Electrochemical Separation of Molybdenum and Tungsten Using Aqueous-Organic Electrolytes

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Article info

Abstract

Molybdenum is one of the valuable metals for the industry; its special properties make it extremely urgent to study the process of separation of molybdenum from other impurities. The article considers the optimization of electrochemical separation of molybdenum from Mo-W system. The electrochemical dissolution of molybdenum and tungsten in solutions of LiCl and NH_4NO_3 in dimethylsulfoxide was studied using polarization curves and calculation of the efficiency of anodic dissolution of molybdenum in the presence of tungsten. The electrolyte with a composition of 0.5 M LiCl; 5.2 M dimethylsulfoxide; 32.2 M water was selected as an effective solution for the electrochemical separation of molybdenum in the potential range of 1.0–2.2 V. Results obtained in this study can be used for the development of selective separation method in the molybdenum production.

1. Introduction

Today, the role of molybdenum in the industry cannot be underestimated. A wide range of unique properties entails widespread use of molybdenum in various industries, such as oil, steel, chemical industries, production of electronic devices, etc. Molybdenum also has the biological value in the composition of nitrogenase protein, which helps to convert atmospheric nitrogen into ammonia [1–4].

Molybdenum compounds are extremely promising as electrodes [5], catalysts [6–10], corrosion resistance additives of steel [11–14], in solar cell systems [15].

The scale of production and consumption of molybdenum in the industry, its special physical and mechanical properties (refractoriness, heat resistance, hardness) make it extremely urgent for efficient processes to process it. Molybdenum samples are often contaminated with various other metal ions, such as tungsten, vanadium, etc. It is of great interest to separate them for further use. Mechanical processing of molybdenum, as well as other rare metals, is difficult since it requires the use of cutting tools or metal preheat to the temperature above the transition from brittle form to ductile one.

An alternative to mechanical processing is chemical methods. The advantages of such methods are high-performance, absence of tensions and structural changes in the surface layer, etc. The chemical etching process is applied for the extraction of molybdenum from systems containing molybdenum and tungsten. In this case, molybdenum is dissolved from Mo-W bimetallic systems often using the solutions of nitric acid, sulfuric acid, hydrochloric acid and hydrogen peroxide [16–19]. All methods of chemical dissolution of molybdenum have a common drawback, namely the process of chemical dissolution is environmentally dangerous. Formed strongly acidic molybdenum solutions have an approximate composition (wt. %): H_2SO_4 –18, HNO_3 – 8, Mo (VI) – 1.6–3,

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and SO_2 and nitrogen oxides [19]. The concentration of Mo (VI) in the washing water reaches 8 $mg \cdot L^{-1}$, while the maximum allowable concentration of molybdenum (VI) is 0.0012 $mg \cdot L^{-1}$. Treatment of wastewater from the molybdenum (VI) to that value is not possible. The drawbacks of these methods also include:

1) formation and emission of nitrogen oxides;
2) high aggressiveness of solutions;
3) etching process is almost uncontrollable;
4) low capture efficiency of molybdenum from the resulted solution (50%).

Currently, to eliminate the disadvantages of the chemical etching method, a significant number of processes are being developed to separate molybdenum from Mo-W systems. Application of ion exchange resins shows significant efficacy, e.g. the use of D301 or D309 macroporous resins allows to extract of tungsten ions selectively in the presence of molybdenum [20–22]. Methods of deposition using iron or manganese salts also made it possible to achieve high separation factor values [23, 24].

Aqueous-organic solutions are widely used to increase the separation efficiency for the Mo-W system [17, 18]. Application of organic compounds improves the selective extraction of molybdenum in weakly acidic media [18] and using of biorecovery agent was investigated for recovery of molybdenum from the waste water [25], the use of phosphoric acid has shown good results in the leaching of tungsten [26]. However, the optimization of the process of electrochemical separation of molybdenum from Mo-W system is still urgent. The problem consists of the selection of the optimal electrolyte for effective separation of molybdenum.

The aim of this work was to study the possibility of selective extraction of molybdenum from bimetallic Mo-W system by anodic dissolution of molybdenum and tungsten in aqueous-organic solutions using the electrolytes of different composition.

