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Electrorecovery of Actinides at Room Temperature

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The electrochemical behavior of U(IV) and U(III) species in room temperature ionic liquids (RTILs) and the relatively low vapor pressure solvents NMP and DMSO is described. These studies have been ongoing in our laboratory to uncover conditions that will lead to the successful bulk electrodeposition of actinide metals at a working electrode surface at room temperature or slightly elevated temperatures. The RTILs we have focused on thus far are based on 1,3-dialkylimidazolium or quaternary ammonium cations and $^{-}N(SO_2CF_3)_2$ anions. Our results from XPS studies of electro-oxidized uranium metal surfaces indicate that uranium metal reacts with the anion from the RTIL, most likely through an initial fluoride abstraction, forming decomposition products that inhibit the bulk electrodeposition of uranium metal. Similar results were found when the organic solvents were used with $TBA[B(C_6F_5)_4]$ as the supporting electrolyte, although the voltammetric data of uranium ions in these solutions is more encouraging in relation to electrodeposition of uranium metal. Preliminary results on the voltammetric behavior and bulk electrodeposition of plutonium species are also presented.

Introduction

There are a large number of purification and processing operations involving actinide species that rely on high-temperature molten salts as the solvent medium. One such application is the electrorefining of impure actinide metals to provide high purity material for subsequent applications. There are some drawbacks to the electrodeposition of actinides in molten salts including relatively low yields, lack of accurate potential control, maintaining efficiency in a highly corrosive environment, and failed runs. With these issues in mind we have been investigating the electrodeposition of actinide metals, mainly uranium, from room temperature ionic liquids (RTILs) and relatively high-boiling organic solvents. The RTILs we have focused on are comprised of 1,3-dialkylimidazolium or quaternary ammonium cations and mainly the $^{-}N(SO_2CF_3)_2$ anion [bis(trifluoromethylsulfonyl)imide ≡ $^{-}NTf_2$]. These materials represent a class of solvents that possess great potential for use in applications employing electrochemical procedures (1). In order to ascertain the feasibility of using RTILs for bulk electrodeposition of actinide metals our research team has been exploring the electron transfer behavior of simple coordination complexes of uranium dissolved in the RTIL solutions. More recently we have begun some fundamental electrochemical studies on the behavior of uranium and plutonium complexes in the organic solvents N-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO). Our most recent results concerning electrodeposition will be presented in this account.

Experimental

The room temperature ionic liquids used for these studies were prepared in our laboratory following previously published literature procedures (2). The solvents dimethylsulfoxide (DMSO - Sigma-Aldrich, ≥99.9%, anhydrous) and N-methylpyrrolidone (NMP - Sigma-Aldrich, 99.5%, anhydrous) were prepared by contact with powdered 4Å molecular sieves for at least one week followed by filtration through dry (24 hours at 500° C), neutral alumina just before each experiment. The supporting electrolyte for voltammetry experiments utilizing organic solvents was tetra-n-butylammonium (TBA) tetrakis(pentafluorophenyl)borate, $[(n\text{-}C_4H_9)_4N][B(C_6F_5)_4]$, at 0.1 M. Preparation and purification were performed according to the literature procedure (3). All experimental work was performed in an inert atmosphere (helium) Vacuum Atmospheres Company glovebox with continuous oxygen and moisture monitoring. Electrochemical experiments were conducted with a PAR 273A potentiostat controlled with a Windows PC running CorrWare from Scribner Associates Inc. A conventional three-electrode configuration consisting of a coiled platinum wire auxiliary, a bare silver wire pseudo-reference, and various working electrodes was employed. The platinum (1 and 2 mm), glassy carbon - GC (1.5 mm), and gold (1 mm) disk working electrodes were from Cypress Systems. The working electrodes were polished with 1 µm and 0.05 µm alumina slurries from Buehler LTD and rinsed with copious amounts of nanopure water before each experiment. During the electroplating experiments the reference electrode was placed in a separate compartment isolated from the bulk solution by a fine glass frit. The $E_{1/2}$ potential for the ferrocene/ferrocenium couple in NMP with 0.1 M $TBA[B(C_6F_5)_4]$ is 0.835 V vs Ag wire. Potentials reported here versus Ag wire can be referenced to the ferrocene/ferrocenium couple by the subtraction of 0.835 V.

