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Electrochemical Separation of Curium and Americium

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Proposal 04-22

Project Title:

Electrochemical Separation of Curium and Americium

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AFCI Research Area: Separations Technology

Abstract:

The objective of this project is to develop a method for the separation of Am from Cm based on electrochemical techniques. Electrochemical systems that allow the thermodynamics of actinide and lanthanide complexes to be systematically evaluated and tuned will be examined. The influence of complex formation on the ability to selectively isolate a given species electrochemically will be evaluated. Metal-ligand complex formation provides a useful derivation technique to increase solubility in solution environments that favor precipitation. In addition, the thermodynamic properties of a complex relative to the isolated species may be shifted to more suitably measurable electrochemical separation regimes. Electrochemical sorption methods are well suited for use in the separation of similar chemical species where the applied potential provides the thermodynamic selectivity required. Traditional separation techniques will be evaluated using common electrodes such as Hg, Au/Hg film, and glassy carbon. In addition, conductive polymer such as polypyrrole will be examined to provide a more novel method of separating and sequestering of actinide and lanthanide chemical species. The polymer composite electrodes will be chemically modified with chelating and the separation of chemical species based on the adsorption/desorption thermodynamics of the polymer relative to the complex or isolate species will be probed. The proposed experiments will provide a comprehensive survey of the effect of complex formation and species on the ability to separate complex mixtures of actinide and lanthanide complexes in aqueous environments using electrochemical methods and modified polymer electrodes.

Work Proposed for Year 2004 - 2005, Goals, and Expected Results:

Year one of the project will develop the lab facilities required for the electrochemical experiments. The electrochemical workstation will be acquired and necessary electrodes, reagents, and supplies will be purchased. The year one goals are to prepare and electrochemically evaluate the complexes and species of interest in this study or species that closely resemble more hazardous counterparts. These studies will be important for the future studies of polypyrrole membranes providing the required thermodynamic data concerning the complexes formed and possible separation of complex mixtures.

Funding Requested:

Funding Year	2004-2005	2005-2006	2006-2007
Total (\$K)	\$131,105	\$117,788	\$120,812

PROPOSAL NARRATIVE

Background and Rationale

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 obtain. Furthermore removal of Cm would reduce difficulties in fuel fabrication.

Separation of Am from Cm is achievable with current methods, mainly column chromatography. Separation of tracer level Am and Cm has been performed with displacement complexing chromatography. [1-4] The separations were examined with DTPA and nitrilotriacetic acid in the presence of Cd and Zn as competing cations. The use of Cd and nitrilotriacetic acid separated trace levels of Am from Cm. However, the displacement complexing chromatography method is too cumbersome to use on a large scale. Ion exchange has also been used to separate trace levels of Cm from Am [5]. In this work Am, Cm, and lanthanides were sorbed to a cation exchange resin at pH 2. Element separation was achieved by adjusting pH and organic complexant. Separation of Cm from Am was performed with 0.01 % ethylenediamine-tetramethylphosphonic acid at pH 3.4 in 0.1 M NaNO₃ with a separation factor of 1.4. Separation of gram scale quantities of Am and Cm has been achieved by cation and anion exchange [6-8]. The methods rely upon the use of α -hydroxyisobutyrate or diethylenetriaminepentaacetic acid as an eluting agent or a variation of the eluant composition by the addition of methanol to nitric acid. The best separations were achieved under high pressure conditions. For these methods the Am fraction contained 10-20 % Cm. By repeating the procedure separation factors greater than 400 were obtained. Unfortunately, these methods do not appear suited to the needs of the AFCI.

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 from a mixture, electrochemically.

