SnO$_2$:F coated austenite stainless steels for PEM fuel cell bipolar plates

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Abstract

Austenite stainless steels (316L, 317L, and 349^{TM}) have been coated with 0.6 μm thick SnO$_2$:F by low-pressure chemical vapor deposition and investigated in simulated polymer electrolyte membrane fuel cell (PEMFC) environments. The results showed that substrate steel has a significant influence on the behavior of the coating. Coated 316L showed a steadily increasing anodic current in PEMFC environments, indicating that it is not suitable for this alloy/coating combination. Coated 349^{TM} showed a cathodic current in the PEMFC anode environment, demonstrating its stability in the PEMFC cathode environment. Coated 317L exhibited a stable anodic current after a current peak (at *ca.* 14 min) in the PEMFC anode environment, and showed an extremely stable low current in PEMFC cathode environment, suggesting the possibility of using SnO$_2$:F coated 317L for PEMFC bipolar plate applications.

ICP results on the corrosion solutions showed that the PEMFC anode environment is much more corrosive than the cathode one. Fresh 316L showed the highest Fe, Cr, and Ni dissolution rates, and coating with SnO$_2$:F significantly reduced the dissolution. Coating the 317L also showed a significant beneficial effect on the corrosion resistance in the PEMFC environments. Coating 349^{TM} steel further improved the already excellent corrosion resistance of this alloy. Trace Sn ions were detected for all coated steels in PEMFC anode environment, but not in the cathode one.

The influence of SnO$_2$:F on the interfacial contact resistance (ICR) is mixed. For 316L and 317L steels, a SnO$_2$:F coating reduced the ICR. For 349^{TM} steel, the SnO$_2$:F coating increased the ICR.
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1. Introduction

The use of stainless steels for bipolar plates in polymer electrolyte membrane fuel cells (PEMFC) has recently attracted a lot of attention [1–14]. Two key barriers are the interfacial contact resistance (ICR) and corrosion resistance in the PEMFC environments. Although previous investigations indicated that fresh austenite stainless steels have fairly low contact resistance and good to excellent corrosion resistance in PEMFC environments [4,6,10–12], better corrosion resistance and lower contact resistance with low-cost materials are necessary. The former is needed to reduce metal ion contamination, which could poison the membrane, while the latter is needed to reduce the resistive losses during operation [1]. To meet such requirements,

researchers have taken a number of approaches including coatings [8,15], surface electrochemical treatment [16], and applying a polymer layer [17].

Thermal nitridation has been one approach for 349^{TM} steel, leading to the discovery that a discontinuous mixture of CrN, Cr$_2$N, and (Cr, Fe)$_2$N$_{1-x}$ (x = 0–0.5) surface particles overlying an exposed γ austenite-based matrix resulted in unacceptably high corrosion rates under simulated PEMFC anodic and cathodic conditions [18]. On the other hand, the same nitridation treatment for super ferritic AISI446 resulted in a nitrogen modification of the native oxide passive layer on the alloy, which significantly decreased the ICR while improving the corrosion resistance in the simulated PEMFC environments [19]. However, the lengthy treatment times used in this process lead us to explore other possible coating alternatives with more rapid processing. Our approach in looking for coatings is to identify base metals with high corrosion resistance and then apply a coating that is not only corrosion resistant but also provides low

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interfacial contact resistance. In this approach, the metal does not need to be pin-hole free since any exposure of the base metal will result in passivation. Previous work has been conducted on applying conductive SnO_2 coatings onto metal substrates for the PEMFC bipolar plate, mostly as a protective coating on a porous substrate or as a catalyst [9,13]. There is a shortage of systematic investigations concerning coating steels in PEMFC environments. In this report, we present our efforts towards coating austenite steel with fluorine doped SnO_2 (SnO_2:F). SnO_2:F, which is widely used in photovoltaic industry, can be easily doped for high conductivity and is known to have good stability in aqueous solutions. So, highly doped SnO_2 may improve the corrosion resistance and lower the contact resistance for stainless steels in a PEMFC environment.

2. Experimental

2.1. Materials and electrochemistry

Stainless steels plates of 316L, 317L, and 349™ were provided by J&L Specialty Steel, Inc. (now part of Allegheny Ludlum). The chemical compositions are given elsewhere [10]. Alloy plates were cut into 2.54 cm × 1.25 cm samples and were processed through #600 grit SiC abrasive paper, rinsed with acetone, and dried with nitrogen gas.

The SnO_2:F coating was deposited in a low-pressure chemical vapor deposition (LPCVD) system. LPCVD has a significant advantage over atmospheric-pressure systems with regard to film uniformity. Reduced pressure enhances the reactants diffusion coefficient; thus the film deposition is very sensitive to substrate temperature. By systematically varying the substrate temperature, total chamber pressure, and total gas flow rate, we were able to control the film properties [20]. Ultrahigh-purity (UHP) tetramethyltin (TMT, Morton International) and bromotrifluoromethane ($CBrF_3$) were used as the tin and fluorine precursors, respectively and UHP-grade oxygen was used as the oxidizer. The forming reaction for the SnO_2 coating is described as:

$$Sn(CH_3)_4(g) + 8O_2(g) = SnO_2(s) + 6H_2O(g) + 4CO_2(g)$$
(1)
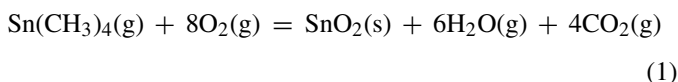
The reaction chamber pressure for the depositions was kept at 6666 Pa (50 Torr) and the deposition temperature was 550 °C. With the high purity precursor and tight deposition parameter control, a very high quality conducting SnO_2:F film was formed. A stylus profilometer (Dektak3) was used to measure the film thickness and a Tencor M-gauge was used to measure the sheet resistance of SnO_2 films on the glass substrate. A 0.6 μm (approximately) thick film of SnO_2:F was formed with a sheet resistance of $8\,\Omega\,\square^{-1}$ (a resistivity of 5 Ω cm).

