Electrodeposition and electrochemical behavior of molybdenum ions in $ZnCl_2$-NaCl-KCl molten salt

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ABSTRACT

In this paper, a method for extracting and refining metallic molybdenum using low-temperature $ZnCl_2$-NaCl-KCl molten salt was proposed. The electrochemical behavior of molybdenum ions in $ZnCl_2$-NaCl-KCl molten salt was investigated in detail, and pure metallic molybdenum was collected on the cathode. The reduction and diffusion processes of Mo(V) ions in $ZnCl_2$-NaCl-KCl molten salt were determined through a series of electrochemical methods. The diffusion coefficients and nucleation modes of Mo(V) ions were also studied, and electrolysis was conducted for a prolonged period at a constant current density. The results indicated that the electrode reduction of Mo(V) ions in $ZnCl_2$-NaCl-KCl molten salt proceeds through a three-step reaction: Mo(V) → Mo(IV) → Mo(III) → Mo at 250°C. The Mo(V) → Mo(IV) reaction was reversible and diffusion-controlled, with a Mo(V) diffusion coefficient of 6.02×10^{-6} cm^2 s^{-1}. Additionally, the nucleation mode of Mo(V) ions was instantaneous nucleation. The products electro-deposited were confirmed of metallic molybdenum with a particle size of less than 1 μm.

Keywords: molybdenum; molten salt; electrochemical behaviors; nucleation mechanism

INTRODUCTION

Molybdenum is a metal with the high melting point, high hardness, good thermal and electrical conductivity and strong corrosion resistance (Huang et al. 2016; Lv et al. 2021a; Lv et al. 2021b; Zhang et al. 2023), and is widely used in the fields of iron and steel, metallurgy, medical treatment, semiconductors and other fields (Luo et al. 2019; Kuroda et al. 2020). Among the various extraction and refining technologies for molybdenum metal, the electrolysis method has shown great potential for development and application with its high efficiency and environmentally friendly characteristics. In the process of electrolytic extraction and refining, the electrolyte composition has an important influence on the electrolysis process due to its different physical and chemical properties. Therefore, the choice of electrolyte composition is extremely important issue for the extraction and purification of molybdenum metal. Depending on the type of electrolyte used in the electrolysis extraction and refining of molybdenum metal, it can be divided into ionic liquid electrolytes and molten salt electrolytes.

Ionic liquid electrolyte is a special liquid substance mainly composed of a large number of cations and anions. Researchers attempted to successfully deposit high-purity and dense molybdenum metal using ionic liquids with high concentrations of acetic acid (Morley et al. 2012), ammonium acetate solution (Kuznetsov et al. 2018), and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) (Tian et al. 2023) as the electrolyte. However, although the ionic liquid electrolyte has the advantages of fine-tuning and low-temperature electrolysis in the preparation of metallic molybdenum, its efficiency is low, with most of the current being used to electrolyze water and produce hydrogen, resulting in a high oxygen content in the product and a slow electrolysis rate.

Compared with ionic liquid electrolytes, molten salt electrolyte electrolysis has the advantages of high current efficiency, fast electrolysis rate and high product purity. Senderoff et al successfully prepared molybdenum metal with high purity by adding K_3MoCl_6 to the molten salts of KCl-NaCl and LiCl-KCl, respectively, and electrolyzing them at 900°C in an inert atmosphere (Senderoff and Brenner, 1954). After that, molybdenum metal with higher purity was successfully prepared from the molten salt system of NaF-KF-MoF_6 (Senderoff and Mellors 1967) at 600°C. In addition to molybdenum halide as solute in molten salt for molten salt electrolysis, researchers have also tried to use molybdenum oxide (Kou et al. 2023; Malyshev et al. 2018; Kushkhov and Adamokova, 2007) and metal molybdates (Kōyama, Hashimoto and Terawaki, 1987) as solutes, which can also successfully prepare molybdenum metal, but the oxygen content in the product will inevitably be higher. Therefore, the extraction and refining of molybdenum metal using molten salt electrolyte, although the current efficiency is high and the electrolysis speed is fast, the temperature required for electrolysis is usually above 450°C, and the energy consumption is high and the requirement of equipment is high. To address this problem, Nakajima et alinvestigated a new low-temperature molten salt system, i.e., $ZnCl_2$-NaCl-KCl system (Nakajima, Nohira and Hagiwara, 2006). $MoCl_3$ was added to the $ZnCl_2$-NaCl-KCl system at 250°C, and molybdenum metal was successfully obtained by electrodepositing on the cathode. The advantage of this molten salt system is that it can realize the electrodeposition of metallic molybdenum at a lower temperature, which will reduce the energy consumption and the volatilization loss of molybdenum chloride. Carrying on electrodepositing in such melt, the current efficiency is much higher than that of ionic liquids, which is a more ideal electrolyte.

