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Cyclic Voltammetric Experiment - Simulation Comparisons of the Complex Mechanism Associated with Electrochemical Reduction of Zr\(^{4+}\) in LiCl-KCl Eutectic Molten Salt

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Nuclear energy increasingly represents an important option for generating largely clean CO\(_2\)-free electricity and zirconium is a fission product that is expected to be present in irradiated fuels. The present investigation addresses the electrochemical reduction of Zr\(^{4+}\) to Zr\(^0\) in LiCl-KCl eutectic molten salt in the temperature range 425–550 \(^\circ\)C using cyclic voltammetry (CV), square-wave voltammetry (SWV) and bulk electrolysis. Simulations of the CV data indicate that the initial reduction proceeds through surface confined steps: Zr\(^{4+}\) + 2e\(^-\) \(\rightarrow\) Zr\(^{2+}\) and Zr\(^{2+}\) + 2e\(^-\) \(\rightarrow\) Zr\(^0\) processes (* adsorbed species) followed by a peak-shaped complex diffusion controlled step that consists of a combination of closely spaced processes associated with the reactions Zr\(^{4+}\) + 4e\(^-\) \(\rightarrow\) Zr\(^0\) and Zr\(^{2+}\) + 3e\(^-\) \(\rightarrow\) Zr\(^{0}\). Zr\(^{2+}\), probably in the form of ZrCl\(_6^+\) is then further reduced to Zr\(^0\) at even more negative potentials. The simulations provide the first quantitative analysis of the thermodynamics and kinetics of the Zr\(^{4+}\) reduction in the LiCl-KCl eutectic.

Pyroelectrochemical processes based on molten chloride or fluoride electrolyte systems have over the past decade received substantial interest for the reprocessing of irradiated nuclear fuel. The renewed interest owes its origin to several attractive features of the pyroelectrochemical approach in comparison to hydrometallurgical reprocessing. Advantages include: 1) the ability to handle different fuel types, i.e., metal, oxide, carbide, nitride, mixed ceramic-metal, ceramic-coated particles; 2) potential for reprocessing freshly irradiated fuel without the need for fuel cooling; 3) small plant footprint compared with hydrometallurgical reprocessing; 4) the absence of organic solvents and 5) favorable criticality, safety and proliferation resistance. Zirconium, a fission product, our material of interest in the present investigation addresses the electrochemical reduction of Zr\(^{4+}\) to Zr\(^0\) in LiCl-KCl eutectic molten salt using potentiometric and polarographic techniques. These authors indicated that Zr\(^{4+}\) to Zr\(^0\) electrode potential is \(-1.22\) V while that of the Zr\(^{4+}\)/Zr\(^0\) process is \(-1.12\) V (vs. Ag/AgCl) at 550 \(^\circ\)C. Electrorefining of zirconium in LiCl-KCl eutectic molten salt also was studied by Kipouras et al. These authors indicated that the predominant cathodic reaction occurs as in, Equation 1

\[
\text{ZrCl}_6^+ + 4e^- \rightarrow \text{Zr}(s) + 6\text{Cl}^- \quad [1]
\]

but also noted that side reactions such as Zr\(^{4+}\) + Zr\(^0\) \(\rightarrow\) Zr\(^{2+}\) and their combinations could reduce the current efficiency. Baboian et al. suggested the irreversible comproportionation reaction, (Equation 2) could occur when the electrolyte is heated and cooled between 450 and 550 \(^\circ\)C whereas Basile et al. described this process in the context of an equilibrium reaction.

\[
\text{Zr}^{4+} + \text{Zr}^0 \rightarrow 2\text{Zr}^{2+} \quad [2]
\]

Sakamura studied the cyclic voltammetry of zirconium in the LiCl-KCl eutectic molten salt at temperatures over the range 450 to 550 \(^\circ\)C using Mo as the working electrode. The initial process at about \(-1.0\) V (vs. Ag/AgCl) was assumed to correspond to the reaction given in Equation 3

\[
\text{Zr}^{4+} + 2e^- \rightarrow \text{Zr}^{2+} \quad [3]
\]

A process observed at about \(-1.2\) V (vs. Ag/AgCl) at 500 \(^\circ\)C was postulated to correspond to the reduction of Zr\(^{4+}\) to Zr\(^0\) and ZrCl\(^2\) as in Equations 4 and 5.

