# EVALUATING METALLIC BIPOLAR PLATES FOR PROTON EXCHANGE MEMBRANE FUEL CELLS [1]

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## Abstract

The proton exchange membrane fuel cell (PEMFC) is one of the most promising technologies for electric energy generation, and bipolar plates are key components of a PEMFC stack. The aim of this work is to evaluate the electrical and corrosion behaviors of stainless steel-based metallic bipolar plates through the development of a methodology that includes the simulation of the PEMFC operating conditions. Uncoated and coated AISI316L stainless steel samples were evaluated in terms of their interfacial contact electrical resistance (ICR) and corrosion behavior in conditions that simulated the PEMFC anodic and cathodic environments. Four types of coating were studied: titanium nitride, chromium nitride, diamond-like carbon and ion-nitriding. The microstructural characterization was made by optical and scanning electron microscopy. The obtained results show that titanium nitride and chromium nitride coated AISI316L presented the best performances, however, still inferior to those of carbon-based materials. The titanium nitride coated AISI316L stainless steel presented an ICR value of 14 milliohms x cm$^2$ at 140 N/cm². The corrosion tests showed that chromium nitride coated samples were more resistant than titanium nitride coated samples, especially in a zero pH solution.

**Keywords:** metallic bipolar plates, electrical characterization, PEMFC.

## AVALIANDO PLACAS BIPOLARES METÁLICAS PARA PILHAS A COMBUSTÍVEL DE MEMBRANA TROCADORA DE PRÓTONS

## Resumo

Pilha a combustível de membrana trocadora de prótons é uma das mais promissoras tecnologias de geração de energia elétrica. As placas separadoras são componentes fundamentais da pilha e são normalmente produzidas com materiais à base de carbono, que apresentam problemas de fragilidade e elevados volume e custos de fabricação. O propósito deste trabalho é desenvolver uma metodologia para avaliação de materiais metálicos para aplicação em placas separadoras e selecionar os materiais mais promissores para pesquisas ulteriores. Amostras de aço inoxidável AISI316L não revestidas ou revestidas com nitreto de titânio, nitreto de cromo, nitretação iônica e DLC (*diamond like carbon*) foram avaliadas quanto à resistência de contato interfacial (RCI) e resistência à corrosão em meios simulando as condições usuais em uma pilha. Os resultados mostram que o aço AISI316L revestido com nitreto de titânio e nitreto de cromo apresentaram melhores desempenhos, contudo inferior às placas à base de grafita. O aço AISI316L revestido com nitreto de titânio apresentou um valor de RCI da ordem de 14 miliohms x cm$^2$ em 140 N/cm². Os testes de corrosão mostraram que as amostras revestidas com nitreto de cromo foram mais resistentes que àquelas revestidas com nitreto de titânio, especialmente em pH igual a zero.

