The Behavior of Dissolved Elements in the Electrolyte of the Molten Carbonate Fuel Cell

Hidekazu KASAI*, Yumi HAYAKAWA, Hidemi UKAI and Shiro YAJIMA

Received December 21, 1995 ; Accepted March 22, 1996

In a molten carbonate fuel cell, some substances deposit in an electrolyte plate during long-term operation. We have been investigating such deposits over the past few years. Major elements contained in the deposits have been identified as Ni and Cr. The amounts of these elements increased with operating time. Ni dissolves from the cathode as nickel ion and is reduced to form metallic particles. On the other hand, Cr dissolves from the surface of cell parts such as the current collector and corrugate plate in the cathode side and deposits in an electrolyte plate as a Cr compound. Both substances deposit to form a layer in the electrolyte plate. The layer containing the Ni deposit and the layer containing the Cr compound are separated. The former layer is close to the anode in the electrolyte plate where the fuel concentration is high. Furthermore, the Cr compound layer is between the cathode and Ni deposit layer. From an XPS analysis, the valency of the Cr is different between the Cr compound in the electrolyte plate and that in the source materials such as Cr_2O_3 and K_2CrO_4 . It is considered that the Cr compound dissolving in the electrolyte plate is reduced and deposits as different chromate salts. According to the long term operation and the deposition mechanisms, it is estimated that these depositions are not limited in amount.

1 INTRODUCTION

The stability of the components in a molten carbonate fuel cell (MCFC) is the most important parameter for achieving long cell life. After more than ten thousand hours of operation, some substances significantly dissolve into the electrolyte plate which causes loss of cell performance.

For example, NiO, which is the standard material of an MCFC cathode, dissolves in the electrolyte plate as nickel ion and deposits as metal particles. The micro and macro structures of the cathode change and the cathode's performance then deteriorates. Furthermore, it is thought that Ni particles form an electrical shunt between the anode and the cathode. This shunt causes electrical shorting.

This phenomenon has been reported ^{1,2)}.

We have been analyzing the components of an MCFC after long-term operation. For almost all cases, Ni and Cr have been identified in addition to the initial elements in the electrolyte plate. The amount of these elements increases with operation time. Furthermore, the deposition state changes with the cell operating conditions such as temperature and gas composition.

We reported ^{3,4)} the behavior of Ni deposition in the electrolyte plate. However, the behavior of the deposition compound containing Cr has not yet been reported and has not yet been discussed. In this paper, we describe the states of the compounds containing Cr in the electrolyte plate and the correspondence between Ni and the compound containing Cr upon the deposition in the electrolyte plate.

2 EXPERIMENTAL AND ANALYSES

2.1 Cell components The molten carbonate

Ishikawajima-Harima Heavy Industry Co., Ltd.

(1-15, Toyosu 3-Chome, Koto-KU, Tokyo, 135, Japan)

Key words : Molten carbonate fuel cell, Nickel, Chrome, deposition,

fuel cell consists of an anode, a cathode, an electrolyte plate and a separator or a holder. Both electrodes have a porous structure for the electrochemical reaction. The separator or holder has two roles. The first one is to distribute fuel gas and oxidization gas to each cell. The second one is to conduct electrical current. The schematic cross section of the MCFC is shown in Fig. 1.

Fig.1 Schematic cross section at view of a cell .

From the point of view of materials, the cathode is made of nickel oxide and the anode is made of Ni-8%Cr alloy. The electrolyte plate is made of lithium aluminate and a carbonate mixture. The holder and the separator are mainly made from stainless steel such as SUS310S and SUS316L. Ni is partially used for the active area in the separator where the fuel gas flows and electrical current flows.

The specifications of the cell components are shown in Table 1. The electrode area of the cells change from 100 cm² to 1 m².

2.2 Cell operation The operating conditions of the cell are shown in Table 2. In the case of a small cell, temperature is nearly uniform across

the cell. On the other hand, in the case of a large size cell, temperature is not uniform in the cell. The operating temperature ranges from 863K to 1023K in the case of a bench scale cell test. As usual in a large size cell, temperature in the gas inlet side of the cell is controlled within 830K to 860K while the temperature in the gas outlet side of a cell is controlled within 930K to 960K.

