Immobilisation of phosphomolybdic (PM) acid by Nafion and the electrochromism of the resulting PM–Nafion films

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The electrochromism of phosphomolybdic (PM) acid in solution and immobilised in Nafion has been investigated. Immobilisation made use of two simple dip-coating techniques which allowed easy modification of the electrochemical activity of the composite films. PM in solution changed from light yellow to blue upon reduction, whereas immobilised PM showed a change from pale yellow to light blue under identical conditions. Electrostatic repulsions between PM anions and negatively charged sulfonic groups in Nafion limited the amount of PM that could be molecularly dispersed in Nafion. This, coupled with the poor conductivity inherent in the Nafion matrix, resulted in suppressed electrochemical reactivities for the composite films. Despite these results, UV–VIS absorption spectra showed marked differences in light absorption between the pristine and coloured forms of immobilised PM, indicative of application potentiality.

Electrochromism is the phenomenon related to changes in colour induced in selected materials by reversible electrochemical processes, where an electron-transfer or a redox reaction takes place.[1–4] Numerous materials, including both inorganic and organic liquids and solids, exhibit electrochromism. Phosphomolybdic (PM) and phosphotungstic (PW) acids of formula $P_2O_5\cdot24MO_3\cdot nH_2O$ (M = Mo, W) are crystalline compounds belonging to the family of heteropolyacids (HPAs).[5] Several HPAs have been shown to be electrochromic and follow similar colouration and bleaching mechanisms as that of MO_3 (M = Mo, W).[6]

In recent years, the observed capability of HPAs to modify persistently metallic, as well as semiconductor, surfaces has prompted electrochemists to use these compounds as surface promoters in electrochemistry.[7–9] Moreover, HPAs are of considerable interest as redox catalysts in a variety of oxidation reactions.[10] The electrocatalytic properties of these compounds as heterogeneous vapour-phase oxidation catalysts have been investigated extensively and are attributed to their reducibility and reoxidisability, strong dissociation constants and ionic conductivities.[11–14] Most previous studies on HPA modified electrodes were conducted with the aim of substituting noble-metal-based catalysts with less expensive materials activated by such compounds.

Promisingly, several HPAs exhibit colouration upon reduction. Thus, there is interest in the study of their electrochemical and electrochromic performance as well as their possible applications in display devices. The electrochromisms of PW powders and PW solutions[15] have been documented. The experimental results showed proton conduction and blue colouration of the materials upon electroreduction. It has been commented that HPAs will be useful as electrochromic materials only if they can be rendered translucent in the bleached state and be obtainable as thin films instead of compressed powders or in solutions.[1,4,16] These attributes are difficult to attain in the pristine form of such materials. Thus far only Shimidzu *et al.*[17] have reported the formation of a composite of PW with polypyrrole for electrochromic applications. In comparison, the electrochromism of PM has rarely been addressed and this work aspires to fill some of the voids. To this end, this paper reports very simple but effective means to immobilize PM as thin films on transparent substrates by Nafion, and the electrochromism of the resulting composite films. In addition, the electrochromism of PM in solution, which has rarely been mentioned in the literature, is also described.

Experimental

All chemicals used were of AR grade. Crystalline phosphomolybdic acid (PM, Merck) was dissolved in deionized water to the desired concentrations. A conventional three-electrode cell was used for all electrochemical experiments. Indium tin oxide (ITO) glass slides (Hampton Scientific) of dimensions 1.2×0.8 cm^2 were used as working electrodes. The counter and reference electrodes were a platinum basket and a saturated calomel electrode (SCE) respectively. Prior to their use, the ITO glasses were cleaned ultrasonically in deionised water followed by rinsing with ethanol.

An Aldrich Nafion solution containing 5 mass% of protonated Nafion 117 (molar mass 1100) in a mixture of low aliphatic alcohols and water (9:1), was used without dilution. The concentration of sulfonic acid groups was 39.7 mmol dm^{-3}. With the pH of the solution at 1.7, approximately 50% of the sulfonic acid was dissociated. Nafion was used to immobilise PM on ITO electrodes by two very simple methods.