\[
\text{Zr}^{4+} + 4e^- \rightarrow \text{Zr}^0 \quad [4]
\]

\[
\text{Zr}^{4+} + 3e^- \rightarrow \text{ZrCl}_6^+ \quad [5]
\]

Sakamura described ZrCl\(_6^+\) proposed in Equation 5, as a product of reduction of Zr\(^{4+}\) as being `insoluble' and `metastable' in the molten salt and supported this hypothesis with electrowinning tests. Furthermore, it was noted that ZrCl\(_6^+\) may be reduced to Zr\(^0\) at potentials more negative than \(-1.3\) V (vs. Ag/AgCl).
A recent voltammetric and chronopotentiometric (CP) study by Ghosh et al. confirmed the presence of processes described by Sakamura. Additional observations were that CV data are complicated by adsorption of Zr\(^{2+}\) at the tungsten-working electrode, and CP transients exhibited two transition plateaus that were said to correspond to Zr\(^{2+}/Zr\(^{3+}\) and Zr\(^{3+}/Zr\(^{4+}\) reductions.

In summary, from the literature reviewed above, it may be concluded that the reduction of Zr\(^{4+}\) to Zr\(^{3+}\) in molten salt media takes place in a series of electron transfer steps such as Zr\(^{4+}/Zr\(^{3+}\), Zr\(^{3+}/Zr\(^{2+}\) and Zr\(^{2+}/Zr\(^{+}\), with disproportionation reactions such as Zr\(^{2+}\) + Zr\(^{2+}\) → Zr\(^{3+}\) + Zr\(^{+}\) (or Zr\(^{3+}\)) and adsorption also being important. However, the papers published on the subject provide only limited qualitative forms of analysis of the complex electrochemical reduction of zirconium. The aim of the present study therefore is to probe the reaction mechanism for zirconium electroreduction in LiCl-KCl eutectic molten salt using cyclic voltammetry, square-wave voltammetry and bulk electrolysis. In particular, a comprehensive attempt at simulation and a decrease in the working-reference electrode gap. The solid obtained on the working electrode was spongy, yellowish and pink in color. After removal from the electrode surface, the solid was mounted in an air-tight container under a nitrogen atmosphere, and transferred to a Bruker D8 diffractometer fitted with Cu tube and SOL-XE detector. Diffraction was acquired over an angular range of 2° to 120° two theta with a step size of 0.03 and a counting time of 10 seconds per point.

**Results and Discussion**

**Experimental Aspects of the Cyclic Voltammetry of Zirconium.**—If Nernstian reduction of Zr\(^{4+}\) to Zr\(^{3+}\) were to occur in a voltammetric experiment, all steps involved in the reaction mechanism would appear to take place simultaneously so the reaction would equate to an overall Zr\(^{4+}/Zr\(^{3+}\) process. However, if the lower Zr\(^{3+}\), Zr\(^{2+}\) and/or Zr\(^{+}\) states are stable and/or adsorbed, electron transfer may be found to take place in a series of consecutive and concurrent steps.

Sakamura reported 13.5 mA current (WE area: 0.325 cm\(^2\)) from 0.00123 mol fraction ZrCl\(_4\) (0.0171 mol kg\(^{-1}\) Zr\(^{4+}\)) at 100 mVs\(^{-1}\) scan rate and 500°C. Preliminary experiments in the present study produced higher current densities and further studies suggested that low concentrations of electroactive zirconium ions formed in the molten bath and hence lower current densities might be attributable to ZrCl\(_4\) and its hygroscopic behavior. Also, it is known that zirconium tetra-chloride reacts readily with O\(^2-\) ions to form ZrOCl\(_2\) and ZrO\(_2\), which can precipitate from the molten salt mixture. Experimental data suggested that ZrOCl\(_2\) and/or ZrO\(_2\), once formed, are very difficult to dissolve and non-electroactive even after HCl\(_0\) cleaning at 500°C. In the present studies, between 1.00 and 1.25% ZrCl\(_4\) (w/w) was added to the bath and currents detected per unit of electrode area were higher than those reported by Sakamura and it was assumed in this study that all zirconium is electroactive. The rest potential became more negative than –1 V (vs. Ag/AgCl) upon addition of ZrCl\(_4\) greater than 1.25% (w/w).

