# ELECTROCHEMICAL REDUCTION OF MOLYBDENUM FROM $KF-B_2O_3-K_2MoO_4$ MOLTEN SALT SYSTEM①

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## ABSTRACT

The mechanism of electroreduction of molybdenum in molten $KF-B_2O_3-K_2MoO_4$ has been studied by means of linear sweep voltammetry, cyclic voltammetry and chronopotentiometry.

**Key words**: molybdenum, electrochemical reduction, $KF-B_2O_3-K_2MoO_4$ melt

## 1 INTRODUCTION

Several papers have been published concerning the electrodeposition of molybdenum from molten salts and coherent molybdenum coating has been obtained in following molten mixtures: chloride salts[1]; fluoride salts[2-5]; oxide salts[6-8]; fluoride oxide salts[9-12] and chloride oxide salts[13-17]. It was shown that the best coating was obtained in molten $KF-B_2O_3-K_2MoO_4$ which has a wider range of operating current density.

A number of works on the technology of molybdenum coating have been published, the mechanism of electroreduction of molybdenum from molten salts has seldom been studied. Senderoff *et al.* studied the electrochemical behavior of molybdenum in molten $KCl-LiCl-K_2MoCl_6$[18] and $KF-LiF-NaF-MoF_6$[19] by chronopotentiometry. They found that the molybdenum ion existing in above mentioned systems is trivalent. The electroreduction is as follows

$$[Mo_2Cl_9]^{3-}+3Cl^- = 2[MoCl_6]^{3-}$$

$$[MoCl_6]^{3-}+3e^- = Mo^o+6Cl^-$$

The reaction is reversible at 800℃ but in fluoride systems it is irreversible at the temperature of 600–800℃. Inman *et al.*[20] studied the mechanism of electroreduction process of Mo in KCl–NaCl melt at 760℃ and found a chemical reaction preceding the charge transfer:

$$Mo^{6+}\ (complex) = 2Mo^{3+}$$

$$Mo^{3+}+3e^- = Mo^o$$

In this study, we aim to reveal the mechanism of electroreduction of molybdenum in molten $KF-B_2O_3-K_2MoO_4$

## 2 EXPERIMENTAL

The experiments were carried out with molten $KF-B_2O_3-K_2MoO_4$ (72–25–3mol%) in a graphite crucible placed in a fully sealed stainless steel can which was heated up to 815 ± 2℃ in a furnace[21]. The measurements were made at a flowing argon atmosphere. The working and reference electrodes were a 1mm diameter platinum and molybdenum wire

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respectively. The graphite crucible was also used as the auxiliary electrode.

All chemicals used were A. R. grade. KF was prepared by dehytrating $KF \cdot 2H_2O$, which was first heated and dehytrated slowly at 80℃ and then dried in vacuum at 200℃ for 20h. $K_2MoO_4$was produced with $MoO_3$. For this purpose, $MoO_3$was dissolved in a KOH solution and the product of the reaction was then washed and dried in vacuum at 200℃, The X-ray diffration analysis showed that the product was pure $K_2MoO_4$.

The prepared, $K_2MoO_4$, $B_2O_3$ and KF powders were mixed and then placed in a graphite crucible and dried in situ at 250℃ for 10h and at 500℃ for 2h in vacuum. Later, we filled the can with pure argon at a slight flow rate and heated the mixture to experimental temperature.

## 3 RESULTS AND DISCUSSION

### 3.1 *Linear Sweep Voltammetry and Cyclic Voltammetry*

The results of linear sweep voltamogram and cyclic voltamogram of the molten KF-$B_2O_3$-$K_2MoO_4$($C_{Mo}=8.33\times10^{-4}$mol/cm$^3$) at 815℃ on the platinum working electrode are shown in Fig.1 and some parameters are

**Table.1 The parameters of linear sweep voltamogram**

| $V$ | $E_{pc}$ | $E_p/2$ | $i_{pc}$ | $i_{pc}/V^{1/2}$ |
|---|---|---|---|---|
| mV/s | mV | mV | A/cm$^2$ | |
| 147 | −255 | −89 | 1.74 | 0.14 |
| 200 | −250 | −93 | 1.93 | 0.14 |
| 250 | −250 | −95 | 2.14 | 0.14 |
| 300 | −250 | −99 | 2.32 | 0.14 |
| 350 | −250 | −100 | 2.48 | 0.13 |
| 400 | −245 | −120 | 2.62 | 0.13 |

$V$: potential sweep rate; $E_{pc}$ and $E_{p/2}$: peak and half peak potentials; $i_{pc}$: peak current density; $i_{pc}/V^{1/2}$: current function.

