THE ELECTROCHEMISTRY OF OXYGEN AND CARBON DIOXIDE AT GOLD ELECTRODES IN MOLTEN Li2CO3-Na2CO3-K2CO3 EUTECTIC

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ABSTRACT

Molten alkali carbonate mixtures are of interest for fuel cell electrolytes. Their solution chemistry in contact with both fuel and oxidant gases is complex and is of significance to the electrode reactions taking place. Preliminary results obtained for ternary Li2-Na2-K2CO3 eutectic at 660°C under oxygen/nitrogen atmospheres, carbon dioxide and argon are discussed. The diffusion coefficient for carbon dioxide is 9 ± 2 x 10^-6 cm^2 sec^-1. The solution under oxygen-nitrogen probably involves the equilibrium

\[ O_2 + O_2^{2-} \rightarrow 2O_2^- \]

and the \( E^\dagger \) for peroxide and superoxide ion reduction are close.

INTRODUCTION

The molten alkali metal carbonates are components of the electrolytes employed in the high temperature fuel cell under development at the present time. The early work on molten carbonate fuel cells stalled on the technology associated with electrode composition and electrolyte immobilization (1). Recent developments have shown that nickel/nickel oxide is a suitable porous electrode material and the development of lithium aluminate tile structures has led to active development of a molten carbonate fuel cell prototype. The current fuel cell technology may be compared to that which existed for many years during the development of the Hall-Heroult process, i.e., a commercially viable technology supported by little in depth understanding of the chemistry and electrochemistry involved.

During the sixties Janz and co-workers and others developed a sound basis for the physicochemical properties of molten carbonates (2). These data were recently drawn together and reviewed by workers at IGT (3). This emphasized the areas in which further contributions to the chemistry and electrochemistry of the molten carbonate fuel cell system were needed.

In particular, the chemistry of the complex interactions between fuel gases, oxidant gases, and the electrolyte is still uncertain although the pioneering work of Appleby (4) has highlighted the importance
of species such as peroxide and superoxide in these systems. On the other hand, the details of the electrode reactions are barely understood, in spite of a number of attempts to measure exchange current densities and identify mechanisms (5,6). The limited success of these studies arises partly from the complexity of the systems and partly because of the level of understanding of the electrochemical problem. The use of relaxation techniques is notoriously difficult (7,8), and much of the work suffers from a lack of an appreciation of this fact.

In any kinetic study, the nature of the reactants and products should be identified prior to detailed mechanism studies. It has been our purpose to secure an understanding of this aspect of the oxygen electrode in molten carbonates before proceeding to a detailed kinetic study, initially employing gold planar electrodes. The treatment of three-dimensional porous electrode made of nickel oxide is a formidable problem, and a data base for smooth gold electrodes has been our goal.

The chemistry of molten carbonates is characterized by acid-base behavior of the carbonate ion modified by the alkali metal cation

\[ \text{CO}_3^{2-} \rightleftharpoons \text{CO}_2 + \text{O}_2^{2-} \]  

Thermodynamic calculations (9) indeed show that the reductive processes vary from carbon deposition in the case of Li_2CO_3 to alkali metal formation in the case of K_2CO_3 reflecting in these melts the differing basicity defined as \( P_{0^{2-}} = -\log[O^{2-}] \). Such behavior has been confirmed experimentally and discussed in more detail (10,11).

On the other hand, the interactive behavior of the molten carbonate with gases such as CO (12), CO_2, and O_2 is little understood. It is likely that in these systems oxygen behaves as an oxidizing acid competing with CO_2 for oxide ion, which results in the formation of peroxide or superoxide ions viz.

\[ 2\text{CO}_3^{2-} + \text{O}_2 \rightleftharpoons 2\text{CO}_2 + 2\text{O}_2^{2-} \]  
\[ 2\text{CO}_3^{2-} + 3\text{O}_2 \rightleftharpoons 2\text{CO}_2 + 4\text{O}_2^{2-} \]  

These equilibria also involve the oxygen/carbon dioxide partial pressure ratio, a quantity of some importance in fuel cell operations. Appleby and Nicholson have interpreted their electrochemical studies in Li_2CO_3 (13), Li_2CO_3-K_2CO_3 and Na_2CO_3-K_2CO_3 (14) in terms of reduction of peroxide (Li_2CO_3) and peroxide and superoxide mixture for various O_2/CO_2 ratios equilibrated with the melts. Thermodynamic data to some extent support these findings (15). The influence of basicity has been inferred also from these results (11).