The $PuCl_3$ used for electrochemical experiments was prepared by the reaction of highly pure, electrorefined plutonium metal and chlorine gas at 900 °C in a tantalum crucible. Full preparatory details and single crystal x-ray diffraction data for $U(OTf)_3(dme)_3$ {where OTf is SO_3CF_3 and dme is 1,2-dimethoxyethane} and $[U(NMP)_8][OTf]_3$ will be published in a separate account shortly. Briefly, $U(OTf)_3(dme)_3$ was prepared by hydriding of U metal at elevated temperature, followed by reaction of UH_3 with triflic acid to give $U(OTf)_3$, which was then dissolved in dimethoxyethane solvent (Sigma-Aldrich, anhydrous 99.5%, vacuum distilled from deep purple solutions containing K/benzophenone) and crystallized at reduced temperature to give pure product. The $[U(NMP)_8][OTf]_3$ was prepared by dissolution of $U(OTf)_3(dme)_3$ in NMP solvent followed by slow crystallization at reduced temperature. $[UCl_6][EMI]_2$ was prepared from the reaction of UCl_4 in tetrahydrofuran (thf) solvent with two equivalents of [EMI]Cl, where EMI = 1,3-ethylmethylimidazolium.

Results and Discussion

We have previously reported on the electrodissolution of uranium metal in $^-NTf_2$ based RTILs, which quantitatively produced emerald green solutions of U(IV) ions supported in some fashion by coordination to the $^-NTf_2$ anion (4). The voltammetry of the resulting U(IV) solutions show a shift in $E_{1/2}$ potential for the U(IV)/U(III) reduction process to a value 1.724 V more positive than the associated couple for $[UCl_6][EMI]_2$

(0.164 V for U(IV)$(NTf_2)_x$ to -1.560 V for UCl_6^{2-} both vs Fc/Fc^+). Unfortunately at potentials negative of the U(IV)/U(III) reduction the voltammetry was not conclusive for the electrodeposition of uranium metal on the surface of various working electrodes (Pt, Au, GC, U), and there were indications that the electrostripped bare uranium metal was interacting with the bulk RTIL solvent in a non-innocent fashion. The most obvious indication of this behavior became evident when the uranium metal working electrode was removed from the inert atmosphere, rinsed with ethanol, and left exposed to air for weeks: the surface of the uranium metal that had been electrolyzed did not oxidize as normally expected for this metal. This result is similar to recent results on the formation of protective films on the surface of magnesium alloys (5). While inhibiting the air oxidation of uranium metal through the use of protective films may be of scientific and technical interest, it seems to be inhibiting our desired result of bulk uranium metal electrodeposition at the surface of a working electrode. A simple voltammogram of the electrostripped uranium metal electrode shown in Figure 1 indicates the presence of an insulating film since the current on the reverse CV scan is larger than the forward current. It appears that at a potential of approximately 1.1 V vs Ag wire the film, formed while the electrode sat in the RTIL solution with no applied potential for several minutes, begins to break down. It should be noted that we attempted to use UH_3 as a starting material for the production of U(III)$(NTf_2)_x$ ions in a reaction with $HNTf_2$, but the lack of reactivity between the two reactants precluded any further study.

