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Electrochemical behavior of zirconium in the LiCl–KCl molten salt at Mo electrode

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ABSTRACT

The electroreduction process of Zr(IV) was studied at molybdenum electrode in LiCl–KCl–K_2ZrF_6 molten salt. The transient electrochemical techniques, such as cyclic voltammetry and chronopotenimetry were used. The experimental results showed that the electrochemical reduction of Zr(II)/Zr and Zr(IV)/Zr(II) were both diffusion-controlled process. In the 773–973 K range, the diffusion coefficients of Zr(ii) and Zr(IV) were determined: $D_{Zr(II)} = 0.15567\exp\{-69.65 \times 10^3 RT(K)\}$ cm^2/s, $D_{Zr(IV)} = 1.09 \times 10^{-4} \exp\{-44.39 \times 10^3 RT(K)\}$ cm^2/s. The activation energy values for the diffusion process were 69.65 kJ/mol and 44.39 kJ/mol, respectively.

1. Introduction

Because of the good nuclear performance and suitable machine properties, zirconium is widely used in nuclear industry [1]. The molten salt electrolysis method is an effective method for the preparation of high-melting point metals and their alloys [2–6]. Though the molten salt electrolysis of zirconium has been widely studied [7–12], the electroreduction process of Zr(IV) ion is not clear yet.

At present, a few studies have been devoted to the electrochemical behavior of Zr in different molten salt systems. The stand potential Zr(IV)/Zr was determined in the molten LiCl–KCl eutectic by Baboian et al. [7]. They found that the Zr(II) and Zr(IV) could coexist in the molten salts between 450 °C and 550 °C, and the ratio of Zr(II)/Zr(IV) increased with the enhancement of temperature. Similar conclusion in the same molten system was educed by Suzuki [8] and Kawase [9]. Basile et al. [10] studied the reduction process of $ZrCl_4$ in the molten NaCl and KCl–LiCl system. They found that Zr(IV) ion was reduced via a four-step reduction mechanism in the molten NaCl melt and two-step in the LiCl–KCl melt. Kipouros and Flengas [11] investigated the oxidation states (+1, +2, +3, +4) of zirconium in alkali metal and fluoride systems over the temperature range 700–750 °. Sakamura [12] investigated the electrochemical behavior of Zr(IV) in LiCl–KCl–$ZrCl_4$ melts over the temperature range 450–550 °C. They found that Zr(I) and Zr(II) both appeared in the melt during the electrodeposition process of Zr. The Zr(IV) ion showed different electrochemical behavior in the reported literatures, which might be attributed to the disaffinity of molten salt system. The different results also show that the further investigation of the electrochemical reduction mechanism of zirconium is indispensable for the electroreduction process.

Our group has tried to explore the electroreduction process of Zr(IV) at molybdenum electrode in the molten LiCl–KCl–K_2ZrF_6 system[9,10]. It was found that Zr(IV) was reduced to Zr metal by a two-step mechanism corresponding to the Zr(IV)/Zr(II) and Zr(II)/Zr transitions. This work planed to further explore the electrochemical behavior of zirconium in the molten LiCl–KCl–K_2ZrF_6 system at molybdenum electrode. The transient electrochemical techniques, such as cyclic voltammetry and chronopotenimetry were used, and the related electrochemical data were obtained.

2. Experimental

2.1. Cell and electrodes

Fig. 1 shows the experimental apparatus. The primary and secondary crucibles were made of high purity (99.9 wt.%) alumina and graphite, respectively. They were positioned in the stainless steel tank outer vessel and heated with the tubular furnace. The temperature measurement was carried out by Chromel–Alumel thermocouple with an accuracy of ±2 K.

The reference electrode was an Ag wire immersed in LiCl–KCl eutectic containing 1.0 mol% AgCl in a Pyrex tube provided with a diaphragm at the bottom. The inert working electrode was molybdenum wire (Ø 1 mm) for the investigation of electrochemical behavior. The lower end of the working electrode was thoroughly polished by SiC paper, and then cleaned in ethanol using the method of ultrasonic cleaning. The active electrode surface was determined after each experiment by measuring the immersion depth of the electrode in the molten salt. A graphite rod (Ø 6 mm) served as a counter electrode. All the experiments were carried out under a carefully purified and dehydrated argon atmosphere.

