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Original Article

Electrochemical behavior of niobium ions in molten KCl-NaCl

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ABSTRACT

The reduction mechanism of Nb(V) in molten KCl-NaCl at 1023 K was investigated by a series of electrochemical techniques such as cyclic voltammetry, square wave voltammetry and chronopotentiometry. It was found that there were three steps in the reduction of Nb(V) as Nb(V)→Nb(III)→Nb(I)→Nb, and electrochemical reaction, Nb(V)→Nb(III), is a quasi-reversible diffusion controlled process. The diffusion coefficient of Nb(V) was also obtained by cyclic voltammetry, square wave voltammetry and chronoamperometry. The relationship between current density and the square root of time shows that the nucleation of niobium belongs to the instantaneous nucleation on molybdenum electrode in molten KCl-NaCl-$NbCl_5$ (0.43×10^{-3} mol/cm^3) at 1023 K at −3.10 V vs. Cl_2/Cl^-. Moreover, the metallic niobium was deposited on molybdenum wire by chronoamperometry, and the products were analyzed by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX). The results showed that the metallic niobium has a high purity of 99.98%.

1. Introduction

As a strategic metal, niobium has many advantages, such as high melting point and boiling point, excellent ductility and corrosion resistance. The increasing industrial demand offers a bright development prospects for metallic niobium [1]. The preparation of metallic niobium by molten salt electrolysis has been widely concerned due to its short process, low cost and sustainable development, and several authors have studied the electrochemical reduction mechanism of niobium ions in fluoride and fluoride-chloride molten salts [2–5]. However, the electrochemical reduction process of niobium ions in molten salt is controversial. Qiao et al. [4] studied the electrochemical reduction of K_2NbF_7 in molten LiF-NaF by cyclic voltammetry, chronopotentiometry and found that the reduction of niobium ions was a two-step reactions as Nb(V)→Nb(IV)→Nb or Nb(V)→Nb(III)→Nb. Mellors and Senderoff [1] discovered that the reduction of K_2NbF_7 was a three-step reduction process in molten LiF-NaF-KF by means of chronopotentiometry: Nb(V)→Nb(IV)→Nb(I)→Nb. In addition, in molten KCl-NaCl-K_2NbF_7, the reduction of niobium ions obtained by Chemla and Konstantinov [6] was a two-step process: Nb(V)→Nb(IV)→Nb. A similar study in molten NaCl-KCl-K_2NbF_7 was developed by Arurault et al. [7], and results showed that Nb(IV) was reduced to Nb via a four-

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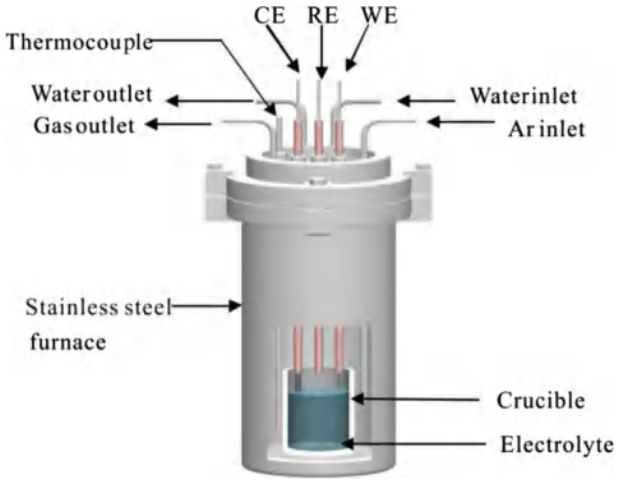

Fig. 1 – Schematic diagram of electrochemical cell.

