

Metal Electrodeposition and Electron Transfer Studies of Uranium Compounds in Room Temperature Ionic Liquids

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Room temperature ionic liquids (RTIL's) comprised of 1,3-dialkylimidazolium or quaternary ammonium cations and one of several anions such as PF_6^- , BF_4^- , or $\text{N}(\text{SO}_2\text{CF}_3)_2$, represent a class of solvents that possess great potential for use in applications employing electrochemical procedures. Part of the intrigue with RTIL's stems from some of their inherent solvent properties including negligible vapor pressure, good conductivity, high chemical and thermal stability, and non-flammability. Additionally, a substantial number of RTIL's can be envisioned simply by combining different cation and anion pairs, thereby making them attractive for specific application needs. We are interested in learning more about the possible use of RTIL's within the nuclear industry. In this regard our research team has been exploring the electron transfer behavior of simple metal ions in addition to coordination and organometallic complexes in these novel solvents. Results from our research have also provided us with insight into the bonding interactions between our current anion of choice, bis(trifluoromethylsulfonyl)imide $\equiv \text{NTf}_2$, and open coordination sites on actinide and transition metal fragments.

This presentation will focus on recent results in two areas: the electrodeposition of electropositive metal ions from RTIL solutions and the electron transfer behavior for several uranium complexes. Details concerning the cathodic electrodeposition and anodic stripping of alkali metals (Na, K) from various working electrode surfaces (Pt, Au, W, Glassy Carbon) will be discussed. Figure 1 displays typical behavior for the electrodeposition of potassium metal from an RTIL containing potassium ions produced through the reaction of KH with $\text{H}[\text{NTf}_2]$. Our efforts with other metal ions, including our results to date with uranium electrodeposition, will be covered during the presentation.

The electron transfer behavior for a number of uranium complexes have been studied with various electrochemical methods including cyclic and square-wave voltammetry, chronoamperometry, and bulk coulometry. Results from these studies will be presented to show the general electron transfer behavior of metal complexes in the RTIL's. As an example, Figure 2 shows the difference in chemical stability of an electrogenerated U(V) anion for two uranyl (U(VI)O_2^{2+}) complexes due to the difference in ancillary ligands about the uranyl moiety. Figure 2a shows a cyclic voltammogram (CV) for the $\text{U(VI)}/\text{U(V)}$ couple of a uranyl complex containing a multi-dentate chelating nitrogen/oxygen ligand (inset in figure). The couple is both chemically and electrochemically reversible. The CV in Figure 2b is that of $[\text{UO}_2\text{Cl}_4]^{2-}$ in which the electrogenerated U(V) derivative is unstable yielding a chemically irreversible wave. For the compound giving rise to the CV in Figure 2a its electrochemical behavior in a conventional non-aqueous electrolyte medium is very similar to that obtained in the RTIL. While this result does not illustrate a distinct advantage for employing the RTIL solvent in this particular case, we believe it effectively demonstrates the ability of the RTIL to be utilized as a solvent/electrolyte medium for detailed electrochemical studies without severe limitations.

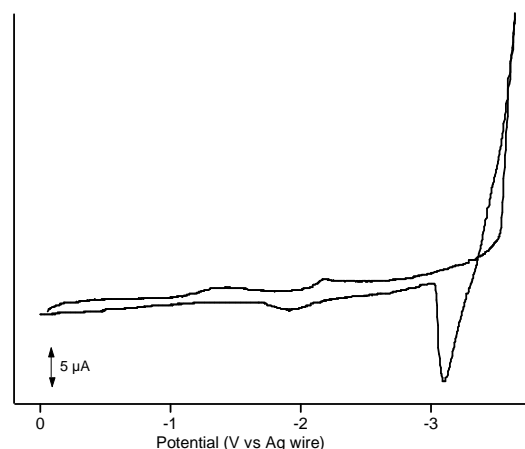


Figure 1. Cyclic voltammogram (0.1 V/s, 1mm Pt disk) of K metal electroplating and stripping from a solution of KH and $\text{H}[\text{NTf}_2]$ in $[(\text{CH}_3)_2\text{N}(\text{C}_3\text{H}_7)(\text{C}_3\text{H}_6)][\text{NTf}_2]$.

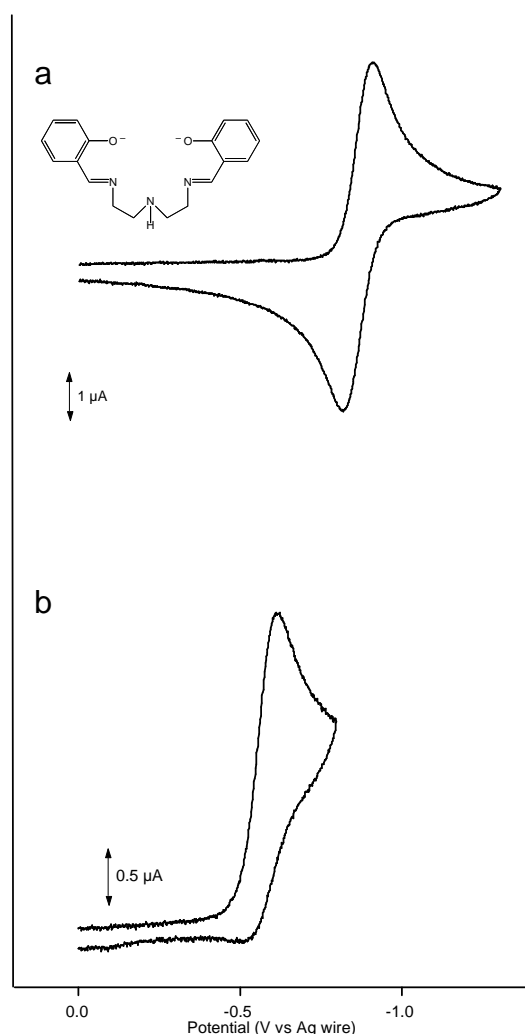


Figure 2. Cyclic voltammograms (0.1 V/s, 1.5 mm GC disk) of (a) $\text{UO}_2(\text{saldiene})$ and (b) $[\text{UO}_2\text{Cl}_4]^{2-}$ in $[\text{ethylmethylimidazolium}][\text{NTf}_2]$.