

The Effect of Electrolyte Composition on the Electrodeposition of Molybdenum from $\text{KF—B}_2\text{O}_3\text{—K}_2\text{MoO}_4$ Melts

II. Voltammetry

^aM. MAKYTA, ^bT. A. UTIGARD, ^aP. ZATKO, ^aA. SILNÝ, and ^aM. CHRENKOVÁ

^a*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava*

^b*University of Toronto, Toronto, Canada M5S 3E4*

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Voltammetric experiments have been carried out to determine the effect of the electrolyte composition on the mechanism of electrodeposition of molybdenum from molten $\text{KF—B}_2\text{O}_3\text{—K}_2\text{MoO}_4$ salts. It was confirmed that during the dissolution of potassium molybdate in molten $\text{KF—B}_2\text{O}_3$ electrolyte both electrochemically active and electrochemically inactive molybdenum-containing species are created. Moreover, at least two electrochemically active molybdenum compounds are present with the first one dominating for $n(\text{Mo})/n(\text{B})$ ratios up to 0.4 and the second one dominating for ratios above 0.66. The electrodeposition of molybdenum metal from the electrochemically active species is a reversible six-electron electrochemical reaction. Results in the above system obtained by the chronopotentiometric method are described in Part I of this series.

The electrodeposition of molybdenum from molten salts may become a suitable method for the formation of compact surface layers of molybdenum on electrical conductive substrates [1, 2]. This method may also be considered for the primary production of molybdenum metal. The analysis of the literature data [1] shows that the process is most successful in electrolytes consisting of a mixture of alkali metal fluoride(s) and boron oxide (or alkali metal borates) to which molybdenum oxide (or alkali metal molybdate) is added [2–7] at temperatures from 800°C to 950°C.

In the first part of this work [1], the influence of the electrolyte composition on the cathode process was investigated using chronopotentiometry. It was found that during the dissolution of K_2MoO_4 in molten $\text{KF—B}_2\text{O}_3$, two types of molybdenum-containing species are created: i) a compound containing electrochemically active molybdenum and ii) a compound containing electrochemically inactive molybdenum. For $n(\text{Mo})/n(\text{B})$ ratios smaller than 0.05 the data from chronopotentiometric measurements [1] could be described by the Sand equation for a simple electrode process controlled by diffusion of the electroactive species to the electrode surface with a diffusion coefficient of $2.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 860°C. This value is slightly higher than the value ($2.00\text{—}2.25 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) obtained by *Li* and *Fan* [8] at 815°C in the melt 72 mole % $\text{KF} + 25$ mole % $\text{B}_2\text{O}_3 + 3$ mole % K_2MoO_4 . For $n(\text{Mo})/n(\text{B})$ ratios larger than 0.05, the molybdate anions form both electrochemi-

cally active and electrochemically inactive molybdenum species. In this case, the electrochemical charge-transfer reaction is preceded by a chemical reaction between the various molybdenum species. In the present work, voltammetry was used to extend the chronopotentiometric investigations reported in [1].

EXPERIMENTAL

The voltammetric experiments were carried out in an electrically resistant tube furnace described previously [1]. The molten salt was held in a platinum crucible (diameter = 32 mm, height = 40 mm) which was also used as the auxiliary electrode. The 1 mm diameter platinum wire working electrode was immersed in the electrolyte by means of a micrometer screw to control the immersion depth. The platinum wire was also used as the reference electrode. All experiments were carried out in argon at 860°C.

Commercially available chemicals of anal. grade were used to prepare the electrolyte. Before use, the chemicals were dried at room temperature in vacuum in the presence of P_2O_5 . During the final purification step, the prepared mixture was dried at 200°C in vacuum for 48 h in the furnace.

A potentiostat HD HAB-151 was used as the source of potential and current—potential curves were recorded by means of a data acquisition system using a DAS-20 AD/DA card.