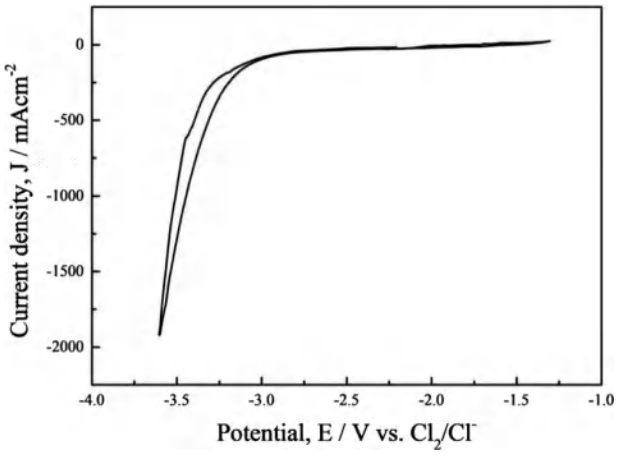

Fig. 2 – Electrochemical window of molten KCl-NaCl on a molybdenum wire electrode; Scan rate: 100 mV/s; RE: Cl_2/Cl^-; CE: graphite.

electron exchange procedure. Lantelme et al. [8] found that the electrochemical reduction process of Nb(V) in molten LiCl-KCl salt was Nb(V)→Nb(IV)→Nb(III)→Nb. The eutectic mixture NaCl-KCl is considered as a standard molten electrolyte and is widely used for the separation, purification and synthesis of various metals [9]. Therefore, the eutectic mixture of molten NaCl-KCl (equimolar) was chosen as electrolyte to study the electrochemical behavior of niobium ions. In this work, Nb(V) was added in eutectic molten KCl-NaCl at 1023 K in the form of $NbCl_5$, and then several electrochemical methods such as cyclic voltammetry, square wave voltammetry, chronoamperometry and chronopotentiometry were carried out to further study the cathodic reduction of niobium ions.

2. Experimental

2.1. *Chemical and electrochemical installation*

The eutectic mixture of KCl (Aladdin Biochemical Technology Co., Ltd., 99.8%) and NaCl (Sinopharm Chemical Reagent Co., Ltd., 99.9%) was dried under vacuum (0.1 Pa) at 573 K for 24 h before used. Subsequently, the mixture was heated to the experimental temperature of 1023 K under a high-purity argon atmosphere (99.999%), and the flow rate of argon was controlled at 30 mL/min. In addition, high-purity hydrogen chloride (99.999%) was blown into the electrolyte to remove the O^{2-} [10]. Prior to the electrochemical work, the molten salt electrolyte used has been pre-electrolyzed in advance. The impurities in the molten salt electrolyte were mainly removed by means of pre-electrolysis. This work used the method of potentiostatic electrolysis to pre-electrolyze molten salt electrolyte. The $NbCl_5$ (Macklin Biochemical Co., Ltd., 99%) was used as the niobium ions source in this experiment. The schematic diagram of experimental apparatus is shown in Fig. 1.

2.2. *Electrodes and electrochemical techniques*

A three-electrode system was used in the experiment. Nickel wire (99.998%) with a diameter of 1.0 mm, graphite rod with a diameter of 5.0 mm, and molybdenum wire with a diameter of 3.0 mm were used as reference electrode, counter electrode and working electrode, respectively. In order to be more comparable, the reference potential was converted to Cl_2/Cl^- in the results and discussion. The potential of the nickel reference electrode with respect to chlorine gas evolution was 1.60 V in molten KCl-NaCl at 1023 K. Cyclic voltammetry (CV), square wave voltammetry (SWV), chronoamperometry (CA) and chronopotentiometry (CP) were performed by AutoLab (PGSTAT302 N). The electrodes should be polished with 2000 mesh SiC paper, then dried with anhydrous ethanol before each test. The working electrode was inserted into the molten salt to a depth of 2.0 mm.