2. Experimental section

2.1. Chemicals

Dimethylsulfoxide (DMSO, *puriss.*) purchased from Sigma Aldrich was used as a solvent. Water was removed from the solvent by drying it over calcium oxide changing the desiccant twice within two weeks. After drying, the solvent was distilled twice in a vacuum (5.3 mmHg). Solvent purity was checked by IR spectroscopy.

Calcium oxide (anhydrous, powder, *puriss.*, Sigma Aldrich) was pre-purified by calcination in flowing dry air at the temperature of 1000 °C.

Lithium chloride (powder, *puriss.*, Sigma Aldrich) was recrystallized three times from deionized water, dried for several days at gradually raising the temperature from 80 to 300 °C in a vacuum oven until a constant weight was obtained. The purity of the salt was checked by IR-spectroscopy for the presence of the OH-group signal.

Studies were also carried out using ammonium nitrate solution (powder, *puriss.*, Sigma Aldrich) in DMSO with different concentrations.

2.2. Preparation of working solutions

The working electrolyte solutions were prepared in 100 mL flasks by placing the compound and bringing the solution to the mark by DMSO according to Table 1. All solutions were prepared in flasks with ground stoppers in a dried box. The box was dried using phosphorus oxide (*puriss.*, Sigma Aldrich), which was changed periodically. Salts were weighted in a separate box, free from solvent vapor, using AR 3130 analytical balance (OHAUS Corp., USA). After preparation, all the electrolytes were tested for water content by IR spectroscopy for the presence of OH-group signal.

Table 1
Preparation of working solutions

Compound	Weight, g	Resulting concentration, M
LiCl	0.8479	0.20
	1.0599	0.25
	2.1197	0.50
NH_4NO_3	8.0043	1.0
	16.0086	2.0
	24.0129	3.0
	32.0172	4.0
	40.0215	5.0

2.3. Procedure and techniques

Study molybdenum and tungsten electrooxidation was conducted by obtaining the current-voltage curves using AUTOLAB PG101/101 M potentiostat-galvanostat (Metrohm Autolab, Switzerland) in a temperature controlled three-electrode cell.

Rotating and stationary molybdenum and tungsten rods, molded in Teflon, were used as a working electrode (anode). Before each experiment, elec-

trodes were polished using micron sandpaper to a mirror finish and washed with the working solution.

When using a stationary electrode, measurements were carried out in the glass three-electrode cell with separate spaces. Before experiments, the cell was washed with a hot soda solution, a large amount of water, and then with deionized water, steamed and dried under vacuum. Immediately before the measurement, the cell was rinsed with a working solution. A platinum plate served as an auxiliary electrode, a silver chloride electrode (Ag/AgCl) was used as a reference electrode placed in a capillary with a saturated electrolyte solution in dimethylsulfoxide.

The instrument was prepared to work before each experiment in accordance with the operating requirements. Electrode polarization was performed at the potentials in the range of 0.00 to +2.0 V, depending on the working electrode used and the conditions of the electrochemical process. Polarization curves were recorded using H-307 XY recorder tablet. The system was deoxygenated by argon purging before each experiment to exclude the possible effect of dissolved oxygen.

2.4. Electrolysis

Electrolysis was carried out in the selected concentration range of the components using the glass electrochemical cell with separated spaces. The cathode was an indifferent metal (Pt), and the anode was the tungsten-molybdenum bispiral, wound on the molybdenum rod. The process was carried out at room temperature and the current density of 220 mA·cm^{-2}. The amount of metal transferred to the solution was established by the difference between the initial and final masses of the anode.

2.5. Analytical measurements

Analytical measurements were carried out for the purity control of chemicals and analysis of the electrolysis products. For this, infrared spectrometry, atomic absorption spectroscopy and X-ray analyses were used.

Atomic absorption analyses for Mo were carried out on AAS1N (Carl Zeiss Jena, Germany) in an air-acetylene flame at the wavelength of 285.2 nm. Molybdenum concentration range was up to 2.5 mg·mL^{-1}. Its content was found using the calibration curve.

X-ray microanalysis on the different electrodes was carried out on JCXA-733 «Superprobe» elec-

tron probe microanalyzer (JEOL, Japan) at the accelerating voltage of 25 kV.

