

Article

Electrochemical Behavior of Niobium Oxide and Titanium Oxide in NaF–Na₃AlF₆ Molten Salt

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Abstract: The Bayan Obo ore deposit is a world-renowned polymetallic coexistence mine that integrates important elements, such as rare earths, iron, niobium, and titanium. The chemical properties of niobium and titanium are similar, and the two often coexist in the Bayan Obo deposit as isomorphs, making them difficult to separate. Therefore, the separation of niobium and titanium is crucial for the efficient utilization of niobium resources in the Bayan Obo ore deposit of China. To discuss the feasibility of separating niobium and titanium by selective electrolysis, cyclic voltammetry and square wave voltammetry were used to study the reduction mechanism of niobium oxide and titanium oxide in NaF–Na₃AlF₆ molten salt. The results revealed significant differences in the diffusion coefficients and reduction steps of Nb⁵⁺ and Ti⁴⁺ during reduction at a molybdenum cathode. At 950 °C, the diffusion coefficient of Nb⁵⁺ during reduction at a molybdenum cathode was 3.57×10^{-6} cm²/s. Also, in the NaF–Na₃AlF₆ system, Nb⁵⁺ underwent a three-step reduction as follows: Nb(V)→Nb(IV)→Nb(III)→Nb. The diffusion coefficient of Ti⁴⁺ during reduction at the molybdenum cathode was 9.92×10^{-7} cm²/s, and Ti⁴⁺ underwent a two-step reduction in the NaF–Na₃AlF₆ system: Ti(IV)→Ti(III)→Ti. When Nb₂O₅ and TiO₂ were both present in the NaF–Na₃AlF₆ system, the deposition potential of niobium metal (−0.64 V) differed from that of titanium metal (−0.77 V). These differences in diffusion coefficient, reduction step, and deposition potential enabled selective electrolytic separation of niobium and titanium.

Keywords: niobium; titanium; selective electrolysis; NaF–Na₃AlF₆

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1. Introduction

The Bayan Obo mine in China is a globally significant polymetallic symbiotic ore deposit. It encompasses rare earths, iron, niobium, titanium, and other essential elements. Notably, niobium, which has an important role in material properties, has a resource amount of 6.6 million tons [1]. However, exploitation of the Bayan Obo mineral resource has primarily focused on the extraction of iron and rare earths, and the utilization rate of niobium resources has been almost zero. The low utilization rate of niobium is mainly because the niobium is low-grade, there are diverse niobium-containing minerals, and there is a fine embedded grain size in the Bayan Obo mine [2]. These characteristics have made the beneficiation and metallurgy of niobium resources extremely difficult; thus, most of the niobium resources have ended up in tailings.

The grade of niobium coexistence ore in the Bayan Obo mine is about 0.10%, and there are as many as 20 types of niobium-bearing mineral phases, including niobite (FeNb₂O₆), aeschynite ((Ce,Nd)(Ti,Nb)₂O₆), pyrochlore ((Ca,Na,Ce)₂(Nb,Ti)₂O₆(F,OH)), ilmenorutile ((Fe,Ti,Nb)O₂), fersmitite (CaNb₂O₆), etc. These niobium-bearing phases contain multiple metal elements in coexistence with one another, and they typically have particle sizes that

do not exceed 20 μm . Often, they are symbiotic or encapsulated with other minerals, and this makes their separation and extraction exceedingly difficult. Furthermore, niobium and titanium have similar chemical properties and ionic radii ($\text{Ti}^{4+} = 0.64 \text{ \AA}$ and $\text{Nb}^{5+} = 0.69 \text{ \AA}$), and they coexist extensively in various niobium-bearing phases; thus, they are inherited into the beneficiation and metallurgy processes of niobium resources. This significantly affects the concentrate grade and product quality. In niobium-containing alloys that are produced via pyrometallurgical processes [3,4] and in niobium oxide that is produced via hydrometallurgical processes [5–9] using Bayan Obo mine materials, the difficulty in separating niobium and titanium leads to low product quality. This severely limits the range of product applications. Therefore, the deep separation of niobium and titanium becomes key to overcoming the challenges of achieving comprehensive utilization of Bayan Obo niobium resources.

Molten salt electrolysis has the advantages of a short process flow, low cost, continuous production, and high product purity; thus, it has been widely applied in industrial production. It is especially effective in the production of high-purity metals, such as high-purity niobium and titanium. Many researchers have studied the electrochemical behavior of niobium ions or titanium ions in fluoride and chloride molten salts. However, niobium and titanium ions in molten salts have multiple valence states, and hence, their electrochemical reduction processes are quite complex.

He et al. [10] proposed that the electrolytic reduction of K_2NbF_7 proceeds via the following steps: $\text{Nb(V)} \rightarrow \text{Nb(IV)} \rightarrow \text{Nb}$. The second step is quasi-reversible and controlled by a diffusion process. Li et al. [11] found that the electrode reduction process of niobium ions at 750 $^\circ\text{C}$ in KCl-NaCl molten salt is the following quasi-reversible three-step reaction: $\text{Nb(V)} \rightarrow \text{Nb(III)} \rightarrow \text{Nb(I)} \rightarrow \text{Nb}$. Wang et al. [12] found that the electrode reduction reaction of Nb(V) in $\text{LiF-NaF-KF-Na}_2\text{O}$ melts is a two-step electrochemical reaction process that involves one and four electrons, respectively, and is as follows: $\text{Nb(V)} \rightarrow \text{Nb(IV)} \rightarrow \text{Nb}$. Matthiesen et al. [13] used cyclic voltammetry to study the electrochemical behavior of F-Nb complexes at 700 $^\circ\text{C}$ in LiF-NaF-KF melts. When K_2NbF_7 was added, the fluorine complex NbF_7^{2-} was introduced into the melt, and its electrochemical reduction process was as follows: $\text{Nb(V)} \rightarrow \text{Nb(IV)} \rightarrow \text{Nb}$. Bailey et al. [14] used cyclic voltammetry and chronopotentiometry to study the electrochemical behavior of Nb(V) in molten LiF-NaF-KF melts; they showed that Nb(V) is reduced in two steps, which are as follows: $\text{Nb(V)} \rightarrow \text{Nb(III)} \rightarrow \text{Nb}$. S. A. Kuznetsov [15] investigated the electroreduction of niobium in chloride fluoride electrolytes used for preparing zirconium powder, and determined the limit density of the cathode diffusion current of niobium discharge and the diffusion coefficient of Nb(V) and Nb(IV) fluoride complexes as a function of temperature. The optimal electrolysis parameters were determined by studying the effects of cathode current density, niobium concentration, and temperature on the current efficiency of cathode electrodeposition.