A profile of the CV experimental data obtained for the reduction Zr\(^{4+}\) is presented in Figure 1a with a switching potential of –1.5 V (vs. Ag/AgCl). Two reduction steps are seen in this potential range. The first feature to note from perusal of Figure 1 is that as expected both cathodic processes vary systematically with temperature. That is, larger currents and reduction at less negative potentials is found at the higher temperatures. Moreover, the initial reduction process was more drawn out (segment AB), than the one obtained at more negative potentials (segment BC). The initial process may involve interaction time, gradually increased to 50 mA, possibly due to dendrite formation and a decrease in the working-reference electrode gap. The solid obtained on the working electrode was spongy, yellowish and pink in color. After removal from the electrode surface, the solid was mounted in an air-tight container under a nitrogen atmosphere, and transferred to a Bruker D8 diffractometer fitted with Cu tube and SOL-XE detector. Diffraction was acquired over an angular range of 2° to 120° two theta with a step size of 0.03 and a counting time of 10 seconds per point.

**Experimental**

High purity LiCl (Aldrich, 99%) and KCl (Merck, 99.999%) were used to prepare the eutectic melt (59% mol LiCl and 41% mol KCl; 65 g of the salt mixture). Known wt% masses of zirconium chloride, ZrCl\(_4\) (Sigma-Aldrich, 99.99%) were added to the eutectic salt, but ICP analysis was used to determine the exact concentrations in the bath. The reactor head consisted of an 8-port borosilicate ground glass vacuum flange. All components were dried at 80°C for at least 12 h prior to assembly. The working electrode (WE) was a 1 mm diameter tungsten wire (W), with the bottom-end rounded off to form a hemicylinder. The oxide layer on a WE was removed with 4000 grit SiC paper, then rinsed with dilute nitric acid and distilled water and dried for least 1 h at 80°C. After about one hour of use, the WE was cleaned once again with the SiC paper and ethanol and then used again. The counter electrode (CE) was a 3 mm diameter x 400 mm glassy carbon rod (SIGRADUR G) encased in an alumina tube of 6 mm OD. The Ag/AgCl reference electrode (REF) was constructed from 0.75 mol kg\(^{-1}\) AgCl dissolved in LiCl-KCl eutectic molten salt in contact with 1 mm diameter silver wire embedded in 6 mm OD x 4 ID x 300 mm quartz tubing sealed with high temperature epoxy resin. The temperature of the eutectic was monitored using a thermocouple (type K, ± 2°C) sheathed in alumina. The eutectic melt was weighed into a glassy carbon crucible (SIGRADUR G, GAZ 12; 50 mm OD x 85 mm H) in a nitrogen filled (< 1 ppm oxygen and water) glove box. The electrochemical reaction was purged first with dry argon gas (99.99%), then sealed and evacuated to about 0.2 mbar. Further dehydration of the salt was undertaken by heating under vacuum at about 300°C for 72 h. After this time, the vacuum was removed and the vessel purged with argon. The temperature was then increased to 425 or 450°C and the zirconium chloride sample added. Numerous preliminary tests were conducted to reduce the sublimation of ZrCl\(_4\) and HCl gas was not used under the conditions finally employed.

An AUTOLAB potentiostat PGSTAT302N from Eco Chemie, driven by Nova 1.6, 1.7 and GPES 4.9 software packages, was used to conduct all the electrochemical experiments. DigiElch 6 (build 12) was used to simulate the CV data. Multiple experiments employing different zirconium concentrations and sweep rates were imported into DigiElch and compared with simulated cyclic voltammograms to extract the required kinetic and thermodynamic properties.

The controlled potential electrolysis experiment, required for identification of ZrCl\(_4\) as a product of reduction, was conducted for about 1 h at –1.2 V (vs. Ag/AgCl) and 500°C with a 0.18 mol kg\(^{-1}\) Zr\(^{4+}\) solution. This electrolysis potential lies just prior to the onset of the second step. The initial current of 20 mA, rather than decaying with

**Figure 1.** (a) Cyclic voltammograms obtained at 425, 475 and 525°C with a sweep rate of 100 mVs\(^{-1}\) in LiCl-KCl eutectic molten salt. [Zr\(^{4+}\)] = 0.0270 molkg\(^{-1}\). WE: W wire (electrode area at: 425°C, 0.410; 475°C, 0.492 and 525°C, 0.507 cm\(^2\)); CE: GC rod; REF, Ag/AgCl; [AgCl] = 0.75 mol kg\(^{-1}\). (b) Plot of peak current density for the second reduction process vs. square root of scan rate indicating that this process is diffusion-controlled.
of the Zr$^{4+}$ with the surface while the second peak shaped process is likely to be associated with diffusion. On reversing the potential scan direction after the second step, two oxidation processes are detected that are scan rate dependent (Figure 1). The symmetrical shape of these components implies oxidation of surface confined species.