IR spectrometry method was used to check the purity of solvents and reagents. Analyses were carried out on IRPrestige-21 (Shimadzu).

3. Results and discussion

3.1. Choice of the solvent

DMSO was chosen as a solvent for the following reasons:

1) DMSO is the most important aprotic solvent, has high solvating ability, coordination with the metal atom goes through a sulfur atom, and high donor properties cause the ability of DMSO molecules to easily displace other ligands from the inner sphere of metal complexes;

2) DMSO is used as a medium for electrochemical studies due to high dielectric permittivity, electrochemical stability in a wide range of potentials;

3) DMSO has an associated structure that can't degrade in a 18.5–189 °C temperature range and when the proton is accepted;

4) in a certain concentration range, the salts dissolved in DMSO form ionic associates.

In addition, DMSO has low toxicity and volatility, relative cheapness and electrochemical stability in a wide range of potentials compared to water.

The advantage of the lithium chloride system (in DMSO) is the good solubility of the reaction products and the low adsorption of the anion, compared to other anions.

3.2. Anodic oxidation in LiCl

Figure 1 shows the polarization curves of the electrooxidation of molybdenum in 0.25 M solution of LiCl in DMSO at different rotational speeds. The sweep speed of the potential was 50 mV·s^{-1}. At the potentials of 0.1–0.75 V, there was a small region of polarizability followed by a sharp increase in the oxidation current with the increase in potentials above 1.5 V. This was due to the formation of lower molybdenum oxides (δ and γ-phases) with high electronic conductivity. Increased sweep speed led to the increased rate of electrochemical dissolution of Mo. In this case, diffusion limited the dissolution of molybdenum. Intensive mixing facilitates the transport of electrolyte molecules to the surface of the metal. Such molecules take a direct part in the formation of a solid surface film, which also inhibits the process of molybdenum dissolution.
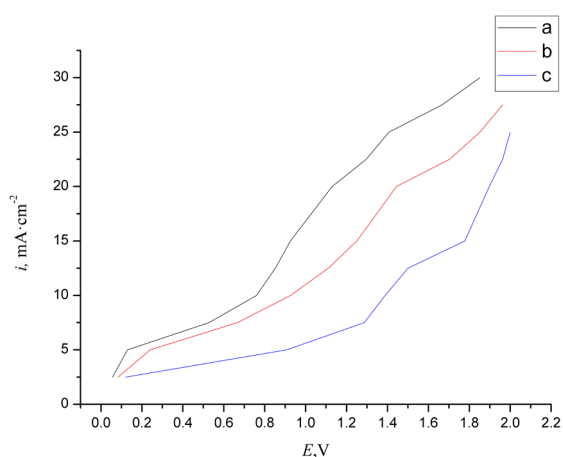
Fig. 1. Polarization curves of anodic dissolution of molybdenum in 0.25 M solution of LiCl in DMSO: a – 1900 rpm; b – 3100 rpm; c – 4600 rpm.
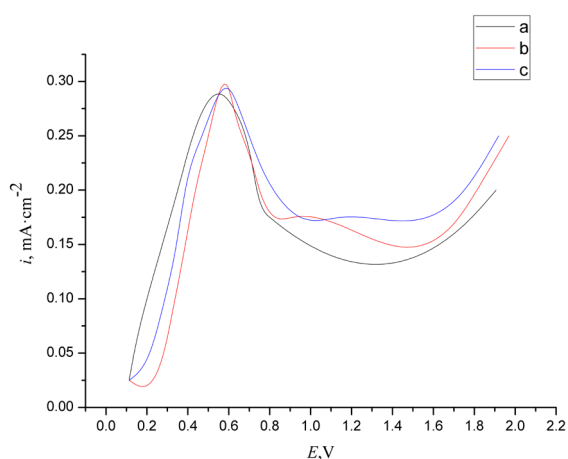

Fig. 2. Polarization curves of anodic dissolution of tungsten in 0.25 M solution of LiCl in DMSO: a – 960 rpm; b – 1360 rpm; c – 3800 rpm.