The electrochemical studies reported here are for the ternary (43.5 mol%), Li_2CO_3 (31.5 mol%), Na_2CO_3 (25 mol%) K_2CO_3 system which is a candidate for fuel cell applications and which enables measurements.
to be obtained over a much wider range of temperatures (400-900°C) than
is possible with Li$_2$CO$_3$ or the binary mixtures. The reported data are
obtained close to the fuel cell operational temperature of 680°C and
supplemented where necessary with results at other temperatures.

EXPERIMENTAL

The ternary carbonate mixture 43.5 mol% Li$_2$CO$_3$, 31.5 mol% Na$_2$CO$_3$,
25 mol% K$_2$CO$_3$ was made up from ACS Fisher chemicals which were further
dried over P$_2$O$_5$ in a vacuum desiccator. The mixture, contained in an
alumina crucible, was slowly evacuated while heating to just above the
melting point (397°C). Surface carbon was removed by treatment with
oxygen which was followed by carbon dioxide to convert any base to
carbonate. The melt was cooled and subsequently handled in the dry
box. The cell consisted of a closed end silica tube capped with a
water-cooled brass head through which various working electrodes were
introduced using "Ace" threaded joints (Figure 1). The electrodes were
gold flags of varying sizes supported on gold wires sealed in alumina
capillary tubes. The working electrode areas were measured in the later
work by an electrochemical method described by Wolfe and Caton (16).
The reference electrode was similar to that described by Danner and
Rey (17). The silver concentration was 0.25M Ag$_2$SO$_4$ in Li$_2$SO$_4$-Na$_2$SO$_4$-
K$_2$SO$_4$ eutectic. The aluminous porcelain tube was separated from the
main compartment via a high purity alumina tube with a pinhole in the
closed end. Cyclic voltammetric and chronopotentiometric measurements
were made using either an AMEL 551 or a PAR 373 potentiostat and a
PAR 175 signal generator. The resultant transients were recorded on
an X-Y recorder or at high frequencies on a Bascom-Turner microprocessor-
controlled data recorder and stored on floppy disc for subsequent analysis.

RESULTS AND DISCUSSION

Argon. Initially, the ternary electrolyte was examined under argon
at lower temperatures to assess the purity of the melt. Figure 2 shows
a low sensitivity cyclic voltammogram indicating the accessible range of
this melt at 430°C. The cathodic peak arises from the reduction of
carbonate to carbon as demonstrated by potential-controlled electrolysis
at these potentials on the substrates. These observations are in agree­
ment with the earlier results of Ingram, Baron and Janz (18) at 600°C.
The sharp stripping peak confirms the presence of an insoluble reduction
product.

High sensitivity (100X more sensitive) cyclic voltammograms are
shown in Figure 3 for several different cell atmospheres at 680°C.

Under argon at the higher sensitivity, an anodic rising current is
seen which, under closer inspection, shows the presence of a shoulder.
The $E_1$ is similar to peaks observed in the presence of added oxide (19).
Thus, even at 680°C some decomposition of the carbonate ion takes place
viz..
CO$_3^{2-}$ (l) $\leftrightarrow$ CO$_2$ (g) + O$_2^-$ (soln) \hspace{1cm} (4)

for which

$$P_{CO_2} = \frac{K}{a_0^2}.$$

Now since the oxide activity is inversely proportional to the CO$_2$ pressure, as the oxide ion activity rises, $P_{CO_2}$ falls and eventually a steady state is reached in which CO$_2$ loss becomes negligibly slow. The observed residual oxide peaks reflect this situation. Preliminary measurements suggest the oxide ion concentration in this case to be 0.8 x 10$^{-6}$ mol-cm$^{-3}$. The oxide ion concentration calculated using the data given by Janz (20) at the dissociation pressure of the carbonate is 0.6 x 10$^{-6}$ mol-cm$^{-3}$. The latter figure represents a lower estimate and our value is therefore reasonable. Further, at the dissociation pressure of CO$_2$ the solubility of CO$_2$ will be small and the cyclic voltammetry will not detect such a low concentration. This is supported by the scan shown in Figure 3. No further peaks are detected in the potential region 0 to -1.506V with respect to CO$_2$/O$_2$ (2:1) reference electrode.