After dissolution, issues such as acid concentration and complex formation in solution dramatically influence the solubility, distribution, and properties of the chemical species. However, complex formation can be utilized to tune the electronic properties providing larger or more feasible experimental separation windows for chemical species with similar thermodynamic properties. More importantly complex formation can influence the relative reactivity in comparison to other species. For example, formation of complexes of UO₂²⁺/UO₂⁺ indicate that oxidation/reduction of a chemical species is strongly influenced by the complex ligand. Uranium complexes (UO₂²⁺/UO₂⁺) with ligands such as Cl⁻, H₂O, C₂H₃O₂⁻, CO₃²⁻, and OH⁻ have been studied and exhibit a range of E_{1/2} values for the reversible oxidation/reduction.[9] A ~1 V difference between the complex formed with Cl⁻ (-0.065 V vs. Ag/AgCl) and OH⁻ (-0.927 V vs. Ag/AgCl) is observed. Based on the potential difference observed between Cl⁻ and OH⁻ for Uranium, complex formation can be considered as a viable parameter for enhancing separation efficiency.[10]

In this project we propose to examine and optimize the separation of Am and Cm using traditional electrochemical methods. A systematic study of the effect of complex formation on the oxidation/reduction and deposition potentials will be conducted to provide a thermodynamic map of Am and Cm species based on complexation with common organic ligands as well as those proposed in the AFCI separation procedures. We are also proposing to use more novel electrochemical materials such as conductive polymer membranes that can be modified to facilitate the capture and separation of chemical species from aqueous environments.[11,12,13] Conductive polymer materials such as polyaniline and polypyrrole are unique in the fact that they require the uptake of positive or negative charge to remain charge neutral as the oxidation state the material is changed using applied potential. The uptake of Am and Cm species in the membrane is based on the physical/chemical properties and electrostatic binding within the polymer membrane [14,15]. The species is expelled when the polymer is electrochemically reduced, changing the

oxidation state of the membrane, making the existing electrostatic interactions unfavorable. Modification of the polymer can also be envisioned through the potential mediated chelation of waste form species using ligands bound within the polymer membrane. This approach is detailed in Figure 1a - 1c which shows a polyaniline membrane modified with gold particles [16]. The dispersed gold acts as a template for the EDTA like thiol binding at the metal surface. The electronic properties of the ligands can be selectively tuned using the applied potential influencing the ability of internal complexes to form. The potential dependence of the ligand will provide the primary mode of separation of similar chemical species. The cumulative study will serve to define the parameters that are the most effective in enhancing the electrochemical separation of chemical species from solution. With this information the selective uptake and sequestering of complexes derived from Cm and Am, as well as the lanthanide homologs, can be examined.

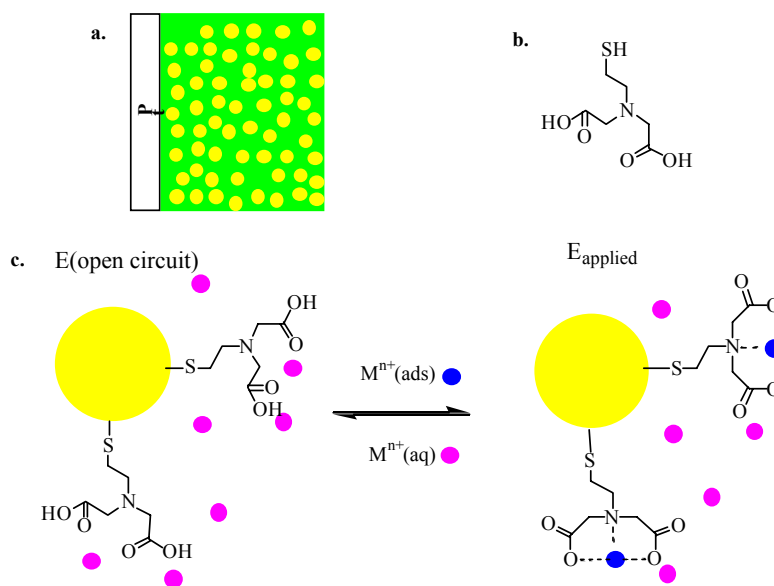


Figure 1. a. Schematic of a conductive polymer/Au composite electrode. b. Chelating ligand to be bound to the gold dispersed in the conductive polymer. c. Potential mediated separation of a metal species from solution using chelation.

Research Objectives:

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: We will examine the thermodynamic oxidation/reduction properties of actinides and lanthanides using electrochemical methods. We will also examine how the oxidation/reduction of actinides and lanthanides change after complex formation.
- 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.

Project Goals: The following are specific goals for year one of the project.