However, the results of the present study only demonstrate the feasibility of extracting metal molybdenum from the $ZnCl_2$-NaCl-KCl molten salt electrolyte. There are few studies on the electrochemical behavior of Mo(V) in low-temperature molten salts, and no uniform conclusions have been drawn. In addition, the molybdenum metal has a complex dissolved valence state during the refining and extraction process. Therefore, it is of great significance to study the electrochemical behavior of high-valent molybdenum ions in the $ZnCl_2$-NaCl-KCl (Moon et al. 2022). In summary, $ZnCl_2$-NaCl-KCl (3:1:1) was chosen as the electrolyte in this study, and thermodynamic calculations and various electrochemical tests were performed to probe deeply into the reduction and diffusion processes of Mo(V) ions. The diffusion coefficient and nucleation mode of molybdenum ions were investigated, and electrodeposition experiments were carried out at a constant current, and molybdenum metal was successfully obtained at the cathode.

EXPERIMENTAL

In this study, a total of 100 g of $ZnCl_2$-NaCl-KCl salt mixture was used as the electrolyte with a molar ratio of 3:1:1. The specific compositions were $ZnCl_2$ (99% purity), NaCl (99.8% purity), and KCl (99.8% purity), which were purchased from McLean Biochemicals Ltd. The salt mixtures were first kept at a constant temperature of 200°C for 4 h to remove residual moisture, followed by a temperature increase to 250°C and maintained for 4 h to ensure that the molten salt mixtures were fully melted and well mixed. This was followed by a 12 h pre-electrolysis treatment, followed by electrochemical tests and deposition experiments. Molybdenum ions were added to the molten salt as $MoCl_5$ (99.9% purity, purchased from Macklin Biochemicals Ltd).

The whole experiment was carried out under argon atmosphere. A three-electrode system was used during the electrochemical tests. In this system, a tungsten wire (1 mm diameter, 99.99% purity) was used as the working electrode (WE), while another tungsten wire was used as the reference electrode (RE) and a graphite rod (10 mm diameter, 99.99% purity) was used as the counter electrode (CE). When constant current electrolysis was performed, a two-electrode system was used, in which molybdenum sheets (50 mm in length, 10 mm in width, and 1 mm in thickness) were used as cathode and anode, respectively, in different electrolysis steps. The electrochemical experiments were recorded by Nova 2.1 software controlled by AutoLab (PGSTAT 302N) and transient electrochemical techniques were used to study the electrochemical behavior of Mo(V) in $ZnCl_2$-NaCl-KCl molten salt. The experiments were carried out at a current density of 0.06 A cm^{-2} in a constant current electrolysis test and the cathodic products were collected. In order to investigate the microstructure and morphology of the cathode products, scanning electron microscopy (SEM, including TESCAN MIRA LMS and ZEISS Sigma 300), as well as energy spectrometry (EDS), were used for the analysis.

RESULTS AND DISCUSSION

3.1. Redox behavior of molybdenum ions in molten salt

The decomposition reactions corresponding to NaCl, KCl, $ZnCl_2$, and $MoCl_x$ ($x \leq 5$) were shown in Equation (1)-(4). Through thermodynamic calculations and the study of Nakajima et al (2006), it was found that the decomposition potential of $ZnCl_2$ is the smallest when compared to NaCl and KCl under 250°C. Therefore, for extraction and refining of molybdenum metal by using this molten salt, the $MoClx$ ($x \leq 5$) decomposition potential must be lower than the $ZnCl_2$ decomposition potential. The Gibbs free energy changes for the reactions (3) and (4) at 250°C were calculated using HSC Chemistry 6.0, from which the decomposition potentials of molybdenum chloride at different valence states as well as the theoretical electrochemical window of the molten salt electrolyte were determined by Equation (5).

The common valence states of molybdenum chloride were more complex (including 5, 4, 3, 2, and 0 valence states) and the calculated decomposition voltages were shown in Figure 1(a). The electrolyte selection criteria for the electrolysis of molten salts was satisfied because the decomposition voltage of $MoCl_x$ (max. -1.13 V) was lower than that at molten NaCl-KCl (-1.74

V) at 750°C. In addition, the reduction order of each valence state of each molybdenum ion in the Figure 1(a) provided theoretical support for the subsequent molybdenum ion reduction process.

$$2NaCl(s) = 2Na(l) + Cl_2(g) \tag{1}$$

$$2KCl(s) = 2K(l) + Cl_2(g) \tag{2}$$

$$ZnCl_2 = Zn + Cl_2(g) \tag{3}$$

$$2MoCl_x = 2MoCl_y + (x - y)Cl_2(g) \tag{4}$$

$$\Delta G = -nE\mathrm{F} \tag{5}$$

Where ΔG represents the change in Gibbs free energy (kJ mol^{-1}); the relationship between x and y is $0 \leq y < x \leq 5$; n is the number of electrons transferred by the reaction (mol); E refers to the reduction potential (V) of the above chloride and sulfide, and F is the Faraday constant (C mol^{-1}).

