Application of Voltammetry for Quantitative Analysis of Actinides in Molten Salts

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Our previous work ("Method Development for Quantitative Analysis of Actinides in Molten Salts" 2015) demonstrated that by following a set of developed procedures and a refined data analysis method, cyclic voltammetry can be used for very precise, real-time quantitative concentration measurements of actinides in molten salts. This work examines the suitability of the established procedures over a wider range of concentrations comparable to those expected in the normal operation of an electrorefiner used in the pyrochemical processing of used nuclear fuel. We found that electrochemical methods can be used for very precise concentration measurements up to approximately 2 wt%. For higher actinide concentrations, the value of the diffusion coefficient decreases and these variations have to be taken into consideration. We also investigated the application of voltammetry for analyzing systems containing multiple elements (U³⁺ and Pu⁴⁺) and found that a zero current baseline determination of the second or succeeding peaks in the voltamogram is not a correct approach, since that peak is affected by the tail from the peak that preceded it. We then used a different method of data analysis that allows for an accurate baseline determination and can be used to analyze systems involving more than one component.

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Pyrochemical reprocessing technology represents a promising alternative to aqueous processes for separating actinides from the remaining irradiated fuel by employing electrolytic methods in a molten salt media. The electrorefiner is the centerpiece of the process, in which uranium (U) and transuranic elements are separated from the bulk of the fission product elements by electrotransport onto a solid or liquid cathode. High-precision, real-time concentration measurements of actinides in molten salts are required to monitor the progress of the process and could be used for material control and accountability measurements. The development of these measurements is essential for implementing and operating a commercial fuel reprocessing facility. Electrochemical techniques are very well-suited for this purpose since they allow rapid real-time measurements, do not require the use of standards, and are compatible with remote handling operations.

Unlike other chemical methods, they do not require the collection and preparation of representative samples, so they avoid problems that can result from contaminating the sample and its degradation. Also, the equipment is not affected by the high radiation field present in a fuel processing operation, and the analytical results can be received in a relatively short time (e.g., less than 2 minutes).

In our previous work, we investigated the applicability of electrochemical methods for quantitative measurements of actinide concentrations in molten salts. We demonstrated that by following a particular set of procedures, and refining data analysis and experimental methods, very precise and reproducible measurements could be achieved. The concentrations of uranium (U) and plutonium (Pu) were calculated from peak currents obtained by cyclic voltammetry (CV), and the results were found to be in a very good agreement with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) concentration measurements, with an extremely small relative error. These results indicate that voltammetry, when properly applied and verified, is a very promising tool for quantitative measurements of actinide concentrations in molten salts. However, its suitability at the various possible experimental conditions expected in the normal operation of an electrorefiner during pyrochemical reprocessing had to be verified.

First of all, the applicability of using voltammetry in molten salts containing higher amounts of electroactive species needed to be examined. In an electrorefiner, the concentration of actinides in the salt can range anywhere from 0.1 to 10 wt%, and that concentration is composed primarily of U and Pu, since the total amount of those actinides in the used fuel is considerably larger than the amount of other actinides, such as neptunium and americium. A majority of previous studies had used concentrations between 0.5 and 1 wt%. Only a few studies had used higher concentrations. Iizuka et al. examined the relationship between peak currents and concentrations of U and Pu ranging from 0.1 to 4 wt% by using normal pulse voltammetry (NPV) and square wave voltammetry (SWV). The researchers found a nonlinear relationship between the peak current and Pu and U concentration in the salt at concentrations larger than about 0.5 wt% when using SWV and larger than about 1.7 wt% when using NPV; however, no quantitative calculations or numerical results were reported. In a different study, Iizuka investigated the concentration dependence of gadolinium (Gd) and cerium (Ce) ions on the respective diffusion coefficients by using chronopotentiometry (CP), but difficulties in defining transition times (τ) at concentrations higher than 0.62 wt% for Ce(III) and 0.45 wt% for Gd(III) were reported. Up to these values, no significant dependence of the concentration on the diffusion coefficient was observed. Pao et al. investigated the reduction of U⁴⁺ to uranium metal in LiCl-NaCl-CaCl₂-BaCl₂ by using CV for concentrations of UCl₃ ranging from 1.8 to 5.6 mol% but did not report any exact values for the diffusion coefficient because of the poor precision of the results. They reported deviations in the shapes of the voltammograms at concentrations higher than 4.9 wt% but did not report any quantitative results. Paek et al. investigated a system composed of Gd and lanthanum (La) in LiCl-KCl eutectic salt by using SWV and observed a large deviation from the linearity of the peak current with the concentration for values higher than 1 wt%. The possible reason for the deviation was attributed to the increased surface area of the working electrode, which is more significant at higher concentrations. However, no information about the method used for area determination was given, and no quantitative results were reported. To date, we have not found information on any other studies using electrochemical methods in molten salts containing electroactive species at concentrations higher than several weight percent. The concentrations studied in our previous work also involved only relatively low amounts of actinides (U³⁺ and Pu⁴⁺) present in the salt (less than 2 wt%). In this work, we examined four additional concentrations of U⁴⁺, ranging from approximately 3.5 wt% to about 9.2 wt%, in order to investigate the effects of concentration changes on electroanalytical measurements.

