Electrodeposition of Mo/MoO$_x$ on Copper Substrate from Dimethyl Sulfoxide Solutions

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Abstract

Molybdenum (Mo) is a refractory metal used principally as an alloying agent in steels, cast irons, and super alloys to enhance hardness, strength, toughness, wear and corrosion resistance and it is also widely used in catalytic applications, lubricants and pigments. The single electrodeposition of Mo from aqueous solutions cannot be achieved but Mo it can be co-deposited as an alloy with iron group metals (induced co-deposition). In this study, the electrodeposition of Mo/MoO$_x$ from dimethyl sulfoxide solutions on a copper substrate has been investigated. Different experimental electrodeposition parameters have been assessed (i.e., supporting electrolyte concentration and small amounts of water to the electrolytic bath) to analyze their influence on mechanism of induced Mo/MoO$_x$ deposition. Linear scan voltammetry has been used to follow up the electrodeposition of Mo/MoO$_x$ films. Film morphology has been characterized using scanning electron microscopy (SEM), compositional analysis was performed using X-ray photoelectron spectroscopy. Mo bearing films were also chemically characterized by ICP-OES analysis. An electrodeposition mechanism was developed and discussed.

Introduction

Molybdenum (Mo) is a refractory metallic element used principally as an alloying agent in steels, cast irons, and super alloys to enhance hardness, strength, toughness, and resistance to wear and corrosion. Moreover, molybdenum is also significantly used in numerous chemical applications, including catalysts, lubricants, and pigments.

The electrodeposition of molybdenum has been attempted in the past by many investigators with little or no success. Electrodeposition of metallic molybdenum from non-aqueous baths (i.e., solutions of molybdenum salts in organic solvents or in liquid ammonia) has also been investigated [1].

During the last few years, the use of non-aqueous solvent for a variety of applications has been widely investigated. Some examples are the use of solvents for chemical synthesis [2], media for electrodeposition of metals [3], electrolyte for electrochemical devices such as batteries [4], and supercapacitors [5]. Many researchers have succeeded in co-depositing Mo together with iron group metals [6-7]. Previous investigations show that it is not possible to electrochemically deposit molybdenum alone from aqueous system, reason being molybdenum metal ions form complexes immediately with OH$^-$ [8]. The objective of the present work is to study the feasibility of using dimethyl-sulfoxide (DMSO) and DMSO/H$_2$O mixtures as electrolytic bath for the electrochemical deposition of molybdenum. Properties of the water–dimethyl sulfoxide system and the density of water – DMSO mixtures have been measured by numerous authors [9-10].

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Experimental

All reagents used were analytical grade. Salts were dried at suitable temperature to remove humidity. The ingredients of the electrolytic bath were as follows: ammonium molybdate ($(NH_4)_6Mo_7O_{24}$), lithium chloride (LiCl), distilled water (DI-H$_2$O) and DMSO.

Different electrolytic baths compositions were studied in order to assess the efficiency and quality of Mo coating. In first case, the plating bath contained ammonium molybdate, DMSO and three different concentrations of LiCl as supporting electrolyte (0.5M, 0.8M, 1M). Among aprotic dipolar solvents (ADRs), one of the most suitable solvent for the electrochemical processes is DMSO due to its properties such as high dielectric constant and solvating power. The selection of supporting electrolytes and indifferent electrolytes must be carefully carried out, as for the selection of solvents. Supporting electrolytes for use in polarography and voltammetry should fulfill the following conditions: (1) they should be soluble in the solvent under study and provide enough conductivity to the solution, (2) they should be resistant to oxidation and reduction and gives a wide potential window, (3) they should not have an unfavorable effect on the electrode reaction to be measured, (4) they should be commercially available at a reasonable cost, and (5) they should not be toxic or dangerous to handle. The conclusion is that the supporting electrolytes for organic solvents are fewer in number than those for aqueous solutions [11]. The second bath consisted of molybdate salt in dimethyl sulfoxide without supporting electrolyte. The solubility of ammonium molybdate in dimethyl sulfoxide in the absence of LiCl was very low and increased with increasing amounts of LiCl.