Figure 1b provides a plot of peak current density vs. square root of the scan rate, \(i^{1/2}\), for the second reduction process. The current increases linearly with the square root of scan rate as the Randles-Sevcik equation predicts, implying that this process is diffusion-controlled. Interestingly, Figure 1b also indicates that the difference in current between 475 and 425 °C for this second reduction step is greater than that between 525 and 475 °C. It is difficult to construct analytical theoretical models for complex reduction processes of this kind, so a practical approach is to compare the experimental behavior with the predictions derived from simulations.\(^{13,14}\)

Figure 2 contains the scan rate dependence of cyclic voltamograms at 475 °C with a Zr$^{4+}$ concentration of 0.027 mol kg\(^{-1}\) (1% wt mass ZrCl\(_4\) added, 0.655 g) in LiCl - KCl eutectic molten salt and with a \(-1.45\) V (vs. Ag/AgCl) switching potential. The cathodic (\(i_pC_1\) and \(i_pC_2\)) and anodic (\(i_A_2\) and \(i_A_3\)) components are designated in this Figure. Clearly, the first reduction step (\(i_pC_1\)) is very drawn out at all scan rates, implying that this reaction is predominantly surface based, in contrast to the second reduction step, which contains a diffusion component.

Figure 3 shows that the peak-to-peak separations \(\Delta E_{pp}\) (\(\Delta E_{pp} = \Delta E_C\) (anodic) – \(E_p\) (cathodic))) for the second reduction process as a function of temperature and scan rate.

Figure 4 provides the scan rate dependence of cyclic voltamograms from 50 to 500 mV s\(^{-1}\) for the reduction of Zr$^{4+}$ at a higher concentration of 0.0445 mol kg\(^{-1}\) in LiCl - KCl (1.25% wt mass ZrCl\(_4\) added, 0.869 g) eutectic molten salt at 500 °C with a switching potential at \(-1.425\) V (vs. Ag/AgCl). Figure 5 shows the corresponding peak-to-peak separation potentials vs. scan rate plot as a function of temperature. The results of the cyclic voltammetric data can be summarized as follows: 1) The reduction of Zr$^{4+}$ is well defined over the temperature range of 425 to 550 °C (698 to 823 K) and concentration range of 0.027 to 0.045 mol kg\(^{-1}\), 2) reduction up to \(-1.45\) V (vs. Ag/AgCl) consists of two major processes. The first reduction step, \(i_pC_1\) probably includes a dominant adsorption component with the second process, \(i_A_2\) having a dominant diffusion component; and 3) oxidation on reversing the scan direction is dominated by a large peak, \(i_A_3\) followed by a smaller process, \(i_A_2\), Sakamukura\(^2\) also reported predominantly two anodic processes peaks at 500 °C using Mo as the WE with the first decreasing and the second increasing in relative importance as the scan rate is increased from 100 to 800 mV s\(^{-1}\) (vs. Ag/AgCl, Figure 4\(^5\)).

Figure 5 also provides the peak-to-peak separation data derived from Figure 4 for the second process vs. scan rate. It can be deduced from analysis of Figures 3 and 5 that \(\Delta E_{pp}\) varies from 260–325 mV at 425 °C to 156–217 mV at 550 °C consistent with the overall irreversibility of this process.

The CV data presented in Figure 2 were obtained at 475 °C with 0.027 mol kg\(^{-1}\) of Zr$^{4+}$, while those in Figure 4 were obtained at 500 °C with 0.0445 mol kg\(^{-1}\). Additional cyclic voltammetric experiments...
were conducted with 0.0428 molkg$^{-1}$ of Zr$^{4+}$ at 475, 500, 525 and 550°C. Figure 6 shows results at 525°C with a switching potential of $-1.375$ V (vs Ag/AgCl). All the cathodic and anodic processes shown in this Figure and with the other conditions are consistent with those shown in Figures 2 and 4 in terms of relative shapes and characteristics.

