Electrochemical Study of Metallic Oxides in Fused Lithium Chloride-Potassium Chloride Eutectic

H. A. Laitinen and B. B. Bhatia

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

ABSTRACT

The oxygen electrode does not behave reversibly in LiCl-KCl at temperatures of 400°-500°C, and at oxide ion concentrations of 0.1-0.2M. The following electrode systems behave reversibly as electrodes of the second kind: Cu/CuO,O==; Pt/PtO,O==; Pd/PdO,O==; Bi/BiOCl,O==. The Ni/NiO,O== and Bi/BiOCl,O== electrodes did not show reversible behavior. Because of the relatively high solubilities of the metal oxides, the applicability of the metal oxide electrodes to the measurement of oxide ion activity is limited to solutions containing oxide ion in concentrations comparable with, or greater than, that contributed by dissolution of the oxides. This limit is 10^-5 M or higher, depending on the system. The relatively high solubility of heavy metal oxides in this solvent is attributed to the great complexing tendency of chloride ion. It is probable that these oxides would be much less soluble in nitrate and sulfate melts and thus their utility as acidity electrodes could be extended to lower oxide concentrations.

A molten alkali metal chloride solvent may be said to be “buffered” with respect to the addition of Lewis acids such as AlCl3, because of the presence of a large excess of the weakly basic chloride ion. On the other hand, such a solvent can be rendered basic by the addition of substances such as oxide ion which are more strongly basic than chloride ion.

The purpose of the present investigation was to determine the feasibility of using the oxygen-oxide ion electrode or metal-metal oxide-oxide ion electrodes for the electrochemical measurement of oxide ion activity in molten lithium chloride-potassium chloride eutectic at 450°. A secondary objective was to determine the solubilities of metal oxides from emf measurements.

There is considerable evidence for the reversibility of the oxygen-oxide ion electrode at temperatures of the order of 1000°C in various melts containing oxyanions. The early work of Baur and Ehrenberg (1) on borates, silicates, etc., and of Treadwell (2) on metal oxides, using quartz or porcelain as an electrolyte and silver as the indicator electrode, had indicated that the oxygen-oxide ion was exhibiting reversible behavior.

Csáki and Dietzel (3) reported on emf measurements in cells involving platinum indicator electrodes in borate melts, but their interpretation of the results has been criticized by Flood, Forland, and Motzfeld (4). Antipin (5) used a graphite electrode, which had been anodized to make it behave as an oxygen electrode, as a reference electrode in cryolite at 1050°C. The investigations of Lux (6) largely in sulfate and phosphate systems at 950°C were the first which clearly showed the feasibility of oxide ion activity measurements using a platinum electrode with oxygen gas. Similar measurements were made by Flood and co-workers (4, 7, 8) who demonstrated that the dependence of the potential on oxide ion activity obeyed the Nernst equation.

Work at lower temperatures has been much more limited in scope. Rose, Davis, and Ellingham (9) made measurements involving oxygen electrodes in molten NaOH containing small concentrations of tin or lead at 400°-700°C and found that the cells behaved reversibly. Hill and co-workers (10) measured emfs of cells of the type

\[ M/\text{MO}/\text{CaO in Li}_2\text{SO}_4-K_2\text{SO}_4/Pt,\text{O}_2 \]
at 550°-750°C and concluded that for iron, copper, and (at temperatures below 658°C) nickel, the cell emf agreed with that calculated from the free energy of formation of the metal oxide. Since both of the electrodes used by Hill, et al. theoretically responded equally to oxide ion activity, the cell emf data did not show whether the potentials of the two types of oxide ion electrodes individually varied properly with oxide ion activity. Selis and co-workers (11) in interpreting the galvanic behavior of a Mg-Ni cell in moist lithium chloride-potassium chloride eutectic, considered that the potential-determining systems were Mg/MgO,O and either Ni/ NiO,O (at temperatures of 445°-535°C) or H₂ Ni/ OH₂O (at temperatures of 380°-440°C). Once again, the individual electrode behavior against a reference electrode that was invariant with oxide ion activity was not determined.

