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f-Element Electrochemistry in Room Temperature Ionic Liquids

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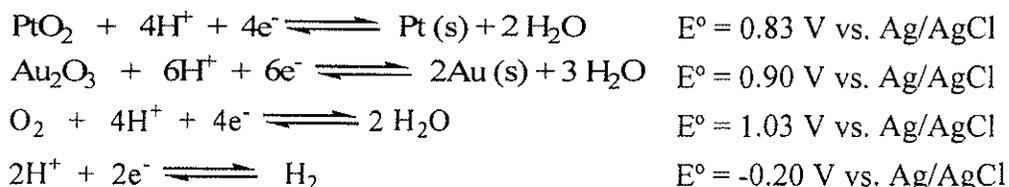
Project Objectives:

This proposal focuses on f-element electrochemistry in room temperature ionic liquids (RTILs). The ultimate goal is to fully characterize the oxidation/reduction of f-elements in RTILs to establish the baseline thermodynamic and kinetic data for these systems. The data will be used to critically evaluate the ability to use electrochemical methods for controlled, potential mediated, separation of f-elements by electroplating on electrodes surfaces. Factors that will influence the ability to measure the redox processes in f-elements in RTIL solutions and electroplating on electrode surfaces include the structure, solubility, and stability of the target species in these solutions. These factors will be addressed using a multidisciplinary research approach with techniques including UV/Vis, and FTIR spectroscopy which will provide structural and stability information. These studies will provide a comprehensive study of the use of RTIL systems in the electrochemical analysis and potential dependent separation of f-elements by electroplating.

This research will address the need to demonstrate, by 2015, progress in understanding, modeling and controlling chemical reactivity and energy transfer processes in solutions at electrochemical interfaces using non-aqueous solutions comprised entirely of organic cations and inorganic/organic anions. Electrochemical studies will examine the interfacial electron transfer processes of f-elements and the potential dependent deposition of f-elements at electrode surfaces. These studies will probe the ability to use RTIL systems in the controlled, potential dependent, separation of f-elements species from complex mixtures.

Narrative:

Exploiting electrochemical differences in the f elements is a promising route to achieving selective, reversible, and tunable separations. However the capacity to examine or let alone systematically quantify and characterize the oxidation and reduction properties of f elements in aqueous solutions is limited. A significant hindrance to the electrochemical analysis of lanthanide and actinide species in aqueous environments remains the potential window afforded in aqueous environments at common working

electrodes including Pt, Au, and glassy carbon (GC) and metal ion hydrolysis in aqueous solutions. For the metal electrode the potential window is constrained and often convoluted by the formation of metal oxides, water oxidation, and hydrogen evolution. The potential window can range from as little as 1.3 V to 2.5 V depending on the electrode composition and the boundary provided by side reactions at positive (water oxidation, metal oxide formation) and negative potentials (hydrogen evolution) as defined by the following reactions [1,2]:

$$PtO_2 + 4H^+ + 4e^- \rightleftharpoons Pt\,(s) + 2\,H_2O \qquad E° = 0.83 \text{ V vs. Ag/AgCl}$$

$$Au_2O_3 + 6H^+ + 6e^- \rightleftharpoons 2Au\,(s) + 3\,H_2O \qquad E° = 0.90 \text{ V vs. Ag/AgCl}$$

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2\,H_2O \qquad E° = 1.03 \text{ V vs. Ag/AgCl}$$

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad E° = -0.20 \text{ V vs. Ag/AgCl}$$