- 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.
- Examine how chelation influences the thermodynamic properties of waste form species.
- Use systematic studies to distinguish the thermodynamic signatures and ability to shift thermodynamic potentials using chelation to enhance separation properties.

Technical Impact:

The successful completion of this project will develop a systematic understanding of variables that influence the electrochemical separation of actinide and lanthanides with a focus on the solution separation of Am from Cm as well as the separation of trivalent actinides from the lanthanides. The thermodynamics of the systems will be explored and correlated with values obtained after complex formation to determine if complexes can be used to assist in the electrochemical separation of chemically similar species. The ligands will include both common organic complexants as well as ligands proposed in the AFCI separations.

Research Approach/Scientific Investigation

Electrochemical Thermodynamics. A systematic study of the thermodynamic properties of actinides and lanthanides in their uncomplexed state will be completed. Differences in chemical reactivity of mixed species are often not sufficient to allow individual species to be distinguished or separated from a mixture. In contrast, electrochemical properties are distinguishable because the ionization potentials and electronic properties are significantly different for each species. For example we are particularly interested in the thermodynamic properties of Am and Cm. The two species have significantly different oxidation/reduction properties, which are mediated by acid concentration and complex formation. For example, the tri-valent state is the most stable species for Americium in both acid and base, Figure 2. However, the potentials for the oxidation and reduction of the trivalent species are significantly different. In fact in base the 2+ species is not thermodynamically stable. The same trend is observed for Cm, Figure 3.

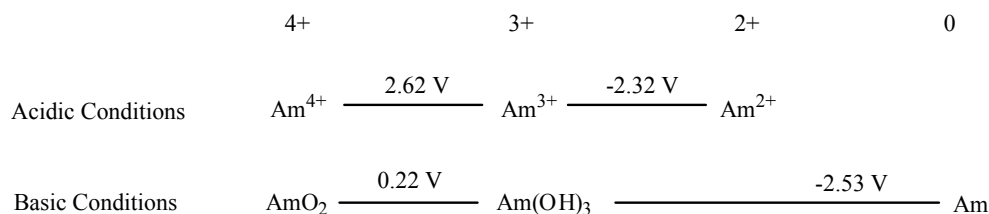


Figure 2. Oxidation/Reduction states of Americium in acid and base.

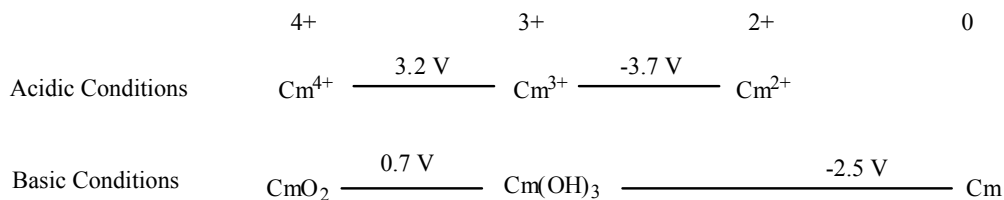


Figure 3. Oxidation/Reduction states of Curium in acid and base.

The chemical reactivity is obvious similar with comparable chemical species and the similar potentials for the 2 electron reduction of each metal hydroxide. However, clear differences are observed in acidic conditions with potentials on the order of 2.62 V for the Am^{3+} to Am^{4+} transition and 3.2 V for the Cm^{3+} to Cm^{4+} transition, respectively. The reduction from the 3+ to 2+ species is also significantly different. With a comprehensive understanding of the thermodynamics the targeted separation of species with very similar chemical properties can be envisioned which exploit the inherent potential differences between species.

Project Plan:

The project objectives will be defined and achieved through the successful completion of the following tasks:

Task 1. Electrochemical characterization of the thermodynamic properties of actinides and lanthanides under different solution conditions.

This task is divided into two parts.

- **Thermodynamics of actinide and lanthanide species under acid/base conditions.**

Current research in the electrochemical characterization of actinides and lanthanides has not been systematically examined and correlated with solution parameters such as pH, and ionic strength. For this project we will examine these properties and use them to assist in the electrochemical separation of species that are not easily separated chemically. For this study we will obtain electrochemical apparatus and materials that will be used for the characterization. The PI has extensive experience in the potential dependent characterization and deposition of metallic species from solution. The DOE collaborator will be consulted concerning the solution conditions of interest and species of interest that will be the most beneficial to this study.

