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David W. Hatchett

University of Nevada, Las Vegas, david.hatchett@unlv.edu

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Task 38

f-Element Electrochemistry in RTIL Solutions: Electrochemical Separation of Lanthanides and Actinides

D.W. Hatchett and K. Czerwinski

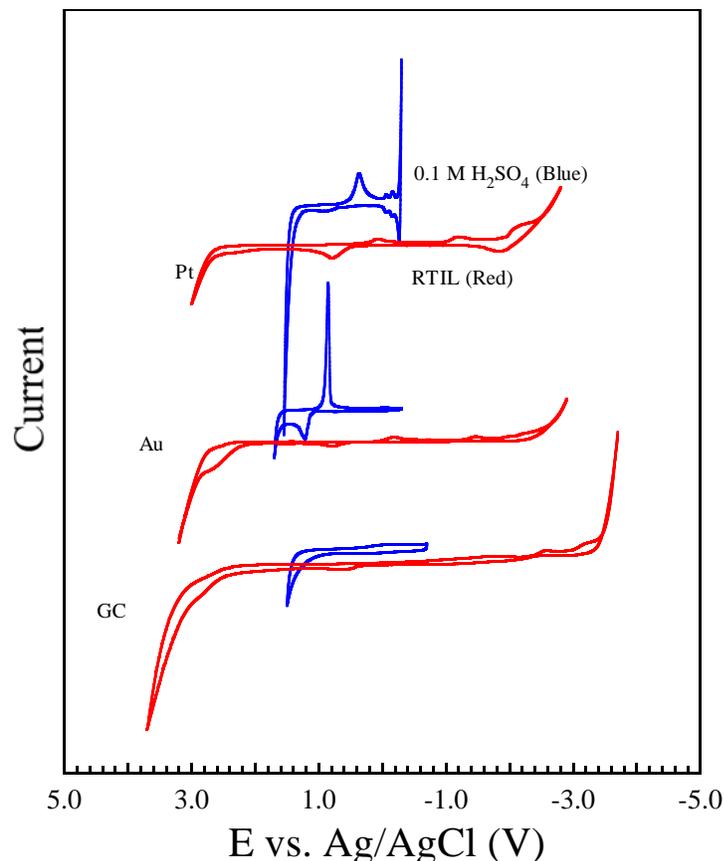
BACKGROUND

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 separations. 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. They are a new starting point for the electrochemical separation of individual species from a mixture.

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 electrode 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.

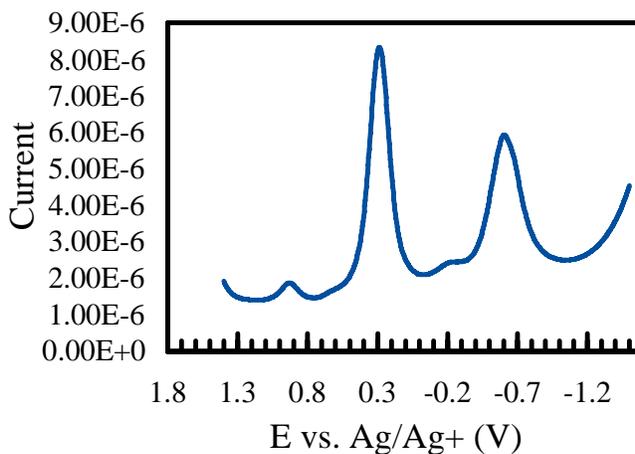
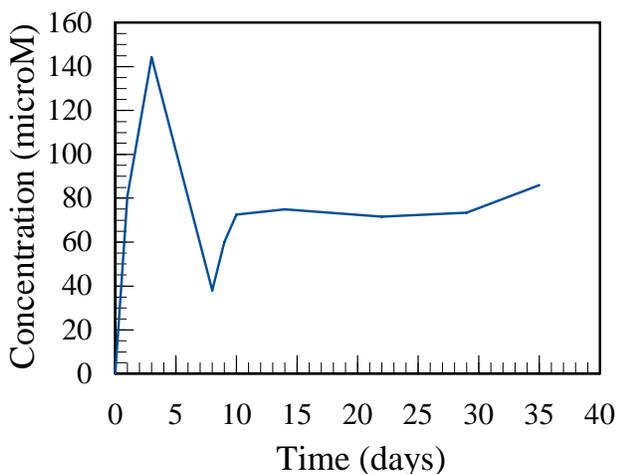
RESEARCH OBJECTIVES AND METHODS

The objective of this project is to use electrochemical techniques to develop a thermodynamic understanding of actinide and lanthanide species in RTIL solutions, and to use this data to effectively separate species with very similar chemical properties. In consultation with a U.S. Department of Energy national program 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



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

sequester individual species from mixtures. This project is in its first year and has successfully completed Phase 1. This research allows for expansion into Phases 2 and 3 for the next year.



