

## Electrochemical behavior of zirconium in the (NaCl-KCl-NaF- ZrO<sub>2</sub>) molten salt

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**Abstract.** As a refractory metal, zirconium has a wide range of applications in many fields. The method of electrode position to produce metal zirconium is more available, it is important to study the behavior of zirconium in the molten salt. The electrochemical reaction mechanism and electrocrystallization process of zirconium in the NaCl–KCl–NaF–ZrO<sub>2</sub> molten salt were studied at 973 K by means of cyclic voltammetry, chronopotentiometry, and chronoamperometry techniques. The results show that the electrochemical reaction process of zirconium in the NaCl–KCl–NaF–ZrO<sub>2</sub> molten salt system is a reversible process and controlled by ion diffusion rate. Zirconium ion in this system is reduced to Zr(0) in only one step and the diffusion coefficient of Zr ion in the system is  $3.274 \times 10^{-5} \text{cm}^2 \cdot \text{s}^{-1}$ . The electrocrystallization process of zirconium is an instantaneous hemispheroid three-dimensional nucleation process.

### Introduction

Zirconium is a silvery white metal with a very high melting point (2125K), and it is a type of high temperature resistant metal [1-3]. Zirconium is widely used in nuclear industry due to the low neutron-absorption cross-section and excellent corrosion-resistance properties, such as the cladding tube of the nuclear fuel because of its excellent nuclear property [4-7]. Zirconium is also applied in the fields such as heat exchanger in petroleum chemical industry, hydrogen storage materials [8], reaction vessel, drying column and piping system equipment and so on.

Owing to the important strategic position of zirconium, many means were developed to produce metal zirconium. Compared with other methods, such as reducing (Kroll) position, the production of zirconium by electrode position is more available for its easier operation, higher metal purity and lower cost. So it is important to study the electrochemical behavior of zirconium in the molten salt.

The behavior of zirconium in different systems of molten salt has been investigated by many researchers. WU [9] studied the electrochemical behavior of zirconium in LiCl-KCl-K<sub>2</sub>ZrF<sub>6</sub> melt at 1023 K. It showed that the electrochemical reduction of Zr<sup>4+</sup> ions is a diffusion-controlled reversible electrochemical reaction, and Zr<sup>4+</sup> is reduced in the two-step transfer of  $\text{Zr}^{4+} \rightarrow \text{Zr}^{2+} \rightarrow \text{Zr}$  and the diffusion coefficient of Zr ion in the system is  $4.22 \times 10^{-6} \text{cm}^2 \cdot \text{s}^{-1}$ . Polyakova [10] found that in NaCl-KCl-ZrCl<sub>4</sub> melt with the addition of NaF, the electrode reaction of zirconium occurs reversibly in a four-electron step reaction:  $\text{Zr}^{4+} + 4\text{e}^- \rightarrow \text{Zr}$ . Chen [11] considered the electrochemical behavior of zirconium in chloride-fluoride melts. It showed that the electrochemical reaction process of zirconium is a double two-electron reduction process with less fluoride, while the Zr<sup>4+</sup> is directly

reduced to Zr(0) when the fluoride is higher.

In this study, the electrode position of zirconium was further studied using NaCl–KCl–NaF–ZrO<sub>2</sub> melt, which will be much simple and stable. The electrochemical behavior of zirconium will be investigated by cyclic voltammetry, chronopotentiometry and chronoamperometry.

## Experimental

**Reagents pretreatment.** Anhydrous analytic purity reagents NaCl: KCl: NaF: ZrO<sub>2</sub>=0.3324:0.3324:0.2849:0.0503 in molar ratio were used in the experiments. All of them were dried under a vacuum for 8h at 473K.

**Electrode selection and preparation.** A three-electrode cell was used for the electrochemical experiments. The pure Pt wire with 0.5 mm in diameter was served as the working electrode, reference electrode and the auxiliary electrode. All electrodes surfaces were polished mechanically to a mirror finish before use. The pure Pt wire were washed with hydrochloric acid and distilled water ultrasonically for more than 5 minutes, and then washed in the alcohol and dried before each measurement.

**Experimental facility.** The temperature of the resistance furnace was controlled by an artificial intellectual controller (Model: AI-808p) and temperature measurements were carried out by the platinum–platinum rhodium thermocouple (Model: S), the electrochemical reduction mechanism and electrocrystallization process of zirconium in NaCl–KCl–NaF–ZrO<sub>2</sub> system were performed by an electrochemical measurement workstation (Model: Zahner IM6ex, Germany).

