



A comparison of carbon coated and uncoated 316L stainless steel for using as bipolar plates in PEMFCs

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ABSTRACT

Two kinds of carbon coated and uncoated 316L stainless steel are studied to use as bipolar plates in fuel cells. The results show that the conductive amorphous carbon film has a low corrosion rate in simulated PEMFC environment. Rather long term potentiostatic tests and SEM investigations indicate that carbon thin films can be a good candidate to use as bipolar plate.

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1. Introduction

Carbon thin films can reveal a wide range of physical and chemical properties that make them suitable for using in high wear resistant [1–4], high corrosion resistant [5], and biocompatible components [5,6], low field emission cold cathodes [7], high efficiency speakers [2], and high capacity data recording hard disks [2,3]. Recently deposition of carbon films on a metallic substrate, such as stainless steel or titanium, are proposed to be used as bipolar plates in polymer electrolyte membrane fuel cell (PEMFC) [8–15]. Bipolar plates, that are a multifunctional component, are most important parts in the PEMFC. However, some problems in the bipolar plates prevent traditional mass production of PEMFCs. Bipolar plates should have good corrosion resistance in the high acidity (pH ~ 2) and high temperature (<60 °C) environment of PEMFC [16]. Also, they should have low surface electrical conductivity [16]. Some materials such as stainless steel, titanium, composites, and coated materials are investigated to be used as bipolar plates [16]. 316L stainless steel is one of the most interesting candidates for using as bipolar plates [17]. But their corrosion resistance in PEMFC environment is unsatisfactory. Also, the high electrical resistant passive layer on stainless steel has a significant role to increase ohm losses in fuel cells [18]. Amorphous carbon films with low sp³

bands have a high chemical stability with low electrical resistance [2,3]. Therefore, it seems that the stainless steel coated with a carbon film is a good candidate. In our previous work, the effect of substrate temperature on the properties of carbon films for using as bipolar plates was studied [19]. In the present paper following our previous work, the carbon coated 316L stainless steel prepared at the substrate temperature of 300 °C that has optimum properties for using as bipolar plate is compared with the uncoated samples.

2. Experimental

Polished 316L stainless steel (Fe–16.4 Cr, 9.32 Ni, 1.94 Mo in wt%) sample with approximate sizes of 10 mm × 10 mm and 2 mm in thickness, and surface roughness of 0.4 nm was used to coat with a carbon film by magnetron sputtering physical vapor deposition process (MS-PVD). Sample preparation method and carbon coating procedure have been explained in the previous work [15]. Here, the deposited sample prepared at 300 °C with a deposition time of 25 min was selected to compare with 316L stainless steel. The thickness of carbon layer measured by a mechanical profile meter was around 200 ± 10 nm. The structure of coating was investigated with a Raman spectroscopy type Labram HR800 at 532 nm line excited with Nd–YAG laser. AFM analysis was used to evaluate the morphology of the carbon film. There is a conventional method to measure interfacial contact resistance (ICR) for bipolar plates in PEMFCs [10–14,17,18]. In this method two pieces of carbon paper are sandwiched between the sample and two copper plates. The electrical resistance of the circuit measured during the compacting force was increased gradually. By measuring ICR of carbon paper and copper plates, the calculated ICR was corrected. A four point-probe instrument is also used to measure electrical resistance of the carbon film. The measured resistance was converted to sheet resistivity by considering ring currents for thin films and the thickness of carbon thin film. Potentiodynamic corrosion tests for both coated and uncoated 316L stainless steel were conducted in 1 M H₂SO₄ with 5 ppm F⁻ ions at 70 ± 3 °C (i.e. simulated PEMFC solution) by a potentiostat

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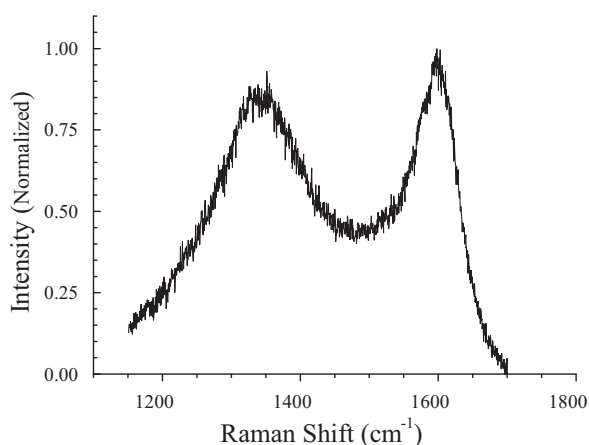


