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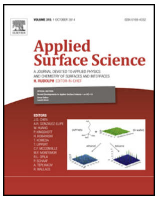

Effects of passive films on corrosion resistance of uncoated SS316L bipolar plates for proton exchange membrane fuel cell application

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ABSTRACT

The effects of passive films on the corrosion behaviors of uncoated SS316L in anode and cathode environments of proton exchange membrane fuel cells (PEMFCs) are studied. Potentiodynamic and potentiostatic polarizations are employed to study the corrosion behavior; Mott-Schottky measurements are used to characterize the semiconductor properties of passive films; X-ray photoelectron spectroscopy (XPS) analyses are used to identify the compositions and the depth profiles of passive films. The passive films formed in the PEMFC anode and cathode environments under corresponding conditions both behave as n-type semiconductor. The passive film formed in the anode environment has a single-layer structure, Cr is the major element (Cr/Fe atomic ratio > 1), and the Cr/Fe atomic ratio decreases from the surface to the bulk; while the passive film formed in the PEMFC cathode environment has a bi-layer structure, Fe is the major element (Cr/Fe atomic ratio < 0.5), and in the external layer of the bi-layer structure Fe content increases rapidly and gradually in the internal layer. SS316L shows better corrosion resistance owing to both the high content of Cr oxide in the passive film and low band bending in normal PEMFC anode environments.

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1. Introduction

Global energy shortage and environment deterioration are burning issues for the entire world and clean hydrogen cycle [1] may be one of the promising solutions. Fuel cell, generating power by electrochemically combining hydrogen and oxygen to form water, is important in the clean hydrogen cycle. Proton exchange membrane fuel cells (PEMFCs) have attracted worldwide attention, since they have many advantages [1]: such as high-efficiency, compact, low noise and vibrations. PEMFCs consist of a set of components, such as membranes, catalytic electrodes, gas diffusion layers and bipolar plates. As one of the critical components, bipolar plates play very important roles in PEMFCs, such as collecting current, distributing hydrogen and oxygen, supporting gas diffusion layer and electrode. Stainless steel is a promising candidate for bipolar plate materials, owing to their good electrical conductivity, high mechanical strength and low processing cost [2,3].

For now, PEMFCs cannot be applied on a global scale because of the durability issues from the components, in which stainless steel bipolar plates will corrode in weak acid PEMFC environment [4]. Although stainless steels can be passivated in PEMFC environments and a layer of passive film is formed on the surface of stainless steel to impede the substrate from reacting spontaneously and violently in corrosion environments [5], the required targets for corrosion resistance of bipolar plates are still not achieved [6] and the passive film will increase the interfacial contact resistance between the carbon gas diffusion layer and the bipolar plate then reduce the efficiency of PEMFCs [7–10].

Numerous attempts have been made to improve the corrosion resistance by fabricating protective coatings, such as Ti-Mo-N films, Nb-carbide diffusion layers, TiN films [11–19] and/or interfacial electric conductivity by fabricating conductive coatings, such as CrN films, TiO_2/Au layers and RuO_2 [20–22]. However, defects, such as inclusions, scratches, pin-holes and micro-cracks in the protective coatings or conductive coatings are inevitable during coating fabrication and bipolar plates assembling processes, thus protection of these areas in the operation of stacks must be provided by

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Table 1
Main chemical composition of SS316L (wt. %).

C	Cr	Ni	Mo	Si	Cu	Fe
0.03	16.9	10.5	2.23	0.516	0.506	Balance

the stainless steel substrates. To achieve the durability targets of bipolar plates for PEMFCs, it is essential to understand the degradation phenomena and mechanism of stainless steels in PEMFC environments. The relationship between the corrosion behavior and corrosion environment were focused in most of previous studies [4,7,23–43], in which only a few [7,38,43] studied the passive films employing electrochemical impedance method. Further fundamental studies, focusing on effects of passive film structure and semiconductor properties on the corrosion characteristics of stainless steel in PEMFC environments, are needed.

Thus the objectives of this work are to study the effects of semiconductor properties of passive films on the corrosion behaviors of uncoated stainless steel in the PEMFC anode and cathode environments and to provide fundamental information for the improvement the durability of stainless steel bipolar plates. In this work, SS316L was chosen since it is a popular metallic material for bipolar plate and many reports have been published on this material in recent years [2,3,44,45].

2. Experimental

In this study, a solution of low acid environment (pH 5) is chosen since it can represent the realistic PEMFC environment [39,46] of 1×10^{-5} M H_2SO_4 with 6×10^{-4} M NaF [39,46–48]. The solution was bubbled with either hydrogen gas (to simulate PEMFC anode) or air (to simulate PEMFC cathode) in the experiments. The amount of each of the simulated solution transferred to the corrosion cell was 1 dm^3. The pre-bubbling hydrogen gas or air was carried out about 1 h before each measurement and the solution was bubbled with hydrogen gas or air during the measurement.

SS316L (the main chemical composition is showed in Table 1) specimens were machined into cylinders with a diameter of 10 mm. The electrode was sealed with polyethylene heat-shrink tube and silicone, and working surface was polished with 800-grit silicon carbide abrasive paper. The detailed electrode fabrication procedure was described previously [47]. Each specimen was rinsed with acetone and de-ionized water before experimental measurements.

