KINETIC AND TRANSPORT PROCESSES FOR FeCl₃ AND CuCl₂ POSITIVE ELECTRODES IN LOW TEMPERATURE MOLTEN SALTS

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ABSTRACT

The transport and kinetic properties of FeCl₃ and CuCl₂ in acidic mixtures of 1-methyl-3-ethylimidazolium chloride and aluminum chloride were determined at a rotating glassy carbon disk electrode. These properties are necessary for evaluation of a model of battery positive electrodes which has been developed. Development of a quantitative analytical technique for determination of the metal chloride species in the melt would have been helpful for monitoring the distribution of active material within the electrode. Quantitative analysis for FeCl₃, FeCl₂, CuCl, CuCl₂ in acidic melts was attempted using UV-Vis spectroscopy. Quantitative analysis for FeCl₃ in acidic melts was also attempted using chronopotentiometry.

INTRODUCTION

Recently secondary Al/FeCl₃ and Al/CuCl₂ batteries were tested using acidic mixtures of 1-methyl-3-ethylimidazolium chloride (MEIC) and AlCl₃ as the electrolyte (1,2). Reticulated vitreous carbon was used as the positive current collector. The positive reactant (FeCl₃ or CuCl₂) was introduced into the current collector by an evaporative impregnation process. The overall reactions for these batteries are

\[
\text{Al} + 3\text{FeCl}_3 = \text{AlCl}_3 + 3\text{FeCl}_2
\]

and

\[
\text{Al} + 3\text{CuCl}_2 = \text{AlCl}_3 + 3\text{CuCl}
\]

Figure 1 shows the discharge curves for an Al/FeCl₃ battery at discharge currents of 20, 50, and 70 mA. One observes that utilization of the positive reactant is dependent upon the discharge current (decreases with increasing current).

The reactions occurring at the positive electrode in these batteries are:

\[
\text{FeCl}_3 + \text{Al}_2\text{Cl}_7^- + e^- = \text{FeCl}_2 + 2\text{AlCl}_4^-
\]

and

\[
\text{CuCl}_2 + \text{Al}_2\text{Cl}_7^- + e^- = \text{CuCl} + 2\text{AlCl}_4^-
\]

where the iron and copper chlorides are assumed to be present as solids. Improvements in polarization and utilization of the positive electrode materials were observed when the specific area of the positive current collector was increased (2). Further, cycling of the batteries (charging and discharging at
constant current) has shown an improvement in cell capacity as the cycling progresses (2). It is believed that there may be redistribution of the active material within the RVC matrix through a dissolution/precipitation mechanism. Cell polarization and utilization are believed to be associated with the coupled effects of kinetics and transport of the active species within the positive current collector. The kinetic processes are enhanced by the available surface area of the collector matrix while the transport processes are facilitated by the open pore structure.

A mathematical model of the steady state electrochemical behavior of metal chlorides in porous electrode matrices has been developed in terms of the kinetic and transport properties of the metal chlorides, the electrolyte, and the physical properties of the porous electrode (3). This model is an extension of one developed by Austin (4). The solution to the mathematical model of the porous electrode will be included here to highlight the important parameters of porous electrode operation. Two forms of the solution exist, the current density distribution in the electrode, \( i \) (mA/cm\(^2\)):

\[
i = nFk^0([A]_b \exp \phi_c - 2[B]_b \exp \phi_a) \frac{(\exp(zP) + \exp(-zP))/((\exp(LP) + \exp(-LP))}{5}
\]

where the \( P \) is:

\[
(P = (k^0A_v/DAm_a)^{1/2}(4\exp\phi_a + \exp\phi_a)^{1/2}).
\]

and the total current, \( I \) (mA), the equation which describes the macroscopic polarization behavior of the electrode:

\[
I = (nFk^0A_{as}/P)([A]_b \exp \phi_c - 2[B]_b \exp \phi_a) \frac{(\exp(LP) - \exp(-LP))/((\exp(LP) + \exp(-LP))}{6}
\]

Definitions of the parameters appearing in these equations are given in Table 4. The current or electrode potential are the adjustable parameters of the model. The electrode potential appears in equations 5 and 6 in the dimensionless potential terms, \( \phi_c \) and \( \phi_a \):

\[
\phi_c = (\phi^0 - \phi)/\beta_c
\]

\[
\phi_a = (\phi^0 - \phi)/\beta_a
\]

where \( \phi \) is the perturbed potential, \( \phi^0 \) is the standard electrode potential, and \( \beta \) is the anodic or cathodic Tafel slope. Modeling and analysis of the discharge-charge behavior of the metal chloride positive electrodes requires the evaluation of the parameters appearing in equations 5 and 6. The current density distribution equation permits calculation of the reaction distribution in the electrode. Development of a quantitative analytical technique for the determination of metal chloride species in the melt would be useful to evaluate the distribution of FeCl\(_3\)/FeCl\(_2\) and CuCl\(_2\)/CuCl in the porous matrix as a function of the history of the electrode.

