MEMBRANE POTENTIALS ACROSS MACOR IN MIXTURES OF MOLTEN BROMIDES

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ABSTRACT

Potentials generated across a Macor membrane in molten NaBr-KBr mixtures were measured. The composition of a melt on one side of the membrane was fixed and the other allowed to vary systematically in the conducted cations. Measurements were made with mixtures of Na-Br-KBr and LiBr-KBr. The best \( K_{Na-K}^{POT} \) and \( K_{Li-K}^{POT} \) were calculated for the systems from the data points. The measured membrane potentials were plotted as a function of the activity of one of the ions in the indicator melt and compared with a curve of the theoretical potentials.

INTRODUCTION

Many ceramics conduct ionically in molten salt solutions at high temperatures. However, most are not exclusive conductors of a single ion. For example, mullite conducts Na\(^+\), K\(^+\), and Li\(^+\) ions (1). Such mixed conduction is believed to occur via a glassy phase in the ceramic.

When this type of ceramic forms a separator in an electrochemical cell, a membrane potential is generated across the conductor. This potential is predicted by the equation:

\[
E_{mem} = \frac{RT}{F} \ln \left( \frac{a(N^+)I + K_{NM}^{POT} \cdot a(M^+)I}{a(N^+)O + K_{NM}^{POT} \cdot a(M^+)O} \right)
\]  \hspace{1cm} (1)

where the \( E_{mem} \) is the potential generated, \( R, T, F \), are the gas constant, the temperature, and Faraday's constant, \( a(N^+)I \) and \( a(N^+)O \) are the activities of the conducted ion \( N^+ \) on either side of the membrane, and \( a(M^+)I \) and \( a(M^+)O \) are the activities of the second conducted ion \( M^+ \) on either side of the
membrane. \( K_{\text{POT}}^{\text{POT}} \) is the potential selectivity coefficient which is a measure of the preference of the membrane for \( M^+ \) over \( N^+ \) as a means of moving ionic current (2). For example, if the potential selectivity coefficient for a mixture of \( \text{NaBr-KBr} \), \( K_{\text{Na-K}}^{\text{POT}} \) is less than 1, a preference for \( \text{Na}^+ \) conduction by the membrane is indicated. If the value is small enough the membrane becomes effectively an exclusive conductor of \( \text{Na}^+ \).

The relationship between the value of potential selectivity coefficient and the composition of a membrane has been established for glasses in aqueous solutions (3). It may hold as well for ceramic membranes in molten salts. This investigation proposes to examine that relationship beginning with Macor. Macor is a machinable glass ceramic produced by Corning and containing approximately 60% crystalline and 40% glassy phases. It is approximately 47% \( \text{SiO}_2 \), 8.5% \( \text{B}_2\text{O}_3 \), 16.7% \( \text{Al}_2\text{O}_3 \), 14.5% \( \text{MgO} \), 9.5% \( \text{K}_2\text{O} \), and 6.3 fluoride by weight. This material was selected because it is commercially available and is replicated by other manufacturers with only slight modifications in composition. In addition glass ceramics have good resistance to high temperatures and have been shown in this work to resist degradation in molten salts.

**EXPERIMENTAL**

A diagram of the experimental apparatus depicted in Figure 1. It and the experimental procedure are fully described in (1). A large mullite tube contained the experimental system. Dry argon flowed throughout the system at all times during the experiments. One gas inlet was directed through the reference melt and the other into the indicator melt. A silver crucible contained the indicator melt, which was changed for each experiment, and the reference melt of constant composition. The Macor was purchased as a rod 2.54 cm. in diameter and 7.62 cm. in length. The rod was machined to form a tube with one end closed and a wall width of either 0.3175 or 0.1587 cm. This tube held the reference melt and the wall of the tube became the membrane determining the potential of the cell.

