

Communications

EQCM Studies on Anodic Oxidation of Metallic Molybdenum in 0.5 M Sulfuric Acid Solution: Molybdenum Blue Formation

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Molybdenum (Mo) has rich chemistry because it has oxidation state ranging from $-II$ to $+VI$ ¹ and coordination number from 0 to 8.² Metallic Mo has dynamic surface chemistry originating from these varieties in oxidation state and coordination number of the element. While metallic Mo and its derived materials have been widely used in the areas of solar cells, battery, photochromism, electrochromism, corrosion etc., most of their fundamental electrochemistry is not uncovered.³ In this communication, we wish to report a preliminary report by the electrochemical quartz crystal microbalance (EQCM) studies on anodic oxidation of metallic Mo in a representative aqueous acid solutions. To the best of our knowledge, this is the first EQCM result on Mo electrode in aqueous solutions. The present work results from the efforts in developing molybdenum as the back contact electrode for CuInGaSe solar cells.⁴

The EQCM instrumentation used in this work consisted of an EG&G model 283A potentiostat, which was coupled to a Seiko EG&G QCA 917 quartz crystal analyzer.⁵ The working electrode consisted of 0.196 cm² Mo sputtered onto titanium/crystal at a frequency of 9 MHz AT-cut quartz (5.7 ng Hz⁻¹ cm⁻²). EQCM measures simultaneously the current and frequency changes with potential applied. Because of the high sensitivities in frequency and current responses, the removal and accumulation of materials on electrode surface can be detected clearly at the minute level in EQCM experiments. Metallic Mo has been known to dissolve into solution or to form the new materials of Mo complexes depending on the environments where it is situated when it is electrochemically oxidized but the exact conditions have been controversial for long time.⁶⁻⁸ In this work, we show the electrochemical anodization conditions leading to the removal of metallic Mo as well as the accumulation of Mo complexes onto the surface of Mo electrode by means of EQCM in 0.5 M sulfuric acid medium. The accumulation of complexes resulted in the formation of the new material of molybdenum blue.

Figure 1 shows the current response and frequency change simultaneously observed when the potential of the Mo/

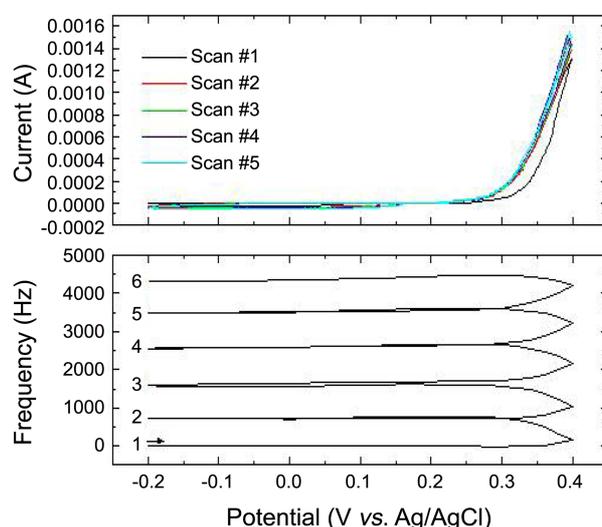


Figure 1. Current and frequency responses during five potential cycles at 20 mV/s from -0.2 V to $+0.4$ V to -0.2 V in 0.5 M sulphuric acid solution.

quartz electrode was cycled at 20 mV/s between -0.2 V and $+0.4$ V starting from -0.2 V versus Ag/AgCl reference electrode in a 0.5 M sulfuric acid solution. The resonance frequency increased stepwise during the five consecutive cycles. Frequency increase reflects that Mo was removed from the surface of Mo electrode to dissolve into the solution. The frequency increment during the first cycle was

Table 1. Frequency shift observed and Mo removed during continuous cyclic voltammetric scans between -0.2 V and $+0.2$ V versus Ag/AgCl

Cycle number	ΔF (Hz)	Δm ($\mu\text{g}/\text{cm}^2$)
5	750	4.3
4	920	5.2
3	980	5.6
2	860	4.9
1	720	4.1