Another important aspect that needed to be considered is the suitability of the method for analyzing a system containing multiple analytes. In the normal operation of the electrorefiner, there are several

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actinides present in the salt, of which U and Pu are the main constituents since their amounts in the spent fuel are significantly larger than the amounts of other minor actinides. We must be able to separately determine the contribution of the reduction peaks corresponding to each element in order to obtain accurate concentration measurements from the voltammogram. Work done previously by Iizuka et al. involved salts containing multiple species (\(\text{U}^{3+}\) and \(\text{Pu}^{3+}\)) as well as other fission products (for example, \(\text{Gd}^{3+}\)); however, no quantitative measurements were performed. The effect of adding \(\text{GdCl}_3\) to the salt was investigated by simple graphical observation of the differentiated NPV peaks, but no quantitative results were reported. For NPV, although linearity was achieved up to about 1.5 wt\%, no equation describing the current in terms of concentration was reported or verified experimentally, and no quantitative results were reported. Our previous work involved only one-component systems (U or Pu), for which determining the baseline was straightforward and reliable. However, when more than one component is present in the system, the baseline for the second or succeeding reduction peak is affected by the tail from the previous peak. Thus, any change in the concentration of the first component could possibly affect the height of the second peak, because the peak current is due to the second component reduction combined with the tail from the preceding reduction peak. When the peaks are symmetrical, resolving this type of overlap is rather simple, but the CV reduction of the preceding reduction peak is affected by the tail from the previous peak. Thus, forward and reliable. However, when more than one component is present in the system, the baseline for the second or succeeding reduction peak is affected by the tail from the previous peak. Thus, any change in the concentration of the first component could possibly affect the height of the second peak, because the peak current is due to the second component reduction combined with the tail from the preceding reduction peak. When the peaks are symmetrical, resolving this type of overlap is rather simple, but the CV reduction peaks are not symmetrical. In this work, we examined the validity of the electroanalytical method described previously with regard to the quantitative concentration measurements of individual components present in binary systems containing both \(\text{U}^{3+}\) and \(\text{Pu}^{3+}\) in the salt.

**Experimental**

All experiments were carried out in a high-purity argon atmosphere glove box by using a three-electrode, small electrochemical cell. The electrochemical cell used in this work is described in our previous report. The working electrode (WE) consisted of a tungsten (W) wire either 0.075 cm or 0.1016 cm in diameter. The surface area of the working electrode was determined by standard addition method, which is described in more detail also in our previous report. A layer of U metal pre-deposited on the walls of the crucible served as the counter electrode to ensure that the counter reaction would not interfere with the reaction occurring at the WE. For the reference electrode, either W or platinum (Pt) wire was used as a quasi-reference electrode (QRE). Although the half-potential of this reference was undefined, its potential was stable on the timescale of the voltammetric measurements. Because the method selected for electrochemical analysis depended on the value of the current rather than the potential, the need for a reference electrode with a well-defined potential was eliminated. For consistency of data representation, all potentials were shifted to the values corresponding to the \(\text{U}^{3+}/\text{U}^0\) reaction.

A schematic diagram of the electrolytic cell is shown in Figure 1. The electrolytic bath was a eutectic mixture of high-purity lithium chloride (LiCl, Aldrich ≥99%) and potassium chloride (KCl, Aldrich ≥99%). About 50 g of LiCl-KCl eutectic was put in a 55-mL Inconel (nickel-chromium-iron alloy 601) crucible and heated with an electric furnace to 773 ± 1 K. The concentration of uranium in the molten salt was adjusted by the addition of LiCl-KCl-50 wt\%UCl₃, which was prepared before the measurements by the reaction of uranium metal with cadmium chloride in LiCl-KCl. The LiCl-KCl-PuCl₃ salt was prepared by chlorination of PuO₂ by using ZrCl₄ of uranium metal with cadmium chloride in LiCl-KCl. The LiCl-KCl-PuCl₃ salt was adjusted by the addition of LiCl-KCl-50 wt\%UCl₃, which was prepared before the measurements by the reaction of uranium metal with cadmium chloride in LiCl-KCl.

**Results and Discussion**

Electrochemical analysis over a wider range of actinide concentrations.—Challenges and optimization of the measurements.— As described in our previous work, cyclic voltammetry was selected as the preferred method for taking highly

| Table I. List of \(\text{U}^{3+}\) salt compositions analyzed with ICP-AES (No. 1 and 3) and TIMS (No. 5, 6, and 7). (\(a\) denotes value obtained based on process knowledge; \(b\) denotes salt concentrations analyzed in our previous work\(^{1}\)). |
|---|---|
| Salt No. | Wt\% |
| 1 | 0.46 ± 0.05 \(b\) |
| 2 | 0.95 \(b\) |
| 3 | 1.73 ± 0.17 \(b\) |
| 4 | 3.55 \(a\) |
| 5 | 4.620 ± 0.013 |
| 6 | 6.837 ± 0.021 |
| 7 | 9.149 ± 0.027 |

To examine the application of voltammetric methods for quantitative measurements in multicomponent systems, we studied different compositions of \(\text{U}^{3+}\) and \(\text{Pu}^{3+}\) in LiCl/KCl eutectic. A list of salt compositions examined in this work is shown in Table II. We prepared salt composition 8 by adding UCl₃ to salt containing approximately 1.4 wt\% PuCl₃. The next three compositions (9, 10, and 11) were prepared by adding more UCl₃ to salt composition 8. Electroanalytical measurements were performed by using a Solatron Modulab system Model HV100 fitted with the standard potentiostat/galvanostat module and controlled with the ModuLab software package.

