



Short communication

## Performance of a high Cr and Ni austenitic stainless steel bipolar plates in proton exchange membrane fuel cell working environments

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## ABSTRACT

Electrochemical behavior of a high Cr and Ni austenitic stainless steel (HCN) is investigated and 316L SS in a simulated proton exchange membrane fuel cell environments is also investigated, and interfacial contact resistance (ICR) is measured before and after potentiostatic polarization. Both stainless steels underwent passivation in both anode and cathode environments for proton exchange membrane fuel cell. Passive current density of HCN is lower than that of 316L SS. An increase in ICR between carbon paper and HCN results from passive film formed during the potentiostatic polarization.

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### 1. Introduction

Proton exchange membrane fuel cell (PEMFC) has drawn many countries' and investigators' attention due to its high efficiency, zero emission of pollution and lower operation temperature. It can be widely used in vehicles, and other areas where portable power sources are needed.

Bipolar plates are the important multifunctional components in the PEMFC stacks. They not only connect the anode of one cell to the cathode of the adjacent but also separate and distribute the reactant gases. Traditional graphite has been used as the bipolar plates for PEMFC because of its excellent corrosion resistance in the low pH environments and low contact resistance. However, its poor mechanical strength and high permeability make it difficult to fabricate low cost thin plate, which is an important challenge to wide commercialization use. Because of relatively high strength, high chemical stability, excellent electrical and thermal conductivities, low cost and permeability, some metallic materials are preferred candidates as another alternative, especially for transportation application.

In general, PEMFC operates at around 80 °C, and water vapor and oxygen coexist in H<sub>2</sub>/air PEMFC stacks. Li et al. [1] found that highly acidic PEMFC operation environment contains the ions of F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>, HSO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, etc. These ions result from the process technology of membrane electrode assembly (MEA)

and dissolution of membrane. The bipolar plate is always in contact with such aggressive environment and undergoes inevitable electrochemical corrosion. A passive film formed on the surface of metal bipolar plate will cause an increase in interfacial contact resistance (ICR) and a decrease in power output of PEMFC. Dissolved metallic cations can enter into the membrane and lead to the degradation in proton exchange rate [2]. In addition, they can also poison the electrode catalysts and change the activity of catalyst. A number of metallic materials investigated include aluminum, stainless steels, titanium, nickel, Ni–Cr alloys and so on.

Stainless steels are the candidate materials to substitute for bulk graphite and can be fabricated to thin sheet (less than 1 mm) and meet the requirement of higher power density. Additions of Cr, Ni and Mo markedly improve corrosion resistance: Ni provides the corrosion resistance in neutral and reducing environment, while Cr and Mo can improve one under oxidizing and neutral condition. It was well known that hydrogen oxidation and oxygen reduction take place in anode and cathode side of PEMFC. Most of the works on stainless steels [3–10] and coated or surface-treated stainless steels [11–15] as the bipolar plates for PEMFCs have been carried out in different laboratories. For the stainless steel bipolar plate, the higher ICR caused by the air-formed oxide film and passive film on the surface is a big challenge in commercial application. Davies et al. [16] pointed out that 310 SS could be used as the bipolar plates because the passive films are thinner and denser than other comparable kinds of stainless steels. Wang et al. [3] showed that 349<sup>TM</sup> has excellent corrosion resistance and lowest ICR among the studied stainless steels, and the performance is related to higher chromium content. Dissolution of Fe<sup>3+</sup> and Cr<sup>3+</sup> is too low to detect in the MEA

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**Table 1**  
Chemical compositions (wt %) of stainless steels.

Material	C	Cr	Ni	Mn	Mo	Si
HCN	0.022	25.94	19.43	1.76	2.03	0.01
316L	≤0.03	16–18	12–14	2.0	2–3	≤1.0

after 100 h of cell operation [17].

