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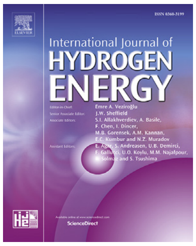

Corrosion-resistant coating for cathode current collector and wet-seal area of molten carbonate fuel cells

MinJoong Kim [a], *JuYoung Youn* [b], *JeongHoon Lim* [a], *KwangSup Eom* [c], *EunAe Cho* [a,*], *HyukSang Kwon* [a,**]

[a] *Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon, 34141, Republic of Korea*

[b] *Energy Conversion System Research Team, Doosan Heavy Industries & Construction, 10 Suji-ro, Suji-gu, Yongin, 16858, Republic of Korea*

[c] *School of Materials and Engineering, Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju, 61005, Republic of Korea*

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ABSTRACT

High-temperature corrosion of metallic bipolar plates is a main problem to limit system reliability of molten carbonate fuel cells (MCFCs). In particular, cathode current collector (CCC) and wet-seal area in the bipolar plates suffer severe corrosion during MCFCs operation. Herein, we are trying to explore facile and cost-effective coating materials and methods to enhance corrosion resistance of CCC and wet-seal area of MCFCs. Cobalt (Co) layer was coated by using electrodeposition method for CCC, and aluminum (Al) layer was coated by using mechanical cladding method for wet-seal area. Co and Al layers were transformed into *in-situ* lithiated oxides, which are $LiCoO_2$ and $LiAlO_2$, by reacting with electrolytes without detachment. These *in-situ* formed oxides efficiently impede formation and growth of corrosion scales by preventing permeation of electrolytes. We believe that Co electrodeposition and Al cladding would be suitable and practical methods for making protective layers to enhance corrosion resistance of CCC and wet-seal area in the MCFCs bipolar plates.

Introduction

To respond to global climate change, demand for eco-friendly power generation systems has been continuously increased. Molten carbonate fuel cells (MCFCs) have attracted much attention as a clean source for large-scale power plants for the future due to their high efficiency and low air pollutant emission. MCFCs operate at high temperatures about 650 °C to completely melt carbonate salts, such as $(Li,K)_2CO_3$ and $(Li,Na)_2CO_3$, that are used as an electrolyte [1]. The high operating temperature enables to get economic advantages by utilizing non-precious metal catalysts and high quality waste heat, but causes severe corrosion of metallic bipolar plates

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* *Corresponding author.*
** *Corresponding author.*
E-mail addresses: eacho@kaist.ac.kr (E. Cho), hskwon@kaist.ac.kr (H. Kwon).

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that directly contact with electrolyte [1]. The high-temperature corrosion is regarded as a main factor to limit system reliability of MCFCs [2,3]. Typically, austenitic stainless steels (AISI 310S, AISI 316L) whose main components are iron and chromium have been used for bipolar plates owing to their high corrosion resistance and high mechanical strength [4,5]. However, these stainless steels cannot ensure the long-term durability target for commercialization of MCFCs [4–10].

In MCFC bipolar plates, cathode current collector (CCC) and wet-seal area particularly suffer severe corrosion [11,12]. CCC is in contact with cathode to transfer electrons from cathode to the next cell. Oxygen environment and high operating voltage of cathode, combined with the molten carbonate flowing out from the cathode, induce severe corrosion of CCC. Wet-seal area, the edge of the bipolar plate, is in direct contact with the molten carbonate electrolyte to form a leak-free gas seal. As a result, corrosion scales, such as lithium iron oxides ($LiFe_xO_y$) and lithium chromium oxide ($LiCr_xO_y$), are formed on the surface of CCC and wet-seal area [6]. These corrosion scales can grow fast at the high operating temperature, resulting in formation of fractures due to increased mechanical stress [1,13]. At wet-seal area, these fractures cause severe leakage of gaseous reactants [11]. CCC has additional issues related with the corrosion scales. Because the corrosion scales have very low electrical conductivity, formation of thick corrosion scales on CCC surface increases contact resistance between CCC and the cathode [14]. In addition, chromium corrosion scales ($LiCr_xO_y$) of CCC can be transformed into chromate salt (K_2CrO_4) by reacting with the electrolyte under the cathode operating condition [15]. The chromate salt is known to be highly soluble in the electrolyte during MCFC operation [16]. Continuous formation and dissolution of the chromate salts leads to severe electrolyte loss [11]. Therefore, the high-temperature corrosion of CCC and wet-seal area can cause severe performance degradation of MCFCs by gas leakage through the bipolar plate, an increase in contact resistance and electrolyte loss.

