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Using numerical models to accelerate electrolyte transport parameter identification

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Abstract

A new electrolyte transport parameter identification methodology, based on the numerical solution of a symmetric Li–Li cell model, is presented. In contrast to available techniques in the literature, where small concentration perturbations are generated in testing setups and linearization is assumed to identify transport properties for the initial salt concentration, large currents are used here to excite nonlinear dynamics able to reveal concentration dependent transport properties. This approach allows a significant reduction in the experimental effort. The proposed methodology is applied to two synthetic experiments. Firstly, an ideal case (where all difficulties associated to stripping and plating dynamics on Li metal surface are neglected) is considered in order to show both the details of the proposed methodology and its performance (specially its robustness, including the effect of the noise level in the voltage measurements in the experiment). A second case considers the effect of complex stripping and plating dynamics to show that, provided (macroscopic) modelling/identification of this dynamics is carried out, the proposed methodology is still able to accurately identify electrolyte transport properties using a simple experimental test setup.

Keywords:

battery, electrolyte parameters, identifiability, model-based parametrization

1. Introduction

Lithium-ion batteries (LIBs) are widely employed in many applications on which society now depends [1]. However, despite almost 30 years of research and development, further investigation is still needed with the ultimate goal of searching high-performance batteries with higher energy density [2][3][4][5][6][7], better rate performance [8][9] [10][11][12] and longer lifespan. In this regard, several authors [13] [14] recently addressed the optimisation work of the design parameters of thick electrodes for various LIB configurations. It is noted for those cases, ion transport, rather than electron transport, is limiting in most cases [15] [16] and demonstrated battery cell performance is highly dependent on the transport and thermodynamic properties of their electrolyte[17]. Another example in which the electrolyte properties play a crucial role is in the so-called Lithium Metal Batteries, the uniformity of lithium deposition as well as lithium stripping mechanisms are severely affected by the transport properties of the electrolyte, as it is shown in [18] [19] and [20]. Regardless of the technology, it is therefore of paramount importance to be able to accurately measure electrolyte properties and ultimately improve them for the continued development of innovative battery technologies.

For a full understanding of the properties electrolyte system, the ionic conductivity (κ), binary diffusion coefficient (D_e), cationic transference number (t_0^+), molar thermodynamic factor and interfacial charge-transfer resistance (R_{ct}) are key parameters[21][2][22][23]. All these transport properties depend, in general, on the lithium ion concentration. Having accurate information of each of these properties, will provide knowledge toward a comprehensive picture of the electrolyte's transport phenomena and support better cell designs.

In spite of the availability of a wide range of experimental techniques, identification of electrolyte properties poses several practical challenges if good identifiability, robustness and limited experimental effort are simultaneously intended (as is the case, in general, with electrode/cell parameters identification; see, for instance, recent reviews [24] and [25]). Since identification of other transport properties poses very similar difficulties, electrolyte diffusivity will be considered here in more detail.

On one hand, in situ and operando techniques are used in literature for estimation of transport properties. In this regards, several authors [26] [27] used $1D^7$ Li NMR imaging and NMR to determine binary diffusion coefficient.

66 They proposed a new cell set-up configuration to identify the lithium ion
 67 concentration gradients under constant current load in a battery cell. Novel
 68 approaches based on operando X-ray photon correlation spectroscopy [28]
 69 have also been considered. Although in situ/operando characterisation opens
 70 new perspectives, significant obstacles to a routine operando characterisation
 71 still remain, such as the ones enumerated in Atkins et al. [29].

72 On the other hand, more classical electrochemical techniques are well
 73 suited and, definitely, more extended for the estimation of the transport
 74 properties. For instance, in literature the electrolyte diffusion coefficient is
 75 typically determined using restricted-diffusion experiments where the relax-
 76 ation of concentration/potential gradients in the electrolyte is monitored.
 77 The relaxation process takes place following cell polarization or after two
 78 fractions of electrolyte with different concentrations are put in contact, un-
 79 til the two phases reach uniform concentration. Measurements can be per-
 80 formed in various experimental setups, including long-time voltage relaxation
 81 for symmetric Li|Li electrochemical cells as first proposed in Ma et al. [30]
 82 and widely used, although other setups can also be used (as, for instance,
 83 identification from steady-state current proposed in [31]. These kind of tech-
 84 niques are used, among other references, in Capiglia et al. [32], [33] or Valoen
 85 et al. [34].

86 Although traditionally analytical solutions are used to identify the elec-
 87 trolyte diffusion coefficient from experimental observations in the above de-
 88 scribed setups, the remarkable increase in processors computing power com-
 89 bined with the development of efficient simulation tools have made the use
 90 of identification techniques based on the numerical solution of the experi-
 91 mental setup more and more frequent. This is the case, for instance, in [35],
 92 [36], [37] or [38] where optimisation techniques are used in order to find val-
 93 ues for the electrolyte diffusion coefficient minimising the difference between
 94 experimental results and numerical model results.

95 It is important to highlight here some points concerning the identification
 96 techniques found in the literature:

- 97 • Documented techniques always consider small perturbations of the lithium
 98 ion concentration in order to identify the electrolyte diffusion coeffi-
 99 cient. Of course, this restriction is essential if an analytical solution is
 100 used in the identification (since no exact solution is available for the
 101 model with concentration-dependent electrolyte diffusion coefficient).
 102 When the numerical solution is used instead, this restriction is only

kept as a way to ensure local identifiability associated to the linearised problem. As a consequence, concentration-dependency increases the number of cells to be assembled (since cells with different initial salt concentration be prepared) and tested. The characterisation experimental effort is then very high.

- In spite of the (above mentioned) very significant increase in computational capacity related to the microprocessor design improvements and the availability of several efficient simulation tools, identification techniques are still rather time consuming. For instance, identification of all the parameters in a cell (making the assumption of concentration independent parameters, leading to a significant reduction of the simulation time) using advanced optimisation algorithms can take as long as 14 hours [39]. Identification of a single parameter (as is the case considered here) requires a significantly shorter time, but still long enough for identification to be carried out after the experiment has concluded. Nevertheless, if computational time can be further reduced so that optimisation is possible to carry identification as the experiment proceeds, and adaptive experimental technique can be proposed. Using this approach, the experimental effort can be reduced (test can be interrupted as soon as the parameter has been identified) and identifiability ensured (for instance adding some validation test before putting an end to the experimental identification).

Against this framework, this paper considers an alternative approach to derive identification techniques for the electrolyte diffusion coefficient (easily extender to other cell parameter identification). This methodology will be based on the following ideas:

- Taking into account that linearization is not needed if the model is solved numerically, larger Li ion concentration variations are considered. In particular, test conditions should ensure that all the interval of Li ion concentration for which electrolyte diffusion coefficient is to identified is visited through the test (so that identification of the corresponding function for this interval is possible). Using this approach there is no need to prepare many cells (with different Li ion concentrations) in order to identify electrolyte diffusion coefficient corresponding to each Li ion concentration, since a single cell can provide this in-

138 formation. This would result in a very significant reduction of the
139 experimental effort during electrolyte characterisation.

- 140 • Since (as previously commented) adaptive testing techniques are envis-
141 aged as a long-term goal, really fast identification techniques must be
142 considered. This requisite implies both the use of efficient optimisation
143 techniques (combining good initial estimates and gradient-based local
144 optimisation methods) and the acceleration of the numerical simulation
145 of the cell (provided by the use of model order reduction techniques,
146 which in contrast to other acceleration techniques [40] does not imply
147 a simplified physics). As a result, on-line identification can be carried
148 out and experimental conditions modified in order to complete (and
149 validate) electrolyte diffusion coefficient estimation in adaptive testing
150 techniques.
- 151 • Being far from the linear case associated to small perturbations of the Li
152 ion concentration considered in the literature, identifiability of the elec-
153 trolyte diffusion coefficient (as a function of the Li ion concentration)
154 must be analysed. Given a parametrisation for the function describing
155 the electrolyte diffusion coefficient, local identifiability can be carried
156 out provided that sensitivities (to each parameter) are computed. In
157 addition, information from these sensitivities makes possible (through
158 the Fisher information matrix) the design of optimal experiments, max-
159 imising parameter identifiability.

160 All in all, in this paper a methodology based in the previous ideas is de-
161 veloped and applied to two synthetic experiments. In order to validate the
162 proposed methodology, identification of the concentration dependent binary
163 diffusion coefficient of non-aqueous electrolyte solutions carried out by two
164 different electrochemical methods in [37] is revisited. Since methods con-
165 sidered in [37] are based on model linearisation, several symmetrical Li-Li
166 cells are used in the experimental setup. The proposed methodology will be
167 tested in this framework in order to prove that identification can be carried
168 out using a single cell and shorter test duration.

169 For the sake of clarity, firstly an *idealised* synthetic experiment will be
170 considered in order to illustrate the proposed methodology. This first ex-
171 periment will neglect all complex phenomena taking place on the Li metal
172 electrodes and affecting to Li stripping and plating kinetics [41], [42].

173 Of course, such complex dynamics on the Li metal surface can not be
174 neglected in real cases since voltage measurements recorded during tests and
175 used in the identification technique can be strongly affected by this dynam-
176 ics (given that generation of significant variations in the Li ion concentration
177 will be provoked by relatively large external currents, such phenomena will
178 be more relevant in the proposed methodology). Some experimental tech-
179 niques propose the use of four electrodes cells [43], [44] in order to isolate
180 overpotential associated to the electrolyte, subtracting those corresponding
181 to stripping and plating phenomena. But even in that case (see [44]) recorded
182 voltages can be affected by stripping/ plating overpotentials.

183 A second synthetic experiment is considered in this paper in order to
184 illustrate the capacity of the proposed methodology to identify electrolyte
185 diffusion coefficient using a two electrodes Li–Li symmetric cell, provided that
186 stripping and plating phenomena can be modelled. Obviously, no attempt
187 will be made here to provide an accurate, general model for stripping and
188 plating phenomena (which, in addition, are strongly linked to solid electrolyte
189 interface, SEI, [45]). In contrast, a simple model inspired by [41] will be
190 considered here in the synthetic experiment.

191 The remainder of this paper is structured in the following way. In section
192 2 the theoretical background is presented where the strategy of the iden-
193 tificability problem is defined. In this section, full order model, reduced
194 order model as well as the pursued optimisation algorithm are introduced.
195 In section 3 two case studies are presented, the first one in which the ap-
196 plication of the proposed theoretical strategy defined in section 2 is derived
197 and the second case, in which a high fidelity full order model is introduced
198 accounting the impact of the morphology evolution along cycling in the strip-
199 ping/plating kinetics, and similar strategy is followed for estimation of the
200 electrolyte diffusion coefficient function. Finally, in section 4 main conclu-
201 sions of the proposed work are presented.

202 2. Theoretical background

203 In this section, the proposed methodology for the parameter estimation
204 is presented. This methodology addresses the aforementioned difficulties.
205 Firstly, a continuum model (called afterwards Full Order Model, or FOM)
206 describing the galvanostatic behaviour of a Li|Li symmetric cell is stated.
207 Then, the derivation of a reduced order model (able to solve very efficiently
208 the FOM using its reduction to a low dimensional model) is introduced.

209 Finally, the proposed optimisation strategy is described, again with a focus
 210 on its efficiency. In particular, use of model sensitivities is made in order
 211 to both implement gradient-based optimisation techniques and assist test
 212 design enhancing parameter identifiability.

213 2.1. Full Order Model

214 In this section, the continuum model capturing the electrochemical be-
 215 haviour of a Li|Li symmetric cell with a separator in between is introduced.
 216 Ion transport is modelled using Nernst-Planck equations and electroneutral-
 217 ity is imposed, which is generally an accurate assumption except outside a
 218 1 – 10 nm charged interfacial double layer region [46] which is here replaced
 219 by an electrical potential jump at the Li foil-electrolyte interface. Asymmet-
 220 ric behaviour of Li metal electrodes in Li|Li symmetric cells (see Koo et al.
 221 [47]) is not considered here either. Anyway, a more realistic description of
 222 Li metal electrodes is discussed later. Apart from ionic diffusion coefficient,
 223 ionic transport properties are considered concentration-independent (since,
 224 as explained, only a concentration-variable transport property is considered
 225 here for the sake of simplicity).