Potentiostatic electrolysis was carried out in molten KCl-NaCl-$NbCl_5$, and the mass of salts was 71.5 g containing 5.0 g of $NbCl_5$. The cathode, which was a molybdenum wire with a diameter of 3.0 mm, was inserted into the melt to a depth of 12.0 mm. After electrolysis, the products on the cathode were washed in an ultrasonic tank containing a solution of water and ethanol for dissolving the salt, and the deposit was detached from the cathodic substrate. Finally, the deposits were characterized by field emission scanning electron microscopy (FESEM, JEOL, JEM-6701 F) equipped with EDX analysis.

3. Results and discussion

3.1. *Electrochemical behavior of niobium ions in molten KCl-NaCl*

Cyclic voltammetry was firstly performed on a molybdenum wire electrode with a scan rate of 100 mV/s at 1023 K in molten KCl-NaCl without niobium ions and the cyclic voltammogram was shown in Fig. 2. The current density between −1.30 V to −3.20 V *vs.* Cl_2/Cl^- was extremely low, and there was no obvious current density peak, which indicated that no redox reaction occurred in this interval. Then a strong cathodic peak occured at around −3.20 V, which associated with the deposition of alkali metal Na.

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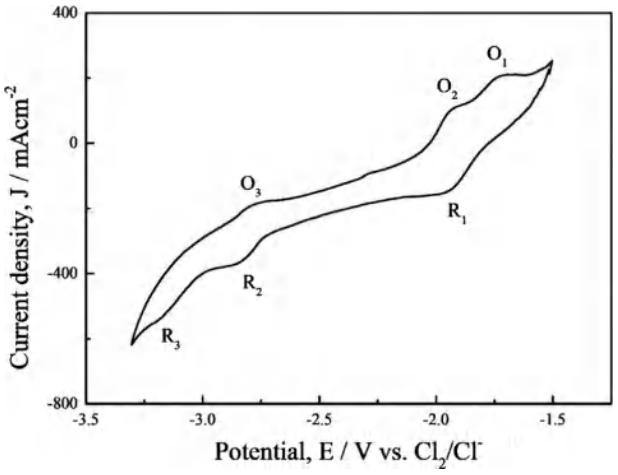

Fig. 3 – Cyclic voltammogram of $NbCl_5$ in molten KCl-NaCl on a molybdenum wire electrode. $C_{NbCl5} = 0.43 \times 10^{-3}$ mol/cm^3; Scan rate: 100 mV/s; RE: Cl_2/Cl^-; CE: graphite.

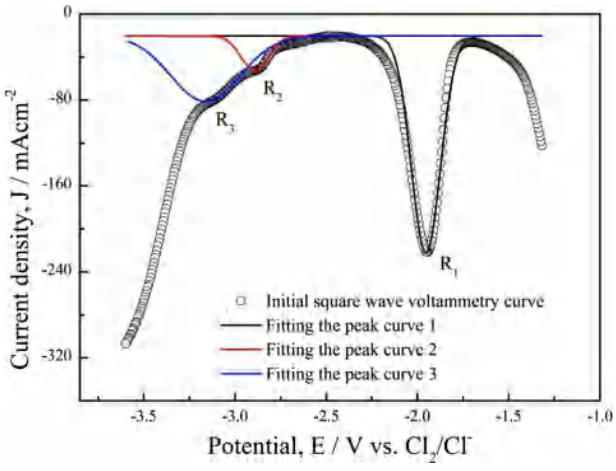

Fig. 4 – Square wave voltammogram of $NbCl_5$ in molten KCl-NaCl; $C_{NbCl5} = 0.43 \times 10^{-3}$ mol/cm^3; Frequency: 20 Hz; WE: molybdenum wire; RE: Cl_2/Cl^-; CE: graphite.