To make the electrodes for the electrochemical measurements, the un-coated side of the sample was polished with #600 SiC paper followed by cleaning with acetone and drying with nitrogen gas. For electrical conduction, this side (backside) was connected to a copper wire with silver paint. The backside and the edges of the samples were mounted with epoxy, leaving the coated side for electrochemical measurements. The sealing process was repeated to eliminate possible leakage.

To simulate an aggressive PEMFC environment, all electrochemical experiments were conducted in 1 M H_2SO_4 + 2 ppm F^- solution at 70 °C [3,10–12,21], and the solution was bubbled thoroughly either with hydrogen gas (for simulating the PEMFC anode environment) or pressured air (for simulating the PEMFC cathode environment) prior to and during the electrochemical measurements. These conditions are for accelerated laboratory tests and effectively simulate the direct contact between the bipolar plate and the membrane.

A conventional three-electrode system was used in the electrochemical measurements. A platinum sheet acted as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode; hereafter electrode potentials will be referred to the SCE unless otherwise noted. We used a Solartron 1287 potentiostat interfaced with a computer and employed dynamic polarization to compare the general electrochemical behavior of the coated steels. In these tests, samples were stabilized at the open circuit potential (OCP) for 5 min. Then the potential was swept from the OCP in the anodic direction with a scanning rate of 1 mV s^{-1}. This scanning rate was based on previous experiments. Potentiostatic polarization experiments were conducted to investigate the corrosion resistance and the film stability on the steel under simulated PEMFC operating conditions. In these measurements, the samples were also stabilized at OCP for 5 min then a specific potential was applied and the current–time curve was registered. Two potentials were chosen for the tests: −0.1 V (equivalent to ∼0.1V_{NHE}) [21] with the solution purged with hydrogen gas for the simulated PEMFC anode environment and 0.6 V (which is equivalent to ∼0.8V_{NHE}) with the solution purged with air for the simulated PEMFC cathode environment. A blank test with a Pt plate (an excellent oxygen reduction reaction catalyst) at 0.6 V in the air-purged solution (70 °C) was conducted to check the possible influence of the oxygen reduction reaction for the SS samples under these conditions. A continuously decaying anodic current was registered, reaching *ca*. 1.2 μA cm^{-2} after ∼10 min. This blank test indicates that the oxygen reduction reaction does not play a significant role in the observed sample current when polarized at 0.6 V in the air-purged solution.

2.2. Interfacial contact resistance

All ICR measurements were carried out at room temperature. The detailed method for conducting the ICR measurements is described elsewhere [10]. In short, two pieces of conductive carbon papers were sandwiched between the stainless steel sample and two copper plates. A current of 1.000 A was provided via the two copper plates and the total voltage drop was registered. The compaction force was gradually increased to determine the dependence of the resistance on the compaction force.

We investigated both fresh and SnO_2:F coated steels. Fresh steel samples were used to investigate the carbon paper/stainless steel interface ($R_{C/SS}$) and were used as a base for comparison. The ICR value of the carbon paper/copper plate interface ($R_{C/Cu}$) was compensated via a calibration, so only the ICR values for the

carbon paper/stainless steel interface are reported here. For the SnO_2:F coated steel samples, the interfacial contact resistance due to the un-coated backside was compensated for via the previous investigation with the fresh steel samples. So only the ICR of the carbon paper/SnO_2:F coated steel interface ($R_{C/TO}$) is reported here.

2.3. Characterization with XRD, AES and ICP

Glancing angle X-ray diffraction (XRD), used to investigate the structures of the bulk and surface layers was conducted via a four-circle Scintag X-1 diffractometer (ThermoLab) with a Cu Kα anode source. To reduce the signal-to-noise ratio for a reasonable test period, a slow scanning speed of $0.02°$ step^{-1} and a preset time of 3 s step^{-1} were applied for all of the measurements.

Auger electron spectroscopy (AES) analysis was used to identify the SnO_2:F coating's composition and for depth profiling, and was carried out with a Phi670 Auger Nanoprobe. The chamber base pressure was 4.0×10^{-8} Pa (3×10^{-10} Torr). The depth profiles were obtained by sputtering with 3 keV argon ions at a current density of around 1 μA mm^{-2}. During the sputtering, the system pressure in the chamber was approximately 6.67×10^{-6} Pa (5×10^{-8} Torr). Based on previous measurements, a reasonable estimate of the sputtering rate was approximately 35 nm min^{-1}.

To quantify the dissolved metallic Fe, Cr, Ni and Sn ions produced during the potentiostatic polarization process, the solutions used in the polarizations (for simulating the PEMFC anode and cathode environments) were collected after testing and analyzed by means of inductively coupled plasma atomic adsorption spectrometry (ICP/AAS). Solution volume was in the range of 80–100 ml. The standardizing solution for ICP analysis, purchased from Inorganic Ventures, Inc. was 1 M H_2SO_4 containing 100 ppm of each of these metallic ions. The system used was a Varian Liberty 150 ICP emission spectrometer controlled by a PC. The detailed procedure is described elsewhere [22].

