Evaluation of Corrosion Resistance of Coated and Uncoated Stainless-Steel Separators at Cathode Side for Molten Carbonate Fuel Cell *1

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In order to evaluate the corrosion resistance of a cathode-side separator for a molten carbonate fuel cell (MCFC), SUS316 and SACC-SUS316 (chromium and aluminum were simultaneously deposited by diffusion into SUS316 austenitic stainless steel substrate using the pack-cementation process) were used as the separator materials. In the case of SUS316, corrosion proceeded via three steps: the formation of a corrosion product until the corrosion product becomes stable; the protection against corrosion until breakaway occurs; and the advancement of corrosion after breakaway. Since SUS316 showed a high corrosion rate in the cathode environment, it would be impossible to use it as a separator without suitable surface modification because of the occurrence of severe stability problems of the cell during long-term operation. In contrast, SACC-SUS316 showed higher corrosion resistance than the present separator material, SUS316. No corrosion was observed on SACC-SUS316 after 480 h at 923 K. Therefore, this material is thought to be very useful as an alternative separator at the cathode side for MCFC in the future.

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1. Introduction

After its development by W. Grove in 1839, the fuel cell was limited to military or aerospace use, such as the Gemini and Apollo plan, etc.1) However, since the shortage of fossil fuels and their environmental pollution have become a serious problem worldwide since the 1970s, much research has been carried out to determine its large-scale and/or small-scale applications such as local power generation, transportation, and supply.2) The molten carbonate fuel cell (MCFC) is one of the most promising devices because it is capable of using a variety of fuels including reformed naphtha or natural gas. A typical fuel cell assembly consists of a porous and stabilized Ni anode and a porous Ni or NiO cathode separated by molten alkali carbonate electrolyte contained within the interstices of a porous LiAlO2 compact.

In spite of the many advantages of MCFC, the problems of separator plate corrosion and cathode dissolution during cell operation3–5) have to be solved prior to its commercialization. The separator is an essential cell component inserted between two units of MCFC; however, it undergoes serious corrosion in the cathode and anode environment due to the high-temperature molten salt electrolyte, the oxidant gas from the anode, and the cathode gas from the anode cell operation. Today, many studies on the development of new alloy materials6, 7) and surface modification methods8, 9) are being carried out to solve the corrosion problem of the separator; however, a substitute material of good corrosion resistance has not been developed yet. Recently, Park et al.5, 10) investigated the characteristics of austenitic stainless steel and the influence of the alloying elements under the conditions for MCFC operation to obtain a substitute separator with improved corrosion resistance. They found that chromium and aluminum simultaneously deposited by diffusion into austenitic stainless steel substrates improved the corrosion resistance of the separator.11)

Therefore, in this research, SUS316 austenitic stainless steel (SUS316), which is widely used as an MCFC separator, and the simultaneous aluminum-chromium-coated SUS316 (SACC-SUS316) were used as separator materials. Then, the corrosion resistance of SUS316 and SACC-SUS316 was evaluated under conditions for MCFC operation by analyzing the element’s behavior and the progress of corrosion.

2. Experimental Procedure

The precursor substrate used in this experiment was austenitic SUS316 (C : 0.06, Si : 0.66, Mn : 0.92, P : 0.02, S : 0.005, Ni : 10.48, Cr : 16.82, Mo : 2.04, Fe : bal, mass%). The substrate was cut into squares of 10 mm × 10 mm (1.0 mm thick) and then washed by ultrasonication in acetone. Then, aluminum and chromium were simultaneously deposited about 50 μm thick by diffusion into the square substrates using the pack-cementation process to form SACC-SUS316.11) Diffusion was carried out via a two-step coating cycle and the pack composition was 80Cr–20Al 100-mesh master alloy (25 mass%), NH4Cl activator (2 mass%), and 100-mesh α-Al2O3 inert filler (73 mass%).

