Corrosion kinetics of 316L stainless steel bipolar plate with chromium carbide coating in simulated PEMFC cathodic environment

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\textbf{A B S T R A C T}

Stainless steel with chromium carbide coating is an ideal candidate for bipolar plates. However, the coating still cannot resist the corrosion of a proton exchange membrane fuel cell (PEMFC) environment. In this work, the corrosion kinetics of 316L stainless steel with chromium carbide is investigated in simulated PEMFC cathodic environment by combining electrochemical tests with morphology and microstructure analysis. SEM results reveal that the steel's surface is completely coated by Cr and chromium carbide but there are pinholes in the coating. After the coated 316L stainless steel is polarized, the diffraction peak of Fe oxide is found. EIS results indicate that the capacitive resistance and the reaction resistance first slowly decrease (2–32 h) and then increase. The potentiostatic transient curve declines sharply within 2000 s and then decreases slightly. The pinholes, which exist in the coating, result in pitting corrosion. The corrosion kinetics of the coated 316L stainless steel are modeled and accords the following equation: \( i_0 = 7.6341t^{-0.5} \), with the corrosion rate controlled by ion migration in the pinholes.

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\textbf{Introduction}

Owing to its virtue of high efficiency, high power density, low temperature operation, fast and easy start-up, etc., proton exchange membrane fuel cells (PEMFC) have promising applications in Electric Vehicles and backup power stations. Although PEMFC is gaining worldwide interest, and attracting governments and the research institutes to spend huge human and material resources on its research and development, and has achieved great advances in recent years, the following problems are still to be solved in its commercialization.

Lifetime \cite{1,2}, for different applications, the requirements for fuel cell lifetime vary significantly, ranging from 5000 h for cars to 40,000 h of continuous operation for stationary applications. The durability of the fuel cell has become one of the technical challenges restricting its commercialization.

Cost High Cost is a major hurdle for commercialization. Only when fuel cell costs are dramatically reduced to the US Department of Energy (DOE) target, will fuel cells be competitive.

Hydrogen Source the lack of infrastructure is also thought as one of the limiting factors of its large-scale application.

Basically, the commercialization process of PEMFC is determined by the development of technology. As one of the key components of PEMFC, bipolar plates occupy not only 70–80% in weight but also about 30% in economic cost. Graphite bipolar plates have been a good start for the commercialization of PEMFC, but their poor mechanical strength and high processing costs make them lack competitiveness in industrial applications. Although metal bipolar plates possess so many advantages such as low-cost, excellent mechanical properties, good electrical and thermal conductivities, etc., they are subject to corrosion. The corrosion generated metallic ions may subsequentially poison the FC catalysts decreasing performance. Additionally, with corrosion, interfacial contact resistance increases because of the formation of passive surface layer films. Thus research on minimizing the corrosion of metallic bipolar plates is needed. Although the coatings of noble metals such as gold or platinum would have excellent chemical stability and conductivity, their high price rules them out for achieving marketability. TiN coatings have received extensive attention, but the pitting corrosion was very high and their fuel cell performance has not been satisfactory in the presence of F\(^-\) \cite{3,4}. Other coatings such Ni-Co-B can resist corrosion in PEMFC
environment, but their performance degrades rapidly [5]. Though amorphous alloys such as Fe_{50}Cr_{14}Mo_{8}Al_{2}Y_{2} and Fe_{44}Cr_{15}-Mo_{1}Y_{2}C_{3}B_{4} have better anti-corrosion performances compared with stainless steel, there is a challenge in making them in large format [6,7]. There is also the concern that recrystallization may occur during use or during cell construction and thus lead to corrosion failure. Thus, attention is focused on coatings for protecting stainless steels. Nitride coatings have been shown to improve the contact resistance of Ni-50Cr alloy [8] and the coating process has been applied to lower Cr content stainless steels. Good results were found for the Ni-Cr alloy AL29-4C steel [9]. Through physical vapor deposition, ion nitriding, forms an intermediate transition layer with Cr and its compounds [9–11], also had good corrosion resistance in PEMFC environment. Fu Yu et al. [12–17] fabricated the chromium nitride and carbon coating for 316L stainless steel, which basically meet the requirements of low contact resistance, high corrosion resistance, and relatively low cost. These beneficial results created a new direction for the surface modification of PEMFC metal bipolar plates. For example, Hyundai Motor Company prepared carbon film containing C on the surface of a metal bipolar plate by chemical vapor deposition. GM company (USA) exploited a graphite coating containing Fe and Cr on the metal bipolar plate surface. Feng, Larji, and Yi et al. deposited amorphous carbon films on the surface of 316L stainless steel and 304 stainless steel by magnetron sputtering method [18–20], respectively.

