

Application of Corrosion-Resistant ATF Materials for PEM Fuel Cells as a Next-Generation Convergence Technology

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1. Introduction

The Fukushima nuclear accident revealed that there was a problem with the safety of the zirconium cladding materials currently in use, and it was a key point that triggered the R&D of accident tolerant fuel claddings (ATFC) with enhanced safety. Accordingly, research on Cr-based alloy technology including a protective oxide film as an oxidation-resistant material for an accident prevention covering material is being actively conducted [1]. In particular, CrAl and FeCrAl materials among accident prevention materials have excellent high-temperature oxidation resistance, strength and stability at high temperatures, and thus have potential to be applied to various fields other than nuclear materials [2],[3]. Therefore, in this study, CrAl and FeCrAl, the core materials of accident-resistant materials, were applied as bipolar plates materials for proton exchange membrane fuel cells (PEMFC) to lead the next-generation convergence technology and national competitiveness.

2. Methods and Results

2.1 corrosion tests

Typically, PEM fuel cells operate in a humid acidic environment. Specifically, the operating temperature range is 80-100° C, and the pH of system is 2-4 [4]. At this time, the protective film on the surface of the metal bipolar plates induce ion dissolution of the temperature, humidity, and pH, and ultimately the base material, thereby causing contamination of the electrolyte and the membrane. Therefore, in order to confirm the durability of the metal bipolar plates, it is essential to conduct a corrosion behavior test (0.5 M H₂SO₄, 80°C) in the simulated environments. Potentiodynamic polarization tests of CrAl and FeCrAl alloys in simulated acidic environment were performed. Corrosion and passivation behavior are analyzed by Butler Volmer equations and Tafel plots [5],[6]. The Butler-Volmer equation is expressed for a current that varies with applied voltage when the overall reaction rate is governed by the charge transfer process. The corrosion behavior of the specimen is expressed as the corrosion potential (E_{corr}) when the value of the current generated on the metal surface equals the anode and cathode currents. The corrosion potential means a potential value at which corrosion starts after the surface protective film is formed. The larger the current density (I_{corr}) value, the

more corrosion occurs due to the activation of electron migration by ion elution. In the potentiodynamic polarization test, the electrochemical corrosion behaviors of CrAl and FeCrAl substrates were compared with that of stainless steel, which is a general metal bipolar plates. The composition of the test alloys are as follows.

Table. 1. composition of the CrAl and FeCrAl, SS316L.

	CrAl	FeCrAl	SS316L
Fe	-	Balance.	Balance.
Cr	80~85%	20~23%	16~18%
Al	15~20%	5~5.8%	-
Ni	-	-	12~15%
C	-	0.08%	0.03%
Mn	-	0.40%	2%
Si	-	0.70%	1%
P	-	-	0.04%
S	-	-	0.03%

The corrosion potential values of the alloy specimens were higher than those of stainless steels, and the corrosion currents were lower. These results suggest that CrAl and FeCrAl alloys have a positive effect on corrosion inhibition properties compared to stainless steels.

$$I = I_0 \left[\exp\left(\frac{-\alpha F \eta}{RT}\right) - \exp\left(\frac{(1-\alpha) F \eta}{RT}\right) \right] \quad (1)$$

I : Electrode current density

η : Activation over potential (defined as $E - E_{eq}$)

α : Charge transfer coefficient

F : Faraday constant

R : universal gas constant

T : absolute temperature

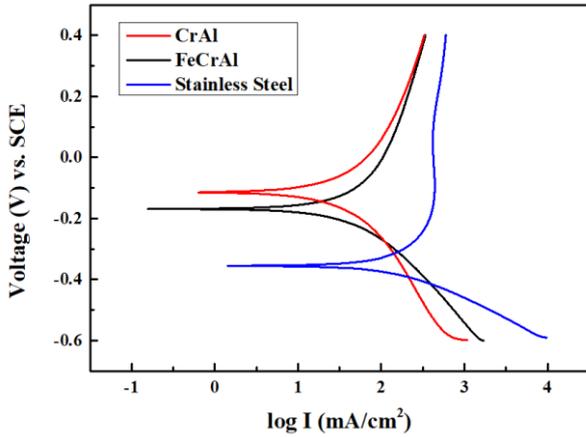


Figure. 1. Potentiodynamic polarization curves of the CrAl and FeCrAl alloy compared stainless steels in a simulated PEMFC conditions (0.5 M H₂SO₄, 80°C).