To evaluate the corrosion resistance of SUS316 and SACC-SUS316 specimens under conditions for MCFC operation,
corrosion experiments were performed under two conditions: the electrolyte environment (EE) and the electrolyte with oxidant gas environment (EOD) in cathode conditions. The EE condition implies that the electrolyte was exposed to air environment. And the EOD condition implies that the fuel gas (Air: CO₂ = 70: 30 vol(%)) was infused into the electrolyte at a flow rate of 3.08 cm³/s. The electrolyte used was a eutectic mixture of Li₂CO₃ (ϕ: 10 μm) and K₂CO₃ (ϕ: 100 μm) which had a ratio of 62 : 38 mol% and was ball-milled for two hours before processing. The total amount of electrolyte was 4.00 kg/m² of specimen surface. All the experiments were performed at 923 K for 480 h. After the corrosion test, the specimens were immersed in a boiling solution of 18%NaOH and 3%KMnO₄ for four hours, and then immersed in 10% diammonium hydrogen citrate followed by washing with distilled water and acetone for complete removal of corrosion products. After drying, the mass loss of the corroded specimen was measured as an indicator of the degree of corrosion. The salts on the specimens were removed by dipping in 5%H₂SO₄ for several seconds, prior to the investigation of elemental behavior and the composition in the cross section of the corroded specimen by SEM and EPMA. The corrosion products were identified by XRD.

3. Results and Discussion

3.1 Basisity of molten carbonate salt

At first, we will consider the basisity of the molten carbonate salt. Using the activity of oxide ion a₀₂⁻, the basisity of molten salt p₀²⁻ is expressed as follow.

\[ p_{O_2} = - \log(a_{O_2^-}) \]  

(1)

In the molten carbonate salt, the activity of oxide ion a₀₂⁻ is given by the following reaction.

\[ CO_3^{2-} \rightleftharpoons CO_2 + O_2^2^- \]

\[ K = \frac{P_{CO_2} \cdot a_{O_2^-}}{a_{CO_3^{2-}}} \]  

(2)

Where, K is the equilibrium constant, P_{CO_2} the partial pressure of CO₂ and a_{CO_3^{2-}} the activity of CO₃²⁻ ion. When a_{O_2^-} in eq. (2) is substituted in eq. (1), we obtain the following equation.

\[ p_{O_2} = - \log(K \cdot a_{CO_3^{2-}}) + \log P_{CO_2} \]  

(3)

In view of the fact that K₂CO₃ is more stable than Li₂CO₃, \( P_{CO_2} \) in the EE condition is estimated to be 42.49 Pa by using the following reaction.¹³)

\[ Li_2CO_3 = CO_2 + Li_2O \quad \Delta G_{f}^0 = 32581 - 288T \text{ J/mol} \]  

(4)

On the other hand, \( P_{CO_2} \) in the EOE condition is estimated to be 3.04 × 10⁴ Pa by assuming CO₂ is in equilibrium in the molten salt and the fuel gas. Therefore, the basisity of the molten salt is estimated as follows.

For the EE condition : \( p_{O_2} = - \log(K \cdot a_{CO_3^{2-}}) - 3.38 \)

For the EOE condition : \( p_{O_2} = - \log(K \cdot a_{CO_3^{2-}}) - 0.52 \)

Unfortunately, the basisity of the molten salt can not be exactly determined because the values of K and a_{CO_3^{2-}} for this molten salt are not found in the thermodynamic data. From above equations, however, the basisity in the EE condition may be presumed to be higher by 2.86 than that in the EOE condition. Furthermore, the basisity in the EE condition may be estimated to be zero by assuming that eq. (2) is equivalent to eq. (4): i.e., a_{CO_3^{2-}} and a_{O_2^-} are equivalent to a_{Li_2CO_3} ≡ 1 and a_{Li_2O}, respectively.

The corrosion test was conducted under these conditions mentioned above.