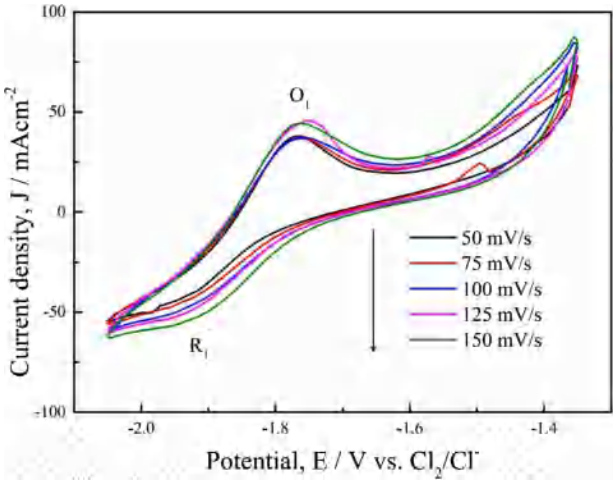

Fig. 5 – Cyclic voltammograms of $NbCl_5$ in molten KCl-NaCl on a molybdenum wire electrode at different scan rates; $C_{NbCl5} = 0.43 \times 10^{-3}$ mol/cm^3; RE: Cl_2/Cl^-; CE: graphite.

In order to obtain information about the reaction of niobium ions, cyclic voltammetry with the scan rate of 100 mV/s was performed on a molybdenum wire electrode after $NbCl_5$ was added into molten KCl-NaCl, and the results were shown in Fig. 3. Three pairs of redox peaks (R_1/O_1, R_2/O_2, R_3/O_3) appeared before the precipitation of alkali metal, which indicated that the reduction of niobium ion was a three-step reactions. The potentials corresponding to the peaks R_1/O_1, R_2/O_2, R_3/O_3 were −1.96 V/−1.75 V, −2.87 V/−1.95 V, −3.07 V/−2.80 V, respectively.

Square wave voltammetry is a more sensitive test than cyclic voltammetry [11]. It is also an accurate method for calculating the number of electrons exchanged in a reversible electrochemical processes. Fig. 4 is the square wave voltammogram at 1023 K at 20 Hz. Moreover, Gaussian fitting analysis was also carried out on the corresponding square wave, and the number of exchanged electrons could be calculated by eq. (1) [12–17].

$$W_{1/2} = 3.52 \times \frac{RT}{nF} \quad (1)$$

Where n is the number of exchanged electrons involved in the reaction, F is the Faraday constant, R is the gas constant 8.314 J/(mol K), T is the temperature in Kelvin. $W_{1/2}$ is the half-wave width.

After calculation, the values were listed here, $n_1 = 1.78 \approx 2$; $n_2 = 1.78 \approx 2$; $n_3 = 1.12 \approx 1$; Thus, the reduction process for niobium ions can be deduced as follows: Nb(V)→Nb(III)→Nb(I)→Nb.

In order to further investigate the electrochemical behavior of niobium ions in molten KCl-NaCl, cyclic voltammetry at different scan rates was carried out and the cyclic voltammograms were shown in Fig. 5. The reduction potential of R_1 changes slightly with the increase of scan rate, indicating that R_1 was a quasi-reversible process. Moreover, in order to determine whether or not the reaction R_1 was controlled by diffusion, the relationship between the peak value of the reaction current density R_1 and the square root of the scan rate was examined. As shown in Fig. 6, R_1 has a linear relationship after linear fitting ($R^2 = 99.6\%$) by Origin, indicating that the reaction R_1 was controlled by diffusion. The diffusion coefficient of Nb(V) ions in molten KCl-NaCl-$NbCl_5$ can be calculated according to eq. (2) [18,19]

$$\frac{I_p}{A} = 0.4463nFC(nF/RT)^{1/2}D^{1/2}\upsilon^{1/2} \quad (2)$$

Where I_P is the peak current (mA), ν is the scan rate (mV/s), 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).

The calculated diffusion coefficient of Nb(V) ions in molten KCl-NaCl-$NbCl_5$ at 1023 K was 3.99×10^{-5} cm^2/s.

