Effects of Temperature, Concentration, and Uranium Chloride Mixture on Zirconium Electrochemical Studies in LiCl-KCl Eutectic Salt

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Abstract

Experimental studies were performed to provide measurement and analysis of zirconium (Zr) electrochemistry in LiCl-KCl eutectic salt at different temperatures and concentrations using cyclic voltammetry (CV). An additional experimental set with uranium chloride added into the system forming $\text{UCl}_3\text{-ZrCl}_4\text{-LiCl-KCl}$ was performed to explore the general behavior of these two species together. Results of CV experiments with ZrCl_4 show complicated cathodic and anodic peaks, which were identified along with the Zr reactions. The CV results reveal that diffusion coefficients (D) of ZrCl_4 and ZrCl_2 as the function of temperature can be expressed as $D_{\text{Zr(IV)}} = 0.00046\exp(-3716/T)$ and $D_{\text{Zr(II)}} = 0.027\exp(-5619/T)$, respectively. The standard rate constants and apparent standard potentials of ZrCl_4 at different temperatures were calculated. Furthermore, the results from mixture of UCl_3 and ZrCl_4 indicate that high concentrations of UCl_3 hide the features of the smaller concentration of ZrCl_4 while Zr peaks become prominent as the concentration of ZrCl_4 increases.

24 1. Introduction

25 Electrochemical processing (also known as pyroprocessing, electrometallurgical, or
26 pyrochemical technology) was first developed by Argonne National Laboratory to treat used
27 metallic sodium-bonded fuel from the Experimental Breeder Reactor-II (EBR-II) [1-3]. This
28 technique is still being used at Idaho National Laboratory (INL) and widely studied by many
29 researchers because it has some advantages when compared with the conventional aqueous
30 processes, including compact space requirement, production of the mixed fuel, and treatment of
31 fast reactor fuel [4]. During irradiation, the metallic sodium bond material is incorporated into
32 the fuel [3], which limits the disposal options due to the highly exothermic reaction with water
33 [5]. In general, the driver fuel, post-irradiation, contains approximately 80.6 wt% uranium (U)
34 and 10.8 wt% zirconium (Zr), with the remainder fission products (FPs) [6]. The used EBR-II
35 driver fuel rods are chopped and loaded into stainless steel fuel dissolution baskets as an anode,
36 which are then lowered into a molten LiCl-KCl eutectic (58 mol% : 42 mol%) salt containing
37 nominally 5 - 10 wt% UCl_3 at 773 K for an electrefining process [6]. Generally, it is operated
38 in a galvanostatic mode, so a current is applied with a cutoff voltage to electrochemically oxidize
39 and dissolve U into the electrolyte salt while Zr and FPs remain in the anode baskets. Overall,
40 the goal of the electrochemical process is to anodically dissolve U at the anode basket and collect
41 pure U at the solid steel cathode.

42 Ideally, as mentioned above, the Zr should remain unoxidized in the anode basket due to
43 the difference in the standard potentials between U and Zr. The reported apparent standard
44 potentials of U and Zr are -1.3 V and -1.22 V vs. Ag/AgCl at 723K, respectively [7 - 9].
45 However, the small difference in the standard potentials causes unavoidable Zr oxidation along

with U. Additionally, in the electrorefining process, the potential applied at the anode basket needs to be sufficiently higher than the standard potential of U/U^{3+} to maintain a high dissolution rate of U at the anode basket [10], resulting in Zr dissolution into the salt. In the early years of electrorefining operation at INL, Zr retention was the primary goal under the U.S. Department of Energy (DOE) demonstration program, while during the Advanced Fuel Cycle Initiative (AFCI), more emphasis had been put on achieving complete actinide dissolution [6]. Zr buildup in the electrorefiner (ER), primarily in the cadmium pool, is illustrated and reported by Li and Simpson [6].