Method A. Bare ITO slides were precoated with Nafion and the Nafion-coated ITO slides were exposed to the PM solution for different periods of time. The resulting composite films were identified as type A films.

Method B. Bare ITO slides were coated with Nafion solutions containing different amounts of dissolved PM. The resulting composite films were identified as type B films.

All the PM–Nafion composite films were dried in air.

Cyclic voltammetry (CV) and chronoamperometry (CA) were carried out at room temperature using the EG&G model 270 electrochemical measurement system. Aqueous 0.1 mol dm^{-3} $LiClO_4$ was used as the supporting electrolyte. CV began with a cathodic sweep from 1.0 V after the system had been conditioned at this potential for 15 s. A Shimadzu UV-3101PC spectrophotometer was used to obtain the UV–VIS spectra of pristine and blue PM–Nafion composite films in aqueous solutions.

Results and Discussion

Electrochromism of PM in solutions

PM was dissolved in deionised water to give a 1 mmol dm^{-3} solution. The solution at this concentration was light yellow. The solution next to the electrode was immediately darkened to blue when a small and negative potential (*ca.* −0.05 V) was applied. The blue colouration could be bleached by applying a positive potential to the electrode, but at a much slower rate relative to colouration. No solid deposit was formed on the electrode. The colouration was due to the localization of a soluble coloured species near the electrode, which would eventually diffuse away and disappear if left alone.

The cyclic voltammogram of a 1 mmol dm^{-3} PM aqueous solution at a scan rate of 50 mV s^{-1} is shown in Fig. 1. $LiClO_4$ (0.1 mol dm^{-3}) was added as the supporting electrolyte. In the cathodic scan, the current began to increase significantly at 0.4 V until the end of the scan was reached. Some small reduction peaks also emerged as shoulders during the scan. The solution next to the electrode turned increasingly blue as the current increased. On the reverse scan, several corresponding oxidation peaks appeared, and the blue PM species was bleached slowly and incompletely relative to colouration. If the reverse scan was not started immediately after the end of the forward scan, and the system was left to stand for some time, the blue colouration began to spread and decolourisation could not be completed in the reverse scan. The species formed upon PM reduction was therefore water-soluble, and deposition of a solid was not possible in this case. Chang *et al.*[18] reported an analogous system of polytungstic anions, and its electrochemical colouration and bleaching by acidified H_2O_2. Cho *et al.*[19] observed a complex anodic voltammetric pattern for PM electrocatalysts at slow scan rates and attributed it to slow reaction kinetics in the formation of unstable higher oxidation state species of PM. Cyclic voltammograms of PM electrocatalysts in a 50% (v/v) water–dioxane mixture with 0.5 mol dm^{-3} H_2SO_4 also showed similar anodic behaviour.[7]

Double-step chronoamperometry was used to assess the speed of electrochromic response in solution. Fig. 2 shows the *I–t* transient of a 0.5 mmol dm^{-3} PM aqueous solution. The ITO electrode was preconditioned at 0.8 V for 15 s to keep the PM solution in its pristine light yellow colour. The potential was then stepped to −0.1 V for 4 s and the solution next to the electrode immediately turned blue. This was followed by an anodic step to 0.8 V for 4 s during which the blue species was progressively bleached and the solution returned to the pristine colour of the PM solution. The ease of PM colouration enabled the use of a small negative potential (−0.1 V) to reduce the effects of hydrogen evolution. It can be seen from the current transient that colouration and bleaching proceeded at noticeably different rates, with more time being needed for bleaching than for colouration. The higher residual current in the electroreduction step could be due to the evolution of small amounts of hydrogen. The chronoamperometric results are therefore in general agreement with the cyclic voltammetric results.