Different surface modification methods have been used to improve the performance of metallic bipolar plates [18–23]. The bipolar plate consisting of substrate and coating has to meet the cost requirement. Furthermore, coating materials and process technology will increase the cost of whole bipolar plate. It is important that the coatings can alleviate but not completely eliminate the electrochemical corrosion resulting from inherent defects. The best way is to select an alloy that has the excellent electrochemical property in the aggressive PEMFC environments and high surface conductivity even after polarization. Therefore, non-coated stainless steels have still drawn considerable attention to use as the bipolar plates for PEMFCs.

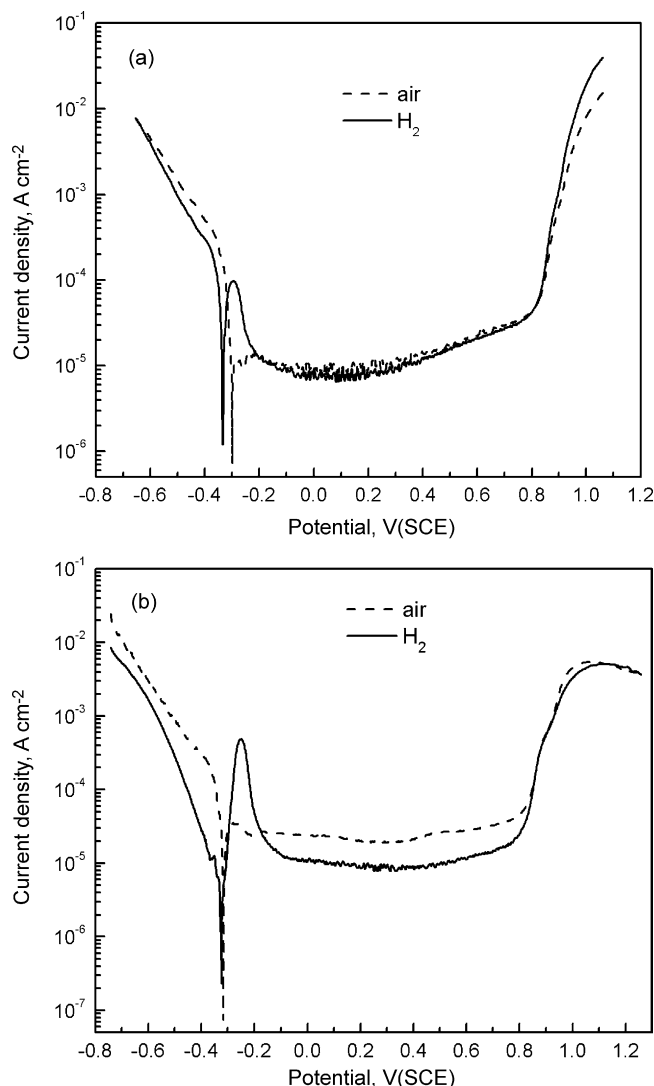
In this study, electrochemical behavior of a high Cr and Ni austenitic stainless steel was investigated in the simulated anode and cathode PEMFC environments. ICR was evaluated as an important parameter for bipolar plate in PEMFC before and after the potentiostatic polarization. In order to assess the applicability of this material to bipolar plate, 316L SS, which is a baseline requirement for metallic bipolar plates, was also investigated in the same condition.

## 2. Experimental

The high Cr and Ni austenitic stainless steel (HCN) used in this work is a commercial plate with a thickness of 5 mm, and its Cr content is higher than that of 316L SS. The chemical compositions of both steels are listed in Table 1. Both were solution-treated at 1000 °C and then water-cooled. HCN and 316L SS plates were cut into the samples with an exposed area of 1 cm<sup>2</sup> for electrochemical measurement. The samples were grounded with 280–1000# abrasive paper and polished mechanically and rinsed with alcohol and dried. The samples were covered with insulating epoxy, only leaving one side exposed for electrochemical measurements.