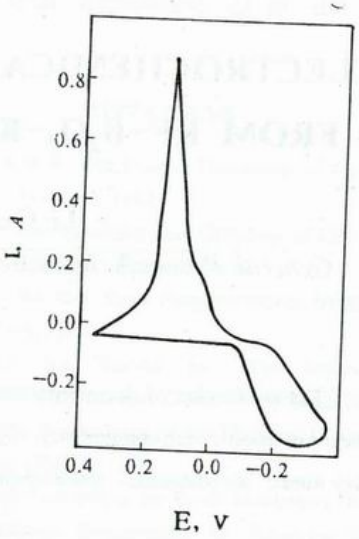


**Fig.1 Typical voltamogram in KF-$B_2O_3$-$K_2MoO_4$ molten salt**

working electrode: Pt, reference electrode: Mo, 815℃ $C_{Mo}=8.33\times10^{-4}$mol/cm$^3$, $A=0.154$cm$^2$, $v=200$mV/s

listed in Table.1. From Fig.1 it can be seen that there is a cathodic wave at the potentical of −0.25 V (vs. Mo reference electrode) which responded to an anodic wave $i_{pa}$ at a potential of 0.16 V and peak current $i_{pa}>i_{pc}$, indicating that the product of the electrochemical reaction is insoluble. An electrodeposition of molybdenum from this melt was carried out at a constant potential (−0.2V) on the platinum strip. A layer of metallic coating which was examined to the molybdenum was obtained by X-ray diffraction. In the experiments we also found that the molybdenum reference electrode immersed in molten electrolyte did not have any erosion caused by the disproportion between metallic molybdenum and its high valent ion $Mo^{6+}$. This phenomenon indicates that there are almost no low valent molybdenum ions in the melt. Therefore, the current efficiency of molybdenum reduction may be approximately suggested as 100%, so the number of total electrons discharged on the

cathode can be calculated as 6 by the increment of the cathode (Pt strip). This fact, on the other hand, shows that the hexavalent molybdenum ion is the only form presented in the melt. A similar result (current efficiency of 95–96%) was obtained by Koyama *et al.*[11] in their technological experiments of molybdenum electroplating using this melt. From the above discussion, we can see that the electroreduction of molybdenum seems to be a single process of discharge of hexavalent molybdenum ions. However, the convolutive treatment[22] reveals that the relationship between $\ln(I_{cl}-I_{c(t)})/I_{c(t)}$ and $E$ deviates from a straight line (see Fig.2) and is close to two lines intercepted at the potential of about −100mV. This indicates that the reduction of $Mo^{6+}$ is not a single electroreduction. From the slope of the line ranging from −0.05V to −0.1V, the electron number(n) can be calculated as 5.2 (5). It follows that the electroreduction of molybdenum in the present melt may be proposed as a stepwise reduction, such as

$$Mo^{6+}+5e^- = Mo^+$$
$$Mo^+ + e^- = Mo^\circ$$

For further analysis, a small amplitude cyclic voltamograms was employed in the present study. Fig.3 shows the cyclic voltamogram under the condition of small changes of cathodic potential. It is clear that there are two electroreduction processes. The first reaction occurs at the cathodic potential of about −45mV and the corresponding anodic peak is at the potential about −100mV. By increasing cathodic polarization, the second anodic wave appears at a potential of about 40mV (see Fig.3–c), but the cathodic wave of the second reaction is superposed on the first wave. This means that the reduction potentials of both reactions are very close. With increasing amplitude of sweep potential, the first and second anodic waves should tend towards superposition (see Fig.3–d) and the cyclic voltamogram will take the form of Fig.1. Thus the stepwise reactions which occurred during the electroreduction of $Mo^{6+}$ were confirmed again by the small amplitude cyclic voltammetry.