- **Thermodynamics of actinide and lanthanide complexes under acid/base conditions.**

Complexes of Uranium (III) – Uranium (VI) with citrate, oxalate, phosphate, humate, alkoxides under various solution conditions have been examined.[9,10,17,18,19,20] In some cases the thermodynamic properties of the complexes have also been examined electrochemically. However in many cases the influence of complexation on the thermodynamic properties has not been examined for individual species for a pre-defined series of ligands. The goal is to find a series of ligands that provide solution stability for the different oxidation states of the lanthanide or actinide species. In addition the series of ligands will be used to vary the thermodynamic potential for oxidation/reduction reactions in an effort to provide a range of accessible potentials that can be used to provide selective electrochemical interactions and efficient electrochemical separation.

Task 2. Electrochemical adsorption/desorption thermodynamics at Hg and Au/Hg electrodes.

- **Thermodynamics of actinide and lanthanide adsorption/desorption.**

The electrochemical adsorption of actinides and lanthanides has not been extensively studied. There are a few examples of actinide adsorption on inorganic substrates such as apatite materials, lanthanum phosphate, montmorillonite, and calcium phytate. In many cases the positively charged actinide or lanthanide species replaces cations within the inorganic matrix thus sequestering the species from solution. However, the uptake is superficial and does not fully permeate the complex inorganic matrix. The adsorption/desorption at Hg or Au/Hg film electrodes can be probed to determine how complex formation influences the process.

Task 3. Electrochemical characterization of oxidation/reduction properties of Am and Cm at conductive polymer electrodes.

- **Potential mediated uptake/expulsion and oxidation/reduction of charged actinide/lanthanide species and complexes in conductive polymers.**

The use of conductive polymer matrices as electrochemical interfaces to examine the thermodynamic properties of actinide and lanthanide species has been largely ignored. However, the materials have advantages over other electrodes. First, they are extremely porous allowing the chemical species to permeate the membrane. The high porosity ensures high surface area which favors sorption. The electrostatics and electron density of the polymer can be used to sequester chemical species through electrostatic interactions. These interactions are reversible and can be used in either the uptake or expulsion of the chemical species from the membrane. In the case of polypyrrole the chemical species must be an anion and the polymer oxidized to facilitate the interactions. For polyaniline, positively and negatively charged species can interact with the polymer as the polymer is reduced or oxidized, respectively.

Task 4.

- **Potential mediated separation actinide and lanthanide species and complexes in conductive polymers containing bound chelators.**

The potential mediated uptake and chelation of actinide or lanthanide species using conductive polymer/gold composite membranes will be examined. The complex ligand will be bound to the gold clusters within the polymer membrane to act as nucleation sites for the actinides or lanthanides. The selectivity of the bound ligand will be evaluated as a function of applied potential. Typically solution pH is the primary method adjusting a chelating ligands affinity for species from solution. The underlying factor in chelation is the free electron density that is created as protons are extracted from the ligand. We plan on using the applied potential to mediate electron density at the ligand rather than manipulating the pH. Studies will be performed on single solution species to determine the thermodynamic potentials required for adsorption/desorption of species by the composite membrane, (Figure 1.). The studies will be expanded to include mixed solution once the thermodynamics of the individual systems are evaluated. The goal is to use the thermodynamic properties to selectively separate and trap individual species from complex mixtures.

Expected Technical Results for Year One:

- a. Systematic evaluation and determination of the thermodynamic properties of actinide and lanthanide species in aqueous environments.
- b. Determine the influence of acid concentration and ionic strength on the thermodynamics.
- c. Evaluate ligands for complex formation and produce complexes of actinides and lanthanides.

