ELECTROCHEMICAL RESPONSE OF STAINLESS STEELS 310, 316L AND NICKEL-RICH ALLOY IN MOLTEN CARBONATE

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ABSTRACT

The corrosion of separator plate/current collector materials in molten carbonate fuel cells is investigated. Although the corrosion resistance of stainless steel Type 310 is better than that of Type 316, the poorly conducting surface oxide layer on Type 310 is a source of significant ohmic resistance in long term operation, where not only corrosion resistant but conductive layer forming materials are needed. A high-nickel content alloy shows better corrosion resistance than 300 series stainless steels. Electrochemical measurements show significant differences in corrosion behavior between completely submerged samples and samples wetted by a carbonate film.

INTRODUCTION

Cathode dissolution leading to electrolyte-matrix shorting, and the corrosion of current collector and separator plate materials are the main life-limiting factors of the state-of-the art MCFC(1,2). These metallic components are also major contributors to the total system cost. Therefore, it is necessary to minimize hardware corrosion and increase cell life to reduce capital cost.

It is well-known that in the corrosion of stainless steel by molten carbonate chromium forms a protective layer or surface oxide scale which causes the substrate not to be further oxidized. The chromium content of the alloy determines whether it forms an interior layer or an external scale. Low oxide diffusivity in the oxide scale can cause chromium to diffuse to the surface. While chromium is oxidized to form \( \text{Cr}_2\text{O}_3 \) at the metal/oxide interface, an FeO layer also forms and may grow at higher rates. A quantitative explanation of the oxidation behavior of alloy systems requires dealing with multi-component diffusion. In addition, the separator has various contact areas with the carbonate melt, whose different surface to volume ratios lead to differences in character of the corrosion process. The wet-seal area resembles most closely the fully immersed condition. On the other hand, the areas exposed to the gas channels can be dry or covered with a thin film due to creeping of the melt from the porous electrode onto the separator or current collector.
Finally, electrochemical analysis of the multi-component corrosion process becomes difficult when different materials have very close oxidation or reduction potentials. In some cases, it is not possible to find sufficient thermodynamic information for reactions to calculate the required electrode potentials. Therefore, in the following analysis we use a combination of information from different sources such as surface and layer analysis, as well as thermodynamic reference works.

**EXPERIMENTAL DETAIL**

A series of experiments were carried out on stainless steel Types 310 and 316L, and a nickel-rich alloy, in a specially designed controlled-atmosphere chamber, furnace and cell\(^3\). A 62% Li\(_2\)CO\(_3\)-38% K\(_2\)CO\(_3\) mixture was used as electrolyte under oxidant gas of 30% CO\(_2\)-70% air compositions. The nickel-rich alloy was also tested in 52% Li\(_2\)CO\(_3\)-48% Na\(_2\)CO\(_3\) electrolyte. The chemical compositions of the alloys are given in Table 1.

The test cell and electrodes are shown in Figure 1. In this half-cell study, two electrodes are compared under open circuit or current load. Potential is measured with reference to a 67% O\(_2\)-33% CO\(_2\) gas mixture. Three different configurations may be used (Figure 2).

However, electrochemical analysis of the corrosion process at a partially immersed electrode is difficult because it involves too many unknown parameters such as meniscus structure and melt thickness. Therefore, only two (fully immersed and thin-film covered) configurations are examined. These electrodes (immersed and thin-film covered) are subjected to an oxidizing environment at the same time. In the case of the alumina-backed electrode configuration, the electrolyte creeps up very fast on the alumina surface, and fills the crevice at the back of the electrode. The electrolyte starts to slowly creep up to form a thin film on the outer surface of the electrode. A meniscus forms at the interface metal-electrolyte-gas atmosphere.

Steady-state polarization and cyclic voltammetry measurements are performed periodically after the electrode is first in contact with the melt. The experimental set-up allows optical observation and camera recording of the different electrodes to determine the effect of wetting by molten carbonate on the surface reactions.

