Electrodeposition of molybdenum oxides from weakly alkaline ammonia-molybdate electrolytes

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Electrochemical deposition is a promising method for the production of thin and dense MoO_x coatings, employed as catalysts, selective solar absorbers and gas sensors. This work aims to investigate the processes of electrodeposition of molybdenum oxides from alkaline baths and to characterize their chemical composition, electrical and electrochemical properties. For the purpose, Mo oxides were deposited galvanostatically on Al substrates, coated by Zn to improve coating adhesion. The chemical composition of the molybdenum oxide surfaces was characterized by X-ray photoelectron spectroscopy (XPS). The stoichiometry of the oxide surfaces, their degree of hydroxylation, and the atomic O/Mo ratio were estimated. The electrical and electrochemical properties of the obtained oxides were characterized by voltammetry and electrochemical impedance spectra in a borate buffer solution. Tentative conclusions on the influence of the deposition current density and the pH of the electrolyte on the composition, electrical and electrochemical properties of the oxides are drawn on the basis of the obtained results.

Keywords: cathodic deposition, molybdenum oxides, alkaline electrolytes, electrochemical impedance spectroscopy

INTRODUCTION

Electric, photoelectric, and electrochemical properties of molybdenum oxides are of primary significancefor a number of important technical applications in such materials as catalysts, selective solar absorbers, and gas sensors [1 – 3]. One of the promising methods to produce molybdenum oxides with optimal properties is their cathodic deposition. Electrodeposition of Mo oxides from acidic electrolytes has been widely investigated [4 – 9], whereas data concerning such deposition from neutral and alkaline media remains relatively scarce [10 – 13]. Alkaline electrolytes are supposed to enable stabilization of molybdenum oxides of mixed valency. This work aims to investigate the processes of electrodeposition of mixed-valency molybdenum oxides from alkaline baths and to characterize their chemical composition, electrical and electrochemical properties.

EXPERIMENTAL METHODS

Mo oxides were deposited on Al substrates (99.99%, working area of 8 cm^2), chemically coated by Zn to improve the adhesion of the films. A conventional three-electrode cell was used with a platinum mesh as a counter electrode, located symmetrically around the working electrode, and a Ag/AgCl/3M KCl electrode as a reference (E =

0.201 V *vs*. SHE). The pH of the electrolytes (8-10) was adjusted by using an NH_3-CH_3COONH_4 buffer, the electroactive salt being $(NH_4)_6Mo_7O_{24}.4H_2O$ (20 g l^{-1}). Electrodeposition was conducted in a galvanostatic regime at a room temperature (22±2 ºC). The range of current densities was between 0.05 and 0.4 A dm^{-2}. The current efficiency of film formation was estimated by a gravimetric method. Steady-state current-potential curves and electrochemical impedance spectra (frequency range of 0.01 Hz – 10 kHz, a.c. amplitude of 10 mV rms) were measured by an Autolab PGSTAT 30/FRA2 apparatus, driven by GPES and FRA software (Eco Chemie, Netherlands). The chemical composition of the obtained molybdenum oxide surfaces was characterized by X-ray photoelectron spectroscopy (XPS). An Escalab II spectrometer with a monochromated Al Kα radiation (1486.6 eV) was used. The analyser pass energy was 100 eV for the survey spectra and 20 eV for the high resolution spectra, the photoelectron take-off angle being 90º.

RESULTS AND DISCUSSION

The dependence of the coating weight on the current density in electrolytes with pH 8-10 is presented in Fig.1. The deposition was conducted up to a constant charge of Q = 240 C dm^2. The weight of the coating decreases about 2.5 times with the increase in the current density of the pH 10 electrolyte. On the other hand, the reduction of
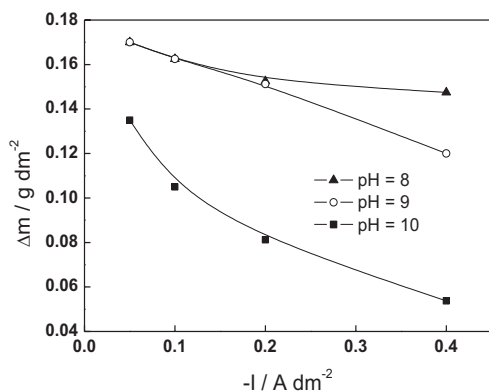