Fig. 1. Raman spectrum of the carbon film deposited on 316L stainless steel substrate.

instrument model EG & G 273A. A Pt wire and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode, respectively. The potential was swept at scan rate of 1 mV/s. The corrosion current density of samples was calculated by linear polarisation method with Corrview software. In order to simulate the actual conditions of a PEMFC in rather long term periods, potentiostatic tests were conducted with the same instrument. For anodic side of bipolar plate -0.1 V vs. SCE with H_2 purging was applied. For cathode side the applied potential was $+0.6$ V vs. SCE purged with O_2 . The total time of test was 8 h and the current points were recorded every 18 s. Concentration of dissolved iron ions after potentiostatic tests were measured by ICP method. After electrochemical tests the surface morphologies of the samples were investigated by scanning electron microscopy.

3. Results and discussion

Fig. 1 shows the Raman spectrum of the carbon film deposited on 316L stainless steel substrate. This Raman spectrum is mainly composed of two broad peaks at around 1580 cm^{-1} and 1340 cm^{-1} . These peaks are named G-band and D-band, respectively. The G band (Graphite) is related to graphite lattice and sp^2 bands.

The D-band (Defect) results from the defects in the graphite crystalline structure. The intensity and width of the D-band are proportional to the resonances of carbon atoms in disordered and defective graphite structure. The stronger intensity and the wide full width at half maximum (FWHM) of the D-band denote an abundance of short range ordered graphite structures or graphite with very small grain size in the carbon film [3,19,20]. The intensity, position and FWHM of G and D bands are gained after Lorentzian deconvolution of Raman spectrum. The data are shown in **Table 1**.

Table 1

Data extracted from Raman spectrum of carbon films by Lorentzian deconvolution.

Band	Intensity	FWHM (cm^{-1})	Shift (cm^{-1})
G	0.91	54	1603
D	1.10	227	1348

If the FWHM of D band is more than 50 cm^{-1} , the intensity ratio of the D band to G band (I_D/I_G), related to in-plane correlation length (L_a) or the size of graphite clusters according to the following relation [3,7,19]:

$$\frac{I_D}{I_G} = cL_a^2 \quad (1)$$

with c equal to around 0.0055 (for L_a in Angstrom). The intensity ratio of the current spectrum is calculated around 1.22. Then the mean size of graphite crystallites is found to be equal $\sim 15\text{ \AA}$ for the selected carbon coating. Therefore, the structure of carbon coating can be related to glassy carbon with short range order.

Fig. 2 shows the AFM image of the carbon coating surface. It is obvious that the structure of the grains is columnar and they grow in the frontier of vertical side of the surface. According to Structural Zone Model (SZM) the ratio of substrate temperature (300°C) to melting point of coating material (3500°C) is less than 0.3.

Then it is expected that the growth of carbon coating follows zone I structure. It should be mentioned that according to the 2D AFM image this morphology is dense enough to cover the entire surface and prevent the corrosive environment from attacking the substrate directly.

The ICR values of uncoated and carbon coated 316L stainless steel as a function of compaction forces are presented in **Fig. 3**. One of the important properties of bipolar plate in PEMFC is low interface contact resistance (ICR) and high conductivity due to minimizing ohms losses and increasing the output power efficiency of the fuel cell. Generally, it is reported that the ICR value should be less than $20\text{ m}\Omega\text{ cm}^2$ for 140 N/cm^2 clamping force [16–18]. At 150 N/cm^2 compaction force, ICR is around $5\text{ m}\Omega\text{ cm}^2$ for carbon coated 316L stainless steel which is very low in comparison with that of uncoated 316L stainless steel ($280\text{ m}\Omega\text{ cm}^2$).

In addition, the electrical sheet resistance of carbon film that was measured by four-probe technique is compared with that of neat stainless steel and graphite (**Table 2**). The electrical resistance of carbon film is lower than stainless steel and even graphite. The high density of charge carriers in amorphous carbon increases conductivity in comparison with crystalline graphite. Therefore, carbon coating with a low electrical resistivity can reduce ohm losses in fuel cells.

