

Task 25

Electrochemical Separation of Curium and Americium

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BACKGROUND

In the AFCI 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 utilized to effectively separate actinide and lanthanide species from complex mixtures. This is based on the general description of electrochemical control of precipitation or dissolution. The selective dissolution or precipitation of a chemical species is based on the thermodynamic potential dependent oxidation/reduction of the chemical species in the solid. Each chemical species has unique electrochemical properties largely based on physical properties such as ionization and chemical potential, which determine the potential for dissolution.

The same thermodynamic properties identified for species dissolution from solids can be used in the deposition of these species at electrochemically controlled interfaces. Evaluating the oxidation/reduction properties and determining the reaction

mechanism of each species in solution is the key to effective separations and optimization of such processes. Thus, it may be possible to selectively separate individual species electrochemically from a mixture.

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 aqueous solution and use this data to effectively separate species with very similar chemical properties. In consultation with our DOE collaborator, electrochemical methods and materials will be evaluated and used to exploit the thermodynamic differences between similar chemical species enhancing our ability to selectively target and sequester individual species from mixtures. The project can be divided into three distinct phases that can be defined by one-year intervals.

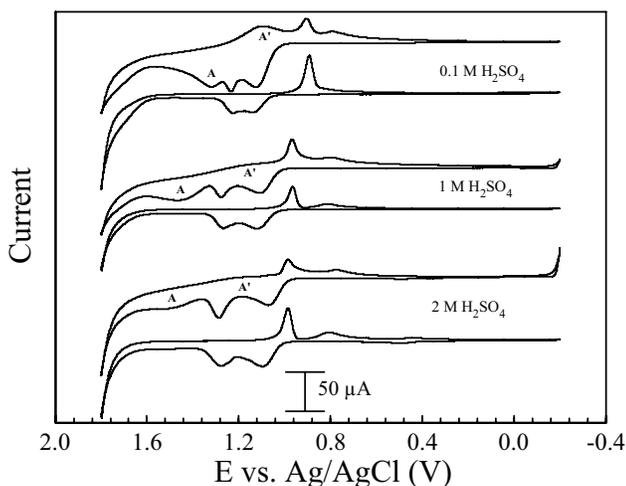
Phase 1: The thermodynamic oxidation/reduction properties of actinides and lanthanides will be examined using electrochemical methods. How the oxidation/reduction of actinides and lanthanides change after complex formation will also be examined.

Phase 2: The thermodynamics studies in phase I will be expanded to include the potential mediated adsorption properties of lanthanide and actinide species at Hg and Au/Hg electrodes. It is expected that the thermodynamics of adsorption will be markedly different than the oxidation/reduction.

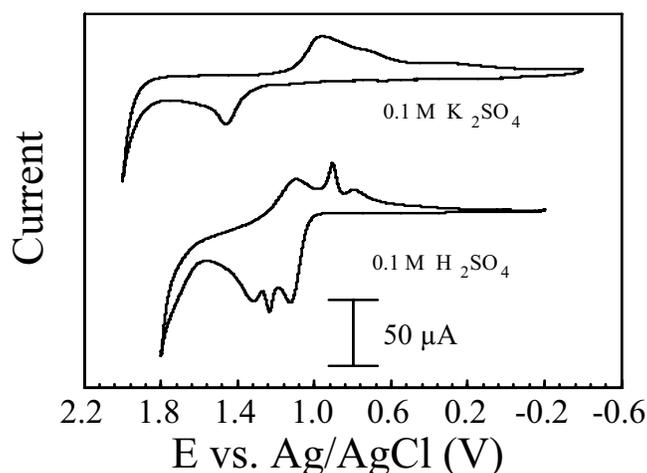
Phase 3: The use of conductive polymer membranes for the uptake and expulsion of complexed and uncomplexed actinide and lanthanide species will be examined. The uptake and selective adsorption and separation of individual actinide and lanthanide species including the isolation of Cm from Am will be examined using conductive polymer/metal composite membranes containing bound chelates. The potential mediated separation of single chemical species within a mixture will be the focus.

The following were specific goals for this year:

- To develop a fundamental understanding of the thermodynamic properties of actinide and lanthanide species such as Cm, Am, Ce, Nd, Eu, Sm prior to complex formation.
- To examine how chelation influences the thermodynamic properties of waste form species.
- To use systematic studies to distinguish the thermodynamic signatures and ability to shift thermodynamic potentials using chelation to enhance separation properties.