Table 1. Chemical composition in wt% of alloys used in the study

| Alloy/Elements | Fe% | Ni% | Cr% | Al% |
|----------------|-----|-----|-----|-----|
| SS 316L        | 69  | 10  | 18  |     |
| SS 310         | 55  | 20  | 25  |     |
| NKK            | 23  | 45  | 30  | 1   |
RESULTS AND DISCUSSION

Open Circuit Potential (OCP)

The open circuit potentials of stainless steel Types 310 and 316L and of high-nickel alloy under CO₂ becomes stable around -1000 mV. The stable potential under CO₂ shows roughly 50 mV potential difference between a fully immersed and a mounted electrode. Under CO₂, these surfaces are indeed stable (i.e., no surface reaction is observed). Steady-state potentials of both immersed and thin-film covered electrodes under CO₂ are given in Figure 3. Table 2 shows corrosion currents and potentials derived from log I-E plots. The data suggest a lower corrosion resistance for thin-film covered electrodes than for immersed electrodes. Stainless steel Type 316L has a lower corrosion resistance than Type 310. High nickel alloy has the lowest corrosion current among these materials.

| sample-(electrolyte) | immersed | immersed | thin-film covered | thin-film covered |
|----------------------|----------|----------|-------------------|-------------------|
| SS310-(Li/K)         | -1023    | 4.1      | -986              | 29.6              |
| SS316-(Li/K)         | -1040    | 23       | -981              | 40                |
| NKK-(Li/K)           | -991     | 3.5      | -878              | 5.9               |
| NKK-(Li/Na)          | -1058    | 1.2      | -970              | 5.1               |

When an O₂/CO₂ mixture is introduced at a partially immersed electrode, most surface reaction is observed on the top portion of the thin-film covered electrode.

The open circuit potential of a thin-film covered electrode under oxidizing gas mixture evolves toward the oxygen reduction potential quickly, i.e., within 2-3 hrs. Figures 4(a) and (b) show open circuit potential decay of stainless steel Types 310 and 316L. If the electrode is wetted by a thin film of carbonate, it easily forms a surface oxide (i.e. FeO and Cr₂O₃). An immersed electrode forms LiCrO₂ under a surface oxide layer. This inner LiCrO₂ layer cannot prevent iron from diffusing out through the outer surface oxide scale. Therefore, the OCP of the immersed electrode cannot reach oxygen equilibrium potential.

As the OCP of a film-wetted electrode evolves, electrolyte intensively moves around the wetted electrode. The forces that drive this movement are generated at the melt/oxide interface, but also appear to accelerate corrosion at the oxide/metal interface. If the thin film on the electrode is rich in lithium, this may affect long-term corrosion behavior because of the more basic character of the film. Due to the low oxygen solubility in the electrolyte layer and the smaller solid-state diffusivities in the alloy, oxygen diffusion from the gas-electrolyte-oxide interface to the metal-oxide interface is slow compared with iron diffusion from the bulk metal to the metal-oxide interface. Thus, the characteristics of the surface oxide layer play an important role. These considerations
also hold for the open circuit potential response of high-nickel alloys. Figures 4(c) and (d) show the potential-time behavior in Li/K and Li/Na electrolytes, respectively. Although, the potential change of thin-film covered electrodes are similar, immersed alloy samples show a response similar to pure nickel\(^4\). The response of thin-film wetted electrode upon changing oxidizing gas to CO\(_2\) is not explained yet.

**Cyclic voltammetry**

When the potential is swept repeatedly, the polarization response of the thin-film wetted electrode (FE) is a current increase without peaks. The overall response of an immersed electrode (IE) under CO\(_2\) gas and under oxidizing atmosphere (see Figure 5) does show distinct peaks. The potential window between 0 and -1600 mV contains several oxidation and reduction peaks. Thermodynamic potentials calculated with reference to the oxygen reduction potential under 67% O\(_2\)- 33% CO\(_2\) gas are given in Table 3. In the following discussion, expressions in parenthesis will refer to the electrochemical reactions in this table.

The most negative equilibrium potential of the elements forming the alloy is that of chromium, at approximately -1500 mV. Therefore, the first anodic oxidation peak when sweeping anodically from -1400 mV (following a previous cathodic sweep) is apparently due to carbon which may result from carbonate decomposition at such negative potentials, and Cr\(_2\)O\(_3\) formation at much more positive potentials than the metal equilibrium potential (C1). LiCrO\(_2\) can also form from chromium at the same potential as Cr\(_2\)O\(_3\) formation (C2). Next, iron, starts to be oxidized at a more positive potential than the stable thermodynamic potential (F1). Starting from oxidation of iron metal, current continuously increases by giving peaks. In the potential range of -900 mV, several reactions may take place simultaneously according to Table 3. Metallic iron can react to form lithiated iron oxide (F2) at -953 mV. Around the same potential, FeO is further oxidized to Fe\(_3\)O\(_4\) (F3). Since formation of Fe\(_2\)O\(_3\) from FeO occurs at -550 mV, LiFeO\(_2\) can only be formed from Fe or FeO. Nickel oxidation starts to occur around -800 mV (N1). Participation of nickel in the surface layer reaction depends on the amount of chromium. The potential necessary to cause lithiation of FeO to LiFeO\(_2\) is approximately -700 mV (F4). Since the very negative scan starting potential causes formation of LiCrO\(_2\). This can be oxidized to Li\(_2\)CrO\(_4\), which occurs at around -500 mV (C3). This peak is also contributed by lithiation of NiO[4].

