STABILIZED ZIRCONIA AS AN OXIDE ION INDICATOR

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ABSTRACT
The suitability of stabilized zirconia-air electrode as an oxide-ion concentration indicator for molten Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$, NaOH and LiF-KF systems has been confirmed. With this indicator, dissociation constants of the reaction: CO$_3^{2-}$ = CO$_2$(g) + O$_2^{-}$ in Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ eutectic melts and the reaction: 2OH$^{-}$ = H$_2$O(g) + O$_2^{-}$ in molten NaOH have been determined to be 4.0 x 10$^{-8}$ [atm] at 873 K and 1.0 x 10$^{-10}$ [atm] at 623 K, respectively. Solubility products of NiO and ThO$_2$ in LiF-KF eutectic melt have also been determined.

In order to explain the characteristic potential response of the stabilized zirconia-air electrode to the oxide-ion concentration, a theoretical equation has been derived taking into account the equilibria in the solid electrolyte between oxygen and three charge carriers: electron, hole and oxide-ion vacancy.

1. INTRODUCTION
Recently, it has been shown that a stabilized zirconia solid electrolyte can be used as an oxide-ion concentration indicator in molten chloride systems and with the use of this indicator, the solubility product of metal oxide[1], [2],[3], and the chemical equilibrium associated with the oxide-ion[4] have been investigated. The author and his coworkers have extended these studies to the molten Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$[5], NaOH[6] and LiF-KF[7] systems and found that the stabilized zirconia-air electrode is suitable for all of these three systems.

This paper describes our recent work with these electrolytes.

2. MOLTEN CARBONATE SYSTEM
Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ eutectic melt has been selected as an example of a molten carbonate, and the suitability of a stabilized zirconia-air electrode for an oxide-ion indicator has been confirmed. The dissociation constant of the melt has been determined by the use of this oxide-ion indicator[5].

Experimental cells are shown in Figs 1 and 2. For an
oxide-ion concentration indicating electrode, yttria or magnesia stabilized zirconia tube (Nippon Kagaku Togyo Co., Ltd.) was used. The inside of the tube was coated with a platinum powder layer which acted as an air electrode. This electrode is called the stabilized zirconia-air electrode and abbreviated as SZAE. The emf measured with this electrode was converted to the potential of the oxygen (1 atm)(Pt)/stabilized zirconia electrode, taking into account the partial pressure of oxygen in air.

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 and 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. In the case of Ni, for example, the anodic and cathodic potential plateau values, E+ and E−, are both in reasonable agreement with the value (-0.88 V) calculated using the thermochemical data [8], [9] for the reaction:

\[ \text{NiO}(s) \rightarrow \text{Ni}(s) + \frac{1}{2} \text{O}_2 (1 \text{ atm}) \]  

As the plateau potential corresponds to the single electrode reaction:

\[ \text{NiO}(s) + 2e^- = \text{Ni}(s) + \text{O}_2^2- \]  

the above result suggests that the SZAE acts effectively as an oxide-ion indicator in a molten carbonate system, with the single electrode reaction:

\[ \frac{1}{2} \text{O}_2 + 2e^- = \text{O}_2^2- \]  

Fig.3 shows a summary of the relationship between the measured plateau potentials of several metal electrodes and the corresponding potentials calculated from thermochemical data [8],[9] on the assumption that the anodic and cathodic plateau potentials (E+, E−) correspond to metal oxide formation and reduction, respectively.

The linear relationship with unit slope in Fig.3 provides strong evidence for the applicability of SZAE as an oxide-ion concentration indicator in a molten carbonate melt. When the partial pressure of CO2 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. Fig.4 shows the potential of SZAE at various CO$_2$ partial pressures over a melt at 873 K. The measured potential is referred to the potential of the same electrode with P$_{CO_2}$=1 atm. A linear relationship with a slope of $\frac{-2F}{RT}$ is observed. Since the dissociation reaction of the molten carbonate is:

$$CO_3^-(1) = CO_2(g) + O^{2-}(1) \quad (4)$$

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

$$E = E^o - \frac{RT}{2F} \ln \left[O^{2-}\right] \quad (5)$$

where $E^o$ is the standard potential, and $\left[O^{2-}\right]$ is the mole fraction of oxide. Eqn.(5) can be written as:

$$E = E^o' + \frac{RT}{2F} \ln P_{CO_2} \quad (6)$$

where

$$E^o' = E^o - \frac{RT}{2F} \ln K_d \quad (7)$$

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

$$K_d = P_{CO_2} \cdot \left[O^{2-}\right] \quad (8)$$

A clear Nernst relationship (eqn.(6)) can be observed in Fig.4 and thus verifies the applicability of the SZAE 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.4. 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 $K_d$ value. The cell shown in Fig.2 was used. After reducing the CO$_2$ partial pressure inside the cell to less than $10^{-5}$ atm by dilution with argon gas, a measured amount of Na$_2$O was added to the melt. Fig.5 shows the relation between the potential of stabilized zirconia-air electrode (SZAE) and an added amount of $\left[O^{2-}\right]$ (as Na$_2$O) at 873 K. As the initial oxide-ion concentration is negligibly small, this added amount of Na$_2$O can be regarded as the oxide-ion concentration in the melt. The slope of the line in Fig.5 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, that will be explained in detail in section 5. As the linear part of Fig. 5 corresponds to the extrapolated portion of the line in Fig.4, 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.6. From these data, the relation

$$\log[O^{2-}] + \log P_{CO_2} = -7.4$$
can be deduced. That is, the dissociation constant of reaction (4) has been determined to be $10^{-7.8} \times (4.0 \times 10^{-8})$ [atm] at 873 K. This value is an order of magnitude higher than the value $10^{-8.75}$ reported by Andersen [10]. The reason for this discrepancy is not yet understood and will be investigated further.

3. MOLTEN SODIUM HYDROXIDE SYSTEM

In the molten hydroxide system, the equilibrium constant $K_1$ of the reaction:

$$20H^- = H_2O(g) + O^{2-} \quad (9)$$

is one of the basic data for the $E$-$pO^{2-}$ diagram. In order to obtain the dissociation constant $K_1$, the following electrochemical cell:

Na/$\beta$-alumina/NaOH(Na$_2$O)/ZrO$_2$-Y$_2$O$_3$/O$_2$(Air) (Pt) using the SZAE described in the preceding section was constructed and by the use of this cell, the standard chemical potential of Na$_2$O dissolved in molten sodium hydroxide and the equilibrium constant of the reaction $20H^- = H_2O(g) + O^{2-}$ could be determined rigorously [6].

The experimental apparatus is shown in Fig.7. Even reagent grade NaOH contains H$_2$O as impurity, so the apparatus was held at 623 K for several days before the experiments in order to eliminate impurities in the gas refining systems. After preparation, known amounts of reagent grade Na$_2$O were added and the emf between the $\beta$-alumina/sodium electrode and the SZAE was recorded using a digital voltmeter or pen recorder with voltage follower, both of which have high input impedance. After addition of Na$_2$O, the emf changed slowly and reached a constant value after about 5 min. When necessary, the atmosphere in the nickel container was adjusted by flowing oxygen-free argon which was presaturated by passing through distilled water at constant temperature.

Fig.8 shows emf response to $O_2$ partial pressure inside the zirconia. Circles represent measured values. All points fit a Nernst slope of $\frac{2.3RT}{4F}$, which indicate the possibility of using stabilized zirconia as an oxide-ion indicating electrode at this temperature (623 K). Fig.9 shows emf response to added Na$_2$O. The inside of the zirconia tube is filled with air. Circles represent experimental values. The solid line indicates a theoretical Nernst slope $\frac{2.3RT}{4F}$. Experimental values at higher oxide-ion concentration deviate slightly from the theoretical line. One of the reasons for the deviation may be due to the deviation of the activity coefficient of sodium oxide from unity. Other possible reason for the deviation will be discussed later in section 5.

From the extrapolation of the solid line in Fig.9, to the point where the mole fraction of Na$_2$O is unity, $E^o$ is determined as 1.71 V, from which it was found that
\( \mu^0(\text{Na}_2\text{O}) \) is \(-4.71 \times 10^5 \text{ J mol}^{-1}\).

Fig. 10 shows the emf response to H\(_2\)O partial pressure over the melt. Circles represent experimental values. The solid line has a theoretical Nernst slope of \( \frac{2.3RT}{2F} \).

Taking into account that the acid-base behaviour of molten hydroxide can be described by the equation:

\[ 2\text{MOH} = \text{H}_2\text{O} + \text{M}_2\text{O} \quad (10) \]

the emf of the cell:

\[ E = E^o - \left( \frac{RT}{2F} \right) \ln a(\text{Na}_2\text{O}) + \left( \frac{RT}{4F} \right) \ln P(\text{O}_2) \quad (11) \]

can be replaced by equation (12):

\[ E = E^o + \frac{RT}{2F} \ln P_{\text{H}_2\text{O}} + \frac{RT}{4F} \ln P(\text{O}_2) + \text{const.} \quad (12) \]

(concentration of OH\(^-\) is extremely large and can be regarded as constant.)

Experimental data are consistent with equation (12). The extrapolated value of emf to \( P_{\text{H}_2\text{O}} = 1 \text{ atm} \) and \( P(\text{O}_2) = 1 \text{ atm} \) is 2.23 V. This value agrees well with the emfs of the corresponding cell reaction:

\[ \text{Na}(l) + \frac{1}{4} \text{O}_2(g) + \frac{1}{2} \text{H}_2\text{O}(g) = \text{NaOH}(l) \quad (13) \]

calculated by thermochémical data (8) and measured by the experiment (11).