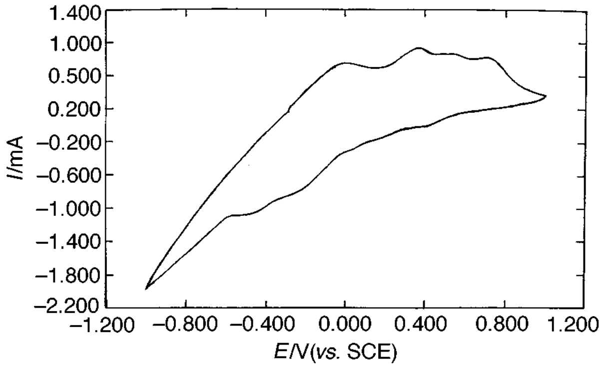

Fig. 1 Cyclic voltammogram of a 1 mmol dm^{-3} PM aqueous solution at 50 mV s^{-1}. 0.1 mmol dm^{-3} $LiClO_4$ was added as the supporting electrolyte.

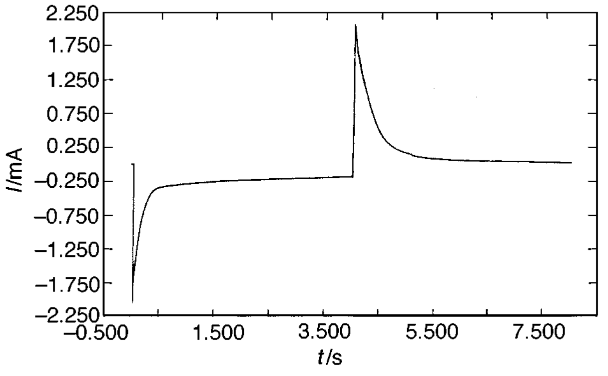

Fig. 2 *I–t* Transient of a 0.5 mmol dm^{-3} PM aqueous solution. The electrode was conditioned at 0.8 V for 15 s before the potential was stepped to −0.1 V for 4 s and then to 0.8 V for another 4 s.

Electrochromism of type A PM–Nafion films

Crystalline PM powder was dissolved in deionized water to concentrations of 1, 5 and 10 mmol dm^{-3}, resulting in light yellow solutions. Nafion-coated ITO electrodes were prepared by dip-coating. Bare ITO electrodes were lowered into the Nafion solution and withdrawn immediately. The Nafion-coated ITO electrodes were kept vertically straight and the solvent was allowed to evaporate in air overnight. PM was subsequently introduced into the Nafion layer by exposing the Nafion-coated ITO electrodes to a given PM solution for a predetermined time, followed by washing in deionized water and drying in air. All resulting PM–Nafion films were pale yellow.

The incorporation of PM into the Nafion layer was hindered by electrostatic repulsions between anionic PM species and the negatively charged sulfonate groups of Nafion. However, a certain amount of PM anions could still be incorporated into Nafion by virtue of a concentration difference across the ion-permeable Nafion membrane.[1] Honda *et al.*[20] fabricated Prussian Blue (PB)-based electrochromic devices through sequential immersions of a Nafion membrane in Fe^{2+} and $Fe(CN)_6{}^{3-}$ solutions. The resulting PB-containing Nafion composite film showed very satisfactory electrochromism. Nafion has also been used to reduce the slow dissolution of electrochromes under application conditions. A good example is given by Shen *et al.*[21] who coated electrochromic WO_3 by Nafion to prolong the life of the former in acidic media.

Fixed PM concentration, varying immersion time (type A1 films). Fig. 3 shows the cyclic voltammograms of Nafion-immobilised PM on ITO slides in aqueous 0.1 mmol dm^{-3} $LiClO_4$ at 50 mV s^{-1}. The electrodes were prepared by exposing Nafion-coated ITO to a 5 mmol dm^{-3} aqueous PM