Due to this behavior, it is clear that Zr has been building up in the ER at INL and must be periodically collected. To develop a method of collecting Zr in a pure (free from U contamination) state, the electrochemical behaviors of U and Zr, both separately and together, in the LiCl-KCl eutectic molten salt must be understood. These actions provide an important motivation to focus on the zirconium electrochemistry as little attention has been paid to it in the past. Early work in 1965 by Baboian et al. [9] provided a specific study on the potentials and stabilities of zirconium chlorides (ZrCl_4 and ZrCl_2) in molten LiCl-KCl at 723 K for low concentrations of Zr (less than 0.05 mol%). Since then, there have been several other experiments and computational models focusing on understanding Zr behaviors in molten salt systems complicated by the low sublimation point (604 K) and hygroscopic properties of ZrCl_4 , along with complex behaviors in the stepwise process [9-17]. However, electrochemical properties of ZrCl_4 including the diffusion coefficient, the apparent standard potential, and the standard rate constant have been poorly accumulated and understood because of the complexity of the Zr ion formations and difficulty of Zr handling as previously mentioned.

In the present study, series of experimental runs were conducted by systematically varying the concentration of ZrCl_4 up to 5 wt% in the molten LiCl-KCl salt at three different temperatures (723, 773, and 823 K) using two electrochemical methods—cyclic voltammetry (CV) and chronopotentiometry (CP). Furthermore, to better reflect the conditions in an operating used nuclear fuel ER, an additional set of experiments with quaternary salt $\text{UCl}_3\text{-ZrCl}_4\text{-LiCl-KCl}$ was also performed to explore the behavior of U and Zr together. It is expected that this research study will offer an enhancement in the electrorefining process for current operation and future process design.

2. Experimental

Experiments were conducted in a sealed glove box with an inert argon atmosphere with O_2 and H_2O concentrations less than 3.0 ppm. A Kerrlab melting furnace for melting and maintaining the salt at desired temperatures was placed inside the glove box as shown in Figure 1(a). There were two experimental schemes: (1) zirconium tetrachloride (ZrCl_4) experiments under different temperatures and concentrations and (2) variations with additional uranium trichloride (UCl_3).

In the first scheme, the salt mixtures were composed of LiCl-KCl eutectic from AAPL (99.99%) and zirconium tetrachloride (ZrCl_4 , 99.5+%) from Alfa Aesar. The salt was loaded into a 16.8 cm tall tapered glassy carbon crucible (Sigradur®, HTW-Germany) with outside diameters of 4.1 cm and 4.5 cm at the bottom and top, respectively, and a wall thickness of 0.3 cm. This glassy carbon crucible was then placed into a magnesium oxide (MgO) secondary crucible to contain any molten salt upon possible breakage of the crucible before loading it into the furnace. The working electrode was a tungsten rod (diameter of 2.0 mm and length of 30 cm,

Alfa Aesar, 99.95%) and the counter electrode was a glassy carbon rod (diameter of 3.0 mm and length of 30 cm, Sigradur®, HTW-Germany). The glassy carbon rod was in contact with the glassy carbon crucible making the entire crucible and rod in contact with the electrolyte the counter electrode. A silver wire in LiCl-KCl-5.0 mol% AgCl (Alfa Aesar, ultra dry, 99.997%) in a Pyrex® body was used as a reference electrode. A view of the electrodes and connections can be seen in Figure 1(b), while the schematic design of the cell is shown in Figure 2.

While ZrCl_4 is soluble and stable in the molten eutectic, pure ZrCl_4 sublimates at 604 K [18], which is lower than the melting point of the LiCl-KCl eutectic, from 621 K to 634 K [19]. To overcome this issue, a modified process was developed to trap ZrCl_4 underneath the LiCl-KCl until the salt melts and all ZrCl_4 can be all dissolved into the eutectic by working with a tapered glassy carbon crucible (see Figure 3). The pure LiCl-KCl eutectic was first melted and consolidated into a single ingot in the tapered glassy carbon crucible. When cooled overnight, the LiCl-KCl ingot was removed from the crucible and approximately 1 cm was cut off the bottom of the salt ingot (see Figure 3(a)). The powdered ZrCl_4 was added to the crucible and the ingot with the bottom cut off was placed over the top of the ZrCl_4 powder in the crucible (Figure 3(b)). Due to the taper, the salt ingot sits tightly against the walls of the crucible and above this powder. With this method, there was no evidence of ZrCl_4 vaporization and inductively coupled plasma mass spectrometry (ICP-MS) analysis of the salt mixtures following each experiment showed that all the ZrCl_4 that was added to the mixture remained in the crucible.

