Chapter VI
Electrochromic(EC) Studies on Tungsten and Molybdenum
Heteropolyoxometalate Thin Films

6.1 Introduction

The transition metal oxides (TMOs) form a group of predominantly ionic solids, which exhibit a wide range of optical and electrical properties. Most of these TMOs are studied as electrochromic (EC) materials. EC is a phenomenon related to persistent and reversible change in optical property, induced electrochemically, whose macroscopic effect is the change in color. These are used in many applications viz. information displays, variable emittance surfaces, variable reflectance mirrors and smart windows etc. Amongst these 'smart windows' have captured the interest of researchers as a means to achieve energy efficiency in buildings. It has become clear that 'smart windows' are able to combine two features that are often thought of as incompatible; energy efficiency (as a result of the curtailing of air conditioning) and indoor comfort (due to less glare and thermal discomfort). Therefore EC materials have been considered as a subset of solar energy materials [1, 2].

Amongst these TMOs, tungsten oxide (WO$_3$) and molybdenum oxide (MoO$_3$) are an extensively studied EC material due to its outstanding electrochromic properties [3–8]. Several adequate deposition techniques such as sputtering, electron beam evaporation, plasma oxidation, chemical vapour deposition, MOCVD, and sol gel process have been used to prepare HPOM thin films. But to our knowledge, chemical bath deposition has not previously been employed to obtain electrochromic tungsten and molybdenum HPOM thin films [9-15].

In the present chapter electrochromic properties of tungsten and molybdenum heteropolyoxometalate thin films prepared by the simple and inexpensive chemical bath deposition technique are discussed.
6.2 Experimental

6.2.1 Substrate Cleaning

Cleanliness of the substrates, for thin film deposition is most important factor. It affects the adherence, smoothness and uniformity of the film. The technique to be adopted for cleaning depends on nature of substrates, degree of cleanliness required and nature of contaminants to be removed. The common contaminants are grease, adsorbed water, air borne dust, lint and oil particles. Cleanliness is the process of breaking the bonds between substrates and contaminants without damaging the substrates. There are various methods to supply energy for breaking such bonds, such as heating, bombarding by ions scrubbing etc. Following cleaning procedure was used for the glass substrates.

1) The substrates were first washed with the neutral detergent solution and then with the double distilled water.
2) The substrates were boiled in chromic acid for few minutes.
3) NaOH treatment was given to remove the acidic contaminants.
4) The substrates were again washed with double distilled water.
5) Lastly, the substrates were ultrasonically cleaned.
6) Drying of the substrates were done in the vapors of the alcohol.

6.2.2 Preparation of conducting FTO coatings on glass substrates

The conducting FTO coatings were prepared using pentahydrated stannic chloride (SnCl$_4$·5H$_2$O) (purity 98%) and ammonium fluoride (NH$_4$F) (purity 95%) as precursor salts. The solution was prepared in double distilled water. The FTO coated conducting glass substrates with 90–95% transparency and sheet resistance of 10–15 Ω/cm$^2$ were obtained at 500°C. These FTO-coated glass substrates were further used as conducting substrates for the deposition of electrochromic tungsten and molybdenum heteropolyoxometalate thin films.
6.2.3 Preparation of precursor solution

Thin films of tungsten HPOM and TI (I) doped tungsten HPOM were prepared by dissolving following AR grade chemicals in double distilled water.

a) 2% solution of phosphotungstic acid. \([ \text{H}_3 (\text{PW}_{12} \text{O}_{40}) ]\) in acetone.

b) 2% aqueous solution of phosphomolybdic acid. \([ \text{H}_3 (\text{PMo}_{12} \text{O}_{40}) ]\)

c) 0.1%, aqueous solution of thallous acetate (\(\text{CH}_3\text{COO}-\text{TI}\))

6.2.4 Deposition of Phosphotungstic acid \([ \text{H}_3 (\text{PW}_{12} \text{O}_{40}) ]\) thin films

For the deposition of thin films of phosphotungstic acid \([ \text{H}_3 (\text{PW}_{12} \text{O}_{40}) ]\), 2% solution of phosphotungstic acid in acetone was taken in 150 cm\(^3\) glass beaker. The cleaned and dried glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in the in this solution. The speed of substrate rotation was kept 40-50 rpm. After 10 minutes, the substrates were taken out side the beaker. After evaporation of acetone solvent, there was white colored and uniform deposition of \([ \text{H}_3 (\text{PW}_{12} \text{O}_{40}) ]\) on glass and FTO substrates. As deposited thin films were dried in constant temperature oven at 80 °C. Thickness of the as deposited films was measured by surface profilometer and it was 508.0 nm.

6.2.5 Deposition of TI (I) doped phosphotungstic acid \([ \text{Tl}_3 (\text{PW}_{12} \text{O}_{40}) ]\) thin films.

90 cm\(^3\) 2 % aqueous solution of phosphotungstic acid was taken in 150 cm\(^3\) capacity beaker having side arm and temperature of this solution was kept at 55 °C. The clean & dry glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in the phosphotungstic acid solution. After five minutes 0.1% aqueous solution of thallous acetate was added drop wise through side arm in phosphotungstic acid solution. The speed of substrate rotation was kept 50-60 rpm. After 1\(1/2\) hour, there was white colored and uniform deposition
of \( [\text{Tl}_3 (\text{PW}_{12} \text{O}_{40})] \) HPOM on glass and FTO substrates. As deposited thin films were dried in constant temperature oven at 80 °C. Thickness of the as deposited films was measured by surface profilometer and it was 418.0 nm.

