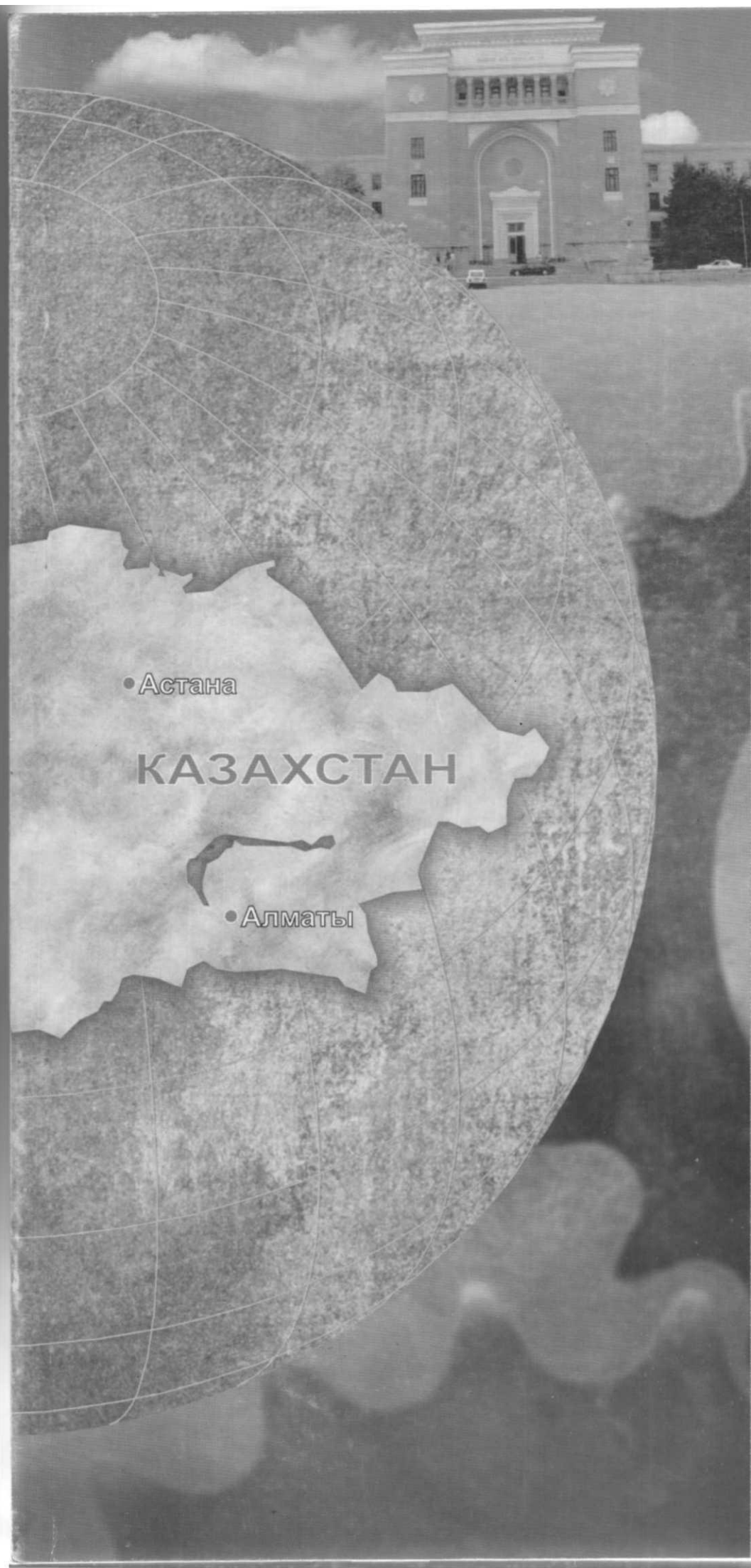




ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

ХАБАРШЫСЫ ВЕСТНИК

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН

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INFLUENCE OF CITRIC AND BORIC ACID ON THE ELECTRODEPOSITION PROCESS OF MOOX FILM FROM DIMETHYL SULFOXIDE

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The electrodeposition of Mo/MoOx from dimethyl sulfoxide has been investigated and influence of bath composition was studied. The Mo/MoOx thin films were deposited on copper substrates by the electrochemical method from dimethyl sulfoxide solution with bath composition citric acid and boric acid. Among the experimental electrodeposition parameters, only the concentration ratio of additional substances to molybdate ions was varied to analyze its influence on mechanism of induced Mo/MoOx deposition. Voltammetry was one of the main techniques, which was used to examine the voltammetric response, revealing that Mo/MoOx deposition depended on the nature of the species in solution. When optimal potential is applied, a colored Mo/MoOx thin film is formed on the electrode. Physical - Chemical ICP-OES analysis was used to corroborate the Mo/MoOx thin film almost presence on the substrate. Intermediate Mo/MoOx was characterized using scanning electron microscopy (SEM), compositional analysis was determined with X-ray photoelectron spectroscopy.