In the present investigation, a platinum(II)-platinum electrode (12) was used for the measurement of the potentials of the oxygen-oxide ion electrode and of various metal-metal oxide-ion electrodes as a function of the concentration of oxide ion.

Previous attempts to measure reversible oxygen potentials, using a platinum foil or graphite rod as an indicator electrode, had been unsuccessful (13). In the present study, a porous graphite electrode was used, again with unsuccessful results, as will be seen below.

For an electrode of the second kind, composed of a metal M, its sparingly soluble oxide MO₇₂, and free oxide ion, the Nernst equation is given by

\[ E = E^o + \frac{RT}{nF} \ln a_{M^{n+}} \]  

For an electrode of the first kind, composed of a metal M, its sparingly soluble oxide MOₓ, and free oxide ion, the Nernst equation is given by

\[ E = E^o + \frac{RT}{nF} \ln a_{M^{n+}} \]

where \( E^o \) is the standard electrode potential of the metal ion-metal electrode, and \( a_{M^{n+}} \) is the activity product of the sparingly soluble oxide. The first two terms on the right hand side of Eq. [3] can be combined to give the standard potential of the electrode of the second kind, or

\[ E = E^o_{oxide} = \frac{RT}{2F} \ln a_{O^2} \]

which is the Nernst equation for the electrode reaction

\[ MO_{\text{solid}} (\text{solid}) + n e^- \rightarrow M + \frac{n}{2} O^2 \]

From previous work on the electromotive force series in LiCl-KCl (12) it may be inferred that activities may be replaced by concentrations in Eq. [1]-[4] if a very dilute solution is chosen as the standard state, at least if the mole fraction of added solute is in the range 10⁻⁴ to 10⁻³. For analytical purposes it will be convenient to adopt the molarity scale of concentration, although simple conversion factors to molality or mole fraction may be applied if desired. The formal potential \( E^o \), written to describe the electrode with soluble reactants at a concentration of 1M, will therefore be written as \( E^o \), the standard potential. At 450°C the Nernst factor 2.303RT/F becomes 0.1434 v, so that the theoretical slope of the plot of potential against \( \log C \), the logarithm of molar concentration of oxide ion, becomes 71.7 mv if a solid uncharged oxide is formed, regardless of the valence of the metal. Deviation from this slope implies a different course of the reaction.

The metals in this study were chosen to have stable oxides at the operating temperature and to be comparatively noble, in order that the electrode potentials would not become excessively negative and therefore subject to interference by traces of reducible impurities in the presence of excess oxide.

**Experimental**

The eutectic mixture of 41 mole % potassium chloride and 59 mole % lithium chloride (melting point 352°C) was used as a solvent system at 450°C, the working temperature in this investigation. The technique of preparation and purification as described in a detailed form earlier (15, 27) was followed. The reference electrode was a platinum plate immersed in a platinum(II) solution prepared in a fritted glass compartment by anodic dissolution with a known quantity of electricity. After each experiment the reference electrode compartment was analyzed by titration for chloride to determine the amount of solvent, and the potential was corrected to a Pt(II) concentration of 1M by calculation using the Nernst equation.

The associated apparatus and equipment used in fused salt methodology has been described elsewhere (16-19).

The oxygen electrode was a porous graphite electrode, of a type described by Senderoff and Mellors (20), which was held in an oxygen atmosphere at 400°C for 5 hr before use.