2.2. Chemicals

The electrochemical behaviors of Zr(IV) were studied in the molten LiCl–KCl–K_2ZrF_6 system. The LiCl–KCl eutectic mixture (LiCl:KCl = 58:42 mol%,

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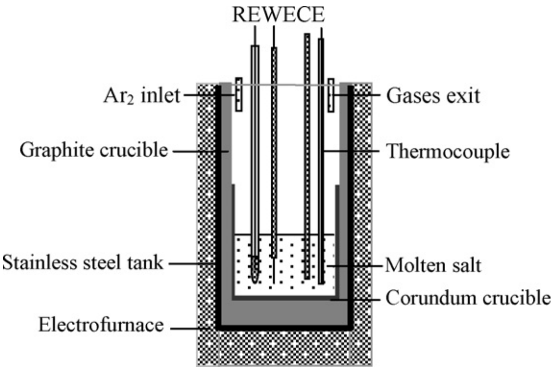

Fig. 1. Apparatus of electrolysis cell.

reagent grade) was dried under vacuum for more than 72 h at 473 K to remove residual water. In order to remove the residual water and some metal impurities, pre-electrolysis was conducted using a molybdenum electrode at −0.3 V (versus Ag/AgCl) for 5 h in a molten LiCl–KCl–K_2ZrF_6 at temperature of every experiment.

2.3. Electrochemical equipment and techniques

All of the electrochemical studies were performed with IM6e electrochemical workstations (Zahner Co.) and the measurement was controlled by the IM6e software package. The transient electrochemical techniques, such as cyclic voltammetry and chronopotenimetry were used.

3. Results and discussions

3.1. Cyclic voltammogram of K_2ZrF_6 in the LiCl–KCl eutectic

It was indicated that the electroreduction of Zr(IV) proceeded a two-step process electrolysis according to our previous experimental results [13,14]. It canalso be seen in Fig. 2. In the cathodic scan, two cathodic current peaks A and B are observed. The cathodic peak B is related to the reduction of Zr(IV)/Zr(II), which corresponds to the following reaction:

$$\text{Peak(B)} : \text{Zr(IV)} + 2e^- \rightarrow \text{Zr(II)} \qquad (1)$$

And cathodic peak A is related to the reduction of Zr(II)/Zr, which corresponds to the following reaction:

$$\text{Peak(A)} : \text{Zr(II)} + 2e^- \rightarrow \text{Zr} \qquad (2)$$

The cathodic peak potential of A and B are not dependent on the sweep rate. It can be concluded that the reduction processes of Zr(II)/Zr and Zr(IV)/Zr(II) are both reversible (or quasi-reversible). According to Bard and Faulkner [15], the following equation gives the relationship among the peak potential, the half peak potential and the number of electrons transferred for an electrochemical reaction producing a soluble product.

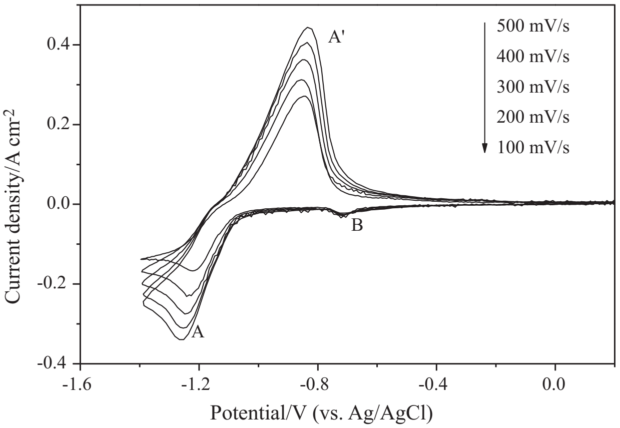

Fig. 2. Cyclic voltammograms at various scan rates for molybdenum electrode in the LiCl–KCl eutectic melt containing 5% K_2ZrF_6 at 923 K.

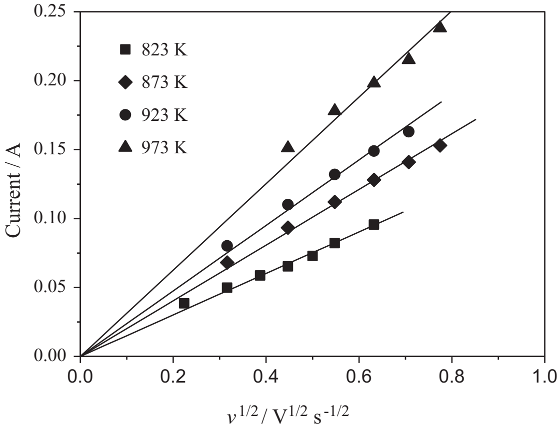

Fig. 3. Dependence of peak currents of the electroreduction reaction of Zr(II) on the sweep potential rate at various temperature.

$$E_P - E_{P/2} = \frac{-2.2RT}{nF} \qquad (3)$$

In the reduction process of Zr(II) to Zr, the number of transferred electrons was determined to be 2 by the above equation. The result confirmed our conclusion in [13]. In the following discussion, the electrochemical performance of the Zr(II)/Zr(0) system and Zr(IV)/Zr(II) system were studied respectively.