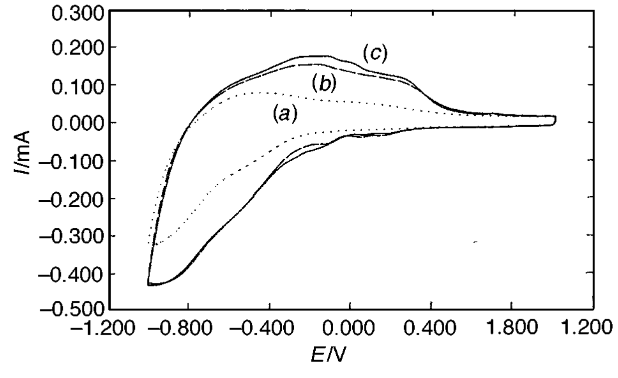

Fig. 3 Cyclic voltammograms of type A1 immobilised PM films in 0.1 mmol dm^{-3} $LiClO_4$–H_2O at 50 mV s^{-1}. The electrodes were prepared by immersion of Nafion-coated ITOs in 5 mmol dm^{-3} PM aqueous solution for different times [(*a*) 30 s, (*b*) 5 min and (*c*) 10 min].

solution for 30 s, 5 min and 30 min. All voltammograms displayed characteristic PM behaviour (see Fig. 1). The electrochemical activity of the composite films was lower than that of PM in solution but their reversibility, in terms of the closeness of the anodic peak to the cathodic end, was better. At the shortest immersion time (30 s), both the cathodic colouration and anodic bleaching currents were relatively small. This was primarily due to limited incorporation of PM in the Nafion, resulting in a low concentration of PM in the composite film. When the immersion time was lengthened to 5 min, more PM permeated and incorporated into the Nafion layer and the resulting PM–Nafion film showed higher colouration and bleaching currents. However, corresponding to the increase in currents, the anodic peak was shifted to a more positive potential, indicating a decrease in electrochemical reversibility. Increasing the immersion time to beyond 5 min did not bring about any significant changes in the voltammograms. This implies that PM incorporation into Nafion has reached saturation after 5 min for the 5 mmol dm^{-3} solution. The saturation time is, of course, dependent on the Nafion layer thickness and the concentration of the PM solution. There are no economic incentives to use an immersion time greater than that needed to saturate Nafion with PM.

Double-step chronoamperometry was carried out to evaluate the electrochromic response of PM–Nafion films to potential steps. The films were initially conditioned at 1.0 V for 15 s. The potential was then stepped to −1.0 V for 4 s and returned to 1.0 V for another 4 s. Larger potential steps were needed to initiate the electrochromic response because of the increased *IR* drop introduced by the Nafion layer. Fig. 4 shows the response of PM–Nafion films prepared using different immersion times, as indicated. The supporting electrolyte was 0.1 mmol dm^{-3} $LiClO_4$ in water. The films after conditioning were pale yellow. The first step (1.0 V→−1.0 V) coloured the films to the characteristic pale blue of reduced PM and the second step (−1.0 V→1.0 V) restored the pristine colour of the films.

With increased immersion time, the response time increased and the response speed decreased. Increasing the immersion time beyond 5 min did not bring about significant changes in the response speed, which agreed well with the voltammetric findings. For each case, the response during the initial stage of colouration (*ca.* 0.5 s) was quite fast and distinct but became slower thereafter. In contrast, all PM coloured in the first step could be completely bleached in *ca.* 1.5 s in the decoloration step.

As has been mentioned previously, an aqueous PM solution showed faster colouration than bleaching, inferring that PM was easier to reduce than to reoxidise. This behaviour was reflected only within the first 0.5 s of the colouration of PM–Nafion films, thereafter the occurrence of the hydrogen evolution reaction (HER) and the matrix effect of Nafion intervened. The poor conductivity of Nafion hampered the effectiveness of charge-transfer reactions except for those occurring immediately next to the electrode.[1,21] As a result, colouration and bleaching became sluggish and slower than the corresponding processes in aqueous solution.

Fixed immersion time, varying PM concentration (type A2 films). Experiments were also carried out using a fixed immersion time of 5 min and different PM concentrations (1, 5 and 10 mmol dm^{-3}). The choice of 5 min was arbitrary (although it did correspond to the near-optimal immersion time for the 5 mmol dm^{-3} solution), and no attempt was made to use factorial experimental design procedures to obtain the optimal preparation conditions from the experimental variables.