**Palavras-chave:** Placas bipolares metálicas; Caracterização elétrica; PEMFC.

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## 1 INTRODUCTION

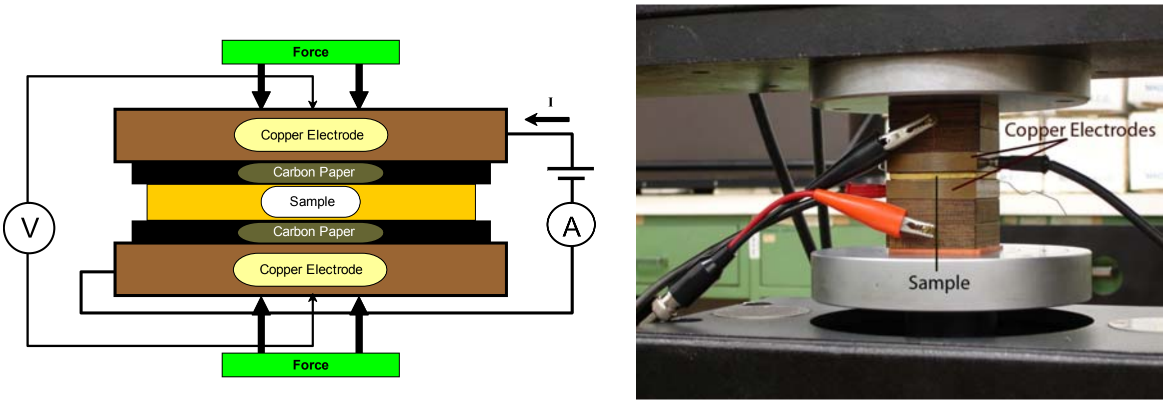
The proton exchange membrane fuel cell (PEMFC) essentially consists of polymer electrolyte membrane, cathodic and anodic electrodes and bipolar plates.(1) The single fuel cells (SFC) constituents of a PEMFC stack are serie-connected by means of bipolar plates, which are multifunctional components in PEMFC stacks, collecting and conducting the electrical current from SFC to SFC, and distributing the reacting gases ($H_2$ and $O_2$) to the respective fuel cell electrodes (2). The basic requirements for the bipolar plate material include high electrical conductivity, good mechanical strength, and good corrosion resistance. Bipolar plates are responsible for most of the mass and volume of a fuel cell stack.(1, 2) Thus, the reduction in the thickness of these components will enable a reduction in size of the stack, this being of interest from both technical and commercial points of view.

The most commonly used bipolar plate material is graphite, which presents ideal corrosion resistance and electrical conductivity.(2,3) Nevertheless, its high cost and the need of intensive machining to form the flow channels limit this material for applications involving high-volume manufacturing. Additionally, graphite is very brittle and lacks mechanical strength, and therefore the thickness of the plates cannot be reduced. This results in thicker plates with bulkier sizes and more elevated weights.(3) In light of these problems, there is great interest in the replacement of the graphite as base material of the PEMFC bipolar plates. Several alternatives to replace the graphite have been considered, such as conductive polymers, carbon–polymer composite materials, graphite-filled polymer, carbon–carbon composite materials, and metals and metallic alloys.(3)

Considerable attention has been recently given to metallic-based bipolar plates due to their high electrical conductivity, acceptable material cost, high strength, low gas permeability, and applicability to mass production. Moreover, metallic materials can be easily machined or stamped to the final form of thin plates with the flow channels, thus significantly reducing the volume and weight of PEMFC. Metallic materials investigated to date mainly include stainless steel, aluminium, titanium and nickel.(4) The major disadvantage of metals is that they are very susceptible to corrosion when exposed to the acidic and humid environments usually containing sulphate, chloride and fluoride ions, and reactant gases inside the PEMFC.(4,5) The corrosion can cause the formation of a passive surface layer, which increases the electrical contact resistance, while the metal dissolution can contaminate the membrane and electrocatalysts. The passivation/dissolution of metallic bipolar plates would cause considerable power loss.(4,5) In order to avoid or minimize the problems associated with the corrosion of metallic materials, one solution is to coat the metallic bipolar plates with protective and conductive coatings. In this study the objective is to develop a methodology for evaluating materials for metal-based bipolar plates and to select, by this method, one or more materials that may be most promising for additional research to PEMFC bipolar plate application. The work is focused on the assessment of two important parameters: the interfacial contact resistance (ICR) and the corrosion resistance in an environment simulating the conditions existing in a PEMFC.

