NEUP Nuclear Energy University Program
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Novel Diamond-Based Spectroelectrochemical Sensors for Advanced Understanding of Radioactive Molten Salt Chemistry

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ABSTRACT:

This NEUP project will advance fundamental understanding of radioactive molten salt chemistry through determination of important redox and thermodynamic properties of nuclear fuel (Uranium(IV/III, U-238) and Plutonium(IV/III, Pu-239)) in both chloride- and fluoride-based (Cl- and F-) molten salts (LiF:KF, FLiNaK, LiCl:KCl, and NaCl:KCl). Such properties include the formal reduction potential (E°'), electron transfer stoichiometry, diffusion coefficient (*D*), activation energy (E_a), gibbs free energy (ΔG_{rxn}), enthalpy (ΔH_{rxn}), and entropy (ΔS_{rxn}). These will be determined as a function of molten salt composition and temperature. The knowledge gained through electrochemical, spectroscopic, and spectroelectrochemical studies will 1) lead to better corrosion control in the molten salt reactor (MSR) and 2) lay the foundation for safeguarding and accounting for nuclear material.

In general, MSRs offer several advantages over traditional light water reactors (LWRs). However, challenges remain before they can be feasibly implemented for nuclear power production. Specifically, corrosion of the reservoir which contains the molten salt and dissolved nuclear fuel. Fuel such as U or Pu is dissolved as Cl or F salt and can typically exist in both the III (*e.g.* UCl_3/UF_3) or IV (*e.g.* UCl_4/UF_4) oxidation state. However, the III state is strongly preferred because the IV state behaves as an oxidizing agent and is corrosive to the reservoir. As such, it is crucial to understand and quantify the oxidation state of U, Pu and other radionuclides present *in situ*. Spectroelectrochemical methods are capable of such quantification, provided the electrodes are capable of withstanding the molten salt conditions.

Throughout this project, boron-doped diamond (BDD) electrodes will be developed for spectroelectrochemical measurements in various molten salts. This will primarily include BDD in both single-crystalline and polycrystalline morphologies. BDD is one of the most rugged electrode materials available; the sp^3-hybridized carbon crystal lattice give the material its superior properties to withstand harsh environments due to its inertness. This combined with the ability to fabricate BDD for spectroelectrochemical measurements make it an attractive electrode material for *in situ* characterization of molten salt structure and determination of important redox and thermodynamic properties.

In the first phase of this project, corrosion/fouling of the BDD electrode surface will be studied. This will be completed in radioactive molten salt environments including U-238 and Pu-239. Experiments at low radionuclide activity (μCi) will be completed at UNLV while those at higher radionuclide activity (mCi) will be completed at PNNL. Exposure to a high energy gamma/neutron source will also be completed at PNNL. To our knowledge, the corrosion of diamond electrodes have never been studied under such conditions. In the second phase of the project, a custom-built spectroelectrochemical cell will be used for determination of the redox and thermodynamic properties listed above.

This research will be completed by a UNLV Radiochemistry PhD student, a UNLV undergraduate student, and UNLV post-doctoral researcher that will be afforded the opportunity to travel to PNNL for certain experiments. This experience combined with the publication potential of this NEUP make it an attractive one for both cutting-edge research and the development of next generation radiochemists.