Electrochemical Behaviour of Mo Ions in Alkali Halide Electrolytes

CRISTINA DONATH, NICULAE ENE*, ELENA NEACSU
Romanian Academy – Institute of Physical Chemistry “Ilie Murgulescu”, 202 Spl. Independentei, 060021, Bucharest, Romania

The electrochemical properties of solution of molybdenum ions in molten alkali halide electrolytes were studied at 1023-1123 K. The chemical and electrochemical stability of solutions is an important parameter, which must be controlled to ensure reproducible electrochemical measurements. Polarization and voltammetric curves at tungsten electrode revealed the existence of a reversible electrochemical process between the species Mo(III) and Mo(0) with a standard potential equal to 812 mV vs. Ag/AgCl reference electrode. The reduction process Mo(III) to Mo(0) appears as a single reversible three-electron exchange couple with significant crystallization problems.

Keywords: molten salts, electrochemistry, molybdenum

The work presented is part of a research project focused on the electrochemistry and electrochemical properties of Mo in molten salts [1-7].

The purpose of this investigation was to determine the electrochemical behaviour of Mo ions in the molten eutectic NaCl-KCl-NaF mixtures at different temperatures and different concentrations on molybdenum ions. Nickel and stainless steel wires and cathodes were used. In order to study the reaction mechanism and to determine the standard reduction potential, the diffusion coefficient and the activity coefficient, cyclic voltammetry was used.

Experimental part

Preparation and purification on the melt

The electrolytic bath consists of a NaCl-KCl-NaF (Merck) eutectic mixture (60.5-22.5-17 molar percent) [8]; all are of advanced purity so that no previous purification was needed.

The alkali halide (analytical grade) was initially dehydrated by vacuum heating. Then the eutectic mixture was melted in a stainless crucible placed in a stainless cell under argon atmosphere. The bath temperature was measured with a calibrated K type thermocouple (precision ± 5 ^{0}C) sheathed in a stainless steel tube, immersed in the electrolyte.

Electrochemical apparatus and electrodes

The electrochemical study was performed in a classical three-electrode cell [9-11]. Cyclic voltammetry was performed with a Tacussel PRT 20-10X potentiostat controlled with the corresponding software package or signal generator E 0507. The Linseis (X,Y, t) LY 1600 recorder was used to register the linear and cyclic voltammograms.

As reference electrode Ag/AgCl was used, which was constituted by a Ag wire (1 mm dia-meter) dipped into a alumina tube containing a solution of AgCl in NaCl-NaF-KCl. Tungsten wire (1 mm diameter) was used as working electrode and graphite (5 mm diameter) was used as counter electrodes. Mo(III) complex chloride compound solution in NaCl-NaF-KCl melt was prepared by direct addition of weighed amount of solid K_3MoCl_6.

Results and discussions

The study of the voltammetric curves recorded with a solution of Mo(III) for potential sweep rates ranging from 0.05 to 1.0 V s^{-1} at 1023 K (fig. 1) shown the linear dependence of the cathodic peak current, I_C, and the anodic peak current, I_A, and the square root of the sweep rate is observed in figure 2.

The peak potentials values do not change with the increase of the scan rate for the values up to 1.0 V s^{-1} (fig. 3), behaviour expected for a diffusion-controlled process. Another reversibility test was performed by obtaining the convolute curves of the voltammograms recorded at different potential scan rate. The fact the convoluted curves are practically identical and independent of the sweep rate, and that the back and forward scans are practically coincident, indicate the reversibility of the reaction Mo(III)/ Mo(0). From all these criteria it can be concluded that the

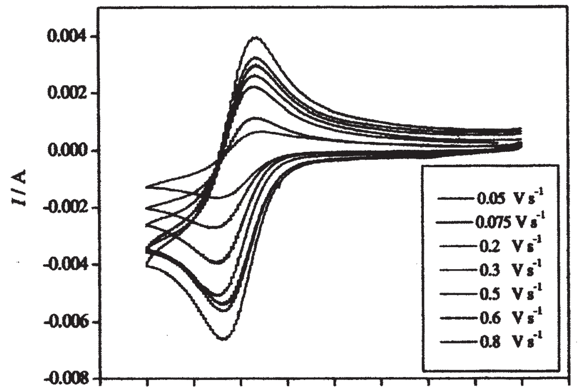

Fig. 1. Cyclic voltammetry for the reduction of K_3MoCl_6 (2·10^{-4} mol/cm^3) on a W electrode (82·10^{-3}cm^2) in the eutectic NaCl-KCl-NaF melt at 1023 K. Sweep rate: is shown in figure

