Electrochemical analysis on the growth of oxide formed on stainless steels in molten carbonate at 650 °C

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ABSTRACT

The oxide growth on stainless steel (SS) 310S and 316L, used as a cathode current collector material of molten carbonate fuel cell (MCFC), were examined in the mixture of 62 mol% Li2CO3−38 mol% K2CO3 at 650 °C by measuring the change in corrosion potential and potentiodynamic response of the alloys and also in terms of impedance analysis on the alloy/oxide layer/electrolyte system. The corrosion potential of SS 316L was in an active region for 12 h-immersion, whereas that of SS 310S drastically increased after 6 h-immersion due to an active to passive transition. The corrosion rate of the two SSs decreased with immersion due to the growth of protective oxide. However, the decrease in the corrosion rate of SS 310S is much greater than that of SS 316L. The oxide formed on the two SSs was found to be duplex layer, composed of inner Cr enriched oxide and outer Fe enriched oxide. However, the inner Cr enriched layer of 310S is more clearly separated from the outer Fe enriched layer than that of SS 316L due primarily to the higher Cr content in SS 310S. The drastic increase in the corrosion potential of SS 310S after 6 h-immersion is closely associated with the growth of the inner Cr enriched oxide layer. The corrosion resistance of SS depends dominantly on the resistance of the inner Cr enriched oxide that is determined form the impedance analysis on the alloy/oxide layer/electrolyte system. The higher corrosion resistance of SS 310S compared with SS 316L results from the more protective inner Cr enriched oxide layer, as confirmed by its higher resistance associated with the higher Cr content in SS 310S.

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Introduction

The molten carbonate fuel cell (MCFC) is a power generation system to convert chemical energy of fuels (hydrogen) directly to electrical energy by electrochemical reactions at a high temperature (above 650 °C). The MCFC has been recognized as an attractive power generation system because of its high electrical efficiency, fuel flexibility and the high grade waste heat recovery [1]. MCFC is composed of anode, cathode, matrix impregnated with carbonate electrolyte and mixture of ceramic powder (usually lithium aluminate, LiAlO₂) and bipolar plate. The bipolar plate with the performance of current collector acts as the single-cell housing, and then provides cell-to-cell electronic connection. During the operation of MCFC, the current collector materials at the cathode side are usually exposed to a eutectic mixture of 62 mol% Li₂CO₃–38 mol% K₂CO₃ and gas mixture of 15 vol.% O₂–30 vol.% CO₂–N₂ balance at 650 °C that is a severe corrosive environment [2–6]. Hence, the selection of an optimum current collector material is essential to long life operation of MCFC.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS 310S</td>
<td>0.039</td>
<td>1.38</td>
<td>0.421</td>
<td>0.042</td>
<td>24.51</td>
<td>19.50</td>
<td>–</td>
</tr>
<tr>
<td>SS 316L</td>
<td>0.028</td>
<td>0.95</td>
<td>0.482</td>
<td>0.032</td>
<td>18.74</td>
<td>9.20</td>
<td>1.96</td>
</tr>
</tbody>
</table>

Stainless steels (SSs) such as 310S and 316L have been used as a cathode current collector (CCC) material due to its high corrosion resistance. The SSs react with carbonate electrolyte to form oxides and soluble chromate on the surface of SS during the operation of MCFC [3]. The oxides grow up with operating time and are divided into outer Fe enriched oxide layer and inner Cr enriched oxide layer [7]. Although the main constituents of the oxides are LiFeO₂ and LiCrO₂ [3,8], their detailed structure is quite complex.

Fig. 1 – Cross-section of high temperature corrosion reactor with the layout of working, reference and counter electrodes.

Fig. 2 – Schematic diagram of 3 electrodes. SSs wire type working electrode, pure gold wire type counter electrode and pure gold wire immersed in carbonate electrolyte reference electrode.

Fig. 3 – Corrosion potential transients of SS 310S and SS 316L, respectively, in the mixture of 62 mol% Li₂CO₃–38 mol% K₂CO₃ at 650 °C.
The formation and growth of the oxides significantly reduce electrical conductivity of CCC. Also the soluble chromate leads to outward transport of Cr ion, thereby resulting in a large electrolyte loss. As a result, the cell performance and long term stability of MCFC is significantly degraded with operation time \[9-11\]. Therefore, the selection of an optimum CCC material based on fully understanding of the oxide formation and growth mechanism is very important to the improvement in the life time of MCFC. Vossen et al. compared the corrosion behaviors of pure metal and some commercial steels such as SS 310, SS 316, Inconel 601, and Kanthal Al in molten carbonate environment by electrochemical tests such as polarization tests and cyclic voltammetry. They claimed that the increase in Cr and Al contents has a beneficial effect on the corrosion resistance of SS and nickel base alloys \[8,12-14\]. However there remains a need for a quantitative evaluation on the corrosion resistance of CCC materials with compositional analysis of the corrosion products or the oxides formed on SS to clarify the relevant corrosion mechanism.