(left) Solubility of UO₂CO₃ in a RTIL solution. (right) Square wave voltammetry of UO₂CO₃ in RTIL after 24 hours.

Phase 1 objectives:

- To prepare and characterize RTIL solutions.
- To examine the electrochemical window and to evaluate the electrochemical properties of lanthanide and actinide species in the non-aqueous ionic environment.

Phase 2 objective:

- To examine the solubility and complex formation of Lanthanide and Actinide species.

Phase 3 objective:

- To examine extraction properties of NTf_2^- ion complexes into RTIL solutions with common ions.

Phase 4 objective:

- To electrodeposit lanthanide and actinide species from RTIL.

RESEARCH ACCOMPLISHMENTS

The advantage of using RTIL solutions and 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 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 $E = -1.90 \text{ V vs. Ag/AgCl}$, well within the negative potential limit for the RTIL at platinum ($-2.6 \text{ V vs. Ag/AgCl}$), gold ($-2.2 \text{ V vs. Ag/AgCl}$), and glassy carbon ($-3.4 \text{ V vs. Ag/AgCl}$) electrodes. The figure on the opposite page (top) provides an example of the potential windows associated with GC, Au, and Pt electrodes in aqueous and RTIL solutions.

ACADEMIC YEAR HIGHLIGHTS

- ◆ Synthesis of bulk quantities of RTIL.
- ◆ Electrochemical characterization of the UO_2^{2+} system.

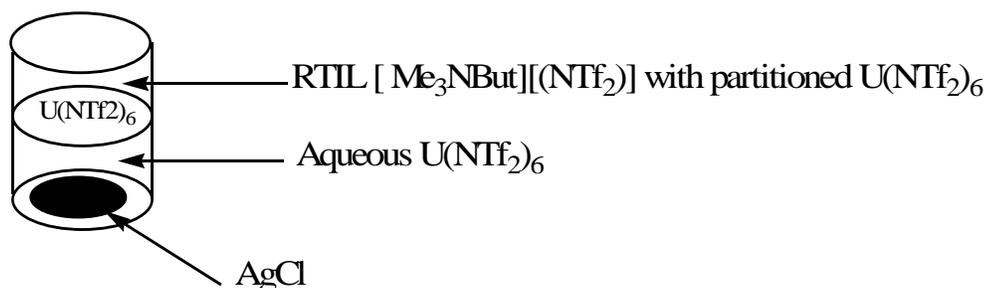
A second advantage is the increased solubility of lanthanide and actinide species in the RTIL. RTIL solutions have been utilized in the waste cycle for extraction of species. These solutions could be useful in the potential dependent separations of lanthanide and actinide species. The figure on the opposite page (bottom) provides the preliminary evaluation of UO_2CO_3 solubility in RTIL. The electrochemical response if UO_2^{2+} is provided also.

Preliminary studies suggest that the extraction and electrode position of lanthanide and actinide species into RTIL solutions is possible. Work will continue with increasing the solubility of target species in RTIL.

FUTURE WORK

- Precipitation/complexation using $\text{Ag}(\text{NTf}_2)$ with chloride derivative of lanthanides and actinides.
- Extraction of the complex using RTIL solutions and common ions.

Future work will focus on the complexation of simple species like CeCl_3 , CeCl_4 . This will be performed through the aqueous precipitation of AgCl and the formation of triflate complexes of Ce. The complexes will then be extracted without the use of additional complexing species such as tributylphosphate (TBP). The goal is to provide a common complex anion for the metal that will allow neutral species to be extracted more efficiently than the TBP/n-Dodecanese system. Once the species are extracted into the RTIL, the electrochemistry will be examined using this solution. The ultimate goal is to electrodeposit and separate a given species using potential dependent methods.



Schematic of experimental set-up for precipitation/complexation using $\text{Ag}(\text{NTf}_2)$.

Research Staff

David W Hatchett, Principal Investigator, Associate Professor, Department of Chemistry
Ken Czerwinski, Associate Professor, Department of Chemistry
Asanga Ranasinghe, Post Doctoral Researcher, Department of Chemistry

Student

Wendy Pemberton, Graduate Student, Department of Chemistry

Collaborator

David Costa, Los Alamos National Laboratory