Protective coating is a commonly-used method to suppress corrosion [17,18]. Aluminum (Al) coating is known to be effective in suppressing corrosion of MCFC bipolar plates since the Al layer is transformed into lithium aluminate ($LiAlO_2$) which has excellent corrosion resistance under the MCFCs operating condition [19,20]. However, $LiAlO_2$ has very low electrical conductivity [21]. Therefore, Al coating can be used only for wet-seal area, not for CCC that needs high electrical conductivity. In the case of CCC, cobalt (Co) is considered as a good candidate for protective coating material. As similar with Al coating, Co layer can be transformed into lithium cobalt oxide ($LiCoO_2$) during MCFCs operation [22]. $LiCoO_2$ has sufficient electrical conductivity and corrosion resistance to be used as a protective layer for CCC [2,8,23]. These coatings for CCC and wet-seal area have been generally conducted by using atomic layered deposition (ALD), thermal spray and slurry coating [19,24,25]. However, these methods have drawbacks that are not suitable for practical use; ALD is too expensive, thermal spray causes thermal deformation and slurry coating cannot ensure uniform coverage. Therefore, exploring facile and cost-effective coating method is an important issue to develop corrosion-resistant CCC and wet-seal area of MCFCs.

In this work, we employed electrodeposition and mechanical cladding as protective coating methods for CCC and wet-seal area of MCFCs bipolar plates, respectively. Since both electrodeposition and mechanical cladding are known to be facile and cost-effective, these methods are practically suitable for corrosion-resistant coating for CCC and wet-seal area of MCFC bipolar plate. On AISI 310S, Co layer was electrodeposited for CCC and Al layer was mechanically cladded for wet-seal area coating. Corrosion-resistance of bare 310S and the coated 310S was evaluated under MCFCs operating conditions.

Experimental

Materials and coating methods

AISI 310S plate was used as a bare material for bipolar plates. Chemical composition of AISI 310S is summarized in Table 1. Before Co electrodeposition, a 310S plate was cleaned in acetone to remove organic impurities and activated in 10% H_2SO_4 solution and 10% HNO_3 + 2% HF solution to remove passive film. First, Co seeds were electrodeposited on the activated 310S plate at a current density of 70 mA/cm^2 for 100 s, and then 15 μm thick Co layer was electrodeposited at a relatively lower current density of 20 mA/cm^2 for 30 min. The first seed electrodeposition can enhance adhesion between the 310S plate and the thick Co layer. The Co-electrodeposited 310S plate was heat-treated at 1000 °C under H_2 gas condition for 2 h to stabilize the Co layer. Al-cladded 310S plate was provided by Chang Sung Corporation. 15 μm thick Al layer was cladded on a 310S plate by mechanical rolling. For comparison, Al layer was coated on a 310S plate by using slurry coating method. Slurry was prepared by mixing Al powder and colloidal silica binder. After slurry coating, the Al slurry-coated 310S plate was heat-treated at 850 °C under reducing environment (5 vol % H_2 + N_2 Gas) to improve adhesion of Al coating layer with the 310S substrate.

Corrosion tests

During MCFCs operation, cathode current collector (CCC) and wet-seal area were exposed to different corrosion environments. To evaluate corrosion resistance under the actual MCFCs operating conditions, we designed corrosion tests for CCC and wet-seal area, respectively. As an electrolyte, $(Li_{0.67}K_{0.33})_2CO_3$ salt was used.

In MCFCs, CCC is in contact with cathode that contains electrolyte. Thus, during operation, molten electrolyte is spread out from the cathode and the CCC comes in contact with a thin electrolyte layer. To simulate the condition, we designed a corrosion test for CCC as depicted in Fig. 1. Two

Table 1 – Chemical composition of AISI 310S.

Element	C	Mn	Si	P	S
Composition (Wt. %)	0.0434	1.35	0.5	0.0025	0.007
Element	Cr	Mo	Ni	N	Cu
Composition (Wt. %)	25.5	0.06	19.6	0.0324	0.05

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