kg⁻¹). This demonstrates the self-sufficient conductive properties of CNT fibers and opens further prospects for EDLC optimization by replacement or elimination of the current collector.

5.3.4.2 Self-discharge properties

Another important aspect for final integration and utilization of EDLC devices is the charge loss due to self-discharge. Fast self-discharge rate of an energy storage system noticeably limits its use in applications that require long-term use without booster charge. This phenomena is associated to parasitic reactions and other side processes and it is evidenced by a voltage drop when the device is not operated. This voltage drop is particularly detrimental for EDLCs since 75% of the energy stored in an EDLC is delivered in the first half of the voltage window and once the voltage decreases to half of the initial value the device needs to be charged again for further employment. Thus, the self-discharge leads to wastage of stored energy lowering the efficiency of electrochemical system and having a significant impact on practical utilization of EDLCs.

In case of batteries self-discharge is a process in which internal chemical reactions reduce the voltage and stored energy. On the contrary, in case of dielectric or electrolytic capacitors the voltage drop (self-discharge) arises from the leakage of current between electrodes, which does not involve any chemical process. EDLCs demonstrate an intermediated behaviour in which both mechanisms can cause self-discharge.

It is considered that the main source of self-discharge is associated with redistribution of charge among the capacitive elements.[3, 353] Broad pore size distribution and high surface area of electrodes normally translates into different time required to form uniform double-layer on all available surface of the material. As a result, outer parts of electrodes charge more rapidly than the bulk. The stop of applying voltage provokes ions to move through the material to equalize the imbalance in the potentials (*Figure 5.17*), which thus is accompanied by reduction of voltage measured at outer part of the electrode. In EDLCs self-discharge can also originate from Faradaic reactions consuming the charge carriers and discharging the surface of electrodes causing a voltage drop.[3, 353, 354] For instance, a presence of impurities or functionalities on electrode surface which undergo oxidation/reduction at the applied voltage can reduce the electrode charge, releasing ions from electric double layer. Third and least studied (due to its simplicity) mechanism of self-discharge is related to

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ohmic leakage between electrodes.[3, 354] It derives from local short-circuits or preferential resistive pathways of the charge connecting two electrodes induced by failure or defects in EDLC design.

As discussed above, the processes determining self-discharge behaviour of EDLCs are complex and cannot be attributed to one individual mechanism. In order to identify the origin of voltage decay, in-depth knowledge of all materials (electrodes and electrolyte), their possible interactions and reactivity and a thorough understanding of charge transfer processes is required. Thereby it is critical to identify reasons accelerating the self-discharge process and find conditions favorable for longer energy storage time.

Figure 5.17. Schemes of the charge redistribution mechanism causing EDLC self-discharge.

Self-discharge phenomena in self-standing EDLCs was investigated by monitoring the voltage drop at open circuit conditions and through the so-called “float current” measurements.[355, 356] The effect of maximum voltage and voltage holding time on self-discharge properties of the device was explored. *Figure 5.18a* represents the voltage decay at OCV for 10 cm² EDLC device at 25 °C after different time of voltage holding at 3.5 V. First, switching the device to OCV after charging to 3.5 V without a voltage holding step reflects on the considerable fading of potential with 1.2 V drop in first 10 min. This drastic drop of voltage is related to charge redistribution in entire electrode porous media necessary to equalize the potential throughout the electrode pores.[357, 358] Whereas, 2 minutes of voltage hold step allows time to reach the desired potential, and thereby minimize the process of charge redistribution that results in considerable slowing the self-discharge rate (only 0.5 V drop in first 10 min). The increase of voltage holding time to 10, 30 and 60 minutes gradually suppresses the voltage decay reflected in flattening of self-discharge curves. The residual voltage after 6 hours at open circuit was as low as 1.5 V if no holding voltage step is applied, whereas it reached above 2.0 V

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when the voltage was hold at 3.5 V for only 2 minutes. The residual voltage increased by 0.1, 0.2 and 0.3 V, respectively, when the applied voltage was hold for 10, 30 and 60 minutes, respectively. Further extension of the holding step to 5 hours shows barely slight delay of voltage fading during initial stage of self-discharge reaching in first two hours nearly similar values of potential. This shows that the charge redistribution noticeable at very short times (2 minutes) is almost fully completed after 1 hour of voltage holding.

Figure 5.18. Self-discharge profiles of 10 cm² EDLC device at a) different charging time and b) various maximum voltages, c) potentiostatic float current response and d) self-discharge energy loss factor (SDLF) at different maximum voltages applied.

Likewise, self-discharge behaviour of a SC is closely linked to the maximum applied voltage. According to Tafel equation[359] describing the relationship between current and overpotential during oxidation or reduction the rate of Faradaic reactions will increase exponentially with the increase in applied voltage. It means that in case of self-discharge caused by Faradaic processes overcharge will accelerate the potential decay. It was also shown that an increase in voltage across the EDLC accelerates the process leading to excess ionic concentration near the electrodes of the cell,

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thus increasing diffusion parameter causing a faster decay of voltage.[354, 360]–[362] Moreover, operating of EDLC at the limit of electrochemical window can provoke an enhancement of self-discharge rate due to decomposition of electrolyte.

The effect of maximum applied voltage on self-discharge of EDLC was investigated and the results are illustrated in *Figure 5.18b*. In order to avoid a coupling of different effects the device was charged to desired voltage and held charged 1 hour before switching to open circuit. As it is observed, the rate of voltage decay is closely related to the maximum voltage applied. In particular, the growth of applied voltage accelerates the rate of voltage drop in initial 60 min from 3.3 mV s^{-1} for 2.5 V to 9 mV s^{-1} after being charged to 3.5 V. At the same time, despite substantial change of the self-discharge rate during first hour, the maximum voltage applied does not influence the self-discharge behaviour of the device upon prolonged open circuit measurement reaching similar slope of the voltage decline in 2-3 hours. The gradual increase of the maximum voltage from 2.5 V to 3.2 V leads to a corresponding raise of voltage values measured after 6 hours at OCV. However, further increase of the maximum voltage does not result in higher residual potentials after 6 hours.

The observed behaviour of EDLC at different maximum voltage can be explained considering two processes which occur simultaneously during the charge of the device. As it is expected, the first process is related to the number of ions near the surface of electrodes forming electric double layer, which is proportional to the voltage applied. Another process is a local increase in ionic concentration, which is not directly associated to formation of the double-layer. Accumulation of an excess ionic concentration does not take place within stable conditions and occurs only when there is a current flow through the capacitor and when the voltage across the electrodes surpasses some critical value. In the tested system, the rise of voltage above threshold value of around 3.3 V results in the formation of an excess ionic concentration near the carbon surface which causes the diffusion of ions to an equilibrium state. Hence, the number of excess charges in electrodes will be reduced manifested in decrease of OCV of the EDLC.

Comparative float current responses extracted from potentiostatic measurements during one hour at different maximum applied voltage are depicted in *Figure 5.18c*. The float current corresponds to the current required to maintain the device at selected constant potential, which is ideally equal to the sum of the currents of all of the processes related to self-discharge (leakage current). At short times ($< 2 \text{ min}$) the current is relatively high due to penetration of charge to interior surface of the porous material, but it rapidly falls, reaching a steady-state current, which is assumed to be equal to the current associated with self-discharge processes. The value of this current is quite small ($< 5 \text{ }\mu\text{A}$) indicating that the amount of additional charge required to maintain EDLC at constant maximum voltage is considerably low. The growth of maximum voltage applied from 2.5V to 3.5V directly reflects in two main features: 1) increase of the time required to reach a steady-state current from nearly 5 to 10

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minutes and 2) increase of the float current value measured after 60 min from 1.9 to 4.4 μA . The amount of time required to achieve the steady-state value of float current is indicative of the amount of charge redistribution in the system, whereas the enhancement in the steady-state leakage current is associated with the growth of the rate of Faradaic reactions involved in self-discharge process.

To better understand the effect of maximum voltage applied on self-discharge properties of the electrochemical system self-discharge energy loss factor (SDLF) was estimated. SDLF represents the ratio of the energy lost over time to the maximum available energy at the charged state. The values were directly obtained from the OCV profiles in *Figure 5.18b* according to the equation $SDLF(t) = 1 - (V(t)/V_0)^2$ and plotted in *Figure 5.18d*. As one can see, in initial 30 minutes the slope of the curves, representing the rate of energy loss during voltage decay, increases gradually with a growth of maximum voltage applied. It achieves nearly double increment with the increase of the V_{max} from 2.5 V (0.03 min^{-1}) to 3.5 V (0.06 min^{-1}). After 2-3 hours curves reach similar rate of energy loss ($\sim 0.007 \text{ min}^{-1}$), which is in expected agreement with the rate of voltage decline.

The comparison of SDLF for the studied EDLC and similar system based on activated carbon (AC) and Pyr₁₄TFSI ionic liquid shows noticeable difference in self-discharge performance.[363] The maximum rest time that should be adopted for $SDLF < 0.1$ at maximum voltage of 3.2 V for CNT fiber-based all-solid system was found to be 18 min compared to 68 min for AC-based liquid EDLC. Such significant deviation indicates that the high rate of voltage decay is related to internal properties of CNT fibers and/or induced during formation of polymer electrolyte, but distinctly independent from IL behaviour. In fact, higher self-discharge rate of CNT-based EDLCs compared to those based on AC is directly associated with superior charge transportation capabilities of the CNT material, which contributes a stronger potential driving force for the self-discharge.[364] Furthermore, despite highly graphitic nature of employed CNT fibers, presence of small content of functional groups and impurities can additionally accelerate the voltage decay. The surface functionalities create a relatively weak bonding between ions and the charged electrode surface and together with impurity species can participate in side reactions.[355, 364, 365] Development of a comprehensive purification method of CNT fibers might enable better understanding self-discharge nature of the EDLC and improve its performance. On the other hand, the effect of solid-state gel polymer electrolytes on self-discharge properties is not widely studied.[366, 367]

Although excellent conductive behaviour of CNT fibers determines high power performance of assembled EDLCs, it also affects quite rapid self-discharge rate common for CNT-based electrodes.[364] The extension of voltage holding step and control of applied maximum voltage allow minimizing the voltage decay in the EDLCs, that provides a prospect for some self-discharge tuning. Moreover, introduction of small additives to PE impeding diffusion of ions (e.g. *via* electrorheological effect of liquid crystals[368]) enables substantial surpassing the self-discharge rate in supercapacitors

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for applications requiring varied energy retentions.

5.3.4.3 Fire-resistive properties

Another critical requirement that should be considered for practical application of any energy storage system is fire safety of the composite material. An important feature of the polymer electrolyte used in this work, which eventually defines safety of electrochemical device, is its non-flammability. Utilization of all-solid electrolyte based on non-flammable polymer and ILs can lower the risk of the EDLC fires and it could possibly lead to more rugged and longer lived device. In order to confirm fire-resistive properties of CNT fiber/PE membrane composite, vertical burning test was performed. As shown in *Figure 5.19* bright flame originated from the specimen could only be observed during the first 6-7 seconds at the first application of the flame. After that, no flame except the burner was observed. The material showed excellent flame retardant property during the vertical burning test, which is classified by VTM-0 rating. Such classification is used for vertical burning test of thin materials that are not capable of supporting themselves in a horizontal position and which demonstrate afterflame ≤ 10 s, afterglow ≤ 30 s and no dripping.

Figure 5.19. Vertical burning test in air on CNT fiber/PE membrane composite with 35 wt.% of the carbon material.

To estimate flame resistive properties of the composite more quantitatively limiting oxygen index (LOI) measurement was carried out. LOI represents the percentage of oxygen in a controlled oxygen-nitrogen atmosphere required to sustain flaming combustion, which directly reflects the potential flammability of a material. The LOI of 21%, corresponding to oxygen content in air, can be considered as a threshold value which defines that a material with $\text{LOI} < 21\%$ will easily burn in air. The results

5.3 Assembling and electrochemical characterization of free-standing flexible all-solid EDLC

of the LOI test suggest that the minimum oxygen concentration needed to support combustion of the samples varied between 40-45%. According to the classification of the materials based on LOI[369] CNT fiber/PE composite can be defined as self-extinguishing materials similar to rigid polyvinyl chloride (LOI = 42-45%) and polyamide imide (LOI = 43%) indicating outstanding flame retardancy of the samples.

The high flame retardant property of the EDLC derives from the low flammability of all three main components of the composite: ionic liquid, polymer and graphitic carbon material. The major part of the composite consists of the PE membrane, 60 wt.% of which is Pyr₁₄TFSI ionic liquid well known for its outstanding nonflammable properties. On the other hand, the rest 40 wt.% of PVDF-co-HFP can provide high char yield during combustion. In this case, the char layer combined with highly stable CNT network acts as a protective barrier preventing the combustion of the polymer electrolyte underlying material. The high-quality barrier prevents combustible gases from feeding the flame and also separates oxygen from burning materials, leading to high flame retardant behaviour of CNT fiber/PE composite.

