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and improve the hydrogen storage properties. These results suggest the possibility of realizing a lightweight battery with higher capacity than those employing alloys at present.

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REFERENCES

1. J. J. G. Willems, *Philips J. Res.*, **39**, 1 (1984).
2. C. Iwakura and M. Matsuoka, *Prog. in Batt. Batt. Mater.*, **10**, 81 (1991).
3. J. J. Reilly and R. H. Wiswall, *J. Inorg. Chem.*, **7**, 2554 (1968).
4. L. Zaluski, A. Zaluska, and J. O. Ström-Olsen, *J. Alloys Compd.*, **217**, 245 (1995).
5. J. Huot, E. Akiba, and T. Tanaka, *ibid.*, **231**, 815 (1995).
6. S. Orimo and H. Fujii, *ibid.*, **232**, L16 (1996).
7. C. Iwakura, S. Nohara, H. Inoue, and Y. Fukumoto, *Chem. Commun.*, 1831 (1996).
8. Y. Q. Lei, Y. M. Wu, Q. M. Yang, J. Wu, and Q. D. Wang, *Z. Phys. Chem.*, **183**, 379 (1994).
9. M. Matsuoka, T. Kohno, and C. Iwakura, *Electrochim. Acta*, **38**, 787 (1993).
10. C. Iwakura, M. Matsuoka, K. Asai, and T. Kohno, *J. Power Sources*, **38**, 355 (1992).
11. C. Iwakura, S. Hazui, and H. Inoue, *Electrochim. Acta*, **41**, 471 (1996).
12. T. Kohno, S. Tsuruta, and M. Kanda, in Extended Abstracts of The Japan Institute of Metals 118th Meeting, p. 176 (1996).
13. T. Kohno, S. Tsuruta, and M. Kanda, *This Journal*, **143**, L198 (1996).

Electrochemical Studies of Chromium(III) and Chromium(II) Chloride Complexes in Basic Aluminum Chloride-1-Methyl-3-ethylimidazolium Chloride Room Temperature Molten Salts

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ABSTRACT

Chromium(III) chloride is complexed as $[\text{CrCl}_6]^{3-}$ in the basic aluminum chloride-1-methyl-3-ethylimidazolium chloride melt, and it can be reduced to a Cr(II) species at a glassy carbon electrode. Absorption spectroscopy and titration experiments suggest that the Cr(II) is complexed as $[\text{CrCl}_4]^{2-}$. The Cr(III)/Cr(II) electrode reaction exhibits slow charge-transfer kinetics with a standard heterogeneous rate constant of $3.27 \times 10^{-6} \text{ cm s}^{-1}$ and a cathodic transfer coefficient of ca. 0.38 in the 44.4/55.6 mole percent (m/o) melt at 27°C. The formal electrode potential of the Cr(III)/Cr(II) chloride redox couple is -0.649 V in the 44.4/55.6 m/o melt. The Stokes-Einstein products of $[\text{CrCl}_6]^{3-}$ and $[\text{CrCl}_4]^{2-}$ complexes are 1.2×10^{-10} and $1.7 \times 10^{-10} \text{ g cm s}^{-2} \text{ K}^{-1}$, respectively.

Mixtures of aluminum chloride (AlCl_3) and certain anhydrous organic halide salts (RCl) such as N-butylpyridinium chloride (BupyCl),¹ 1-methyl-3-ethylimidazolium chloride (MeEtimCl),² and 1,2-dimethyl-3-propylimidazolium chloride (DMPimCl),³ form ionic liquids at room temperature. These ambient temperature molten salts have proven to be useful solvents for electrochemical studies of many inorganic, organometallic, and organic compounds. In addition, they have been employed for the electroplating of metals, for semiconductor electrochemistry, and for batteries. Several reviews^{4,5} concerning these molten salts have been published in the literature.

The room temperature haloaluminate molten salts are termed acidic, basic, or neutral when the AlCl_3 :RCl molar ratio is greater than, less than, or equal to 1, respectively. It has been shown that Al_2Cl_7^- and AlCl_4^- are the dominant anions in acidic melts, whereas free Cl^- and AlCl_4^- are the dominant anions in basic melts. The electrochemical window of the melt depends on the melt composition. The "neutral" melt possesses the widest electrochemical window, which is, however, difficult to maintain. It has been shown that the "neutral" composition can be maintained by buffering an initially acidic melt with NaCl.⁶ There is

considerable interest in the use of buffered room temperature melts as electrolytes for rechargeable batteries.⁷⁻¹⁰

Although basic room temperature melts have proven to be excellent solvents for the anionic chloride complexes of transition metal elements, it has been realized that the electrochemistry of a solute in the melt can sometimes be complicated by trace amounts of protonic and oxide impurities. Recently, methods for the removal of these interfering species have been developed.^{11,12} In addition, a vacuum-tight electrochemical cell¹³ has been employed to minimize the influence of trace dioxygen on the electrochemical results in the melts.