On the other hand, there was a rather sharp current rise (with a maximum at 0.5–0.7 V) of the electrical oxidation of tungsten in 0.25 M solution of LiCl in DMSO (Fig. 2). The oxidation rate decreased in a relatively small range of potentials (from 0.70 to 1.00 V) and followed by a slight increase of 30% in the range from 1.00 to 1.75 V. The region of the passive state was limited by the repressive potential, which was accompanied by the formation of oxygen compounds of WO_3 (α-phase). This fact agrees with the literature. The maximum at the potential of +0.70 V and the subsequent decrease in the rate of anodic dissolution of tungsten indicated a complete coating of the surface by the oxides of a poorly conductive film of α-phase.

3.3. Anodic oxidation in NH_4NO_3

The use of ammonium nitrate instead of LiCl

as an electrolyte for anodic dissolution of molybdenum is the most interesting from a practical point of view. At the concentrations of ammonium nitrate of 1–4 M (pH=4–5), the current increased continuously and sharply with increasing potential, not reaching the current limit (Fig. 3). The area of active metal oxidation covered a wide range of potentials (from 0.5 V and higher), and the polarization curve did not have a current limit site. An increase of concentration from 4 to 5M leads to a clear increase in the current (Fig. 3, lines d and e). Intensive oxidation of molybdenum in ammonium nitrate was due to the participation of anions in the process of electrical dissolution. The electrolyte anions participated in the process of de-passivation of individual metal sections (adsorption displacement of passivating oxygen from the metal surface) and in the elementary ionization act of metallic atoms, resulting in the increase of dissolution process rate.

In addition, dissolving molybdenum in ammonium nitrate led to electrolytical conversion of the surface oxide to a soluble compound. This compound accelerated the transition of metal oxides to the solution with increasing polarization. The product of oxidation of molybdenum oxides was ammonium molybdate. Formation of black flakes of molybdenum dioxide was observed at the initial stage of molybdenum electro-oxidation, the precipitate was then peeled off from the electrode and dropped to the bottom of the cell. A part of MoO_2 then converted into a soluble form, ammonium molybdate, since the amount of suspended particles in the electrolyte decreased by the end of the electrolysis. In this case, the oxide layer also did not reduce the metal oxidation rate.
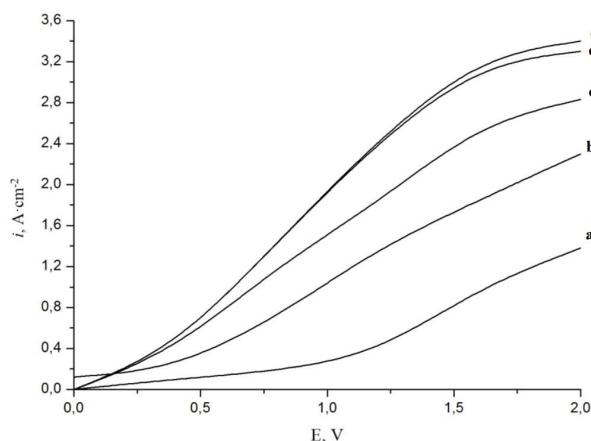

Fig. 3. Polarization curves of anodic oxidation of molybdenum in solutions of ammonium nitrate of various concentrations: a – 1 M; b – 2 M; c – 3 M; d – 4 M; e – 5 M.
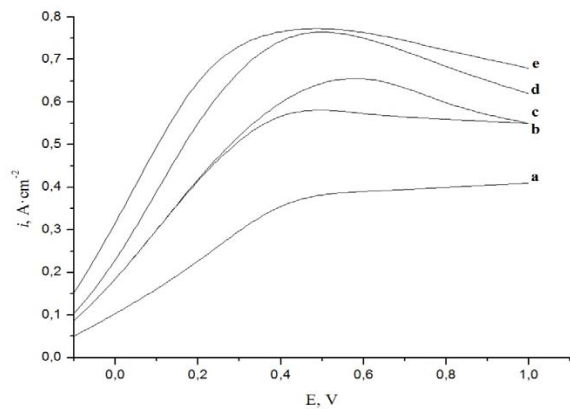
Fig. 4. Polarization curves of anodic oxidation of tungsten in solutions of ammonium nitrate of various concentrations: a – 1 M; b – 2 M; c – 3 M; d – 4 M; e – 5 M.