According to Lantelem's research [16], the cathodic process of tetravalent titanium ions in the NaCl-KCl molten salt system undergoes three reduction stages: $\text{Ti(IV)} \rightarrow \text{Ti(III)} \rightarrow \text{Ti(II)} \rightarrow \text{Ti}$. Chen et al. [17] investigated the cathodic process of Ti^{4+} in the NaCl-KCl eutectic salt system, and they concluded that Ti^{4+} undergoes the following processes on a platinum electrode: $\text{Ti(IV)} \rightarrow \text{Ti(III)} \rightarrow \text{Ti(II)} \rightarrow \text{Ti}$. This is essentially consistent with Lantelem's findings. Robin et al. [18] concluded that during the cathodic reduction process of TiF_6^{2-} it is first reduced to TiF_6^{3-} regardless of the type of metal cathode and that the cathodic reduction process of TiF_6^{3-} varies greatly depending on the type of cathode metal. Li et al. [19] determined the cathodic process of tetravalent titanium ions at 700 $^\circ\text{C}$ in the molten $\text{LiF-NaF-KF-K}_2\text{TiF}_6$ system on platinum metal, and this could be represented as $\text{Ti(IV)} \rightarrow \text{Ti(III)} \rightarrow \text{Ti}$. They concluded that the nucleation process of titanium on the platinum electrode is instantaneous nucleation. Jiao et al. [20] studied the electrochemical behavior of titanium ions in chloride melts, such as NaCl-KCl-TiCl_x and $\text{NaCl-KCl-LiCl-TiCl}_x$. From the results of electrochemical research on low-valent titanium ions on metal cathodes, Zhou et al. [21] prepared high-purity titanium that had different morphologies. Zhao et al. [22] comprehensively evaluated the electrochemical process of Ti deposition using

cyclic voltammetry and square wave voltammetry. The electrode reaction mechanisms and particle evolution principles in molten salt during this electrolysis process were discussed. It indicated that titanium chloride in lower valence (TiCl_3) with a more productive advantage could exist as an intermediate, and Ti^{3+} ions were reduced to Ti metal by a two-step mechanism corresponding to the following pathway: $\text{Ti}^{3+} \rightarrow \text{Ti}^{2+} \rightarrow \text{Ti}$.

The abovementioned literature focused only on electrochemical research of niobium ions or titanium ions and proved that molten salt electrolysis is an effective method for preparing high-purity niobium and titanium metals. However, systematic studies on the electrochemical behavior of niobium and titanium oxides in molten salts, especially in cases where niobium and titanium are both present, have not yet been reported. Developing technology for molten salt electrolytic separation of niobium and titanium has yet to be explored. In this work, niobium oxide and titanium oxide in the $\text{NaF}\text{--}\text{Na}_3\text{AlF}_6$ molten salt system were systematically studied using electrochemical testing, and the evolution of niobium and titanium states during molten salt electrolysis, and the potential conditions for selective electrolytic separation between niobium and titanium were explored. This research provides a theoretical basis for developing technology for molten salt electrolytic separation of niobium and titanium in the Bayan Obo coexistence mine.

2. Experimental Methods

Reagents used for electrochemical testing included niobium pentoxide (Nb_2O_5), titanium dioxide (TiO_2), sodium fluoride (NaF), and cryolite (Na_3AlF_6), which were analytical grade and were produced by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). The experimental setup (Figure 1) included an electrochemical workstation (Aut 84847), a tubular high-temperature furnace, and an electrolytic cell. The electrolytic cell used a molybdenum wire as the working electrode (WE), a graphite crucible as the counter electrode (CE), and a molybdenum wire as the reference electrode (RE). The molybdenum wire was sheathed in a protective alumina sheath.

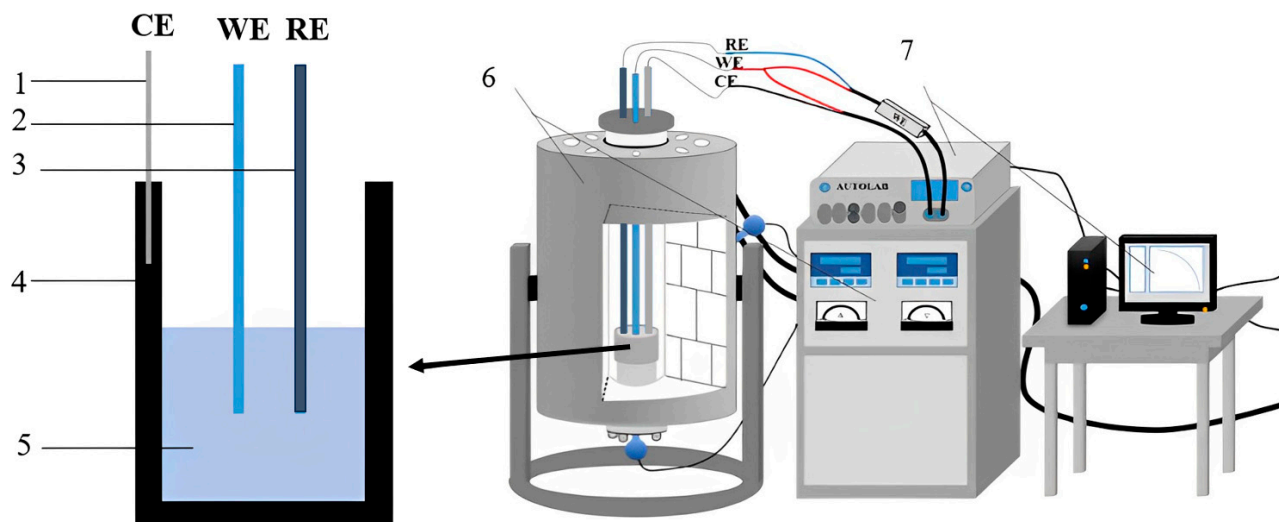


Figure 1. Schematic diagram of the experimental system. 1—Stainless steel bar; 2—working electrode; 3—reference electrode; 4—graphite crucible (counter electrode); 5—molten salt; 6—tubular high-temperature furnace; 7—electrochemical workstation.

Before electrochemical tests were conducted, molten salt electrolysis (42 wt% NaF –58 wt% Na_3AlF_6) was subjected to vacuum drying. Pre-electrolysis was carried out using the constant potential electrolysis method to remove impurities. The electrolyte was mixed with niobium oxide and titanium oxide, and the mixture was placed in a crucible in the electrolytic cell. The electrolytic cell was then placed in a tubular heating furnace. The temperature was increased while argon gas (purity $\geq 99.99\%$) was introduced at a flow rate of 0.5 L/min. When the temperature reached 950 °C and the materials were

completely melted, the electrolytic cell was set up and connected to the electrochemical workstation. After the workstation was started and the control software Nova 1.0 was initiated, the open circuit potential (OCP) of the electrolysis cell was tested, and electrode potentials were adjusted. Subsequent tests were conducted using a three-electrode system for cyclic voltammetry (CV) and square wave voltammetry (SWV). The test schemes are listed in Table 1.

Table 1. Experimental scheme.