The electrochemical and spectrochemical properties of the electrolytes and redox systems under consideration here have been studied by others, e.g. the
binary electrolyte (5), iron chloride (6-8), copper chloride (9, 10), and Al$_2$Cl$_7$ reduction (11, 12).

This paper focuses on the estimation of the appropriate chemical and physical properties for evaluation of the model.

**EXPERIMENTAL**

The synthesis and purification of the MEIC was conducted in a manner similar to that of Wilkes and coworkers (5). Aluminum chloride (Fluka) was purified by vacuum sublimation. Anhydrous FeCl$_3$ (Fisher), FeCl$_2$ (Cerac), CuCl$_2$ (Cerac), and CuCl (Cerac) were not purified further. All experiments were conducted under a helium and nitrogen atmosphere in a Vacuum Atmospheres Company glove box at ambient temperature. The moisture level was maintained below 1 ppm and the oxygen level was maintained below 10 ppm. The temperature within the dry box was measured daily.

The binary mole fraction of AlCl$_3$ in the test electrolyte was 0.58 except for the aluminum transport experiments which were conducted in a 0.505 electrolyte. The iron and copper chlorides were introduced into the test electrolyte as the anhydrous solids. Viscosities of several of the ternary and binary solutions were measured using a Brookfield Model LVTD plate and cone viscometer. These measurements were conducted at 25°C. UV-Vis spectra of the binary and ternary solutions were obtained with a Hewlett Packard 845IA Diode Array Spectrophotometer using a 1 cm path length.

The FeCl$_3$ and CuCl$_2$ transport and kinetic experiments were conducted with a rotating glassy carbon disk electrode, RGCDE (Pine Instruments). The Al$_2$Cl$_7$ transport experiments were conducted using an aluminum disk electrode fabricated in-house consisting of a 6.25 mm aluminum rod (Alfa Products, m5N) which was insulated on the sides by a PTFE sleeve 3.25 mm thick. Rotation of the working electrodes was provided by a Pine Rotator (Model MSR). The reference electrode was an aluminum plated platinum wire immersed in a 0.505 melt and separated from the working electrode compartment by an ultra-fine porosity glass frit (Witeg Scientific, Anaheim, CA.; Catalog # 2.350.P5). The aluminum cylinder counter electrode (Alpha Products, m5N) was also separated from the working electrode compartment by a fine porosity glass frit (Catalog # 2.350.P5). The electrochemical measurements were made using a PARC Model 273 Potentiostat-Galvanostat equipped with a current interrupt IR compensation device. The data were collected and stored on an IBM PC/XT using the PARC Headstart software.

**RESULTS**

UV-Vis spectroscopy was chosen as the quantitative analytical technique for determination of the metal chloride species in the melt. Absorption data for the metal chloride species (FeCl$_3$, FeCl$_2$, CuCl$_2$, and CuCl) in the melt was obtained by pointwise subtraction of the binary melt spectrum from the ternary melt spectrum for each of the metal chlorides. The resulting absorption peak was attributed to the metal chloride. Table 1 shows the absorbance wavelength regions for each of the metal chloride species and the binary melt. The spectroscopic results indicate that the metal chlorides and the melt absorb in the same wavelength region. While UV-Vis spectroscopy proved unsuccessful as a
quantitative analytical technique, chronopotentiometry of FeCl₃ ternary solutions indicated that this technique may be useful.

Figures 2 and 3 are linear sweep voltammograms (scan rate = 5mV s⁻¹, 1000 RPM) for FeCl₃ reduction and CuCl₂ reduction, respectively, at a RGCDE in the test electrolyte. In the case of FeCl₃, both kinetic (charge transfer) and mass transport controlled regions are observed. The Tafel slope and exchange current density for this redox reaction were obtained from slow potential sweeps (scan rates 0.5 to 0.25 mV s⁻¹) in the kinetic controlled region (see Table 2). The linear sweep voltammogram for CuCl₂ reduction indicates that this reaction is immediately transport controlled. In this case the limiting current provides a lower bound for the exchange current density of this reaction.