5.4 Optimization of EDLC architecture and configuration for target application

5.4.1 Evaluation of application restrictions and EDLC capabilities for required conditions

Excellent performance of materials and electrochemical systems estimated from standard laboratory experiments often becomes irrelevant for practical use. A more representative examination of materials and energy storage devices should be performed in the context of real application. However, the rapidly growing number of studies dedicated to flexible or structural supercapacitors is mainly limited by laboratory tests and do not entirely represent practical impact of performed research on existing technology. Although the laboratory testing of initial performance of materials and EDLCs is always necessary, the final application imposes additional requirements on laboratory based devices during moving towards industrial prototype, e.g. employ scalable and reproducible fabrication method, optimize thickness and area of electrodes, establish stacking of EDLCs in one device, obtain long-term cycling performance and long shelf life and achieve low self-discharge rate. Some of these aspects were considered during development of large-area flexible EDLC, such as scaling up the fabrication process and achievement of reproducible electrochemical properties. Nevertheless, implementation of EDLCs performance in the bounden form of a final scope induces further restrictions which should be counted in order to fulfill all necessary requirements.

5.4 Optimization of EDLC architecture and configuration for target application in the aircraft interior

As an example, one of the objectives of this thesis was to develop a stack prototype operated under certain conditions which are predetermined by a real application. The target application of the all-solid EDLC required opening a specific mechanical component integrated into the aircraft interior. The application restrictions limit the component opening response to maximum 2 seconds.

In order to evaluate the electrochemical characteristics defined by the component and required to open it, preliminary test was performed by applying different constant currents and measuring the voltage during powering the mechanism. The results of chronopotentiometry test shows that the component acts as a resistor exhibiting 10.37 Ohm. The energy and power calculated from the values of current, voltage and opening time are shown in *Figure 5.20* and represent the restrictions of the mechanical component (most relevant parameters are included in *Table 5.6*).

Figure 5.20. Restrictions of the mechanical component obtained by chronopotentiometric characterization of the device.

As one can see, the minimum power required to activate the mechanism was found to be 3W at the voltage limit of 5.5 V and current of 0.53 A corresponding to energy as high as 29.1 J (see *Table 5.6*). However, under these conditions the component is opened after 10 s, which is far too long according to the specifications. Consequently, it is necessary to increase both voltage and current to shorten the discharge time to 2 seconds, exceeding the power restriction while reducing the energy demand. As shown in *Figure 5.20* and *Table 5.6*, the final requirements that should be accomplished by the EDLC prototype to open the component within 2 seconds are: 7.1 V, 0.68 A, 9.7 J and 4.9 W of voltage, current, energy and power, respectively.

5.4 Optimization of EDLC architecture and configuration for target application in the aircraft interior

Table 5.6. Restrictions of the mechanical component and electrochemical characteristics of an individual 100 cm² EDLC device obtained from constant resistance (10.37 Ohm) discharge.

		Voltage, V	Current , A	Opening/Discharge time, s	Energy, J	Power, W
Minimum electrochemical requirements	to activate the component	5.5	0.53	10	29.1	3
	to activate the component within 2 seconds	7.1	0.68	2	9.7	4.9
Electrochemical characteristics of 100 cm ² EDLC		3.0	0.29	2	1.9	0.9

To design the final prototype cable to fulfill the application requirements it is necessary to determine the performance of large-area EDLC in real conditions. Conventional discharge test at constant current is not realistic because the component acts as a resistor. Therefore, to estimate the correct values of effective energy and power the discharge experiment should be carried out at constant resistance of 10.37 Ohm, corresponding to the resistance of the mechanical component. In addition, a voltage holding step of 2 minutes was applied before discharging in order to ensure more complete charge of the device and avoid instant self-discharge at OCV due to charge redistribution (see section 5.3.4). *Figures 5.21a,b* represent the comparison of discharge profiles obtained for single 100 cm² EDLC at constant current of -0.5 A and at constant resistance of 10.37 Ohm after being charged to 3.5 V. It can be clearly noticed that the area under discharge curve at the constant resistance, which is proportional to the energy delivered by the EDLC, significantly surpasses the area under discharge profile at constant current (*Figure 5.21a*). On the other hand, the value of current measured during the discharge at constant resistance experiences a continuous decrease from 0.32 A to 0.22 A in absolute numbers (*Figure 5.21b*). Significant deviation of voltage and current from linear functions does not allow using the simplified equation for energy ($E_{real} = CV^2/2$). To estimate the amount of available energy in EDLC to power the component, integral form of the following equation $E_{real} = \frac{1}{m} \int_{t_1}^{t_2} I(t)V(t)dt$ should be used. Fitting of voltage and current profiles shows that curves are in good agreement with exponential functions $V(t) = 0.636 + 2.586 * e^{-0.054t}$ ($R^2=0.9992$), and $I(t) = -0.062 - 0.25 * e^{-0.055t}$ ($R^2=0.9992$), respectively. The values obtained from integration of the energy equation and their corresponding power ($P_{real} = E_{real}/t$) are represented in *Figure 5.21c*. As summarized in *Table 5.6*, the total effective energy and power obtained in the timeframe from 0 to 2 s were found to be 1.9 J and 0.9 W, respectively. This data clearly demonstrates that the electrochemical parameters of a single 100 cm² cell are insufficient to fulfill the component restrictions.

In fact, to fulfill the requirements it is necessary to connect several individual EDLC cells in series or in parallel in the final EDLC stack. Several alternative cell assemblies can be considered: cells can be stacked in series or in parallel to increase the voltage or current, respectively, or combination of parallel and series connection can be employed. The simplest approach to overcome the energy/power

5.4 Optimization of EDLC architecture and configuration for target application in the aircraft interior

restrictions of the desired application is to connect several cells in series that enables increasing the maximum voltage, current ($I = V/R$, where R is constant) and, consequently, the energy stored. An estimation of performance of n series connected devices, assuming the voltage and current increasing by n -fold, results in energy and power increasing by n^2 -fold. Thus, two 100 cm^2 EDLCs in series can provide 7.6 J of energy ($1.9 \text{ J} \times 2^2$) and 3.6 W of power ($0.9 \text{ W} \times 2^2$) in 2 seconds, which are lower than the minimum required (9.7 J and 4.9 W). Whereas, three devices in series deliver 17.1 J ($1.9 \text{ J} \times 3^2$) and 8.1 W ($0.9 \text{ W} \times 3^2$), sufficient to fulfill both energy and power requirements. Therefore, three cells is the minimum number of EDLCs connected in series necessary to activate the component in less than 2 seconds.

Figure 5.21. Comparison of a) voltage and b) current discharge profiles obtained at constant current of -0.5 A and at constant resistance of 10.37 Ohm for 100 cm^2 EDLC device. c) Real values of energy and power calculated for a single 100 cm^2 EDLC discharged at constant resistance by integration of $I(t)$ and $V(t)$ functions.

In order to verify admissible charge distribution amongst EDLCs connected in series, CD test of two 4.5 cm^2 devices connected in series has been performed. *Figure 5.22* shows CD profiles obtained at

5.4 Optimization of EDLC architecture and configuration for target application in the aircraft interior

5 mA cm⁻² for two individual devices independently and connected in series. Both EDLCs demonstrate similar performance obtaining 2.14 and 2.18 Wh kg⁻¹ of energy density and 1.10 and 1.16 kW kg⁻¹ of power density, respectively (*Table 5.7*). The electrochemical characteristics of the two devices connected in series (shown in *Table 5.7*) are in well accordance with the rules of series circuit, namely, $R_{\text{tot}} = R_1 + R_2$ and $\frac{1}{C_{\text{tot}}} = \frac{1}{C_1} + \frac{1}{C_2}$. Furthermore, the absolute values of energy and power of the devices connected in series are double those for the individual devices. This demonstrates a negligible deviation from ideal behaviour and confirm the excellent performance of series connected cells without any clear side effect or imbalance in charge distribution.

Figure 5.22. CD profiles at 5mA cm⁻² obtained for two individual 4.5 cm² EDLC device connected in series.

Table 5.7. Electrochemical characteristics of two individual EDLCs connected in series calculated from CD results at 5 mA cm⁻².

EDLC	CNT fiber mass, mg	Potential, V	Discharge time, s	Capacitance, mF	ESR, Ω cm ²	Energy density, Wh kg ⁻¹	Power density, kW kg ⁻¹	Coulombic efficiency, %
EDLC 1	12	3.5	7	290	115	2.14	1.10	98.5
EDLC 2	12	3.5	6.72	303	103	2.18	1.16	98.4
EDLC (1+2) in series	24	7	7.5	161	216	2.38	1.14	99.8

5.4.2 Design of EDLC configuration based on application requirements

Despite the fact that three cells are sufficient for operation of the mechanical component, one additional EDLC was employed in order to mitigate the voltage decay caused by self-discharge of the device. A preliminary experiment of the component opening by four 100 cm² EDLC cells laminated individually and connected in series confirmed that the size and the number of devices were enough

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to successfully power the component mechanism. In an attempt to optimize the design, four 100 cm² cells separated by a thin plastic, to avoid short circuit, and connected in series were stacked, pressed and laminated together resulting in a laminated pouch EDLC stack as shown in *Figure 5.23*.

Figure 5.23. Scheme of the fabrication of SC prototype by stacking four EDLC cells, pressing them together and laminating inside of the plastic pouch.

The contribution of different components to the final weight of the prototype in *Figure 5.24* depicts distinction between four individual laminated devices (left) and one prototype consisted of four stacked cells laminated together (right). The highest weight contribution in individual devices accounts for the plastic pouch which takes around 60% of the total mass. The stacking configuration enables reducing the weight of the prototype by almost half (from 42 g to 23.9 g) by minimizing contribution of the plastic pouch. It should be noticed that additional thin plastic isolator was introduced in the stack to prevent short-circuit. However, the contribution of this lightweight element to the total weight of the stack is not significant (~6%). Furthermore, the pie chart representing EDLC with stacked cells denotes that 40 wt.% of the prototype correspond to polymer electrolyte. Thickness

Figure 5.24. Pie charts showing contribution of different EDLC components to the final weight of the prototype for 4 individual (left) and stacked (right) cells configuration.

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of PE membrane was designedly exceeded up to 105 μm to ensure that no local short-circuit would appear. However, experiments at lab scale demonstrated that the reduction of this thickness is perfectly feasible (up to 35 μm) and might result in additional weight saving.

The mass and thickness of all components of the EDLC stack prototype are summarized in *Table 5.8* including the estimated mass and thickness of these elements in an “optimized configuration”. For instance, by applying a bipolar configuration additional weight and thickness savings can be achieved. The bipolar configuration can be described as a cell stack in which CNT fibers are deposited on both sides of a thin host material, thereat there is a double layer on each side of each bipolar electrode but with opposite polarity. This enables avoiding cell interconnection which would otherwise be required. Moreover, the use of bipolar electrodes might improve electrochemical performance of large area EDLCs by minimizing the current path between cells connected in series. In unipolar electrode design a long current pass along thin current collector of both electrodes and intercell connector often cause an ohmic loss decreasing the power density and voltage efficiency. In contrast, a bipolar electrodes design eliminates the need of additional intercell connection and isolators and enables considerable reduction of the ohmic loss, which becomes independent of the cell area and configuration. Furthermore, due to the excellent electric conductivity of CNT fibers, aluminum current collector (amounted to 24 wt.%) might be replaced by a lighter nonconductive substrate (e.g. mylar plastic) without noticeable reduction of electrochemical properties, as demonstrated in section 5.3.4.

Table 5.8. Weight and thickness of components of fabricated 100 cm² EDLC stack and its “optimized configuration”.

Components of EDLC stack prototype	Total mass in fabricated prototype, g	Estimated mass for optimized prototype, g	Thickness in fabricated prototype, μm	Estimated thickness for optimized prototype, μm
CNT fibers	0.64	0.57	40	40
PE membrane	9.68	3.23	420	140
Substrate	5.63	1.6	208	115
Isolator	1.48	0	69	0
Plastic cover	6.5	6.5	240	240
Total device	23.93	11.9	977	535

Although the contribution of carbon material to the overall mass of the EDLC is negligible, slight reduction of CNT fiber mass might be reached by thermal annealing as-spun material from carbon impurities (*Figure 4.9*). Utilization of thinner and lighter plastic for lamination of electrochemical system has not been considered, whilst it can be an effective tool for additional weight reduction. Finally, the thickness of final assembled device does not exceed 1.0 mm with total mass of around 24 g, but the assessment of possible optimization predicts 40-50% reduction in weight and thickness which are directly correlated to specific electrochemical characteristics of the system.