Electrolyte System	Test Method	Scan Rate
NaF–Na ₃ AlF ₆	CV	50 mV/s
NaF–Na ₃ AlF ₆ –2 wt% Nb ₂ O ₅	CV, SWV	50 mV/s, 75 mV/s, 100 mV/s
NaF–Na ₃ AlF ₆ –2 wt% TiO ₂	CV, SWV	50 mV/s, 75 mV/s, 100 mV/s
NaF–Na ₃ AlF ₆ –2 wt% Nb ₂ O ₅ –2 wt% TiO ₂	CV	50 mV/s

3. Results and Discussion

3.1. Electrochemical Behavior of NaF–Na₃AlF₆ Molten Salt

Figure 2 shows the cyclic voltammetry curve of NaF–Na₃AlF₆ molten salt. No oxides were added to the system, and hence, there should be no elemental electrodeposition. However, a reduction peak can be observed at point A (−0.50 V) in the figure. This is likely because Al₂O₃ from the protective alumina sheath around the molybdenum wire electrode dissolved into the molten salt.

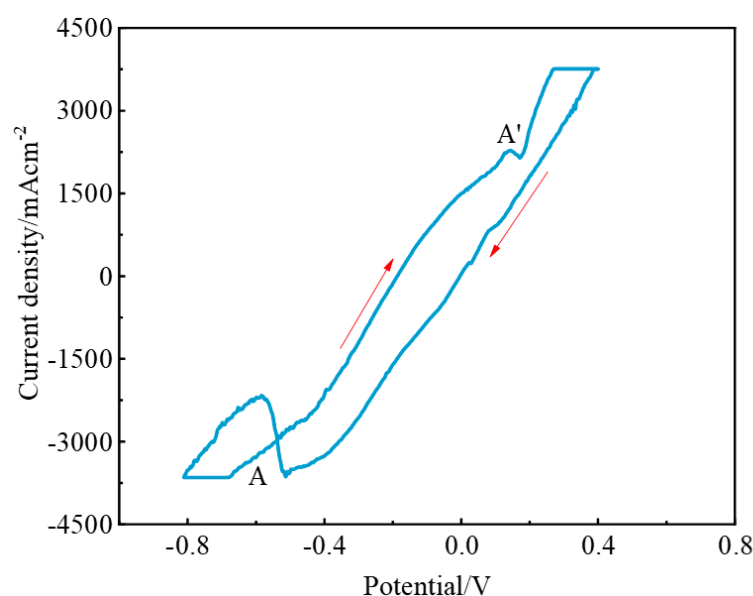


Figure 2. Cyclic voltammetry curve of NaF–Na₃AlF₆ molten salt (scan rate: 50 mV/s; temperature: 1223 K).

3.2. Electrochemical Behavior of the NaF–Na₃AlF₆–2 wt% Nb₂O₅ Molten Salt System

Figure 3 shows the cyclic voltammetry curve of the NaF–Na₃AlF₆–2 wt% Nb₂O₅ molten salt system on a Mo electrode. There are four reduction peaks in the negative scan from 0.5 V to −1.5 V. Compared to the cyclic voltammetry curve of the NaF–Na₃AlF₆ molten salt system, additional reduction peaks (A, B, and D) are observed after TiO₂ was added. The corresponding potential of reduction peak C (−0.50 V) is consistent with the peak potential that is observed in the cyclic voltammetry curve of the NaF–Na₃AlF₆ molten salt system. It is believed that this is caused by dissolution of the alumina tube, corresponding to the reduction peak of Al³⁺. The reduction peaks at A, B, and D have potentials of 0.09 V, −0.38 V, and −0.68 V, respectively, and this indicates that the reduction process of Nb⁵⁺ is divided into three steps.

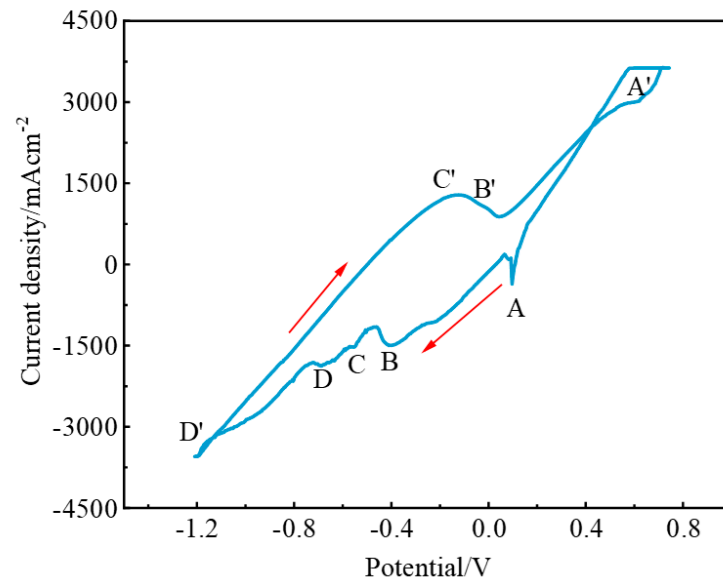


Figure 3. Cyclic voltammetry curve of the NaF–Na₃AlF₆–2 wt% Nb₂O₅ molten salt system on the Mo electrode (scan rate: 50 mV/s; temperature: 1223 K).

Figure 4 shows cyclic voltammetry curves of NaF–Na₃AlF₆–2 wt% Nb₂O₅ obtained at different scan rates. It is observed that both the cathodic peak current density and the corresponding cathode peak potential vary with respect to the scan rate. The absolute value of the ratios of each reduction peak current density to the corresponding oxidation peak current density is not equal to one. Both the oxidation and reduction peak current densities increase with the scan rate. The reduction peak potential shifts to a lower potential, and the oxidation peak potential shifts to a higher potential.

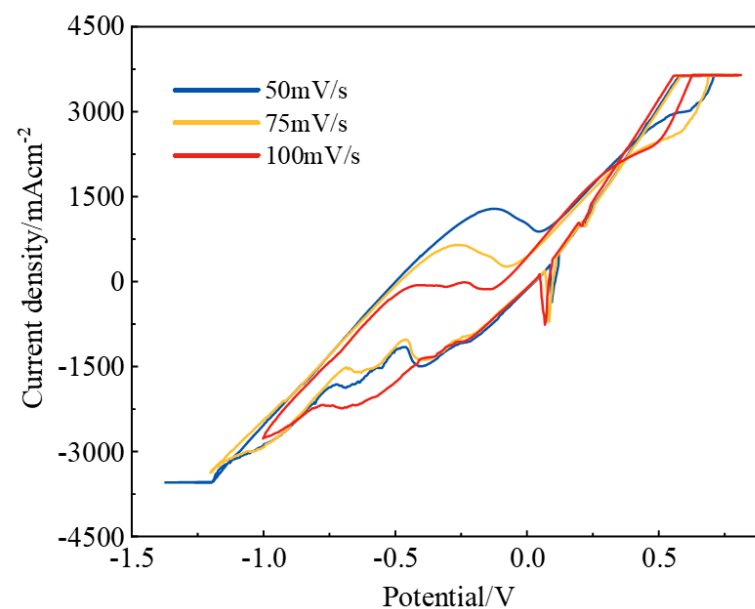


Figure 4. Cyclic voltammetry curves of the NaF–Na₃AlF₆–2 wt% Nb₂O₅ molten salt system at different scan rates (scan rate: 50 mV/s, 75 mV/s, and 100 mV/s; temperature: 1223 K).