3. Results and discussion

3.1. XRD and AES characterization

Typical glancing angle XRD patterns of the SnO_2:F coated 349^{TM} stainless steel are shown in Fig. 1. At a glancing angle of $5°$, both the austenite structure of the steel and the coated SnO_2:F are observed in the diffraction pattern. This is corresponds to a relatively deeper sampling of the surface. With decreasing glancing angle, both the austenite and SnO_2:F peaks decrease. At glancing angle of $1°$, the austenite peaks are negligible and can be ignored. On the other hand, all of the SnO_2:F peaks still have a reasonable intensity. This indicates that the investigated area is only the SnO_2:F coating. XRD patterns suggest that the SnO_2:F coating is in the 1 μm range, in fair agreement with the profilometer measurement.

The AES depth profile in Fig. 2a shows the tin oxide coating on a 349^{TM} stainless steel substrate. Initially, only Sn and O are present, while the main steel composition elements only appear
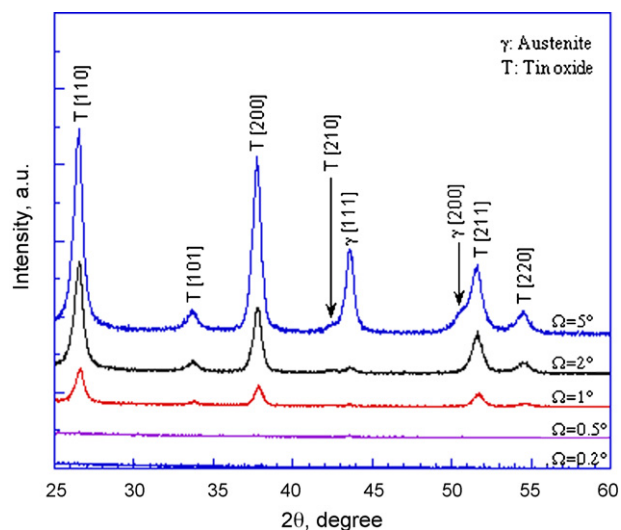

Fig. 1. Glancing angle X-ray diffraction patterns for 349^{TM} coated with fluorine doped tin oxide. Corresponding grazing angles (Ω) are marked on the right side of the patterns.
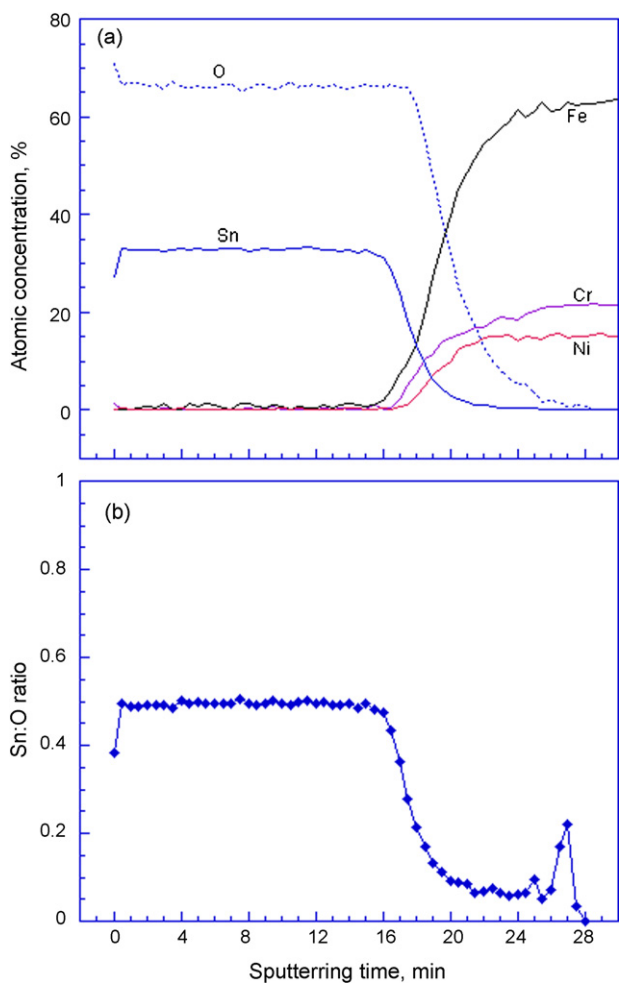

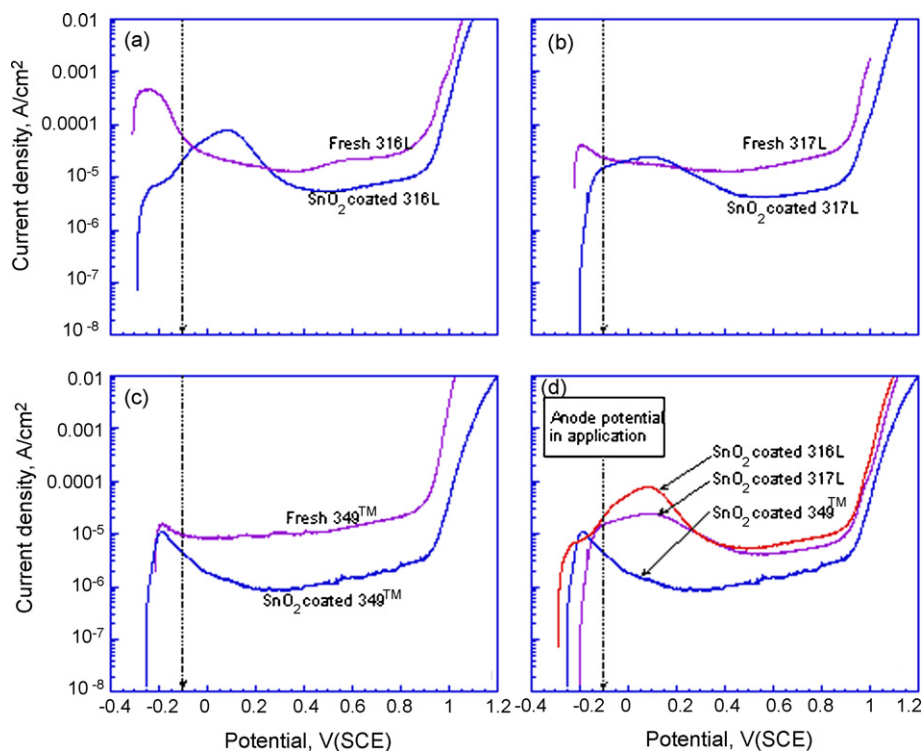Fig. 2. AES depth profile for SnO_2:F coated 349^{TM} steel (a); and the Sn:O ratio of the surface coating (b).

