SPECTROELECTROCHEMISTRY IN ROOM TEMPERATURE HALOALUMINATE IONIC LIQUIDS

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ABSTRACT

A fiber optic based, microprocessor controlled spectroelectrochemistry system suitable for the remote acquisition of transmission spectroelectrochemical data is described. This system utilizes a commercial fiber optic spectrophotometer and employs a reticulated vitreous carbon optically transparent electrode. It can be used to collect data in reactive liquids that are isolated in a glove box or other controlled atmosphere environment. The system is completely controlled by two linked microprocessors that collect both electrochemical and spectral data simultaneously. The application of this system is demonstrated through experiments with the tris(2,2'-bipyridine)ruthenium(II)/(III) and hexachloroiridate(III)/(IV) redox systems in the aluminum chloride-1-methyl-3-ethylimidazolium chloride room temperature ionic liquid.

INTRODUCTION

The application of spectroelectrochemical techniques to investigations in molten salts has been reviewed (1). Research in this area has been conducted in both high temperature melts (2-5) and in ionic liquids that are molten at or near room temperature (6,7). Research in our laboratory is concerned with transition metal halide and oxide halide complex chemistry in room temperature
haloaluminate ionic liquids (8) like aluminum chloride-1-methyl-3-ethylimidazolium chloride (AlCl₃-MeEtImCl) (9). In order to fully explore this chemistry, we have constructed a microprocessor controlled, fiber optic based spectroelectrochemistry system and a cell with a reticulated vitreous carbon optically transparent electrode (RVC-OTE) (10). The latter was constructed from Teflon and fused silica. This cell is designed specifically for use with these reactive solvents. The properties of reticulated vitreous carbon or glassy carbon foam electrodes have been discussed (11).

The main advantage of the spectroelectrochemistry system described herein is that it can be used to acquire data directly inside a controlled atmosphere glove box while the spectrophotometer and electrochemical instrumentation remain outside and accessible. Some of the techniques that can be carried out with this system are chronoamperometry, chronocoulometry, chronoadsorptometry, voltammetry, voltadsorptometry, and spectropotentiostatic experiments. In this article we describe this spectroelectrochemical system and illustrate the implementation of these techniques in room temperature haloaluminate melts.

**SPECTROELECTROCHEMISTRY SYSTEM**

The construction of the RVC-OTE cell and cell holder have been described (10). The major instruments that comprise the spectroelectrochemistry system are a Guided Wave Model 100-2 optical waveguide spectrum analyzer, a Tandy Model 1000 microcomputer, a 16-bit microcomputer (IBM-PC/AT equivalent), an AMEL Model 552 potentiostat, an AMEL Model 566 function generator, and a PARC Model 379 digital coulometer with a BCD output.

The Guided Wave spectrophotometer was equipped with both tungsten and deuterium light sources, a silicon diode detector, and a 1200 lines mm⁻¹ concave holographic grating. The Tandy computer was equipped with 128 Kb RAM on the mother board, an RS-232 serial communications board, and a TanPak 512 Kb RAM expansion card (Hard Drive Specialist) with an additional serial port and quartz clock. The 16-bit microcomputer was equipped with 1 Mb RAM, a 20 Mb hard disk, a serial interface card, a parallel I/O BCD card (MetraByte), and an ADALAB-PC (Interactive Microware) interface card. This card was furnished with both differential integrating and
successive approximation 12-bit analog/digital converters, two 12-bit
digital/analog converters, and a four channel multiplexer. A schematic
diagram of the system is shown in Figure 1.

The Tandy computer was used to control the Guided Wave spectrophoto­
meter and acquire spectral data through a proprietary interface card and
software supplied by the instrument manufacturer. The 16-bit computer,
which served as the master unit, was used to control the start of an
experiment by simultaneously triggering the AMEL function generator
through a digital trigger and initiating spectral acquisition by the Tandy
1000/Guided Wave spectrophotometer through a serial communications link.
The sweep voltage from the function generator was monitored with one
channel of the four channel multiplexer by using the integrating A/D
converter. The second channel was used to sample the current at the
coulometer during an experiment. The BCD link was used to monitor the
charge. Alternately, one of the digital/analog converters was sometimes
used in place of the analog function generator to generate waveforms.
Processing of both spectral and electrochemical data was carried out with
LOTUS 123 software.

