Electrochemistry of soluble $\text{UO}_2^{2+}$ from the direct dissolution of $\text{UO}_2\text{CO}_3$ in acidic ionic liquid containing water

Wendy J. Pemberton, Janelle E. Droessler, John M. Kinyanjui, Kenneth R. Czerwinski, David W. Hatchett*\(^{1,}\)

**Department Chemistry, University of Nevada Las Vegas, 4505 Maryland Parkway, Box 454009, Las Vegas, NV 89154–4003, USA**

**A R T I C L E   I N F O**

**Article history:**
Received 27 December 2012
Received in revised form 5 January 2013
Accepted 10 January 2013
Available online 29 January 2013

**Keywords:**
Uranyl
Dissolution
 Ionic liquid
Deposition

**A B S T R A C T**

The direct dissolution of $\text{UO}_2\text{CO}_3$ in neat and “wet” ionic liquid (IL) trimethyl-n-butyrammonium bis(trifluoromethanesulfonyl)amide $\lfloor $Me$_3$N$^+$/Bu$^+$$\rfloor$[TFSI]$^{-}$ is examined. The ionic liquid serves as both the solvent for the direct dissolution of $\text{UO}_2\text{CO}_3$(s) and the electrolyte solution for the electrochemical analysis of the soluble uranyl species. The solubility data indicate that displacement of the $\text{CO}_3^{2−}$ occurs slowly due to the low concentration of protons available from residual water in the pristine IL. Enhanced dissolution of $\text{UO}_2\text{CO}_3$ through the formation of carboxylic acid $\text{H}_2\text{CO}_3$ is achieved after the addition of acid, bis(trifluoromethanesulfonyl)amide (HTFSI) and water. The soluble uranyl cation can then coordinate with the TFSI$^−$ anion in place of the displaced $\text{CO}_3^{2−}$ anion following the decomposition of carboxylic acid and the purging of $\text{CO}_2$(g) and water from the IL. The solubility of $\text{UO}_2\text{CO}_3$ was examined using liquid scintillation counting of $^{233}\text{U}$ for the pristine ionic liquid. The “wet” ionic liquid containing HTFSI and soluble $\text{UO}_2\text{CO}_3$ was evaluated using UV/vis spectroscopy before and after dissolution. The electrochemical deposition of uranium species from ionic liquid was evaluated using cyclic voltammetry. The potential mediated deposition of uranium species was achieved and verified using scanning electron microscopy (SEM) and the solid uranium deposits were evaluated using energy dispersive X-ray emission spectroscopy (EDX).

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The solubility, coordination and speciation of f-elements in ionic liquids (IL) has been the focus of numerous studies because purely ionic systems have unique physical properties that can be exploited in comparison to aqueous, organic, or molten salt systems [1]. For example, ILs can be used to evaluate the electrochemical properties of f-elements, while minimizing the impact of side reactions typically encountered in aqueous environments [1]. Moreover, the physical properties of the cation/anion pair of the ionic liquid provide a significantly larger potential window when compared to water, encompassing the thermodynamic potentials required for the reduction of f-elements to metal [2,3]. The choice of the cation is critical because reduction of the species can occur at potentials that preclude the electrochemical reduction of actinides to metal [4,5]. The trimethyl-n-butyrammonium cation provides relatively low viscosity and melting point when combined with the TFSI anion and it is electrochemically stable at negative potentials that encompass the reduction of actinide species [1–4]. Ionic liquids also have negligible vapor pressure and high thermal stability in contrast to common organic solvents. Finally, ionic liquids do not require the elevated temperatures thereby reducing the energy requirements in comparison to the associated molten salt systems [6,7].

The electrochemical study of f-elements in ionic liquid can be complicated by the inherent low solubility of f-elements in purely ionic solvents. Solvent extraction from aqueous solutions [8,9] has been utilized to introduce f-element species into ionic liquids. Extraction is typically achieved by first dissolving the f-elements in aqueous acid solutions followed by two-phase extraction of the soluble species into the IL using complexing agents [10,11]. The extraction can be complicated by the crossover of neutral water and ion species at the phase boundary increasing possible contaminants in the IL [9]. Crossover effects can be minimized provided the aqueous solution composition is precisely controlled. More recently, species such as $\text{Pu(IV)}$, $\text{Th(IV)}$, and trivalent lanthanides have been extracted into IL without the need of additional complexing agent [12,13]. The results suggest that extraction may be an effective way of pre-concentrating some f-elements in IL.

