

# Characterization of Electrodeposited Molybdenum Black Surface Coatings

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Molybdenum black has been produced in thin coating form (3  $\mu\text{m}$ ) on prepared aluminium surfaces by the method of electrodeposition. The microstructure of the coating has been identified as one of flat irregular platelets belonging to a material which can be described as quasi-amorphous. Its chemical composition is 90 wt%  $\text{MoO}_2 \cdot 2 \text{H}_2\text{O}$  and 10 wt%  $\text{Ni}(\text{OH})_2$ . Mo-black appears to be a good absorber of solar radiation. Absorbance values as high as 93% have been measured for the visible region of the solar energy spectrum. It has been identified that the coating is of semiconducting nature and that the dominant conduction mechanism is the Schottky emission mechanism. Photoelectrochemical measurements have finally provided evidence for photon-induced electrochemical processes at the Mo-black electrodes.

**Key words:** Molybdenum black, Electrodeposition, Amorphous semiconductor, Schottky emission.

## Introduction

The search for an efficient conversion of solar energy into other useful forms such as thermal, electrical or chemical energy has become one of the most important challenges of future research and technology. To achieve any of these conversions, certain devices are needed and their fabrication necessitates the use of special materials.

In the case of a direct solar-electrical conversion, these materials are initially required to exhibit semi-conducting behaviour and to absorb most of the incident solar radiation. One area of solar energy research is associated with the possible discovery of such materials, and a common initial approach is to establish a standard procedure of material preparation. Among other known methods of material preparation, electrodeposition is often preferred because of its simplicity, ease of use and low cost.

The aim of this work has been to examine the optical, electrical, microstructural and photoelectrochemical properties of electrodeposited molybdenum black, a material which was first discovered by Hoffman and Hull [1].

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## Experimental

### *Coating Preparation, Microstructure and Composition*

Mo-black has been produced by cathodic electrodeposition on prepared surfaces of aluminium from a solution of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$  [1]. The plating equipment consisted of two lead anodes on either side of the specimen, a low voltage variable power supply, a smoothing unit, a Rheostat and a Philips pH-meter. All preparations were carried out under thermostatically controlled conditions.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffractometry, x-ray photoelectron spectroscopy, chemical analysis and x-ray microanalysis were employed to examine the microstructure of the coatings and identify their chemical composition. The instrumentation used belonged to the Experimental Techniques Centre and Industrial Chemistry Dept. of Brunel University in London.

### *Optical Measurements*

Measurements of diffuse reflectance over the wavelength range 0.34–0.8  $\mu\text{m}$  were made with an Optica CF4NJ Spectrometer equipped with an integrating sphere. Measurements of specular reflectance over the same range were made using an Edwards modulated

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beam photometer. These were combined to give values of total reflectance over the same range. The latter have been compared with total reflectance measurements over the wavelength range 0.34–2.1  $\mu\text{m}$  made at the U.K. National Physical Laboratory.

#### *Electrical Measurements*

These were made in a  $4 \times 10^{-5}$  Torr vacuum. A specimen of Mo-black, coated on both sides of aluminium, was positioned vertically inside the vacuum test chamber and in between two tungsten heating filaments. Mica was used to insulate the specimen from all conducting surroundings. Silver paint was used to provide the electrical contacts on the Mo-black coating and on the aluminium substrate. A PK 1 type patch thermocouple supplied by Comark was also mounted on the coating. The vacuum system used was an Edwards high vacuum speedivac model 12E7/114 unit. A Coutant Electronics power supply was used to provide the specimen with voltage differences in the 1–30 Volt range. The coating temperature measuring unit was a Comark electronic thermometer connected to the thermocouple. The current flowing between the coating and the substrate was measured with a Keithley 610C electrometer, and voltages were measured with a digital voltmeter connected across the coating substrate. Current-voltage characteristics were produced for a constant temperature of 22 °C. Current-temperature characteristics were produced for a constant applied voltage of 10 Volts.