Results from investigations of the first-row transition metal ions in AlCl_3 -MeEtimCl and AlCl_3 -BupyCl melts show that, in the basic melt, stable tetrahedral chloro complex anions are dominant for iron(III), iron(II),¹⁴ cobalt(II),¹⁵ nickel(II),¹⁶ and copper(II).¹⁷ However, the coordination of these inorganic ions in the acidic melt is very different from that in the basic melt and is not clearly understood. Extended x-ray absorption fine structure (EXAFS)¹⁸ and fast atom bombardment mass spectrometric (FAB-MS)¹⁹ results indicate that Co(II), Mn(II), and Ni(II) are coordinated by three bidentate AlCl_4^- ions to produce a complex of the general type, $[\text{M}(\text{AlCl}_4)_3]^-$ in the acidic AlCl_3 -MeEtimCl melt. The electrochemical behav-

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ior of these transition metal ions also depends on the melt composition. For instance, Fe(II) and Co(II) can be reduced to the corresponding metals in acidic melt but not in basic melt.^{14,15}

Interest in the electrochemistry of chromium compounds in molten salts and especially in chloride electrolytes originates from their use as cathode materials in thermally activated batteries.^{20,21} In LiCl-KCl melt, Cr(III) can be reduced to the metal via a two-step process in which the intermediate species is precipitated as CrCl₂.²² In alkali chloride-aluminum chloride molten salts such as 66-14-20 m/o AlCl₃-KCl-NaCl, CrCl₃ is insoluble whereas CrCl₂ is soluble.²³ Hussey *et al.*²⁴ studied the electrochemical behavior of chromium in the sodium chloride-saturated AlCl₃-NaCl electrolyte. They reported that Cr(III) was reduced to Cr(II) through a quasi-reversible charge-transfer process and that Cr(II) could be further reduced to the metal. Moffat²⁵ recently reported that Cr-Al alloys can be produced from acidic AlCl₃-NaCl and from the room temperature melt, AlCl₃-TMPAC (trimethylphenylammonium chloride) melts. De Long and Trulove have also examined Cr-Al alloys in room temperature melts.²⁶ Scheffler²⁷ attempted to study the electrochemistry of Cr(III), added as CrCl₃, in the basic AlCl₃-MeEtimCl melt. He reported that the reduction of Cr(III) chloride is complicated by the presence of proton impurities and that stable products of this reduction process could neither be obtained nor be characterized in these melts. Therefore, we have reexamined the electrochemistry of Cr(III) in basic AlCl₃-MeEtimCl melts from which all traces of proton impurities have been removed, and the results are reported herein.

Experimental

Apparatus.—All electrochemical experiments were conducted inside a nitrogen-filled glove box equipped with a dry train/oxygen removal column (Vacuum Atmospheres HE-493). Electrochemical experiments were performed with an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat interfaced to an IBM-compatible personal computer equipped with EG&G 270 software. The airtight electrochemical cell was identical to those described in a previous article.¹³ For conventional voltammetric experiments, including rotating disk electrode voltammetry, a glassy carbon (GC) disk electrode (Pine Instruments, geometric area 0.126 cm²) was used as the working electrode. Bulk electrolysis experiments were carried out in this same cell except that the GC electrode was replaced by a large surface area platinum-gauze electrode. All potentials are reported *vs.* the Al³⁺/Al couple in the 66.7/33.3 m/o melt. Rotating-disk-electrode voltammetry was conducted with a Pine Instruments Co. Model AFMSR electrode rotator. All electrochemical experiments were performed at 29 ± 1°C.

Absorption spectra in the wavelength range between 250 and 900 nm were recorded with a JASCO Model V-550 double-beam UV-Vis spectrophotometer, and spectra in the wavelength range between 400 and 1600 nm were recorded with a Varian Cary-5 spectrophotometer. The solutions for study were examined in 1 and 10 mm path length fused silica cells fitted with airtight Teflon caps.