The direct dissolution of actinide and lanthanide species has also been achieved using preformed complexes with ligands common to the ionic liquid. For example, complexes of $[\text{Th(TFSI)}_6\text{(HTFSI)}_2]$2$\text{H}_2\text{O}$ where the TFSI is the bis(trifluoromethanesulfonyl)amide ion (N(SO$_2$CF$_3$)$_2$) [14] and Ln(TFSI)$_3\text{(H}_2\text{O)}_3$ (Ln=$\text{La(III)}, \text{Sm(III)},$ and $\text{Eu(II)}$) [15] have been successfully prepared and dissolved directly into the ionic liquid.
trimethyl-n-butylammonium bis[trifluoromethanesulfonfonyl]imide, [Me₃N⁺Bu⁻][TFSI]. In addition, the dissolution of UO₂(TFSI)₂ and UO₂(TFSI)₂·H₂O has been achieved in a variety of ionic liquid solutions containing the TFSI anion [16,17]. However, synthesis in aqueous solution can be influenced by water coordination minimizing possible interactions with weakly coordinating ligands such as TFSI prior to dissolution in IL [18,19]. For example, the absorbance of UO₂(TFSI)₂·H₂O when dissolved into various ionic liquids is consistent with hydrated uranyl ion [UO₂(H₂O)₆]²⁺ suggesting that the TFSI ion is not the primary coordinated species when the complex is prepared from aqueous solution [16–19]. The question remains if water coordination with uranyl cation is inhibited during the direct dissolution of UO₂CO₃ in ionic liquid containing water when compared to the UO₂(TFSI)₂·H₂O complex produced in aqueous synthesis.

Alternatively, "task specific" ionic liquids that contain acid functionalized cations have been used to dissolve metal species into ionic liquids [20,21]. The betaine cation is the zwitterion 1-carboxy-N,N,N-trimethylmethaneammonium hydroxide where the carboxyl moiety acts as the coordinating group for metal solubilization [20,21]. Similar carboxylic functionalized cations have been produced to dissolve metal oxides where they can be reacted stoichiometrically with the protonated cations [22]. However, the presence of water also plays a role with increased solubility in "wet" ionic liquid which may be due to the ability of the hydrophobic ionic liquid to interact with the metal oxide surface [22]. Using these methods many trivalent lanthanides (e.g. Sm₂O₃, Eu₂O₃, and Nd₂O₃) and UO₂ were dissolved directly into the ionic liquid without addition of secondary acid species. Although the carboxylic functional group plays an important role in the formation of the uranyl complex during the dissolution process the role of water is equally important in providing solvated protons for the reaction [22,23].

The previous studies suggest that the use of acid functionalized groups and water may be beneficial in the dissolution and solubility of lanthanide and actinide species in ionic liquids. However, the direct dissolution of f-element species in the ionic liquids using secondary acid species common to the ionic liquid has not been extensively studied. The dissolution of uranyl carbonate using HTFSI can be explored through the formation of carbonate intermediate and the production of water and CO₂ as byproducts:

\[
\text{UO}_2(\text{CO}_3) + 2\text{HTFSI} \rightleftharpoons \text{UO}_2^{2+} + 2\text{TFSI}^- + \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} \uparrow + \text{CO}_2
\]

Previously, bis[trifluoromethanesulfonfonyl]amide (HTFSI) has been utilized to produce protic ionic liquids with a variety of different cations [24]. The evolution of hydrogen in ionic liquid solutions has been demonstrated suggesting that the protons within the ionic liquid are partially dissociated from HTFSI [24]. In addition, the acidity of ionic liquids containing HTFSI or carboxylic acids was evaluated using various protic indicators [25,26]. Both studies suggest that proton dissociation from the acid is diminished in ionic liquid when compared to aqueous solution environments, reducing the overall acid strength. Therefore the role of water within the ionic liquid may be important in increasing the dissociation of protons from HTFSI which will likely influence the direct dissolution of f-elements in ILs [24–26]. In addition, the role of water has been examined in the formation and reduction of gold oxide in IL solutions containing water without additional acid. The data suggest that the addition of water provides sufficient proton to the IL such that the oxidation/reduction of Au can be resolved electrochemically, Eq. (2) [27].

\[
\text{Au}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Au} + 3\text{H}_2\text{O}
\]

The direct dissolution of UrO₂CO₃ complex into ionic liquid using either carboxyl functionalized cations or through the addition of HTFSI has not been extensively studied. Moreover, interfacing common aqueous species such as UrO₂CO₃ through the direct dissolution into ionic liquid may be useful in evaluating species that normally interact in natural environments. A more detailed understanding of the dissolution of UrO₂CO₃ and the speciation and electrochemical behavior of soluble species in ionic liquid, [Me₃N⁺Bu⁻][TFSI], may also be useful in evaluating the use of ionic liquids for more common uranium fission products. For example, recent studies have evaluated the electrolytic dissolution of simulated fuels in carbonate solutions through the formation of UrO₂CO₃ [28,29]. The uranyl carbonate could be an important component of some reprocessing schemes where UO₂CO₃ is precipitated to achieve separation of the uranyl ion. The subsequent dissolution of UO₂CO₃ into ionic liquid solutions may therefore be relevant in the recovery of the uranyl species. Finally, UO₂⁺ is a common species encountered in typical separation schemes and an understanding of the chemical and electrochemical properties of the species in ionic liquids is important regardless of the initial species used in the dissolution.