Formation of Cr\(_2\)O\(_3\) or LiCrO\(_2\) surface layers is a very important step in building the corrosion protection characteristic of Fe-Cr-Ni alloys. Lithium chromite is probably less protective and does not prevent further internal oxidation. Cr\(_2\)O\(_3\) is preferable to protect the alloy from further being oxidized. Following the main peak at -500 mV, the current decreases until dissolution of chromium into the melt as CrO\(_4^{2-}\) takes place (C4). This process occurs with a lot of bubble formation and color change of the melt. The location of this peak is the same for Types 310 & 316L.
An anodic potential scan causes gas evolution from the surface only at potentials more positive than -600 mV. It is very likely that the anodic current peak above -600 mV is caused by an electrode process which causes CO₂ generation, for example (C3) or (C4).

Table 3: Equilibrium potentials calculated from thermodynamic data

| Potential, V | Reaction |
|-------------|----------|
| -0.1        | (O) 1/2O₂ + CO₂ + 2e⁻ → CO₃⁻ |
| -0.2        | (C4) LiCrO₂ + 2CO₃⁻ → Li⁺ + CrO₄²⁻ + 2CO₂ + 3e⁻ |
| -0.3        | (C3) LiCrO₂ + Li⁺ + 2CO₃⁻ → Li₂CrO₄ + 2CO₂ + 3e⁻ |
| -0.4        | (F5) FeO + Li⁺ + CO₃⁻ → LiFeO₂ + CO₂ + e⁻ |
| -0.5        | (F4) 2Fe₃O₄ + CO₂ → 3Fe₂O₃ + CO₂ + 2e⁻ |
| -0.6        | (N1) Ni + CO₂ → NiO + CO₂ + 2e⁻ |
| -0.7        | (F3) 2Fe₂O₃ + CO₂ → 3FeO + CO₂ + 2e⁻ |
| -0.8        | (F2) Fe + Li⁺ + 2CO₂ → LiFeO₂ + 2CO₂ + 3e⁻ |
| -0.9        | (C2) Cr + Li⁺ + 2CO₃⁻ → LiCrO₂ + 2CO₂ + 3e⁻ |
| -1.0        | (C1) 2Cr + 3CO₂ → Cr₂O₃ + 3CO₂ + 6e⁻ |
| -1.1        | (C) CO₃⁻ + 4e⁻ → C + 3O²⁻ |
| -1.2        | (F1) Fe + CO₃⁻ → FeO + CO₂ + 2e⁻ |

The reverse cathodic scan starts from 0 mV with carbonate formation (O) and possibly with chromate reduction if it is not removed from the surface. The alloys we are dealing with here consist of three different elements: nickel, chromium and iron, therefore, sometimes peaks related to the oxidation or reduction of two different elements may overlap with each other if their potentials are close. Also, a high valence oxide of iron may become a lower valence oxide at a potential anywhere between -600 to -1200 mV. Between peak (F3) and that assigned to LiFeO₂ (F2), the current is very flat over a range of approximately 400 mV. This may be caused by structural changes in the lattice. Removal of lithium or iron (if any higher valence oxide such as LiFe₂O₄ is formed) from the lattice structure reduces the magnitude of the current and keeps it constant until further reduction occurs. If the degree of delithiation does not exceed a certain level, nothing happens until the potential approaches -1100 to -1200 mV. The more clearly defined peak (F1) around -1100 mV is considered to be reduction of FeO and LiFeO₂ to metallic iron. At the end of the cathodic scan, a current increase is caused by metallic chromium formation and carbonate decomposition.
Optimal resolution of the peaks corresponding to various electrochemical reactions on Type 316L is obtained only at very slow scan rates opposite to type 310. As Figures 5 and 6 show, differences may be due to lower percentages of chromium and nickel in Type 316L.

