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Review of Cyclic Voltammetry Measurements for Uranium in FLiNaK Molten Salt

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Abstract

The electrochemical behavior of uranium FLiNaK molten salts is explored, focusing on cyclic voltammetry (CV) as a powerful tool for redox characterization and diffusion studies. Through a comprehensive review of recent research, the study highlights the significance of CV in understanding electrode kinetics, material compatibility, and process optimization in molten salt environments. The findings underscore the potential of FLiNaK molten salt reactors in advancing nuclear energy technologies, fuel processing, and waste management strategies. Collaborative interdisciplinary efforts are emphasized to address challenges and accelerate innovation in electrochemical methods for nuclear applications.

Keywords: Uranium Fluoride, Cyclic Voltammetry, Molten Salt

1 Introduction

In recent years, research on molten salt technologies has garnered significant attention in the field of nuclear energy, driven by the potential to revolutionize reactor design, fuel processing, and waste management. Among the various molten salt systems under investigation, uranium-based fluoride molten salts have emerged as a promising avenue for advancing next-generation nuclear technologies. This literature review aims to provide a comprehensive overview of recent advancements in uranium molten salt research and their implications for the nuclear energy sector. A previous review was given by Hege et al. [1]. Their review gave a large overview of cyclic voltammetry (CV) for uranium-containing alkali metal halide molten salts. This review will seek to dive deeper into the specifics for CV of actinide-containing fluoride molten salts and the differences in techniques and results between studies. This review will focus on FLiNaK.

Molten salt reactors (MSRs) represent a distinct class of nuclear reactors that utilize liquid fluoride or chloride salts as both the coolant and the fuel medium. Unlike traditional water-cooled reactors, MSRs offer several inherent advantages, including improved safety features, higher operating temperatures, and enhanced fuel cycle efficiency [2]. Within this context, uranium molten salt systems present unique opportunities for addressing key challenges in nuclear energy, such as reactor sustainability, proliferation resistance, and waste minimization.

One of the primary advantages of uranium molten salt systems is their ability to efficiently utilize a wide range of fissile and fertile materials, including thorium and recycled nuclear waste. By operating in the thorium-uranium fuel cycle, MSRs can potentially leverage thorium’s abundant reserves to produce sustainable and proliferation-resistant nuclear energy [3]. Moreover, the inherent online reprocessing capability of molten salt reactors enables continuous removal of fission products and the extraction of valuable isotopes, thereby minimizing waste generation and enhancing resource utilization.

Electrochemistry plays a crucial role in uranium molten salt systems, particularly in the context of fuel processing and reprocessing. Electrochemical techniques, such as molten salt electrolysis, offer efficient means for separating and purifying uranium and other actinides from the molten salt stream. These processes not only facilitate the extraction of valuable fuel materials but also enable the transmutation of radioactive isotopes, contributing to waste management and nuclear non-proliferation efforts [4].

The findings from uranium molten salt electrochemistry research have significant implications for the future of nuclear energy, with potential applications ranging from small modular reactors to advanced nuclear fuel cycles. By providing
insights into processing technologies and electrochemical techniques, this literature review seeks to contribute to the broader discourse on the role of molten salt systems in shaping the next generation of nuclear power.

1.1 FLiNaK

FLiNaK is a eutectic mixture of LiF, NaF, and KF that has garnered much attention in the realm of molten salt reactors and other applications such as thermal energy storage [5]. This attention is due to its favorable thermal properties. Uranium is mixed with salt typically as UF₄ and then purified. One purification method that has been studied is through electrochemical methods. Zuo et al. published one such purification method that employed the redox of hydrogen on a nickel electrode [6]. They found that compared to traditional purification methods such as HF gas, high purification efficiency was achieved. This study was done on FLiNaK without uranium and would need to be studied to find if it has the same efficiency when uranium is introduced into the salt. In addition to salt purification, other electrochemical methods have been studied specifically for fuel processing for separating uranium from FLiNaK. This is an important aspect of waste management for nuclear power.

2 Methods

Cyclic voltammetry (CV) is a high-performance electrochemical method used to investigate redox behavior in solution species. The method involves applying a linear varying potential to the electrochemical cell and measuring the current response. Cyclically sweeping the potential between the two limits, usually at a controlled scanning speed, to generate the voltammogram, which provides information on the electrochemical reactions taking place at the interface between the electrode and the solution. When it comes to molten salts, CV is a useful tool for studying the electrochemical behavior of species in liquid salt environments at high temperatures. According to Bard et al., it is one of the most widely used electrochemical techniques [7].

