Actinides and Rare Earths Focus Topic
Room 318 - Session AC+LS+MI-WeA

Chemistry and Physics of the Actinides/Rare Earths

Moderator: Krzysztof Gofryk, Idaho National Laboratory

2:20pm **AC+LS+MI-WeA-1** ***Novel Preorganized Ligands for Selective and Efficient Separation of f-Elements , Santa Jansone-Popova,*** Oak Ridge National Laboratory **INVITED**

Selective separation of f-elements (lanthanides and actinides) is challenging to realize due to their very similar properties. For example, lanthanides exist predominantly in 3+ oxidation state and their ionic radii decrease across the lanthanide series on average by only 0.01 Angstrom per unit increase in atomic number. Organic molecules (ligands) capable of magnifying these effects and selectively recognizing one element over another are extensively sought after. Implementation of such ligands in separating f-elements would result in substantial cost and energy savings. The neutral organic molecules decorated with at least four donor atoms (oxygens and/or nitrogens), designed to complex with metal ions and that do not undergo conformational change in the process, demonstrate exceptional size selectivity.[1-3] The innate rigidity and size of the cavity in addition to the electronic structure of ligands provide the means to control the selectivity across the trivalent f-element series by design. On the contrary, organic molecules with donor groups that are connected to freely rotating single bonds show high affinity for metal ions that are more Lewis acidic.[4] Superior performance of preorganized ligands in two immiscible solvent system in selectively separating adjacent lanthanides or lanthanides from actinides will be discussed in detail. More specifically, the chemistry of hydrophobic and hydrophilic bis-lactam-1,10-phenanthroline-based ligands having four donor atoms will be presented, focusing on the separation of adjacent lanthanides (e.g., Nd-Pr, Tb-Gd, Ho-Dy) and Americium-Europium pair separation. Additionally, the contrasting performance of rigid ligands decorated with two to four donor atoms will be shown and compared to their non-preorganized counterparts.

[1] Healy, M. R.; Ivanov, A. S.; Karslyan, Y.; Bryantsev, V. S.; Moyer, B. A.; Jansone-Popova, S. *Chem. Eur. J.*, **2019**, *25*, 6326.

[2] Karslyan, Y.; Sloop, F. V.; Delmau, L. H.; Moyer, B. A.; Popovs, I.; Paulenova, A.; Jansone-Popova, S. *RSC Adv.*, **2019**, *9*, 26537.

[3] Jansone-Popova, S.; Ivanov, A. S.; Bryantsev, V. S.; Sloop, F. V.; Custelcean, R.; Popovs, I.; Dekarske, M.; Moyer, B. A. *Inorg. Chem.*, **2017**, *56*, 5911.

[4] Stamberga, D.; Healy, M. R.; Bryantsev, V. S.; Albisser, C.; Karslyan, Y.; Reinhart, B.; Paulenova, A.; Foster, M.; Lyon, K.; Moyer, B. A.; Popovs, I.; Jansone-Popova, S. *Inorg. Chem*. **2020**, *59*, 17620.

3:00pm **AC+LS+MI-WeA-3 Impact of Noncovalent Interactions on Actinide Structural Chemistry*, Karah E. Knope,*** Georgetown University*; J. Wacker,* Lawrence Berkeley National Lab*; M. Shore,* Georgetown University **INVITED**

