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Electrodeposition of Mo/MoO$_x$ Thin Film on Nickel Substrate From Dimethyl-Sulfoxide: Assessing Electrolytic Bath Characteristics

Akbar Dauletbay*[a], Washington Braida[b], MihailNauryzbaev[a], Leila Kudreeva[a]

[a] al-Farabi Kazakh National University, Chemical and Chemical Technology Department, al- Farabi 71, 050040, Almaty, Kazakhstan.
[b] Stevens Institute of Technology, Center for Environmental System, Hoboken, NJ 07030, USA

adauletbay@gmail.com

Non-stoichiometric mixed-valent molybdenum oxide (MoO$_x$) films were deposited on nickel substrates by electrodeposition from dimethyl-sulfoxide (DMSO) solution. Different experimental electrodeposition parameters (i.e., supporting electrolyte concentration and small amounts of water on the electrolytic bath) have been assessed in order to analyze their influence on the mechanism of induced Mo/MoO$_x$ deposition. Cyclic voltammetry was used to assess the electrochemistry of the process while morphological changes of the deposited films were monitored by scanning electron microscopy (SEM). SEM images of the molybdenum oxide film show that the characteristic snowed structure on the film surface become more prevalent during the transition from the oxidized state to the reduced state without signification change in the Root Mean Square (RMS) surface roughness value. Furthermore, energy dispersive (X-ray) spectroscopy (EDS) studies show that the presence of water in the electrolytic bath has great effect on the morphology of the films.
Keywords: molybdenum , reduction, lithium, molybdate.

1. Introduction

The advent of the missile, space industries and modern military technologies has spurred interest in refractory metals of the group IV, V and VI in general and molybdenum in particular, due to their high melting points, good thermal properties and excellent mechanical properties was recently confirmed (Holliday, 1965). Bucklow (1983) has reported that molybdenum has been classified as a strategically sensitive material and its conservation and efficient use may thus become a priority.. Electrodeposition of molybdenum from molten salts is of considerable industrial interest for the following reasons: (i) molybdenum cannot be electrodeposited from aqueous solution; (ii) since molybdenum is generally scarce and expensive, it is more desirable to use them as a thin coating on the appropriate substrate rather as a bulk were described (Senderoff and Mellors 1966, Koyama et al 1986).

Molybdenum has been electrodeposited from a variety of molten electrolyte systems including fluorides (Gabriel et all, 1999), chlorides (Gabriel et al, 1994; and Senderoff and Mellors 1965, 1966, 1967) and mixed electrolytes (Li and Fan, 1991; Ye and Li, 1991; McCawley and Charlie, 1969). The authors previous work addressed Mo deposition on Cu substrates using dimethylsulfoxide electrolytic baths (Dauletbay et al, 2011). From a practical application standpoint, chemical and electrochemical stability of these systems is a factor of paramount importance. The purpose of the present work is to study the influence of electrolytic bath based on dimethyl-sulfoxide (DMSO) and DMSO/H_2O mixtures for the electrochemical deposition of molybdenum. 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. Properties of the water/dimethyl-sulfoxide system and the density of water/DMSO solutions have been measured by numerous authors and reported elsewhere (Markarian et al, 2005; Torres et al, 2006; Crande et al, 2007).

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2. Experimental

All reagents used were analytical grade. Salts were dried at a suitable temperature to remove humidity. The components of the electrolytic bath were as follows: ammonium molybdate ($(NH_4)_6Mo_7O_{24}$), lithium chloride (LiCl), distilled water (DI-H_2O) and DMSO.

Two different electrolytic baths were studied in order to assess the deposition efficiency and quality of Mo coatings. In the first case, the plating bath contained ammonium molybdate, DMSO and 1M LiCl as supporting electrolyte. The second bath consisted of molybdate salt in dimethyl-sulfoxide with variable water content (i.e., 0.005M, 0.05M, 0.5M). 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-Figure 1) using a potentiostat/galvanostat, model VersaSTAT 3 (Princeton Applied Research). Data were processed using the VersaStudio software.