Carbide or nitride layers on stainless steel surface exhibit good conductivity and good resistance to corrosion, and appear likely to be used in commercial applications for PEMFC bipolar plates. Despite these developments few researchers focus on the corrosion kinetics of stainless steel bipolar plates with a chrome carbide coating in PEMFC cathodic environment. Research on the corrosion process of stainless steel with coatings not only can evaluate its anti-corrosion characteristic but also is in favor of knowing its effect on membrane electrode assembly and the performance degradation of PEMFC stack. In this paper, the corrosion performance of 316L stainless steel with a chrome carbide coating is tested by electrochemical methods. Combined with the results of morphology and structure, its corrosion kinetics was determined and modeled. Since 316L stainless steel with a chrome carbide coating will be an alternative materials for PEMFC bipolar plates, these results are essential for knowing the mechanism of corrosion of stainless steel with chrome carbide coatings, and providing guidance for further improvement. Meanwhile, the results are also beneficial for monitoring the corrosion and evaluating the lifetime of 316L stainless steel bipolar plates with chromium carbide coating in PEMFC stacks.

**Experimental details**

**Materials**

The test materials were 316L stainless steel with chrome carbide coating (20 mm × 20 mm × 1 mm) offered by Sunrise Power Co. Ltd. The samples were ultrasonically cleaned for 15 min in acetone, and then dried. The corrosion solution was 0.5 mol·L⁻¹ H₂SO₄ + 5 mg·L⁻¹ HF solution prepared with 18 MΩ ultrapure water (Beijing Xiangshun Yuan Co. Ltd.). In order to simulate PEMFC cathodic environment, the solution was continuously bubbled with air and was maintained at 80 °C. All the reagents used were analytical reagents.

**Electrochemical tests**

The electrochemical tests were conducted on VMP3 electrochemical workstation (EG&G company) using a three electrode system. The cleaned sample with 1cm² exposed area, used as the working electrode. The reference electrode and the counter electrode were a saturated calomel electrode (SCE) and Pt net (20 mm × 20 mm), respectively. The cyclic potentiodynamic polarization was recorded from open circuit potential to more positive voltages with a scan rate of 1 mV·s⁻¹. When the current density reached 1 mA·cm⁻², the reverse sweep was initiated. The run was stopped when the reverse curve intersected the forward curve. Electrochemical impedance spectroscopy (EIS) measurements was tested at open circuit potential when the sample was immersed in the simulated solution for more than 30 min. During test, the frequency was swept from 100 kHz to 0.01 Hz while the ac amplitude was 5 mV. EIS data were analyzed by ZsimpWin software. Unless noted otherwise, all the tests were performed at room temperature and all the potentials refereed to SCE.

In order to evaluate the coating’s stability, potentiostatic transient polarization was performed in simulated PEMFC cathodic environment. The applied potential was 0.6V. Based on the potentiostatic transient curve, the corrosion kinetics equation of the stainless steel having coating was obtained.

