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On-line Optical Spectroscopy to Characterize Chemistry of the Transuranic Elements in Molten Salts

August 2019

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Abstract

This project was targeted to design, build, and employ a spectroelectrochemical setup for the characterization of molten salts containing radioactive elements. This is a unique capability now housed at the Radiological Processing Laboratory (RPL) of PNNL. Initial work focused on the characterization of molten salts containing uranium, filling literature gaps regarding redox behavior, diffusion coefficients, and speciation. The setup was further modified/relocated to a glove box to allow for the study of transuranic elements, where significant research is needed to fill in literature gaps and fundamental understanding of behavior within molten salts.

Acknowledgments

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1.0 Tasks and Milestones for FY19

FY 19 was broken into 3 tasks:

Task 1: Continue characterization of U within chloride melts in radiological fume hood
Task 2: Build and test spectroelectrochemical system within a glove box
Task 3: Demonstration of spectroelectrochemical characterization of TRU species in glove box
Milestone (completed): Demonstrate characterization of TRU in salt melt

Task 1 has been ongoing for the entirety of FY 19. Electrochemical characterization has provided insight into behavior of U within LiCl:KCl eutectics, where conditions studied include a range of U concentration (1-5 wt%), a range of temperatures (from 500-900°C), and a range of electrode types (e.g., platinum, tungsten, carbon). Overall, the team has been able to generate the data needed to fill several literature gaps including the diffusion coefficients of U as a function of oxidation state and temperature. Figure 1 presents an example of an electrochemical scan rate study used to determine the diffusion coefficient of U within the LiCl:KCl salt melt. Additionally, the application of optical spectroscopy has enabled the team to characterize U signatures in UV-vis absorbance as well as Raman spectroscopy, where Raman spectroscopy represents another literature gap for U within salt melts.

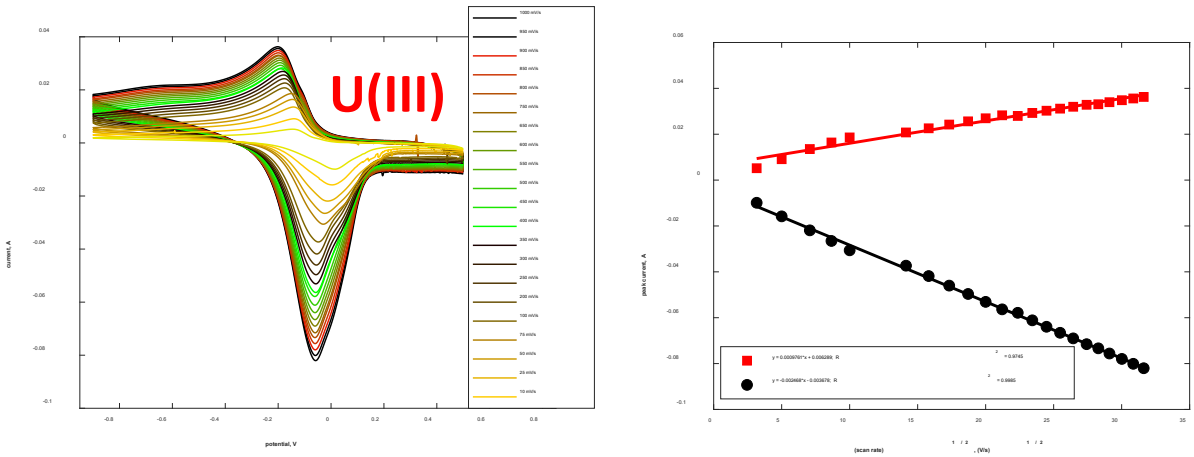

Figure 1: cyclic voltammograms of U 1 wt% U within a LiCl:KCL eutectic where scan rate was varied (left) and resulting Randles-Sevcik plots used to calculate diffusion coefficients (right)

Task 2 involved setting up and testing a spectroelectrochemical system within a glove box. This brought new capabilities to RPL where our team can now characterize transuranic species within salt melts. Identifying space, obtaining necessary approvals, and installing fibers and cables into the box was the primary focus of FY 19. Following complete installation, the team prepared a 1 wt% Pu sample within a LiCl:KCl eutectic and demonstrated successful spectroelectrochemical characterization of the TRU species. Pictures of the setup and examples of experimental data are presented in Figure 2.