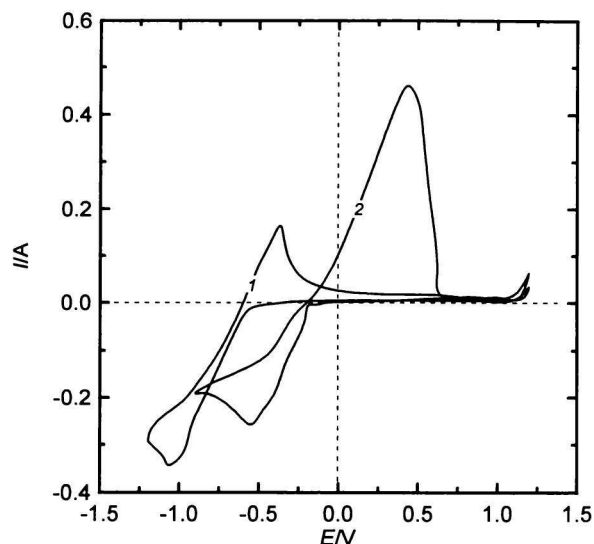


Fig. 1. Voltammetric curve recorded at 860°C. Scan rate 1 V s⁻¹, electrode area 36.5 × 10⁻⁶ m². 1. KF + 3 mole % B₂O₃, 2. KF + 3 mole % B₂O₃ + 1 mole % K₂MoO₄.

RESULTS AND DISCUSSION

The voltammetric experiments in molten KF—B₂O₃—K₂MoO₄ were carried out in three different basic electrolyte systems

- Series 1. 97 mole % KF + 3 mole % B₂O₃
- Series 2. 99 mole % KF + 1 mole % B₂O₃
- Series 3. 96 mole % KF + 4 mole % K₂MoO₄

to which K₂MoO₄ (for the first and second series) and B₂O₃ (for the third one) were added. The K₂MoO₄ mole fraction was varied from 0.125 mole % ($c = 39 \text{ mol m}^{-3}$) to 6 mole % ($c = 2010 \text{ mol m}^{-3}$) and the B₂O₃ mole fraction was varied from 0.5 mole % ($c = 140 \text{ mol m}^{-3}$) to 20 mole % ($c = 5610 \text{ mol m}^{-3}$). The scan rate was varied from 0.1 to 9 V s⁻¹. The accuracy of measurements concerning the determination of the potential and current is ± 4 %.

Fig. 1 (curve 1) shows cyclic voltammetric curve recorded in the electrolyte containing 97 mole % KF and 3 mole % B₂O₃. The rate of polarization of the working electrode was 1 V s⁻¹. During cathodic polarization up to -1.2 V only one reduction process starting at -0.58 V is observed. This reduction process is ascribed to the electrodeposition of boron [1, 9]. Further cathodic polarization (not shown in the figure) leads to a continuous increase of the cathodic current until the electrodeposition potential of potassium is reached at approximately -1.6 V. During polarization reversal, an anodic peak is observed at -0.37 V representing the dissolution of the electrodeposited boron. The anodic peak observed at +1.13 V represents the oxidation of oxide anions [9]. The integration of the cathodic and anodic parts of the cyclic voltammogram

shows that the electrodeposition of boron is an irreversible electrode process. The reversibility increases with increasing scan rate as the ratio of the cathodic to anodic integral varies from 12.3 for a scan rate of 0.1 V s⁻¹ to 2.1 for a scan rate of 9 V s⁻¹.

The addition of potassium molybdate to the KF—B₂O₃ electrolyte brings about changes in the shape of the voltammetric curves (curve 2). Compared to curve 1, a new reduction process is observed starting at -0.18 V creating a cathodic peak at -0.53 V. By carrying out potentiostatic electrolysis in the potential region from -0.18 V to -0.50 V, it was shown that this cathodic peak represents the reduction of Mo(VI) to molybdenum metal. Similarly to the first part of this study [1], the electrodeposition potential of boron was shifted to more negative values by adding K₂MoO₄. The gradual increase of K₂MoO₄ causes the disappearance of this peak, and it is not observed at 1 mole % K₂MoO₄ in the melt (curve 2). At that and higher mole fractions, only the electrodeposition of molybdenum is registered. Similarly, only one anodic peak at a potential +0.43 V is recorded during anodic polarization up to the oxidation potential of O²⁻ ions. A second series of voltammetric measurements was carried out using an electrolyte containing 99 mole % KF and 1 mole % B₂O₃. The character of the voltammetric curves was the same as with 3 mole % B₂O₃.