**Table II. List of \(\text{U}^{3+}\) and \(\text{Pu}^{3+}\) salt compositions analyzed with ICP-AES. (\(a\) denotes value obtained based on process knowledge).**

| Salt No. | U (wt\%) | Pu (wt\%) |
|---|---|---|
| 8 | 0.45 ± 0.05 | 1.42 ± 0.14 |
| 9 | 1.00 \(a\) | 1.31 \(a\) |
| 10 | 1.99 \(b\) | 1.28 \(b\) |
| 11 | 4.35 ± 0.44 | 1.44 ± 0.14 |
precise, quantitative actinide concentration measurements in molten salts. Equation 1 describes the peak current as a function of concentration for reversible reactions involving the formation of an insoluble product.18,19

\[
i_p(CV) = 0.61AC_i\sqrt{\frac{F^2n^3D_v}{RT}}
\]  

Here \(A\) is the area of the working electrode (cm²), \(v\) is the scan rate (Vs⁻¹), \(T\) is the temperature of the melt (K), \(D_i\) is the diffusion coefficient of the electroactive species (cm²s⁻¹), \(n\) is the number of electrons involved in an electrode reaction, and \(R\) is the universal gas constant (Jmol⁻¹K⁻¹). Initial electrochemical measurements using CV on salt concentrations 4–7 shown in Table I were taken under the same experimental conditions as those used previously1 for salt concentrations 1–3 from Table I; namely, a 0.075-cm-diameter working electrode and 50-mVs/s scan rate. We observed that with an increasing concentration of \(U^{3+}\) in the salt, these measurements show deviations from typically shaped voltammograms. Instead of a sharp reduction peak in the CV wave, a corresponding loop and/or line is seen. An example of a CV in which the reduction peak has a distorted shape is shown in Figure 2 for salt composition 7. The most likely reason for this behavior is that at higher concentrations, the depletion effect does not occur at small-diameter electrodes and at relatively slow scan rates. This occurrence is similar to the effect that is observed for ultra-microelectrodes at lower concentrations.20–22 In CV, as the potential changes toward more negative values, the surface concentration of the electroactive species drops; hence, the flux to the surface and consequently the current increase. At relatively low concentrations, mass transfer reaches a maximum rate and declines as the depletion effect sets in. What is observed is therefore a peak-shaped voltammogram;18,20 At higher concentrations, however, as the potential becomes more negative, the surface concentration does not drop to zero, and mass transport of the electroactive species is no longer the limiting step of the reaction. Because there is no depletion of the electroactive species, the current continues to grow, which results in a line or a loop instead of a peak in the current-potential curve. The presence of a loop in the cyclic voltammogram was observed in previous work by Fukasawa et al.3 and Shirai et al.21 It is often interpreted as a result of nucleation phenomena occurring during the electrodeposition of metal at an inert electrode. Such behavior may indicate that nucleation and growth processes have become a limiting step of the reaction, as opposed to the mass transport of electroactive species or the kinetics of the electrochemical reaction.

If the absence of depletion of electroactive species at the electrode surface is indeed the cause of the unusual shapes of voltammograms at higher concentrations, then increasing the electrode size or increasing the scan rate should increase the rate of the depletion and produce a peak on the cathodic sweep. Figure 3 shows the effect of the increasing area of the electrode (from 0.205 to 0.390 cm²) on the shape of the voltammogram. It shows that proper optimization of the voltammetry parameters (scan rate, electrode diameter) can result in peak-shaped voltammograms. On the other hand, as described in our previous work,4 in order to use CV peak currents for quantitative calculations, the assumptions used to derive the relationship between peak current and concentration (Equation 1) — namely, reversibility of the reaction, unit activity of the deposit, and linear diffusion approximation — have to be realized and verified. Therefore, in order to use the CV peak current, the scan rate can be increased only up to a point at which the reaction remains limited by mass transport and fulfills reversibility requirements. Also, the diameter or surface area of the working electrode can be enlarged only up to a point at which the unit activity of deposit is a valid assumption.