Figure 5 shows the relationship between the reduction peak potential of Nb⁵⁺ and the logarithm of the scan rate. The data indicate that there is a nearly linear relationship between the reduction peak potential and the logarithm of the scan rate. By combining data for the changes in oxidation–reduction peak current density and potential with respect to the scan rate, it is deduced that the first step in the reduction of Nb⁵⁺ is an irreversible

process. For an irreversible electrochemical reaction process, the difference in values between the peak potential and the half-peak potential, which is expressed as $|E_p - E_{p/2}|$, should satisfy Equation (1) [23]. According to Equation (1), the charge transfer coefficient (α) of the reduction of Nb^{5+} at the Mo cathode is calculated to be approximately 0.97.

$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha n F} \quad (1)$$

where E_p represents the peak potential (V), $E_{p/2}$ is the half-peak potential (V), R is the gas molar constant [8.314 J/(mol·K)], T is the temperature (K), α is the charge transfer coefficient, n is the number of electron transfers, and F is Faraday's constant (96,485 C/mol) [24]. n is calculated as $n_A = 3$ and is based on the electron transfer number at this potential, as obtained in the following text.

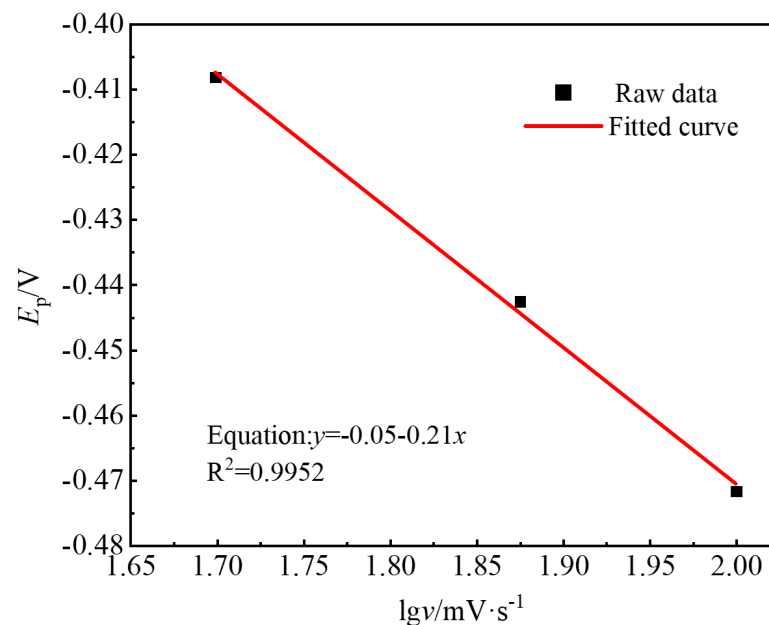


Figure 5. Relationship between the reduction peak A potential and the logarithm of the scan rate in the NaF–Na₃AlF₆–2 wt% Nb₂O₅ molten salt system.

Figure 6 shows the relationship between the reduction peak A current density and the square root of the scan rate. As seen in the figure, the current density value of the reduction peak for Nb^{5+} increases with an increase in the scan rate, and there is a linear relationship with the square root of the scan rate. This indicates that the reaction is controlled by the diffusion of Nb^{5+} in the system [25]. At this point, the relationship between the peak current density and the scan rate can be calculated using the Randles–Sevcik equation, which can be expressed as Equation (2) [26].

$$I_p = 0.4958 \left(\frac{anF}{RT} \right)^{\frac{1}{2}} nF(Dv)^{\frac{1}{2}} AC_0 \quad (2)$$

where I_p represents the peak current density (A), D is the diffusion coefficient (cm^2/s), v is the scan rate (V/s), A is the electrode working area (cm^2), and C_0 is the initial concentration of Ti^{4+} (mol/cm^3).

Using the previously obtained charge transfer coefficient (α) of 0.97 and assuming complete ionization of Nb_2O_5 in the molten salt, the diffusion coefficient D of Nb^{5+} in the NaF–Na₃AlF₆ system at 950 °C is calculated to be approximately $3.57 \times 10^{-6} \text{ cm}^2/\text{s}$.

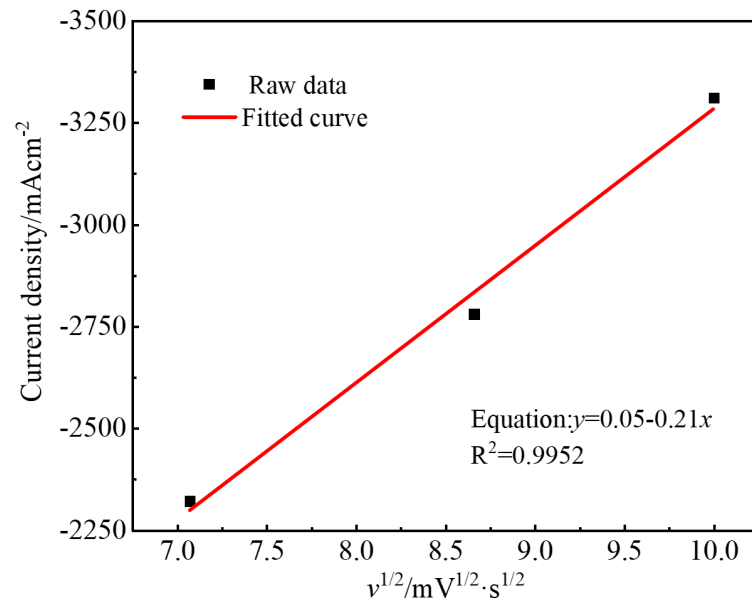


Figure 6. Relationship between the reduction peak A current density and the square root of the scan rate in the NaF–Na₃AlF₆–2 wt% Nb₂O₅ molten salt system.

Figure 7 shows the square wave voltammetry curve of the NaF–Na₃AlF₆–2 wt% Nb₂O₅ molten salt system on the Mo electrode. Four reduction peaks (R_I , R_{II} , R_{III} , and R_{IV}) are observed. Among them, the reduction potential of peak R_{III} corresponds to the reduction potential of Al^{3+} , whereas the reduction potentials of R_I , R_{II} , and R_{IV} correspond to niobium ions. After Gaussian fitting of the square wave voltammetry curve and combining Equation (3) [27], which relates the half-peak width $W_{1/2}$ of the reduction peak to the number of electrons transferred in the reduction reaction, the number of electrons transferred for different reduction peaks can be calculated as follows:

$$W_{1/2} = \frac{3.52RT}{nF} \quad (3)$$

where $W_{1/2}$ represents the half-peak width (V), F is Faraday's constant (96,485 C/mol), T is the Kelvin temperature (K), and R is the gas constant (8.314 J/(mol·K)).

