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Electrochemical Separation of Curium and Americium


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Task 25

Electrochemical Separation of Curium and Americium

D.W. Hatchett and K. Czerwinski

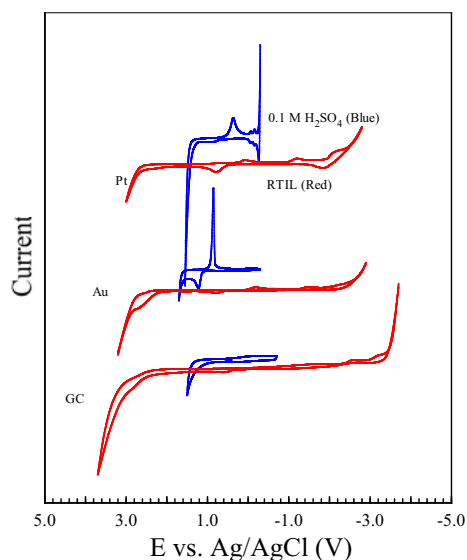
BACKGROUND

In the Transmutation Research Program the separation of the trivalent actinides Am and Cm from the trivalent lanthanides, and even each other, has been identified as an area of particular interest. The removal of lanthanides from trivalent actinides is necessitated for the neutron economy of a fuel containing Am and Cm. Furthermore, a fuel containing only Am would ease the demands on a reactor for transmutation. The destruction rate of Cm isotopes in a reactor is comparable to their decay rate. Separation and storage of the Cm, and reintroduction into the fuel of the Pu daughters, is a transmutation option that can be explored if a suitable method for the separation of Cm from Am is obtained. Furthermore, removal of Cm would reduce difficulties in fuel fabrication.

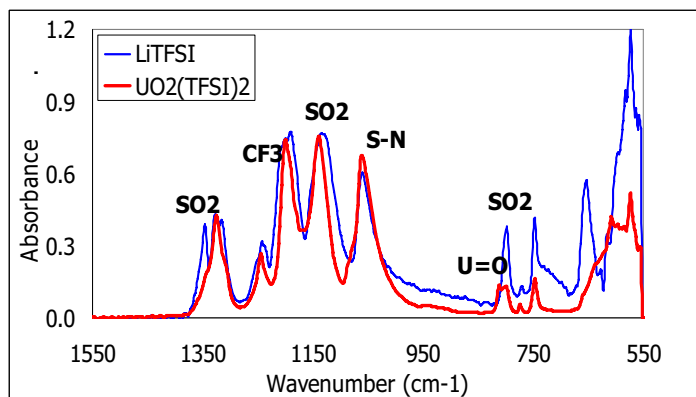
Electrochemical methods can be used to effectively separate actinide and lanthanide species from complex mixtures. This is based on the unique electrochemical properties of each specific target species. In studies it has been found that with the exception of Ce, aqueous solutions provide unsuitable electrochemical windows to effectively evaluate the thermodynamic properties that are useful for chemical separation. Therefore a more novel approach was examined which eliminated the aqueous solution with a Room Temperature Ionic Liquid (RTIL) solution. RTIL solutions do not suffer from the side reactions that are prominent in aqueous environments. In addition the potential window is much larger for the RTIL solutions. The RTIL solutions are a new starting point for the electrochemical separation of individual species from a mixture.

RESEARCH OBJECTIVES AND METHODS

The objectives of this project are to use electrochemical tech-



Electrochemistry of GC, Au, and Pt electrodes in RTIL ([MeBu₃N][NTf₂]) (red) and 0.1 M H₂SO₄ (blue).



The IR spectra show the typical RTIL anion Li(TFSI) (blue), and UO₂ complexed to TFSI (red). The shift of the SO₂ peak at 1350cm⁻¹ indicates TFSI complexation, and the peak around 810cm⁻¹ indicates the presence of a U=O bond.

niques to develop a thermodynamic understanding of actinide and lanthanide species in RTIL solution, and to use this data to effectively separate species with very similar chemical properties. In consultation with a national laboratory collaborator, electrochemical methods and materials will be evaluated and used to exploit the thermodynamic differences between similar chemical species, enhancing the ability to selectively target and sequester individual species from mixtures. This project is in its third year and has successfully completed phases 1 and 2. Phase 3 has been partially completed. The tasks have been expanded to include a fourth phase.

Phase 1

Evaluate thermodynamic oxidation/reduction properties of Ce using electrochemical methods.

Phase 2

Evaluate the thermodynamic properties of chelated Ce, Sm, and Eu at carbon, platinum and gold electrodes.