Fig. 3. Anodic behavior of fresh and SnO_2:F coated stainless steels in 1 M H_2SO_4 + 2ppm F^- at 70 °C purged with H_2. The anode potential in the PEMFC application is marked. (a) Fresh and SnO_2:F coated 316L; (b) fresh and SnO_2:F coated 317L; (c) fresh and SnO_2:F coated 349^{TM}; (d) SnO_2:F coated steels.

at longer sputtering times. Fig. 2b shows the Sn:O ratio as a function of the sputtering time. It gives the general chemical composition of SnO_2 coating. It should be mentioned that F acts only as dopant and its concentration is not high enough to change the composition of the coating. Using the half value of the Sn:O ratio as the boundary of the SnO_2:F and substrate steel, it took 18.0 min to sputter off the oxide coating. With a sputtering rate of 35 nm min^{-1}, the coating thickness is then 0.63 μm, in excellent agreement with the estimated value of 0.6 μm from the deposition conditions as well as the XRD patterns.

3.2. Dynamic polarization of SnO_2:F coated stainless steels

Anodic polarization curves of SnO_2:F coated stainless steels in 1 M H_2SO_4 + 2ppm F^- at 70 °C are displayed in Figs. 3 and 4. Fig. 3 shows the results when the solution was purged with hydrogen gas and a PEMFC anode operation potential of around −0.1 V according to [21], marked in the figure. In general for all the three steels tested in PEMFC anode environment, the OCP of the coated steel is very similar to that of the fresh substrate. However it is interesting to note that the coating has a significant influence on the anodic polarization behavior of the steels in the PEMFC anode environment and it also depends on the steel substrate. For 316L steel, the SnO_2:F coating decreases the peak passivating current *ca.* one order of magnitude, while shifting the passivating potential (the critical potential at peak passivating current) *ca.* 0.35 V anodic (from *ca.* −0.25 V to *ca.* 0.10 V), Fig. 3a. The result of this change in the polarization curve suggests that the coated 316L steel may experience a current peak during potentiostatic polarization in a PEMFC anode

environment. The peak at *ca.* 0.1 V is then due to the influence of SnO_2:F coating. Note that the passivation current (lowest current in the passivation region) of the SnO_2:F coated 316L is much lower than that of the fresh steel.

Similar results can be seen with SnO_2:F coated 317L, Fig. 3b, however the current is not as large as in the case of 316L. The passivating current for bare 317L is almost one order of magnitude lower than that of bare 316L. The passivating potential for coated 317L is shifted *ca.* 0.30 V anodic from *ca.* −0.20 V to *ca.* 0.10 V. Therefore, −0.1 V is also located somewhere near the peak of the polarization curve, which indicates that a current peak will be expected if polarized at −0.1 V. As for 349^{TM} however, the SnO_2:F coated steel shows a lower peak passivating current as well as a much lower passivation current than the fresh steel for the entire passivation region, Fig. 3c. The passivation region width for 349^{TM} is not affect by the coating. Thus, −0.1 V is inside the passivation region, as in the case of the fresh sample. Fig. 3d summarizes the three steels. It is interesting to note that the anodic behavior of the coated steels in the PEMFC anode environment depends very much on the substrate steel, though a generally lower current is obtained with the coated steel than the fresh ones. It should also be mentioned that SnO_2 may experience some instability at −0.1 V (see Section 3.3 below).