**Surface morphology analysis**

The topography and the cross-section of the coating was investigated by scanning electron microscopy (Philips, XL-30TMP), X-ray diffraction meter (D/MAX-Ultima+, Rigaku Corporation), X-ray photoelectron spectroscopy (XPS, SHIMADZU-AMICUS) system equipped with a water-cooled Mg-anode at a total power dissipation of 120 W (12 kV, 10 mA).

**Results and discussion**

**Cyclic potentiodynamic polarization**

Fig. 1 showed the SEM cross-section and topography of the sample. From Fig. 1(a), the thickness of the coating was about 240 nm. Before polarization, it was relatively rough and had pinholes. It became smoother and the pinholes grew slightly after polarization. The spherical nodules and pinholes in the surface were seen to be active and displayed preferential loss during polarization. Thus, the polarized specimens tended to become smooth and the pinholes increased slightly.

Fig. 2 showed the cyclic potentiodynamic polarization curve of a coated sample in simulated PEMFC cathodic environment. From Fig. 2, when the polarization potential was below 0.6 V, the current density maintained at 0.04 μA·cm⁻². While the polarization potential was above 0.6 V, the current density increased significantly with increase in polarization potential. While in the reverse sweep, a small hysteresis loop was found. The formation of a hysteresis loop indicated that pitting had taken place, and the loop size can be interpreted with the extent of pitting [21,22]. Conversely, the smaller the hysteresis loop was, the less susceptible was the surface to pitting [23]. Since the coating prepared by pulsed bias arc ion plating had pinholes, it is clear that the corrosive ion can penetrate through the coating and result in corrosion. Although the coated sample had a very small hysteresis loop and showed better corrosion resistance, pitting corrosion would inevitably be observed and be accompanied by general corrosion. The smoother surface and the more enlarged the pinholes, the greater the corrosion observed, thus supporting the above deduction.

Figs. 3 and 4 showed the surface phases of the coated sample before polarization and the surface analysis using X-ray photoelectron spectroscopy (XPS) after polarization. From Fig. 3, the coating was composed of Cr and Cr₂C₃, and there was no diffraction peak of Fe. The Cr signal in the analysis was due to the presence of a Cr...
layer which was used to increase the adhesion between the Cr₃C₂ coating and the matrix. Combining the results of SEM and XRD, it is clear that the stainless steel matrix was completely covered by Cr and Cr₃C₂ except there were pinholes on the surface.

From Fig. 4a, XPS analysis shows Cr, Fe, C and O atoms were found on the surface of the polarized sample. The peaks found at 573.8 eV, 576.4 eV, 583.3 eV and 586.2 eV were identified as Cr₂p₁/₂ and Cr₂p₃/₂, respectively. The peak of C₁s was at 282.5 eV, 284.6 eV and 288.5 eV. The peaks at 710.4 eV, 717.0 eV and 723.3 eV were identified as Fe₂p₁/₂ and Fe₂p₃/₂, respectively. The peak at 531.9 eV was from O₁s. More detailed analysis based on the standard energy spectrum data and literature [24,25] revealed that the Cr₂p₃/₂ peak in Cr₂O₃ was found at 576.4 eV, the Cr-O bond in O₁s peak can be assigned to 531.5 eV. The peak position of Fe₂p₃/₂ (between 710 and 711.2 eV) had been investigated by many researchers [26,27]. The Fe₂p₁/₂ peak for Fe₂O₃ had associated satellite peaks, which was located approximately 8 eV higher than the main Fe₂p₃/₂ peak [28]. The Fe₂p₃/₂ for Fe₂O₄ hadn’t a satellite peak [28]. The binding energies of Fe₂p₃/₂ and Fe₂p₁/₂ obtained from the present study were 710.4 eV, 717.0 eV and 723.3 eV, respectively. The satellite peak obtained at 717.0 eV was clearly distinguishable and did not overlap either the Fe₂p₃/₂ or Fe₂p₁/₂ peaks, which mean Fe₂O₃ existed in the oxides [28]. The other peaks manifested that there also had Fe₂O₄. The results indicated that there were oxides of Cr and Fe on the surface of polarized sample. No Fe species was seen in XRD analysis (Fig. 3) prior to polarization, so that the XPS detection of iron oxide after polarization indicated that corrosion of the matrix must had taken place. The corrosion mechanism must have been from a corrosive ion penetrating the coating, and migrating to the matrix where dissolution of the iron took place. The pathway for this corrosion was almost certainly the pinholes in the film. Along with the developing of corrosion process, the corroded species would have had difficulty in diffusing into the bulk solution and hence would accumulate in the pinholes, and this process would hinder the corrosion rate. In addition, the stainless steel can passivate if there was sufficient oxygen available. Enlarging pinholes would be expected to increase this oxygen availability and slowed the corrosion process down.