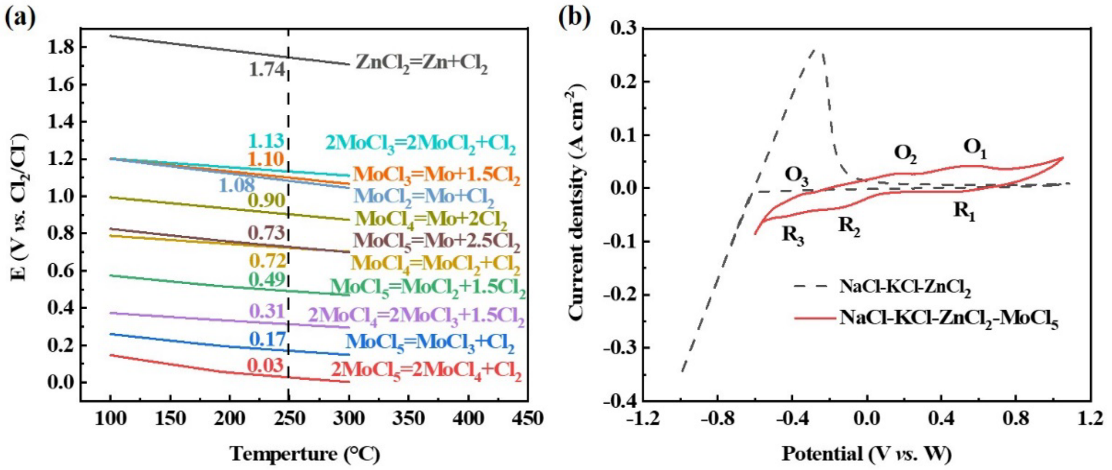

Figure 1. (a) Molybdenum chloride and zinc chloride theoretical decomposition voltage as a function of temperature (all thermodynamic data from HSC 6.0 in activity (α = 1)); (b) Cyclic voltammograms before and after the addition of $MoCl_5$ in the molten $ZnCl_2$-NaCl-KCl salt; scan rate: 0.25 V s^{-1}

The results of the cyclic voltammetry (CV) tests, conducted before the addition of $MoCl_5$, were shown as the gray line in Figure 1(b). The reduction of Zinc ions began near -0.6 V *vs*. W, and there were no significant current density peaks observed between 1.1 V and -0.6 V, suggesting that no other reduction reactions occurred in this voltage range. Therefore, it was determined that the electrolyte system was suitable for performing electrochemical tests. After the addition of $MoCl_5$, the voltammetric curve appeared as the red line in Figure 1(b). Three pairs of distinct current density peaks (R_1/O_1, R_2/O_2, and R_3/O_3) were observed, indicating that molybdenum ions were involved in redox reactions. Furthermore, all these reduction reactions of molybdenum ions occurred before the precipitation of Zinc ions, demonstrating that the selection of the $ZnCl_2$-NaCl-KCl-$MoCl_5$ system was feasible for the extraction and refining of molybdenum metal.

The cyclic voltammograms obtained after the addition of $MoCl_5$ were further analyzed through Figure 2(a), where it can be seen that the reduction peaks R_1, R_2, and R_3 occurred at reduction potentials of 0.52 V, -0.08 V, and -0.42 V (*vs*. W), respectively. Based on these observations, it can be inferred that the reduction of molybdenum ions occurred in three distinct steps. Subsequently, the electrochemical behavior of Mo(V) was further investigated using the more precise square wave voltammetry (SWV) technique. The results obtained from this analysis are presented in Figure 2(b), where three distinct electrode reduction reactions R_1, R_2, and R_3 can be observed at potentials of 0.53 V, -0.05 V, and -0.45 V (*vs*. W), respectively. These findings suggest that the conversion of Mo(V) to metal in the $ZnCl_2$-NaCl-KCl molten salt involves three reduction processes, which is consistent with the results obtained from the previously conducted cyclic voltammetry tests.

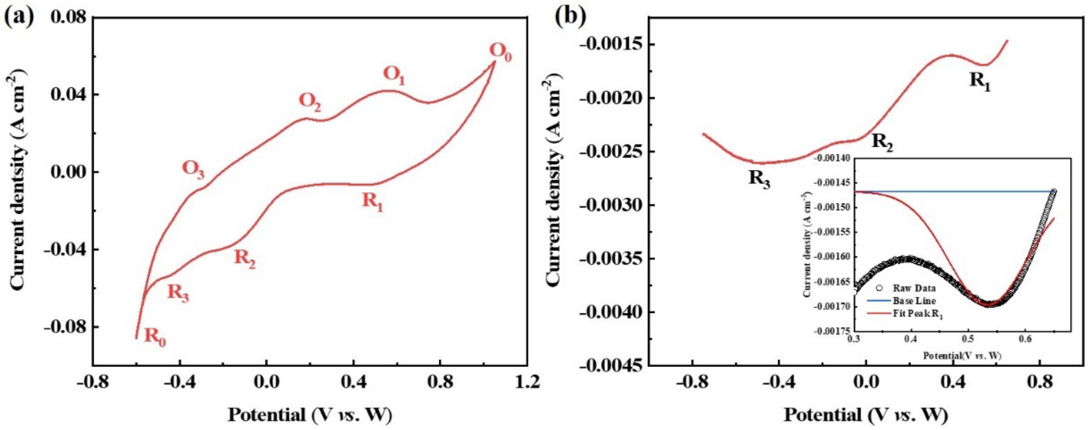

Figure 2. Electrochemical test plots after addition of $MoCl_5$ to $ZnCl_2$-NaCl-KCl molten salt: (a) cyclic voltammetry; scan rate: 0.25 V s^{-1}; (b) square-wave voltammetry; scan frequency: 25 Hz; inset: Gaussian fit to R_1 peaks