The current study evaluates the direct dissolution of UrO₂CO₃ in pristine IL containing residual water and "wet" [Me₃N⁺Bu⁻][TFSI] containing HTFSI with added water at room temperature. The soluble species from the dissolution process are characterized using liquid scintillation counting and UV/vis spectroscopy. The properties of the carbonate ligand are specifically exploited to increase the solubility of the f-element species and provide a pathway for incorporating the actinide species into the ionic liquid. The spectroscopy provide insight into the dissolution mechanism of UrO₂CO₃ and electrochemical measurements are used to probe the oxidation/reduction properties of the soluble UrO₂⁺ species. Electrochemical methods are also utilized in the potential dependent deposition of uranium species from the ionic liquid and SEM/EDX analyses are used to examine and confirm the chemical deposits on the Au electrode surface.

2. Experimental

2.1. Chemicals

All chemicals used in the synthesis of the ionic liquid were reagent grade and used without further purification. Lithium bis[trifluoromethanesulfonfonyl]imide (LiTFSI) salt was purchased from VWR. The bis[trifluoromethanesulfonfonyl]amine (HTFSI), N,N-Dimethyl-n-butylamine (Me₂NBu), and the methyl iodide (Mel) were purchased from Sigma–Aldrich.

2.2. Synthesis of ionic liquid trimethyl-n-butylammonium bis[trifluoromethanesulfonfonyl]imide

The synthesis of the IL was based on a previously published procedure [30]. The IL, [Me₃N⁺Bu⁻][TFSI], was purified by passing the solution through a column of activated alumina. Finally, the IL was placed under a vacuum and gently warmed overnight. The final product [Me₃N⁺Bu⁻][TFSI] was characterized via IR-spectroscopy. The water content in the [Me₃N⁺Bu⁻][TFSI] was determined to be 0.285 ± 0.008% by weight using Karl Fischer titrations.

2.3. Synthesis of uranyl carbonate

The synthesis of the uranyl carbonate was based on literature procedures [31–33]. The synthesis was initiated by combining 240 mg of uranyl nitrate composed of ²³⁸U and 60 mg of ²³⁵U in a reaction vessel containing 50 ml of DI water. The solution was then adjusted from pH 2 to pH 5 via the addition of sodium carbonate. The pH was selected to favor the formation of the mono-carbonate species [31–34]. The resulting solution was subsequently bubbled with CO₂ gas for one week to ensure sufficient time to complete
2.4. Dissolution of uranyl carbonate

The dissolution of UO₂CO₃ without the addition of HTFSI or water was initialized after placing 0.3 g of finely ground uranyl carbonate containing ²³³U along with 39.3 ml of [Me₃N⁺Bu][HTFSI] in a 50 ml centrifuge tube. The water content of the pristine IL was determined using Karl Fischer titration, 0.285% by weight. Constant stirring of the reaction vessel contents was executed using a spin vane with a continuous argon gas purge. The centrifuge tube was disconnected from the gas and centrifuged for 10 min at given time intervals prior to measurement. An aliquot was removed and saved for analysis using both liquid scintillation counting and UV/vis spectroscopy over the course of 80 days.

The direct dissolution was also examined by placing 0.0251 g of UO₂CO₃ in 15 ml of [Me₃N⁺Bu][HTFSI] containing 0.1 M HTFSI, producing 5 mM soluble UO₂²⁺ in IL. The dissolution of UO₂CO₃ sample was completed within a few hours without the addition of water. Finally, a set of 50 mM UO₂CO₃ samples containing 0.2475 g UO₂CO₃ in 15 ml of deionized water or ionic liquid with 0.5 M HTFSI was prepared. The uranyl carbonate dissolved completely in the aqueous solution within 10 min of mixing. In contrast, the dissolution of UO₂CO₃ in the IL did not occur after 24 h. To facilitate the dissolution, 2 ml of 0.5 M HTFSI in H₂O was added to the sample to enhance the deprotonation of the acid in the ionic liquid and increase solubility [22,23]. The sample was sonicated resulting in the complete dissolution of the solid and then centrifuged to assist the separation of the two distinct phases (aqueous and IL). The sample was purged with argon to eliminate the water phase until only the IL was visible. The resulting solution was measured using Karl Fischer titration which provided a measure of the water content after purging the IL, 1.28%. For comparison the IL containing 0.5 HTFSI prior to dissolution was 0.298% by mass. Finally, the water content for the 5 mM soluble UO₂²⁺ in IL solution obtained from the direct dissolution of UO₂CO₃ without the addition of water to facilitate dissolution was 0.524% by mass.