In the study of metal oxides the solvent was compartmented into medium porosity fused alumina or zirconia tubes. Prior to their actual use the tubes were soaked in hydrochloric acid for a few days in order to remove any basic oxides incorporated as binding agents in the tubes. After this treatment, the tubes were washed thoroughly with distilled water and dried at 500°C before they were inserted in the melt. There was no evidence for the presence of any objectionable species in the melt due to the use of these tubes. The residual current was found to be the same whether alumina or zirconia tubes or fritted glass compartments were used. Glass frits were used only when the study was purely qualitative in nature, for instance, when it was desired to observe color changes in the system. The solutes, generally anhydrous metallic salts, were added to the compartmentation tubes with the aid of a small platinum scoop which was mounted on a glass handle. At times, coulometric generation of metal ions by anodic oxidation of pure metal foils or wires was employed. At the conclusion of each experiment, the chloride content of each compartment was determined by argentometric titration as described elsewhere (12). Thus, knowing the volume of the solution in the compartment, the concentration of solute at the time of measurement could be calculated.
The anhydrous metallic oxides were prepared as follows: Calcium oxide, platinum(II) oxide, and bismuth(III) oxide were made by vacuum desiccation of commercially available anhydrous samples. Lithium oxide was prepared from an analytical grade sample of lithium hydroxide monohydrate according to a procedure outlined by Brauer (21). Nickel(II) oxide (22), copper(I) oxide (21), palladium(II) oxide (23), and bismuth(III) oxychloride (21) were prepared according to available procedures.

Results and Discussion

The oxygen electrode, when dipped into solutions 0.09M to 0.21M in lithium oxide, was found very slow to reach equilibrium at temperatures of 400°-500°C. After 6-7 hr, the potential usually had reached a constant value, the final potentials at 450°C being -0.212, -0.328, and -0.407 v against a 1M Pt(II) reference electrode, at oxide ion concentrations of 0.094, 0.167, and 0.21M, respectively. These data do not yield a linear semi-logarithmic plot, and the rate of change of potential with concentration is much greater than predicted by the Nernst equation. The slope of the "best" straight line is about 0.6 v rather than the theoretical 0.0717 v. Similar behavior was observed at 400° and 500°C. It is concluded that reversible behavior could not be achieved under the conditions of the present study. It is likely that carbon takes part in the potential-determining reaction, in view of the finding by Smirnov, et al. (24) that at 800°C in KCl-NaCl saturated with CaO, the potential-determining reaction of a carbon electrode is

\[ 2Ca^{++} + CO_2 + 4e^- = C + 2CaO \]

Consequently, the drifting potentials and nonequilibrium character in the present study are probably due to mixed electrode processes.

The following metal oxides were studied in this investigation: copper(I) oxide, nickel(II) oxide, platinum(II) oxide, palladium(II) oxide, bismuth(III) oxide. In addition, bismuth oxychloride was compared with bismuth(III) oxide. The general procedure was to add a weighed amount of an anhydrous metal oxide to the melt collected in a zirconia tube and to measure the potential after each addition of oxide and no change in potential was observed on subsequent additions of oxide. For following the reversibility of these electrode systems, varying amounts of lithium or calcium oxide were added to establish the oxide ion concentration. These oxides are known to be fairly soluble in lithium chloride-potassium chloride eutectic.

To calculate the equilibrium concentration of oxide ion, it was necessary to take into account the contribution from the solubility of the metal oxide.

Table I. Potential of Pd, PdO Electrode at Various Concentrations of Added Oxide Ion

<table>
<thead>
<tr>
<th>Total CaO added, mg</th>
<th>CaO added, stoichiometric molar conc.</th>
<th>( [O=] ) corr, molar</th>
<th>( E ) (Cell B), volt measured</th>
<th>( E ), volt, versus 1M Pt reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0</td>
<td>( 7.0 \times 10^{-5} )</td>
<td>(-0.2371)</td>
<td>(-0.3594)</td>
</tr>
<tr>
<td>7.8</td>
<td>0.0168</td>
<td>( 2.06 \times 10^{-5} )</td>
<td>(-0.2700)</td>
<td>(-0.3023)</td>
</tr>
<tr>
<td>15.9</td>
<td>0.0342</td>
<td>( 3.60 \times 10^{-5} )</td>
<td>(-0.2962)</td>
<td>(-0.4058)</td>
</tr>
<tr>
<td>23.0</td>
<td>0.0494</td>
<td>( 5.07 \times 10^{-5} )</td>
<td>(-0.2992)</td>
<td>(-0.4215)</td>
</tr>
</tbody>
</table>