In the second scheme, the behavior of ZrCl_4 together with UCl_3 in the LiCl-KCl eutectic was studied as there is nominally 10 wt% UCl_3 in the LiCl-KCl electrolyte during the pyrochemical treatment of used nuclear fuel in the Mark-IV ER [6]. For similitude with this ER, depleted UCl_3 provided by INL as a 75 wt% mixture in LiCl-KCl eutectic was chosen. The UCl_3

concentration was slightly less than 10 wt% (9.80 and 8.34 wt%) with two experiments containing a low (0.497 wt%) and a high (4.17 wt%) concentration of ZrCl_4 . To minimize depleted uranium waste, the UCl_3 - ZrCl_4 - LiCl - KCl salt mixtures were prepared by adding ZrCl_4 to 10.0 wt% UCl_3 - LiCl - KCl mixture prepared for previous pure uranium experiments [24]. The cutting of the salt ingot as described above would spread UCl_3 sawdust throughout the glove box, so a modified method was undertaken in preparing the salt mixture. A 25.1 wt% mixture of ZrCl_4 - LiCl - KCl was prepared utilizing the vapor trapping method described previously, maintaining the salt at temperature for five hours to allowing for a complete dissolution. This salt with the ZrCl_4 pre-dissolved in the LiCl - KCl eutectic was then added to the 10.0 wt% UCl_3 - LiCl - KCl mixture to achieve the desired ZrCl_4 concentrations.

The heating process was the same for both experimental schemes. The furnace was heated at 4 K/min to avoid thermal shock on the glassy carbon crucible to approximately 813 K for the pre-heating process. During that period, the electrodes were positioned over the top of the crucible to be pre-heated during furnace heating as well. Then, the temperature was adjusted to the desired operating temperature. Prior to initiating the electrochemical runs, the electrodes were lowered into the molten salt resulting in working electrode surface areas ranging from 0.583 cm^2 to 0.785 cm^2 depending on the experimental sets. The working electrode surface area was calculated based on the measured immersion depth of the electrode indicated by a line of adhered salt after removing from each experiment. Once the salt mixture reached the desired temperature, the electrochemical experiments were initiated. A Princeton Applied Research VersaSTAT 4-400 potentiostat with *VersaStudio* software was used for all electrochemical experiments and data collection. The experimental program is summarized in Table 1.

3. Results and Discussion

3.1 Cyclic voltammetry (CV) and chronopotentiometry (CP) of ZrCl₄-LiCl-KCl

Cyclic voltammograms of ZrCl₄ were recorded under four concentrations at three different temperatures (723, 773, and 823 K) and several scan rates, as shown in Figure 4. All CV results show very similar complex behavior. As an example, the 1.07 wt% ZrCl₄ CVs (Figure 4(b)) show three cathodic peaks (A_c, B_c, and C_c) and two anodic peaks (A_a and B_a). It is clear that the peak potential shifts slightly negative for the reduction peaks and positive for the oxidation peaks with increasing scan rate. This behavior indicates that the reactions must be considered irreversible. It should be noted that peak identification has been performed through a review of the Zr studies by several researchers [10, 15, 17]. As the potential is scanned from 0.5 V in the negative direction, the first reaction to occur is Zr(IV) being reduced to Zr(II), resulting in Peak A_c at approximately -1.06 V, which is

As the potential is scanned further in the negative direction Zr(II) may be reduced to Zr metal while some remaining Zr(IV) may be reduced to insoluble ZrCl, resulting in Peak B_c at approximately -1.5 V; these are

Continuing further in the negative direction, both ZrCl and Zr(IV) are fully reduced to Zr metal at approximately -1.85 V, which are

At -2.4 V, the potential scan was reversed and the first oxidation reactions that may occur are shown by the large Peak B_a at approximately -0.5 V.