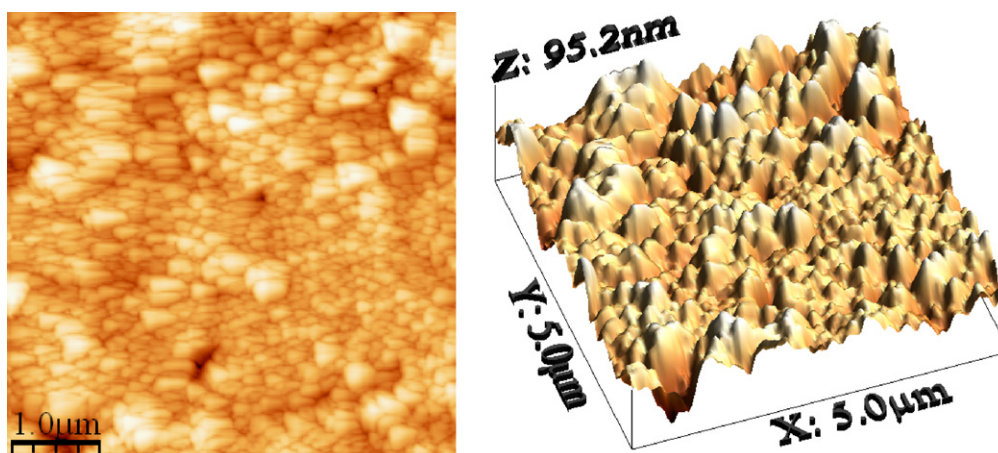


Fig. 2. AFM image of the carbon coating surface.

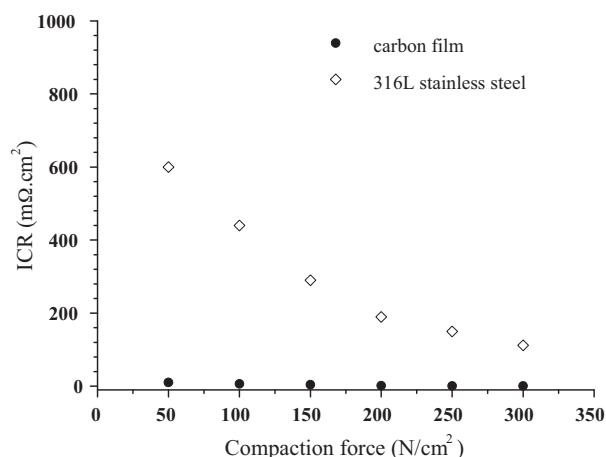


Fig. 3. ICR values of uncoated and carbon coated 316L stainless steel as a function of compaction forces.

Table 2
Electrical resistance of materials that measured by four-probe technique.

Material	Electrical resistance (mΩ cm)
Stainless steel	47 ^a
Graphite	62 ^a
Carbon coating	26

^a Extracted from Ref [12].

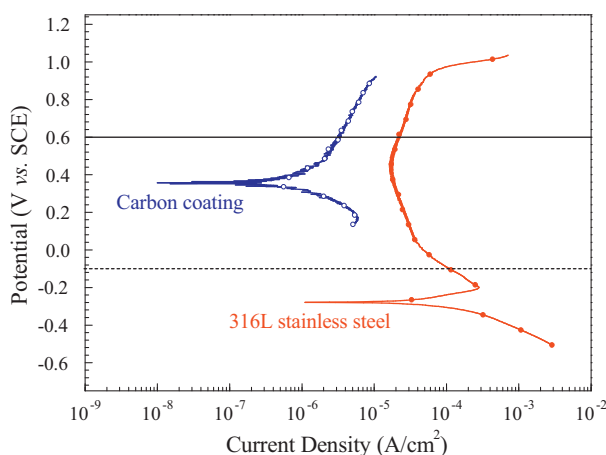


Fig. 4. Potentiodynamic polarisation curves of 316L stainless steel and carbon coated 316L stainless steel in simulated PEMFC solution.

Table 3
Corrosion parameters obtained from potentiodynamic curves in Fig. 1.