6.2.6 Deposition of Phosphomolybdic acid \([H_3 (\text{PMo}_{12} \text{O}_{40})]\) thin films

For the deposition of thin films of phosphomolybdic acid \([H_3 (\text{PMo}_{12} \text{O}_{40})]\), 2% solution of phosphomolybdic acid in acetone was taken in 150 cm\(^3\) glass beaker. The cleaned and dried glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in this solution. The speed of substrate rotation was kept 40 - 50 rpm. After 10 minutes, the substrates were taken outside the beaker. After evaporation of acetone solvent, there was yellow colored and uniform deposition of \([H_3 (\text{PMo}_{12} \text{O}_{40})]\) on glass and FTO substrates. As deposited thin films were dried in constant temperature oven at 100 °C. Thickness of the as deposited films was measured by surface profilometer and it was 467.0 nm.

6.2.7 Deposition of Ti (I) doped Phosphomolybdic acid \([\text{Tl}_3 (\text{PMo}_{12} \text{O}_{40})]\) thin films.

90 cm\(^3\) 2 % aqueous solution of phosphomolybdic acid \([\text{Tl}_3 (\text{PMo}_{12} \text{O}_{40})]\) was taken in 150 cm\(^3\) capacity beaker having side arm and temperature of this solution was kept at 55 °C. The clean & dry glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in the phosphomolybdic acid solution. After five minutes, 0.1% aqueous solution of thallous acetate was added drop wise through side arm in phosphomolybdic acid solution. The speed of substrate rotation was kept 50-60 rpm. After 1\(\frac{1}{2}\) hour, there was yellow colored and uniform deposition of \([\text{Tl}_3 (\text{PMo}_{12} \text{O}_{40})]\) HPOM on glass and FTO substrates. As deposited thin films were dried in constant temperature oven at 100 °C. Thickness of the as deposited films was measured by surface profilometer and it was 508.0 nm.
6.3 Results and discussion

6.3.1 Electrochemical characterizations of tungsten HPOM thin films

For the electrochemical characterization, the standard three-electrode electrochemical cells of the following configuration was used:

Glass / FTO / [ H₃(PW₁₂O₄₀) ] / 0.5 M LiClO₄ / Pt / SCE

Glass / FTO / [ Ti₃(PW₁₂O₄₀) ] / 0.5 M LiClO₄ / Pt / SCE

Where, [ H₃(PW₁₂O₄₀) ] and [ Ti₃(PW₁₂O₄₀) ] thin films acts as a working electrode (area of electrode used for EC characterization was 1 cm²), LiClO₄ is an Li⁺ ion source electrolyte. Saturated calomel electrode (SCE) was used as a reference electrode to which all measured voltages were referred and Pt acts as the counter electrode.

6.3.1. a Optimization of potential window for electrochemical characterizations:

In order to optimize potential window for electrochemical characterizations initially we have carried out cyclic voltammogram of bare FTO substrate in the potential range ±1.0 V. Fig. 6.1 shows cyclic voltammogram of bare FTO substrate, from figure it is observed that the reduction current increases rapidly beyond -0.7 V and an oxidation peak was observed at -0.450 V. To avoid the contribution of conducting FTO substrate in the redox reaction of electrochromic tungsten heteropolyoxometalate thin film, potential window is optimized in between 0.5 to -0.7V and all the voltametric studies were carried out in the optimized potential range.
Fig. 6.1 Cyclic Voltammogram for bare FTO substrate recorded in 0.5 M LiClO$_4$ electrolyte.

6.3.1.b Cyclic Voltammetry (CV) of Phosphotungstic Acid (PTA) and Ti$^+$ doped Phosphotungstic Acid (TlPTA)

Fig. 6.2 and Fig. 6.3 shows cyclic voltammograms of PTA and TlPTA recorded at 100 mV/sec scan rate after 1st cycle with linear potential sweep between -1.0 to +1.25 mV (Versus SCE).

Fig. 6.2 Cyclic voltammogram of phosphotungstic acid (PTA) thin film at 100mV/sec scan rate
Fig. 6.3 Cyclic voltammogram of Ti\textsuperscript{+} doped phosphotungstic acid (Ti\textsubscript{3}PTA) thin film at 100mV/sec scan rate

The threshold voltage (E\textsubscript{τ}), the voltage corresponding to rapid surge of Li\textsuperscript{+} ionic intercalation into the (H\textsubscript{3}PO\textsubscript{4}) (WO\textsubscript{3})\textsubscript{12} and Ti\textsuperscript{+} doped phosphotungstic acid (Ti\textsubscript{3}PO\textsubscript{4})(WO\textsubscript{3})\textsubscript{12} thin films is indicated in Fig.6.2 and Fig. 6.3. During the cathodic potential scan (from 1.25 to -1.0 mV) simultaneous intercalation of electrons and Li\textsuperscript{+} ions into the film causes reduction of W\textsuperscript{6+} to W\textsuperscript{5+} and hence the film gets blue colored. In its reduced state film appears bluish. During the anodic potential scan (from -1.0 to +1.25 mV) deintercalation of Li\textsuperscript{+} ions causes the bleaching of film and film appears white. The redox chemical reaction associated with coloration and bleaching of phosphotungstic acid (H\textsubscript{3}PO\textsubscript{4}) (WO\textsubscript{3})\textsubscript{12} and Ti\textsuperscript{+} doped phosphotungstic acid (Ti\textsubscript{3}PO\textsubscript{4}) (WO\textsubscript{3})\textsubscript{12} thin film can be represented as:

\[
\begin{align*}
[(H_3PO_4) (W^{6+}O_3)_{12}] + x Li^+ + xe^- & \rightarrow [ Li_x (H_3PO_4) (W^{5+}O_3)_{12}] \quad \text{---6.1} \\
\text{PTA (colorless)} & \quad \text{PTA (blue)} \\