Electrochemical measurements were performed in a conventional three electrode Flat Cell Kit (model K0235) using a potentiostat/galvanostat, model VersaSTAT 3 from Princeton Applied Research equipment and VersaStudio software.

The layers were deposited on a copper (99.9%) foil substrate (working electrode), which was prepared by mechanical polishing the exposed side sand paper. Geometric surface area of copper surface exposed was 1 cm^2. A platinum mesh (4 cm^2) served as anode (counter electrode). The distance between electrodes was approximately 9cm. A standard calomel electrode was used as a reference. The cell configuration allows for the contact of the electrode's silver wire with electrolyte solution by a plastic tube that runs close to the working electrode.

Electrochemical experiments were performed in quiescent conditions (i.e., no stirring). Voltammetric measurements were carried out at a scanning rate of 50mV s^{-1}, from 0 to - 3V negative potentials. Only one cycle was run in each voltammetric experiment. Recurrent potential pulses experiments were performed a constant potential and time.

The deposits were examined with Auriga cross-beam scanning electron microscope (SEM) from Carl Zeiss NTS, the elemental composition was determined by an incorporated X-ray analyzer Oxford INCA X-max 80 SDD EDS system. The efficiency of Mo deposition was estimated by comparing the deposition and the chemical analysis of the films. For chemical analysis, the deposits were dissolved in 5 ml of a 5% nitric acid solution and the resulting samples were analyzed using a Varian Vista MPX inductively coupled plasma spectrophotometer with an optic emission detector (ICP-OES). Certified standard solutions of molybdenum ions containing iridium as an internal standard were used to calibrate the instrument.

Results and Discussion

Preliminary electrochemical study

In polarography and voltammetry, supporting electrolytes play various roles, i.e., to make the electrolytic solution conductive, to eliminate migration currents that may flow in their absence, to control reaction conditions by varying acid-base properties and/or complexing ability of the solution and by changing the double-layer structure at the electrode. The indifferent electrolyte in potentiometry is also important as it adjusts ionic strength and gives appropriate reaction conditions to the solution. The selection of supporting electrolytes and indifferent electrolytes must be carefully carried out, as for the selection of solvents.

Based on a review of the literature [11], LiCl was chosen as supporting electrolyte. Moreover, the influence of LiCl on dimethyl sulfoxide (DMSO) electrochemical properties was further examined. A preliminary voltammetric study was carried out using three different concentration levels of LiCl in DMSO, namely 0.5M, 0.8M, 1M. When 0.5M, 0.8M, 1 M LiCl was present in solution, a reduction

current was detected between – 0 and - 3V in the voltammetric response. For each concentration, three reduction peaks were found which shifted to more positive potentials as the concentration of LiCl increased. This behavior may be explained by LiCl strong influence on some physical properties of DMSO, namely activity coefficients, conductivities, viscosities [12] For the DMSO/0.5M LiCl system, a three steps reduction was observed with reduction peaks - 1.25 V, - 1.85V, and - 2.8V (Fig. 1, curve a). In the system containing 0.8M LiCl the peaks shifted to - 0.95 V, - 1.75V, and - 2.50V, respectively (Fig. 1, curve b). Finally, for the system containing 1M LiCl, the three reduction peaks appeared at - 0.85V, - 1.75V, and - 2.45V, respectively (Fig. 1, curve c).