3.2 Coating characteristics of SACC-SUS316

Figure 1 is a SEM micrograph that shows the coating characteristics of the SACC-SUS316 specimen obtained by the pack cementation of SUS316. During simultaneous aluminum-chromium coating, the two-step coating cycle was applied so that both gas-state diffusion and homogeneous solid-state diffusion could be induced. As shown in the figure, the coated layer consists of an outer layer (A) and an underlying multiphase zone (B). The small precipitates inside B were dispersed homogeneously with spherical large precip-
3.3 Corrosion rate

Figure 3 shows the mass loss per unit area of SUS316 and SACC-SUS316 specimens under the EE and EOE conditions.

In the SUS316 specimen, the corrosion seems to be a first-order reaction since the mass loss that corresponds to the amount of corrosion products is linearly proportional to the logarithm of time. Regarding the corrosion rate, it proceeds in three steps. For the corrosion of the SUS316 specimen under the EE condition, the first step involves the formation of corrosion products up to two hours during which the corrosion proceeds rapidly with a corrosion rate (the gradient of log W vs. log t plot in Fig. 3) of about 0.82. In the second step, however, the gradient of log W vs. log t plot decreases to 0.25 due to the protective action of the corrosion products formed in the first step. In the third step following the breakaway point, the corrosion rate increases again, where the gradient of log W vs. log t plot is about 0.64. The total mass loss is about 6.6 kg/m² after the 480 h corrosion test. Since marked corrosion is found in the Cr-depleted zone, it is believed that Cr element is converted to Cr₂₃C₆ at 923 K in the first step. In the second step, however, the Cr compound formed in the corrosion reaction acts as a protective layer and thus, the corrosion rate decreases with time. This stable corrosion product layer (A and B in Fig. 3) breaks after 240 h as it is exposed to the hot molten salt of the excessively corrosive environment, and thus the corrosion rate increases again.

Under the EOE condition, the gradient of log W vs. log t plot of the SUS316 specimen is about 0.68, which is lower than 0.82 in the formation step of the corrosion product under the EE condition. In the second step up to 240 h, the gradient of log W vs. log t plot is 0.29, which indicates very effective corrosion resistance, even though the specimen is exposed to severe oxidizing atmosphere on the cathode side. However, in the third step following the breakaway at point A, the gradient of log W vs. log t plot is 0.71, which is larger than
0.64 under the EE condition. Moreover, the total mass loss after 480 h is 11.46 kg/m², which is considerably high compared with 6.6 kg/m² under the EE condition. The reason for this is that the stable Cr oxide layer formed under the EOE condition containing the oxidizing gas shows effective corrosion resistance, in agreement with the results of Evans and Stott[18,19] who investigated the characteristics of austenitic stainless steels under an oxidizing environment. However, this stable oxide layer is broken on exposure to the hot molten salt of the severe oxidizing environment for a long time, and the corrosion rate increases again. Therefore, judging from the corrosion rate and the degree of corrosion obtained under the conditions for MCFC operation, it is evident that during prolonged cell operation, corrosion of the separator on the cathode side will bring about a serious stability problem. As described in Section 3–1, the basisity in the EOE condition was estimated to be higher by 2.86 than that in the EE condition. Therefore, the difference of oxidation behavior in the two conditions is judged to be due to the influence of basisity on the corrosion. Recently, one of the authors investigated the oxidation behavior of SUS310S austenitic stainless steel (Ni : 18.34, Cr : 24.14, mass%) under the same conditions in this experiment.[5,10,11] He found that the SUS310S austenitic stainless steel showed quite similar oxidation behavior involving the three steps, though the total mass loss in the SUS310S after 480 h was about only half of the SUS316 in this experiment. The difference of the total mass loss in the both stainless steels is considered to be due to the difference of Ni and Cr concentration in their matrix.

