DETERMINATION OF THE DISSOCIATION CONSTANT OF MOLTEN $Li_2CO_3/Na_2CO_3/K_2CO_3$ USING A STABILIZED ZIRCONIA OXIDE-ION INDICATOR

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Summary

An $Li_2CO_3/Na_2CO_3/K_2CO_3$ eutectic melt has been selected as an example of a molten-carbonate system and the suitability of a stabilized zirconia–air electrode as an oxide-ion concentration indicator for this melt has been confirmed.

With this indicator, the dissociation constant of the reaction

$$CO_3{}^{2-}(\ell) = CO_2(g) + O^{2-}(\ell)$$

in this melt has been determined to be

$$K_d = P_{CO_2}[O^{2-}] = 4.03 \times 10^{-3} \text{ Pa at 873 K}$$

Reproducible measurements were obtained throughout the experiment and this method might find further application in the study of reactions related to the oxide ion in carbonate melts.

Introduction

Molten carbonate is a useful material for application in many future energy processes, such as molten-carbonate fuel cells (MCFCs), thermal energy storage, nuclear waste processing, coal gasification, etc. [1, 2]. To use this melt for such purposes, it is necessary to know the behaviour of the oxide ion in the melt. For example, in the case of the MCFC, the oxide ion has a marked effect on the reactions at both the cathodic and anodic electrodes, as well as on the corrosion behaviour of the electrode and cell construction materials [3].

Recently, it has been shown that a stabilized zirconia solid electrolyte can be used as an oxide-ion concentration indicator in many melt systems

[4 - 9]. However, to date, no attempt to use such a material as an oxide-ion indicator in molten-carbonate systems has been reported.

In this paper, an $Li_2CO_3/Na_2CO_3/K_2CO_3$ eutectic melt has been selected as an example of a molten-carbonate system, and the suitability of a stabilized zirconia–air electrode as an oxide-ion indicator has been investigated. Using this indicator, the dissociation constant of the melt has been determined.

Experimental method and apparatus

The experimental cells employed in this study are shown in Figs. 1 and 2. Commercial Li_2CO_3, Na_2CO_3 and K_2CO_3 (Reagent Grade, Wako Chemicals Co. Ltd.) were mixed and the eutectic mixture (Li_2CO_3: 0.435, Na_2CO_3: 0.315, K_2CO_3: 0.250 mole fraction, melting point 670 K [10]) was vacuum dried for over 48 h at 473 K (200 °C). The eutectic mixture was then melted at the given operating temperatures in a high purity alumina crucible (Nippon Kagaku Togyo Co. Ltd., SSA-S) and under a dry carbon dioxide gas atmosphere.

An yttria or magnesia stabilized zirconia tube (Nippon Kagaku Togyo Co. Ltd.) was used as the indicator electrode for the oxide-ion concentration. The inside of the tube was coated with a platinum powder layer that acted as an air electrode. This electrode is termed the stabilized zirconia–air electrode (abbreviated to SZAE in this paper). The e.m.f. measured with this electrode was converted to the potential of the O_2 (1.01×10^5 Pa) (Pt)/stabilized zirconia electrode, taking into account the partial pressure of oxygen in air.
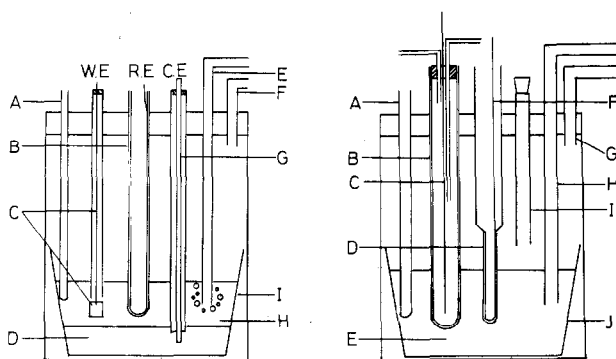

Fig. 1. Experimental cell: A, chromel–alumel thermocouple; B, stabilized zirconia; C, nickel; D, tin; E, gas inlet; F, gas outlet; G, molybdenum; H, molten carbonate; I, alumina crucible.

Fig. 2. Experimental cell: A, chromel–alumel thermocouple; B, mullite tube; C, Au wire; D, stabilized zirconia; E, molten carbonate; F, Pt wire; G, gas outlet; H, gas inlet; I, sodium oxide inlet; J, alumina crucible.