In addition, the peak potentials of R_1, R_2, and R_3 did not change with increasing scan rate or scan frequency in Figure 3(a) and Figure 4(a), which indicates that R_1, R_2, and R_3 are reversible reactions. Where the number of transferred electrons corresponding to the reduction peak R_1 can be calculated by Equation (6) (Krause and Ramaley, 1969; O'Dea, Osteryoung and Osteryoung, 1981; Aoki et al. 1986):

$$W_{1/2}=3.52\frac{RT}{n\mathrm{F}} \tag{6}$$

A Gaussian fit was applied to R_1 in the square-wave voltammogram, and the fitted curve is presented in the inset of Figure 2(b). The half-wave width of R_1 was determined to be 0.16. The number of electrons transferred corresponding to R_1 was calculated to be approximately 0.99, which was close to 1, indicating that the reduction step represented by the R_1 peak was Mo(V) → Mo(IV). Subsequently, Mo(IV) was reduced to metallic molybdenum through two further steps, R_2 and R_3. The reduction reaction of the Mo(IV) ion can be referenced to our previous determination in NaCl-KCl (Zhang et al. 2024): Mo(IV) → Mo(III) → Mo. Therefore, it is inferred that R_2 and R_3 correspond to the reduction steps of Mo(IV) → Mo(III) and Mo(III) → Mo, respectively. In conclusion, the reduction process of Mo(V) in the $ZnCl_2$-NaCl-KCl molten salt was Mo(V) → Mo(IV) → Mo(III) → Mo. This was consistent with the order of the Mo(V) reduction potential calculated thermodynamically in Figure 1(a).

3.2. Diffusion coefficient of molybdenum ions in molten salt

To further investigate the kinetics of the electrode process of molybdenum ions in $ZnCl_2$-NaCl-KCl molten salt, cyclic voltammetry experiments were conducted at various scan rates within the scan interval of 0.9 V to -0.7 V (*vs*. W). The resulting cyclic voltammetry curves were presented in Figure 3(a), and the correlation between the potential of the reduction peak R_1 and the logarithm of the scan rate was depicted in Figure 3(b). The peak potential of R_1 hardly varied with increasing scan rate and tended to level off with a value of 0.53 V (*vs*. W), which indicated that the R_1 reduction was reversible (Yuan et al. 2021). The relationship between the maximal current density of reaction R_1 and the square root of the scan rate was subsequently investigated. As demonstrated in Figure 3(b), the peak current density of the reduction reaction R_1 was linear with the square root of the scan rate, indicating that the electrode reduction reaction R_1 was controlled by diffusion.

The diffusion coefficient of Mo(V) ions in molten $ZnCl_2$-NaCl-KCl was determined by Equation (7) (Liu et al. 2019)

When the reactants and products were both soluble.

$$I_p = 0.4463 \frac{(n\mathrm{F})^{3/2} A D^{1/2} C_0 v^{1/2}}{(\mathrm{R}T)^{1/2}} \tag{7}$$

When the product was insoluble, Equation (8) could be used to determine the diffusion coefficient.

$$I_p = 0.6102 \frac{(nF)^{3/2} A D^{1/2} C_0 v^{1/2}}{(RT)^{1/2}} \tag{8}$$

Where *Ip* is the peak current (A), v is the scan rate (V s^{-1}), and C_0 is the bulk concentration of the reducible ion (mol cm^{-3}). The concentration C_0 was determined to be 2.24×10^{-5} mol cm^{-3}. A is the surface area of the W working electrode (cm^2), and D is the diffusion coefficient of Mo(V) (cm^2 s^{-1}). Mo(V) ions were calculated to have a diffusion coefficient of 6.02×10^{-6} cm^2 s^{-1} in molten $ZnCl_2$-NaCl-KCl at 250°C.