In the simulated PEMFC cathode environment, similar polarization curves were observed. SnO_2:F coated 316L shows a similar passivating current as that of the fresh 316L, and the passivating potential shifts around 0.15 V anodically from *ca.* −0.20 V to *ca.* −0.05 V, Fig. 4a. This shift is less than that in the PEMFC anode environment. Due to this shift, the passiva-
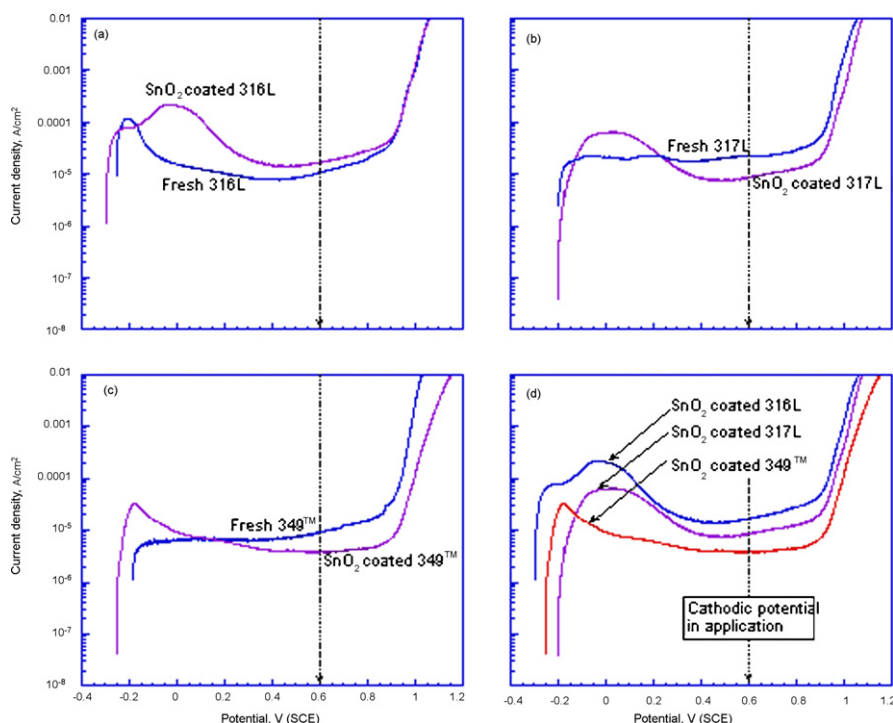
Fig. 4. Anodic behavior of the bare and SnO$_2$:F coated stainless steels in 1 M H$_2$SO$_4$ + 2ppm F$^-$ at 70 °C purged with air. The cathode potential for the PEMFC application is marked. (a) Fresh and SnO$_2$:F coated 316L; (b) fresh and SnO$_2$:F coated 317L; (c) fresh and SnO$_2$:F coated 349^{TM}; (d) SnO$_2$:F coated steels.

tion potential region is reduced for the SnO$_2$:F coated 316L. The current at 0.6 V for SnO$_2$:F coated 316L is lower than that for fresh 316L under identical conditions. This suggests a beneficial effect for the SnO$_2$:F coated 316L in a PEMFC cathode environment. For the SnO$_2$:F coated 317L a higher passivating current was noted compared to that of the fresh 317L, Fig. 4b. The passivating potential shifts from *ca.* −0.07 V for fresh 317L to *ca.* 0.04 V for SnO$_2$:F coated 317L. And while the passivation potential region of the SnO$_2$:F coated 317L is decreased, the current at 0.6 V for the SnO$_2$:F coated 317L is also decreased, indicating the beneficial effect of the coating for 317L in this environment.

A similar beneficial effect is registered with SnO$_2$:F coated 349^{TM}, Fig. 4c, though it shows a higher passivating current than the fresh steel in PEMFC cathode environment. Therefore, the polarization behavior of the coated steels in the PEMFC cathode environment again depends very much on the composition of the substrate steel. For comparison, the polarization curves of the coated steels are summarized in Fig. 4d. Comparing Figs. 4d with 3d, we see that the polarization curves are rather similar, suggesting that the purging gas does not have a significant influence on the anodic behavior of the coatings. In both environments, the behavior of the coated steels is in the order: 349^{TM} > 317L > 316L, in agreement with our previous investigation with fresh steels [10].

3.3. Potentiostatic polarization of SnO$_2$:F coated stainless steels

The corrosion resistance and the SnO$_2$:F coating stability are very important for the application as a PEMFC bipolar plate, since the anode operating potential of around −0.1 V is near the corrosion potential for SnO$_2$:F coated steels, Fig. 3. Thus, we conducted potentiostatic polarization measurements for the coated steels in a solution purged with hydrogen gas; the current–time behavior is shown in Fig. 5.

As soon as the potential is applied, there is a sharp current decrease for all the coated alloys. SnO$_2$:F coated 316L then experiences a current peak of *ca.* 140 μA cm^{-2} at *ca.* 10 min polarization, inset of Fig. 5. The current decreases after this peak and then stabilizes after *ca.* 50 min of polarization. This continues for around *ca.* 200 min, it then increases gradually and reaches *ca.* 80 μA cm^{-2} at the end of the test. SnO$_2$:F coated
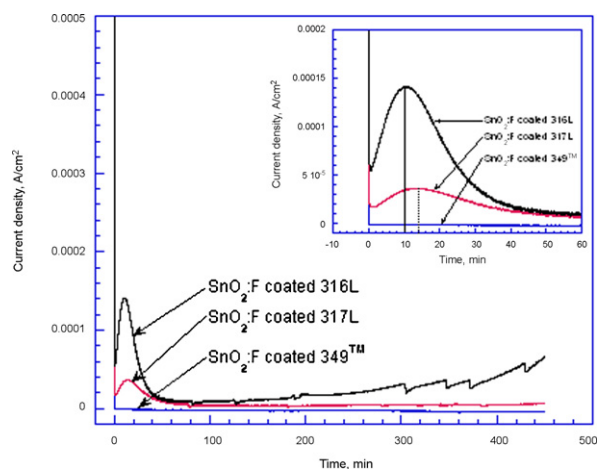

Fig. 5. Transient currents of SnO$_2$:F coated stainless steels at −0.1 V in 1 M H$_2$SO$_4$ + 2 ppm F$^-$ at 70 °C purged with hydrogen gas. Insert shows the transient currents in the first hour of testing.