Capabilities at UNLV and National Laboratories

The electrochemical analysis of complexes and materials used for this study will be accomplished at UNLV using facilities at HRC equipped to handle actinide and lanthanide materials. Both the spectroscopic and electrochemical apparatus required for these studies will be housed Dr. Czerwinski's laboratory. Dr. Czerwinski has chemistry facilities for performing the electrochemical and spectroscopic experiments using actinide and lanthanide species. The polymer/metal composite studies and electrochemical analysis of the polymeric material, ligands, and thiol chelator will be conducted in Dr. Hatchett's laboratory using existing electrochemical and spectroscopic apparatus. Chemical characterization of actinide and lanthanide complexes will be examined using UV/Vis spectroscopy with a fiber optic spectrophotometer. Metal to ligand charge transfer transitions can be probed using spectroscopy to determine the degree individual ligand species interact with the metal species in the actinide and lanthanide complexes. Other equipment available include a state of the art FTIR spectrometer/microscope for detailed chemical analysis, optical microscopes, SEM, and XPS all currently available at UNLV in various departments. X-ray absorption fine structure (XAFS) studies on the extracted actinide and lanthanide species can be performed with DOE partners at either ANL or SRTC using the synchrotron facilities at Brookhaven or ANL. XAFS includes EXAFS (extended x-ray absorption fine structure spectroscopy) and XANES (x-ray absorption near edge spectroscopy). EXAFS is an atom-specific local structure probe used to determine the molecular structure of a species. Data can yield information including average interatomic distances and the number and chemical identities of neighbors within 5 to 6 Å of a selected atom species.[21]

Equipment Requested for TRP User Labs:

- a. An electrochemical workstation and computer are required for the electrochemical studies. This system will provide the apparatus required for all electrochemical experiments and will be housed in Dr. Czerwinski's laboratory. This laboratory is rated to handle radioactive materials required for these studies. The electrochemical workstation will consist of a bipotentiostat/galvanostat and a PC to run the system, acquire and store data.

Project Timelines with Milestones and Deliverables:



Timeline Narrative:

The project will be conducted over a three-year period beginning in the fall of 2004. During the first year, the electrochemical analysis will focus on determining the thermodynamic properties of actinides and lanthanides in aqueous environments of variable acid concentration, ligand, and ion strength. Equipment required for the electrochemical characterization will be purchased within the first month of the project

with a two-month window for performing the first electrochemical experiments. The thermodynamic data from the first year studies will be compared to thermodynamic data from complexes of actinides and lanthanides to determine the influence of chelation on the oxidation/reduction properties conducted during the end of the first year and beginning of the second. In addition, UV/VIS spectroscopy will be used to examine complex formation in-situ. The time dependent studies will be used to determine the rate of complex formation as a function of solution conditions. The oxidation state of the complexes will also be probed using spectroscopy. In the second year the potential dependent uptake and expulsion of un-complexed and complexed actinides and lanthanides will be examined at Hg and Au/Hg film electrodes. These studies will be expanded to include polymer membranes in the second year. The potential dependent uptake and expulsion actinide and lanthanide species will be examined. Finally in year three the potential dependent uptake of actinide and lanthanide species in Polymer/metal/bound chelator composite membranes will be examined with the goal of separating individual species from mixtures. The ultimate goal is to selectively separate chemically similar Am from Cm using the experimentally obtained thermodynamic data in years one and two. The proposed work will be the focus of scientific publications and presentations at national meetings. In addition, the work is expected to result in the publication of a thesis based masters degree in year two and a Ph.D. in year four after the project start date.

Timeline, Major Milestones and Deliverables for Year One.

Tasks	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug
1. Electrochemistry of Actinides and Lanthanides												
----Apparatus acquisition and Setup.												
----Thermodynamic measurements of native species.												
----pH and Ionic strength measurements.												
2. Ligand Complex formation with Actinides and Lanthanides												
----In-situ UV/Vis spectroscopy of complex formation.				↓			↓					↓
Reporting Requirements												
Travel for meetings with Collaborators.												

 Quarterly Report
  Annual Report

Both of the principal investigators will attend American Chemical Society meetings, American Nuclear Society meetings, Materials Research Society meetings, and/or Electrochemical Society meetings. Students will also be encouraged to present talks and posters at scientific meetings. We will meet with the DOE collaborators at semi-annual meetings. Based on these discussions further meetings will be arranged as needed. Phone conversations will serve as the primary mode of communications between meetings.

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