#### *Photoelectrochemical Measurements*

These were made using a standard electrochemical set up which involved a conventional 3 electrode electrochemical glass cell, a DD50SU Sycopel Scientific potentiostat connected to a linear sweep generator, and an X-Y-t-recorder. Platinum foil and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The Mo-black working electrodes were prepared to have an active coating area of about 1  $\text{cm}^2$ . Silver conducting paste was used to provide the electrical contacts, epoxy resin provided the insulation from the electrolyte and a thin glass tube was used to cover the wiring. The electrolyte used was a buffer solution of 0.1 M  $\text{H}_3\text{BO}_3$ , 0.1 M  $\text{Na}_2\text{B}_4\text{O}_7$  and 0.1 M  $\text{NaClO}_4$  (pH = 8). All experiments were performed under nitrogen gas atmosphere for eliminating currents due to oxygen generation. Measurements were made

both in the dark and under illumination from a tungsten-halide lamp (SUN 1000, power 750–1000 W). A 7 cm thick water filter was placed between the lamp and the cell to absorb most of the infrared which would cause a substantial rise in the temperature of the electrolyte.

## **Results and Discussion**

#### *Coating Preparation*

Mo-black can easily be produced by electrodeposition from a bath containing  $30 \text{ g l}^{-1}$   $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  and  $150 \text{ g l}^{-1}$   $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ . Two different processes were used for cleaning the aluminium substrates prior to deposition. One of them involved boiling of the substrates in a  $15 \text{ g l}^{-1}$  sodium carbonate and sodium silicate solution for 8 min, and the other involved immersion in a  $250 \text{ g l}^{-1}$  NaOH solution for 10 min. Uniform, adherent and stable coatings have been produced with bath temperatures in the range 60–65 °C, deposition times of 30 min, and current densities of  $3 \text{ mA cm}^{-2}$ . Coatings were slightly glossy and almost black in appearance.

The NaOH cleaning process prior to deposition has enabled the preparation of stable coatings whilst the sodium carbonate-silicate process was proven inappropriate and has resulted in less stable coatings.

The presence of nickel in the coating ensures better adherence and an almost black colour of Mo-black [1, 2].

#### *Microstructure, Composition and Chemical Stability*

Mo-black coatings have a microstructure of relatively flat irregular platelets separated by large and deep cracks as shown by scanning electron microscopy (Figure 1). This morphology remained essentially the same after immersion of the coatings in electrolytes and upon illumination. However, the width of the cracks was doubled. X-ray diffractometry has revealed an unusual diffraction pattern consisting of only one broad peak at about  $4^\circ\theta$  using Cuka rays with a wavelength of 0.179 nm. This corresponds to a periodic lattice spacing of 1.3 nm and may indicate that some crystalline order exists in one lattice direction. Transmission electron microscopy gave evidence for the formation of polycrystalline regions within the amorphous matrix (Figure 2). Coatings can be described as quasi-amorphous or polycrystalline rather than completely

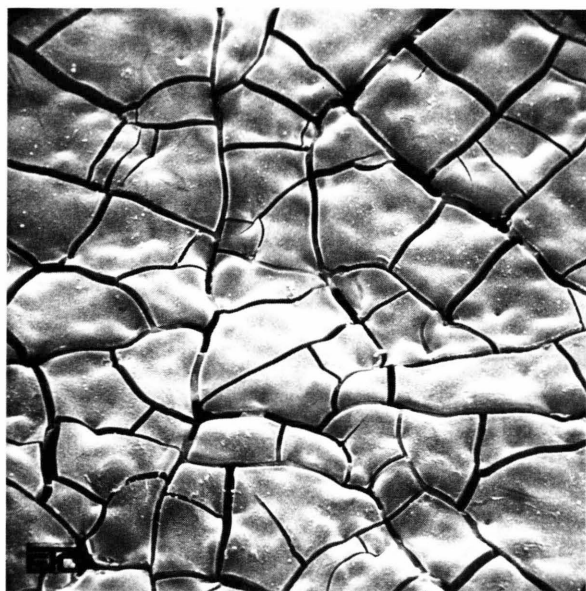


Fig. 1. Scanning electron micrograph of electrodeposited molybdenum black.