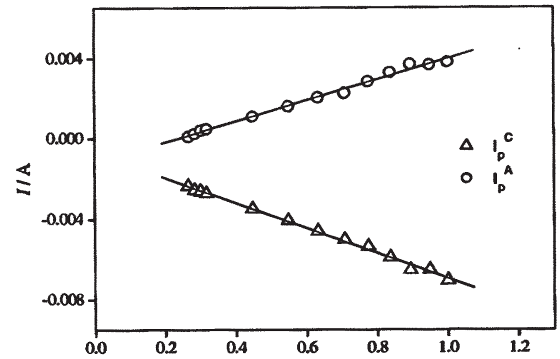

Fig. 2. Variation of cathodic and anodic peak current for the reduction of K_3MoCl_6 (2·10^{-4} mol/cm^3) as a function of the potential scan rate, on a W electrode (82·10^{-3} cm^2) in the eutectic NaCl-KCl-NaF melt at 1023 K

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* email: nene@chimfiz.icf.ro

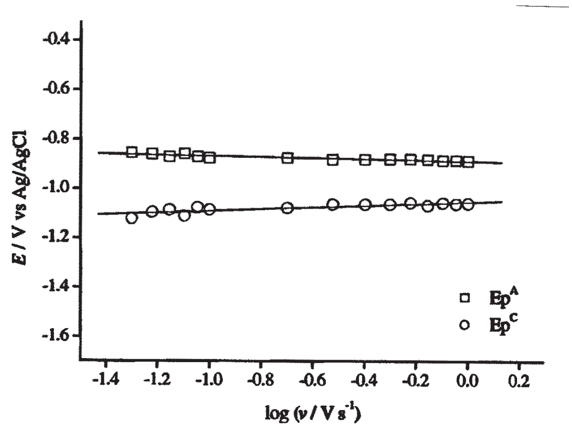

Fig. 3. Variation of cathodic and anodic peak potential for the reduction of K_3MoCl_6 ($2\cdot10^{-4}$ mol/cm^3) as a function of the potential scan rate, on a W electrode ($82\cdot10^{-3}$cm^2) in eutectic NaCl-KCl-NaF melt at 1023 K

reduction reaction Mo(III)/Mo(0) on W electrode is a reversible process controlled by a diffusion of the electroactive species to electrode.

For a reversible change transfer, the convoluted curves should obey the following equation [12-13]:

$$E = E_{1/2} + 2.303\frac{RT}{nF}\log\frac{(m^* - m)}{m}$$

$$\text{where: } E_{1/2} = 2.303\frac{RT}{nF}\log\left(\frac{D_R}{D_O}\right) \qquad (1)$$

and, m is the semi-integral of the current density (A), m^* the cathodic limiting value of these functions (A), E^0 is the standard potential of Mo(III)/Mo(0) system, $E_{1/2}$ the half-wave potential (V), D_R and D_O the reduction and oxidation diffusion coefficients (cm^2 s^{-1}), respectively.

The logarithmic analysis of a convoluted curve corresponding to a solution of Mo(III) at a sweep rate at of 0.2 V s^{-1}, according to this model, is given in figure 4, in which it is observed that the electrode potential varies linearly with log[m* - m / m]The standard potential of the redox couple Mo(III)/Mo(0) was obtained using the linear least square analysis of the linear part of the data. If we assume that $D_R \approx D_o$ (1) can be writen as:

$$E = E^o + 2.303\frac{RT}{nF}\log\frac{(m^* - m)}{m} \qquad (2)$$

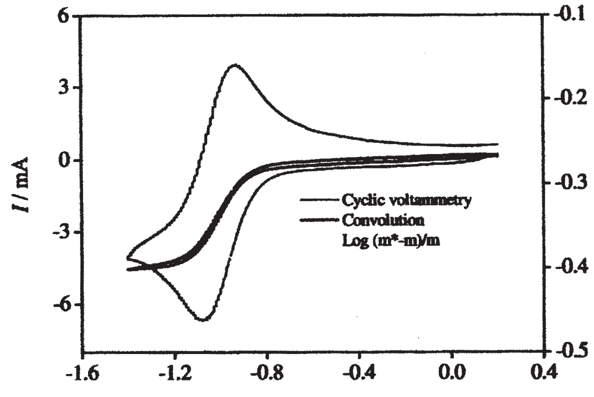

Fig. 4. Cyclic voltammograms for the reduction of K_3MoCl_6 ($2\cdot10^{-4}$ mol/cm^3) on a W electrode ($82\cdot10^{-3}$cm^2), its corresponding convoluted curve (heavy lines) and the logarithmic analysis of this convolutes date (—) following a reversible model in the eutectic NaCl-KCl-NaF melt at 1023 K, sweep rate = 0.2 V s^{-1}

The slope of the linear part of this curve is 0.022, which is very close to the value expected for a reversible exchange process of three electrons (0.0239).