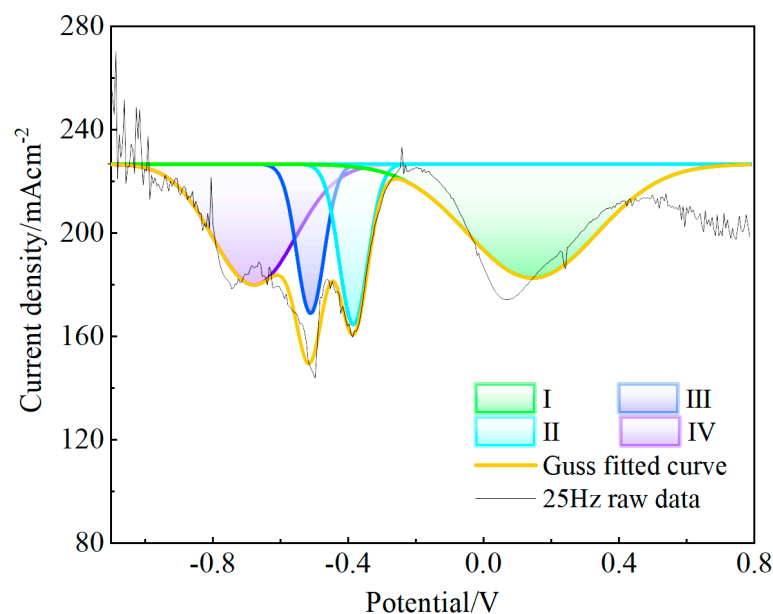


Figure 7. Square wave voltammetry curve of the NaF–Na₃AlF₆–2 wt% Nb₂O₅ molten salt system on the Mo electrode (frequency: 25 Hz; temperature: 1223 K).

The following are found from the calculations: $n_I = 0.82 \approx 1$, $n_{II} = 3.36 \approx 3$, $n_{III} = 3.41 \approx 3$, and $n_{IV} = 1.37 \approx 1$. Therefore, it is inferred that the pentavalent niobium ion undergoes a three-step reduction in the NaF–Na₃AlF₆ system, and these steps are as follows: Nb(V)→Nb(IV)→Nb(III)→Nb. The reduction of Al³⁺ [Al(III)→Al] occurs at −0.5V. The results for square wave voltammetry and cyclic voltammetry agree well in terms of the measured reduction potentials.

3.3. Electrochemical Behavior of the NaF–Na₃AlF₆–2 wt% TiO₂ Molten Salt System

Figure 8 shows the cyclic voltammetry curve of the NaF–Na₃AlF₆–2 wt% TiO₂ molten salt system on a Mo electrode. There are three reduction peaks in the negative scan from 0.5 V to −1.2 V. The corresponding potential of reduction peak B is consistent with the peak potential that is observed in the cyclic voltammetry curve of the NaF–Na₃AlF₆ molten salt system, corresponding to the reduction peak of Al³⁺. The reduction peaks at A and C have potentials of −0.43 V and −0.84V, respectively, and this indicates that the reduction process of Ti⁴⁺ is divided into three steps. There is a current density disturbance at C, which should be caused by metal phase precipitation.

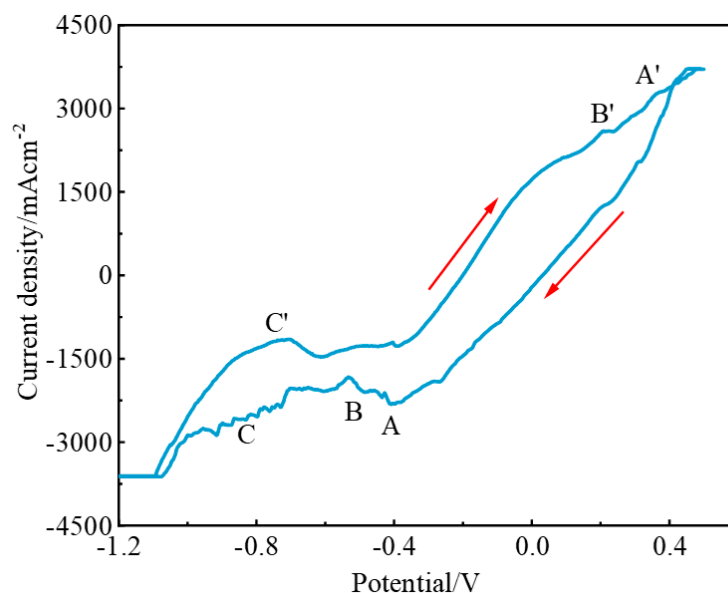


Figure 8. Cyclic voltammetry curve of the NaF–Na₃AlF₆–2 wt% TiO₂ molten salt system on the Mo electrode (scan rate: 50 mV/s; temperature: 1223 K).

Figure 9 shows cyclic voltammetry curves of NaF–Na₃AlF₆–2 wt% TiO₂ obtained at different scan rates. Figure 10 shows the relationship between the reduction peak potential of Ti⁴⁺ and the logarithm of the scan rate. There is a nearly linear relationship between the reduction peak potential and the logarithm of the scan rate. By combining data for the changes in oxidation–reduction peak current density and potential with respect to the scan rate, it is deduced that the first step in the reduction of Ti⁴⁺ is an irreversible process. According to Equation (1), the charge transfer coefficient (α) of the reduction of Ti⁴⁺ at the Mo cathode is calculated to be approximately 0.28.

Figure 11 shows the relationship between the reduction peak A current density and the square root of the scan rate. The current density value of the reduction peak for Ti⁴⁺ increases with an increase in the scan rate, and there is a linear relationship with the square root of the scan rate. This indicates that the reaction is controlled by the diffusion of Ti⁴⁺ in the system. Using the previously obtained charge transfer coefficient (α) of 0.28 and assuming complete ionization of TiO₂ in the molten salt, the diffusion coefficient D of Ti⁴⁺ in the NaF–Na₃AlF₆ system at 950 °C is calculated to be approximately $9.92 \times 10^{-7} \text{ cm}^2/\text{s}$, which is much less than the diffusion coefficient D of Nb⁵⁺.

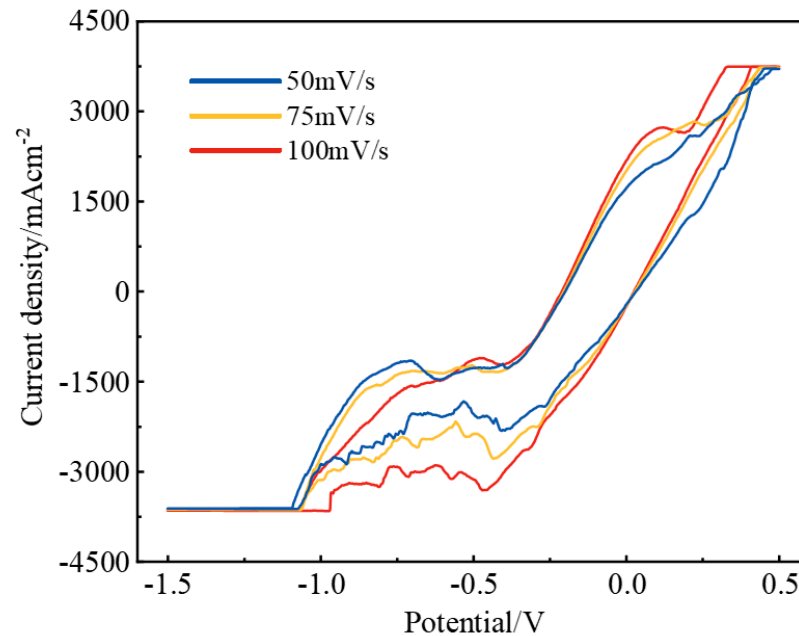


Figure 9. Cyclic voltammetry curves of the NaF–Na₃AlF₆–2 wt% TiO₂ molten salt system at different scan rates (scan rate: 50 mV/s, 75 mV/s, and 100 mV/s; temperature: 1223 K).

