

R. Thangamuthu · S. M. Senthilkumar ·  
K. Chandrasekara Pillai

## Octacyanomolybdate-doped-poly(4-vinylpyridine) ionomer film electrode for the electrocatalytic oxidation of L-ascorbic acid

Received: 28 August 2005 / Revised: 24 September 2005 / Accepted: 30 September 2005 / Published online: 15 November 2005  
© Springer-Verlag 2005

**Abstract** Poly(4-vinylpyridine) (PVP)-based anion exchange polymers are not studied as much as cation exchange polymers Nafion and Eastman Kodak AQ for electroanalytical applications. Similarly, octacyanomolybdate  $[\text{Mo}(\text{CN})_8^{4-}]$  has not been studied much as a redox mediator. This communication presents results from examinations of the behaviour of  $\text{Mo}(\text{CN})_8^{4-}$ -doped PVP ionomer film electrode to highlight the opportunities for realization of the application of this composite electrode for L-ascorbic acid ( $\text{AH}_2$ ) estimation via electrocatalytic mediation in acidic medium. The modified electrodes were characterized by cyclic voltammetry and rotating disc electrode voltammetry. PVP coatings possess strong anion-binding capacity for  $\text{Mo}(\text{CN})_8^{4-}$  mediator with an extraction coefficient of 990, and electrostatically cross-linked PVP films offer insignificant resistance to permeation of  $\text{AH}_2$ , facilitating a cross-exchange reaction between the substrate and the mediator in the entire film volume. They show effective electrocatalytic oxidation of  $\text{AH}_2$ , with the oxidation potential of  $\text{AH}_2$  decreased by  $\sim 200$  mV in overpotential compared to that at bare electrode.  $\text{Mo}(\text{CN})_8^{4-}$ /PVP composite electrode does not respond to the more common interferents of L-ascorbic acid estimation even at high positive potentials. These and several other attractive potentialities of the modified electrode are demonstrated by direct determination of  $\text{AH}_2$  in a commercial vitamin C tablet without any special treatment, with the value closely agreeing ( $\pm 0.75\%$ ) with the reference method.

**Keywords** Ionomer-modified electrode · Poly(4-vinylpyridine) ·  $\text{Mo}(\text{CN})_8^{3-/4-}$  · L-ascorbic acid · Electrocatalytic oxidation

### Introduction

Polymer-coated electrodes incorporating functional redox molecules have attracted great interest for their applications in several fields especially in electrocatalysis and electroanalysis, including biosensor development [1, 2]. Among the various electroactive polymer electrodes developed, conducting and redox types have been widely studied compared to ion exchange film-polymer electrodes [1–3] because mediator components are covalently linked to the polymer backbone in the former's polymer composites, thus reducing catalyst leaching from the electrode surface—a problem quite often encountered with later type electrodes. Despite this weakness, polyelectrolyte-coated electrodes offer several advantages such as practical simplicity and convenience, since any desirable ionic species can be very conveniently incorporated into a polyelectrolyte film via ion exchange [4–9]. Ion exchange is normally performed by simply immersing a polymer-coated electrode into a dopant solution, with or without potential cycling. Electrostatic interactions are the basis of the binding of oppositely charged species to the polymer. It is well established [4–9] that ion exchange is quite fast and that this feature is especially useful for easily regenerating the activity of the electrode upon repetitive measurements [1–3, 6, 7, 10, 11]. In the present work, we describe the electrocatalytic activity of a protonated poly(4-vinylpyridine) (PVP) film electrostatically cross-linked with octacyanomolybdate  $[\text{Mo}(\text{CN})_8^{4-}]$  anion towards ascorbic acid ( $\text{AH}_2$ ) oxidation, and we show that this ionomeric-film-modified electrode fulfils the characteristics required for good catalysis and is very competitive in terms of sensitivity, linear detection range and selectivity compared to several previously developed electrodes for ascorbic acid estimation, based on conducting polymers, viz. polypyrrole [12] and polyaniline [13, 14]; redox polymers

R. Thangamuthu · S. M. Senthilkumar ·  
K. Chandrasekara Pillai (✉)  
Department of Physical Chemistry,  
University of Madras,  
Guindy Campus,  
Chennai, 600 025, India  
e-mail: kc\_pillai@yahoo.com  
Fax: +91-44-22352494

*Present address:*  
R. Thangamuthu  
Department of Chemical Engineering,  
National Yunlin University of Science and Technology,  
Yunlin, Taiwan, ROC

(organic and inorganic) such as  $[\text{Os}(\text{bpy})_2(\text{PVP})_{10} \text{Cl}]\text{Cl}$  [15], electropolymerized Ni(II) tetraaza macrocyclic compound  $[\text{Ni}(\text{II})(\text{Tet-a})]$  [16] and nickel pentacyanonitrosylferrate films [17]; screen-printed carbon electrode (SPCE) impregnated with the electrocatalyst 2,6-dichlorophenolindophenol lanthanum salt (DCPI) [18]; and carbon paste electrode (CPE) spiked with ferrocene carboxylic acid ( $\text{FcCOOH}$ ) [19]—in all of which redox mediator molecules are either covalently attached to or entrapped in 3D matrices.

Our interest in PVP film electrode electrostatically doped with  $\text{Mo}(\text{CN})_8^{4-}$  ions arose because, in the overwhelming majority of previous electrocatalysis and amperometric chemical and biological sensor works utilizing polyelectrolyte coatings as mediator-entrapping matrices, only polyanionic polymers, viz. Nafion and Eastman Kodak AQ, are most abundantly used [20]. Polycationic polymers that are presently available—such as vinylpyridine-based polymers [PVP [4, 21, 22], quaternized PVP [23, 24], poly(acrylamide/vinylpyridine) copolymer gel [25] and ternary copolymer [26]], poly(L-lysine) [27] and siloxane-based pyridinium polymers [6, 8]—are not found in many applications [20]. On the other hand, these cationic polymers doped with anionic redox components [such as  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{W}(\text{CN})_8^{4-}$ ,  $\text{Mo}(\text{CN})_8^{4-}$  and  $\text{IrCl}_6^{3-}$ ] have been extensively used as model electroactive polymer systems, and entire studies with these composites have been directed towards understanding such phenomena [e.g., general properties of polymer-modified electrodes [4, 6, 8], charge transport in polymer membranes [23, 24] and testing and verifying [6, 22, 25–27] various theories proposed for electrocatalysis at electroactive polymer-modified electrodes [28–30]. The potential utility of electroactive PVP ionomer coatings in electroanalytical applications is not fully explored.