Noncovalent interactions (NCIs) have received significant attention over the past several years. This interest is fueled by recent examples that have shown that these interactions, which exist beyond the first coordination sphere of a metal ion, can be used to isolate novel structural units, push chemical equilibria, and tune redox behavior. As illustrated by these examples, it has become clear that consideration of NCIs is important for understanding the overall chemical behavior of a metal ion. Taken together with our group's interest in the factors that govern actinide speciation and reactivity, our recent work has thus focused on the solution and solid-state structural chemistry of actinide complexes and clusters that form from acidic aqueous solution in the presence of heterocycles capable of N-H hydrogen bonding interactions. Specifically, we have examined the identity (i.e. composition, charge, coordination number) of actinide structural units that precipitate from monoanionic ligands systems including Br^{1-}, Cl^{1-}, and NO$_3^{1-}$ with N-heterocycles ranging from pyridinium to terpyridinium. While bromide, chloride, and nitrate all form weak relatively weak complexes with the actinides (Th-Pu), clear effects of NCIs are present only in the chloride ligand system with chloride rich (e.g. [Th(H$_2$O)$_2$Cl$_6$]$^{2-}$) to chloride poor (e.g. [Th(H$_2$O)$_7$Cl$_2$]$^{2+}$) complexes having been observed. By contrast, speciation is much more limited in the Br^{1-} and NO$_3^{1-}$ ligand systems. Presented here will be an overview of our experimental and computational efforts to understand the effects of NCIs on phase formation.

4:20pm **AC+LS+MI-WeA-7 XPS Characterization of a Pu-7at.%-Ga Alloy*, Paul Roussel,*** AWE, UK*; K. Graham, S. Hernandez, J. Joyce, T. Venhaus,* Los Alamos National Laboratory

Gallium is often used in small concentrations (<10 at. %) as an alloying element with plutonium to stabilize the face centred cubic phase.Most XPS analyses of these plutonium materials have focused on low concentration alloys (< 4 at. %) where it is difficult to measure the signal and effects of gallium.Here we report the analysis of a higher alloy concentration of Pu$_{0.93}$Ga$_{0.07}$ in the as received state, during sputter depth profiling and following oxidation either from the addition of Langmuir quantities of oxygen or the in situ environment of the ultra high vacuum system.Quantification of the spectra has been undertaken by comparison of the elastic peak intensity and this has allowed us to test the recently reported relative sensitivity factors for plutonium [1]. The higher alloying concentration has permitted quantification of gallium in both the metal and oxides and, for the first time, the gallium chemical state plot for both alloy and oxide has been determined along with those of plutonium and oxygen.In addition to this we highlight a novel method to quantify the C1s peak which overlaps with the Pu5p$_{1/2}$ photoemission line and demonstrate the effect of gallium on the in situ oxidation rate of this alloy.

1) P. Roussel, A. J. Nelson, Quantitative XPS of plutonium: Evaluation of the Pu4f peak shape, Relative Sensitivity Factors and estimated detection limits, Surf. Interface Anal. https://doi.org/10.1002/sia.7083.

4:40pm **AC+LS+MI-WeA-8 Nanoscale Uranium Oxide: Correlating Colloidal Synthesis Pathways with Structure at the Atomic and Nanometer Length Scale*, Liane Moreau,*** Washington State University

Nanoscale uranium oxide is of interest for the development of advanced nuclear fuels and its importance in the corrosion of conventional fuel pellets and trends in uranium mobility within environmental systems. Knowledge of nanoscale properties of uranium oxide, however, are limited due to 1) a lack of synthetic methods capable of forming monodisperse actinide oxide nanoparticles and 2) the challenges associated with characterization of complex interfaces. Organic-phase colloidal approaches prove promising towards the synthesis of actinide oxide nanoparticles due to precedence for formation of highly monodisperse transition metal oxide nanoparticles, and the capability to synthesize particles in rigorously air- and water-free environments. Three systems will be discussed which exploit colloidal uranium oxide synthesis. The first explores oxidation kinetics in UO$_2$ nanoparticles. Synthesis is paired with X-ray diffraction and X-ray spectroscopy to compare nanoparticle oxidation trends with those observed in bulk counterparts under controlled oxidative environments. The second traces the formation mechanism of UO$_2$ nanoflowers and demonstrates the role of solvent interactions in anisotropic growth. The established growth patterns are particularly interesting as anisotropic growth in transition metal counterparts have traditionally depended on surface binding species and trace impurities rather than solvent chemistry. The third system investigates the deposition of uranium oxide onto iron nanoparticle cores, which serves as an analogue to environmental systems where uranium and plutonium have shown to preferentially bind to Fe-based minerals. The high-surface area particles provide a means to investigate the interface in atomistic detail. In describing the aforementioned systems, X-ray focused approaches and characterization method development will be discussed, which prove critical to resolving structural attributes and making connections between synthetic parameters and resulting atomic and nanoscale structure.