The potential window that is available for the electrochemistry of f-elements, based on the reactions, is between -0.2 and 1.03 V. However this potential range can be expanded under non-standard state conditions based on changing the electrode material and solution conditions employed. Regardless of the ability to expand the potential window, the systematic study of f-element electrochemistry is prohibitive in aqueous solutions.
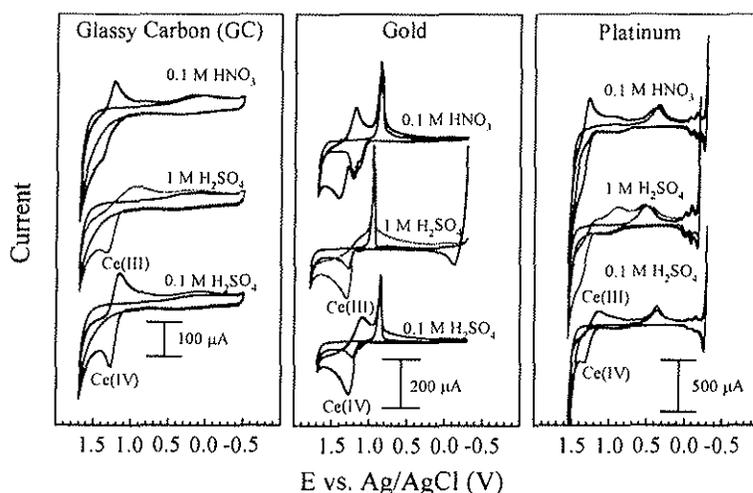
The electrochemistry of Ce(III)/Ce(IV) redox couple illustrates the difficulty of examining f-elements in aqueous solution. The Ce couple is one of the most studied f-element systems in aqueous environments, with literature available as early as the turn of the century. The system has been used as a model for rare earth elements in its group based on the ability to exist as a tetravalent and trivalent form. The Ce(IV) cation is chemically stable, remaining in aqueous solution for several weeks before converting to Ce(III). Ce(IV) is also interesting, electrochemically, because of its very positive reduction potential (1.75 V vs. Ag/AgCl). The oxidation of water is a significant interference to electrochemical investigations of Ce(III) oxidation in aqueous solution. A great deal of experimental effort has been devoted to elucidating cerium's redox chemistry and its resolution from side reactions in acidic solutions. This has mainly involved the manipulation of 1) the material, structure, and reactivity of the working electrode and 2) the solution characteristics, complex formation and stabilization of the Ce species in the aqueous environment.

In early literature accounts, only Ce(IV) reduction was examined at conventional electrodes such as platinum due to the difficulties associated with resolution of the oxidation of Ce(III) [3,4]. Ce(III) oxidation remained elusive even with the use of the dropping mercury electrode [5, 6]. Desideri et al. examined the reduction of Ce(IV) in H_2SO_4 solutions using polarography at a bubbling platinum electrode [7]. It was found that lower acid concentrations moved the reduction to less positive potentials. However, this desirable effect was counteracted by extensive hydrolysis of cerium species in solution. Reversibility of the Ce(IV)/Ce(III) redox couple was only attainable at H_2SO_4 concentrations greater than 7 M.

Pt oxide formation on the electrode also influences the reduction of tetravalent cerium [8]. The effect is variable, since the formation of Pt oxide duration of the experiment never truly reached a steady state. This finding was in contradiction to earlier work by Galus and Adams who found no experimental evidence of a Pt oxide influence

on the redox properties of Ce [9]. There have been attempts to produce standardized Pt oxide films to minimize any possible influence on the voltammetry [10]. Investigation of oxygen adsorption at gold electrodes showed that the oxide formation occurred independently of the cerium concentration in solution [11]. However, contrary to the behavior of platinum oxide, the gold oxide layer was found to behave as a good electronic conductor, and no influence on Ce(IV) reduction was observed. Conflicting results have also been presented in the literature on Au electrodes by Kiekens et al. Specifically, the Ce(III)/Ce(IV) redox peaks were non-Nernstian at Au oxide electrodes ($\Delta Ep > 59$ mV, $Ip_a/Ip_c \neq 1$) [12].

It is obvious from current and past literature that significant ambiguity exists in regarding the composition of the "optimum working electrode" and "optimum solution conditions" for the Ce(IV)/Ce(III) redox system. In addition, the lack of electrochemical analysis of other systems in aqueous environments suggests that the Ce redox couple is actually unique among f-elements. To understand the limitation of aqueous systems we have examined the Ce(III)/Ce(IV) redox couple in aqueous solutions at Au, Pt, and GC electrodes. The goal of the work was to elucidate optimum conditions for this redox couple, as defined by minimal kinetic limitations (high redox peak currents), reversibility (Nernstian response), and resolution (sufficient separation from the background currents caused by the oxidation of water, hydrogen evolution, and oxide formation).
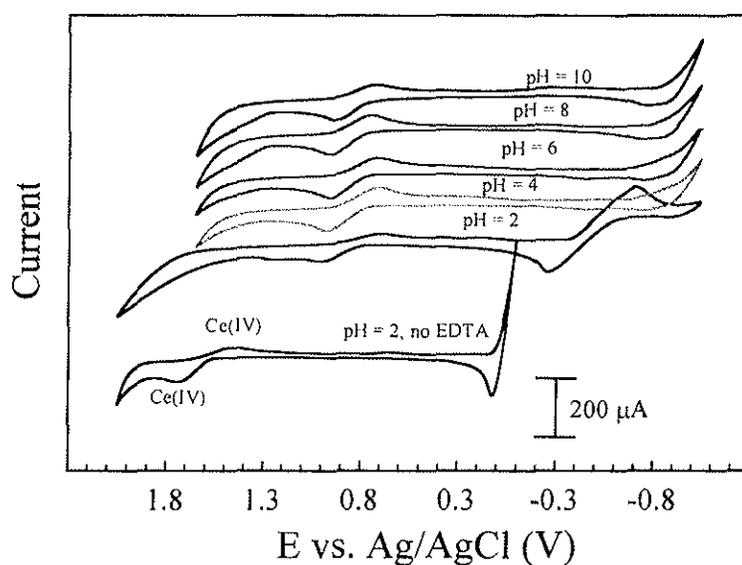

