The Anodic Behaviour of Oxide Ion at Glassy Carbon Electrode in LiF-KF Eutectic Melt

Yasuhiko ITO*, Toshihide TAKENAKA*, Keiko EMA* and Jun OISHI*

The anodic behaviour of the oxide ion at glassy carbon electrode in LiF-KF eutectic melt was investigated by the chronopotentiometry, potential sweep method and the potential step method, together with IR spectroscopy and gas chromatography. The potential sweep method was the most suitable for monitoring the oxide ion concentration in the melt and estimating the value of the diffusion coefficient of the oxide ion in the melt. The diffusion coefficient of the oxide ion in the melt was estimated to be 5×10^{-5} cm²/sec at 550°C. The reaction rate constant, k_t , of the irreversible anodic oxidation of oxide ion in the melt and the roughness factor of the glassy carbon electrode were estimated to be about 10^{-2} cm/s and 7, respectively. The oxide ion contamination level of a melt, that was vacuum dried before melting and was contained in a high purity alumina crucible, was estimated to be about 250 ppm (F⁻ basis). The possibility of electrolytic purification of the melt was also suggested. The results obtained should be also useful when considering the consumption of graphite moderator in the MSBR.

1 Introduction

Molten fluoride is a useful material for use in many future energy processes, such as the Molten Salt Breeder Reactor, heat storage systems, etc. To use this melt for such purposes, it is necessary to monitor the concentration of oxide ion in the melt and to control it to a desirable level, because the oxide ion concentration strongly influences corrosion of the container material and the precipitation characteristics of dissolved species, which in turn largely determine plant lifetime and process efficiency. In order to monitor and control the oxide ion concentration level, electrochemical methods might play an important role, and in this sense, the anodic behaviour of oxide ion in fluoride melt becomes an important subject. From this viewpoint, Manning and Mamantov¹⁾ have studied the electrochemical behaviour of oxide ion in several molten fluorides and described that the anodic reaction of oxide ion at glassy carbon electrodes does not give reproducible results. It is, however, still interesting to know the details of the anodic behaviour of oxide ion at glassy carbon electrodes. That is, if the glassy carbon elec-

trode shows reproducible electrochemical behaviour, it can be used as an oxide ion concentration indicator. In addition, if it works well, it can be used for the purpose of the electrochemical elimination of oxide ion from the fluoride melt, and in this case, electrolytic products are only gases and the contamination of metallic ion or other species will be minimized.

From a different viewpoint, concerning the Molten Salt Breeder Reactor, the behaviour of the glassy carbon electrode would supply basic informations about the consumption of graphite moderator.

In this paper, LiF-KF eutectic melt has been selected as an example of a fluoride melt, and detailed studies have been carried out on the anodic behaviour of oxide ion at glassy carbon electrode in this melt, using several conventional electrochemical methods, as well as IR spectroscopy and gas chromatographic analysis of the evolved anode gas.

2 Experimental Method and Apparatus

Commercial LiF and KF (Reagent Grade, Wako Chemicals Co., Ltd.) were mixed and the eutectic mixture was vacuum dried for over two nights at 200°C, after which it was then melted in a high purity alumina crucible (Nippon Kagaku Togyo Co. Ltd., SSA-S) under

* Department of Nuclear Engineering, Faculty of Engineering Kyoto University (Sakyo-ku, Kyoto 606)

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an argon (water content < 10 ppm) atmosphere at 550°C . This procedure is not a rigorous one to prepare oxide-free fluoride melt, because residual oxide ion cannot be removed unless the melt is fused under, for example, H_2 -HF gas mixture²⁾. Also, the alumina crucible may introduce some oxide ion into the melt. But in our case, this insufficiency is not a serious problem because, as mentioned later, one of the purposes of the experiments was to estimate the oxide ion contamination level resulting from this kind of insufficient experimental condition.

The oxide ion concentration in the melt was controlled by adding the appropriate amount of dry, CO_2 -free Li_2O (supplied by Prof. K. Niki, Yokohama National University). For the IR spectrum and gas chromatographic analysis of the evolved anode gas, the electrolytic cell and sampling line were arranged as shown in Fig. 1. A 5 mm diameter glassy carbon rod (Touhoku Kyowa Carbon Co. Ltd.) was used as the working electrode. Liquid tin was used as the counter electrode to absorb deposited alkali metal (Li and K) as an alloy. Molybdenum wire was used as the lead for the liquid tin cathode. Solid Al-Alkali-metal alloy was used as a quasi-reference electrode. This electrode maintains a potential of about 0.1 V *vs.* the alkali-metal deposition potential in the same melt, although there is still some thermodynamic uncertainty in the precise value of this potential.