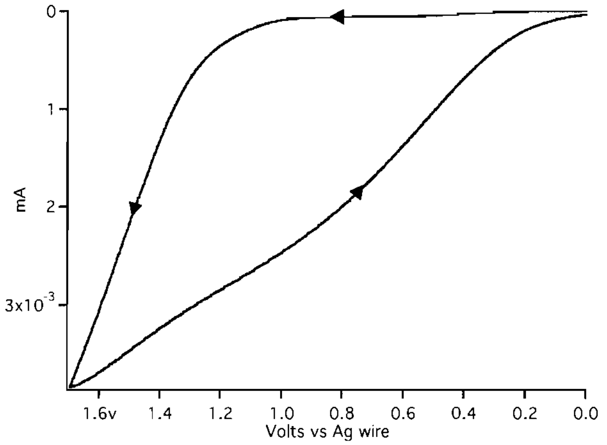

Figure 1. Cyclic voltammogram of an electrostripped U metal working electrode in the RTIL [EMI]$[NTf_2]$ with U(IV)$(NTf_2)_x$ present. Scan rate was 0.1 V/s.

In order to obtain some qualitative data about the nature of the uranium electrodeposition process we decided to utilize the inherent radioactivity of uranium to detect its presence on a Pt working electrode surface by alpha spectroscopy. The methodology used involved the application of a potential negative enough to possibly deposit uranium metal, followed by removal of the electrode from the inert atmosphere glove box for analysis. This method would expose the electrode to air and lead to oxidation of any uranium metal on the surface, but the study would still indicate whether or not uranium was being deposited on the surface of the electrode at potentials more negative than the U(IV)/U(III) couple. Due to self-attenuation of alpha particles from relatively thick surfaces, only a very thin layer of material was deposited amounting to approximately 350 μg of U metal on a 1cm^2 surface. The alpha spectroscopy results were positive for the presence of uranium on the surface of the electrode. A blank Pt metal electrode that was also exposed to the solution of uranium ions with the absence of any applied potential showed essential no alpha activity.

We have also utilized x-ray photoelectron spectroscopy (XPS) to obtain additional information about the surface of the electrostripped uranium electrode. The uranium metal was prepared by electrolysis at a potential of approximately 1.5 V vs Ag wire in the [(i-propyl)(n-propyl)N(Me)$_2$][NTf$_2$] RTIL until active dissolution had been sustained for several hours. The electrode was then removed from the RTIL solution, rinsed with anhydrous ethanol, cut to approximately 1 cm^2 size, and finally mounted within the inert atmosphere transfer chamber. The transfer chamber integrates with the XPS instrument so that the integrity of the inert atmosphere is maintained during transfer. The sample was studied initially without any disruption to the surface and subsequently after the surface was sputtered with argon ions to obtain data on the nature of the film below the outer surface. The results from the XPS data show an outer surface that is mainly comprised of a 1:1 cation to anion ratio of native RTIL solvent. This is likely due to material that was not removed during the wash procedure with anhydrous ethanol. After sputtering the XPS data shows peaks associated with the RTIL constituents in which the fluorine 1s peak is in a different chemical environment than that displayed in the intact anion. Additionally there are uranium peaks present that are not indicative of U(IV) or uranium metal, but instead are more accurately described as a low-valent uranium species. We believe this low-valent uranium species may be some type of uranium fluoride complex. This result is not completely unexpected since low-valent actinides are very effective at abstracting fluoride from various molecules. However, the result does indicate that a bare uranium metal surface undergoes an interaction with the RTIL solvent that appears to hinder the solvents ability to be an adequate medium for bulk electrodeposition of uranium metal. Further sputtering shows the presence of the native uranium metal electrode. Our results are in-line with results reported on the decomposition products when Li metal is exposed to solutions containing the $^{-}$NTf$_2$ anion (6). There was no indication from the XPS data that the uranium formed an oxide species.