Carbon Dioxide. Changing from argon to carbon dioxide atmosphere above the melt resulted in the development of a reduction peak at $E_1 \approx$-1100 with respect to the CO$_2$/O$_2$ (2:1) reference. The reduction peak showed a reverse anodic peak, much less than expected for a reversible system. There was a slight dependence of peak potential on scan rate for the limited range of scan rates. Using the solubility data reported by Appleby and Van Drunen (21) at 700°C, and assuming no temperature dependence between their working temperature and our temperature of 660°C, (for n = 1 from $\Delta E_D/2$) the diffusion coefficient for carbon dioxide is 9 ± 2 x 10$^{-6}$ cm$^2$sec$^{-1}$.

According to Andersen (15),

$$K_D = \frac{P_{CO_2} N_{O_2^-}}{N_{CO_3}} = 1.77 \times 10^{-8} \text{ atm}$$

Thus, at 1 atmosphere CO$_2$, the concentration of oxide ions will be $\approx$10$^{-10}$ mol-cm$^{-3}$, well below the detection limit of cyclic voltammetry. This is then consistent with the disappearance of the oxide wave under a carbon dioxide atmosphere.

Oxygen-Carbon Dioxide 3:1 Mixture. The cyclic voltammograms under this mixture at comparable sensitivities to those used for CO$_2$ and argon are rather featureless (Fig. 3). The carbon dioxide solubility was not detected. New equilibria (2) and (3) may now control the solution chemistry and suppress lower oxidation states of oxygen.
Oxygen–Nitrogen Mixtures. The introduction of differing oxygen-nitrogen mixtures has a dramatic effect on the solution chemistry which is highlighted both in the cyclic voltammetric and chronopotentiometric responses at gold electrodes. Figures 3, 4 and 5 illustrate typical cathodic and anodic scans from the open circuit potential of the gold electrode. Figure 6 shows the variation of peak current with gas composition at scan rates up to 250 mV-sec⁻¹ and Figure 7 shows the variation of $\tau^\frac{1}{4}$ ($\tau$ = transition time) as a function of applied current $i$ and gas atmosphere. The Sand equation is clearly verified and $E_{\tau}/4$ was apparently independent of applied current density indicating the presence of a diffusion-controlled reaction.

The observation that the rest potential lies within the cyclic voltammetric envelope is interesting because it indicates the presence of more than one redox species at equilibrium. An attempt to resolve these species can be made by recognizing the relationship between the concentration of the solution species undergoing reduction, the Sand constant, and the oxygen partial pressure. Again, it is anticipated that reactions such as (2) and (3) will reach a steady state since it is actually the $P_{O_2}/P_{O_2}$ ratio that ultimately fixes the equilibrium. The coexistence of peroxide ions and superoxide ions under varying oxygen partial pressure must also be considered in addition to the reactions in reactions (2) and (3). This is expressed by

$$O_2^2^- + O_2 \rightleftharpoons 2O_2^- \quad (5)$$

The various relationships derived between the Sand constant $i\tau^{\frac{1}{4}}$ and the oxygen partial pressure are given in Table 1. The cyclic voltammetric data are not subject to this analysis because (a) the Randles Sevcik equation is dependent on the model, i.e., $\chi(i)_{\text{max}}$ is a variable function which depends on whether the product of reaction is soluble, insoluble, and coupled to subsequent chemical reactions or whether the electrochemical reaction is reversible or irreversible under the experimental conditions, and (b) the value of "n" the number of electrons in the overall reaction (diffusion control) or the number of electrons in the rate determining step times $\alpha$ the transfer coefficient (kinetic control) appear in the slope.

From the limited data so far available, the slope observed is close to the theoretical (Fig. 8) 0.5. This implies that either peroxide ions are the solution species if a single moiety is present or more reasonably that the equilibrium (5) controls the solution chemistry and superoxide ions are the electroactive species. This latter choice is supported by the cyclic voltammetric data. Diagnostic potential analysis of the cyclic voltammograms using $\Delta E_p/2 = E_p-E_{p/2}$ in particular, shows the initial cathodic cycle to involve 3 electrons in a diffusion controlled process consistent only with superoxide ion being reduced.