5.4 Optimization of EDLC architecture and configuration for target application in the aircraft interior

5.4.3 Electrochemical properties of EDLC stack and its performance in operation

Before testing the EDLC stack prototype in real operation its electrochemical performance was examined in our pilot plant by galvanostatic CD measurements using a battery charger. *Figure 5.25a* depicts CD profiles of the prototype stack when it is charged up to a maximum voltage of 14 V (3.5 V each cell in series), revealing equilateral triangular shape and accordingly high coulombic efficiency. Calculated energy and power densities, represented in a Ragone plot in *Figure 5.25b*, are very similar to those obtained by single 100 cm² EDLC device when normalized by the mass of CNT fibers. This demonstrates the excellent behaviour of the EDLC stack showing electrochemical performance close to the theoretical one and validating the fabrication method. As expected, the values of power and energy density decrease considerably when normalized by the total mass of the stack.

Figure 5.25. a) CD profiles at different current densities and b) Ragone plots, representing specific energy and power normalized by mass of active material and total mass of EDLC, obtained for four cells SC prototype.

Table 5.9 presents the comparison of electrochemical properties of the assembled EDLC stack prototype, the “optimized configuration” and a commercial Maxwell BCAP0010 supercapacitor.[370] There is a large distinction in capacitance and equivalent series resistance between the fabricated EDLC based on CNT fibers and polymer electrolyte (80 mF g⁻¹ and 4 Ω) and commercial SC based on AC and TEABF₄/ACN liquid electrolyte (2.86 F g⁻¹ and 75 mΩ). The major impact determining such difference in electrochemical properties of the EDLCs derives from lower mass fraction of active material in the flexible device. The weight of CNT fibers corresponds to < 3 wt.% of total prototype, when highly compacted AC in commercial supercapacitors usually accounts for 20-30 wt.%. Furthermore, larger specific surface area of AC with respect to CNT fiber (about one order of

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magnitude) and higher ionic conductivity of organic electrolyte in comparison with the PE additionally contribute to the distinction in the performance. At the same time, wide potential window of the IL-based PE gives rise to maximum energy density (0.5 Wh kg^{-1}), which still remains inferior to commercial SC (2.9 Wh kg^{-1}). The maximum power density of the fabricated device (0.93 kW kg^{-1}) also exhibits lower value compared to commercial liquid-based SC (6.9 kW kg^{-1}). As shown above, preliminary assessment of further optimization of the device reveals prospect to decrease the weight of EDLC by factor of two, utilizing a thinner PE membrane, getting rid of isolator and reducing the mass of substrate by employing bipolar electrodes.

Table 5.9. Comparison of electrochemical characteristics normalized by total mass of the device for commercial Maxwell BCAP0010 supercapacitor, fabricated 100 cm^2 EDLC stack and optimized EDLC device.

EDLC	Mass, g	Maximum voltage, V	ESR, Ω	Capacitance, F/g	Max Energy density, Wh kg^{-1}	Max Power density, kW kg^{-1}
Maxwell BCAP0010	3.5	2.85	0.075	2.86	2.9	6.9
Fabricated EDLC prototype	24	14	4	0.08	0.5	0.93
Optimized device	12	14	<4	0.16	1.0	1.86

The final test of the device opening the mechanical component was performed by charging EDLC connected to battery charger equipment (Delta Power Supply SM 18-50) to 14V, holding the potential during 1 min and monitoring the voltage decay at open-circuit, while discharging the EDLC stack connected to the component. The voltage profile of discharging EDLC device during powering the component in *Figure 5.26* reveals four sharp drops of the voltage corresponding to the consumption of stored energy by the resistor. It can be seen that integration of four cells provides sufficient energy and power to activate the component four times consecutively. As is evident, every subsequent activation of the component takes more time that is related to decrease of the voltage and current, or equally to the decay of remaining energy and power in the EDLC. Noticeably, after first discharge the prototype is capable to preserve adequate values of voltage and current to reopen the component within 2 seconds. Long-term test, considering prolonged self-discharge of the EDLC device was not conducted. However, small values of current ($5\text{-}10 \mu\text{A}$) required to maintain the device at selected constant voltage of 3.5V indicate that the voltage decay can be mitigated through an external current supply with negligible energy consumption.

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Figure 5.26. Discharge profile of the EDLC prototype during activating the mechanical component.

5.5 Fabrication of ultra-high power density transparent EDLC

5.5.1 Assembling and characterization of all-solid EDLC based on single filament CNT fiber

The dependence of the electrochemical performance of EDLC based on Pyr₁₄TFSI liquid electrolyte on the mass loading (i.e. thickness) of CNT fiber electrodes was investigated in Chapter 4, showing that energy density remains independent with respect to the electrode thickness, whereas the power density is inversely proportional to it. To confirm that similar dependence can be achieved in all-solid configuration, all-solid EDLCs based on the polymer electrolyte were assembled employing CNT fiber electrodes with varied mass loading from 35 $\mu\text{g cm}^{-2}$ to 2.40 mg cm^{-2} . Assembled supercapacitors were tested by galvanostatic CD experiments in two electrode Swagelok® cell. The plot of calculated energy and power densities is shown in *Figure 5.27*. The value of energy is independent of electrode's mass loading while the value of power is inversely proportional to CNT fibers mass per unit area. Observed dependence between power density and electrode's gravimetric density is predicted behaviour caused by proportional increase in discharge time at higher electrode's thickness assuming high electronic conductivity and full accessibility of material's surface area.

Clear linear trend of power vs $1/\text{mass loading}$ indicates that reduction of CNT fibers gravimetric density to the production limit implemented in single filament will result in ultra-high power density of all-solid EDLC. Theoretical prediction based on equation obtained from fitting of experimental data shows that utilization of single filament electrodes with a mass loading of around 3.5 $\mu\text{g cm}^{-2}$

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will raise the value of EDLC power density up to 1.2 MW kg^{-1} . This value is extremely high and lay in the upper power range for conventional dielectric capacitors (*Figure 1.1*).

Figure 5.27. Energy density and power density of symmetric all-solid EDLC at different mass loading of CNT fibers (two electrodes) calculated from CD measurements performed at 3.5V operating voltage and 5 mA cm^{-2} current density.

In order to assess the possibility of achieving this predicted ultra-high power density and to explore the prospect of thin carbon electrodes in all-solid EDLC, single filaments of CNT fibers were produced and deposited directly on aluminum foil. As-spun material exhibits highly porous structure and after densification with acetone forms a transparent thin film with width of around 1.5 cm (*Figure 5.28a*). Adjusted synthesis conditions enables producing highly-porous fibers consisting of highly graphitized CNTs with a few layers demonstrated in *Figure 5.28b,c*. The mass loading of single filament was estimated based on linear density of 5 min spun fiber, considering its mass and winding rate of the spinning process, which was found to be $3.50 \pm 0.05 \mu\text{g cm}^{-2}$ (for two electrodes).

Figure 5.28. a) Single-filament film of CNT fibers after densification with acetone, b) SEM and c) TEM images demonstrating porous system of fibers and highly graphitic structure of CNTs.

Electrochemical performance of single-filament films of CNT fibers was evaluated by assembling a symmetric EDLC using PE membrane in a two-electrode Swagelok cell and testing it by galvanostatic charge-discharge. Comparison of CD profiles (*Figure 5.29a*) of EDLCs based on single-filament CNT

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electrodes ($3.5 \mu\text{g cm}^{-2}$) and conventional high mass loading CNT fibers (1.27 mg cm^{-2}) are shown in *Figure 5.29*. Both charge-discharge profiles show similar triangular behaviour with high coulombic efficiencies. Noticeably, similar values of ohmic drop indicate negligible influence of electrode's thickness on ESR of EDLC. Moreover, quite similar slopes of the discharging curves indicate that electrode thickness does not affect significantly the specific capacitance ($C \sim 1/\text{slope}$) of the two EDLC. In fact, specific capacitance of single filament EDLC is only slightly higher than for high mass loading EDLC (31.2 F g^{-1} vs. 27.5 F g^{-1} at current density of 1 mA cm^{-2}). This small difference might be attributed to a more effective impregnation of polymer electrolyte into ultrathin film of carbon material. Fairly similar values of resistance and capacitance indicate that no considerable difference in specific energy density caused by decrease of fibers mass loading is expected.

Figure 5.29. Comparison of a) CD profiles obtained at 5 mA cm^{-2} and b) Ragone plots for single-filament ($3.5 \mu\text{g cm}^{-2}$) and high mass loading (1.27 mg cm^{-2}) CNT fiber-based EDLCs.

Ragone plot in *Figure 5.29b* representing specific energy and specific power calculated from discharge curves confirms sustention of gravimetric energy density in the same range of values after considerable reduction of CNT mass loading. The maximum energy density achieved at 1 mA cm^{-2} for the single filament EDLC was 12.3 Wh kg^{-1} (84.6 nWh cm^{-2}). However, substantial reduction of the mass loading was translated into a huge enhancement of specific power, reaching 1579 kW kg^{-1} at 10 mA cm^{-2} (10.86 mW cm^{-2}) compared to 10 kW kg^{-1} of conventional high mass-loading electrode. Observed outstanding performance of CNT fiber-based EDLC can be attributed to combination of excellent intrinsic properties of electrode material (high surface area with accessible meso and macropores and superior electrical conductivity) and polymer electrolyte (wide potential window and good ionic conductivity).

5.5.2 Assembly of free-standing transparent EDLC and characterization of its optical and electrochemical properties

As demonstrated in section 5.3.4, high electrical conductivity of CNT fibers enables replacing aluminum foil by a nonconductive substrate and assemble EDLCs without use of current collector.

5.5 Fabrication of ultra-high power density transparent EDLC

Direct deposition of the thin single filament film on a transparent substrate or PE membrane gives access to the transparency of CNT fiber electrodes. Thereby, the composite consisted of two CNT fiber films electrically separated by the transparent PE membrane can act not only as high power energy storage system but also as a transparent device. In order to assess the transparency of CNT fiber/PE/CNT fiber composite single filament CNT film was directly deposited on both sides of the PE membrane. The optical transmittance of the EDLC and its components were measured and depicted in *Figure 5.30a*. High optical transparency of the PE membrane with transmittance of 95% accompanied by ~90% transmittance of single filament CNT fiber results in fairly high transparency of the assembled EDLC which possesses 74% of optical transmittance at the wavelength of 550 nm.

Figure 5.30. a) Transmittance spectrum of CNT fiber/PE/CNT fiber composite, PE membrane and single layer of CNT fiber, and the photograph of the composite film showing its transparent character (inset) b) The photograph of free-standing transparent EDLC device.

Free-standing transparent EDLC was assembled and tested by employing aluminum terminals laminated together in a transparent plastic pouch (*Figure 5.30b*). It stands to mention that aluminum foil is employed exceptionally for simplification of the design and further can be replaced by thin and transparent conductive substrate, e.g. PEDOT, ITO-PET etc. Charge-discharge test reveals slight declension of EDLC performance when compared with experiments performed in Swagelok cell (*Figure 5.31a*). The maximum values of specific power and energy reached 1370 kW kg^{-1} and 10 Wh kg^{-1} , respectively, when gravimetric capacitance achieved 29 Fg^{-1} . Observed deviation of electrochemical properties for free-standing device is related to increased ESR from 40 to 50 Ohms, which is clearly seen in Nyquist plots obtained from EIS measurements (*Figure 5.31b*). This increase might be associated with higher pressure provided by pistons in Swagelok cell that ensures better contact between the electrodes and current collector.

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Figure 5.31. a) CD profiles obtained at 2 mA cm^{-2} and b) Nyquist plots obtained for single-filament ($6.9 \text{ } \mu\text{g cm}^{-2}$) and high mass loading (1.27 mg cm^{-2}) CNT fiber-based EDLCs.

It is worthy to highlight that utilization of current collector in single-filament configuration is more relevant than for thick CNT fiber electrodes. As was showed in Chapter 4, ESR of relatively thick electrodes does not depend on the mass loading or thickness of electrodes. However, once the electrode thickness falls below a threshold value its properties, especially the electric conductivity, become thickness dependent. This phenomenon is known as percolation effect and it is measured for various kinds of materials.[371–375] It is associated with limited number of links providing conducting paths in low density films. Thereby, below the percolation threshold, the in-plane resistance increases that directly reflects on higher ESR of the EDLC. The percolation scaling law is highly dependent on the aspect ratio (length/diameter) of the average CNT bundle and due to the highly one dimensional nature of CNTs and CNT bundles, the percolation threshold is very low (typically less than 1% surface coverage). This shows that although single filament CNT fibers provide high transparency owing to their low thickness, doing so entails a corresponding increase in sheet resistance with implications for current conduction. Thus, the problem can be solved by use of thicker electrodes, scarifying transmittance and power density to some extent, or employment of additional current collector.

Table 5.10 summarizes the performance of transparent and flexible EDLCs reported in literature. It can be observed that free-standing device based on single-filaments of CNT fibers exhibits outstanding electrochemical behaviour, demonstrating superior energy density and the highest value of power density achieved so far. Therefore, the combination of good optical transparency, high flexibility and excellent energy storage capabilities makes CNT fiber/IL-b-PE composite one of the most attractive EDLC systems application in power-integrated flexible optoelectronic systems, i.e. displays, light-emitting diodes, touch sensors or photovoltaics.