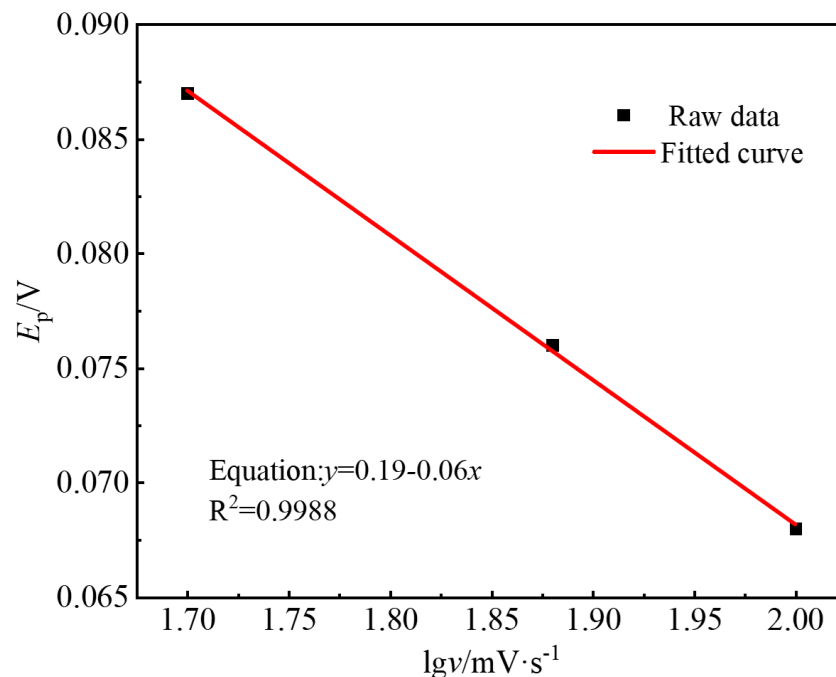


Figure 10. Relationship between the reduction peak A potential and the logarithm of the scan rate in the NaF–Na₃AlF₆–2 wt% TiO₂ molten salt system.

Figure 12 shows the square wave voltammetry curve of the NaF–Na₃AlF₆–2 wt% TiO₂ molten salt system on the Mo electrode. Three reduction peaks (R_I , R_{II} , and R_{III}) are observed. Among them, the reduction potential of peak R_{II} corresponds to the reduction potential of Al^{3+} , whereas the reduction potentials of R_I and R_{III} correspond to titanium ions. After Gaussian fitting of the square wave voltammetry curve and combining Equation (3), the following are found: $n_I = 3.36 \approx 3$, $n_{II} = 2.85 \approx 3$, and $n_{III} = 0.77 \approx 1$. Therefore, it is inferred that the reduction of Al^{3+} [$Al(III) \rightarrow Al$] occurs at $-0.5V$, and the tetravalent titanium ion undergoes a two-step reduction: $Ti(IV) \rightarrow Ti(I) \rightarrow Ti$.

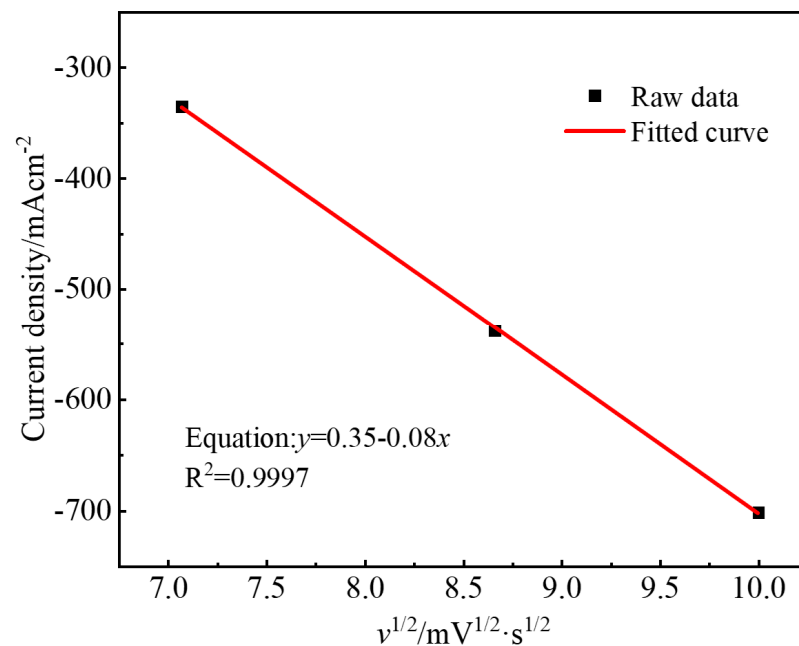


Figure 11. Relationship between the reduction peak A current density and the square root of the scan rate in the NaF–Na₃AlF₆–2 wt% TiO₂ molten salt system.

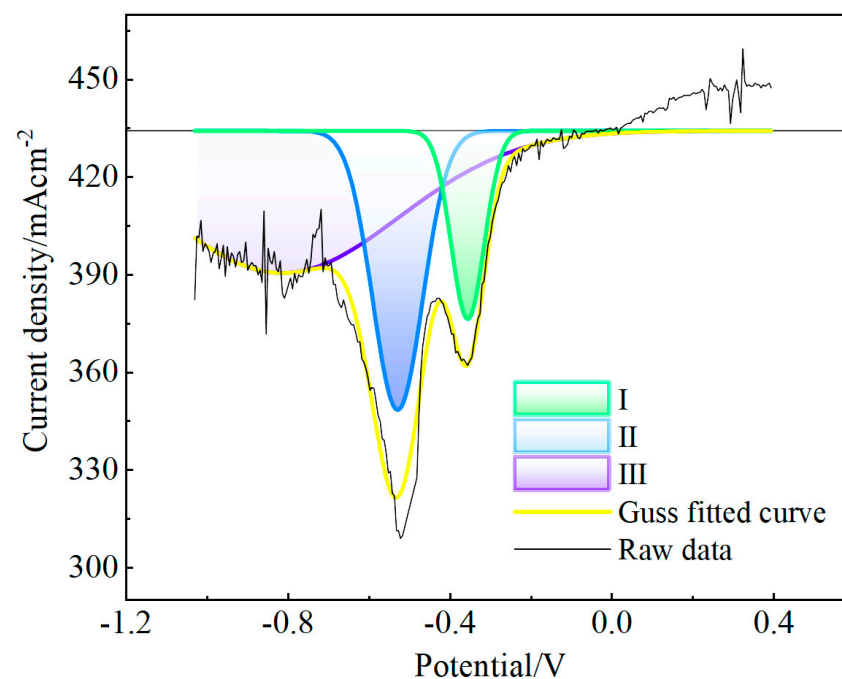


Figure 12. Square wave voltammetry curve of the NaF–Na₃AlF₆–2 wt% TiO₂ molten salt system on the Mo electrode (frequency: 25Hz; temperature: 1223K).