226 Lithium ion concentration in the electrolyte, c_e , can be obtained from a
 227 transport equation in the electrolyte. This equation reads

$$\epsilon_e \frac{\partial c_e}{\partial t} - \frac{\partial}{\partial x} \left(D_e^{eff} \frac{\partial c_e}{\partial x} \right) = 0 \quad \text{with } 0 < x < L_{sep} \text{ and } t > 0 \quad (1)$$

where ϵ_e and D_e^{eff} represent electrolyte porosity and effective diffusivity, respectively. Mass conservation equation (1) must be completed with the following boundary conditions

$$- D_e^{eff} \frac{\partial c_e}{\partial x} \Big|_{x=0} = \frac{(1 - t_0^+) I_{app}(t)}{AF} \quad \text{with } t > 0 \quad (2)$$

$$- D_e^{eff} \frac{\partial c_e}{\partial x} \Big|_{x=L_{sep}} = \frac{(1 - t_0^+) I_{app}(t)}{AF} \quad \text{with } t > 0 \quad (3)$$

228 and initial condition

$$c_e(x, 0) = c_e^0 \quad \text{with } 0 < x < L_{sep} . \quad (4)$$

229 where I_{app} represents the current intensity, A the cell (transversal) area, t_0^+
 230 the transport number and F the Faraday constant.

231 On the other hand, from the ionic current expression

$$\frac{I_{app}(t)}{A} = -\kappa \frac{\partial \phi_e}{\partial x} - \kappa_D \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{1}{c_e} \frac{\partial c_e}{\partial x} \quad (5)$$

232 where κ is the ionic conductivity and κ_D a parameter which can be written
 233 in terms of the ionic conductivity and mean molar activity coefficient $f_{\pm}$ as
 234 $\kappa_D = \frac{2\kappa RT}{F} (1 - t_+^0)$, the electrolyte potential drop between both electrodes
 235 $\phi_e(L_{sep}, t) - \phi_e(0, t)$, can be easily obtained as

$$\begin{aligned} \phi_e(L_{sep}, t) - \phi_e(0, t) = \\ \int_0^{L_{sep}} \left(-\frac{I_{app}(t)}{\kappa} - \frac{\kappa_D}{\kappa} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\partial \ln c_e}{\partial x}(x, t) \right) dx \end{aligned} \quad (6)$$

236 To complete computation of Li|Li symmetric cell voltage drop, overpo-
 237 tentials on each lithium foil must be computed. In order to that, the cor-
 238 responding kinetics (in this paper, Butler–Volmer will be used) should be
 239 inverted. This will be discussed later.

In the proposed methodology, the numerical solution of the nonlinear dif-
 fusion problem (1)–(4) is carried out using a P_1 finite element discretization.
 Finite element techniques represent a particular case of Galerkin methods.
 These methods consider the solution of a so-called variational formulation
 (or weak form) in a finite dimensional space vector V_h . In the solution of the
 present problem for c_e this formulation leads to searching $c_e^h(x, t)$ in V_h for
 any t and such that

$$\begin{aligned} \int_0^{L_{sep}} \epsilon_e \frac{\partial c_e^h}{\partial t} v_h dx + \int_0^{L_{sep}} D_e^{eff} \frac{\partial c_e^h}{\partial x} \frac{dv_h}{dx} dx = \\ = -\frac{(1 - t_+^0) I_{app}(t)}{AF} v_h(L_{sep}) + \frac{(1 - t_+^0) I_{app}(t)}{AF} v_h(0) \quad \text{with } t > 0 \end{aligned} \quad (7)$$

240 for all v_h in the vector space V_h . The space discretization leads then to a
 241 initial value problem for a system of ordinary differential equations. The
 242 size of this system is given by the number of degrees of freedom in V_h . In
 243 a P_1 finite element discretization this is the number of nodes used in the
 244 mesh. It must be taken into account that although this is a one-dimensional
 245 problem, the number of nodes can be somehow large since a boundary layer
 246 (associated to large concentration gradients arising when a not very small

current is applied to the cell, as needed in order to identify concentration-dependent properties as explained below) must be captured by the numerical model.

Numerical time integration of equation (7) with (a projected on V_h) initial condition (4) can be done using Backward Euler scheme, in order to avoid (strict) numerical stability constraints in the selection of time integration steps. This scheme reads

$$\begin{aligned} \int_0^{L_{sep}} \epsilon_e \frac{c_e^{h,k+1} - c_e^{h,k}}{\Delta t} v_h dx + \int_0^{L_{sep}} D_e^{eff} \frac{\partial c_e^{h,k+1}}{\partial x} \frac{dv_h}{dx} dx - \\ = - \frac{(1 - t_0^+) I_{app}(t_{k+1})}{AF} v_h(L_{sep}) + \frac{(1 - t_0^+) I_{app}(t_{k+1})}{AF} v_h(0) \end{aligned} \quad (8)$$

where $c_e^{h,k}$ and $c_e^{h,k+1}$ represent approximations of the lithium concentration c_e at the k -th and $k + 1$ -th time steps, respectively, and Δt the time step.

The implementation of this finite-element based FOM is carried out in a Python code using the open-source FEniCS library <https://fenicsproject.org/>. Most computationally demanding operations are written in Fortran, compiled and linked to the Python code in order to reduce the simulation time.

2.2. Reduced order model

Among other reduced order modelling (ROM) techniques, some methods consider the solution of the physical model using a Galerkin method with an *ad hoc* selection of the finite dimensional space V_h . Using this approach, where the continuum model is projected onto a low-dimensional subspace, the resulting ROM can be solved with a very significant reduction of the computational effort, in comparison with the FOM (see, for instance, [48], [49], [50] or [51]).

Following this approach, two phases must be considered: in a first, offline phase the *ad hoc* space vector V_h is selected and the ROM equations are assembled, then in a second, online phase an inexpensive time integration is carried out providing an accurate numerical solution of the physical model. Several techniques to build V_h (in the offline phase) can be considered. An efficient alternative is based on the Proper Orthogonal Decomposition ([52],[53],[54]) of a database of the model solutions. Elements of a basis for V_h , that will be called *solution modes*, can be easily computed using the so-called *method of snapshots*.

274 Thus, in order to build a ROM for the nonlinear diffusion problem (1)–(4)
 275 a database of representative solutions must be computed. This database can
 276 be obtained solving the FOM for a suitable combination of concentration–
 277 dependent electrolyte diffusion coefficients and electric current profiles.

278 Once this database has been completed, as mentioned, mode extraction is
 279 carried out using proper orthogonal decomposition (POD) and the so-called
 280 *method of snapshots* proposed by Sirovich [52]. FOM solutions are stored
 281 as columns of a matrix A and a singular value decomposition (SVD) of this
 282 matrix, $A = U\Sigma V^T$, is computed. Columns of (orthogonal) matrix U provide
 283 an (ordered) orthogonal basis to describe FOM solutions in the database. Not
 284 only the set of columns of U associated to non-zero singular values (in Σ)
 285 can exactly reproduce FOM solutions in A , but an approximation will be
 286 obtained if a smaller number of columns of U is kept instead. In this sense,
 287 (ordered) columns of U constitute an optimal selection when approximation
 288 of FOM solutions by the linear combinations of a small number of elements
 289 is considered (see [52] or [59]).

290 More precisely, let $\{\mathbf{x}_n\}_{n=1}^{N_{snap}}$ be the columns of the matrix A (*i.e.* the
 291 FOM solutions in the database), N_{svd} the number of non-zero singular value
 292 decomposition, $\{\sigma_j\}_{j=1}^{N_{svd}}$ the (decreasingly) ordered set of non-zero singular
 293 values, and $\mathbf{u}_j$, $\mathbf{v}_j$ the j -th columns of matrices U and V , respectively. Matrix
 294 A (containing N_{snap} FOM solutions) can be exactly represented by

$$A = \sum_{j=1}^{N_{svd}} \sigma_j \mathbf{u}_j \mathbf{v}_j^T$$

295 or approximated if only the first M terms are retained

$$A \simeq \hat{A} = \sum_{j=1}^M \sigma_j \mathbf{u}_j \mathbf{v}_j^T$$

296 Approximation error of FOM solutions contained in A can be easily ob-
 297 tained from decay of singular values since

$$\frac{\|A - \hat{A}\|_F}{\|A\|_F} = \frac{\sum_{j=M+1}^{N_{svd}} \sigma_j^2}{\sum_{j=1}^{N_{svd}} \sigma_j^2}$$

298 and, when singular values decay fast enough, last quotient can, in turn, be
 299 approximated by $\frac{\sigma_{M+1}}{\sigma_1}$. As a result, from the inspection of singular values

300 a decision on the number of *modes* (*i.e.* number of columns of U) to be
 301 retained as a function of the required accuracy in the representation of the
 302 database solutions can be easily established. Nevertheless, it must be taken
 303 into account that the previous selection is only related to the accuracy of the
 304 representation of FOM solutions in the database and not to the accuracy of
 305 the ROM solutions. In particular, in order to reach a particular accuracy
 306 in the solution of the ROM, all terms in the projected equations must be
 307 computed accurately enough [55].

308 In linear problems, all terms appearing in the ROM (derived by apply-
 309 ing the Galerkin method with V_h generated from POD modes) can be pre-
 310 processed in the offline phase. As a consequence, in the online phase only
 311 computation in a (very) low-dimensional space must be carried out. Non-
 312 linear problems instead lead to the online computation of terms in the (orig-
 313 inal) high dimension space. For instance, in this case (where nonlinearity
 314 arises from concentration-dependent diffusivity) the electrolyte diffusion co-
 315 efficient must be computed over the whole domain at each iteration. Thus
 316 computational speed-up can be significantly reduced unless this difficulty
 317 is overcome. One possibility comes from the reconstruction of the diffusion
 318 coefficient from a few measurements, as proposed by the Discrete Empirical
 319 Interpolation Method ([56],[57]). Using this approach, during the generation
 320 of a database, also snapshots of the electrolyte diffusion coefficient must be
 321 collected. From these snapshots a basis for diffusion coefficient interpolation
 322 is built using POD/SVD (see also [58] and [59]). Functions in this second
 323 basis will be called *diffusivity modes*.

324 In the proposed ROM lithium ion concentration in the electrolyte, c_e , is
 325 approximated using

$$c_e(x, t) \simeq \sum_{i=1}^{N_c} a_i^c(t) \phi_i(x) = \Phi(x) \mathbf{a}^c(t) \quad (9)$$

326 where $\{\phi_i\}_{i=1}^{N_c}$ represent the *solution modes* computed in the offline phase.

