Polarization Phenomena at β"-Alumina/Molten Salt Interface

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Abstract

The polarization at the interface between β"-alumina solid electrolyte and AlCl3-NaCl melt has been studied at 473 K by ac impedance spectroscopy, using cells equipped with a β"-alumina disk. Impedance spectra at the interface were observed at frequencies lower than 400 Hz. The melt composition influences a little on the impedance spectra in the cell with a dried β"-alumina disk. The damped surface of the β"-alumina obstructs the movement of sodium ions from the melt into the damped layer of the β"-alumina. The damped layer induces quite high polarization at the interface, when the acidic melt is utilized.

Introduction

Sodium batteries designated as sodium/β"-alumina/molten salt have been studied for electric vehicle and load leveling applications. Several kinds of this type batteries were proposed such as Na/SbCl3(1), Na/SCl4 (2,3), Na/SeCl4 (4–7), Na/NiCl2(8,9), Na/FeCl2 (10). These cells usually utilize AlCl3–NaCl melts. The pretreatment of the β"-alumina often influences on the charge–discharge behavior of these cells, especially when the acidic chloroaluminate melt is utilized.

The polarization at two interfaces, between β"-alumina and liquid sodium and between β"-alumina and the molten salt, should be reduced to improve the charge and discharge properties (11–13). In this paper, the effects of the surface conditions of β"-alumina and the acidity of molten salt have been studied by ac impedance spectroscopy to clarify the polarization mechanism at the interface between β"-alumina and AlCl3–NaCl melts.

Experimental

An experimental cell, type-I, composed of Pyrex glass compartments filled with AlCl3–NaCl melts as shown in Fig.1. Two identical compartments were separated by means of a Li2O–doped β"-alumina disk (16 mm diameter and 2 mm thickness) produced by Mitsubishi Heavy Industry Company. The β"-alumina disk was sealed with Schott 8338 glass, of which the expansion coefficient is similar to that of β"-alumina.
The sealed $\beta''$-alumina disk was connected to Pyrex glass with two kinds of sealing glass tubes. Each compartment was equipped with a whirlpool aluminum electrode, which was located at a distance of ca. 6 mm from the $\beta''$-alumina surface. This cell was washed with organic solvents in an ultrasonic cleaning equipment, and was dried under vacuum at 723 K for one week prior to use. Another cell without the $\beta''$-alumina disk, type-II, was used to study the electrode reaction of aluminum. This cell was equipped with a 99.999% pure aluminum microelectrode as the working, a coiled aluminum wire as the counter and an aluminum reference electrode.

Melt preparation and most experimental procedures have been described previously (6,7). Impedance spectrum was measured in frequency range from 0.1 Hz to 100 kHz by using a Solatron Instruments Model 1260 impedance/gainphase analyzer, Model 1287 potentiostat, and a Toyo Technica CAP-1 electrochemical software. The impedance data were recorded and analyzed with a NEC Model PC-9801 personal computer.

RESULTS AND DISCUSSION

Impedance Spectra at $\beta''$-Alumina/Molten Salt Interface

A well-defined impedance spectrum could be measured with the type-I cell. Figure 2 depicts typical spectra for the cell containing basic AlCl$_3$–NaCl melts in both compartments. The current density is calculated as a value for unit surface area of the $\beta''$-alumina disk. The impedance spectrum consists of two overlapped arcs; i.e., arcs–A and –B in Fig.2. The value of dc bias influence little on the arc–A. On the other hand, the higher the current flows, the smaller the size of the arc–B becomes. Considering the cell configuration, an equivalent circuit for this cell, as shown in Fig.3, consists of the aluminum electrode impedance, the melt resistance $R_m$, the impedance at $\beta''$-alumina/molten salt interface $Z_v$ and the $\beta''$-alumina impedance caused by grain boundary $Z_{gb}$ and grain bulk $Z_b$. It was reported that the impedance of the grain boundary and grain bulk of the $\beta''$-alumina appeared at quite high frequency such as several MHz (14). Therefore, the arc–A and arc–B in Fig.2 correspond to the electrode reactions of aluminum electrodes and the interfaces between $\beta''$-alumina and molten salt.

