The Effect of Electrolyte Composition on the Electrodeposition of Molybdenum from KF—B_2O_3—K_2MoO_4 Melts

I. Chronopotentiometry

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Chronopotentiometric experiments have been carried out to determine the effect of the electrolyte composition on the mechanism of electrodeposition of molybdenum from molten KF—B_2O_3—K_2MoO_4 salts. During the dissolution of potassium molybdate in the KF—B_2O_3 electrolyte, two types of molybdenum-containing species, electrochemically active and electrochemically inactive, are created. The electrochemically active molybdenum compound is created by a chemical reaction with boron containing constituents in the melt. Electrochemically inactive molybdenum species are created by the reaction of K_2MoO_4 with fluoride anions. A chemical reaction between these two species was found to precede the one-step charge-transfer reduction of Mo(VI). The diffusion coefficient of the electrochemically active molybdenum compound was determined to be 2.8×10^{-9} m^2 s^{-1}

Electrodeposition from molten salts appears to be a progressive method for the formation of compact metallic surface layers on electrically conductive substrates. This method is especially useful when the coatings cannot be prepared by electrolysis in aqueous solutions, as it is in the case of refractory metals.

Literature review of the electrodeposition of molybdenum shows that several types of molten salts have been tested. On the basis of the electrochemical species used, they can be divided into two main groups: i) systems containing either K_3MoCl_6 [1—5] or K_3MoF_6 [6] dissolved in alkali metal halides, mainly chlorides and fluorides; ii) systems using compounds of molybdenum containing oxides, such as molybdenum oxide, MoO_3 [7—9], alkali metal molybdates [7, 10—13], and $CaMoO_4$ [14]. Supporting electrolytes include: LiCl—KCl [8], sodium and lithium metaborates [7], KF—$Na_2B_4O_7$ [10], KF—$Li_2B_4O_7$ [13], KF—B_2O_3 [11, 15] and $CaCl_2$—CaO [14].

The influence of the temperature, current density, and the electrolyte composition on the character of the electrodeposited product has been studied. It was shown [15] by comparing the results of molybdenum electrodeposition from several types of electrolytes, 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 as the electrochemically active component.

As reported previously [1—13, 15], electrodeposition of smooth, well adherent molybdenum layers from binary MeF—Me_2MoO_4 mixtures is for not quite clear reasons not feasible. However, a small addition (1 mole %) of boron oxide to the electrolyte facilitates the electrodeposition of molybdenum layers. The presence of boron compounds probably modifies the structure of the melt which results in changes to the cathode process.

The mechanism of the cathode process has been extensively studied in chloride-based electrolytes containing either Me_3MoCl_6 [16] or Me_2MoO_4 [8, 15, 17, 18] as electrochemically active species. For pure chloride electrolytes [16] the reduction of Mo(III) proceeds in a single three-electron irreversible step. It was found that the irreversibility of the process decreases with increasing temperature from 600 °C to 750 °C. Chloride melts containing dissolved molybdenum(VI) oxide and alkali metal molybdates have been found unsuitable for electrodeposition of molybdenum because the primary product of the cathodic reaction is molybdenum(III) oxide which is insoluble in the chloride melt.

The mechanism of the electrodeposition process of molybdenum from potassium molybdate dissolved in a KF—B_2O_3 molten mixture has been investigated by *Li* and *Fan* [19]. The authors declared the process to proceed in two consecutive charge-transfer electrode reactions: Mo(VI) → Mo(I) → Mo(0). The diffusion coefficient of Mo(VI) species in the melt was determined to be in the range of 1.99—2.25 $\times 10^{-9}$ m^2 s^{-1}

In the present work, chronopotentiometry was used to determine the effect of the electrolyte composition on the mechanism of the cathode process in the electrodeposition of molybdenum from KF—B_2O_3—K_2MoO_4 melts.

EXPERIMENTAL

The furnace tube which was closed by an air-tight, water-cooled head consists of a sintered corundum tube with an internal molybdenum anticorrosive lining. The molten salt was held in a platinum crucible (diameter = 32 mm, height = 40 mm) which was also used as the auxiliary electrode. The working electrode which was made of a 1 mm diameter platinum wire, 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 the experiments were carried out in argon at a small overpressure and at a temperature of 860 °C.

Commercially available chemicals of anal. grade were used to prepare the electrolyte. Before use, all 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.

