VOLTAMMETRIC STUDY OF WATER IN MOLTEN LiCl-KCl EUTECTIC

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ABSTRACT

The in situ determination of water in molten LiCl-KCl eutectic and a study of its electrochemical behavior were undertaken using the technique of linear sweep voltammetry. Two reversible reduction peaks with $E_{1/2}$ of about 1.61 V and 0.47 V (vs. a LiAl reference electrode) that were observed in the cyclic voltammogram of water-equilibrated LiCl-KCl on platinum electrodes at 390°C are attributed to one-electron transfers to H$_2$O and OH$^-$ respectively. The anodic oxidation of O$^-$ was also examined and found to correspond to a reversible two-electron transfer process. Proportionality of peak currents to concentration of H$_2$O, OH$^-$ and O$^-$ provide a basis for an electroanalytical method of detecting these species in the melt.

INTRODUCTION

Molten salts constitute a class of solvent system suitable for high temperature applications. The LiCl-KCl eutectic, in particular, has been extensively studied because of its use as an electrolyte in the production of lithium and in thermal batteries. The determination of impurities in this electrolyte was of interest in a program to develop Li(Al)/FeS$_x$ (x = 1 or 2) batteries for load leveling in electric utility systems and for electric vehicle applications. Water appears to be the main contaminant in the chloride salts, and its reaction products are the most difficult impurities to remove from the molten salt. In the present work, the technique of linear sweep voltammetry was used for the in situ determination of water and its reaction products, and for investigations of their electrochemical behavior.

EXPERIMENTAL

The voltammetric study was carried out inside a glovebox under high purity helium atmosphere. Figure 1 shows the set-up of experimental apparatus. The cell consisted of a 100-ml platinum crucible which was used as container for the electrolyte and at the same time acted as the counter electrode. As the working electrode, a 0.4-cm x 0.6 cm x 0.025 cm platinum plate attached to the tip of a 0.04-cm diameter platinum wire sheathed in glass, was used. Glassy carbon and tungsten rods were also tried as working electrodes but the former showed much higher residual currents than platinum, while extraneous peaks were observed when using tungsten. All voltammograms were henceforth taken with platinum. The reference electrode consisted of a
lithium-aluminum alloy (39 at. % Li) whose composition lies in the α + β region of the Li-Al phase diagram (5-45 at. % Li). This has been shown to give a stable and reproducible potential of 305 mV anodic of Li/Li⁺ at 390°C. The electrode was prepared by melting the alloy at about 750°C in an alumina crucible and attaching leads of 0.32-cm diameter tungsten or copper rod while rapidly cooling. A 1-cm diameter alumina tube with a 0.025-cm hole at the bottom was used as the reference electrode compartment. The thermocouple sheath consisted also of an alumina tube.

The LiCl-KCl eutectic electrolyte was of polarographic grade obtained from Anderson Physics Laboratories (Champaign, Illinois) where it is purified following the procedure of Laitinen et al. Water was introduced into the molten salt during the voltammetric experiment by passing helium, which was humidified by bubbling through saturated salt solutions of LiCl, MgCl₂, and Mg(NO₃)₂ at 25°C, and allowing equilibrium inside the furnace well to be established. The vapor pressure of water above these solutions at 25°C are 2.61, 7.84 and 12.35 Torr respectively. Equilibration and voltammetric measurements were done at 390° and 480°C where data on the solubility of water in fused LiCl-KCl are given as 30.5 and 11.3 micromole H₂O/mole LiCl-Torr respectively. Furnace temperature control was within ±2° at each temperature setting.

Single sweep and cyclic voltammetry scans were made with a Princeton Applied Research Model 173 Potentiostat/Galvanostat coupled to a PAR Model 175 Universal Programmer. The current-voltage curves were plotted with a Hewlett-Packard Model 7040A X-Y recorder.