CV in the electrochemical measurements of molten salts provides several key benefits and insights, such as:

1) Redox characterization: CV allows researchers to characterize the redox behavior of species in molten salt systems, such as determining oxidation and reducing potentials, and identifying electroactive species with their concentration dependencies.

2) Electrodes Kinetics: By analyzing the shape and characteristics of voltammogram experiments, information on electrode kinetics (e.g., electron transfer rates, reaction mechanisms) can be found, which are essential for understanding and optimizing electrochemical processes within molten salt environments.

3) Materials compatibility: CV allows for the measurement of material stability and material resistance over several potential cycles, helping to select and design the appropriate electrode materials for use in molten salt applications.

4) Process optimization: By understanding and manipulating experimental parameters (e.g. scan rate, temperature, etc.), one can optimize electrochemical processes and achieve desired outcomes more efficiently and effectively.

This review will focus on CV measurements made on uranium based FLiNaK systems and is limited to the past 15 years. Several works have been completed that have studied uranium FLiNaK salt with CV. Table 1 displays the works that will be reviewed. This review is limited to uranium fluoride analytes.

3 Results and Discussion

In 2019, Han et al. studied the oxidation of UF₄ in FLiNaK salt via oxygen sparging [8]. They found that the UF₄ converted to UO₂F₂ and confirmed this via CV. These CV measurements used a scan rate of 0.1 V/s using an electrode setup as shown in Table 1. The result from their CV is shown in Figure 1. Additional CV measurements for before and after oxidation are found in the work by Han et al.
Table 1: Overview of Selected Works.

<table>
<thead>
<tr>
<th>Author</th>
<th>Analyte</th>
<th>WE/CE/RE</th>
<th>Temp (C)</th>
<th>Crucible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Han</td>
<td>UF₄</td>
<td>Pt/Au/Pt</td>
<td>550</td>
<td>Pt</td>
</tr>
<tr>
<td>Jiang</td>
<td>UF₄</td>
<td>W/Graphite/Ni</td>
<td>550</td>
<td>Graphite</td>
</tr>
<tr>
<td>Korenko</td>
<td>UF₄</td>
<td>Ni/Glassy Carbon/Ni</td>
<td>530</td>
<td>Glassy Carbon</td>
</tr>
<tr>
<td>Hoover</td>
<td>UF₄/UF₃</td>
<td>Ni/Inconel/Glassy Carbon</td>
<td>500</td>
<td>Ni</td>
</tr>
<tr>
<td>Shaltry</td>
<td>UF₃</td>
<td>Ta/Ta/Ni</td>
<td>500-600</td>
<td>--</td>
</tr>
</tbody>
</table>

Figure 1: Cyclic voltammogram of FLiNaK with 1.5 wt% UF₄. WE area: 0.165 cm². Data digitized using WebPlotDigitizer v4.7 [9] from Ref. [8].

The diffusion coefficient of U(III) was not calculated in this study, so it will be calculated here according to the Berzins-Delahay equation assuming electrochemical reversibility [7]:

\[ I_p = -0.6105 \times \left( \frac{n^3F^3}{RT} \right)^{1/2} AD^{1/2} CV^{1/2} \] (1)

where \( I_p \) is peak current, \( n \) is number of electrons transferred, \( A \) is surface area, \( D \) is the diffusion coefficient, \( C \) is concentration, \( v \) is the scan rate, \( F \) is Faraday’s constant, \( R \) is universal gas constant, and \( T \) is Temperature.

From Figure 1, the peak current for the uranium electrodeposition is approximately -0.15 A/ cm². The salt was prepared with 3.15g UF₄ and 31.85g FLiNaK, and given the density of the mixed salt to be approximately 2.077 g/cm³ [10], the concentration of uranium in the salt is 0.000594 mol/cm³. With this value and Eq. (1), the calculated diffusion coefficient is \( 4.83 \times 10^{-7} \) cm²/s. It should be noted that the analysis of this system is complicated due to the many processes occurring including the diffusion of U⁴⁺ to the electrode surface, the reduction of U⁴⁺ to U³⁺, the diffusion of U³⁺ away from the electrode surface, and the reduction of U³⁺. A similar analysis was done by Shen et al. [11] and the reader is referred to their work for a resource on existing analysis approaches for electrodeposition.