Chemicals.—Anhydrous aluminum chloride (Fluka, 99%) was sublimed *in vacuo* two times at 210°C with NaCl and stored in sealed Pyrex tubes prior to use. MeEtimCl and DMPrimCl were synthesized according to the previously published procedures.^{2,3} Melts were prepared by mixing the appropriate amounts of AlCl₃ and RCl. Proton impurities were removed from the melt by evacuating the melt as recommended in the literature¹¹ before every experiment. Chromium(III) chloride, CrCl₃ (Johnson-Matthey, anhydrous, 99.99%) and chromium(II) chloride, CrCl₂ (Strem, anhydrous, 99.9%), were used as received.

Results and Discussion

The dissolution of chromium(III) chloride, CrCl₃, in basic AlCl₃-MeEtimCl is an extremely slow process at room temperature, and it was necessary to raise the tem-

Table I. Absorption spectroscopic data for chromium chloride complexes.

Species	Solvent	λ , nm (ϵ , M ⁻¹ cm ⁻¹)	Reference
[CrCl ₆] ³⁻	44.4/55.6 m/o AlCl ₃ -MeEtimCl	792(43), 546(45)	This work
[CrCl ₆] ³⁻	LiCl-KCl ^a	800, 541	28
CrCl ₃	CsCl ^b	830, 580	28
[CrCl ₄] ²⁻	44.4/55.6 m/o AlCl ₃ -MeEtimCl	945(83) ^c	This work
[CrCl ₄] ²⁻	LiCl-KCl ^a	1020 ^c	34

^a 400°C.

^b 650°C.

^c Broad-band.

perature of the melt to 90°C in order to increase the dissolution rate. The dissolution of CrCl₃ produces a violet-blue solution; these solutions appeared to be quite stable. A typical absorption spectrum of a Cr(III) solution prepared with a 44.4/55.6 m/o melt is shown in Fig. 1a. Spectroscopic data taken from this spectrum are collected in Table I along with the pertinent literature data. The overall appearance of the spectrum in Fig. 1a is very similar to that reported for the [CrCl₆]³⁻ complex ion.²⁸ Adjusting the acidity of this solution to the neutral point by the addition of AlCl₃ resulted in a precipitate that is identical in appearance to CrCl₃. Absorption spectroscopic data also show that when K₂CrO₄ was added to the basic AlCl₃-MeEtimCl melt, a solution of [CrCl₆]³⁻ was obtained, indicating that the Cr(VI) was reduced by the melt. This probably occurs through reaction with chloride ion.

The cyclic voltammetric behavior of [CrCl₆]³⁻ in basic melt is dependent upon the surface condition of the GC disk electrode. In order to observe a reproducible response, it was necessary to clean the electrode surface, either by polishing it with a Kimwipe or by stepping the electrode potential to 0.9 V for 10 s, before each voltammetric scan. Alternatively, reproducible voltammograms were obtained if the electrode was allowed to sit in the solution at open-

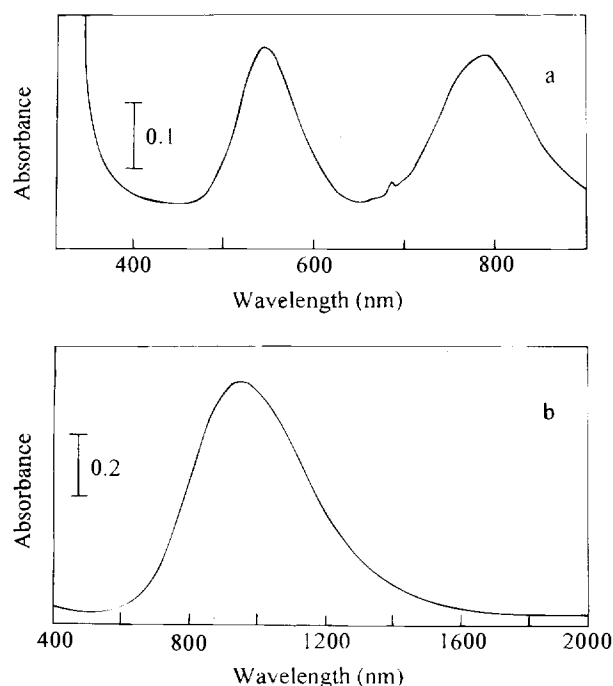
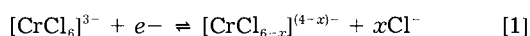


Fig. 1. Absorption spectra of chromium(III) and -(II) chloride complexes in 44.4/55.6 m/o AlCl₃-MeEtimCl melt at 27°C: (a) 6.79 mM [CrCl₆]³⁻; and (b) 9.43 mM [CrCl₄]²⁻ that was produced by exhaustive reduction of a 9.43 mM [CrCl₆]³⁻ solution at a potential of -1.40 V.