From other studies [10, 15, 17], a ZrCl/Zr⁴⁺ anodic peak was observed at about -0.9 V versus Ag/Ag⁺ reference while the peak disappeared when the cathode potential was swept more negative than -1.6 V versus Ag/Ag⁺ reference. Therefore, the ZrCl/Zr⁴⁺ anodic peak was not observed in the present study. The small hump on the shoulder of Peak B_a, marked A_a, is likely the oxidation of Zr(II) to Zr(IV).

Figures 4(a) – 4(d) also display the effect of temperature on recorded CV data sets. As temperature is increased, the effect appears qualitatively similar to increasing concentration—peak heights increase and peak potentials shift in the positive direction. It can be seen that temperature may be used to enhance the peak detection for low concentration studies. For example, peak A_c becomes more prominent as temperature increases, which can be seen in Figure 4(a). However, as the concentration increases (4.98 wt% as an example), the temperature effect was minimal in changing the peak height. Peak enhancement and peak potential shift with increasing temperature were barely found at the high concentration cases.

The effects of concentration at the three different temperatures can be seen in Figure 5. As expected, the peak heights increase when the concentration increases, implying that higher current density results from higher bulk concentration due to an increase in mass transfer rates. The peak potential shifts in the positive direction with increasing temperature at low

concentrations (0.57 wt% to 2.49 wt%); however, the opposite peak characteristic can be observed at the concentration of 4.98 wt%. At the high concentration, limiting current occurs late due to that the oxidants are continuously provided from the bulk salt to the electrode surface. The peak C_c is not clearly observed at 0.57 wt% $ZrCl_4$ in comparison to the other concentrations leading to the conclusion that, at this low concentration, $ZrCl$ is either not formed at the electrode surface as in Eq. (2b), or $ZrCl$ is formed, but it is not reduced to Zr metal via Eq. (3a).

CP was performed on the four different $ZrCl_4$ salt compositions at three temperatures. The resulting chronopotentiograms for the 0.57 wt% $ZrCl_4$ salt mixture at 823 K and various applied driving current densities are shown in Figure 6 as an example. Similar trends have been observed for other concentrations. Figure 6 shows several plateaus corresponding to the different reactions that can occur in the LiCl-KCl eutectic. The first plateau at approximately -1.3 V is most likely corresponding to Peak B_c in the cyclic voltammograms as indicated in Figure 4 (b); therefore, this would likely represent the diffusion limited reaction of $Zr(II)/Zr$ implying the diffusion of $Zr(II)$. The second plateau at approximately -1.7 V corresponds to Peak C_c in the CVs (see Figure 4 (b)), and the reduction of $ZrCl$ to Zr. Other plateaus beyond a potential of -2 V were difficult to determine. In comparison to the CV measurements, CP is of relatively low value for a system with so many redox couples; therefore, CV results were further analyzed to explore the electrochemical behaviors of Zr elements in LiCl-KCl salt.

3.2 Diffusion coefficient of Zr^{4+} and Zr^{2+} in LiCl-KCl salt

As the zirconium system is irreversible, the Delahay equation [20] was chosen to determine information about the reactions occurring in the system; that is,

$$\frac{i_{pc}}{\sqrt{v}} = 0.4958 nFSC \sqrt{\frac{n\alpha F D_{ox}}{RT}} \quad (6)$$

where i_{pc} is the cathodic peak current density in voltammetry, v is the scan rate, n is the number of electrons transferred, α is the transfer coefficient, F is the Faraday constant ($C \text{ mol}^{-1}$), S is the working electrode area (cm^2), C is the concentration (mol cm^{-3}), D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), R is the universal gas constant ($J \text{ mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K). Figure 7 shows a representative plot of peak current density versus square root of scan rate for the 1.07 wt% ZrCl_4 mixture at 773 K. From the slope of the line, if the number of electrons transferred during the reaction is known, the diffusivity of the oxidized species can be determined. In case of irreversible reaction, $n\alpha$ can be calculated by using the difference between the cathodic peak potential and the half peak potential, which can be expressed by