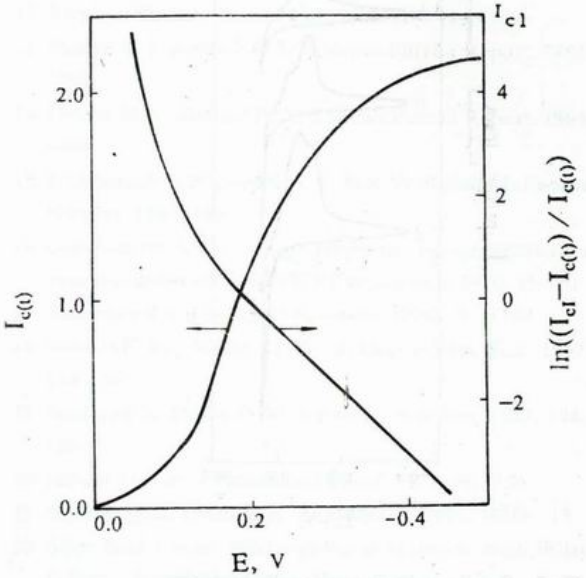


**Fig.2 Variation of $I_{c(t)}$ and $\ln(I_{cl}-I_{c(t)})/I_{c(t)}$ with E in convolutive treatment**

$I_{c(t)}$—convolutive transform current;

$I_{cl}$—convolutive transform limiting current[22]

Concerning the reversibility of the reactions, as has been shown in Fig.1 and Table 1, the peak potentials of cathodic wave representing the second reaction, and the current funtions $i_{pc}/V^{1/2}$ are independent of the potential sweep rate. Therefore, the second reaction can be considered to be reversible. As regards to the first step, it seems to be less reversible because of little change of $E_{p/2}$ towards the negative direction. So it may be defined as a quasi-reversible reaction.

Based on the equation(1) deduced from convolutive treatment, the diffusion coefficient of hexavalent molybdenum ion $D$ can

be determined as $1.99\times10^{-5}cm^2/s$.

$$I_{cl}=nFD^{1/2}C^{o} \quad (1)$$

where $I_{cl}=2.15$ (from Fig.2); $C^{o}$ is the concentration of molybdenum ion in the melt ($8.33\times10^{-4}mol/cm^3$)

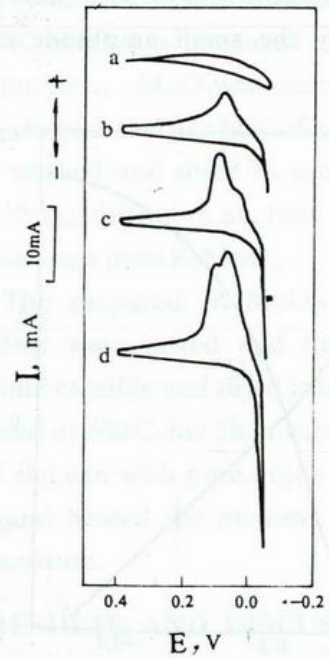


**Fig.3 Small amplitude cyclic voltammogram**

### 3.2 *Chronopotentiometry*

This experiment was carried out at the current density of $1.96-3.00A/cm^2$. The typical chronopotentiograms are shown in Figs.4 and 5 and the data obtained from Fig.4 are summarized in Table 2.

**Table 2 Results of chronopotentiometry**

| | | | | | |
|---|---|---|---|---|---|
| $i$, $A/cm^2$ | 1.96 | 2.22 | 2.31 | 2.64 | 3.00 |
| $\tau$, s | 1.15 | 0.84 | 0.77 | 0.56 | 0.44 |
| $i\tau^{1/2}$ | 2.08 | 2.04 | 2.03 | 1.98 | 1.99 |
| $D$, $\times10^{-5}$ $cm^2/s$ | 2.37 | 2.28 | 2.26 | 2.15 | 2.17 |

mean value $\overline{D}=2.25\times10^{-5}cm^2/s$

From Fig.4 and Table 2 it is clear that the values $i\tau^{1/2}$ for different experiments have a little change. Fig.5 demonstrates that the transition times of cathodic and anodic processes are equal: $\tau_c=\tau_a$, indicating insolubility of the reaction product; and there is a difference in step potentials of both processes. All these facts may be attributed to some irreversibility of the first reaction step.

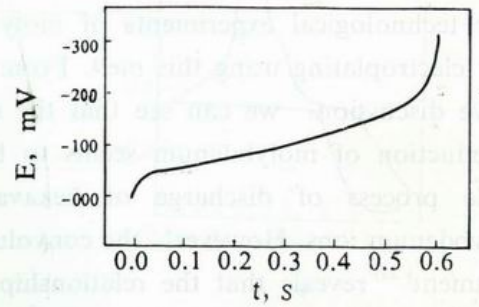


**Fig.4 Cathodic chronopotentiogram for $KF-B_2O_3-K_2MoO_4$ 815℃**
($C^{o}=8.33\times10^{-4}mol/cm^3$, I=406mA, A=0.154$cm^2$)

