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Electrochemical measurement of high concentrations of UCl_3 and $GdCl_3$ in molten LiCl-KCl eutectic

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ABSTRACT

Electrochemical methods have been developed to measure metal ion concentrations in spent nuclear fuel electrorefiner by correlating concentration with current response. Analytes UCl_3 and $GdCl_3$ were studied in LiCl-KCl eutectic solvent at 773 K. A mixture matrix, which consisted of varying concentrations of UCl_3 and $GdCl_3$ from 1 to 10 wt% and from 1 to 3 wt%, respectively, was tested. Optimized normal pulse voltammetry (NPV) measurements were made on this mixture matrix and used for the concentration correlations. The accuracy of the prediction was improved by including solution resistance compensation and minimizing the working electrode surface area. The presence of $GdCl_3$ showed no effect on the U^{3+} NPV reduction current, but high U concentrations affected the Gd^{3+} NPV reduction current. This is speculated to be due to increased migrational current in the molten salt mixture. The average relative measurement errors obtained were 1.6% and 2.7% for UCl_3 and $GdCl_3$ respectively.

1. Introduction

Pyroprocessing is currently being used at Idaho National Laboratory (INL) for treatment of irradiated, sodium bonded fuel from the Experimental Breeder Reactor-II in two electrorefiners operated in the Fuel Conditioning Facility. The Republic of Korea (ROK) is also researching the same process technology for potential inclusion in commercial facilities aimed at processing spent pressurized water reactor fuel. Implementation of pyroprocessing in non-weapons states such as the ROK will require development and implementation of international safeguards by the International Atomic Energy Agency (IAEA). Electrorefiners are used to separate U/TRU metal from metallized spent nuclear fuel, which may eventually lead to production of recycled fuel for fast reactors. Such electrorefiners contain a pool of molten salt consisting of eutectic LiCl-KCl, 5–10 wt% UCl_3, and variable concentrations of TRU and fission product chlorides [1]. While commercial system scale has not been determined or published, the INL electrorefiners are considered engineering scale and each contain about 500 kg of salt. Pu inventory in each electrorefiner can reach 25 kg, which is equivalent to over three significant quantities of Pu by definition of the IAEA. Electrorefiners used for commercial scale pyroprocessing would certainly be larger and likely contain more salt. Thus, electrorefiners should be considered a high-risk target for diversion of Pu and adequately safeguarded. Currently, the IAEA has no reference approach for safeguarding a pyroprocessing facility, as there have been no facilities built in non-weapons states subject to international safeguards. The traditional international safeguards approach is based on nuclear material accountancy, which requires the ability to perform inventories of special nuclear material (including Pu) to verify operator/state declarations. Once the spent fuel is loaded into an electrorefiner and processed, its item-based identify vanishes. Some of the Pu partitions into the salt phase as $PuCl_3$, some remains in the fuel basket (anode), and some can be deposited onto a cathode [2]. Depending on how the operator runs the process, the rules for partitioning can be changed to meet the operator's goals. Both the fuel basket and cathode can be removed, counted, weighed, and assayed as a unique item. The salt, however, remains in the electrorefiner over many fuel processing campaigns and cannot be completely removed. Therefore, it is essential to be able to determine the amount of Pu in the salt in situ at any point in time. INL tracks Pu in the salt by sampling and using a mass tracking application [3]. This approach is slow, due to the long times needed for sample analysis, and does not meet the accuracy and timeliness requirements for international safeguards, so there is a need for the development of a better method - preferably one that works in real time or near real time.

The electrochemical properties of molten eutectic LiCl-KCl

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containing fission product and actinide chlorides can be utilized for developing measurement methods. Such methods require only three robust rods or wires that can be immersed into the molten salt to measure the concentration of metal ions in the molten salt mixture in real-time. Research on electrochemical sensor development in such salt mixtures has been the subject of several recent publications [4–15]. However, a challenge that arose during previous research is that multi-element correlations in a mixture with high concentration of UCl_3 could not be achieved, and the correlations at low concentrations needed to be improved. This is important because the UCl_3 concentration in the electrorefiner can often go up to about 10 wt%. In addition, the overall correlations must be improved for better concentration prediction.

The most widely applied electrochemical methods in molten salt systems are cyclic voltammetry (CV), chronoamperometry (CA), and normal pulse voltammetry (NPV). CV appears to be the most popular electrochemical method, as it yields both qualitative and quantitative information about the analyte. There are typically two current peaks in the cyclic voltammogram for an analyte - an oxidation peak and a reduction peak. The relationship between the reduction peak current and analyte concentration for deposition of metal on solid electrode is described by the Berzins-Delahy equation [16]. The peak current and concentration are directly proportional if all the other terms are kept constant (surface area, scan rate, diffusion coefficient, number of electrons transferred, and temperature). A disadvantage of CV method is that it scans a wide range of potentials, causing multiple electrochemical reactions to occur with each cycle. The working electrode will be under deposition potential for a significant amount of time, as a result, electrode surface growth is inevitable. When surface area growth occurs, it skews the peak current versus concentration correlation. CA and NPV are similar methods that can be used in more limited potential ranges and optimized to mitigate WE area growth. In CA, the potential is kept constant, and the diffusion limited current response is described by the Cottrell equation [17]. The potential applied needs to be negative enough to create a large overpotential so that the reaction kinetics would be fast enough for the electrochemical reaction to be diffusion limited. The limitation of CA is that one needs to know the reduction potential of each species precisely to applied the correct potential, and it fails to distinguish between two or more reduction processes occurring simultaneously. Thus, it only works for measuring concentration of a single analyte in a molten salt mixture.