3.4. Electrochemical Behavior of the NaF–Na₃AlF₆–2 wt% Nb₂O₅–2 wt% TiO₂ Molten Salt System

Figure 13 shows the cyclic voltammetry curve of the NaF–Na₃AlF₆–2 wt% Nb₂O₅–2 wt% TiO₂ molten salt system. By combining this with the cyclic voltammetry curve of the NaF–Na₃AlF₆–2 wt% Nb₂O₅ system (Figure 3), the reduction processes and corresponding reduction potentials of the NaF–Na₃AlF₆–2 wt% Nb₂O₅–2 wt% TiO₂ system are obtained and listed in Table 2. There are noticeable differences between the reduction potentials of TiO₂ and Nb₂O₅ in NaF–Na₃AlF₆ molten salt. When both TiO₂ and Nb₂O₅ are present,

the deposition potential of niobium metal (-0.64 V) differs from the deposition potential of titanium metal (-0.77 V). This difference in deposition potentials enables the selective electrolytic separation of the two.

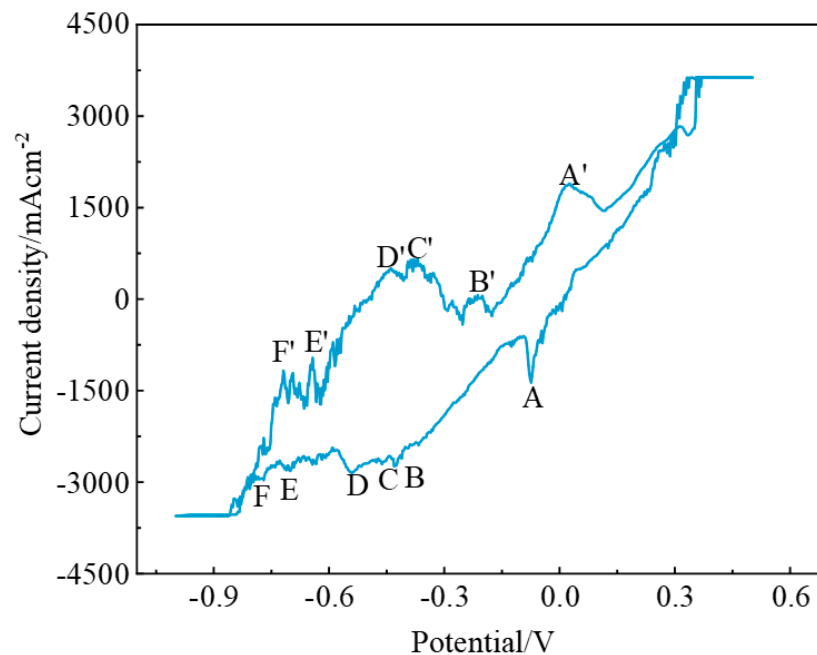


Figure 13. Cyclic voltammety curve of the NaF–Na₃AlF₆–2 wt% Nb₂O₅–2 wt% TiO₂ molten salt system (scan rate: 50mV/s; temperature: 1223K).

Table 2. Reduction processes and corresponding reduction potentials of Nb₂O₅ and TiO₂ in different molten salts.

Reduction Process	Reduction Potential		
	NaF–Na ₃ AlF ₆ – 2 wt% Nb ₂ O ₅	NaF–Na ₃ AlF ₆ – 2 wt% TiO ₂	NaF–Na ₃ AlF ₆ – 2 wt% Nb ₂ O ₅ –2 wt% TiO ₂
Nb (V)→Nb (IV)	0.09 V	–	–0.07 V
Ti (IV)→Ti (I)	–	–0.43 V	–0.43 V
Nb (IV)→Nb (I)	–0.38 V	–	–0.46 V
Nb (I)→Nb	–0.68 V	–	–0.64 V
Ti (I)→Ti	–	–0.84 V	–0.77 V

4. Conclusions

The separation of niobium and titanium is crucial for the efficient utilization of niobium resources in the Bayan Obo polymetallic coexistence mine. Using selective electrolysis on molten salts offers a promising approach for achieving this separation. However, systematic studies on the electrochemical behavior of Nb₂O₅, TiO₂, and their mixtures in NaF–Na₃AlF₆ molten salt have been lacking. In this paper, cyclic voltammetry and square wave voltammetry were used to study the reduction mechanism of niobium oxide and titanium oxide in NaF–Na₃AlF₆ molten salt. The results revealed significant differences in the diffusion coefficients and reduction steps of Nb⁵⁺ and Ti⁴⁺ during reduction at a molybdenum cathode. At 950 °C, the diffusion coefficient of Nb⁵⁺ during reduction at a molybdenum cathode was 3.57×10^{-6} cm²/s. Also, in the NaF–Na₃AlF₆ system, Nb⁵⁺ underwent a three-step reduction as follows: Nb(V)→Nb(IV)→Nb(I)→Nb. The diffusion coefficient of Ti⁴⁺ during reduction at the molybdenum cathode was 9.92×10^{-7} cm²/s, and Ti⁴⁺ underwent a two-step reduction in the NaF–Na₃AlF₆ system: Ti(IV)→Ti(I)→Ti. When Nb₂O₅ and TiO₂ were both present in the NaF–Na₃AlF₆ system, the deposition potential of niobium metal (-0.64 V) differed from that of titanium metal (-0.77 V). These differences in

diffusion coefficient, reduction step, and deposition potential enabled selective electrolytic separation of niobium and titanium.

In future work, we plan to use selective electrolysis to produce high-purity niobium metal from mixtures of niobium oxide and titanium oxide based on the differences in their electrochemical behaviors.