In an effort to synthesize and isolate stable U(III) complexes as potential starting materials for uranium electrodeposition, we were successful in preparing and obtaining single-crystal x-ray diffraction data for the complex U(OTf)$_3$(dme)$_3$. Unfortunately the preliminary voltammetric behavior of this compound in neat RTIL and in 1,2-dimethoxyethane solvent with RTIL as supporting electrolyte was not very encouraging. The compound displayed two very closely spaced oxidation waves likely due to the U(III)/U(IV) couple. The two waves presumably arise from slightly different structures in solution, which follows from the two different crystal orientations uncovered in the solid state. We then decided to look at the voltammetric behavior of the U(OTf)$_3$(dme)$_3$ complex in NMP and DMSO solvents due to the positive results we were observing in these solvents for the electrodissolution of uranium metal. As shown in the top CV of Figure 2, the U(OTf)$_3$(dme)$_3$ complex undergoes a quasi-reversible oxidation to the U(IV) species, and there are no additional voltammetric waves observed at potentials positive of the U(III)/U(IV) couple. However, as displayed in the CV on the bottom of Figure 2 at potentials negative of the U(III)/U(IV) couple two small closely spaced waves are observed at approximately -0.5 V with an additional large reduction wave at -1.25 V.

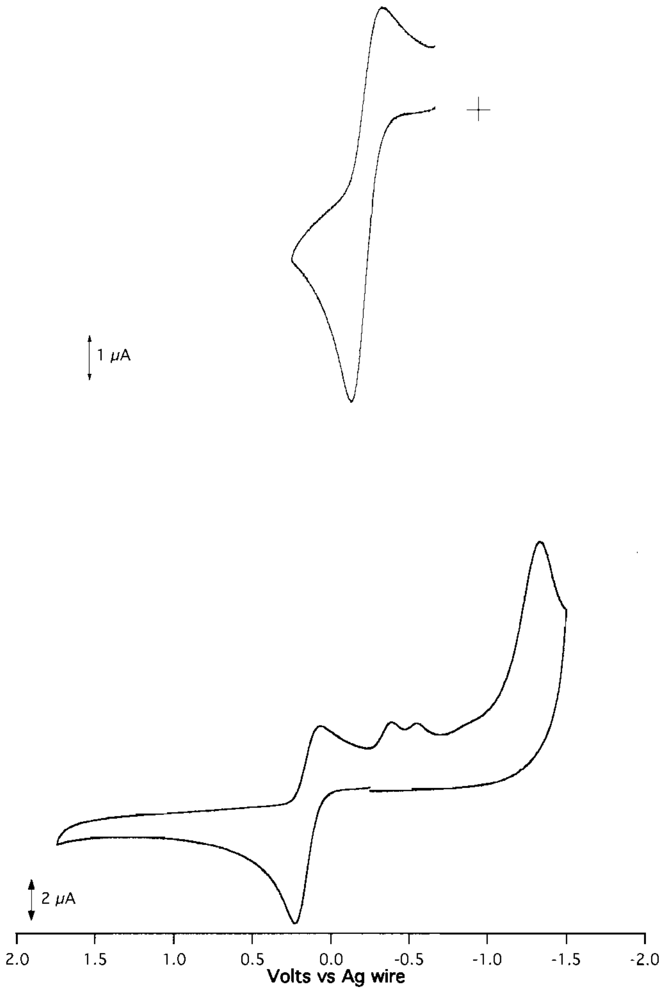

Figure 2. Cyclic voltammograms of $U(OTf)_3(dme)_3$ in NMP/0.1M $TBA[B(C_6F_5)_4]$ at 0.1 V/s and a 1.5 mm glassy carbon disk working electrode versus Ag wire reference electrode.