It may be interesting to note that  $\text{Mo}(\text{CN})_8^{4-}$ -doped PVP and  $\text{Mo}(\text{CN})_8^{4-}$ -doped poly(L-lysine) ionomer film electrodes are some of the first examples cited in the literature as capable of exhibiting catalytic properties; however, the systems studied to date involve only model outer-sphere electron transfer couples, such as  $\text{Fe}^{3+}$  reduction,  $\text{Fe}^{2+}$  oxidation [21] and  $\text{Co}(\text{tpy})_3^{2+}$  oxidation (where tpy=terpyridine) [27]. The only electroanalytical application of  $\text{Mo}(\text{CN})_8^{4-}$ /PVP ionomer composite electrode is the ion exchange voltammetry work by Lorenzo and Abruna [11], who used  $\text{Mo}(\text{CN})_8^{4-}$ -doped quaternized PVP-modified electrode to estimate  $\text{Ag}^+$  ions via a non-faradaic preconcentration method. The octacyanomolybdate complex,  $\text{Mo}(\text{CN})_8^{3-/4-}$ , is an interesting candidate as a redox center, since it is highly reversible, fast-reacting, pH-independent, stable in both oxidized and reduced forms, and unreactive with  $\text{O}_2$ . Schroder and Scholz [31] have used the silver complex of  $\text{Mo}(\text{CN})_8^{4-}$  (V/IV) in microscopic in situ diffuse reflectance spectroelectrochemical studies to understand the interface region where the charge transfer process starts and its direction of advancement in the solid phase. Taniguchi et al. [32] have demonstrated that it is a highly active mediator in dissolved state for the oxidation of flavoproteins such as lactate oxidase and sarcosine oxidase. Moreover, Pelizzetti

et al. [33] have shown that, in a solution of 1 M  $[\text{H}^+]$  composition and 1 M ionic strength,  $\text{Mo}(\text{CN})_8^{3-}$  oxidizes L-ascorbic acid at 20°C at an exceptionally faster rate, with the second-order homogeneous rate constant being  $665 \text{ M}^{-1} \text{ s}^{-1}$ . Because of these potentialities, the PVP/ $\text{Mo}(\text{CN})_8^{4-}$  composite electrode is expected to provide a highly stable and sensitive electrocatalytic system for  $\text{AH}_2$  oxidation and its estimation. Our present objective in this work is to highlight results on several basic properties of this chemically modified electrode, such as (1) the anion-binding ability of the resulting PVP ionomer film, (2) charge transport in the film in the absence of substrate (ascorbic acid), (3) ascorbic acid diffusion in the PVP film—key factors that invariably control the catalytic performance of a modified electrode [5, 28–30]. The effects of pH, interferents and electrode stability on  $\text{AH}_2$  oxidation are also described.  $\text{Mo}(\text{CN})_8^{4-}$ /PVP composite electrode is proved to possess a strong binding capacity for  $\text{Mo}(\text{CN})_8^{4-}$ , less restricted  $\text{AH}_2$  diffusion in the film, excellent mediated activity for  $\text{AH}_2$ , strong electroinactivity for several interferents and minimal propensity for electrode surface fouling, which allow an easy-to-perform, fast, selective and sensitive method for the convenient amperometric estimation of L-ascorbic acid in pharmaceutical drug formulation without any special treatment. Moreover, the ascorbic acid content estimated by the PVP/ $\text{Mo}(\text{CN})_8^{4-}$  composite electrode fell within  $\pm 0.75\%$  of the value obtained by the Association of Analytical Communities (AOAC) method [34]. Note that the catalytic electrochemical oxidation of ascorbic acid on modified electrodes is a continuous research interest, and it has been reported recently on electrodes modified by cobalt hexacyanoferrate [35] or metal tetrabenzoporphyrins [36].

## Experimental details

$\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  was prepared following the reported method [37], and PVP was obtained by the polymerization of 4-vinylpyridine monomer (Fluka) using 2,2'-azobis(isobutyronitrile) (Fluka) as the initiator [38]. The weight average molecular weight ( $M_w$ ) of PVP determined viscometrically was  $5.2 \times 10^5$ . L-ascorbic acid was recrystallized twice from distilled water. All other chemicals were of Analar grade and were used without further purification. Double-distilled water passed through an activated charcoal column was used to prepare all experimental solutions.

PVP-coated glassy carbon (GC) electrodes (geometric area  $0.19 \text{ cm}^2$ ; Pine Instruments Co., USA) were prepared by droplet evaporation of  $7 \mu\text{l}$  of a 0.2% (wt/vol) methanolic PVP solution followed by drying for 12 min at room temperature. Before coating with PVP, the electrode was polished to a mirror finish with graded emery papers (1/0, 2/0, 3/0, 4/0 and 6/0 Kohinor products, India), degreased with trichloroethylene, smoothed on a polishing cloth, washed with copious amounts of double-distilled water and dried.  $\text{Mo}(\text{CN})_8^{4-}$ -doped PVP ionomer film electrodes were fabricated by dipping PVP-coated electrodes in 0.1 M  $\text{H}_2\text{SO}_4$  containing 2 mM  $\text{Mo}(\text{CN})_8^{4-}$  for 30 min.

A Pt electrode of large surface area and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All experimental solutions were deaerated with purified nitrogen for 30 min before the commencement of electrochemical measurements at  $27 \pm 0.2^\circ\text{C}$ . A Wenking potentiostat (ST 72), coupled with a Wenking signal generator (VSG 83) and a Graphtec X–Y–t recorder (WX 2300), was used to record cyclic voltammograms. An electrode rotator from Pine Instruments Co. was employed in rotating disk electrode measurements.

## Results and discussion

Electrochemical response from  $\text{Mo}(\text{CN})_8^{4-}$ /PVP ionomer film electrode in the absence of L-ascorbic acid

When an  $\text{Mo}(\text{CN})_8^{4-}$ /PVP-film-modified GC electrode was scanned continuously by cyclic voltammetry from 0 to 1,200 mV with a scan rate ( $\nu$ ) of  $20 \text{ mV s}^{-1}$  in  $0.1 \text{ M H}_2\text{SO}_4$ , a pair of redox peaks was observed at 560 and 500 mV, as illustrated in Fig. 1 (curve a). The characteristics of reversible redox processes shifted from adsorption-controlled to diffusion-controlled as the scan rate increased. At  $\nu < 10 \text{ mV s}^{-1}$ ,  $[\partial \log(i_{\text{pa}})/\partial \log(\nu)]$  was close to unity, and it was equal to 0.5 at faster scan rates in  $0.1 \text{ M H}_2\text{SO}_4$  for the above electrode doped with different amounts of  $\text{Mo}(\text{CN})_8^{4-}$  ion. Along with these changes, peak potential difference  $\Delta E_p$  values also increased from 20 to 135 mV with increasing scan rate.