were first calculated to a platinum(II) concentration of 1M, to give the figures in the last column. From the standard potential of the Pd(II),Pd electrode \((-0.214 \text{ v vs. } 1 \text{M Pt(II)})\), estimates of the solubility product of PdO were made, using the stoichiometric concentrations of calcium oxide added (column 2). The two values \((6.63 \text{ and } 6.49 \times 10^{-5})\) estimated from the higher added oxide concentrations were averaged to give \(6.56 \times 10^{-5}\). From the solubility product, using a quadratic solution, the corrected oxide ion concentrations were calculated. The oxide ion concentration of a saturated solution of PdO without added CaO would be expected to be equal to the square root of the solubility product, or \(8.1 \times 10^{-5} \text{M}\). From the standard potential of palladium and the measured emf, a Pd(II) concentration of \(9.38 \times 10^{-5} \text{M}\) is calculated. This suggests that some initial oxidation of Pd, promoted by the presence of oxide ion, had occurred before the oxygen had been completely flushed from the system. A better estimate of initial oxide concentration is given by \(K_p/9.38 \times 10^{-5} = 7.0 \times 10^{-5} \text{M}\).

The solubility of each metal oxide was estimated by three procedures: (a) from the measured potential of the metal in a solution saturated with its oxide, (b) from measurements of the voltammetric (polarographic) diffusion current of a solution saturated with the oxide, and (c) from \(E_{\text{oxy}}\), defined as the standard potential of the metal, metal oxide electrode obtained from the experimental curve of electrode potential against logarithm of oxide ion concentration extrapolated to a concentration of 1M (Eq. [4]).

Two alternate procedures were used to prepare half-cells. In the first, a metal was dissolved anodically in the melt and lithium or calcium oxide was subsequently added. In the second, a weighed amount of anhydrous metal chloride was added to the melt containing the soluble calcium or lithium oxide. A brief discussion of each metal-metal oxide system studied will now be given. For each electrode system, a plot of logarithm of molarity of oxide vs. potential against 1M platinum reference electrode has been made. These plots are depicted in Fig. 1, 2, and 3. In each figure the points are connected.
Nickel(II) oxide.—The nickel-nickel oxide couple, NiO + 2e⁻ = Ni + O²⁻, was the first to be studied. Nickel is known to form NiO as a stable oxide and no oxychloride of this metal is known. The concentration of nickel calculated from the potentials is 3.3 × 10⁻⁴ mole liter⁻¹. The concentration found from a polarogram taken of a saturated solution of NiO in the melt was 3.2 × 10⁻⁴ mole liter⁻¹. A plot of log [O²⁻] vs. E, shown in Fig. 1, showed a considerable departure from the theoretical slope and therefore indicated irreversibility of the system. The slope calculated by the least squares method is 53 mv as compared to a theoretical slope of 71.7 mv for a reversible half reaction. The Eₜ value can approximately be quoted as −1.23 v which corresponds to the solubility of ca. 10⁻⁴ moles/liter, calculated from the theoretical slope. The experimental points on the figure are scattered and thus very little theoretical significance can be attached to the Eₜ value. The value −1.23 v is more positive than expected from Eₜ and solubility of NiO estimated polarographically (−1.297 v).

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Platinum(II) oxide.—A saturated solution of PtO in equilibrium with solid oxide when brought in contact with the platinum foil electrode registered a potential of \(-0.0546\) vs. a \(3.28 \times 10^{-4}\) M Pt(II) reference. This potential was stable over a long period (4-5 hr). From the potential the solubility of PtO was calculated to be \(3.32 \times 10^{-2}\) moles liter\(^{-1}\). The effect of additional increasing amounts of CaO on the potential was also followed. A plot of log \([\text{O}^=]\) vs. \(E\) is shown in Fig. 2. The slope of the plot is 72.5 mv and \(E^\text{oxide}_{\text{eq}}\) is \(-0.3385\) v. The solubility calculated from the \(E^\text{oxide}_{\text{eq}}\) value is \(4.36 \times 10^{-3}\) moles liter\(^{-1}\) which is in good agreement with the measured value.

