

This is the peer reviewed version of the following article: Thomas J. Morley, Leah Penner, Paul Schaffer, Thomas J. Ruth, François Bénard, Edouard Asselin, The deposition of smooth metallic molybdenum from aqueous electrolytes containing molybdate ions, *Electrochemistry Communications*, Volume 15, Issue 1, 2012, Pages 78-80, ISSN 1388-2481, which has been published in final form at <https://doi.org/10.1016/j.elecom.2011.11.026>. This article may be used for non-commercial purposes in accordance with Elsevier terms and conditions for use of self-archived versions.

## **The Deposition of Smooth Metallic Molybdenum from Aqueous Electrolytes Containing Molybdate ions**

Thomas J. Morley <sup>a</sup>, Leah Penner <sup>b</sup>, Paul Schaffer <sup>a</sup>, Thomas J. Ruth <sup>a, c</sup>, François Bénard <sup>c</sup>,  
Edouard Asselin <sup>b</sup>

<sup>a</sup> Nuclear Medicine, TRIUMF, 4004 Wesbrook Mall, Vancouver, BC, Canada  
V6S 2L9

<sup>b</sup> Materials Engineering, University of British Columbia, 309-6350 Stores Road,  
Vancouver, BC, Canada V6T 1Z4

<sup>c</sup> Molecular Oncology, British Columbia Cancer Agency, 601 West 10th Avenue,  
Vancouver, BC, Canada V5Z 1L3

### **Abstract**

This paper details the electrodeposition of metallic molybdenum from an aqueous electrolyte containing molybdate ions. The deposition is performed in an acetate bath that contains a high (up to 10 M) concentration of acetate. The molybdenum deposits are thick (up to 20

μm), adherent and were characterized by XRD and XPS analysis. The deposition is inefficient, with most of the current (up to 99%) used in the electrolysis of water to generate hydrogen. The effect of acetate concentration, pH, additives and current on the deposition efficiency and physical properties of the molybdenum deposit were investigated and optimized to obtain smooth, adherent coatings.

## 1 Introduction

The unique properties of molybdenum are often exploited as coatings to increase the thermal and wear resistance of materials. [1] They are most often manufactured by sintering, pressing or spraying molybdenum powder at elevated temperature, rather than electroplating. [2, 3] The dearth of reports describing the electrodeposition of molybdenum is most likely due to its highly oxophilic nature and stability of its oxides, especially in water. Attempts to electrochemically reduce and deposit molybdenum from molybdate ( $\text{MoO}_4^{2-}$ ) ions produces either a poorly adherent mixed oxide, [4–6] or a thin ( $<0.1 \mu\text{m}$ ) metallic film. [7] Thicker (up to  $3 \mu\text{m}$ ) metallic molybdenum has been deposited in the presence of fluoride ions, [8] and even thicker ( $>3 \mu\text{m}$ ) coatings can be co-deposited in the presence of one of the iron-group metals (Ni, [9] Co [10] and Fe [11]) to give an alloy. However these alloys generally contain less than 50% molybdenum and may not be suitable for applications requiring pure molybdenum.

Thick ( $\leq 500 \mu\text{m}$ ) metallic molybdenum deposits, via electrodeposition, have been reported by using non-aqueous electrolytes. [12, 13] Such processes utilize a molten chloride salt or oxide melt electrolyte, generated by melting together the molybdenum salt with one or more alkali salts at high temperatures ( $>800 \text{ }^\circ\text{C}$ ). However, the high temperatures and water-sensitive molybdenum salts require significantly more complex and specialized equipment. The

concept of bringing together the benefits of both aqueous and molten salt electrolytes by employing a saturated aqueous salt electrolyte has remained largely unexplored. To our knowledge only one report details such an approach, [14] and describes a lustrous, white metal, adherent deposit of molybdenum up to 1.5  $\mu\text{m}$  thick from an electrolyte containing molybdates and a high ( $>5$  M) concentration of co-salt.