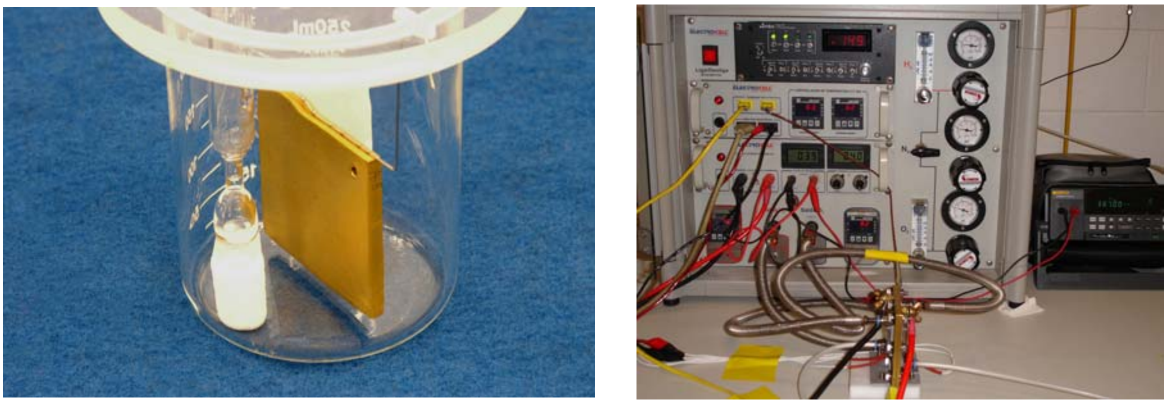
## 2 EXPERIMENTAL

The AISI 316L stainless steel was chosen as the substrate material for this study because its availability and relatively low cost. The coatings analyzed were: diamond-like carbon (DLC), chromium nitride (CrN), titanium nitride (TiN) and that obtained by ionic nitriding of the substrate. The sample specimens were cut into pieces of about 20 $cm^2$ (4 mm thickness), polished with #600 grit SiC abrasive paper and cleaned with ethanol and organic-based solvent and the respective coating was applied. DLC, CrN and TiN coatings were applied by PVD (physical vapor deposition). The samples were identified as A (titanium nitride), B (chromium nitride), C (ion nitrided), D (diamond-like carbon) and F (without coating). Samples with dimensions 95 x 95 x 4 mm were utilized in single fuel cell assembly. Scanning electron microscopy (SEM) was used to analyze the microstructure of the as-received specimens as well as those submitted to corrosion endurance tests.
The apparatus for ICR measurements (Figure 1) is basically the same as described in references.(6-8) The method consists in measuring the ICR between stainless steel-based samples and conductive carbon paper (Ballard, P50T model). Two pieces of carbon paper were sandwiched between the respective sample and two copper plates. The contact resistance was obtained by means of a Data Logger Fluke Hydra Series II. The apparatus operates with the principle of the four-wire current–voltage measurement eliminating transition and lead resistances. The potential difference (V) across the cell was measured while a fixed electrical current (I) was passed through the arrangement. The current applied (PS 6000 current source) was in the range 90–900 mA. The compaction force was gradually increased with the use of an Instron hydraulic press. The complete methodology of this test is described in the references (6-8). The experimental apparatus used in the corrosion tests and in the evaluation of performance of the single fuel cells are shown, respectively, in Figures 2a and 2b, and experimental procedures can be found in Silva's thesis.(9) The solution used in endurance corrosion tests without polarization was $10^{-3}$ M $H_2SO_4$ + 1.5 x $10^{-4}$ M HCl + 15 ppm HF, at 60°C, with oxygen or hydrogen continuously bubbled to simulate the cathode or the anode environment, respectively.(8) Corrosion tests with polarization were performed with the same solution described above and also with a solution of 1 M $H_2SO_4$+ 2 ppm $F^-$, pH = 0, 70°C, bubbled with air (cathode) or hydrogen (anode).(6)



(a) (b)

**Figure 1.** (a) Schematic illustration of the device (measurement cell) for the testing of interfacial contact resistance (ICR); (b) Photo of the arrangement of the test using the four terminals method to measure the ICR.



(a) (b)

**Figure 2.** Experimental apparatus used in: (a) corrosion tests; (b) evaluation of performance of the single fuel cells.