Higher concentrations of actinides in the salt introduced an additional challenge for electroanalytical measurements. We found that it is much more challenging to achieve the repeatability of measurements when this condition exists. One possible reason is that the much higher background currents degrade the quality of the data. Also, for salts with higher concentrations of electroactive species, the effect of an increase in area due to the electrodeposition on the working electrode is much more significant than it is for salts with lower concentrations, even when the time of measurement is short. The problem of repeatability was solved by modifying the conditioning procedures between each test (described in more detail in our previous work1) and by increasing the duration of resting periods to achieve the same conditions at the electrode/electrolyte interface. We observed that even without any cleaning steps being applied, significant degradation of the current occurred on successive voltammograms. Pov et al.14 studied concentration ranges of \(U^{3+}\) from 5 to 9 wt% and reported difficulties in obtaining consistent results. Iizuka et al.15 also reported difficulties in defining CP transition times at concentrations higher than 0.62 wt% for Ce⁴⁺ and 0.45 wt% for Gd⁴⁺. Because none of the studies reported using any conditioning or renewing protocols between measurements, it is likely that the inconsistencies were caused by changes at the electrode/electrolyte interface, which degraded the current response. Repeatable and consistent data can be obtained only when a proper conditioning protocol, consisting of waiting periods and cleaning potentials, is used between each measurement.

Concentration calculations.—To calculate the concentration of \(U^{3+}\) in the salt, we used the standard area addition described in detail in our previous work.3 In this method, the peak currents are plotted as a function of the controlled immersion depth (\(h\)) of the working electrode, and from the slope of a generated linear plot (\(\Delta_i/\Delta h\)) described by Equation 2, the concentration \(C_i\) is calculated.

\[
\frac{\Delta I_p}{\Delta h} = 1.92C_i\sqrt{\frac{n^2F^2D_v}{RT}}
\]

As mentioned earlier and demonstrated in our previous work, this method gave very accurate and precise concentration measurements.
for salt concentrations 1–3 listed in Table I. We used the same approach to obtain cyclic voltammograms at different immersion depths for salt concentrations 4–7 by using a range of scan rates and different diameters of working electrodes. Based on the concentration studied, we chose a suitable scan rate and electrode diameter that would generate peak-shaped voltammograms and also satisfy the reversibility condition, linear diffusion approximation, and unit activity of the deposits. We repeated each test several times by changing the immersion depths in both directions in order to ensure the reproducibility of the measurements and obtain the relative error of the collected measurements.

Table III. Values of slopes (mA/cm) obtained for salt compositions 4, 5, 6, and 7 listed in Table I.

| Salt No. | Slope (mA/cm) | % Error (99.9% CI) |
|---------|---------------|-------------------|
| 4       | 63.62 ± 0.94  | 1.48              |
| 5       | 84.14 ± 0.77  | 0.92              |
| 6       | 107.7 ± 1.9   | 1.76              |
| 7       | 148.5 ± 1.3   | 0.87              |

As can be seen, the precision of the obtained slopes is very good, with a small relative error similar to that found in the results obtained previously\(^1\) for lower U\(^{3+}\) concentrations (concentrations 1–3 in Table I). The results indicate that the reproducibility of the data is not affected by the increase in the U\(^{3+}\) concentration in the salt and that high-precision, repeatable results are achievable when proper cleaning procedures and experimental parameters are applied.

To examine the accuracy of the technique, the concentration of U\(^{3+}\) was calculated from Equation 2 on the basis of the same assumption of a constant value of the diffusion coefficient of U\(^{3+}\) in the salt \((D_{U^{3+}} = 1.45 \text{ cm}^2/\text{s})\) that was used previously for calculations done for salt concentrations 1–3. Table IV shows the results of the calculations obtained for salt No. 4–7, together with concentrations measured by using ICP-TIMS analysis. As can be seen, there is a significant discrepancy between the values of the concentrations obtained by using the electrochemical method and values obtained by using the TIMS analysis technique. Also, it is evident that the higher the concentration of U\(^{3+}\) in the salt, the larger the difference between these two values. It is clear that even though the precision and reproducibility of the obtained measurements are comparable to the results obtained for salts containing lower amounts of U\(^{3+}\), the proximity of the measurement results to the actual values is significantly poorer. These results indicate that there are some changes occurring at higher concentrations of the electroactive species (more than 2 wt%) that affect the measurements. These changes must be taken into account in order to obtain accurate measurements.

Possible causes of discrepancies at higher concentrations.—One possible explanation for deviation could be the change in the salt density caused by the increase in the amount of heavy metal ions. It was found, however, that any increase in the salt density would result in further decrease of electroanalytical concentration values shown in Table IV and therefore, this possibility was eliminated. Another possible reason for deviation is the change in the diffusion coefficient value caused by the amount of electroactive species present in the salt. The diffusion coefficient is independent of the solute particle concentration only in the case of an ideal mixture (in which the solute particles do not interact when inside the solvent). When a large number of solute electroactive ions are present, interactions among them may become substantial and cause the diffusion coefficient to become dependent on the concentration of the solute.\(^{24,25}\) In this case, the interactions among the ions and their effect on the diffusion coefficient need to be considered when electrochemical techniques are being used for quantitative analysis.