A similar study was conducted by Jiang et al. [12] in 2017. Along with CV, they also performed chronopotentiometry and found a diffusion coefficient of \( 1.339 \times 10^{-6} \) cm²/s for U(IV) in FLiNaK at 550 °C. Their salt used 1.96 wt% UF₄ which is higher than the salt used by Han et al. [8]. The result of their CV with a scan rate of 0.1 V/s is shown in Figure 2. This study also found a method to separate U from FLiNaK via electrowinning which is an electrochemical process used to extract metal ions from a solution using an external source of electricity. A notable strength of this study lies in its comprehensive approach, combining CV with chronopotentiometry to explore electrochemical behavior and diffusion properties.

Another study focusing on the separation of uranium from FLiNaK was performed by Korenko et al. [13] in 2013. They focused on the reduction of U⁴⁺ ions to metal. The result of their CV is shown in Figure 3.
Their salt used a higher uranium percent than the previous two studies with 2.58 wt% UF₄. Based on the results of the CV, it was concluded that the rate of the electrode reaction exceeded the rate of mass transfer, but that was not enough to say it was diffusion controlled. The peak potentials are slightly shifted as compared to Jiang et al. [12] which is likely due to the change in uranium percent, temperature, and electrode materials. Furthermore, the decay of the U deposition peak seems to not follow the usual decay. The high concentration used in this study is not ideal for CV measurements.

Diffusion coefficients for this study were calculated by the authors and found to be $1.64 \times 10^{-5}$ cm²/s for U⁴⁺ and $1.76 \times 10^{-5}$ cm²/s for U³⁺. These are an order of magnitude greater than those found by Jiang et al. [12] and two orders greater than calculated for Han et al. above. This could be due to surface area growth or natural convection which are common non-idealities at higher concentrations. The 20-degree temperature difference is not enough to explain this difference, so more data is necessary to confirm these studies.

Hoover et al. [14] studied both UF₄ and UF₃ as shown in Figure 4. The purpose of their study was to look at separation of uranium from FLiNaK in two forms. The first salt with UF₄ used 0.8 mol% and the second with UF₃ used 1.1 mol%. A strength of this study is the comparative analysis of two uranium forms, providing insights into separation techniques. Differences in peak potentials, shapes, and currents between UF₄ and UF₃ provide valuable information about the reactivity and stability of uranium species in the molten salt environment. However, a weakness is the limited exploration of the underlying mechanisms driving the separation processes, which could enhance the understanding of the electrochemical behavior in uranium FLiNaK systems.

The last study reviewed comes from Shaltry et al. [15] from 2020. The purpose of this study was to determine kinetic parameters and diffusivity of uranium (UF₃) in FLiNaK. Results of this study are shown in Figure 5. This was the only study that showed scans at various temperatures. The diffusion coefficient was calculated by the authors. It was $2.04 \times 10^{-5}$ cm²/s at 773 K and $5.27 \times 10^{-5}$ cm²/s at 873 K. The first value was off the reported value from the study by Korenko et al. [13] by only $0.28 \times 10^{-5}$ cm²/s. A strength of this research is the comprehensive analysis of temperature effects on diffusion coefficients, offering valuable insights into the thermal dependence of electrochemical processes. The peaks seem to be more stretched than the other studies which could be due to IR drop.
Figure 5: Cyclic voltammograms of UF₃ in FLiNaK with a scan rate of 50 mV/s. Temperatures are in K. WE area: 0.1425 cm². Data digitized using WebPlotDigitizer v4.7 [9] from Ref. [15].

A summary of the results described above is shown below in Table 2. The differences between the studies yielded different results and it is important to understand how these differences affected the data. The diffusion coefficients for Hoover et al. were not calculated in their work or this work due to insufficient information.

The main difference between the studies is the composition of uranium in the salt. The limited range of salt compositions and the range of diffusion coefficients questions the generalizability of their findings to a broader spectrum of uranium concentrations. Another potential weakness is the limited varying of scan rates. Only Hoover et al. [14] varied scan rates.

There are numerous gaps and opportunities for improvement in the utilization of electrochemical methods. One notable gap that has been highlighted in the literature is the necessity for a more systematic exploration of how experimental parameters impact electrochemical behavior. This was demonstrated briefly in the study conducted by Jiang et al. [12]. The differences in the diffusion coefficients were explained to be because of experimental conditions. By conducting comprehensive parametric studies, researchers can enhance their understanding of redox reactions and diffusion processes in FLiNaK. This, in turn, will improve the predictive capabilities of electrochemical models.