At low scan rates, in addition to non-zero peak separation, it was also observed that voltammetric peaks possessed a full-width-at-half-maximum potential  $E_{\text{FWHM}}$ , which was significantly different from 90.6 mV, as expected in an ideal one-electron process [39, 40]. The interaction parameter ( $r$ ) for the  $\text{Mo}(\text{CN})_8^{4-}$ /PVP system was calculated using the equation  $i_{\text{pa}} = nF\nu Q_t / RT(4 - 2r\Gamma_t)$  following the procedure suggested by Facci and Murray [41] from the voltammetric charge  $Q_t$ , the total amount of dopant in the film  $\Gamma_t$  and the slope of  $i_{\text{pa}}$  vs  $\nu$  plot [42, 43]. In the above equation,  $Q_t$  represents the charge consumed in the complete oxidation of film species, and both  $Q_t$  and  $\Gamma_t$  are calculated from the area under the baseline-corrected anodic peak.  $r$  was calculated to be  $-1.03 \times 10^6 \text{ cm}^2 \text{ mol}^{-1}$  for the above 0.2% (wt/vol) PVP film containing  $1.91 \times 10^{-7} \text{ mol cm}^{-2}$   $\text{Mo}(\text{CN})_8^{3-/4-}$  dopant concentration. The negative value indicates destabilizing repulsive interactions within the PVP film between redox active centers. Thus,  $\Delta E_p$  variation with  $\log(\nu)$  for the  $\text{Mo}(\text{CN})_8^{4-}$ /PVP system can be associated with slow electron transfer kinetics (at electrode/film interface) along with interactions between redox sites (within the film) [5].

The formal potential of the  $\text{Mo}(\text{CN})_8^{3-/4-}$  system confined to the electrode surface within the PVP film (i.e.  $E_{\text{sur}}^{0'}$ ), obtained as  $(E_{\text{pa}} + E_{\text{pc}})/2$  (where  $E_{\text{pa}}$  and  $E_{\text{pc}}$  are the anodic and cathodic peak potentials, respectively, at a slow scan rate of  $5 \text{ mV s}^{-1}$ ), is 530 mV. This value is similar to that of the molecular analogue dissolved in solution

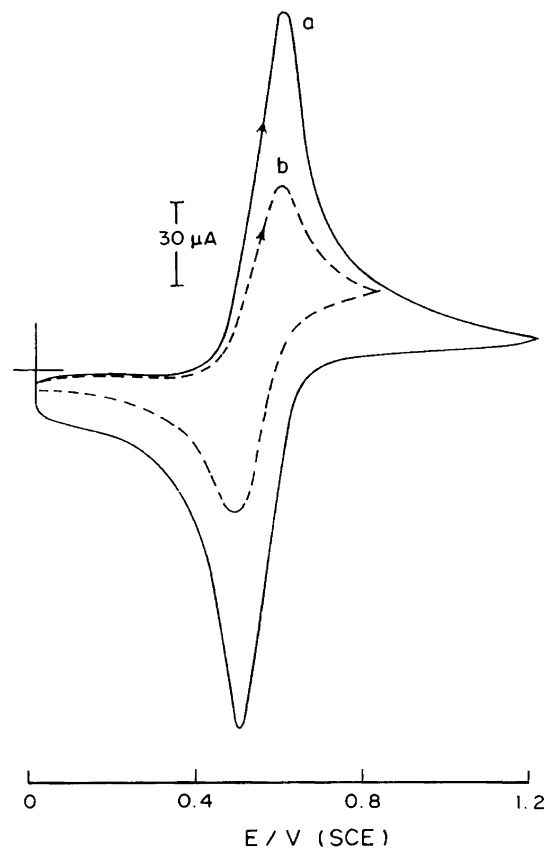


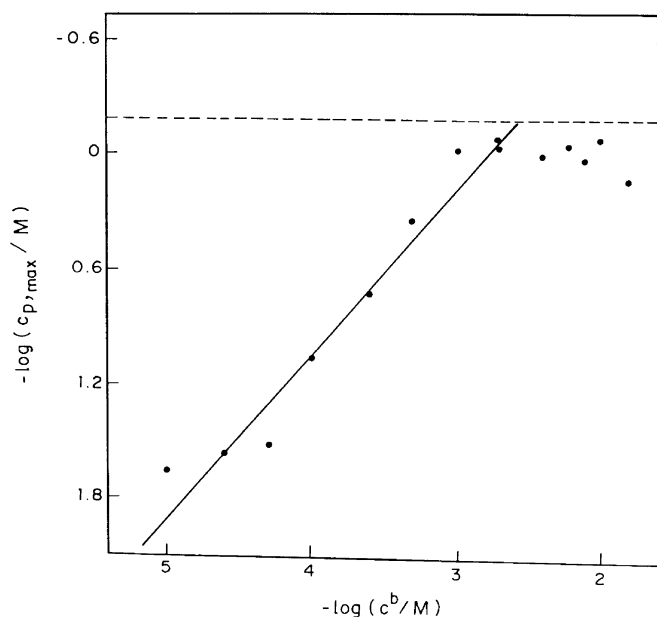
Fig. 1 (a) Cyclic voltammogram of  $\text{Mo}(\text{CN})_8^{4-}$ /PVP-film-coated GCE in  $0.1 \text{ M H}_2\text{SO}_4$ . (b) Cyclic voltammogram of  $2 \text{ mM Mo}(\text{CN})_8^{4-}$  at bare GCE in  $0.1 \text{ M H}_2\text{SO}_4$ . Scan rate =  $20 \text{ mV s}^{-1}$

(Fig. 1, curve b). This is in contrast to the behaviour of the  $\text{Mo}(\text{CN})_8^{3-/4-}$  redox couple in the conducting polymer poly(*N,N*-dimethylaniline) film, which shows that  $E_{\text{sur}}^{0'}$  is 60 mV more positive than  $E_{\text{sol}}^{0'}$  [44]. These observations in PVP are taken to indicate that there is no preferential interaction of the ionomer film for any half of the  $\text{Mo}(\text{CN})_8^{3-/4-}$  redox couple, or that the environment in the polymer is not greatly different from the solution for the complex [8], signifying the more uniform homogeneous nature of the PVP film in the present work. Further support is provided by the observation that the diffusion coefficient of ascorbic acid in the PVP film is somewhat close to its diffusion coefficient in aqueous solution, as will be discussed later. Note that, in Fig. 1, peak currents at a modified electrode are larger than those at a bare electrode in the same loading solution because a large number of electroactive ions may be bound in the protonated polymer. The concentration of the complex within the protonated PVP coating is much higher (0.64 M) than its concentration (0.002 M) in the loading solution (see later). Experiments involving the distribution of  $\text{Mo}(\text{CN})_8^{4-}$  in the PVP film and in solution were conducted to evaluate the electrostatic-binding capacity of the PVP film towards  $\text{Mo}(\text{CN})_8^{3-/4-}$  ions—a key factor signifying the performance of an ionomer film as a sensor electrode.