RESULTS AND DISCUSSION

The cyclic voltammograms of water as the solute in molten LiCl-KCl showed two reduction waves at about 1.6 and 0.5 V vs. LiAl (see Figs. 2 and 3). These waves were studied at scan rates of 10 to 100 mV/sec, temperatures of 390 and 480°C, and water concentrations of 1.45 x 10⁻⁸, 4.36 x 10⁻⁵, and 6.87 x 10⁻⁶ mole/cm³. The theory developed by Nicholson and Shain was used to interpret the voltammograms.

Through the use of standard KOH additions, the wave at 0.5 V was attributed to OH⁻ reduction, the wave at 1.6 V was therefore assumed to result from the reduction of water itself. The latter is clearly reversible (Fig. 2) with a half-wave potential, \( E_{1/2} \), (which occurs at a point 85.17% up the wave) of 1.61 V vs. LiAl. From measurements of the peak potential, \( E_p \), and half-peak potential, \( E_{p/2} \), the number of electrons, \( n \), involved in the charge transfer was calculated using the relations

\[
E_p = E_{1/2} - 1.109 \frac{RT}{nF}
\]

\[
E_{p/2} = E_{1/2} + 1.09 \frac{RT}{nF}
\]
At 390°C, the differences $E_p - E_{1/2}$ and $E_p/2 - E_{1/2}$ should theoretically equal $0.0633\, V$ and $0.0622\, V$ respectively. Experimental values are $-0.075 \pm 0.01\, V$ and $0.075 \pm 0.01\, V$ giving $n = 1.19 \pm 0.16$ for the number of electrons involved in the water reduction wave. The variation of peak current ($i_p$) with the square root of scan rate ($v$) at each of the concentrations studied showed a linear relationship indicating diffusion control for the process. Figure 4 shows typical plots at the two temperatures studied. Plots of $i_p/v^{1/2}$ vs. $v$ (Fig. 5) and $i_{pa}/i_{pc}$ (where $i_{pa}$ and $i_{pc}$ are the peak currents of the anodic and cathodic portions of the wave respectively) vs. $v$ (Fig. 6) were conducted to test for the presence of adsorption or coupled chemical reaction. The constancy of $i_p/v^{1/2}$ and $i_{pa}/i_{pc}$ with $v$ indicate the absence of adsorption of reactant or products. There is an apparent increase in $i_p/v^{1/2}$ at the slowest scan rate (10 mV/sec) which could be due to the presence of a catalytic current. It is, however, difficult to separate this effect from that of convection at such a slow scan rate. Peak currents at a given scan rate were found to be proportional to the water concentration (and partial pressure) as shown in Fig. 7. From the slope of plots of $i_p/v^{1/2}$ vs. $C_w$ (Fig. 5) and $i_p$ vs. $v^{1/2}$ (at constant $C_w$), apparent diffusivities of water were calculated using the equation:

$$i_p = 0.452 \frac{n^3/2F^{3/2}}{R^{1/2}T^{1/2}} \frac{AD^{1/2}C_w}{v^{1/2}}$$  

(3)

where $i_p$ is the peak current in amperes, $n$ the number of electrons, $F$ the Faraday constant, $R$ the gas constant, $T$ the absolute temperature, $A$ the electrode area in cm$^2$, $D$ the diffusion coefficient in cm$^2$/sec, $C_w$ the water concentration in mole/cm$^3$ and $v$ the scan rate in volts/sec. Values of diffusivity for water obtained in this manner averaged $3.1 \pm 0.5 \times 10^{-5}$ cm$^2$/sec at 390°C and $8.0 \pm 0.8 \times 10^{-5}$ cm$^2$/sec at 480°C.

The $OH^-$ reduction wave is shown in Fig. 3 and corresponds also to a reversible process with $E_{1/2}$ of 0.47 V vs. LiAl at 390°C. The value of $n$ calculated from the measured values of $E_p$, $E_{1/2}$ and $E_{1/2}$ was $1.06 \pm 0.09$. Diffusion control of the process is evident from the $i_p$ vs. $v^{1/2}$ plot of Fig. 8. Calibration curves of peak current vs. $OH^-$ concentration were constructed using standard KOH additions. A linear relationship was found as shown in Fig. 9. The height of the $OH^-$ wave was usually about four times that of the water peak in the Anderson salt indicating another source of $OH^-$ in addition to that arising possibly from water reduction. Addition of small amounts of Li$_2$O to the melt resulted in much higher $OH^-$ peak currents upon equilibration with water.