Diffusion coefficients for FeCl₃ and CuCl₂ species and Al₃Cl⁻ were computed from limiting current measurements at RDE. The computed diffusivities and the Dµ/T quantities for the species are presented in Table 3.

DISCUSSION

The exchange current densities cannot be used directly in the model while the Tafel slopes can. The exchange current densities are used to compute the standard specific rate constant used in the model. For example the standard specific rate constant for FeCl₃ reduction can be estimated from

\[ k^o = i_0 / \left( nF[FeCl₃] \right) \]

The mean value, based on the data in Table 2, is 8 \times 10^{-6} \text{ cm/s}. Other investigators have reported values on the order of 10^{-4} (6) and 10^{-5} (7), at 30 and 40 °C, respectively. These data were obtained by using a technique proposed by Galus and Adams (13).

Since there were no Tafel data for the copper system, i.e. cupric ion reduction was immediately mass transport limited, neither exchange current density nor Tafel slope could be determined. The limiting current density, 49 \times 10^{-3} \text{ mA/cm}^2, was used as a lower bound for the exchange current density in the calculation of the standard specific rate constant. The mean value was 3 \times 10^{-4} \text{ cm/s}. Nanjundiah and Osteryoung found values on the order of 3 \times 10^{-4} at 40°C in basic BPC melts (9). Since the Tafel slope obtained for ferric chloride reduction was consistent with a one electron transfer process, this value was used as a basis for the Tafel slope for the cupric/cuprous reaction in the model.

The diffusivity of Al₃Cl⁻ is required for the model (see Eq. 3-6). The value of the Dµ/T quantity computed here is approximately twice that reported by Donahue and Wilkes, 1.3 \times 10^{-10} in similar melts (11). Robinson and Osteryoung, using multiple techniques and three different electrodes, obtain diffusivities in the range 3.5 - 10 \times 10^{-7} \text{ cm}^2/\text{s} (12).

The remaining Dµ/T groups, while not necessary for the model, permit direct comparison with these measurements and those of others. Dµ/T for the FeCl₃ species is in agreement with that obtained in n-butyl pyridinium chloride/aluminum chloride (BPC/AlCl₃) melts using limiting current measurements (7). The Dµ/T quantities for the iron and copper species are smaller than those reported by others in similar systems (8) and (9, 10), respectively. Nevertheless, these Dµ/T data are consistent with suggestions that
the Cu(II) is complexed as Cu(AlCl₄)₂⁻ (9) while the Fe(III) complex is suggested to be FeCl₄⁻ (7).

Using the estimated kinetic and transport parameters and the physical properties for 80 ppi RVC, the total current equation can be revised for the specific cases of the FeCl₃ and CuCl₂ porous electrodes using a 0.58 electrolyte. The evaluated model parameters specific for each reaction are shown in Table 5. The revised equation for the FeCl₃ electrodes is:

\[ I = \frac{(1.95 \times 10^5/P)(2[B_b]\exp\Phi_a - [A_b]\exp\Phi_e)}{(\exp(LP) - \exp(-LP))/((\exp(LP) + \exp(-LP)))} \]

where \( P \) is:

\[ (26.7)(4\exp\Phi_a + \exp\Phi_e)^{1/2}. \]

The revised equation for the CuCl₂ electrodes is:

\[ I = \frac{(7.30 \times 10^6/P)(2[B_b]\exp\Phi_a - [A_b]\exp\Phi_e)}{(\exp(LP) - \exp(-LP))/((\exp(LP) + \exp(-LP)))} \]

where \( P \) is:

\[ (163)(4\exp\Phi_a + \exp\Phi_e)^{1/2}. \]

The remaining parameters in the model are the operating parameters - either current or potential.

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Table 1. Spectroscopic Data for Copper Chlorides and Iron Chlorides in 0.58 AlCl₃/MEIC.

| System               | λ_{abs} (nm) |
|----------------------|--------------|
| Blank Binary         | 183-244      |
| FeCl₃ Ternary        | 258,358      |
| FeCl₃ Ternary        | 244          |
| CuCl₂ Ternary        | 248,334      |
| CuCl₂ Ternary        | 249          |

Table 2. Tafel Slopes and Exchange Current Densities for FeCl₃ in X=0.58 AlCl₃/MEIC

| 10⁶ FeCl₃ (mole/cm³) | 10⁶ i₀ (A/cm²) | b (mV) |
|----------------------|---------------|--------|
| 4.15                 | 6.2           | 132    |
| 4.70                 | 1.6           | 133    |
| 7.62                 | 3.8           | 143    |

