

Long-term corrosion tests of stainless steel and aluminium alloys in simulated direct methanol fuel cell environments

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Keywords: Material tests, Corrosion rate, DMFC, Weight loss test, Bipolar plate

1. Introduction

Traditionally, high density graphite has been used in laboratory tests as bipolar plates (BP) material for fuel cells due to its excellent corrosion resistance and low contact resistance. However, the commercial development of fuel cells out of the laboratories shows the drawbacks of this material. The graphite is very brittle and presents a low mechanical resistance, which makes it difficult to use in many applications, such as transport where the fuel cells suffer the vehicle vibrations. Moreover, graphite BP fabrication is arduous and costly, preventing its use on a large scale [1].

Metals naturally arise as potential candidates for their use in BP. Stainless steel (SS) and aluminium (Al) are two of the most promising metals due to their high mechanical resistance and chemical stability, good thermal and electrical conductivity and low cost. Moreover, a very thin (≈ 1 mm) BP can be easily manufactured by stamping techniques. This is a relevant point for applications in which the weight and space are limitant conditions, for example, in aerospace or marine applications [2].

The main disadvantage of SS and Al is the corrosion suffered in an aggressive environment such as that taking place inside direct methanol fuel cells (DMFC). On the one hand, the release of metal ions during the corrosion of bipolar plates can contaminate the membrane and poison the catalysts. On the other hand, the corrosion leads to the BP deterioration due to the weight loss and the formation of passivation oxide layer which increases the contact resistance between the bipolar plate and the electrode.

The aim of this work is to study the long-term behaviour of SS 316L and Al 6061 in simulated environment for their use as bipolar plates in DMFC. It is easy to find electrochemical studies of these materials in simulated DMFC environments, but their behavior in long-term tests is less common. The influence of methanol in the corrosion rate in acidic media of these two materials is also investigated.

2. Experimental

2.1 Simulated environments

The corrosion behaviour of SS 316L and Al 6061 was studied in two different acid methanol solutions. In order to

simulate anodic and cathodic conditions, the methanol concentration changes from one solution to another. Thus, a solution of 1 M CH₃OH + 1 M H₂SO₄ + 5 ppm HF was used as anodic simulated environment, while the cathodic solution was composed of 0.01 M CH₃OH + 1 M H₂SO₄ + 5 ppm HF. The presence of methanol in the cathodic solution is intended to simulate the methanol crossover through the membrane in actual DMFC. During DMFC operation the perfluorosulphonic acid membrane can release H⁺, SO₄²⁻ and F⁻ ions. That is why H₂SO₄ and HF were added to the solutions [3].

2.2 Corrosion tests

In order to simulate the DMFC operating temperature, the samples of SS 316L and Al 6061 were placed in the solutions at 70 °C at time zero. After 9, 20 and 40 days some samples were extracted from the solutions and tested. In order to evaluate the metals corrosion behaviour, weight loss and potentiodynamic tests were carried out. The metal corrosion surface was also investigated by an optical microscope.

For *weight loss tests*, the samples were extracted from the solutions and cleaned with plenty of water. Each material was immersed in its respective stripper solution during 10 min to remove adhered oxidation products. The solution for SS consists of a HCl solution with hexamethylenetetramine, which is a corrosion inhibitor, while in the case of Al is a diluted solution of HNO₃. Then, the samples were weighted and the resulting values were compared to the weights of the same samples measured before starting the tests. Later, the surface of these samples were studied under microscope at three different magnifications, 50, 150 and 220.

The samples for *potentiodynamic tests* were only cleaned with water and the tests were carried out in anodic and cathodic freshly solutions. At the beginning of potentiodynamic tests, each sample was stabilised at its open circuit potential for 20 min. For SS 316L the potential sweep range was from -0.5 V to 0.5 V vs Ag/AgCl (1 M KCl), while the potential sweep range for Al 6061 was from -1.0 V to 0.0V vs Ag/AgCl (1 M KCl). In order to reduce the influence of effects such as diffusion, the scan rate in all tests was 1 mV s⁻¹. Electrochemical tests were conducted in a three

electrode cell with Ag/AgCl (1 M KCl) as reference electrode and a Pt mesh as counter-electrode.