Parameter	Uncoated 316L	Carbon coated 316L
Corrosion potential (E_{corr}), mV vs. SCE	-279	+354
Corrosion current density (i_{corr}), A/cm ²	-2.4×10^{-5}	-1.3×10^{-7}
Current density at +0.6 V vs. SCE, A/cm ²	-2.2×10^{-5}	-3.2×10^{-6}
Current density at -0.1 V vs. SCE, A/cm ²	$+1.1 \times 10^{-4}$	Less than $+5 \times 10^{-6}$

Fig. 4 shows the potentiodynamic polarisation curves of 316L stainless steel and carbon coated 316L stainless steel in simulated PEMFC solution. The corrosion current density and corrosion potential of these two samples are summarized in Table 3. The corrosion potential of carbon coated 316L stainless steel is considerably more than that of uncoated samples. It shows that corrosion tendency of

this sample in the simulated fuel cell solution is significantly less than 316L stainless steel. Also, corrosion current density of carbon coated sample ($<1.3 \times 10^{-7}$ A/cm²) is less than uncoated 316L stainless steel ($<2.4 \times 10^{-5}$ A/cm²).

The lower corrosion current density means less dissolution and better durability of the specimen in PEMFC environment. For carbon coated 316L stainless steel, the corrosion current density is less than 1.6×10^{-6} A/cm² which is a value recommended by Department of Energy (DOE) as a target value until 2010 [16–18].

In actual PEMFC working conditions, the anode and cathode potentials are about -0.1 V vs. SCE and 0.6 V vs. SCE, respectively. In Fig. 4 solid lines and dashed lines show cathodic and anodic potentials of fuel cell, respectively. In the anodic potential, both samples are located in the anodic branch. In other words, corrosion will take place in uncoated and coated 316L stainless steel. However, for uncoated stainless steel cathodic potential are located in the passive region. Some authors reported that, although formation of the passive film on the 316L stainless steel will reduce the corrosion rate dramatically, this protective layer is electrically non-conductive [16,18]. Formation of high electrical resistance passive layer on the bipolar plates will increase internal ohm losses in the fuel cell. According to potentiodynamic curve in Fig. 4, for the carbon coated 316L stainless steel there is no evidence of passivation. Therefore, reduction in fuel cell performance could not happen in the bipolar plates coated with carbon layer.

At anodic potential of fuel cell, 316L stainless steel will be located in the passive region the same as cathodic potential. However, for carbon coated stainless steel, anodic potential of fuel cell is located in the cathodic branch of potentiodynamic curve.

At cathodic branch of potentiodynamic curves, just reduction reactions, like hydrogen evolution, are provided and no corrosion will happen.

SEM photographs of carbon coated and uncoated 316L stainless steel after potentiodynamic test are shown in Fig. 5. It is obvious that the surface of carbon coating is damaged by corrosive agent attack leaving the scratches on the surface (shown by arrows). It seems that, at high potentials, high gas evolution rates at pin-holes and defects can erode carbon films mechanically. In uncoated 316L stainless steel, formation of mass corrosion product with intergranular cracks and pitting corrosion are seen (shown by arrows). This phenomenon is reported by some authors [21,22] in the literature.

According to Yu et al. [22], the grain boundary corrosion in 316L stainless steel after polarisation test in simulated fuel cell environment can refer to the formation of chromium carbide precipitates (Cr_{23}C_6) at the grain boundaries that increase intergranular corrosion due to the decrease in chromium content in the areas close to the boundaries.

Contrary to their declaration it should be mentioned that formation of chromium carbide in 316L stainless steel is less possible because the carbon content in 316L stainless steel is very low for the formation of carbides (less than 0.02 wt%). Actually, 316L stainless steel resists the intergranular corrosion due to chromium depletion. It seems that at high electrochemical potentials the tendency of passive layer to break and the formation of pits will increase. Therefore, the intergranular and pitting corrosion could be due to the thickening and break down of the passive layer.

The potentiostatic curves of uncoated and carbon coated 316L stainless steel at PEMFC cathodic potential are seen in Fig. 6. In this paper negative current means anodic current and vice versa. According to Fig. 6, both samples are corroded in the cathodic conditions. However, the anodic current density of carbon coated sample is less than uncoated 316L stainless steel (Table 4).