Figure 1. Electrochemistry of the Ce(III)/Ce(IV) redox couple at a GC, Au, and Pt electrodes in aqueous solutions of H_2SO_4 and HNO_3 [Ce(III)] = 6 mM, v = 100 mV/s. Background cyclic voltammetry is included for clarity to distinguish redox processes from side reactions of solvent or the electrode.

Analysis of the cyclic voltammetry in Figure 1 for the graphite electrode indicates that the response is quasi-reversible with $\Delta E_p > 59$ mV and $Ip_a/Ip_c \approx 1.30$, in 0.1 M H_2SO_4 [13]. The GC electrode showed the most resolved voltammetric response in comparison to both Au and Pt electrodes due to the oxide formation and dissolution reactions at the metal electrodes in all solutions studied. The oxidation/reduction of Ce becomes more irreversible ($\Delta Ep >> 59$ mV and $Ip_a/Ip_c \neq 1$) as the acid concentration increases for all electrodes studied indicating the electron transfer process is kinetically limited. The decrease in redox peak magnitude may be enhanced by increased complex formation of cerium cation with hydrosulfate and sulfate anion at elevated concentrations. The response in 0.1 M HNO_3 is less resolved when compared to 0.1 M H_2SO_4 indicative of a lower degree of complex formation between Ce and NO_3^- relative to HSO_4^- or SO_4^{2-}. The data demonstrate the importance of electrode composition, electrolyte composition,

and concentration of acid on Ce electrochemistry. The solution requirements impose very narrow constraints for the elucidation of the Ce redox couple and preclude the study of other species entirely. We have been unable to observe either Sm(II)/Sm(III) or Eu(II)/Eu(III) redox couple electrochemistry within the potential window provided by a variety of aqueous environments.

The stability of Ce and ligand species from H_2SO_4 suggests that complex formation can be effective in the solution stabilization of the redox couple. Therefore, complexation may be effective in shifting thermodynamic potentials into regions that allow the electrochemistry to be resolved. The influence of metal/ligand complex formation and stabilization and elucidation of Ce redox processes in aqueous solutions using EDTA is examined in Figure 2. The goal was to shift the redox potential for the Ce couple to potential regions devoid of side reactions in aqueous solutions.


Figure 2. Electrochemistry of the Ce(III)/Ce(IV) redox couple at a Platinum electrode uncomplexed and complexed with EDTA as a function of pH. [EDTA] = 12 mM [Ce(III)] = 6 mM, v = 100 mV/s. Free [Ce(III)] = 6 mM is shown on the bottom of the figure for comparison.

The data show that the Ce redox couple can be elucidated in solutions that would normally result in precipitation of the species as cerium hydroxide if uncomplexed with EDTA. For reference Ce(III) would precipitate as $Ce(OH)_3$ at pH values greater than 7.7. However, we find the redox couple is stable at pH values ranging from 2 to 10. The chelation of Ce results in the shift in the thermodynamic potential for the redox couple on the order of 0.8 V relative to free Ce. In the same manner we were able to elucidate the electrochemical response of Sm(II)/Sm(III) and Eu(II)/Eu(III) EDTA complexes in aqueous solution (not shown). The conclusions that can be drawn from Figures 1 and 2 are straightforward. The electrode composition is an important factor in the resolution of the electrochemical response in aqueous solutions. GC electrodes are not kinetically hindered in comparison to Au and Pt electrodes because they do not form oxide layers in aqueous solution. Water determines the ultimate potential window available based on water oxidation and hydrogen evolution reactions at positive and negative potentials, respectively. Finally, complex formation and stabilization of chemical species is one method for shifting species to more accessible potential ranges in aqueous solutions. In summary, aqueous systems do not allow the systematic analysis of f-element electrochemistry due to thermodynamic and kinetic limitations of the target species in the

aqueous environment. Therefore, an alternative solvent system must be utilized which minimizes the limitations of aqueous systems.