[(Ti_3PO_4) (W^{6+}O_3)_{12}] + x Li^+ + xe^- & \rightarrow Li_x (Ti_3PO_4) (W^{5+}O_3)_{12} \quad \text{---6.2} \\
\text{TIPTA (colorless)} & \quad \text{TIPTA (blue)}
\end{align*}
\]
To maintain charge neutrality in the cell as a whole, oxidation must occur at the carbon electrode. It is known that there are hydroxyl groups on the carbon surface; these can undergo the following oxidation reaction,

\[ \text{C-OH} \overset{\text{e}^-}{\longrightarrow} \text{C=O} + \text{H}^+ + \text{e}^- \]  

--- 6.3

The liberated proton can be injected into the PTA, maintaining charge neutrality in the cell as a whole, with the electron completing the external circuit. Combining equations 1 and 2 the net electrochemical reaction is

\[ \text{C-OH} + (\text{H}_3\text{PO}_4) (\text{W}^{6+} \text{O}_3)_{12} \overset{\text{e}^-}{\longrightarrow} \text{C=O} + (\text{H}_4\text{PO}_4) (\text{W}^{5+} \text{O}_3)_{12} \]  

--- 6.4

\[ \text{PTA} \]

\[ \text{C-OH} + (\text{Tl}_3\text{PO}_4) (\text{W}^{6+} \text{O}_3)_{12} \overset{\text{e}^-}{\longrightarrow} \text{C=O} + (\text{Tl}_4\text{PO}_4) (\text{W}^{5+} \text{O}_3)_{12} \]  

--- 6.5

\[ \text{TIPTA} \]

In Fig. 6.4 photographs of Tungsten HPOM thin films in its (a) colored and (b) bleached state are shown.

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Fig. 6.4  Photographs of Tungsten HPOM thin films in its (a) colored and (b) bleached state
6.3.1.c Cyclic Voltammetry (CV) at different scan rates

Fig. 6.5 and Fig. 6.6 shows CV spectra recorded for phosphotungstic acid (PTA) and Tl⁺ doped phosphotungstic acid (Ti₃PO₄) (WO₃)₁₂ thin films at different scan rates (20, 40, 60, 80, 100 mV/sec). The inset shows the plots of cathodic / anodic peak potentials as a function of square root of scan rates. The linear increase in both anodic and cathodic peak potentials with respect to increasing scan rate indicates that the associated mechanism is diffusion controlled. The plot of cathodic and anodic peak potentials as a function of square root of scan rates is shown in the inset of Fig. 6.5 and Fig. 6.6. The diffusion constant for the Li⁺ ions (D_{Li⁺}) is calculated using the well-known Cottrell's Eq. 6.4.

\[ D^{1/2} = \frac{I_{pc}}{2.72 \times 10^5 \times n^{3/2} \times C_o \times A \times \nu^{1/2}} \quad \text{--------- 6.4} \]

Where, \( I_{pc} \) = cathodic peak potential, \( \nu \) = scan rate (mV/sec), \( n \) = number of electrons, \( C_o \) = electrolyte Concentration (0.5 M), \( A \) = Area of film

Fig. 6.5 Cyclic Voltammograms recorded for the phosphotungstic acid (PTA) thin film at different scan rates. Inset shows plot of cathodic / anodic peak potentials as a function of square root of scan rate.
Fig. 6.6 Cyclic Voltammograms recorded for the Tl$^+$ doped phosphotungstic acid (Tl PTA) thin films at different scan rates. Inset shows plot of cathodic / anodic peak potentials as a function of square root of scan rate.

From the slope of the curve of the cathodic / anodic peak current versus square root of scan rates in the linear part, the diffusion coefficients were calculated. For PTA it is found to be $9.49 \times 10^{-11}$ cm$^2$/sec and $6.96 \times 10^{-11}$ cm$^2$/sec for intercalation and deintercalation process, respectively and for TlPTA it is found to be $4.8 \times 10^{-10}$ cm$^2$/sec and $6.09 \times 10^{-11}$ cm$^2$/sec for intercalation and deintercalation process, respectively [16-18].