5.5 Fabrication of ultra-high power density transparent EDLC

Table 5.10. Comparison of transparent and flexible SCs.

Electrode material	Electrolyte	Capacitance of the device, F g ⁻¹	Energy, Wh kg ⁻¹	Power, kW kg ⁻¹	Transparency, %
CNT fibers (this work)	Pyr ₁₄ TFSI/PVDF-co-HFP	29	10	1370	74
graphene[376]	H ₃ PO ₄ -PVA	N/A	2.94	438.6	67
Co ₃ O ₄ [111]	H ₂ SO ₄ -PVA	N/A	3.01	1.15	51
SWCNTs[377]	H ₂ SO ₄ -PVA	17.5	N/A	N/A	75
graphene[378]	H ₂ SO ₄ -PVA	17.3	0.88	118	73
graphene[379]	KCl (liquid)	135	15.4	7.2	N/A
SWCNTs[380]	TBAPF ₆ -PMMA/PC-ACN	34.2	19	21.1	82
SWCNTs[381]	LiClO ₄ -EC/DEC/DMC (liquid)	22.5	12.5	13.9	60
CNTs+In ₂ O ₃ [382]	LiClO ₄ -EC/DEC/DMC (liquid)	64	1.3	7.5	62
CNTs[346]	H ₃ PO ₄ -PVA	29.2	2.4	0.9	75
graphene paper[383]	H ₂ SO ₄ -PVA	55	7.64	3.4	46.5

5.6 Summary

Polymer electrolyte membranes produced by casting method using PYR₁₄TFSI ionic liquid and different polymeric matrices, including PVDF, PVDF-co-HFP and pDADMATFSI, demonstrate different properties in terms of ionic conductivity and mechanical stability. PVDF-co-HFP based PE exhibits the optimum balance between mechanical properties and ion mobility. The exploration of multifunctional properties of PVDF-co-HFP-based membranes at different polymer/IL weight ratios indicates an appropriate combination of mechanical robustness and ionic conductivity at 60 wt.% of IL. The membrane exhibits 4.5×10^{-4} S cm⁻¹ of room temperature conductivity, 14 MPa of modulus and 3.4 MPa of tensile strength.

The comparison of two distinctive approaches for assembling of all-solid EDLCs by i) casting impregnation of PE solution on top of the CNT electrodes, and ii) utilizing a pre-cast PE membrane sandwiched between two electrodes, reveals different impact on EDLC performance. Impregnation of electrodes from the solution of PE mixture leads to considerable variation of EDLC properties and poor reproducibility of obtained values owing to nonhomogeneous distribution of PE among CNT fiber pores and formation of an isolating layer between CNT fibers and the current collector. EDLC

5.6 Summary

assembled by sandwiching PE membrane between carbon electrodes in Swagelok cell evinces reproducible electrochemical performance very close to that obtained using IL, which was taken as a benchmark to evaluate the efficiency of all-solid EDLC.

Study of pressure impact on the performance and efficiency of self-standing EDLC denotes that energy storage capabilities of supercapacitor are closely related to a degree of compression of the device mostly due to improved impregnation of the electrolyte at higher pressure and better electrical contact between CNT fibers and current collector. To assemble a free-standing flexible EDLC device and overcome the problem of required pressure, a simple assembly method based on room-temperature pressing of two CNT fiber sheets and a polymer electrolyte membrane with further lamination of the composite in plastic pouch was proposed. The process was applied to scale up the fabrication of flexible EDLCs producing devices as large as 100 cm^2 with electrodes fabricated in-house. Electrochemical measurements indicate similar properties for the laminated self-standing device compared to those obtained under high pressure in Swagelok cell, highlighting the efficiency of the assembly process. The maximum gravimetric capacitance, energy and power densities realized in a self-standing EDLC were 28 F g^{-1} , 11.4 Wh kg^{-1} and 46 kW kg^{-1} , respectively. Moreover, scaling-up of the device assembly up to 100 cm^2 results in only slight reduction of electrochemical properties.

Large-area devices demonstrate high flexibility and can be repeatedly bent and folded 180° without degradation of their properties. In fact, bending produces reversible increases in energy density owing to locally improved polymer infiltration as a consequence of bending stress. Mechanical testing of CNT fiber sheet/PE membrane/CNT fiber sheet EDLC structure based on electrodes comprising highly oriented CNTs reveals excellent mechanical properties of the composite, obtaining maximum tensile strength of 53 MPa (39 MPa SG^{-1}), Young's modulus of 790 MPa (577 MPa SG^{-1}) and calculated specific toughness of 3.7 J g^{-1} at fiber volume below $14\text{ vol.}\%$. The assessment of the composite's performance, considering tensile properties of an individual filament can be realized in an electrode and the membrane thickness reduced by a forth, predicts an increase of specific modulus and strength to 0.37 GPa SG^{-1} and 18 GPa SG^{-1} , respectively.

The feasibility of fabricating current collector-free EDLCs based on CNT fibers was demonstrated by replacement of the metallic current collector by non-conductive mylar plastic. The assembled free-standing device exhibited reproducible electrochemical performance similar to that with conductive metallic substrate confirming self-sufficient conductive properties of CNT fibers. The study of self-discharge behaviour of all-solid EDLCs indicates fairly fast voltage decay at open circuit, apparently attributed to highly conductive behaviour of CNT fibers and high values of operating voltage, which can be improved by adjusting the voltage holding step and control of potential applied. Fire test of CNT fiber/PE membrane composite reveals outstanding flame retardancy of the samples corresponding to self-extinguishing type of material.

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Analysis of required optimization of the EDLC prototype for the objective application considering activation of specific mechanical component, suggests employment no fewer than three cells connected in series. The optimization of the prototype design was achieved by stacking four 100 cm^2 cells connected in series and separated by a thin plastic isolator, enabling reducing the weight contribution of plastic pouch and total mass of the system. The device assembled by stacking, pressing and sealing together four EDLC cells obtains similar values of specific energy and power to a single 100 cm^2 EDLC, which were found to be sufficient to activate the required component consecutively four times.

CNT fibers possess an inverse dependence of the film thickness (or mass per unit area) and the power of all-solid EDLCs that foreshows huge enhancement of power density by minimizing the electrode thickness. All-solid symmetric EDLC implemented in single filament size of CNT fibers with mass loading of $3.5\text{ }\mu\text{g cm}^{-2}$ demonstrates ultra-high power density up to 1579 kW kg^{-1} (10.86 mW cm^{-2}) and energy density similar to high mass loading CNT fibers. Excellent measured transmittance of thin CNT fiber films (90%) and PE membrane (95%) enables assembling free-standing flexible and transparent EDLC showing 74% of the total composite transmittance. Free-standing single filament EDLC device shows optimal electrochemical properties in self-standing state with high values of specific capacitance (29 F g^{-1}), energy (10 Wh kg^{-1}) and the highest gravimetric power density of 1370 kW kg^{-1} so far realized in transparent state.

CHAPTER 6

Development of structural EDLC based on CNT fiber/polymer electrolyte interleaves and CF/epoxy laminates

Unlike flexible supercapacitors capable to withstand mainly bending, twisting or stretching without significant influence on electrochemical performance, structural energy storage systems preserve high capacitive properties under different mechanical stresses approaching conventional structural composites. The benefit of such devices with dual functions is quite vast, providing perceptible savings in weight and volume. However, high mechanical stability of the structural EDLC imposes substantial restrictions on the composite's architecture and on its constituents including electrodes, electrolyte and substrates.

The Chapter 6 discusses fabrication and characterization of structural supercapacitor based on all-solid thin sandwich structures of CNT fiber veils and an ionic liquid-based polymer electrolyte embedded between carbon fiber plies and followed by infusion and curing of epoxy resin. In *Section 6.1* a simple method to produce structural composite supercapacitor and its electrochemical behaviour during infusion, gelation and curing of epoxy resin are examined. *Section 6.2* presents the effect of mechanical stress on electrochemical properties of structural composite through in situ galvanostatic charge-discharge and impedance measurements during flexural bending test. The tensile, neutral and compressive scenarios were explored for a device containing EDLC interleaves at different ply positions.

6.1 Fabrication of structural EDLC

An approach to improve interlaminar properties of the composite and achieve a compromise between mechanical stability and energy storage capabilities is introduced in *Section 6.3*. The envisaged design is based on grid-shaped interleaves that mechanically interconnect CF plies with epoxy resin. The capacitive behaviour of such composites and their mechanical properties also studied. At the end, *Section 6.4* reveals additional aspects of the composite's multifunctionality, including strong encapsulating properties of CF/epoxy laminate protecting embedded interleaf from exposure to humid environment. Alternative EDLC architectures considering removal of electrode substrate and utilization of CF as part of active material are investigated. The analysis of multifunctional efficiency of the composite and its potential optimization to offer a desired weight reduction is discussed.

6.1 Fabrication of structural EDLC

6.1.1 Integration of EDLC interleaves in CF-based composite

The fabrication of structural energy storage systems has followed mainly two approaches: the development of *multifunctional structures* and the development of *multifunctional materials*. The first strategy is centered on physical embedding of devices into structural composites in a way that the composite takes the role of a component of energy storage system. Thus, a reduction in weight with respect to monofunctional systems is obtained. For instance, such structures were produced by embedding thin-film batteries within composite laminates.[384, 385] Practically, these devices act as sandwich structure achieving low mechanical stability quite limited for further improvements by delamination problems.

Another technique is to explore actual multifunctional electrode and electrolyte materials that simultaneously store energy and bear high mechanical loads. Such systems obtain excellent mechanical properties approaching the performance of conventional composites. For example, structural supercapacitors were manufactured by employing CF fabric electrodes separated by a structural glass fiber fabric and infused with a multifunctional polymeric electrolyte, such as IL-epoxy resin matrix.[102, 106] However, electrochemical properties of such devices remain very low owing to inherent limitations conditioned by low surface area of carbon fibers, common structural reinforcement, and low ionic conductivity of epoxy-based electrolytes, prevalent structural matrix.

A combined approach is to build a structural supercapacitor incorporating interleaf devices pre-assembled using unidirectional fabrics of CNTs and polymer electrolyte. As was discussed in Chapter 5, the thin all-solid CNT fiber/PE structure shows remarkable multifunctionality and in addition to excellent capacitive behaviour exhibits exceptional flexibility and mechanical stability, which ideally suits for their integration into laminated composite. Such interleaf based on CNT fibers

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can potentially improve the interlaminar properties of traditional carbon fiber reinforced composites (CFRP) by means of their high toughness and strong adhesion to the plies between which it embedded, increasing resistance to delamination.[386] Utilization of such thin EDLC as an interleaf between CF laminas mechanically joined by stiff epoxy resin and tailoring the composite architecture should provide desired synergy and balance between energy storage capabilities and structural functions.

Figure 6.1a depicts the fabrication process of the structural EDLC composites. Overall, the method consists in producing a lay-up of CF (Hexcel G0926) with a thin EDLC interleaf between layers, and then infusing the fabrics with a thermosetting resin (Ashland Inc. Derakane 8084). The interleaf is itself a thin sandwich structure comprising a polymer electrolyte membrane between two CNT fiber sheets deposited on a thin aluminum support and produced by simply applying a required minimum pressure to achieve sufficient impregnation of the PE membrane into CNT fiber porous electrodes. The EDLC samples required for this study were around 4 cm² dictated by the size of a typical composite beam subjected to bending tests, although the self-standing EDLC can be easily scaled up to 100 cm² without significant loss of its performance, as discussed in Chapter 5. Interleaves were laid down between CF fabric layers, in most cases using a thin insulating plastic tape to avoid the CF short circuiting the device.