After traversing these negative voltammetric processes and scanning positive again the behavior at the working electrode surface changes. Referring to Figure 3 now, which contains a series of two consecutive voltammograms starting at -0.3 V, there is a complete absence of the U(III) to U(IV) oxidation wave and a new oxidation wave has appeared at approximately 1.65 V. On the second cycle, and also on the return scan of the first cycle, the waves associated with the U(III)/U(IV) reappear. Our interpretation of these results involves the electrodeposition and subsequent electrostripping of uranium metal from the working electrode surface. The two small waves centered around -0.5 V likely arise from nucleation phenomena associated with initial stages of uranium electrodeposition. The voltammetry described here is highly reproducible. Subsequent to the voltammetric studies on $U(OTf)_3(dme)_3$ a crystal structure of $[U(III)(NMP)_8][OTf]_3$ was obtained from low-temperature crystallization, in which all inner sphere OTf and dme ligands are replaced by eight inner sphere NMP ligands bonded through their respective oxygen atoms. This result is similar to a previous finding we made where three of the inner sphere chloride ligands of UCl_4 are replaced by DMSO ligands to give the crystal structure $[UCl(DMSO)_7]Cl_3$ (7).

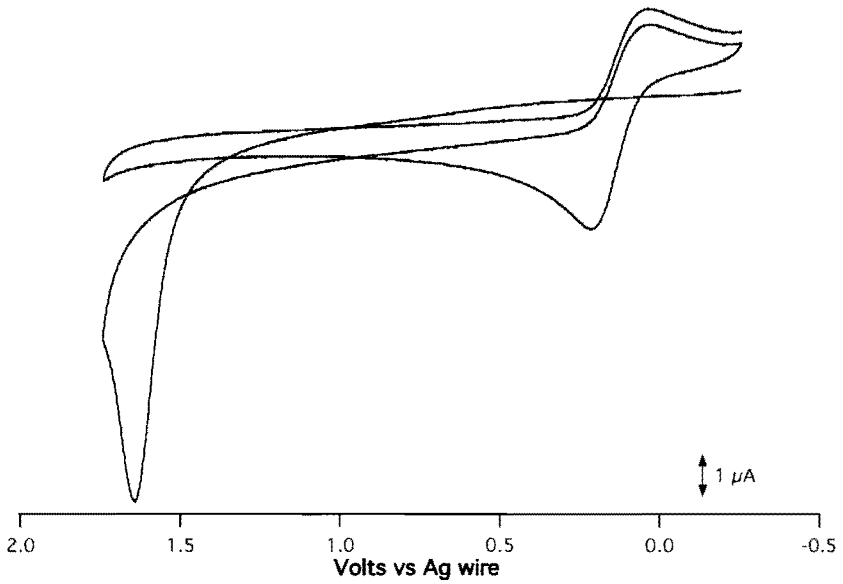

Figure 3. Cyclic voltammogram of $U(OTf)_3(dme)_3$ in NMP/0.1M $TBA[B(C_6F_5)_4]$ at 0.1 V/s, 1.5 mm glassy carbon disk versus Ag wire reference obtained after scanning to -1.75 V on the previous voltammogram.

The voltammetric behavior of U(IV), either from UCl_4 or anodic electrodissolution of uranium metal, in NMP and DMSO solvents with 0.1M $TBA[B(C_6F_5)_4]$ as supporting electrolyte looks qualitatively similar to the voltammetry of the $U(OTf)_3(dme)_3$ complex in NMP. A related study has been published recently in DMSO solutions with ClO_4 based supporting electrolytes (8). An example of this voltammetric behavior is shown in Figure 4, which contains CV traces of the solvent supporting electrolyte background with an overlay of the response with the analyte UCl_4. The CV scan with the analyte in solution starts at 0V and proceeds first in the negative direction and then back towards positive potentials. The negative scan shows an initial peak, attributed to the U(IV) to U(III) oxidation, that is not well resolved due to the broad wave that appears just after this process. The broad ill-defined electrode process is likely due to the electrodeposition of uranium metal at the working electrode surface. On the return scan in the positive direction the electrodeposited material is stripped from the working electrode surface just negative of 1.0 V vs Ag wire. Subsequent CV traces obtained in this experiment possessed excellent reproducibility at Pt, Au, and glassy carbon working electrodes. In order to identify the presence of uranium metal on the surface of a working electrode we utilized XPS analysis on a piece of Pt metal. A bulk solution of U(IV) ions was prepared through electrodissolution of uranium metal in NMP/0.1M $TBA[B(C_6F_5)_4]$. Voltammetry of this solution showed the characteristic electrodeposition process at negative potentials with the coupled stripping wave on the reverse scan at positive potentials. A Pt flag was used as the working electrode for the bulk deposition of uranium at -2.0 V vs Ag wire for 10 minutes. The working electrode was removed from the solution of U(IV) ions, rinsed with pure NMP solvent, cut to appropriate size, and mounted in the inert atmosphere XPS transfer chamber for subsequent analysis. The results from the XPS analysis are qualitatively similar to the