2.5. Karl Fischer titration

Karl Fischer titrations of the ionic liquid were performed using a Mettler Toledo DL-32 titrator to determine the water content. Standards were used to calibrate the instrument using a HYDRANAL water standard 1.0 (H₂O 1.011 ± 0.003 mg/g) prior to analyzing ionic liquid samples in triplicate. The instrument was operated with 100 ml of the HYDRANAL analyte Coulomat A and 5 ml HYDRANAL cationlyte Coulomat CG (Fluka).

2.6. Electrochemical setup

All electrochemical measurements were conducted using a CH Instruments CHI 770 potentiostat. A three electrode setup was utilized in all the measurements. The working electrodes were either a glassy carbon disc (3 mm diameter), an Au disc (1.6 mm diameter), or an Au sheet (1 cm x 1 cm). An Ag/Ag⁺ (0.1 M AgNO₃ in IL) non-aqueous reference electrode was utilized [37]. The reference electrode was standardized with respect to a [Me₃N⁺Bu][HTFSI] solution containing 4 mM ferrocene providing an offset potential of +0.416 V vs. Ag/AgCl. All cyclic voltammograms are referenced versus Ag/AgCl (3 M KCl) based on the Ag/Ag⁺ electrode and the Fc/Fc⁺ redox couple. A platinum sheet counter electrode (1.25 cm x 1.25 cm) was immersed in solution to ensure a surface area of 150% relative to the working electrode area. Cyclic voltammetry was obtained for solutions that were degassed with desiccated Ar prior to measurement.

2.7. Ultra-violet–vis (UV/vis) spectroscopy

UV/vis spectra were collected using a dual beam Cary 6000 UV-Vis-NIR IR spectrophotometer using quartz cuvettes under ambient conditions in the spectral range between 200 and 800 nm. The UV/vis spectra of the pristine ionic liquid solution was obtained after degassing with argon for seven days and was unchanged. The results indicate that the argon does not appreciably influence the UV/vis response of the ionic liquid. All UV/vis spectra were collected versus a suitable blank cell containing either ionic liquid with or without the addition of HTFSI. All solutions containing soluble UO₂CO₃ were purged with Ar to facilitate decomposition of any carbonyl acid and reduction of residual CO₂ and water prior to measurement.

2.8. Liquid scintillation counting (LSC)

Measurements of the ²³³U were obtained by adding 100 µg of IL solution with the ²³³U tracer to 10 mg of scintillation cocktail. Masses were used rather than volume to reduce potential pipeting errors due to the viscosity of ionic liquid. Data was obtained using a Perkin Elmer Precisely Liquid Scintillation Analyzer Tricarb 3100TR instrument. The activity observed from the LSC was converted to total concentration of uranium using the experimental determination of 24% ²³³U enrichment.

2.9. Scanning electron microscopy (SEM) and energy dispersive X-ray emission spectroscopy (EDX)

The SEM images and EDX measurements of the electrochemical deposits were obtained using a JOEL JSM-5610 scanning electron microscope equipped with a secondary electron and backscatter electron detectors. The electrochemical deposits were evaluated without any additional surface pretreatment.

3. Results and discussion

3.1. Dissolution of UO₂CO₃ in [Me₃N⁺Bu][HTFSI] without HTFSI

The possible dissolution mechanism for UO₂CO₃ and the complexation of soluble UO₂²⁺ with TFSI is provided in Scheme 1. The solubility in the IL should be directly influenced by the

\[
\text{UO}_2\text{CO}_3(s) + 2\text{H}^+ \rightarrow \text{UO}_2^{2+} + \text{H}_2\text{CO}_3
\]

\[
\text{H}_2\text{O} + \text{CO}_2 + \text{Ar} \rightarrow \text{CO}_2(g)
\]

Scheme 1. Possible dissolution mechanism for UO₂CO₃ in [Me₃N⁺Bu][HTFSI].
formation and decomposition of carbonic acid in the IL. In addition, TFSI complexation with soluble uranyl ion would be directly linked to dissociative loss of the carbonate species. The mechanism suggests that the availability of protons in solvent systems including IL and water will directly influence the dissolution of $\text{UO}_2\text{CO}_3$ and the ultimate solubility of $\text{UO}_2^{2+}$.

