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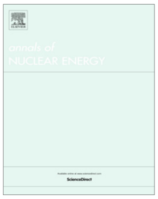

Electrochemical behavior of dysprosium and lanthanum in molten LiF-NaF-KF (Flinak) salt

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ABSTRACT

Cyclic voltammetry (CV) analysis was performed to determine the behavior of Dysprosium (Dy) and Lanthanum (La) in molten FLiNaK salt (LiF-NaF-KF: 46.5–11.5–42 mol%) and to understand the mechanism driving the electrochemical reactions. The goals of these experiments are to understand the behavior of contaminants and nuclear fission products related to the Fluoride Salt-cooled High-Temperature Reactor (FHR) concept, and to generate a reliable source of electrochemical properties in fluoride salts. The tests were performed at 600–650–700 °C for Dy and 650–700–750 °C for La in a glassy carbon crucible contained within an inert argon atmosphere. A platinum wire quasi-reference electrode exhibited stable potential throughout experiments and allowed for thermodynamic reference between test species and known redox couple (F_2/F^-). The electrochemical reduction of Dy and La (assumed three-electron, single-step transfer) maintained quasi-reversibility at the solid tungsten electrode for scan rates of 160 mV/s and below during CV. For scan rates of 200 mV/s and above, significant deviation from reversibility was evidenced by increasing separation between anodic and cathodic peaks. For Dy^{3+}, the diffusion coefficient was calculated as $\mathcal{D}\ [cm^2/s] = 0.0538 * \exp(-6193/T(K))$ and the activation energy $E_a = 51.5$ kJ/mol. The diffusion coefficient of La^{3+} was calculated as $\mathcal{D}\ [cm^2/s] = 14.252 * \exp(-15285/T(K))$ and the activation energy $E_a = 127$ kJ/mol. The apparent potential of the La^{3+}/La^0 redox reaction was determined as $E^{0*}[V\ vs.\ K^+/K] = -0.368 + 0.001119 * T[K]$ and for the Dy^{3+}/Dy^0 reaction as $E^{0*}[V\ vs.\ K^+/K] = 0.0626 + 0.00088 * T[K]$.

1. Introduction

The Fluoride High-Temperature Reactor (FHR) is an emerging nuclear reactor concept that combines desirable characteristics of previous reactor developments. The FHR is also a bridge in technology between today's light water reactors (LWRs) which use solid fuel and water coolant, to molten salt reactors of the future that utilize molten salt coolant and dissolved liquid fuel. The FHR design incorporates low-pressure liquid fluoride salt coolant, coated particle fuel, and an entirely passive decay heat removal system. FHRs operating at very high temperatures increase the thermal energy transfer and subsequently the efficiency.

Research in fluoride salts was popular in the U.S. during the Molten Salt Reactor Program (1958–1976) at Oak Ridge National Laboratory. The program operated the Aircraft Reactor Experiment in 1954 and the Molten Salt Reactor Experiment (MSRE) in 1964–1969 (Rosenthal et al., 1969). Considerable effort was dedicated to identifying candidate reactor designs and adequate materials. These efforts considered molten fluoride salt, specifically ^7LiF-BeF_2 ("Flibe"), as a viable primary coolant for the MSRE. Due to the high toxicity of beryllium in Flibe, LiF-NaF-KF ("Flinak") is used as a surrogate of Flibe and considered as a secondary or tertiary reactor coolant. The successful operation of the MSRE proved that molten fluoride salt reactors can be reliably constructed and controlled.

The FHR concept requires a primary coolant cleanup system to mitigate the contamination from leaking fission products and ingress of moisture and oxygen. This system should allow online processing of the primary coolant for continuous reactor operation. As an ionic fluid, molten fluoride salts lend themselves to electrochemical-based separation methods for purification. Pyroprocessing-based methods, combined with molten salt/liquid metal extraction processes, seem to be a reliable path towards online coolant purification (Straka et al., 2011).

Certain contaminating species encountered in the operation of the FHR may pose significant problems to different systems such

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as neutronics, heat transfer, decay heat generation, corrosion, and redox control. The first step toward the development of a cleanup system must be a fundamental understanding of the physical properties of significant species that may be encountered throughout the operation of the FHR. Then, data from experiments and models can help identify a suitable cleanup method which can be tested and verified. This is the pathway for development of the FHR cleanup system, as illustrated Fig. 1.

The thermodynamic properties obtained from this work play an important role in tabulating physical data of fluoride salts such as diffusion behavior, redox potential, and reaction mechanism. For example, this research is critical to many molten fluoride salt applications outside of nuclear engineering such as solar energy storage, corrosion, and benchmarking electrochemical fluoride research in general. Most molten salt electrochemical research has been dedicated to experiments in molten chlorides such as LiCl-KCl (Chuchvalcova Bimova et al., 2008; Huang et al., 2014; Straka and Tulackova, 2008). These experiments help establish common practices for molten salt research. However, fluoride salts pose unique challenges including higher boiling points and higher corrosivity. More recent advances in fluoride salt chemistry have been the result of a renewed interest in molten salt technologies including the FHR (Straka et al., 2011; Shim et al., 2018; Korenko et al., 2018; Hoover et al., 2014, 2016; Olson et al., 2009).