The current paper describes carefully optimized conditions under which thick ( $>5$   $\mu\text{m}$ ) metallic deposits of molybdenum can be obtained from aqueous molybdate containing electrolytes. The deposition efficiency and physical characteristics of the deposit were found to be highly dependent on the pH of the electrolyte, yielding a non-crystalline molybdenum metal layer, completely reduced from its oxide form(s).

## **2 Experimental**

In a typical experiment, potassium acetate (25 g, 255 mmol), ammonium acetate (20 g, 260 mmol) and ammonium heptamolybdate (250 mg, 1.0 mmol) were dissolved in water (25 ml) contained in a jacketed beaker, preheated to 30  $^{\circ}\text{C}$  and stirred at 800 rpm. A typical electrolyte has a viscosity of 11.4 mPa. The pH of the solution was adjusted with either concentrated acetic acid or ammonium hydroxide. A platinum gauze anode (70  $\times$  50 mm) was held parallel, at a distance of 40 mm, to a pre-cleaned (by 1200 grade SiC paper, acetone and water) copper cathode (with 32  $\times$  11 mm working surface area). The cathode was held in place using a PTFE holder that exposes only one face to the electrolyte. The electrodes were connected to a potentiostat (Princeton Applied Research model 273A). After 1 h the current was stopped, the cathode removed, washed with distilled water, dried under vacuum, weighed and characterized using the techniques outlined below. Optical microscopy was performed using a Nikon Eclipse MA200. SEM and EDX spectra

were obtained using a Hitachi S3000-N microscope. XRD spectra were obtained using a Bruker D8 powder diffractometer and XPS spectra were obtained using an Omicron and Leybold Max200 spectrometer.

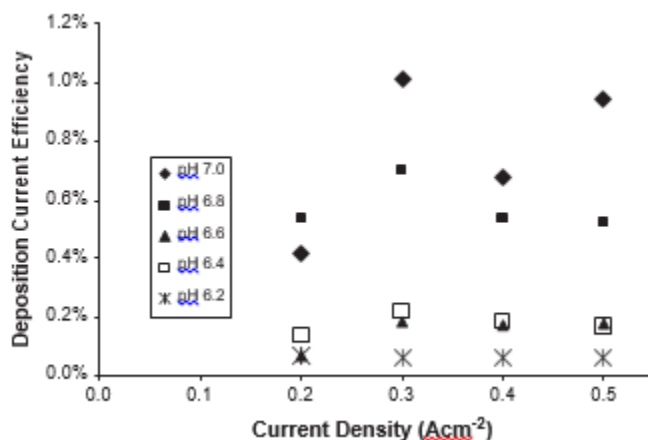


Fig. 1. Effect of pH (6.2–7.0) and current density (0.2–0.5 Acm<sup>-2</sup>) on d.c.e over a one hour experiment.

### 3 Results and Discussion

#### 3.1 Optimization of Bath and Electrode Composition

With the aim of developing an electrolyte that would promote deposition of thick coatings of molybdenum, a series of baths were tested that contained a high (up to 10 M) concentration of acetate, formate, phosphate or chloride salts at ambient temperature and neutral pH. Of these initial trials, only the acetate baths resulted in thicker (>1 μm), lustrous deposits, a result consistent with the only other previous report. [14] The molybdenum deposit obtained

from this process (>99.9% Mo by EDX analysis) had a nodular, non-smooth surface (see Fig. 2). Metallic deposits were obtained using molybdenum trioxide and sodium, potassium and ammonium molybdates interchangeably, without any noticeable difference in the deposition. Molybdate concentrations were varied between 1 and 100 mM, with no effect on deposition, suggesting that the electrolyte is already saturated. Stirring rate did not affect molybdenum deposition with the large volumes of hydrogen generated likely dominating mass transport.