A potentiostat HD HAB-151 was used as the source of potential. The observed voltage *vs.* time curves were recorded by means of a data acquisition system using a DAS-20 AD/DA card.

RESULTS AND DISCUSSION

The chronopotentiometric experiments in the KF—B_2O_3—K_2MoO_4 system were carried out with two different compositions of the basic electrolyte, 98.5 mole % KF + 1.5 mole % B_2O_3 and 97 mole % KF + 3 mole % B_2O_3. The K_2MoO_4 content in these two basic electrolytes was varied from 0.05 to 0.4 mole % and from 0.125 to 6.00 mole %, respectively. In order to carry out the electrochemical calculations, the molar concentrations were recalculated to volume concentrations (mol m^{-3}).

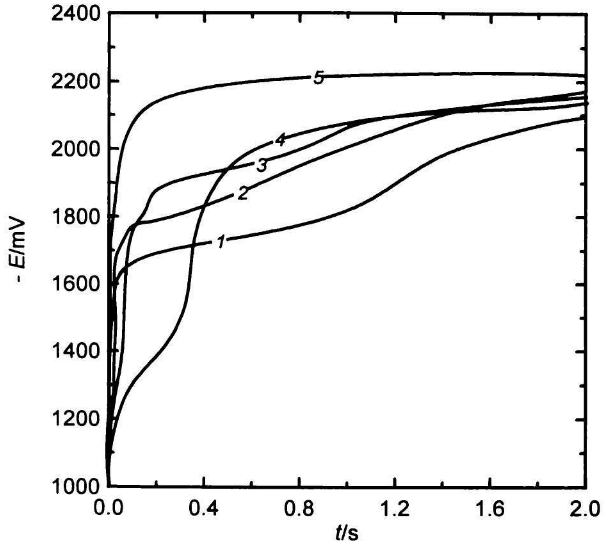

Fig. 1. Chronopotentiometric curves recorded in the system KF—B_2O_3—K_2MoO_4 containing 3 mole % B_2O_3 at different mole fractions of K_2MoO_4 in the melt; current 0.1 A, electrode area 36.5 × 10^{-6} m^2, temperature 860 °C. *1.* 0 mole % K_2MoO_4, *2.* 0.05 mole % K_2MoO_4, *3.* 0.1 mole % K_2MoO_4, *4.* 0.4 mole % K_2MoO_4, *5.* pure KF.

Fig. 1 shows the chronopotentiometric curves recorded in melts containing 1.5 mole % B_2O_3 and different mole fractions of K_2MoO_4. It is observed that there are remarkable changes in the shape of the chronopotentiometric curves brought about by an increase in the concentration of potassium molybdate in the melt. Curve *1* recorded in the basic electrolyte without K_2MoO_4 exhibits only one chronopotentiometric wave indicating an electrode reaction starting at − 1.67 V The second electrode process starting approximately at − 2.03 V does not create a chronopotentiometric wave with a clearly defined transition time. This second electrode process is characterized by a continuous increase of the potential with time until reaching the reduction potential of potassium at approximately −2.19 V These two electrode processes are ascribed to the reduction of B(III) from tetrafluoroborate anions [20] and from oxoborate anions ($B_4O_7^{2-}$ BO_2^-) [21], respectively. It is necessary to point out that there is a dynamic chemical equilibrium between the boron containing species in the melt.

By the addition of 0.05 mole % of K_2MoO_4 to the basic electrolyte (curve *2*), the electrodeposition potential of boron is shifted to −1.76 V and a new chronopotentiometric wave develops at −1.25 V Further additions of potassium molybdate to the electrolyte cause a gradual increase of the transition time of the process starting at −1.25 V and a decrease of the transition time for the electrodeposition of boron. These changes in the shape of chronopotentiometric curves with increasing mole fraction of molybdenum (curve *3*) continue until reaching 0.4 mole % K_2MoO_4 (curve *4*). At this content, the chronopotentiometric wave corresponding to the electrodeposition of boron disappears and only one wave is observed. With a higher content the shape of the curve does not change. However, further increases above 0.4 mole % K_2MoO_4 cause a small drop in the transition time. A chronopotentiometric curve (curve *5*) recorded in the KF—K_2MoO_4 molten system (0.4 mole % K_2MoO_4) with no B_2O_3 is shown in Fig. 1 for comparison purposes. This curve demonstrates that no electrode reaction takes place on the cathode until the electrodeposition potential of potassium is reached at approximately −2.19 V.