In this study, we focused on the initial stage in the formation and growth of the oxides on the commercial CCC materials, SS 310S and SS 316L, to examine their corrosion behaviors in the MCFC environment. At the initial stage of the
oxide formation, chemical composition and structure of the oxides or the corrosion products formed on SS are rapidly changed, which may significantly affect the overall lifetime of CCC material. It is objective of the present work to examine the growth of oxides on SSs by analyzing the electrochemical and compositional behaviors of the alloy/oxide layer/electrolyte system with placing an emphasis on the effects of Cr content on the oxidation resistance, and hence to determine the critical factor that may significantly affect the corrosion resistance of the SSs in the MCFC environment.

**Experimental**

The electrochemical performances of 310S and 316L SSs in a simulated MCFC environment were performed using an alumina crucible that were inserted into a high temperature corrosion reactor made of Inconel alloy. Fig. 1 shows details in the reactor with the layout of working, reference and counter electrodes. The working electrodes are SS 310S and SS 316L sheets that were commercially produced. Table 1 shows chemical compositions of the two SSs. The main difference in the chemical compositions between the two SSs is Cr and Ni content. SS 310S has higher Cr and Ni content compared with those in SS 316L. Fig. 2 shows schematically 3 electrodes that were used in the electrochemical tests; a wire type working electrode, a counter electrode made of 99.999% pure gold wire, and a reference electrode made of pure gold wire immersed in carbonate electrolyte containing LiAlO2, all of which are covered with an alumina tube with a very tiny hole (diameter ~ 0.3 mm) at the bottom. The tiny hole allows an electrochemical contact between the carbonate electrolyte in the reference electrode compartment and that in the reactor compartment. The electrolyte in the reference electrode was...
The corrosion behavior of each alloy in the simulated MCFC environment was determined by measuring the corrosion potential transient and potentiodynamic response for the alloy. For the corrosion potential measurement, specimen was immersed in the carbonate electrolyte during 12 h with 15 s sampling rate. The potentiodynamic tests were carried out at 1 h, 3 h, and 12 h after the immersion, with a scanning rate of 1 mV/s from an initial potential of −50 mV active to the corrosion potential, the two SSs are in an electrochemically active state. With increasing electrode potential, the two SSs go abruptly from −0.55 V to −0.2 V, implying a dramatic change in the growth of protective oxide formed on 310 SS, and thereafter it became almost constant until 12 h-immersion. To examine what reaction occur at each stage we did potentiodynamic test and EIS test at each stage.

**Table 2** - Effects of immersion time on the corrosion potential ($E_{corr}$) and corrosion current density (Icorr) of SS 310S and SS 316L in the mixture of 62 mol% Li$_2$CO$_3$−38 mol% K$_2$CO$_3$ mixture at 650 °C.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Immersion time (h)</th>
<th>Corrosion potential (mV vs. Au [O$_2$/CO$_2$ = 1/2])</th>
<th>Corrosion current density (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS 310S</td>
<td>1</td>
<td>−841.5</td>
<td>8.731 E−5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>−639.0</td>
<td>7.856 E−5</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>−273.1</td>
<td>3.264 E−5</td>
</tr>
<tr>
<td>SS 316L</td>
<td>1</td>
<td>−887.1</td>
<td>1.377 E−4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>−871.9</td>
<td>1.384 E−4</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>−851.0</td>
<td>1.031 E−4</td>
</tr>
</tbody>
</table>

purged with the gas mixture of 67 vol.% CO$_2$ + 33 vol.% O$_2$ throughout the tests. All potentials mentioned in this study are referred to the equilibrium potential for the reaction (CO$_2$ = CO$_2$ + 1/2O$_2$ + 2e$^-$) that occurs at the reference electrode.

The inlet gases introduced into the reactor were air at 100 cc/min and CO$_2$ at 50 cc/min, respectively. The outlet gas was led through a water lock to prevent air inlet. The carbonate electrolyte composition was a standard mixture of 62 mol% Li$_2$CO$_3$ and 38 mol% K$_2$CO$_3$. The reactor temperature was kept at 650 °C throughout the electrochemical tests.