A common criterion used to determine the reversibility of an electrode process is to compare the ratio of the total cathodic to anodic charge passing through the working electrode. It should be close to unity for a reversible electrode process. For the first series of experiments, this ratio varied from 1.0 to 1.1 for K₂MoO₄ mole fractions from 1 to 6 mole %, in the second and third series of experiments this ratio varied from 1.0 to 1.2. In all the experiments it was found to be independent of the scan rate and it is concluded that the electrodeposition of molybdenum from KF—B₂O₃—K₂MoO₄ is a reversible charge-transfer electrode reaction.

According to *Delahay* [11], the current for a reversible deposition of an insoluble substance under the conditions of a simple charge-transfer electrode reaction controlled by the diffusion of the electrochemically active species to the electrode is described by

$$I = \frac{2(nF)^{3/2}}{\pi^{1/2}(RT)^{1/2}} D^{1/2} A c \nu^{1/2} \varphi[(\sigma t)^{1/2}] \quad (1)$$

where D is the diffusion coefficient (m² s⁻¹), A denotes the electrode surface area (m²), c is the concentration of the electrochemically active component in the electrolyte (mol m⁻³), ν is the scan rate of the working electrode (V s⁻¹), t denotes time (s), and $\varphi[(\sigma t)^{1/2}]$ is a current factor acquiring the value 0.541 for the maximum on the voltammetric curve; the other symbols have their conventional meaning and

$$\sigma = \frac{nF}{RT} \nu \quad (2)$$

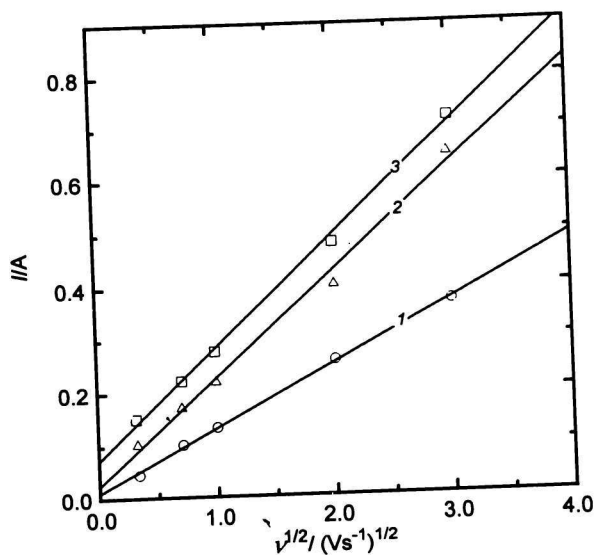


Fig. 2. The peak current (I_p) vs. the square root of the scan rate ($\nu^{1/2}$) in molten KF—B₂O₃—K₂MoO₄ containing 3 mole % B₂O₃, temperature 860 °C, electrode area $36.5 \times 10^{-6} \text{ m}^2$. 1. 0.125 mole % K₂MoO₄, 2. 0.25 mole % K₂MoO₄, 3. 0.5 mole % K₂MoO₄.

By introducing $n = 6$ and $T = 1133 \text{ K}$ in eqn (1), the peak current becomes

$$I_p = 2.771 \times 10^6 \times D^{1/2} A c \nu^{1/2} \quad (3)$$

From eqn (3) it follows that the peak current should increase linearly with the square root of the potential scan rate and the concentration. Fig. 2 shows the peak current (I_p) vs. the square root of the scan rate ($\nu^{1/2}$) measured in the first series of experiments for K₂MoO₄ mole fractions of 0.125 mole %, 0.250 mole %, and 0.5 mole %, respectively. It is seen that eqn (3) is fulfilled only at the lowest mole fraction of K₂MoO₄. At higher contents, including others not shown, the dependence of I_p vs. $\nu^{1/2}$ is linear but does not pass through zero. This is caused, as found by Makyta *et al.* [1], by the fact that the kinetics of the electrode process is influenced by a preceding chemical reaction.