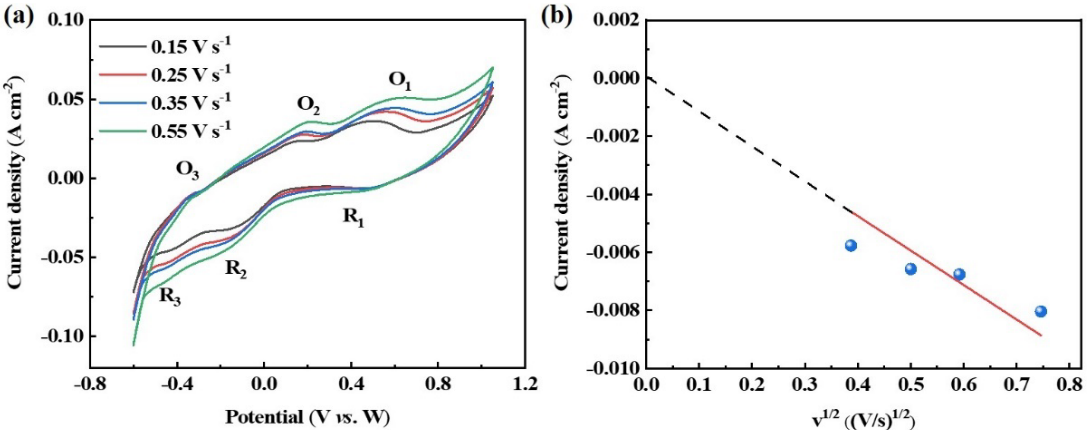

Figure 3. (a) Cyclic voltammograms of $MoCl_5$ in molten $ZnCl_2$-NaCl-KCl on a tungsten wire electrode at different scan rates; (b) The relationship between the current density and the square root of scan rate.

To further confirm the findings above, we conducted square wave voltammetry at various frequencies. The test results are displayed in Figure 4(a). The responsive R_1, R_2 and R_3 potentials barely changed as the applied frequency increased. The linear fitting results were given in Figure 4(b), which related the peak current density linearly to the square root of frequency. This was consistent with the finding made by cyclic voltammetry and leads to the conclusion that the electrode reduction reaction R_1 was a reversible diffusion reaction. The diffusion coefficient was calculated by Equation (9) and Equation (10) (Song et al. 2016).

$$I_p=nFAC_0\frac{1-\Gamma}{1+\Gamma}\left(\frac{Df}{\pi}\right)^{1/2} \tag{9}$$

$$\Gamma=\exp\left(\frac{nF\Delta E}{2RT}\right) \tag{10}$$

where ΔE is the amplitude of SWV (0.02 V), and f indicates the frequency. The diffusion coefficient of Mo(V) in molten $ZnCl_2$-NaCl-KCl at 250°C was calculated to be 5.61×10^{-6} cm^2s^{-1}. This was about on the same scale as what was discovered during cyclic voltammetry testing.

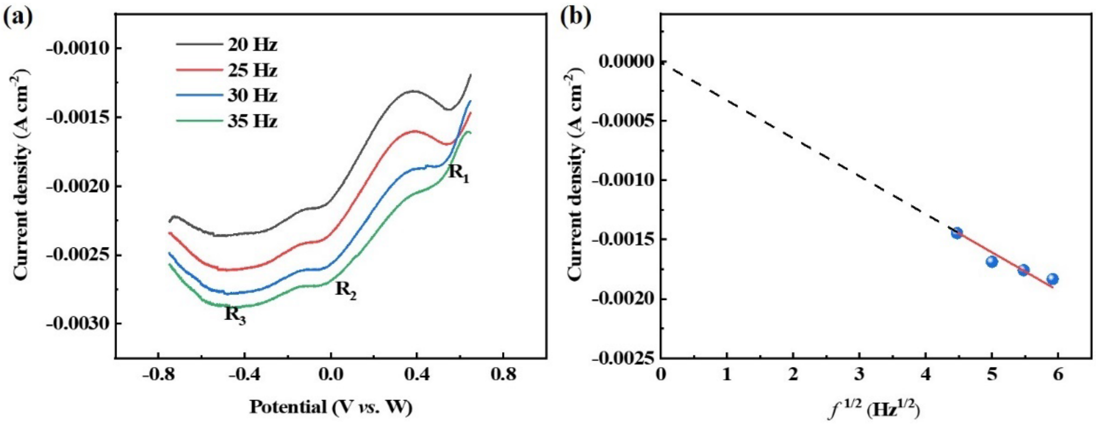

Figure 4. (a) Square wave voltammetry of $MoCl_5$ in molten $ZnCl_2$-NaCl-KCl on a tungsten wire electrode at different frequencies; (b) The relationship between the current density and the square root of frequency.

3.3. Nucleation mode of molybdenum ions

In this paper, the $MoCl_5$ nucleation mode was further investigated by using the time-current method, as shown in Figure 5(a). Its time-current curve is shown in Figure 5(a). The applied potential was set to -0.55 V *vs*. W. The current decreased rapidly and stabilized with time, which was attributed to the fact that molybdenum would be deposited on the electrode at this potential, resulting in a decrease in the molybdenum ion concentration in the vicinity of the electrode, which led to a rapid decrease in the current because molybdenum ions in the molten salt were unable to diffuse to the surface of the electrode in time to replenish it. However, as the reaction proceeds, the diffusion rate of molybdenum ions on the cathode surface and the deposition rate of molybdenum gradually reached a dynamic equilibrium, which led to the gradual stabilization of the current. This also showed that the reduction of Mo(V) ions was controlled by diffusion.