## 3 RESULTS AND DISCUSSION

Figure 3 shows the average values of ICR of the as-received samples. The ICR decreases markedly with increasing compression between the plates. In practical conditions this compression is limited to a value around 140 N/cm$^2$ to prevent damage to other fuel cell components. According to the DoE (United States Department of Energy) studies,$^{(10)}$ an ICR value less than or equal to 20 mΩ.cm$^2$ at 140 N/cm$^2$ is a target for the development of PEMFC bipolar plates. As shown by Figure 3 the characteristic ICR values for C and D coated samples are very high in relation to DoE target value and, therefore, these coatings were excluded of the subsequent evaluations. Stainless steel without coating (F samples) also presents high ICR values due to the dielectric characteristics of the atmospherically formed oxide layer. However, these samples were also included in subsequent tests for comparative purposes.

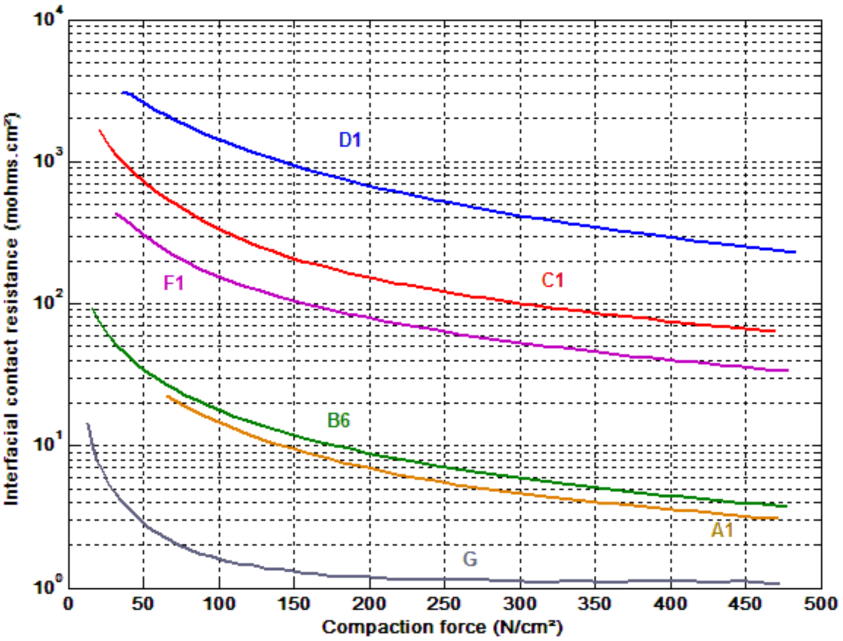


**Figure 3.** ICR values against compression force. Samples: A1 (titanium nitride), B6 (chromium nitride), C1 (ion nitrided), D1 (diamond-like carbon), F1 (without coating) and G (conventional graphite for PEMFC bipolar plates).

Microscopic observations, roughness measurements and ICR values obtained under various surface preparations of the samples suggest that the main factor that determines the major differences between the ICR values of different samples is the electrical resistivity of the material of the surface layer, and not its roughness. This is demonstrated, for example, by a series of tests on AISI316L uncoated samples (F samples) whose surface was treated to obtain different roughness levels. Figure 4 shows the ICR x versus compression force curve of F samples as received and after sand blasting, sandpapering or polishing, obtaining a roughness range of 0.09µm to 8.22µm. Note that the ICR is greatly reduced as a function of the surface treatment, regardless of the roughness achieved. The reduction of ICR is caused by mechanical removal of the oxide-rich layer. This is a temporary effect, because the samples stored in atmospheric conditions showed a gradual increase in ICR with the time, returning to the original ICR values about 500 hours after the surface treatment.