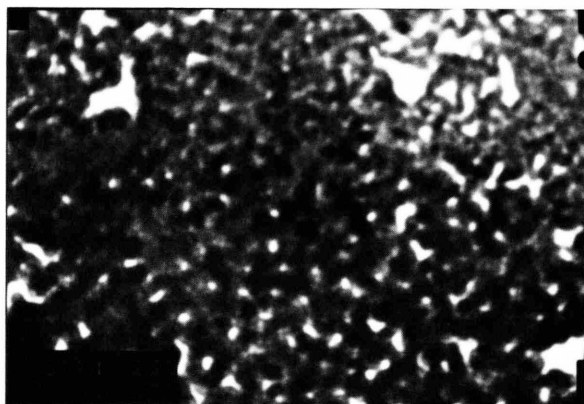


Fig. 2. Transmission electron micrograph of electrodeposited molybdenum black.

amorphous [3]. Immersion in electrolytes did not change the nature of the coatings. The fact that the material is amorphous might present a difficulty in the transport of charge carriers through the lattice due to rapid recombinations. X-ray photoelectron spectroscopy identified the O1s, Mo 3p 3/2 and Mo 3d 5/2 as mean peaks. Their count rates increased as a result of immersion in electrolytes while their binding energies remained fixed.

Chemical analysis, weight loss on heating in vacuum and ESCA provided evidence for the presence of  $\text{MoO}_2 \cdot 2\text{H}_2\text{O}$  in the electrodeposited coatings as suggested by Jost et al. [4]. The weight percentages of Mo and Ni in the coating are 53.5 and 6.4%, respectively. This gives molecular proportions of approx. 5 to 1 for  $\text{MoO}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ni}(\text{OH})_2$ , respectively. X-ray microanalysis confirmed the existence of Mo and Ni as main elements.

The stability of the coatings in electrolytic environments was examined for immersion times ranging from a few days to 2–3 weeks and was found to depend upon the substrate cleaning process prior to deposition, planting conditions and nature of the electrolytes. It is obvious that a slow degradation process is taking place, and the fact that the electrolyte may diffuse through the cracks of the coating and corrode the substrate itself makes this process even more complicated and difficult to understand [5]. The problem may be difficult to overcome by better preparation of the deposits.

#### *Optical Properties*

The total reflectance of Mo-black ranged from 7 to 27% (Figure 3). Assuming that % absorbance = 100% – % reflectance is a good approximation for this type of coating, Mo-black is found to exhibit a nearly constant absorbance of approx. 93% for the wavelength range of 0.4–0.9  $\mu\text{m}$ . Beyond 0.9  $\mu\text{m}$ , absorbance decreases steadily down to a value of 73% at 2.1  $\mu\text{m}$ . These results indicate that Mo-black is a good absorber of solar radiation especially in the visible region of the spectrum.

#### *Electrical Properties*

The current-voltage characteristics for a constant coating temperature of 22 °C and the current-temperature characteristics for a constant applied voltage of 10 V showed that the resistance of the specimen decreases with increasing voltage or temperature. This was a first indication that the Mo-black coating is semiconducting. In search for a dominant conduction mechanism of an amorphous material, the Schottky [6], the Poole-Frenkel [7] and the ionic conduction [6] mechanisms have been investigated.

An expression for the Schottky current suggested by Pollack [8] is

$$I = AST^2 \exp \left\{ -\frac{W}{k} + C \left[ \frac{V}{Ka} \right]^{1/2} \right\} / T, \quad (1)$$

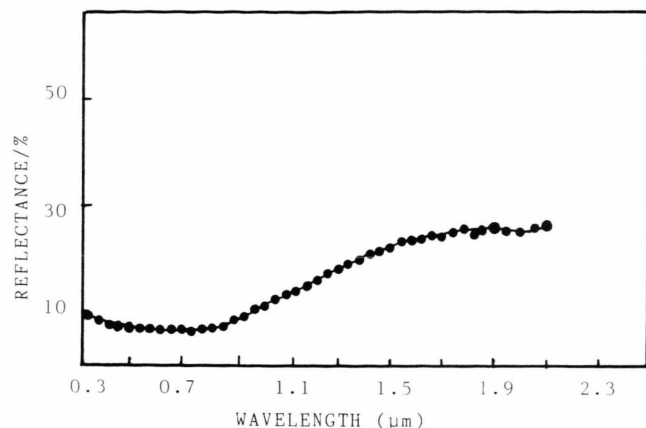


Fig. 3. Spectral reflectance vs. wavelength of electrodeposited molybdenum black.