The effect of concentration on the voltammograms of PM–Nafion composite films is shown in Fig. 5. For the 1 mmol dm^{-3} case, both the cathodic colouration and the anodic bleaching currents were smaller. The anodic peak was, however, closer to the cathodic end of the scan, indicating better electrochemical reversibility for electrochromism. This observation can be understood in terms of a low concentration of PM in the Nafion layer. Immersion for 5 min was probably inadequate for a dilute PM solution to fully saturate the Nafion layer. A subsequent increase in electrochromic activity was possible with increased immersion time. On the other hand, there were no substantial changes in the voltammetric features when the PM concentration was increased beyond 5 mmol dm^{-3}. In relation to the 1 mmol dm^{-3} solution, the cathodic and anodic currents were higher and the anodic peak was located at a more positive potential, indicating that more PM had permeated into the Nafion layer resulting in a higher concentration of immobilised PM. Since 5 min immersion was adequate for the 5 mmol dm^{-3} PM solution to saturate the Nafion layer, further increasing the PM concentration to 10 mmol dm^{-3} would only lead to a faster approach to saturation, but not to any increase in the electrochromic activity of the composite films. If statistical design of experiment procedure is followed, an optimal electrochromic response (in terms of activity, reversibility, response time and cost-effectiveness of preparation) from a defined domain of immersion time and PM concentration could be identified. Nevertheless, the present unoptimised results do verify that Nafion is PM-permeable and that it is easily saturated by PM because of the electrostatic repulsions between PM anions and the negatively charged sulfonate groups of Nafion.

The electrochromic performance of these films was again tested by chronoamperometry and the resulting *I*–*t* transients are shown in Fig. 6. The experimental conditions were the same as those used for Fig. 4. The films after conditioning showed a pale yellow colouration, which changed to pale blue

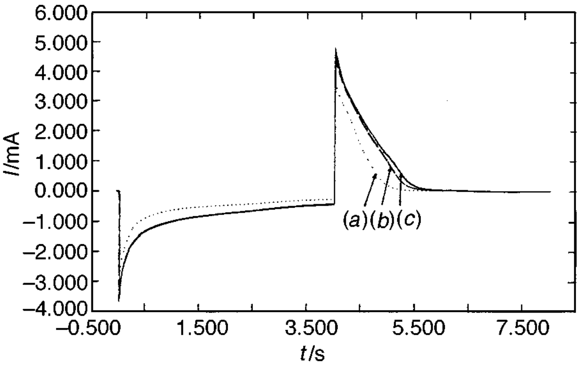

Fig. 4 Double-step chronoamperometric curves of type A1 immobilised PM films in 0.1 mol dm^{-3} $LiClO_4$–H_2O. The potential was stepped between −1.0 and 1.0 V for 4 s in each interval; (*a*) 30 s, (*b*) 5 min, (*c*) 10 min.

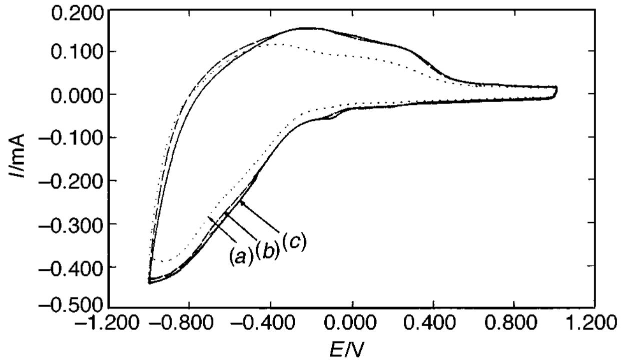

Fig. 5 Cyclic voltammograms of type A2 immobilised PM films in 0.1 mol dm^{-3} $LiClO_4$–H_2O at 50 mV s^{-1}. The electrodes were prepared by immersing Nafion-coated ITOs in aqueous PM solutions of different concentrations [(*a*) 1, (*b*) 5 and (*c*) 10 mmol dm^{-3}] for 5 min.