Fig. 2. Linear scan voltammogram of 1 M LiCl + x M $(NH_4)_6Mo_7O_{24}$ in dimethyl sulfoxide solution, at 50 mV/s scan rate. (a) x = 0.0025; (b) x = 0.005; (c) x = 0.01. Intensity also represents the numerical value of current density and the working electrode area was 1 cm^2.
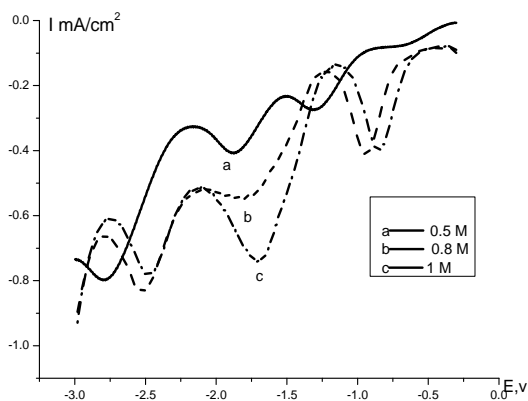

Fig. 1. Linear scan voltammogram of (a) 0.5 M; (b) 0.8M; (c) 1 M LiCl in dimethyl sulfoxide solutions, at 50 mV/s scan rate. Intensity also represents the numerical value of current density and the working electrode area was 1 cm^2.

The concentration of ammonium molybdate in DMSO varied from 0.0025M to 0.01M for solutions containing 1M LiCl as a supporting electrolyte. The addition of ammonium molybdate to the LiCl/DMSO solution resulted in a change of the electrochemical behavior of the system as shown in Figure 2. Two reduction peaks were observed in the 0 to – 3V interval. As the molybdate concentration increased from 0.0025M to 0.01M, the first reduction step shifted to more positive values from ~ – 1.2V for 0.0025M to ~ – 0.8V for 0.01M. On the other hand, an increase in molybdate concentration shifted the second reduction peak to more negative values (from around – 1.6V to around – 2.2V) as it can be observed in Fig. 2. In all cases the intensity of the current associated to the reduction peaks was larger than for the case without molybdate.
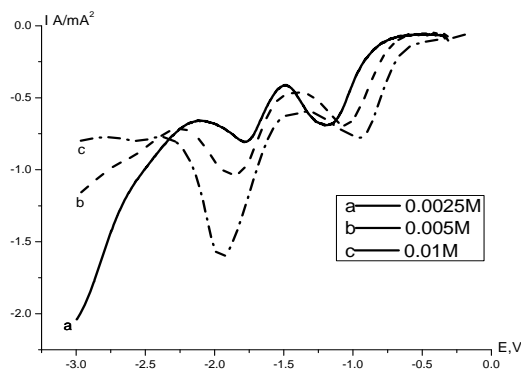
In order to interpret the experimental results the quantum-chemical computations were carried out for DMSO molecule and three complexes with Li^+ approaching DMSO molecule from the side of oxygen atom and sulfur atom and two Li^+ cations approaching DMSO molecule from the sides of oxygen and sulfur atoms. Figure 2 also shows one reduction peak less than Figure 1 in the same voltage interval. The apparent disappearance of the peak may be attributed to the unresolved polarogram. Assuming that the peaks belong to DMSO molecule, the reason of that may be that the presence of molybdate leads to a shift of the ionization potential of DMSO. Analogous shift occurs in case of the binary system with LiCl. The value of ionization potential is directly related to the red-ox potential of the compound. In order to investigate the effects of complex formation and the shifts of peaks of polarization curves the quantum-chemical computations were carried out at Hartree-Fock level in cc-pvdz basis. Ionization potential is estimated as the energy of HOMO and electron affinity is estimated as the energy of LUMO. The electron affinity is closely related to the reduction potential. The increase of the electron affinity leads to the increase of the reduction potential. The lowering of the electron affinities signifies the lowering of the reduction potential, which may serve as the qualitative explanation of the shifts in polarographic spectra. The dependence of the value of the electron affinity on the number of lithium ions forming the complex with DMSO complex may also serve as the explanation of the degree of the shift of polarographic waves with the increase of concentration of LiCl in the solution. Moreover, the presence of ammonium cations may also influence decomposition of DMSO.