As mentioned earlier in the text, only a few studies had used electrochemical techniques in molten salt electrolytes that had concentrations of electroactive species higher than a few weight percent. The typical concentration ranges were between 0.5 and 1 wt%. No detailed studies on the change in electrochemical parameters with concentration have been published. To investigate possible variations among the ions and their effect on the diffusion coefficient need to be considered when electrochemical techniques are being used for quantitative analysis.

Because all the measurements were obtained at the same temperature, the plot of \(\frac{\Delta I_p}{\Delta h} \cdot \frac{1}{\sqrt{D_i}}\) versus \(C_i\) should be linear if \(D_i\) is independent of the U\(^{3+}\) concentration in the salt. Such behavior would indicate that U\(^{3+}\) ions do not interact with each other when inside the salt and that the assumption of an ideal mixture is valid. A plot of the seven different U\(^{3+}\) concentrations listed in Table I is shown in Figure 5.

As can be seen, the plot is linear only up to approximately 2 wt% U\(^{3+}\). With further increases in the salt concentration, the data points deviate from the linearity. Figure 5 clearly shows that increasing the concentration of the electroactive species in the salt results in peak currents that are no longer directly proportional to the concentration. Because all of the experiments were conducted at the same temperature, the only parameter left in Equation 3 that could have changed during the experiment is the diffusion coefficient, \(D_i\).

\[
p = \frac{\Delta I_p}{\Delta h} \cdot \frac{1}{\sqrt{D_i}} = 1.922 C_i \frac{\sqrt{n_i F^3 D_i v}}{RT}
\]

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\[D_i = \frac{\Delta I_p}{\Delta h} \cdot \frac{\sqrt{RT}}{1.922 C_i \sqrt{m_i F^3}}\]

Table IV. List of U\(^{3+}\) salt concentrations obtained by using electrochemical measurements and ICP-TIMS method. (* denotes value obtained based on process knowledge).

| Salt No. | ICP-TIMS (wt%) | Electroanalytical (wt%) |
|---------|----------------|-----------------------|
| 4       | 3.55*          | 2.94 ± 0.04           |
| 5       | 4.620 ± 0.013  | 4.05 ± 0.04           |
| 6       | 6.837 ± 0.021  | 4.98 ± 0.09           |
| 7       | 9.149 ± 0.027  | 6.99 ± 0.06           |
The decrease in the U\textsuperscript{3+} concentration becomes higher, the diffusion coefficient decreases.

As can be seen, for U\textsuperscript{3+} concentrations lower than 2 wt%, using a constant value of the diffusion coefficient was a valid approach, and the concentration calculations obtained for salt concentrations 1–3 were in a very good agreement with the actual values.\textsuperscript{1} However, as the concentrations become higher, the diffusion coefficient decreases.

The decrease in the U\textsuperscript{3+} diffusion coefficient is caused by the attractive interactions among particles. This may reveal a tendency to combine or form clusters when the concentration reaches a certain threshold.\textsuperscript{24,25}

Because the value of diffusion coefficient changes as the concentration is increased above 2 wt% of U\textsuperscript{3+}, Equation 2 cannot be directly used for determining the concentration. One option is to obtain a nonlinear fit of the data in Figure 4 and use it as a calibration curve for determining the U\textsuperscript{3+} concentration. This approach is not very accurate, however, because the diffusion coefficient depends on the salt composition; also, the presence of different ions (e.g., other actinides, fission products, lanthanides) may also affect its value. Therefore, a different method is needed to measure the diffusion coefficient independently of concentration and to detect any changes in its value caused by changes in concentration or salt composition.

Analysis of multicomponent systems.—Concentration calculations.—As mentioned earlier, one of the main challenges when voltammetry is used for multiple component systems is determining a reliable baseline for peak height measurements. To examine the validity of the electroanalytical method described previously\textsuperscript{1} for quantitative concentration measurements of individual components present in in multicomponent systems, several binary systems containing both U\textsuperscript{3+} and Pu\textsuperscript{3+} in the salt were studied; they are shown in Table II.

An example of CVs at different WE immersion depths for salt composition 8 is shown in Figure 6. Cathodic peak currents corresponding to the reduction of both U\textsuperscript{3+} and Pu\textsuperscript{3+} are clearly observable and well-defined, however, as can be seen, the baselines for the Pu\textsuperscript{3+}/Pu\textsuperscript{4+} reduction peaks are affected by the tails from the U\textsuperscript{3+}/U\textsuperscript{0} peaks. For the single-component systems that were examined previously, the baseline determination was straightforward and reliable. For multicomponent systems, however, if simply the zero current baseline is used for the peak current measurement, then any change in the concentration of U\textsuperscript{3+} could affect the height of the Pu\textsuperscript{3+}/Pu\textsuperscript{4+} reduction peak and contribute to an error in the Pu\textsuperscript{3+} concentration calculations. It was shown in the previous section that for concentrations of electroactive species in the salt lower than 2 wt%, the diffusion coefficient can be assumed to be constant, and the concentration of the electroactive species in the salt can be accurately calculated by following the procedures that were developed in our previous work.\textsuperscript{1} Because the Pu\textsuperscript{3+} concentration was less than 2 wt% for all compositions, and the change in the U\textsuperscript{3+} concentration was relatively small for salt compositions 8, 9, and 10, accurate concentration calculations of both U and Pu should be obtained by using the developed method. This method is not recommended for composition 11, however, because the U\textsuperscript{3+} concentration is greater than 2 wt%.