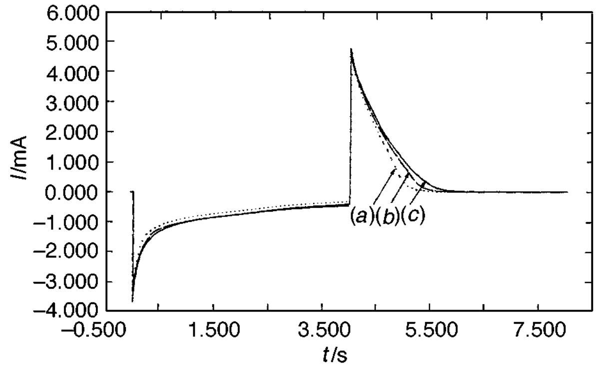

Fig. 6 Chronoamperometric curves of type A2 immobilised PM films in 0.1 mol dm^{-3} $LiClO_4$–H_2O. The potential was pulsed between −1.0 and 1.0 V for 4 s in each step; (*a*) 1, (*b*) 5, (*c*) 10 mmol dm^{-3}.

during colouration but returned to the pristine colour after bleaching.

Similar to Fig. 4, the current transient slowed after the first 0.5 s of colouration. Bleaching, on the other hand, was more efficient and all of the PM coloured in the first potential step could be completely bleached in *ca.* 1.5 s. The peak current in bleaching was also higher than that in colouration. With the increase in PM concentration, the response time increased and the response speed decreased, but the increase was less conspicuous when the solution concentration was increased from 5 to 10 mmol dm^{-3}. The parallel with the voltammetric behaviour of these films is quite evident.

Electrochromism of type B PM–Nafion Films

In this alternative method of PM immobilisation, PM was dissolved in a Nafion solution and applied to the surface of ITO electrodes by dip-coating. The resultant PM–Nafion composite films after solvent evaporation were light yellow. Their electrochemical characterizations in 0.1 mol dm^{-3} aqueous $LiClO_4$ followed the same procedures as described earlier.

As PM was dissolved directly into the Nafion solution, the limit of PM incorporation was determined by the solubility of PM in Nafion, although electrostatic repulsions could still operate on the molecular level to result in separate microscopically dispersed phases of Nafion and PM in the composite. Fig. 7 shows the voltammograms of several PM–Nafion films which were prepared by coating ITO directly with PM–Nafion solutions of different PM concentrations (1, 5 and 10 mmol dm^{-3} PM). With increasing PM concentration in Nafion, both cathodic and anodic currents continued to increase. This is unlike type A films, where the increase in electrochromic activity stopped at 5 mmol dm^{-3}. Only slight increases were possible due to the poor conductivity of Nafion. Increasing the PM concentration again brought about a positive shift in the first anodic peak. Similar to Fig. 1, more than one anodic peak was detected, which may be indicative of the presence of a separate PM phase in the composite. Again the increase in activity came at the expense of a decrease in electrochemical reversibility. Although the electrochromic reversibility of these films was reduced by virtue of a higher concentration of immobilised PM, most major voltammetric features are qualitatively similar to those of type A films.

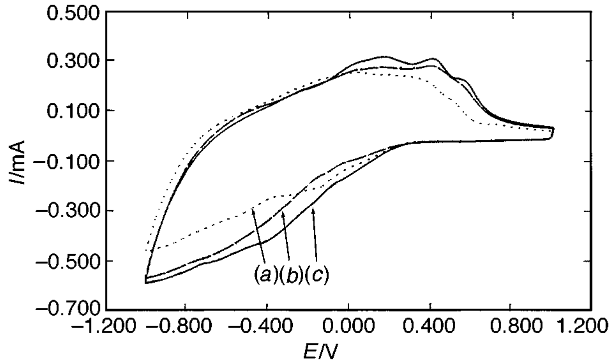

Fig. 7 Cyclic voltammograms of type B immobilised PM films in 0.1 mol dm^{-3} $LiClO_4$–H_2O at 50 mV s^{-1}. The electrodes were prepared by dip-coating bare ITO in mixed PM and Nafion solutions of different PM concentrations [(*a*) 1, (*b*) 5 and (*c*) 10 mmol dm^{-3}].