Table 1
Electron affinities and ionization potentials of DMSO complexes

Complex	Ionization potential/ Hartree	Electron affinity/ Hartree	Shift of electron affinity/ Hartree
DMSO	-0.3568	0.1669	0
DMSO-Li$^+$ (O)	-0.0437	0.0242	0.1427
DMSO-Li$^+$ (S)	-0.0409	0.0181	0.1488
DMSO-Li$_2^+$ (S-O)	-0.0065	0.0011	0.1658

But Figure 3 depicting linear scan voltammogram of 0.01M (NH$_4$)$_6$Mo$_7$O$_{24}$ + xM dimethyl sulfoxide solution shows a peculiar effect produced by the absence of LiCl in the system. The change of the nature of the voltammogram is hard to be explained by the arguments used above and additional studies are needed to be carried out in order to provide a profound explanation.

Molybdenum (or MoO$_x$) films were deposited from DMSO/LiCl solutions containing different concentration of ammonium molybdate by applying different but constant potentials for 20 minutes.

The deposited films appear to be very thin. ICP-OES analysis of the solutions obtained after dissolving the films confirmed the presence of molybdenum (as a metal or oxide (MoO$_x$) in these films (Table 2). Furthermore, ICP-OES analysis revealed that for potentials more positive than -0.95V and ammonium concentration smaller than 0.002M Mo deposits were not formed.

Influence of water on the deposition process

The influence on the electrodeposition process of the presence of water in the electrolytic bath was also studied. Solutions containing 0.01M constant

molybdate concentration and variable water concentration (i.e., 0.005M; 0.05M; 0.5M) in the DMSO solution were used in the study. ICP-OES analysis revealed that the addition of water to the system resulted in larger deposition of Mo than in the previous experiments without water.
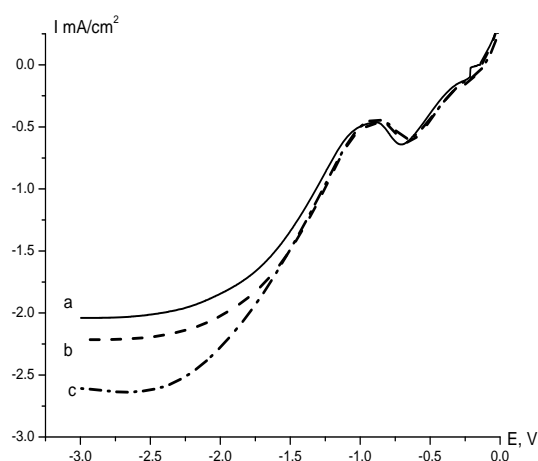

Fig. 3. Linear scan voltammogram of 0.01M (NH$_4$)$_6$Mo$_7$O$_{24}$ + xM dimethyl sulfoxide solution, at 50 mV/s scan rate. (a) x= 0.005; (b) x=0.05; (c) x= 0.5.

Table 2
IPC-OES analysis of solution obtained after dissolving films in 5 ml of 5% nitric acid. The bath employed for preparing the films contained 0.01M concentration of molybdate and variable water concentrations

E[V] / C[mol L^{-1}]	0.75	0.95	-1	-1.2	-1.5	-1.75	-1.85	-2
0.005	0.00	0.009	0.0089	0.0262	0.0422	0.0828	0.1440	0.2472
0.05	0.00	0.0015	0.0109	0.0554	0.0728	0.1629	0.2669	0.5702
0.5	0.0013	0.0649	0.1589	0.5986	0.9926	1.1890	1.5193	1.9207

Characterization of the deposits

Several deposits were prepared from 0.01M molybdate (alone or in the presence of 1M LiCl) in