AVERAGE: 136

Table 3. D and D_μ/T for FeCl₃, CuCl₂, and Al₂Cl₇⁻ in AlCl₃/MEIC

| 10⁶ FeCl₃ (mole/cm³) | 10⁷ D (cm²/s) | 10¹⁰ D_μ/T (gcm/s²K) |
|----------------------|---------------|----------------------|
| 3.18                 | 7.4           | 3.6                  |
| 11.9                 | 7.6           | 3.7                  |
| 18.3                 | 7.3           | 3.6                  |
| 32.7                 | 6.0           | 2.9                  |

AVERAGE: 7.1 3.5

| 10⁷ CuCl₂ (mole/cm³) | 10⁷ D (cm²/s) | 10¹⁰ D_μ/T (gcm/s²K) |
|----------------------|---------------|----------------------|
| 1.51                 | 2.0           | 1.0                  |
| 1.53                 | 2.5           | 1.2                  |
| 1.54                 | 1.3           | 0.6                  |
| 1.57                 | 1.8           | 0.9                  |

AVERAGE: 1.9 0.9

| 10⁵ Al₂Cl₇⁻ (mole/cm³) | 10⁷ D (cm²/s) | 10¹⁰ D_μ/T (gcm/s²K) |
|------------------------|---------------|----------------------|
| 9.26                   | 5.7           | 3.2                  |
| 9.26                   | 5.1           | 2.8                  |

AVERAGE: 5.4 3.0
Table 4. Model Parameters

| Adjustable Parameters | Model Parameters |
|-----------------------|------------------|
| $\phi_a$              | Anodic dimensionless potential |
| $\phi_c$              | Cathodic dimensionless potential |
| $i$                   | Current density (mA/cm$^2$) |
| $I$                   | Total apparent current (mA) |

| Constant Parameters                      | Model Parameters |
|------------------------------------------|------------------|
| $n$                                      | Number of electrons transferred in electrochemical reaction (eq/mole) |
| $F$                                      | Faraday's constant, 96,500 (coul/eq) |
| $k^0$                                    | Standard specific rate constant (cm/s) |
| $A_b$                                    | Bulk concentration $\text{AlCl}_3$ (mole/cm$^3$) |
| $B_b$                                    | Bulk concentration $\text{AlCl}_4^-$ (mole/cm$^3$) |
| $L$                                      | Electrode thickness (cm) |
| $D_{\text{am}}$                          | Diffusion coefficient of $\text{AlCl}_3$ with respect to mixture (cm$^2$/s) |
| $A_{\text{xs}}$                          | Cross-sectional area of electrode perpendicular to current flow (cm$^2$) |
| $A_v$                                    | Specific area of electrode (cm$^2$/cm$^3$) |
| $\epsilon$                              | Porosity of electrode |

Table 5. Model Parameters for $X=0.58$ AlCl$_3$/MEIC and 80 ppi RVC.

| Parameters | FeCl$_3$ | CuCl$_2$ |
|-----------|----------|----------|
| $n$ (eq/mole) | 1        | 1        |
| $F$ (coul/eq) | 96,500   | 96,500   |
| $k^0$ (cm/s) | $8 \times 10^{-6}$ | $3 \times 10^{-4}$ |
| $A_b$ (mole/cm$^3$) | $1.54 \times 10^{-3}$ | $1.54 \times 10^{-3}$ |
| $B_b$ (mole/cm$^3$) | $2.51 \times 10^{-3}$ | $2.51 \times 10^{-3}$ |
| $L$ (cm) | 0.48     | 0.48     |
| $D_{\text{am}}$ (cm$^2$/s) | $5.96 \times 10^{-7}$ | $5.96 \times 10^{-7}$ |
| $A_{\text{xs}}$ (cm$^2$) | 4.9 | 4.9 |
| $A_v$ (cm$^2$/cm$^3$) | 51.5 | 51.5 |
| $\epsilon$ | 0.97 | 0.97 |
Figure 1. Discharge curves for an Al/FeCl₃ battery at discharge currents of 20, 50, and 70 mA.

Figure 2. Linear sweep voltammogram for Fe(III) reduction at a RGCDE in 0.58 AlCl₃/MEIC (3.0 mM Fe(III) scan rate = 5 mV/s, 1000 RPM).

Figure 3. Linear sweep voltammogram for Cu(II) reduction at a RGCDE in 0.58 AlCl₃/MEIC (1.5 mM Cu(II) scan rate = 5 mV/s, 1000 RPM).