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**SPECTROELECTROCHEMISTRY IN MELTS:
APPLICATIONS TO MOLTEN CHLOROALUMINATES**

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ABSTRACT

Spectroelectrochemistry is an effective approach to studies of redox chemistry in solutions. We have recently initiated UV-visible spectroelectrochemical studies in molten chloroaluminates ($\text{AlCl}_3\text{-NaCl}$ mixtures) using a silicon vidicon rapid-scan spectrometer. Electrodes made from glassy carbon foam and metal grids are used in optically transparent thin layer cells. The solute species of interest are the oxidation products of sulfur and some of the Group IVB-VIB transition metal ions. In this paper the apparatus and the initial results are described.

MASTER

INTRODUCTION

The use of spectroelectrochemistry as a tool for studying redox chemistry in solutions has developed rapidly over the last several years (1). This technique yields simultaneous spectral and electrochemical information useful in the elucidation of mechanisms of redox reactions. By using appropriate experimental designs, short-lived intermediate species, which may be undetectable electrochemically, can be studied.

The transmission mode spectroelectrochemical experiment involves the use of an optically transparent electrode (OTE), i.e. an electrode which is transparent in the spectral region of interest. Radiation of the desired wavelengths is passed through the solution and the OTE where a portion is absorbed by the solute species. The attenuated radiation is then measured to give a spectrum. Spectroelectrochemistry most commonly involves the UV-visible-IR spectral regions, but it has been applied to ESR, NMR and mass spectrometry as well (1).

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We are currently developing UV-visible spectroelectrochemical techniques for studying redox systems in molten chloroaluminates (mixtures of AlCl_3 and alkali halides). Solute chemistry in these melts is quite dependent on the melt acidity (2-4). The acid-base properties of the chloroaluminate melts near the 1:1 AlCl_3 -NaCl mole ratio can be described by the equilibrium (5-9)

AlCl_4^- is the predominant anion in the equimolar AlCl_3 -NaCl melt. As the acidity is increased, Al_2Cl_7^- becomes more abundant (5-9).

To date we have examined by spectroelectrochemistry the reduction of niobium (V) and the oxidation of sulfur in chloroaluminate melts. The use of OTE's to study species in melts spectroelectrochemically has not been reported previously.

EXPERIMENTAL

A block diagram of the spectrometer/data acquisition system used to carry out spectroelectrochemical experiments is shown in Figure 1. The spectrometer is a silicon-vidicon based rapid-scan spectrometer (RSS) which is controlled by the PDP-8/I minicomputer. To obtain an absorption spectrum of a sample, white light is passed through the sample and into a polychromator where it is dispersed by a grating. A 400 nm wide segment of this spectrum is directed across the face of the vidicon detector, where it is read as light intensity vs. wavelength by an electron beam. The sweep frequency of this beam can be adjusted so that spectra may be acquired at time intervals varying from 10 msec to 5 sec. Since the spectrometer operates in a single-beam mode, a 100% transmission spectrum (with no sample in the beam) is also acquired and the absorbance spectrum is calculated using the computer. Spectra are stored either on disk or cassette tape. An absorption spectrum can be viewed either on a CRT display, or displayed on an X-Y recorder. A potentiostat is also interfaced to the system; this makes it possible to synchronize the start of spectral data acquisition with the initiation of the electrochemical experiment as well as to simultaneously acquire and store both spectral and electrochemical data. A more detailed description of the spectrometer and the computer interface system is available (10).

A typical cell used to carry out molten salt spectroelectrochemical experiments is illustrated in Figure 2. The optically transparent electrode consists of a piece of porous glassy carbon (11), a platinum screen or a tungsten grid. The OTE is inserted into the quartz cuvette, the pathlength of which ranges from 0.25 mm to 2.00 mm, and the OTE assembly is held in place by a Cajon vacuum fitting. The counter electrode is a platinum foil electrode and the reference electrode is an aluminum wire in a separate fritted compartment.