**Experimental process.** Take the reagent in to the crucible which is made of high purity graphite, and put the crucible into the resistance furnace, then heated to the working temperature 973 K under dry and inert argon atmosphere and keeping for 3.5 hours.

## Results and discussion

**Cyclic voltammetry.** Fig1 shows the voltammograms of the zirconium electrode in the NaCl–KCl–NaF–ZrO<sub>2</sub> system at 973 K. In the voltammograms, only one reduction peak(R) at -0.935V is observed. The correlation data obtained from Fig. 1 are shown in Table 1. Constant potential electrolysis on Cu electrode was carried out at -0.935 V for 10 min. It is found that gray film material on the cathode is zirconium which is proved by EDS (Fig. 2).

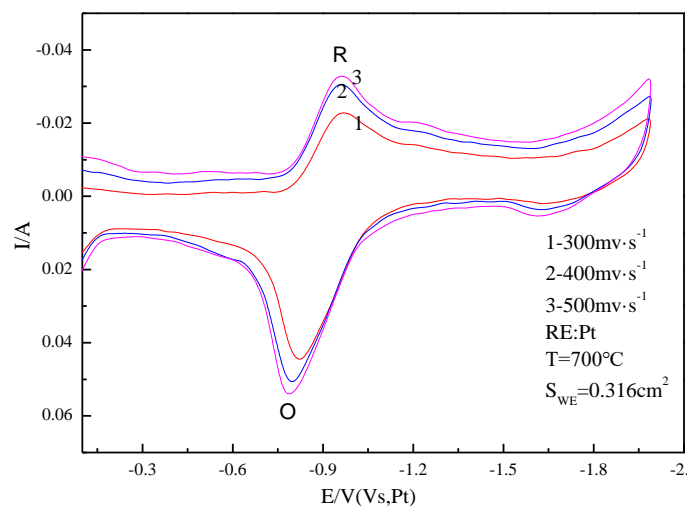


Fig.1 Cyclic voltammetry curve of NaCl-KCl-NaF-ZrO<sub>2</sub> molten salt system

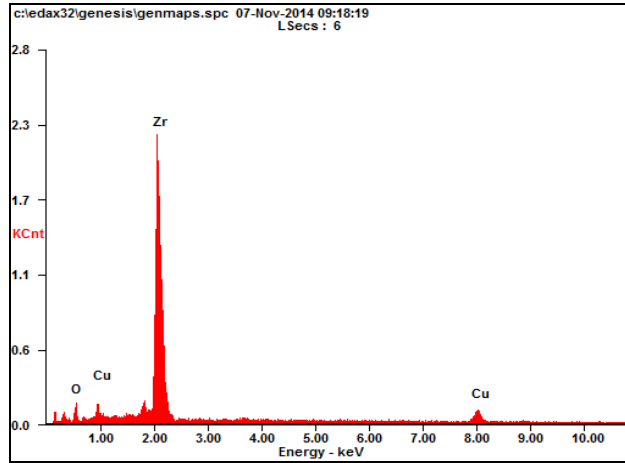


Fig.2 EDS diagram of cathode product at the peak of cathode potential

Table1 Parameters in cyclic voltammetry curve of the molten salt

No.	scanning rate/V·s-1	$I_{pc}/A$	$i_{pc}/A \cdot cm^{-2}$	$E_{pc}/V$	$E_{pc/2}/V$	$E_{pc}-E_{pc/2}$	$i_{pc}/v^{1/2}$
1	0.3	-0.0207	-0.0654	-0.9574	-0.9413	-0.0161	-0.0038
2	0.4	-0.0228	-0.0722	-0.9427	-0.9294	-0.0133	-0.0036
3	0.5	-0.0255	-0.0805	-0.9385	-0.9234	-0.0151	-0.0036

In the voltammetric curves recorded at different potential scanning rates clearly shows that the values of  $E_{pc}$  and  $E_{pa}$  are essentially unchanged when the scanning rate is increasing, and that  $i_{pa}/i_{pc} > 1$ . Based on the above analysis, it can be seen that the electrode process corresponding to the reduction peak of R is a reversible process and the product is insoluble [12].