From this agreement, it was found that the equilibrium described by eqn. (9) really exists in this system. Then, \( K_1 \) of this reaction calculated from the above experimental data is \( 1.0 \times 10^{-10} \text{ atm} \).

4. MOLTEN FLUORIDE SYSTEM

LiF-KF eutectic melt has been selected as an example of a fluoride melt, and after the suitability of stabilized zirconia-air electrode (SZAE) for an oxide ion indicator has been confirmed, the solubility products of several kinds of oxides in this melt were determined [7],[12].

The experimental cell is shown in Fig. 11.

For an oxide ion concentration indicating electrode, yttria, calcia or magnesia stabilized zirconia tubes were used. The measured emf was converted to the potential of the oxygen(Pt)/stabilized zirconia electrode versus the Li-K/Li\(^+\), K\(^+\) electrode potential. The oxide-ion concentration in the melt was controlled by adding the appropriate amount of dry Na\(_2\)O (Aldrich Co. Ltd.). For the solubility product measurements of several kinds of oxides, commercial oxides (Wako Chemicals Co. Ltd.) were added into the melt, and the potential of the SZAE was measured at several values of the amount of added oxides. The other method of determining solubility products is to titrate a dissolved finite amount of metallic ion by oxide-ion, using SZAE as an oxide-ion indicator. The results obtained by both methods are in good agreement as shown later. Fig. 12 shows the relation between emf of the cell:
Li-K/LiF-KF-O\textsuperscript{2-}/stabilized ZrO\textsubscript{2}/O\textsubscript{2} (Pt) and oxide ion concentration. Clear Nernst relation can be observed between potential and oxide ion concentration, though a deviation from the Nernst line is observed in the higher concentration range. The other point to be noted is that the potential value depends on the kind of stabilized zirconia used. This behaviour can be explained by the theoretical equation which will be described in the following section.

Fig.13 shows the relation between Pt(O\textsubscript{2})/stabilized zirconia/LiF-KF-O\textsuperscript{2-} electrode potential and the added amount of NiO. When the amount of NiO in the melt is increased gradually, the potential shift is not so clear in an early stage, due to the contaminating oxide-ion, but when the added amount of NiO exceeds the contamination level, the potential shifts towards the negative side obeying the Nernst equation. And when NiO is saturated in the melt, the potential remains constant at any amount of added NiO even in the region where the Nernst relation would otherwise hold. From the figure of the potential shift obtained by the addition of NiO, $K_{sp}$ values can be calculated, though by a calculation, initial oxide-ion concentration due to the contamination should be carefully taken into account. $K_{sp}$ values thus obtained is $1.3 \times 10^{-6}$ at 823 K.

Fig.14 shows the relation between Pt(O\textsubscript{2})/stabilized zirconia/LiF-KF-O\textsuperscript{2-} electrode potential and the added amount of ThO\textsubscript{2}. From the figure of the potential shift obtained by the addition of ThO\textsubscript{2}, $K_{sp}$ can be estimated as $1.3 \times 10^{-9}$ at 823 K.

Fig.15 shows the relation between Pt(O\textsubscript{2})/stabilized zirconia/LiF-KF-O\textsuperscript{2-} electrode potential and the added amount of Na\textsubscript{2}O when ThF\textsubscript{4} is dissolved in the melt at a finite concentration. From this titration curve, the $K_{sp}$ value can be estimated by curve fitting, to be $K_{sp} = 1.1 \times 10^{-9}$ at 823 K. The two values are in fairly good agreement and hence the results are concluded to be reliable.

5. THEORETICAL RELATION BETWEEN POTENTIAL OF SZAE AND OXIDE ION CONCENTRATION

As stated above, a clear Nernst relation can be observed in all molten salt systems so far examined. However, in every case, a deviation from the Nernst line is observed in the higher concentration range. The other point to be noted is that the potential value depends on the kind of the stabilized zirconia used.