Composites were then fabricated by vacuum assisted resin transfer molding method using a [0°]₈ lay-up. Vacuum bag resin infusion consists in producing resin flow along the fabric lay-up driven by a negative pressure gradient. *Figure 6.1b* shows a photograph of the composite during fabrication, with the electric cables attached to the device visible. *Figure 6.1c* shows optical and electron micrographs of the laminate cross-section showing the EDLC interleaf inbuilt between CF layers in the cured sample. As it can be observed, the fabrication procedure of structural EDLC achieves good integration of the components in the CF/EDLC/epoxy laminate. The resin was able to fill the carbon fabric with the EDLC device, allowing formation of a continuous ply structure without large voids and defects. Synchrotron tomography measurements (see *Figure 6.2*) confirm that the insertion of the EDLC interleaf does not impede adequate flow of the resin surrounding the interleaf and the subsequent consolidation of the CF fabric layers. Small voids are mostly detected at the EDLC interleaf edges (*Figure 6.2a,b*) and caused by the presence of the thin plastic tape used to electrically insulate the EDLC interleaf from the CF tows. The gaps between the tape and interleaf also give rise to emergence of tiny voids along EDLC (*Figure 6.2c*) but their contribution is negligible. The vacuum applied during resin infusion provide additional compression on the interleaf, which might be accompanied by better impregnation of PE membrane into CNT fiber electrodes. Importantly, created compression also provides a good contact between aluminum substrate and CNT fibers, observed in the electron

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Figure 6.1. Infusion of epoxy into CF/EDLC/CF lay-up. (a) Scheme of the fabrication of structural supercapacitor composite by stamping a CNT fiber-based EDLC interleaf, embedding it between CF plies and infusion/curing of epoxy resin. (b) Photographs of a CF/EDLC/CF lay-up during epoxy infusion and of the 4 cm² EDLC interleaf embedded in it (inset). (c) Optical micrograph of composite cross-section (top) showing successful integration of EDLC/CF/epoxy in the laminate and scanning electron micrograph (bottom) of integrated EDLC interleaf.

micrograph (*Figure 6.1c*), which ensures minimized gaps between current collector and electrode material and uniform charge transfer. Good compaction of the components of EDLC interleaf during infusion process is of particular interest since it avoids the presence of gap between current collector and CNT fibers that might be filled with resin flow. This would result in the formation of resin isolating layers affecting uniform distribution of the current, increased resistance and thus deteriorating the electrochemical properties of the entire device. It stands to mention that the use of aluminum current collector is accounted for its function as a flat rigid support, which promotes uniform distribution of applied pressure and therefore enables homogeneous impregnation of PE into CNT fibers. However, as was showed in Chapter 5, aluminum foil can be easily replaced by a thin non-conductive substrate without scarifying EDLC's electrochemical performance.

Figure 6.2. Soft X-ray computed tomography images of cross-sectional area of structural EDLC showing a) presence of voids at the interleaf edges and b) no considerable voids along the interleaf.

6.1.2 In situ electrochemical measurement of EDLC during epoxy infusion and curing

In situ charge-discharge tests were performed during infusion, gelation and further curing of epoxy resin in order to evaluate the impact of these fabrication steps on electrochemical performance of the supercapacitor. CD profiles in *Figure 6.3a* are very similar showing negligible changes in electrochemical behaviour of EDLC after infusion. Coulombic efficiency remains high, at 99%, and ESR low at 24 Ohm cm². After complete curing of epoxy, which takes 48 hours at room temperature, there is a small change in the CD profile (*Figure 6.3a*) with ESR increasing up to 35 Ohm cm², which can be attributed to local damage to the sample after removal the peel-ply and distribution media layers used for fabrication of the composites. SEM and X-ray tomography examination of the interleaves (see *Figures 6.1c* and *6.2*, respectively) shows absence of epoxy resin both inside of CNT fiber pores and between electrodes and aluminum foil, which rules out the possibility of the EDLC interleaves being damaged during the infusion step.

As *Figure 6.3b* shows, energy density (normalized by mass of active material) remains nearly constant at 6.40 Wh kg⁻¹ during epoxy infusion and after curing. The high energy density of the sample under full EDLC operational conditions (3.5 V and 20 mA cm⁻²) is possible because of the excellent electrochemical properties of the EDLC interleaf itself that uses CNT fibers and soft polymer electrolyte. As abovementioned, other capacitive structural composites employing high-performance CF electrodes and structural polymer electrolytes have typically suffered from a very high ESR (0.42-300 kOhm cm²). As a consequence, these structural devices could not bear typical currents and were only tested at 0.4-40 μA cm⁻². [102, 387] This is mainly attributed to the very low ionic conductivity of the employed structural polymers electrolytes, mostly based on highly cross linked three-dimensional polymer networks. For instance, the ionic conductivity of PEGDGE epoxy containing 10 wt.% ionic liquid electrolyte is 2.8×10^{-5} S cm⁻¹, which is more than one order of magnitude lower compared to the PVDF-co-HFP/Py₁₄TFSI polymer electrolyte (3.6×10^{-4} S cm⁻¹ for 60 wt.% IL) and 2-3 orders lower than for liquid electrolytes. Such a feature is arisen from the inverse relation between ionic conductivity and mechanical properties that indicates limitations of structural solid PEs for effective operation of structural power composites.

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Figure 6.3. Electrochemical properties of structural EDLC composite during fabrication by vacuum bag resin infusion. (a) Charge-discharge profiles at 5 mA cm^{-2} of EDLC before infusion, after infusion and after curing of epoxy resin. (b) Energy density obtained for different stages of infusion and curing.

6.2 *In situ* electrochemical characterization of structural EDLC during mechanical tests

In virtually all studies of structural power composites with dual mechanical and energy storage functions, the electrochemical and mechanical properties are investigated independently. However, the targeted applications require analysis of interdependent influence of composite's properties. For instance, the employment of multifunctional structural EDLCs implies that the device can withstand high mechanical stresses and store energy. However, most reports do not consider how electrochemical system behaves under static or dynamic loads. High resistance of structural electrolytes and poor capacitive behaviour of CF complicate exploration of changes in electrochemical properties of structural devices exposed to mechanical stresses. This reflects the challenge in producing composite structures corresponding to full electrochemical cells and with low internal electrical resistance, which apart from stable functioning at broad operation conditions can be used to study both mechanical and electrochemical properties in the same system, and more so to explore the dependence between these properties. Utilization of the EDLC interleaves based on CNT fiber electrodes and PE membrane that possess low ESR and high coulombic efficiency integrated into CF/epoxy laminate enables the simultaneous study of electrochemical and mechanical properties as shown below.

In order to study different ply level stress states a composite with 8 CF layers $[0]_8$ and three 4 cm^2 EDLC interleaves was produced. The EDLC interleaves were placed between the first and second layer, (EDLC_1C), in the neutral plane (EDLC_2N) and between seventh and eighth layers

6.2 In situ electrochemical characterization of structural EDLC during mechanical tests

(EDLC_3T), respectively (see Figure 6.4a). The different position of the interleaves in the laminate enables studying their properties under compression (EDLC_1C), neutral (EDLC_2N) and tension (EDLC_3T) stress states.

Figure 6.4. (a) Schematic illustration of EDLCs locations and mechanical forces under applied load. (b) CD profiles measured at 5 mA cm⁻², (c) specific capacitance and (d) Ragone plot obtained for EDLC_1C, EDLC_2N and EDLC_3T integrated into the structural composite. (e) Photograph of three EDLC devices embedded into structural composite independently powering red LEDs.

After composite fabrication the embedded EDLCs were tested individually and showed nearly identical electrochemical performance (Figures 6.4b-d). The maximum obtained specific capacitance,

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energy and power densities varied in the range of 27-29 F g⁻¹, 10.2-11.5 Wh kg⁻¹ and 4.8-5.8 kW kg⁻¹, respectively, similar to typical values for the all-solid EDLC with the corresponding mass loading of CNT fibers (3.2-3.5 mg cm⁻²). All three devices could independently power three red LEDs (*Figures 6.4e*) confirming excellent electrochemical performance.

In situ charge-discharge and impedance spectroscopy measurements were carried out during 4-point bending on rectangular cross-section beams according to ASTM D7262 standard (*Figure 6.5a*).[388] Maximum flexural stress (σ) and strain (ϵ) in the beams were calculated from the total force recorded with the load cell and the displacement of the actuator of the testing frame. *Figure 6.5a* shows photographs of the sample in the unstrained state and under a large deflection (~ 30 mm). In this range, the composite deformed elastically (*Figure 6.5b*) and without any indication of mechanical reduction of bending modulus due to the presence of the three EDLC interleaves. The chord modulus obtained from the σ - ϵ curve (*Figure 6.5b*) was $\Delta\sigma/\Delta\epsilon \approx 52$ GPa, which was within the range of the control sample without interleaves. This fact indicates a good stress transmission between the plies of the CF and the EDLC interleaves during bending.

Figure 6.5. Mechanical properties of the structural composite. (a) Photographs of the flexural test setup at the initial and bent states. (b) Comparison of stress-strain curves obtained for the structural composite containing three embedded EDLC interleaves and a reference composite produced without interleaves.

Electrochemical measurements were performed during 4-point bending up to a flexural stress of $\sigma \approx 70$ MPa. CD and impedance spectroscopy measurements were collected roughly every 10 MPa of bending stress for each of the EDLC interleaves. *Figures 6.6a-c* show that pronounced alterations of electrochemical behaviour occur during initial load of 2.6 MPa, especially for interleaf under tension (EDLC_3T). The energy densities of all three EDLC interleaves increase, whereas the most remarkable enhancement of about 30% was observed for EDLC_3T. Such change in energy density

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Figure 6.6. *In situ* electrochemical characterization during four point bending flexural test of the structural supercapacitor composite. (a) Relative energy, (b) ESR and (c) Specific capacitance obtained from CD at 5 mA cm^{-2} measured during bending, for the interleaves under compression (EDLC_1C), neutral (EDLC_2N) and tensile (SC_3T) stress states. Nyquist plots for the different interleaves integrated into the structural composite during the bending test d) EDLC_1C, e) EDLC_2N and f) EDLC_3T.

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was caused by the increase in capacitance (*Figure 6.6c*) and by a drop in ESR (*Figure 6.6b*) which was corroborated by CD test and impedance measurements (*Figure 6.6f*). The transverse compaction during 4-point bending test in EDLC_3T results in enhanced capacitance probably due to improved infiltration of the polymer electrolyte into the porous CNT fiber electrode, as previously seen in CNT fiber-based flexible thin EDLCs under severe bending (see section 5.3.3 in Chapter 5). Smaller increment in energy density observed in the interleaves in the neutral plane (EDLC_2N) and the compressive region (EDLC_1C) might be attributed to a better electrical contact in all EDLC layers, induced by the pressure applied during 4-point bending.

Upon further enhancement of the stress up to 15 MPa, EDLC_3T exhibits a moderate reduction in energy and capacitance and slight increase of resistance, which reach constant values and do not change with further increase of applied load. The data imply a relaxation period reflected in partial membrane withdrawal from CNT fibers after instant infiltration of polymer electrolyte at initial stress. This results in small decrement of effective surface area filled by electrolyte and slight increase of separation layer between two electrodes causing alterations of capacitance and ESR.

Further increase of the bending stress does not translate into any distinct alterations in electrochemical properties of the EDLC_2N device. As the neutral layer of the sample experiences close to zero bending stresses, growing flexural load does not have a drastic impact on the EDLC interleaf located in the neutral plane. On contrary, significant deviation of electrochemical properties at high bending stresses was observed for the interleaf under compression (EDLC_1C), exhibiting a 22% drop of energy density at 70 MPa. This is mainly due to a change in ESR, which increases by about 60% relative to the unstrained state (*Figure 6.6b*). The comparison of Nyquist plots obtained for the EDLC_1C (*Figure 6.6d*), EDLC_2N (*Figure 6.6e*) and EDLC_3T (*Figures 6.6f*) corroborates that the rise of ESR at high stresses was detected only for the interleaf exposed to compressing force. This increase is due to local losses of electrical contact, attributed to transverse opening deformation of the device caused by the in-plane compressive stresses at this ply.

Complete unloading of applied stress demonstrates full recovery of original performance for EDLC_1C device. The fact that the final value of the resistance obtained after relieving the load is lower than in the strained states suggests that most of the contact losses are reversible in EDLC_1C device. Despite small variation in capacitance and ESR, that EDLC interleaf exhibits 100% of energy retention after decompression. On the other hand, EDLCs located in the neutral plane and the tensile region show a decline of resistance by 14% and 19% resulting in enhancement of the energy density of EDLC_2N and EDLC_3T of around 10-12% relative to the values obtained before bending test. These results illustrate that, electrochemical properties of the interleaves can be reasonably preserved or even improved after withstanding static loads causing permanent changes within the elastic region of the composite. Overall, the observed change in the electrochemical properties of the interleaves is

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relatively small considering the large deformation of the composite structure.

Figures 6.7a and 6.7b depict electron micrographs of cross sections of interleaves in the compressive ply (buckled device) and tensile ply, respectively. They reveal significant deformation of the interleaf under compression and nearly unaffected structure of the interleaf under tension, which are in good agreement with the observed electrochemical performance.

Figure 6.7. SEM images of the composite cross-section after the bending test. The micrographs correspond to areas near the interleaf edge, for the samples subjected to compression (SC_T) (a) and tension (SC_B) (b) stresses.

6.3 Mechanical interconnection using perforated interleaves

6.3.1 Structure of the composite

While having very high power and energy densities, the EDLC interleaf layer in the composite is essentially an internal defect. Since the polymer electrolyte in the EDLC is very soft, with a tensile modulus of 14 MPa, its corresponding shear modulus is very low. It implies that resistance to the opening/sliding between adjacent layers is considerably small and the interleaf causes delamination in the composite. For instance, a preliminary lap shear test on the composite with embedded EDLC indicates that the shear modulus and shear strength in the interleaf layer are negligible, and the CF ply is easily detached from the EDLC without applying any considerable force. Yet, the simple interleaf's architectures and fabrication method used here open the possibility to produce engineered structures that mitigate the reduction in interlaminar properties. As an example, an EDLC interleaf with a grid structure was produced with the view that upon integration in the composite epoxy would flow through the holes and mechanically interconnect CF plies, as schematically showed in Figure 6.8a. This leads to a composite structure with adjacent lamina mechanically joined by stiff epoxy connectors (similar to structural columns or pillars) that ensures a more efficient transmission of shear stresses through the interfaces of the beam. The sample consisted of a 32 cm² EDLC with 21 holes of 1 cm diameter (~15.5 cm² of effective electrode area) (Figure 6.8b), interleaved in a composite as described above.