DMSO with varying water contents (i.e., 0M, 0.005M, 0.05M, 0.5M). Since electro-reduction of molybdenum was suggested to occur in the potential region below – 0.913V; a sample was

prepared by potentiostatic electrodeposition at -1.2V for 20 minutes. A green-yellowish colored film was deposited over the Cu substrate. Figure 4 shows a surface SEM image of the deposited film. SEM examination revealed that the deposits were neither homogenous nor coherent when they were formed from 1 MLiCl + 0.01M molybdate solution in the absence of water. Table 3 shows the EDS results for the deposited film at two locations. In the region identified as Spectrum 1 the film contained 15.14% of Mo and in the region identified as Spectrum 2, the Mo content was just 2.60%. The relative high percentage of oxygen suggests the presence of mixed metallic molybdenum-molybdenum oxide film. Small amounts of the chloride and sulfide were also detected in supporting electrolyte and the DMSO. Higher concentrations of Mo were associated with the star-like deposits while the smooth areas of the substrate were associated with much smaller Mo concentration.
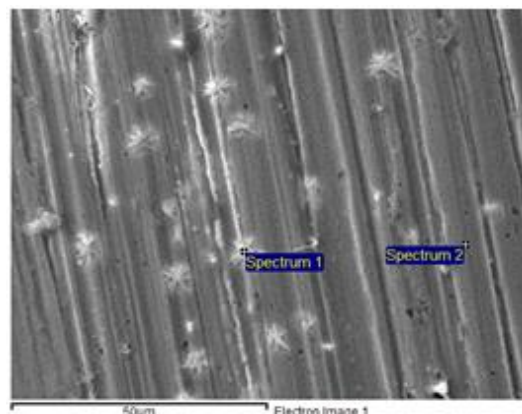

Fig. 4. SEM micrograph of a deposit obtained recurrent potentially pulses at – 1.2V on metallic copper substrate, 1M LiCl + 0.01M molybdate in DMSO solution.

Table 3

EDS results micrograph of a deposit obtained recurrent potentially pulses at – 1.2 V on metallic copper substrate, 1 M LiCl + 0.01 M molybdate in DMSO solution.

Elements (%)	C	O	S	Cl	Mo	Cu	Total
Spectrum 1	4.01	21.66	0.64	0.30	15.14	58.25	100.00
Spectrum 2	4.65	5.84	0.40	0.26	2.60	86.25	100.00
Average	4.33	13.75	0.52	0.28	8.87	72.25	100.00

A second potentiostatic electrodeposition was performed at – 1.5V for 20 minutes. Figure 5 shows a surface SEM image of the electrodeposited film. Fig. 5 (a), (b) and (c) show a surface SEM image of the film that obtained from 0.005M (a); 0.05M (b); 0.5M (c) H_2O + 0.01M molybdate DMSO solutions. After the potentiostatic electrodeposition, the substrate surface was covered with smooth but dense green-yellowish Mo film. As in the deposition performed at – 1.2V, the deposited film was also very thin (inserts of Figures 5a and 5b). However, the highest water concentration (i.e., 0.5M) resulted in the deposition of a different kind of film (insert in Figure 5c). The micrograph clearly shows a large amount of molybdenum snow flake-like formations on the copper substrate.
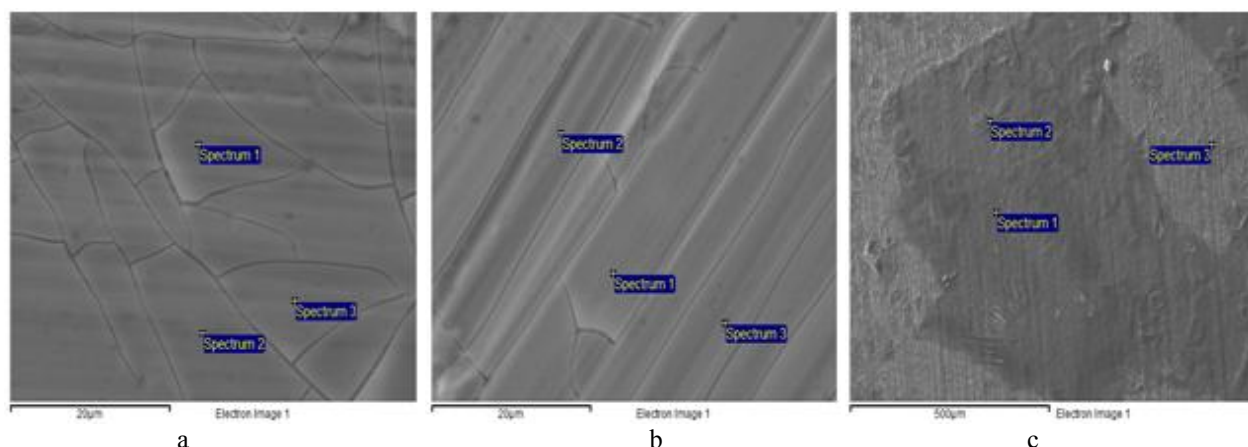