317L also shows a polarization peak of *ca*. 35 $\mu A\,cm^{-2}$ at *ca*. 14 min. This peak indicates that the surface is passivated and the current of the SnO_2:F coated 317L is very low and stable after the passivating peak with a current of *ca*. 3.5–6.0 $\mu A\,cm^{-2}$ until the end of the test. Such passivating peaks are in agreement with the corresponding dynamic polarization curves, Fig. 3, where −0.1 V is located at the active potential region of coated 316L and 317L steels. As a reference, an anodic current of 5 $\mu A\,cm^{-2}$ for iron corresponds to *ca*. 39 $\mu m\,year^{-1}$ thinning rate if all the current is used for metal dissolution. The higher passivating current at the passivating peak with coated 316L is also in agreement with the higher passivating current noted during the dynamic polarization experiment. On the other hand, the passivation of the SnO_2:F coated 316L appears to be not as protective, thus this surface experiences an anodic current increase even after the passivating peak. This, again, indicates that the performance of the SnO_2:F coating depends on the substrate steel.

SnO_2:F coated 349^{TM} steel shows a different polarization behavior. A cathodic current is obtained as soon as the potential is applied. Moreover, the current is very stable during the whole polarization period at *ca*. −2.5 to −4.0 $\mu A\,cm^{-2}$. A cathodic current indicates that the coated surface is cathodically protected and the anodic dissolution of the material is significantly eliminated. Under these conditions, reduction of Sn^{2+} from SnO_2 is also possible thermodynamically. Compared to the bare steel [10], the SnO_2:F coating has a beneficial effect on the corrosion resistance of 349^{TM} steel in the PEMFC anode environment.

The cathode environment in PEMFCs is oxygen reduction and the environment is oxidizing. We conducted potentiostatic measurements at 0.6 V in a solution purged with air and the typical current–time behavior is shown in Fig. 6. As soon as the potential is applied, the current decays quickly. All the coated steels stabilize within around 20 min, inset of Fig. 6. This again, is in agreement with the dynamic polarization results of the materials, Fig. 4, in which 0.6 V is in the middle of the passivation region for all of the coated alloys. Interestingly, SnO_2:F coated 316L shows the lowest stable current of *ca*. 0.20–0.30 $\mu A\,cm^{-2}$. The current, however, shows an almost linear increase after *ca*.

300 min of polarization and reaches *ca*. 4.1 $\mu A\,cm^{-2}$ at the end of the experiment, indicating the limited stability of the coating on 316L in this environment. SnO_2:F coated 317L shows an extremely stable current of *ca*. 0.40–0.50 $\mu A\,cm^{-2}$ during the whole polarization period. Compared to its behavior in the PEMFC anode environment, the performance in the PEMFC cathode environment for coated 317L is much improved. SnO_2:F coated 349^{TM} also shows high stability with current in the range of 1.3–1.5 $\mu A\,cm^{-2}$, albeit higher than that of coated 317L steel.

These electrochemical measurements indicate that the performance of SnO_2:F coated steels depends significantly on the substrate alloy composition, with coated 349^{TM} having the best behavior in both simulated PEMFC environments. SnO_2:F coated 317L shows promising behavior, especially in a PEMFC cathode environment. It could become a candidate material for PEMFC bipolar application if the anodic dissolution in the PEMFC anode environment could be solved.

3.4. Interfacial contact resistance

We investigated the interfacial contact resistance (ICR) between samples of SnO_2:F coated stainless steels and carbon paper at different compaction forces and the results are shown in Fig. 7. For comparison, the ICR behavior for fresh 316L steel is also given in Fig. 7. The influence of the SnO_2:F coating on the ICR is mixed for the different substrate steels. For the 316L and 317L alloys, lower ICR values are obtained for the coated steels as compared with those of the fresh steels, which means that a SnO_2:F coating has a beneficial effect on the ICR with the best results seen with 317L steel. In the lower compaction force region, this improvement is significant for both alloys. In the higher compaction force region, however, the beneficial effect of SnO_2:F coating almost disappears, especially in the case of 316L. For 349^{TM} steel, the SnO_2:F coating does not improve the ICR values in the lower compaction force region. On the contrary, some increase in ICR is seen with the coated 349^{TM} steel at compaction forces over 50 $N\,cm^{-2}$, Fig. 7. This indicates an
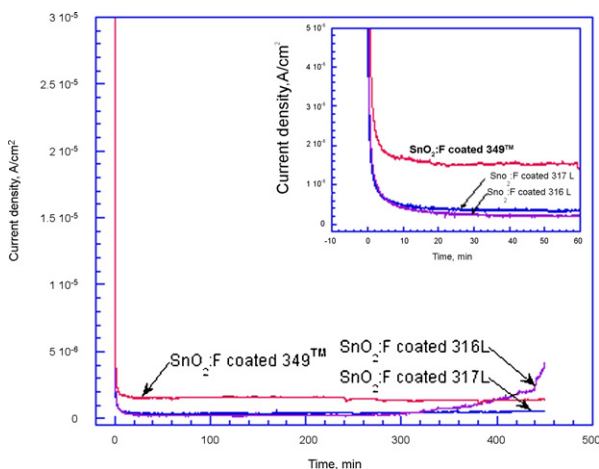

Fig. 6. Transient currents of SnO_2:F coated stainless steels at 0.6 V in 1 M H_2SO_4 + 2 ppm F^- at 70 °C purged with pressured air. Insert shows the transient currents in the first hour of testing.
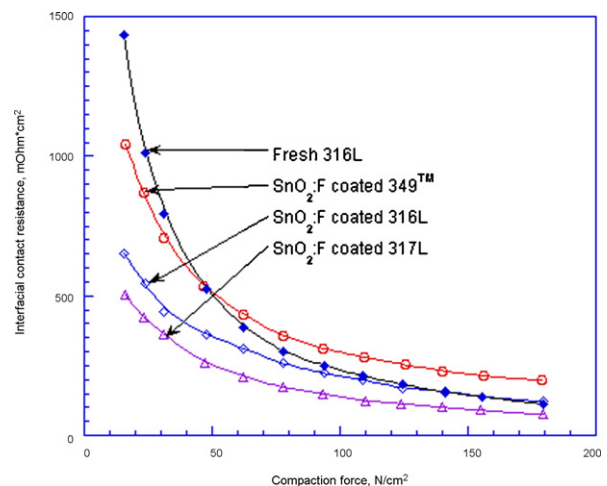

Fig. 7. Interfacial contact resistances for SnO_2:F coated austenite stainless steels and carbon paper at different compaction forces. Interfacial contact resistance with bare 316L is for comparison.