Evolved anode gas was trapped in the gas sampler in a conventional manner.

A similar cell shown in Fig. 2, was used for electrochemical analysis. In this case, however, an aluminum plate, having an area of 10

Fig. 1 Electrolytic cell and gas sampling line

Fig. 2 Cell for electrochemical analysis

cm^2 and a width much greater than that of the working electrode, was used as the alkali-metal-absorbing counter electrode in order to minimize the effects of convection. The vertical surface of the glassy carbon rod was covered with a high purity alumina pipe, (Nippon Kagaku Tokyo Co. Ltd., SSA-S), in order to limit the active area only to the bottom of the rod. Penetration of the melt into the electrode-pipe interface was not observed after the experiments.

All experiments were carried out at 550°C .

3 Results and Discussion

3.1 Chronopotentiometry

Figure 3 shows an example of the experimental results obtained by chronopotentiometry. The chronopotentiogram is not so simple due to the discharge of fluoride ion on the carbon surface, which may form several types of surface compounds. Similar tendency was reported by Lantelme, Damianacos and Chemla³⁾, for the anodic reaction in cryolite melt. At least, however, first plateau in the figure might be attributed to the discharge of oxide ion. To confirm this, potentiostatic electrolysis was carried out and evolved anode gas was analysed qualitatively.

The electrode potential was kept at 3.0 V *vs.* the quasi-reference electrode, which corresponds to the potential region of the first plateau in

Fig. 3 Typical chronopotentiogram
 $[\text{O}_2^{2-}]_{\text{added}} : 0.3 \text{ mol}\%$ (F^- basis), $i_0 : 80 \text{ mA}$

the chronopotentiogram. In the IR spectrum, absorbance due to CO and CO_2 was clearly observed and that due to COF_2 or CF_4 is not observed at all. The presence of large amount of oxygen in the evolved gas was confirmed by gaschromatography.

This fact might suggest that, at least in the potential region of the first plateau, oxide ion discharge reaction is the predominant one.

3.2 Potential sweep method

Figure 4 shows a sample voltammogram obtained by the potential sweep method.

A clear current peak is observed in the figure, although current fluctuation is observed at the potential around 3.6 V vs. the quasi-reference electrode.

The potential of 3.6 V at which perturbation is observed in Fig. 4 corresponds to the potential at which potential fluctuation is observed in Fig. 3. Addition of the peroxide ion into the melt increases the current of the first peak, but does not show new peak. Thus, this current increase can not be attributed to a direct

Fig. 4 Typical potential sweep curve
 $[\text{O}_2^{2-}]_{\text{added}} : 0.15 \text{ mol}\%$ (F^- basis), scan rate : 2.0 V/s

electrochemical discharge of peroxide ion, but might be attributed to a discharge of the oxide ion which is produced by, for example, disproportionation reaction,

That is, peak current of the first peak might be analysed by considering only a discharge of the oxide ion in the melt. An irreversible reaction is suggested by the fact that no peak current is observed during the reverse scan. These observations might be attributed to the diffusion controlled irreversible anodic reaction of the oxide ion in the melt. As expected, in accordance with Nicholson's well known equation⁴⁾ for an irreversible diffusion controlled reaction :

$$\left. \begin{aligned} i &= nFAC_0 \sqrt{\pi D_0 b} \chi(bt) \\ b &= \alpha n_a Fv/RT \end{aligned} \right\} \quad (1)$$

the peak current changes linearly with the added amount of oxide ion in the melt at constant scan rate as shown in Fig. 5, and with the square root of the scan rate at constant oxide ion concentration as shown in Fig. 6. Here, v denotes the potential scan rate; t , the time from the beginning of the scanning; α , the transfer coefficient of the charge transfer step; n , the number of electrons transferred during the rate determining step; and A the electrode area. The other symbols in the equation have their conventional meanings. χ is the special function which has been evaluated numerically by Nicholson and Shain⁴⁾.

Concerning Fig. 5, it is noteworthy that each

Fig. 5 Relation between peak current and $[\text{O}_2^{2-}]_{\text{added}}$ at various scan rates

scan rate : $\circ$; 1.0 V/s, $\bullet$; 0.5 V/s, $\triangle$; 0.2 V/s, $\blacktriangle$; 0.1 V/s

Fig. 6 Relation between peak current and square root of scan rate at various oxide ion concentrations [O²⁻]_{added}: ○; 0.230 mol% (F⁻ basis), ●; 0.116 mol% (F⁻ basis), △; 0.0 mol% (F⁻ basis)

straight line intersects the x-axis at the same concentration, -0.025 mol%, of O²⁻_{added}. This means that before adding Li₂O into the melt, 0.025 mol% O²⁻ was already present in the melt as a contaminant. The oxide ion concentration level of the LiF-KF eutectic melt that was prepared according to the method described in section 2 is, then, estimated to be around 250 ppm (F⁻ basis).