Ghosh et al.$^{8,10}$ reported an additional anodic process at $-0.37$ V with a significant peak current (Figure 4, 0.0884 molkg$^{-1}$ ZrCl$_4$ at 550°C) which was attributed to the reaction $\text{Zr}^{2+} \rightarrow \text{Zr}^{4+} + 2e^-$. In the present work, the process assigned to this reaction is the one designated as $I_{pA_2}$ which is well removed from $-0.37$ V (see details below). However, in this work, a minor process was occasionally observed at $-0.37$ V with high scan rates (Figure 6b) and is possibly associated with monolayer dissolution of zirconium oxide/oxychloride/Zr$^{4+}$/ZrCl$_4$. Sakamura$^7$ avoided any possibility of detecting an anodic peak at $-0.37$ V since the initial and final potentials used in the cyclic voltammetry were $-0.4$ V (vs. Ag/AgCl). The variation in this process is probably due to the differences in salt treatments. Ghosh et al.$^{10}$ appears to have heated LiCl-KCl and ZrCl$_4$ together at 455°C under a chlorine gas atmosphere. Preliminary studies conducted in this work indicated that when the eutectic salt and ZrCl$_4$ are mixed before the drying process, oxygen monolayers present on the salt appear to readily react with ZrCl$_4$ even in the presence of vacuum and once zirconium oxychloride is formed it is difficult to dissolve even with HCl(g).$^{12}$

Sakamura$^7$ reported a third reduction process when the switching potential was extended to even more negative values than considered to date. Figure 7 confirms the presence of additional reduction involving a nucleation-growth mechanism when the potential is switched at $-1.7$ V (vs. Ag/AgCl). Under these conditions, the second oxidation process $I_{pA_2}$ becomes greatly enhanced, relative to $I_{pA_1}$, implying that the product of the third and second reduction steps is common and presumably zirconium metal (Zr). Thus, process $I_{pA_2}$ is attributed to stripping of zirconium metal from the electrode surface.

**Controlled Potential Electrolysis.**—XRD analysis in the 20 range from 20 to 40 of the product formed by bulk electrolysis at $-1.2$ V (vs Ag/AgCl) (Figure 8) indicates the presence of amorphous material with the major diffraction component being attributable to the eutectic salt and ZrCl. The eutectic salt shows strong preferred orientation that precluded the observation of the 35 and 47.5 2θ degree peaks reported by Sakamura.$^7$ Chemical analyzes also indicated the presence of the...
Table I. Summary of Reactions and Parameters Used to Simulate the Cyclic Voltammograms.\(^a\)

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>(E^\circ) / V (vs. Ag/AgCl)</th>
<th>(k_a)</th>
<th>(K_{eq})</th>
<th>(k_f) / s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(Zr^{4+} = Zr^{2+})</td>
<td>425°C</td>
<td>475°C</td>
<td>525°C</td>
<td>(1 \times 10^3)</td>
</tr>
<tr>
<td>2.</td>
<td>(Zr^{4+} + 2e^- = Zr^{2+})</td>
<td>(-1.169)</td>
<td>(-1.077)</td>
<td>(-1.079)</td>
<td>(15 \text{ s}^{-1})</td>
</tr>
<tr>
<td>3.</td>
<td>(Zr^{2+} + 2e^- = Zr^0)</td>
<td>(-1.240)</td>
<td>(-1.176)</td>
<td>(-1.049)</td>
<td>(20 \text{ s}^{-1})</td>
</tr>
<tr>
<td>4.</td>
<td>(Zr^{4+} + 3e^- = Zr^0)</td>
<td>(-1.515)</td>
<td>(-1.470)</td>
<td>(-1.430)</td>
<td>(5 \text{ cm s}^{-1})</td>
</tr>
<tr>
<td>5.</td>
<td>(Zr^0 = Zr^{2+})</td>
<td>(-1.55)</td>
<td>(-1.50)</td>
<td>(-1.460)</td>
<td>(10 \text{ cm s}^{-1})</td>
</tr>
<tr>
<td>6.</td>
<td>(Zr^{2+} + 4e^- = Zr^0)</td>
<td>(-0.864)</td>
<td>(-0.823)</td>
<td>(-0.806)</td>
<td>(500 \text{ s}^{-1})</td>
</tr>
<tr>
<td>7.</td>
<td>(Zr^0 = Zr^{4+})</td>
<td>(-0.852)</td>
<td>(-0.815)</td>
<td>(-0.782)</td>
<td>(500 \text{ s}^{-1})</td>
</tr>
<tr>
<td>8.</td>
<td>(Zr^{2+} = Zr^{4+} + 3e^-)</td>
<td>(-1.430)</td>
<td>(-1.460)</td>
<td>(-1.480)</td>
<td>(10 \text{ cm s}^{-1})</td>
</tr>
<tr>
<td>9.</td>
<td>(Zr^0 = Zr^{4+} + 4e^-)</td>
<td>(-0.852)</td>
<td>(-0.815)</td>
<td>(-0.782)</td>
<td>(500 \text{ s}^{-1})</td>
</tr>
</tbody>
</table>