Other electrodes, not shown for clarity, include a platinum or tungsten wire working electrode for cyclic voltammetry, and an extra platinum foil electrode. The melt is added via a filling tube (not shown) in the top of the cell which is then sealed under vacuum. The cell is mounted in a suspension assembly by means of the support ring, and this assembly is then lowered into an optical furnace. The furnace consists of a glass tube wrapped with a nichrome heating element, and contains two quartz windows through which spectra are taken. The furnace temperature is controlled by using a variable voltage transformer. A tungsten lamp and a xenon arc lamp serve as light sources.

SPECTROELECTROCHEMICAL STUDY OF THE REDUCTION OF NIOBIUM (V)

The redox chemistry of transition metals in Groups IVB-VIB in chloroaluminate melts is unusual because of the tendency to form metal clusters in which the metal exists in an unusually low oxidation state (2,4,12-14). The electrochemical reduction of Nb(V) in both acidic (mole % $\text{AlCl}_3 > 50$) and basic (mole % $\text{AlCl}_3 < 50$) chloroaluminates has been previously reported (4). Potentiometric and spectroscopic studies of Nb(V) in AlCl_3 -KCl melts have also been performed (15). In basic melts the first step of the reduction of the bright-yellow Nb(V) results in the formation of purple Nb(IV). The spectroelectrochemistry of this reduction was studied at a Pt screen OTE in a NaCl-saturated (basic) melt at 225°C. Figure 3 illustrates the spectra obtained during the course of the reduction. At $t = 0$ sec, an absorption band at 300 nm due to Nb(V) is observed. Following a potential step to the diffusion plateau of the first reduction wave, two new absorption bands appear at 275 nm and ~350 nm. Previous spectra of Nb(IV) obtained in this melt (14), in solid phase (16), and in another solvent (17) show bands near 285 nm and 325 nm, plus other lower wavelength bands. The reported band positions vary by as much as 10-15 nm. Figure 4 shows a thin-layer coulogram of this reduction calculated from chronoamperometric data obtained simultaneously with spectral data. The charge value obtained from this curve yields an n-value of 0.99, thus confirming a simple electrochemical reduction.

In acidic melts, the reduction of Nb(V) proceeds through an ECE mechanism to produce a Nb(III) species (4) as shown below:

This reduction was studied spectroelectrochemically in an acidic melt (AlCl_3 -NaCl 63-37 mole %) at 225°C, and the resulting spectra are shown in Figure 5. The Nb(V) band at 300 nm disappears as the reduction is carried out, and no new bands are observed. The slight increase

in absorbance seen at the longer wavelengths is probably due to the formation of a precipitate containing Nb(III) (14). Because this precipitate apparently was deposited on the screen OTE, it could be reoxidized completely to Nb(V), as indicated by the reappearance of the band at 300 nm. Thin-layer coulometry carried out simultaneously with spectral acquisition gave an n-value of 2.2.

SPECTROELECTROCHEMICAL STUDY OF SULFUR OXIDATION

The electrochemistry of sulfur in molten chloroaluminates is of considerable importance to the development of a molten salt battery using a sodium anode and positive oxidation states of sulfur as the cathode (18,19); it has been investigated in both basic and acidic melts (20-22). Because sulfur can be oxidized to higher oxidation states in acidic melts, its chemistry in these melts is of greater importance to the battery work. In acidic $\text{AlCl}_3\text{-NaCl}$ melts sulfur is oxidized in three steps, the final product being S(IV) as indicated by voltammetry and controlled-potential coulometry (22). Both Raman (23) and potentiometric (24,25) studies have indicated that S(IV) is present as SCl_3^+ .

We are using spectroelectrochemistry to study further the mechanism of the oxidation of sulfur in acidic chloroaluminates. By oxidizing elemental sulfur in the melt to S(IV), at least five intermediate oxidation states can be produced (24,25). Several of these species have characteristic absorption maxima which can be used to ascertain the species present as a function of the potential applied to the OTE.