The dissolution of $\text{UO}_2\text{CO}_3$ in the IL, $[\text{Me}_3\text{N}^+\text{Bu}^-][\text{TFSI}]$, without added water or acid was initiated and evaluated daily for one week with no measurable change in the liquid scintillation counting (LSC) baseline. The measurement was the repeated after initiating degassing with dry argon and the liquid scintillation measurements for the dissolution of $\text{UO}_2\text{CO}_3$ in IL as a function of time is provided in Fig. 1. The data indicate that the dissolution of $\text{UO}_2\text{CO}_3$ occurs within two days (2.5 μM) after the Ar degassing is initiated. It is clear from the plot that the dissolution of $\text{UO}_2\text{CO}_3$ in IL is relatively slow with the maximum concentration of $\sim$160 μM soluble $\text{UO}_2^{2+}$ reached after approximately 40 days. The mechanism for dissolution suggests that the purging can be used to facilitate the decomposition of $\text{H}_2\text{CO}_3$ and removal of water and carbon dioxide produced in the process. The dissolution process is likely inhibited by the lack of proton available in the pristine ionic liquid which minimizes the solubility of $\text{UO}_2\text{CO}_3$. The data also suggests that the residual water in the IL (0.285% by weight) may play a role in the dissolution of $\text{UO}_2\text{CO}_3$ providing sufficient proton concentration to initiate the process. Therefore, the proposed mechanism was evaluated for the dissolution of $\text{UO}_2\text{CO}_3$ containing the conjugate acid HTFSI dissolved in the ionic liquid $[\text{Me}_3\text{N}^+\text{Bu}^-][\text{TFSI}]$. The goal was to increase the proton concentration and the ultimate solubility of $\text{UO}_2\text{CO}_3$ without introducing species other than TFSI that may coordinate with the soluble uranyl ion.

For comparison, the dissolution of $\text{UO}_2\text{CO}_3$ (50 mM) in both IL and water containing 0.5 M HTFSI was evaluated using UV/vis spectroscopy (Fig. 2). The background UV/vis spectra of 0.5 M HTFSI in water and IL are also provided for reference to the absorbance bands associated with the dissolution of $\text{UO}_2\text{CO}_3$ in both solvent systems. The UV/vis absorbance associated with HTFSI dissolved in water is characterized by a single band at $\sim$255 nm with relatively low absorbance when compared to the absorbance band centered at 280 nm for the acid species in IL. The wavelengths for the absorbance maximum for each solvent system highlight the difference in dissociation of protons from HTFSI for water and the higher concentration of the TFSI anion in the IL. Moreover strong absorbance is observed for the IL solution containing HTFSI between 200 and 240 nm when compared to the acid dissolved in water. The absorbance spectra for the direct dissolution of the solid $\text{UO}_2\text{CO}_3$ ($\sim$50 mM) in water and the IL are also provided in Fig. 2. The complete dissolution of $\text{UO}_2\text{CO}_3$ in water containing HTFSI was rapid with simple mixing. In contrast, the complete dissolution of the $\text{UO}_2\text{CO}_3$ did not initially occur in theionic liquid containing HTFSI. The addition of 2 ml of water resulted in the complete dissolution of $\text{UO}_2\text{CO}_3$ in the IL containing 0.5 M HTFSI. The addition of water solvates the proton in the IL which facilitated the dissolution of $\text{UO}_2\text{CO}_3$. The method is consistent with the improved dissolution of lanthanide oxides in “wet” IL solutions [22,23].

It is unlikely that there is a change for the soluble species during the dissolution process for either solvent system given the preferential hexavalent oxidation state of uranium [38]. Therefore, it is assumed that the soluble species in solution is the uranyl ion, $\text{UO}_2^{2+}$, in both solutions. Furthermore, the absorbance spectra provided in Fig. 2 for the dissolution of $\text{UO}_2\text{CO}_3$ in water and IL are very similar indicative of similar soluble species. The characteristic absorbance bands between 350 and 450 nm are consistent with f-electron transitions associated with U(VI) complexes including uranyl nitrate, trifluoromethanesulfonate $[\text{SO}_3\text{CF}_3]_2^-$, bis(trifluoromethanesulfonyl)amide [TFSI, $\text{N(SO}_3\text{CF}_3)_2^-$] and chloride in both solvents [16–19,39,40]. In addition, there is a dramatic change in the absorbance at higher energy (lower wavelength) with high absorbance intensities relative to the baseline of HTFSI in either water or IL. Similar absorbance at lower wavelength for lanthanide species has been previously attributed to ligand to metal charge transfer complexes which have been observed for weakly coordinating ligands, including TFSI which act as sensitizing agents for high energy electronic transitions [41]. The combination of absorbance bands at low energy associated with water solvated $\text{UO}_2^{2+}$ and higher energy bands indicative of TFSI suggests that the anion interacts with the soluble uranium species in the presence of water for both solvent systems.

