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**Molten Carbonate Fuel Cell Program
Progress Report for Periods
October 1-December 31, 1977
January 1-March 31, 1978**

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CHEMISTRY DIVISION

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PROGRESS REPORT FOR PERIODS
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SUMMARY

During this period progress has been made in the simulation of mass transport relaxation in molten carbonate fuel cells as a guide to the design of experiments for the measurement of needed transport and thermodynamic properties of molten carbonates. A new tile electrolysis cell was completed and experiments initiated to measure emf relaxations after electrolysis of carbonate tiles and to search for possible concentration gradients. A cell was designed and constructed, and experiments initiated, for the measurement of the emf of concentration cells with transference in Li_2CO_3 - K_2CO_3 mixtures, in order to determine the relative mobilities of lithium ion and potassium ion relative to carbonate. Experiments were initiated also on determining the equilibrium lithiation of NiO in Li_2CO_3 - K_2CO_3 melts under CO_2 - O_2 atmospheres. A survey of literature on physical properties of stoichiometric and nonstoichiometric NiO was carried out.

I. Simulation of Mass Transport Relaxation (C. E. Vallet)

The mass transport model⁽¹⁾ has been applied to evaluate the effects of changes in the diffusion coefficient in the mobility difference of cations Li^+ and K^+ , and of the previously neglected but probably significant activity coefficient on the predicted polarization emf during electrolysis and decay following electrolysis.

The emf, on open circuit, between anode and cathode is related to the concentration at both electrodes by⁽²⁾:

$$E = - \frac{1}{2F} \int_{X''}^{X'} \frac{t_L^C - X_L}{1 - X_L} \frac{d \mu_{L,C}}{d X_L} d X_L \quad (1)$$

where X' and X'' are the concentrations (mole fraction) of Li_2CO_3 at the anode and at the cathode respectively; t_L^C is the (internal or Hittorf) transference number of lithium relative to carbonate ions; X_L is the mole fraction of Li_2CO_3 ; $\mu_{L,C}$ is the chemical potential of Li_2CO_3 in the Li_2CO_3 - K_2CO_3 mixture. The transference number may also be expressed in terms of the mobilities of Li^+ and K^+ relative to CO_3^{2-} , $t_L^C = \frac{X_L U_L}{X_L U_L + (1-X_L) U_K}$.

Figure I.1 illustrates the effects of the transport parameters (transference number, interdiffusion coefficient) and of the activity coefficient on the predicted polarization potential difference between the electrodes during an electrolysis at constant current followed by a relaxation on open circuit at a temperature of 650°C. In Fig. I.1a the computations are done for a hypothetical ideal binary electrolyte mixture (0.5 K_2CO_3 -0.5 Li_2CO_3) with an interdiffusion coefficient of $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Figure I.1a shows the curves obtained with the assumption of constant mobility ratios U_L/U_K of 1.5 or 2, and with the assumption of a transference number of lithium relative to carbonate calculated as $t_L^C = 2.82 X_L^2 - 1.82 X_L^3$. In the latter case, the mobility ratio U_L/U_K varies with composition, being less than 1 for $X_L < 0.56$ and greater than 1 for $X_L > 0.56$. In all three cases the steady state is reached after comparable times of electrolysis, but the magnitude of the potential

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Fig. I.1 Effect of transport and thermodynamic parameters on the time dependence of the emf (open circuit) of anode relative to cathode during electrolysis and following relaxation.

- (a) No activity coefficient correction, $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $r = u_L/u_K = 1.5, 2.0$; dashed line is calculated with transference number given by $t_L^C = 2.82 X_L^2 - 1.82 X_L^3$.
- (b) Activity coefficient given by Eq. (17), $D = 1 \times 10^{-5}$, $r = 1.5, 2.0$.
- (c) No activity coefficient correction, $D = 20, 10, 4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $r = 2$.
- (d) Same D and r as (c) but with activity coefficient correction.