The cell may be described,

\[
\text{M}^1\text{Br} (\text{mol} \%=\text{X}), \text{M}^2\text{Br} (\text{mol}\%=\text{100-X-Y}), \text{AgBr} (\text{mol}\%=\text{Y}) | \text{Ag} | \text{Macor} | \text{M}^1\text{Br} (\text{ref} = 10 \text{ mol}%), \text{M}^2\text{Br} (\text{ref} = 85\text{mol}%), \text{AgBr} (\text{ref} = 5\text{mol}%) | \text{Ag}
\]

where \( \text{M}^1\text{Br} \) and \( \text{M}^2\text{Br} \) define either the combination, NaBr-KBr or NaBr-LiBr, the mole fractions \( \text{X} \) and \( \text{Y} \) vary from 10-90%, ref stands for the reference melt composition. Both electrodes were silver wire.
The indicator melt, the Macor tube containing the reference melt and the electrodes were sealed into the mullite chamber and the temperature of the system raised to 760°C. Equilibration of the temperature required approximately 1-2 hour. After this time the electrodes were lowered into the melts and readings were taken every minute until a stable potential was reached.

To insure that the membrane potential was equal to the measured cell potential the contribution to the potential from the electrodes was fixed at 0.00 volts. Both electrodes were the same silver wire and the mole fraction of AgBr was adjusted in the indicator melt to make the activity of AgBr in that melt the same as in the reference melt. Activities of AgBr in each indicator melt were determined using the equation (4),

\[ RT \ln \gamma_x = k_{12}N_1N_2 + (k_{x1}N_xN_1 + k_{x2}N_xN_2)(N_1 + N_2) \]  

for a ternary solution where \( x \) indicates AgBr and 1 and 2 the alkali metal bromide components of the mixture, \( \gamma_x \) is the activity coefficient of AgBr, and \( k \) is the interaction coefficient of the pair of components indicated by the subscript. Activity coefficients for each system of alkali metal bromides were calculated with the same equation using appropriate interaction coefficients (5-9).

RESULTS AND DISCUSSION

The Macor membrane resisted degradation in the molten salts very well. It lasted, on average several weeks longer than did mullite in earlier experiments. The resistance of the Macor membrane to degradation may be explained by its microstructure and the nature of failure in such membranes. Earlier work with a mullite membrane indicated that failure usually occurs through crack propagation begun through a corrosion process. In the Macor membrane the mica crystalline phase, which makes the ceramic machinable with ordinary tool steel, inhibits crack growth.

The measured membrane potentials for NaBr-KBr melts are plotted as a function of the activity of Na\(^+\) in the indicator melt in Fig. 2. \( K_{Na-K}^{POT} \) values were calculated for each measurement using equation 1 and the measured membrane potentials. They are shown as a function of the activity of the Na\(^+\) ion in the melt in Fig 3. The \( K_{Na-K}^{POT} \) is clearly a constant within reasonable experimental error indicating that the membrane potentials may be predicted by equation 1. Values of \( K_{Na-K}^{POT} \) are shown in Fig. 3 for two membranes, one 0.3175 cm and the other, 0.1587 cm thick. As expected in these early experiments the thickness of the membrane had no effect on the potential.
selectivity coefficient. It did however significantly affect the time required for the system to come to equilibrium. With the 0.125 cm membrane the system required approximately 2.5 hours, but with the 0.0637 cm membrane 1.5 hours was required.

The best value, $K_{Na-K}^{POT} = 0.452$, was calculated using a commercial curve fitting program. This value was substituted into equation 1 to generate the theoretical potential line shown in Fig. 2. The experimental values agree quite well with this theoretical line making the calculation of membrane potentials with this $K_{Na-K}^{POT}$ a practical matter.

The value of $K_{Na-K}^{POT} = 0.452$ indicates that the membrane has a slight preference for conducting Na$^+$ over K$^+$ ions ($K_{Na-K}^{POT} < 1$) although the size of this number suggests that both ions are easily conducted. This result contrasts with the $K_{Na-K}^{POT}$ found for mullite (1) which indicated a greater preference for Na$^+$ ($K_{Na-K}^{POT} = 0.048$). Unlike the mullite the assumption of exclusivity of conduction across a Macor membrane at any activity of K$^+$ in a mixed melt would lead to serious error in the calculation of a membrane potential.