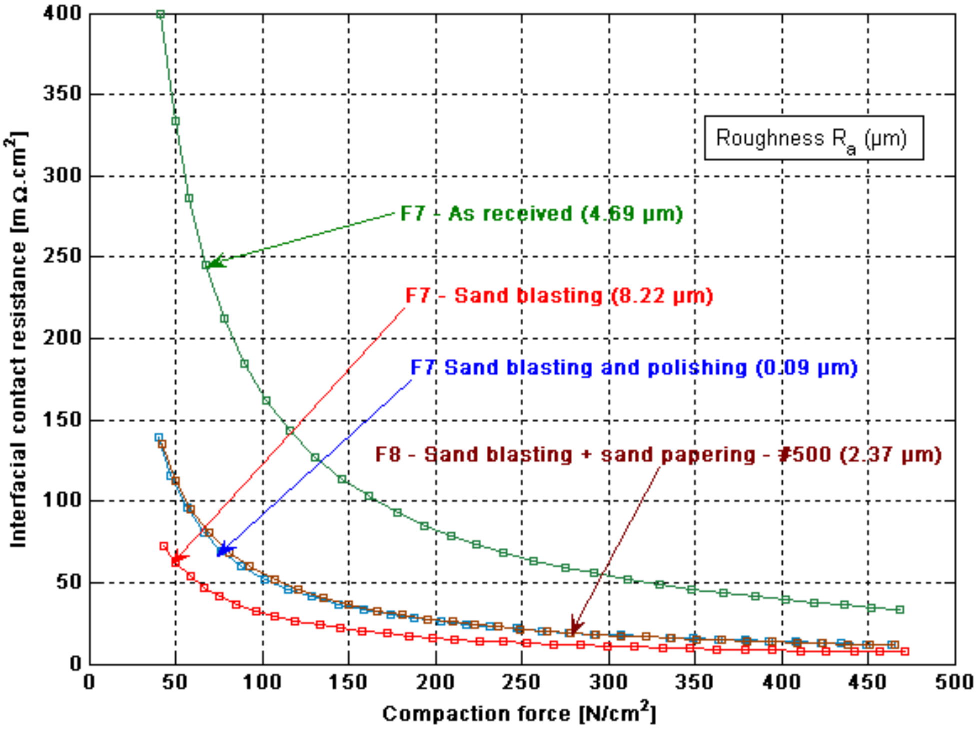


**Figure 4.** ICR results as a function of the compression force for F7 and F8 samples with different surface roughness.

Figure 5 illustrates the results obtained for endurance corrosion immersion test in cathode condition, showing the evolution of the corrosion potential for A, B and F samples. Note that the samples coated with CrN stabilized in higher potentials than the other samples, which is indicative of greater corrosion resistance. Large oscillations of corrosion potential are mainly associated with changes in temperature, since the solution was allowed to cool to room temperature after eight hours daily and on weekends. Visual observation of the samples after endurance corrosion test in cathode condition showed only a slight increase in the surface brightness, similar to the result of a chemical cleaning. Moreover, the quantitative analysis of the metals dissolved in the solution showed that the corrosion was negligible in all samples. SEM analysis (Figure 6) indicated the absence of pitting corrosion as well. Similar remarks are also valid for immersion tests under anode simulated conditions.(9)