6.3.1. d Cyclic voltammetry (CV) for testing of durability of phosphotungstic acid (PTA) and Tl$^+$ doped phosphotungstic acid thin films

Fig.6.7 and Fig.6.8 shows CV spectra recorded for phosphotungstic acid (PTA) and Tl$^+$ doped phosphotungstic acid (Tl$_3$PO$_4$) (WO$_3$)$_{12}$ thin films for its 100$^{th}$, 200$^{th}$, 500$^{th}$ and 1000$^{th}$ cycle. From the figures, it was observed that with an increase in number of cycle threshold voltage ($E_t$), the voltage corresponding to rapid surge of Li$^+$ ions in to the phosphotungstic acid (PTA) and Tl$^+$ doped phosphotungstic acid (Tl$_3$PO$_4$) (WO$_3$)$_{12}$ film shifts anodically. The observed shift in $E_t$ indicates opening of conductive channels leading to easy insertion of ions
in the phosphotungstic acid (PTA) and Tl$^+$ doped phosphotungstic acid (Tl$_3$PO$_4$) (WO$_3$)$_{12}$ thin films. It is also observed that the anodic peak potential shifts anodically, which is a consequence of the requirement of excess energy for the egress of intercalated ions with respect to the number of cycles.

Fig. 6.7 Cyclic voltammograms recorded for the phosphotungstic acid (PTA) thin films for durability testing.

Fig. 6.8 Cyclic voltammograms recorded for the Tl$^+$ doped phosphotungstic acid (Tl PTA) thin films for durability testing.
6.3.1.e Chronoamperometry (CA)

A typical CA trace obtained during coloration and bleaching of as deposited phosphotungstic acid (PTA) and Ti$^+$ doped phosphotungstic acid ($\text{Tl}_3\text{PO}_4$, $\text{WO}_3$)$_{12}$ thin films is shown in Fig. 6.9 and Fig. 6.10. During the experiment, the voltage was stepped from its rest potential of 0.0 V to -0.5 V for 10 s (coloration) and then reversed to +0.5 V for next 10 s (bleaching). From the current versus time transients, it is clearly observed that both coloration current ($I_c$) and bleaching current ($I_b$) following the steps were smooth and decreased continuously with time. The decrease of current with time is due to increase in chemical potential of cations Li$^+$, as intercalation proceeds, according to the following relation [19]

$$n = V_A - \Delta\mu(x)/Ne \quad 6.5$$

Where, $V_A$ is the applied voltage, $\Delta\mu(x)$ is the change in the chemical potential across the barrier and $N$ is the Avogadro’s number. This decrease in current with time has been used to measure the speed of EC response of iridium oxide thin films.

The response time is defined as the time required for the intercalation/deintercalation current to stabilize at its lowest value.

![Fig. 6.9 Chronoamperometric (CA) plot recorded for phosphotungstic acid (PTA) thin films](image)
The coloration time \( t_c \) and bleaching time \( t_b \) for PTA and TIPTA were calculated from the current time transients and are shown in Table 6.1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Response time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( t_c ) (sec)</td>
</tr>
<tr>
<td>PTA</td>
<td>4.8</td>
</tr>
<tr>
<td>TIPTA</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Table 6.1 \((t_c)\) and \((t_b)\) values for PTA and TIPTA

6.3.1.f Chronocoulometry (CC)

To study \( \text{Li}^+ \) ion intercalation, de-intercalation process with respect to time, chronocoulometry was carried out at potential steps of \( \pm 0.5 \) V (versus SCE), for a step of 10 s. Fig. 6.11 and Fig. 6.12 shows corresponding chronocoulometry (CC) curve from which amount of charge intercalated \( (Q_i) \), amount of charge de-intercalated \( (Q_{di}) \) and hence residual charge \( (Q_{i}-Q_{di}) \) has been calculated. The
electrochromic reversibility of the phophotungstic acid (PTA) and Ti$^+$ doped phophotungstic acid (Ti$_3$PO$_4$) (WO$_3$)$_{12}$ thin film is calculated using relation 6.6 [20-21].

\[
Reversibility = \frac{Q_{di}}{Q_i}
\]  

The phophotungstic acid (PTA) thin film exhibited electrochromic reversibility up to 47%. and Ti$^+$ doped phophotungstic acid (Ti$_3$PO$_4$) (WO$_3$)$_{12}$ thin films exhibited electrochromic reversibility up to 54%.

Fig. 6.11 Chronocoulometric (CC) plot recorded for for PTA-10 thin film
6.3.1. g Iono-optical studies

Coloration and bleaching of phophotungstic acid (PTA) and TI\textsuperscript{+} doped phophotungstic acid (TlPTA) thin films was carried out by applying a potential step of ±0.5 V for a fixed time. The various parameters derived from the electrochemical characterization of chemicaly deposited phophotungstic acid (PTA) thin films are given in Table 6.2. The transmittance spectra were recorded for the phophotungstic acid (PTA) and TI\textsuperscript{+} doped phophotungstic acid (TlPTA) thin films in it’s as deposited (A), Colored (C) and bleached (B) states in the wavelength range of 350 nm to 850 nm, at room temperature. The optical absorption by the thin layer is described by the dimensionless quantity ($\alpha t$), which is called optical density (OD). The change in optical density ($\Delta$OD) of phophotungstic acid (PTA) and TI\textsuperscript{+} doped phophotungstic acid (TlPTA) thin films

Table 6.2. Various parameters derived from the electrochemical characterization for PTA and TlPTA