The corrosion behavior of each alloy in the simulated MCFC environment was determined by measuring the corrosion potential transient and potentiodynamic response for the alloy. For the corrosion potential measurement, specimen was immersed in the carbonate electrolyte during 12 h with 15 s sampling rate. The potentiodynamic tests were carried out at 1 h, 3 h, and 12 h after the immersion, with a scanning rate of 1 mV/s from an initial potential of −50 mV active to the corrosion potential. Then, the protectiveness of oxide layer formed on the surface of each SS was examined by EIS measurements on the alloy/oxide layer/electrolyte system. The EIS measurements were obtained with an AC signal of amplitude 10 mV peak to peak at the corrosion potential in the frequency ranging from 10$^3$ Hz−10$^{-2}$ Hz. All EIS data were fitted to appropriate equivalent circuits using computer software program Z-man. After 12 h-immersion, the chemical compositions of oxides formed on the surface of each alloy were measured across the oxide layers by SEM and EDS. In addition, long time (~3000 h) immersion tests were carried out on the two SSs in the standard mixture of 62 mol% Li$_2$CO$_3$−38 mol% K$_2$CO$_3$ at 650 °C for comparing the oxide growth behaviors between the SSs.

**Results and discussion**

**Corrosion potential measurements**

Fig. 3 shows corrosion potential transients of SS 310S and SS 316L in the mixture of 62 mol% Li$_2$CO$_3$−38 mol% K$_2$CO$_3$ at 650 °C. The corrosion potential of each SS increased in the noble direction with immersion time due to the formation of oxide layer on the surface of SS. The corrosion potential of SS 310S is more noble than that of SS 316L over the whole immersion time due probably to the formation of more protective oxide layer. After 1 h-immersion, the corrosion potential of SS 316L increased linearly with time, suggesting the oxide layer formed on SS 316L is less protective. On the other hand, the corrosion potential transient curve of SS 310S is divided into three stages depending on the change of a slope in the transient curve. At the first stage from −1.0 V to −0.6 V for 1.5 h from the beginning of immersion, the corrosion potential increased rapidly in the noble direction. At the second stage from −0.6 V to −0.55 V for 4 h from the end of first stage, the corrosion potential increased with a lower slope than that of first stage. At the third stage, the corrosion potential increased abruptly from −0.55 V to −0.2 V, implying a dramatic change in the growth of protective oxide formed on 310 SS, and thereafter it became almost constant until 12 h-immersion. To examine what reaction occur at each stage we did potentiodynamic test and EIS test at each stage.

**Potentiodynamic polarization response**

Fig. 4(a) shows potentiodynamic polarization responses for SS 310S and SS 316L, respectively, in the mixture of 62 mol% Li$_2$CO$_3$−38 mol% K$_2$CO$_3$ at 650 °C at 1 h-immersion. At corrosion potential, the two SSs are in an electrochemically active state. With increasing electrode potential, the two SSs go abruptly from −0.55 V to −0.2 V, implying a dramatic change in the growth of protective oxide formed on 310 SS, and thereafter it became almost constant until 12 h-immersion. The corrosion potential of SS 310S (−845.1 mV) is more noble than that of SS 316L (−887.1 mV) due probably to the higher Ni content. Further, the corrosion rate (8.731 E−5 A/cm$^2$) of SS 310S was much lower than that of SS 316L (1.377 E−4 A/cm$^2$). Fig. 4(b) shows potentiodynamic polarization responses for SS 310S and SS

**Fig. 7** – An equivalent circuit proposed on the alloy/oxide layer/electrolyte system of SS 310S and SS 316L in the mixture of 62 mol% Li$_2$CO$_3$−38 mol% K$_2$CO$_3$ at 650 °C.
316L, respectively, in the electrolyte at 3-h immersion, or at the second stage. Although the corrosion potential (−639.0 mV) of SS 310S is more shifted in the noble direction compared with that of SS 316 (−871.9 mV), the two alloys are still in an active state at the corrosion potential. The corrosion rate of SS 310S (7.856 E−5 A/cm²) is much lower than that of SS 316L (1.384 E−4 A/cm²). Fig. 4(c) shows potentiodynamic polarization responses SS 310S and SS 316L, respectively, in the electrolyte at the third stage. The corrosion potential of SS 310S is −273.1 mV in the passive region. The stable corrosion potential of SS 310S at the third stage indicates that the stable corrosion product or the protective oxide film is formed on the

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**Fig. 8** — Nyquist plots for the alloy/oxide layer/electrolyte system of SS 310S in the mixture of 62 mol% Li₂CO₃−38 mol% K₂CO₃ at 650 °C together with the simulated fit.