Using the cell shown in Fig. 1, preliminary experiments were conducted at 780 K to confirm that the zirconia electrode effectively acts as an oxide-ion indicator. Several kinds of metal electrode, for example Ni and Cu, were used as working electrodes; each electrode was polarized anodically using liquid tin as a counter-electrode. The anodic polarization under constant current was measured against the SZAE. After reaching the potential (E_+) of the anodic-polarization plateau, each working electrode was then cathodically polarized (again under constant current) and the potential (E_-) of the corresponding plateau was recorded. The plateau potentials thus obtained should correspond to the formation and the reduction of the metal oxides, respectively. In order to confirm this, the measured potentials were compared with the calculated values.

In the case of tin oxide, liquid tin contained in the bottom of the cell was used as a working electrode, and nickel plate served as a counter-electrode.

When the partial pressure of CO_2 over the melt is varied, the potential of the SZAE should change according to the Nernst relation. This was tested by carrying out experiments in the cell shown in Fig. 2. The partial pressure of CO_2 was controlled by dilution with argon gas in a gas-mixing apparatus (KOFLOC GM-2A, Kojima Seisakusho Co. Ltd.). Potential measurements were obtained using a digital multimeter (Takeda Riken Kogyo Co. Ltd., TR6844, internal impedance $>10^3$ MΩ).

An "oxygen electrode" $(P_{O_2} = 3.38 \times 10^4$ Pa and $P_{CO_2} = 6.75 \times 10^4$ Pa [11]) was used as a reference electrode. The electrode was separated from the bulk melt by a mullite tube in order to prevent mixing of the electrolytes.

When necessary, the oxide-ion concentration in the melt was controlled by adding an appropriate amount of dry Na_2O (Aldrich Co. Ltd.).

Results and discussion

A typical chronopotentiogram for the anodic polarization and the subsequent cathodic polarization of an Ni working electrode is shown in Fig. 3. The ohmic drop and the overvoltage are almost negligible owing
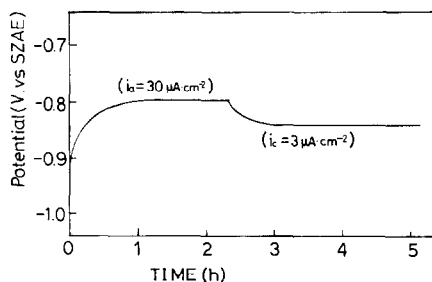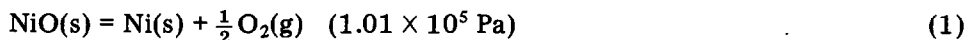

Fig. 3. Chronopotentiogram of an Ni electrode in a carbonate melt at 780 K.

to the low applied current. The anodic and cathodic potential plateau values, E_+ and E_-, are both in reasonable agreement with the value (-0.88 V) calculated using the thermodynamic data [12, 13] for the reaction

$$NiO(s) = Ni(s) + \tfrac{1}{2}O_2(g) \quad (1.01 \times 10^5 \text{ Pa}) \qquad (1)$$

As the plateau potential corresponds to the single-electrode reaction

$$NiO(s) + 2e^- = Ni(s) + O^{2-} \qquad (2)$$
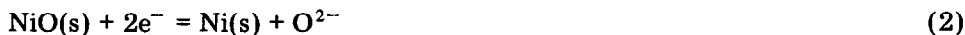
the above result suggests that the SZAE acts effectively as an oxide-ion indicator in a molten-carbonate system, with the single-electrode reaction

$$\tfrac{1}{2}O_2 + 2e^- = O^{2-} \qquad (3)$$

Figure 4 shows a summary of the relationship between the measured plateau potentials of several metal electrodes and the corresponding potentials calculated from thermochemical data [12, 13], based on the assumption that the anodic and cathodic plateau potentials (E_+, E_-) correspond to metal-oxide formation and reduction, respectively.

In the case of the cathodic polarization of a copper electrode, two plateaux were observed. These correspond to two types of copper oxides, CuO and Cu_2O, and are both plotted in Fig. 4. For silver, an anodic plateau but not a cathodic plateau was observed; this may be due to the thermal instability of electrochemically formed Ag_2O [12]. The rest potential of the "oxygen reference electrode" measured against the SZAE is also plotted in the Figure. A linear relationship with unit slope is observed and this provides strong evidence for the applicability of SZAE as an oxide-ion concentration indicator in a molten-carbonate melt.