Room temperature ionic liquids (RTILs) are a class of ionic solutions that provide an unique solution environment for the electrochemistry of f-elements. RTILs show significant promise due to the elimination of side-reactions at the metal electrodes from oxide formation/dissolution and reaction with water and acid. The systems are designed to provide similar characteristics as molten salts without requiring the same harsh temperature regimes. Common cations used to prepare RTIL solutions include imidazoles, pyridinium, ammonium, phosphonium, and sulfonium ions paired with a variety of anions including halides, BF_4^-, $CF_3CF_2CF_2CO_2^-$, $N(CN)_2^-$, to name a few. RTIL solutions can be moisture sensitive, limiting their use in air as is the case for most RTIL solutions containing chloroaluminate ($AuCl_3$ reacted with an acid chloride salt). For our purpose we will focus on systems that are stable in air to avoid the need to use an inert atmosphere in electrochemical experiments. The following schematic illustrates the wide range of RTIL solutions available from a disubstituted pyrrolidinium cation that can form an ionic complex with some typical anions.

Cation
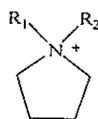
R$_1$ = Methyl, Ethyl, Butyl, Propyl, iso Propyl
R$_2$ = Methyl, Ethyl, Butyl, Propyl, iso Propyl

Scheme 1. The number of theoretically possible combinations between a cation species (15 possible disubstituted pyrrolidinium cations) with eleven possible anions.

Anions

F^-, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, AsF_6^-, $N(CN)_2^-$, $CF_3SO_3^-$, $C_4F_9SO_3^-$, $N(CFSO_2)_2^-$ etc...

165 possible combinations of Cation/Anion RTIL solutions.

The schematic shows that RTILs can be systematically varied by changing the organic cation and anion pairs. Thus combinatorial approaches with anions can be used to identify RTIL systems with variable solubility and affinity for chemical species. The number of possible RTIL solutions is large when all the possible cation/anion pairs are considered. This approach is not possible in aqueous solutions where the properties of the solvent, water, are static. In addition, the potential windows of RTILs are not constrained by the same limitations as aqueous solutions.

The electrochemical window for RTIL system is based primarily on the reduction of the cation and oxidation of the anion used to make the solution. The potentials for cation reduction and anion oxidation in RTIL solutions typically occur at more positive and negative potentials than water oxidation and hydrogen reduction, respectively. Therefore, the potential window is significantly larger for RTILs ranging from approximately 4.5 to 6 V [14,15]. Figure 3 illustrates the potential windows obtained in aqueous solutions of 0.1 M H_2SO_4 (blue line) and the RTIL, tri-n-butylmethylammonium bis(trifluoromethylsulfonyl)imide ([MeBu$_3$N][NTf$_2$], red line) at GC, Au, and Pt electrodes. For each electrode the positive and negative potential limits provide an absolute potential window of approximately 4.5 V for Pt, 5.0 V for Au, and 6.0 V for GC.
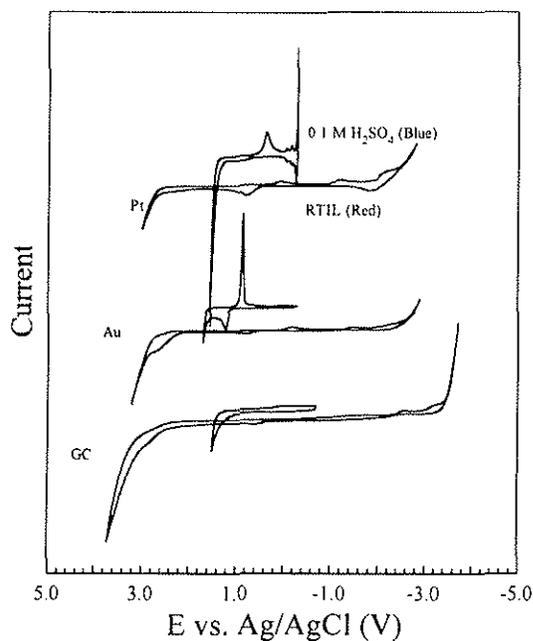
Figure 3. Electrochemistry of GC, Au, and Pt electrodes in RTIL ([MeBu₃N][NTf₂]), (Red) and 0.1 M H₂SO₄, (Blue).