327 As previously described, see equation (8), formulation of the Galerkin
 328 method (with V_h the vector space spanned by $\{\phi_i\}_{i=1}^{N_c}$) and discretization
 329 using Backward Euler scheme leads to the system of N_c nonlinear equations
 330 for the coefficient vector $\mathbf{a}^{c,k+1}$ at each time step

$$[\mathbf{M}] \frac{\mathbf{a}^{c,k+1} - \mathbf{a}^{c,k}}{\Delta t} + [\mathbf{K}(\mathbf{a}^{c,k+1})] \mathbf{a}^{c,k+1} = \mathbf{b}^{k+1} \quad (10)$$

331 with

$$M_{ij} = \int_0^{L_{sep}} \epsilon_e \phi_i \phi_j dx \quad b_i = \frac{(1 - t_+^0) I_{app}}{AF} (\phi_i(L_{sep}) - \phi_i(0)) \quad (11)$$

$$K_{ij}(\mathbf{a}^c) = \int_0^{L_{sep}} D_e^{eff} \left(\sum_{i=1}^{N_c} a_i^c \phi_i(x) \right) \frac{d\phi_i}{dx} \frac{d\phi_j}{dx} dx \quad (12)$$

332 It can be easily shown that DEIM interpolation techniques allows to pre-
 333 process the computation of the stiffness matrix $\mathbf{K}$. It must be taken into
 334 account that $D_e^{eff}(\sum_{i=1}^{N_c} a_i^c \phi_i(x))$ will be approximated using the *diffusivity*
 335 *modes* $\{\psi_i\}_{i=1}^{N_D}$ (also computed in an offline phase)

$$D_e^{eff} \left(\sum_{i=1}^{N_c} a_i^c \phi_i(x) \right) \simeq \sum_{i=1}^{N_D} a_i^D \psi_i(x) = \Psi(x) \mathbf{a}^D \quad (13)$$

336 and $\mathbf{a}^D$ are computed by solving an interpolation problem

$$\sum_{i=1}^{N_D} a_i^D \psi_i(x_k) = D_e^{eff} \left(\sum_{i=1}^{N_c} a_i^c \phi_i(x_k) \right) \quad \text{for } k = 1, 2, \dots, N_D \quad (14)$$

337 for a set of (previously computed) points $\{\psi_i\}_{i=1}^{N_D}$ selected in order to have
 338 a well-conditioned interpolation problem. As a result, $\mathbf{a}^D$ can be obtained
 339 solving a linear system (with a fixed matrix) where the right hand term is
 340 obtained evaluating the diffusivity coefficient on a small number of points

$$\Psi_{\text{DEIM}} \mathbf{a}^D = D_e^{eff}(\Phi_{\text{DEIM}} \mathbf{a}^c) \quad (15)$$

341 and the stiffness matrix can be written as

$$K_{ij}(\mathbf{a}^c) = \sum_{k=1}^{N_D} R_{ijk} a_k^D = \mathbf{R} \mathbf{a}^D \quad \text{with} \quad R_{ijk} = \int_0^{L_{sep}} \frac{d\phi_i}{dx} \frac{d\phi_j}{dx} \psi_k dx; \quad (16)$$

342 Nonlinear system of equations (10) with DEIM approximation (13) can
 343 be solved using Newton method, thus obtaining

$$\begin{aligned}
& [\mathbf{M}] \frac{\mathbf{a}_{m+1}^{c,k+1} - \mathbf{a}_m^{c,k}}{\Delta t} + \\
& + [\mathbf{K}(\mathbf{a}_m^{c,k+1})] \mathbf{a}_m^{c,k+1} + \left(\frac{\partial [\mathbf{K}]}{\partial \mathbf{a}^c} (\mathbf{a}_m^{c,k+1}) \mathbf{a}_m^{c,k+1} + [\mathbf{K}] (\mathbf{a}_m^{c,k+1}) \right) (\mathbf{a}_{m+1}^{c,k+1} - \mathbf{a}_m^{c,k+1}) = \\
& = \mathbf{b}^{k+1} \quad (17)
\end{aligned}$$

344 where $\mathbf{a}_m^{c,k}$ represents the approximation of the lithium concentration modes
 345 coefficients vector $\mathbf{a}^c$ for the m -th Newton iteration at the k -th time step.
 346 The term $\frac{\partial [\mathbf{K}]}{\partial \mathbf{a}^c}$ arising from (Newton) linearization is given by

$$\frac{\partial [\mathbf{K}]}{\partial \mathbf{a}^c} (\mathbf{a}^c) = \mathbf{R} \frac{\partial \mathbf{a}^D}{\partial \mathbf{a}^c} (\mathbf{a}^c) = \mathbf{R} \Psi_{\text{DEIM}}^{-1} \frac{dD^{eff}}{dc} (\Phi_{\text{DEIM}} \mathbf{a}^c) \Phi_{\text{DEIM}} \quad (18)$$

347 where, as explained, most information can be preprocessed and only compu-
 348 tation at DEIM points is involved in the online phase.

349 2.3. Optimisation algorithm

350 The parameter estimation problem is solved by minimising some norm of
 351 the difference between the calculated voltage from the reduced order model
 352 for a particular choice of the diffusivity parameters $\mathbf{p}$, $V_{\text{mod}}(t; \mathbf{p})$, and the
 353 voltage measured in an experiment, $V_{\text{exp}}(t)$. Assuming the voltage is mea-
 354 sured in the experiment at times $\{t_k\}_{k=1}^{N_t}$ and using (the square of) l_2 norm,
 355 the problem can be written as

$$\mathbf{p}_{\text{opt}} = \underset{\mathbf{p}}{\text{argmin}} \sum_{k=1}^{N_t} \frac{1}{V_{\text{ref}}^2 N_{\text{ref}}} (V_{\text{mod}}(t_k; \mathbf{p}) - V_{\text{exp}}(t_k))^2 \quad (19)$$

356 where (for practical reasons) the objective function has been rescaled (in
 357 order to have $f_{\text{obj}} \sim 1$).

358 The simulated voltage, V , is obtained from the model as the addition of
 359 three components

$$\begin{aligned}
V(t; \mathbf{p}) = & (\phi_s(L_{\text{sep}}, t; \mathbf{p}) - \phi_e(L_{\text{sep}}, t; \mathbf{p})) \\
& + (\phi_e(L_{\text{sep}}, t; \mathbf{p}) - \phi_e(0, t; \mathbf{p})) - (\phi_s(0, t; \mathbf{p}) - \phi_e(0, t; \mathbf{p})) \quad (20)
\end{aligned}$$

360 where ϕ_s stands for the electric potential at the lithium foil surface (and
 361 assumed to be constant all along the lithium foil due to the lithium high

electric conductivity). The first and last of these components correspond to overpotentials on the lithium foil surface and is modelled using Butler–Volmer kinetics. A critical aspect in the kinetics modelling corresponds to the description of the exchange current density. This issue will be discussed in detail below. The second contribution in $V(t; \mathbf{p})$ is computed, as previously described, by equation (6) resulting from the integration of the charge conservation equation in the electrolyte (using the computed lithium ion concentration).

Effective minimisation algorithms need to compute derivatives of the objective function with respect to minimisation parameters (so-called derivative free algorithms instead lead to very poor convergence properties and would lead to a rather slow diffusivity identification method). In order to compute derivatives of the objective function, access to the derivatives of the electrolyte lithium ion concentration with respect to any diffusivity parameter at any time during the simulated period, $\frac{\partial \phi_e}{\partial p_i}(x, t; \mathbf{p})$, must be obtained. Such derivatives are called (model) sensitivities and, as described in the appendix Appendix A, they are obtained as the solution of a companion initial value problem that can be solved in parallel with the problem for ϕ_e itself. It is important to note that sensitivities carry out very relevant information concerning parameter identifiability and can be of critical relevance in order to design effective cell tests. This point will be considered in detail below.

In order to close the identification problem, electrolyte diffusivity parameterization is considered. Following [37], a model with two parameters is selected. According to this model, electrolyte diffusivity is described as an exponential function of the lithium ion concentration in the electrolyte phase, c_e , as

$$D^{eff}(c_e) = D_0 \exp(-\alpha_D c_e) \frac{\epsilon_e}{\tau_e}, \quad (21)$$

being D_0 and α_D the two parameters to estimate in this problem. Again for practical reasons, both parameters are scaled obtaining

$$D^{eff}(c_e; \mathbf{p}) = D_0^{ref} p_1 \exp\left(-\alpha_D^{ref} p_2 c_e\right) \frac{\epsilon_e}{\tau_e}, \quad (22)$$

where D_0^{ref} and α_D^{ref} are values obtained from bibliography, and p_1 and p_2 are the terms to estimate (with $p_1 \sim p_2 \sim 1$). This simple electrolyte diffusivity parameterization has been selected for the sake of simplicity, but

the methodology presented in this paper can be straightforwardly extended to any other parameterization (such as the use of spline interpolation or polynomial fitting).

Several optimisation techniques and initial iterate selection strategies will be considered below. Both efficiency and robustness are critical aspects in the developed methodology. These aspects will be discussed in the context of two case studies in the following sections.

An outline of the proposed methodology, summarising the procedure presented above, is shown in Figure 1.

insert Figure 1

3. First case study: a simple, ideal case

Electrolyte diffusivity identification problem in [37] is revisited here in order to highlight benefits from the methodology proposed in the previous section. In particular, it will be shown that a very significant reduction in the experimental effort can be obtained since preparation of cells with different salt concentrations is no longer needed in order to identify a concentration-dependent electrolyte diffusivity. Robustness of the proposed methodology will be also discussed.

As mentioned, identification of electrolyte diffusivity from galvanostatic tests of a symmetric Li|Li cell described in [37] is considered. Using the identified diffusivity in [37] a synthetic test is designed here. Instead of experimental results, FOM results will be used for $V_{exp}(t)$ (some noise will be latter added in order to prove the technique robustness) obtained using a fine mesh. The ability of the proposed methodology to recover the *right* model will then be tested.

Again following [37], a Butler-Volmer kinetic model with constant exchange current density, i_0 , will be used. Thus lithium surface morphology modification during cycling is not considered at this stage (a more realistic model will be proposed in the next section). Overpotential, η , at each lithium foil will then be given by

$$I_{app}(t) = i_0 \left(\frac{c_e}{c_e^0} \right)^\gamma \left(\exp \left(\frac{\alpha F}{RT} \eta \right) - \exp \left(\frac{-\alpha F}{RT} \eta \right) \right) \quad (23)$$

424 In Ehrl [37] concentration dependent binary diffusion coefficient is deter-
 425 mined from the short-term and the long-term relaxation behaviour after a
 426 pulse or a steady-state polarization experiment for two-electrode cells (using
 427 lithium metal electrodes and separator in between). Since both techniques
 428 require for small electrolyte concentration variations along cell in order to
 429 use the proposed analytical approximation, several cells (with different salt
 430 concentration) must be prepared in order to account for the concentration
 431 dependencies.

432 Here instead a single galvanostatic test is proposed. Since electrolyte dif-
 433 fusivity at different lithium ion concentration must be identified, it is clear
 434 that pulses with relatively large currents should be employed (in order to pro-
 435 duce large variations of ion concentration in the electrolyte). Test conditions
 436 similar to those corresponding to chronopotentiometry experiments, leading
 437 to partial depletion of lithium ion near an electrode, should provide infor-
 438 mation on electrolyte diffusivity for low values of ion concentration. Since
 439 also a significant increase of ion concentration will take place in the opposite
 440 electrode, in a test with a two electrode cell voltage measurements always
 441 combine information from low and high ion concentration and identifiability
 442 is not at all immediately guaranteed. Thus, diffusivity identifiability for a
 443 particular galvanostatic profile should be carefully analysed. In this paper,
 444 following the previous remarks, a profile with three pulse and relaxation peri-
 445 ods is proposed: the first pulse corresponds to a small current (its relaxation
 446 phase would make possible to identify electrolyte diffusivity corresponding
 447 to initial ion concentration), a second one is intended to lead to significant
 448 variations of the ion concentration near the electrodes (in order to explore
 449 variation of electrolyte diffusivity with ion concentration near the initial con-
 450 centration), and a third one with significant depletion of ion concentration
 451 (exploring electrolyte diffusivity for very low and large ion concentrations).

452
 453 To guide the selection of current intensity, I_{app} , and pulse duration, t_{pulse} ,
 454 for a galvanostatic test able to identify (concentration dependent) electrolyte
 455 diffusivity a (rough) estimate of the concentration variation can be used.
 456 Making the hypothesis that the concentration variations within the diffusiv-
 457 ity zone of the electrolyte has a linear behaviour whose value is prescribed
 458 by the boundary conditions, applied current intensity, pulse duration, and
 459 concentration variation (near each electrode), Δc_e , are related by

$$I_{app} \sim \Delta c_e A F \sqrt{\frac{D_e^{eff}}{2t_{pulse}(1 - t_+^0)}}. \quad (24)$$

460 It must be observed that the shorter the pulse time is, the better the
 461 estimation is because additional restrictions to the lithium diffusion in the
 462 electrolyte (during the pulse) will give rise to larger variations of the con-
 463 centration near the lithium metal foils (as clearly seen in Figure 2b) and
 464 experimental results will then exhibit the effects of diffusivity for a large con-
 465 centration interval (as intended in the experiment, to identify concentration-
 466 dependent diffusivity).

467 Furthermore, the previous relationship provides an upper bound of Δc_e
 468 (since the diffusion boundary layer is slightly thicker than predicted by a
 469 linear profile).