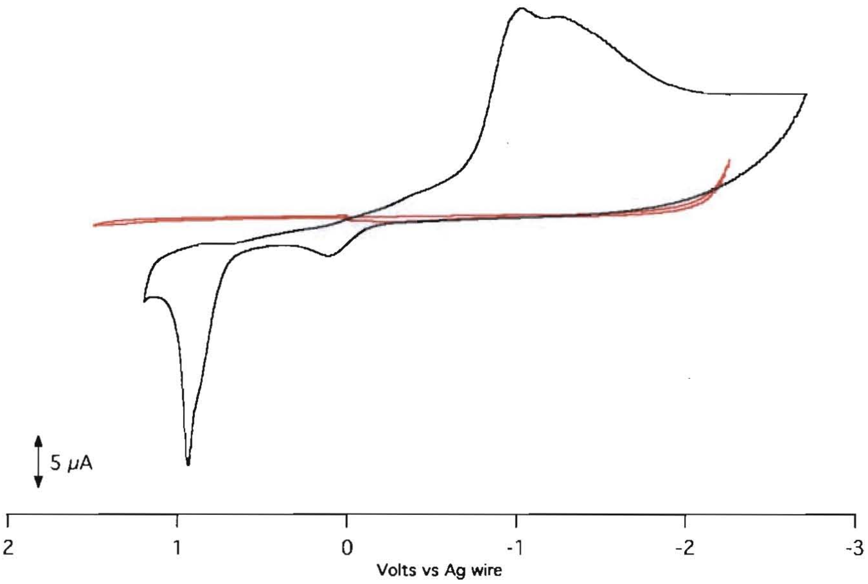

Figure 4. CV traces of NMP/0.1M TBA[B(C_6F_5)$_4$] background (low current trace) and with added UCl_4 (~5 mM) at 0.1 V/s and a 2 mm Pt disc working electrode.

situation that was noted previously for the electro-oxidized piece of uranium metal in an RTIL. The outer surface of the plated Pt electrode shows products from the bulk solution that were not fully washed away including U(IV) ions. Once the surface of the Pt electrode was sputtered with Ar ions the energy of the uranium and fluorine peaks shifted. In the case of the uranium peaks the shift is consistent with the presence of lower-valent ions likely associated with fluorine. So it appears from this analysis that any uranium metal that may have been deposited during the bulk deposition step abstracted fluorine from the anion of the supporting electrolyte, which is similar to what was evidenced with the RTIL studies. This particular supporting electrolyte anion was chosen for its ability to produce highly conductive solutions and its non-coordinating/weakly coordinating properties (3). Although we were hopeful that fluoride abstraction would not occur with this anion at uranium metal surfaces it appears that this was indeed the case. It is clear at this point that an effective bulk electrodeposition process for uranium, and likely the actinides in general, will need to rely on RTILs and/or organic solvent/supporting electrolyte combinations that do not possess accessible fluoride.