In addition, the current density of carbon coated 316L stainless steel decreases continuously and even reaches zero after 8 h. Longer potentiostatic tests are necessary to evaluate this phenomenon

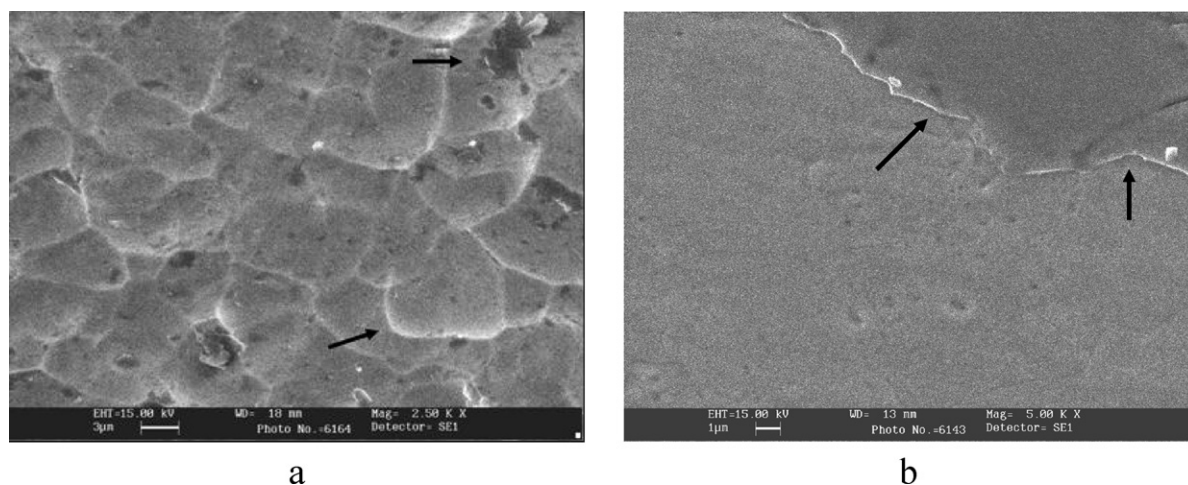


Fig. 5. SEM photographs of (a) carbon coated and (b) uncoated 316L stainless steel after potentiodynamic test.

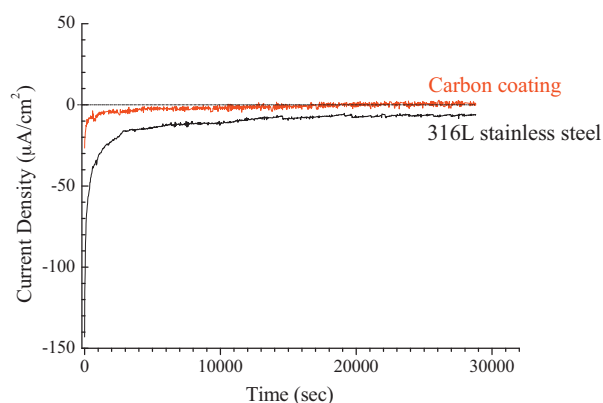


Fig. 6. Potentiostatic curves of uncoated and carbon coated 316L stainless steel at PEMFC cathodic potential.

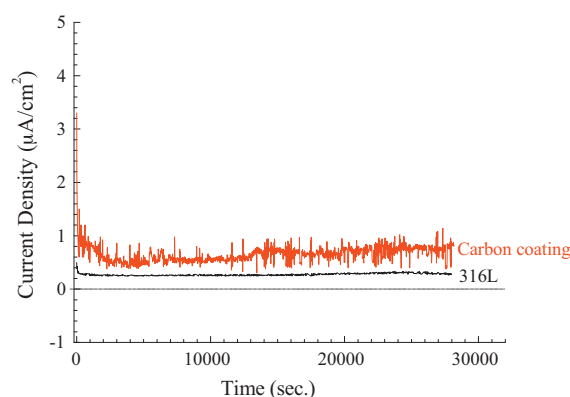


Fig. 7. Potentiostatic curves of carbon coated and uncoated 316L stainless steel in simulated anodic condition.

Table 4

Mean current densities extracted from potentiostatic curves in Figs. 3 and 4.