An oxidation wave at about 2.55 V vs. LiAl also appeared prominently in the voltammogram of LiCl-KCl electrolyte that had not been rigorously purified. Using Li$_2$O additions, this wave was attributed to the oxidation of $O^\circ$. Figure 10 shows the wave to be reversible with $n \sim 2$ being obtained from the separation between anodic and cathodic
peaks. Plots of $i_p$ vs. $v^{1/2}$ (at a given concentration) and $i_p$ vs. $C_{O^m}$ (for a definite scan rate) (see Figs. 11 and 12) were used to obtain the diffusivity of $O^m$ in the melt at 390° and 480°C. Values of $2.8 \pm 0.4 \times 10^{-6}$ and $7.0 \pm 0.6 \times 10^{-6}$ cm$^2$/sec respectively were obtained.

The emphasis in the present work had been in the development of a relatively simple electroanalytical method for detecting water contamination in molten LiCl-KCl eutectic. No attempt was made to identify the products in the reduction of water and $OH^-$, nor in the oxidation of $O^m$. The products of the latter two reactions can be deduced from the potentiometric measurements of Kanzaki and Takahashi.

The proportionality between peak current and concentration (likewise $v^{1/2}$) as found in the present work indicates the utility of cyclic voltammetry for the analysis of chloride melts. Application to some cases has been done in this laboratory. The apparent diffusivities of water calculated from the present work are of the correct order of magnitude as may be expected from extrapolation of diffusivity data on water in nitrate and acetate melts to the higher temperature involved in this work. Measured diffusion coefficients of $O^m$ are in reasonable agreement with that obtained by Kanzaki and Takahashi. The observed voltammetric behavior of water itself suggests that the charge transfer product in the reduction appears sufficiently long lived to apply the first order theory of Nicholson and Shain.

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THERMOCOUPLE IN ALUMINA TUBE

Fig. 1. Experimental Set-up of Voltammetric Cell

WATER INLET

COOLING COILS

WATER OUTLET

LI\textsubscript{2}AI REFERENCE ELECTRODE INSIDE ALUMINA TUBE

FURNACE

GLASS BEAKER

PT. FLAG WORKING ELECTRODE

PT. DISH COUNTER ELECTRODE AND ELECTROLYTE CONTAINER

Fig. 2. Voltammogram for the Reduction of Water

CH\textsubscript{2}O = 4.36 mM, T = 390°C

Scan Rate = 50 mV/sec

580
Fig. 3. Cyclic Voltammogram for OH⁻ Reduction
T = 390°C,
Scan Rate = 200 mV/sec

Fig. 4. Dependence of Peak Current on Scan Rate

Fig. 5. Variation of \( \frac{i_p}{v^{1/2}} \) with Scan Rate for Water Reduction

Fig. 6. Average Ratio of Anodic and Cathodic Peak Currents
Fig. 7. Dependence of Peak Current on the Partial Pressure and Concentration of Water
T = 390°C,
Scan Rate = 100 mV/sec

Fig. 8. Variation of Peak Current with Scan Rate for OH⁻ Reduction
T = 390°C

Fig. 9. Dependence of Peak Current on KOH Concentration

Fig. 10. Cyclic Voltammogram for the Oxidation of O²⁻
T = 390°C,
Scan Rate = 50 mV/sec
C₅Li₂O = 0.1 wt. %
Fig. 11. Variation of Peak Current with Scan Rate for $O^{\text{2-}}$ Oxidation

Fig. 12. Dependence of Peak Current on $\text{Li}_2\text{O}$ Concentration