A unique aspect of the RVC-OTE cell is the positioning of a porous
barrier between the OTE cavity and the reference and counter electrode
compartments (10). This barrier virtually eliminates the edge currents
common to many OTE cells, especially those constructed from minigrids,
where one or more edges of the OTE electrode are exposed to the bulk
solution containing the electroactive solute. No bulk solution containing
electroactive solute need be present in this cell. In addition, the
solution for analysis can be weighed directly into the OTE compartment; no
prior calibration of the volume of this compartment is necessary.

SPECTROELECTROCHEMISTRY EXPERIMENTS

Room temperature haloaluminate melts are relatively viscous compared to
conventional solvents. As a consequence, the diffusion coefficient for a
given electroactive species in these melts is usually one or more orders
of magnitude smaller than in conventional solvents like water or aceto­
nitrile. Hence, the current observed during an electrochemical experiment
with the melt is much less than that observed with most conventional solvents, and longer times are required to accumulate the charge corresponding to complete electrolysis of a given number of moles of solute. Consequently, sweep experiments like cyclic voltammetry must be undertaken at very slow voltage scan rates.

**Chronocoulometry and Chronoabsorptometry.** Chronoabsorptometric techniques involve selective monitoring of the absorbance arising from one or more of the species consumed or produced during an electrode reaction initiated with a potential step. Chronocoulometric charge-time and chronoabsorptometric absorbance-time plots for the oxidation of tris(2,2'-bipyridine)ruthenium(II) cation ([Ru(bipy)$_3$$^{2+}$] in the 60 mole % AlCl$_3$-MeEtimCl melt, which resulted from stepping the potential of the RVC-OTE from 0.70 to 1.50 V versus Al in the 66.7 mole % AlCl$_3$-MeEtimCl melt, are shown in Fig. 2. The [Ru(bipy)$_3$$^{2+}$/3$^+$] electrode reaction has been found to be reversible and uncomplicated by coupled homogeneous chemical steps in a similar molten salt system, aluminum chloride-1-butylpyridinium chloride (12). The chronoabsorptometric plot was obtained by monitoring the [Ru(bipy)$_3$$^{2+}$ absorbance maximum located at 454 nm. The theoretical charge expected based on the exhaustive one-electron oxidation of the [Ru(bipy)$_3$$^{2+}$ cation in the solution that was weighed into the RVC-OTE was 0.01221 coulombs. An uncorrected experimental value of 0.01224 coulombs was recorded during this experiment, and this value suggests that $n = 1.00$. These results illustrate the complete retention of the electroactive solute in the RVC-OTE, and they suggest that [Ru(bipy)$_3$$^{2+}$ undergoes the expected one-electron oxidation to [Ru(bipy)$_3$$^{3+}$]. The chronoabsorptometric plot is essentially a mirror image of the chronocoulometric plot. The flat response of the latter plot (Fig. 2), which is observed after approximately 2800 s have elapsed, illustrates the absence of edge effects associated with this cell.

**Voltammetry and Voltabsorptometry.** Voltabsorptometric techniques involve the simultaneous acquisition of both potential and absorbance data during a potential sweep experiment (13). These techniques are especially useful for selective monitoring of an electrode reaction in the presence of large background currents or currents arising from other electroactive solutes that are oxidized or reduced in the same potential region as the
species of interest. In order to apply these techniques, an accessible spectral region must be available in which either the oxidized or reduced form of the redox couple of interest exhibits absorption and in which there is no absorption by any species that may be participating in parallel redox reactions.

The cyclic voltammetric and voltabsorptometric responses that were obtained from the application of a 0.2 mV s\(^{-1}\) potential sweep program to the RVC-OTE, which contained the same \([\text{Ru(bpy)}_3]^{2+}\) solution used in Fig. 2, are shown in Figs. 3 and 4, respectively. The triangular potential sweep program that was used for these experiments extended from 0.90 to 1.50 and back to 0.90 V. The wavelength was monitored at 454 nm in order to record the voltabsorptometric response.