In some experiments PtO was generated internally by anodizing platinum foil in the melt in the presence of an excess of CaO. Although the measurements agreed with those obtained by direct addition of PtO, the establishment of equilibrium was so slow that it took almost 24 hr to make four measurements. Stirring of the solution or passing of small current (ca. 1 µa), while the measurements were made, did not speed the attainment of equilibrium appreciably.

Palladium(II) oxide.—Following the procedure explained above, the solubility of PdO from potential measurements was calculated as \(9.4 \times 10^{-3}\) moles liter\(^{-1}\). The plot of log \([\text{O}^=]\) vs. \(E\) shown on Fig. 2 gives a slope of 74.2 mv and \(E^\text{oxide}_{\text{eq}}\) \(-0.514\) v. The solubility calculated from \(E^\text{oxide}_{\text{eq}}\) is \(8.1 \times 10^{-3}\) moles liter\(^{-1}\). The attainment of equilibrium in this system was also extremely slow. From the experimental data, however, the electrode system appears to behave as a reversible electrode of the second kind.

Bismuth (III) oxide.—In studying the Bi/Bi\(_3\)O\(_5\)O\(_3\) system, a re-evaluation of the standard potential of the Bi(III)/Bi electrode was made. Using a tungsten electrode in contact with a molten Bi pool, a value of \(-0.63\) v vs. 1M Pt(II)/Pt on the molarity scale was found. This value is in agreement with the value of \(-0.64 \pm 0.01\) v reported elsewhere (24), using a tungsten contact, rather than the previous value of \(-0.553\) v reported elsewhere (12), using a platinum contact. This disagreement may be attributed to alloy formation between platinum and liquid bismuth.

Experimental values of the potential of a bismuth electrode in the presence of sufficient solid BiO\(_2\) to form a solid phase, and with varying concentrations of oxide ion, added as CaO, are given in Fig. 3. The electrode potential followed the empirical equation

\[ E = -1.023 - 0.042 \log [\text{O}^=] \]  \[6\]

from which \(K_{\text{eq}} = 3.2 \times 10^4\) using Eq. [3]. The slope of the logarithmic plot (42 mv), however, does not agree with the theoretical value of 71.7 mv given in Eq. [4]. The value of \(K_{\text{eq}}\) can also be estimated from the potential of the bismuth pool in the presence of BiO\(_2\) but in the absence of added CaO (\(-0.8543\) v vs. 1M Pt), from which \([\text{Bi}^{4+}] = 2.06 \times 10^{-3}\). If it is assumed that \([\text{O}^=] = 3/2 \times 3.09 \times 10^{-4}\), a value of \(K_{\text{eq}} = [\text{Bi}^{4+}][\text{O}^=] = 5.0 \times 10^{-4}\) is estimated, differing by almost an order of magnitude from the estimate made from the intercept.

From the fact that the theoretical Nernst slope is not observed, however, it can be inferred that the simple solubility equilibrium of BiI\(_2\), is not reached. If BiI\(_2\) dissolves through the intermediate formation of BiO\(^-\), the theoretical Nernst slope would not be affected as long as solid BiI\(_2\) were present at equilibrium. If BiI\(_2\) interacts to form a new solid phase of BiOCI and is present in excess so that both solid phases exist, then the equilibrium

\[ \text{BiI}_2(\text{solid}) + 2\text{Cl}^- = 2\text{BiOCI(liquid)} + \text{O}^= \]  \[7\]

would correspond to a fixed oxide ion (and therefore bismuth ion) activity. Addition of excess oxide ion would merely change the relative amounts of the two solid phases. On the other hand, if all the BiI\(_2\) were converted to a new solid phase of BiOCI, then, in accordance with the half reaction

\[ \text{BiOCI} (\text{solid}) + 3e^- = \text{Bi} + \text{O}^= + \text{Cl}^- \]  \[8\]

a Nernst slope of 2.3 RT/3F (47.8 mv) would be expected. The concentration of oxide ion, however, would depend on the amount of BiI\(_2\) as well as CaO which had been added. To clarify this point, a separate study of the Bi/BiOCI,O\(_3\) electrode was made.