Additionally, there is a need for more extensive comparative studies, as exemplified by the work of Korenko et al. [13]. These studies would evaluate the performance of different electrochemical techniques in characterizing uranium behavior in FLiNaK. By highlighting the strengths and limitations of methods such as cyclic voltammetry, researchers can optimize experimental procedures and data interpretation strategies. This will enhance the reliability of electrochemical analyses in uranium molten salt systems. Through combining electrochemical results with theory, researchers can gain insights into complex phenomena such as mass transport limitations and electrode kinetics. This will ultimately lead to more efficient strategies for fuel processing and reprocessing in molten salt reactors.

Table 2: Summary of Results.

<table>
<thead>
<tr>
<th>Author</th>
<th>Analyte</th>
<th>Analyte (wt.%)</th>
<th>Temp (C)</th>
<th>Scan Rate (V/s)</th>
<th>Peak Current (A)</th>
<th>Diffusion Coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Han</td>
<td>UF₄</td>
<td>1.5</td>
<td>550</td>
<td>0.1</td>
<td>0.102</td>
<td>4.83 × 10⁻⁷ (U³⁺)</td>
</tr>
<tr>
<td>Jiang</td>
<td>UF₄</td>
<td>1.96</td>
<td>550</td>
<td>0.1</td>
<td>0.08</td>
<td>1.339 × 10⁻⁶ (U⁴⁺)</td>
</tr>
<tr>
<td>Korenko</td>
<td>UF₄</td>
<td>2.58</td>
<td>530</td>
<td>0.05</td>
<td>0.92</td>
<td>1.64 × 10⁻⁵ (U⁴⁺) 1.76 × 10⁻⁵ (U³⁺)</td>
</tr>
<tr>
<td>Hoover</td>
<td>UF₄</td>
<td>6.0</td>
<td>500</td>
<td>0.025</td>
<td>0.38 /cm²</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>UF₃</td>
<td>7.2</td>
<td>500</td>
<td>0.025</td>
<td>0.68 /cm²</td>
<td>---</td>
</tr>
<tr>
<td>Shaltry</td>
<td>UF₃</td>
<td>7.2</td>
<td>500</td>
<td>0.05</td>
<td>0.58 /cm²</td>
<td>2.04 × 10⁻⁵ (U³⁺)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.05</td>
<td>0.9 /cm²</td>
<td>5.27 × 10⁻⁵ (U⁴⁺)</td>
</tr>
</tbody>
</table>

^Calculated in this work
Lastly, fostering interdisciplinary collaborations is crucial for addressing the multifaceted challenges in uranium FLiNaK salt systems, as emphasized in the study by Hoover et al. [14]. Collaboration between electrochemists, materials scientists, and nuclear engineers is essential. Researchers can accelerate innovation in electrochemical methods for nuclear applications by leveraging diverse expertise and perspectives.

The insights gained from these cyclic voltammetry studies in uranium FLiNaK molten salt systems hold significant promise for practical applications in various areas of nuclear energy and materials science. The understanding of the electrochemical behavior of uranium species in FLiNaK environments is crucial as these studies pave the way for advancements in fuel processing, reactor design, and waste management strategies. With the insights gained from electrochemical studies, researchers and industry professionals can advance the development of next-generation nuclear technologies and contribute to the sustainable and safe utilization of molten salt reactors in the nuclear energy sector.

4 Conclusions

In this review, the synthesis of findings from uranium FLiNaK studies has revealed the critical role of cyclic voltammetry measurements in showing the electrochemical processes governing uranium FLiNaK systems. By highlighting the importance of understanding mass transfer limitations, electrode reactions, and separation techniques, this review contributes to the advancement of knowledge in optimizing uranium extraction and purification methods in molten salt environments. In this review, a new diffusion coefficient for UF₄ was also calculated from past experimental data.

The collective findings from the studies underscore the significance of cyclic voltammetry measurements in explaining the electrochemical behavior of uranium in FLiNaK salt systems. These insights provide advancements in fuel processing, purification techniques, and waste management strategies within the realm of molten salt reactors and nuclear energy applications. These Collaborative efforts could also improve the quality of measurements (minimize surface area growth, ohmic drop effects, etc.) by leveraging others’ expertise and drive the optimization of uranium extraction and processing in molten salt environments for the advancement of next-generation nuclear technologies.

5 Acknowledgements

AI tools were used in the writing of this paper including ChatGPT and PDF.ai. All plots were recreated, and original plots should be used for further analysis.

6 References