The advantage to eliminating aqueous side reactions and expanding the potential window is that previously inaccessible electrochemical reactions may be resolved. For example the potential controlled deposition of Ti has been achieved in RTIL. Electrodeposition of Ti from aqueous environments has been achieved through intermediate Titanate/Benzoquinone hybrid films that can then be heated to 450°C to form TiO_2 thin films. However, direct deposition has not been achieved due to the low stability of Ti^{2+} and Ti^{4+} species in aqueous environments [16]. In contrast, the direct deposition of $TiCl_2$ and $TiCl_4$ has been achieved at Au and graphite electrodes in RTIL [17,18]. The stability of Ti^{2+} and Ti^{4+} in the RTIL is enhanced relative to the ion in aqueous environments [19]. The reduction of Ti in RTILs implies that similar approaches can be used in the reduction and deposition with f elements. The potential dependence of the process is a factor which can be exploited to achieve the selective reduction of a single metallic species providing enhanced separation capabilities. The stability of the species in the RTIL is the key.

A survey of the literature regarding the electrochemical analysis of f-elements in RTIL solutions provides an understanding of the benefits of the systems and possible applications. For example the electrochemical analysis of f-elements has been achieved in RTIL solutions including the species Pu(IV), Np(IV), U(IV), U(VI), Th(IV), Eu(III), La(III), and Sm(III) [20, 21, 22, 23, 24]. These studies are not comprehensive in nature and examine only a small percentage of RTIL systems available for the electrochemical study of f-elements. However, they do provide the proof of principal for further studies in RTIL solutions. In fact, these studies have confirmed that it is possible to electrochemically deposit Eu(0) and Th(0) from RTIL solutions. For example, Eu(0) was electrochemically deposited from solutions containing Eu-[NTf₂]₃ (NTf₂ = [N(SO₂CF₃)₂]⁻) using the RTIL tert-methylphosphonium bistriflimide, [Me₄P][NTf₂] at elevated temperature (160 °C) [25]. The following complex, [Th(NTf₂)₄(HNTf₂)]·2H₂O has been used to electrochemically deposit as Th(0). Reaction of the Th(0) deposit with residual water from the complex resulted in the formation of ThO_2 (s) at the electrode surface

from the RTIL solution, [Me$_3$BuN][NTf$_2$] [23]. Finally, there is evidence that La(III) and Sm(III) can be reduced electrochemically to their metallic state in RTIL solutions of [Me$_3$BuN][NTf$_2$] at Pt electrodes. In theses studies the La and Sm were complexed with NTf$_2^-$ prior to dissolution in the RTIL. These studies demonstrate that RTIL solutions can be used to effectively probe the oxidation/reduction of f-element complexes. In addition the potential mediated deposition of f-elements is possible indicating the controlled separation of chemical species is thermodynamically feasible. For example, the reduction of Pu^{3+}, Am^{2+}, Am^{3+}, Cm^{3+}, and U^{3+} all occur before E = -1.90 V vs. Ag/AgCl, well within the negative potential limit for the RTIL at platinum (-2.6 V vs. Ag/AgCl), gold (-2.2 V vs. Ag/AgCl), and glassy carbon electrode (-3.4 V vs. Ag/AgCl) in the RTIL solutions shown Figure 3. Complex formation can also be used to shift the oxidation/reduction potentials to more favorable regimes allowing more controlled, tunable electrodeposition of species.

In some cases electrochemical measurements have been coupled with spectroscopic measurements to provide information concerning the electronic structure of the material as a function of oxidation state of the species and composition of the RTIL solutions [21, 23, 24]. Critical assessment of the stability of chemical species as a function of solution parameters has been examined for Np and Pu complexes in RTIL solutions spiked with water. The RTIL solution was shown to provide a stable environment regardless of water contamination with no decomposition of the Np(IV) or Pu(IV) complex in [BuMeIm][NTf$_2$] [20]. Similar results were observed for U(IV) and U(VI) chloride complexes in [BuMeIm][NTf$_2$] and [MeBu$_3$N][NTf$_2$] RTIL solutions. The results show that each species was stable in the RTIL with comparable structure when compared to the solid state species [21, 22]. These results suggest that the RTIL solutions can provide enhanced solubility relative to aqueous environments without large changes in energy and structure of the f-element.