$$\left| E_{pc} - E_{p/2} \right| = 1.857 \frac{RT}{n\alpha F} \quad (7)$$

where E_{pc} is the cathodic peak potential, and $E_{p/2}$ is the half peak potential (the potential at the point where the current is half of the peak current), which was measured at the half peak current ($I_{p/2}$) determined by dividing the peak current (I_p) by two. The calculated values of $n\alpha$ are listed in Table 2. A transfer coefficient of 0.4, which has also been used for reactions in the molten LiCl-KCl for modeling purposes [21, 22], results in values that are much closer to the expected number of electrons transferred. An accurate baseline for Peak C_c was not possible, and therefore the half peak potential, $E_{p/2}$, could not be determined and the same analysis using Eq. (7) could not be performed. Assuming two electrons transferred for Peaks A_c and B_c and a transfer coefficient of 0.4, the diffusion coefficients of Zr(IV) and Zr(II) were calculated from the slopes indicated by Eq. (6) at each temperature. All calculated values are listed in Table 2, revealing slightly smaller values than the published Zr (IV) diffusivity values by Yamada and co-workers

[23]. There was no discernable trend in diffusion coefficient at these studied concentrations. The reported values are all mean values. For Peak C_c, the likely oxidized species is the insoluble ZrCl₃ indicating that it does not diffuse in the molten LiCl-KCl eutectic; therefore, there is no diffusivity value associated to it. Although Eq. (6) leads to the assumption that the data should have an intercept of zero, the experimental results do not fully fit this assumption. That is, in reality, a non-zero intercept can exist when a capacitive current is present in the system, as appears to be the case with zirconium. The calculated diffusion coefficients are reasonable values for liquid phase diffusion and are in the same general range as those reported by Lee et al. in 2012 [15]. Diffusivity tends to follow an Arrhenius temperature dependence of

$$D = D_0 \exp \left(\frac{-E_D}{RT} \right) \quad (8)$$

where D_0 is the pre-exponential factor (cm²/s), and E_D is the activation energy for the diffusion of the species (J/mol). The natural log of the calculated diffusivities of Zr(IV) and Zr(II) are plotted against the inverse temperature, from which D_0 and E_D were calculated. These values are indicated in Table 3 along with the published values of D_0 and E_D by Yamada and co-workers [23].

3.3 Apparent standard potential of Zr⁴⁺ and Zr²⁺ in LiCl-KCl salt

To calculate the apparent standard reduction potentials of the zirconium system, for a soluble/insoluble irreversible redox couple, Eq. (9) can be utilized [7]:

$$E_{pc} = E^{0*} - \frac{RT}{n\alpha F} \left[0.78 - \ln k_s + \ln \left(\sqrt{\frac{n\alpha F D_{ox}}{RT}} \right) \right] \quad (9)$$

where k_s is the standard rate constant (cm/s). Since k_s values have not been well reported, the rate constant was estimated by using the following equation from Ghosh et al. [14]:

$$k_s = 2.18 (n\alpha)^{1/2} \left(\frac{DFv}{RT} \right)^{1/2} \exp \left(\frac{\alpha^2 nF}{RT} (E_p^c - E_p^a) \right) \quad (10)$$

where E_p^c and E_p^a are the cathodic and anodic peak potentials, respectively. Both peak potentials were obtained at Zr concentrations of 0.57 wt% and 1.07 wt% because distinctive peak signatures can be read at a lower concentration range. The values of $n\alpha$ and diffusion coefficient used in Eqs. (9) and (10) were based on the previous calculations (listed in Table 2). The estimated values of k_s are listed in Table 4 and the apparent standard potentials are summarized in Table 5. There were no discernable trends to the apparent standard potential data with concentration; therefore, the reported values are the mean across all studied concentrations. It should be noted that conversion to the Cl_2/Cl^- reference was performed by using the Ag/AgCl data from Yang and Hudson [25]. The apparent standard potential of Zr(IV)/Zr(II) at 773 K was -0.825 V which is difficult to compare with the reported data due to the dispersed values: Ghosh [14] and Fabian et al. [16] reported -1.077 V and -0.11 V, respectively. On the other hand, the apparent standard potentials of Zr(II)/Zr in the present study agree well with the published data at these temperature ranges [9, 14, 16].