In contrast, in the SACC-SUS316 specimen, there is no mass loss under the EE and EOE conditions even after the 480 h corrosion test. The reason is that in the case of the SACC-SUS316 specimen, the intermetallic compound layer such as NiAl and Ni₃Al, etc. formed on the surface of the SUS316 specimen during simultaneous aluminum-chromium coating as shown in Fig. 1, seems to provide a high corrosion resistance. Even under the excessively oxidizing environment due to the EOE condition, mass loss is not observed even after the 480 h corrosion test. It is considered that the ease of formation of the stable oxide layer under the oxidizing environment as well as the formation of the intermetallic compound layer on the surface of the SACC-SUS316 specimen brings about a much higher corrosion resistance. Therefore, taking the corrosion rate into account, it is suggested that for the application of SUS316 as an MCFC separator, proper surface treatment to convert it into SACC-SUS316 has to be carried out to enhance its corrosion resistance. In particular, an improvement of the coating process and/or a treatment of the
coated surface will yield a higher corrosion resistance.

3.4 Corrosion behavior and elemental analysis

Figure 4 shows SEM images and EPMA results taken along the cross section of a SUS316 specimen to observe the behavior of the elements in SUS316 under the EOE condition with increasing corrosion time. After the 1 h corrosion test, which corresponds to the first step of corrosion [Fig. 4(a)], Fe, Cr, and Ni are observed to diffuse into the electrolyte/specimen interface, with the diffusion of Cr being the most distinct. It is assumed that the Cr oxide layer is formed from a directional reaction of Cr and oxygen existing in the oxidant gas on the cathode side and a corrosion product is formed at the electrolyte/specimen interface. The Cr oxide layer shows high corrosion resistance even under the EOE condition. However, the Cr oxide layer moves into the matrix as the corrosion product develops at the electrolyte/specimen interface, the α zone. Therefore, as can be seen in Fig. 4(b) for the specimen after the 96 h corrosion test, Fe is enriched in the α zone of the interface, where the corrosion product is eventually formed [Fig. 4(c)], and Cr is enriched in the β zone of the corrosion product/matrix region, which develops into the corrosion protection layer later on. The results indicate that Fe preferentially reacts with the electrolyte to form the corrosion product containing Fe in the α zone, and that Cr and Ni are dispersed into the matrix. In the 240 h corroded specimen, the corrosion product is expected to spall from the matrix interface of the specimen [A in Fig. 4(c)].

Figure 5 exhibits the distribution of the elements in the 480 h corroded SUS316 specimen: Fe is enriched in the formation zone of the corrosion product (α zone), Cr in the corrosion protection zone of the corrosion product/matrix interface (β zone), and Ni in the innermost and Cr-depleted zone (γ zone) of the specimen. Therefore, judging from this elemental behavior, the corrosion product under the EOE condition is presumably a compound containing Fe and is expected to spall from the matrix interface of the specimen.

The corrosion depth is about 15 µm after the 96 h corrosion test, which is similar to that of a separator exposed to the molten salt electrolyte condition (EE). In the 240 h corroded specimen, the corrosion depth is about 18 µm, which is slightly higher than that of a separator under the EE condition, namely, 15 µm. In contrast, in the 480 h corroded specimen, the corrosion depth is about 25 µm as shown in Fig. 5(a); this is, however, a result of subsequent corrosion after the corrosion product spalled from the specimen after approximately 240 h under the EOE condition.

This corrosion depth result agrees with the corrosion rate analysis in Section 3.3, that is, the gradient of log W vs. log t plot of 0.68 under the EOE condition is lower than that under the EE condition in the first step, while the gradient of log W vs. log t plot of 0.29 is similar to 0.25 under the EE condition.

