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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

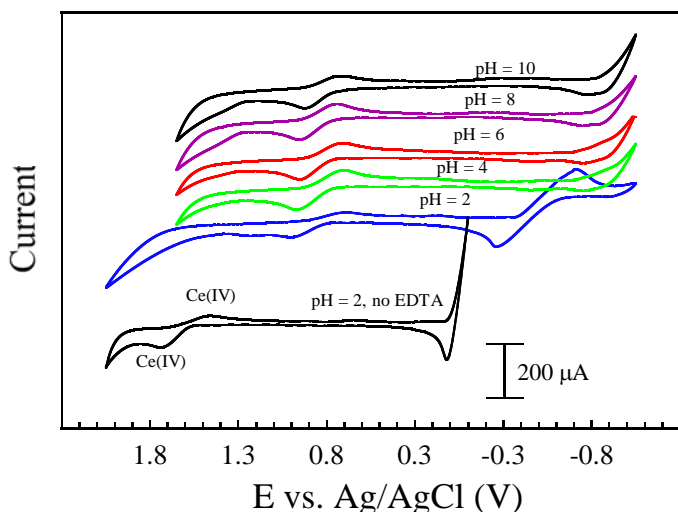
BACKGROUND

In the Advanced Fuel Cycle Initiative 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 the lanthanides from the trivalent actinides is necessitated for 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 as 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. It has been found through study 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.



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.

RESEARCH OBJECTIVES AND METHODS

The objective was to use electrochemical techniques to develop a thermodynamic understanding of actinide and lanthanide species in RTIL solutions, and use this data to effectively separate species with very similar chemical properties.

In consultation with a DOE collaborator, electrochemical methods and materials were 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, in its third year, successfully completed phases 1, 2. Phase 3 was partially completed. The project expanded to include phase 4.

Phase 1

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

Phase 2

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

Phase 3

Examined the use of conductive polymer membranes for the uptake and expulsion of complexed and uncomplexed actinide and lanthanide species. The uptake and selective adsorption and separation of individual actinide and lanthanide species, including the isolation of Cm from Am, still needs to be examined using conductive polymer/metal composite membranes containing bound chelates. Follow-on work was conducted under a new TRP project (Task 38).

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.

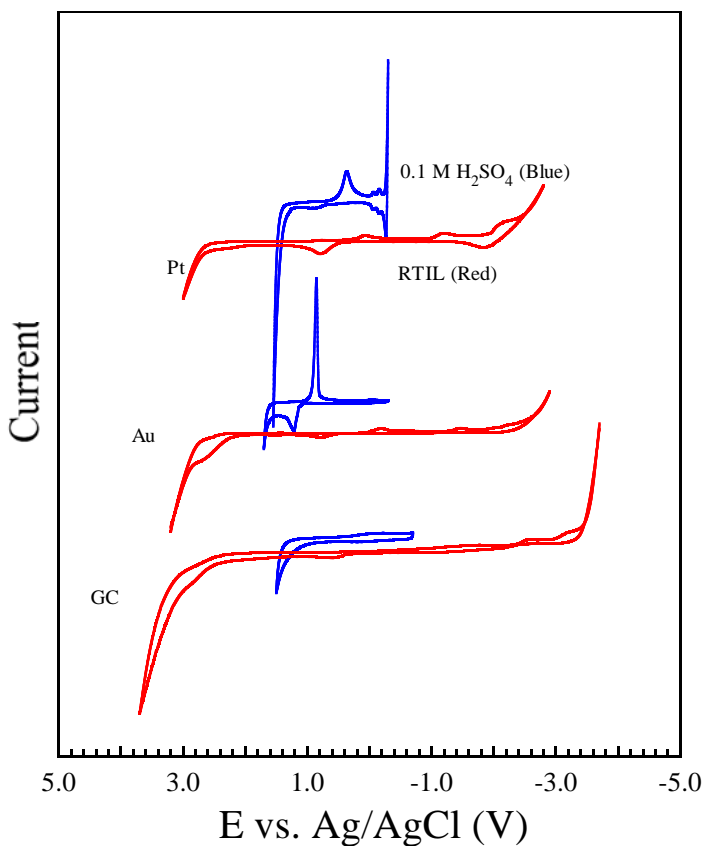
The following were specific goals for 2007-2008:

- 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.

Follow-on work was conducted under a TRP Task 38.

RESEARCH ACCOMPLISHMENTS

The research accomplishments can be separated into aqueous and non-aqueous systems. The initial goal of the research was to examine the thermodynamic properties of lanthanide and actinide species in aqueous solutions. It was apparent from the initial studies that the ability to examine lanthanide and actinide species was limited in aqueous solution. However, there was success in re-



Electrochemistry of Gc, Au, and Pt electrodes in RTIL ($[MeBu_3N][NTf_2]$), (Red) and $1.0\text{ M H}_2\text{SO}_4$, (Blue).

solving the Ce redox couple in aqueous solution. In addition, complexation with EDTA provided increased stability of the Ce redox couple at pH values that would typically lead to the precipitation of $Ce(OH)_x$ ($x = 2$ or 3). The voltammetric response of the Ce redox couple before and after EDTA complex formation is illustrated (see opposite page).

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 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 $E = -1.90\text{ V vs. Ag/AgCl}$, 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 electrode ($-3.4\text{ V vs. Ag/AgCl}$).

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 preliminary evaluation of RTIL solutions relative to normal aqueous conditions is also illustrated.

TASK 25 PROFILE

Start Date: July 2004

Completion Date: December 2007

Follow-on Task: "f-Element Electrochemistry in RTIL Solutions: Electrochemical Separation of Lanthanides and Actinides," TRP Task 38.

Theses Generated:

Sandra Elkouz, M.S. Thesis, Department of Chemistry, "Complexation and Electrode Effects on the Electrochemical Behavior of the Cerium(IV)/Cerium(III) Redox Couple," April, 2007.

Journal Articles:

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).

D.W. Hatchett, S. Elkouz, P. Houlihan, K. Czerwinski, "Electrochemical properties of Ce/EDTA complex in alkaline solutions," *Electrochimica Acta*, submitted 2008.

S. Elkouz, K. Czerwinski, and D.W. Hatchett, "The Electrochemical Characterization of Ce at Au, Pt and Glassy Carbon Electrodes: Influence of pH and Ionic Strength," manuscript submitted, 2006.

Conference Proceedings:

S. Elkouz, K. Czerwinski, and D.W. Hatchett, "The Electrochemical Characterization of Ce at Au, Pt and Glassy Carbon Electrodes: Influence of pH and Ionic Strength," 209th Electrochemical Society Meeting, Denver, CO, May 9 – 13, 2006.

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