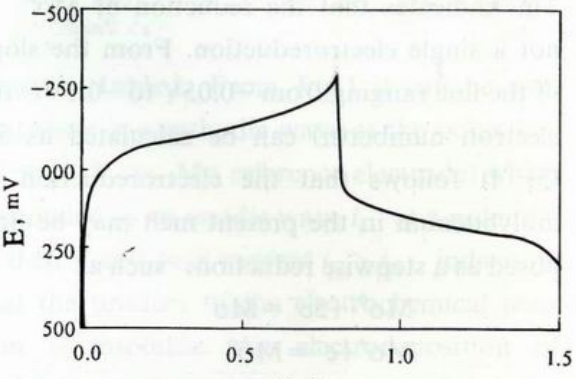


**Fig.5 Cathodic-anodic chronopotentiogram in $KF-B_2O_3-K_2MoO_4$ Pt, 815℃**
A=0.154$cm^2$, $i_c=i_a=311mA$, $C=8.33\times10^{-4}$ mol/$cm^3$, cathodic on the left, anodic on the right.

As has been proved, for a consecutive charge transfer reaction $O\overset{n_1e^-}{\rightleftharpoons}O_1\overset{n_2e^-}{\rightleftharpoons}R$, if the standard potentials of both stepwise reaction are close enough, only one wave can be observed on the chronopotentiogram. In this case, the Sand equation can be expressed as follows[23]

$$i\tau^{1/2}=(n_1+n_2)F\pi^{1/2}D^{1/2}C^{o}/2 \quad (2)$$

In our study, $n_1+n_2=6$. Using equation (2) and data listed in Table 2, the diffusion

coefficients of $Mo^{6+}$ $D$ for various conditions of experiments can be calculated and are shown in Table 2. The mean value is $2.25\times10^{-5}cm^2/s$ which is in accordance with the data obtained in cyclic voltammetry. Thus, the diffusion coefficient of $Mo^{6+}$ determined in this experiment can be regarded as more reasonble.

## 4 CONCLUSION

1 Molybdenum ions which exist in molten $KF-B_2O_3-K_2MoO_4$ containing metallic Mo are still in hexavalent state.

2 The electroreduction of molybdenum in this melt at 815℃ has been found to be a consecutive charge transfer reaction

$$Mo^{6+}+5e^-=Mo^+ \quad \text{(quasi-reversible)}$$

$$Mo^++e^-=Mo^o \quad \text{(reversible)}$$

3 The diffusion coefficient of $Mo^{6+}$ has been determined to be $1.99—2.25\times10^{-5}cm^2/s$ by different methods.

### REFERENCES


1 Senderoff S, Brenner A. J Electrochem Soc. 1954, 101: 16

2 Senderoff S. Met Rev. 1966, 11: 97

3 Mellors G W, Senderoff S. U S Pat. 688546

4 Suri A K, Bose D K. Met Trans. 1974, 5: 451

5 Suri A K, Grupt C K. Met Trans. 1975, 6: 453

6 McCawley F X, Wycle C. J Electrochem Soc. 1969, 166: 1208

7 Барабошкин А Н физическая химия и злектрохимия расплавленных солей и твердых злектролитов. 1979, 2: 3

8 Барабошкин А Н. и др. Зашита металлов. 1981, 17: 371

9 Merganlt P. Compt Rend. 1955, 241: 1755.

10 Koyama K *et al.* Trans J I M. 1984, 25: 265

11 Koyama K *et al.* Trans J I M. 1984, 25: 804.

12 Koyama K *et al.* Trans J I M. 1985, 26: 198.

13 Heinen H J, Zadra J B. U S Mines Bureau Report. 1961, 5797

14 Heinen H J, Zadra J B. U S Mines Bureau Report. 1964, 6444

15 Khlebnikov I, Nadolskii A P. Met Volframa Molibdena Niobiya. 1967, 163

16 Барабошкн А Н, и др. Научные труды института злектрохимии уф АН СССР Сверлловск. 1970, 15: 51

17 Шадобая В Л и др. злектрохимия. 1976, 12: 1723

18 Senderoff S, Meller G W. J Electrochem Soc. 1967, 114: 56

19 Senderoff S, Meller G W. J Electrochem Soc. 1967, 144: 586

20 Inmam D *et al.* J Electroanal Chem. 1971, 29: 134

21 Ye Shangyun, Li Guoxun. Rare Metals. 1991, 10(1): 15

22 Allen Bard J *et al.* Electrochemical Methods. John Wiley & Sons, Inc. 1980, 237

23 Tin Shaowu. Electrochemical Methods. Beijing: Science Press, 1984, 164