The stability of f-element complexes in RTIL solutions can also be exploited in multi-phase extraction, enhancing partitioning of select chemical species from the aqueous environment into the ionic environment. Room temperature ionic liquids have been suggested for the extraction and separation of lanthanide and actinides species from fission elements [26,27,28]. Specifically, RTILs would be used due to their unique solvation properties to create environments to address difficulties encountered in traditional nuclear separations [29]. Although extraction of group f elements using RTIL solutions is not the focus of this proposal, it must be considered an advantage of these systems. The ability to form complexes using ions specific to a given RTIL is a useful technique for enhancing solubility of the given f-element in the RTIL. In some cases the ions used in the preparation of the RTIL have been used to complex a species of interest to enhance solubility [20-25].

Research Approach

Electrochemistry

The electrochemistry of f-elements in RTIL solutions can be divided into three tasks:

- The identification of RTIL cation/anion pairs that are suitable for the electrochemical studies of f-elements.

- The electrochemical characterization of RTIL solutions with respect to the working electrode composition, the potential windows afforded, and the ability to incorporate the f-elements in the ionic liquid.

- The electrochemical oxidation/reduction properties of f-elements in RTIL solutions and electroplating of f-elements at inert electrode surfaces using cyclic voltammtery and electrochemical impedance spectroscopy.

Identification of suitable cation/ion pairs for electrochemical studies of f-elements in RTIL solutions is critical. The choice of suitable RTIL solutions is based on the stability and solubility of the actinide/lanthanide species in the solutions. If the goal is to understand the thermodynamic and kinetic processes associated with the potential dependent separation of f-elements, then it is critical that RTIL solutions that are not suitable for these electrochemical studies to be eliminated. For example water sensitive RTIL solutions prepared with chloroaluminate will not be studied due to degradation of the cation species in the presence of water at negative potentials that would prohibit the electrodeposition of U, Pu, Am, or Cm. In addition, the use of immidizolium cations is not feasible for our studies due to the irreversible reduction of the cation and ring degradation at negative potentials prohibiting the electrodeposition of U, Pu, Cm, or Am [30]. Rather, we will examine quaternary ammonium cations with a variety of weakly complexing anions such as bistriflimide, halides, and acidic organic cations such as paratoluenesulfonic acid. RTIL solutions that have combined quaternary ammonium cations with bis(trifluoromethylsulfonyl)imide (bistriflimide, NTf_2) have shown promise in the electrodeposition of Eu, Sm, and Th, without significant degradation of the cation [23, 24, 25]. We have already produced RTIL solutions that utilize quaternary ammonium cations with bistriflimide (Figure 3) ([$MeBu_3N$][NTf_2]). To date, we have produced a total of 6 different RTIL solutions that utilize two quaternary ammonium cations ($MeBu_3N$ and Me_3BuN) with 3 different anions (Cl⁻, Br⁻, and NTf_2⁻). We also have the ability to produce additional quaternary ions using other organic functionalities such as iso-propyl, butyl, ethyl, and propyl groups. Literature surveys of previous electrochemical studies of f-elements in RTIL solutions will be utilized to identify RTIL systems that show promise. With the target RTIL systems identified experimental factors such as working electrode composition, solution composition influence on the potential window, complex formation, and stability of the target species will be examined for each system.

The literature regarding the use of RTIL solutions in the electrochemistry of f-elements is far from comprehensive and is difficult to compare directly due to the lack of universal, reproducible reference potential. The ability to compare the thermodynamic potentials of f-element electrochemistry is complicated due to assumptions made with respect to the reference electrodes employed. To this point the measurements have been performed using Ag/Ag⁺ quasi reference electrodes with MeCN and Ag⁺ ion, Ag/AgI with RTIL as the fill solution, and Ag⁺ quasi reference using the ferrocene redox couple

(Fc/Fc$^+$) as an internal standard in the electrochemical cell [20, 21, 22, 23, 24, 25]. The potential of these electrodes are not easily compared because solution conditions, junction potentials, and cell resistance are different and can influence the half-cell potential for the reference. To truly compare different species and RTILs a stable reference electrode must be employed in RTIL studies. We will use a reference electrode that has been shown to be stable in a variety of RTIL solutions and conditions which utilizes an Ag wire with either AgNO$_3$ (silver nitrate) or Bu$_4$NCl (tetrabutylammonium chloride) dissolved in a minimum volume of acetonitrile mixed with the RTIL such that the concentration of cation in the reference is 0.1 M. Reference electrodes constructed using the two different cations showed reproducible/stable electrochemical potentials relative to ferrocene. For these studies the reference electrode potential was determined experimentally to be +0.400 V vs. NHE [31]. More importantly, the study provided stable reference electrodes with high reproducibility which allows the potentials from electrochemical measurements in RTIL solutions to be expressed with respect to established lanthanide and actinide oxidation/reduction potentials in the literature and from tables.