The Mo layers were deposited on a nickel (99.99% purity) foil substrate (working electrode), which was prepared by mechanical polishing the exposed side with sand paper. Geometric surface area of nickel surface exposed was 1 cm^2. A platinum mesh (3 cm^2) served as anode (counter electrode). The distance between electrodes was approximately 9 cm. 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 running close to the working electrode.

Figure 1: Electrochemical three electrode flat cell kit (K0235).

Electrochemical experiments were performed in quiescent conditions (i.e., no stirring). Voltammetry measurements were carried out at a scanning rate of $25mVs^{-1}$, 0 to -3V to 0 cyclic potentials. Only one cycle was run in each voltammetry experiment. Recurrent potential pulses experiments were performed a constant potential and time.

The deposits were examined with Aurigacross-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 of the film's amount and thickness.

3. Discussion

In polarography and voltammetry, supporting electrolytes play various roles, i.e., to make the electrolytic solution conductive, to eliminate migration current that may flow in its absence, and to control reaction conditions by varying acid-base properties and 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 it is the case for the selection of solvents, As such, supporting electrolytes for organic solvents are fewer in number than those for aqueous solutions. Based in a review by Dunnett and Gasser(1965). LiCl was chosen as supporting electrolyte. LiCl reportedly has strong influence on some physical properties of DMSO, namely: activity coefficients, conductivities, viscosities (Izutsu, 2002).

3.1. Preliminary electrochemical study

Preliminary studies examined LiCl influence on DMSO electrochemical properties. The preliminary voltammetry study was carried out using 1M concentration of LiCl in DMSO. When LiCl was present in solution, two reduction currents were detected in the cyclic voltammetric response (0V to -3V to 0V). The first step in DMSO electrochemical reduction current appears at around -1.62V and the second step around -2.4V (Figre 2a, lower branch). When the scan reversed, a typical nucleation loop was detected with two oxidation peaks centered at -1.70V and -2.64V (Figure 2a, upper branch). Kuvancheva (2003) proposed the following reaction mechanisms for the conduction with simple electro reduction of DMSO:

(CH3)2SO + e- ↔ (CH3)2SO-. ↔ CH3SO- + CH3. (1)

Moreover, the formed radical-anion further decomposed as follows (Kozlova, 2003):

nCH3SO- ↔ -(SO)n- + nCH3. (2)

The addition of 0.01M ammonium molybdate to the LiCl/DMSO solution resulted in a change of the electrochemical behavior of the system as shown in Figure 2 (curve b). Four big and small (around -1V, -1.95V, -2.3V, -2.75V) reduction peaks were observed in the cyclic voltammogram. In the presence of molybdate, the reduction peaks shifted to more positive values than for the LiCl/DMSO solution. On the other hand, sharp reduction currents were measured at the more negative potentials for the molybdate/LiCl/DMSO solution. In all cases the intensity of the current associated to the reduction peaks was larger than for the case without molybdate. In this study molybdate reduction process appears to be irreversible (Figure 2 curve b), as oxidation peaks were not detected during the positive scan process.

Of the peaks were observed in the cyclic voltammograms, the peaks observed in the cyclic voltammogram corresponds to the one-step discharge of the molybdate ions to MoO2 or Mo, and decomposition of DMSO by influence of ammonium and molybdate ions.

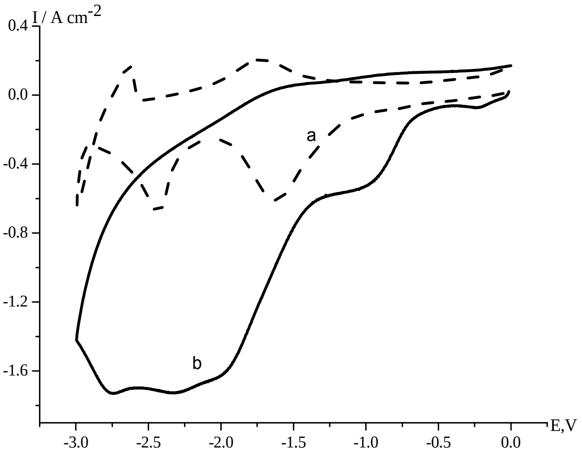

Figure 2: Cyclic scan voltammogram of 1M LiCl (curve a) and 1M LiCl + 0.01M $(NH_4)_6Mo_7O_{24}$(curve b) in DMSO solution, at 25 mV/s scan rate.