Influence of acid concentration on the redox properties of 6mM Ce(NO₃)₃. The redox couple Ce³⁺/Ce⁴⁺ are labeled using A and A'. The background in the supporting electrolyte is presented below the cyclic voltammetry for the solution containing Ce. Working electrode was an Au disk.



Influence of acid concentration on the redox properties of 6mM $\text{Ce}(\text{NO}_3)_3$ with constant ionic strength $\mu = 0.3 \text{ M}$. Working electrode was an Au disk.

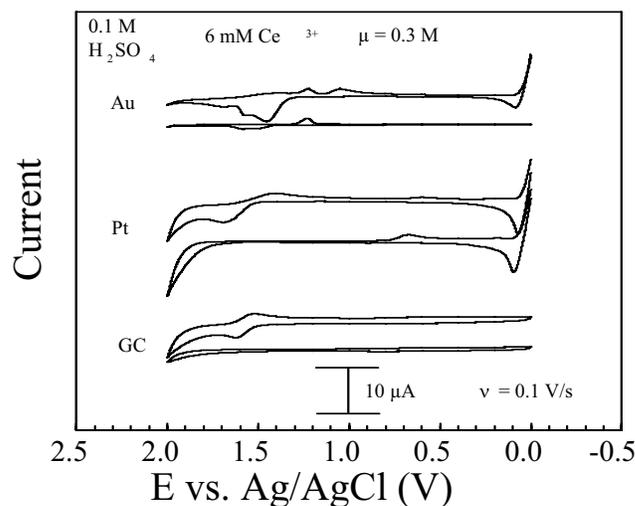
The effect of Ce oxidation and reduction was also examined with respect to the ionic strength of the solution. In these studies the concentration of K_2SO_4 was used to replace the H_2SO_4 supporting electrolyte solutions. The goal of this study was to distinguish the role of ionic strength versus pH for the Ce electrochemistry. The results are presented in the figure (above left) for a system with an ionic strength of $\mu = 0.3 \text{ M}$. The data suggests that acidity is the key variable in the system with higher resolution and lower splitting of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple.

The voltammetric response was also obtained at Au, Pt and glassy carbon electrodes. Resolution for each electrode is quite different. Peak splitting for each electrode provides information regarding the reversibility of the reaction. The figure (above right) shows the voltammetric response for the three electrodes under optimum acid conditions. Pt and glassy carbon electrodes display higher resolution in comparison to Au due to the lack of background signal in supporting electrolyte. In addition, the peak splitting for Pt and glassy carbon is sufficiently small in comparison to Au indicating the reaction is more reversible at these two electrodes. Glassy carbon has the smallest peak splitting indicating the electrode has the best thermodynamic reversibility.

Significantly different results are obtained for acetate buffer solutions at $\text{pH} = 7.5$. The data at this pH is characterized by a loss of electrochemical resolution for the Au and Pt electrodes. The redox properties of Ce at glassy carbon is still visible with lower resolution and larger peak splitting. In each case the reversibility and resolution of the redox couple is diminished.

ACADEMIC YEAR HIGHLIGHTS

- ◆ "The Electrochemical Characterization of Ce at Au, Pt and Glassy Carbon Electrodes: Influence of pH and Ionic Strength," by S. Elkouz, K. Czerwinski, and D.W. Hatchett, manuscript in preparation (2005).



Influence of working electrode composition on the redox prop-

FUTURE WORK

Future work will focus on identifying the optimized solution parameters for other species of interest including Sm, Eu, and Nd. The redox properties of these species will require that a systematic treatment be employed to determine the stability of the redox species as a function of solution pH, species concentration, and ionic strength. The task will be hindered by the lack of published data on the given systems. The goal is to understand the redox properties such that they can be optimized and manipulated to provide an effective method to differentiate individual species in complex mixtures.

In the immediate future the complexation and speciation of Ce and Sm will be examined. How the oxidation/reduction of actinides and lanthanides change after complex formation will be examined. The goal is to shift the thermodynamic potentials to ensure that species can be distinguished and separated from complex mixtures. A thorough understanding of parameters such as ionic strength and pH are critical in complex formation and will be the basis for these studies.

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