Preliminary electrochemical experiments have been performed on the behavior of plutonium metal and plutonium ions in DMSO solutions with TBA[B(C_6F_5)$_4$] as supporting electrolyte. The electrodissolution of Pu metal was performed at a potential of 1.25 V vs Ag wire and proceeded smoothly. The resulting solution of Pu(III) ions displayed a quasi-reversible wave attributed to the P(III)/Pu(IV) couple. When pure $PuCl_3$ was added to the solution the position of the wave did not change. The only change in the voltammogram was an increase in the peak current levels as displayed in Figure 5, where the CV traces were scanned from potentials positive of the Pu(III)/Pu(IV) couple to more negative values. This indicates that once $PuCl_3$ is dissolved in a solution of DMSO/TBA[B(C_6F_5)$_4$] it forms the same species as the electrodissolved Pu ions. Since there are no chloride ligands available with the electrodissolved species it follows that in solution the $PuCl_3$ exists as a [Pu(DMSO)$_x$][anion]$_3$ type species with no inner-sphere

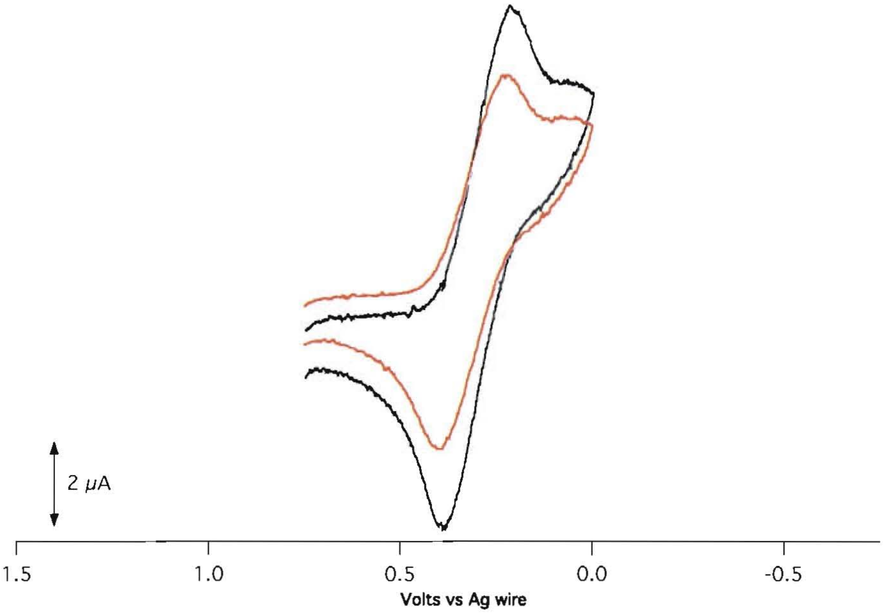

Figure 5. Cyclic voltammograms of "Pu(III)" ions in DMSO/0.1M TBA[$B(C_6F_5)_4$] at 0.1 V/s and a 2 mm Pt disc working electrode before and after addition of $PuCl_3$.

chloride, which is similar to the behavior of UCl_4 noted earlier. We have not yet tried to isolate single crystals of this species for x-ray analysis, but that work is in progress. At potentials negative of the Pu(IV)/Pu(III) couple there is indeed a second reduction process with a relatively large peak current and no coupled return wave. This peak is tentatively assigned as the reduction of Pu(III) ions to Pu metal. At this stage the Pu(III)/Pu(0) process has not been studied in great detail, but Figure 6 is included to display the typical voltammetric response for this process for five consecutive cycles. After the five cycles were obtained a scan to positive potentials revealed a relatively small oxidation wave close to the Pu(IV)/Pu(III) couple that may be the stripping of Pu metal from the working electrode surface. More detailed studies are needed to further characterize this plating/stripping process for Pu in DMSO. However, we have performed a bulk electrodeposition from a solution of electrogenerated Pu(III) ions at a Pt electrode surface to subsequently determine, through Auger analysis, if plutonium is actually being deposited onto the electrode surface. Due to limitations in our laboratory at the time these Pu experiments were conducted the electrode containing the electrodeoposited material had to be exposed to air for introduction into the Auger spectrometer. While this method still enables the identification of plutonium on the surface of the electrode as PuO_2, it inhibits the ability to determine if the plutonium was deposited as metal or as an oxide. The Auger results did indeed confirm the presence of PuO_2, and plans are currently under way to enable the inert atmosphere transfer and analysis of the electrodeposited material for future experiments.