difference after a given time of electrolysis and at the steady state varies strongly with the mobility ratio. The steady state potential difference is 1.5 mV for a mobility ratio $U_L/U_K = 1.5$, and is near 4 mV for a mobility ratio of 2. Two different assumptions for the mobilities or the transference number, $U_L/U_K = 1.5$ and $t_L^C = 2.82 X_L^2 - 1.82 X_L^3$, leading to concentration gradients with opposite signs, give very similar potential-time curves. Since the tendency towards separation is driven by the mobility difference of the two cations, the sign of $(X' - X'')$ resulting from electrolysis is determined by the sign of $(t_L^C - X_L)$, with the more mobile cation accumulating at the cathode. Hence, as can be seen from Eq. (1), the sign of the measured potential difference is insufficient to determine the sign of the concentration gradient (as it would be if the electrodes were reversible to one of the ions of like charge) unless the sign of $(t_L^C - X_L)$ is known. Figure I.1b shows the effect of the activity coefficient on the computed potential differences with the assumptions of mobility ratios of 1.5 and 2. A plausible composition dependence of the activity coefficient in the $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ mixtures may be obtained by assuming the excess chemical potential of Li_2CO_3 at 650°C equal to the partial excess enthalpy of Li_2CO_3 at 900°C derived from the heat of mixing measurements of Andersen and Kleppa⁽³⁾. The excess chemical potential of Li_2CO_3 , in J mole^{-1} , thus is taken as

$$\mu_{\text{Li}_2\text{CO}_3}^E = RT \ln \gamma_{\text{Li}_2\text{CO}_3} \approx H_{\text{Li}_2\text{CO}_3}^E = -49371.2 X_{\text{K}_2\text{CO}_3}^2 + 22175.2 X_{\text{K}_2\text{CO}_3}^3 \quad (2)$$

Figure I.1b shows that the activity coefficient from Eq. (2) gives rise to larger calculated potential differences. E.g., with a mobility ratio of 2, a calculated steady state potential difference of near 4 mV under the assumption of ideality for the $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ mixture becomes 12 mV when the activity coefficient is included. Changes in the transference number and the introduction of an activity term do not influence significantly the rate of decay of the potential difference on open circuit following an electrolysis. Figures I.1c and I.1d illustrate the effect of the interdiffusion coefficient on the potential difference-time curves. The lowest value of the diffusion coefficient ($4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) gives the largest potential difference at the end of the electrolysis and the

longest time required to reach the steady state. The overall time to relax to zero potential is longer. With $D = 4 \times 10^{-6}$, the potential difference halves in about 7 minutes instead of 1.7 minutes for $D = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

These observations suggest an empirical method for estimating the interdiffusion coefficient and the transference number in a binary electrolyte in which direct measurements may be more difficult. Relaxation curves of the potential difference between anode and cathode may be monitored following electrolyses for various times and at various current densities. The initial rate of decay, which appears to depend little on the transference number, can be used to estimate the value of the interdiffusion coefficient, D , by matching the initial portion of a calculated decay curve with the experimental curve. Various plausible concentration dependences of the transference number may thus be tested to provide a better match of the calculated curve to the experimental curve and a better fit for the transference number. However, as pointed out earlier, the sign of the emf following electrolysis is not sufficient to indicate which ion is the more mobile, unless the sign of the concentration gradient between the electrodes is known. Independent potential measurements of concentration cells, where the compositions in both compartments are fixed, will give the sign of $(t_L^C - X_L)$, and such measurements have been initiated. These measurements will also provide a calibration of the observed potential difference in terms of the compositions at the electrodes. The compositions at the electrodes can be calculated by using the numerical solution of the diffusion migration equation with the estimated values of D and t_L^C . The corresponding observed potential difference may be compared to that derived from the calibration in checking the consistency of the result.

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II. EMF Relaxation in Electrolyzed Molten Carbonate Fuel Cell Tiles (H. R. Bronstein and J. I. Padova)

In an operating molten carbonate fuel cell the electrode reactions may be represented as

or

Carbonate ion is thus seen to be the electroactive constituent in the melt, being produced at one electrode and consumed at the other. The net current can be represented in terms of the migration of Li^+ and K^+ relative to CO_3^{2-} so that a knowledge of the transport properties is important⁽¹⁾. Under conditions of high current drain, if a sufficient difference exists between the electrical mobilities of the nonelectroactive constituents (Li^+ and K^+ ions), a variation in the normal ratio, i.e., concentration gradients within the melt⁽²⁾, might develop. The physical properties of the melt which are concentration dependent would change, and in an extreme case this phenomenon could lead to precipitation of Li_2CO_3 or K_2CO_3 ⁽³⁾. Computations⁽²⁾ have indicated the conditions under which such concentration gradients could occur.