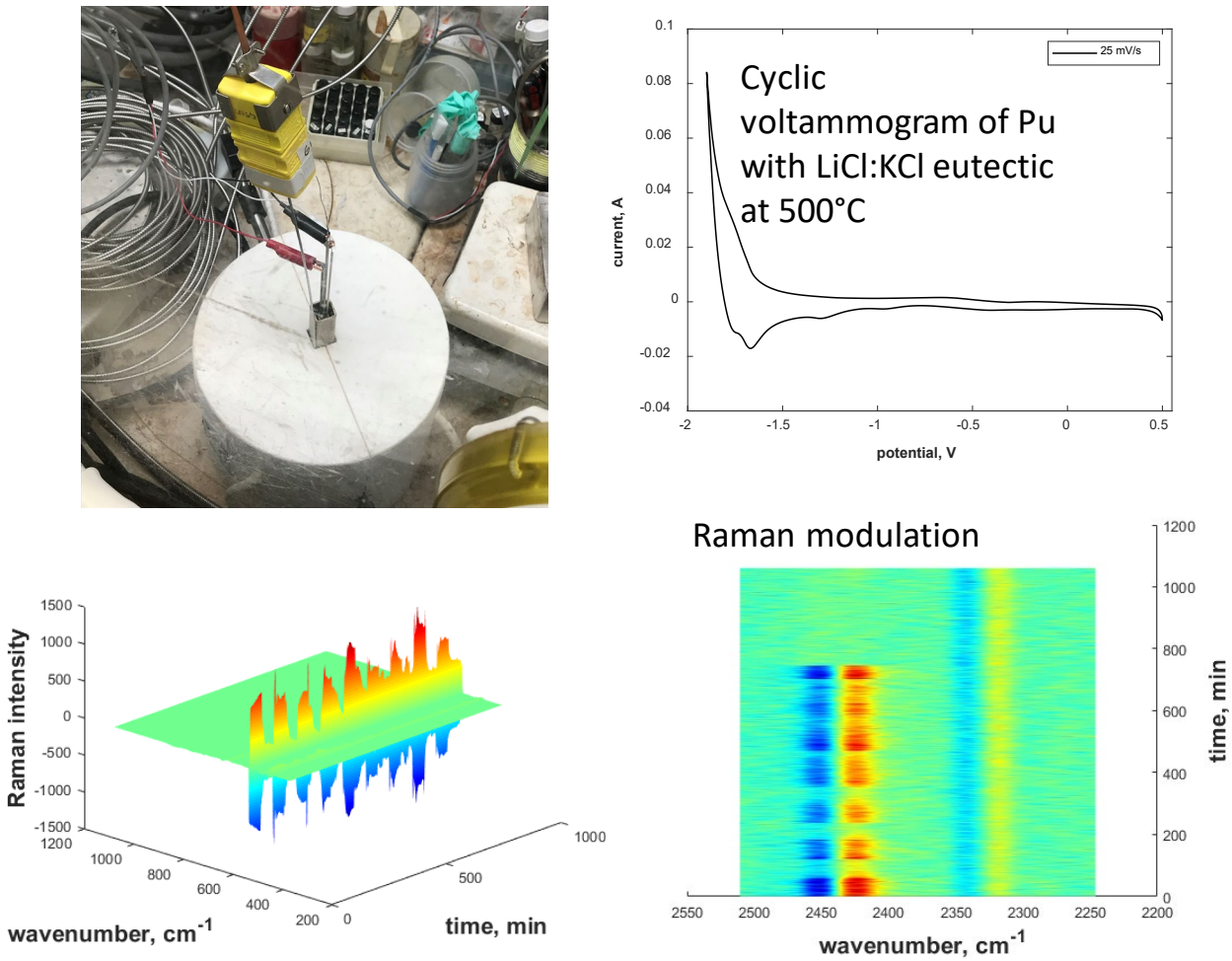

Figure 2: picture of glove box spectroelectrochemical setup (top left), electrochemical cyclic voltammogram of 1 wt% Pu within LiCl:KCl eutectic at 500°C (top right), and optical spectroscopy results of modulating Pu between the 3+ and 4+ oxidation states for UV-vis (bottom left) and Raman (bottom right)

2.0 Follow-on Work

This LDRD project was instrumental in allowing the team to develop new capabilities that have directly led to several proposals for follow-on funding and project work. This includes planned work with Flibe Energy under an existing GAIN project as well as proposals that have been submitted to support work with several industry partners.

The team is also actively writing manuscripts to detail the findings under this LDRD project. Manuscripts will address several literature gaps including the characterization of U diffusion coefficients and spectral fingerprints. Additionally, characterization of the Pu system within the salt melt will represent a major step forward as there is little to no literature on the electrochemical and spectroscopic characterization of Pu within chloride melts.

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