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Figure 6.8. Structural supercapacitor composite with mechanically interconnected plies via the use of grid EDLC interleaves. (a) Schematic of the envisaged structure. (b) Photograph of a 32 cm² grid EDLC interleaf.

Synchrotron X-ray tomography was used to confirm that epoxy resin successfully flowed in the through-the-thickness direction between the adjacent plies via the machined interleaf holes. *Figure 6.9a* presents a 3D X-ray tomography image of a section of the sample after the bending test. The sample volume clearly contains a cylindrical region of epoxy interconnecting two laminae, as well as showing part of the EDLC interleaf delimiting this region. Inspection of the EDLC edge shows the presence of voids, which according to X-ray tomography analysis account for 1% of the volume in the full composite (*Figure 6.9b*) and roughly 8-13% of the porosity in the interconnecting epoxy volume in the hole. These voids are undesired defects, mainly caused by the presence of dielectric tapes used to insulate the electrodes electrically from the CF layer. Avoiding these voids could be achieved by substituting the isolating tapes by thin polymer electrolyte membrane and using the CF as active electrode (*vide infra*) and evidently in composites with electrically insulating fibers. More detailed structure of the composite containing grid EDLC interleaf can be seen in 2D images extracted from different parts of the volume and included in *Figure 6.9c*.

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Figure 6.9. High-resolution (a), (b) 3D and (c) 2D tomography images confirming penetration of epoxy resin through channels in the interleaf and representing the volume fraction of voids (red) appearing at the edge of the EDLC.

6.3.2 Mechanical and electrochemical properties

First, the composites with the grid and non-perforated EDLC interleaves were subjected to lap shear test. *Figure 6.10a* depicts shear stress-displacement curves for the samples with entire and perforated EDLCs. As it is seen, the presence of entire interleaf between CF plies results in the mechanical failure of the composite at negligible force applied, and thus the shear strength of such structure is close to zero. CF interconnection by epoxy through the holes in the interleaf has a clear positive impact on the shear deformation. Although the shear strength is only 2.2 MPa, the composite with embedded grid EDLC demonstrates a substantially improved resistance to the opening/sliding between adjacent layers.

The composites with the grid EDLC interleaves were also characterized by 4-point bending test and compared against the sample with non-perforated EDLC device. As a control sample, similar composite without EDLC interleaves was fabricated and tested. Bending stress-strain curves

6.3 Mechanical interconnection using perforated interleaves

(Figure 6.10b) show that all samples had a similar elastic response and bending modulus, indicating effective shear stress transmission through the CF plies. The supercapacitor composites containing entire and grid-type EDLCs exhibited almost identical stress-strain curves showing evidence of non-linear deformation at around 60 MPa and failure by localized buckling at 153 MPa, whereas the control sample presented linear-elastic behaviour up to fracture at 215 MPa.

Despite very similar stress-strain curves the composites with non-perforated and grid-type EDLCs exhibit different behaviour during buckling. As shown in Figure 6.10c bending test indicates that failure was triggered at the interleaf edges and the sample with grid interleaf suffers less pronounced delamination at the edges of embedded device compare to structural composite with entire EDLC, demonstrating better fastening of CF laminas. Although such improvement remains imperceptible in mechanical performance of the structural composite during bending, distinct delamination at EDLC/CF interface noticeably increases probability of the device failure. Furthermore, with the Al current collector and tape layers, the interleaf thickness is comparable (0.56 mm) to that of a CF lamina (0.4 mm). Thus, plies are distorted in this region in order to accommodate the thickness variation imposed by the EDLC interleaf, producing stress concentrations that generate damage and local ply buckling upon loading. Further optimization of the composite structure by removing some of the redundant elements in the interleaves, such as aluminum foil and double adhesive isolator, and reducing the thickness of the polymer electrolyte membrane can reduce the effect of disorder introducing through interleaf integration.

Figure 6.10. (a) Bending stress-strain curves obtained for control bare composite and structural supercapacitors containing grid and non-perforated EDLC interleaves, (b) digital images of 4 point bending test setup after buckling of structural composites containing grid (bottom) and non-perforated (top) EDLC interleaves, (c) shear stress-displacement curves obtained for the composites containing entire and perforated EDLC interleaves.

Charge-discharge profiles, with the time normalized by the mass of active material, demonstrate nearly identical electrochemical properties for entire and perforated EDLC interleaves, proportional to the effective electrode area (Figure 6.11a). Ragone plot in Figure 6.11b compares power and energy densities normalized by the total mass of structural composites obtained for samples containing

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entire and modified EDLC devices. The observed difference in electrochemical properties is mostly attributed to the difference in effective electrode area (32 cm^2 and 15.5 cm^2 for entire and perforated EDLC, respectively). Interestingly, the supercapacitor could still be charged and discharged after composite fracture, retaining its coulombic efficiency of 99%, 93% of power density and 69% of energy density (Figure 6.11c).

Figure 6.11. Comparison of electrochemical performance of regular 32 cm^2 EDLC interleaf and a modified sample with grid structure containing 18 holes. (a) Charge-discharge profiles at 5 mA cm^{-2} and (b) Ragone plots (energy and power are normalized by the total mass of composite) obtained for structural composites containing entire and modified EDLC devices. The energy and power densities of the grid electrode are *pro rata* with effective area. (c) Charge-discharge curves obtained at 5 mA cm^{-2} before and after buckling of the structural composite.

Considering the total mass of the 32 cm^2 sample, including fiber reinforced polymer (FRP) and EDLC interleaf, the composite has 88 mF g^{-1} of capacitance, 37.5 mWh kg^{-1} of energy density and 30 W kg^{-1} of power density. But clearly, an increase of weight fraction of electrochemical system by introducing additional interleaves between all the plies would provide a *pro rata* increase in these properties. Indeed, the highest values of energy storage obtained in this study for the composite containing three integrated EDLC interleaves are 174 mWh kg^{-1} of energy density and 54 W kg^{-1} of

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power density. Overall, the use of these interleaves enables a range of multifunctional properties, dictated by factors such as: the shape of the interleaves in terms of hole area, number and size of holes; and the position and number of interleaves in the laminate.

Table 6.1 presents a summary of electrochemical and mechanical performance of reported structural supercapacitors. The comparison indicates that the samples in this study have the highest values of power density (30 W kg^{-1}) and energy density (37.5 mWh kg^{-1}) reported for composites with mechanical properties in the structural range, 1 to 3 orders of magnitude above previous reports, albeit with compressive properties most likely short of those obtained using carbon aerogel-modified CFs.

Table 6.1. Properties of structural supercapacitor composites.

Electrode material	Electrolyte	Capacitance, F g^{-1}	Energy, Wh kg^{-1}	Power, W kg^{-1}	Mechanical properties, MPa
CNT fiber/PE interleaf in CFRP (This work)	Thermoplastic + Pyr ₁₄ TFSI	0.088	0.037	30	$S_{\text{lex}} = 153$ $E_{\text{flex}} = 60\,000$
Carbon fiber + carbon aerogel[106]	PEGDE + 10% IL	0.602	0.001	0.033	$G_{12} = 8710$ $S_{12} = 895$
Carbon fiber[102]	PEGDE + IL + 0.1M LiTFSI	0.052	- (0.001, expected)	- (2.68, expected)	$E = 18000$ $X_C = 7.5$
CNT-grafted carbon fiber[389]	MTM57 + IL + LiFSI	0.01	0.01	0.031	$G_{12} = 450$ $S_{12} = 14$ $E = 61200$ $X_C = 153$
Carbon fiber[347]	CD552 + SR494 + 0.825M LiIm	0.093	0.021	0.15	$E/\text{SG}^a = 12000$ $G_{12}/\text{SG} = 310$
CNT fibers (Chapter 5)	Thermoplastic + [PYR ₁₄][TFSI]	6.7	0.91 ^b	3700 ^b	$E = 790$ ^c $S_{11} = 53$ ^c
MWCNTs/ABA/polyaniline-modified carbon fiber[390]	CF ₃ SO ₃ Li + PEG copolymer	0.125	0.017	-	$S_{\text{lex}} = 21$ $E_{\text{flex}} = 2900$

^a) Normalized by specific gravity (SG). ^b) Electrochemical properties normalized by device weight without metallic current collector or encapsulation material, ^c) Tensile test of active material and polymer electrolyte membrane.

6.3.3 Envelope of multifunctional properties

Some analytical examples illustrating the envelope of multifunctional properties are showed in Figure 6.12. Composite energy (E) and power (P) densities can be calculated as

$$E = \frac{E_s n A_{\text{eff}}}{m_{\text{interleaf}} + m_{\text{CF}} + m_{\text{epoxy}}}, \quad (6.1)$$

and

$$P = \frac{P_s n A_{\text{eff}}}{m_{\text{interleaf}} + m_{\text{CF}} + m_{\text{epoxy}}}, \quad (6.2)$$

6.3 Mechanical interconnection using perforated interleaves

where E_s and P_s are energy and power densities of individual EDLC per unit planar area, n is the number of EDLC interleaves, A_{eff} is their effective planar area and, $m_{interleaf}$, m_{CF} and m_{epoxy} are the mass of the different components. The planar area is simply the projected area of the device from top view. Trivially, $m_{interleaf} = \rho t n A_{eff}$, where ρ is the EDLC volumetric density and t is its thickness. Interlaminar properties such as shear modulus G_{12} can be similarly expressed as a function of A_{eff} as

$$G_{12} = G_{12}^* (1 - A_{eff}), \quad (6.3)$$

With equations 6.1-6.3 one can easily predict the energy density, power density and shear modulus of a range of interleaf designs, with properties following the behaviour in *Figure 6.12*. Such a simple estimation allows to evaluate the optimal balance between conflicting electrochemical and mechanical requirements for a particular application, determined by interleaves' design.

Figure 6.12. Predicted shear modulus (G_{12}), a) Energy density and b) Power density as a function of the interleaf area. The prediction is for $n = 1$, $t = 0.56$ mm. Maximum shear modulus of 4.3 GPa corresponds to pure epoxy.

6.4 Additional aspects of multifunctionality

6.4.1 Encapsulating properties of the composite

The ingress of water in ionic liquid-based EDLCs causes a dramatic reduction of the electrochemical stability window of the ionic liquid and degradation of device properties,^[337] hence the use of pouch shells and other encapsulation media, which evidently increase the weight of the device, are necessary. Because of its relatively low permeability to water, cross-linked epoxy is an inherent barrier for water. Therefore, apart from its mechanical functions, in energy storing composite the epoxy matrix can take the key function of encapsulation of the electrochemical system. To demonstrate this, electrochemical properties of a fractured structural EDLC composite was tested before and 12 hours after complete immersion in water (*Figure 6.13*). *Figure 6.13a* shows that CD profiles are nearly identical, with

6.4 Additional aspects of multifunctionality

capacitance, power and energy density values within 4% of those in the dry state. For reference, a plain self-standing EDLC interleaf has a 45% drop in energy after 12 hours of immersion in water (Figure 6.13b).

Figure 6.13. Encapsulation of the EDLC interleaf by epoxy. Comparison of CD profiles before and 12 hours after immersion in water for a) structural and b) free-standing SC.

6.4.2 Optimization of the composite architecture

The device configuration used so far contains various elements that could be simplified or removed in order to improve properties and/or reduce weight. This is the case of the insulator between conductive CF and the device and the aluminum current collector, which inhibit adequate infusion of epoxy resin and can easily cause delamination. Utilization of alternative structural components or composite's configuration enables replacing or eliminating the redundant materials. For instance, the double-sided adhesive insulator can be replaced by thin polymer electrolyte membrane. This approach enables disposing the aluminum current collector of the EDLC assembly but using carbon fibers as alternative electrode, which might additionally contribute to capacitance of the electrochemical system.

As a first step in this direction, a structural composite where both the CNT fibers and the CF act as active electrodes, without recourse to metallic supports, external current collectors or plastic tape insulators was produced. This is realized by embedding polymer electrolyte membranes between CNT fibers veils and CF tows, as schematically shown in Figure 6.14a. Unlike the samples discussed above, where the pre-formed EDLC was embedded between plies, in Figure 6.14a the EDLC composite array is assembled layer by layer. The polymer electrolyte membranes play a dual role acting both as separator, avoiding the electrical contact between CNT and CF electrodes, and as an ion conductor media connecting them ionically. It is worthy to highlight, that replacement of thick plastic tape insulator by thin dual functional polymer electrolyte membrane not only enables saving the final weight of the device but also endows CF structural component with energy storage capabilities. As

6.4 Additional aspects of multifunctionality

depicted in *Figure 6.14a*, ionically connected CNT fibers and CF can act as an EDLC system improving the energy storage capacities of the integrated structural composite.