Introduction. Molybdenum is called refractory metal. About 80% of molybdenum produced is used in metallurgical applications such as alloys. The ability of molybdenum to withstand extreme temperatures without significantly expanding or softening makes it useful in applications that involve intense heat, including the manufacture of armour, aircraft parts, electrical contacts, industrial motors and filaments. Molybdenum is also used in steel alloys for its high corrosion resistance and weldability. Molybdenum contributes further corrosion resistance to "chrome-moly" type-300 stainless steels (high-chromium steels that are corrosion-resistant already due to their chromium content) and especially so in the so-called austenitic stainless steels (such as alloy AL-6XN). Molybdenum acts by increasing lattice strain, thus increasing the energy required to dissolve out iron atoms from the surface.

The electrodeposition of molybdenum has been attempted in the past by many investigators with little or no success. Electrodepositions of metallic molybdenum from non-aqueous baths (i.e., solutions of molybdenum salts in organic solvents or in liquid ammonia) have been investigated [1–2]. During the last few years, the use of non-aqueous solvent for a variety of applications has been widely investigated. Many researchers have succeeded in co-depositing Mo together with iron group metals [3–12]. 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[–] [13, 14]. The purpose of the present work is to study the feasibility of using DMSO and DMSO/H₂O mixtures as electrolyte for the electrochemical deposition of molybdenum.

Experimental work. All reagents used were analytical grade. Salts were dried at suitable temperature to remove humidity. The composition of the electrolytic bath was as follows: ammonium molybdate ((NH₄)₆Mo₇O₂₄), LiCl, boric acid (H₃BO₃), citric acid C₆H₈O₇, distilled water (DI H₂O) and DMSO.

In order obtain Mo coating; two different electrolytic baths were studied. The 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 with sand paper one side. Geometric surface area of copper plates was 1 cm². A platinum mesh (4 cm²) 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 that runs close to the working electrode.

Electrochemical experiments were performed in quiescent conditions, voltammetric experiments were carried out at 50 mV s^{–1}, scanning initially towards 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 an X-ray analyzer incorporated Oxford INCA X-max 80 SDD EDS system equipment. The efficiency of deposits preparation was calculated by comparing the deposition charge 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 rhodium as an internal standard were used to calibrate the instrument.

Results and discussion. Based in a review of the literature [15-17], boric and citric acid were chosen as addition species, two kinds of voltammetric responses were observed the citric and boric acid concentration range.

For LiCl + molybdate solutions in the presence of citric acid 0.001 and 0.01M, boric acid 0.003 and 0.03M, deposition began slightly after -1V (Fig. 1, 2). The negative scan revealed a double reduction peak on the both of figures, which might be showed the electrodeposition of Mo/MoO_x occurs two steps, first step should be Mo/MoO_x, and second step should be higher valance of molybdenum compound or reduction of bath composition. But the positive scan revealed no oxidation peak, which was supposed deposition of molybdenum compound doesn't get oxidation process.

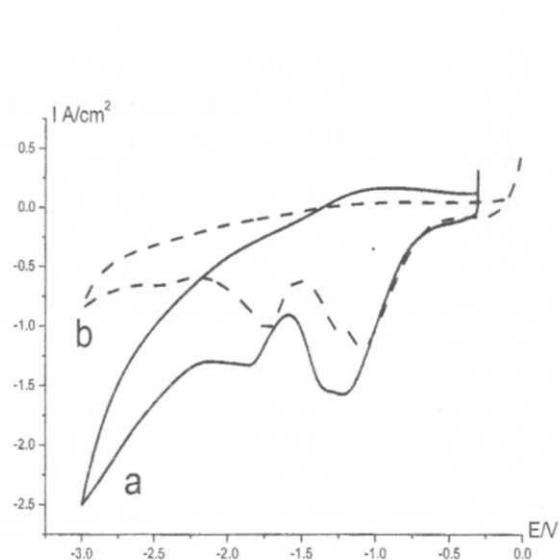


Fig. 1. Cyclic scan voltammogram of 1 M LiCl + 0.01 M (NH₄)₆Mo₇O₂₄ xM citric acid in dimethyl sulfoxide solutions, at 50 mV/s scan rate. (a) x = 0.001, (b) x = 0.01