The diffusion coefficient was calculated to be $1.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ based on the results from the electrolyte containing 0.125 mole % K₂MoO₄. This value is lower than the value based on chronopotentiometric measurements ($2.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [1]). This is probably caused by the fact that the experimental conditions do not fulfil the conditions set in eqn (1). This equation was derived by assuming unit activity of the electrodeposited element on the surface of the electrode. The IR drop in the electrolyte also affects the accuracy of the measurements. In the further treatment of the experimental data, the value of the diffusion coefficient as determined by the chronopotentiometric measurements was accepted. This value is considered to be

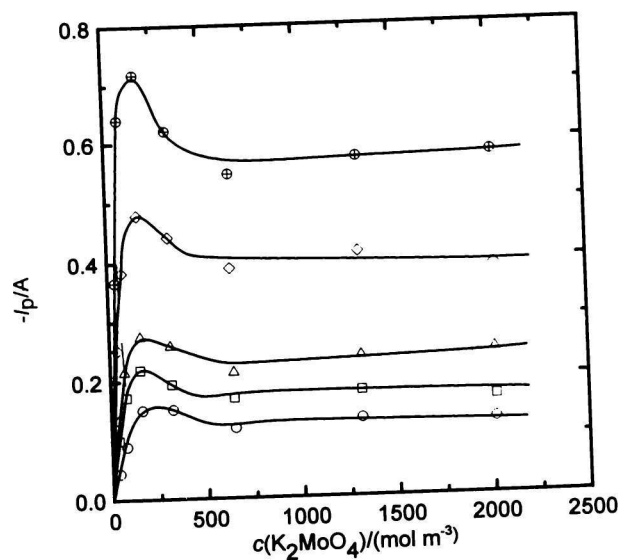


Fig. 3. The peak current (I_p) vs. mole fractions of K₂MoO₄ for various scan rates, 860 °C, electrode area $36.5 \times 10^{-6} \text{ m}^2$, in the KF—1 mole % B₂O₃—K₂MoO₄ melt. ○ 0.1 V s⁻¹, □ 0.5 V s⁻¹, △ 1 V s⁻¹, ◇ 4 V s⁻¹, ⊕ 10 V s⁻¹

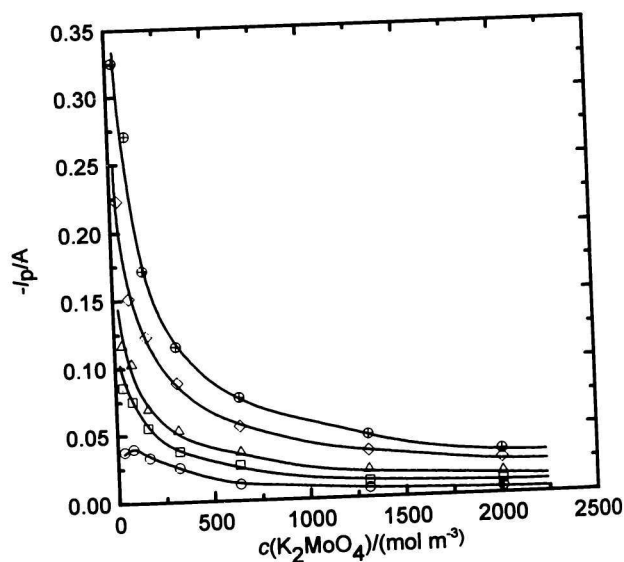


Fig. 4. The peak current (I_p) vs. mole fraction of K₂MoO₄ for various scan rates, 860 °C, electrode area $36.5 \times 10^{-6} \text{ m}^2$, in the KF—3 mole % B₂O₃—K₂MoO₄ melt. ○ 0.1 V s⁻¹, □ 0.5 V s⁻¹, △ 1 V s⁻¹, ◇ 4 V s⁻¹, ⊕ 10 V s⁻¹

more precise as the transition time in chronopotentiometric measurements does not depend on the activity of the electrodeposited element.

As previously mentioned, the peak current, I_p , is proportional to the concentration of electrochemically active species in the electrolyte as expressed by eqn (3). The peak current (I_p) is plotted vs. the concentration (c) for the first and second series of experiments in Figs. 3 and 4, respectively. It is seen that the