Fig. 5. SEM cross-sectional images and EPMA of SUS316 under the electrolyte/oxidant gas (air + CO₂) environment condition (EOE) for 480 h. (a) Image and line-analysis, (b) Fe map, (c) Cr map and (d) Ni map.
condition in the second step. Therefore, SUS316 shows high corrosion resistance in the primary corrosion step. However, the gradient of \( \log W \) vs. \( \log t \) plot of 0.71 in the third step is much higher than 0.64 under the EE condition. Therefore, judging from these aspects of corrosion, it is considered that marked corrosion after the formation of the corrosion product prevents untreated SUS316 from being used as a separator for an extended period of time. Figure 6 displays the
concentration distribution of elements in the specimen after the 480 h corrosion test. The α zone of the corrosion product consists of 94 mass%Fe, and the β zone of the corrosion product has 34 mass%Cr; both of the Fe and Cr concentration are two times higher than those in the matrix composition. The γ region consists of approximately 33 mass%Ni.

Figure 7 shows a SEM image and EPMA results taken along the cross section of a SACC-SUS316 specimen after the 480 h corrosion test under the EOE condition. The coated layer consists of an outer layer (A) and an underlying multiphase zone (B), as indicated in Fig. 1. Fe and Cr are uniformly distributed throughout the specimen, and Ni and Al are homogeneously dispersed in the coated layer with a slightly greater enrichment near the specimen surface. This result clearly indicates much higher corrosion resistance compared with the SUS316 specimen (Figs. 4 and 5). It is considered that in the initial step of corrosion during which corrosion products are formed under the EOE condition, CrFeNi, which is the typical precipitation phase of austenitic stainless steel, LiFeO₂, LiFe₂O₅ and (Cr, Fe) oxide phases coexist; however, LiFeO₂ peak remained dominant even after 480 h, as shown in Figs. 8(c) and (d), which indicates that LiFeO₂, which was formed as a corrosion product in the initial step of corrosion, was transformed into LiFeO₂ with time. Since this LiFeO₂ peak remained dominant even after 480 h, as shown in Figs. 8(c) and (d), the final corrosion product is evidently LiFeO₂ under the EOE condition. This XRD analysis also confirms the results described in Section 3–4 that the corrosion product at the electrolyte/specimen interface consists mainly of Fe. Park et al. 10) reported that in the formation of corrosion products of the separator on the cathode side under conditions for MCFC operation, the corrosion mechanisms involving the direct reaction of electrolyte and specimen, and that of the electrolyte and oxides occur at the same time. Therefore, it is considered that in the initial step of corrosion during which corrosion products are formed under the EOE condition, CrFeNi, which is the typical precipitation phase of austenitic stainless steel, LiFeO₂, LiFe₂O₅ and (Cr, Fe) oxides coexist; however, with time LiFeO₂ is converted into LiFeO₂ with a low oxygen, in which excess oxygen reacts with Fe element diffused from the matrix, thereby proceeding the corrosion.

Figure 9 shows the diffraction results after the 480 h corrosion test for the SACC-SUS316 specimen under the EOE condition. As mentioned in the SEM-EPMA results of Section 3–3, the main diffraction peaks of NiAl and Ni₃Al did not differ from those of the original SACC-SUS316 specimen before corrosion test (Fig. 2). Therefore, judging from the diffraction results of the corrosion products formed under the EOE condition, it is considered that the corrosion product at the electrolyte/specimen interface consists mainly of Fe. Park et al. 10) reported that in the formation of corrosion products of the separator on the cathode side under conditions for MCFC operation, the corrosion mechanisms involving the direct reaction of electrolyte and specimen, and that of the electrolyte and oxides occur at the same time. Therefore, it is considered that in the initial step of corrosion during which corrosion products are formed under the EOE condition, CrFeNi, which is the typical precipitation phase of austenitic stainless steel, LiFeO₂, LiFe₂O₅ and (Cr, Fe) oxides coexist; however, with time LiFeO₂ is converted into LiFeO₂ with a low oxygen, in which excess oxygen reacts with Fe element diffused from the matrix, thereby proceeding the corrosion.