a   b   c

Fig. 5. SEM micrograph of a deposit obtained recurrent potentially pulses at -1.5V on metallic copper substrate, xM H_2O + 0.01M molybdate in DMSO solution. (a) x = 0.005M; (b) x = 0.05M; (c) x = 0.5M.

An elemental analysis, EDS, was done to evaluate the composition of deposited compounds on the substrate surface as shown in Table 4. The Mo content across the substrate for the deposits obtained using 0.005M and 0.05M water content was fairly uniform and in agreement with the smooth appearance of the surface. The rougher deposits obtained from the solution containing 0.5M water shows also large variation in Mo content (almost 3-fold) and a higher Mo content. Oxygen percentages were fairly similar for 0.005M and 0.05M water content in the bath. However, Mo% increased almost 2-fold with increased water

content. As such the average [O]/[Mo] % ratio were 1.48 and 0.9 for water contents 0.005M and 0.05M, respectively. For the largest water content and despite the largest variations in Mo content across the substrate surface, the ratio was % [O]/[Mo] ratio was fairly constant at about 0.9. Those values suggest different stoichiometry for the deposits, which are composed by a mixture of Mo and molybdenum oxides. The atomic O:Mo ratios suggested by the EDS are 8.87:1, 5.26:1, 5.36:1, for water contents 0.005M, 0.05M, and 0.5M, respectively.

Table 4

EDS results micrograph of a deposit obtained at -1.5 V on metallic copper substrate, xM H$_2$O + 0.01M molybdate in DMSO solution. x = 0.005M (a); x = 0.05M (b); x = 0.05M (c).

Fig. 5	Elements	C	O	S	Cu	Mo	Total
a	Spectrum 1	6.18	13.05	0.39	71.53	8.85	100.00
	Spectrum 2	6.42	13.50	0.38	71.05	8.65	100.00
	Spectrum 3	5.72	12.57	0.36	72.39	8.96	100.00
	Average	6.11	13.04	0.38	71.65	8.82	100.00
b	Spectrum 1	7.92	15.22	0.15	58.11	18.60	100.00
	Spectrum 2	7.60	14.60	0.13	61.27	16.40	100.00
	Spectrum 3	8.02	15.48	0.07	60.78	15.65	100.00
	Average	7.85	15.10	0.12	60.05	16.88	100.00
c	Spectrum 1	7.52	12.85	0.00	63.85	15.78	100.00
	Spectrum 2	10.2	37.51	0.00	5.210	47.08	100.00
	Spectrum 3	8.72	27.26	0.00	38.47	25.55	100.00
	Average	8.82	25.87	0.00	35.84	29.47	100.00