circuit potential for about 10 min before each scan was initiated. A typical cyclic voltammogram of $[\text{CrCl}_6]^{3-}$ in the 44.4/55.6 m/o AlCl_3 -MeEtimCl melt at a GC disk electrode is shown in Fig. 2a. This voltammogram consists of a single reduction wave with a peak potential, E_p^c , of about -1.20 V and an associated oxidation wave with a peak potential, E_p^a , of about -0.49 V. No other redox waves were observed within the electrochemical window of the melt. The large peak potential separation, ΔE_p , which increases significantly as the scan rate is increased, suggests that the $[\text{CrCl}_6]^{3-}$ electrode reaction is complicated by slow charge-transfer kinetics.²⁹ In order to determine the number of electrons transferred during the reduction of $[\text{CrCl}_6]^{3-}$, a Nernst plot was constructed for this reaction in the 44.4/55.6 m/o melt by using controlled-potential electrolysis to adjust the concentration ratio of $[\text{CrCl}_6]^{3-}$ to its reduced species in a solution initially containing only $[\text{CrCl}_6]^{3-}$. The concentration ratios in these solutions were determined with rotating-disk-electrode voltammetry, and the equilibrium potentials were recorded as a function of the concentration ratio. The least squares slope of the plot, 0.053 V, compares favorably with the theoretical value of 0.060 V for a one-electron charge-transfer process at this temperature, suggesting that the $[\text{CrCl}_6]^{3-}$ is reduced to a Cr(II) species.

Similar voltammetric behavior was observed in the 49.0/51.0 m/o melt, except that the peak potentials shifted significantly to more positive values, suggesting the possibility that chloride ion is lost from $[\text{CrCl}_6]^{3-}$ during the reduction process.³⁰ Thus, the reduction of $[\text{CrCl}_6]^{3-}$ is probably of the type



Many transition metal chloride complexes react with oxide impurities in basic AlCl_3 -MeEtimCl melts to form oxychloro complexes.^{13,31} However, the formation of the corresponding oxychloro complexes via the interaction of oxide with $[\text{CrCl}_6]^{3-}$ does not seem to be favored, because no change in the voltammetric behavior of basic melt containing $[\text{CrCl}_6]^{3-}$ could be detected after the addition of oxide (introduced as Li_2CO_3). In addition, triphosgene, an

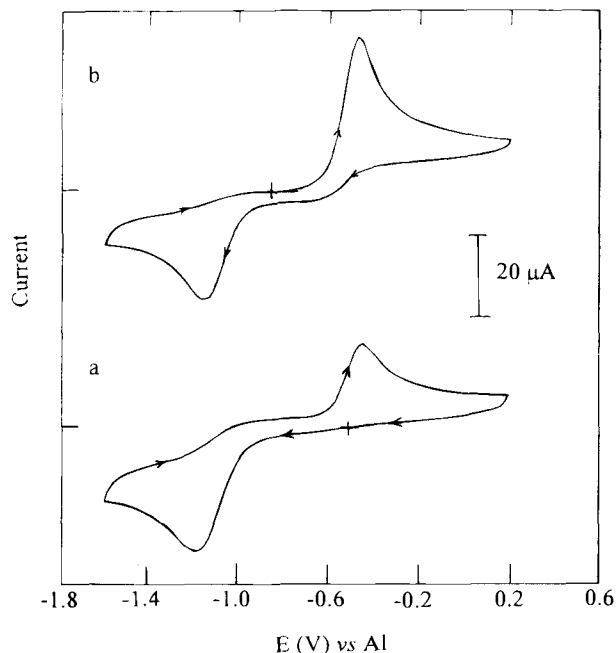


Fig. 2. Cyclic voltammograms of chromium(III) and -(II) chloride complexes at a GC disk electrode in 44.4/55.6 m/o AlCl_3 -MeEtimCl melt at 29°C : (a) 10.5 mM in $[\text{CrCl}_6]^{3-}$; and (b) 10.5 mM in $[\text{CrCl}_6]^{2-}$ that was produced by the electrolytic reduction of the preceding solution at a potential of -1.40 V. The sweep rates were 100 mV/s.

effective oxide removal reagent,³ showed no effect on the voltammetric behavior of $[\text{CrCl}_6]^{3-}$ solutions. Similar behavior has been reported for tungsten(V) and -(IV) chloride complexes in basic AlCl_3 -MeEtimCl.³³