Figure 4 shows the polarization curves of anodic oxidation of tungsten in the solution of NH_4NO_3. Curves were shifted to the region of more negative potentials compared with the molybdenum dissolution curves. The largest value of the oxidation current, observed in 4–5 M NH_4NO_3, was 0.7 A·cm^{-2}. As the potential increased, the profile of the tungsten oxidation curve changed: at the potential of -0.30 to 0.50 V, the current rose from zero to the maximum value attained at E = 0.50 V, followed by constant current region. This indicated the formation of oxygen compounds WO_3 (α-phase).

3.4. Calculation of the efficiency coefficient

The obtained data allowed calculating the values of the efficiency coefficient of anodic dissolution of molybdenum in the presence of tungsten at various potentials and different concentrations of water and LiCl using the formula:

$$K_{eff} = i_{Mo}/i_W,$$

where i_{Mo} and i_W are the densities of the currents of anodic dissolution Mo and W, respectively, for the same potentials.

A comparison of the values of the currents of molybdenum and tungsten anodic dissolution showed that the rate of anodic dissolution of molybdenum significantly exceeded that for tungsten. In the case of molybdenum, the dissolution process is limited by diffusion, while for tungsten – by the formation of a passive film on the electrode surface.

The content of water affected the dissolution process differently with increasing potential (Fig. 5). An increase in water content increased the ef-

ficiency coefficient of anodic dissolution of Mo. However, in nitrate solutions, the efficiency coefficient was smaller than for LiCl solutions (Fig. 6–7).
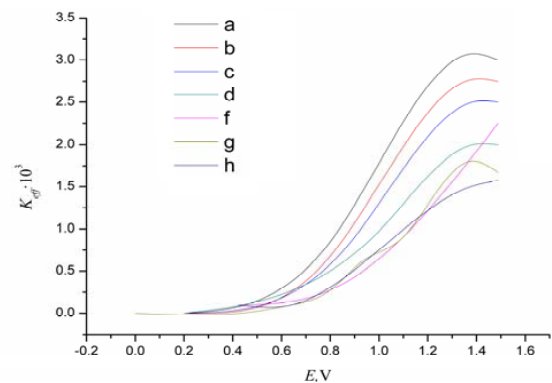

Fig. 5. Dependence of the efficiency of anodic dissolution of molybdenum in 2 M LiCl on the potential at different water content: a – 32.2 M; b – 25.6 M; c – 44.5 M; d – 50.0 M; f – 27.8 M; g – 17.8 M; h – 17.5 M.
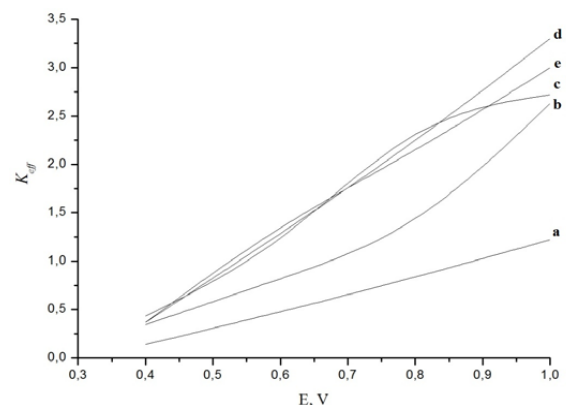

Fig. 6. Dependence of the efficiency of anodic dissolution of molybdenum and tungsten on the potential at different concentrations of NH_4NO_3: a – 1 M; b – 2 M; c – 3 M; d – 4 M; e – 5 M.
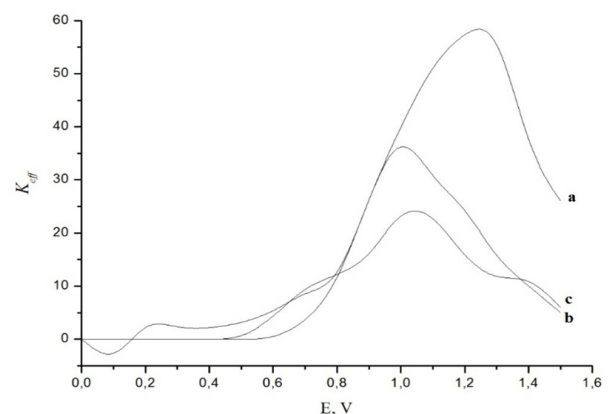

Fig. 7. Dependence of the efficiency of anodic dissolution of molybdenum on the potential at different concentrations of LiCl: a – 0.5 M; b – 0.2 M; c – 0.25 M.