**Fig. 9** — Nyquist plots for the alloy/oxide layer/electrolyte system of SS 316L in the mixture of 62 mol% Li₂CO₃−38 mol% K₂CO₃ at 650 °C together with the simulated fit.
surface of SS 310S. Hence, the abrupt increase in corrosion potential of SS 310S at the onset of the third stage in Fig. 3 is closely associated with the formation of protective oxide. On the other hand SS 316L is still in the active state due probably to the formation of less protective layer. Hence, the corrosion rate of SS 310S (3.264 E−5 A/cm²) is much lower than that of SS 316L (1.031 E−4 A/cm²).

The quantitative values of corrosion potential and corrosion current density of the two alloys, measured from the potentiodynamic tests, are shown as a function of immersion time in Fig. 5. The corrosion potential of SS 310S increased more in the noble direction with immersion time compared with that of SS 316L due to probably to the formation of protective film. Hence the corrosion rate of SS 310S decreased more than that of SS 316 with immersion time. In conclusion, the corrosion rate of SS 316L, expressed by the corrosion current density, is much higher than that of SS 310S over the whole immersion in the molten carbonate environment.

**Surface analysis and electrochemical impedance spectroscopy tests**

The protectiveness of the oxide layer formed on the surface of each SS was examined in terms of the elemental analysis and EIS measurement on the alloy/oxide layer/electrolyte system. Fig. 6(a) and (c) is SEM image on the cross-section of SS 310S and SS 316L, respectively, after 12 h-immersion in the mixture of 62 mol% Li₂CO₃–38 mol% K₂CO₃ at 650 °C. An oxide layer with 8–10 μm thickness was formed on the surface of each SS. Fig. 6(b) and (d) shows chemical composition profile in depth across the oxide layer along the line marked in the Figures. It is evident from Fig. 6(b) and (d) that the oxide is composed of inner Cr enriched layer and outer Fe enriched layer. For SS 310S, the inner Cr enriched layer is more clearly separated from the outer Fe enriched layer due primarily to the high Cr content; the inner Cr layer contains very low Fe content and vice versa. On the other hand, the oxide layer of SS 316L is composed of outer diffused Fe enriched layer with some Cr oxide and the inner Cr enriched layer with Fe oxide and Ni oxide to some level. The Cr concentration in the inner layer of SS 316L is much lower than that in the inner layer of SS 310S due to the lower Cr content in SS 316L. These results are good agreement with those of the previous report on the composition analysis of oxides carried out on the preoxidized specimens (1 h at 750 °C in O₂−CO₂ gas mixture) of SS 310S and SS 316L by Yuh et al. [15]; the inner oxide on SS 310S contains more Cr than that formed on SS 316L (see Table 2).

Based on the SEM and EDS analysis in Fig. 6, we proposed an equivalent circuit on the alloy/oxide layer/electrolyte system for SS 310S and SS 316L as shown in Fig. 7. Each component in the equivalent circuit is as follows: R1 is the solution resistance, R2 is the resistance of the outer Fe enriched oxide, R3 is the resistance of the inner Cr enriched oxide. C1 is the interfacial capacitance between electrolyte and oxide, C2 is the capacitance of the inner Cr enriched oxide, C3 is the capacitance of the inner Cr enriched oxide. W1 is the Warburg impedance of the outer Fe oxide, and W2 is the Warburg impedance of the inner Cr oxide. The impedance values for the alloy/oxide layer/electrolyte system of SS 310S at immersion time of 1 h, 3 h, and 12 h, were measured in the frequency range of 10² Hz−10⁻² Hz, and then optimized based on the proposed equivalent circuit model, to extract values of the important parameters in the model. Fig. 8 shows that there is a good corresponding between the optimized data and the measured impedance data. The impedance measurements and optimization treatments were similarly done on the alloy/oxide layer/electrolyte system of SS 316L, and then the results are shown in Fig. 9. Table 3 shows the extracted elements of the equivalent circuit such as R1, R2 and R3 for SS 310S and SS 316L.