Figure 5 shows the potential of the SZAE at various CO_2 partial pressures in a melt at 873 K. The measured potential is referred to the potential of the same electrode with $P_{CO_2} = 1.01 \times 10^5$ Pa. A linear relationship with a slope of 2.3 RT/2F is observed (F is the Faraday constant, 9.65×10^4 C mol^{-1}; R is the gas constant, 8.31 J mol^{-1} K^{-1}; T is the temperature, K). Since the dissociation reaction of the molten carbonate is
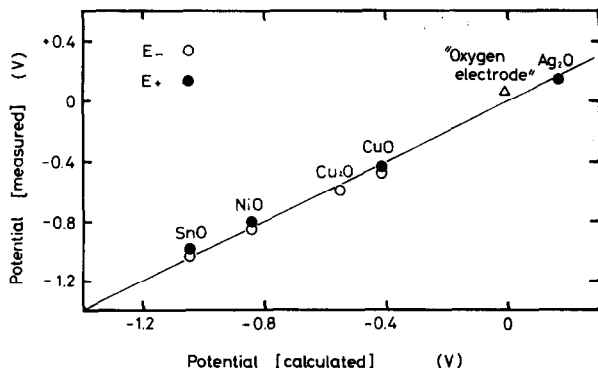

Fig. 4. Measured *versus* calculated potential of a stabilized zirconia–oxygen electrode in a carbonate melt at 780 K.
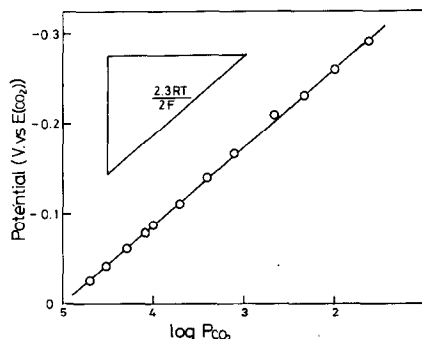
Fig. 5. Potential of a stabilized zirconia–air electrode at various CO_2 partial pressures over a carbonate melt at 873 K. $E(CO_2)$ = potential of SZAE at $P_{CO_2} = 1.01 \times 10^5$ Pa.

$$CO_3{}^{2-}(\ell) = CO_2(g) + O^{2-}(\ell) \tag{4}$$

the potential of the SZAE should obey the following Nernst equation (5) when it responds to the oxide-ion concentration:

$$E = E_0 - \frac{RT}{2F} \ln[O^{2-}] \tag{5}$$

where E_0 is the standard potential, and $[O^{2-}]$ is the mole fraction of oxide. Equation (5) can be written as

$$E = E_0{}' + \frac{RT}{2F} \ln P_{CO_2} \tag{6}$$

where

$$E_0{}' = E_0 - \frac{RT}{2F} \ln K_d \tag{7}$$

and K_d is the dissociation constant of reaction (4), and can be expressed as

$$K_d = P_{CO_2}[O^{2-}] \tag{8}$$

A clear Nernst relationship (eqn. (6)) can be observed in Fig. 5 and thus verifies the applicability of the stabilized zirconia as an oxide-ion indicator.

If the concentration of the oxide ion is known at each CO_2 partial pressure over the melt, then the dissociation constant K_d in eqn. (8) can be calculated from each experimental point in Fig. 5. However, it is very difficult to determine the oxide-ion concentration in equilibrium with CO_2 of a definite partial pressure. Thus, a separate experiment was conducted in order to determine the value of K_d. The cell shown in Fig. 2 was used. After reducing the CO_2 partial pressure inside the cell to less than 1.0 Pa by dilution with argon gas, a measured amount of Na_2O was added to the melt.

Figure 6 shows the change in potential after the introduction of Na_2O. It can be seen that the potential shifts towards the negative direction immediately after the Na_2O is introduced, then passes through a minimum
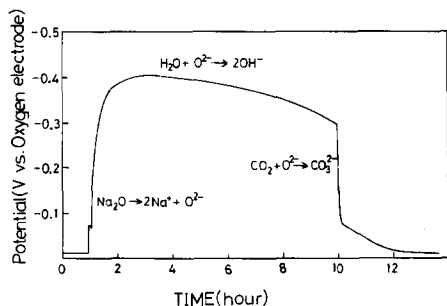
Fig. 6. Potential change after the addition of Na_2O to a carbonate melt at 873 K.

value, and finally shifts gradually towards less negative values. This latter potential shift may be attributed to a gradual decrease in the oxide-ion concentration due to the formation of hydroxide species, *i.e.*

$$H_2O + O^{2-} \longrightarrow 2OH^- \tag{9}$$

Evidence in support of this suggestion is provided by the data presented in Fig. 7 that show the total alkali-ion concentration ($[OH^-]$ + $2[O^{2-}]$) in the melt as determined by the chemical analysis method of Andersen [14]. Melt samples were collected after a long-term equilibration of the melt with H_2O gas of 50 Pa and CO_2 gas of various partial pressures. As the slope of the line in Fig. 7 is -0.5, the total alkali-ion concentration is almost equal to the hydroxide-ion concentration in the melt. That is, added oxide ion may be decreased by the reaction (9) due to the small amount of water in the cover gas.