3.4 CV experiments in UCl_3 - ZrCl_4 - LiCl - KCl and analysis

CV experiments were performed on two LiCl - KCl - ZrCl_4 - UCl_3 mixtures at 773 K. The CVs for the 0.497 wt% ZrCl_4 - 9.80 wt% UCl_3 are shown in Figure 8(a). When comparing this result with the 0.57 wt% ZrCl_4 CVs seen in Figure 4(a) and the 10.0 wt% UCl_3 CVs reported in Hoover [24], which are overlaid in Figure 8(b), it is clear that the relatively high concentration of UCl_3 hides some of the features of the smaller concentration of ZrCl_4 . The main location where any ZrCl_4 effects are evident appears on the positive potential side of the large anodic Peak C_a . At approximately -0.5 V (see Figure 8(a)), there is a small hump, labeled B_a , on the large anodic

peak, which is likely caused by the Zr/Zr(II) oxidation peak as observed in Figure 8(b). The presence of ZrCl₄ is more prominent in the CVs from the 4.17 wt% ZrCl₄ - 8.34 wt% UCl₃ mixture as seen in Figure 9(a). Through a comparison of the data shown in Figures 9(a) and 9(b), it is clear that zirconium has a substantial effect on the appearance of the CVs in the 4.17 wt% ZrCl₄ - 8.34 wt% UCl₃ mixture. The large anodic peak B_a at -0.3 V is most likely due to the Zr/Zr(II) oxidation. There is also the appearance of an anodic peak at approximately -1.0 V, labeled D_a in Figure 9(b). As discussed previously, several studies [10, 15, 17] showed an anodic peak corresponding to the oxidation of ZrCl if it was not fully reduced to metal during the cathodic sweep. This peak is likely an evidence of that oxidation reaction. With the large amount of uranium present in the mixture, the ZrCl is likely not fully reduced to metal during the cathodic sweep leaving some ZrCl to oxidize during the following anodic sweep. This could be a possible impediment to electrorefining pure Zr metal in the presence of large UCl₃ concentrations. Figure 10 illustrates the peak current density versus square root of scan rate for the cathodic peaks. Figure 10(a) plots peak currents of A_c, B_c, and C_c (for the 0.497 wt% ZrCl₄ - 9.80 wt% UCl₃ from Figure 8(a)), and Figure 10(b) plots peak currents of A_c, B_c, and C_c (for the 4.17 wt% ZrCl₄ - 8.34 wt% UCl₃ from Figure 9 (a)). The high degrees of linearity ($R^2 > 0.98$) lead to the conclusion that these reactions are indeed diffusion limited. These figures show a non-zero intercept, likely due to the effect of the capacitive current present with the reactions of zirconium.

4. Conclusions

Two experimental schemes to measure and interpret the collected data for fundamental electrochemical separations were accomplished: (1) zirconium and (2) uranium and zirconium in

combination. Based on the results of the first scheme, several conclusions can be drawn. It appears that not all ZrCl is fully reduced to Zr metal. The results show that peak heights increase and peak potentials shift in the negative direction as temperature increases. This implies that temperature may be used as a tool for enhanced peak detection for any low concentration studies. In addition, two distinct plateaus can be observed in the CP plots at -1.3 V for peak B_c and -1.7 V for peak C_c .

Assuming that the transfer coefficient is 0.4 [21, 22], the number of electrons transferred is calculated to be close to two, as expected for both the Zr(IV)/Zr(II) and Zr(II)/Zr redox couples. Table 6 provides a summary of electrochemical and thermodynamic properties of zirconium calculated from experimental data in LiCl-KCl eutectic at different temperatures. The values of D_0 and E_D for Zr(IV) are in agreement with the values reported in Yamada et al. [23]. The standard potential values of Zr(IV)/Zr(II) are slightly smaller than published values, while the apparent standard potential of Zr(II)/Zr agrees with the reported data.