The differential voltabsorptometric wave (Fig. 4b) was obtained by differentiation of the data in Fig. 4a, and it matches Fig. 3 closely for this reversible, uncomplicated electron transfer reaction. Half-wave potentials of 1.24 V were calculated from both Figs. 3 and 4b. These values are in good agreement with the estimate of \(E_{1/2} = 1.22\) V that was determined with cyclic voltammetry at a glassy carbon disk electrode in a separate experiment.

Spectropotentiostatic Experiments.- The spectropotentiostatic technique involves the measurement of absorption spectra after Nernstian equilibrium has been attained at the OTE following steady-state potential steps (14). This technique is useful for obtaining estimates of iR free formal cell potentials, \(E^0\) (14). Significant potential errors due to uncompensated cell resistance are sometimes present in formal potentials originating from voltammetric measurements. The spectropotentiostatic technique provides a viable non-potentiometric method for estimating \(E^0\). In these experiments the applied potential, \(E_a\), is used to control the ratio \([\text{Red}]/[\text{Ox}]\); when equilibrium has been achieved in the solution entrained in the OTE, the absorption spectrum is recorded. Both \(E^0\) and \(n\) for a redox reaction can be calculated from a series of absorption spectra recorded at different \(E_a\) by monitoring the absorbance of the electroactive species in the OTE at a selected wavelength and then plotting the data according to the following equation (14):
\[ E_a = E^{0*} + \frac{2.3RT}{nF} \log\left(\frac{A_{\text{Red}} - A}{A - A_{\text{Ox}}}\right) \]

\( A_{\text{Red}} \) and \( A_{\text{Ox}} \) correspond to the absorbance of the completely reduced solution, the absorbance of the completely oxidized solution, and the absorbance of the solution at some \( E_a \) value intermediate between those used to establish \( A_{\text{Red}} \) and \( A_{\text{Ox}} \) respectively.

A series of spectropotentiostatic experiments for the \([\text{IrCl}_6]^{2-}/3-\) redox system in the 49.0 mole % \( \text{AlCl}_3\)-MeEtimCl room temperature ionic liquid are shown in Fig. 5. In each experiment, the RVC-OTE was held at \( E_a \) until current ceased to flow and the optical response at 494 nm became constant. A plot of \( E_a \) versus \( \log\left(\frac{A_{\text{Red}} - A}{A - A_{\text{Ox}}}\right) \), which was derived from the series of spectropotentiostatic experiments shown in Fig. 5, is shown in Fig. 6. The slope of this plot is 0.062 V at 40.0 °C (0.062 V is expected for \( n = 1 \)), and the intercept is \( E^{0*} = 0.37 \) V. The latter compares favorably with a value of \( E^{0*} = 0.37 \) V that was calculated from voltammetric data obtained with a glassy carbon rotating disk electrode.

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Figure 1. Schematic diagram of the spectroelectrochemistry system.
Figure 2. Chronocoulometric (----) and chronosorptometric (-- ) responses for the oxidation of a 0.60 mM solution of (Ruthenium)2+ in 60.0 mol % AlCl3-Me2ImCl at 40.0 °C at the RVC-OBE. The potential was stepped from an initial value of 0.70 to 1.50 V, and the wavelength was monitored at 454 nm.
Figure 3. Cyclic voltammetric wave for the solution described in Fig. 2 at the RVC-OTE. The scan rate was 0.20 mV s\(^{-1}\).
Figure 4. (a) Cyclic voltabsorptometric and (b) differential cyclic voltabsorptometric waves for the solution described in Fig. 2 at the RVC-OTE. The scan rate was 0.20 mV s\(^{-1}\), and the absorbance was monitored at 454 nm.
Figure 5. Absorption spectra that were recorded at various applied potentials during a spectro-potentiostatic experiment with 2.09 mM [IrCl₆]^{2-} in 49.0 mole % AlCl₃-MeEtimCl at 40.0 °C at the RVC-OTE: (a) 0.600, (b) 0.450, (c) 0.425, (d) 0.400, (e) 0.375, (f) 0.350, (g) 0.325, and (h) 0 V.
Figure 6. Plot of $E_a$ versus $\log\left(\frac{[A_{\text{Red}} - A]}{[A - A_{\text{Ox}}]}\right)$.