3.2. 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 DMSO were used in the study.

The cyclic scan voltammetry response (Figure 3) showed that the small and basically same reduction current was detected in advance in the three curves (Figure 3 a, b, and c) up to potential around -1.5V. Moreover, thin and dark deposition films appeared with increasing concentration of water. For all solutions, continuous deposits of metallic molybdenum or molybdenum oxides formed starting at -1Vor more negative potentials. The addition of water up to 0.5M (Figure 3, curve c) resulted in more negative reduction current. The mechanism and final reduction product depend on the acid–base properties of the solution, whose variation (namely, the variation of the water concentration) allows controlling the electrode processes. In the studies performed the molybdate reduction process is also irreversible, because oxidation peaks were not detected during positive scan measurements. The discharge of the molybdate ions to Mo_2O_3, MoO_2 or Mo occurs in the range from -1V to -1.5V. At potentials more negative than -1.5V dendrite growth rather than the deposition of a new phase of molybdenum or molybdenum composition occurs.

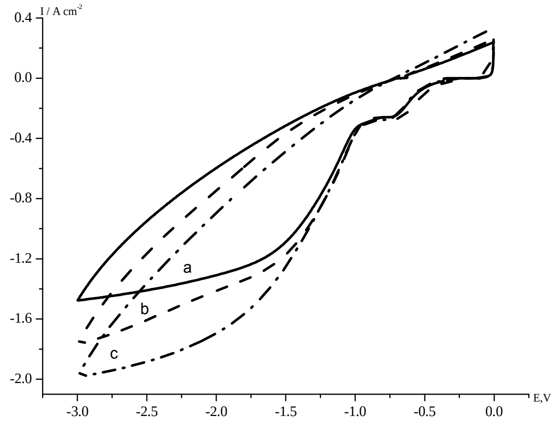

Figure 3: Cyclic scan voltammogram of 0.01M $(NH_4)_6Mo_7O_{24}$ + xM H_2O in DMSO solution, at 25 mV/s scan rate. (a) x = 0.005M; (b) x = 0.05M; (c) x = 0.5M.

3.3. Characterization of the deposits

Several deposits were prepared from DMSO electrolytic baths containing 1M LiCl + 0.01M molybdate, and in the absence of supporting electrolyte, LiCl, but containing 0.005; 0.05; 0.5M H_2O + 0.01M molybdate. The morphological analysis was performed in order to quantify the content of molybdenum in the films and to correlate the type of the film to the electrochemical response.

Aqueous electro-reduction of molybdenum was suggested to occur in the potential region below -0.913V in the presence iron group metals. Samples were prepared by potentiostatic electrodeposition at -1.2 V for 20 minutes. A green-yellowish colored film was deposited over the Ni substrate. Figure 4a shows a surface SEM image of the deposited film. SEM examination revealed that the films were either homogenous or coherent when they were deposited from 1M LiCl + 0.01M molybdate solution in the absence of water.

Table 1 shows the EDS results for the deposited film at Spectrum1 location. In the region identified asSpectrum1 the film contained 13.84% molybdenum. The EDS spectrum also showed that the thin film contained 15.40% oxygen. The relative high percentage of oxygen suggests the presence of a mixed metallic molybdenum-molybdenum oxide film. Chloride and sulphide were also detected from the supporting electrolyte and the DMSO.