470

471 In the context of the application example considered here, (where the
 472 identification problem considered in [37] is revisited) to estimate the applied
 473 current in each of the three pulses, it is assumed that the correct order of
 474 magnitude of the effective diffusivity, D_{eff}^e , is known and 30 second current
 475 pulses will be used in the test.

476 Thus, using an educated guess for D_{eff}^e , fixing t_{pulse} (to 30 seconds) and A
 477 as well as assuming t_+^0 known, equation 24 can then be used to relate current
 478 intensity I_{app} and expected concentration variations Δc_e near the lithium
 479 metal electrodes. With the goal of exploring increasingly larger concentration
 480 intervals around the initial salt concentration $c_e^0 = 1M$ with each new pulse,
 481 values of I_{app} can then be selected.

482 Thus, pulses with current intensities (considering a coin cell with an area
 483 A near 2 cm^2) of the order of magnitude of 1 mA will give rise to concen-
 484 tration variations about 0.05 M, suitable for the first pulse in the considered
 485 test plan. For the second pulse, a current intensity of 10 mA is estimated for
 486 reaching a concentration variation of 0.5 M, while a variation near depletion
 487 in one of the electrodes would be obtained if a 20 mA current pulse is applied.

488

489 A synthetic test following the previous guidelines is then prepared. Sym-
 490 metric Li|Li cell parameters are adapted from Table II of [37]. As explained,
 491 the proposed galvanostatic testing protocol consists on three pulse and re-
 492 laxation periods. Details of this protocol are shown in Table 1.

493 In order to prepare an efficient identification tool, a reduced order model

Table 1: Experiment scheme.

Current [mA]	Period start time [s]	Period finish time [s]
1	0	30
0	30	60
-10	60	90
0	90	120
20	120	150
0	150	500

(ROM) must be built to significantly accelerate the simulation of the galvanostatic test for each assumed concentration-dependent diffusivity during optimisation iterations. As previously explained, in an offline phase, a database of solutions must be collected. From this collection of simulated solutions, reduced basis for lithium ion concentration and electrolyte diffusivity can be computed. Values of parameters (according to diffusivity parameterization described in section 2.3) used to build such database are taken from a parametric space widely enough that identification algorithms evaluate the objective function inside it.

In particular, the first parameter (p_1 , related to the magnitude of the diffusivity) is selected in the interval $[0.3, 1.3]$ and the second one (p_2 , linked the dependence of the diffusivity on the concentration) is taken in the interval $[-0.3, 1.3]$. A set of 64 cases is solved by combining 8 values of each parameter uniformly distributed in the described intervals.

It is important to remark that parameters used in the reference solution are not included in this database. Using information from this database, a reduced order model is prepared following the methodology presented in section 2.2. As much information for this model as possible is preprocessed in order to significantly accelerate the numerical simulation of the test using the ROM.

Taking into account comments in the previous section, the number of modes to be retained in the ROM is decided upon observation of the singular

517 values in the decomposition. More precisely, the following criteria

$$\frac{\sqrt{\sum_{j=i+1}^N \sigma_j^2}}{\sqrt{\sum_{j=1}^N \sigma_j^2}} < 10^{-4} \quad (25)$$

518 is used to select the number of modes to be retained as the smaller value of i
 519 verifying this condition. The above selection determines a number of modes
 520 able to guarantee that fields stored in the database can be reconstructed
 521 (using this number of modes) with a relative root mean squared error smaller
 522 than 10^{-4} . Using this criteria, 13 and 8 modes must be retained for the
 523 concentration and the diffusivity, respectively. A ROM with these numbers
 524 of modes is then prepared.

525 Results corresponding to the simulation of the experiment presented in
 526 Table 1 are shown in Figure 2 for the ROM and the FOM with 100 elements,
 527 and a FOM with 10000 elements, named as REF, which is the mesh used for
 528 obtaining V_{exp} values. As clearly seen the error introduced by reduced order
 529 modelling is very small and similar to the FOM in comparison with REF
 530 solution. In contrast, computational effort is greatly reduced. In terms of
 531 computation time, the solution of the complete (finite element) model, FOM,
 532 needs about 10 seconds (on a Intel® Core™ i7-10700 CPU @ 2.90GHz $\times$
 533 16 processors) whereas the reduced order model (implemented using Python
 534 and a library of compiled basic functions, programmed in Fortran) is solved
 535 in 0.3 seconds. This significant reduction in the simulation time will be crit-
 536 ical in order to prepare an efficient identification methodology.

537

538 insert Figure 2

539

540 Using this ROM to simulate the voltage resulting from the galvanostatic
 541 test, the BFGS (Broyden-Fletcher-Goldfarb-Shanno) gradient-based optimi-
 542 sation algorithm, [60], from Scientific Python, SciPy. Identification is per-
 543 formed in two steps. First, an initial guess is computed using the relaxation
 544 after the first pulse, considering the diffusivity as a constant, $p_2 = 0$. After-
 545 wards, the last two relaxation intervals are used for identifying the diffusivity
 546 lithium ion concentration-dependence. Optimisation is stopped when objec-
 547 tive function gradient is about 10^{-6} .

548

549 An objective function is then built measuring errors between the reference
 550 voltage and simulated voltage for any parameter selection during relaxation

551 periods. Voltages are measured each 0.2 seconds (for all the duration of each
 552 relaxation period). This objective function can thus be written as

$$f_{obj}(\mathbf{p}) = \sum_{l=1}^3 \sum_{k=1}^{N_l} \frac{1}{V_{l,ref}^2 N_{l,ref}} (V_{mod}(t_k^l; \mathbf{p}) - V_{exp}(t_k^l))^2. \quad (26)$$

553 Parameter identification with described parameters (corresponding to the
 554 minimisation of the previous objective function) takes 59 iterations and about
 555 30 seconds (on a Intel® Core™ i7-10700 CPU @ 2.90GHz × 16 processors)
 556 to produce a solution satisfying the stopping criteria. Figure 3 shows the
 557 results from this identification. In Figure 3a both the voltage for the reference
 558 solution (computed using the finite element model described above) and the
 559 voltage obtained (using a preprocessed ROM obtained from the described
 560 database) for the identified diffusivity $D_e^{eff}(c_e)$ are shown. Agreement of
 561 both voltages (during relaxation periods) is very good as seen in Figure 3a
 562 and confirmed in Figure 3c showing relative error between the two voltages
 563 (below 0.1 % all along the whole test plan). Figure 3b compares diffusivity
 564 coefficients, $D_e^{eff}(c_e)$, used to compute the reference solution (taken from
 565 [37]) and that identified by the proposed technique. Finally, values reported
 566 in [37] from tests of different cells (and used to fit the $D_e^{eff}(c_e)$ function used
 567 in the reference solutions) are plotted with the identified function in Figure
 568 3d.

569 insert Figure 3

570 The proposed methodology has proved to be very efficient in this simple
 571 case. Small errors in voltage and good results in diffusivity identification
 572 are associated both to the efficiency of the minimisation algorithm and the
 573 selection of the proposed test plan. Using some modifications of the previous
 574 problem, it will be shown the methodology is also quite robust.

- 575 • To make the example more realistic, some noise will be added to the
 576 reference solution. Added noise with a normal distribution will be
 577 used. Otherwise, the same testing protocol and identification param-
 578 eters previously described are considered. Noise distribution with zero
 579 mean and a standard deviation of 0.05 mV is added to the reference
 580 solution in the previous example. Identification results are shown in

581 Figure 4. As seen in this figure, small errors in voltage and diffusivity
582 identification are still found.

583 insert Figure 4

584 • In order to reduce the experimental data to be processed (and, to a
585 lesser degree, the computational cost of the identification technique)
586 voltage can be measured during a relatively short period of each relax-
587 ation. Using the previous problem, it is now considered a case where
588 voltage is measured only at the shaded periods shown in Figure 5 dur-
589 ing relaxation periods. The same sampling period of 0.2 seconds is
590 used. Identification results are shown in Figure 5 as well. As seen,
591 similar quality identification results are obtained in a time about 45
592 seconds (due to the increase of evaluations of the objective function
593 until identification).

594 insert Figure 5

595 • Finally, the effect of the choice of diffusivity parameterisation is con-
596 sidered. A new reference solution is computed using a second order
597 polynomial. This polynomial is obtained through a least squares fit-
598 ting from diffusivity data in [37]. No other change in the problem is
599 made and all identification parameters from the previous example are
600 kept. As shown in Figure 6, there is no noticeable deterioration of the
601 diffusivity identification.

602 insert Figure 6

603 In order to summarise the performance of the proposed methodology in
604 this application example, Table 2 collects information regarding the four
605 identification problems described above.

606 4. Second case study: a realistic case

607 As shown in the previous section, the proposed methodology can (quite)
608 significantly reduce the required experimental load for electrolyte transport

Noise	Approximation	Sampling	Initial guess, p_{10} $p_{20} = 0$	Identified parameters		Iterations	CPU time [s]
				p_1	p_2		
No	exponential	complete	0.6373	0.9983	0.9975	59	30
Yes	exponential	complete	0.6388	1.0224	1.0507	117	50
No	quadratic	complete	Not applicable			43	20
No	exponential	incomplete	0.6373	1.0029	1.0078	103	45

Table 2: Identification results corresponding to problems considered in first case study, section 3. Since quadratic approximation uses a different parameterisation, no information on the parameters is shown.

properties estimation. Nevertheless, in the previous analysis a quite *ideal* scenario was considered: namely, it was assumed that lithium metal surface charge transfer phenomena were not affected by the (highly nonuniform) lithium deposition and dissolution processes. As a consequence, a constant exchange current density, i_0 , was used in the model and pulse and relaxation profiles are considered to be identical at each cycle (provided the same current and pulse duration are used) from the very first cycle (after cell preparation) on.

When a *real* cell is tested, a number of complex phenomena associated to the lithium deposition and dissolution processes (as well as some secondary reactions) makes the previous hypothesis on a constant exchange current density clearly unrealistic. This fact can be illustrated with a simple experiment as described below where a Li-Li symmetric cell is prepared and exposed to galvanostatic cycles.

In the preparation of this cell, electrodes consist of Albemarle commercial lithium with a thickness of 50 μm , and diameters of 18.2 and 15.0 mm. CR2025 (HOHSEN) symmetric cells were assembled in an argon-filled glove box using two lithium discs as electrodes. A separator (Microfiber Whatman) soaked with 100 μL of the commercial 1 M $\text{LiPF}_6\text{EC}/\text{DMC}$ 2%VC electrolyte (Solvionic) was inserted between the two lithium electrodes. Cells were cycled galvanostatically at 25 $^\circ\text{C}$ in a BaSyTec Cell Test System (Germany), applying 30 cycles at 0.2mA/cm².

Figure 7 shows the recorded voltage during this galvanostatic cycling. As clearly shown, there is a remarkable change of the observed voltage during pulses as cycling proceeds. Such transition from *peaking* to *arcing* is typically observed in experiments and is, of course, inconsistent with a hypothesis of

635 constant exchange current density, i_0 .

636 insert Figure 7

637 On the other hand, Butler–Volmer kinetics suggests an almost linear re-
638 lationship between current intensity and recorded voltage in pulses (at least
639 for small values of current intensity). Although this can be observed after
640 very long cycling intervals (see [62]), extremely long transient periods can
641 appear. Figure 8 shows the voltage measured during galvanostatic cycling
642 for different applied current densities. As it can be observed, there is a clear
643 non-linear relationship between current intensity and voltage.

644

645 insert Figure 8

646

647 A number of complex phenomena, related to the evolution of the lithium
648 metal surface along the experiment, can explain the observed behaviour. On
649 the one hand, highly inhomogeneous lithium stripping and deposition pro-
650 cesses are expected to occur during initial stages of cycling. Original solid
651 electrolyte interface (SEI) must be broken to initiate lithium stripping. Us-
652 ually, relative large overpotentials are required to break this original SEI and
653 slight heterogeneities give rise to the formation of pits where lithium stripping
654 is concentrated. Quite similarly, lithium deposition is favoured by the pres-
655 ence of some nucleation seeds. As a result, deposition leads to the formation
656 of lithium dendrites. Pits and dendrites offer preferred sites for lithium depo-
657 sition and stripping, respectively, when cell polarity is reversed. Only after
658 a relatively large number of cycles lithium surface will evolve into an almost
659 homogeneous mushy state, [61].