The impedance spectra for the aluminum electrode reaction in the basic AlCl$_3$–NaCl melts were measured by using the $\beta''$-alumina–free cell (type-II), in order to separate it from the impedance at the interface. A typical Nyquist plot for the aluminum deposition displays a quite small arc–C at high frequencies and a large arc–D at low frequencies as shown in Fig.4. The impedance spectrum for the anodic dissolution of aluminum is similar to that for the deposition. The time constants for these circles were compared, in order to separate the impedance at the $\beta''$-alumina/melt interface from that of the aluminum electrode reactions. The time constant was estimated by complex nonlinear least squares fitting (15). In this study we assume that a depressed arc is caused by a simple parallel circuit consisting of resistance and constant–phase element (CPE). The time constant of the arc–A in Fig.2 is $7.8 \times 10^{-5}$
s\(^{-1}\), that is similar to \(9.9 \times 10^{-5} \text{ s}^{-1}\) for the arc-C in Fig.4. These results on the time constant suggest the arc-A observed at high frequencies in the type-I cell correspond to the electrode reactions of aluminum. The depressed shape of the arc-C indicates that the rate-determining step may be the charge transfer.

Comparing the impedance spectra at frequencies lower than 10 Hz, the arc-B in Fig.2 is different from the arc-D in Fig.4. The straight-like shape of the arc-D suggests the diffusion process in the electrochemical reaction of aluminum. Therefore, we can conclude that the arc-B corresponds to frequency response from the interface between \(\beta''\)-alumina and molten salt. It should be, however, noticed that the arc-B involves somewhat the influence of the electrode reaction of aluminum. In the later discussion, the arc-B with dc bias of 0.5 mAcm\(^{-2}\) will be used as the reference spectrum to investigate the effects of the melt composition and wet surface of \(\beta''\)-alumina.

**Effects of Melt Composition**

Figure 5 depicts the impedance spectra measured in a type-I cell, in which the melt of one compartment was replaced by 63/37 AlCl\(_3\)-NaCl. The positive current in this figure indicates that sodium ions migrate from the acidic to the basic melt. The radius of the arc-B at low frequencies becomes short by replacing the melt to be acidic, although the arc-A at high frequencies changes little. This tendency becomes clearer as shown in Fig.6, when both compartments are filled with the 63/37 melt. These results suggest that sodium ions can move easily from the acidic melt to the \(\beta''\)-alumina and vice versa, comparing to the case of the NaCl saturated melt. Weak Coulomb's force between sodium ion and Al\(_2\)Cl\(_7\)\(^-\) ion may cause the easier transfer of the sodium ion at the interface.

**Effects of Water on \(\beta''\)-Alumina**

It is known that the cell resistance becomes quite high especially at charging in sodium/acidic molten salt cells, when moisture remains on the surface of the \(\beta''\)-alumina. Figure 7 depicts the typical impedance spectra measured in the type-I cell with wet \(\beta''\)-alumina. The real axis in this figure is compensated to zero to simplify the comparison of the results. One side of the well-dried \(\beta''\)-alumina disk in the cell was exposed to the atmosphere for three days, before loading the melt. The positive current in this figure indicates that sodium ions migrate from the damped surface to the dried one in the \(\beta''\)-alumina. The impedance spectrum at the interface depends on the current direction in this cell containing the NaCl saturated melt. The positive current increases the impedance at low frequencies, whereas the arc-B obtained with the opposite direction of the current is similar to the results for the dried \(\beta''\)-alumina. The moisture adsorbed on the \(\beta''\)-alumina surface clearly obstructs the movement of sodium ions from the basic melt into the damped layer of the \(\beta''\)-alumina.