The nucleation mode of molybdenum ions can also be determined by the relationship between time and current in the chronoamperometry method. The nucleation modes are generally categorized into two: progressive nucleation and transient nucleation (Khelladi et al. 2009; Tylka, Willit and Williamson, 2017) :

For instantaneous nucleation:

$$I(\mathrm{t})=\frac{zFN_0\pi(2DC)^{3/2}M^{1/2}}{\rho^{1/2}}t^{1/2} \tag{11}$$

For progressive nucleation:

$$I(\mathrm{t})=\frac{2z\mathrm{F}K_nN_0\pi(2D\mathrm{C})^{3/2}M^{1/2}}{3\rho^{1/2}}t^{3/2} \tag{12}$$

where I (t) is the polarization current at time t; t is the polarization time (s); Z is the ion valence state; N_0 is the initial nucleation number; M is the atomic weight of the deposit (g mol^{-1}); K_n is the nucleation constant; and ρ is the density of the deposit (g cm^{-3}).

The current versus square root of time was shown in Figure 5(b) and (c). The relationship between the current and the square root of time in Figure 5(b) remained linear after fitting, whereas the relationship between the current and the third power of the square root of time in Figure 5(c) had a poor correlation after fitting. Thus, molybdenum ions nucleated in a transient mode.

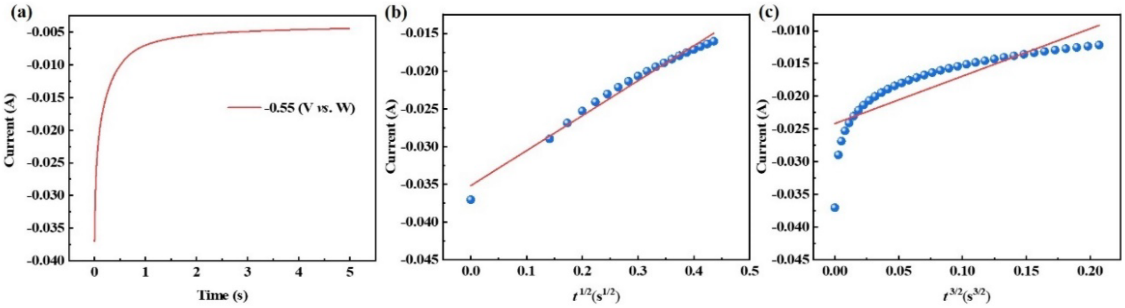

Figure 5. (a) Timing current curve of $MoCl_5$ in $ZnCl_2$-NaCl-KCl molten salt; applied potential: -0.55 V *vs*. W; (b) The relationship between the current and the square root of time; (c) The relationship between the current and the square root to the third power of time.

The diffusion coefficients and nucleation modes of Mo ions in different molten salt systems are shown in Table 1, and there are differences in the results in the molten salt system. This phenomenon may be due to different ionic species in the molten salt electrolyte, different experimental temperatures and the use of electrodes.

Table 1 Diffusion coefficients and nucleation modes of Mo ions obtained in different molten salt systems

Molten salt	T(°C)	Diffusion coefficient (cm^2 s^{-1})		n	Nucleation mode	Reference
		CV	SWV			
NaCl-KCl-$MoCl_5$	750	1.22×10^{-4}	1.67×10^{-4}	2	progressive	(Zhang et al. 2024)
$ZnCl_2$-NaCl-KCl-$MoCl_5$	250	6.02×10^{-6}	5.61×10^{-6}	1	instantaneous	This work

3.4. Electrodeposition of molybdenum

After a series of electrochemical tests, in this paper, constant current electrolysis was carried out in molten $ZnCl_2$-NaCl-KCl-$MoCl_5$ (1.0 wt.%) at 250°C in a two-electrode system. The current density was set at 0.06 A cm^{-2} and the electrolysis time was 20 h. Molybdenum sheets were used as cathode and anode, respectively. During the electrolyzing of molybdenum metal, the anode molybdenum metal was oxidized and dissolved as molybdenum ions, which diffused to the cathode and were reduced to metal. The voltage change during the constant electrolysis process was recorded as shown in Figure 6(a), and it can be found that the voltage was maintained near 1.65 V with little change during the electrolysis process, indicating that the electro-refining process was stable. After 20 h of electrolysis, a black deposit was collected at the cathode as shown in the inset in Figure 6(a). The product was ultrasonically cleaned and vacuum-dried. The electrolysis product was analyzed and detected using SEM and EDS, as shown in Figure 6(b), the cathode product after electrolysis was metallic molybdenum and showed an irregular granular shape with particle size less than 1 μm, and this shape may be due to the transient nucleation of molybdenum ions in the electrochemical deposition process.