<table>
<thead>
<tr>
<th>Sample Id</th>
<th>Qi ($\mu$C/cm$^2$)</th>
<th>Qdi ($\mu$C/cm$^2$)</th>
<th>(Qi - Qdi) ($\mu$C/cm$^2$)</th>
<th>Reversibilit%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTA</td>
<td>-0.002989</td>
<td>-0.001394</td>
<td>-0.001595</td>
<td>47%</td>
</tr>
<tr>
<td>TlPTA</td>
<td>-0.004390</td>
<td>-0.002015</td>
<td>-0.002375</td>
<td>54%</td>
</tr>
</tbody>
</table>
thin film at 630 nm, in its colored state and bleached state, is calculated using relation (6.7)

\[ \Delta OD = \ln \left( \frac{T_b}{T_c} \right) \]  

\[ \text{----------------- (6.7)} \]

Where, \( T_b \) and \( T_c \) is the transmittance of the phophotungstic acid (PTA) and \( \text{Ti}^+ \) doped phophotungstic acid (TlPTA) thin films in its colored and bleached states, respectively. Fig. 6.13 and Fig. 6.14 shows the transmittance spectra recorded for the phophotungstic acid (PTA) and \( \text{Ti}^+ \) doped phophotungstic acid (TlPTA) thin films in its as deposited (A), colored (C) and bleached (B) states. To describe the efficiency of the charge to induce absorption in an electrochromic device is to introduce the coloration efficiency (CE). The CE is defined as the change in optical density (\( \Delta OD \)) per unit inserted charge and it is calculated using relation (6.8) and it is found to be 139.91 C/cm\(^2\) for PTA 97.88 C/cm\(^2\) for TlPTA

\[ CE = \frac{\Delta OD}{\Delta Q} \]  

\[ \text{----------------- (6.8)} \]

Where, \( \Delta Q \) is the amount of charge intercalated in the sample to cause change in optical density (\( \Delta OD \)), which was estimated by integrating the area under the curve of current density versus time [22-26].

![Fig.6.13 The transmittance spectra of the phophotungstic acid (PTA) thin film as deposited (A), colored (C) and bleached (B) states.](image)
Fig. 6.14 The transmittance spectra of the Tl+ doped phophotungstic acid (TlPTA) thin film as deposited (A), colored (C) and bleached (B) states.

6.3.2 Electrochemical characterizations of molybdenum HPOM thin films

For the electrochemical characterization, the standard three-electrode electrochemical cell of the following configuration was used

Glass / FTO / [H$_3$(PMo$_{12}$O$_{40}$)] / 0.5 M LiClO$_4$ / C / SCE

Glass / FTO / [Tl$_3$(PMo$_{12}$O$_{40}$)] / 0.5 M LiClO$_4$ / C / SCE

where, [H$_3$(PMo$_{12}$O$_{40}$)] and [Tl$_3$(PMo$_{12}$O$_{40}$)] thin films acts as a working electrode (area of electrode used for EC characterization was 6 cm$^2$), LiClO$_4$ is an Li$^+$ ion source electrolyte. Saturated calomel electrode (SCE) was used as a reference electrode to which all measured voltages were referred and C is a platinum wire, which acts as the counter electrode.
6.3.2.a Optimization of potential window for electrochemical characterizations:

In order to optimize potential window for electrochemical characterizations initially we have carried out cyclic voltammogram of bare FTO substrate in the potential range ±1.0 V. Figure 6.1 shows cyclic voltammogram of bare FTO substrate, from figure it is observed that the reduction current increases rapidly beyond -0.7 V and an oxidation peak was observed at -0.450 V. To avoid the contribution of conducting FTO substrate in the redox reaction of electrochromic molybdenum heteropolyoxometalate thin film, potential window is optimized in between 0.5 to -0.7V and all the voltammetric studies were carried out in the optimized potential range.

![Cyclic voltammogram for FTO substrate recorded in 0.5 M LiClO$_4$ electrolyte.](image)

6.3.2.b Cyclic Voltammetry (CV) of Phosphomolybdic Acid (PMA) and Ti$^+$ doped Phosphomolybdic Acid (TIPMA)

Fig.6.16 and Fig.6.17 shows cyclic voltammograms of PMA and TIPMA recorded at 100 mV/sec scan rate after 1st cycle with linear potential sweep between 1.0 to 1.25 mV (Versus SCE).
The threshold voltage ($E_T$), the voltage corresponding to rapid surge of Li$^+$ ionic intercalation into the \((H_3PO_4)(MoO_3)_{12}\) and Ti$^+$ doped phosphomolybdic acid
(Tl₃PO₄)(MoO₃)₁₂ thin films is indicated in Fig. 6.16 and Fig. 6.17.

During the cathodic potential scan (from 1.25 to -1.0 mV) simultaneous intercalation of electrons and Li⁺ ions into the film causes reduction of Mo⁶⁺ to Mo⁵⁺ and hence the film gets blue colored. In its reduced state film appears bluish. During the anodic potential scan (from -1.0 to +1.25 mV) deintercalation of Li⁺ ions causes the bleaching of film and film appears yellow. The redox chemical reaction associated with coloration and bleaching of phosphomolybdic acid (H₃PO₄)(MoO₃)₁₂ and Tl⁺ doped phosphomolybdic acid (Tl₃PO₄)(MoO₃)₁₂ thin film can be represented as:

\[
\text{[(H₃PO₄)(Mo}^{6+}{O₃)}₁₂\text{]} + x \text{Li}^+ + x\text{e}^- \leftrightarrow \text{[Li}_x\text{(H₃PO₄)(Mo}^{5+}{O₃)}₁₂\text{]} \quad \text{--- 6.9}
\]