3. Results and discussion

The *weight loss test* results for SS 316L and Al 6061 in anodic and cathodic solutions are shown in Fig. 1, which depicts the corrosion rate versus time. As expected, the corrosion rate decreases with time in all cases because of the passivation layer formation, which hinders the corrosion process. The corrosion rate in Al 6061 is higher than in SS 316L, independently of the test solution. In the case of Al, a greater presence of methanol in the working solutions implies a higher corrosion rate. This is a clear drawback for the use of Al alloys in DMFCs.

However, SS 316L shows the opposite trend, the presence of methanol in working solution produces a stabilizing effect with regard to the corrosion. This behaviour has been previously reported for other type of stainless steel, such as SS 304, by electrochemical tests, and may be due to the reduction of protons mobility [4]. The proton transport between water molecules in aqueous methanol solution is the most energy favourable transport method. Thus, when the methanol concentration increases, the relative amount of water decreases, decreasing the H⁺ mobility and the corrosion rate. Moreover, the oxygen solubility in methanol solutions increases with methanol concentration and this dissolved oxygen eases a passivation layer formation.

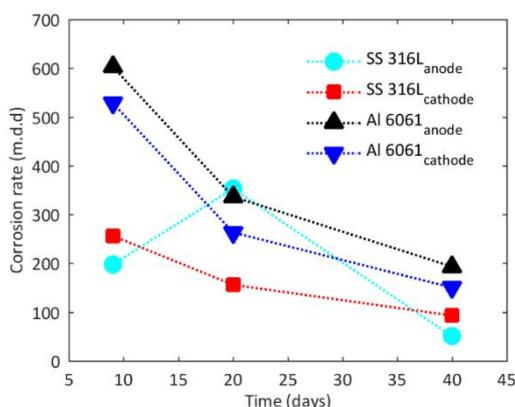


Fig. 1. Results of the weight loss test.

The curves obtained during *potentiodynamic tests* have been analysed by Tafel method in order to estimate their main features.

The general trend is that the polarization resistance increases with time for both materials, while corrosion current decreases. This suggests the formation of an oxide layer on the surface of the samples, which prevents them from higher oxidation. Polarization resistance increase and current density decrease, show a less metal ions dissolution with time, which is in line with the results of weight loss tests.

Moreover, the corrosion potential of SS 316L in anodic solution is higher than in cathodic solution, indicating a less corrosion trend of the stainless SS in anodic solution.

Due to the highly aggressive environment in which the long term tests have been carried out, the samples of both

materials have suffered a significant deterioration. The effects of the tests can be seen with the naked eye.

Aluminium samples changed their metallic sheen by a matt white color and their smooth surfaces by a rough ones. In the case of SS 316L, the samples modified their metallic gray by a charcoal gray.

Fig. 2 shows a microscope image of Al 6061 sample after 40 days in anode test solution at 70 °C. Both materials, Al 6061 and SS 316L, have suffered a homogeneous corrosion in both working solutions, anodic and cathodic.



Fig. 2. Al 6061 microscope image (x220) after 40 days in anodic solution at 70 °C.

4. Conclusions

The long-term tests show that SS 316L is a better choice than Al 6061 for its use in DMFCs. The SS 316L corrosion rate is lower than that of Al. Moreover, the SS 316L surface is passivated faster in presence of methanol, while Al 6061 shows the opposite trend.

Due to the adverse effects on the membrane and the catalysts of the metal ions released by the SS, it is necessary to analyse other materials and coatings and to test them in similar conditions to operating DMFC.

5. Acknowledgements

The authors would like to acknowledge the Spanish Ministry of Economy and Competitiveness and European Regional Development Funds through the Research Project ENE2014-53734-C2-2-R and the Comunidad de Madrid and the European Social Funds through the Research Project S2013MAE-2975 PILCONAER.

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