Controlled-potential electrolysis experiments were conducted with solutions of $[\text{CrCl}_6]^{3-}$ at an applied potential of -1.40 V in order to obtain solutions of $[\text{CrCl}_{6-x}]^{(4-x)-}$. The exhaustively reduced solutions were light green-blue in color, and the total charge consumed during the electrolysis reveals an n value of 1.1 ± 0.1 , which agrees well with the n value proposed in Eq. 1. A typical cyclic voltammogram of one of the reduced solutions is shown in Fig. 2b. It is clear from this figure that the same redox couple that was accessible in the $[\text{CrCl}_6]^{3-}$ solution is still accessible in this solution. However, $[\text{CrCl}_{6-x}]^{(4-x)-}$, the one-electron reduction product of $[\text{CrCl}_6]^{3-}$, is now the principle electroactive species present in solution following reduction. A typical absorption spectrum of $[\text{CrCl}_{6-x}]^{(4-x)-}$ in 44.4/55.6 m/o AlCl_3 -MeEtimCl is shown in Fig. 1b. The main feature of this figure is a broad absorption band covering the wavelength range from 546 to 1600 nm and centered at about 946 nm. This spectrum is similar to that reported for the $[\text{CrCl}_4]^{2-}$ chloride complex in a LiCl - KCl mixture.³⁴

Solutions of Cr(II) in basic AlCl_3 -MeEtimCl melts could also be prepared by the direct dissolution of CrCl_2 . The cyclic voltammograms of these solutions were identical to those resulting from the reduction of Cr(III). To determine the stoichiometry of the dissolved Cr(II) species, titration experiments were conducted in neutral melt. In a typical titration experiment, a precisely weighed quantity of CrCl_2 was first introduced into a cell containing a weighed portion of neutral melt. Because there were no free chloride ions present in the neutral melt, the CrCl_2 remained as solid. Following this, precisely weighed portions of MeEtimCl were added to this mixture. Upon the addition of MeEtimCl, CrCl_2 dissolved by complexing with the chloride ions, and the oxidation current of the Cr(II) chloride increased after each addition of MeEtimCl until finally an excess amount of chloride ions had been added. The results from a typical experiment are presented in Fig. 3. In this figure $m_{\text{Cl}}/m_{\text{Cr}}$ represents the ratio of the number of the moles of the added MeEtimCl to the total number of the moles of CrCl_2 initially present, and $m_{\text{Cr}}^f/m_{\text{Cr}}$ represents

* Caution: Triphosgene is hazardous and must be handled with care. The effectiveness of the triphosgene for the removal of oxide was first tested with the $[\text{TiCl}_6]^{2-}$ system. The results showed that when triphosgene was in excess, $[\text{TiOCl}_4]^{2-}$ was converted to $[\text{TiCl}_6]^{2-}$. The excess triphosgene itself could be electrochemically reduced at ca. -1.60 V. However, this reduction wave does not interfere with the reduction wave of $[\text{CrCl}_6]^{3-}$.

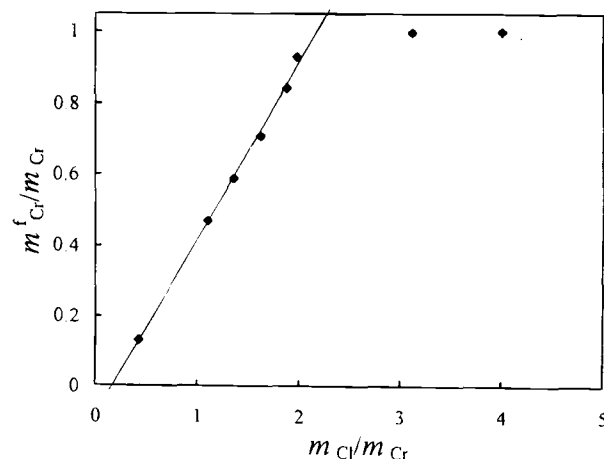


Fig. 3. Plots of $m_{\text{Cr}}^f/m_{\text{Cr}}$ vs. $m_{\text{Cl}}/m_{\text{Cr}}$ resulting from amperometric titration experiments. The solid line was calculated from the least squares slope and intercept of the experimental data.

Table II. Electrochemical data for chromium chloride complexes in AlCl₃-MeEtimCl at 29°C.