The electrochemical measurement was conducted in a ZAHNER IM6e system with a potentiostat controlled by a computer. A conventional three-electrode system is consisted of a platinum sheet, a saturated calomel electrode and the stainless steel sample. They act as the counter, reference and work electrode, respectively. The reference electrode is contacted with the used solution by a Luggin capillary. Previous studies [24] have shown that the aqueous solution is acidic (pH=1–4) in operating H<sub>2</sub>/air PEMFC stacks at the beginning of operation, and the water is almost pure after some time of operation. So, 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup> was selected to simulate the aggressive PEMFC environment. The samples were stabilized in the solution at open circuit for 30 min. The polarization curve was recorded at the scanning rate of 1 mV s<sup>-1</sup>. To evaluate the performance of HCN under the operation condition of PEMFC, the potentiostatic polarization was carried out in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup>. Two potentials (−0.1 V<sub>SCE</sub> and +0.6 V<sub>SCE</sub>) were applied to the samples in simulated anode/cathode condition, and the current–time curves were recorded. All electrochemical experiments were carried out at 70 °C. The solution was sparged with H<sub>2</sub> for anode condition and with air for cathode condition. The surface morphology of the samples was examined by means of SEM after potentiostatic polarization.

Variation of ICR with compaction force was measured using the method described by Wang et al. [3] at room temperature. An electrical current of 100 mA was selected to decrease heat effect and

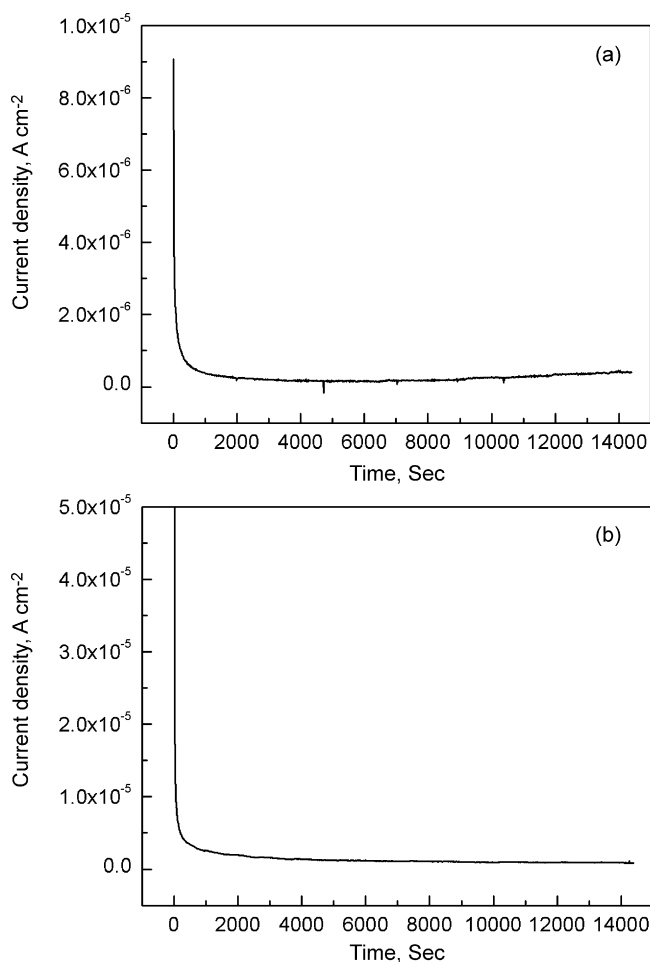


**Fig. 1.** Polarization curves of 316L and HCN in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup> at 70 °C purged with H<sub>2</sub> and air (a) HCN and (b) 316L.

was provided from an YJ-10A type galvanostat via the two copper plates. The compaction force was applied by screwing a screw nut and a lead screw and was recorded with a type of MCK-C compaction sensor and a special force gauge. The electrical resistivity of HCN and 316L SS was measured by four-point probe method. At the same time, the sum of  $R_{\text{system}}$  (refers to the resistance of measurement system including the instruments and connective wires) and  $R_{\text{Cu}}$  (corresponding to the resistance of the two copper plates) remain unchanged during the whole measurement. Thus,  $R_{\text{C/SS}}$  (ICR between stainless steel with air-formed oxide film and carbon paper) and  $R_{\text{C/PF}}$  (ICR between stainless steel with passive film and carbon paper) were obtained.