The thickness of the PVP film ( $L$ ) was  $2.2 \mu\text{m}$ , obtained from its density ( $0.65 \text{ g cm}^{-3}$ ) and the quantity used. The

concentration of  $\text{Mo}(\text{CN})_8^{4-}$  incorporated into the PVP film was estimated with the formula  $c_p = Q_v/nFA_cL$ . In this equation  $A_c$  is the electrode geometric area and  $n=1$ .  $c_p$  is related to the concentration  $c^b$  of  $\text{Mo}(\text{CN})_8^{4-}$  in bulk solution and tends to a constant  $c_{p,\text{max}}$  with increasing immersion time at a fixed concentration of  $\text{Mo}(\text{CN})_8^{4-}$  ions. The ratio  $\kappa$  of  $c_{p,\text{max}}$  to  $c^b$ , defined as the ion exchange distribution coefficient [5], was calculated from  $c_{p,\text{max}}$  measurements for several bulk concentrations  $c^b$ . The ion exchange isotherm describing the detailed dependence of  $c_{p,\text{max}}$  on  $c^b$  is shown in Fig. 2. The plot between  $-\log(c_{p,\text{max}})$  vs  $-\log(c^b)$  is linear within the solution concentration range of  $1 \times 10^{-5}$  to  $2 \times 10^{-3}$  mol  $\text{dm}^{-3}$  and attains saturation at high concentrations.  $\kappa$  was found to be a constant of 990 in the linear concentration range where the film is not saturated [5]. Since the value of  $\kappa$  is relatively large and the rate of equilibrium of  $\text{Mo}(\text{CN})_8^{4-}$  between the PVP film and the solution is relatively slow, this suggests that the loss of  $\text{Mo}(\text{CN})_8^{4-}$  by diffusion from the film to the solution is very small [5]. This is further confirmed by the fact that, on continuous potential cycling between 0 and 1,200 mV in 0.1 M  $\text{H}_2\text{SO}_4$  under rigorous operational conditions (potential scan rate =  $1 \text{ mV s}^{-1}$ ; electrode rotation rate = 1,000 rpm), the PVP/ $\text{Mo}(\text{CN})_8^{4-}$  electrode containing a  $1.91 \times 10^{-7}$  mol  $\text{cm}^{-2}$   $\text{Mo}(\text{CN})_8^{3-/4-}$  dopant concentration exhibited only a less than 2% leakage of  $\text{Mo}(\text{CN})_8^{3-/4-}$ , monitored by the repeated determination of  $I_t$ , over the 7-h testing period, indicating the persistent binding of  $\text{Mo}(\text{CN})_8^{3-/4-}$  complex into the protonated polymer. Thus, the  $\text{Mo}(\text{CN})_8^{4-}$ /PVP-modified GCE will be considerably stable.

When  $c^b = 2 \times 10^{-3}$  mol  $\text{dm}^{-3}$ , the concentration of the complex in the film ( $c_{p,\text{max}}$ ) was  $0.64$  mol  $\text{dm}^{-3}$ . Thus, the apparent charge percolation diffusion coefficient  $D_{\text{app}}$  of



**Fig. 2** Concentration of  $\text{Mo}(\text{CN})_8^{4-}$  incorporated into a PVP film electrode ( $c_{p,\text{max}}$ ) as a function of solution  $\text{Mo}(\text{CN})_8^{4-}$  concentration ( $c^b$ ). The dashed line corresponds to a concentration based on complete utilization of all pyridinium groups

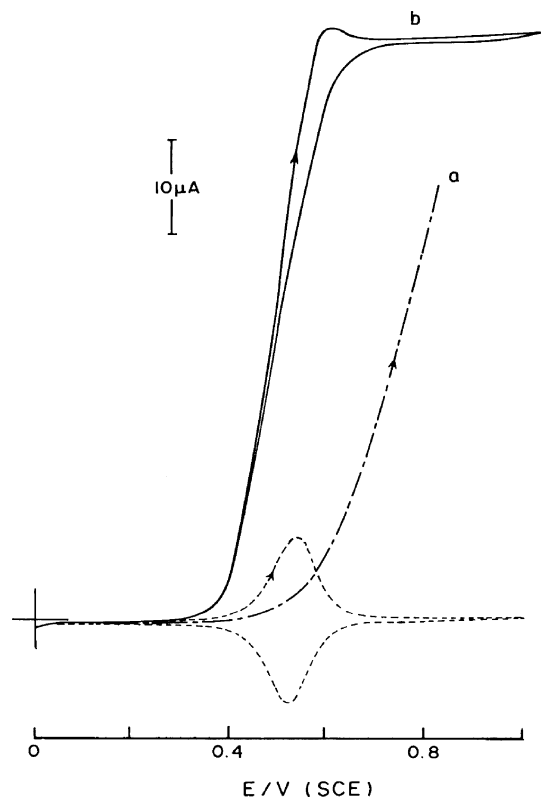
$\text{Mo}(\text{CN})_8^{4-}$  in the film was  $5.6 \times 10^{-9}$   $\text{cm}^2 \text{ s}^{-1}$  from CV measurements and was  $8.0 \times 10^{-9}$   $\text{cm}^2 \text{ s}^{-1}$  from chronocoulometry [38]. These values are relatively in good agreement and are about 1,000 times less than that in solution ( $6.1 \times 10^{-6}$   $\text{cm}^2 \text{ s}^{-1}$ ) [32]. The smaller diffusion coefficient indicates a much reduced mobility within the protonated PVP film, signifying stronger  $\text{Mo}(\text{CN})_8^{4-}$  PVP binding through electrostatic cross-linking.