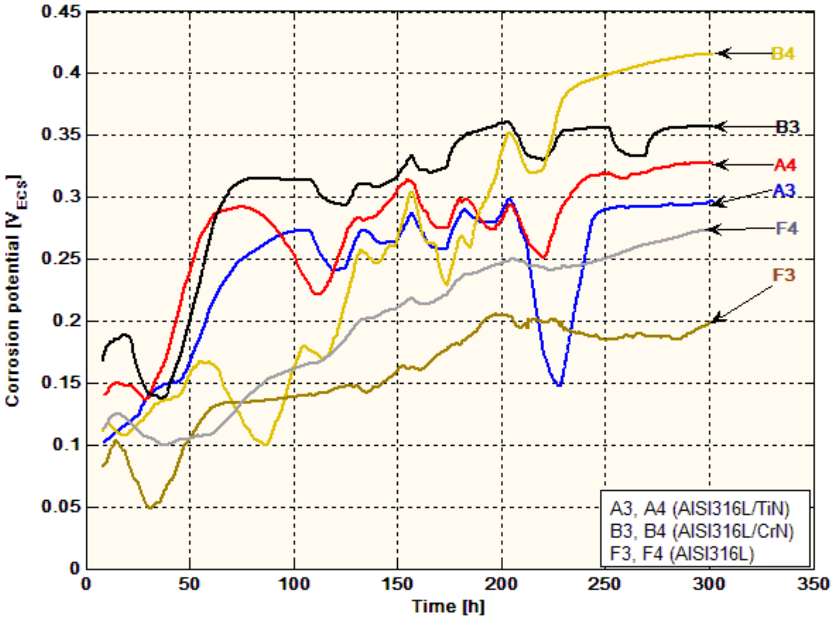


**Figure 5.** Evolution of the corrosion potential in endurance immersion tests in cathode condition (solution $10^{-3}$ M $H_2SO_4$ + 1.5 x $10^{-4}$ M HCl + 15 ppm HF, pH = 3, 60°C, $O_2$ gas).

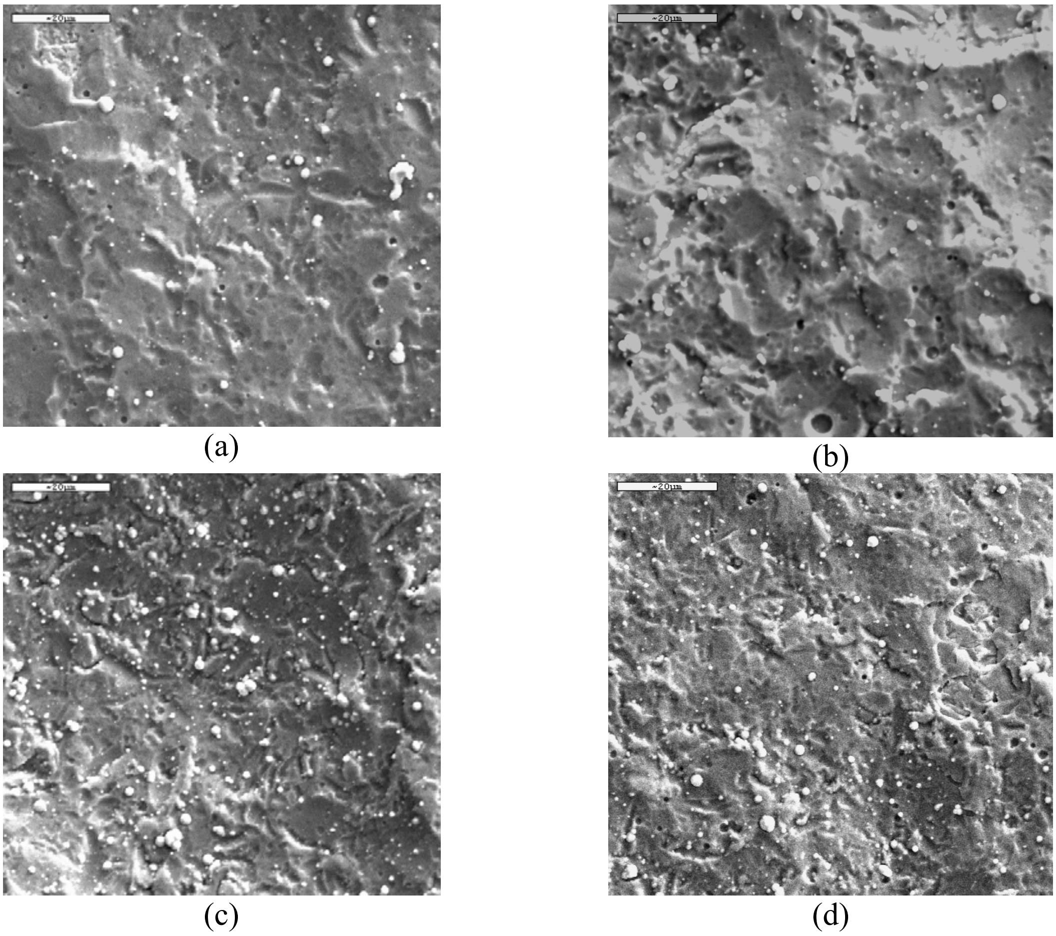

(a) (b) (c) (d)

**Figure 6.** SEM photomicrographs of AISI316L/TiN specimen before (a) and after 500 h of corrosion endurance test (b); AISI316L/CrN specimen before (c) and after 500 h of corrosion endurance test (d).