Square wave voltammetry at different frequencies was carried out to verify results from cyclic voltammetry and the square wave voltammograms were shown in Fig. 7. There

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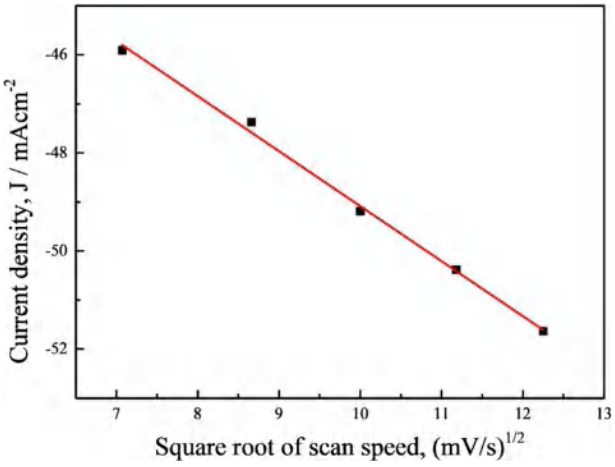

Fig. 6 – The relationship between the current density and the square root of scan rate.

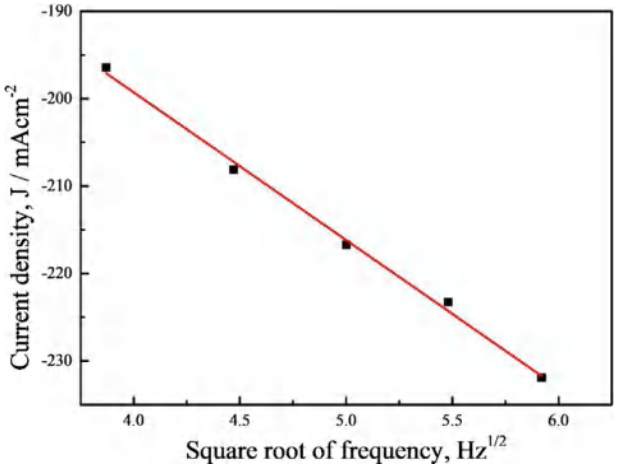

Fig. 8 – The relationship between the current density and the square root of frequency.

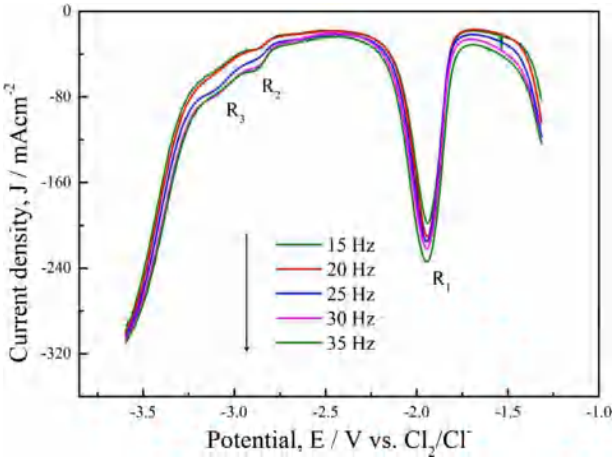

Fig. 7 – Square wave voltammetry of $NbCl_5$ in molten KCl-NaCl on a molybdenum wire electrode at different frequencies; $C_{NbCl5} = 0.43 \times 10^{-3}$ mol/cm^3; RE: Cl_2/Cl^-; CE: graphite.