PMA (Yellow) \hspace{2cm} PMA (blue)

\[
\text{[(Tl₃PO₄)(Mo}^{6+}{O₃)}₁₂\text{]} + x \text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x\text{(Tl₃PO₄)(Mo}^{5+}{O₃)}₁₂\text{]} \quad \text{--- 6.10}
\]

TIPMA (Yellow) \hspace{2cm} TIPMA (blue)

To maintain charge neutrality in the cell as a whole, oxidation must occur at the carbon electrode. It is known that there are hydroxyl groups on the carbon surface; these can undergo the following oxidation reaction,

\[
\text{C-OH} \leftrightarrow \text{C=O} + \text{H}^+ + \text{e}^- \quad \text{-------- 6.11}
\]

The liberated proton can be injected into the PMA, maintaining charge neutrality in the cell as a whole, with the electron completing the external circuit. Combining equations 6.9 and 6.11 the net electrochemical reaction is

\[
\text{C-OH} + \text{(H₃PO₄)(Mo}^{6+}{O₃)}₁₂ \leftrightarrow \text{C=O} + \text{(H₄PO₄)(Mo}^{5+}{O₃)}₁₂ \quad \text{------- 6.12}
\]

PTA

Combining equations 6.10 and 6.11 the net electrochemical reaction is
In Fig. 6.18 photographs of molybdenum HPOM thin films in its (a) colored and (b) bleached state are shown.

![Photographs of molybdenum HPOM thin films in its (a) colored and (b) bleached state](image)

**Fig. 6.18** Photographs of molybdenum HPOM thin films in its (a) colored and (b) bleached state

### 6.3.2.c Cyclic Voltammetry (CV) at different scan rates

Fig.6.19 and Fig.6.20 shows CV spectra recorded for phosphomolybdc acid (PMA) and Tl\(^+\) doped phosphomolybdc acid (Tl\(_3\)PO\(_4\)) (MoO\(_3\))\(_{12}\) thin films at different scan rates (20, 40, 60, 80, 100 mV/sec). The inset shows the plots of cathodic / anodic peak potentials as a function of square root of scan rates. The linear increase in both anodic and cathodic peak potentials with respect to increasing scan rate indicates that the associated mechanism is diffusion controlled. The plot of cathodic and anodic peak potentials as a function of square of scan rates is shown in the inset of Fig.6.19 and Fig.6.20.

The diffusion constant for the Li\(^+\) ions (D\(_{Li^+}\)) is calculated using the well-known Cottrell's Eq. 6.14.

\[
D^{1/2} = \frac{I_{pc}}{2.72 \times 10^5 \times n^{3/2} \times C_o \times A \times V^{1/2}} \tag{6.14}
\]
Where, $I_{pc}$ = cathodic peak potential, $\nu$ = scan rate (mV/sec), $n$ = number of electrons, $C_o$ = electrolyte Concentration (0.5 M), $A$ = Area of film

Fig. 6.19 Cyclic voltammograms recorded for the phosphomolybdic acid (PMA) thin films at different scan rates. Inset shows plot of cathodic / anodic peak potentials as a function of square root of scan rate.

Fig. 6.20 Cyclic voltammograms recorded for the Ti$^+$ doped phosphomolybdic acid (Ti PMA) thin films at different scan rates. Inset shows plot of cathodic / anodic peak potentials as a function of square root of scan rate.
From the slope of the curve of the cathodic / anodic peak current versus square root of scan rates in the linear part, the diffusion coefficient calculated for PMA $2.90 \times 10^{-10} \text{cm}^2/\text{sec}$ and $3.64 \times 10^{-11} \text{cm}^2/\text{sec}$ for intercalation and deintercalation process, respectively and for TIPMA to be $5.84 \times 10^{-10} \text{ cm}^2/\text{sec}$ and $2.87 \times 10^{-11} \text{ m}^2/\text{sec}$ for intercalation and deintercalation process, respectively [16-18].

6.3.2.d Cyclic voltammetry (CV) for testing of durability of Phosphomolybdic Acid (PMA) and Ti$^+$ doped phosphomolybdic acid

[(Ti$_3$PO$_4$)(MoO$_3$)$_{12}$] thin films

Fig.6.21 and Fig.6.22 shows CV spectra recorded for phosphomolybdic acid (PMA) and Ti$^+$ doped phosphomolybdic acid [(Ti$_3$PO$_4$)(MoO$_3$)$_{12}$] thin films for its 100 $^{th}$, 500 $^{th}$ and 1000 $^{th}$ cycle. From the figures, it was observed that with an increase in number of cycle threshold voltage ($E_\tau$), the voltage corresponding to rapid surge of Li$^+$ ions in to the phosphomolybdic acid (PMA) and Ti$^+$ doped phosphomolybdic acid (Ti$_3$PO$_4$)(MoO$_3$)$_{12}$ film shifts anodically. The observed shift in $E_\tau$ indicates opening of conductive channels leading to easy insertion of ions in the phosphomolybdic acid (PMA) and Ti$^+$ doped phosphomolybdic acid (Ti$_3$PO$_4$)(MoO$_3$)$_{12}$ thin films. It is also observed that the anodic peak potential shifts anodically which is a consequence of the requirement of excess energy for the intercalated ions with respect to the number of cycles.
Fig. 6.21 Cyclic voltammograms recorded for the phosphomolybdic acid (PMA) thin films for durability testing.