Although the absorbance for both samples is sufficiently high that no quantitative information can be derived, the data indicates that dissolution of $\text{UO}_2\text{CO}_3$ in IL and water results in the formation of $\text{UO}_2(\text{TFSI})_2$ complexes and cannot be simply attributed to free TFSI ligand. Direct comparison of the data provided in Fig. 2 with other uranyl complexes dissolved in IL is complicated because the spectral region between 200 and 350 nm is not typically examined or shown [16–19,34,35]. However, a large absorbance shoulder at lower wavelengths is often observed in the spectra suggesting that
the UO$_2^{4+}$ may have higher energy electronic transitions in IL environments. For example, previous work for the direct dissolution of [8mim]$_2$UO$_3$Br$_4$ into IL shows an intense absorbance band at lower wavelengths consistent with the absorbance shown in Fig. 2 [42]. The high absorbance observed for the dissolution of UO$_2$CO$_3$ in both solvent systems may be indicative of coordination of the soluble UO$_2^{4+}$ species with TFSI$^-$ in both water and IL.

3.2. Electrochemistry of UO$_2$CO$_3$ in IL [Me$_3$N][TFSI]

The voltammetric response of an Au electrode in IL containing 50 mM soluble UO$_2$CO$_3$ is provided as a function of increasing potential window in Fig. 3. The background cyclic voltammetry for an Au electrode in [Me$_3$N][TFSI] containing 0.5 M HTFSI (dashed line) is also provided for reference in Fig. 3c. The assignment of the voltammetric waves and corresponding reactions are provided in Table 1. The voltammetric waves observed for the IL containing 0.5 M HTFSI in IL are based on previous voltammetric studies for Au electrodes in ionic liquid containing HTFSI [43]. For example, the voltammetric wave labeled II has been attributed to the reductive adsorption of H$^+$ which is followed by the subsequent reduction and reaction of H$^+$ with the surface adsorbed species to produce H$_2$ gas at the Au electrode [44]. In addition, the voltammetric waves labeled VI and VII were previously assigned to the oxidation of the gold electrode and reduction of the oxide, respectively, based on Eq. (2) [27]. The voltammetric responses provided in Fig. 3 indicate that there is a sufficient amount of water and dissociated proton such that the oxidation/reduction of Au can be resolved in the IL solution.

Finally, wave IV has been previously attributed to the reduction of water in IL solution which produced OH$^-$ and H$_2$ [44]. The potential window utilized in Fig. 3a encompasses the oxidation/reduction of the Au surface and the reduction of soluble UO$_2^{4+}$ to the pentavalent UO$_2^{5+}$ species, wave I. The reverse process for the oxidation of the pentavalent UO$_2^{5+}$ species is initially absent in the cyclic voltammetry suggesting that the reduction of UO$_2^{4+}$ is irreversible. However, an oxidative processes, wave I′, is resolved after extending the negative potential limit which can be attributed to the oxidation of UO$_2^{4+}$ to UO$_2^{5+}$. In addition, when the potential is expanded to more negative potential an additional reduction waves emerges, wave III, which is assigned to the initial deposition of UO$_2$ (ads) through a two electron reduction process. It is likely that the reduction of wave I′ is tied to the surface oxidation of UO$_2$ (ads) deposited on the Au surface, followed by the oxidation of pentavalent uranium species back to the hexavalent state. Previous studies support the two electron reduction of UO$_2^{4+}$ and formation of either solvated U(IV) in IL or surface deposited UO$_2$ (ads) on the electrode surface [45,46]. However, the lack of additional oxidative processes on the reverse scan suggests that the reductive deposition of the majority of the uranium species at the gold electrode is largely irreversible.

The sequential cyclic voltammetry associated with the reductive deposition of UO$_2$ (ads) is provided in Fig. 4 encompassing the potential window for the reduction process associated with wave III. The voltammetric response associated with wave III decreases with increasing voltammetric cycles. In addition, the voltammetry associated with the reduction/oxidation of UO$_2^{5+}$ decreases in intensity (wave I′/wave I′′), while the peak splitting increases. The data suggests that the surface deposition of uranium species at the gold electrode occurs as the negative potential is extended past −1 V vs. Ag/AgCl. Furthermore, surface modification of the gold electrode with uranium species changes the electrode properties relative to the bulk gold electrode which reduces the current with each sequential scan. However, the oxidation/reduction of the gold surface is still visible suggesting the UO$_2$ (ads) deposits do not completely cover the electrode surface.