The relationship between the peak current and the scanning rate is shown in Fig.3. It shows that the peak current of R is related to the scanning rate  $v$  and they show a strict linear relation. In keeping with the theory of linear voltammetry [13], it means the electrochemical reaction process of  $Zr^{4+}$  in this system is controlled by ion diffusion rate. Then the relationship of  $E_{pc}$ ,  $E_{pc/2}$ , and electron number  $n$  can be expressed as follows [14].

$$E_{pc} - E_{pc/2} = \frac{-0.77RT}{nF} \tag{1}$$

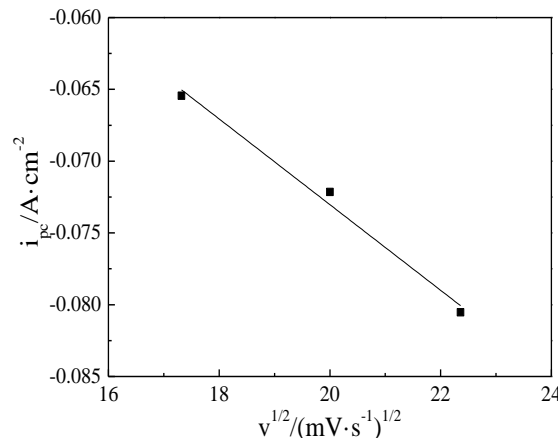


Fig.3 Relationship between  $i_{pc}$  and  $v^{1/2}$

Where  $E_{pc/2}$  is the half peak potential,  $E_{pc}$  is the half peak potential,  $n$  is reacting electron number,  $F$  is the Faraday constant( $96485 \text{ C}\cdot\text{mol}^{-1}$ ),  $R$  is the gas constant,  $T$  is the experiment temperature (973 K).

Taking the experiment data  $E_{pc} - E_{pc/2}$ (Table 1) to Eq. (1), the reacting electron number  $n$  of Peak R in Fig. 1 is shown in Table 2. The average value of  $n$  is 4.38. It can be estimated to be 4. It can be inferred that the main existence form of Zr ion was  $\text{Zr}^{4+}$  in the system, and Zr(IV) was reduced to Zr(0) in only one step. Then, the electrode reaction on the cathodic reduction peak could be written as:

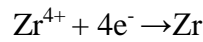


Table2. Electron numbers calculated at different scanning rates

No.	scanning rate/ $\text{V}\cdot\text{s}^{-1}$	$E_{pc} - E_{pc/2}$	$n$
1	0.3	-0.0161	4.00
2	0.4	-0.0133	4.85
3	0.5	-0.0151	4.28

**Chronopotentiometry.** The NaCl–KCl–NaF–ZrO<sub>2</sub> molten salt system was investigated using chronoamperometry at 973 K(Fig. 4). The change of electric potential on curve o–a can be explained as ohmic polarization of the solution on the electrode surface for a sudden constant current applied to the system. As a result of zirconium deposited on the cathode under a constant current polarization, the electric potential increases to the characteristic value (location b) of this reducing reaction. With the reduction of electrical activity  $\text{Zr}^{4+}$  and the precipitation of zirconium on the cathode, the concentration ratio of matters in oxidation state to matters in reduction state changes continuously with the electrolysis time. When the concentration ratio is closed to 1, the electric potential caused by a certain amount of electron in unit time changes slowly, as is shown on curve b-c. When the diffusion rate of electrical activity  $\text{Zr}^{4+}$  on the electrode surface is slower than the electrode reaction rate, for the reason of the concentration polarization, the electric potential is increases greatly as shown on curve c–d. On location d, the concentration of the reactant on the electrode surface decreases to zero, and the electric potential changed rapidly, that means that a new ion electrochemical reduction process to occur on the electrode.

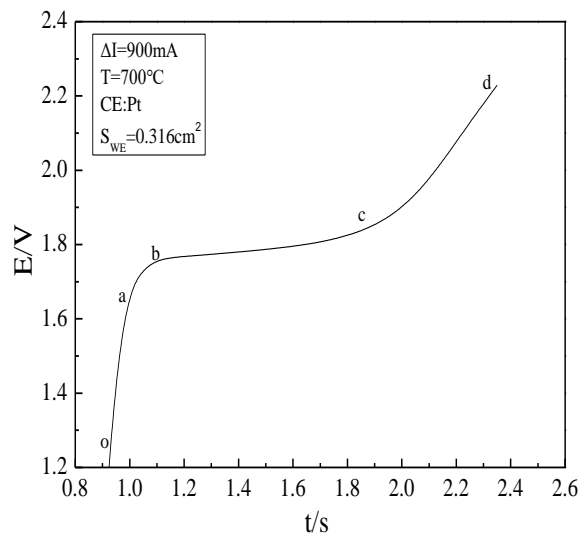


Fig.4 Chronopotentiometry curve of NaCl-KCl-NaF-ZrO<sub>2</sub> molten salt system