Figure 6.14. Alternative structural composite supercapacitor architectures using both CNT fibers and CF as active material, without current collector, separator or insulating layers. (a) Scheme of different EDLC configurations in the composite. (b) Charge-discharge profiles comparing CNT fiber/CNT fiber and CNT fiber/CF device configurations (c) Photographs of the structural supercapacitor powering a red LED in the two configurations.

In fact, such CF/CNT fiber configuration was successfully charged and discharged (*Figure 6.14b*) with high coulombic efficiency (98%) and providing sufficient power to light a red LED (*Figure 6.14c*). As expected, energy and power densities of the resulting arrangement was lower than for CNT/CNT configuration (*Figure 6.14b*) due to the lower surface area of the CF ($0.2 \text{ m}^2\text{g}^{-1}$ vs. $256 \text{ m}^2\text{g}^{-1}$ for CNT fibers). Further optimization of the composite architecture by parallel connection of CNT/CNT and CF/CNT configurations inside of the composite structure will result in enhanced energy storage properties. This is the key to produce devices with asymmetric distribution of load and a charge between electrodes/reinforcing elements. These preliminary results open a new avenue for energy storage in multifunctional structures combining CF and CNT fibers.

6.4 Additional aspects of multifunctionality

6.4.3 Analysis of multifunctionality

The main motivation for the development of multifunctional composites consists in achieving the level of maturity at which the device offers a weight saving relevant for a wide range of applications (e.g. aerospace, portable electronics, road transport). It means that the mass of multifunctional system should be below the total mass of conventional monofunctional electrochemical and structural devices. The ultimate weight saving determined by multifunctional performance of the structural composite can be achieved through the balance between conflicting electrochemical and mechanical properties. This is a challenging task demanding not only modification of the constituents (FRP, CNT fiber electrodes, PE membrane and EDLC configuration) but also optimization of the composite architecture.

To analyze the level of multifunctionality of the composite based on CNT fiber/PE interleaves its electrochemical and mechanical properties were compared to monofunctional systems considering a conventional supercapacitor (Maxwell BCAP0010, Energy = 2.9 Wh kg⁻¹)[370] and the control [0°]₈ fiber reinforced polymer (E = 60 GPa) as benchmark electrochemical and structural components, respectively. *Figure 6.15a* shows the plot of energy density against longitudinal Young's modulus calculated for different configurations of embedded EDLCs. The values of energy density at varied mass fraction of energy storage constituent were estimated as $Energy(x) = x \times Energy(EDLC)$, where x is the mass fraction of the EDLC interleaf and $Energy(EDLC)$ is the intersection of the plot with the vertical axis, corresponding to specific energy density normalized by the mass of EDLC. Young's modulus was calculated assuming that the composite follows the rule of mixture, and $E(x) = x \times E_{EDLC} + (1 - x) \times E_{FRP}$, where E_{EDLC} and E_{FRP} correspond to longitudinal Young's modulus of the EDLC and the bare [0°]₈ fiber reinforced polymer, respectively.

The black dashed line shows the combination of monofunctional systems. Evidently, both energy and modulus are proportional to the mass fraction of its corresponding monofunctional component. The green line corresponds to the results of this work. While they are still below the level for weight reductions, it is of interest to analyze the effect of different plausible improvements to these materials on their multifunctional performance. *Figure 6.15a* shows, for example, that feasible modification of EDLC by removal of aluminum current collectors (Al cc) and a reduction of PE membrane thickness would produce substantial improvements in performance, particularly for multifunctional composites with high energy density requirements (red line). The observed enhancement of the composite's electrochemical properties is accompanied by slight increase in mechanical performance of the device caused by enlarged mass fraction of CNT fibers.

6.4 Additional aspects of multifunctionality

Figure 6.15. Multifunctional properties of structural power composites. (a) The plot of energy density vs Young's modulus at different mass fraction of electrochemical component estimated for alternative EDLC's configurations. (b) Multifunctional plot showing contribution of electrochemical and mechanical efficiencies in structural composites.

In contrast, an increase in the Young's modulus of the CNT fiber fabrics to 30 GPa approaching the values for structural composite (purple curve), would not lead to large performance improvements (purple line). According to the analysis, a more promising method to improve multifunctional performance is to introduce pseudocapacitive metal oxides in the CNT fiber fabric, which has been recently demonstrated to produce monofunctional materials with high energy density (e.g. MnO₂).[391] Specific energy density of the all-solid SC based on CNT fibers decorated by MnO₂ was found to be around 16 Wh kg⁻¹ at 3 V which is more than 2 times higher compare to pristine material (7 Wh kg⁻¹ at 3 V). Coupled with optimization of membrane thickness, this would lead to a multifunctional composite material providing sufficient mechanical and energy storage properties to offer a weight saving (orange line).

A more general approach to examine multifunctional performance of the structural power composites consists in calculating an efficiency index (μ_{mf}) as the sum of the electrochemical and ($\mu_{\text{energy}} = \text{Energy}_{(\text{mf})}/\text{Energy}_{(0)}$) and mechanical ($\mu_{\text{modulus}} = E_{(\text{mf})}/E_{(0)}$) efficiencies with respect to the monofunctional materials. Here $\text{Energy}_{(\text{mf})}$ and $\text{Energy}_{(0)}$ refer to energy density of multifunctional material and the conventional device, respectively, and $E_{(\text{mf})}$ and $E_{(0)}$ to the longitudinal Young's moduli of multifunctional and monofunctional composites, respectively. In these terms, weight reductions at a materials level correspond to $\mu_{\text{mf}} > 1$.

The plot in Figure 6.15b compares the reference monofunctional system (black line) with different multifunctional materials. For reference, Figure 6.15b includes literature data corresponding to structural supercapacitor composites with CNT-grafted CF active material, GF fabrics separator and a multifunctional matrices based on IL and Li salt. These systems have mechanical efficiency near

6.4 Additional aspects of multifunctionality

unity, but a relatively low energy density ($\mu_{\text{energy}} \sim 0.001\text{-}0.004$), leading to μ_{mf} around 0.82 - 1.00.[389] The use of EDLC interleaves based on CNT fibers and the PE noticeably raises the value of μ_{energy} while preserving μ_{modulus} close to 1, although with μ_{mf} currently at 0.95. But the analysis shows that integrating pseudocapacitive metal oxides and optimizing the interleaf device architecture will lead to μ_{mf} around 1.02 - 1.13. Very importantly, a key feature of the multifunctional architectures introduced in this work is that they enable tailoring composite properties by controlling the mass fraction of electrochemical and FRP components to meet a particular balance of mechanical and electrochemical contributions.

6.5 Summary

The simple fabrication method of a structural composite supercapacitor was demonstrated through embedding of CNT fibers/polymer electrolyte interleaves between carbon fiber fabrics followed by infusion and curing of thermosetting polymer. The technique enables achieving good integration of the components in the CF/EDLC/epoxy laminate with a continuous ply structure and a small number of voids and defects at the EDLC interleaf edges accounted to less than 1% of the total volume. Once embedded in the composite structure, the EDLC interleaves had similar electrochemical properties as before, with coulombic efficiency of 98% and low ESR of 35 Ohm cm² even when charged to 3.5V.

In situ electrochemical measurements during 4-point bending performed on the composite with EDLC interleaves at different ply positions reveal distinctive electrochemical behaviour for the tensile, neutral and compressive scenarios. For the EDLC interleaf experiencing tensile force changes in ESR and capacitance caused by improved infiltration of the polymer electrolyte produce 30% increase in energy density upon bending, 10% of which remain preserved after complete unloading of the applied stress. Smaller increment in energy density observed for the interleaf in the neutral plane was attributed to improved electrical contact in the EDLC layers, caused by the applied pressure. The device undergoing high compression stress experiences local losses of electrical contact, related to transverse opening deformation. This provokes considerable increment of ESR and reduction of energy density by 22%. Electrochemical properties were essentially recovered after unload of applied stress demonstrating excellent stability of embedded EDLCs. Even after sample failure by buckling the devices could still be charged and discharged, with 69% and 93% of the initial energy and power densities, respectively.

The produced composites exhibited high power density of 30 W kg⁻¹ combined with energy density of 37.5 mWh kg⁻¹. Although their interlaminar properties are expected to be substantially reduced by the presence of the soft-matrix interleaves, the presence of EDLC interleaves embedded into CF composite does not significantly influence mechanical properties achieving 60 GPa and 153 MPa of

6.5 Summary

the flexural modulus and flexure strength, respectively. As a demonstration of the engineering possibilities to improve interlaminar properties offered by these materials grid-shaped interleaves were produced. Synchrotron 3D tomography showed that the employment of perforated EDLCs leads to epoxy regions interconnecting CF plies through holes in the interleaf. Bending test indicated that the sample with grid interleaf suffers less pronounced delamination at the edges of embedded device compare to structural composite with entire EDLC that demonstrates better fastening of CF laminas, while preserving nearly identical electrochemical properties. The ability to change the shape and size of the hole pattern in the interleaf open a wide range of design parameters to optimize multifunctional properties of the device and obtain desired composite performance.

Among additional aspects of composite's multifunctionality encapsulation of the electrochemical device and alternative architectures of the system were explored. Strong encapsulating properties of CF/epoxy laminate was demonstrated by electrochemical test of the structural composite showing similar performance before and 12 hours after being immersed to water. As pointers for potential improvements in electrochemical properties, the possibility to use both CF and CNT fibers as electrodes was realized by embedding PE membranes between CNT fibers veils and CF tows. This enables to reduce the weight by elimination of electrical insulators and metallic current collector while increasing the fraction of composite material used for energy storage. Furthermore, the ionic connection between CF and CNT fibers through PE membrane discloses additional capacitive contribution of proposed configuration. The analysis of the composite's multifunctionality reveals that the assembled device does not reach the level of multifunctional efficiency at which it offers weight saving. Preliminary assessment of feasible improvements by optimization of the interleaf device architecture anticipates the prospect to achieve sufficient mechanical and energy storage properties to surpass the limit of required multifunctionality providing a weight reduction.

CHAPTER 7

Conclusions and Future outlook

For the sake of a better understanding, in the final chapter the main conclusions have been associated to the specific aspects addressed during this PhD thesis. Moreover, some insights or hints derived from the results of the work were also included as future outlook.

Multifunctional properties of CNT fibers

It has been demonstrated that macroscopic fibers of CNTs produced by the direct spinning method possess an excellent combination of high electrical conductivity, specific surface area and mechanical properties, and thus are attractive elements in multifunctional devices, particularly supercapacitors, with augmented mechanical performance. The direct spinning process enables large control of structural and morphological features of CNTs, such as the degree of CNTs alignment in the fibers, tailored by the draw ratio of the fiber spinning. This thesis provided an extensive study on the electrochemical properties of such fibers and their integration in various multifunctional devices.

Electrochemical characterization of CNT fibers in Pyr₁₄TFSI ionic liquid revealed moderate values of specific capacitance in half-cell (78 F g⁻¹) and full-cell EDLC device (32 F g⁻¹) resulting in 14 Wh kg⁻¹ of energy density. The values of power density were closely associated with electrode mass loading (i.e. thickness) through an inverse relationship and thus should be taken as relative to

7 Conclusions and Future outlook

the mass of CNT fibers per unit area. The cyclability test of the EDLC device at 3.5 V over 10000 CD cycles revealed excellent stability with capacitance retention of > 93%.

Electrochemical measurements also indicated that in fibers made of highly graphitized CNTs of few layers (3-5) capacitance increases substantially with applied bias. This feature was directly related to the contribution of quantum capacitance, which follows the density of states near the Fermi level and becomes accessible in low dimensional system. As such, it must be seen as an intrinsic feature of these nanocarbon-based electrodes. The results suggest that modification of electronic structure of the CNTs can affect quantum capacitance and alter energy storage capabilities of the material.

Therefore, exploring different methods to change the electronic structure of CNTs during CVD growth[258], chemical doping of nanotubes with heteroatoms[392] or functionalization[300, 301] might offer an opportunity to influence electrochemical performance of the fibers. The first approach might be of particular interest due to the possibility of controlling the type of the CNTs during fiber spinning in terms of diameter, number of the layers and potentially chiral angel distribution.[215]

For instance, the layer-dependent electric properties can be investigated for CNT fibers by tailoring the type of nanotubes *via* adjustment of the sulfur promoter concentration in the precursor mixture during CVD growth of CNTs. However, it will be very challenging to analyze the electronic properties of the system composed of a mixture of CNT bundles since the assembly of individual nanotubes into a bundle leads to an electronic structure with substantially increased number of states, really difficult to predict.[393] Furthermore, macroscopic fibers of CNT always contain a certain distribution of diameters and chiral angles, where the joint DOS results from superposition of individual DOS losing some single-molecule features. Therefore, the influence of CNT structure on quantum capacitance of individual nanotubes will be noticeably mitigated in CNT fibers that makes more complicated to determine and attribute the changes in quantum capacitance and overall electrochemical behaviour of the material to the specific alterations in its structure.