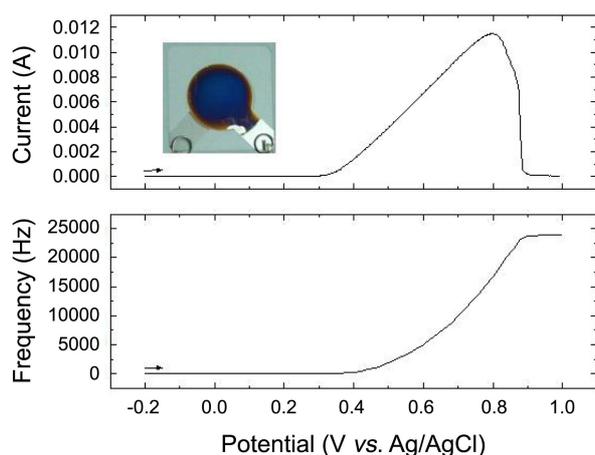


Figure 2. Current and frequency responses during linear potential sweep at 20 mV/s from -0.2 V to $+1.0$ V in 0.5 M sulphuric acid solution. Inset shows the molybdenum blue produced at $+0.9$ V.

720 Hz, which amounts to a removal $4.1 \mu\text{g}/\text{cm}^2$ or a removal of 2.6×10^{16} Mo atoms per cm^2 if the material removed is assumed to be pure Mo. Table 1 summarizes the frequency shifts and Mo removal observed during the five consecutive cycles and shows that the increment in frequency shift first increased as the number of potential cycles increased for the first three cycles and that it then decreased for the next two cycles, suggesting that the surface became rougher and thus the surface area increased as the potential cycle or dissolution increased for the first three cycles by 10–20% per each cycle. The current response changed in a similar way with the potential scans continued. The observations are compatible with the previous reports by means of voltammetry alone.⁶ Bojinov *et al.* reported that in the potential range -0.5 to 0.0 V Mo was spontaneously passivated and transpassive dissolution started at 0.0 V (*vs.* saturated mercurous sulphate electrode or $+0.67$ V *vs.* SHE) in 85% H_3PO_4 solutions. Except the exact potential values and the media used, the passivation and transpassivation phenomena observed in this work are similar to their results as shown below. The potential value of $+0.4$ V *vs.* Ag/AgCl is in the middle of rising part of current function and in fact the frequency increase starts at much less potentials applied as can be seen in the Figure 1.

Although the resonance frequency increased steadily or the removal of Mo continued when the potential was scanned upto *ca.* $+0.9$ V, it did not take place beyond that potential. Figure 2 shows the current response and frequency change observed while the potential of the Mo electrode was swept at 20 mV/s from -0.2 V to 1 V *versus* Ag/AgCl in a 0.5 M sulfuric acid solution. Although the current was initially at the background level, the sharply rising current was observed above *ca.* $+0.25$ V. Once the current reached a maximum value, it decayed abruptly down to the background

level, suggesting that the non-conductive film was forming on the surface of Mo electrode. A clearer evidence of the etching of metallic Mo electrode and the accumulation of new materials at the surface of the Mo electrode can be seen through the change of frequency function. The resonance frequency increased continuously upto the potential where the current reached the background level and remains unchanged even when the potential scan continued upto $+1.0$ V or returned to the initial value of -0.2 V, indicating that the non-conductive film was formed on the surface of Mo electrode when the potential of the Mo electrode reached *ca.* $+0.9$ V. When the Mo electrode was removed after the linear sweep voltammetric experiment was finished at $+1.0$ V or at the potential more positive than *ca.* $+0.9$ V, the blue-colored molybdenum film was found as shown in the Figure 2 inset. The molybdenum blue formed was stable in the ambient laboratory conditions. The previous work shows that variously colored Mo films could be formed on metallic Mo electrode but at much higher voltages.⁹ Molybdenum blue has been known as giant wheel-shaped clusters with nanostructured cavities, displaying exceptional aesthetic beauty in homogeneous solution for some time.¹⁰ The molybdenum blue produced at the metallic Mo surface by low potential applied in aqueous solution may be a surface analogue to the giant solution complex. The structure and physical properties need to be delineated for successful applications of the thin metallic Mo films in coloring area and the work is in progress in this direction.

In conclusion, the first EQCM results at metallic Mo electrode were presented to show dissolution and film forming potential regions at the surface of electrode in sulphuric acid solutions and the insoluble film was found to be blue in color and electrically insulating.

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