#### Electrocatalytic activity of $\text{Mo}(\text{CN})_8^{4-}$ /PVP coatings

$\text{Mo}(\text{CN})_8^{4-}$ /PVP-modified electrodes can electrocatalyse the oxidation of L-ascorbic acid in 0.1 M  $\text{H}_2\text{SO}_4$ , as indicated in Fig. 3. Rotating disk electrode (RDE) voltammograms are obtained for ascorbic acid at bare GCE (curve a) and at  $\text{Mo}(\text{CN})_8^{4-}$ /PVP-coated GCE (curve b). Direct oxidation at the bare electrode occurs at high potentials with  $E_{1/2} = 800$  mV [6]. The oxidation of  $\text{AH}_2$  at the polymer-modified electrode starts earlier (shifts 200 mV to the negative direction compared with that at the bare GCE) and the anodic peak current of the modified electrode is increased several fold. The occurrence of limiting current centered at  $E_{\text{sur}}^0$  of the  $\text{Mo}(\text{CN})_8^{4-}$  redox sites within the polymer film suggests the catalytic oxidation of  $\text{AH}_2$  by the complex  $5^+$  cation, which is formed by the electrochemical oxidation of the  $4^+$  cation within the film matrix. All these features are indicative of a purely outer-sphere electron transfer reaction [45]. As the concentration of  $\text{AH}_2$  increases under the constant amount of  $\text{Mo}(\text{CN})_8^{4-}$  complex, the height of the wave near 530 mV increases.

Permeation of  $\text{AH}_2$  through the PVP film was estimated by the RDE method [46, 47]. The RDE voltammogram for the electrocatalytic oxidation of  $\text{AH}_2$  at a  $\text{Mo}(\text{CN})_8^{4-}$ -doped PVP electrode showed a single wave, which was a composite of the mediated oxidation of  $\text{AH}_2$  by electrogenerated  $\text{Mo}(\text{CN})_8^{3-}$  in the PVP film and of the direct oxidation of film-permeating  $\text{AH}_2$  at the underlying bare electrode [38]. In order to separate these two waves,  $\text{WCN}_8^{4-}$  ion, which bears the same structure and charge as that of  $\text{Mo}(\text{CN})_8^{4-}$  but possesses different redox properties [ $E_{\text{sol}}^0 = 260$  mV (SCE)] [27], was used as a surrogate counter-ion by replacing  $\text{Mo}(\text{CN})_8^{4-}$  [ $E_{\text{sol}}^0 = 530$  mV (SCE)] to maintain the PVP coating at a comparable electrostatic cross-linking state [26]. With the PVP/ $\text{WCN}_8^{4-}$  electrode, there were two waves in the regions 250–500 and 600–1,000 mV corresponding to catalytic oxidation and direct oxidation of  $\text{AH}_2$ , respectively. The plateau current of the second wave that was corrected for the limiting current of the first wave was used to calculate the effective diffusion coefficient of  $\text{AH}_2$  in the film  $\kappa D_{\text{AH}_2,\text{P}}$  where  $\kappa$  is the extraction coefficient. A complete analysis of the catalytic and film permeation processes of the PVP/ $\text{W}(\text{CN})_8^{4-}$ / $\text{AH}_2$  system will be described in detail in a forthcoming paper.

The  $\kappa D_{\text{AH}_2,\text{P}}$  value of ascorbic acid in the PVP film was estimated as  $(4.45 \pm 0.81) \times 10^{-7}$   $\text{cm}^2 \text{ s}^{-1}$ , which is one order of magnitude lower than the reported value of  $6.6 \times 10^{-6}$   $\text{cm}^2 \text{ s}^{-1}$  for the diffusion coefficient of  $\text{AH}_2$  in 1 M  $\text{H}_2\text{SO}_4$  [48]. Compared to several film-permeating electroactive



**Fig. 3** RDE voltammograms of 1 mM L-ascorbic acid obtained at a bare GC electrode (a) and a  $\text{Mo}(\text{CN})_8^{4-}/\text{PVP}$ -film-modified GCE (b) in 0.1 M  $\text{H}_2\text{SO}_4$ . The dotted line is for the blank solution at the  $\text{Mo}(\text{CN})_8^{4-}/\text{PVP}$ -film-modified electrode. Scan rate =  $1 \text{ mV s}^{-1}$ ; rotation rate = 1,000 rpm

molecules that generally display effective diffusion coefficients in the film two to three orders less than solution-diffusion coefficients [46, 47], the transport rate of  $\text{AH}_2$  in the PVP film, being only a factor of ten less than that of diffusion in solution, indicates that the interior of the electrostatically cross-linked PVP film represents a rather fluid medium and offers less impediment to molecular transport. This particular behaviour serves advantageously for the present 3D-anchored  $\text{Mo}(\text{CN})_8^{4-}/\text{PVP}$  catalytic electrode, since most of the relatively immobile mediator sites can participate in a mediation reaction with the substrate, which enters the film from the contacting solution quite easily; hence, the mediation reaction occurs throughout the immobilized film, leading to 3D catalysis. The electrocatalytic activity of an electroactive polymer film is essentially controlled by several dynamic molecular processes, and the theoretical model developed by Andrieux et al. [28] and Andrieux and Saveant [29, 30] provides a well-known and much utilized basis for testing the extent to which catalysts in coatings participate in the production of catalytic currents. A detailed quantitative analysis of steady-state current potential data in terms of the above model was carried out by using the diagnostic criteria proposed by Andrieux and Saveant and also by constructing kinetic zone diagrams [38]. The results also show that the mediated catalytic reaction occurs in the entire film

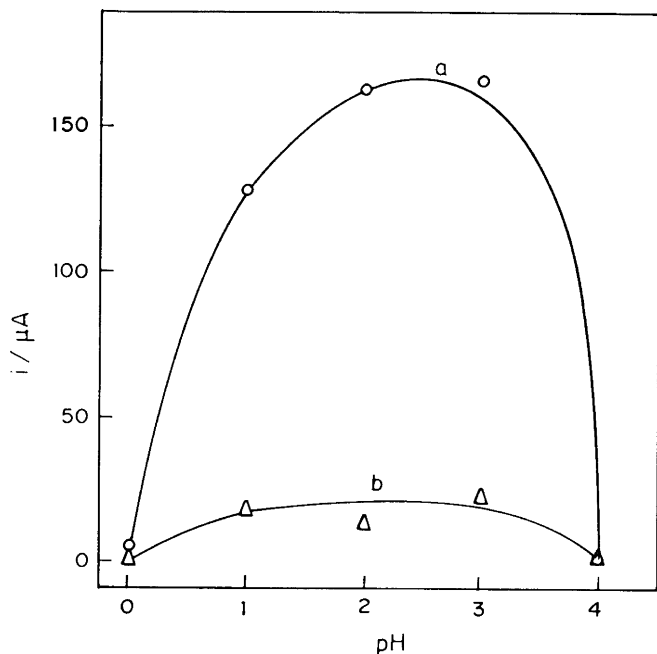
region for thin films at high substrate concentrations. Variations in reaction zone were noticed, depending on film thickness, dopant density and substrate concentration. These details will be published separately elsewhere.