The potential window of each RTIL solution identified must be evaluated and compared to the known potentials for the oxidation/reduction and electrodeposition of each species. The elements to be examined include Ce, U, Pu, Am, and Cm. The potential window will be evaluated to determine if the negative potential limit is sufficiently low to allow the lanthanides and actinides to be reduced to their metallic forms. Provided the potentials in RTIL solutions are significantly different it should be possible to electrochemically deposit species on the inert electrode. Working electrodes utilized will include Pt, Au, and Glassy Carbon with a Pt counter electrode and the RTIL reference electrode discussed previously. For all electrochemical studies cyclic voltammetry will be the primary technique used to evaluate the RTIL solutions containing the f-elements. The technique will be used to determine the reversibility of oxidation/reduction processes, thermodynamic potentials, and to calculate the free energy of the electrochemical processes. In addition, electrochemical impedance will be used to examine the transport and kinetics of the f-elements in RTIL solutions. In these studies the Nyquist plots of f-element electrochemistry will be generated and the electron transfer and diffusion limited processes will be evaluated to obtain electron kinetics and transport properties of the species.

Electrochemical studies of f-elements that exist are often focused on comparative analysis of a limited number of f-elements in a single class of RTIL solutions. For example the studies by Bhatt et al. have focused primarily on RTIL solutions prepared with the weekly complexing bistriflimide ion (NTf$_2^-$) and quaternary ammonium cations. In a few cases quaternary phosphonium and quaternary arsenate ions were substituted for the ammonium cation [23, 24, 25]. However, these studies demonstrate the importance of the complex formation of Th, La, Sm, and Eu with the anion NTf$_2$ and the ability to incorporate these species into RTIL solutions. The complex formation between the anion and the lanthanide or actinide species provides enhanced solubility in the RTIL. However in every case the complex is not converted directly to the RTIL. It is typically isolated in non-aqueous solvent, crystallized by solvent evaporation, re-crystallized, and then dissolved in the RTIL of choice. Although isolation of the complex will be required for spectroscopy it is not necessarily required for the electrochemical studies. We

propose to use the acidic forms containing the anion (HNTf$_2$, paratoluenesulfonic acid) whenever possible to directly dissolve the actinide/lanthanide species to form an anion solution. The RTIL will be formed by the addition of the cation to this solution without pre-isolation of the complex. In this manner anionic solutions of f-elements can be produced using a standardized procedure. The solution produced in this manner provides a chemically stable environment for the lanthanide or actinide allowing the storage, use and archival of samples as needed. In addition, this approach will allow a variety of actinide and lanthanide species to be incorporated into a single RTIL anion solution to represent more realistic waste form solutions that can be utilized for the potential dependent separation of f-elements.

Project Performance Site

The University of Nevada, Las Vegas is the primary site where the research will be performed. Dr. Hatchett's research laboratories in the department of chemistry will be the setting for electrochemical studies that do not utilize radioactive species. The preparation and characterization of RTIL solutions, preparation of f-element complexes for inclusion into the ionic liquid, and electrochemical impedance measurements will be performed in the laboratories in the chemistry department. FTIR and UV/Vis spectroscopic analysis will be conducted in the department of chemistry also.

The University of Nevada, Las Vegas has the capability and expertise to perform experiments studies on the actinides and technetium. UNLV has an established radiochemistry research program and offers a doctoral degree in the subject. The laboratory has the appropriate equipment and licenses for performing studies with solid phase and spectroscopic quantities of actinides and technetium.

Project Timeline:

To achieve the objectives for developing a tunable electrochemical based separation of actinides in RTILs the following areas will be examined:

- RTIL preparation/identification and the solubility and speciation of f elements in selected RTILs
- Electrochemistry and spectroscopy of f elements in the identified RTILs.