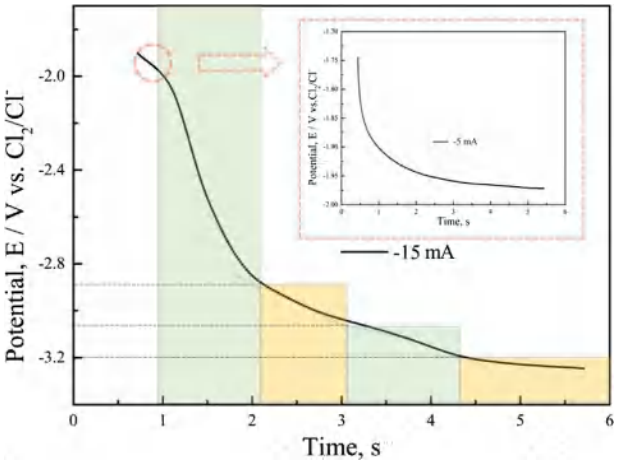

Fig. 9 – Chronopotentiogram of $NbCl_5$ in molten KCl-NaCl at −15.0 mA at 1023 K, $C_{NbCl5} = 0.43 \times 10^{-3}$ mol/cm^3.

was almost no shift in the reduction reaction R_1. In addition, the relationship between the peak value of the reaction R_1 current density and the square root of the frequency was shown in Fig. 8, and it was found to be a linear relationship by fitting the data through Origin software ($R^2 = 99.6\%$). The reaction category could be judged based on the relationship between the current density and the square root of the frequency as eq. (3) [20,21]. Therefore, the reaction R_1 was a quasi-reversible diffusion reaction corresponding to the results of the cyclic voltammograms curves at different scan rates described above.

$$\frac{I_p}{A} = nFC\frac{1-\Gamma}{1+\Gamma}\sqrt{\frac{Df}{\pi}}\Gamma = \exp\left(\frac{nF\Delta E}{2RT}\right) \quad (3)$$

where f represents the frequency (Hz) and is the square wave amplitude (V). The square wave amplitude in this work was 0.02 V and the concentration C was determined to be 0.43×10^{-3} mol/cm^3. According to eq. (3), the diffusion coefficient of Nb(V) in molten KCl-NaCl-$NbCl_5$ at 1023 K was calculated to be 1.01×10^{-5} cm^2/s.

Chronopotentiometry was also carried out to study the reduction mechanism of Nb(V) and the applied current was −15.0 mA, as shown in Fig. 9. The curve in the chronopotentiogram showed four platforms, the first platform appeared at −1.96 V which corresponds to the reduction of Nb(V) to Nb(III), which was consistent with the platform potential when the applied current was −5.0 mA. In addition, the second platform appeared at −2.87 V which corresponds to the reduction of Nb(III) to Nb(I) and the third platform was found at −3.07 V which corresponds to the reduction of Nb(I) to Nb. Thus, it was corresponding to the results of cyclic voltammetry and square wave voltammetry. Moreover, the fourth platform in Fig. 9 corresponds to the precipitation of alkali metals: Na(I)→Na.

Chronoamperometry was also used to verify the above results, and the Chronoamperogram was shown in Fig. 10. When the applied potential was −3.10 V, the current density was observed to be roughly divided into two parts: (I) Rapid decrease of current density indicates that the continuous precipitation of niobium leads to a decrease of the concentration

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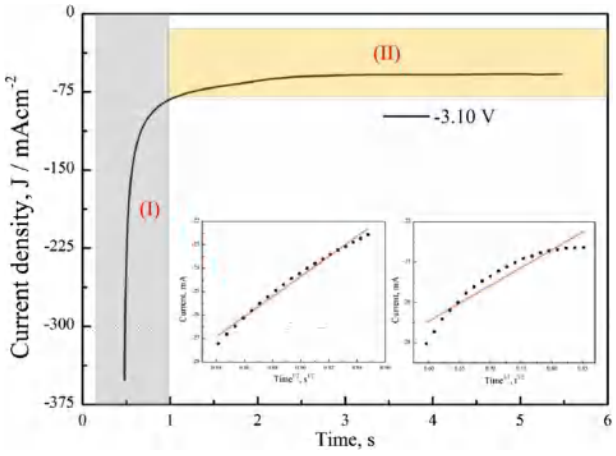

Fig. 10 – Chronoamperogram of $NbCl_5$ in molten KCl-NaCl at −3.10 V at 1023 K.