NPV is comprised of a series of CAs with progressively changing applied potential. Each CA is called a pulse. The time that potential is applied is the pulse time. The magnitude of potential deductions is the step potential. Between each pulse, the potential is increased back to a base potential, which should cause the deposited metal to be oxidized back into the molten salt. The time spent at base potential is called the interval time. A current sample is taken at the very end of each pulse; therefore, and thus the pulse time is used for the time variable in the Cottrell equation. When the applied potential is negative enough, all pulses thereafter would be purely diffusion controlled, which means the sampled current will be invariant. As a result, a plateau would occur in an NPV potential vs current plot. The pulse time is very short, so there would be insignificant working electrode area growth. Unlike CA the plateau indicates the reaction is diffusion limited; thus, the Cottrell equation can be applied. If there were more analytes present, the NPV plateau for the ion that has the least negative reduction potential would appear first. When the applied pulse potential reaches the reduction potential for the next ion, a second plateau would start to occur and build on top of the first plateau, and so on for any additional ions.

The U/Mg system was studied in the authors' previous research [18], where $MgCl_2$ was used as surrogate for $PuCl_3$ due to the similar reduction potentials between the two elements. Salts used in this study were UCl_3 and $GdCl_3$. Spent fuel contains a significant concentration of rare earth fission products. Gd can be considered to be representative of those fission products, given the similar electrochemical properties of the rare earth chlorides. This system is more challenging than the previous one studied, because the reduction potential of Gd^{3+}/Gd is more negative than Mg^{2+}/Mg (Table 1). Thus, the U^{3+}/U reduction plateau needs to be kept flat for a wider range of potentials. A number of modifications were made to the method to overcome this challenge, including compensating for electrolyte resistance, reducing working electrode area, and optimizing the NPV method parameters.

2. Experimental

All experiments were conducted in a glovebox (PureLab HE, Innovative Technologies). The glovebox was filled with argon (UN1006, Airgas), so the moisture and O_2 levels in the glovebox were both maintained under 1 ppm. The molten salt mixtures studied were composed of various concentrations of LiCl-KCl eutectic (99.99% anhydrous, SAFC Hitech), UCl_3 (anhydrous, synthesized in house), and $GdCl_3$ (99.99% anhydrous, Alfa-Aesar). The salts are weighed by a precision balance (ML204, Mettler Toledo). The molten salt mixture was heated by a muffle furnace (Thermolyne FB1315M), and the temperature was maintained at 773 ± 1 K. The molten salt mixture was contained in a 100-ml alumina crucible (AL-2100, AdValue Technology). A 250-ml alumina crucible (AL-2250, AdValue Technology) was used as a safety secondary containment in case the 100-ml alumina crucible fails. According to Kuznetsov et al. [20], alumina interacts with LiCl-KCl-UCl_4 melt to form uranium oxychloride complexes. In our work reported in this paper, UCl_3 was used, and the potential was almost always at or below U^{3+}/U^{4+} to prevent the production of UCl_4 to form uranium oxychloride complexes. Thus, the concentration of any uranium oxychloride complexes formed were negligible compared to UCl_3.

The electrochemical methods were carried out by a potentiostat (Metrohm Autolab PGSTAT302N) and three electrodes. The working electrode (WE) was a 0.5-mm diameter W wire (99.95%, Alfa Aesar). The inert counter electrode (CE) was a 3-mm diameter glassy carbon rod (Alfa Aesar). The inert CE would ensure there was no concentration change in the salt mixtures. The reference electrode (RE) was a silver wire (99.999%, Alfa Aesar) in contact with AgCl (99.9%, Stem chemicals) in a 6-mm outside diameter mullite tube (MLCOE7A, Ceramic Solutions) with a wall thickness of 1 mm. The open end of the mullite tube was enclosed by a silicon stopper.

The submerged surface area of the WE was difficult to measure; therefore, a standard addition method [6] was applied to normalize the area. For each electrochemical test, the current density is calculated by the change in current divided by the change in WE surface area. Thus, current density was measured by the slope of differential current plotted versus differential WE area. The height

Table 1
Standard reduction potential of elements in eutectic LiCl-KCl at 773 K (vs Cl^-/Cl_2) [19].

Couple	E_o (V)
Gd(III)-Gd(0)	−2.95
Mg(II)-Mg(0)	−2.85
Pu(III)-Pu(0)	−2.75
U(III)-U(0)	−2.49
U(IV)-U(0)	−2.24
U(IV)-U(III)	−1.51