High nickel alloys show fewer but more distinct peaks compared to stainless steels. These peaks are mainly Ni dominated. The current levels are also lower compared to stainless steels (Figure 7).

**Surface-layer analysis**

The possible layer products of Types 310 and 316L stainless steel have been determined by Yokokawa (5) from thermodynamic data. They depend on log $P_{CO_2}$, log($a_{CO_2}/a_{Fe}$) and log $P_{O_2}$. Yokokawa suggests a layer sequence of Cr/Fe$_2$O$_3$/LiCrO$_2$/LiFe$_2$O$_3$/K$_2$Cr$_2$O$_7$ for Type 310 and Fe$_2$Cr$_2$O$_3$/Fe$_2$O$_3$/Fe$_3$O$_4$/LiFe$_2$O$_3$/LiFe$_2$O$_3$ for Type 316L.

The corrosion layers found by cross-sectional analysis of Type 310 may be compared for the effect of carbonate contact on the formation of corrosion products. In the case where the electrode is fully immersed in the carbonate mixture, the most inner layer is mainly chromium oxide (positions D & H in Figure 8(a)). These areas are depleted in Fe and Ni. Chromium content gradually decreases from bulk metal to the metal/electrolyte interface. Since Fe diffuses to this interface to form a thick oxide surface layer, the layers below the surface are richer in Cr.

The thin-film wetted electrode forms a compact and thin layer of oxides. The layer thickness at the inner side close to the bulk melt (ceramic facing bottom part) is thicker than at the top which is only slightly wetted by carbonate (Figure 8(b)). Thin-film side which has had less contact with carbonate, shows spreading of chromium oxide at the metal/oxide interface. As electrolyte wetting becomes less and less toward the top of the electrode, this behavior is observed at both sides of the electrode.

Layers formed with a thin-film wetted configuration show concentration differences at the top and the bottom of the electrode, at the gas-facing as well as ceramic-facing side. At the bottom, the most outer layers are continuous and Cr and Fe rich. Below this, a region rich in Fe and Ni occurs. Between this layer and the metal/oxide interface, spreading of chromium oxide is observed. At the top, fewer layers can be distinguished by microprobe analysis. In both gas and ceramic-facing sides, the layer just below the surface is very rich in Cr. At the top of the sample, the overall thickness of the oxide layer becomes less. The more stronger wetted side (ceramic-facing) has a ~ 10% thicker oxide layer than the gas facing side. The thickness are given in Table 4.

Figures 9(a), (b), (c) and (d) show map analyses of oxide layers on thin-film wetted electrodes at the ceramic-facing side. An approximately 8 μ thick iron rich surface layer is observed (b). The region below that is about 6 μ thick and rich in chromium (d). The thickness of the most interior Cr$_2$O$_3$ layer is ~ 5 μ and consists mostly of Fe and Ni oxides. Open areas around the dark regions (a) are iron and nickel. Concentration profiles for immersed and thin-film covered electrodes are given in Figures 10(a), (b).
Table 4. Thickness of oxide layers

| condition            | thickness, μm | thickness, μm | thickness, μm |
|----------------------|---------------|---------------|---------------|
|                      | top           | middle        | bottom        |
| outer inner          | outer inner   | outer inner   | outer inner   |
| Thin-film wetted     | 13            | 15            | 14            |
|                      | 18            | 19            | 22            |
| Thin-film wetted     | spreading oxide | spreading oxide | spreading oxide |
| Immersed             | 31            | 25            |               |

Overall, immersed samples have much thicker oxide layers than thin-film wetted ones. In the thin-film wetted electrode configuration, layer thickness decreases from bottom to top as the thickness of the carbonate film decreases.

CONCLUSION

(1). The significant differences observed in this study between immersed and film-wetted electrodes, summarized in (3) and (4) below, suggest that half-cell studies have to mimic actual cell conditions to yield results that are useful for the improvement of materials and long-term performance of the MCFC. However, alloy composition is the primary factor concerning corrosion resistance.

(2). The OCP as well as CV characteristics are affected by the nickel and chromium content of ternary alloys:

(a) The observed OCP decay of alloys suggests that the higher the chromium and nickel content, the faster a protective layer forms. Type 310 stainless steel contains more chromium and nickel than Type 316L. This helps the formation of a more protective, continuous sub-scale. In Type 316L, iron may diffuse outward and break the thin Cr₂O₃ protective scale. Thereby, lithium may more easily diffuse into the alloy and Fe or Cr cations may diffuse toward the oxide/electrolyte interface, facilitating corrosion.

