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On-line Monitoring of Actinide Concentrations in Molten Salt Electrolyte

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INTRODUCTION

Pyroprocessing, a treatment method for spent nuclear fuel (SNF), is currently being studied at the Idaho National Laboratory. The key operation of pyroprocessing which takes place in an electrorefiner is the electrochemical separation of actinides from other constituents in spent fuel. Efficient operation of the electrorefiner requires online monitoring of actinide concentrations in the molten salt electrolyte. Square-wave voltammetry (SWV) and normal pulse voltammetry (NPV) are being investigated to assess their applicability to the measurement of actinide concentrations in the electrorefiner.

The Need for Online Monitoring

Electrorefining is the main step in SNF pyroprocessing in which two types of cathodes are used to separate useful actinides from fission products. Uranium is selectively collected when an external current is applied between an anode (where spent fuel segments are introduced into the system) and a solid cathode. As uranium collects at the solid cathode, the relative concentrations of transuranic elements in the electrolyte gradually increase. The relative concentration of plutonium ions ($[Pu^{3+}]:[U^{3+}]$) is of greatest interest because other transuranic elements exist at much lower concentrations. When the relative amount of plutonium ions in the electrolyte is sufficiently high, the operator activates a liquid cadmium cathode to simultaneously collect uranium, plutonium, and other transuranic elements. The ratio $[Pu^{3+}]:[U^{3+}]$ varies widely during electrorefining operations and prompt determination of this quantity is needed to guide operators in switching between the two cathodes. [1]

Voltammetry

Voltammetry is a proven electroanalytical method used for measuring the concentrations of dilute species in solution. The applicability of SWV and NPV to the measurement of actinide concentrations in molten salt electrolyte is being evaluated in this study. In each of these methods, a potential is applied to the cell and the resulting current can be correlated to give the concentration of the species of interest. The resulting voltammogram (current vs. potential plot) displays peaks in the current near the redox potential of ionic species in the solution representing the reduction of those ionic species. Peak current values are related to the bulk concentrations of their respective ions in solution, and a correlation can be developed to describe that dependence.

Voltammetry is considered a suitable method for measuring actinide concentrations in the molten salt of the electrorefiner because it provides rapid, accurate *in situ* measurement of the concentrations of multiple species in solution. [2]

DESCRIPTION OF THE ACTUAL WORK

At the Idaho National Laboratory, voltammetric experiments will be conducted with a LiCl-KCl-UCl_3-$PuCl_3$ system to determine appropriate correlations relating the concentrations of uranium ions and plutonium ions in the molten salt electrolyte of the electrorefiner to their related peak currents in a voltammogram. High-temperature (~500°C) LiCl-KCl eutectic salt serves as the solvent in the system. As the facilities and materials for these experiments are costly, preliminary experiments on a surrogate system will be conducted with objectives to 1) determine the type of voltammetry (square-wave or normal pulse) most applicable to the LiCl-KCl-UCl_3-$PuCl_3$ system, 2) increase understanding of the experimental procedure and proper experimental parameters, and 3) determine the likelihood of success with the LiCl-KCl-UCl_3-$PuCl_3$ system.

The chosen surrogate system (LiCl-KCl-$LaCl_3$-$MgCl_2$) includes lanthanum ions and magnesium ions. These ions are considered satisfactory surrogates because the difference between their standard redox potentials in the eutectic salt is similar to the difference in potentials of uranium and plutonium (~0.3 V). The electromotive force series showing the standard redox potentials of all the ions of interest in this study are shown in Table I [3].

TABLE I. Electromotive Force Series in LiCl-KCl Eutectic, 450°C.

Couple	E° (V)
U(III)-U(0)	-2.218
Pu(III)-Pu(0)	-2.535
La(III)-La(0)	-2.877
Mg(II)-Mg(0)	-2.580

Square-wave and normal pulse voltammograms are being generated using both a lanthanum system (LiCl-KCl-$LaCl_3$) and a separate magnesium system (LiCl-KCl- $MgCl_2$). The solute ion concentration in each system is varied from 0 wt% to 3 wt%. Results of these experiments are analyzed to determine which method (square-wave voltammetry or normal pulse voltammetry) is most applicable to the actinide-molten salt system of interest.

The technique selected will then be used to study the multi-component LiCl-KCl-$LaCl_3$-$MgCl_2$ system. Voltammograms will be generated with relative ion concentrations ($[La^{3+}]:[Mg^{2+}]$) ranging from 0 to 10 by adding $MgCl_2$ incrementally to an initial solution of LiCl-KCl-1.5 wt% $LaCl_3$.

RESULTS

The experiments described are in process. A correlation relating the concentrations of lanthanum ions (La^{3+}) and magnesium ions (Mg^{2+}) in molten salt solution to their respective peak reduction currents given in a voltammogram is anticipated. The success or failure of this work with a surrogate system will give an indication of the probability of success of future work with the uranium-plutonium-molten salt system of more direct interest.

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