2.2 Water contact angle tests

For hydrophobicity, the surface water contact angles of CrAl and FeCrAl alloy samples and stainless steel were measured with a single drop of 3 μ L of water on the surface via the sessile-drop method using a contact angle analyzer (SEO, Phoenix 300). In this case, the surface free energy of the solid surface associated with the corrosion phenomenon can be calculated by measuring the contact angle. The contact angle between the droplet and the solid surface can be expressed by the equation of state for the surface free energy. The contact angle refers to the angle at the solid-liquid surface in the solid-liquid-gas boundary. This occurs when the liquid is thermodynamically balanced on the solid surface, resulting in a force balance. The contact angle is described using Young's equation, which is determined by the interaction of the interfacial tension at the gas-liquid-solid boundary γ_{sv} , γ_{lv} , and γ_{sl} are the interfacial energy vectors of solid-gas, liquid-gas, and solid-liquid, respectively. The higher the interaction, the smaller the value. Young's equation for determining the contact angle was originally based on an analysis of the force balance among the three surface tensions involved [7],[8].

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta_y \quad (2)$$

γ_{sv} : Solid-vapor interfacial free energy
 γ_{lv} : Liquid-vapor interfacial free energy
 γ_{sl} : Solid-liquid interfacial free energy
 θ : Water contact angle

According to Young's equation, the contact angle can be expressed as a function of the surface energies of the droplet and solid. An equation based on the Good-

Girifalco-Fowkes model that explains the surface free energy.

$$\gamma_{sl} = \gamma_s + \gamma_{lv} - 2\phi(\gamma_s\gamma_{lv})^{1/2} \quad (3)$$

$$\gamma_{lv}(1 + \cos \theta_y) - 2\phi(\gamma_s\gamma_{lv})^{1/2} \quad (4)$$

The Fowkes model is based on the assumption that it is irrelevant to the molecular composition of liquids and solids, intermolecular attractions, and liquids. Therefore, 73 mJ/m², which is the surface tension of water at room temperature (20°C), was used as the γ_{lv} value. The parameter values are listed in Table. 1. The hydrophobic surface minimizes the water contact area with the metal surface through its high water repellency, preventing the main corrosive ions from entering the surface. This also implies that it slows the breakdown of the metal oxide layer and prevents further corrosion of the metal surface. The hydrophobicity of the metal surface can affect electron transport, specifically reducing corrosion when the surface comes into contact with water in acidic environments, such as the corrosive environment of PEM fuel cells. In other words, the surface of the hydrophobic CrAl and FeCrAl alloys protect the exposed surface from external attack.

Table. 2. Surface free energy of the solid calculated by the water contact angle of the specimens.

Samples	Surface tension of water at 20°C (γ_{lv}) mJ/m ²	Contact angle (θ)	Surface free energy of solid (γ_s) mJ/m ²
CrAl	73	97.65°	13.71
FeCrAl	73	81.63°	23.61
SS316L	73	61.32°	39.42

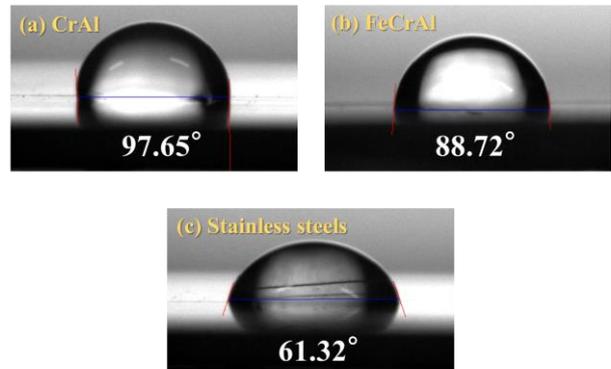


Figure. 2. Water contact angles results of (a) CrAl, (b) FeCrAl

and (c) stainless steel specimens.

3. Conclusions

For corrosion resistance analysis, electrochemical corrosion tests in simulated PEM fuel cells environments reveal that the CrAl and FeCrAl alloys exhibit superior anti-corrosion durability that alloys were found to resist attacks from corrosive ions. In particular, the hydrophobicity of the surface can act to reduce the possibility of corrosion by inducing a low surface energy value, and improve the water management ability of the bipolar plates. As a result, CrAl and FeCrAl alloys have great potential for application to bipolar plates as corrosion-resistant materials compared to stainless steels. New applications of accident-resistant cladding materials can be used as a promising way to effectively protect metal bipolar plates, leading to the development of next-generation convergence technology.

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