In this thesis the electronic structure of CNTs was modified by introduction of different surface functional groups. Functionalization of CNT fibers was performed through the gas-phase reaction conditions using UV-generated ozone, which enables preserving CNT fiber morphology at both the macro- and the micro-scale. It was demonstrated that short ozone treatment of CNT fibers (15 min) had a beneficial effect on their tensile properties manifested in an increase of specific strength and Young's modulus, but cause a reduction in electrical conductivity. Furthermore, the method also allowed a fairly accurate control of a degree of CNT fiber functionalization by simply varying the reaction time. Introduction of functional groups in CNT fibers improved hydrophilic properties of the material and endowed their use in electrochemical systems with aqueous electrolytes.

Specifically, improved hydrophilic behaviour of functionalized CNT fibers along with newly-

7 Conclusions and Future outlook

acquired redox active functional groups resulted in increase of specific capacitance from 14 F g^{-1} to 46 F g^{-1} after 2 hours of ozone treatment obtained in 1M KOH electrolyte. This was translated into higher values of specific capacitance (from 7 to 30 F g^{-1}) and energy density (from 0.34 to 1.29 Wh kg^{-1}) of a symmetric SC. The effect of functionalization was also studied in Pyr₁₄TFSI ionic liquid, which should minimize pseudocapacitive contribution and wetting limitations. The extension of the ozone exposure time led to a clear diminution of the differential capacitance dependence on the bias potential, which indicated fading of quantum capacitance dominance but significant rise of total capacitance from 29 to 45 F g^{-1} . The effect was also evidenced for the symmetric EDLC which exhibited an enhancement in energy density from 13.5 to 17 Wh kg^{-1} .

As a part of future work, an improvement of electrochemical performance of CNT fibers by deposition of redox active materials based on transition materials or conducting polymers should be explored. In fact, some on-going research in our group is now focused on using CNT fibers as an excellent highly-porous conducting scaffold for incorporation of pseudocapacitive elements. In particular, electrochemical deposition of MnO₂ onto CNT fibers reveals a substantial raise of their electrochemical properties.[391] The specific capacitance obtained for SC device assembled with MnO₂-CNT fiber electrodes (60 minutes of total MnO₂ deposition time) in Pyr₁₄TFSI electrolyte was increased from 30 to 82 F g^{-1} with respect to bare CNT fiber EDLCs. Such enhancement causes a perceptible growth of energy density from 14 to 30 Wh kg^{-1} , although achieving a small decay of specific power from 25 to 17 kW kg^{-1} . Optimization of deposition conditions, posttreatment techniques and study of other synthetic methods for metal oxide will enable to enlarge capacitive properties of CNT fibers and tune the balance between energy, power and electrochemical stability of the system. Moreover, a rapid development of novel pseudocapacitive materials with advanced electrochemical properties will provide a wide variety of promising candidates which can be coupled with multifunctional CNT fiber electrodes.

Development of all-solid flexible supercapacitor based on CNT fibers

In order to employ CNT fibers for fabrication of all-solid EDLCs, in this thesis several polymer electrolyte (PE) membranes were produced by casting method using Pyr₁₄TFSI ionic liquid (IL) and different polymeric matrices. The PE based on PVDF-co-HFP copolymer demonstrated the optimum balance between mechanical properties and ion mobility. Specifically, an appropriate combination of mechanical robustness and ionic conductivity was found to be at 60 wt.% of IL and 40 wt.% of the polymer. The membrane exhibited $4.5 \times 10^{-4} \text{ S cm}^{-1}$ of room temperature conductivity, 14 MPa of Young's modulus and 3.4 MPa of tensile strength. Thermal analysis of the membrane reveals some characteristic features of the PE, such as increased fraction of amorphous PE, reduced glass transition temperature, suppressed cold crystallization/melting of IL and partial self-aggregation of IL at higher

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IL content. These features led to PE membrane providing good mechanical stability and ionic conductivity.

After exploring different fabrication methods, the assembling of all-solid EDLC was performed by sandwiching the PE membrane between two CNT fiber electrodes under pressure. The final step consisted in laminating the device in a plastic pouch using a conventional laminating machine. This simple method evinced reproducible electrochemical performance of self-standing EDLC devices as large as 100 cm^2 with maximum gravimetric capacitance of 28 F g^{-1} , energy density of 11.4 Wh kg^{-1} and power densities of 46 kW kg^{-1} , similar to those obtained under high pressure in Swagelok cell. The efficiency and performance of the all-solid EDLC to a large extent depend on the amount of pressure applied during assembling of the device. This suggest that further improvements on the device assembly should try to correlate impregnation to the viscoelastic properties of the membrane at the point of infiltration.

It is important to highlight that this easy fabrication method of flexible supercapacitors might greatly expedited assembling process compared to conventional methods, which normally include preparation of carbon slurry with electrode material and additives, knife pasting or doctor blading of carbon ink onto a current collector, drying of electrodes, assembling and stacking of cells, filling with liquid electrolytes and vacuum sealing of the device. The fabrication method developed within this PhD thesis can be easily scale-up to industrial level using conventional manufacture machinery and shortening the duration of device fabrication.

Another important aspect of this work was to quantify the flexible character of the developed EDLCs. In this sense, large-area devices were repeatedly bent and folded 180° without degradation of their electrochemical properties. Furthermore, tensile test of CNT fiber/PE membrane/CNT fiber EDLC structure composed of highly aligned CNT material revealed excellent mechanical properties, achieving maximum tensile strength of 53 MPa (39 MPa SG^{-1}), Young's modulus of 790 MPa (577 MPa SG^{-1}) and specific toughness of 3.7 J g^{-1} at fiber volume below $14\text{ vol.}\%$.

The mechanical stability of the composite system would be significantly enhanced by optimization of cooperative load bearing between individual CNT fiber filaments and tailoring CNT fiber volume fraction. If the tensile properties of an individual filament can be implemented in an electrode and the volume fraction approached the values for traditional fiber-reinforced polymer composites of $50\text{-}60\%$, the resulting structure would reach specific strength of approximately 0.37 GPa SG^{-1} and specific modulus of 18 GPa SG^{-1} . Such approaches to further improvement of EDLC's mechanical properties will be an important part of future directions.

One of the objectives of this thesis was the design of a large area EDLC device capable to fulfil the requirements of a specific target application. In particular, EDLC prototype was optimized for

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powering a mechanical component and further integration into the aircraft interior. A stack configuration of EDLC prototype based on four individual 100 cm² cells connected in series was fabricated in order to reach an optimum structure and accomplish the restrictions of the application. The proposed design enables to power the mechanism consecutively four times and, importantly, to achieve considerable reductions in the volume and weight of the device.

Despite exhibiting sufficient electrochemical properties predefined by the practical application, the flexible EDLC prototype still demonstrates a performance inferior to commercial EDLCs. However, several options for further optimizations of the system remain feasible. A noticeable reduction in the weight and thickness of the device can be achieved employing a bipolar configuration of electrodes, minimizing the thickness of PE membrane or/and by increasing the fraction of active carbon material that will also affect tensile properties of the composite. In addition, the use of lighter and thinner plastic pouch will allow to fabricate a more compact device with a lower portion of redundant material.

Additional features of EDLC based on CNT fibers were also investigated. For instance, high electrical conductivity of CNT fibers enabled getting rid of metallic current collector, which evinced electrochemical performance similar to that of a common EDLC containing metallic component. Besides capacity, energy and power density, another important electrochemical characteristic such as self-discharge of EDLC was studied in detail. It was demonstrated that the high electrical conductivity of the CNT fibers along with large operating voltage caused fast initial self-discharge of the EDLC. However, this intrinsic effect could be tuned to some extent by extension of the voltage holding step and by controlling the maximum voltage applied. Since for some applications (electric vehicles, aircrafts, etc) safety is of paramount importance, fire resistance of the developed EDLC was examined. The devices exhibited outstanding flame retardancy corresponding to self-extinguishing type of material. Thereto, low flammability of PVDF-co-HFP polymer matrix, graphitic carbon material and non-flammability of ionic liquid promote outstanding flame retardant property of the EDLC structures.

As mentioned above, the CNT fiber direct spinning process enables control of the electrode mass loading and thickness. This was used to assemble all-solid EDLCs with single-filament CNT fiber films (~20 nm thick) with large power density and high transparency. A free-standing laminated all-solid EDLC device based on PE membrane and highly transparent (T=90% at $\lambda=550$ nm) assembly of CNTs showed the transmittance of 74% at the wavelength of 550 nm and extremely high gravimetric power density of 1370 kW kg⁻¹, substantially exceeding state-of-the-art of transparent supercapacitors.

Although outstanding performance of transparent EDLCs was successfully demonstrated in small devices, further scaling up can have certain limitations related to percolation effect in thin conductive films.[375] Thus, a part of future directions should address this challenge. To solve the problem of

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thickness dependent electrical conductivity several approaches can be applied. First, to ensure low ESR in large area devices the use of current collector frame is required. In this instance, the transparent nature of large area EDLCs can be preserved employing grid-like patterned current collectors covering only a small part of the devices area.[394] Alternatively, resistance can be reduced through deposition of two-three overlapped CNT fiber filaments. This implies a drop in optical transmittance of the electrodes and the final device, but can be optimized to reach a balance between transparency of the system and its electrochemical capabilities.

Development of structural supercapacitor based on CNT fiber/polymer electrolyte interleaves and CF/epoxy laminates

High multifunctionality of the CNT fiber/polymer electrolyte composites manifested in their exceptional mechanical stability and excellent capacitive behaviour suggests the prospect of using these structures for fabrication of fully structural EDLCs. In this PhD thesis, CNT fibers/polymer electrolyte interleaves were integrated between carbon fiber fabrics followed by infusion and curing of thermosetting polymer forming a continuous CF/EDLC/epoxy laminate ply structure. The infusion and further curing of the resin induced negligible deviation in the performance of the interleaf, exhibiting 98% of coulombic efficiency, 35 Ohm cm² of ESR and >97% of energy retention.

In situ galvanostatic charge-discharge measurements during 4-point bending test of the composite with EDLC interleaves at different ply positions helped to estimate the impact of applied stress on the properties of devices with specific location. EDLC interleaf under tensile tension experienced significant increase in energy density upon bending, caused by improved infiltration of the polymer electrolyte which produces positive changes in ESR and capacitance. The interleaf located in the neutral plane of the composite experiences close to zero stress and thus does not show a significant alteration in the performance. On the contrary, EDLC interleaf undergoing compression demonstrates reduction of electrochemical properties mainly associated to transverse opening deformation translated into local losses of electrical contact. However, a relief of applied stress recovers the initial electrochemical performance of the device. The apparent alterations in the behaviour of interleaves can be assumed to be reproducible in elastic region of the composite. But even after plastic deformation and sample failure by buckling the devices is still capable to retain 69% of the initial energy density and 93% of the initial power.

It is important to mention that the presence of the soft-matrix interleaves does not cause a pronounced drop in mechanical performance, achieving 60 GPa and 153 MPa of the flexural modulus and flexure strength, respectively. In fact, power and energy densities corresponding to 30 W kg⁻¹ and 37.5 mWh kg⁻¹, respectively, represent the highest values reported for structural power composites. However, the interlaminar properties of the composites, particularly in shear, are really poor but could be improved

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utilizing preformed grid-shaped interleaves. In order to solve this problem we proposed an architecture where CF plies are interconnected by epoxy penetrated through the holes in perforated EDLC. This led to structural EDLC with higher resistance to delamination, remarkable increase in shear strength of the composite and similar electrochemical properties.

Such engineering approach opens a possibility to tune the properties of the composite according to the needs of specific application. The predicted linear dependence between shear modulus and effective area of the interleaf can be used as fairly accurate estimation for optimization of the multifunctional performance. As a future work, the effect of various designs of the interleaf having different shape and size of the hole pattern on shear properties of the structural power composite should be examined. In addition, other factors, such as position and the number of interleaves in the laminate need to be further considered to obtain a desired combination of electrochemical and mechanical properties.

Even so, fabricated structural power composite does not reach the level of multifunctional efficiency at which it offers weight saving. However, an assessment of feasible improvements anticipated the prospect to achieve sufficient mechanical and energy storage properties to surpass the limit of required multifunctionality providing a weight reduction. This can be done by removal of metallic current collector, increase of CNT fiber fraction in the EDLC interleaf (i.e. reduction of PE membrane thickness) and deposition of pseudocapacitive metal oxides onto CNT fibers (e.g. MnO_2).

The concept of multifunctional supercapacitors based on CNT fibers creates a general framework of multifunctional electrochemical energy storage systems which should be considered as a starting point for the development of more sophisticated devices, such as flexible or structural batteries.

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