Plots of Pu\textsuperscript{3+}/Pu\textsuperscript{4+} reduction peak currents measured by using a zero current baseline at different immersion depths for salt compositions 8, 9, 10, and 11 are shown in Figure 7. As can be seen, although concentration of Pu\textsuperscript{3+} did not change for salt compositions 8, 9, 10, and 11, the slope doubled from 20.67 to 42.24 mA/cm with the increasing U\textsuperscript{3+} concentration in the salt. If we were to use the values of these

**Table V. Values of U\textsuperscript{3+} diffusion coefficients at 773 K calculated from Equation 4 for salt concentrations listed in Table I.**

| Salt No. | U\textsuperscript{3+} (wt%) | 10\textsuperscript{9} D\textsubscript{1} cm\textsuperscript{2}/s |
|----------|-----------------------------|--------------------------|
| 1        | 0.46 ± 0.05\textsuperscript{b} | 1.51 ± 0.01               |
| 2        | 0.95\textsuperscript{b}      | 1.52 ± 0.03               |
| 3        | 1.73 ± 0.17\textsuperscript{b} | 1.57 ± 0.01               |
| 4        | 3.55\textsuperscript{a}      | 0.94 ± 0.02               |
| 5        | 4.620 ± 0.013                | 1.07 ± 0.01               |
| 6        | 6.837 ± 0.021                | 0.77 ± 0.03               |
| 7        | 9.149 ± 0.027                | 0.67 ± 0.01               |

**Figure 5.** Relationships between concentration of U\textsuperscript{3+} (wt%) and values of p (Equation 3) for salt concentrations 1–7 listed in Table I.

**Figure 6.** Cyclic voltammograms obtained at different immersion depths of WE for salt composition 8 shown in Table II (v = 50 mV/s).

**Figure 7.** Relationships between Pu\textsuperscript{3+}/Pu\textsuperscript{4+} reduction peaks and electrode immersion depths for salt compositions 8, 9, 10, and 11.
slopes to calculate the Pu\(^{3+}\) concentration by employing the method described previously (Equation 2 with an average diffusion coefficient value of Pu\(^{3+}\) \(D_i = 1.6 \times 10^{-5} \text{ cm}^2/\text{s}\)), the resultant values would be considerably different from the actual values. Results using CV slopes are compared with the analytical values in Table VI.

As can be seen, the error associated with the Pu baseline determination is quite significant and increases as the concentration of U\(^{3+}\) in the salt increases. One option would be to make the measurement of the Pu peak current using the decaying current of the first wave as the baseline. However, this method of baseline determination is not very accurate, depends on many factors (e.g. reversibility of the reaction, peak separation) and is not suitable for high-precision quantitative measurements. Therefore, a method that achieves better baseline resolution between peaks is needed to enable the accurate determination of peak height without showing any effects from other nearby peaks in the voltammogram.

**Semi-differential analysis method development.**—To solve the problem of baseline determination for a system containing multiple components, we examined different analyses that result in a better baseline determination and an increased peak height/width ratio. One of the promising methods we found was semi-differential (SD) analysis, which is generated by taking a derivative of semi-integrated current versus potential data. The semi-integration (SI) method has been frequently used to transform cyclic voltammograms into forms resembling the steady-state curves by using the convolution principle. In cases in which diffusion of the electroactive species is the only mode of mass transfer, the current reaches its limiting value, which is independent of the excitation signal. In theory, the transformation of the current \(m(t)\) should reach a limiting value \(m_i\), indicated in the data by the presence of a flat plateau, as described by Equation 5.

\[
m_i = -nF AC_i D_i^{0.5}
\]

In practice, however, instead of a flat plateau, the observed transformation of the current continuously increases with the potential, which causes inaccuracy in the determination of \(m_i\). This behavior is especially true for a system involving an insoluble product. The SD method uses the derivative of the semi-integrated voltammogram, and it generates symmetrical, peak-shaped voltammograms with increased peak height/width ratios, making it much easier to determine the baseline than it is when the original cyclic voltammogram is used. Figure 8 shows current versus potential plots of the original cyclic voltammetry data, the semi-integral data, and the SD data for salt composition 8 from Table II. The red and purple lines show the Pu\(^{3+}/Pu^{0}\) peak baselines for the CV and SD plots, respectively. As can be seen in Figure 8, there is definitely better baseline resolution between the U and Pu peaks in the SD plot, giving a Pu peak that is independent of the U peak. The SD method has the advantages of high sensitivity and high resolvability for the species and provides a better baseline for the Pu\(^{3+}/Pu^{0}\) peak. The fundamentals of SD analysis were established by Goto and others (Goto and Ishoo, Dalrymple, Oldham et al.), who derived an equation of a semi-differentiated peak current \(e_{p}\) corresponding to a reversible reaction involving the soluble-soluble reaction (Equation 6).