Fig.1 Dependence of the mass of the coating on current density in electrolytes with different pH.

weight in the pH 9 solution is from 0.17 to 0.12 g dm^{-2}, being even smaller in the pH 8 electrolyte. The influence of the deposition current density on the weight of the coatings can be explained by the occurrence of two parallel reactions, the molybdenum oxide formation and the hydrogen evolution. It can be concluded that the highest current efficiency is achieved in the pH 8 electrolyte at current densities of 0.05 – 0.2 A dm^{-2}.
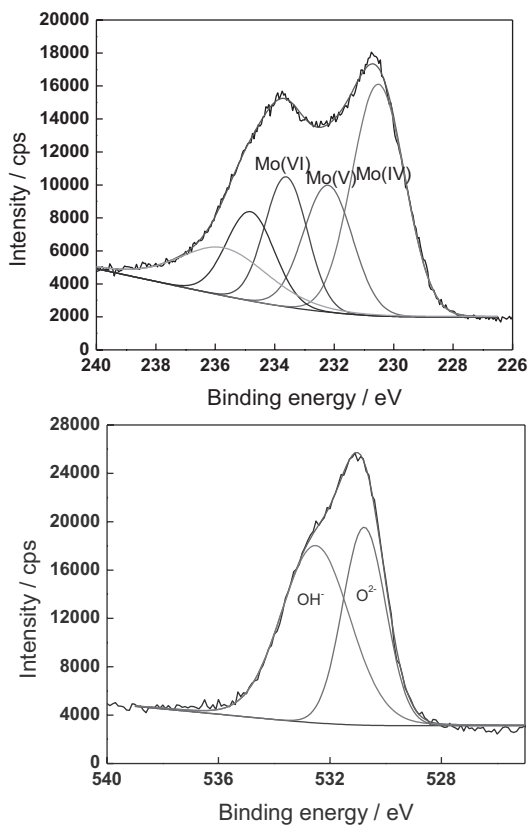

Fig. 2 Detailed Mo3d and O1s XPS spectra at surface of the film formed by cathodic deposition in a pH 8 electrolyte.
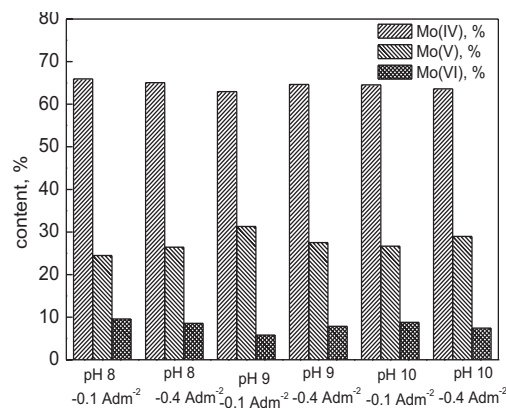
Fig. 3 Distribution of the valence states of Mo as depending on electrolyte pH and current density.

The chemical composition of the obtained molybdenum oxide surfaces was characterized by X-ray photoelectron spectroscopy (XPS). As an example, the Mo3d and O1s spectra for oxides, formed in an electrolyte with pH 8 at current density of –0.1 A dm^{-2}. are shown in Fig. 2. The results indicate the formation of mixed valency oxides. containing Mo (IV), Mo (V), and Mo (VI).
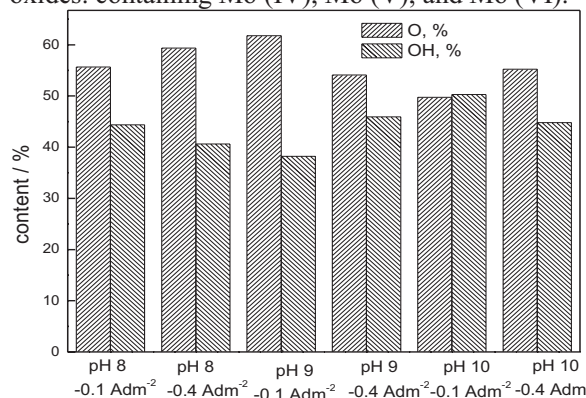

Fig. 4 Percentages of oxygen bound as oxide and hydroxide as depending on pH and current density.