The square root of the transition time is drawn

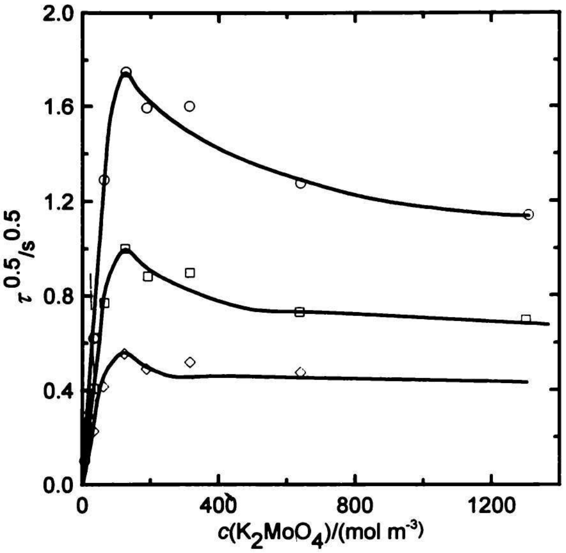

Fig. 2. The dependence $\tau^{1/2} = f(c(K_2MoO_4))$ for various currents recorded in the system $KF—B_2O_3—K_2MoO_4$ containing 1.5 mole % B_2O_3; temperature 860 °C, electrode area 36.5 × 10^{-6} m^2 ○ 0.04 A, □ 0.06 A, ◇ 0.1 A.

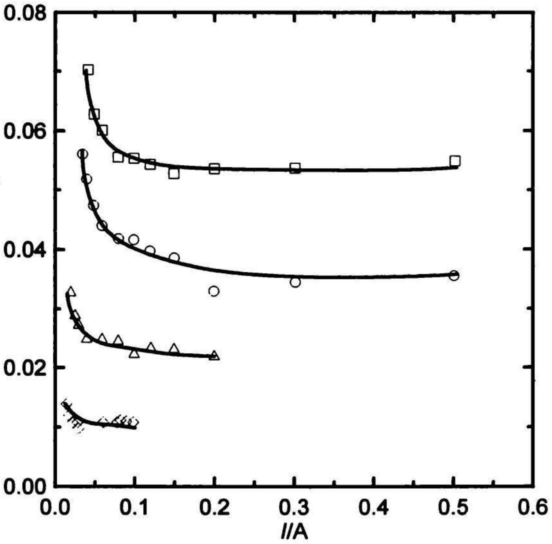

Fig. 3. The dependence $I\tau^{1/2} = f(I)$ for various mole fractions of K_2MoO_4 in the electrolyte. Content B_2O_3 in the melt 1.5 mole %. Temperature 860 °C, electrode area 36.5 × 10^{-6} m^2 ◇ 0.05 mole % K_2MoO_4, △ 0.1 mole % K_2MoO_4, ○ 0.2 mole % K_2MoO_4, □ 0.4 mole % K_2MoO_4.

in Fig. 2 as a function of the K_2MoO_4 concentration at three different currents. Initially, the square root of the transition time increases with increasing K_2MoO_4 concentration before reaching a maximum. Further concentration increases lead to a slight decrease in the transition time.

These results indicate that during the dissolution in the $KF—B_2O_3$ molten mixture, potassium molybdate reacts with some of the structural species present in the melt under the creation of new species. The bonding energy of molybdenum in the molybdenum containing species in the $KF—B_2O_3—K_2MoO_4$ is obviously lower than that in the binary $KF—K_2MoO_4$ system. The decrease in the bonding energy is manifested by the decrease of the electrodeposition potential of molybdenum under the potential of potassium, allowing for the deposition of molybdenum metal from the melt.

Fig. 3 shows a plot of the product $I\tau^{1/2}$ *vs.* the current for different mole fractions of K_2MoO_4 in the electrolyte. This type of plot is frequently used as a diagnostic tool to determine the mechanism of the electrode processes. For a simple charge-transfer reaction, which is governed by the diffusion of the electrochemically active component of the electrolyte to the electrode surface, the product $I\tau^{1/2}$ should be proportional to the bulk concentration of the electrochemically active species and independent of the current. This relation is described by the Sand equation

$$I\tau^{1/2} = \frac{nFAD^{1/2}\pi^{1/2}c}{2} \qquad (1)$$

where τ is the transition time (s), n the number of electrons taking part in the electrode reaction, F the Faraday constant (96487 C mol^{-1}), D the diffusion coefficient ($m^2\ s^{-1}$), c the concentration of the electrochemically active substance (mol m^{-3}), A the surface area of the electrode (m^2), and I is the current (A).