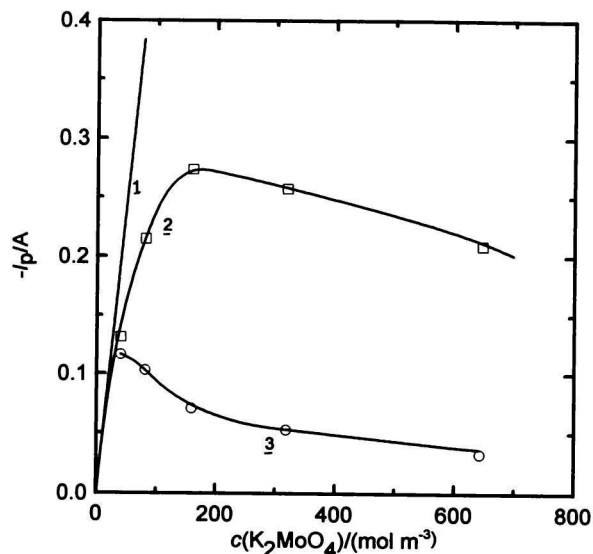


Fig. 5. Comparison of the experimental I_p vs. $c(\text{K}_2\text{MoO}_4)$ dependences with theoretical line calculated according to eqn (3). Scan rate 1 V s^{-1} , temperature 860°C . 1. Theoretical line, 2. KF—3 mole % B_2O_3 — K_2MoO_4 , 3. KF—1 mole % B_2O_3 — K_2MoO_4 .

peak current passes through a maximum with increasing amounts of K_2MoO_4 for electrolytes containing 3 mole % B_2O_3 (Fig. 3). On the contrary, the second series of experiments with 1 mole % B_2O_3 is characterized by a continuous decrease of I_p with increasing concentrations of molybdenum in the melt (Fig. 4).

A comparison of I_p vs. c dependences recorded at a scan rate of 1 V s^{-1} with that calculated according to eqn (3) is shown in Fig. 5. Curve 2, which represents the experimental results of the first series of measurements, merges with the theoretical line as the concentration of potassium molybdate approaches zero. This was observed for all the scan rates employed. Curve 3 of this figure demonstrates that the concentrations of molybdenum used in the second series of measurements were too high to obtain the fit with theoretical line at small concentrations. Voltammetric measurements carried out in the melt with K_2MoO_4 mole fractions less than 0.125 mole % did not provide reproducible results.

Based on these results and according to *Makyta et al.* [1], it is concluded that the dissolution of potassium molybdate proceeds under the creation of two types of molybdenum-containing species. The first one is electrochemically active and it enables the electrodeposition of Mo from the melt. The second type is electrochemically inactive and it is probably identical with molybdenum compound present in molten KF— K_2MoO_4 . The experimental results indicate that the electrochemically active compound is preferentially formed at high surpluses of B_2O_3 . In this case, the equilibrium between the various molybdenum constituents of the melt is shifted in favour of the elec-

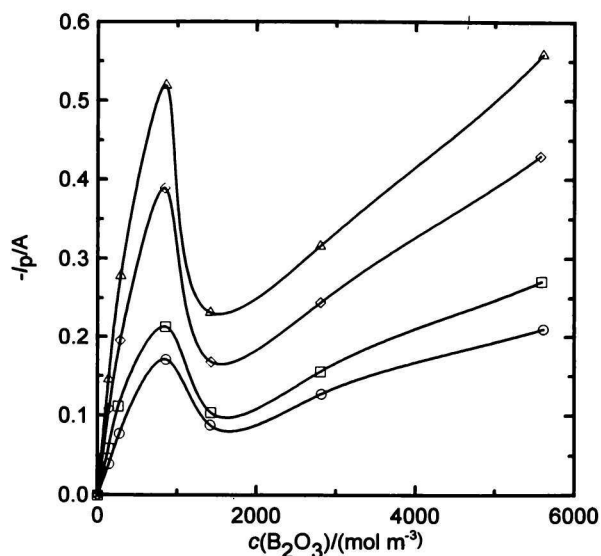


Fig. 6. The peak current (I_p) vs. $c(\text{B}_2\text{O}_3)$ for various scan rates in molten KF— B_2O_3 — K_2MoO_4 containing 4 mole % K_2MoO_4 , temperature 860°C , electrode area $36.5 \times 10^{-6} \text{ m}^2$ \circ 0.1 V s^{-1} , \square 0.5 V s^{-1} , \diamond 1 V s^{-1} , Δ 4 V s^{-1}

trochemically active species. Hence, all the molybdenum is in the electrochemically active form which is demonstrated by the merging of the experimental curve (curve 2) with the theoretical one (curve 1) in Fig. 5. This is also supported by the fact that I_p vs. $\nu^{1/2}$ plot passes through zero (Fig. 2) at a low concentration of K_2MoO_4 . In this case, the experimental conditions fulfil the conditions of a simple electrode process controlled by diffusion. With increasing concentration of molybdenum, both electrochemically active and electrochemically inactive molybdenum species are formed. This situation is characterized by a deviation of the experimental data from the theoretical ones. In the second series of experiments, the mole fraction of B_2O_3 was too small (1 mole %) so that even the smallest addition of potassium molybdate (0.125 mole %) dissolved both active and inactive molybdenum species.