\[
e_p = \frac{n^2 F^2 AC_i \sqrt{D_i}}{2RT}
\]

A plot of \(e_p\) versus the immersion depth of the working electrode, \(h\), has a slope given by Equation 8, where \(d\) is the diameter of the electrode. Similar to Equation 2, this equation can be used to calculate the concentration \(C_i\). It should also yield accurate, highly precise results to the degree that the terms in the equation are well known and the error is small.

\[
\frac{\Delta e_p}{\Delta h} = \frac{1.57dn^2 F^2 C_i \sqrt{D_i}}{RT}
\]

**Semi-differential current measurements.**—Commercially available software (Condecon 2001) was used to transform cyclic voltammograms into SD plots by first semi-integrating the current-potential data and then taking the first derivative with respect to potential. An example of SD plots at different immersion depths for salt composition 8 is shown in Figure 9.

---

**Table VI. Values of Pu\(^{3+}\) compositions obtained for salt compositions 8, 9, 10, and 11.** (\(^a\) denotes value obtained based on process knowledge).

| Salt No. | Actual (wt%) | CV (wt%) | % Difference |
|---------|--------------|----------|--------------|
| 8       | 1.42 ± 0.14  | 1.32 ± 0.01 | 7.04         |
| 9       | 1.31\(^a\)  | 1.73 ± 0.02  | 32.1         |
| 10      | 1.28\(^a\)  | 2.11 ± 0.04  | 64.8         |
| 11      | 1.44 ± 0.14  | 3.08 ± 0.12  | 113.9        |

---

**Figure 8.** CV, semi-integrated CV, and semi-differentiated CV obtained for salt composition 8 (scan rate = 50 mV/s, \(T = 773 \text{ K}\)).

They also derived an equation describing \(e_p\) for the case of irreversible processes; however, no studies were done to establish equations for reactions involving soluble-insoluble reactions. Therefore, in order to use this technique for actinide concentration calculations, equations that describe a semi-differentiated peak current for processes involving the formation of an insoluble product had to be derived. By following the steps used to derive \(e_p\) for soluble-soluble reactions and an equation that describes potential in terms of semi-integrated current \(m(t)\), we derived an equation that describes SD current peaks for a case in which the soluble oxidant is reversibly reduced to an insoluble species (Equation 7). A detailed description of the steps used in the derivation process is provided in Appendix.

\[
e_p = \frac{n^2 F^2 AC_i \sqrt{D_i}}{2RT}
\]
In order to effectively use this modified analysis method for concentration measurements, the validity of the derived relationship describing the SD peak current \( i_p \) to be verified. For that reason, \( U^{3+} \) concentrations were calculated by using the values of both slopes \( \Delta V_{3+} \) and \( \Delta V_{0+} \) described by Equations 2 and 8, respectively. The plots generated from using both methods for salt compositions 8, 9, and 10 are shown in Figures 10 and 11.

Concentrations of \( U^{3+} \) calculated by using both electroanalytical methods CV and SD are shown in Table VII, along with concentrations obtained either from process knowledge or by using ICP-AES. The values obtained from using both electro-analytical methods are clearly in very good agreement and have a high degree of precision. This result verifies the validity of the derived equation (Equation 7) and the accuracy of the approach used in its derivation.

Once the validity of Equations 7 and 8 was confirmed, the equations were used to calculate the \( Pu^{3+} \) concentration for salt compositions 8, 9, 10, and 11. The results are shown in Table VIII. They clearly demonstrate the advantage of the SD method over the simple analysis method peak measurement and yields incorrect results for concentration calculations. A different method of data analysis that transforms CV data into symmetrical peaks with increased height/width ratios was identified. We demonstrated that this analysis technique successfully allows the determination of an accurate baseline for a second peak or any succeeding peaks and can thus be used for concentration measurements of any electroactive species in a multicomponent system.

### Table VII. Values of \( U^{3+} \) compositions obtained from using CV and SD electroanalytical techniques and ICP-AES (* denotes salt compositions analyzed in our previous work).

| Salt No. | Actual (wt%) | CV (wt%) | SD (wt%) |
|----------|--------------|----------|----------|
| 8        | 0.45 ± 0.05  | 0.52 ± 0.01 | 0.558 ± 0.003 |
| 9        | 1.00*        | 1.06 ± 0.03 | 1.017 ± 0.006  |
| 10       | 1.99*        | 1.68 ± 0.05 | 1.731 ± 0.005  |

### Table VIII. Values of \( Pu^{3+} \) compositions obtained from using CV and SD electroanalytical techniques and ICP-AES (* denotes salt compositions analyzed in our previous work).

| Salt No. | Actual (wt%) | CV (wt%) | SD (wt%) |
|----------|--------------|----------|----------|
| 8        | 1.42 ± 0.14  | 1.32 ± 0.01 | 1.37 ± 0.01  |
| 9        | 1.31*        | 1.73 ± 0.02 | 1.46 ± 0.01  |
| 10       | 1.28*        | 2.11 ± 0.04 | 1.264 ± 0.008 |
| 11       | 1.44 ± 0.14  | 3.08 ± 0.12 | 1.445 ± 0.007 |

concentration measurements, as reflected by extremely small relative error in the measurements.