Electrochemical experiments were carried out using a conventional three-electrode setup. The specimen served as the working electrode and a platinum sheet (ca. 1.5 cm^2) as the counter electrode. The reference electrode was a saturated calomel electrode (SCE, +0.242 V vs. normal hydrogen electrode (NHE)) with a bridging solution of saturated KCl, against which all the potentials reported herein were measured. The corrosion solution was kept at 70 °C with the corrosion cell immersed in a temperature controlled water bath [49].

All electrochemical measurements were performed with a PAR 273A potentiostat (AMETEK) coupled with a Model 5210 lock-in amplifier (AMETEK). The "PowerSuite" software was used for electrochemical data acquisition and processing. Each experiment was repeated by using at least three specimens to ensure reproducibility of the results.

Before potentiodynamic experiments, the specimen was polarized cathodically for 10 min to remove oxides on the specimen surface and then stabilized at open circuit potential (OCP) for 1 h. During potentiodynamic tests, specimens were polarized at a scanning rate of 1 mV s^{-1} in a potential range from −0.2 V vs. OCP to 1.2 V vs. SCE. In potentiostatic tests, specimens were polarized for 5 h at different simulated environments, in which the polarization potentials were set at −0.1 V to simulate the typical PEMFC anode potential and 0.6 V to simulate the typical PEMFC cathode potential.

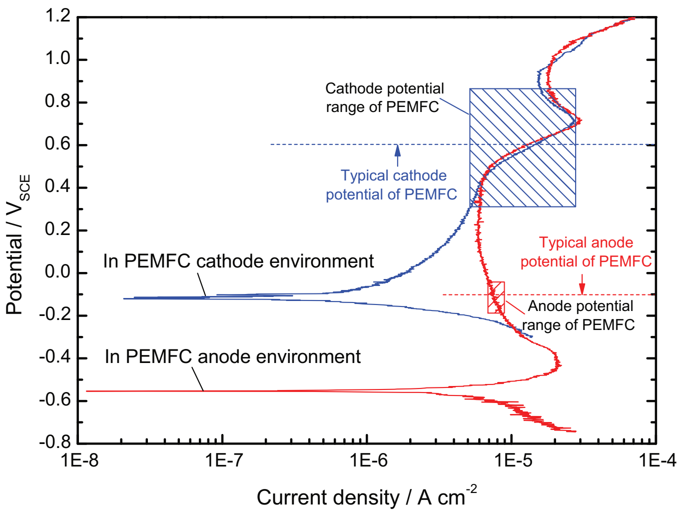

Fig. 1. Comparison of potentiodynamic polarization curves of SS316L in simulated PEMFC anode and cathode environments. Shadows show the corresponding potential range of PEMFC anode and cathode.

Mott-Schottky measurements were performed to obtain the semiconductor properties, such as the flatband potential and n-type/p-type conductivity, of the passive films in the simulated PEMFC environments. In Mott-Schottky measurements, potential sweeps were carried out from 0.8 V to −0.6 V. The data acquisition frequency was 188 Hz. The detailed description about this measurement procedure can be found in [46].

X-ray photoelectron spectroscopy (XPS) was employed to identify the composition and the depth profile of the passive film formed on the specimen, which was potentiostatically polarized in different environments for 5 h. The composition profiles of elements Fe 2p, Ni 2p, Cr 2p and O 1s in the passive films were analyzed with an AXIS UltraDLD X-ray photoelectron spectroscope (Kratos Analytical) using a monochromatic Al Ka radiation X-ray source (1486.6 eV). Binding energies were referenced to the C 1s peak at 285.1 eV. The chamber base pressure was 1.7×10^{-9} Torr (2.266×10^{-7} Pa). Sputtering was performed at a pressure of about 1.7×10^{-6} Torr (2.266×10^{-4} Pa) with a 3.0 keV argon ion beam, while the sputtered area was 2 mm × 2 mm. The sputtering rate was around 3.3 nm min^{-1}. The data processing of the different peaks were calculated by the Vision Processing Software by Kratos Analytical.

3. Results and discussion

3.1. Potentiodynamic and potentiostatic measurements

Fig. 1 shows comparison between the potentiodynamic polarization curves of SS316L in the simulated PEMFC anode and cathode environments, respectively. The potential fluctuation ranges of PEMFC anode and cathode are marked with shadows on the polarization curves. The polarization curve of SS316L in PEMFC anode environment passes through an active region, a passive region and a transpassive region as the potential increases from the equilibrium potential. It is a typical active-passive behavior. The anode potential fluctuation of PEMFC [6,50,51], 0.15 V from −0.19 to −0.04 V (0.052–0.202 V vs. NHE) (fluctuation of current density is ca. 2 $\mu A\,cm^{-2}$), is small and lies in the passive region of SS316L. According to Pourbaix diagram [52], Fe is unstable and will dissolve, while Cr can be oxidized to trivalent Cr in this potential range at pH 5. Thus, passive films consisting of rich chromium can be easily

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