## 3. Results and discussion

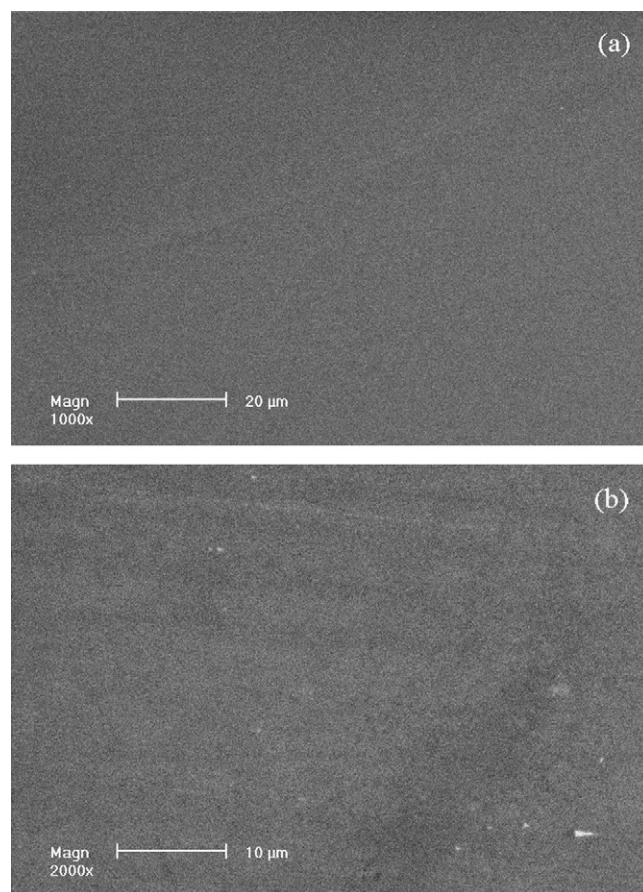
The corrosion behavior and stability of passive film are the major factors affecting the properties for stainless steel bipolar plates. The polarization curves of HCN and 316L SS in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup> at 70 °C are shown in Fig. 1. Both steels exhibit the passivation behavior in simulated PEMFC environments. The active region is very narrow, and the wide passive regions appear on the polarization curves. The anode (−0.1 V<sub>SCE</sub>) and cathode (+0.6 V<sub>SCE</sub>) potentials for PEMFC operation are in the passive region



**Fig. 2.** Current density–time relationship of HCN in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup> at 70 °C (a) purged with H<sub>2</sub> at +0.1 V<sub>SHE</sub> and (b) purged with air at +0.8 V<sub>SHE</sub>.

of HCN and 316L SS, as shown in Fig. 1. For both steels, the passive current density, which is the lowest current density needed to maintain the passive film, is slightly higher in air bubbled solution than in H<sub>2</sub> bubbled one. In comparison with 316L SS, the lower passive current density for HCN in both simulated PEMFC environments has resulted from its higher Cr and Ni contents. From this point, HCN can be used as the promising bipolar plate material for PEMFC.