3.5 Phase transformation of corrosion product

Figure 8 shows the XRD patterns of the corrosion product of the SUS316 specimen under the EOE condition as a function of time. In the pattern of the specimen obtained after the 1 h corrosion test [Fig. 8(a)], CrFeNi, LiFeO₂, LiFe₂O₅ and (Cr, Fe) oxide phases were observed. The fact that the main diffraction peak turned out to be that of LiFeO₂ in the specimen after the 96 h corrosion test [Fig. 8(b)] indicates that LiFeO₂, which was formed as a corrosion product in the initial step of corrosion, was transformed into LiFeO₂ with time. Since this LiFeO₂ peak remained dominant even after 480 h, as shown in Figs. 8(c) and (d), the final corrosion product is evidently LiFeO₂ under the EOE condition. This XRD analysis also confirms the results described in Section 3–4 that the corrosion product at the electrolyte/specimen interface consists mainly of Fe. Park et al. 10) reported that in the formation of corrosion products of the separator on the cathode side under conditions for MCFC operation, the corrosion mechanisms involving the direct reaction of electrolyte and specimen, and that of the electrolyte and oxides occur at the same time. Therefore, it is considered that in the initial step of corrosion during which corrosion products are formed under the EOE condition, CrFeNi, which is the typical precipitation phase of austenitic stainless steel, LiFeO₂, LiFe₂O₅ and (Cr, Fe) oxides coexist; however, with time LiFeO₂ is converted into LiFeO₂ with a low oxygen, in which excess oxygen reacts with Fe element diffused from the matrix, thereby proceeding the corrosion.

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SUS316 specimen, the intermetallic compound layer of NiAl and Ni$_3$Al formed on the surface prevented the reaction between elements in the electrolyte and the specimen, thereby giving a very high corrosion resistance. It is considered that even if the uneven diffusion coating layer exists in the SACC-SUS316 specimen, the formation of the much more refined intermetallic compound layer under the EOE condition and the ease of formation of the oxide layer by reacting with oxygen will provide a very high corrosion resistance.

On the other hand, the underlying multiphase zone of the coated layer consisted of the homogeneously dispersed small precipitates of $\zeta$-$\text{Cr}_5\text{Al}_8$, as described in Fig. 1. Therefore the simultaneously coated Cr element seems to diffuse into the matrix. The Cr element may be presumed to play an important role in stabilizing the austenitic matrix and also improving the corrosion resistance of the matrix.

4. Conclusion

In order to evaluate the corrosion resistance of the separator plate on the cathode side for molten carbonate fuel cell, SUS316 and SACC-SUS3160 (chromium and aluminum simultaneously deposited on SUS316 austenitic stainless steel substrate by pack-cementation process) were used and following experimental results were obtained.

(1) In the case of SUS316, corrosion proceeded via three steps: the formation of corrosion products until stable corrosion products are realized; the protection against corrosion until breaking occurs; and the advancement of corrosion after breaking.

(2) From the standpoint of the behavior of elements in SUS316 after the stable corrosion product, Fe is enriched in the formation zone of the corrosion product, Cr in the corrosion protection zone of the corrosion product/matrix interface, and Ni in the innermost and Cr-depleted zone of the specimen.

(3) The final corrosion product was LiFeO$_2$. The formation rate of LiFeO$_2$ was so high at the initial step; however, when Cr oxide acted as a protective layer, the formation rate became lower with time.

(4) Taking the corrosion rate into account, the application of SUS316 as an MCFC separator would be impossible without suitable surface modification because of the severe problem of cell stability during long-term operation.

(5) In the case of the SACC-SUS316 specimen, no corrosion took place even after the corrosion test of 480 h due to the formation of an intermetallic compound layer.

(6) SACC-SUS316 showed better corrosion resistance than the present separator, SUS316. Therefore, the SACC-SUS316 may become a very useful separator for MCFC in the future.

REFERENCES