Fig. 3 shows that the product $I\tau^{1/2}$ does not follow this theoretical function derived for simple charge-transfer electrode reactions [1]. The value of $I\tau^{1/2}$ increases with decreasing current in the region below 0.1 A for all the concentrations tested. This type of behaviour may be explained in two ways:

i) The transport of the electrochemically active substance to the electrode surface is not purely a diffusion process but it is also influenced by convection (in our case τ varies from 0.3 to 1 s) in the electrolyte. This situation may occur in chronopotentiometric measurements at low currents due to the long time required to reduce the concentration of the electrochemical species at the electrode surface to zero.

ii) The kinetics of the electrode process is influenced by a preceding chemical reaction [22]. The thermodynamic equilibrium between reducible (electrochemically active) and nonreducible (electrochemically inactive) molybdenum species will be shifted by the electrolysis process. Based on the Le Chatelier principle, the system tries to restore the equilibrium and, consequently, to produce more of the reducible molybdenum species.

The mechanism of the electrode process with preceding chemical reaction has been quantitatively described by *Delahay* and *Berzins* [23, 24] as follows

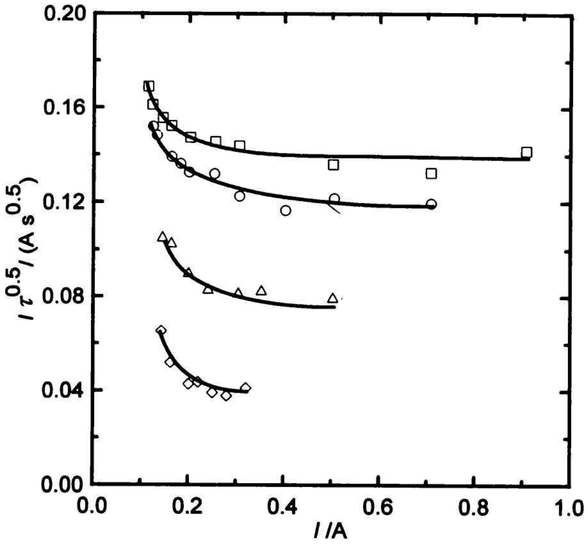

Fig. 4. The dependence $I\tau^{1/2} = f(I)$ for various mole fractions of K_2MoO_4 in the electrolyte containing 3.0 mole % B_2O_3. Temperature 860 °C, electrode area 36.5×10^{-6} m^2 ◇ 0.125 mole % K_2MoO_4, △ 0.25 mole % K_2MoO_4, ○ 0.5 mole % K_2MoO_4, □ 1 mole % K_2MoO_4.

$$I\tau^{1/2} = \frac{nFAD^{1/2}\pi^{1/2}c}{2} - \frac{I(\pi^{1/2}/2)\,\mathrm{erf}\,[(k_\mathrm{f}+k_\mathrm{b})^{1/2}\tau^{1/2}]}{K(k_\mathrm{f}+k_\mathrm{b})^{1/2}} \tag{2}$$

where k_f, k_b are the forward and backward rate constants of the preceding chemical reaction, K is the thermodynamic equilibrium constant, and c is the bulk concentration in the electrolyte. The error function for long transition times τ (at low current densities) approaches unity and $I\tau^{1/2}$ will be no longer independent of the current I. On the other hand, when the value of error function is less than 0.1 (high currents, small τ), eqn (*2*) is reduced to

$$I\tau^{1/2} = (\pi^{1/2}/2)nFAD^{1/2}c\frac{K}{1+K} \tag{3}$$

Eqn (*3*) predicts that at high current densities $I\tau^{1/2}$ should be independent of the current and that it should be proportional to the concentration of the electrochemically active species and to the ratio $K/(1+K)$. For large values of the equilibrium constant K, the ratio $K/(1+K)$ approaches unity and eqn (*3*) becomes the Sand equation. Therefore, for large values of the equilibrium constant it becomes impossible to distinguish the mechanism of an electrode process with a preceding chemical reaction from that of a simple charge-transfer electrode reaction.