In order to obtain direct experimental measurements of possible composition changes occurring in the electrolyte and in the electrodes, an electrolysis apparatus^(3,4) was designed and constructed. This particular apparatus had rather high lead to lead resistance (of the order of 10 ohms) suggesting high contact resistance between tile and the NiO electrodes, contributing to the observed high joule heating. Thermocouples placed at the collector plates registered temperature increases upon passage of current greater than expected for I^2R heating of the electrolyte. A new apparatus was designed and constructed during this period and is illustrated in Fig. II.1. The new apparatus enabled a greater and more uniform pressure to be applied to the cell sandwich, which greatly reduces the previously high contact resistance. The use

Fig. II.1 Cell for electrolysis of $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-LiAlO}_2$ tiles between Ni(NiO) electrodes under $\text{CO}_2\text{-O}_2$ atmosphere, and measurement of emf relaxation after current flow.

of identical electrodes and the same gas mixture for each electrode eliminate the need for wet seals. The potential changes resulting from current flow are measured relative to the very small bias potential between nearly identical electrodes, rather than relative to varying and much larger potential differences resulting from the different electrode reactions of fuel and oxidant gases. The electrolyte tile* is a disk about 0.2 cm thick and 2 cm in diameter. Porous nickel disks* are pressed against the tile faces by the perforated stainless steel current lead disks. The temperature at each electrode is monitored by the thermocouples as shown. The porous nickel disks are oxidized in situ at 873°K to NiO (oxygen) electrodes by the operating gas mixture $\text{CO}_2:\text{O}_2$ (67-33% by volume). Operating tests have been completed, and systematic measurements of the emf relaxation following electrolysis as a function of electrolysis time, current density and temperature are under way.

*Supplied by Drs. J. Ackerman and K. Kinoshita, Argonne National Laboratory.

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III. Concentration Cells with Transference (J. I. Padova and H. R. Bronstein)

Among the needed transport coefficients in molten carbonate fuel cell electrolyses are the inner cation transference numbers relative to the carbonate ion. These are in general determined by one of three methods: Hittorf (electrolysis method) type measurements, moving boundary measurements or study of emf cells with transference. For molten salt mixtures at high concentrations, where a reversible electrode exists, the third method may be most appropriate. It is being applied to molten carbonate mixtures using the cell indicated below.

It has been previously shown⁽¹⁾ that in concentration cells with transference and two electrodes reversible to the common ion, the emf E_c of the cell is given by

$$-FE_c = +\Delta G = \int_I^{II} \frac{t_{\text{Li}}^{-y}}{1-y} \frac{d \mu_{\text{Li}_2\text{CO}_3}}{dy} dy \quad (1)$$

where y is the equivalent fraction of the Li_2CO_3 in the melt.

Expression (1) leads to

$$\frac{d (FE_c)}{dy} = - \frac{t_{\text{Li}}^{-y}}{1-y} \frac{d \mu_{\text{Li}_2\text{CO}_3}}{dy} \quad (2)$$

The estimation of the transference numbers from the change of the emf with the Li_2CO_3 fraction requires a knowledge of the change in chemical potential of the same species with lithium carbonate content in the melt. These values may be obtained from the phase diagram⁽²⁾ and heat of mixing data⁽³⁾ of the system $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$. Even without accurate activity coefficients, however, the sign of (t_{Li}^{-y}) and hence the more mobile ion may be obtained directly from the sign of the experimental emf.

An apparatus to conduct such experiments has been designed and constructed and is shown in Fig. III.1. The initial experiments will be carried out with saturated solutions corresponding to either side of the phase diagrams and concentrations read at each temperature.

The electrochemical cell consists essentially of two compartments, a cylindrical alumina crucible containing one solution of $\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ into which the second compartment, an alumina tube, is situated. The junction between the two solutions is provided by a creeping film from the solution of $\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ in the inner tube through a 13 mil diameter hole. The electrodes are gold tubes one in each compartment with perforated gold discs at the end. They will serve as bubblers for the $2\text{CO}_2\text{-O}_2$ gas mixtures, and thermocouples (gold covered) are contained therein for checking the temperatures at both the anode and cathode. The system is enclosed in a high cylindrical quartz furnace (not shown on the figure) which is monitored by an additional thermocouple and can be evacuated or flushed with dry gas (CO_2 or $\text{CO}_2 + \text{O}_2$ mixtures).