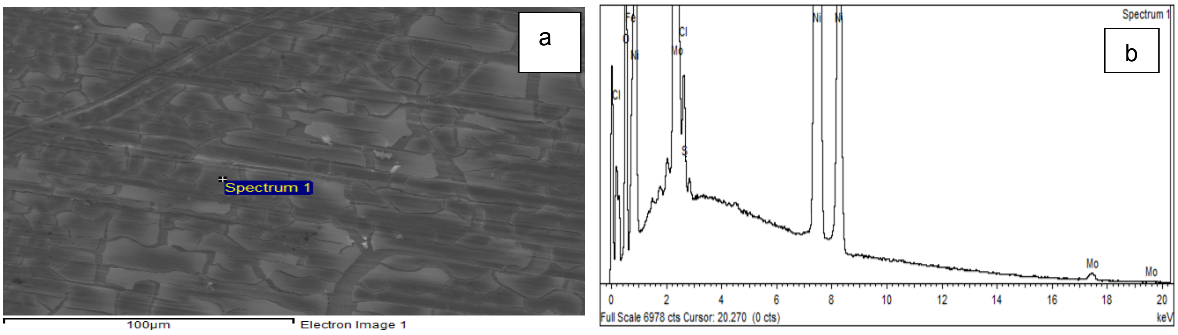

Figure 4: SEM micrograph (a) and EDS (b) result of a deposit obtained by potentiostatic electrodeposition at -1.2V on metallic nickel substrate (1M LiCl + 0.01M molybdate in DMSO solution).

The rougher deposits obtained from the solution containing 0.5M water shows also large variation in Mo content (almost 5-fold, spectrum1) and a higher Mo content.

A second set of potentiostatic electrodeposition experiments were performed at -1.5V for 20 minutes using a solution without supporting electrolyte and different water contents. Figure 5 shows a surface SEM image of the electrodeposited film. Figure 5a, 5b and 5c 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 and homogenous but dense green-yellowish Mo film. As in the deposition performed at -1.5V, 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 nickel substrate.

Table 1: EDS results micrograph of a deposit obtained at -1.2 V on metallic nickel substrate, 1M LiCl + 0.01M molybdate in DMSO solution.

Figure 6	Elements	C (%)	O (%)	Cl (%)	S (%)	Ni (%)	Mo (%)	Total (%)
	Spectrum 1	9.65	15.40	0.93	0.40	59.78	13.84	100

The growth of Mo/MoO_X crystal appears to be time dependent. The micrograph (Figure 5c) clearly shows that the molybdenum or molybdenum oxide crystals gradually grow to cover up on the nickel substrate. For example, the area marked as spectrum 3 contains very small amounts of molybdenum (0.82% Mo), the area described as spectrum 2 contains still small amounts of molybdenum but 5-6 fold larger (4.50% Mo). Finally, the area identified as spectrum 1 contains large amounts of molybdenum (50.96% Mo).