The standard potential of the Mo(III)/Mo(0) system was determined from the data of the anodic and cathodic peak potential measurement in the cyclic voltammograms at different potential scan rates, according to the following equations [14-15]:

$$E^0 = \frac{E_p^a + E_p^c}{2} \qquad (3)$$

$$E_{1/2} = E_p + 1.109\frac{RT}{nF} \approx E^0 + 2.303\frac{RT}{nF}\log\left(\frac{D_R}{D_O}\right)^{1/2}$$

If we assume that $D_R \approx D_o$ therefore $E_{1/2} \approx E^o$ and equation 3 can be expressed as follows:

$$E^0 = E_p + 1.109\frac{RT}{nF} \qquad (4)$$

The standard potential of Mo(III)/Mo(0) was determined at temperatures ranging from 1023 K to 1123 K, the average values obtained are summarized in table 1.

Table 1

STANDARD POTENTIAL OF THE Mo(III) / Mo(0) REDOX SYSTEM IN NaCl-KCl-NaF MELT; K_3MoCl_6 (2 . 10^{-4} mol / cm^3)

T (K)	E^0 (V vs. Ag/AgCl)
1023	- 0.812 ± 0.05
1053	- 0.803 ± 0.05
1123	- 0.789 ± 0.05

The experimental values show that the potential values become more positive as the temperature increases in the temperature range used.

$E^o_{Mo(III)/Mo(0)} \approx D_o$ was also determined from logarithmic analysis of the convoluted curves of the voltammograms, as it was mentioned above, by applying equation 2.

The diffusion coefficient of molybdenum electroactive species in the eutectic NaCl-KCl-NaF was determined using cyclic voltammetry technique, by applying the appropriate equations. These measurements were made using different concentration of K_3MoCl_6. Variation of the diffusion coefficient with the temperature was studied in the range 1023-1123 K. By cyclic voltammetry, the diffusion coefficient was calculated from the values of the cathodic peak current, according the Randles-Sevcick equation [16]:

$$I_p = 0.4463\, nFSC_0\left(\frac{nF}{RT}\right)^{1/2} v^{1/2} D^{1/2} \qquad (5)$$

where I_p is the cathodic peak current (A), C_0 is the Mo(III) concentration in the bulk solution (mol cm^{-3}), S the electroactive area of the electrode (cm^2) and D the Mo(III) diffusion coefficient (cm^2 s^{-1}). From the relation between the peak current and the square root of the potential scan rate, appropriate values for the diffusion coefficient of Mo(III) species could be obtained, $D_{Mo(III)} = (4.3 \pm 0.4) \cdot 10^{-5}$ cm^{2}s^{-1}, in good agreement with literature data [17-18]. The values of the diffusion coefficient can by related to the solvodynamic mean radii (R) of the electroactive Mo(III) species by the Stokes-Einstein relation [19]:

$$R = \frac{kT}{6\pi\eta D}$$

where k is the Boltzman constant and η the viscosity.

In these the condition the value of parameter, R is about 3.9 Å. This result shows the high degree of complexation of the molybdenum electroactive species in the electrolyte and explains the low value of the diffusion coefficient of Mo(III). Comparing this value with the radius of the Mo(III) ion (0.8 Å) [20] it results that the solvation processes (the complexation of this ion with the oppositely charged nearest neighbouring chloride ions in the melt) of the electroactive species is substantiated.

Assuming that only $(MoCl_6)^{3-}$ species, with an octahedral arrangement of chloride ligands is present in the electrolyte, radius of electrochemical active species ranging from minimum 3.2 Å to maximum 4.4 Å can be calculated. Thus, $[MoCl_6[^{3-}$ can be assumed to be the electroactive predominant species in molten electrolyte.

This result is in good agreement with the solvation radius calculated from the Stakes-Einstein equation. Based on the diffusion coefficient at the temperature in range 1023-1123 K the temperature dependence of the diffusion coefficient was established like this:

$$\log D = 3.489 - \frac{8442.6}{T} \qquad (6)$$

A plot of $\log D$ *vs.* $1/T$ is shown in figure 5.