Similarly, when the reduction potential is extended to more negative potentials, −2 V vs. Ag/AgCl, the voltammetric response decreases dramatically with each sequential scan (Fig. 5). The formation and reduction of gold oxide is lost after four voltammetric

![Fig. 3. Cyclic voltammetry of an Au electrode in soluble UO$_2$CO$_3$ (50 mM) in IL [Me$_3$N][TFSI] containing 0.5 M HTFSI in the potential range between (a) 2.4 to −0.2 V, (b) 2.4 to −1.1 V and (c) 2.4 to −2.1 V. Cyclic voltammetry of an Au electrode in IL [Me$_3$N][TFSI] containing 0.5 M HTFSI in the potential range between 2.4 and −2.1 V is provided for comparison (dashed line). Electode area = 7.07 × 10^−2 cm$^2$, scan rate = 50 mV/s.](image1)

![Fig. 4. Sequential cyclic voltammetry of an Au electrode in soluble UO$_2$CO$_3$ (50 mM) in IL [Me$_3$N][TFSI] containing 0.5 M HTFSI in the potential range between 2.4 and −1.1 V for the first −10 cycles. Cyclic voltammetry of an Au electrode in IL [Me$_3$N][TFSI] containing 0.5 M HTFSI in the potential range between 2.4 and −2.1 V is provided for comparison (dashed line). Electrode area = 7.07 × 10^−2 cm$^2$, scan rate = 50 mV/s.](image2)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Proposed reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I/I′</td>
<td>UO$_2^{2+}$ + e$^-$ → UO$_2^{+}$</td>
</tr>
<tr>
<td>II</td>
<td>H$_2$O + e$^-$ → H$<em>2$ + OH$^-$ and, H$</em>{ads}$ + H$_2$ + e$^-$ → H$_2$ [44]</td>
</tr>
<tr>
<td>III</td>
<td>UO$_2^{3+}$ + 2e$^-$ → UO$_2$ (ads)</td>
</tr>
<tr>
<td>IV</td>
<td>H$_2$O + e$^-$ → (1/2)H$_2$ + OH$^-$ [44]</td>
</tr>
<tr>
<td>V</td>
<td>UO$_2^{2+}$ + 2e$^-$ → UO$_2$ (ads) bulk</td>
</tr>
<tr>
<td>VI/VI′</td>
<td>AuO$_2$ + 6H$^+$ + 6e$^-$ → 2Au + 3H$_2$O [27]</td>
</tr>
</tbody>
</table>

Table 1

Summary of the proposed reactions and peak assignments for an Au electrode in IL containing soluble UO$_2^{4+}$ with HTFSI.
cycles (Inset) indicating that the gold surface is modified with UO$_2$ surface deposits. The voltammetric waves I and I' are also not resolved in any of the voltammetric cycles after the negative potential is extended. The voltammetric waves associated with proton adsorption and hydrogen evolution at the gold electrode are also completely absent after four voltammetric cycles, wave II. Finally, waves III and V diminish rapidly with each successive cycle. The loss of surface activity and diminished voltammetry with respect to soluble UO$_2$$^{2+}$ suggests that the electrodes surface has been sufficiently modified that the bulk properties are more consistent with deposited uranium species rather than gold electrode. The voltammetry of IL solutions containing 5 mM soluble UO$_2$$^{2+}$ in IL containing 0.1 M HTFSI from the direct dissolution of UO$_2$CO$_3$ was also examined (Fig. 6). The voltammetric response for the ionic liquid containing soluble UO$_2$CO$_3$ (5 mM) in IL is similar in the potential range between 0 V and −2 V which was utilized in Figs. 4 and 5. However, the voltammetric range encompassing the oxidation/reduction of the soluble UO$_2$$^{2+}$ in IL is significantly different at lower concentration. The oxidation/reduction of the gold electrode can be observed at +1.4 V and +2.0 V for waves VI/VI', respectively. In addition, the reduction of the gold oxide at the working electrode is followed by a reduction of UO$_2$$^{2+}$ from the hexavalent state to the pentavalent species (0.4 V vs. Ag/AgCl). The reduction of UO$_2$$^{2+}$ was previously observed in Fig. 3a and assigned as wave I. In contrast, the oxidation of U(V) to U(VI) is resolved in the reverse scan, wave I’, without extending the reduction potential window. The results suggest that the disproportionation of pentavalent uranium species to U(VI) and U(IV) occurs as uranium concentration increases and the stability of the pentavalent uranium species is higher in the IL solution at lower concentration. In addition, the IL solution with 50 mM UO$_2$$^{2+}$ contains a higher concentration of proton and water which may influence the stability of the pentavalent species. These observations are consistent with experimental studies and modeling of U(V) stability which indicate that both the U(VI) concentration and proton availability largely dictate disproportionation [47,48].