Redox system	Solute	AlCl ₃ (m/o)	E ^{o/a} (V)	10 ⁷ D ^b (cm ² s ⁻¹)	10 ¹⁰ ηD/T (g cm s ⁻² K ⁻¹)	10 ⁶ k ^o (cm s ⁻¹)	α
Cr(III)/Cr(II)	[CrCl ₆] ³⁻	44.4	-0.649	1.29	1.2 ± 0.1	3.27	0.38
Cr(II)/Cr(III)	[CrCl ₄] ²⁻ c	44.4		1.80	1.6 ± 0.1		
Cr(III)/Cr(II)	[CrCl ₆] ³⁻	49.0	-0.596	3.31	1.3 ± 0.1	5.79	0.37
Cr(II)/Cr(III)	[CrCl ₄] ²⁻ c	49.0		2.26	1.8 ± 0.1		

^a Estimated from Nernst plots.

^b Average value from stationary and rotating-disk-electrode voltammetry.

^c Produced by electrolytic reduction of [CrCl₆]³⁻.

the fraction of the number of the moles of CrCl₂ that dissolved after each addition of MeEtimCl. The reciprocal of the slope of this plot reflects the number of chloride ions that are consumed per CrCl₂ molecule during the dissolution process. During the titration, no appreciable current due to the oxidation of chloride ion was observed until the m_{Cl}/m_{Cr} ratio exceeded 2. When the ratio was larger than 2, chloride ion oxidation became apparent, and the oxidation current of Cr(II) approached a constant value, indicating that all of the CrCl₂ had dissolved and that excess chloride was present. The average value of the reciprocal of the slope obtained from three independent titration experiments is 2.1 ± 0.1 , indicating that two chloride ions are consumed by each molecule of CrCl₂ upon dissolution. Thus, Cr(II) is complexed as [CrCl₄]²⁻ in basic melt. This result is consistent with the absorption spectroscopic data and the electrochemical reaction scheme that is proposed in Eq. 1 for the reduction of [CrCl₆]³⁻.

The charge-transfer kinetics of the Cr(III)/Cr(II) couple was also investigated at a GC electrode with rotating-disk-electrode (RDE) voltammetry; plots of the current for the reduction of [CrCl₆]³⁻ at a GC-RDE as a function of the square root of the angular velocity, ω, of the electrode constructed from data appearing in the rising portion of the voltammogram was curved as expected for a quasi-reversible reaction. However, plots of $1/i$ vs. $\omega^{-1/2}$ were linear in accordance with the equation³⁴

$$1/i = 1/i_k + 1/i_{1,c} = 1/i_k + 1/(0.620nFAC_0D_0^{2/3}v^{-1/6}\omega^{1/2}) \quad [2]$$

In Eq. 2, $i_{1,c}$ is the limiting current for the reduction of [CrCl₆]³⁻, i_k is $nFAk_f(E)C_0$, where n is the number of electrons transferred, F is the Faraday constant, A is the geometric area of the electrode, C_0 is the concentration of [CrCl₆]³⁻, and $k_f(E)$ is the potential dependent heterogeneous rate constant for the reduction. Values for $k_f(E)$ are calculated from the intercepts of the plots of $1/i$ vs. $\omega^{-1/2}$, and the standard heterogeneous rate constant, k^o , and cathodic transfer coefficient, α, are determined from the slope and intercept of the plot of $\ln k_f(E)$ vs. E according to the equation³⁴

$$\ln k_f(E) = \ln k^o - \alpha nFE/RT \quad [3]$$

The average values for k^o and α from several experiments are given in Table I. Slow charge-transfer kinetics have also been observed for other transition metal chloride redox couples that undergo a change in coordination during electrochemical reduction in basic AlCl₃-MeEtimCl.^{13,36,37}

Solutions of [CrCl₄]²⁻ are stable when stored in an airtight container, but this species slowly converts to [CrCl₆]³⁻ in about a week if it is exposed to trace oxygen in the dry box atmosphere. This phenomenon also has been reported for some other reduced chloride species such as [YbCl₅]³⁻ (2 days)³⁶ and [EuCl₄]²⁻ (4 days)³⁶ in basic AlCl₃-MeEtimCl melts. However, the oxidation rate for [CrCl₄]²⁻ is much slower than those for [YbCl₅]³⁻ and [EuCl₄]²⁻. In fact, the oxidation rates correlate well to the formal potentials of the respective couples: Yb(III)/Yb(II) at ca. -1.620 V, Eu(III)/Eu(II) at ca. -0.908 V, and Cr(III)/Cr(II) at ca. -0.649 V.