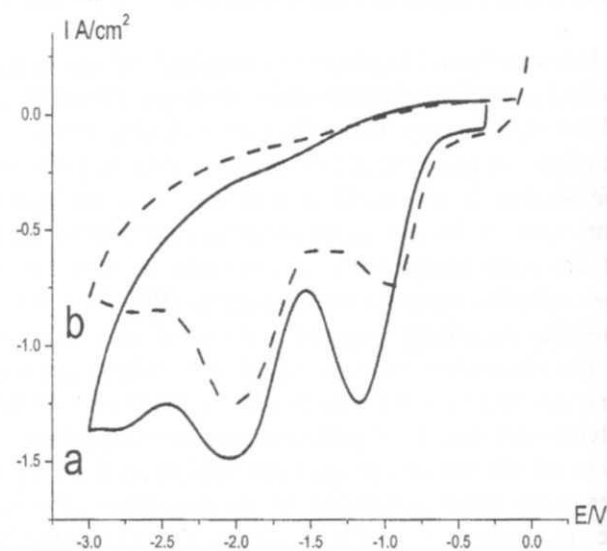


Fig. 2. Cyclic scan voltammogram of 1 M LiCl + 0.01 M (NH₄)₆Mo₇O₂₄ xM boric acid in dimethyl sulfoxide solutions, at 50 mV/s scan rate. (a) x = 0.003; (d) x = 0.03

Moreover, the charge involved in the first and second reduction processes were decreased by increasing the citric and boric acid concentration (Fig. 1 and 2, curve a, b).

Can be supposed, citric and boric acid was more helpful for decomposition of DMSO, also prevented deposition of molybdenum compounds. Because both of these acids produce more protons. Table 1 corroborated this supposition. The films were deposited to sue recurrent potential pluses methods different constant potentials and time (20 minutes). Furthermore, ICP-OES analysis revealed that the molybdenum compound decreased greatly when the presence of acids in the bath solution.

A sample was prepared by potentiostatic electrodeposition at -1.2 V for 20 minutes. It was formed from 1M LiCl + 0.01 M (NH₄)₆Mo₇O₂₄ dimethyl sulfoxide solution presence 0.001M boric acid. A green-yellowish colored film was deposited over the Cu substrate. Figure 3 shows a surface SEM image of the deposited film. SEM examination revealed that the deposits were homogenous and coherent. Table 3 shows the EDS results for the deposited film at three locations. Every location's molybdenum percentage is approximately similar, that was corroborate the film was spread co-ordinate on the substrate.

Table 1. 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 acid concentrations

C/ mol·L ⁻¹ \ E/V		0.75	-1	-1.2	-1.35	-1.75	-1.90	-2	-2.15
citric	0.001	0	0.0019	0.0119	0.0254	0.0368	0.0429	0.0469	0.0519
	0.01	0	0.0005	0.0089	0.0162	0.0222	0.0314	0.0340	0.0402
boric	0.003	0	0.0061	0.0113	0.0246	0.0420	0.0490	0.0593	0.0653
	0.03	0	0.0017	0.0093	0.0154	0.0218	0.0315	0.0372	0.0499

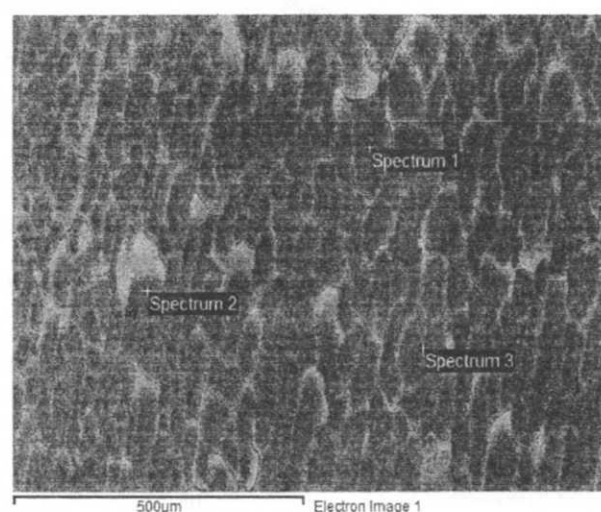


Fig. 3. SEM micrograph of a deposit obtained recurrent potential pulses at -1.2V on metallic copper substrate, 1M LiCl + 0.01M molybdate in DMSO solution presence 0.001M boric acid.