Bi(III) oxychloride.—The bismuth electrode in the presence of solid BiOCI and added CaO was found to obey the equation

\[ E = -0.935 - 0.045 \log [\text{O}^=] \]  \[9\]

in good agreement with the theoretical equation

\[ E = E^\text{ni=bi}_{\text{eq}} + RT/3F \ln K_{\text{eq}} - 0.0478 \log [\text{O}^=] \]  \[10\]

where \(K_{\text{eq}} = [\text{Bi}^{4+}][\text{O}^=]\).

From the intercept, \(K_{\text{eq}} = 4.2 \times 10^4\). From the potential in the absence of added oxide (\(-0.782\) v vs. 1M Pt), a bismuth ion concentration \([\text{Bi}^{4+}] = 6.6 \times 10^{-4}\) and \(K_{\text{eq}} = 4.4 \times 10^4\) are calculated, in good agreement with the value calculated from the intercept. Moreover, from the polarographic wave height for saturated BiOCl, a solubility of \(6.9 \times 10^{-4}\), corresponding to \(K_{\text{eq}} = 4.8 \times 10^4\), was estimated.

It may be concluded that the electrode Bi/BiOCl,O\(_3\) is behaving reversibly and that the above estimates of the solubility are therefore valid. It is interesting to note that these data indicate no appreciable interaction between Bi\(^{4+}\) and O\(^=\) to form a complex such as BiO\(^-\).

Returning now to the behavior of BiO\(_2\), it is clear from a comparison of Eq. [8] and [9] that, at the same added oxide ion concentration, the BiO\(_2\) electrode showed a more negative potential than the corresponding BiOCI electrode. If BiO\(_2\) were to interact according to Eq. [7] to produce BiOCI and oxide ion, the oxide ion concentration would be increased and qualitatively the electrode potential would be shifted in the negative direction as actually observed. The slope, however, would be affected because the oxide appearing from reaction [7] would exert more influence at low concentrations than at high concentration of added oxide ion. It appears probable that some interaction occurs between solid BiO\(_2\) and the melt, but that either the reaction is not as simple as represented by Eq. [7] or the system is slow to come to equilibrium, or...
both. In an event, the Bi/Bi₂O₅⁺ electrode cannot be regarded as a reversible oxide ion electrode.

Acknowledgment

The porous graphite used in the fabrication of the oxygen electrode was kindly provided by Dr. Seymour Senderoff, of the National Carbon Company. The authors extend their appreciation to the Office of Ordnance Research and the Diamond Ordnance Fuze Laboratory for the financial support of this project and for the research assistantship held by one of them (B. B. Bhatia).

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REFERENCES


Solutions of Some Alkali Halides in the Pure Liquids and in Mixtures of N-Methylacetamide and Dimethylformamide

Lyle R. Dawson and Walter W. Wharton

Department of Chemistry, University of Kentucky, Lexington, Kentucky

ABSTRACT

Dielectric constants, densities, and viscosities of N-methylacetamide, dimethylformamide, and of mixtures of these liquids have been determined at five temperatures. Conductances, densities, and viscosities of solutions of sodium and potassium bromides and potassium iodide in various mixtures of these solvents have been measured at ten-degree intervals from 20° to 50°C. Variations in the dielectric constant of the solvent over the range 35-165 showed no influence on the degree of dissociation of these salts; they are essentially completely dissociated in all of the solvent mixtures studied. Differences in mobilities of the ions are explained in terms of various specific types of solute-solvent interactions.

During the past few years Dawson and co-workers have published from This Laboratory several papers describing the properties of solutions of electrolytes in solvents having high dielectric constants. Very large degrees of dissociation and correspondence with the theoretical Onsager (1) conductance relationships to concentrations much greater in these solutions than in water are attributable to a considerable extent to the high dielectric constants. The investigation reported in this paper was designed to study the influence of large changes in dielectric constant on the degree of electrolytic dissociation and the mobilities of the ions of some univalent bromides and iodides. It was expected that