Condition	Sample	Mean current density (A/cm ²)
Anodic (−0.1 V vs. SCE and hydrogen bubbling)	Uncoated 316L	2.7×10^{-7}
	Carbon coated 316L	6.5×10^{-7}
Cathodic (+0.6 V vs. SCE and oxygen bubbling)	Uncoated 316L	-8.4×10^{-6}
	Carbon coated 316L	-7.6×10^{-7}

exactly. It is well known that, during corrosion reactions, reduction reactions especially hydrogen gas evolution take place. In one step of hydrogen reduction reaction, atomic hydrogen (H) will be produced. Atomic hydrogen has a high tendency to dangle with sp^3 carbon bonds. In conductive amorphous carbon films, there are about 5% sp^3 bonds [2–4]. Then during potentiostatic tests a number of dangling bonds of C–H are created. These dangling C–H bonds can increase the corrosion resistance of carbon coated substrates [10]. Probably, the formation of dangling bonds of C–H due to reduction reaction of hydrogen on the surface of carbon coating can increase the corrosion potential and shift the current density towards cathodic currents.

In Fig. 7, potentiostatic curves of carbon coated and uncoated 316L stainless steel in simulated anodic condition are illustrated. Both samples present cathodic current in which any effect of corrosion cannot be observed. The behavior of carbon coated samples was predictable according to potentiodynamic curve in Fig. 4. However the trend of uncoated 316L stainless steel at anodic condition

is not well understood but similar trend has been reported in the literature [14,21,22].

All authors who have studied on the potentiostatic behavior of stainless steel in simulated PEMFC solution, have reported the cathodic currents in anodic conditions without suggesting an evident reason for this controversy. It is possible that different conditions imposed during the potentiostatic and potentiodynamic tests bring about this contrasting result. In potentiodynamic conditions, the potential is unstable and gradually changes but in potentiostatic tests the electrochemical potential is constant and it seems that this condition is more stable thermodynamically. Nevertheless, according to Table 4 the current densities of coated and uncoated 316L stainless steel are positive (cathodic) indicating no corrosion will happen. The cathodic current density in carbon coated stainless steel is more than uncoated sample, meaning that the cathodic protection in coated sample is more effective. However, it should be mentioned that at high cathodic current density a problem arises due to the increase of hydrogen evolution rate which leads to the formation of open blisters on the surface of the coatings.

SEM micrographs of carbon coated and uncoated 316L stainless steel surface after potentiostatic tests are shown in Fig. 8. The arrows show initiating pitting corrosion on the uncoated 316L stainless steel. The number of pits on the 316L stainless steel in cathodic conditions is more than the ones in anodic conditions.

There is no evidence of corrosion on the surface of carbon coated samples in anodic and cathodic conditions.