3.2. Electrochemical studies of the Zr(II)/Zr(0) system

The relationship between the reduction and oxidation peak currents and the square root of sweep rate is shown in Fig. 3. As can be seen that the plots of the peak current A versus the square root of scan rate on molybdenum electrode in the temperature range 823–973 K, are linear and through the zero point which indicates that the reaction is diffusion controlled.

For a diffusion controlled electrochemical reaction, the diffusion coefficient of Zr(II) in the molten salt can be calculated using Eq. (4) [15]:

$$I_P = 0.4463(nF)^{3/2}(RT)^{-1/2}AD^{1/2}Cv^{1/2} \qquad (4)$$

where I_P is the peak current (A), v is the potential scan rate (V s^{-1}), A is the surface area of the working electrode (cm^2), C is the bulk concentration of the reducible ion (mol cm^{-3}) and D is the diffusion coefficient (cm^2 s^{-1}). The results are shown in Table 1.

The influence of temperature on the value of diffusion coefficient of Zr(II) was determined by plotting ln D versus the reverse of absolute temperature (shown in Fig. 4). A straight line was obtained which showed the validity of the Arrhenius law in the reduction process of Zr(II) (expressed as Eq. (5)) [15]:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (5)$$

where D_0 is the pre-exponential factor, E_a is the activation energy (kJ mol^{-1}), and T is the absolute temperature. Finally, the diffusion coefficient of Zr(II) in LiCl–KCl–K_2ZrF_6 is formulated as follows:

$$\ln D = -1.86 - 8377T^{-1} \qquad (6)$$

Table 1
Experimental values of D of Zr(II) species at various temperatures.

Temperature (K)	823	873	923	973
D ($\times 10^{-5}$ cm^2/s)	0.59	1.11	1.62	2.98

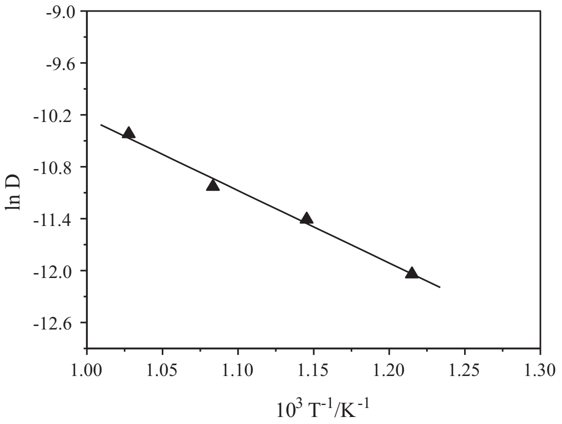

Fig. 4. Variation of diffusion coefficient of Zr(II) with temperature in LiCl–KCl.

From this equation, the temperature dependence of the diffusion coefficient was established, and the activation energy value for the diffusion process could be extracted, being $E_a = -69.65$ kJ/mol which was independent of the temperature. The pre-exponential term D_0 was calculated to be 0.15567 cm^2 s^{-1}.

3.3. Electrochemical studies of the Zr(IV)/Zr(II) system

In order to further investigate the reduction mechanism of Zr(IV), chronopotentiometry was carried out on a molybdenum working electrode in the LiCl–KCl–K_2ZrF_6 melt at various current intensity. The experiment temperature was controlled between 773 K and 973 K. Fig. 5 shows the evolution of the chronopotentigrams with the applied current intensity at 823 K. The τ_a corresponds to peak B and τ_b corresponds to peak A of the cyclic voltammetry (shown in Fig. 2). The potential of the first plateau in chronopotentiometric curves did not shift in the direction of negative with the increasing of current density. This result further indicated that the electrochemical reduction of Zr(IV) to Zr(II) should be a reversible electrochemical reaction.

For each temperature (773–793 K), several current intensities were applied and the plots of i (current intensity) versus $\tau_a^{-1/2}$ yielded a straight line. The lines passed through the origin as expected (shown in Fig. 6). This phenomenon shows that Sand's law (Eq. (7)) is available. It also can be concluded that the electrochemical reduction of Zr(IV) to Zr(II) is a diffusion-controlled process [15]. For each temperature, the diffusion coefficient of Zr(IV) was calculated using the Sand equation [15]:

$$i\tau^{-1/2} = 0.5nFCA(\pi D)^{1/2} \qquad (7)$$

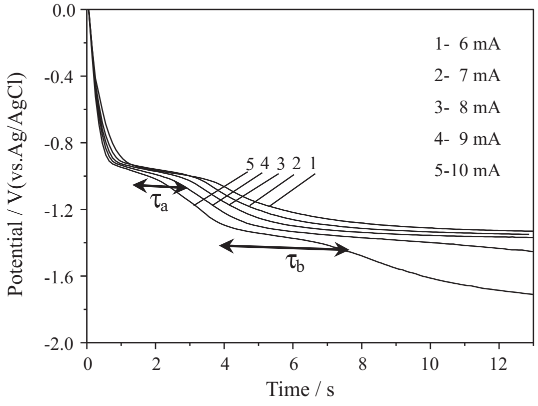

Fig. 5. Chronopotentiogram for molybdenum electrode in K_2ZrF_6-LiCl–KCl melt at 823 K.