The chronoamperometric response of the type B PM–Nafion films is shown in Fig. 8. The films after conditioning were light yellow, and changed to light blue during colouration and returned to light yellow after bleaching. The chronoamperometric response was similar to that of the type A films, except that the response times for colouration and bleaching were generally longer, and the peak currents were more similar. These changes arose because of the higher concentration of PM in Nafion which imposed a negative effect on the respond speed. The current response in the first 0.5 s of colouration was still fast, but a subsequent slowing of response was nonetheless observed. In the following bleaching step, all the PM coloured in first step could be completely bleached in *ca.* 3 s.

With increasing PM concentration, the response time increased slightly, which was consistent with the slight increase of both colouration and bleaching currents in the voltammograms. The changes in the response currents and response times with concentration were smaller because of a larger immobilised PM fraction in these films compared to type A films. Lower electrochemical reversibility aside, method B does offer a more expedient and convenient method for the immobilisation of PM in Nafion. The PM loading in the film can be adjusted through the PM concentration in the solution. The homogeneity of the composite layer may, however, be compromised at too high a loading level.

UV–VIS spectroscopy

The optical absorption spectra of a type B film prepared from a 5 mmol dm^{-3} PM solution in Nafion are shown in Fig. 9. The pristine form of the film was light yellow and was held at −0.5 V for 2 min in 0.1 mol dm^{-3} $LiClO_4$ until it turned light blue. The absorbance of the pristine film decreased with wavelength in the region 350 to *ca.* 500 nm and remained nearly constant thereafter at a relatively low level of absorption. A broad absorption occurred, however, for the light blue film, the absorbance decreased from 350 to *ca.* 500 nm and then increased with further increase in the wavelength. In addition, the intensity of absorption increased with increasing negative potentials in steps with the response of the cathodic current to the same electrical stimulations. All type A films also

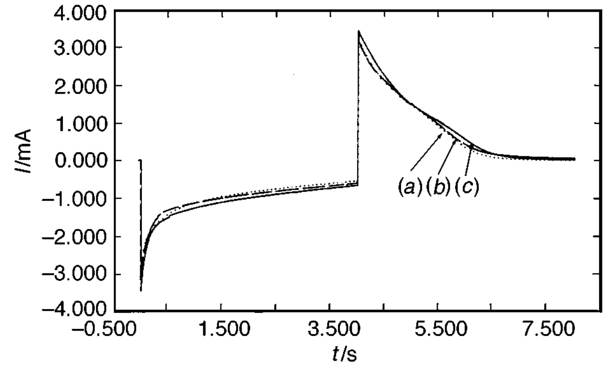

Fig. 8 Double-step chronoamperometric curves of type B immobilised PM films in 0.1 mol dm^{-3} $LiClO_4$–H_2O. The potential was stepped between −1.0 and 1.0 V for 4 s in each interval; (*a*) 1, (*b*) 5, (*c*) 10 mmol dm^{-3}.

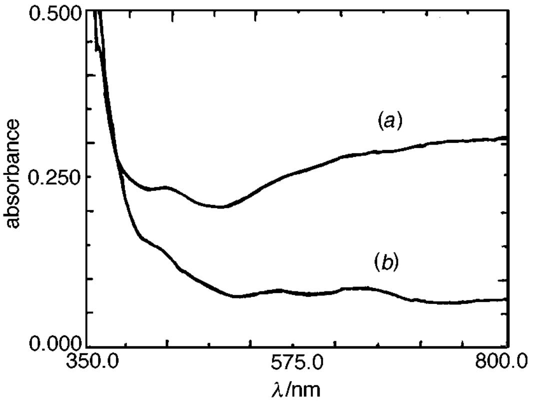

Fig. 9 UV–VIS spectra of coloured (*a*) and pristine (*b*) type B films. The films were prepared from a 5 mmol dm^{-3} PM solution in Nafion, and held at −0.5 V for 2 min to change from light yellow to light blue.

exhibited similar optical characteristics under identical conditions.