In order to further understand corrosion resistance of HCN, the stability of passive film was studied by potentiostatic polarization in simulated PEMFC environment. The potential of  $-0.1 V_{SCE}$ , the operating potential under the anodic PEMFC condition bubbled with hydrogen, was applied to HCN. The current density drops rapidly at the beginning of polarization and then gradually stabilizes, as shown in Fig. 2(a). This is related to the formation of the passive film. Once the passive film covers on the whole surface of the sample under this condition, the current density maintaining the passive film is decreased. The relatively stable current density indicates that the passive film is stable under the anodic operation of PEMFC. In the cathodic PEMFC environment bubbled with air, the potential of  $+0.6 V_{SCE}$  was applied to the sample. It can be seen that this steel also exhibits the passivation behavior, as shown in Fig. 2(b). The time required for the formation of the passive film is less than that under anodic operation condition, which can be related to the different thickness and composition of the passive film formed in simulated anodic and cathodic environments. Oxygen dissolved in the cathode environment is beneficial to the formation of passive film. This shows that the passive film



**Fig. 3.** Surface morphology of HCN after potentiostatic polarization in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup> at 70 °C (a) purged with H<sub>2</sub> at +0.1 V<sub>SHE</sub> and (b) purged with air at +0.8 V<sub>SHE</sub>.

formed on HCN appears to be very stable in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup> sparged with air.

The surface morphology of HCN was examined after potentiostatic polarization by means of SEM to observe the effect of electrochemical polarization on the surface character. The results indicate that only uniform corrosion was observed on the surface of the samples, and no pit was found, as shown in Fig. 3.

Conductivity is one of the most important properties for the bipolar plate because electron transfers across the bipolar plates during the PEMFC operation, while the surface conductivity of the bipolar plate is more important than that of the inside. Fig. 4 shows  $R_{C/SS}$  for HCN and 316L SS as a function of compaction force. ICR decreases markedly at lower compaction force, then slowly, and does not change almost at higher compaction force. This is related to an increase in contact area between stainless steel and carbon paper with increasing the compaction force. Many investigators' have also obtained similar results [3–9]. At the compaction force of  $150 N cm^{-2}$ ,  $R_{C/SS}$  is approximately  $30 m\Omega cm^2$  for HCN with air-formed oxide film and is lower than  $200 m\Omega cm^2$  for 316L SS under the same condition. The air-formed oxide film on HCN is similar to that on 349<sup>TM</sup> and 316L SS, which can be related to their austenitic structure [3]. Wang et al. [3] also pointed out that the lower ICR for 349<sup>TM</sup> is related to its higher Cr content.

Once the metallic bipolar plate is in contact with the aggressive PEMFC environments, the passive film will be formed on the surface. ICR for HCN as a function of compaction force after potentiostatic polarization for 4 h is shown in Fig. 5. It can be seen that  $R_{C/PF}$  increase markedly after passivation in the simulated PEMFC environments at an applied potential of anode ( $-0.1 V_{SCE}$ ) and cath-

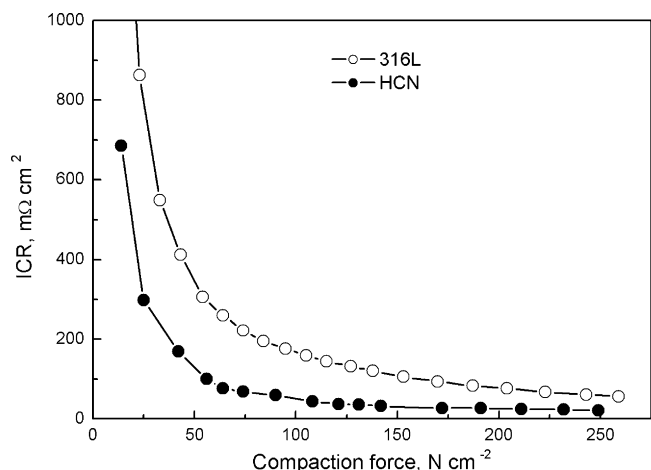


Fig. 4. ICR of HCN and 316L at different compaction forces.