To gain a deeper insight into the electrochemical properties of the KF— B_2O_3 — K_2MoO_4 system, the third series of voltammetric measurements was carried out using KF with 4 mole % K_2MoO_4 . In this series of measurements, B_2O_3 was added to the melt creating the electrochemically active molybdenum compound in the presence of high surpluses of K_2MoO_4 . Fig. 6 shows that for all scan rates, I_p exhibits a maximum at 3 mole % B_2O_3 and a minimum at 5 mole % B_2O_3 . This indicates that depending on the $n(\text{Mo})/n(\text{B})$ ratio, there are at least two electrochemically active molybdenum species in the melt. The first one is dominating at B_2O_3 mole fractions up to 3 mole % and the second one is dominating above 5 mole % B_2O_3 . The medium region between 3 and 5 mole %

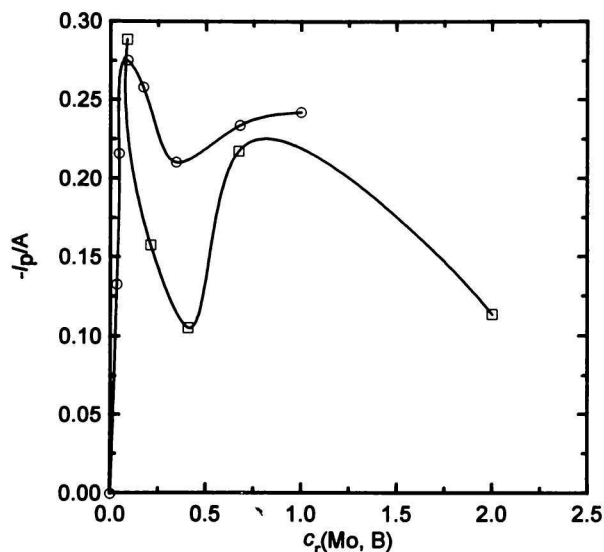


Fig. 7. The peak current (I_p) vs. relative concentration of molybdenum ($n(\text{Mo})/n(\text{B})$) in the electrolyte $\text{KF}-\text{B}_2\text{O}_3-\text{K}_2\text{MoO}_4$, temperature 860°C , electrode area $36.5 \times 10^{-6} \text{ m}^2$, scan rate 1 V s^{-1} ○ First series, □ third series.

B_2O_3 is characterized by a continuous change of the mole fractions of both species.

The peak current decreased with increasing concentration of molybdenum in the melt for all three series of measurements. Fig. 7 shows I_p vs. the $n(\text{Mo})/n(\text{B})$ ratio for the first and third series of measurements. It can be seen that the minimum and maximum values of the curves are approximately at the same $n(\text{Mo})/n(\text{B})$ ratio. It is suggested that the ionic structure of the melt changes in these regions characterized by a steep increase or decrease of the peak current.

CONCLUSION

The voltammetric measurements in the molten $\text{KF}-\text{B}_2\text{O}_3-\text{K}_2\text{MoO}_4$ system are in a good agreement with the results obtained by chronopotentiometry. It

was found that the dissolution of potassium molybdate in the $\text{KF}-\text{B}_2\text{O}_3$ melt creates both electrochemically active and electrochemically inactive species. At least two electrochemically active compounds exist, the first one is dominating in melts with $n(\text{Mo})/n(\text{B})$ ratios up to approximately 0.4 and the second one is dominating above 0.66. The reduction process of $\text{Mo}(\text{VI})$ is a simple six-electron reversible electrochemical reaction which is influenced by a preceding chemical equilibrium reaction between electrochemically active and inactive compounds.

The electrochemical measurements clearly demonstrate the effect of the melt composition on the mechanism of the electrodeposition of molybdenum from the molten $\text{KF}-\text{B}_2\text{O}_3-\text{K}_2\text{MoO}_4$.

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