Subsequent reversal of the cathodic sweep produced an anodic peak (Fig. 4) whose $\Delta E_p/2$ is consistent with $n = 2$, implying

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The second cycle of the voltammogram (cathodic) produced a peak whose \( \Delta E_{p/2} \) are now consistent with \( n = 2 \), i.e.,

\[
2\text{O}^2- + 2e \rightarrow \text{O}_2 + 2\text{e}^- \tag{6}
\]

Table 2 illustrates this potential data. The involvement of oxide ions as the final reduction product is supported by the observation that no further reduction peaks are observed beyond about -350 mV vs. CO\(_2\)/O\(_2\) (2:1) reference electrode.

The results imply that the reduction potentials of superoxide ion and peroxide ions may be very close in this melt. Appleby has reported such overlap for the reduction of these ions in Li\(_2\)CO\(_3\)/K\(_2\)CO\(_3\). Further work is underway to confirm this identification of the solution species and to investigate the influence of small controlled amounts of CO\(_2\) in the gas streams. The kinetics of these processes will then be open to direct measurement.

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| No. | Solution Reaction | Equation | Chronopotentiometric/O₂ Partial Pressure Dependence | Slope |
|-----|------------------|----------|-----------------------------------------------|-------|
| 2   | Peroxide Formation | \( \frac{1}{n} \log \frac{\Pi_{\text{FA}}}{\Pi_{\text{FA}^2}} = 0.51 \log P_{\text{O}_2} - \log K'_{n} \) | 0.5 |
| 3   | Superoxide Formaon | \( \frac{1}{n} \log \frac{\Pi_{\text{FA}}}{\Pi_{\text{FA}^2}} = 0.75 \log P_{\text{O}_2} - \log K''_{n} \) | 0.75 |
| 5   | Peroxide Reduced  | \( \frac{1}{n} \log \frac{\Pi_{\text{FA}}}{\Pi_{\text{FA}^2}} = - \log P_{\text{O}_2} - \log K'_{n} \) | -1.0 |
| Atmosphere | First Cathodic Cycle | Second Cathodic Cycle | Anodic Cycle |
|------------|----------------------|-----------------------|--------------|
|            | $\Delta E_{p/2}$ mV | $\Delta E_{p/2}$ mV | $\Delta E_{p/2}$ mV |
| 100% $O_2$ | 86 ± 3               | 95 ± 3                | 101 ± 2      |
| 22% $O_2$/78% $N_2$ | 66 ± 1               | 84 ± 2                | 102 ± 5      |
| 10% $O_2$/90% $N_2$ | 67 ± 4               | 87 ± 4                | 115 ± 6      |
| n = 3      | n = 2                | n = 2                 |              |

$\Delta E_{p/2} = \frac{176}{n}$ at 660°C for $ox = ne \xrightarrow{\mathit{Red}} 2ox \xrightarrow{\mathit{Red + ne}}$ (22) at 660°C.
Fig. 1. Cell for electrochemical measurements in carbonate melts.

A - Carbonate Melt  
B - Gold Flag Electrode  
C - Ag/Ag$_2$SO$_4$ in (LiNaK)$_2$SO$_4$  
D - Silica or Pyrex  
E - Alumina Crucible  
F - Gas Bubbler

Fig. 2. Low sensitivity cyclic voltammogram, ternary carbonate melt, T = 430°C. Atmosphere argon, 200 mV-sec$^{-1}$, Au sphere area 0.08 cm$^2$. Insert (Ref. 18) - (1) CO$_2$, (2) argon atmosphere, T = 600°C.
Fig. 3. Cyclic voltammetry in carbonate melt under different atmospheres. Sweep under pure oxygen; 100% O\textsubscript{2} rate = 100 mV-sec\textsuperscript{-1}, area = 0.367 cm\textsuperscript{2}, atmosphere, Au electrode, T = 680°C.

Fig. 4. Cyclic voltammogram rate = 125 mV-sec\textsuperscript{-1}.

Fig. 5. Variation of peak current as a function of scan rate and oxygen partial pressure. T = 660°C.
Fig. 6. Chronopotentiogram at gold electrode under pure oxygen. Applied current density = 3.27 mA/cm$^2$, rest potential = -226 mV vs. CO$_2$ 67%/O$_3$ 33%, reference electrode.

Fig. 7. Variation of $\tau^3$ with reciprocal current and oxygen partial pressure. $T = 660^\circ$C.

Fig. 8. Chronopotentiometric function plotted vs. oxygen partial pressure.