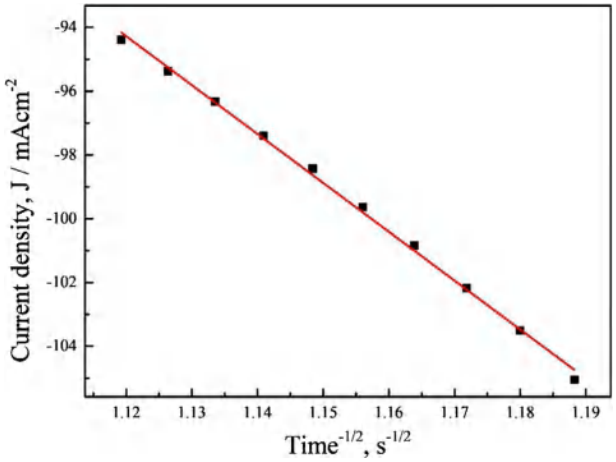

Fig. 11 – The relationship between current density and reciprocal of the square root of time.

of niobium near the electrode, and the niobium ions in the molten salt cannot diffuse to the surface of the electrode in time. (II) After a period of time, the current density tends to be balanced and in a straight line indicating a balance between diffusion rate and precipitation rate of niobium ions. It can be considered from the chronoamperogram that the electrochemical reduction process of niobium ions in the molten salt was diffusion-controlled. The diffusion coefficient of niobium ions can be calculated by Cottrel eq. (4) [22]

$$\frac{I}{A} = -\frac{nFD^{1/2}C}{\pi^{1/2}t^{1/2}} \tag{4}$$

Where I is the current (mA) and t is the reaction platform time (s).

According to Fig. 10, the relationship between current density and reciprocal of the square root of time was shown in Fig. 11. The current density has a good linear relationship with reciprocal of the square root of time ($R^2 = 99.7\%$). Therefore, the cathodic reduction reaction of Nb(V) ions in this molten salt system was controlled by diffusion, and the diffusion coefficient of Nb(V) ions in molten KCl-NaCl-$NbCl_5$ at 1023 K was 1.06×10^{-5} cm^2/s. Diffusion coefficients were listed in Table 1, which compared the results obtained by difference researchers and various methods. The different results may be attribute to the different of electrodes, temperatures, and different niobium feedstock.

In addition, the nucleation process of niobium ions was also discussed in this work. There are two types of nucleation modes: instantaneous nucleation and progressive nucleation. The relation between current and time was deduced in the document [27]. The nucleation model was as follows,

For instantaneous nucleation, according to eq. (5):

$$I(t) = \frac{zFN_0\pi(2DC)^{3/2}M^{1/2}}{\rho^{1/2}}t^{1/2} \tag{5}$$

For progressive nucleation, according to eq. (6):

$$I(t) = \frac{2zFK_nN_0\pi(2DC)^{3/2}M^{1/2}}{3\rho^{1/2}}t^{3/2} \tag{6}$$

Where N_0 is the initial nucleation number, z is the valence number, M is the atomic weight for deposits (g/mol), ρ is the density for deposits (g/cm^3), $I(t)$ is the polarization current when the time is t, t is the polarization time (s), and K_n is the nucleation constant.

The relationship between current and the square root of time was observed by chronoamperometry, as shown in the insert of Fig. 10, which was basically linear ($R^2 = 98.6\%$). The relationship between the current and the square root of time to the third power was basically linear, and the R^2 was equal to 89.2%, which was lower than the fitting result of between the current and the square root of time, indicating that the nucleation of niobium ions pertains to the instantaneous nucleation [28–30].