660

661 At the same time, evolution of the solid electrolyte interface (formed and
662 broken along each cycle) is still not well known. SEI dynamics involve ex-
663 change of several species (including lithium ions) and possibly interacts with
664 other electrochemical phenomena (including double layer formation and rup-
665 ture), then exhibiting different time scales. In particular, considering gal-
666 vanostatic tests, SEI dynamics is observed to induce fast voltage variations
667 at the beginning of cell relaxation after galvanostatic pulses, and may be
668 responsible for a long term residual voltage at the end of cell relaxation pe-

riods, [62], [63]. Accurate modelling of the involved phenomena would, quite likely, need both *ab initio* and molecular dynamics simulations (in order to identify relevant phenomena) and the derivation of some *upscaling* technique (in order to incorporate subscale information into a continuum, macroscale model). See, for instance, [Sitapure20], [Hankins21], [Lee21], [Sarkar22] and [Parmananda22].

Resuming the design of an efficient transport properties identification technique, it is important to stress that in the methodology presented in the previous sections not only the rate of voltage decay during relaxation is used to estimate the electrolyte diffusivity (as is the case in standard tests) but the actual voltage during relaxation is also important to identify this diffusivity (since the difference between predicted and observed voltage is minimised). This means that voltage at the beginning of the relaxation phase needs to be well modelled and any residual voltage at the end of the relaxation phase should be identified as well.

According to all these considerations, the identification technique presented in the previous section must: (1) incorporate a detailed modelling of the lithium stripping/deposition kinetics, and (2) demonstrate that identification is still efficient using such complex models. The first point is well out of the scope of this paper (active research is being done by several authors on this topic), and here only the second point will be considered. In particular, a second synthetic experiment will be designed to test the performance of the proposed methodology in a realistic case.

The synthetic experiment will concentrate on the variable kinetics of lithium stripping/deposition during first galvanostatic, associates (as previously explained) to inhomogeneous phenomena on the lithium metal surface. In order to capture these phenomena, Wood *et al.* [64], introduced a model capable to provide detailed explanation to the following mechanisms: (1) when dendrite nucleation occurs, (2) how those dendrites evolve as a function of time, (3) when surface pitting occurs during Li electrodisolution and (4) kinetic parameters that dictate overpotential as the electrode morphology evolves. For this purpose, they employed a modified form of the current-overpotential relationship, by including in the Butler-Volmer equation parameters that account for the roughness of the electrode surface for one side, and the effective heterogeneous rate constant that depended upon the morphology of the electrode for the other side.

707

708 The model developed by Wood *et al.* [64] is revisited here in order to
 709 derive a synthetic experiment. In particular, the equation (23) is modified to

$$i_{app} = \gamma F k^0 \left(c_{Li} \exp \left(\frac{(1-\alpha)F}{RT} \eta \right) - c_e \exp \left(-\frac{\alpha F}{RT} \eta \right) \right), \quad (27)$$

710 where γ refers to the roughness of the lithium metal surface, which is assumed
 711 1 for this case; c_{Li} is the surface concentration of metallic lithium and it is
 712 calculated as $c_{Li} = \rho_{Li}/M_{Li}$, where ρ_{Li} is the lithium density and M_{Li} the
 713 lithium molar weight; and k^0 is an effective rate constant that depends on
 714 the morphology of the lithium metal surface as in [64]. In order to account
 715 for inhomogeneity in the lithium stripping/deposition kinetics, the effective
 716 rate constant is expanded to include contributions from kinetically fast and
 717 slow processes (fast lithium stripping is related to the existence of pits and
 718 fast lithium deposition to the presence of dendrites):

$$k^0 = \theta_f k_f^0 + \theta_s k_s^0, \quad (28)$$

719 where θ_f and θ_s (θ_s being calculated as $(1-\theta_f)$) are the fractions of the lithium
 720 metal surface area with fast and slow kinetics, respectively, (θ_f is then re-
 721 lated to the density of pits and dendrites on the lithium metal surface) and
 722 k_f^0 and k_s^0 are the rate constants of the fast and slow processes, respectively,
 723 assumed constant as in Wood *et al.* [64].

724

725 Although the parameter θ_f is derived from simple geometrical arguments
 726 in [64], a *data-driven* approach (to mimic observed voltage profiles during
 727 galvanostatic tests) will be followed here. In particular, θ_f will be modelled
 728 as a function of two variables: the amount of lithium stripped/deposited Q
 729 and the amount of lithium exchanged throughout the experiment $\hat{Q}$. These
 730 parameters are expected to be strongly correlated with SEI morphology evo-
 731 lution and active lithium consumption.

732

733 More precisely, θ_f will be described by the following correlation:

$$\theta_f = (1 - \exp(-aQ)) \exp(-b\hat{Q}) + (1 - \exp(-c\hat{Q})), \quad (29)$$

734 where a , b and c are constants that can be tuned in order to obtain a voltage
 735 profile similar to those from experiments. Q and $\hat{Q}$ can be straightforwardly
 736 computed from

$$Q = \int_0^t \frac{i_{app}(\tau)}{F} d\tau, \quad (30)$$

$$\hat{Q} = \int_0^t \frac{|i_{app}(\tau)|}{F} d\tau. \quad (31)$$

737 where i_{app} represents the applied current density.

738

739 Figure 9 shows the simulated voltage using the numerical model described
 740 in section 2.1 (hereafter called *High-fidelity FOM*) using the revisited model
 741 of [41] for kinetics described below with the following selection of parameters:
 742 $a = 4.72$, $b = 0.15$ and $c = 0.01$.

743 insert Figure 9

744 As shown, this model is able to capture the change of the shape of the
 745 galvanostatic voltage response from *peaking* to *arcing*. Both the shape of
 746 voltage profiles and the duration of transient phenomena can be controlled
 747 by parameters a , b and c . As previously explained, an accurate description of
 748 the kinetics evolution is not intended here and only a model capturing realis-
 749 tic voltage profiles is looked for in order to understand the performance of the
 750 proposed methodology in realistic conditions. As a consequence, correlation
 751 (29) with the above selection of parameters will be used in the preparation
 752 of the synthetic experiment.

753

754 Identification methodology explained in the previous section is repeated
 755 here: (a) a reference solution (afterwards considered as an experimental volt-
 756 age profile) is computed using the *High-fidelity FOM*, (b) a set of galvanos-
 757 tatic tests is solved using also this FOM in order to prepare a reduced order
 758 model (ROM), (c) a preprocessed ROM is built using the information col-
 759 lected in the previous step, and (d) an optimisation algorithm (using the
 760 developed ROM) is run in order to identify the electrolyte diffusion coeffi-
 761 cient as a function of the electrolyte concentration.

762

763 In a first example, a testing protocol avoiding the transition period (where
 764 important changes in lithium stripping/deposition kinetics due to a lithium
 765 metal surface modification are observed) is proposed. From the experimen-
 766 tal work carried out within the laboratory, it is demonstrated that after 30

767 cycles the voltage profile remains relatively constant. Taking this evidence
768 as a baseline, the following testing protocol is proposed. Firstly, 30 contin-
769 uous cycles are conducted. After these continuous cycles, 1 hour relaxation
770 period is included. Finally, after the relaxation time, the sequence of 3 pulses
771 proposed in the previous section, with 10 minutes of relaxation after each of
772 the pulses, is applied.

773

774 Of course, computational cost of electrolyte diffusion coefficient for this
775 example will be much larger than in the case considered in the previous sec-
776 tion if transient period (corresponding to 30 cycles used in cell conditioning)
777 is simulated at each optimisation step. In this case each simulation (with a
778 ROM) can take several seconds, and diffusion coefficient identification can
779 last a few minutes.

780

781 But since only recorded voltage during the final sequence of three pulses
782 will be used in the identification and a long relaxation period follows the 30
783 cycles period (ensuring than a homogeneous concentration profile and a zero
784 cell voltage will be obtained at the end of the relaxation period, indepen-
785 dently of cell parameters) simulation of this transient period is not needed.
786 Additional reductions in the optimisation can be obtained as well is good ini-
787 tial estimates of the mean electrolyte diffusion coefficient can be found (for
788 instance, voltage relaxation after the first pulse in the 3 pulse sequence can
789 provide a good estimate using the slope of the logarithm of the voltage as in
790 [37]). Following these observations, computational effort can be significantly
791 reduced.

792

793 As in the ideal case, a 100 non uniform element mesh has been used in the
794 model, concentrating nodes near electrolyte corners for capturing correctly
795 the non linearities, and a database of 64 numerical solutions has been built
796 running simulations inside the parametric space given by $p_1 \in [0.3, 1.3]$ and
797 $p_2 \in [-0.3, 1.3]$.

798

799 For the identification problem (using the same 10^{-4} tolerance in the rela-
800 tive root mean squared error than in the ideal case considered in the previous
801 section to select the number of modes to be retained),

802 a ROM with 10 and 5 modes for the lithium ion concentration and the
803 diffusivity, respectively, has been built. A BFGS optimisation algorithm (im-
804 plemented in Scientific Python, SciPy) is used for minimising the objective

function presented in equation (26), evaluating it only throughout the relaxation intervals.

Figure 10 shows results of the identification methodology using a synthetic experiment along the previous guidelines. As shown in the figure, the proposed technique identifies correctly the electrolyte diffusion coefficient, as was the case in the *ideal* case considered in the previous section, taking about 40 seconds for the identification problem and 1 second for each simulation.

insert Figure 10

Identification is also robust concerning the presence of noise in the recorded voltage, provided the noise is not too high. Figure 11 shows the corresponding identification results when the reference voltage is contaminated with a white noise with 0.1 mV of amplitude. It can be seen that identification is reached with a maximum relative error less than 2%.

insert Figure 11

Although encouraging, previous identification results are not surprising. Since a cell conditioning has been previously performed, the case is not quite different from the *ideal* (synthetic) experiment considered in the previous section. On the other hand, since cell conditioning could require a large number of cycles, total time required to complete electrolyte diffusion coefficient can be extremely long since even if the computational time taken by the proposed methodology is very low, the experiment will take a long time.

Thus, a much more challenging case is now considered. In this case, identification will be performed using a much shorter cycling period, allowing to significantly reduce the duration of the experiment. Cell conditioning will be reduced to only 5 cycles, and relaxation periods after each pulse in the 3 pulse sequence will be reduced to 60 seconds in the considered (synthetic) test. But, as previously explained, significant variations in lithium stripping / deposition take place during this period. It is important to analyse if electrolyte diffusion coefficient can still be efficiently identified by the proposed methodology using this accelerated testing protocol. If proven, a very significant reduction in the experimental effort during electrolyte characterisation can be achieved.

839

840 In contrast to the previous case, initial cycling must be solved at each op-
 841 timisation iteration since cell state at the beginning of the 3 pulse sequence
 842 will depend on the electrolyte diffusion coefficient. As a consequence, nu-
 843 merical simulation of the protocol at each optimisation iteration will take
 844 a longer computational time (about 90 seconds for the whole identification
 845 computation and 1 second for each simulation).

846 Identification results are shown in Figure 12. As clearly observed, elec-
 847 trolyte diffusion coefficient is still very efficiently identified showing the ability
 848 of this methodology to work also under these conditions.

849 insert Figure 12

850 Identification results for this second case study are summarised in Table
 851 3.

Condit. [cycles]	Identif. window	Noise	Init. p_{10} $p_{20} = 0$	Identif. param.		Iter.	CPU time [s]
				p_1	p_2		
30	3 pulses	No	0.6402	0.9977	0.9955	32	40
30	3 pulses	Yes	0.6697	0.9797	0.9545	39	50
5	condition + 3 pulses	No	0.6376	1.0395	1.0888	48	60

Table 3: Identification results corresponding to problems considered in second case study, section 4

.