5:00pm **AC+LS+MI-WeA-9 Chemical Speciation Mapping of Spent Nuclear Fuel Using Soft X-Ray Spectromicroscopy at the Advanced Light Source*, Alexander Ditter,*** *D. Smiles, D. Lussier,* Lawrence Berkeley National Laboratory (LBNL)*; A. Altman,* Northwestern University*; M. Bachhav, L. He,* Idaho National Laboratory*; M. Mara,* Northwestern University*; S. Minasian,* Lawrence Berkeley National Laboratory (LBNL)*; C. Degueldre,* Lancaster, UK*; D. Shuh,* Lawrence Berkeley National Laboratory (LBNL)

A nuclear reactor is a complex environment, with high temperatures, large temperature gradients and a multitude of fission products in various states. Spent nuclear fuel offers a key window into this environment, but is an important object of study in its own right, particularly with regards to the release of radioisotopes into the environment. The oxidation of spent nuclear fuel is especially important as this can govern the transport and solubility of fission products. To study this process, a focused ion beam (FIB) was used to make thin sections of a low burnup spent fuel pellet at Idaho National Laboratory. These FIB sections were then measured at the O K-edge, U N$_{4,5}$-edges and Ce M$_{4,5}$-edges at the scanning transmission x-ray microscope (STXM) at Advanced Light Source (ALS) Beamline 11.0.2. O K-edge results were analyzed by a modified form of non-negative matrix factorization and revealed two main components, the bulk of the sample which is made up primarily of UO_2, and a thin (est. 8 nm) layer of UO_{2+x} on the surface of the FIB section. This oxidation occurred after FIB sectioning as a thin layer over the entire sample. Cerium measurements showed that the Ce (~ 0.4 wt. %) is at least predominantly in the 3+ oxidation state, though a small contribution of tetravalent cerium cannot be ruled out, representing the first known measurements of Ce oxidation state in spent nuclear fuel. This work lays the foundations for future STXM measurements of FIB sections of spent nuclear fuel which can be expanded to mixed-oxide, uranium nitride, or other advanced fuels.

5:20pm **AC+LS+MI-WeA-10 Structural, Thermodynamics, and the Electronic Properties of Al, Ga, In, and Tl Stabilized δ-Pu***, **Sajib Barman**, S. Hernandez,* Los Alamos National Laboratory

The 5*f* electrons in plutonium show mystifying character contrary to other elements in the periodic table, where there are six solid state phases of plutonium that undergo five solid-state phase transformations in a relatively short temperature range. The low temperature α-phase is brittle and has a monoclinic structure where the high temperature δ-phase is ductile and has an FCC structure. From a metallurgical point of view, the ductile δ-Pu is mostly important due to its favorable elasticity compared to the brittle α-Pu. Therefore, stabilizing δ-Pu at room temperature can be done by alloying with Group IIIA elements (X = Al, Ga, In, and Tl). Nevertheless, the alloyed δ-Pu stability zones highly depend on the alloying content, where the stability zone decreases with increasing atomic number of the Group IIIA elements. In this work, we will present a systematic density functional theory investigation of the thermodynamic stability of alloyed δ-Pu with Group IIIA elements as a function of alloying content (3.125, 6.25, and 9.375 at. %). We have calculated that the δ-Pu-Ga alloys have the highest thermodynamic stability compared to the other Group IIIA alloys, where the stability trend follows Pu-Ga > Pu-Al > Pu-In > Pu-Tl at 0K. After volume optimization, the volume contracts for Pu-Ga and Pu-Al alloys, while the volume expands for Pu-In and Pu-Tl alloys with increasing alloy content. Finally, we will show the electronic structure analysis to discuss the electronic interaction between Pu and the Group IIIA elements within the δ-matrix.

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Author Index

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