

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. 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.

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 a national laboratory collaborators, 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 1 examined the thermodynamic oxidation/reduction properties of actinides and lanthanides using electrochemical methods and examined how the oxidation/reduction of actinides and lanthanides change after complex formation.

Phase 2 expanded the thermodynamics studies in Phase I to include the chelation of properties Ce, Sm, and Eu at carbon, platinum and gold electrodes. It was expected that the thermodynamics of chelated species would be markedly different than the oxidation/reduction of unbound species.

Phase 3 will examine the use of conductive polymer membranes for the uptake and expulsion of complexed and uncomplexed actinide and lanthanide species and examine the uptake and 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.

The potential mediated separation of single chemical species within a mixture will be the focus.

The following were specific goals for this year:

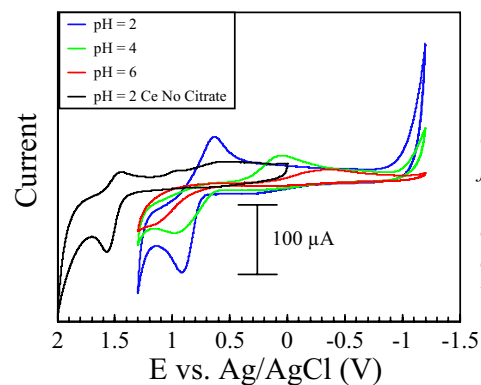
- To develop a fundamental understanding of the thermodynamic properties of actinide and lanthanide species such as Cm, Am, Ce, Nd, Eu, and Sm after complex formation.
- To examine how chelation influences the thermodynamic properties of waste form species.
- To use systematic studies to distinguish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

RESEARCH ACCOMPLISHMENTS

The thermodynamic characterization of Ce^{3+}/Ce^{4+} redox couple and other lanthanide species has been completed in various supporting electrolytes (0.3 M $NaNO_3$, 0.5 M HNO_3 , and H_2SO_4 at concentrations of 0.1 M, 1.0 M, 2.0 M, and 4.0 M). The results show that the Ce^{3+}/Ce^{4+} redox couple can be successfully resolved in aqueous environments. While the potential range was suitable for the resolution of the Ce^{3+}/Ce^{4+} redox couple it was insufficient for others. Species such as Eu and Sm were not resolved within the potential limitation of the aqueous system.

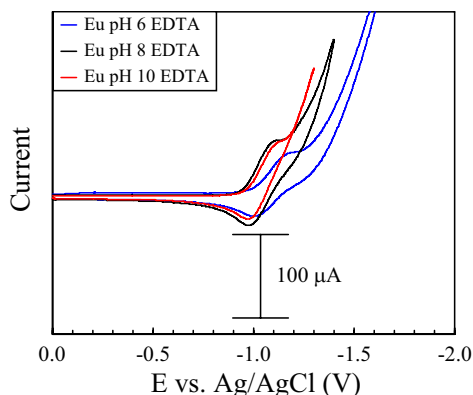
To expand the ability to resolve the electrochemical response of other species besides the Ce^{3+}/Ce^{4+} redox couple the chelation properties of ligands such as EDTA, NTA, and Citrate were utilized. The Ce^{3+}/Ce^{4+} redox couple was examined first due to the fact that the electrochemistry of the unbound species has been fully characterized.

These studies were expanded to include other chelating species with similar results including citrate. The figure below shows the chelation of Ce by citrate as a function of pH. The data for bound and unbound Ce are shifted relative to each other indicating that the thermodynamics of bound species is much different than the unbound. The difference in redox potentials for Ce bound by EDTA and Citrate indicate that chelation can be used effectively to separate species in solution. It is also apparent that the pH dramatically influences the voltammetry in citrate solutions. This is not the case for EDTA with stable redox chemistry over a pH



Electrochemistry of Ce and Ce/Citrate chelated species as a function of pH. The unbound Ce (black) and Ce/EDTA (blue) at pH = 2 are shown with Ce/EDTA at pH = 4 and pH = 6.