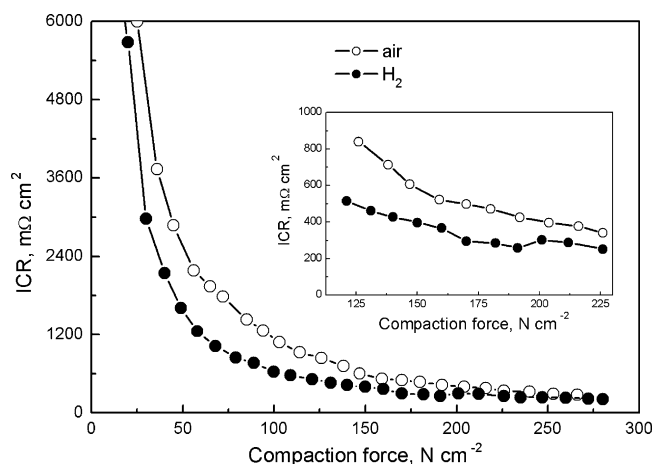


Fig. 5. ICR as a function of compaction force of HCN before and after potentiostatic polarization for 4 h in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup> at 70 °C.

ode (+0.6 V<sub>SCE</sub>) operation condition. In comparison with the results of Fig. 4, ICR for HCN all increases markedly at the same compaction force. The change of ICR is because composition of the passive film formed in simulated PEMFC environments is different from that of air-formed oxide film. Cr is a main passivation element electrochemically, therefore, stainless steels with higher Cr content are to passivate easier. The air-formed film on 2205 stainless steel is composed of iron oxides and chromium oxide without a dominating species, while the passive film is consisted of chromium oxide [4]. Iron is selectively dissolved during the passivation process, and chromium enriched seems not to be depleted. Nickel is not found in the surface passive film and the thickness of passive film decreases with increasing Ni content in the steels [25]. Kumagai et al. [26] showed that relatively thin film enriched with chromium oxide was formed in the solutions with lower pH. In addition, Wang et al. [3] show that the air-formed oxide film is thinner than the passive film formed on the surface of stainless steel. On the other hand,  $R_{C/PF}$  of HCN is higher in the solution purged with air at +0.6 V<sub>SCE</sub> than that in the solution purged with H<sub>2</sub> at -0.1 V<sub>SCE</sub>, as shown in Fig. 5. Surface oxidation of HCN is easier in the air-purged solution than in the H<sub>2</sub>-sparged one, which results in a thicker passive film formed

in the simulated cathodic environment of PEMFC than that in the simulated anodic one. At the compaction force of 150 N cm<sup>-2</sup>,  $R_{C/PF}$  of HCN is about 560 mΩ cm<sup>2</sup> at +0.6 V<sub>SCE</sub> in the simulated cathodic environment, while  $R_{C/PF}$  is about 390 mΩ cm<sup>2</sup> at -0.1 V<sub>SCE</sub> in the simulated anodic environment. Therefore, both  $R_{C/PF}$  of HCN in the simulated solutions are too high to use as bipolar plates in PEMFC stacks.

According to the above results, HCN has excellent corrosion resistance in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup> at 70 °C; however, the higher ICR between the carbon paper and passive film formed on the surface in the simulated anodic and cathodic environments at the specified potential prevents the bare HCN to be used as the bipolar plate material for PEMFC. Some further work is needed to improve the surface conductivity after the passive film formed on HCN.

#### 4. Conclusion

Corrosion behavior of the high Cr and Ni austenitic stainless steel has been investigated in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 2 ppm F<sup>-</sup> purged with H<sub>2</sub> or air at 70 °C simulating the anode or cathode operating environment for PEMFC. The results show that the excellent corrosion resistance results from the higher Cr and Ni content. In view of this point, this steel can be used as a candidate material for the bipolar plate under PEMFC operating condition. ICR between the carbon paper and stable passive film formed during potentiostatic polarization at -0.1 V<sub>SCE</sub> and +0.6 V<sub>SCE</sub> is higher than that between the carbon paper and air-formed oxide film. This is because the thickness and composite of the former are different from that of the later.

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