### Summary and Discussion

In our study of a wider range of actinide concentrations in molten salts, we found that increasing the concentration of the electroactive species introduced additional challenges for electrochemical analysis in terms of the electrode pretreatment and interpretation of voltammetric data. Appropriate optimization of the voltammetry parameters and cleaning procedures was required to obtain repeatable and consistent data. The effect of concentration change on the diffusion coefficient had to be investigated as well. We found that electrochemical methods can be used for very precise concentration measurements for a single-component system up to approximately 2 wt%. For higher actinide concentrations, a constant value of the diffusion coefficient cannot be assumed, since its value decreases with increasing concentration. Because these variations need to be taken into consideration, a new method that will measure the diffusion coefficient independently of salt concentration is needed. This method will be developed in future work.

This work also shows that for systems involving more than one component, a zero-current baseline determination of the second or succeeding peak in the voltammogram is not a correct approach, because that peak is affected by the tail from a preceding peak. Therefore, any change in the concentration of the first component affects the second peak measurement and yields incorrect results for concentration calculations. A different method of data analysis that transforms CV data into symmetrical peaks with increased height/width ratios was identified. We demonstrated that this analysis technique successfully allows the determination of an accurate baseline for a second peak or any succeeding peaks and can thus be used for concentration measurements of any electroactive species in a multicomponent system.

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### Appendix: Derivation of Relationship for Semidifferential Peak Current for Reversible Deposition of Insoluble Product

For a case in which the soluble oxidant is reversibly reduced to an insoluble product \( (O^{n+} + ne^{-} \rightarrow R) \), the Nernst equation (Equation A1) is replaced by Equation A2, in which the activity of the reduced species was assumed to be unity \( (a_R = 1) \).

\[
E = E^\circ + \frac{RT}{nF} \ln \left( \frac{a_R}{a_O} \right) \quad [A1]
\]

\[
E = E^\circ + \frac{RT}{nF} \ln \left( \frac{a_R}{a_O} \right) \quad [A2]
\]
Oldham\textsuperscript{30} and Grenness and Oldham\textsuperscript{31} solved the diffusion equation (A3) by using the initial condition (A4) and two boundary conditions (A5 and A6) and obtained the results shown in Equation A7:

\[
\frac{\partial C_t(x)}{\partial t} = D_i \frac{\partial^2 C_t(x)}{\partial x^2} \tag{A3}
\]

\[C_t(x, 0) = C_o \tag{A4}\]

\[C_t(\infty, t) = C_o \tag{A5}\]

\[\frac{\partial C_t(0, t)}{\partial x} = \frac{i(t)}{nAFD_i} \tag{A6}\]

\[C_t(0, t) = C_o - \frac{m(t)}{nAF\sqrt{D_i}} \tag{A7}\]

Here \(C_o\) is the initial concentration of the electroactive species, \(i(t)\) is a cathodic current, \(A\) is the working electrode area, \(F\) is Faraday’s constant, \(D_i\) is the diffusion coefficient of the electroactive species, and \(m(t)\) is the semi-integral of the current \(i(t)\) with respect to time \(t\) described by Equation A8.

\[m(t) = \frac{d^{-0.5}}{dm} \ln i(t) \tag{A8}\]

The limiting value of \(m(t)\) when \(t \to \infty\) is described by Equation A9.

\[m(\infty) = nAFC_i \sqrt{D_i} \tag{A9}\]

Equations A7 and A9 are valid when transport of the electroactive species is controlled solely by semi-infinite linear diffusion. In this case, Equation A2, describing reversible reactions at electrochemical equilibrium, is applicable and can be rewritten as Equation A10, where \(E^*\) is a formal potential of the electrode reaction.

\[E(t) = E^* + \frac{RT}{nF} \ln C_t(0, t) \tag{A10}\]

Using Equation A7 and A9, Equation A10 can be rearranged as A11 or A12.

\[E(t) = E^* + \frac{RT}{nF} \ln \left(\frac{C_t}{2}\right) + \frac{RT}{nF} \ln \left(\frac{m(\infty) - m(t)}{m(\infty)}\right) \tag{A11}\]

Equation A12 can be rewritten as a relationship describing \(m(t)\) in terms of \(E(t)\) explicitly. The result is shown in Equation A14.

\[m(t) = m(\infty) - \frac{m(\infty)}{2} \exp\left(\frac{nF}{RT} \left(E(t) - E_{1/2}\right)\right) \tag{A14}\]

Finally, when Equation A9 for \(m(\infty)\) is plugged into Equation A16, the equation describing the peak height in terms of concentration \(C_t\) is shown in Equation A17.

\[e_p = -\frac{nAFC_i \sqrt{D_i}}{2} \left(\frac{nF}{RT}\right) = -n^2F^2AC_t \sqrt{D_i} \tag{A17}\]

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