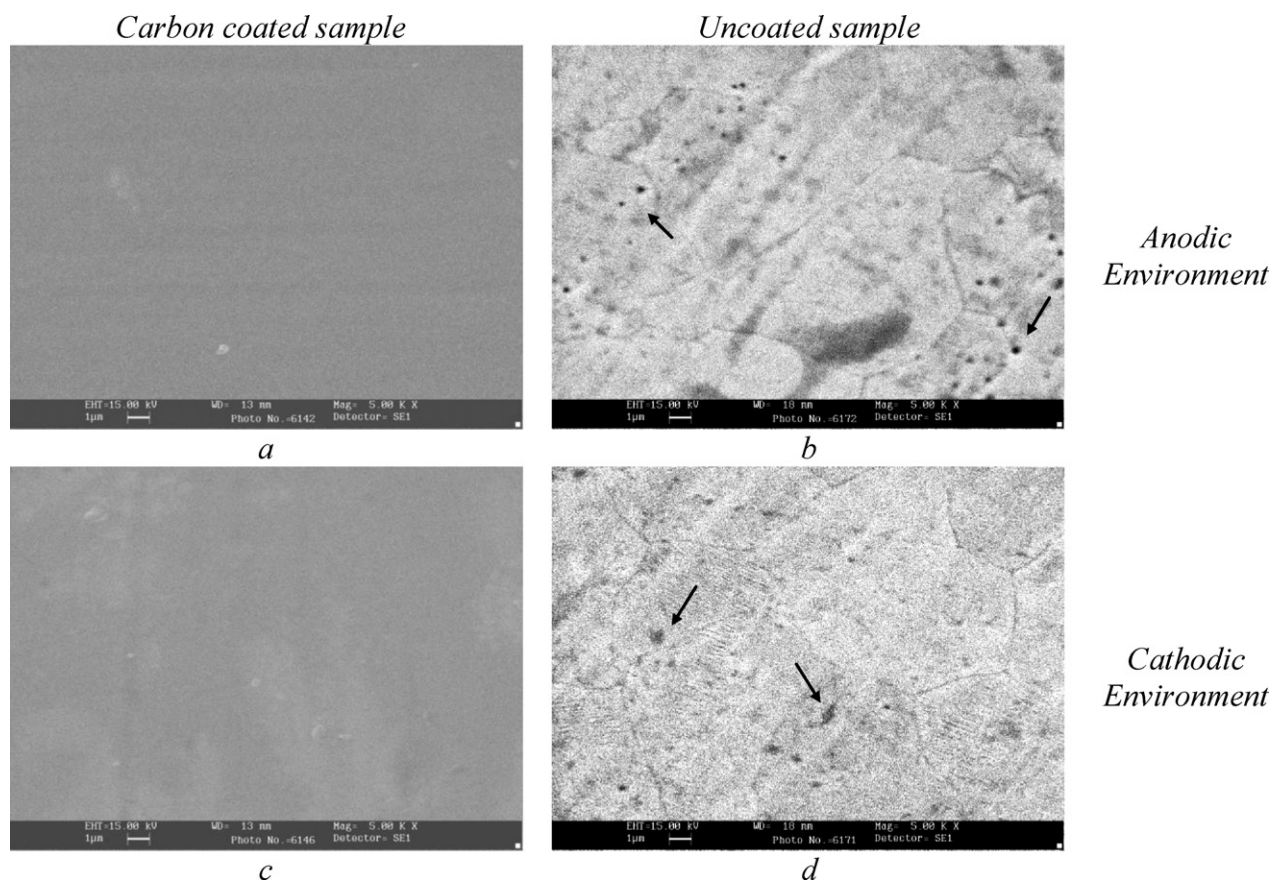


Fig. 8. SEM photographs of carbon coated (a and c) and uncoated 316L stainless steel (b and d) after potentiodynamic test for anodic potential (a and b) and cathodic potential (c and d).

Table 5

Dissolved iron concentration after potentiostatic tests.

Condition	Sample	Dissolved iron ions concentration (mg/l)
Anodic (−0.1 V vs. SCE and hydrogen bubbling)	Uncoated 316L	0.49
	Carbon coated 316L	0.06
Cathodic (+0.6 V vs. SCE and oxygen bubbling)	Uncoated 316L	0.98
	Carbon coated 316L	0.07

After potentiostatic tests dissolved iron ion concentration was measured by ICP method. The concentrations of Fe ions for various conditions are summarized in Table 5. In actual fuel cell operation, dissolved metallic ions due to corrosion migrate to the polymer electrolyte membrane. If the amount of metallic ions in the membrane reaches more than 10 mg/l, it can degrade fuel cell performance by poisoning the membrane [10]. According to Table 5, after 8 h potentiostatic test 0.98 mg/l Fe ions of uncoated samples are dissolved in the solution. Assuming a constant corrosion rate during the test, Fe ion concentration of 613 mg/l in the solution can be estimated for 5000 h. If just 5% of dissolved ions migrate towards the membrane, one can predict that the concentration of Fe ions in the membrane after 5000 h reaches 31 mg/l which is higher than critical concentration. It should be mentioned that dissolution of other metallic ions, i.e. Cr and Ni, has been ignored. When carbon coating is used as a protective coating on 316L stainless steel, the amount of Fe ions in the membrane is 3 mg/l after 5000 h operation. In other words, after 15,000 h, the concentration of metallic ions reaches the critical concentrations.

4. Conclusions

In this study a thin carbon film was coated on 316L stainless steel by magnetron sputtering physical vapor deposition. The electrical properties and the corrosion resistance of carbon coated samples compared with uncoated 316L stainless steel shows a substantial strong improvement in the cited properties. It seems that stainless steel coated by an electrically conductive and protective carbon layer can be a suitable candidate for using as a bipolar plate in polymer electrolyte membrane fuel cells.

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