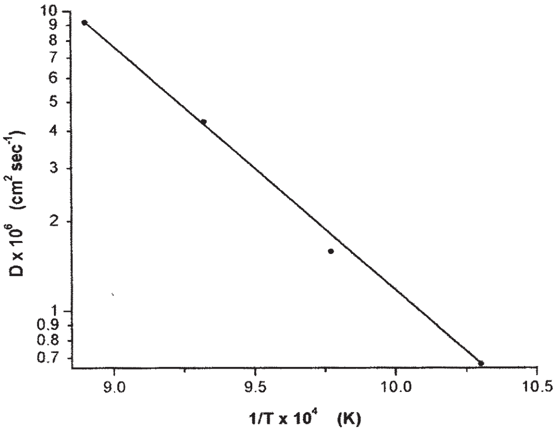

Fig. 5. Variation of the diffusion coefficient with the temperature. K_3MoCl_6 concentration is $(2\cdot10^{-4}$ mol/cm$^3)$

The activation energy calculated from the slope of this line is 8.44 kcal mol^{-1}, and may be compared with the value of 11.9 kcal mol^{-1} for trivalent molybdenum ions obtained by Senderoff in KCl-LiCl solvent [21].

Results and discussion

From the cyclic voltammetry data, the electroreduction of the K_3MoCl_6 from chloride-fluoride electrolytes on tungsten electrode occurs as a single three-electron reversible step. The process was slown with diffusion-controlled mass transfer.

A 3-electron reversible reduction of a mononuclear Mo(III) compound, with no kinetic complication by any preceding chemical reaction has been shown by cyclic voltammetry. However, as far as the earlier [21] proposed existence of a polynuclear species such as $[Mo_2Cl_9[^{3-}$ concerned, no unambiguous conclusion from electro-chemical measurements can be reached because the determinations of the corresponding concentrations were not sufficiently precise.

From our study, we can however conclude that the mononuclear species $[MoCl_6[^{3-}$ should be predominant.

Based on the study it is not possible to determine whether the polyatomic cluster (mononuclear, binuclear or polynuclear) anions, $[MoCl_6[^{3-}$ or $[Mo_2Cl_9[^{3-}$ are present and, if so, whether the electrode reaction occurs and the rate is limited, and therefore reversibility was not unambiguously established:

$$[MoCl_6]^{3-}_{(liq)} + 3e^- \rightarrow Mo_{(s)} + 6Cl^-_{(liq)}$$

$$2[MoCl_6]^{3-}_{(liq)} + 3e^- \leftrightarrow [Mo_2Cl_9]^{3-}_{(liq)} + 3Cl^-_{(liq)}$$

$$[Mo_2Cl_9]^{3-}_{(liq)} + 6e^- \rightarrow 2Mo_{(s)} + 9Cl^-_{(liq)}$$

Conclusions

The electrochemical and chemical properties of K_3MoCl_6 were studied using tungsten as working electrode in the molten NaCl-KCl-NaF eutectic at different temperatures (1023-1123 K).

The electrochemical study performed in this paper indicates that the reduction reaction Mo(III)/Mo(0) occurs in a single step with transference of three electrons and the electrode process shows reversible behavior at temperature range 1023-1123 K.

This fact is surprising because in NaCl-KCl-NaF electrolyte at Ni or stainless steel, in the same conditions, reduction process Mo(III)/Mo(0) is irreversible [5, 6, 22-26].

This aspect can be explained through different interactions between Mo adatom or atom (produced at cathode after electro reduction process) with the metallic cathode.

Thus, the interaction in the Mo-W system is more different than for Mo-Ni or Mo-stainless steel system. This behaviour is also proved by the differences Mo-W system phase diagram and Mo-Ni system phase diagram [27, 28].

However as the temperature increases, the electrochemical reduction process Mo(III)/Mo(0) presents a deviation from the reversible behaviour.

The standard potential of the redox couple Mo(III)/Mo(0) was determined using cyclic voltammetry as $E^o_{Mo(III)/Mo(0)} = -0.810\pm0.020$ V vs. Ag/AgCl reference electrode at 1023 K. This standard potential, apparently, in the range of 1023-1123 K shows a decrease as the temperature increases.

The diffusion coefficients of Mo(III) ions obtained by cyclic voltammetry techniques show a temperatures dependence according to the Arrhenius law in the NaCl-KCl-NaF melt.

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