While the mechanism and redox potentials of lanthanides in fluoride melts are well-reported in literature, data regarding the kinetics of such reactions are severely lacking and mainly limited to nuclear fuel elements such as uranium and thorium. Furthermore, comparison of results is hindered due to a lack of consensus on methods of analysis as well as the variation in experimental setups and reference electrodes. Much of the current literature regarding kinetic behavior in fluoride melts is restricted to structural material corrosion.

The mechanism and redox potentials for many actinides and lanthanides in Flinak, Flibe, and LiF-CaF_2, were investigated against a Ni/Ni^{2+} reference electrode and reported by Bimova, et al. (Chuchvalcova Bimova et al., 2008). Huang et al. investigated the diffusion behavior of Eu (another lanthanide) in Flinak and determined the diffusion coefficient and activation energy for the soluble-soluble system resulting in $D = 0.8\text{–}2.41 \times 10^5\ cm^2/s$ and $E_a = 38.9 \pm 4.6$ kJ/mol for Eu(III) and $D = 1.25\text{–}2.98 \times 10^5\ cm^2/s$ and $E_a = 34.7 \pm 1.6$ kJ/mol for Eu(II) (Huang et al., 2014). Straka et al. reported a 2-step reduction mechanism for Nd, Gd, and Eu but indicated that metal deposition was impossible to detect due to hindrance from melt decomposition (Straka and Tulackova, 2008). The observed 2-step mechanisms for Nd and Gd in Flinak are confirmed by Shim et al. (2018) Korenko et. Al. proposed a 2-step mechanism for the reduction of Sm in Flinak as a single-electron transfer followed by a two-electron transfer but only the first step of the reduction was observed (Korenko et al., 2018). Other studies have investigated actinides and lanthanides in chloride salts using similar methods. Hoover et. al. identified diffusion coefficients, reduction potentials, and activity coefficients of UCl_4 and UCl_3 as well as Zr in LiCl-KCl (Hoover et al., 2014, 2016).

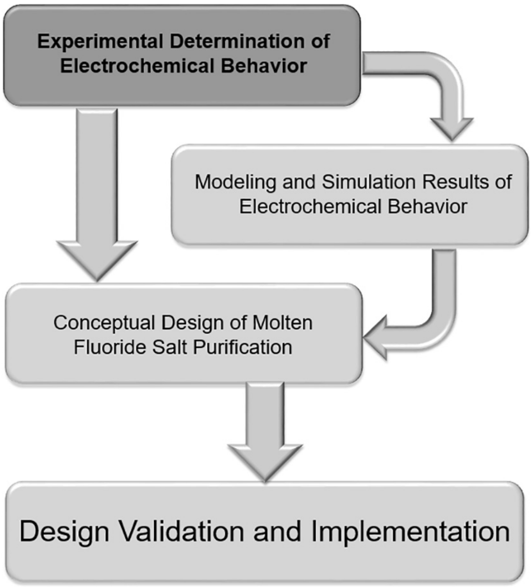

Fig. 1. Roadmap for the development of a fluoride salt purification system.

This paper focuses on the procedure and analysis of cyclic voltammetry (CV) experiments. Cyclic voltammetry is a powerful electroanalytical technique that is used to study a variety of redox reactions, determine product stability, detect the presence of intermediate species, and characterize electron transfer kinetics and reaction thermodynamics. Thermodynamic data can be extracted from a CV curve due to its potential-controlled nature. Also, since the scan rate of the CV test considers the time factor of the experiment, kinetic parameters can be calculated as well. Thus, CV is a widely popular method and can be used to compare calculated properties from other electrochemical methods.

These studies focus on the determination of fission product and contaminant properties in molten Flinak using experimental electrochemical data. The work presented here focuses on behavior of dysprosium and lanthanum, which are both lanthanides and common fission product, and were chosen to represent such portion of the elements generated throughout reactor operation. The system was tested at temperatures of 650–700-750 °C for La and 600–650–700 °C for Dy. In between each electrochemical test, a cleaning procedure was performed aimed towards restoring the molten salt system to its initial equilibrium state. This cleaning procedure consists of applying a "cleaning potential" to the system for a chosen amount of time. The cleaning potential is chosen as a value slightly more positive than the potential window of the test species. This applied potential oxidizes the remaining layer of deposited metal on the electrode surface back into solution. Any remaining metal deposited on the electrode will alter the initial conditions of the next test and the data would not be reliable.

To successfully analyze the electrochemical behavior of a test species in Flinak salt, the redox reaction must occur within the electrochemical window of the molten salt. At sufficiently low potentials, cations constituting the salt will reduce in order of more negative Gibbs free energy of formation (K → Na → Li) while the anion F^- will oxidize to F_2 at a more positive potential (Hoover et al., 2014). The Gibbs free energy of formation for fluorides also demonstrates the ability of tungsten to act as an inert electrode, as the free energy value is much more positive than other materials that may be tested.

2. Experiment

2.1. Chemicals

The selected electrolyte for this research is molten LiF-NaF-KF salt (46.5–11.5–42 mol%, respectively). Available thermodynamic data for molten salts, including Flinak and Flibe, are found in a 2006 report from Oak Ridge National Laboratory (Hoover et al., 2016). The salt was prepared in the lab by weighing the constituent salts in the given eutectic ratio. Once weighed, the dry mixture was mixed and stirred by hand in the test crucible. Mixing and testing were carried out in a glove box from Inert Technology with a controlled argon atmosphere that maintained the O_2 and H_2O