Table 1 Specifications of cells .

component	material	thickness (mm)	porosity (%)
holder separator	SUS310S or SUS316L Ni or SUS310S		
anode	Ni+8%Cr	0.7 ~0.8	50~60
electrolyte plate	LiAlO2 +Li2CO3 / K2CO3 (62/38 or 70/30)	0.9 ~1.1	55~60
cathode	NiO (in-situ type)	0.7 ~0.8	60~70

Table 2 Operating conditions of a cell .

anode gas	H ₂ /CO ₂ /H ₂ O = 67/17/17
cathode gas	Air/CO ₂ = 70/30
temperature	590°C ~ 750°C
current density	150mA/cm ²

The gas flow configuration is a co-flow type. The longest operating time of such cells is over 20000 hours. The operation pressure is usually kept constant and ranges from 1 atm to 5 atm.

2.3 Analysis methods The Ni and Cr concentrations in the electrolyte plate were measured by atomic absorption analysis. A cross section of the electrolyte plate was observed using a microscope and was analyzed by EPMA. Surfaces of the separator and holder were analyzed using the X-ray diffraction method.

In order to analyze the surface of the cell components, we used two types of XPS (ESCA). One (SHIMAZU ESCA650B) analyzes a wide surface area of a sample at one time. The other analyzes a spot surface of a sample and can move the measurement spot. Both analyzers use Mg-K α as the X-ray source and can clean the sample surface using Ar-etching.

3 RESULTS AND DISCUSSION

3.1 Amount of Ni and Cr in the electrolyte

3.1.1 Effect of operating time The amount of nickel and chrome increases with the operating time as shown in Fig. 2 and Fig. 3. These increasing curve were found not to be linear with time. According to the results obtained after a long operating time, the amounts of both depositions were considered not to attain saturation.

Fig. 2 Change of the Ni amount with time

3.1.2 Effect of temperature The effect of temperature on the amounts of Ni and Cr deposits are different. From the investigation of the effect of operating cell temperature, the amount of Ni deposition decreases with an increase in cell temperature while the amount of Cr compound increases with an increase in cell

temperature as shown in Fig. 4.

Fig. 3 Change of the Cr amount with time

Fig. 4 Change of the amount of deposition in the electrolyte with temperature after 500 hours operation at 100cm cell.

The dissolution rate of a cathode is considered to change with the concentration of Ni²⁺ ion in the carbonate mixture. The relationship between cell operating temperature and the amounts of Ni deposition is considered to be due to the equilibrium solubility of NiO, which decreases with an increase temperature in the carbonate mixture^{5,6}.

The solubility of Cr₂O₃ in the carbonate increases with an increase in temperature. The dependence of the amount of deposited Cr compounds is considered to be due to this solubility behavior.

3.2 State of deposits

3.2.1 Figure of deposits The optical micrograph of a typical cross section of the cell is shown in Fig. 5. A layered structure parallel to the electrode appeared in the electrolyte plate. A yellow or brown layer was observed near the cathode. Next to this layer, we found a layer of metallic particles. From EPMA measurements, it was determined that the yellow or brown layer contains Cr and the metal particles are made of Ni. The distribution of Ni, Cr and Al in the electrolyte plate was determined by the scanning EPMA measurement as shown in Fig. 6.

Fig.5 Optical microphotograph of the electrolyte plate cross section after testing

The distributions of Ni and Cr are distinctive. Considering the solubility of Ni in the carbonate mixture, it is thought that almost all Ni in the electrolyte plate forms metallic particles. On the other hand, the Cr compound forming particles were not observed using the optical microscope. The diameter of the Ni particles was mainly several tens of using micron, and large grains containing several particles were recognized.

Fig.6 Result of EPMA at the cross section of the electrolyte plate

Fig.7 Location and outline of the deposition layers in the electrolyte plate obtained from the result of EPMA. Cross sectional view along a gas flow. Limit of Ni deposit ; (■), and order between Ni and Cr; (□))

3.2.2. Position of deposit layer The positions and thickness of these layers in the electrolyte plate are not similar in the cell. We observed these layers along the electrolyte plate using EPMA. The schematic diagram of the cross sectional layer structure state in the electrolyte plate is shown in Fig. 7.