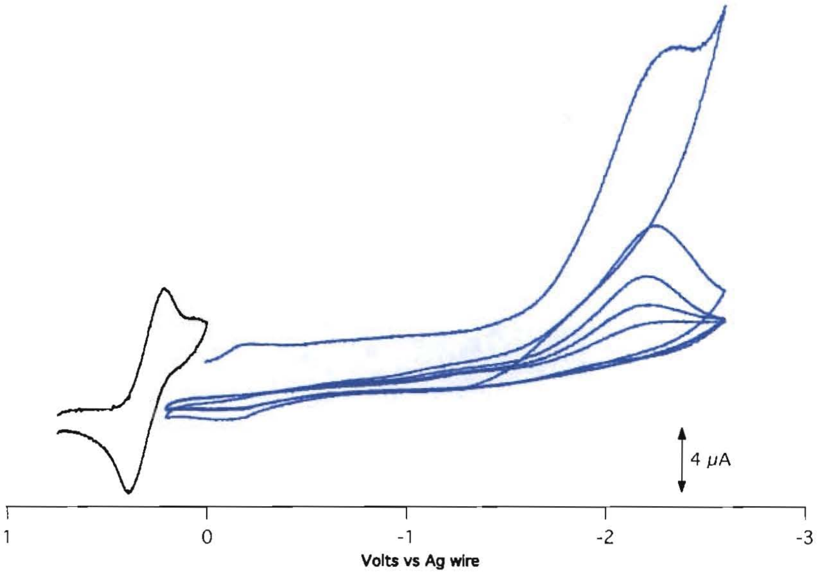

Figure 6. Cyclic voltammograms of "Pu(III)" in DMSO/0.1M TBA[B(C_6F_5)$_4$] at 0.1 V/s and a 2 mm Pt disc working electrode showing the large reduction wave attributed to the electrodeposition of plutonium metal.

Conclusion

The qualitative electrochemical behavior for U(IV) and U(III) ions in [N(SO_2CF_3)$_2$]$^-$ based RTILs and the organic solvents NMP and DMSO with TBA[B(C_6F_5)$_4$] as supporting electrolyte has been described. The results presented here detailing our repeated attempts at the full reduction of uranium ions to uranium metal show that the bulk deposition is inhibited by the reactivity of the initially deposited uranium and the [N(SO_2CF_3)$_2$]$^-$ anion from the RTIL. It appears from our data that the anion reactivity at uranium is due to fluoride abstraction by the uranium metal to form a low-valent uranium fluoride, which in some way stops further electrodeposition. While the voltammetric data in NMP and DMSO with TBA[B(C_6F_5)$_4$] supporting electrolyte show more promising behavior, the lack of electrochemical data supporting long-term bulk electrodeposition coupled with the XPS results indicating reactivity of the supporting electrolyte anion also limits the effectiveness of these solvent/supporting electrolyte combinations. The judicious choice of supporting electrolyte for one of these organic solvents may indeed lead to the desired result of bulk electrodeposition of uranium metal at room temperature. This likely also holds true for future experiments on plutonium, but we have no data at this point to suggest plutonium metal abstracts fluoride from the anions discussed here. Current work in our laboratory is focused on learning more about the details surrounding low-valent Pu electrochemistry in non-aqueous solvents and uncovering alternative ionic liquids and/or organic solvent supporting electrolyte combinations that are effective for bulk uranium (actinide) electrodeposition.

Acknowledgements

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