Ten hours after the introduction of Na_2O, CO_2 gas was fed into the cell. The potential was found to return to the same value recorded before the evacuation of the cell (Fig. 6). This demonstrates the good reproducibility of the experiment. After obtaining the potential corresponding to the initial CO_2 pressure, a different amount of Na_2O was added and a similar potential change was observed.
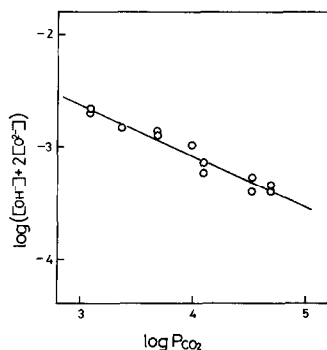

Fig. 7. Relation between the total alkali-ion concentration and CO_2 partial pressure for a carbonate melt at 873 K.

Figure 8 shows a plot of the above-measured minimum potential values against the various amounts of Na_2O added. As the initial oxide-ion concentration is negligibly small, this added amount of Na_2O can be regarded as the oxide-ion concentration in the melt. The slope of the line in Fig. 8 is almost equal to the theoretical value up to an oxide-ion mole fraction of about $10^{-2.5}$. A possible cause of the deviation from the straight line at higher concentrations may be the semiconducting nature of the stabilized zirconia itself [15], which will be explored in detail in a separate paper [16].

As the linear part of Fig. 8 corresponds to the extrapolated portion of the line in Fig. 5, the relation between the potential of the SZAE and the oxide-ion concentration, or CO_2 partial pressure, can be obtained as shown in Fig. 9. From these data, the relation

$$\log[O^{2-}] + \log P_{CO_2} = -7.4 \tag{10}$$

can be deduced. That is, the dissociation constant of reaction (4) has been determined to be 4.03×10^{-3} Pa at 873 K. This value is an order of magnitude higher than the value 1.80×10^{-4} Pa reported by Andersen [14]. The reason for this discrepancy is not yet understood and will be investigated further.
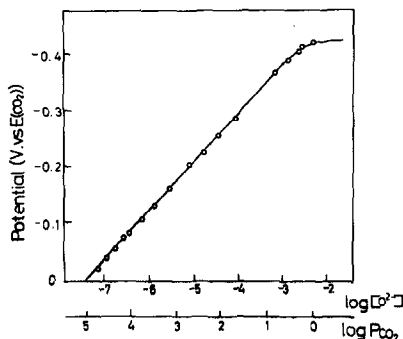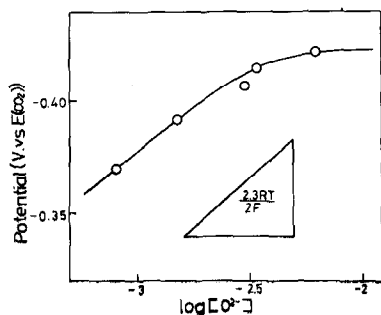

Fig. 8. Relation between the potential of a stabilized zirconia–air electrode and the amount of $[O^{2-}]$ (as Na_2O) added at 873 K. $E(CO_2)$ = potential of SZAE at P_{CO_2} = 1.01×10^5 Pa.

Fig. 9. Potential of a stabilized zirconia–air electrode *versus* oxide-ion concentration and CO_2 partial pressure over a carbonate melt at 873 K. $E(CO_2)$ = potential of SZAE at P_{CO_2} = 1.01×10^5 Pa.

Conclusions

An $Li_2CO_3/Na_2CO_3/K_2CO_3$ eutectic melt has been selected as an example of a molten-carbonate system and the suitability of a stabilized zirconia–air electrode as oxide-ion concentration indicator has been confirmed. Using this indicator, the dissociation constant of the reaction

$$CO_3{}^{2-}(\ell) = CO_2(g) + O^{2-}(\ell)$$
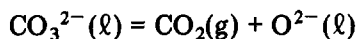
in this melt has been determined to be:

$$K_d = P_{CO_2}[O^{2-}] = 4.03 \times 10^{-3} \, Pa \quad \text{at 873 K}$$

After the experiment, the stabilized zirconia and mullite tubes were examined carefully: neither mechanical damage nor chemical corrosion could be observed. Reproducible measurements were obtained throughout the experiment. Whereas the ruggedness of stabilized zirconia has been reported previously [17], the good stability of mullite is surprising since the material is unstable from a thermodynamic viewpoint [18]. However, it should be pointed out that both stabilized zirconia and mullite are less stable when the oxide-ion concentration is greater that 10^{-3} mole fraction.

It is suggested that the stabilized zirconia–air electrode may find wide application in further studies of the equilibrium related to the oxide ion in other carbonate melts at various temperatures.

Acknowledgement

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