The surface fractions of Mo different valency statesfor films, obtained in all the studied electrolytes, are summarized in Fig. 3. The films consist mainly of Mo (IV) (65%) and Mo (V) (25–30%). The proportion of the valency states of Mo in the film was not found to depend neither on the pH nor on the current density within the experimental error.

The surface concentrations of oxygen, bound as oxide and hydroxide and calculated from the O1s spectra for the three electrolytes are presented in Fig. 4 as a function of the deposition current density. The presence of a significant amount of hydroxide (40%) for the films, formed in the three electrolytes, is an indication for a hydroxylated surface. The films, formed in the electrolyte of pH

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8 at both current densities, and the film, formed in the solution of pH 9 at the lower current density, are less hydroxylated than those, formed in the pH 10 solution. The values of the O / Mo ratio vary between 2.5 and 3.2, which is another indication that the Mo in the surface film has a mixed valence. In general, the surface film can be denoted as $MoO_x(OH)_y$ in accordance with the hypotheses of other authors [14].

The electrochemical stability of the obtained oxides with respect to oxidation was characterized by measuring the steady-state current vs. the potential curves in an inert borate buffer solution (pH 7.3). The current vs. the potential curves of $MoO_x(OH)_y$, deposited at a current density of 0.2 A dm^{-2}, are presented in Fig.5. The open circuit potential (OCP) of $MoO_x(OH)_y$ electrode depends slightly on the pH of the film formation and is located in the range of –0.87/– 0.85 V.
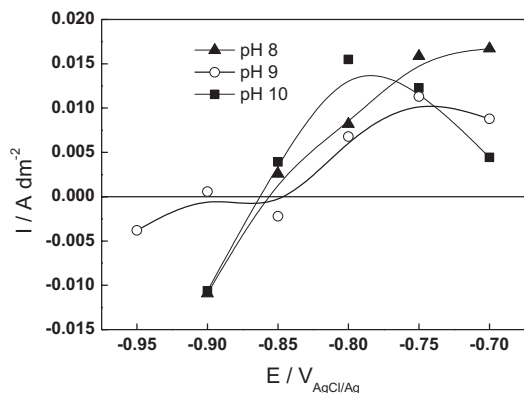

Fig. 5 Current - potential curves of molybdenum oxides in a pH 7.3 borate buffer as dependence on the pH of the deposition electrolyte at a current density 0.2 A dm^{-2}.

At potentials less negative than the OCP, the current density reaches a maximum. This maximum is observed at the potential which is more negative. It is more negative at higher pH values of the forming electrolyte. The current-potential curves in this area are similar due to the oxidation of Mo(IV) in the film to a higher valency.

Fig. 6 shows the impedance spectra of $MoO_x(OH)_y$ films, obtained in the studied electrolytes at different current densities, measured at the rest potential in a pH 7.3 borate buffer The values of the impedance magnitude at low frequencies are in the range of 20–100 Ωcm^2, i.e the films are fairly ionically conductive, and the impedance spectra are most likely dominated by the processes at the film/electrolyte interface. The impedance diagrams do not significantly depend on either the deposition current density or on the pH of the electrolyte, in

accordance with the fact that the films have almost identical chemical composition.