The experimental potentials were also plotted in Fig. 4 using a modification of equation 1 proposed by Eisenman et al. (10),

$$E_{mem} = \frac{RT}{nF} \ln \left( \frac{a(Na^+)_{1/n} + a(K^+)_{1/n}}{a(Na^+)_ref + a(K^+)_ref} \right)$$

where $n$ is a correction for the nonideality of sites on the surface of the membrane. $K_{Na-K}^{POT}$ and $n$ were calculated to best fit the data ($K_{Na-K}^{POT} = 0.428$, $n = 1.077$) and were used to generate the theoretical line in Fig. 4. The results indicate that this modification does not improve the fit of the experimental data to the theoretical curve, suggesting that relationship does not depend on the ideality of surface exchange sites on the membrane.

The measured membrane potentials for KBr-LiBr melts are plotted in Fig. 5. Using the same method as that for NaBr-KBr melts the best value of $K_{Li-K}^{POT} = 0.1178$ was calculated and used to generate the theoretical line shown in Fig. 5. Agreement between the measured and theoretical potentials is less than in the Na-K system. The measured potentials are plotted again in Fig. 6 with a theoretical curve generated from equation 3 and $K_{Li-K}^{POT} = 0.2265$ and $n = 0.5954$. Using the Eisenman modification of equation 1 improves the
correlation between experimental data and theoretical but the agreement is still not as good as that found for the Na-K system. Since the measured cell potentials were reproducible, and since a very similar problem was observed with the mullite membrane in the Li-K system the error may be due to factors other than experimental procedure. The interaction coefficients and calculated activity coefficients indicate that this system is much more removed from the ideal than is the Na-K system. Any error in the interaction coefficients would lead to a just such systematic error as appears in the experimental data.

In this system the \( K_{\text{Li-K}}^{\text{POT}} \) indicates the membrane shows a preference for the conduction of Li\(^+\) over K\(^+\) this preference being greater, \( K_{\text{Li-K}}^{\text{POT}} < K_{\text{Na-K}}^{\text{POT}} \), than that for Na\(^+\) over K\(^+\). Overall the mullite conducted Na\(^+\) to a greater extent than Li\(^+\) and Li\(^+\) to a greater extent than K\(^+\). In the Macor system, even without the results from the third system, the likely preferred order of conduction will be Li\(^+\) > Na\(^+\) > K\(^+\). It seems reasonable to assume that the difference in transport numbers is due to the difference in the composition of the conducting phases. Additional work is planned with different glass ceramics to examine this idea further.

SUMMARY

The potentials measured across Macor in molten NaBr-KBr and LiBr-KBr solutions are predicted quite well by equation 1. Use of Eisenman's modification of equation 1 does not improve the correlation of data with theory in the Na-K system, but does improve the agreement for the Li-K system. The value of the potential selectivity coefficients suggests a tentative ranking of conductivity, Li\(^+\) > Na\(^+\) > K\(^+\) for a Macor membrane. Again this order is different from that observed for a mullite membrane suggesting that the composition of the glassy phase is likely different as well.

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Silver wire Ag/Ag elec-
trode
Silver—
Crucible MACOR
tube with Ag/Ag
electrode Ref melt
MBr-M^2Br
mixture (m)

Fig 1: Diagram of Experimental Apparatus.

Fig 3: Potentials selectivity coefficients calculated from measured cell potentials as a function of activity NaBr where O = 0.317 cm. and O = 0.159 cm.

Fig. 2: Membrane potentials as a function of activity NaBr where O = measured potentials and — = theoretical potentials when $K_{Na-K} = 0.452$

Fig 4: Membrane potentials as a function of activity NaBr where O = measured potentials and — = theoretical potentials when $K_{Na-K} = 0.428$ and $n = 1.077$. 

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Fig 5: Membrane potentials as a function of activity LiBr where O = measured potentials and — = theoretical potentials when $K_{Li-K}^{POT} = 0.1178$.

Fig 6: Membrane potentials as a function of activity LiBr where O = measured potentials and — = theoretical potentials when $K_{Li-K}^{POT} = 0.2264$ and $n = 0.5954$. 

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