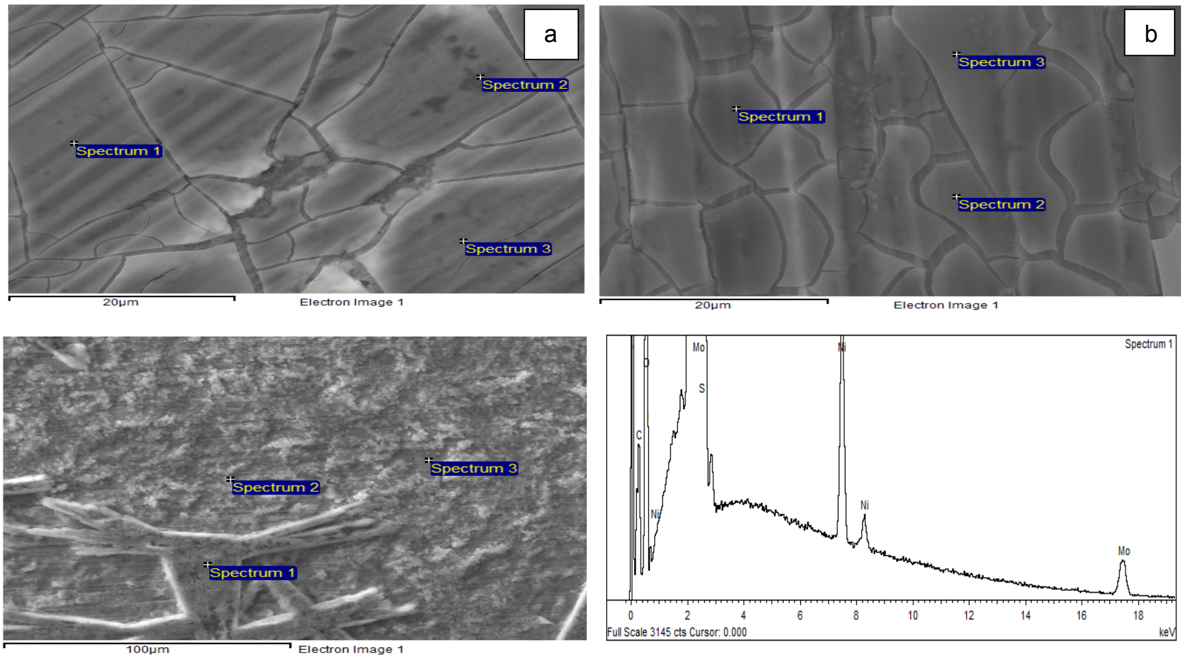

Figure 5: SEM micrographs (a, b, c) and EDS (d) result of a deposit obtained by potentiostatic electrodeposition at -1.5V on metallic nickel substrate (0.005M-0.5M H_2O+ 0.01M molybdate in DMSO solution).

An elemental analysis, EDS, was done to evaluate the composition of deposited compounds on the substrate surface as shown in Figure 5d. The EDS result of Fig. 5d is corresponding Fig. 5c microphotograph spectrum 1 point. 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.

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 1.08 and 0.74 for water contents 0.005M and 0.05M, respectively. For the largest water content and despite the large variations in Mo content across the substrate surface, the ratio was [O]/[Mo] was fairly constant at about 0.79. 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. These experiments indicated that the film was composed mainly of molybdenum and oxygen.

The colored molybdenum oxides deposits obtained appears to correspond to sub-stoichiometric molybdenum oxides, whose color is related to the presence of oxygen vacancies (Sabhapathi et al, 1995). For these oxides, an associated intercalation reaction Scarminio et al (1997) is favored. During electrochemical formation, ions in solution are inserted into the film (protons, lithium or ammonium ions). 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 (Rout and Bandyopadhyay, 2007).

Table 2: EDS results micrograph of a deposit obtained at -1.5 V on metallic nickel substrate, x M H_2O + 0.01M molybdate in DMSO solution. x = 0.005M (a); x = 0.05M (b); x = 0.5M (c).

Figure 6	Elements	C (%)	O (%)	S (%)	Ni (%)	Mo (%)	Total (%)
a	Spectrum 1	4.23	9.85	0.27	75.10	10.55	100.00
	Spectrum 2	5.40	12.19	0.27	71.14	11.00	100.00
	Spectrum 3	5.29	11.37	0.31	73.60	9.48	100.00
	Average	4.97	11.12	0.29	73.28	10.34	100.00
b	Spectrum 1	4.99	13.08	0.17	60.18	21.18	100.00
	Spectrum 2	6.52	15.47	0.04	59.85	18.12	100.00
	Spectrum 3	6.59	14.72	0.00	59.99	18.69	100.00
	Average	6.03	14.42	0.07	60.01	19.47	100.00
c	Spectrum 1	10.04	34.67	0.73	3.60	50.96	100.00
	Spectrum 2	5.69	7.08	0.43	82.30	4.50	100.00
	Spectrum 3	6.70	2.90	0.81	88.77	0.82	100.00
	Average	7.48	14.88	0.66	58.23	18.76	100.00

Conclusions

Electrochemical deposition of molybdenum and molybdenum coatings from DMSO, and DMSO/H_2O systems was achieved. The advantages of DMSO solutions over other types of electrochemical baths are the low cost and relatively low toxicity of reagents.

A relationship between the electrochemical response during the deposition and the type of deposit formed on the electrode has been found. The four reduction peaks detected in voltammetry experiments are related to Mo/MoO_Xformation in 1M LiCl + 0.01Mmoybdate DMSO solution. 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 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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