852 5. Conclusion

853 In this work, an efficient methodology for concentration dependent elec-
 854 trolyte transport properties identification has been proposed. This methodol-
 855 ogy has been illustrated with identification of electrolyte diffusion coefficient
 856 revisiting [37]. The basic underlying idea of the proposed methodology is
 857 to exploit nonlinear behaviour of the cell dynamics, what is in sharp con-
 858 trast to usual techniques, based on model linearization. As a consequence,
 859 the resulting identification methodology is able to significantly reduce the
 860 experimental effort needed to characterise Li ion concentration dependent

861 transport properties when compared with the usual approach (as made in
862 [37]) given that there is no need to assemble a different cell for each Li ion
863 concentration at which electrolyte diffusion coefficient is to be estimated.
864 Instead a single cell can be used, as shown in the paper.

865 The proposed methodology has proven to be very robust. In particular,
866 this methodology is quite insensitive to the presence of noise, so that not
867 very accurate experimental equipment's are required. At the same time, ef-
868 fective electrolyte diffusion coefficient identification can be carried out using
869 two electrode Li–Li symmetric cells even in the presence of strong, complex
870 phenomena of Li stripping and plating phenomena, provided these phenom-
871 ena can be identified in turn. Although accurate modelling of Li stripping
872 and plating phenomena is difficult, the proposed identification methodology
873 would avoid the use of four electrode cells or very long cell conditioning
874 cycles.

875 Computational load associated to electrolyte diffusion coefficient identifi-
876 cation under this approach is very low. This is based on the local optimisation
877 algorithm and the use of model order reduction techniques. As commented
878 in the paper, some care must be taken concerning selection of initial opti-
879 misation iterates and construction of a solution database in order to obtain
880 an accurate reduce order model. This low computational cost opens the
881 possibility of developing adaptive identification tests, since each identifica-
882 tion step (corresponding to a given test cycle) can be carried out on-line.
883 Thus, in contrast to the usual approach (a fixed test plan and an *a posteriori*
884 identification using recorded experimental results), a software tool to control
885 experimental conditions can be developed. This software will adaptatively
886 derive experimental conditions appropriate to identify electrolyte diffusion
887 coefficient (or other transport property) and test the cell using these condi-
888 tions, iterating until effective identification can be assessed.

889 In contrast to the approach described in the literature (see, for instance,
890 [65]), optimisation of the experimental conditions following this methodol-
891 ogy would be carried out for each particular electrolyte to be identified and
892 no *a priori* information on the parameter to be identified is needed (though
893 an educated guess for this parameter would indeed speed-up the identifi-
894 cation algorithm). Also, inexpensive computation of solution sensitivities
895 would allow on-line analysis of practical identifiability [66]. To the authors'
896 knowledge this approach remains unexplored in the literature.

897 In order to implement the possibility suggested above, progress on at least
898 two aspects must be gained:

- 899 • Experimental test conditions proposed in this paper has been heuris-
900 tically derived. Nevertheless, in more complex cases, an automatic
901 selection of test cycles should be implemented. Computation of sensi-
902 tivities carried out in the proposed methodology makes this selection
903 fairly easy using optimal design of experiments through maximisation
904 of the Fisher information matrix, [65].
- 905 • Modelling stripping/plating phenomena is essential in order to apply
906 the developed methodology to real identification problems. Description
907 of all microscale phenomena in this process is, of course, an extraordi-
908 nary task which is the object of many research groups. Nevertheless,
909 such a description is not needed in the framework of the identification
910 methodology. Instead, a phenomenological description of local overpo-
911 tentials would be enough. Although difficult, this is an immeasurably
912 more modest and feasible objective.

913 A final remark on the extension of the ideas explored in this paper may be
914 worth. Since the core of the proposed methodology is an efficient optimisation
915 technique (based on the use of reduced order models and the computation
916 of sensitivities) the extension to deal with optimisation problems in battery
917 design or battery operation seems natural. As illustrated by recent reviews
918 on optimisation of battery design ([67], [68]), battery charging protocol ([69]),
919 or battery control ([70]) (see also recent papers [Berliner22], [Wang22] and
920 [Jiang22] on charging optimization) a challenging point in all these techniques
921 is the integration of simultaneously accurate and fast models.

922 The use of (preprocessed) reduced order models presented in this paper
923 can be refined to further accelerate the numerical solution of an accurate
924 model. This model solution acceleration can be achieved with the use of
925 time-adaptive reduced order models [55] and also reinforced in the frame-
926 work of an optimisation algorithm with parameter-adaptive model order re-
927 duction strategies (explored in [71] for cell optimisation and proven to be
928 very efficient).

929 The (strongly) multiscale nature of the underlying battery models repre-
930 sents indeed an additional challenge in the acceleration of the model solution.
931 Nonetheless, model order reduction techniques can somehow deal effectively
932 with scale integration. This is the case, for instance, with particle subscale
933 modelling in p2D cell models as shown in [55]. Hopefully, this kind of tech-
934 niques could be extended to multiscale battery and battery packs models in
935 the framework of battery optimisation or battery control problems.

936 A research programme to tackle some of the above mentioned aspects is
937 under development by the authors.

938

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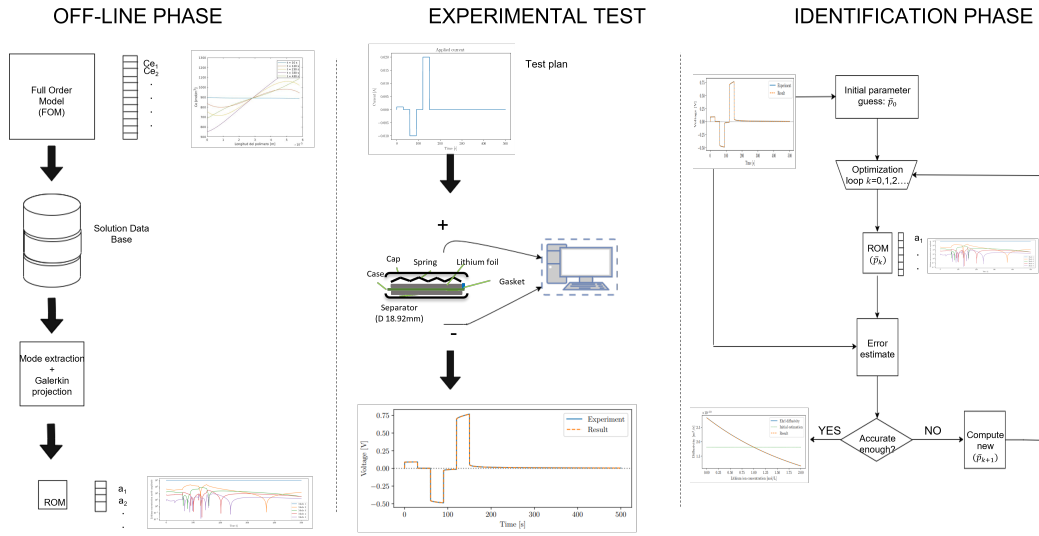
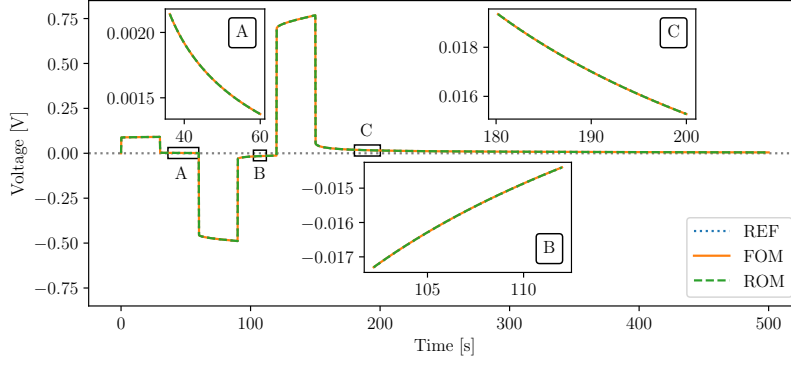
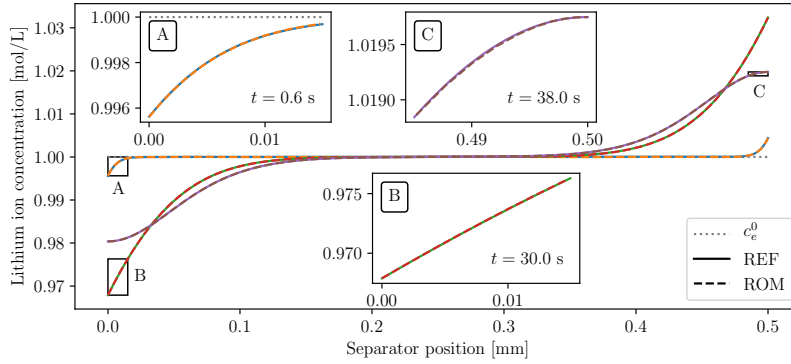


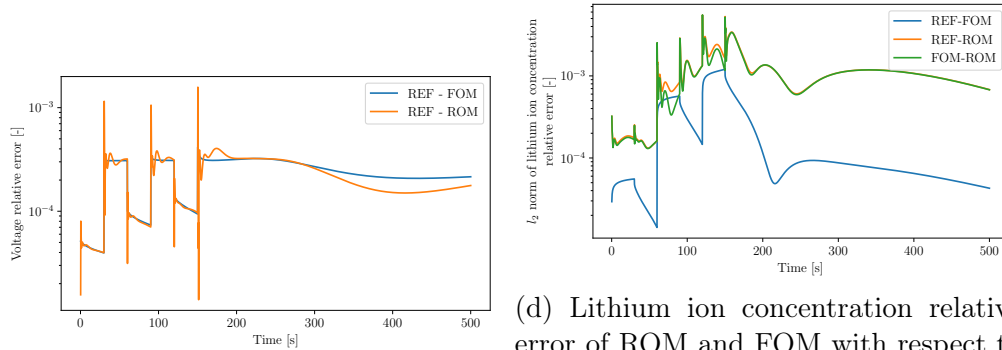
Figure 1: Outline of the proposed methodology for the identification of the electrolyte diffusivity.



(a) Voltage time series. Three detailed sights are included corresponding to the first seconds of each relaxation interval



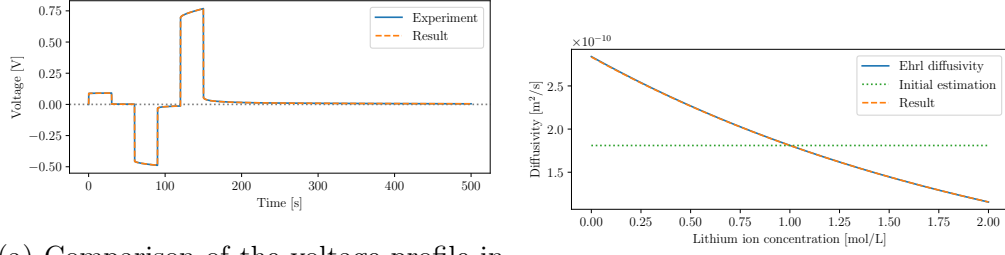
(b) Lithium ion concentration profiles at three different times ($t = 0.6s$, $t = 30s$ and $t = 38s$). Three detailed views (A, B and C) are also included to show concentration profiles near lithium metal electrodes.