As mentioned already, the cross-exchange reaction between  $\text{AH}_2$  and  $\text{Mo}(\text{CN})_8^{3-}$  is quite rapid in solution phase [33]. A similar fast cross-exchange reaction can be expected to take place within the PVP film, since the oxidative power of the bound  $\text{Mo}(\text{CN})_8^{3-}$  remains unchanged upon its immobilization in the PVP ionomer film (since  $E_{\text{sur}}^{0r} = E_{\text{sol}}^{0r}$ ) and since the PVP coating also does not greatly affect the film permeation of  $\text{AH}_2$ . Collectively, all these features indicate that the  $\text{Mo}(\text{CN})_8^{4-}/\text{PVP}$  assembly can function well as a sensor for the determination of  $\text{AH}_2$ .

The pH dependence of the catalytic activity of the electrode was investigated in the pH range 0–4 by monitoring the ascorbic acid oxidation current, using the RDE method, at 570 mV in  $1-10^{-4}$  M  $\text{H}_2\text{SO}_4$  acid solutions. Note that the formal potential of the mediator is independent of pH. As it is illustrated in Fig. 4, the catalytic current is maximum in the pH range 1–3. This behaviour is similar to the cyclic voltammetric anodic peak current of the electrode in pure base electrolyte in the absence of  $\text{AH}_2$  (curve b). The decrease in currents at high pH is due to the gradual deprotonation of the pendent pyridine in the PVP polymer chain with a  $\text{p}K_a = 3.3$  for PVP [49], yielding a film devoid of mediator ions [i.e.  $\text{Mo}(\text{CN})_8^{4-}$ ] in the matrix beyond pH 3.3. On the other hand, small currents at very low pH ( $\sim 0$ ) may exist because excessive protonation could produce films of compact thickness as a result of strong electrostatic cross-linking between the mediator ions and the protonated N sites, resulting in deeply attenuated charge percolation and substrate permeation within the film. Thus, pH 1 in the maximum range was selected for further experiments.

As an application of this catalytic reaction to a  $\text{AH}_2$  sensor, we measured the chronoamperometric current responses of  $\text{Mo}(\text{CN})_8^{4-}/\text{PVP}$  film electrode as a function of the standard addition of  $\text{AH}_2$  solution. The plots are shown in Fig. 5. These curves were recorded for a constant applied potential of 570 mV, with the electrode rotated at 1,000 rpm. It is evident that the modified electrode rapidly responds to minute concentration changes within 5 s and attains steady catalytic current values that remain relatively constant for several minutes at each addition (curve a). This can be contrasted with the continuously decreasing current response at each addition, which is recorded with a bare GCE under similar experimental conditions, shown as curve b in Fig. 5. Remembering that ascorbic acid detection at bare carbon electrode surfaces causes rapid and severe electrode surface fouling resulting in deterioration of electrode sensitivity [50, 51], undiminished currents in  $i-t$  responses for the  $\text{Mo}(\text{CN})_8^{4-}/\text{PVP}$  film electrode testify its capability in preventing the adsorption of inhibitory substances from solution. This result, along with very rapid response times, is significant from the view point of practical applications.

Figure 5 shows that the response current of the  $\text{Mo}(\text{CN})_8^{4-}/\text{PVP}$  film electrode increases with  $\text{AH}_2$  concen-

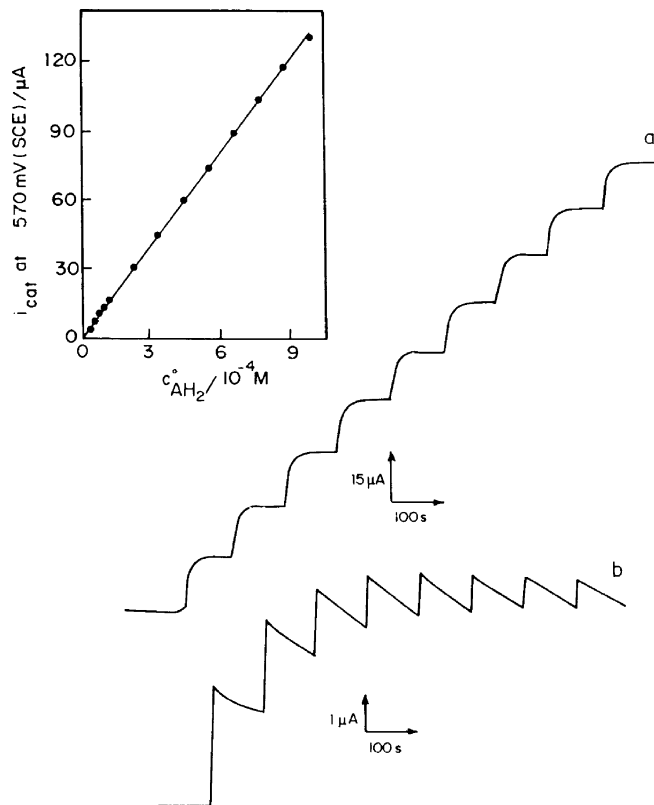


**Fig. 4** pH dependence of (a) catalytic oxidation current of 1 mM L-ascorbic acid at a rotating  $\text{Mo}(\text{CN})_8^{4-}$ /PVP-film-modified GCE in corresponding pH solutions (at  $E=570$  mV; rotation rate=1,000 rpm;  $\nu=1$  mV s $^{-1}$ ); (b)  $\text{Mo}(\text{CN})_8^{4-}$  oxidation current of a stationary  $\text{Mo}(\text{CN})_8^{4-}$ /PVP film electrode in pure supporting electrolytes of different pH values (at  $E_{\text{pa}}=530$  mV;  $\nu=1$  mV s $^{-1}$ ). Solutions of  $1-10^{-4}$  M  $\text{H}_2\text{SO}_4$  acid were used for pH 0–4

tration, offering a linear calibration plot from  $1.1 \times 10^{-5}$  to  $9.8 \times 10^{-4}$  mol dm $^{-3}$  (inset), with a correlation coefficient of 0.9999 (number of points=18) and a sensitivity of  $687 \mu\text{A mM}^{-1} \text{cm}^{-2}$ . The limit of detection (LOD) was  $5.5 \times 10^{-6}$  mol dm $^{-3}$  at a 3:1 signal-to-noise (S/N) ratio. A comparison of the performance of our electrode with that of other modified electrodes developed from conducting polymers [12–14], redox polymers [15–17], screen-printed carbon [18] and carbon paste [19] is given in Table 1.