In order to reveal whether a preceding chemical reaction influences the mechanism of the cathode process during the electrodeposition of molybdenum, a second series of the chronopotentiometric experiments were carried out. The basic electrolyte was made up of a mixture of KF—3 mole % B_2O_3. By varying the mole fraction of potassium molybdate from 0.125 to 6 mole %, it was found that the changes in the shape of the chronopotentiometric curves with increasing molybdate content were the same as those observed in the first series of experiments with 1.5 mole % B_2O_3 (Fig. 4). At constant current densities, the transition time increased with increasing K_2MoO_4 mole fraction up to 1 mole %. Further additions of molybdenum were accompanied by a slight decrease in the transition time.

In both series of experiments at sufficiently high potassium molybdate contents in the melt, only one wave was observed on the chronopotentiometric curves. This took place for K_2MoO_4 mole fractions above 0.4 mole % in the melt containing 1.5 mole % B_2O_3 and above 1 mole % in the melt containing 3 mole % B_2O_3. This observation together with previous results [15] indicates that the charge transfer in the electrodeposition of molybdenum from KF—B_2O_3—K_2MoO_4 melts proceeds in one six-electron step.

The results of the chronopotentiometric measurements in the melt containing 3 mole % B_2O_3 are summarized in Fig. 4 where the product $I\tau^{1/2}$ is plotted *vs.* the current for various mole fractions of potassium molybdate. Similarly to the first series of experiments with 1.5 mole % B_2O_3, the product $I\tau^{1/2}$ also exhibits a dependence on the current. The product $I\tau^{1/2}$ is constant for currents above approximately 0.2 A while it increases with decreasing currents below this value. This corresponds to a transition time of 0.1 s for the electrolyte containing 0.125 mole % K_2MoO_4 and 0.2 s for the electrolyte containing 0.25 mole % K_2MoO_4. These transition times are fairly high and it may be suggested that under the given experimental conditions they are already influenced by convection of the electrolyte.

To compare the results of the two series of experiments, a relative concentration of molybdenum in the electrolyte is defined.

$$c_\mathrm{r}(\mathrm{Mo,B}) = (\text{mole fraction of } K_2MoO_4)/ /(2 \times \text{mole fraction of } B_2O_3)$$

Based on the experimental data shown in Figs. 3 and 4, the value of product $I\tau^{1/2}$ from the region, where $I\tau^{1/2}$ is independent of the current, is plotted in Fig. 5 as a function of the relative concentration of molybdenum in the electrolyte $c_\mathrm{r}(\mathrm{Mo,B})$. It is observed that for both B_2O_3 mole fractions 1.5 and 3.0 mole %, the product $I\tau^{1/2}$ passes through a maximum at approximately the same relative concentration (0.15—0.16). Further increases of $c_\mathrm{r}(\mathrm{Mo,B})$ lead to a slight decrease in the value of the product $I\tau^{1/2}$ These results indicate that the dissolution of potassium molybdate in the molten KF—B_2O_3 mixture is accompanied by a

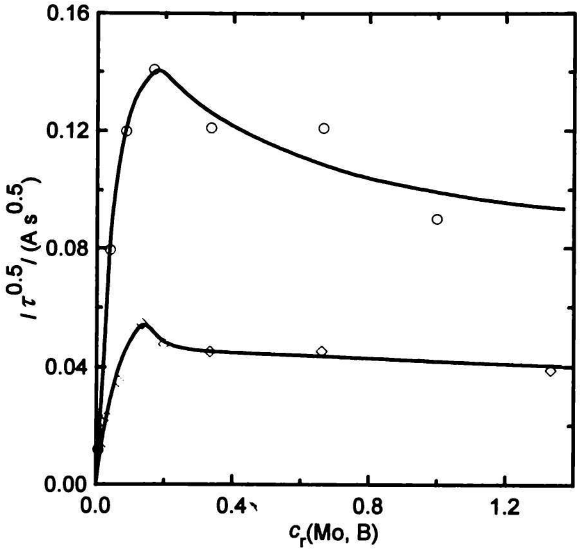

Fig. 5. The dependence of $I\tau^{1/2}$ *vs.* relative concentration of molybdenum in the electrolyte for melts with different mole fractions of B_2O_3. Temperature 860 °C, electrode area 36.5×10^{-6} m^2 ◇ 1.5 mole % B_2O_3, ○ 3.0 mole % B_2O_3.