The electrochemical cell and furnace were tested over the experimental temperature range of 500°C to 800°C and under vacuum. The salt mixtures are to be loaded into the cell and dehydrated in situ by standard techniques before commencing the experiments. Since the solutions are saturated either with K_2CO_3 (outer compartment) or Li_2CO_3 (inner compartment) there should be no concentration changes due to mass transport through the creeping film, and concentrations will be fixed by the temperature at which the experiment is performed. However since the mobility ratio might change from $U_{\text{Li}}/U_{\text{K}} > 1$ to $U_{\text{Li}}/U_{\text{K}} < 1$, further measurements at various concentrations are planned to characterize the mobilities and evaluate the possibility of component separation in fuel cell tiles.

Fig. III.1 Concentration cell with transference.

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IV. Nickel Oxide Electrode Studies (H. R. Bronstein and J. Braunstein)

Lithiation, or substitution of a Li^+ for a Ni^{2+} ion accompanied by oxidation of Ni^{2+} to Ni^{3+} , (which is chemically equivalent to formation of LiNiO_2) in an NiO lattice is known to occur in an oxidizing atmosphere at high temperatures (1300–1800°C)⁽¹⁾. This not only imparts higher electrical conductivity because of delocalization of the excess positive charge, but is thought to be responsible for the electrocatalytic activity of NiO fuel cell electrodes⁽²⁾. Significant literature exists on the properties of NiO in the range between the stoichiometric, insulator, state and the nonstoichiometric, metal deficient, semi-conductor state, as well as on the effect of foreign ion impurities such as lithium on electronic conductivity and on catalytic activity as an oxygen electrode. Listed in the accompanying bibliography is a selection of publications from 1950 to the present which covers many of these properties. The following tabulation indicates some of the properties of interest and the specific references dealing with them.

Table IV.1 NiO Properties and Bibliography Reference Numbers

<u>Properties</u>	<u>Reference No.</u>
Stoichiometry	1, 4, 6, 7, 12, 16
Insulator	1, 6, 7, 10, 16
Magnetic	4, 6
Electrical conductivity	1, 6, 10, 12, 14, 16
Catalytic activity	9, 16, 22, 25, 30, 31
Crystal structure	1, 3, 4, 7, 18, 23
Electrochemical behavior	8, 13, 17, 22, 24, 25, 28, 31
Preparation, lithiation and foreign ion effect	1, 2, 3, 4, 7, 10, 12, 14, 16, 19, 21, 22, 26, 27
Theory	1, 2, 4, 5, 6, 7, 14, 20
Hall effect	15
Thermodynamic properties	16, 19, 29
Electrical and optical properties	20

In a molten carbonate fuel cell, the cathode is formed in situ by oxidation of the original porous nickel electrode by the cathode gas $\text{CO}_2:\text{O}_2$ (2:1) at the operating temperature 823-923°K. Lithiated single crystal NiO has been extensively studied as an electrode in aqueous solutions, but these crystals have been formed under conditions differing vastly from those existing in the molten carbonate fuel cell. Experiments are underway with stoichiometric single crystals of NiO immersed in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (62-38 mole %) melts for various time intervals and oxidizing conditions and at temperatures of an operating fuel cell. The extent of oxidation and Li penetration will be determined by analytical techniques such as SEM, ion microprobe and flame emission spectroscopy. In the initial experiments single crystals were submerged in the melt under a cover gas of $\text{CO}_2:\text{O}_2$ (2:1) and held at temperature of 923°K for a period of 100 hours. Chemical analyses have indicated the crystals to contain 50 ppm lithium, which would correspond to 0.06 mole percent replacement of Ni by Li. It is not known yet whether the lithium is uniformly distributed through the crystals or resides on the surface. A profile study using SEM and ion microprobe techniques should yield the desired information. This concentration, if uniformly distributed, is insufficient to significantly enhance the electronic conductivity of NiO. Further experiments will be done under controlled higher oxidizing conditions and temperature in an attempt to define the oxidative substitution equilibrium

and ultimately to prepare such an electrode of well defined surface area to study cathodic electrode kinetics.

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