**Table 3 – Extracted elements of the equivalent circuit for SS 310S and SS 316L at each stage.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Immersion time (h)</th>
<th>Interfacial resistance, R1 (Ω·cm²)</th>
<th>Fe enriched oxide resistance, R2 (Ω·cm²)</th>
<th>Cr enriched oxide resistance, R3 (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS 310S</td>
<td>1</td>
<td>0.70</td>
<td>0.57</td>
<td>70.66</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.41</td>
<td>0.76</td>
<td>126.20</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.32</td>
<td>0.99</td>
<td>241.51</td>
</tr>
<tr>
<td>SS 316L</td>
<td>1</td>
<td>19.34</td>
<td>0.71</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.14</td>
<td>0.40</td>
<td>29.50</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>2.92</td>
<td>7.11</td>
<td>81.99</td>
</tr>
</tbody>
</table>

![Fig. 10 – Effects of immersion time on the inner Cr enriched oxide resistance (R3) for SS 310S and SS 316L. Calculated from the EIS data in Figs. 8 and 9.](image-url)
For SS 316L, the interfacial resistance between electrolyte and oxide, $R_1$, is decreased with immersion time due to dissolution of metal ion such as Fe. In contrast, the oxide resistance, $R_2$ and $R_3$, increased with immersion time. $R_3$ is much greater than the other resistances, $R_1$ and $R_2$, and therefore the corrosion resistance of SS 316L is mainly depends on $R_3$.

Fig. 10 shows the effects of immersion time on the inner Cr enriched oxide resistance ($R_3$) of each SS, suggesting that the corrosion resistance of each SS increased with immersion time. It is evident from the comparison between the $R_3$ transient (Fig. 10) and the $i_{corr}$ transient (Fig. 5(b)) that the decrease in corrosion rate of SS with immersion time is closely associated with the formation and growth of inner Cr enriched oxide. The inner Cr enriched oxide formed on the surface of SS 310S after 6 h-immersion appears to act as a protective oxide layer because the corrosion potential of SS 310S maintained a constant value of $-0.2$ V after the immersion time as shown in Fig. 3. The inner Cr enriched oxide formed on SS 316L is much less protective than that on 310S as confirmed by the large difference in $R_3$ between the two SSs.

Fig. 11 represents SEM image on the cross sectional oxide layer formed on the surface of SS 310S and SS 316L, respectively, after 3000 h-immersion in the mixture of 62 mol% Li$_2$CO$_3$–38 mol% K$_2$CO$_3$ at 650 °C. Evidently, the oxide layer (212 μm) formed on the surface of SS 316L has much thicker than that (69 μm) of SS 310S as expected from the large difference in the resistance of the inner Cr-enriched oxide layer ($R_3$) between the two SSs, as presented in Fig. 10. Fig. 12 shows the effects of immersion time on the oxide thickness of the two SSs. It appears that the growth of oxide layer of 310S follows a quasi-parabolic rate law due to the protective nature of the inner Cr enriched oxide layer. On the other hand, the growth of oxide layer of 316L seems to follow a quasi-linear rate law because of the less protective nature of the oxide. It is noteworthy that the thickness of oxide layer of SS exposed for a long period such as 3000 h can be predicted in terms of the value of $R_3$ measured at an initial stage or the resistance of the inner Cr enriched oxide that has been formed for a short period of 12 h.

Conclusions

1. The corrosion potential of SS 310S is noble to that of SS 316L due primarily to the formation of more protective oxide layer in SS 310S over the whole immersion time (~12 h). The corrosion potential of SS 316L was in an active region for 12 h-immersion, whereas that of SS 310S drastically increased after 6 h-immersion due to a transition of an active state to a passive state.

2. The corrosion rate of SS 310S, determined from its potentiodynamic response, much lower than that of SS 316L over the whole immersion time. The corrosion rate of the two SSs decreased with immersion due to the growth of protective oxide. However, the decrease in the corrosion rate of SS 310S with immersion time is much greater than that of SS 316L.

3. The oxide formed on the two SSs was found to be duplex layers, composed of inner Cr enriched oxide and outer Fe enriched oxide, as confirmed by SEM and EDS analysis. However, the inner Cr enriched layer of 310S is more clearly
separated from the outer Fe enriched layer than that of SS 316L due primarily to the higher Cr content in SS 310S.

4. The drastic increase in corrosion potential of SS 310S after 6 h from immersion is closely associated with the growth of the inner Cr enriched oxide layer. The corrosion resistance of SS is closely associated with the resistance \( R_3 \) of the inner Cr enriched oxide that is determined from the impedance analysis on the alloy/oxide layer/electrolyte system.

5. The higher corrosion resistance of SS 310S compared with SS 316L is due presumably to the formation of more protective inner Cr enriched oxide layer, as confirmed by its higher resistance \( R_3 \) compared with that of SS 316L, a result of higher Cr content in SS 310S.

6. The growth of oxide layer of 310S follows a quasi-parabolic rate law due to the protective nature of the inner Cr enriched oxide layer. On the other hand, the growth of oxide layer of 316L seems to follow a quasi-linear rate law because of the less protective nature of the oxide.

REFERENCES