The electrodeposition does not appear to be dependent on the cathode material and thick molybdenum deposits were obtained routinely on copper, steel, iron, nickel, molybdenum, tantalum and rhodium. With an aluminum cathode, a significant amount of degradation was noted during the electrodeposition. Platinum was found to be the optimum anode for the electrolysis, since graphite anodes degraded during the process.

### ***3.2 Effect of current density and pH on deposit***

The composition of the electrolyte and deposition conditions was optimized towards maximizing thickness and density of the deposit, while maintaining structural stability and bonding to the cathode. Electrolyte pH was investigated, and it was found that the pH in the cathodic compartment of the cell increased dramatically over time due to the hydrogen evolution reaction (HER). Both electrodes were placed in a single cell to mitigate this effect and the pH of the electrolyte was found to be stable ( $\pm 0.2$ ) throughout the course of the experiment (2 h). Below pH 5.5 no metallic deposit was obtained, while above pH 8.5 the deposits became less compact, lustrous and adhesive to the cathode. A detailed study of the effect of pH and current density on the deposition current efficiency (d.c.e.) is shown in Fig. 1.

The efficiency of molybdenum deposition is extremely low in all cases, with most (> 98%) of the

available current being used in the HER, due to the reduction potential of molybdenum metal being lower than that of water. [15] However, other metals have a lower reduction potential than molybdenum (i.e. Zn, Ni, Mn) and are routinely electroplated from aqueous electrolytes. Thus, the observed low efficiency may be due to molybdenum participating as a catalyst for water reduction. [16] We hypothesize that once a thin metal film has been deposited, hydrogen production is accelerated by molybdenum itself, diverting almost all the cell current through this pathway and away from further molybdate reduction.

The microstructure of the deposit was also heavily influenced by the pH of the electrolyte. Smooth, dense deposits were obtained at pH 6.6 and below, while nodular, poorly adhesive deposits were obtained at pH 6.8 and above. The poor adherence is a result of the molybdenum layer peeling away from the cathode and indicates the presence of tensile stress within the deposit. The smoother, adherent deposit obtained below pH 6.6 may be a result of its slower growth rate. The addition of low concentrations of bone glue (less than 2 mg/L) to electrolytes with a pH above 6.8 resulted in a slightly smoother deposit.

The significant effect of electrolyte pH is unexpected, since the local pH at the cathode would normally be higher than bulk, due to the HER. However, the buffering effect of concentrated ammonium acetate and the significant mass transfer at the cathode, due to the large volumes of hydrogen produced, may lead to little change in pH at this surface. The observed increase in the d.c.e would then be a result of the suppression of the HER, since the potential for the HER decreases as pH is increased.

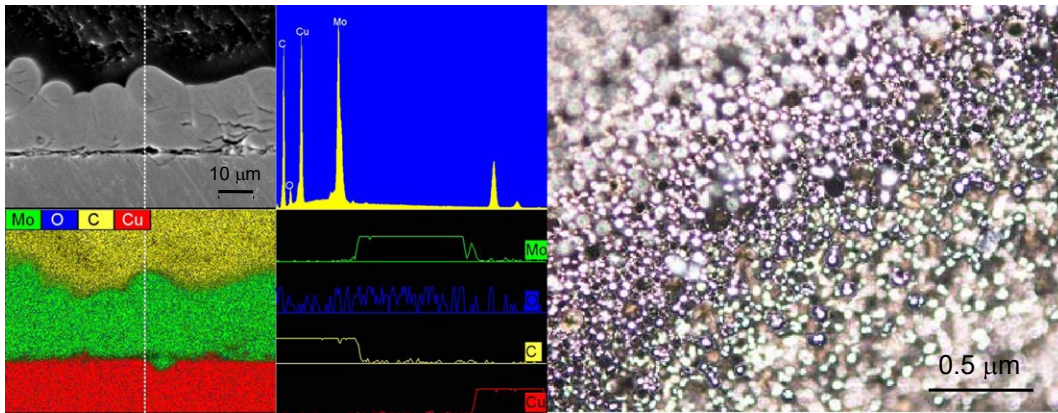


Fig. 2. Deposit obtained from an electrolyte containing ammonium molybdate (10 mM) and acetate (8 M) at pH 7.0 and  $0.4 \text{ A cm}^{-2}$  after 10 h. Left — SEM/EDX analysis of a molybdenum deposit on copper, cross sectioned into epoxy resin. Right - by optical microscopy ( $50 \times$  magnification).