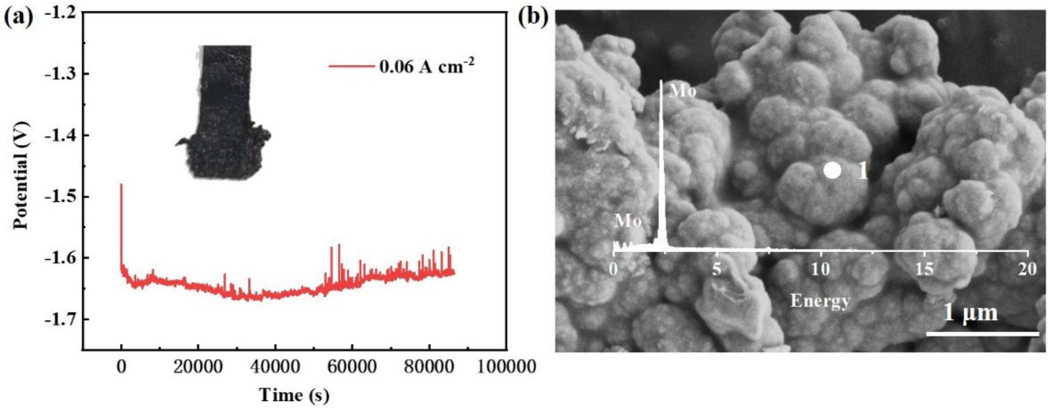

Figure 6. (a) Time voltage curve at constant current density; inset: Cathode after 20 h electrolysis; (b) SEM image of cathode product and the results of EDS analysis at point 1.

CONCLUSIONS

In this paper, the electrochemical behavior of Mo(V) ions in molten $ZnCl_2$-NaCl-KCl at 250°C was investigated in detail. In the three-electrode system, thermodynamic calculations and a series of electrochemical tests were conducted to determine that Mo(V) in $ZnCl_2$-NaCl-KCl molten salt was reduced to molybdenum metal in three steps, namely, Mo(V) → Mo(IV) → Mo(III) → Mo, and the electrode reduction process was a diffusion-controlled reversible reaction. The diffusion coefficients of Mo(V) were calculated to be 6.02×10^{-6} cm^2s^{-1} and 5.61×10^{-6} cm^2s^{-1}, respectively. Subsequently, the nucleation of Mo(V) ions in $ZnCl_2$-NaCl-KCl molten salts was determined to be a transient nucleation process through the use of the constant current method. Finally, electrolytic refining was performed for a prolonged duration at a current density of 0.06 A cm^{-2}, and the electrolytic process remained stable, resulting in the collection of metallic molybdenum at the cathode with a particle size of less than 1 μm. It indicates that $ZnCl_2$-NaCl-KCl holds potential as an electrolyte molten salt for the electrolytic extraction and refining of molybdenum metal.

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REFERENCES

Aoki, K., K. Tokuda, H. Matsuda, and J. G. Osteryoung. 1986. Reversible square-wave voltammograms independence of electrode geometry. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 207(1-2), 25-39.doi:10.1016/0022-0728(86)87060-7

Huang, Z., J. Liu, X. Deng, H. Zhang, L. Lu, Z. Hou, and S. Zhang. 2016. Low temperature molten salt preparation of molybdenum nanoparticles. *International Journal of Refractory Metals & Hard Materials* 54, 315-321. doi:10.1016/j.ijrmhm.2015.08.01

Khelladi, M. R., L. Mentar, A. Azizi, A. Sahari, and A. Kahoul. 2009. Electrochemical nucleation and growth of copper deposition onto FTO and n-Si(100) electrodes. *Materials Chemistry and Physics* 115(1), 385-390.doi:10.1016/j.matchemphys.2008.12.017

Kou, Q., W. L. Jin, C. T. Ge, J. Pang, J. Zhang, G. M. Haarberg, S. J. Xiao, and P. Wang. 2023. Preparation of molybdenum coatings by molten salt electrodeposition in Na_3AlF_6-NaF-Al_2O_3-MoO_3 system. *Coatings* 13(7), 1266.doi:10.3390/coatings13071266

Kōyama, K., Y. Hashimoto, and K. Terawaki. 1987. Smooth electrodeposits of molybdenum from KF-$Li_2B_4O_7$-Li_2MoO_4 fused salt melts. *Journal of the Less Common Metals* 132(1), 57-67.doi:10.1016/0022-5088(87)90174-3

Krause, M. S. and L. Ramaley. 1969. Analytical application of square wave voltammetry. *Analytical Chemistry* 41(11), 1365-1369.doi:10.1021/ac60280a008

Kuroda, P. A. B., M. L. Lourenço, D. R. N. Correa, and C. R. Grandini. 2020. Thermomechanical treatments influence on the phase composition, microstructure, and selected mechanical properties of Ti–20Zr–Mo alloys system for biomedical applications. *Journal of Alloys and Compounds* 812, 152108.doi:10.1016/j.jallcom.2019.152108

Kushkhov, K. B. and M. N. Adamokova. 2007. Electrodeposition of tungsten and molybdenum metals and their carbides from low-temperature halide-oxide melts. *Russian Journal of Electrochemistry (Translation of Elektrokhimiya)* 43(9), 997-1006.doi:10.1134/s1023193507090030

Kuznetsov, V. V., M. A. Volkov, D. A. Zhirukhin, and E. A. Filatova. 2018. Electroreduction of Mo(VI) compounds in ammonium-acetate solutions(Article). *Russian Journal of Electrochemistry (Translation of Elektrokhimiya)* 54(11), 1006-1011.doi:10.1134/s1023193518130256