(b) Since the alloys consist of three or four different elements, CV peaks related to the oxidation or reduction of one element may overlap with oxides of the other two elements. This makes interpretation of CV's much more difficult than in pure-metal corrosion. Nevertheless, in combination with OCP and surface layer analysis, CV's can give insight in the sequence of corrosion processes.

(3). A compact(thin) and dual-structured oxide layer is required for good corrosion protection by any candidate material, and this is affected by the degree of wetting:

(a) The film-wetted alloy forms a much more compact layer, due to the passive surface oxide layer formed under high oxygen activity, than the same alloy immersed in a deep layer of carbonate. The corrosion layer thickness close to the bulk melt is thicker than at the top of the sample where it is only slightly wetted.

(b) One other distinction is that a surface contacting a thin carbonate film forms a spreading Cr₂O₃ layer while a deeply immersed surface forms a continuous inner layer of Cr₂O₃ much more slowly and less reliably.
The corrosion protection provided by the film wetted electrode is related to convection at the melt/oxide interface (via the meniscus) and to gas access (via the film):

(a) When Types 310 and 316L are wetted by a thin film of carbonate, the potentials of both alloys approach the oxygen reduction potential within a few hours. This is explainable by easy access of oxygen to the metal/electrolyte interface. A protective scale forms before lithium ions penetrate and can and take part in the corrosion process. When electrodes are fully immersed, the diffusion of lithium into, and cations (Fe, Ni and Cr ions) out of the alloy, overtakes the oxide layer formation process. Alloy inter-diffusion coefficients, therefore, are an important consideration in comparing and understanding the corrosion behavior of stainless steels and alloys.

(b) The lithium content of the electrolyte film appears to determine the corrosion rate by making the electrolyte film more basic. If porous oxide layers are filled with carbonates, it causes internal lithiation of oxide products. This process lowers the lithium concentration and increases potassium concentration. However, when the surface layer is stable and inner layers form a spinel, then these stable oxides do not allow lithium to diffuse into the inner structure. In this case, a gradual lithium gradient is established to a certain thickness. Beyond that critical thickness, oxides are not lithiated.

(5) These results suggest that pre-oxidation can be a solution to obtain a compact oxide layer. Adding Al to alloy leads to a very stable oxide layer, but increases its resistivity. Alloy behavior under continuously polarized conditions has to be investigated for more realistic corrosion predictions.

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Figure 1. Detail of cell and electrode configuration showing immersed and thin-film covered electrodes.

Figure 2. (a) Schematics of possible electrode configurations in the electrolyte: (1) fully immersed, (2) partially immersed and (3) thin-film wetted, (b) detail of partially immersed electrode configuration.
Figure 3. Steady-state polarization curves on (a) immersed and (b) thin-electrolyte-film covered electrodes. NKKI-K stands for (I)mmersed NKK alloy in Li-(K) carbonate, and NKKF-Na stands for (F)ilm-covered electrode in Li-(Na) carbonate electrolyte.
Figure 4. OCP response of stainless steel (a) 310, (b) 316L in Li-K electrolyte and high nickel alloy in (c)Li-K and (d) Li-Na electrolytes. Solid line: wetted electrode, dashed line: immersed electrode.
Figure 5. Polarization response of an immersed stainless steel Type 310 under 15% \( \text{O}_2 \)-30% \( \text{CO}_2 \)(solid line) and 100% \( \text{CO}_2 \)(dashed line) at 100 mV/s scan rate

Figure 6. Polarization response of immersed stainless steel Type 316 under 15% \( \text{O}_2 \)-30% \( \text{CO}_2 \)(solid line) and 100% \( \text{CO}_2 \)(dashed line) at 1 mV/s scan rate
Figure 7. Polarization response of immersed high-nickel alloy under 15% O₂-30% CO₂ (solid line) and 100% CO₂ (dashed line) at 100 mV/s scan rate in (a) Li-K, (b) Li-Na carbonate
Figure 8. Cross-section of (a) immersed and (b) thin-film covered SS 310
Figure 9. Map analysis on the (a) cross-section of thin-film covered Type 310 for (b) Fe, (c) Ni and (d) Cr
Figure 10. Concentration profiles at the cross-section of (a) immersed and (b) thin-film covered Type 310 stainless steel.