Table 1 Binding energies (eV) of Mo3d orbitals obtained by XPS in comparison to known references. <sup>a</sup>[20], <sup>b</sup>[19].

	This work	References				
		Graphite <sup>a</sup>	Mo(0) <sup>b</sup>	Mo(III) <sup>b</sup>	Mo(IV) <sup>b</sup>	Mo(VI) <sup>b</sup>
<b>C1s</b>	285.0	284.2	—	—	—	—
<b>Mo3d3/2</b>	231.7	—	230.9	232.9	233.4	235.1
<b>Mo3d5/2</b>	228.5	—	227.7	229.7	230.2	231.9

### 3.3. Effect of Acetate Concentration

The acetate concentration in the electrolyte affects both the deposition rate and the microstructure of the deposit. In electrolytes at pH 7.2 metallic deposits were obtained in the range of 1.6:1 to

3.5:1 mole ratios of water to acetate. A mixture of colored oxides was obtained in the range 3.5:1 to 4.5:1, with ratios above 4.5:1 only black oxide deposits were obtained. The optimal ratio was found to be 1.9:1, which yielded a smooth dense molybdenum metal deposit. By decreasing the acetate concentration beyond this value a lower d.c.e and a less adhesive deposit was obtained.

At high acetate concentrations water may be less available due to solvation of the salts. The water activity in a typical electrolyte used here was calculated to be 0.125. [17] If the water is not as available for reduction to hydrogen, there may be a decreased flux through the HER and a concurrent increase in charge available for reduction of molybdate, increasing the deposition rate. A second effect of a high acetate concentration could be the stabilization of transient, lower valence molybdenum species as it is reduced. [14]

### ***3.4 Analysis of Deposit***

The molybdenum deposits were characterized by EDX, XRD and XPS. EDX (Fig. 2) suggests that the deposit is predominantly molybdenum, however this does not rule out the presence of a molybdenum oxide. XRD analysis of the deposit failed to yield any peaks, suggesting that the deposit is amorphous or that the grains are nanometric. [18] The XPS analysis results are shown in Table 1. The C1s binding energy obtained is offset from literature data by 0.8 eV, which when subtracted from the Mo3d data gives binding energies identical to those reported for reduced Mo(0) metal. [19] This suggests that it is reduced molybdenum metal that is deposited and not an oxide.

## **4 Conclusions**

Herein, we have demonstrated that thick, adherent deposits of metallic molybdenum can be



deposited from aqueous electrolytes containing molybdate ions. The electrolyte requires a high concentration of acetate ions, with the pH of the electrolyte having a dramatic effect on deposition efficiency and deposit microstructure. Smooth deposits were obtained in baths with a pH of less than 6.6, with a water to acetate ratio of 1.9 to 1. The deposit is amorphous in nature and consists of completely reduced molybdenum metal with very little or no oxygen detected. Deposition of molybdenum metal using an aqueous-based electrolyte that uses economical, readily available molybdate substrates significantly reduces the complexity of forming molybdenum coatings, and may find an application in wear resistance of materials.

### **Acknowledgements**

This work was supported by grants RMIPJ 389546–09 from the Natural Sciences and Engineering Research Council of Canada and MIS-100934 from the Canadian Institutes of Health Research. Additional financial support was provided by TRIUMF and Natural Resources Canada.