\(^a\) A superscripted asterisk (*) denotes an adsorbed species. Other species are assumed to be soluble. For example, in step 3, Zr^{4+} indicates that zirconium metal is adsorbed (present as a thin film while Zr^{0} in step 6 represents a very small concentration of dissolved zirconium metal at the electrode-solution interface. In step 7 virtually all Zr^{0} metal is present as a film, \(K_{eq} = 10^{15}\). The maximum surface coverage used was \(\sim 10^{-5} \text{ moles cm}^{-2}\). In some cases, simulations are relatively insensitive to a particular parameter, in the sense that they may be varied with the outcome resulting in little difference in agreement between simulated and experimental data, e.g., \(k_f\) value of 10 cm s\(^{-1}\) in step 6. In the simulations, linear diffusion, Butler-Volmer electrode kinetics and Frumkin isotherms were assumed with no interaction between the surface confined species (a = 0).

Simulations of the Cyclic Voltammetry.— Simulations using a wide range of mechanisms were undertaken in an attempt to mimic the first two processes derived from reduction of Zr^{4+}. Simulations using the parameters shown in Table I provide the results shown in Figure 9. It can be seen that for both concentrations of Zr^{4+} over the temperature range from 425 to 550°C that simulations with the finally chosen mechanism successfully mimic the experimental scan rate and other characteristics. That is, excellent agreement is obtained between the simulated and experimental data under all conditions examined. In a complex mechanism such as the one proposed, the excellent accord of simulated and experimental data does not guarantee that a unique set of simulated parameters has been obtained in order to match the experimental data. Nevertheless, the excellent agreement does present some confidence that the basic features are now identified. Accordingly, the CV experimental data is now interpreted as follows: (a) the Zr^{2+} \(\rightarrow\) Zr^{4+} step is formed by a large and favorable equilibrium constant (b) the first process consists predominantly of the reduction process Zr^{4+} \(+2e^-\) \(\leftrightarrow\) Zr^{2+} and the simulation closely mimics the drawn out nature of this essentially confined process. (c) the peak shaped second reduction process represents a complex reaction with a significant diffusion component. (d) the overall reaction is irreversible.

Table I summarizes the parameters used to simulate cyclic voltammograms for the first two steps in the reduction of Zr^{4+} in LiCl - KCl eutectic molten salt at 425, 475 and 525°C and 2 Zr^{4+} concentration levels.

Table II provides peak potentials for process I_pC_2 derived experimentally, Baboian et al.\(^1\) reported a value of \(-1.120 \text{ V (vs Ag/AgCl)}\) at 550°C which is in reasonable agreement with that \(-1.058 \text{ V (vs Ag/AgCl)}\) obtained in this work also at 550°C. Table II summarizes eutectic salt. The dominance of ZrCl over zirconium metal, when electrolysis is undertaken at \(-1.2 \text{ V (vs Ag/AgCl)}\) agrees with the findings reported by Sakamura.\(^4\)

Table II. Peak Potentials for \(E_p\) (Process I_pC_2) and Diffusion Coefficient values (D) for Zr^{4+} determined from simulation as a function of temperature in LiCl-KCl eutectic molten salt.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>425</th>
<th>450</th>
<th>475</th>
<th>500</th>
<th>525</th>
<th>550</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_p) (I_pC_2), V (vs. Ag/AgCl)</td>
<td>(-1.18)</td>
<td>(-1.16)</td>
<td>(-1.12)</td>
<td>(-1.09)</td>
<td>(-1.06)</td>
<td>(-1.05)</td>
</tr>
<tr>
<td>D, cm(^2) s(^{-1})</td>
<td>1.25</td>
<td>1.30</td>
<td>1.40</td>
<td>1.50</td>
<td>1.65</td>
<td>1.75</td>
</tr>
</tbody>
</table>