The effects of the damped layer were studied by using the cells washed with water. Figures 8 and 9 show the impedance spectra with these cells containing the basic and acidic melts, respectively. Although the cells were dried under vacuum at
723 K, the polarization became higher in both cells. These figures, however, suggest that the influence of the damped surface depends on the melt composition. While the impedance spectrum changes little with time in the cell containing the NaCl saturated melt, the damped surface layer of β"-alumina induces an increase in the polarization with time for the cell containing the acidic melt. Therefore, the effect of water adsorbed on or absorbed in β"-alumina induces high polarization in the cell utilizing the acidic AlCl₃-NaCl melt. The mechanism of this difference of melt acidity should be studied in future.

CONCLUSION

The drying of β"-alumina is quite important to reduce the polarization at the β"-alumina/AlCl₃-NaCl melt, especially when the cell utilizes an acidic melt. The damped surface of the β"-alumina obstructs the movement of sodium ions from the melt into the solid electrolyte.

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REFERENCES

1. A. M. Chreitzberg, J. W. Consolloy, M. R. Manning and J. C. Sklarchek, J. Power Sources, 3, 201 (1978).
2. G. Mamantov, R. Marassi, M. Matsunaga, Y. Ogata, J. P. Wiaux and E. J. Frazer, J. Electrochem. Soc., 127, 2319 (1980).
3. J. Caja, T. D. J. Dunstan and G. Mamantov, Proc. 36th Power Sources Conf., p.337 (1994).
4. M. Matsunaga, K. Kitagawa and K. Hosokawa, Denki Kagaku, 51, 847 (1983).
5. M. Matsunaga and K. Hosokawa, Yoyuen (Molten Salts), 30, 83 (1987).
6. M. Matsunaga, T. Gouda, R. Otogawa and K. Hosokawa, Nippon Kagaku Kaishi, 8, 1466 (1988).
7. M. Matsunaga, M. Morimitsu, S. Obata, K. Hosokawa, K. Rikihisa and K. Adachi, J. Electrochem. Soc., 141, 2413 (1994).
8. J. Coetzer, J. Power Sources, 18, 377 (1986).
9. R. C. Galloway, J. Electrochem. Soc., 134, 256 (1987).
10. R. J. Wedlake and A. R. Tilley, Bull. Electrochem., 4, 41 (1988).
11. M. W. Breiter, B. Dunn and R. W. Powers, Electrochim. Acta, 25, 613 (1980).
12. D. S. Demott, J. Electrochem. Soc., 127, 2312 (1980).
13. A. Katagiri, J. Hvistenedahl, K. Shimakage and G. Mamantov, J. Electrochem. Soc., 133, 1281 (1986)
14. A. Hooper, J. Phys. D: Appl. Phys., 10, 1487 (1977).
15. J. R. Macdonald, Impedance Spectroscopy, pp.16-20, pp.180-182, John Wiley & Sons, New York (1987)

Fig.1 Typical geometry of an experimental cell (type-I).

Fig.2 Impedance spectra at 473 K for the type-I cell containing basic melts. AC amplitude is 53 μAcm⁻².

Fig.3 The equivalent circuit of the type-I cell shown in Fig.1.
Fig. 4 Impedance spectrum for the deposition of aluminum in a NaCl saturated melt at 473 K.

Fig. 5 Impedance spectra by replacing the melt of one compartment to 63/37 AlCl₃-NaCl in type-I cell.

Fig. 6 Effects of the melt composition on the impedance spectrum.
dc bias
- 0.5mA cm$^{-2}$ for dried $\beta''$-alumina
- 0.5mA cm$^{-2}$ for wet $\beta''$-alumina
- -0.5mA cm$^{-2}$ for wet $\beta''$-alumina

Fig. 7 Dependence of the direction of dc current direction on impedance spectra, when the one side of the $\beta''$-alumina disk contains water.

- 1Hz
- 0.1 Hz

Fig. 8 Effects of the damped surface of the $\beta''$-alumina on the impedance spectra. Melt composition is NaCl saturated melt

- 1st (after 0.96 ks)
- 2nd (after 0.60 ks)
- 3rd (after 7.08 ks)
- 4th (after 8.40 ks)
- 5th (after 9.84 ks)

Fig. 9 Effects of the damped surface of the $\beta''$-alumina on the impedance spectra. Melt composition is 63/37.