Two to three time constants are observed in the impedance spectra, the corresponding semicircles in the impedance plane being significantly depressed. This feature can be taken as an
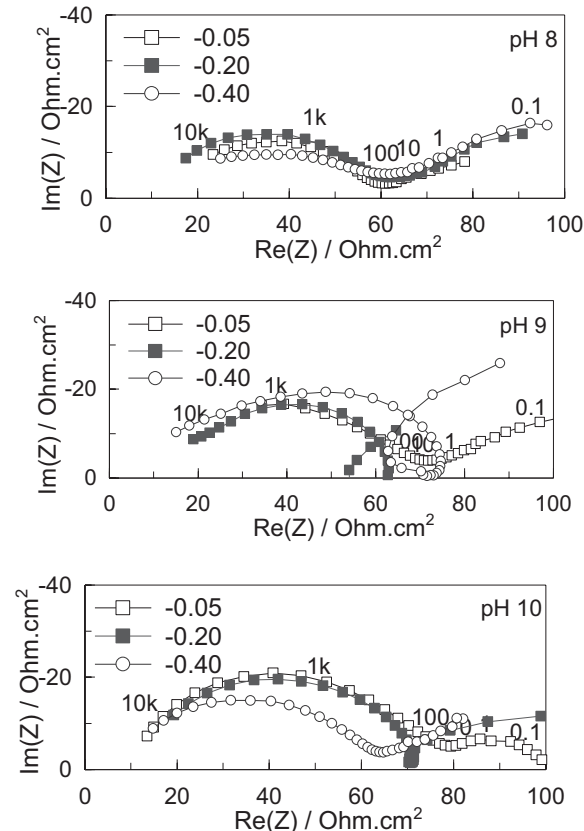
Fig. 6 Impedance spectra of $MoO_x(OH)_y$ in a pH 7.3 borate buffer at open circuit as depending on the pH of the deposition electrolyte at different current densities (A dm^{-2}).

indication for the geometric and/or energetic heterogeneity of the film/solution interface. The processes that take place in an open circuit in an inert electrolyte can be interpreted, due to the oxidation of Mo (IV), to higher valencies coupled with water reduction. Initial estimates of the capacitance of the film from the high-frequency semicircles indicate the presence of a thin layer with semiconductor properties [14, 15]. At lower frequencies, transport impedance is detected, most probably due to the transfer of protons and electrons through the mixed-conducting oxide.

CONCLUSIONS

Cathodic electrodeposition of molybdenum oxides on Zn-coated Al from alkaline electrolytes with different pH and current densities was studied in this work. The electrochemical stability of the

obtained oxides was characterized by voltammetry and electrochemical impedance spectroscopy in a plain borate buffer solution. The chemical composition of the obtained molybdenum oxide surfaces was assessed by X-ray photoelectron spectroscopy (XPS). The following main conclusions can be drawn from the obtained results:

• The charge efficiency for cathodic deposition of molybdenum oxide from alkaline heptamolybdate baths is the highest at pH 8. The effect of the deposition current density on the charge efficiency is accordingly the smallest in electrolytes with this pH value.

• The cathodic deposit can be described as a layer with a good electronic and ionic conductivity and of typical composition of $MoO_x(OH)_y$.

• The electrodeposition regime (pH of the electrolyte and current density) does not influence substantially neither the composition of the coating nor its electric properties.

• To clarify the mechanism of modification of oxides during anodic polarization, additional studies in a wider range of potentials, combined with the determination of the surface chemical composition, are needed.

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ЕЛЕКТРОХИМИЧНО ОТЛАГАНЕ НА МОЛИБДЕНОВИ ОКСИДИ ИЗ СЛАБО АЛКАЛНИ ЕЛЕКТРОЛИТИ, СЪДЪРЖАЩИ АМОНИЕВ МОЛИБДАТ

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(Резюме)

Електрохимичното отлагане е един от най-обещаващите методи за получаване на тънки и плътни MoO_x покрития, които намират приложение като катализатори, селективни слънчеви абсорбери и газови сензори. Настоящата работа има за цел да изследва процесите на електроотлагане на молибденови оксиди от алкални електролити, както и да характеризира техния химичен състав, електрични и електрохимични свойства. За целта, молибденови оксиди са отлагани галваностатично върху алуминиеви субстрати, покрити с контактно отложен Zn за подобряване на адхезията. Химичният състав на получените молибденово-оксидни повърхности е характеризиран чрез рентгенова фотоелектронна спектроскопия (XPS). Определени са стехиометрията на оксидните повърхности, тяхната степен на хидроксилиране и съотношението О/Мо. Електричните и електрохимични свойства на филмите са изследвани чрез волтаметрия и електрохимична импедансна спектроскопия в боратен буферен разтвор. На базата на получените резултати са направени предварителни заключения за влиянието на плътността на тока и рН на електролита върху химичния състав, електричните и електрохимични свойства на оксидите.