In order to explain such characteristics, a theoretical relation between the potential of SZAE and oxide ion concentration was deduced as in the following [13]: In the stabilized zirconia, there are three equilibria among oxygen and three charge carriers: electron, hole and...
oxide ion vacancy. Thus,

\[ O_0 = O^{2-} + V_{O^2} \]  \hspace{1cm} (14)
\[ O_0 = \frac{1}{2} O_2 + V_{O^2} + 2e^+ \]  \hspace{1cm} (15)
\[ \frac{1}{2} O_2 + V_{O^2} = O_0 + 2e^+ \]  \hspace{1cm} (16)

Taking into consideration the above three equilibria, a relation between potential and oxide-ion concentration can be derived as follows: Potential difference between the position \( i \) and \( j \) can be expressed as:

\[ E_{ij} = \phi(i) - \phi(j) = \frac{RT}{F} \ln \frac{a_{\text{V}_{O^2}}(j)}{a_{\text{V}_{O^2}}(i)} \frac{t_{i}^{l}}{Z_{l}^{l}} \]  \hspace{1cm} (17)

where

\[ t_{i}^{l} = k_{l} a_{\text{V}_{O^2}} a_{V_{O^2}} + k_{e} a_{e} a_{e} \]  \hspace{1cm} (18)

and

\[ k_{l} = \frac{Z_{l} U_{l}}{\gamma_{l}} \]  \hspace{1cm} (19)

Integrating equation (17) with appropriate boundary conditions based on the calculation model shown in Fig.16, equation (20) can be derived. Details will appear in the separate paper (13).

\[ E = E^0 - \frac{RT}{2F} \ln \left[ O^{2-} \right] + \frac{RT}{2F} \ln \left( 1 + K[O^{2-}] \right) \]  \hspace{1cm} (20)

\( (K : \text{constant, but depends on the characteristics of stabilized zirconia}) \)

According to eqn.(20), the Nernst equation holds when \( [O^{2-}] \) is much smaller than \( \frac{1}{K} \), and when \( [O^{2-}] \) is increased, positive deviation from the Nernst line will be observed. Hence, this eqn.(20) explains well the behaviour of SZAE described above.

6. CONCLUSION

The suitability of the stabilized zirconia-air electrode (SZAE) for the oxide-ion concentration indicator in molten Li\(_2\)CO\(_3\)-Na\(_2\)CO\(_3\)-K\(_2\)CO\(_3\), NaOH and LiF-KF systems have been confirmed. And as examples of the application of this indicator, dissociation constants of the reaction:

\[ \text{CO}_3^{2-}(\text{s}) = \text{CO}_2(\text{g}) + O^{2-}(\text{s}) \]

and

\[ 2\text{OH}^- = \text{H}_2\text{O}(\text{g}) + O^{2-}(\text{s}) \]

have been determined to be \( 4.0 \times 10^{-8} \) [atm] at 873 K and \( 1.0 \times 10^{-10} \) [atm] at 623 K, respectively.

Solubility products of NiO and ThO\(_2\) in LiF-KF eutectic melt have also been determined.

Finally, in order to explain the characteristic potential response of the stabilized zirconia-air electrode to the oxide-ion concentration, a theoretical relation between potential of stabilized zirconia-air electrode and
oxide-ion concentration has been derived taking into account the equilibria among oxygen and three charge carries: electron, hole, and oxide ion vacancy.

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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

Fig. 3 Relation between measured and calculated potentials of stabilized zirconia-air electrode (at 780 K)

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Fig. 4 Potential of stabilized zirconia-air electrode at various CO₂ partial pressures over the melt (at 873 K)

Fig. 5 Relation between potential of stabilized zirconia-air electrode and the added amount of Na₂O ([O²⁻]) (at 873 K)
Fig. 6 Relation between potential of stabilized zirconia-air electrode and the oxide concentrations and/or CO₂ partial pressure over the carbonate melt (at 873 K)

Fig. 7 Experimental cell

A: Thermocouple
B: Gas bubbler (H₂O, Ar)
C: Gas outlet
D: Na₂O inlet
E: Ar gas inlet
F: O₂ or air inlet (outlet)
G: Ar gas outlet
H: Nickel container
I: Alumina crucible
J: Alumina tube
K: B-alumina
L: Molten sodium
M: Molten NaOH
N: Zirconia tube
O: Pt powder
P: Lead wire (stainless steel or molybdenum)
Fig. 8 Emf response to $O_2$ partial pressure inside the zirconia (at 623 K)

Fig. 9 Emf response to added $Na_2O$ (at 623 K)

Fig. 10 Emf response to $H_2O$ partial pressure over the melt
Fig. 11 Experimental cell

A: Thermocouple  
B: Zirconia electrode  
C: M/M⁺ electrode  
(M: Alkali metal)  
D: Reference electrode  
E: Glassy carbon

Fig. 12 Potential - log[O²⁻]  
LiF-KF eutectic at 823 K
Fig. 13 Relation between Pt(O$_2$) / stabilized zirconia / LiF-KF-O$_2^-$ electrode potential and the added amount of NiO (mole fraction)

Fig. 14 Potential - \(\log[\text{ThO}_2]\) LiF-KF eutectic at 823 K

\[ K_{sp} = 1.3 \times 10^{-9} \]
Fig. 15 Potential - $\log [O^{2-}]_{\text{add}}$
LiF-KF eutectic at 823 K

Fig. 16 Calculation model