Fig. 6.22 Cyclic voltammograms recorded for the Ti\(^+\) doped phosphomolybdic acid (Ti PMA) thin films for durability testing.
6.3.2.e Chronoamperometry (CA)

A typical CA trace obtained during coloration and bleaching of as deposited phosphomolybdic acid (PMA) and Ti⁺ doped phosphomolybdic acid (Ti₃PO₄) (MoO₃)₁₂ thin films is shown in Fig. 6.23 and Fig. 6.24. During the experiment, the voltage was stepped from its rest potential of 0.0 V to -0.5 V for 10 s (coloration) and then reversed to +0.5 V for next 10 s (bleaching). From the current versus time transients, it is clearly observed that both coloration current ($I_c$) and bleaching current ($I_b$) following the steps were smooth and decreased continuously with time. The decrease of current with time is due to increase in chemical potential of cations Li⁺, as intercalation proceeds, according to the following relation [19].

$$n = \frac{V_A - \Delta \mu (x)}{Ne} \quad \text{(6.15)}$$

Where, $V_A$ is the applied voltage, $\Delta \mu (x)$ is the change in the chemical potential across the barrier and $N$ is the Avogadro’s number. This decrease in current with time has been used to measure the speed of EC response of iridium oxide thin films.

The response time is defined as the time required for the intercalation/deintercalation current to stabilize at its lowest value. The coloration time ($t_c$) and bleaching time ($t_b$) were calculated from the current time transients and found to be, for PMA $t_c = 3.4$ s and $t_b = 1.3$ s, for Ti PMA $t_c = 3.8$ s and $t_b = 1.7$ s.
Fig. 6.23 Chronoamperometric (CA) plot recorded for phophotungstic acid (PTA) thin film.

Fig. 6.24 Chronoamperometric (CA) plot recorded for Tl$^+$ doped phosphomolybdic acid (TIPMA) thin film.

The coloration time ($t_c$) and bleaching time ($t_b$) for PMA and TIPMA were calculated from the current time transients and are shown in Table 6.3.
Table 6.3 coloration time ($t_c$) and bleaching time ($t_b$) for PMA and TIPMA

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Response time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_c$ (sec)</td>
</tr>
<tr>
<td>PMA</td>
<td>3.4</td>
</tr>
<tr>
<td>TIPMA</td>
<td>3.8</td>
</tr>
</tbody>
</table>

6.3.2.f Chronocoulometry (CC)

To study Li$^+$ ion intercalation, de-intercalation process with respect to time, chronocoulometry was carried out at potential steps of ±0.5 V (versus SCE), for a step of 10 s. Fig. 6.25 and Fig. 6.26 shows corresponding chronocoulometry (CC) curve from which amount of charge intercalated ($Q_i$), amount of charge de-intercalated ($Q_{di}$) and hence residual charge ($Q_i - Q_{di}$) has been calculated. The electrochromic reversibility of the phosphomolybdic acid (PMA) thin film is calculated using relation 6.16 [20-21].

$$\text{Reversibility} = \frac{Q_{di}}{Q_i} \quad \text{---------- (6.16)}$$

The phosphomolybdic acid (PMA) thin film exhibited electrochromic reversibility up to 58% and Tl$^+$ doped phosphomolybdic acid (Tl$_3$PO$_4$) (MoO$_3$)$_{12}$ thin films exhibited electrochromic reversibility up to 56%.
Fig. 6.25 Chronocoulometric (CC) plot recorded for PMA-10 thin film.

Fig. 6.26 Chronocoulometric (CC) plot recorded for Tl$^+$ doped phosphomolybdic acid (TIPMA) thin film.
Table 6.4. Various parameters derived from the electrochemical Characterization

<table>
<thead>
<tr>
<th>Sample Id</th>
<th>Qi (µC/cm²)</th>
<th>Qdi (µC/cm²)</th>
<th>(Qi - Qdi) (µC/cm²)</th>
<th>Reversibility %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMA</td>
<td>0.0062</td>
<td>0.0022</td>
<td>0.0040</td>
<td>35</td>
</tr>
<tr>
<td>TIPMA</td>
<td>0.0052</td>
<td>0.0024</td>
<td>0.0028</td>
<td>47</td>
</tr>
</tbody>
</table>

6.3.2.g Iono-optical studies

Coloration and bleaching of phosphomolybdic acid (PMA) and TI⁺ doped phosphomolybdic acid thin films (TIPMA) was carried out by applying a potential step of ±0.5 V for a fixed time. The various parameters derived from the electrochemical characterization of chemicaly deposited phosphomolybdic acid (PMA) thin films are given in Table 6.4 The transmittance spectra were recorded for the phosphomolybdic acid (PMA) and TI⁺ doped phosphomolybdic acid thin films (TIPMA) thin films in its as deposited (A), Colored (C) and bleached (B) states in the wavelength range of 350 nm to 850 nm, at room temperature. The optical absorption by the thin layer is described by the dimensionless quantity (αt), which is called optical density (OD). The change in optical density (ΔOD) of phosphomolybdic acid (PMA) and TI⁺ doped phosphomolybdic acid (TIPMA) thin films at 630 nm, in its colored state and bleached state, is calculated using relation (6.17)

\[ ΔOD = \ln \left( \frac{Tb}{Tc} \right) \]