The voltammetry in Figs. 3a and 6 is consistent with previous studies that show the reduction of UO$_2$$^{2+}$ produces a stable pentavalent uranium species in 1-butyl-3-methyl-imidazolium ionic liquid solutions [49,50]. The electrochemical response of uranyl chloride in 1-butyl-3-methylimidazolium nonafluorobutane-sulfonate (bmimNO) also shows similar behavior at negative potentials consistent with sequential reduction of the uranyl ion [51]. The reduction has been previously assigned to the multi-step reduction of UO$_2$$^{2+}$ through a stable pentavalent intermediate to U(IV). Finally, the scan rate dependence was examined to ensure the oxidation/reduction processes for wave I and I' are consistent with solution rather than surface processes. The linear dependences for the plots of peak currents for waves I and I' versus the square root of the scan rate ($v^{1/2}$) are indicative of diffusion limited solution processes rather than surface adsorption of uranium species (Inset).

### 3.3. SEM and EDX analyses of U deposits

Although the voltammetry presented suggests that the deposition of uranium species at gold electrodes occurs, it does not provide any direct evidence. SEM was conducted to confirm that the surface deposition of uranium species was achieved. The potentials utilized for deposition were at sufficiently negative potentials, −2 V, to ensure that any deposits remain on the gold electrode surface. The clean Au electrode surface is provided in Fig. 7a with the scale bar provided in the top left corner (100 µm) for comparison to Au surfaces with uranium deposits. The SEM image of uranium deposits at the same magnification (100×) and applied surface potential of 20 kV are provided in Fig. 7b. The gold surface and uranium deposits are labeled for clarity. In addition, the SEM of uranium deposits at higher magnification (500×) is provided in Fig. 7c. The uranium surface deposits are visible on the Au surface in Fig. 7b and c. EDX analysis of the surface deposits is provided in Fig. 8 for the Au surface prior to deposition (dashed line) and after deposition of uranium species on the electrode surface (solid line). The EDX spectra for the uranium deposits show characteristic bands associated with the deposition of uranium species which are
The 500 species, initiated in UO2CO3(s) uranium deposits, occurs. The direct dissolution and solubility of UO2CO3(s) was increased from 5 mM to 50 mM with the addition of HTFSI and water indicating that the solubility is enhanced through the increased dissociation of the acid allowing for proton facilitated displacement of CO32−. The UV/vis data suggest that UO22+ is the soluble species and in the IL solution as well as in water. In addition, the soluble UO22+ was evaluated electrochemically and the reduction of U(VI) to form the stable intermediate U(V) was resolved. Additional reduction processes were elucidated and attributed to the two electron reduction of UO22+ to UO2 and the subsequent deposition of uranium species at the electrode surface. The surface deposits were identified using SEM and EDX analyses which indicates that the deposits are consistent the deposition of uranium oxide at the gold surface. Finally, the methods detailed in the manuscript provide a pathway for increasing the solubility of actinide or lanthanide carbonates in ILs so that the electrochemical properties and the potential dependent deposition of F-element species at an electrode surface can be evaluated.

**Acknowledgements**

The authors wish to thank Nick Smith for his assistance with obtaining the UV/vis spectra. In addition, we would like to thank Dr. Anthony Hechanova and the UNLV Transmutation Research Program, as well as our funding source, GNEP TRP Task 59028G. The authors are indebted to Thomas O’Dou and Trevor Low for their invaluable assistance with laboratory safety and management.

**References**


La[N(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}]\textsubscript{3}][H\textsubscript{2}O]_\textsubscript{5}, and an investigation of La, Sm, and Eu electrochemistry in a room-temperature ionic liquid, [Me\textsubscript{2}N\textsubscript{2}Bu][N(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}], Inorganic Chemistry 44 (2005) 4934.


[18] I. Billard, C. Gaillard, C. Hennig. Dissolution of UO\textsubscript{2}\textsuperscript{2+} and U\textsuperscript{4+} in some lanthanide oxides in Binnemans, effect of acid and water and formation of UO\textsubscript{2}N\textsubscript{2}O\textsubscript{5}\textsuperscript{\textsuperscript{\textsuperscript{3}}}+, Dalton Transactions 37 (2007) 4214.


[30] A.J. Bhatt, I. May, V.A. Volkovich, D. Collison, M. Helliewell, I.B. Polovov, R.G. Lewin, Structural characterization of a lanthanum bis(triflimide) complex, La[N(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}]\textsubscript{3}[H\textsubscript{2}O]\textsubscript{5}, and an investigation of La, Sm and Eu electrochemistry in a room-temperature ionic liquid [Me\textsubscript{2}N\textsubscript{2}Bu][N(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}], Inorganic Chemistry 44 (2005) 4934.