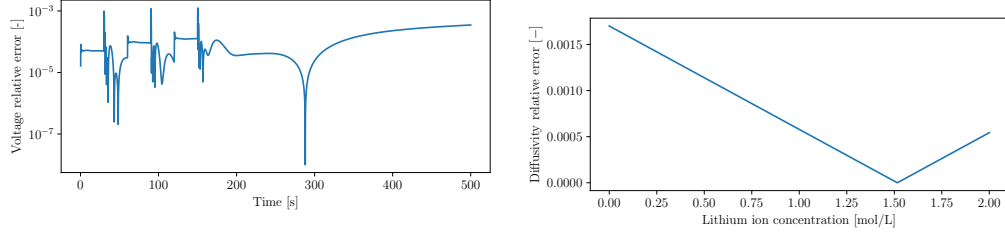
(c) Voltage relative error of ROM and REF solution, and between ROM and FOM with respect to REF solution

(d) Lithium ion concentration relative error of ROM and FOM with respect to REF and FOM, obtained as the l_2 norm of relative error vector along the whole domain for every time

Figure 2: Results obtained from simulating the experiment defined in Table 1 for a ROM and FOM with 100 elements, and a FOM with 10000 elements, named as REF

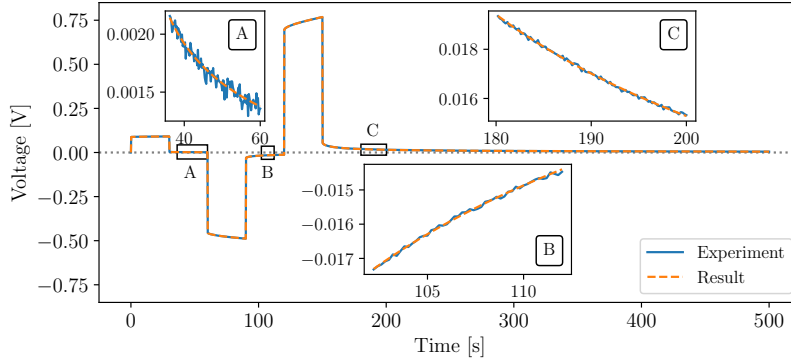


(a) Comparison of the voltage profile in the FOM model, called Experiment in (b) Comparison of the real electrolyte the legend, and the result of the ROM coefficient diffusion pattern, taken from model with the electrolyte diffusion co- Ehrl and the value obtained solving the efficient extracted from the optimisation optimisation problem problem

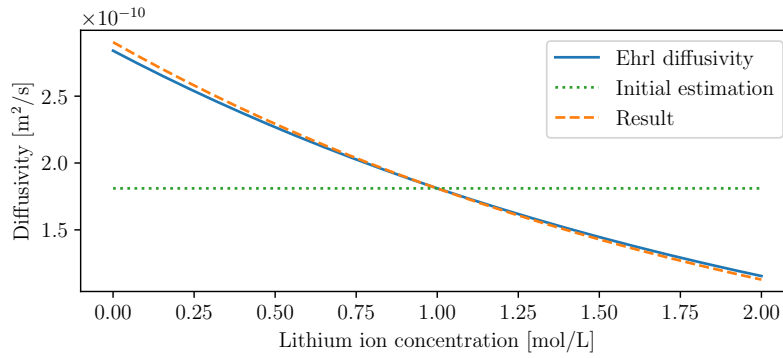


(c) Relative error of the voltage from FOM and the one obtained from the ROM with the optimum electrolyte co- (d) Relative error of the diffusion coefficient used in the FOM and the optimum electrolyte coefficient.

Figure 3: Ideal case. Optimisation problem results taken FOM model simulations as real experiments and assuming there is no noise in the measurement

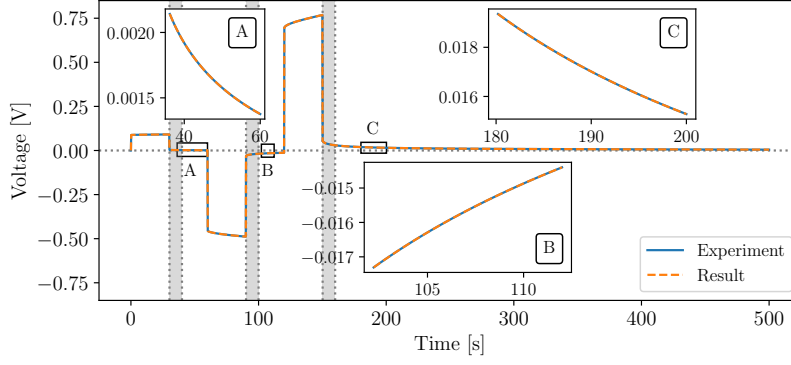


(a) Comparison of the voltage profile in the FOM model, called Experiment in the legend, and the result of the ROM model with the electrolyte diffusion coefficient extracted from the optimisation problem

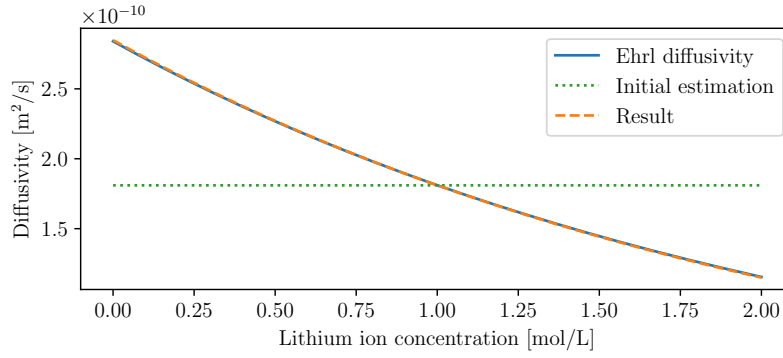


(b) Comparison of the real electrolyte coefficient diffusion pattern, taken from Ehrl and the value obtained solving the optimisation problem.

Figure 4: Ideal case. Optimisation problem results taken FOM model simulations as real experiments with normal noise

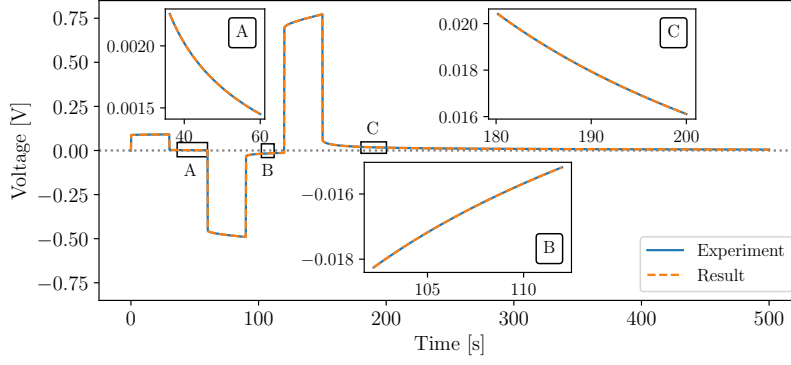


(a) Comparison of the voltage profile in the FOM model, called Experiment in the legend, and the result of the ROM model with the electrolyte diffusion coefficient extracted from the optimisation problem

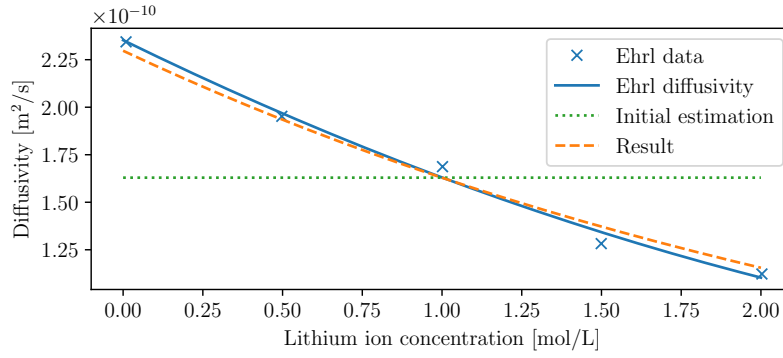


(b) Comparison of the real electrolyte coefficient diffusion pattern, taken from Ehrl and the value obtained solving the optimisation problem

Figure 5: Ideal case. Optimisation problem results taken FOM model simulations as real experiments assuming there is no noise in the measurement but with low number of data



(a) Comparison of the voltage profile in the FOM model, called Experiment in the legend, and the result of the ROM model with the electrolyte diffusion coefficient extracted from the optimisation problem



(b) Comparison of the real electrolyte coefficient diffusion pattern, taken from Ehrl and the value obtained solving the optimisation problem

Figure 6: Ideal case. FOM model simulations as real experiments assuming D_e has polynomial dependency with the c_e and there is no noise in the measurement and data taken from the whole relaxation profiles

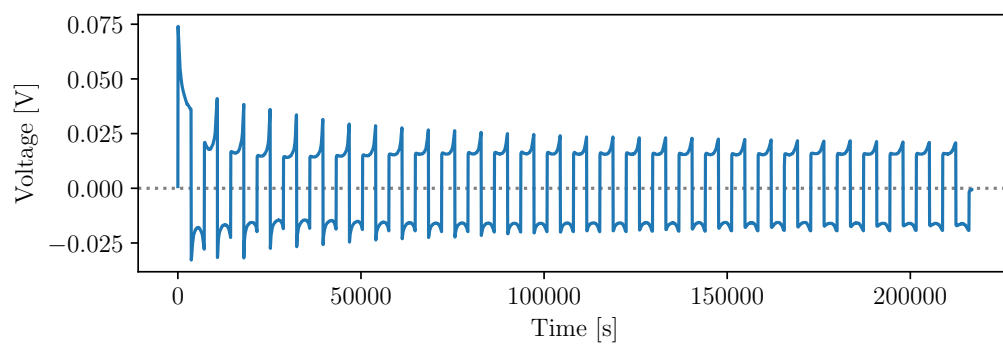


Figure 7: Experimental galvanostatic cycling voltage profiles for a Li-Li symmetric coin cell cycled at 0.2 mA/cm^2 for 30 cycles

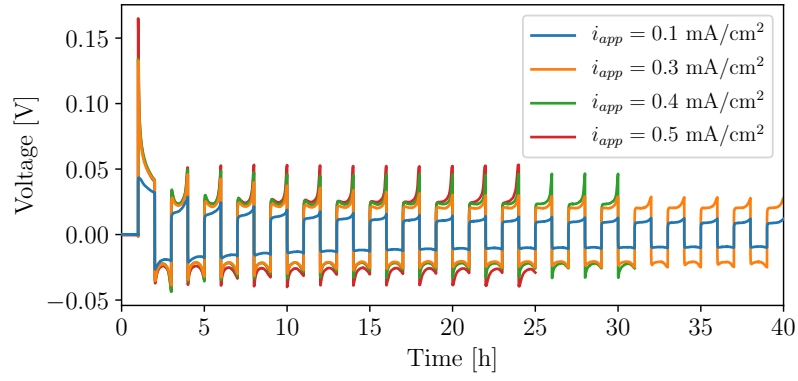


Figure 8: Voltage during galvanostatic cycling tests for different applied current densities

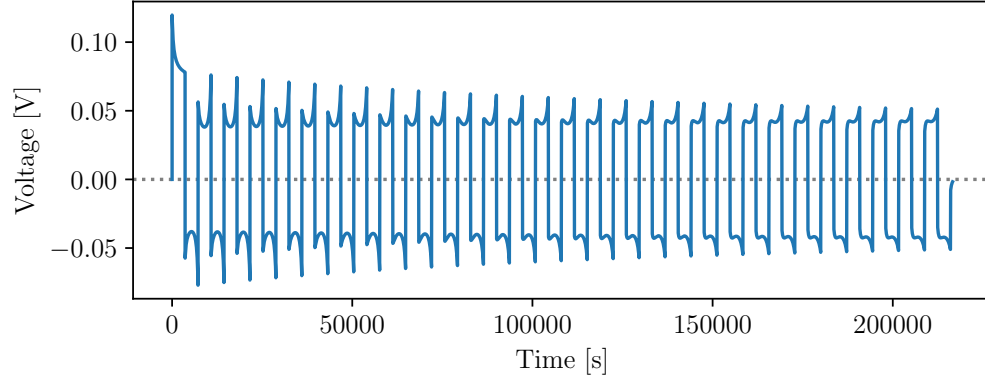
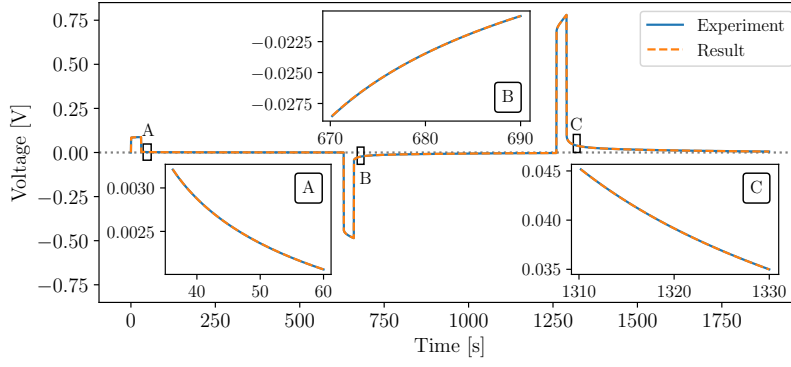
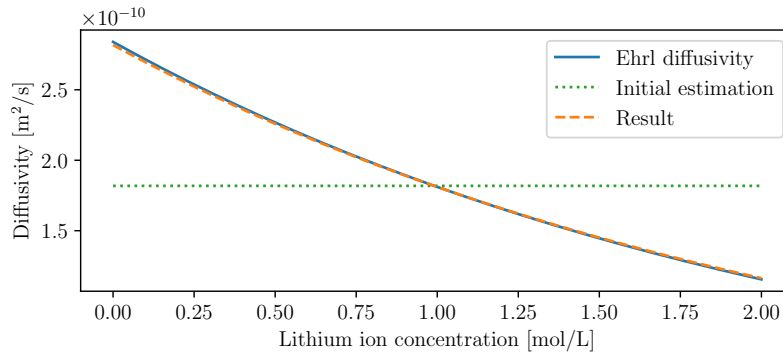