Where, Tb and Tc is the transmittance of the phosphomolybdic acid (PMA) thin film in its colored and bleached states, respectively. Fig. 6.27 and Fig. 6.28 shows the transmittance spectra recorded for the phosphomolybdic acid (PMA) and TI⁺ doped phosphomolybdic acid (TIPMA) thin films respectively in its as deposited (A), colored (C) and bleached (B) states. To describe the efficiency
of the charge to induce absorption in an electrochromic device is to introduce the coloration efficiency (CE). The CE is defined as the change in optical density ($\Delta OD$) per unit inserted charge and it is calculated using relation (6.8).

$$CE = \frac{\Delta OD}{\Delta Q}$$  \hspace{1cm} (6.18)

Where, $\Delta Q$ is the amount of charge intercalated in the sample to cause change in optical density ($\Delta OD$), which was estimated by integrating the area under the curve of current density versus time [22-26].

Fig.6.27 The transmittance spectra of the phosphomolybdic acid (PMA) thin film as deposited (A), colored (C) and bleached (B) states.
Fig. 6.28 The transmittance spectra of the Ti$^+$ doped phosphomolybdic acid (Ti PMA) thin film as deposited (A), colored (C) and bleached (B) states.

### 6.4 Conclusions

Tungsten and molybdenum HPOM thin films with polycrystalline and cubic spinal structure have been successfully deposited on the FTO-coated conducting glass substrates, using low cost chemical bath deposition technique. The films formed were uniform and well adherent. The film shows good EC properties.

### Table 6.5 Various parameters obtained from cyclic voltammetry and chronoamperometry studies of tungsten HPOM thin films.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Response time</th>
<th>$I_{pc}$ $\mu$A/cm$^2$</th>
<th>$I_{pa}$ $\mu$A/cm$^2$</th>
<th>Diffusion constant, cm$^2$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_c$ (sec)</td>
<td>$t_b$ (sec)</td>
<td></td>
<td>$I_{pc}$</td>
</tr>
<tr>
<td>PTA</td>
<td>4.8</td>
<td>3.4</td>
<td>-1.54 x 10^{-4}</td>
<td>1.32 x 10^{-4}</td>
</tr>
<tr>
<td>TIPTA</td>
<td>5.4</td>
<td>3.8</td>
<td>-6.22 x 10^{-4}</td>
<td>1.1 x 10^{-4}</td>
</tr>
</tbody>
</table>
Table- 6.6 Various electrochromic parameters calculated from electrochemical and iono-optical studies of tungsten HPOM thin films

<table>
<thead>
<tr>
<th>Sample Id</th>
<th>Qi (µC/cm²)</th>
<th>Qdi (µC/cm²)</th>
<th>(Qi - Qdi) (µC/cm²)</th>
<th>Reversibility (%)</th>
<th>Tb (%)</th>
<th>Tc (%)</th>
<th>Δ OD</th>
<th>CE cm²/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTA</td>
<td>-0.0030</td>
<td>-0.0014</td>
<td>-0.0016</td>
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<td>TIPTA</td>
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<td>-0.0021</td>
<td>-0.0024</td>
<td>54</td>
<td>49.5</td>
<td>18.5</td>
<td>0.43</td>
<td>97.88</td>
</tr>
</tbody>
</table>

Table- 6.7 Various parameters obtained from cyclic voltammetry and chronoamperometry studies of PMA and TIPMA thin films

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Response time tc (sec)</th>
<th>Response time tb (sec)</th>
<th>Ipc (µA/cm²)</th>
<th>Ipa (µA/cm²)</th>
<th>Diffusion constant, cm²/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ipc</td>
<td>Ipa</td>
<td></td>
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<tr>
<td>PMA</td>
<td>3.4</td>
<td>1.3</td>
<td>-4.16 x 10⁻⁴</td>
<td>1.68 x 10⁻⁵</td>
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<tr>
<td>TIPMA</td>
<td>3.8</td>
<td>1.7</td>
<td>-6.22 x 10⁻⁴</td>
<td>1.1 x 10⁻⁴</td>
<td>4.22 x 10⁻¹⁰</td>
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<td></td>
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</tbody>
</table>

Table- 6.8 Various electrochromic parameters calculated from electrochemical and iono-optical studies of PMA and TIPMA thin films

<table>
<thead>
<tr>
<th>Sample Id</th>
<th>Qi (µC/cm²)</th>
<th>Qdi (µC/cm²)</th>
<th>(Qi - Qdi) (µC/cm²)</th>
<th>Reversibility (%)</th>
<th>Tb (%)</th>
<th>Tc (%)</th>
<th>Δ OD</th>
<th>CE cm²/C</th>
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<tbody>
<tr>
<td>PMA</td>
<td>0.0062</td>
<td>0.0022</td>
<td>0.0040</td>
<td>35</td>
<td>23</td>
<td>6</td>
<td>0.66</td>
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<td>TIPMA</td>
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<td>14</td>
<td>7</td>
<td>0.27</td>
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By observing various parameters obtained from cyclic voltammetry, chronoamperometry and ionooptical studies of tungsten and molybdenum HPOM thin films (Table 6.5 to 6.8) it is clear that, reversibility of phosphotungstic acid (PTA) and phosphomolybdc acid (PMA) increases after doping thallium but coloring efficiency (CE) decreases.
References