When ZrCl_4 is combined with UCl_3 , CV results reveal that a high concentration of UCl_3 hides some of the important features of the smaller concentration of ZrCl_4 . There is limited distinctive features of zirconium that can be observed from the low Zr concentration CV data sets. The presence of zirconium becomes prominent as the concentration of ZrCl_4 increases. Additionally, it is possible to expect that the ZrCl is likely not fully reduced to metal during the cathodic sweep leaving some ZrCl to oxidize during the following anodic sweep. This is seen with large amounts of uranium present in the mixture. This may also create a possible impediment to electrorefining pure Zr metal in the presence of large UCl_3 concentrations.

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Table 1 Program for two experimental schemes

Exp. No.	Concentration, wt%		Electrochemical		Temperature (K)
	(Actual)		Methods		
	ZrCl ₄	UCl ₃	CV	CP	
1	0.5 (0.57)	0	YES	YES	723, 773, 823
2	1.0 (1.07)	0	YES	YES	723, 773, 823
3	2.5 (2.49)	0	YES	YES	723, 773, 823
4	5.0 (4.98)	0	YES	YES	723, 773, 823
5	0.5 (0.497)	10 (9.80)	YES	NO	773
6	5.0 (4.17)	10 (8.34)	YES	NO	773

Table 2 Calculated product of number of electrons transferred and transfer coefficient along with diffusion coefficients for Zr(IV) and Zr(II) at 723, 773, and 823 K in the molten LiCl-KCl eutectic.

Peak	Product of electrons transferred and transfer coefficient, $n\alpha$			Diffusion Coefficient, D (cm ² /s)		
	723 K	773 K	823 K	723 K	773 K	823 K
A_c: Zr(IV)	0.85	0.825	0.93	3.06×10^{-6}	2.86×10^{-6}	5.82×10^{-6}
B_c: Zr(II)	0.75	0.65	0.875	1.27×10^{-5}	1.47×10^{-5}	3.33×10^{-5}

Table 3 Zr(IV) and Zr(II) diffusion Arrhenius temperature dependence factors

Peak	D_0 (cm ² /s)		E_D (kJ/mol)	
	Current	Literature	Current	Literature
	Work	Ref. [22]	Work	Ref. [22]
Zr(IV)	4.60×10^{-4}	3.58×10^{-3}	30.9	37.0
Zr(II)	0.0270	N/A	46.7	N/A

Table 4 The standard rate constant for Zr at 723, 773, and 823 K in the LiCl - KCl
eutectic

Peak	Standard Rate Constant, k_s (cm/s)		
	723 K	773 K	823 K
A_C: Zr(IV)/Zr(II)	7.37×10^{-5}	6.65×10^{-5}	3.26×10^{-5}
	($\pm 3.07 \times 10^{-5}$)	($\pm 4.71 \times 10^{-6}$)	($\pm 1.69 \times 10^{-5}$)
B_C: Zr(II)/Zr	2.56×10^{-4}	1.79×10^{-4}	3.01×10^{-4}
	($\pm 5.93 \times 10^{-5}$)	($\pm 1.0 \times 10^{-4}$)	($\pm 1.70 \times 10^{-4}$)

Table 5 Apparent standard reduction potentials for Zr at 723, 773, and 823 K in the LiCl-KCl eutectic

Peak	Temp.	Apparent Standard Reduction Potential, E^{0*} (V vs Ag/AgCl (5 mol%))			
		This study	Ref. 8	Ref. 13	Ref. 15
A_C: Zr(IV)/Zr(II)	723 K	- 0.847 V ($\pm$ 0.043 V)	N/A	N/A	- 1.169 V
	773 K	- 0.786 V ($\pm$ 0.015 V)	N/A	-0.11 ($\pm$ 0.02 V)	- 1.077 V
	823 K	- 0.737 V ($\pm$ 0.105 V)	N/A	N/A	- 1.079 V
B_C: Zr(II)/Zr	723 K	- 1.17 V ($\pm$ 0.013 V)	- 1.12 V	N/A	- 1.24 V
	773 K	- 1.11 V ($\pm$ 0.046 V)	N/A	- 1.11 V ($\pm$ 0.02 V)	- 1.17 V
	823 K	- 1.08 V ($\pm$ 0.025 V)	N/A	N/A	- 1.049 V

