

Study of Corrosion behavior of the Separator for MCFC

Gwi-Yeol Kim^a

*School of Electrical Engineering, University of Ulsan,
San 29, Muger 2-dong, Nam-gu, Ulsan 680-749, Korea*

^aE-mail : gwiyeol@ulsan.ac.kr

(Received October 31 2007, Accepted December 7 2007)

The molten carbonate fuel cell has conspicuous feature and high potential in being used as an energy converter of various fuel to electricity and heat. However, the molten carbonate fuel cell which use strongly corrosive molten carbonate at 650 °C have many problem. Systematic investigation on corrosion behavior of stainless steels has been done 62 mole% Li₂CO₃ and 38 mole% K₂CO₃ melt at 923 K by using steady-state polarization method and electrochemical impedance spectroscopy method. It was found that SUS 310L and Al coating specimen may be the best choice among the alloys tested in this study for molten carbonate fuel cell component material.

Keywords : Fuel cell, Molten carbonate, Separator, Corrosion behavior

1. INTRODUCTION

A fuel cell is an electrochemical cell which can continuously convert the chemical energy of a fuel and an oxidant to electrical energy by a process involving an essentially invariant electrode-electrolyte system. Fuel cells work at high efficiency with emission levels far below the most strict standards[1,2].

Usually, molten carbonate fuel cell is operated around 650 °C, at which temperature the electrolyte is molten and serves as a good ionic conductor. One of the material problems is the severe corrosion of the metallic components, such as the separator[3-5]. This corrosion is recognized as hot corrosion: dissolution of metal into molten carbonate[6-8].

Corrosion has been a major problem in the historical development of molten carbonate fuel cell and understanding the corrosion behavior of metals in carbonate melts is essential to obtain a leading principle in development of corrosion-resistant metallic components for molten carbonate fuel cell technology[9,10].

The objectives of this study is to get the leading principal for developing the corrosion tolerable alloys for metal component materials of molten carbonate fuel cell.

This paper reports systematic studies of corrosion behavior of SUS304, SUS304L, SUS316, SUS316L, SUS310L alloys in 62 mole% Li₂CO₃ and 38 mole% K₂CO₃ melt at 923 K by using steady-state polarization method and electrochemical impedance spectroscopy method.

2. EXPERIMENTAL

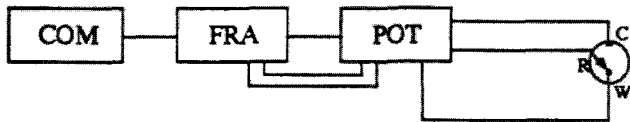
The eutectic mixture of 62 mole% Li₂CO₃ and 38 mole% K₂CO₃, so called eutectic in (Li+K)CO₃ melts, was used as a solvent. An electrochemical cell consisting of pure alumina products was placed in a silica cell container.

The whole assembly was placed in a vertical tube furnace regulated with a panel-mount digital temperature controller and a thermocouple. The regulation was ±1 °C and melt temperature were monitored directly with a thermocouple immersed in the melts. Measurements were carried out after establishing equilibrium with respect to gas compositions and temperatures. The gas was bubbled into the melt for at least 5 h after the melt temperature reached a steady value.

The working electrodes were fully immersed flag-type electrodes with a geometric surface area of 1.0 cm².

SUS304, SUS304L, SUS316, SUS316L, SUS310L and coated specimens were tested in the study. All test pieces were vacuum-annealed at 1,123 K for 12 h and polished to mirror finish with fine alumina powder. The reference electrode compartment containing a thick gold wire(1 mm diameter) with a pin hole which acted as a junction to the bulk melt. The corrosion products formed in the melt were analyzed by an XRD(Shimadzu XD610).

Impedance measurements were carried out at the rest potential using Solartron 1250 in a frequency range from 0.1 Hz to 10 kHz, and analyzed by the non-linear parameter fitting based on the Simplex method with the postulated equivalent circuit using the frequency response



COM:computer, FRA:frequency response analyzer
 POT:potentiostat, R:reference electrode
 W:working electrode, C:counter electrode

Fig. 1. Schematic diagram of the impedance measurements.

of potentiostat at high frequency end and by the low reliability of the data at lower frequency end. Figure 1 shows experimental device.