According to Sand equation [15, 16], the relation between the transition time  $\tau$  and the diffusion coefficient  $D$  of electrical activity ion in the solution can be derived by:

$$D = \frac{\tau \cdot 2^2 \cdot i^2}{n^2 \cdot F^2 \cdot \pi \cdot C^2} \quad (2)$$

There  $C$  is the concentration of  $ZrO_2$ ,  $\tau$  is the transition time,  $i$  is the constant current density,  $n$  is reacting electron number,  $F$  is the Faraday constant ( $96485 \text{ C}\cdot\text{mol}^{-1}$ ). Depend on the chronopotentiometry curve, taking the data extracted from Fig.4 and diffusion coefficient  $D$  of electrical activity  $Zr^{4+}$  figured out by Eq. (2), and list it in Table(3). The diffusion coefficient of  $Zr^{4+}$  in the system is  $3.274 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ . According to the characteristic equation of  $E-t$  curve under constant current electrolysis, when the electrode process is reversible and the product is insoluble or irreversible,  $E$  and  $\ln(\tau^{1/2} - t^{1/2})$  are linear relation. The electric potential  $E$  and  $\ln(\tau^{1/2} - t^{1/2})$  obtained from Fig.4 and Table 3 are strict linear relation as shown in Fig.5, from which it can be inferred that the electrode process of zirconium in the  $NaCl-KCl-NaF-ZrO_2$  system is a reversible process, which is the same as that measured by cyclic voltammetry.

**Electro crystallization process of zirconium.** The electro crystallization process of zirconium in the  $NaCl-KCl-NaF-ZrO_2$  molten salt system was investigated using chronoamperometry at 973 K (Fig.6).

As is shown in Fig.6, each curve shows a process controlled by ion diffusion rate And have experienced several stages of change, that indicates the electro crystallization nucleation of zirconium on the cathode. At first, the double layer of zirconium electrode is charged and the first nuclei of zirconium form, so the current increases to a high value in a very short time.

Table3 Data from chronopotentionmetry curve of  $NaCl-KCl-NaF-ZrO_2$  molten salt system

$I/A$	$i/A \cdot \text{cm}^{-2}$	$\tau/s$	$D/ \text{cm}^2 \cdot \text{s}^{-1}$	$\bar{D}/ \text{cm}^2 \cdot \text{s}^{-1}$
0.9	2.848	1.010	$3.444 \times 10^{-5}$	$3.274 \times 10^{-5}$
1	3.165	0.737	$3.104 \times 10^{-5}$	

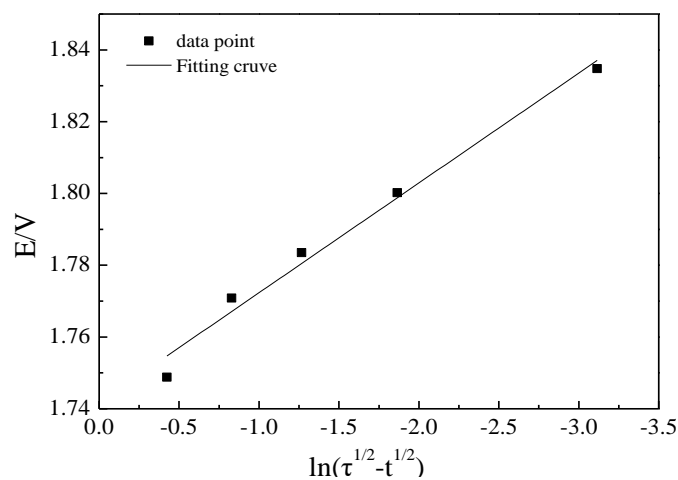


Fig.5 Relationship between  $E$  and  $\ln (\tau^{1/2}-t^{1/2})$

Taking curve (b) in Fig.6 as an example, data of current  $I$  and time  $t$  from curve (b) are presented in Table 4. Curves of  $I-t^{1/2}$  and  $I-t^{3/2}$  are shown in Fig. 7.