Phase 3

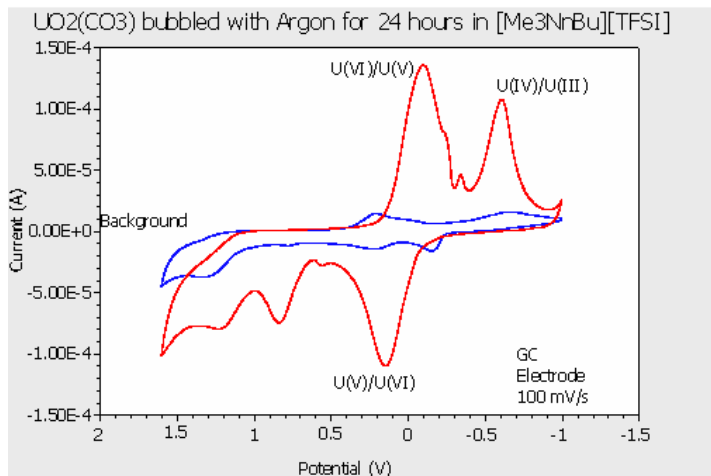
Examine the use of conductive polymer membranes for the uptake and expulsion of complexed and uncomplexed actinide and lanthanide species.

This phase still needs to examine the uptake, selective adsorption and separation of individual actinide and lanthanide species, including the isolation of Cm from Am, using conductive polymer/metal composite membranes containing bound chelates.

Phase 4

Prepare and characterize RTIL solutions. Examine the electrochemical window and evaluate the electrochemical properties of lanthanide and actinide species in the non-aqueous ionic environment.

The following were specific goals for this year:



CV of UO_2 -TFSI complex formed by added $UO_2(CO_3)$ directly to the RTIL and using Argon to remove the carbonate from the system.

- To prepare RTIL solutions.
- To evaluate the potential window of RTIL solutions.
- To develop a fundamental understanding of the thermodynamic properties of actinide and lanthanide species (such as Cm, Am, Ce, Nd, Eu, and Sm) in RTIL solutions.

RESEARCH ACCOMPLISHMENTS

The electrochemical window for RTIL systems is based primarily on the reduction of the cation and oxidation of the anion used to make the solution. The potential window is significantly larger for RTILs ranging from approximately 4.5 to 6 V when compared to aqueous environments. The figure to the left 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 ($[MeBu_3N][NTf_2]$, 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.

The advantage to eliminating aqueous side reactions and expanding the potential window is that previously inaccessible electrochemical reactions may be observed. These systems provide a huge potential window for the observation of oxidation and reduction of lanthanides and actinides. In addition, the potential mediated deposition of f-elements is possible - indicating that 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 in the before

ACADEMIC YEAR HIGHLIGHTS

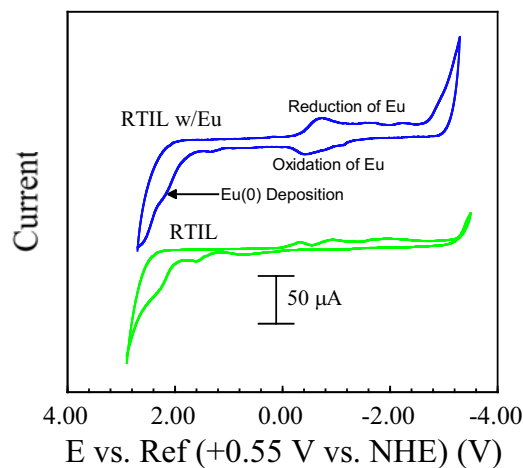
- ♦ Sandra Elkouz, M.S. thesis, UNLV Chemistry Department, "Complexation and Electrode Effects on the Electrochemical Behavior of the Cerium(IV)/Cerium(III) Redox Couple," April 2007.
- ♦ S. Elkouz, P. Houlihan, K. Czerwinski, and D.W. Hatchett, "The influence of electrode composition, pH, and ionic strength on the redox properties of Ce(IV)/Ce(III)," Submitted to *Electrochimica Acta*, April 2007 (Ms. Ref. No.: EA-S-07-00835).

mentioned figure. The preliminary electrochemical characterization of Eu in RTIL is shown in the figure below.

Through using infrared (IR) and ultraviolet-visible spectra, it was observed that the uranyl did complex to the anion of the RTIL. However, a more interesting way to complex the uranyl to the RTIL is by adding uranyl carbonate directly to the RTIL and then using Argon gas to remove the carbonate. The results yielded a soluble UO_2 -bis(trifluoromethylsulfonyl)amide (TFSI) complex that produced reversible electrochemical reactions with Uranium including the U(VI)/U(V) couple. The Cyclic Voltammogram (CV) also yielded the U(IV)/U(III) couple. This method could prove to be very useful in observing the electrochemistry of any metal-carbonate species.

FUTURE WORK

Future work will focus on the development of RTIL solutions suitable for the potential mediated oxidation/reduction and deposition of lanthanide and actinide species. The ultimate goal is to separate individual species using the electrochemical potential of species.



Electrochemistry of Eu at a Pt electrode in RTIL ($[MeBu_3N][NTf_2]$).

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