Table 6 Summary of electrochemical and thermodynamic properties of zirconium calculated from experimental data in LiCl-KCl eutectic

	Diffusion coefficient, D (cm ² /s)			Apparent standard potential, E ^{0*} (V vs Cl ₂ /Cl ⁻)		
	723 K	773 K	823 K	723 K	773 K	823 K
Zr(IV)/Zr(II)	3.06×10^{-6}	2.86×10^{-6}	5.82×10^{-6}	-1.915	-1.853	-1.802
	$D = 4.60 \times 10^{-4} \exp\left(\frac{-30,900}{RT}\right)$			$E^{0*} = 0.0011T - 2.733$		
Zr(II)/Zr	1.27×10^{-5}	1.47×10^{-5}	3.33×10^{-5}	-2.236	-2.198	-2.149
	$D = 0.0270 \exp\left(\frac{-46,700}{RT}\right)$			$E^{0*} = 0.0009T - 2.872$

Figure 1 (a) Experimental setup in the glove box with (b) close-up view of the electrodes and connections.

Figure 2 Experimental setup within the glove box with (a) Al_2O_3 sheathed thermocouple, (b) tungsten working electrode, (c) Ag/AgCl (5 mol%) reference electrode, (d) glassy carbon counter electrode lead, (e) glassy carbon crucible/counter electrode, (f) MgO secondary crucible, (g) eutectic LiCl-KCl salt containing UCl_3 and/or ZrCl_4 , and (h) Kerrlab furnace.

Figure 3 (a) The bottom of the LiCl-KCl ingot is cut off as part of a method to ensure ZrCl_4 is dissolved into the eutectic, (b) Diagram of the ZrCl_4 trapping method developed for this experimental study (not drawn to scale).

(a)

(b)

(c)

(d)

Figure 4 Cyclic voltammograms showing the temperature effect of (a) 0.57 wt%, (b) 1.07 wt%, (c) 2.49 wt% and (d) 4.96 wt% ZrCl_4 in the molten LiCl-KCl eutectic.

Figure 5 The effect of concentration on CV at (a) $T = 723$ K and $v = 200$ mV/s, (b) $T = 773$ K and $v = 200$ mV/s, and (c) $T = 823$ K and $v = 400$ mV/s.

Figure 6 Chronopotentiograms for 0.57 wt% ZrCl_4 in LiCl-KCl eutectic salt at 823 K.

Figure 7 Peak current density versus square root of scan rate for cathodic peaks in the 1.07 wt% ZrCl₄ cyclic voltammogram at 773 K.

Figure 8 (a) Cyclic voltammograms of 0.497 wt% ZrCl_4 and 9.80 wt% UCl_3 mixture in the LiCl-KCl eutectic at 773 K. (b) Individual cyclic voltammograms of 0.57 wt% ZrCl_4 and 10 wt% UCl_3 mixture in the LiCl-KCl eutectic at 773 K from Ref. [23].

Figure 9 (a) Cyclic voltammograms of 4.17 wt% ZrCl_4 and 8.34 wt% UCl_3 mixture in the LiCl-KCl eutectic at 773 K. (b) Individual cyclic voltammograms of 4.98 wt% ZrCl_4 and 10.0 wt% UCl_3 in the LiCl-KCl eutectic at 773 K from Ref. [23].

Figure 10 (a) Peak current density versus square root of scan rate for cathodic peaks in the 0.497 wt% $ZrCl_4$ - 9.80 wt% UCl_3 cyclic voltammograms at 773 K. (b) Peak current density versus square root of scan rate for cathodic peaks in the 4.17 wt% $ZrCl_4$ - 8.34 wt% UCl_3 cyclic voltammograms at 773 K.