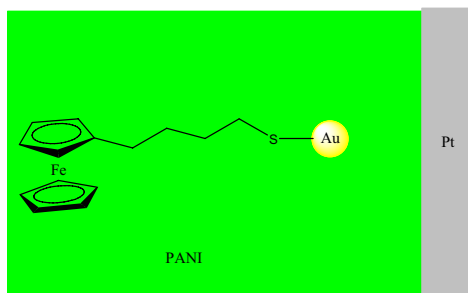
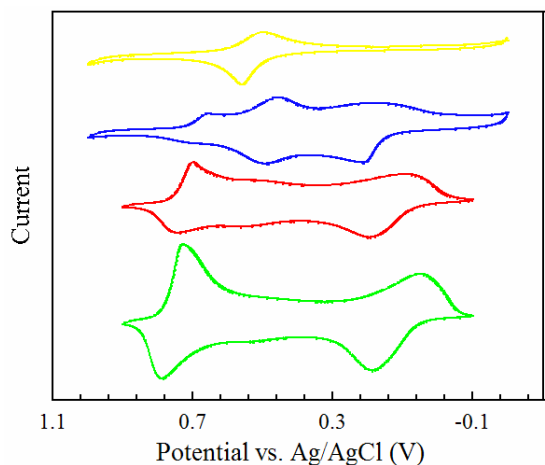
Electrochemistry of Eu/EDTA chelated species as a function of pH.



range from 2 to 12.

The success of shifting the redox potentials for Ce bound to species such as EDTA and citrate ion suggest that species that were not resolved when unbound may be resolved after chelation. For example, the figure above shows the voltammetric response of Eu which was not resolved when unbound, after chelation with EDTA. The redox chemistry has been shifted such that the oxidation and reduction Eu/EDTA can be resolved at very negative potentials. This species should precipitate as a hydroxide at the pH values presented in this figure. However, EDTA stabilizes the species at higher pH values allowing the electrochemistry to be resolved. The voltammetry at pH = 6 is more fully resolved than at the other pH values. However, the oxidation and reduction can be resolved at all three pH values. The redox chemistry of the Sm/EDTA species has also been successfully observed.

The last phase of this research is based on the electrochemical



Acid doping of PANI in HClO₄ before uptake of Au (green) and after (red). Redox properties of a PANI/Au/FcThiol membrane in HClO₄ (blue) and Au/FcThiol (yellow). A schematic of the PANI/Au/FcThiol is provided to the right for clarity.

ACADEMIC YEAR HIGHLIGHTS

- ◆ 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.
- ◆ 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.

separation of americium and curium. The proof of principal for this experiment is shown in the figure below left. In this figure the doping of polyaniline (PANI) is shown (green) followed by the second doping (red) after the uptake and reduction of Au particles in the polymer membrane. These particles will be used to affix the chelating ligand and then the applied potential will be used to facilitate complexation and speciation. To test the ability of the Au particles interaction with thiol molecules a simple five carbon thiol with a ferrocene tail was allowed to interact with the PANI/Au membrane. The results are shown in blue in the figure with a schematic of the system to the right. For comparison the oxidation and reduction of the ferrocene thiol at a planar gold electrode is shown in yellow in the figure. The oxidation and reduction of ferrocene is clearly visible in the polymer indicating the gold particles are electroactive and can act in potential mediated chemical reactions. The ultimate goal is to use this in separation reactions using an EDTA/thiol ligand that was synthesized in the lab.

FUTURE WORK

Future work will focus on the potential mediated chelation of lanthanide and actinide species using the system described above. A thorough understanding of the influence of pH and ionic strength and how these parameters influence the thermodynamics of species such as Eu, Ce, and Sm has been attained. Initially, planar Au electrodes will be used to chelate the species of interest in the absence of polymer to determine the potential for chelation for individual species. With this information the potential to control the chelation of individual species will be used. The ultimate goal is to separate individual species, thus providing highly efficient separation through potential mediation.

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