The diffusion coefficient of the oxide ion also can be estimated from these experiments.

If we assume $\alpha n_a = 1$, the diffusion coefficient of the oxide ion in the melt is calculated to be $5 \times 10^{-5} \text{ cm}^2/\text{s}$ by applying equation (1) and using many other data obtained under different conditions*¹.

3.3 Potential step method

As discussed above, it has been concluded that the anodic oxidation of oxide ion at glassy carbon electrode in LiF-KF eutectic melt is a diffusion controlled irreversible process.

In this section, the rate constant of this

irreversible reaction is estimated by the potential step method. Figure 7 shows an example of the transition curve obtained by the potential step method. According to the theory⁵⁾, the relation between the current i and the rate constant k_t , the concentration C , the diffusion coefficient D and the electrode area A is expressed as follows:

$$i = nFAk_t C (1 - 2k_t t^{1/2} / \pi^{1/2} D^{1/2}) \quad (2)$$

under the assumption that $(k_t/D^{1/2})t^{1/2} \ll 1$. If the electrode roughness factor β is incorporated into equation (2), it becomes:

$$i = nF\beta A k_t C (1 - 2k_t t^{1/2} / \pi^{1/2} D^{1/2}) \quad (3)$$

As is seen in Fig. 8, a linear relation between current and the square root of time is

Fig. 7 Typical potential step curve

[O²⁻]: 0.2 mol% (F⁻ basis), potential was stepped from rest potential to 3.0 V (vs. alkali-metal deposition potential) at time 0, and from 3.0 V (vs. alkali-metal deposition potential) to rest potential at time 100 ms

Fig. 8 Relation between current and square root of time

[O²⁻]: 0.2 mol% (F⁻ basis), potential was stepped from rest potential to 3.0 V (vs. alkali-metal deposition potential)

*¹ The assumption that $\alpha n_a = 1$ has not a rigorous theoretical basis, but it seems reasonable to consider this value to stay around 1 (eg. $\alpha = 0.5$, $n_a = 2$). So, as a representative value, the value of 1 has been chosen for this estimate. This assumption yields reasonable values for the diffusion coefficient, so that at least the order of magnitude of the diffusion coefficient can be considered to be reliable.

To make the situation clearer, exact values of the diffusion coefficient should be determined by other methods, after which the value of αn_a can then be obtained. This is the subject of a future report.

Fig. 9 Relation between logarithm of current deviation and time (initial current decrease in Fig. 8)

observed over the range 10~100 ms.

By substituting a diffusion coefficient value of $5 \times 10^{-5} \text{ cm}^2/\text{s}$ and a concentration of $C=0.2$ mol% (which was measured by a separate potential sweep experiment) into equation (3), the values of β and k_f are estimated from this straight line to be 7 and $7.0 \times 10^{-3} \text{ cm/s}$ respectively.

The sharp current decrease over the time range of 0~10 ms in Fig. 8 might be attributed to the double layer electrode capacity. This is confirmed by the linear relation between the logarithm of the current deviation (from the straight line) and time, as seen in Fig. 9. From the slope of the line in Fig. 9 and the value of 7 for the roughness factor, the double layer capacity is calculated to be $400 \mu\text{F}/\text{cm}^2$, which seems several times higher compared with many other double layer capacity data⁹⁾.

4 Conclusions

The anodic behaviour of the oxide ion at

glassy carbon electrode in LiF-KF eutectic melt was investigated by the chronopotentiometry, potential sweep method and the potential step method, together with IR spectroscopy and gas chromatography. Among the electrochemical methods, the potential sweep method was the most reliable for monitoring the oxide ion concentration in the melt and for estimating the value of the diffusion coefficient of the oxide ion in the melt. The diffusion coefficient of the oxide ion in the melt was estimated to be $5 \times 10^{-5} \text{ cm}^2/\text{s}$ at 550°C .

The possibility of electrolytic purification of the melt was also suggested. The reaction rate constant, k_t , of the irreversible anodic oxidation of oxide ion in the melt and the roughness factor of the glassy carbon electrode were estimated to be about 10^{-2} cm/s and 7, respectively.

The oxide ion contamination level of a melt, that was vacuum dried before melting and was contained in a high purity alumina crucible, was estimated to be about 250 ppm (F^- basis).

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