3. RESULTS AND DISCUSSION

Figure 2, Fig. 3, and Fig. 4 shows the steady state polarization curves of SUS 316, SUS 316L and SUS 310L in (Li+K)CO₃ at 923 K.

When the Ni or Cr contents were increased. E_{corr} were shifted to anodic and i_{corr} were decreased. Clearly, the corrosion stability of iron were improved by the Ni or Cr addition.

Thus determined i_{corr} were summarized in Fig. 5 as a function of Ni, Cr contents and coated specimens. In both cases, the i_{corr} decreased with increasing Ni or Cr contents and coating Al. The corrosion resistivity depends on the stability and compactness of corrosion product layer at the metal surface.

According to the X-ray diffraction measurement of corrosion product layer. the main product of Fe-based alloys were found to be Li₂Fe₃O₄.

When Ni and Cr were added, NiO and LiCrO₂ were formed with Li₂Fe₃O₄ in the corrosion product layer. Thus, it was concluded that NiO and LiCrO₂ were more stable than Li₂Fe₃O₄. in molten carbonate, and these oxides of second additives improved the corrosion resistivity of Fe-based binary alloys. It is well known that the most stable oxide in molten carbonate is LiAlO₂, so that it may be possible to improve the corrosion resistivity further by adding Al.

In case of steady state polarization, it is necessary to apply large overpotential to obtain i_{corr}. This may introduce the unrecoverable damages to the corrosion product layer at metal/electrolyte interface.

On the other hand, the impedance spectra method uses the small amplitude of nominal 5 mV rms at the rest potential which corresponds to the E_{corr} in this cases, this may enables us to obtain i_{corr} without any damaging to the corrosion product layer.

Furthermore, it may be possible to obtain the structural information of the corrosion product layer if the wide band Impedance Spectra is analyzed properly.

Therefore, the analysis of impedance spectra of the corrosion impedance of these alloys were also carried out.

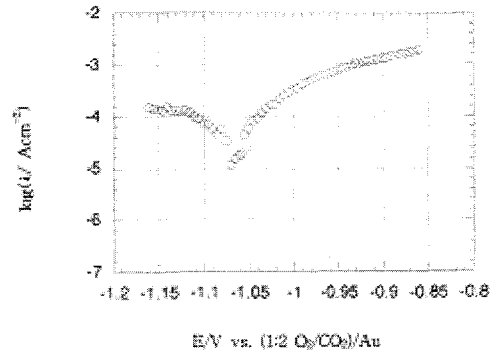


Fig. 2. Steady state polarization curves of SUS 316.

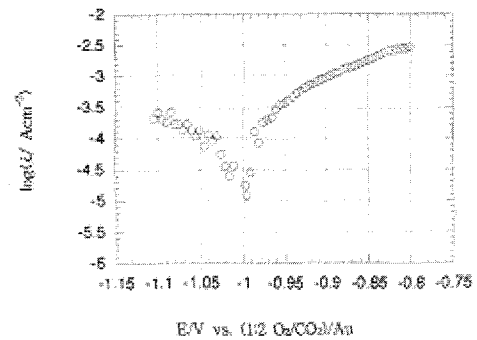


Fig. 3. Steady state polarization curves of SUS 316L.

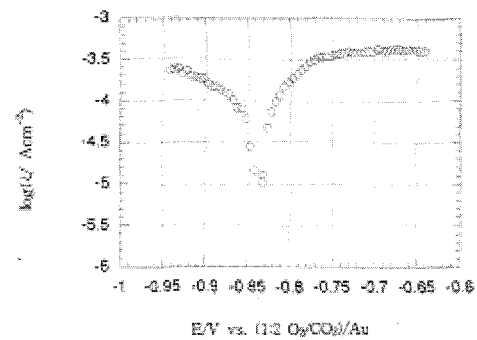


Fig. 4. Steady state polarization curves of SUS 310L.