Liu, S. Y., L. J. Wang, K. C. Chou, and R. V. Kumar. 2019. Electrolytic preparation and characterization of VCr alloys in molten salt from vanadium slag. *Journal of Alloys and Compounds* 803, 875-881.doi:10.1016/j.jallcom.2019.06.366

Luo, L., Y. Zhou, Y. Zhang, X. Zan, J. Liu, X. Zhu, and Y. Wu. 2019. Current status and development trend of toughening technology of molybdenum-based materials. *Chinese Journal of Nonferrous Metals* 29(3), 525-537.doi:10.19476/j.ysxb.1004.0609.2019.03.12

Lv, C., H. D. Jiao, S. L. Li, Y. S. Che, S. X. Li, C. Liu, J. L. He, and J. X. Song. 2021a. Liquid zinc assisted electro-extraction of molybdenum. *Separation and Purification Technology* 279, 119651.doi:10.1016/j.seppur.2021.119651

Lv, C., S. L. Li, Y. S. Che, H. T. Chen, Y. C. Shu, J. L. He, and J. X. Song. 2021b. Study on the molybdenum electro-extraction from MoS_2 in the molten salt. *Separation and Purification Technology* 258, 118048.doi:10.1016/j.seppur.2020.118048

Malyshev, V., A. Gab, D. Shakhnin, C. Donath, E. I. Neacsu, A. M. Popescu, and V. Constantin. 2018. Influence of electrolysis parameters on mo and w coatings electrodeposited from tungstate, molybdate and tungstate-molybdate melts(Article). *Revista de Chimie* 69(9), 2411-2415.doi:10.37358/rc.18.9.6544

Moon, J., K. Myhre, H. Andrews, and J. McFarlane. 2022. Potential of electrolytic processes for recovery of molybdenum from molten salts for ^{99}Mo production. *Progress in Nuclear Energy* 152, 104369.doi:10.1016/j.pnucene.2022.104369

Morley, T. J., L. Penner, P. Schaffer, T. J. Ruth, F. Bénard, and E. Asselin. 2012. The deposition of smooth metallic molybdenum from aqueous electrolytes containing molybdate ions. *Electrochemistry Communications* 15(1), 78-80.doi:10.1016/j.elecom.2011.11.026

Nakajima, H., T. Nohira, and R. Hagiwara. 2006. Electrodeposition of metallic molybdenum films in $ZnCl_2$–NaCl–KCl–$MoCl_3$ systems at 250°C. *Electrochimica Acta* 51(18), 3776-3780.doi:10.1016/j.electacta.2005.10.041

O'Dea, J. J., J. Osteryoung, and R. A. Osteryoung. 1981. Theory of square wave voltammetry for kinetic systems. *Analytical Chemistry* 53(4), 695-701.doi:10.1021/ac00227a028

Senderoff, S. and A. Brenner. 1954. The electrolytic preparation of molybdenum from fused salts: Ⅰ. electrolytic studies. *Journal of the Electrochemical Society* 101(1), 16-17.doi:10.1149/1.2781198

Senderoff, S. and G. Mellors. 1967. Electrodeposition of coherent deposits of refractory metals: V. Mechanism for the deposition of molybdenum from a chloride melt. *Journal of the Electrochemical Society* 114(6), 556.doi:https://10.1149/1.2426648

Song, Y., S. Q. Jiao, L. W. Hu, and Z. C. Guo. 2016. The cathodic behavior of Ti(III) ion in a NaCl-2CsCl melt. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science* 47(1), 804-810.doi:10.1007/s11663-015-0521-9

Tian, H. X., Q. J. Gang, Y. Ying, L. Xin, L. T. Jun, and L. ing. 2023. Approaches to electrodeposit molybdenum from ionic liquid. *Rare Metals* 42(7), 2439-2446.doi:10.1007/s12598-018-1040-z

Tylka, M. M., J. L. Willit, and M. A. Williamson. 2017. Electrochemical nucleation and growth of uranium and plutonium from molten salts. *Journal of the Electrochemical Society* 164(8), H5327-H5335.doi:10.1149/2.0471708jes

Yuan, R., C. Lv, H. L. Wan, S. l. Li, Y. s. Che, Y. c. Shu, J. l. He, and J. x. Song. 2021. Electrochemical behavior of vanadium ions in molten LiCl-KCl. *Journal of Electroanalytical Chemistry* 891, 115259.doi:10.1016/j.jelechem.2021.115259

Zhang, H. K., S. L. Li, Z. P. Lv, Y. Fan, and J. X. Song. 2023. The role of zinc sulfide in the electrochemical extraction of molybdenum. *Separation and Purification Technology* 311, 123290.doi:10.1016/j.seppur.2023.123290

Zhang, H., Z. Lv, S. Li, J. He, Y. Fan, and J. Song. 2024. Electrochemical behavior and cathodic nucleation mechanism of molybdenum ions in NaCl-KCl. *Separation and Purification Technology* 329, 125121.doi:10.1016/j.seppur.2023.125121