**EIS results**

Fig. 5 showed the Nyquist diagram of the coated sample immersed in simulated PEMFC cathodic environment for different times. The EIS spectra showed the characteristic of a single capacitive resistance within the tested time. The capacitive resistance was found to first decrease and then increase with the longer duration in the electrolyte. The equivalent circuit (Fig. 6) was used to fit these EIS data and the fitting results were shown in Table 1 where, Rs – solution resistance, CPE – Constant phase element, Rₓ – reaction resistance, W – Warburg impedance.

From Table 1, it is clear that CPE and Rₓ decreased gradually with time elapsed between 2 to 32 h, which meant the corrosion rate increased gradually. At the initial stage, as seen in the SEM Fig. 1a, there were many surface active sites which were preferentially dissolved in the electrolyte (Fig. 1b). In addition, the surface film and the pinholes would also be susceptible to corrosion. Therefore it is not unexpected that the capacitive resistance and
the reaction resistance slowly decreased. When the immersion time exceeded 32 h, C and R began to increase and hence the bipolar plate’s corrosion rate decreased. At longer immersion times, pitting corrosion would become the dominant corrosion process and would accelerate slowly. Evidence for this can be seen in the results of SEM analysis for 20 and 80 h exposures. Fig. 7 showed the surface morphology of the coated sample after immersion in simulated PEMFC environment for different times. The dissolution of uneven active points on the surface was accompanied by pinholes expanding (Fig. 7a) during immersion. When immersion time was over 80 h, some of the coating had delaminated and became detached (Fig. 7b). At this stage surface roughness increased. Although the surface of 316L stainless steel was covered by the intermediate transition layer (having Cr and its compounds) and Cr$_2$C$_2$, the corrosion of matrix under the coating still occurred. The oxide of Fe found in XPS further confirmed that the stainless steel matrix was corroded. With longer immersion times, some corrosion products would deposited back to the surface and the pinholes, resulting in the capacitive resistance decreased and the reaction resistance increased.

**The potentiostatic transient polarization curve**

The potentiostatic transient polarization curve of the coated sample in simulated PEMFC cathodic environment was shown in Fig. 8. From Fig. 8, the transient polarization curve declined sharply within 2000 s, and then decreased slightly. The average value was about 0.07 μA cm$^{-2}$. According to the results of SEM, corrosion...
occurred mainly from the pinholes on the surface once the surface roughness was lost. With longer times, some of the pinholes were enlarged and some corrosion extended from these pinholes under the coating to cause a trench or groove. Since the destruction of bipolar plate was mainly contributed by the corrosion through pinholes, it can be treated as pitting corrosion. Due to the complexity of the process, some simplification was necessary before the kinetic equation for the pitting corrosion of bipolar plate could be established [29–33]. Firstly, the pinholes were treated as one integral whole. Secondly, the corrosion current was mainly from the corrosion occurring within the pinholes and the contribution from general corrosion was neglected; Finally, the pitting corrosion was controlled by ion migration. Based on these hypothesises, the relationship between pitting depth (h) and current density (i_0) was obtained according to Faraday's law [32,33]:

$$n = \frac{Q}{z \cdot F} = \frac{i \cdot t}{z \cdot F}$$  \hspace{1cm} (1)
$$i_0 = \frac{i}{n}$$  \hspace{1cm} (2)