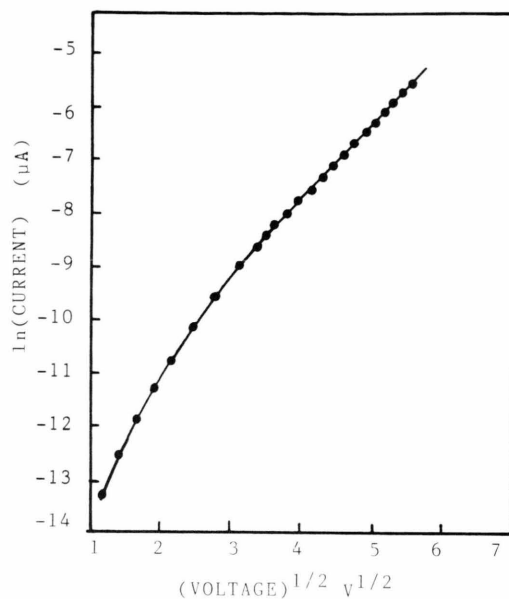


Fig. 4. Test of Schottky conduction under constant temperature.

where  $A$  is Richardson's constant,  $S$  the specimen active area,  $W$  the effective metal-insulator work function,  $k$  Boltzmann's constant,  $C$  is 4.389 with  $V$  in Volts and  $a$  in cm,  $K$  is the dielectric permittivity and  $a$  the coating thickness.

A plot of  $\ln I$  versus  $V^{1/2}$  was found to be linear for applied voltages greater than 10 Volts (Fig. 4), and a plot of  $\ln \left( \frac{I - I_t}{T^2} \right)$  versus  $1/T$  was also found to be linear (Figure 5).  $I_t = 1.8 \mu\text{A}$  was the temperature independent current at 298 K due to tunneling. The linearity of these plots provided evidence that the dominant conduction mechanism is the Schottky mechanism [6, 9]. This conclusion was also supported by the non-linearities of plots of  $\ln I$  vs.  $V$  (test of ionic conduction) and  $\ln I$  vs.  $1/T$  (test of Poole-Frenkel conduction), which show that these two conduction mechanisms are not dominant.

Schottky emission is normally an electric field activated mechanism. But if no ionic conduction is dominant, and this is here the case, the Schottky mechanism can also be activated by photons [10]. Finally, the quantity in square brackets of (1) is equated with the slope of the experimental line in Fig. 5 to give a value of 1.2 eV for the effective metal-insulator work function,  $W$ , which is essentially the Schottky barrier height at the substrate-coating interface.

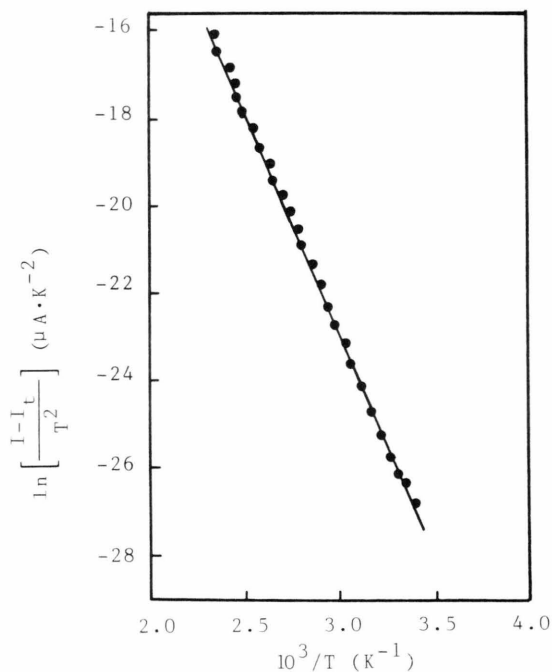


Fig. 5. Test of Schottky conduction under high electric field.