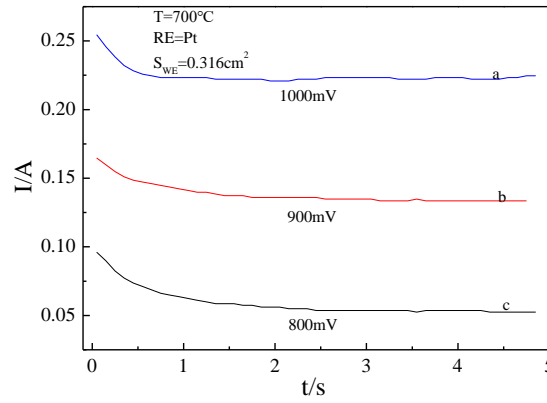
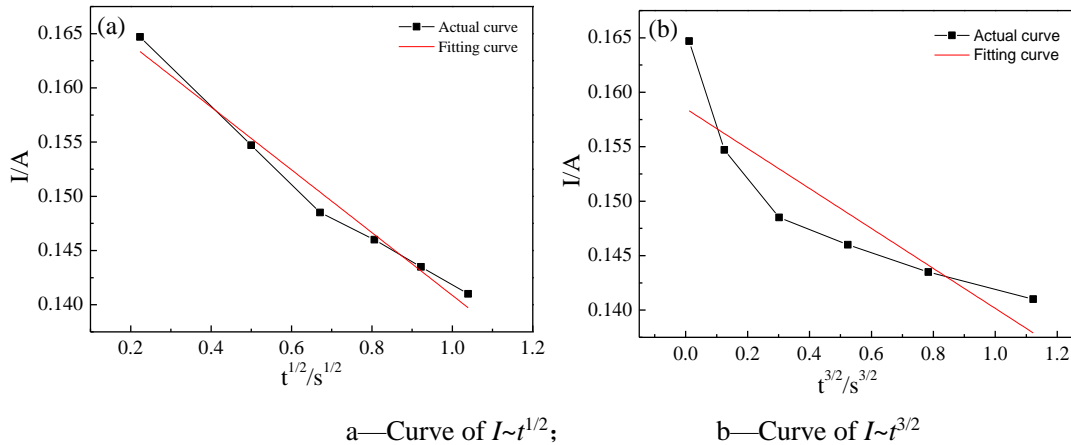


Fig.6 Chronoamperometry curve of NaCl-KCl-NaF-ZrO<sub>2</sub> molten salt system

According to hemispheroid three-dimensional nucleation theory [12], when the electrocrystallization process is controlled by diffusion of metallic atom on electrode surface and is progressive nucleation growth, the relation of I to t is represented by Eq.(3):

Table4 I and t data from curve b of fig.6

t/s	I/A	$t^{1/2}/s^{1/2}$	$t^{3/2}/s^{3/2}$
0.05	0.1647	0.2236	0.0112
0.25	0.1547	0.5000	0.1250
0.45	0.1485	0.6708	0.3019
0.65	0.1460	0.8062	0.5240
0.85	0.1435	0.9220	0.7836
1.05	0.1410	1.0392	1.1224



a—Curve of  $I \sim t^{1/2}$ ; b—Curve of  $I \sim t^{3/2}$

Fig.7 Curve of  $I \sim t^{1/2}$  and curve of  $I \sim t^{3/2}$

$$i = \frac{2}{3} zF \pi K_n N \left( \frac{M}{\rho} \right)^{1/2} (2C_0^* D)^{3/2} t^{3/2} \quad (3)$$

There z, F, Kn, N, D, M, q, C<sub>0</sub> are reacting electron number, Faraday constant, nucleation rate constant, maximum crystal nucleus density, diffusion coefficient of ion, atomic weight of electrodeposit, density of electrodeposit, and concentration of ion.

When the electrocrystallization process is instantaneous nucleation growth, the relation of I to t is represented by Eq.(4)

$$i = nF\pi N \left( \frac{M}{\rho} \right)^{1/2} (2C_0^* D)^{3/2} t^{1/2} \quad (4)$$

As is shown in Fig.7, the fitting degree of a is better than b, I and  $t^{1/2}$  are the linear relation. It can be inferred that the electrocrystallization process of zirconium in the NaCl–KCl–NaF–ZrO<sub>2</sub> system is an instantaneous hemispheroid three-dimensional nucleation.

## Conclusions

The electrochemical reaction mechanism and electrocrystallization process of zirconium in the NaCl–KCl–NaF–ZrO<sub>2</sub> (X<sub>NaCl</sub>:X<sub>KCl</sub>:X<sub>NaF</sub>:X<sub>ZrO<sub>2</sub></sub>=0.3324:0.3324:0.2849:0.0503) molten salt were studied at 973 K:

- (1) The electrochemical reaction process of zirconium is a process controlled by ion diffusion rate, and the electrode reaction mechanism is:  $Zr^{4+} + 4e^- \rightarrow Zr$
- (2) Under the experimental conditions, the diffusion coefficient of Zr ion in the system is  $3.274 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ .
- (3) The electrocrystallization process of zirconium in the NaCl–KCl–NaF–ZrO<sub>2</sub> system is an instantaneous hemispheroid three-dimensional nucleation process.

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