Experimental diffusion coefficients for both [CrCl₆]³⁻ and [CrCl₄]²⁻ in the basic AlCl₃-MeEtimCl melt are given in Table II. These diffusion coefficients were estimated from RDE limiting currents. Each value represents the average value of several individual experiments. The Stokes-Einstein products, ηD/T, which are inversely proportional to the radii of the diffusing entities for these two species, are also included in this table. It has been shown³⁷ that the value of ηD/T for most transition metal chloride complex ions in these melts is dependent upon the overall charge on the complex; a complex ion with an overall charge of 3- generally exhibits a smaller ηD/T than a complex ion with an overall charge of 2- does. The values of ηD/T, and hence the solvodynamic radii for both [CrCl₆]³⁻ and [CrCl₄]²⁻, do not appear to vary significantly with melt composition and are perfectly consistent with those found for transition metal complex ions with the overall charge of 3- and 2- in similar melts.³⁷ The fact that the value of ηD/T for Cr(II) is larger than that for Cr(III) also supports the conclusion that Cr(II) is complexed as [CrCl₄]²⁻ rather than [CrCl₆]³⁻, which would be expected to exhibit a smaller value of ηD/T than [CrCl₆]³⁻.

The electrochemistry of Cr was also examined in the AlCl₃-DMPrimCl melt under the same conditions. The behavior that was observed was similar to that described previously; in spite of the more negative potential limit of this melt compared to the basic AlCl₃-MeEtimCl melt (about 0.5 V), no reduction of Cr(II) to the metal was observed.

Conclusions

In proton free basic AlCl₃-MeEtimCl melt, [CrCl₆]³⁻ can be reduced to [CrCl₄]²⁻, which is stable in the melt unless exposed to trace oxygen. The electrochemical behavior of chromium chloride complex species in basic AlCl₃-MeEtimCl melt is different from those observed in the alkali metal chloride-based melts. In both LiCl-KCl²² and AlCl₃-NaCl²⁴ melts, Cr(III) could be reduced successively to Cr(II) and Cr metal, whereas in basic AlCl₃-MeEtimCl melt, Cr(III) can be reduced only to Cr(II).

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REFERENCES

1. J. Robinson and R. A. Osteryoung, *J. Am. Chem. Soc.*, **101**, 323 (1979).
2. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, *Inorg. Chem.*, **21**, 1263 (1982).
3. P. R. Gifford and J. B. Palmisano, *This Journal*, **134**, 610 (1987).
4. (a) R. A. Osteryoung, in *Molten Salt Chemistry*, G. Mamantov and R. Marassi, Editors, p. 329, D. Reidel Publishing, Holland (1987); (b) C. L. Hussey, *Pure Appl. Chem.*, **60**, 1763 (1988).