For the area near the gas inlet, the layer containing nickel particles is far from the anode and particles are scattered in a narrow region. On the other hand, in the area near the gas outlet, the layer of nickel particles is close to the

anode, and particles are scattered over a wide region. This distribution of Ni particles have been usually observed in other cells regardless of cell size.

The concentration of H_2 in the fuel gas is lower at the outlet than at the inlet because of the consumption of H_2 during the anode reaction. Also, the change in the concentration of oxidative gas is similar. A reductive-oxidative potential in the electrolyte plate is considered to change both with the H_2 concentration and oxidative gas concentration.

It is considered that the appearance of the layer containing Ni particles corresponds to the reduction potential and its gradient in the electrolyte plate and the amount of Ni deposit is proportional to the amount of dissolved Ni ion. Furthermore, the Ni dissolution rate is affected by the CO_2 partial pressure in the cathode gas.

According to the above mentioned scheme, the reductive and oxidative potentials in the layer containing the Cr compound is considered to be located in the more oxidative atmosphere than the layer containing the Ni deposit.

The appearance of both the Ni deposit layer and the layer containing the Cr compound deposits are schematically shown in Fig. 7.

3.3 Result of XPS

3.3.1 Measurement of XPS In order to identify the Cr compound, we use two types of XPS as mentioned in the following paragraph. Because the samples have a rough surface and are covered with carbonate, we treated these surfaces with Ar-etching from 20 minutes to 120 minutes to make the XPS peak of Cr distinctive and to stabilize its position among the spectra. However, the binding energy values of the $Cr_{2p_{2/3}}$ peak identified in the spectra using

two XPS systems are different. One reason for this effect is the charging on the sample's surface.

Because there is much noise in both spectra, the $Cr_{2p_{2/3}}$ peaks could not be treated for peak resolution by curve fitting. It appears that each peak consists of a single peak.

3.3.2 Wide area measurement A sample of the electrolyte plate attached to the anode was divided in the middle of the electrolyte plate as shown in Fig. 8. The two surfaces were measured by XPS. One is the anode and the other is that of the dividing interface.

Fig. 8 Value of $Cr_{2p_{2/3}}$ peak of the Cr compound from XPS (wide area) and values of the reference samples in the literature.

From the results of elemental analysis and X-ray diffraction, Cr compounds identified on the cell parts of the cathode side are Cr_2O_3 and K_2CrO_4 . Also, it was identified the Cr compounds in the anode are $LiCrO_2$ and Cr_2O_3 . $LiCrO_2$ is formed by the reaction of Cr_2O_3 and Li_2CO_3 . The XPS peak of the Cr compound from the surface of the anode is estimated to be that of $LiCrO_2$ because all the Cr_2O_3 on the surface reacts with Li_2CO_3 to form $LiCrO_2$.

The binding energy value of the Cr_{2p2/3} peak identified from XPS of the anode agrees with that for LiCrO₂ in the literature⁴⁾. There is about a 3eV gap between the Cr_{2p2/3} peak of K₂CrO₄ (Cr⁺⁶) and LiCrO₂ (Cr⁺³) in the same report. As for the XPS data obtained from the dividing interface, the binding energy value of the Cr_{2p2/3} peak is close to that of LiCrO₂. However, it is slightly bigger than that identified for the anode surface. The relation of these binding energy values are shown in Fig. 8.

Fig. 9 Value of Cr 2p_{2/3} peaks at several positions in the electrolyte plate from XPS (spot).

3.3.3 Spot measurement XPS spot measurements were done on the cross section of the cell as shown in Fig. 9. The binding energy of the Cr_{2p2/3} peak changes within about a 1.5eV difference. The binding energy values of the Cr peak from the electrolyte plate are lower than the that from anode which is about 576eV. This difference is similar to the result observed using the wide area XPS as mentioned in the previous section. These binding energy values were obviously different from that for K₂CrO₄.