3.2. *Electrolytic product analysis*

Potentiostatic electrolysis was carried out at 1023 K in molten NaCl-KCl-$NbCl_5$. The electrodeposition potential of the metallic niobium was about −3.07 V ys. Cl_2/Cl^- according to above analysis. So the electrodeposition potential was selected to be −3.10 V in this research. High-purity graphite rod was used as anode and high-purity molybdenum wire with a diameter of 3.0 mm was used as cathodic. The electrolysis duration was 8 h. After electrolysis, the product was ultrasonically cleaned, and then dried. The sample was analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

Fig. 12 **(a)** showed the morphology of the electrolysis product. The product was a block structure, and the distribution is relatively loose. Fig. 12 **(b)** was an EDX analysis of the electrolysis product, and the results showed that the main element was niobium with a mass percentage of 99.98%. A small amount of oxygen in the sample may be derived from air with a mass percentage was 0.02%.

4. Conclusions

Using a three-electrode system, the electrochemical behavior of Nb(V) in molten KCl-NaCl at 1023 K was studied systematically. It was found that the reduction process of

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Table 1 – Comparison of Nb(V) diffusion coefficient results obtained by various methods.

Molten salt	Diffusion coefficient, D				Reference
	Cyclic voltammetry	Square wave voltammetry	Chrono-amperometry	Chrono-potentiometry	
KCl-NaCl	3.99×10^{-5} cm^2/s	1.01×10^{-5} cm^2/s	1.06×10^{-5} cm^2/s	–	This work
KCl-NaCl	–	–	–	1.83×10^{-5} cm^2/s	[23]
KCl	–	–	1.32×10^{-5} cm^2/s	1.41×10^{-5} cm^2/s	[24]
LiF-NaF-KCl	8.30×10^{-6} cm^2/s	–	–	–	[25]
LiF-NaF	–	1.61×10^{-5} cm^2/s	–	–	[26]

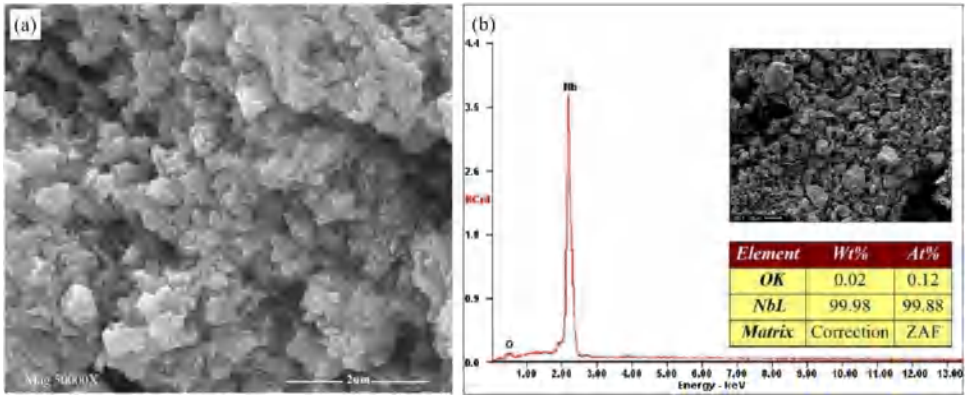

Fig. 12 – (a) The SEM image of the product of −3.10 V potentiostatic electrolysis; (b) The result of EDX analysis.

niobium ions was a quasi-reversible three-step reaction, and the reaction was controlled by diffusion. The cyclic voltammetry, square wave voltammetry and the chronoamperometry were used to analyze the diffusion coefficients of Nb(V), which were 3.99×10^{-5} cm^2/s, 1.01×10^{-5} cm^2/s and 1.06×10^{-5} cm^2/s respectively. The results were slightly different due to experimental accuracy, but it was still an order of magnitude and therefore acceptable. In addition, the nucleation process of the reaction was determined by chronoamperometry, which was instantaneous nucleation. At the end of the experiment, the reaction product was obtained by chronoamperometry. The product was analyzed by SEM and EDX techniques, and results showed that the product was metallic niobium which had high purity of 99.98%.

Conflict of interests

The authors declare no conflict of interest.

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