### Table 1

<table>
<thead>
<tr>
<th>Exposure time/h</th>
<th>Rs (Ω.cm²)</th>
<th>Ccrc (µF.cm⁻²)</th>
<th>n</th>
<th>Rt (Ω.cm²)</th>
<th>W (S.cm⁻⁰.⁵)</th>
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<tr>
<td>2</td>
<td>4.52</td>
<td>2.48E–05</td>
<td>0.95</td>
<td>7.59E+05</td>
<td>4.05E–06</td>
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<td>9.26E+05</td>
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<tr>
<td>6</td>
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<td>1.37E+06</td>
<td>4.19E–06</td>
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<tr>
<td>8</td>
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<td>2.24E–05</td>
<td>0.96</td>
<td>1.75E+06</td>
<td>6.98E–06</td>
</tr>
<tr>
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<td>1.22E+06</td>
<td>8.48E–06</td>
</tr>
<tr>
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<td>0.96</td>
<td>7.88E+05</td>
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<tr>
<td>56</td>
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<td>0.96</td>
<td>1.06E+06</td>
<td>3.20E–06</td>
</tr>
<tr>
<td>68</td>
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<td>0.96</td>
<td>1.27E+06</td>
<td>3.70E–06</td>
</tr>
<tr>
<td>80</td>
<td>3.93</td>
<td>2.31E–05</td>
<td>0.96</td>
<td>1.37E+06</td>
<td>3.87E–06</td>
</tr>
</tbody>
</table>

**Fig. 5.** The Nyquist plot of the coated sample immersed in simulated PEMFC cathodic environment.

**Fig. 6.** The Nyquist plot of the coated sample immersed in simulated PEMFC cathodic environment.

**Fig. 7.** SEM of the coated sample after immersed 20 h and 80 h in simulated PEMFC cathodic environment.

**Fig. 8.** Potentiostatic transient curve in simulated cathodic environment.
The derivative of pitting depth with respect to time is calculated:

$$\frac{dh}{dt} = \frac{i_0 \cdot M}{z \cdot F \cdot \rho}$$  \hspace{1cm} (4)

The process of the corroded metal ions diffusing from pinhole to bulk solution was in accord with Fick's law [29] (Eq. (6)).

$$n = \frac{D \cdot S \cdot (c_s - c_b)}{h} \cdot t$$  \hspace{1cm} (6)

where \(D\) – the diffusion coefficient, m² s⁻¹;
\(c_s\) – the concentration of metal ions at the bottom of pit, mol·L⁻¹;
\(c_b\) – the concentration of metal ions in bulk solution, mol·L⁻¹.

Since the development of pitting corrosion was supposed to be controlled by the oxygen reduction at the film surface, \(c_s\) was constant because the metal ions at the bottom of pit were saturated. \(c_b\) can be regarded as zero because the metal ions' concentration in bulk solution was very low. So these equations, Fick's law and Fara-}

Comparing Eq. (12) with Eq. (11) it is found that they had the same power index and the correlation coefficient was 0.996, which supported the claim that the development of the corrosion through the pit was controlled by the ion migration.

**Conclusions**

By electrochemical techniques, the corrosion kinetics of 316L stainless steel with chromium carbide coating was investigated in PEMFC cathodic environment. The EIS results indicated that the capacitive resistance and the reaction resistance first slowly decrease (2–32 h) and then increase, which mean the corrosion rate increased first and then decreased. Although the chromium carbide coating had high corrosion resistance and acted as a barrier layer inhibiting the substrate from corrosion, some pinholes found in the coating, ultimately lead to failure of the coating by a pitting corrosion mechanism. The corrosion kinetics equation of the coated 316L stainless steel was \(i_0 = 7.6341t^{-0.5}\) in simulated PEMFC cathodic environment, which meant the corrosion was controlled by the ion migration in the pinholes.

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