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References

1. She, H.D.; Fan, H.R.; Yang, K.F.; Li, X.C.; Yang, Z.F.; Wang, Q.W.; Zhang, L.F.; Wang, Z.J. Complex, multi-stage mineralization processes in the giant Bayan Obo REE-Nb-Fe deposit. *Ore Geol. Rev.* **2021**, *139*, 104461. [\[CrossRef\]](#)
2. Zhang, B.; Ma, C.; Wang, R.; Liu, C.; Jiang, M. Selective Smelting Reduction of Metal Oxides in REE-Nb-Fe Deposit. *JOM* **2022**, *74*, 993–1001. [\[CrossRef\]](#)
3. Zhang, S.; Rao, M.; Xiao RYou, J.; Li, G. Beneficiation of Nb and Ti carbides from pyrochlore ore via carbothermic reduction followed by magnetic separation. *Miner. Eng.* **2022**, *180*, 107492. [\[CrossRef\]](#)
4. Zhang, S.H.; Rao, M.J.; Xiao, R.D.; You, J.X.; Li, G.H.; Jiang, T. Enrichment of Nb and Ti from carbonatite pyrochlore ore via calcining-slaking followed by gravity separation. *Int. J. Min. Sci. Technol.* **2022**, *32*, 615–626. [\[CrossRef\]](#)
5. Zhang, B.; Xue, X.; Yang, H. A novel process for recovery of scandium, rare earth and niobium from Bayan Obo tailings: NaCl-Ca(OH)₂-coal roasting and acid leaching. *Miner. Eng.* **2022**, *178*, 107401. [\[CrossRef\]](#)
6. Zhang, B.; Liu, C.J.; Li, C.L.; Jiang, M.F. A novel approach for recovery of rare earths and niobium from Bayan Obo tailings. *Miner. Eng.* **2014**, *65*, 17–23. [\[CrossRef\]](#)
7. Sun, L.; Yu, H.; Meng, F.; Qi, T.; Zheng, S.; Peng, Y.; Wang, L. A novel method for the separation of niobium and titanium from sulfuric acid-oxalate solutions using N235 and MIBK. *Hydrometallurgy* **2021**, *205*, 105748. [\[CrossRef\]](#)
8. Sun, L.; Yu, H.; Meng, F.; Qi, T.; Wang, L.; Peng, Y. Recovery of niobium and titanium from ilmenorutile by NaOH roasting-H₂SO₄ leaching process. *J. Mater. Res. Technol.* **2021**, *15*, 2575–2583. [\[CrossRef\]](#)
9. Sun, L.; Zhang, X.; Wang, L. Separation and extraction of niobium from H₂SO₄ solution containing titanium and iron impurities. *Sep. Purif. Technol.* **2022**, *295*, 121207. [\[CrossRef\]](#)
10. Li, H.E.; Lu, X.G.; Chen, C.Y.; Li, Q.; Li, C.H.; Zhong, Q.D. Metal niobium by solid oxygen-ion membrane. *Chin. J. Nonferrous Met.* **2008**, *18*, 1336–1341.
11. Li, C.; Li, S.; Che, Y.; Li, J.; Shu, Y.; He, J.; Song, J. Electrochemical behavior of niobium ions in molten KCl-NaCl. *J. Mater. Res. Technol.* **2020**, *9*, 9341–9347. [\[CrossRef\]](#)
12. Christensen, E.; Wang, X.D.; Barner JH, V.; Ostfold, T.; Bjerrum, N.J. The Influence of Oxide on the Electrodeposition of Niobium from Alkali Fluoride Melts. *Cheminform* **2010**, *25*, 141. [\[CrossRef\]](#)
13. Matthiessen, F.; Christensen, E. The Redox Chemistry of Niobium(V) Fluoro and Oxofluoro Complexes in LiF-NaF-KF Melts. *J. Electrochem. Soc.* **1996**, *143*, 1793–1799. [\[CrossRef\]](#)
14. Bailey, R.A.; Yoko, T. High-temperature electroplating of chromium from molten FLINAK. *J. Appl. Electrochem.* **1986**, *16*, 737–744. [\[CrossRef\]](#)
15. Kuznetsov, S.A. Electrolytic production of niobium powder from chloride—Fluoride melts containing compounds of niobium and zirconium. *Russ. J. Electrochem.* **2000**, *36*, 509–515. [\[CrossRef\]](#)
16. Lantelme, F.; Salmi, A. Electrochemistry of Titanium in NaCl–KCl Mixtures and Influence of Dissolved Fluoride Ions. *J. Electrochem. Soc.* **1995**, *142*, 3451–3456. [\[CrossRef\]](#)
17. Chen, G.S.; Masazumi, O.; Takeo, O. Electrochemical studies of titanium ions (Ti⁴⁺) in equimolar KCl–NaCl molten salts with 1 wt% K₂TiF₆. *Electrochim. Acta* **1987**, *32*, 1637–1642. [\[CrossRef\]](#)
18. Robin, A.; Lepinay, J.D. Determination of the apparent standard potential of the Ti/Ti(III) system in the LiF–NaF–KF eutectic using voltammetry, chronopotentiometry and open-circuit potentiometry. *Electrochim. Acta* **1991**, *36*, 1009–1012. [\[CrossRef\]](#)

19. Jun, L.; Bing, L. Electrochemical reduction and electrocrystallization process of B(III) in the LiF-NaF-KF-KBF₄ molten salt. *Rare Met. Mater. Eng.* **2007**, *36*, 15–19. [[CrossRef](#)]
20. Jiao, H.; Zhang, L.; Jiao, S. Electrochemical Behavior of Titanium Ions at Liquid Metal Cathodes in Molten Salts. In *Proceedings of the 13th World Conference on Titanium*; Venkatesh Venkatesh, V., Pilchak, A.L., Allison, J.E., Eds.; John Wiley & Sons: San Diego, CA, USA, 2016; Volume 28, pp. 183–186.
21. Yuan, T.C.; Weng, Q.G.; Zhou, Z.H.; Li, J.; He, Y.H. Preparation of High-Purity Titanium by Molten-Salt Electrolysis Process. *Adv. Mater. Res.* **2011**, *284–286*, 1477–1482. [[CrossRef](#)]
22. Ma, M.; Wang, D.; Wang, W. Extraction of titanium from different titania precursors by the FFC Cambridge process. *J. Alloys Compd.* **2019**, *25*, 6107–6114. [[CrossRef](#)]
23. Wei, Y.; Yang, W.; Guo, H. Functional COFs for Electrochemical Sensing: From Design Principles to Analytical Applications. *ChemistrySelect* **2023**, *8*, 2365–6549. [[CrossRef](#)]
24. Pogliano, U.; Durbiano, F.; Serazio, D. A system for controlling electrical and chemical parameters in the Faraday constant determination by dissolution of silver. *Meas. Sci. Technol.* **2011**, *22*, 055102. [[CrossRef](#)]
25. Su, C.; An, M.; Yang, P.; Gu, H.; Guo, X. Electrochemical behavior of cobalt from 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid. *Appl. Surf. Sci.* **2010**, *256*, 4888–4893. [[CrossRef](#)]
26. He, X.; Hou, B.; Li, C.; Zhu, Q.; Jiang, Y.; Wu, L. Electrochemical mechanism of trivalent chromium reduction in 1-butyl-3-methylimidazolium bromide ionic liquid. *Electrochem. Acta* **2014**, *130*, 245–252. [[CrossRef](#)]
27. Halford, G.C.; Personick, M.L. Bridging Colloidal and Electrochemical Nanoparticle Growth with In Situ Electrochemical Measurements. *Acc. Chem. Res.* **2023**, *56*, 1228–1238. [[CrossRef](#)] [[PubMed](#)]

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