It can be seen that for both concentrations of Zr^{+4} over the temperature range from 425 to 550°C that simulations with the finally chosen mechanism successfully mimic the experimental scan rate and other characteristics. That is, excellent agreement is obtained between the simulated and experimental data under all conditions examined. In a complex mechanism such as the one proposed, the excellent accord of simulated and experimental data does not guarantee that a unique set of simulated parameters has been obtained in order to match the experimental data. Nevertheless, the excellent agreement does present some confidence that the basic features are now identified. Accordingly, the CV experimental data is now interpreted as follows: (a) the Zr^{2+} \(\rightarrow\) Zr^{4+} step is formed by a large and favorable equilibrium constant (b) the first process consists predominantly of the reduction process Zr^{4+} \(+2e^-\) \(\leftrightarrow\) Zr^{2+} and the simulation closely mimics the drawn out nature of this essentially confined process. (c) the peak shaped second reduction process represents a complex reaction with a significant diffusion component. (d) the overall reaction is irreversible.
the diffusion coefficient values determined from simulation, which were assumed to be equal for all dissolved species. Caravaca et al.16 and Fabian et al.11 have also reported the diffusion coefficient values in the low 10−5 cm².s−1 range for gadolinium, neptunium and lanthanum, respectively in the LiCl-KCl electrolyte system.

Square-Wave Voltammetry of Zirconium.— Cyclic voltammetry with simulation of the theory has been the electrochemical technique of choice employed to probe the mechanism of reduction of Zr⁴⁺. Square-wave voltammetry provides improved resolution and discriminates against the capacitative current and at least qualitatively can be advantageously used to probe the reaction mechanism more effectually than cyclic voltammetry.17 SWV data were obtained with a 20 mV pulse height or amplitude (Eₚₛ) and 5 mV step potential (ΔEₛ) at frequencies of 9, 16, 25, 36, 49 and 64 Hz (scan rate, mVs⁻¹), 45, 80, 125, 180, 245 and 320 Hz.

Figure 10a shows a SWV for the reduction of Zr⁴⁺ at 550°C. The initial adsorption dominated first reduction process Zr⁴⁺ + 2e⁻ ↔ Zr²⁺ is again seen at about −1.1 V (vs. Ag/AgCl). However, the second predominant diffusion based process described in the cyclic voltammetry is now split into two steps with peak potentials at about −1.18 V and −1.225 V, illustrating that there is a multi-electron reduction closely spaced charge-transfer processes. Furthermore, as shown in Figure 10b the dependence of the major peak current on the square root of the frequency is linear as expected for mass transport by diffusion.18

Conclusions

Since zirconium is a fissile product in nuclear fuels and is also used in the preparation of metallic fuels, it is important to understand its electrochemistry in pyroelectrochemical reprocessing of spent nuclear fuel. Simulation of the pyroelectrochemical complex cyclic voltammetric data was conducted and excellent agreement was obtained with a designated mechanism and experimental data at two concentrations of Zr⁴⁺ (0.027 and 0.043 molkg⁻¹) over the temperature range of 425 to 550°C and scan rates from 50 to 500 mVs⁻¹. Simulations indicate that the Zr⁴⁺ → Zr⁴⁺⁺ process has a large equilibrium constant so that the initial reduction step is predominantly a surface confined of Zr⁴⁺⁺ + 2e⁻ ↔ Zr²⁺⁺ process. Simulations closely mimic the drawn out sigmoidal shaped nature of the initial reduction step. The second peak shaped reaction step is complex, but consists of combination of unresolved Zr²⁺⁺ + 2e⁻ ↔ Zr²⁺, Zr⁴⁺⁺ + 4e⁻ → Zr⁴⁺, Zr⁴⁺⁺ + 3e⁻ → Zr⁵⁺ reactions with a significant diffusion component. Zr²⁺⁺ is probably ZrCl and can be reduced to Zr⁰ at more negative potentials. Their symmetrical shape implies that the oxidation components in cyclic voltammograms are a result of surface confined processes. SWV data provide evidence of closely spaced steps in the second reduction process.

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References