Voltammetry for quantitative analysis of actinides in molten salts

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Various voltammetric techniques, such as cyclic or square wave voltammetry, were used to study the electrochemical properties of actinides dissolved in a LiCl - KCl eutectic melt. High-precision measurements of actinide concentrations in molten salts are the main focus of our process monitoring studies. Use of electroanalytical techniques for quantitative analysis presents several challenges that have to be addressed before they can successfully be used for concentration measurements.

Multi-component systems present even more challenges because the baseline for succeeding reduction peaks are affected by the "tail" from the previous peak. Without a reliable baseline, accurate measurements required for quantitative analysis cannot be made. A well understood but not commonly used technique for manipulating the current vs. time data (semi-differential analysis) was applied and it resulted in symmetrical reduction peaks with increased height/width ratio. It successfully allowed the determination of an accurate baseline for the succeeding peaks and therefore is useful for concentration measurements of any electroactive species in the multicomponent system. Figures 1,2 and 3 illustrate current vs. voltage data of the reduction wave of cyclic voltammogram, the semi-integral data, and the semi-differential data for system containing U^{3+} and Pu^{3+} in molten LiCl/KCl. As can be seen, better baseline resolution between U and Pu peaks is achieved using semi-differential analysis. In addition, the advantages of high sensitivity and high resolvability are also achieved.

An additional challenge for making quantitative measurements is obtaining a well-defined area of the electrode. Area determination was performed by standard area addition, which employs incremental changes of immersion depth for a cylindrical electrode. The observed change in current is correlated directly to the change in immersion depth in a Randles-Sevick model. The method was improved to give a better precision by using a wider range of immersion depths and taking multiple measurements.

A range of salt compositions containing U and Pu in molten LiCl/KCl were studied and the requirements needed to obtain high-precision measurements were evaluated. A protocol was developed to establish a repeatable and representative electrode/electrolyte interface to test various salt conditions. Ensuring reproducible test conditions for the electrode surface at the beginning of each step is the key requirement for quantitative measurements. This reproducible electrode surface was accomplished by applying proper cleaning procedures and waiting periods between each test. Other

requirements include verifying the assumptions of semi-infinite linear diffusion and kinetic reversibility of the reaction over a range of voltammetry parameters (e.g. scan rate, frequency, size of the electrode, etc.). It was demonstrated that once all the conditions are satisfied, voltammetry coupled with the method of standard area addition can be effectively used to provide high precision measurements of actinides in the molten salts. With a 99.9% confidence interval, the error in measured concentrations averages ~1%.
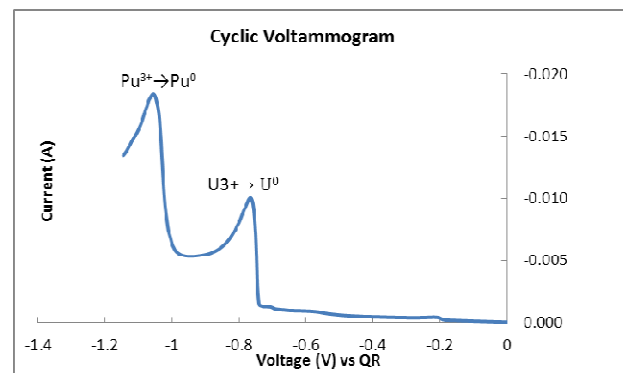

Figure 1. Plot of CV for system containing U^{3+} (0.5wt %) and Pu^{3+} (1wt %) in molten LiCl/KCl.
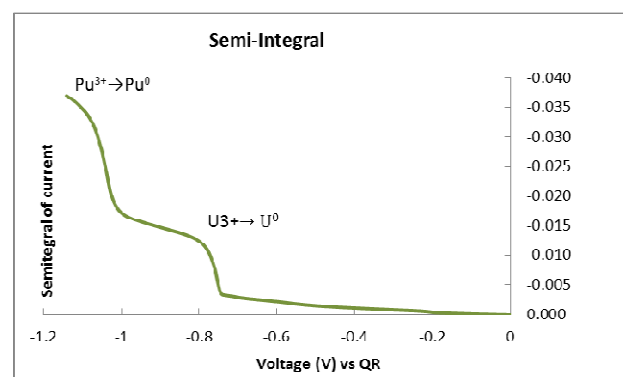

Figure 2. Plot of semi-integral for system containing U^{3+} (0.5wt %) and Pu^{3+} (1wt %) in molten LiCl/KCl.
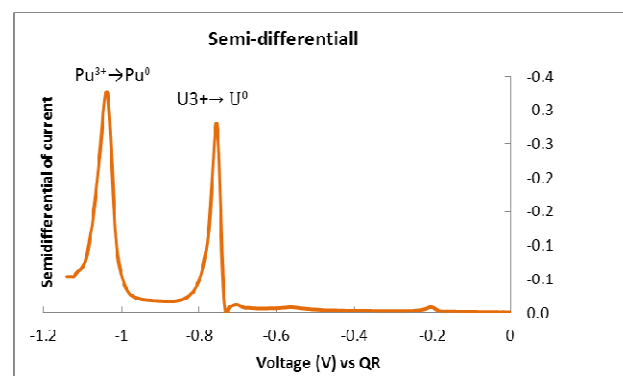

Figure 3. Plot of semi-differential for system containing U^{3+} (0.5wt %) and Pu^{3+} (1wt %) in molten LiCl/KCl.