### Photoelectrochemical Measurements

The semiconducting nature of the electrodeposited Mo-black has urged us to investigate the photoelectrochemical behaviour of this material. Figure 6 shows the current-voltage characteristics of the Mo-black

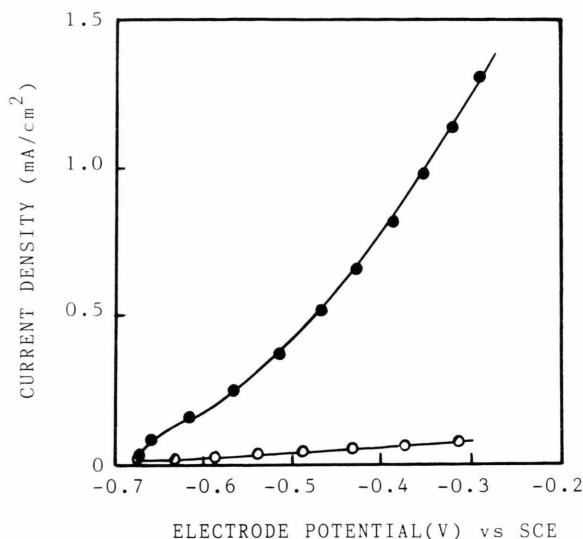


Fig. 6. Current-voltage characteristics of Mo-black electrodes in contact with a Borax solution in dark (○) and under illumination (●).

electrodes in contact with a borax solution under steady state conditions. The maximum photocurrent was observed at  $-300$  mV vs. SCE, while for more anodic potentials high dark currents were observed due to the electrodisolution of the coating. An interesting feature has been that the increase of the photocurrent was not abrupt but time dependent. This may

be attributed to an inherent property of the bulk of the coating such as hopping or relaxation [11]. Measurements of the photovoltage under open circuit conditions gave negative values ranging from  $100$ – $150$  mV. This result provides evidence for the n-type semiconducting nature of the coating, a fact which is also supported by the shape of the I–V curve in Figure 6.

Finally, it has been observed that, as a result of intensive and prolonged illumination, the photocurrents decreased while the dark currents increased. This may be attributed to photocorrosion of the coating, which has resulted upon contact of the electrolyte with the aluminium substrate.

## Conclusions

Mo-black is a material which, when electrodeposited in thin coating form on aluminium surfaces, is characterized by the following properties: (i) it is amorphous and of semiconducting nature forming a Schottky barrier at the coating-metal interface, (ii) it is a good absorber of solar radiation especially for wavelengths belonging to the visible region of the solar spectrum and (iii) it exhibits photoelectrochemical behaviour when the coating-electrolyte interface is illuminated. Further work should include studies related to the stabilization of the material against photo corrosion and to its behaviour in the presence of various redox systems.

[1] R. A. Hoffman and R. O. Hull, *Proc. Amer. Electroplaters Soc.* **1**, 45 (1939).  
 [2] R. Hoseini, Dissertation, Brunel University, London 1981.  
 [3] K. W. Andrews and D. J. Dyson, *Interpretation of Electron Diffraction Patterns*, pp. 15, 228, Adam Hilger Ltd. 1971, 2nd ed.  
 [4] P. Jost, P. Langrange, M. Wolff, and J. P. Schwing, *Proc. 1st Int. Conf. on Chemistry and Uses of Molybdenum*, Climax Molybdenum Co., London 1973, p. 90.  
 [5] E. Deltombe and M. Pourbaix, *Corrosion* **14**, 496 (1958).

[6] D. S. Campbell and A. R. Moreley, *Rep. Prog. Phys.* **34**, 283 (1971).  
 [7] A. K. Jonscher, *Thin Solid Films* **1**, 213 (1967).  
 [8] S. R. Pollack, *J. Appl. Phys.* **34**, 877 (1963).  
 [9] K. Farmakis, Dissertation, Brunel University, London 1982.  
 [10] S. R. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, Plenum Press, New York 1980, pp. 299–333.  
 [11] W. van Roosenbroeck and H., C. Casey Jr., *Phys. Rev. B* **5**, 2154 (1972).