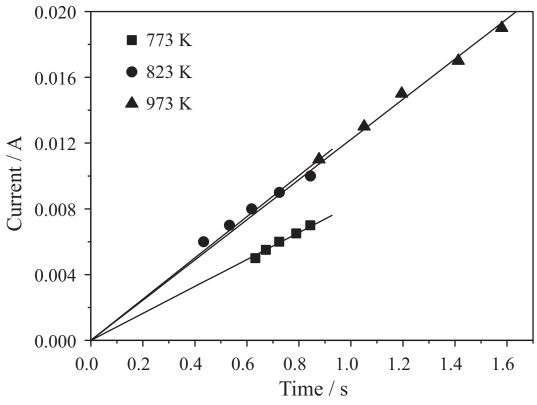

Fig. 6. Relation between I and $\tau_a^{-1/2}$ on Mo electrode.

Table 2
Experimental values of D of Zr(IV) species at various temperatures.

Temperature (K)	773	823	973
D ($\times 10^{-7}$ cm^2/s)	1.07	2.54	4.40

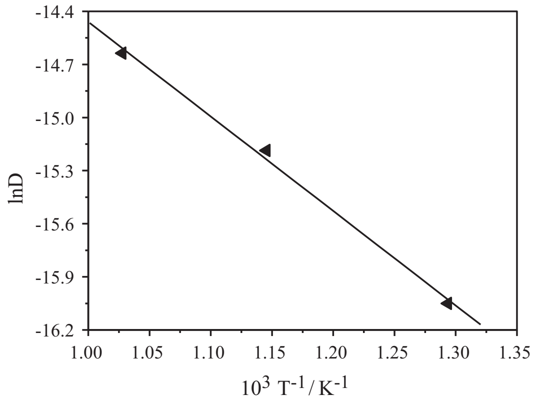

Fig. 7. Variation of diffusion coefficient of Zr (IV) with temperature in LiCl–KCl.

where i is the current (A), τ is the transition time (s), C is the bulk concentration of the reducible ion (mol cm^{-3}). Table 2 shows the diffusion coefficient of Zr(IV) in LiCl–KCl–K_2ZrF_6 at several temperatures obtained by the chronopotentiometry techniques.

The influence of temperature on the value of diffusion coefficient of Zr(IV) was also determined by plotting ln D versus the reverse of absolute temperature (shown in Fig. 7). A straight line was obtained as respected. The diffusion coefficient of Zr(IV) in LiCl–KCl–K_2ZrF_6 was formulated as follows (according to the Arrhenius law):

$$\ln D = -9.12 - 5339T^{-1} \qquad (8)$$

From this equation the temperature dependence of the diffusion coefficient of Zr(IV) was established. The activation energy value for the diffusion process also could be extracted, being $E_a = 44.39$ kJ/mol which was independent of the temperature. The pre-exponential term D_0 was calculated to be 1.09×10^{-4} cm^2 s^{-1}.

4. Conclusions

The electrochemical behavior of Zr(IV) was studied in the eutectic LiCl–KCl mixture at molybdenum electrode by various electrochemical techniques. The electrochemical redox processes of Zr(IV)/Zr(II) and Zr(II)/Zr (0) were found to be a diffusion-controlled process.

The diffusion coefficients of Zr(IV) and Zr(II) at different temperatures, as well as activation energy value for the diffusion process of Zr(IV) and Zr(II) in LiCl–KCl–K_2ZrF_6 molten salt were determined by the chronopotentiometry and cyclic voltammetry techniques: $_{\mathrm{Zr(II)}} = 0.15567\exp\{-69.65\times10^3/RT(K)\}\mathrm{cm}^2/\mathrm{s}$, $D_{\mathrm{Zr(IV)}} = 1.09\times10^{-4}\exp\{-44.39\times10^3/RT(K)\}\,\mathrm{cm}^2/\mathrm{s}$; $D_{\mathrm{Zr(II)}}{:}E_A = 69.65\,\mathrm{KJ\,mol}^{-1}$, $D_{\mathrm{Zr(IV)}}{:}E_A = 44.39\,\mathrm{KJ\,mol}^{-1}$.

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