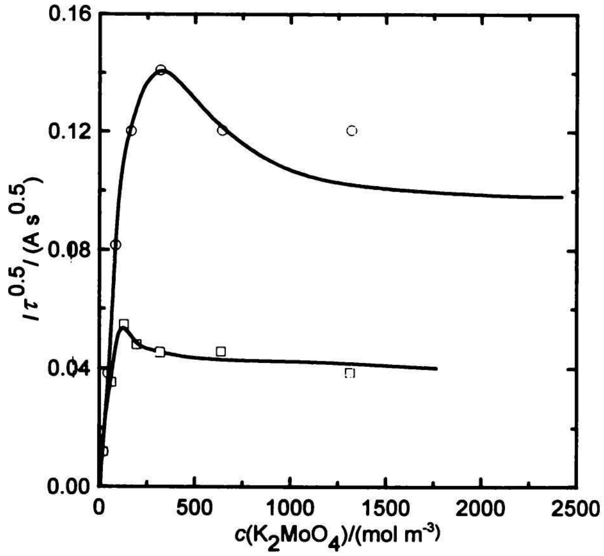

Fig. 6. The dependence of $I\tau^{1/2}$ *vs.* concentration of K_2MoO_4 in the electrolyte for melts containing 1.5 (□) and 3.0 (○) mole % B_2O_3. Temperature 860 °C, electrode area 36.5×10^{-6} m^2

chemical reaction with boron containing constituents ($B_4O_7^{2-}$, BO_2^-, BF_4^-) and fluoride ions (F^-). The chemical reactions with boron containing constituents create new species containing electrochemically active molybdenum. *Rawson* [25] described the multi-atom polyanions present in the melt of MoO_3-based glasses. These ions consist of MoO_6 groups and contain boron as a central atom. An investigation on the structure and physicochemical properties of the KF—B_2O_3—K_2MoO_4 melt [26, 27] is supporting this idea. On the other hand, the reaction of potassium molybdate with fluoride anions gives species containing electrochemically inactive molybdenum. These species are probably identical with those present in the molten KF—B_2O_3 mixture. When all the boron used to create electrochemically active molybdenum species is consumed, the further dissolution of molybdate anions proceeds to the form of electrochemically inactive molybdenum species only. The chemical equilibria between the various species in the melt are most probably those which precede the charge-transfer electrode reaction.

Fig. 5 shows that the product $I\tau^{1/2}$ increases linearly with increasing relative concentration of molybdenum up to approximately 0.05. Over this value the deviation from linearity is observed in both series of experiments. This indicates that for relative molybdenum concentrations between 0 and 0.05, the product $I\tau^{1/2}$ is proportional to the concentration of molybdenum in both melts. Moreover, it is assumed that for large surpluses of B_2O_3 over K_2MoO_4 in the melt, the chemical equilibrium is shifted in favour of the electrochemically active molybdenum species. In this case, nearly all the molybdenum present in the melt is in the electrochemically active form and its concentration is equal to that of K_2MoO_4 in the electrolyte.

According to the above discussion, the experiments carried out with a relative molybdenum concentration less or equal to 0.05 fulfil the conditions of validity of the Sand equation [1]. In Fig. 6 the product $I\tau^{1/2}$ is plotted as a function of the absolute concentration of potassium molybdate in the melt for mole fractions of B_2O_3 equal to 1.5 and 3.0 mole %, respectively. It is seen that when the concentration of molybdenum in the melt approaches zero, the two curves merge into a single line. This confirms that in both melts with different content of boron oxide, the same amount of electrochemically active molybdenum species is created during the dissolution of K_2MoO_4 in the basic KF—B_2O_3 melt. Based on a regression analysis of the data obtained at the two lowest K_2MoO_4 concentrations for the two melts and forcing the line to pass through zero, the diffusion coefficient of the electrochemically active molybdenum species was calculated to be 2.8×10^{-9} m^2 s^{-1} This value is in a good agreement with the value determined by *Li* and *Fan* [19].

The above discussion shows that in the region of relative concentration of molybdenum up to 0.05, the kinetics of the cathode process is not affected by the preceding chemical reaction. In this region, the ratio of $n(B_2O_3)/n(K_2MoO_4)$ is larger than 10. In the region where the ratio $n(B_2O_3)/n(K_2MoO_4)$ varies from 10 to 2.5, the molybdate anion dissolves and forms both electrochemically active and electrochemically inactive species. Further additions of K_2MoO_4 to the melt lead to the creation of only inactive molybdenum compounds. In this concentration region, boron compounds serve as transformers of electrochemically inactive molybdenum compounds to electrochemically active form.

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