Table 2
Results of analysis of electrolyte solution after electrolysis

Electrolyte composition	Concentration, mg·L^{-1}	
	Mo	W
0.5M LiCl, 32.2 M H$_2$O, 5.2M DMSO	98.247±0.001	0.022±0.001

The process of molybdenum recovery from bi-metallic Mo-W systems was the most effective at 0.5 M LiCl in 5.2 M DMSO, with the water content of 32.2 M in the potential range of 1.0–2.2V. The use of these parameters for the electrolysis resulted in a significant dissolution of molybdenum in comparison with tungsten, and this concentration range was most suitable for carrying out selective dissolution (Table 2). Thus, in 0.5 M LiCl electrolyte, the concentration of molybdenum transferred to the solution was ~ 4000 times higher than the concentration of tungsten.

Considering the nitrate solutions, Table 3 presents the comparative data on the effect of the electrolyte composition and pH on the dissolution of molybdenum and tungsten. The dissolution of Mo occurred in all the electrolytes studied. However, the highest dissolution rate was achieved in ammonium nitrate at pH=4–5. The product of metal oxidation in the nitrate medium was ammonium molybdate, followed by the formation of ammonium paramolybdate. This commercial product can be obtained in one stage, which will have a significant benefit in the production process.

Dissolution of tungsten was not observed at pH=4–5. Tungsten was oxidized only in alkaline media, and its dissolution rate was commensurable with this of molybdenum. This is a significant difference in the electrochemical behavior of molybdenum and tungsten, which can be used to select the condition for selective extraction.

Table 3
The process of anodic oxidation of molybdenum and tungsten in electrolytes of various composition[a]

Concentration of the electrolyte, M	Composition	Molybdenum			Tungsten		
		E_{ip},V	i_p, A·cm^{-2}	V, g·cm^{-2}·h^{-1}	E_{ip},V	i_p, A·cm^{-2}	V, g·cm^{-2}·h^{-1}
1	NH$_4$NO$_3$ pH=4–6	1.2$^+$	0.5	0.65	-	-	-
2		1.2$^+$	0.9	0.95		-	-
3		1.2$^+$	1.4	1.14	-	-	-
4		1.2$^+$	1.6	1.26	-	-	-
5		1.2$^+$	2.0	1.30	-	-	-
1	NH$_4$NO$_3$ pH=10	0.9	0.2	-	0.4	0.4	0.2
2		-	-	-	0.4	0.6	0.5
3		0.9	0.5	0.40	0.4	0.8	0.6
4		-	-	-	0.5	0.7	0.6
5		1.0	0.7	0.41	0.4	0.8	05

[a] The anodic oxidation of molybdenum in all electrolytes resulted in the formation of dark oxide film on the surface of the electrode (anode). E_{ip} is the potential corresponding to the region of the limiting current, i_p is the limiting current density, V – the rate of anodic dissolution of the metal. Conditions under which the limiting current was not observed are marked with "+". In this case, the values of the current density for certain values of the potential are given in the column "i_p".

4. Conclusions

Based on the analysis of the polarization curves of anodic oxidation, it was established that the most efficient extraction of molybdenum from bi-metallic Mo-W systems occurs in the electrolyte with composition of 0.5 M LiCl; 5.2 M DMSO; 32.2 M H$_2$O in the potential range of 1–2.2 V. The ratio of the rates of anodic dissolution of Mo and W was 4000:1, which made it possible to use the

proposed solution as an electrolyte for the selective dissolution of molybdenum in the presence of tungsten (K_{eff} = 4000). The proposed method increases significantly the selectivity of molybdenum dissolution, improves working conditions and simplifies the process.

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