It may be noted that the values for our PVP/ $\text{Mo}(\text{CN})_8^{4-}$  system are comparable with other results. The LOD value for PVP/ $\text{Mo}(\text{CN})_8^{4-}$  ( $5.5 \mu\text{M}$ ) is smaller by nearly half compared to that for SPCE/DCPI ( $10 \mu\text{M}$ ) and CPE/FcCOOH ( $10.8 \mu\text{M}$ ). But it is higher compared to those of other electrodes, as listed in Table 1. The sensitivity obtained in the present ionomer working system ( $687 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ) is relatively higher than those of a polyaniline-modified Ni electrode ( $200 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ) and the SPCE/DCPI system ( $15 \pm 0.1 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ), but is lower than that of a polypyrrole-modified Pt electrode ( $1,606 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ). The linear range obtained in the present work ( $11 \mu\text{M}-0.98$  mM) is wider than that reported for either a conducting polymer polypyrrole ( $16 \mu\text{M}-1.2$  mM) or a redox polymer  $[\text{Os}(\text{bpy})_2(\text{PVP})_{10}\text{Cl}]\text{Cl}$  ( $100 \mu\text{M}-1$  mM) or the CPE/FcCOOH system ( $34.8 \mu\text{M}-0.49$  mM). Its range is similar to that possessed by SPCE/DCPI electrode.

A recently reported, a cationic Tosflex ionomer film containing a  $\text{Fe}(\text{CN})_6^{3-}$  mediator for  $\text{AH}_2$  estimation [52] is also included in Table 1. Note that sensitivity of the PVP system was improved by twofold compared to that of the



**Fig. 5** Chronoamperometric response as a function of added L-ascorbic acid at (a)  $\text{Mo}(\text{CN})_8^{4-}$ /PVP-film-modified GCE; (b) bare GCE. Each step represents a 100  $\mu\text{l}$  addition of a 0.05 M ascorbic acid solution. Electrode potential=570 mV; rotation rate=1,000 rpm. Inset: The calibration plot for the  $\text{Mo}(\text{CN})_8^{4-}$ /PVP-film-modified electrode

Tosflex film. Furthermore, the linear relationship between the current and the concentration for the PVP/ $\text{Mo}(\text{CN})_8^{4-}$  electrode extends the working range to much higher concentrations (up to 0.96 mM) compared to that of the Tosflex/ $\text{Fe}(\text{CN})_6^{4-}$  electrode (0.05 mM).

The stability of the film electrodes was tested by monitoring the response current in successive measurements, with the electrode maintained at 570 mV and rotated at 1,000 rpm. The relative standard deviation value for eight successive determinations of  $1.0 \times 10^{-4}$  mol dm $^{-3}$  ascorbic acid was less than 4%, exhibiting good reproducibility. Depletion of mediator after more than 15 analyses was evident in the more than 20% loss of sensitivity of the response. However, the original sensitivity of the electrode could be restored by simple reimmersion in a  $\text{Mo}(\text{CN})_8^{4-}$  soaking solution for 5–10 min, after which further multiple analyses were possible. Note that the PVP film, once formed on the electrode surface, could be used continuously for several measurements for more than 3 months. The easy regeneration of the modified electrode and the fact that the response of the regenerated electrode is identical to the original electrode make this polymer electrode attractive.

Interference experiments were performed by comparing the response of a number of possible interferents with that of 2 mM  $\text{AH}_2$  in 0.1 M  $\text{H}_2\text{SO}_4$ . The interferents *o*-aceta-

**Table 1** Comparison of the efficiency of some modified electrodes used in the electrocatalysis of ascorbic acid (AH<sub>2</sub>)

Substrate electrode	Matrix	Incorporated mediator	pH	Shift in potential <sup>a</sup> (mV)	$E_{app}$ <sup>b</sup>	Linear range	Sensitivity ( $\mu\text{A mM}^{-1}\text{ cm}^{-2}$ )	LOD <sup>c</sup> ( $\mu\text{M}$ )	Reference
Pt	Polypyrrole	–	7.0		500 mV (SCE)	16 $\mu\text{M}$ –1.11 mM	1,606 <sup>d</sup>		[12]
GCE or SPCE	Polyaniline	–	6.0		100 mV (SCE)	0.4 $\mu\text{M}$ –2 mM		0.4	[13] <sup>e</sup>
Ni	Polyaniline	–	0.1 M H <sub>2</sub> SO <sub>4</sub>	AH <sub>2</sub> not oxidized on Ni	300 mV (SCE)	500 $\mu\text{M}$ –35 mM	200 <sup>f</sup>		[14]
GCE	[Os(bpy) <sub>2</sub> (PVP) <sub>10</sub> Cl]Cl	Os <sup>3+/2+</sup>	7.0	300	290 mV (SCE)	100 $\mu\text{M}$ –1 mM		1 at 2:1 S/N ratio	[15]
GCE	Ni(II)(Tet-a)	Ni <sup>3+/2+</sup>	6.0	200	500 mV (Ag/AgCl)	0.5 $\mu\text{M}$ –1 mM		0.47	[16]
Al	NiPCNF	Fe <sup>3+/2+</sup>	7.2	AH <sub>2</sub> not oxidized on Al	600 mV (SCE)	1 $\mu\text{M}$ –5 mM		0.3	[17]
SPCE	Ethyl cellulose	DCPI	7.25	350–450	100 mV (Ag/AgCl)	10 $\mu\text{M}$ –1 mM	(15±0.1)	10	[18]
CPE	CPE	FeCOOH	5.0	248	320 mV (Ag/AgCl)	34.8 $\mu\text{M}$ –0.49 mM		10.8	[19]
GCE	Tosflex	Fe(CN) <sub>6</sub> <sup>3-/4-</sup>	5.0	200	300 mV (Ag/AgCl)	10 $\mu\text{M}$ –0.05 mM	368		[50]
GCE	PVP	Mo(CN) <sub>8</sub> <sup>3-/4-</sup>	0.1 M H <sub>2</sub> SO <sub>4</sub>	200	570 mV (SCE)	11 $\mu\text{M}$ –0.98 mM	687	5.5	

<sup>a</sup>The values are calculated vs the oxidation potential of ascorbic acid at an unmodified electrode

<sup>b</sup>Applied potential in amperometry

<sup>c</sup>LOD at a 3:1 S/N ratio

<sup>d</sup>From Fig. 12 of Lyons et al. [12]

<sup>e</sup>Data for batch mode

<sup>f</sup>From Fig. 3 of Rajendra Prasad and Munichandraiah [14]

midophenol, *o*-acetylsalicylic acid, citric acid, L-cysteine, glucose, uric acid, sodium sulphite, catechol, L-Dopa and dopamine were tested. None of the compounds, except dopamine, caused any observable interference to the determination of AH<sub>2</sub> even when they were present at a high concentration of 25 mM (uric acid was limited to 0.2 mM by its solubility). This particular behaviour, in combination with a rapid electrocatalytic ascorbic acid oxidation reaction, provides high selectivity for AH<sub>2</sub> with respect to other compounds, which makes the amperometric sensor electrode free from the above electroactive species even at high positive potentials where AH<sub>2</sub> is oxidized at bare GCE.

