Advancements Toward Molten Salt Spectroelectrochemistry

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Objectives

To assess the molecular structures and chemistry that govern ***optical indicators*** of molten salt reactors (MSRs) by establishing molten salt spectroscopic monitoring capabilities and leveraging them for spectroscopic interpretation to develop online monitoring capabilities.

Introduction

➢ **Online Monitoring**
- Provides **electronic** and **vibrational** signatures to characterize and monitor in real-time species in the core
- Key benefits are nondestructive data collection, radiation worker dose reduction, and proliferation risk minimization

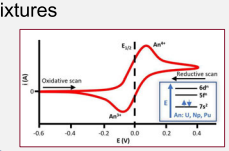
➢ **UV-Vis and Raman Spectroscopy**

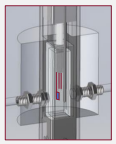
Produces **elemental specific** information for actinides [U, Pu] and other fission products

Probes the **chemical environment**, gives overall geometry and speciation information

➢ **Questions**
- What chemistry is taking place that can contribute to **corrosion and precipitation effects**?
- How does the concentration of the analyte affect the **speciation** of the metal in the melt?

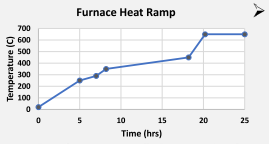
➢ **Plan**
- Measure the **diffusion coefficient** of U through molten salts
  - »Test method: $EuCl_3$-LiCl-KCl
- Use diffusion coefficients to inform molecular dynamic simulations of molten salt U mixtures





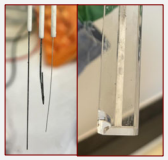
Methods and Validation

➢ **Goals**
- Validate all instruments inside the furnace at room temperature
- Engineer a reproducible system for electrodes so that they do not touch and can be inserted at high temperatures
- Implement a controlled heating and cooling ramp with logging capabilities

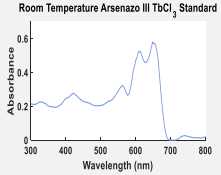


Mines furnace controlled temperature for heat ramp.

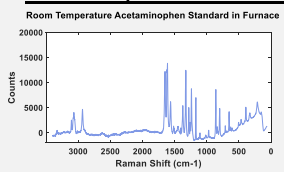
➢ **Heat Challenges**
- Quartz cuvettes chip with heat
- Electrodes become brittle after one experiment



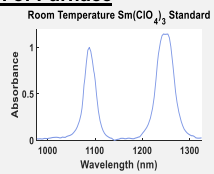
➢ **Room Temperature Validation of Furnace**



UV-Vis spectrum of arsenazo III complexed with $TbCl_3$ at a 0.49 mole ratio.



Raman spectrum of acetaminophen inside Mines furnace; integration time: 30 sec, 100% laser power, dark subtracted, baseline subtracted.

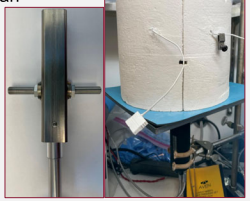


NIR spectrum of 0.3 M $Sm(ClO_4)_3$ inside Mines furnace.

Accomplishments
- Fiberoptic cables are optically aligned
- Raman laser focal point is within the 2mm cuvette pathlength
- Electrochemical cable calibration successful

Molten Salt System

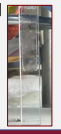
➢ **Experimental Design**
- Equipped for UV-Vis, Raman and electrochemical experiments
- Furnace reaches temperatures of 650°C
- Experiments performed in an inert atmosphere glovebox
- Corrosion resistant design

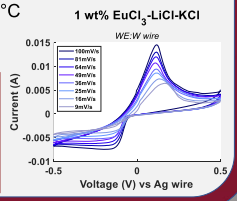


➢ **High Temperature Electrochemistry**

First molten salt electrochemistry melt successes
- Proper heat/cool ramps to 650°C
- Electrodes assembled with no short circuits
- Featureless background
- No corrosion of cell materials

Experiment details
- Quartz cell: 1g of salt





Future Work

➢ **Diffusion Coefficient**
- Determine the diffusion coefficients in reversible, quasi-reversible, and irreversible systems with SEC and compare to standard electrochemical techniques
- Determine the diffusion coefficient for Ln(III) in the LiCl-KCl eutectic melt
- Determine the diffusion coefficient for U(III) and U(IV) in molten salt mixtures
- Use results to inform molecular dynamics

➢ **High Ln(III) Loading Measurements**
- Determine possible redox potential changes with increasing Ln(III) concentrations in LiCl-KCl
- Determine diffusion differences at higher analyte concentrations

➢ **Raman Spectroscopy**
- Define the bonding characteristics and behavior of U with the salt constituents

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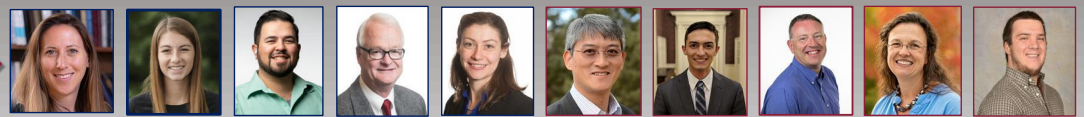
Project Team



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