### **References**

- [1] M. Laribi, A.B. Vannes, D. Treheux, Study of mechanical behavior of molybdenum coating using sliding wear and impact tests, *Wear* 262 (2007) 1330–1336.
- [2] H.S. Huang, K.S. Hwang, Deoxidation of molybdenum during vacuum sintering, *Metallurgical and Materials Transactions A* 33 (2002) 657–664.
- [3] F. Habashi (Ed.), *Handbook of Extractive Metallurgy*, WILEY-VCH, Heidelberg, Germany, 1997.
- [4] M.P. Zach, K.H. Ng, R.M. Penner, Molybdenum nanowires by electrodeposition, *Science* 290 (2000) 2120–2123.
- [5] R.S. Patil, M.D. Uplane, P.S. Patil, Structural and optical properties of electrodeposited molybdenum oxide thin films, *Applied Surface Science* 252 (2006) 8050–8056.
- [6] V.M. Nagirnyi, R.D. Apostolova, E.M. Shembel, Electrodeposition of molybdenum oxide and its structural characteristics, *Russian Journal of Applied Chemistry* 79 (2006) 1438–1442.

- [7] S. Daolio, M. Fleischmann, D. Pletcher, A Study of the Deposition of Molybdenum at a Vitreous Carbon Cathode from an Aqueous Citrate Bath, *Journal of Electroanalytical Chemistry* 130 (1981) 269–275.
- [8] N.D. Ivanova, S.V. Ivanov, E.I. Boldyrev, O.A. Stadnik, Electrodeposition of metal molybdenum from electrolytes containing hydrofluoric acid, *Protection of Metals* 42 (2006) 354–358.
- [9] M.P. Pavlov, N.V. Morozova, V.N. Kudryavtsev, Electrodeposition of nickel- molybdenum alloys from ammonium citrate baths containing intermediate valence molybdenum compounds, *Protection of Metals* 43 (2007) 459–464.
- [10] E. Pellicer, E. Gomez, E. Valles, Use of the reverse pulse plating method to improve the properties of cobalt-molybdenum electrodeposits, *Surface and Coatings Technology* 201 (2006) 2351–2357.
- [11] N.R. Elezovic, V.D. Jovic, N.V. Krstajic, Kinetics of the HER on Fe-Mo film deposited on mild steel support in alkaline solution, *Electrochimica Acta* 50 (2005) 5594–5601.
- [12] N. Ene, C. Donath, Texture of electrolytic Mo deposition from molten alkali halide, *Journal of Optoelectronics and Advanced Materials* 8 (2006) 708–711.
- [13] G.J. Kipouros, D.R. Sadoway, The Electrodeposition of Improved Molybdenum Coatings from Molten-Salts by the use of Electrolyte Additives, *Journal of Applied Electrochemistry* 18 (1988) 823–830.
- [14] M.J. Ksycski, L.F. Yntema, The Electrodeposition of Molybdenum from Aqueous Solutions, *Journal of the Electrochemical Society* 96 (1949) 48–56.
- [15] M. Dekker, *Standard Potentials in Aqueous Solution*, IUPAC, New York, USA, 1985.
- [16] H.I. Karunadasa, C.J. Chang, J.R. Long, A molecular molybdenum-oxo catalyst for generating hydrogen from water, *Nature* 464 (2010) 1329–1333.
- [17] O. Weres, L. Tsao, Activity of Water Mixed with Molten-Salts at 317-Degrees-C, *Journal of Physical Chemistry* 90 (1986) 3014–3018.
- [18] O. Younes, L. Zhu, Y. Rosenberg, Y. Shacham-Diamand, E. Giladi, Electroplating of amorphous thin films of tungsten/nickel alloys, *Langmuir* 17 (2001) 8270–8275.
- [19] C.R. Clayton, Y.C. Lu, A Bipolar Model of the Passivity of Stainless-Steel - the Role of Mo

Addition, *Journal of the Electrochemical Society* 133 (1986) 2465–2473.

[20]C. Hinnen, D. Imbert, J.M. Siffre, P. Marcus, An In-Situ XPS Study of Sputter- Deposited Aluminum Thin-Films on Graphite, *Applied Surface Science* 78 (1994) 219–231.