Table 1
Fe, Cr, Ni ion concentration for bare and coated steels after polarization in PEMFC environments (average of three samples)

Material	Ion concentration in PEMFC anode environment after 7.5 h (ppm)				Ion concentration in PEMFC cathode environment after 7.5 h (ppm)			
	Fe	Cr	Ni	Sn	Fe	Cr	Ni	Sn
316L	21.18	4.60	2.49		9.02	1.94	1.41	
317L	3.98	0.65	0.39		1.29	–	–	
349^{TM}	1.70	0.12	–		1.47			
SnO$_2$:F/316L	10.83	1.97	1.38	0.49	1.12	0.10	0.11	–
SnO$_2$:F/317L	4.03	0.69	0.56	0.19	0.87	–	–	–
SnO$_2$:F/349^{TM}	1.27	–	–	0.10	1.07	–	–	–

unexpected effect of the coating on the ICR. At this time, the reason for this mixed influence is not clear.

The ICR measurements indicate that the contact resistance of 317L is reduced due to the SnO$_2$:F coating, while the same coating on 316L does not impact the ICR values. On the other hand, the SnO$_2$:F coating increases the ICR values of 349^{TM}. Combining the anodic behavior of the SnO$_2$:F coated alloys in PEMFC environments, we see that SnO$_2$:F coated 317L could be an alternative candidate for a PEMFC bipolar plate.

3.5. Dissolved metallic ions

The metallic ions dissolved during the potentiostatic polarization for 7.5 h with fresh and SnO$_2$:F coated steels were analyzed by with ICP and the results are shown in Table 1.

In general for all the alloys tested, regardless if they are coated with SnO$_2$:F or not, more metallic ions are generated in the anode environment than in the cathode environment, indicating that the anode environment is much more corrosive than the cathode one. This is reasonable since the PEMFC anode environment is reductive and the cathode one is oxidative, and the passive film of stainless steels is much more stable in an oxidative environment than in a reductive one. As expected, Fe has the highest concentration of all dissolved ions in all cases. This is in agreement with our previous XPS investigation concerning passive film where Fe was selectively dissolved and Cr was enriched at the surface [12,23]. Fresh 316L generates the highest concentration of metallic ions for all three of the alloys tested, and approximately double the concentration was obtained in the PEMFC anode environment than in the PEMFC cathode environment. When 316L is coated with SnO$_2$:F, the metal ion concentration in the PEMFC anode environment is reduced by half compared with the fresh alloy, indicating that the SnO$_2$:F coating provides some protection under these conditions.

Around 0.5 ppm Sn is detected for the coated 316L in the PEMFC anode environment. The low Sn dissolution rate suggests that this reaction is diminished by others, especially the selective dissolution of iron. In the PEMFC cathode environment, the dissolved Fe is down to the 1 ppm level, the Cr, Ni and Sn concentrations are negligible. This means that the coating provides better protection in the simulated PEMFC cathode environment than in the anode one. The analysis is in excellent agreement with the polarization curves for coated 316L where current in the PEMFC anode environment (Fig. 5) is much higher

than that in PEMFC cathode one. This is also true for 317L steel where the content of dissolved metallic ions is practically unaffected by the SnO$_2$:F coating when polarized in the PEMFC anode environment, except for trace Sn detected for coated 317L. In this environment, fresh 317L steel shows a much a lower corrosion rate (not shown) and over five times lower dissolved metallic ions than 316L. In the PEMFC cathode environment, however, 317L shows excellent behavior, with only ppm levels of dissolved Fe. Coating with SnO$_2$:F improves the already low corrosion rate, in agreement with the polarization curve, Fig. 6. Previously, we determined that 349^{TM} was one of the best candidate steels in PEMFC environments with a low corrosion rate [10]. The dissolved metallic ions in both PEMFC environments give ppm levels of Fe and trace Cr, confirming the low dissolution rate of the alloy and its high corrosion resistance. Coating the steel with SnO$_2$:F also improves the already excellent corrosion resistance of this alloy. Barely detectable levels of Sn^{2+} ions are noticed for coated 349^{TM} in the PEMFC anode environment, much lower than coated 317L in the same environment. The polarization curves (Figs. 5 and 6) of the coated alloy are in excellent agreement with the ICP analysis (Table 1), where coated 317L is the best in the PEMFC cathode environment. Nevertheless, Table 1 suggests that SnO$_2$:F coated 317L could be a good candidate for PEMFC bipolar plate application. However, the interfacial contact resistance of this alloy needs further improvement.

4. Conclusions

We investigated SnO$_2$:F coated austenite stainless steels in 1 M H$_2$SO$_4$ + 2 ppm F$^-$ at 70 °C purged either with hydrogen gas or pressured air to simulate a bipolar plate environment in a PEMFC application. Dynamic polarization measurements indicated that the coated steels have lower passivating currents than bare ones in hydrogen gas purged solution; and they have higher passivating currents than the bare ones in air purged solution. The substrate steel has a greater influence on the polarization curve than the purge gases.