Table 2. EDS results micrograph of a deposit obtained recurrent potential pulses at -1.2 V on metallic copper substrate, 1 M LiCl + 0.01 M molybdate in DMSO solution presence 0.001M boric acid

Spectrum	C	O	S	Cl	Cu	Mo	Total
Spectrum1	4.35	10.90	0.24	0.13	78.07	6.31	100.00
Spectrum2	5.37	12.44	0.09	0.00	75.74	6.36	100.00
Spectrum3	5.53	15.17	0.06	0.14	71.26	7.85	100.00

The relatively 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.

Conclusions. Among aprotic dipolar solvents (ADRs), one of the most suitable solvent for the electrochemical processes is dimethyl sulfoxide (DMSO) because of its properties such as high dielectric constant and solvating power. However, supporting electrolyte is important for ADRs, LiCl was used for supporting electrolyte and was examined the influence to DMSO electrochemical properties.

Many researchers have succeeded in co-depositing Mo together with iron group metals and with additional species citrate and boric acid [18-21], so this work although test additional species citric and boric acid, but the results not good for DMSO solutions. Reason is that complexation between molybdate and citrate is stronger, as demonstrated by the corresponding complex formation constants ($\text{HMoO}_4\text{Cit}^{4-}$, $\log K_1 = 8.08$; $\text{H}_2\text{MoO}_4\text{Cit}^{3-}$, $\log K_2 = 6.27$; $\text{H}_3\text{MoO}_4\text{Cit}^{2-}$, $\log K_3 = 21.74$). The complexation is broken when the presence of iron group metals in solutions.

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ДИМЕТИЛСУЛЬФОКСИД ЕРІТІНДІСІНЕН МОО_x ҚАБЫРШАҒЫН ЭЛЕКТРОТҮНДІРУДА ЛИМОН ЖӘНЕ БОР ҚЫШҚЫЛДАРЫНЫҢ ӘСЕРІ

Бұл жұмыста диметилсульфоксид ерітіндісінен Мо/МоОх электрохимиялық тұндыру және электролиз құрамының әсері зерттелді. Мыс төсемесінде құрамында лимон және бор қышқылдары бар диметилсульфоксид ерітіндінен электрохимиялық тотықсыздану нәтижесінде Мо/МоОх жұқа қабыршағы түзілді. Молибдат ионының электрохимиялық тотықсыздануына лимон және бор қышқылдарының әртүрлі катынастағы концентрациясында Мо/МоОх қабыршағының түзілу механизміне әсері қарастырылды. Мо/МоОх электрохимиялық тұндыру ертінді табиғатына тәуелді екені анықталды. Электрод бетінде түсті Мо/МоОх қабыршағының түзілуіне тиімді потенциал (-1,2В) екені анықталды. Оптика-эмиссиондық спектроскопия құрылғысының көмегімен электрод бетінде Мо/МоОх қаптамасының бар екендігі дәлелденді. Электрод бетінде түзілген қабыршақтың үлкейтілген фотосуреттері түсіріліп, рентген спектрлі талдаулары жасалды.

Акбар Дәулетбай^{*1}, Вашингтон Брайда², Михаил Наурызбаев¹, Лейла Кудреева¹

ВЛИЯНИЕ ЛИМОННОЙ И БОРНОЙ КИСЛОТЫ НА ПРОЦЕСС ЭЛЕКТРООСАЖДЕНИЯ ПЛЕНКИ МОО_x ИЗ ДИМЕТИЛСУЛЬФОКСИДА

Исследованы электроосаждение Мо/МоОх из раствора диметилсульфоксида и влияние состава электролита. На медном подложке из раствора диметилсульфоксида в котором содержится лимонная и борная кислота образовался тонкая пленка Мо/МоОх. Рассмотрено влияние соотношения концентрации лимонной и борной кислоты на механизм образования пленки Мо/МоОх. При потенциале -1,2В формируется тонкая Мо/МоОх пленка на электроде. По результатам рентгеноспектрального анализа, оптико-эмиссионной спектроскопии и электронной микроскопии можно предположить, что наличие этих ионов способствует образованию на поверхности металлической подложки Мо/МоОх пленки.

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