Figure 9: Simulation results of the modified model representing galvanostatic cycling voltage profiles for a Li-Li symmetric coin cell cycled at 0.2 mA/cm^2 for 30 cycles. During the earlier cycles, peaking behaviour can be observed, while in the latest cycles, arcing behaviour with a characteristic arc reaching a plateau at the end of each half cycle

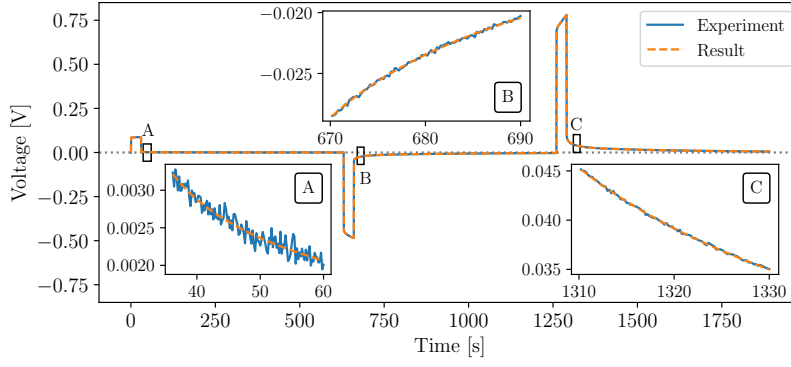


(a) Comparison of the voltage profiles

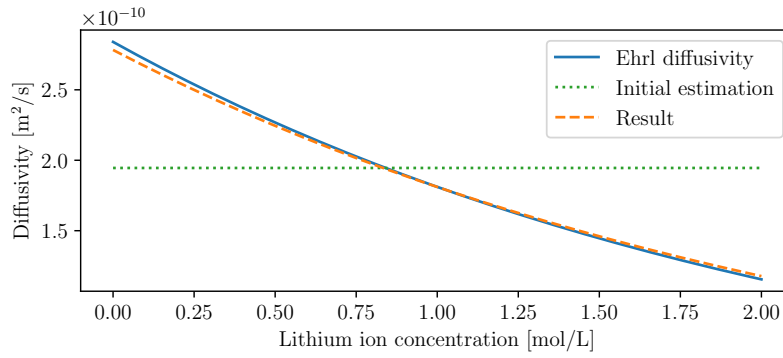


(b) Comparison of the electrolyte diffusion coefficient

Figure 10: Realistic case. FOM model simulations as real experiments without a noise

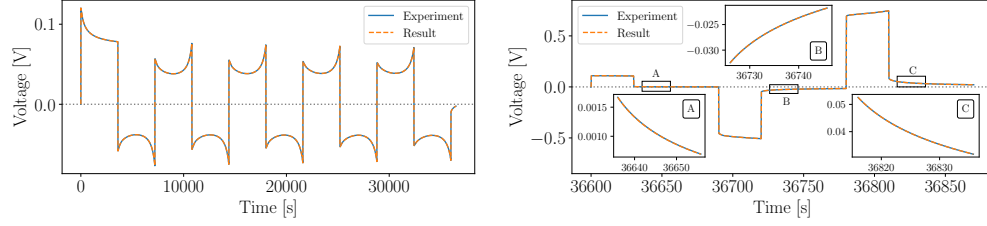


(a) Comparison of the voltage profiles

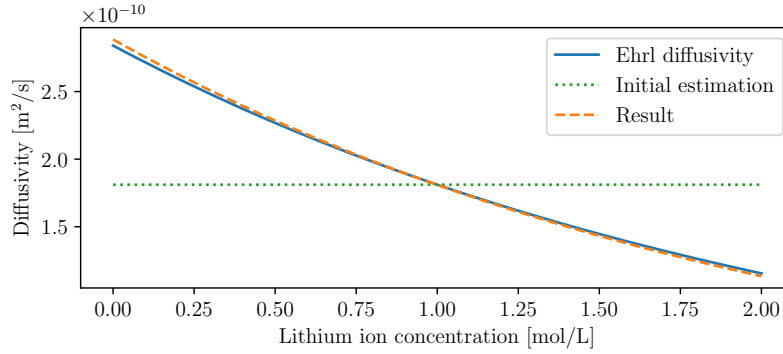


(b) Comparison of the electrolyte diffusion coefficient

Figure 11: Realistic case. FOM model simulations as real experiments with a noise



(a) Comparison of the voltage profile in cycling (b) Comparison of the voltage profile in the identifiability study



(c) Comparison of the electrolyte diffusion coefficient

Figure 12: Realistic case. FOM model simulations as real experiments with a reduced duration of the experiment

1086 Appendix A. Sensitivity matrix calculation

1087 A key ingredient in the developed identification methodology is the use of
 1088 sensitivities (they are used both in gradient-based optimisation techniques
 1089 and local identifiability analysis). Sensitivity matrix (here reduced to a vector
 1090 since a single model output V is considered) is defined by the derivatives of
 1091 the model output components with respect to each parameter.

1092 From the decomposition of the simulated voltage V given by equation
 1093 (20), sensitivity vector components corresponding to a parameter vector $\mathbf{p}$
 1094 evaluated at time t , are given by

$$S_i(t, \mathbf{p}) = \frac{\partial V}{\partial p_i}(t, \mathbf{p}) = \frac{\partial \eta}{\partial p_i}(L_{sep}, t, \mathbf{p}) + \frac{\partial \Delta \phi_e}{\partial p_i}(t, \mathbf{p}) - \frac{\partial \eta}{\partial p_i}(0, t, \mathbf{p}) \quad (\text{A.1})$$

1095 where $\eta(x, t, \mathbf{p})$ is the overpotential and $\Delta\phi_e$ is the potential difference be-
 1096 tween both sides of the electrolyte

$$\Delta\phi_e(t, \mathbf{p}) = \phi_e(L_{sep}, t, \mathbf{p}) - \phi_e(0, t, \mathbf{p})$$

1097 The derivative of the overpotential respect to the parameters can be ex-
 1098 pressed in terms of the derivative of the Li ion concentration using the ki-
 1099 netics. Using the standard form of Butler–Volmer (as done in the *ideal* case
 1100 considered for the first application example, in section 3) in equation (23 and
 1101 taking derivative in p_i (observing that i_{app} is constant)

$$\gamma \frac{i_{app}}{c_e} \frac{\partial c_e}{\partial p_i} + i_0 \left(\frac{c_e}{c_e^0} \right)^\gamma \left(\exp \left(\frac{\alpha F}{RT} \eta \right) + \exp \left(\frac{-\alpha F}{RT} \eta \right) \right) \frac{\alpha F}{RT} \frac{\partial \eta}{\partial p_i} = 0 \quad (\text{A.2})$$

1102 When the more realistic case (presented in section 4) is considered, the
 1103 counterpart equation (27) must be used. In this case, the following expression
 1104 is obtained

$$\begin{aligned} \gamma F k^0 \left((1 - \alpha) c_{Li} \exp \left(\frac{(1 - \alpha) F}{RT} \eta \right) + \alpha c_e \exp \left(-\frac{\alpha F}{RT} \eta \right) \right) \frac{F}{RT} \frac{\partial \eta}{\partial p_i} - \\ - \gamma F k^0 \left(\exp \left(-\frac{\alpha F}{RT} \eta \right) \right) \frac{\partial c_e}{\partial p_i} = 0 \quad (\text{A.3}) \end{aligned}$$

1105 Taking derivatives with respect to p_i in the expression for the ionic current
 1106 given by equation (5), an additional equation relating derivatives of $\Delta\phi_e$ and
 1107 c_e is obtained (where it must be taken into account that the ionic conductivity
 1108 and the thermodynamic factor are defined as a function of the electrolyte
 1109 concentration)

$$\begin{aligned} \frac{\partial \Delta\phi_e}{\partial p_i} = \int_0^{L_{sep}} \frac{i_{app}}{\kappa^2} \frac{\partial \kappa}{\partial c_e} \frac{\partial c_e}{\partial p_i} - \frac{\kappa_D}{\kappa} \frac{1}{c_e} \frac{\partial^2 \ln f_{\pm}}{\partial \ln c_e^2} \frac{\partial c_e}{\partial p_i} \frac{\partial \ln c_e}{\partial x} \\ - \frac{\kappa_D}{\kappa} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\partial}{\partial x} \left(\frac{1}{c_e} \frac{\partial c_e}{\partial p_i} \right) dx \quad (\text{A.4}) \end{aligned}$$

1110 Using equations (A.2), (A.3) and (A.4) all contributions to the sensitiv-
 1111 ity vector can be expressed in terms of $\frac{\partial c_e}{\partial p_i}$. In the (preprocessed) reduced

1112 order model used in the cell simulation, Li ion concentration $c_e(x, t, \mathbf{p})$ is
 1113 approximated using a decomposition

$$c_e(x, t, \mathbf{p}) \simeq \sum_{j=1}^{N_c} a_j^c(t, \mathbf{p}) \phi_j(x) \quad (\text{A.5})$$

1114 with modes $\{\phi_j(x)\}_{j=1}^{N_c}$ independent of $\mathbf{p}$. In a consistent approach

$$\frac{\partial c_e}{\partial p_i}(x, t, \mathbf{p}) \simeq \sum_{j=1}^{N_c} \frac{\partial a_j^c}{\partial p_i}(t, \mathbf{p}) \phi_j(x) \quad (\text{A.6})$$

1115 The system of ordinary differential equations associated to the reduced
 1116 order model reads

$$[\mathbf{M}] \frac{d\mathbf{a}^c}{dt} + [\mathbf{K}(\mathbf{a}^c)] \mathbf{a}^c = \mathbf{b} \quad (\text{A.7})$$

1117 where $[\mathbf{M}]$ and $[\mathbf{K}]$ are the mass and stiffness matrices defined in equations
 1118 (11) and (12), respectively. Derivatives with respect to parameters in $\mathbf{p}$
 1119 can be taken in this system in order to obtain a system of (linear) ordinary
 1120 differential equations for $\frac{\partial a_j^c}{\partial p_i}$. This system can be written (taking into account
 1121 that the mass matrix $[\mathbf{M}]$ does not depend on $\mathbf{p}$) in matrix form as

$$[\mathbf{M}] \frac{d}{dt} \left(\frac{\partial \mathbf{a}^c(t)}{\partial \mathbf{p}} \right) + [\mathbf{K}] \frac{\partial \mathbf{a}^c(t)}{\partial \mathbf{p}} + \frac{\partial [\mathbf{K}]}{\partial \mathbf{p}} \mathbf{a}^c = 0, \quad (\text{A.8})$$

1122 where $\frac{\partial [\mathbf{K}]}{\partial \mathbf{p}}$ corresponds to the matrix which results of taking the derivative
 1123 of the stiffness matrix with respect to the parameters and can be also de-
 1124 composed as

$$\frac{\partial [\mathbf{K}]}{\partial \mathbf{p}} = \mathbf{R} \frac{\partial \mathbf{a}^D}{\partial \mathbf{p}} = \mathbf{R} \Psi_{\text{DEIM}}^{-1} \frac{\partial D_{\text{DEIM}}^{\text{eff}}}{\partial \mathbf{p}}. \quad (\text{A.9})$$

1125 System given by equation (A.8) and providing information on sensitivities
 1126 must be solved simultaneously with system (A.7).