At −0.1 V, the SnO$_2$:F coated 316L and 317L showed an anodic current peak at about 10–14 min of polarization. The current for coated 316L then steadily increases, indicating this combination is not suitable for a PEMFC anode environment. Coated 317L exhibited a stable anodic current after the peak, suggesting the possibility of using this material in a PEMFC

anode environment. Coated 349[TM] showed a cathodic current in a simulated PEMFC anode environment, indicating that the material is somehow cathodically protected. So, the behavior of coated 349[TM] is the best of the ones tested in the PEMFC anode environment. At 0.6 V, coated 316L showed stable anodic current until around 300 min of polarization, followed by an increase in corrosion current. On the other hand, coated 317L showed an extremely stable and low current (close to 0) throughout the whole test period. Its behavior was even better than coated 349[TM] in this environment.

For both bare and SnO_2:F coated stainless steels, the ICP results showed that the PEMFC anode environment is much more corrosive than the cathode one. Fresh 316L gives the highest dissolution rate in the PEMFC anode environment. Coating with SnO_2:F reduced the dissolution rate of 316L to half of the value of the uncoated steel in the PEMFC anode environment and 1/8 of the value in the PEMFC cathode environment. Coating the 317L also showed a significant beneficial effect on the metallic ion concentration in the PEMFC cathode environment, although it did show a significant improvement in the PEMFC anode environment. Coating 349[TM] steel further improved the already excellent corrosion resistance of this alloy. Less than 1 ppm of Sn^{2+} was detected for all the coated steels in the PEMFC anode environment, indicating a low dissolution of the coating. This reaction could be diminished by selective dissolution of iron.

The influence of SnO_2:F on the ICR is mixed. For 316L and 317L steels, a SnO_2:F coating showed a beneficial effect, reducing the ICR. For 349[TM] steel, the SnO_2:F coating increased the ICR. It is clear that the composition of the substrate steel has a significant impact on the SnO_2:F coating, thus impacting the ICR values. It is possible that SnO_2:F coated 317L could be used as bipolar plates in a PEMFC. And finally, it is not surprising to note that coatings and base metal alloys must be matched for optimum performance.

Acknowledgements

References

[1] B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345.
[2] M.S. Wilson, C. Zawodzinski, Fuel Cell with Metal Screen Flow Field, US Patent No. 6,037,072 (2000).
[3] R. Hornung, G. Kappelt, J. Power Sources 72 (1998) 20.
[4] R.C. Makkus, A.H.H. Janssen, F.A. de Bruijn, R.K.A.M. Mallant, J. Power Sources 86 (2000) 274.
[5] P.L. Hentall, J.B. Lakeman, G.O. Mepsted, P.L. Adcock, J.M. Moore, J. Power Sources 80 (1999) 235.
[6] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, J. Power Sources 86 (2000) 237.
[7] J. Scholta, B. Rohland, J. Garche, in: P.R. Roberge (Ed.), Proceedings of the Second International Symposium on New Materials for Fuel Cell and Modern Battery Systems, Ecole Polytechnique de Montreal, Canada, 1997, p. 300.
[8] M. Li, S. Luo, C. Zeng, J. Shen, H. Lin, C. Cao, Corros. Sci. 46 (2004) 1369.
[9] A.J. Appleby, S. Gamburzev, Electronically Conducting Fuel Cell Component with Directly Bonded Layers and Method for Making the same, US Patent No. 6,828,054 (2004).
[10] H. Wang, M.A. Sweikart, J.A. Turner, J. Power Sources 115 (2003) 243.
[11] H. Wang, J.A. Turner, J. Power Sources 128 (2004) 193.
[12] H. Wang, G. Teeter, J.A. Turner, J. Electrochem. Soc. 152 (2005) B99.
[13] B. May, D.R. Hodgson, Fuel Cells and Fuel Cell Plates, US Patent No. 6,790,554 (2004).
[14] L. Ma, S. Warthesen, D.A. Shores, J. New Mater. Electrochem. Syst. 3 (2000) 221.
[15] J. Wind, R. Späh, W. Kaiser, G. Böhm, J. Power Sources 105 (2002) 256.
[16] S.-J. Lee, C.-H. Huang, J.-J. Lai, Y.-P. Chen, J. Power Sources 131 (2004) 162.
[17] N. Cunningham, D. Guay, J.P. Dodelet, Y. Meng, A.R. Hill, A.S. Hay, J. Electrochem. Soc. 149 (2002) A905.
[18] H. Wang, M.P. Brady, G. Teeter, J.A. Turner, J. Power Sources 138 (2004) 86.
[19] H. Wang, M.P. Brady, K.L. More, H.M. Meyer III, J.A. Turner, J. Power Sources 138 (2004) 79.
[20] X.N. Li, T.A. Gessert, T. Coutts, Appl. Surf. Sci. 223 (2004) 138.
[21] R.L. Borup, N.E. Vanderborgh, Proceedings of the Material Research Society Symposium, vol. 393, Materials Research Society, USA, 1995, p. 151.
[22] R.N. Bhattacharya, A. Duda, D.S. Ginley, J.A. DeLuca, Z.F. Ren, C.A. Wang, J.H. Wang, Physica C 229 (1994) 145.
[23] H. Wang, J.A. Turner, On the passivation of 349[TM] stainless steel in a simulated PEMFC cathode environment, ECS Transactions, vol. 1, No. 6 (2005) 263: Proton Exchange Membrane Fuel Cells V, in Honor of Supramaniam Srinivasan—eds: T. Fuller, C. Bok and C. Lamy.