The marked difference in light absorption between the two forms of PM in the wavelength range 350–800 nm is desirable for practical electrochromic applications such as smart windows. The optical absorbance in the coloured state can be varied through manipulation of the PM concentration in Nafion and the magnitude of the applied cathodic potential. A good colouration can therefore be attained with a smaller amount of electrochrome and/or lower energy input, resulting in substantial savings in the operating cost of the electrochromic devices. The simple methodologies outlined here have removed a major hindrance to the use of HPAs for electrochromic applications, namely their immobilisation on transparent optical substrates.

Conclusions

The electrochromism of phosphomolybdic (PM) acid in solution and in a series of PM–Nafion composite films was investigated by means of cyclic voltammetry, chronoamperometry and UV–VIS spectroscopy. PM in solution changed from light yellow to blue upon reduction, whereas the composite films showed a change from pale yellow to light blue under identical conditions. By using Nafion, PM could be immobilized on ITO substrates as thin films by two very simple but effective methods, thereby removing a major hindrance to the use of PM in electrochromic applications.

The experimental results showed that the composition of the PM–Nafion composite films could be tailored and hence their electrochromic properties (such as activity, reversibility, response speed and optical contrast) could also be manipulated as desired by changing the PM concentration in aqueous solution and/or the immersion time of Nafion-coated ITO in this solution as well as the concentration of PM dissolved directly in the Nafion solution. However, owing to electrostatic repulsions between PM anions and the negatively charged sulfonate groups of Nafion, and the poor conductivity of the Nafion matrix, the extent of incorporation was limited and Nafion was easily saturated by PM, leading to relatively low electrochromic activity for the composite films. On the other hand, the electrochromic reversibility of PM–Nafion films was better than that of PM solution because immobilisation led to increased availability of electroactive species in the electrode proximity. UV–VIS spectroscopy showed marked differences in light absorption between as-prepared and coloured immobilised PM species that are suitable for practical applications.

References

1 P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism: fundamentals and applications*, VCH, Weinheim, 1995.
2 C. G. Granqvist, *Appl. Phys. A*, 1993, **56**, 1.
3 B. W. Faughnan and R. S. Crandall, in *Top. Adv. Phys.*, 1980, **40**, 181.
4 C. M. Lampert, *Sol. Energy Mater.*, 1984, **11**, 1.
5 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 1972, p. 950.
6 B. Tell and S. Wagner, *Appl. Phys. Lett.*, 1978, **33**, 837.
7 B. Keita and L. Nadjo, *J. Electroanal. Chem.*, 1988, **243**, 87.
8 B. Keita, L. Nadjo and J. M. Saveant, *J. Electroanal. Chem.*, 1988, **243**, 105.
9 O. Savadogo, *J. Electrochem. Soc.*, 1992, **139**, 1082.
10 R. Standberg, *Acta Chem. Scand., Ser. A*, 1975, **29**, 359.
11 M. Akimoto, H. Ikeda, A. Okabe and E. Echigoya, *J. Catal.*, 1984, **89**, 196.
12 M. Ai, *J. Catal.*, 1981, **71**, 88.
13 M. Akimoto, K. Shima, H. Ikeda and E. Echigoya, *J. Catal.*, 1984, **86**, 173.
14 M. Mizuno, T. Watanabe and M. Misono, *J. Phys. Chem.*, 1985, **89**, 80.
15 P. Stonehart, J. C. Koren and J. S. Brinen, *Anal. Chim. Acta*, 1968, **40**, 65.
16 A. Donnadieu, *Mater. Sci. Eng. B*, 1989, **3**, 185.
17 T. Shimidzu, A. Ohtani, M. Aiba and K. Honda, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 3941.
18 I. F. Chang, B. L. Gilbert and T. J. Sun, *J. Electrochem. Soc.*, 1975, **122**, 955.
19 K. Cho, S. O. Chung, K. Ryu, K. Kim, J. H. Choy and H. Kim, *Synth. Met.*, 1995, **69**, 481.
20 K. Honda and H. Hayashi, *J. Electrochem. Soc.*, 1987, **134**, 1330.
21 P. K. Shen, H. T. Huang and A. C. C. Tseung, *J. Mater. Chem.*, 1992, **2**, 497.

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