Figure 7 shows the polarization curves in simulated cathode environment. The CrN coated samples showed the best results, ie, lower dissolution currents, followed by the samples without coating, which in turn showed better corrosion resistance than TiN coated samples. In the latter samples, the corrosion occurred mainly at the interface between the substrate and the coating, causing the detachment of undissolved coating particles from the substrate during the test. The corrosion process takes place at the interface due to the penetration of the solution through microcracks and adhesion failures of the coating. The interface is more active than the surface of steel without coating, which explains the dissolution current being higher in A samples than in F samples.$^{(11)}$

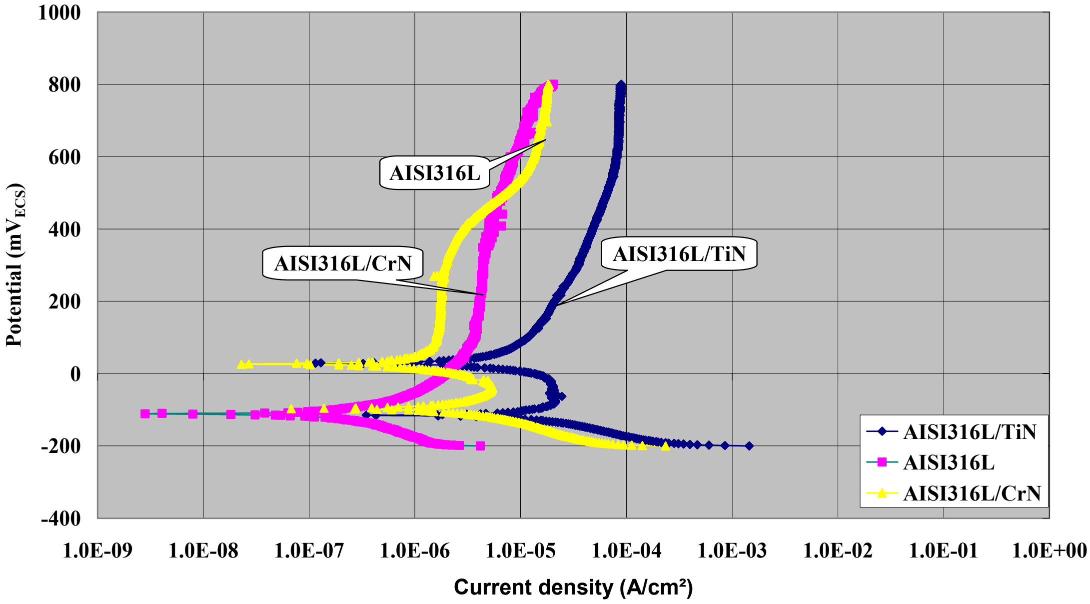
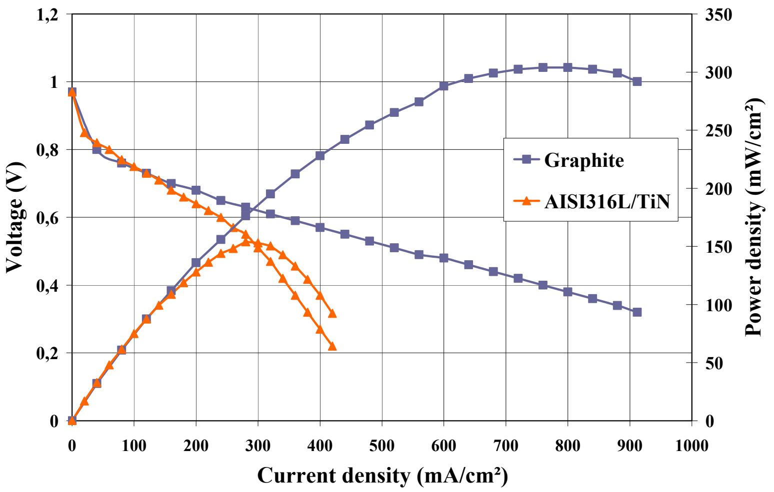
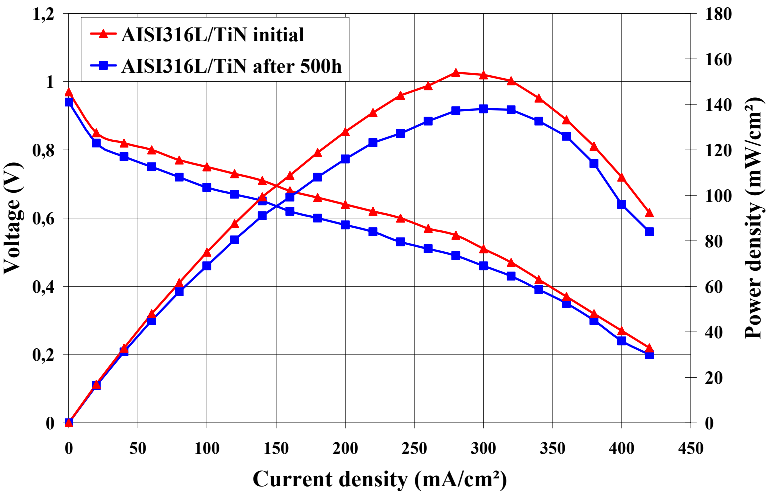