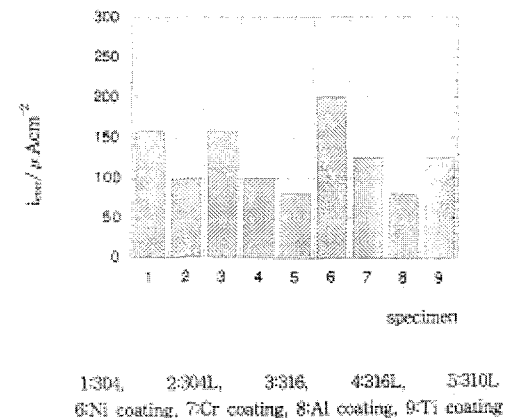


Fig. 5. Corrosion current characteristics of the specimens.

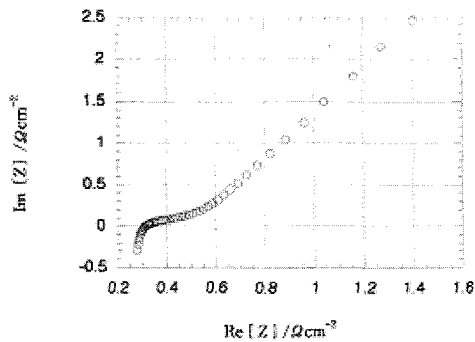


Fig. 6. EIS Spectra of SUS 316L.

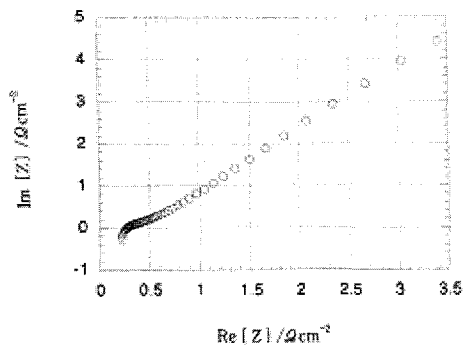


Fig. 7. EIS Spectra of Al coating specimen.

Figure 6 and Fig. 7 show the impedance spectra of the corrosion impedance of SUS 316L and Al coating specimen in (Li+K)CO₃ melt at 923 K. Frequency range was 1 Hz to 60 kHz with equally divided to 10 point per decade.

The corrosion impedance increased with increasing Ni or Cr contents.

However, we could not obtain any clear semi-circular arc and diffusion like impedance in these plots.

This may be attributed to the complicated structure of corrosion products layer. The metal surfaces covered with thin film of its oxide if the metal is exposed to the corroding environment. If this surface film is compact and stable enough to cover the metal surface perfectly, the corrosion rate or corrosion current is very small because this surface film works as corrosion protective layer.

4. CONCLUSION

The corrosion behavior of iron based alloys has been investigated using steady-state polarization measurements and electrochemical impedance spectroscopy in (62+38)mole% (Li+K)CO₃ at 923 K under a pure CO₂.

As a conclusion, SUS 310L and Al coating specimen may be the best choice among the alloys tested in this study for molten carbonate fuel cell component material from the view point of both corrosion resistance and the conductance of the corroded scale.

REFERENCES

- [1] K. Kordesch and G. Simader, "Fuel Cells and Their Applications", VCH Publishers. Inc., p. 9, 1996.
- [2] W. Vielstich, A. Lamm, and H. A. Gasteiger, "Handbook of Fuel Cells", John Wiley & Sons., p. 905, 2003.
- [3] F. Zenith and S. Skogestad, "Control of fuel cell power output", Journal of Process Control, Vol. 17, p. 333, 2007.
- [4] A. J. Bard and L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications", John Wiley & Sons, New York, p. 120, 1980.
- [5] J. R. Macdonald, "Impedance Spectroscopy, Emphasizing Solid Materials and Systems", John Wiley & Sons, p. 54, 1987.
- [6] Leo J. M. J. Blomen and Michael N. Mugerwa, "Fuel Cell Systems", Plenum, p. 465, 1993.
- [7] N. Q. Minh and T. Takahashi, "Science and Technology of Ceramic Fuel Cell", Elsevier, p. 147, 1995.
- [8] A. J. Appleby, "Fuel Cell Technology: Status and Future Prospects", Energy, Vol. 21, p. 521, 1996.
- [9] US Department of Energy, "Fuel Cell Handbook", John Wiley & Sons, 5th edition, p. 110, 2000.
- [10] T. Fukui, H. Okawa, S. Oharaand, and M. Naito, "Performance of NiO cathode covered with LiCoO₂ for MCFC", 2000 Fuel Cell Seminar, p. 215, 2000.