5. (a) C. L. Hussey, in *Chemistry of Nonaqueous Solutions: Current Progress*, G. Mamantov and A. I. Popov, Editors, Chap. 4, VCH, New York (1994); (b) R. T. Carlin and J. S. Wilkes, *ibid.*, Chap. 5.
6. T. J. Melton, J. Joyce, J. T. Maloy, J. A. Boon, and J. S. Wilkes, *This Journal*, **137**, 3865 (1990).
7. C. L. Yu, J. Winnick, and P. A. Kohl, *ibid.*, **138**, 339 (1991).
8. J. Fuller, R. A. Osteryoung, and R. T. Carlin, *ibid.*, **142**, 3632 (1995).
9. G. E. Gray, P. A. Kohl, and J. Winnick, *ibid.*, **142**, 3636 (1995).
10. B. J. Piersma, D. M. Ryan, E. R. Schumacher, and T. L. Riechel, *ibid.*, **143**, 908 (1996).
11. M. A. M. Noel, P. C. Trulove, and R. A. Osteryoung, *Anal. Chem.*, **63**, 2892 (1991).
12. I-W. Sun, E. H. Ward, and C. L. Hussey, *Inorg. Chem.*, **26**, 4309 (1987).
13. I-W. Sun and C. L. Hussey, *ibid.*, **29**, 3670 (1990).
14. T. M. Laher and C. L. Hussey, *ibid.*, **21**, 4079 (1982).
15. C. L. Hussey and T. M. Laher, *ibid.*, **20**, 4201 (1981).
16. R. J. Gale, B. Gilbert, and R. A. Osteryoung, *ibid.*, **18**, 2723 (1979).
17. C. Nanjundiah and R. A. Osteryoung, *This Journal*, **130**, 1312 (1983).
18. A. J. Dent, K. R. Seddon, and T. Welton, *J. Chem. Soc., Chem. Commun.*, 315 (1990).
19. A. K. Abdul-Sada, A. M. Greenway, K. R. Seddon, and T. Welton, *Org. Mass Spectrom.*, **24**, 648 (1992).
20. D. A. Nissen, *This Journal*, **126**, 176 (1979).
21. D. M. Bush, Sandia Laboratories, Albuquerque, NM, Technical Report SC-RR-69-497A (1972).
22. S. C. Levy and F. W. Reinhardt, *This Journal*, **122**, 200 (1975).
23. E. E. Marshall and L. F. Yntema, *J. Phys. Chem.*, **46**, 353 (1942).
24. C. L. Hussey, L. A. King, and J. K. Erbacher, *This Journal*, **125**, 561 (1978).
25. T. P. Moffat, *ibid.*, **141**, L115 (1994).
26. H. C. De Long and P. C. Trulove, in *Molten Salts*, R. T. Carlin, S. Deki, M. Matsunaga, D. S. Newman, J. R. Selman, and G. R. Stafford, Editors, PV 96-7, p. 276, The Electrochemical Society Proceedings Series, Pennington, NJ (1996).
27. T. B. Scheffler, Ph.D. Dissertation, University of Mississippi, University, MS (1984).
28. (a) D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963); (b) G. Harrington and B. R. Sundheim, *Ann. N. Y. Acad. Sci.*, **79**, 950 (1960).
29. R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
30. S. K. D. Strubinger, I-W. Sun, W. E. Cleland, Jr., and C. L. Hussey, *Inorg. Chem.*, **29**, 993 (1990).
31. (a) H. Linga, Z. Stojek, and R. A. Osteryoung, *J. Am. Chem. Soc.*, **103**, 3754 (1981); (b) P. A. Barnard and C. L. Hussey, *This Journal*, **137**, 913 (1990).
32. T. B. Scheffler and C. L. Hussey, *Inorg. Chem.*, **23**, 1925 (1984).
33. G. P. Smith, in *Molten Salt Chemistry*, M. Blander, Editor, p. 451, John Wiley & Sons, New York (1964).
34. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, New York (1980).
35. W-J. Gau and I-W. Sun, *This Journal*, **143**, 170 (1996).
36. W-J. Gau and I-W. Sun, *ibid.*, **143**, 914 (1996).
37. C. L. Hussey, I-W. Sun, S. K. D. Strubinger, and P. A. Barnard, *This Journal*, **137**, 2515 (1990).

Relative Dielectric Constant Measurements in the Butyronitrile-Chloroethane System at Subambient Temperatures

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ABSTRACT

By means of electrochemical impedance spectroscopy, the relative dielectric constant was measured as a function of composition and temperature in the butyronitrile-chloroethane system from -35 to -105°C . A customized cell was designed by iterative optimization; the equivalent circuit was used to assess the impacts of the electrical properties of the sample, the limitations of the instrumentation, and the data reduction technique. To account for strong local ordering effects due to molecular association in these solutions, a new model, termed "extended Kirkwood-Onsager" (EKO), was developed. For solutions rich in chloroethane, structural features are inferred with this model.

Introduction

As part of a systematic study of the physical chemistry of butyronitrile (BN), chloroethane (CE), and their solutions, the relative dielectric constant was determined as a function of temperature and composition by electrochemical impedance spectroscopy (EIS). Growing awareness of the potential advantages of processing materials at subambient temperatures had stimulated interest in cryogenic electrochemistry.²⁰ This work was conducted within the framework of a search for liquids that can serve as low-temperature electrolytes for the electrochemical modulation of superconductivity in cuprate materials, such as $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$.²²

The relative dielectric constant of BN has been studied by a number of authors¹⁻³ at and near room temperature. Values of the relative dielectric constant of CE as a function of temperature have been reported by two authors.^{4,5} This work extends the temperature ranges of the relative

dielectric constants for pure BN and CE and measures the dependence of the relative dielectric constant of the binary solutions as a function of temperature and composition.

In order to cope with the high specific impedances of these liquids while minimizing stray capacitance, a customized apparatus was designed. This paper describes the apparatus, reports the measured values of the relative dielectric constant as a function of temperature and solution composition, and interprets the results using a modification of the Kirkwood model.

Experimental

In the experience of the authors, it was found that optimal design of an experiment for EIS measurements derives from focusing on the electrical characteristics of the system and the relationships among cell design, experimental protocol, and data reduction (see Fig. 1). The complex interplay among these various factors is quantified by the equivalent circuit.

The equivalent circuit is a mathematical and physical model of the electrical behavior of an electrochemical system. There are three representations of the equivalent cir-

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