Elemental sulfur was dissolved in an acidic chloroaluminate melt ($\text{AlCl}_3\text{-NaCl}$ 63-37 mole %); this solution was studied spectroelectrochemically at platinum and carbon OTE's at 225°C. Thin-layer coulometry was carried out on the first oxidation wave by holding the potential of a Pt OTE at + 1.65V. N-values ranging from 0.14 to 0.16 were obtained. These results agree with those obtained through exhaustive bulk coulometry (22). An n-value of 0.125 would correspond to the formation of S_{16}^{2+} (or S_8^+), while an n-value of 0.25 would indicate formation of S_8^{2+} . The intermediate value suggests that a mixture of these species is formed. The spectra shown in Figure 6, obtained at a carbon OTE, substantiate this supposition. As the oxidation takes place, three absorption bands appear approximately simultaneously at 16600 cm^{-1} (600 nm), 13700 cm^{-1} (730 nm) and 10200 cm^{-1} (980 nm). The latter two bands achieve a maximum absorbance after about four minutes and begin to decrease as the first band continues to increase. This can be seen clearly from the absorbance-time profiles illustrated in Figure 7. According to previously published work (24,25), the 600 nm band is attributed to S_8^{2+} and the 730 nm and 980 nm bands are due to S_{16}^{2+} . This first oxidation step then produces a mixture of S_{16}^{2+} (or S_8^+) and S_8^{2+} . Marassi et al. (22) have proposed mechanisms involving chemical reactions which could account for these results.

The spectra shown in Figure 8 were obtained by stepping the potential of the carbon OTE from 1.65V (plateau of the first wave) to 1.85V (just past the plateau of the second wave). The band at 13700 cm^{-1} , due to S_{16}^{2+} (or S_8^+) immediately vanishes while the band at 16600 cm^{-1} (S_8^{2+}) initially increases. This band then slowly disappears as S_8^{2+} is oxidized to S(I). In a similar experiment carried out at a Pt screen OTE, but recording spectral data at shorter wavelengths, bands at ca. 26300 cm^{-1} (380 nm) and $\sim 31000\text{ cm}^{-1}$ (323 nm) appeared as the oxidation proceeded. At least one and perhaps both of these bands can be attributed to the formation of S(I) (as S_2^{2+}) (25). The third sulfur oxidation wave is not very interesting for spectroelectrochemical study because the S(IV) product does not exhibit any absorption in the visible region (25).

CONCLUSION

We have demonstrated that spectroelectrochemistry can be carried out successfully in melts using optically transparent electrodes. The correlation of the spectral data with the electrochemical results has proven very helpful in determining what species are formed during the reduction or oxidation, thereby yielding insight into the mechanisms of the electrochemical processes in melts.

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Figure 1. Block diagram of the system used for spectroelectrochemical experiments

Figure 2. Typical spectroelectrochemical cell used in the molten salt studies. The reference electrode is isolated from the bulk melt by a porous ceramic frit

Figure 3. Spectra obtained during the reduction of Nb(V) in the NaCl-saturated chloroaluminate melt. Potential stepped from 1.5V to 1.0V vs. the Al(III)/Al reference electrode in the NaCl-saturated melt. OTE: Pt screen. Pathlength: 0.25 mm. Conc. Nb(V): 0.0015 molal

Figure 4. Charge vs. time plot for the thin-layer coulometric reduction of Nb(V) in the NaCl-saturated chloroaluminate melt. Potential stepped from 1.5V to 0.9V vs. the Al(III)/Al reference electrode in the NaCl-saturated melt. OTE: Pt screen

Figure 5. Spectra obtained during the reduction of Nb(V) in $\text{AlCl}_3 - \text{NaCl}$ (63-37 mole %) melt. Potential stepped from 1.5V to 0.9V vs. the Al(III)/Al reference electrode in the 63-37 melt. OTE: Pt screen. Pathlength: 0.25 mm Conc. Nb(V): 0.0036 molal

Figure 6. Spectra obtained during the oxidation of sulfur at a glassy carbon OTE in the $\text{AlCl}_3 - \text{NaCl}$ (63-37 mole %) melt. Potential stepped from 1.3V to 1.65 V vs. the Al(III)/Al reference electrode in the 63-37 melt. Conc. S: 0.013 molal

Figure 7. Absorbance vs. time plots for the three absorbance bands shown in Figure 6. Pathlength: 2.0 mm

Figure 8. Spectra obtained during the oxidation of sulfur at a glassy carbon OTE in the $\text{AlCl}_3 - \text{NaCl}$ (63-37 mole %) melt. Potential stepped from 1.65 V to 1.85V vs. the Al(III)/Al reference electrode in the 63-37 melt. Conc. S: 0.013 molal