The proposed research is planned over a three-year period. Dr. Hatchett will direct all electrochemical studies and Dr. Czerwinski will be responsible for directing the spectroscopic studies. The first year work will focus on the preparation/identification of RTIL systems suitable for the electrochemistry of f elements. The synthesis of targeted RTIL systems, complex formation of the f-element using the anion from the RTIL, and the direct incorporation of complexes formed between f-elements and RTIL anions will all be evaluated in year two. Spectroscopy of the f-element complexes used in the electrochemical studies will be examined separately and incorporated in the RTIL. UV/Vis and FTIR analysis of the materials will be performed. The second and third year of the project will focus on the electrochemistry of f-elements in the RTIL solutions identified and synthesized in years one and two. The thermodynamic potentials obtained

during the oxidation and reduction of the f-elements from electrochemical experiments will be used to calculate the free energy of the complex in the RTIL. The electrochemical deposition of a variety of f-elements including U, P, Am, Cm and Ce will be evaluated using RTIL solutions and complexes prepared in years one and two. Evaluation of deposits will be conducted to determine speciation of the deposit and the chemical reactions for the deposition processes. Electrochemical impedance studies will also be conducted in addition to cyclic voltammetry. The data will allow the transport properties (diffusion controlled) and electron transfer kinetics to be evaluated for the RTIL systems. This information will be used to determine the most favorable conditions for potential mediated separation of the f-element species.

Year 1 (Anticipated Start Date of September 2007)
- The synthesis of cations/anions needed to prepare RTILs.
- Preparation of RTIL solutions based on literature studies.
- Basic spectroscopic analysis of RTIL solutions.
- Electrochemical analysis of RTIL solutions. Evaluation of potential windows and stability of solutions under the electrochemical conditions useful for f-element analysis.

Year 2
- Direct synthesis of RTIL solutions from anion/f-element complexes and cations.
- Acidification of RTIL solutions employing f-element complexes formed using organic acids followed by cation inclusion.
- Electrochemistry of f-elements in RTIL solutions. Oxidation/reduction of f-elements in RTIL solutions.
- Preliminary studies of the potential mediated deposition of f-elements from RTIL solutions.
- Spectroscopic analysis of isolated f-element complexes and f-element complexes in RTILs using UV-Vis and FTIR spectroscopy

Year 3.
- Electrochemical studies of the potential mediated deposition of f-elements at inert electrodes.
- Evaluation of the kinetics of electron transfer and transport properties of f-elements in RTIL solutions using electrochemical impedance spectroscopy.
- Evaluation of the thermodynamic properties and free energy of electrochemical processes of f-elements in RTILs.
- The continued spectroscopic analysis of isolated f-element complexes and f-element complexes in RTILs.

Deliverables
- Quarterly reports to update and evaluate progress, discuss problems, and allow for re-focusing of research goals.
- Ph.D. Degree completion of the graduate student by the end or close to the end of project.

- Peer reviewed research publications in scientific journals from the studies outlined in years one through three.
- Bi-annual reports detailing experiments/calculations performed, data collected, and results.
- Final report detailing experiments/calculations performed, data collected, and results and conclusions to be submitted at the end of the project.

The following table illustrates the timeline for each component of the research proposal.

Time (Years)	1				2				3			
Time (Months)	3	6	9	12	15	18	21	24	27	30	33	36
Order Materials/Chemicals	■	■	■	■								
Synthesis of RTIL components.	■	■	■	■								
Preparation of RTIL solutions.	■	■	■	■	■	■						
Spectroscopy of RTIL solutions.			■	■	■	■						
Electrochemistry of RTILs.			■	■	■	■						
Oxidation/reduction of f-elements in RTILs			■	■	■	■	■	■				
Synthesis of RTIL solutions from anion/f-element complexes					■	■	■	■	■			
Synthesis of acidic RTIL solutions from anion/f-element complexes					■	■	■	■	■	■	■	
Electrodeposition of f-elements from RTIL solutions.						■	■	■	■	■	■	■
Spectroscopic analysis of isolated f-element complexes.					■	■	■	■	■		■	■
Spectroscopic analysis of f-element complexes in RTILs.					■	■	■	■	■	■	■	■
Electrochemical kinetics and transport in f-elements in RTILs								■	■	■	■	■
Thermodyamics of f-elements in RTILs (experimental)								■	■	■	■	■
Quarterly Reports	■	■	■	■	■	■	■	■	■	■	■	■
Semi-Annual Reports		■		■		■		■		■		■

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