3.4 Mechanism of deposition

3.4.1 Nickel particles The source of Ni is

mainly the NiO of the cathode. NiO dissolves in the carbonate as Ni²⁺ ion. This process is explained as follows.⁸⁾

The dissolving nickel ion diffuses from the cathode to the anode in the electrolyte, and is reduced as metallic particle by hydrogen that diffuse from the anode.

3.4.2 Chrome compounds It is clear that the source of Cr is mainly the corrosion layer of the parts on the cathode side such as the current collector. From the post-test analysis, the Cr content of the anode does not change and from the mass balance of Cr among the anode, the cathode and the electrolyte plate, the total amount of Cr exceeds that of the initial value. The surface of the stainless steel used for the cathode side parts are covered with a chrome oxide film (Cr₂O₃). This oxide reacts with carbonate and form M₂CrO₄ (M=Li,K) under the cathode gas conditions. The reaction is as follows.

Also chromate ion might be reduced by hydrogen that diffuses from the anode.

According to Hsu's phase diagram⁹⁾ for chromate-carbonate, it is considered that M is mainly K under the cathode gas conditions. From our analytical results, almost all chromate compounds on the active area of the cathode side parts were recognized to be K₂CrO₄. This chromate dissolves into the carbonate through

the cathode and diffuses from the cathode to the anode. Along with this diffusion, the valence of chrome might change from Cr^{6+} to Cr^{3+} in the electrolyte plate, because the equilibrium partial pressure of O_2 in the electrolyte plate decreases as it approaches the anode. According to Hsu's phase diagram, under the cathode gas conditions, K_2CrO_4 is stable, and under the anode gas conditions, LiCrO_2 is stable.

The Cr compound forming layer in the electrolyte plate is not still identified. This compound obviously differs from K_2CrO_4 .

4 CONCLUSIONS

Two elements, Ni and Cr, accumulate in the electrolyte plate of a molten carbonate fuel cell during its long-term cell operation. Ni deposition and Cr compound deposition form a layer in the electrolyte. The two layers are separate on the electrolyte plate. The location and the outline of the two layers in the electrolyte plate reflect the reductive and oxidative atmospheres in the electrolyte plate.

The Cr compound-forming layer in the electrolyte plate has not been identified. The valency of Cr differs from 6 or 3 based on an XPS analysis.

The protection of the dissolution of the cell components and the deposition in the electrolyte plate are an important concern for making a long life cell. It is necessary to clarify these phenomena for the commercialization of a molten carbonate fuel cell.

This work has been conducted under a contract from NEDO (New Energy and Industrial Technology Development Organization) and MCFC Research Association (Technology Research Association for Molten

Fuel Cell Power Generation System) as part of the New Sunshine Program of MTTI (Ministry of Industrial Trade and Industry). We appreciate their advice and support.

REFERENCES

- 1) H.R.Kunts and J.W.Pandolfo, *J. Electrochem. Soc.*, **139**, 1549 (1992).
- 2) Y.Mugikura, T.Abe, S.Yoshioka and H. Urushibata, *J.Electrochem.Soc.*, **142**, 2971 (1995).
- 3) H.Kasai, A.Suzuki and S.Sato, *NIKKA*, **8**, 1345(1988).
- 4) H.Kasai and A.Suzuki, *Proc.THIRD INTERNATIONAL SYMPOSIUM ON CARBNATE FUELCELL TECHNOLOGY*, 1993, ISBN 1-56677-072-6.
- 5) K.Ota, T.Shinjo and N. Kamiya, *Denki Kagaku*, **55**, 327(1987).
- 6) K.Ota and N.Kamiya, *J.Electrochem.Soc.*, **139**, 667 (1992), March 1992.
- 7) J.F.Moulder, W.F.Stickle, P.E.Sobol, K.D.Bomben, "*Handbook of X-ray Photoelectron Spectroscopy*", Perkin-Elmer(1992).
- 8) C.E.Baumgartner, *J. Am. Ceram. Soc.*, **69**, 162 (1986).
- 9) H.S.Hsu, J.H.DeVan, and M.Howell, *J.Electrochem.Soc.: Electrochemical Science and Technology* **134**, 2146 (1987).