Reaction mechanism

Based on results of experimental studies the following reaction mechanism is proposed to be responsible for the conduction with simple electro reduction of DMSO [13]:
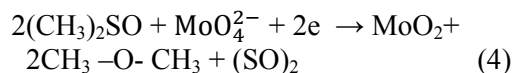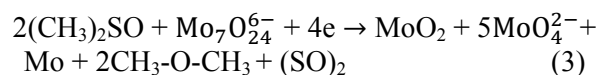
$$(CH_3)_2SO + e^- \rightarrow (CH_3)_2SO^{\cdot-} \rightarrow CH_3SO^{\cdot-} + CH_3^{\cdot} \quad (1)$$

And further formed to carry on decompositon anion [14]:

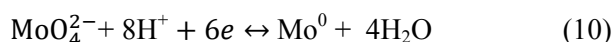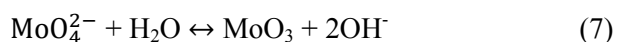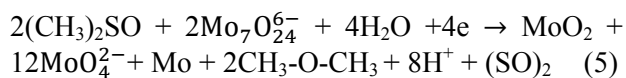$$nCH_3SO^{\cdot-} + e^- \rightarrow -(SO)n + nCH_3^- \quad (2)$$

The colored molybdenum oxides obtained at optimal potentials from molybdate bath may correspond to substoichiometric molybdenum oxides, whose color is related to the presence of

oxygen vacancies [15]. For these oxides an associated intercalation reaction [16] is favored. During electrochemical formation, ions in solution are inserted into the film (protons, lithium or ammonium ions). Then, the formation of molybdenum oxides can be explained by these reactions:

$$2(CH_3)_2SO + Mo_7O_{24}^{6-} + 4e \rightarrow MoO_2 + 5MoO_4^{2-} + Mo + 2CH_3\text{-}O\text{-}CH_3 + (SO)_2 \quad (3)$$

$$2(CH_3)_2SO + MoO_4^{2-} + 2e \rightarrow MoO_2 + 2CH_3\text{-}O\text{-}CH_3 + (SO)_2 \quad (4)$$

In the presence of water, the molybdenum oxide deposits at more negative potentials and as the initial film of molybdenum oxide is formed, significant hydrogen evolution occurs and the

possible inclusion of protons may lead to the formation of blue molybdenum oxide [17].

$$2(CH_3)_2SO + 2Mo_7O_{24}^{6-} + 4H_2O + 4e \rightarrow MoO_2 + 12MoO_4^{2-} + Mo + 2CH_3\text{-}O\text{-}CH_3 + 8H^+ + (SO)_2 \quad (5)$$

$$Mo_7O_{24}^{6-} + 4H_2O \leftrightarrow 7\,MoO_4^{2-} + 8H^+ \quad\quad (6)$$

$$MoO_4^{2-} + H_2O \leftrightarrow MoO_3 + 2OH^- \quad\quad (7)$$

$$6H^+ + 6\,e \leftrightarrow 6\,H^0 \quad\quad (8)$$

$$MoO_3 + 6H^0 \leftrightarrow Mo^0 + 3H_2O \quad\quad (9)$$

$$MoO_4^{2-} + 8H^+ + 6e \leftrightarrow Mo^0 + 4H_2O \quad\quad (10)$$

Conclusions

Results obtained have demonstrated that Mo/MoO$_x$ is formed in induced molybdenum deposition from non-aqueous solutions.

A relationship between the electrochemical response during the deposition and the type of deposit formed on the electrode has been found. The two reduction peaks detected in voltammetric experiments are related to Mo/MoO$_X$ (peak I, II) formation. Potentiostatic experiments are in agreement with these results.

A combination of techniques (spectroscopy and wet chemistry) and the electrochemical studies were used to characterize molybdenum oxide formation during induced molybdenum electrodeposition. The SEM shows the formation of a thin film on the electrode substrate, over which molybdenum begins to deposit. Results obtained from EDS and ICP-OES have demonstrated that molybdenum oxides are deposited from DMSO solutions. However, it is not possible to rule out the presence of Mo oxides produced by oxidation of the freshly deposited metallic molybdenum or sub-stoichiometry Mo oxides.

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