**Figure 7.** Polarization curves at 0.33 mV/s. Samples in cathode condition. Solution: 1 M $H_2SO_4$+ 2 ppm $F^-$; pH = 0; 70°C; bubbled with air.

Figure 8(a) shows the performance curves of two single PEMFCs in their initial conditions, one fuel cell having being built with conventional graphite-based end plates and the other one with TiN/AISI316L coated end plates. At the open-circuit potential and at low-current densities (until 170 mA/cm$^2$) the electrochemical performances of the two fuel cells are similar. However, for current densities higher than 170 mA/cm$^2$ the curves showed considerable discrepancies, with the maximum power of the graphite-based unit being twice that of the metallic end plate unit. Figure 8(b) shows the performance curves of the single PEMFC made with TiN/AISI316L coated end plates after 500 hours of operation, as compared to the performance of this fuel cell in the initial conditions. A possible ageing effect of the fuel cell with time was shown by a small decrease (5% or less) of the voltage values for the same current densities, especially in the ohmic polarization region (50 mA/cm$^2$to 300 mA/cm$^2$). Preliminary investigations carried out after the operation time suggested that the relatively poor performance of the fuel cell made with metallic end plates (Figure 8(a)) could be associated with assembly problems or with thermal diffusion aspects related to this unit. Incipient signals of corrosion in TiN/AISI316L coated end plates were also found. Additional tests of longer duration should be performed to verify the evolution of this corrosion process and its effect on the ageing of the fuel cell.



(a)



(b)

**Figure 8.** Electrochemical performance curves of single PEMFC: (a) comparative analysis – fuel cells with graphite and AISI316L/TiN plates; (b) PEMFC with AISI316L/TiN plates - Initial and after 500 hours of operation.

## 4 CONCLUSIONS

Four different types of coatings applied on AISI316L stainless steel samples were evaluated concerning their suitability for use in metallic bipolar plates. Titanium nitride (TiN) coatings showed the best interfacial contact resistance, namely, 14 mΩ.cm$^2$ at 140 N/cm². Chromium nitride (CrN) coatings, on the other hand, showed better corrosion behavior than TiN. With the methodology developed in this study it was possible to select candidate coatings for AISI316L stainless steel aiming further detailed studies concerning its application as metallic bipolar plates in fuel cells.

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