The analytical utility of the PVP/Mo(CN)<sub>8</sub><sup>4-</sup> electrode was demonstrated by applying it for the determination of ascorbic acid content in a pharmaceutical vitamin C tablet (Glaxco, India). The tablet was powdered, dissolved in 0.1 M H<sub>2</sub>SO<sub>4</sub> and filtered. The clear filtrate was used for the direct determination of its ascorbic acid content. The

average value of seven successive determinations was 491.0±7.9 mg. The result is close to the value of 487.3 mg, which was obtained by titrimetry with 2,6-dichlorophenolindophenol as titrant (AOAC method) [34]. This proves that the Mo(CN)<sub>8</sub><sup>4-</sup>-doped PVP ionomer-film-modified electrode can be applied well in practice as a sensitive and selective amperometric ascorbic acid sensor.

## Conclusions

With the help of experimental results obtained in this study, the prepared Mo(CN)<sub>8</sub><sup>4-</sup>-doped PVP-modified electrode is clearly shown to offer several attractive advantages for the estimation of L-ascorbic acid. (1) The Mo(CN)<sub>8</sub><sup>4-</sup>-modified PVP film electrode prepared on GCE by simple droplet evaporation method displays excellent catalytic activity towards the oxidation of L-ascorbic acid in 0.1 M H<sub>2</sub>SO<sub>4</sub>

via a redox mediation mechanism, reducing overpotential by ~200 mV. (2) The electrostatically cross-linked PVP film represents a more uniform, homogeneous and fluid-like medium, and it offers insignificant resistance to the permeation of ascorbic acid, facilitating a cross-exchange reaction between the substrate and the mediator in the entire film volume. (3) PVP/Mo(CN)<sub>8</sub><sup>4-</sup> coatings prevent electrode surface fouling by oxidation products and do not respond to many common electrochemical interferents even at high positive potential. (4) Analytical performance (especially sensitivity) of the present ionomer electrode is considerably improved over several other modified electrodes, including polymer electrodes. (5) The PVP/Mo(CN)<sub>8</sub><sup>4-</sup> film exhibits excellent stability, showing strong anion-binding capacity for Mo(CN)<sub>8</sub><sup>4-</sup> mediator (extraction coefficient=990) under hydrodynamic conditions, but the film shows good stability for 15 determinations. The characteristics of the original electrode could be restored by dipping into Mo(CN)<sub>8</sub><sup>4-</sup> solution for 5–10 min and by reusing for further determinations. Such regeneration and continuous reuse are possible for a period of 3 months. Finally, this electrode was employed for the estimation of L-ascorbic acid in a vitamin C pharmaceutical product by the constant potential hydrodynamic amperometry method, and good correlation with the standard titration method was obtained within these limitations.

**Acknowledgements** We are gratefully indebted to the Council of Scientific and Industrial Research and the University Grants Commission, India, for financial support and to Prof. Isao Taniguchi of Kumamoto University, Japan, for providing facilities during the preparation of this manuscript and for helpful discussions.

## References

- Lyons MEG (1996) *Electroactive polymers electrochemistry*, Part 2. Plenum, New York
- Murray RW (1992) *Molecular design of electrode surfaces*. Techniques of chemistry series, vol XXII. Wiley, New York
- Leech D (1996) Analytical applications of polymer-modified electrodes. In: Lyons MEG (ed) *Electroactive polymers electrochemistry*, Part 2, Chap 10. Plenum, New York
- Oyama N, Anson FC (1980) *J Electrochem Soc* 127:247, 640
- White HS, Leddy J, Bard AJ (1982) *J Am Chem Soc* 104:4811
- Kuo KN, Murray RW (1982) *J Electroanal Chem* 13:3798 (and references therein)
- Krishnan M, Zhang X, Bard AJ (1984) *J Am Chem Soc* 106:7371
- Harrison DJ, Daube KA, Wrighton MS (1984) *J Electroanal Chem* 163:93
- Qi Z, Pickup PG (1998) *Electrochim Acta* 43:1005
- Gehron MJ, Anna Brajter-Toth (1986) *Anal Chem* 58:1488
- Lorenzo E, Abruna HD (1992) *J Electroanal Chem* 328:111
- Lyons MEG, Breen W, Cassidy J (1991) *J Chem Soc Faraday Trans* 87:115
- Connell PJO, Gormally C, Pravda M, Guilbault GG (2001) *Anal Chim Acta* 431:239
- Rajendra Prasad K, Munichandraiah N (2002) *Anal Chem* 74:5531
- Doherty AP, Stanley MA, Vos JG (1995) *Analyst* 120:2371
- Bae Z, Park J-H, Lee S-H, Chang H-Y (1999) *J Electroanal Chem* 468:85
- Pourmaghi-Azhar MH, Rajmi-Nerbin H (2000) *J Electroanal Chem* 488:17
- Florou AB, Prodromidis MI, Tzouvara-Karayanni SM, Karayannis MI (2000) *Anal Chim Acta* 423:107
- Raof J, Ojani R, Kiani A (2001) *J Electroanal Chem* 515:45
- Iwuoha EI, Smyth MR (1996) Polymer-based amperometric biosensors. In: Lyons MEG (ed), *Electroactive polymers electrochemistry*, Part 2, Chap 11. Plenum, New York
- Oyama N, Sato K, Matsuda H (1983) *J Electroanal Chem* 115:149
- Lindholm B (1988) *J Electroanal Chem* 250:341
- Fritsch-Faules I, Faulkner LR (1992) *Anal Chem* 64:1118, 1127 (and references therein)
- Tjarnhage T, Skarman B, Lindholm B, Sharp M (1996) *Electrochim Acta* 41:367 (and references therein)
- Van Koppenhagen JE, Majda M (1987) *J Electroanal Chem* 236:113 (and references therein)
- Sharp M, Montgomery DD, Anson FC (1985) *J Electroanal Chem* 194:247 (and references therein)
- Anson FC, Ohsaka T, Saveant JM (1983) *J Am Chem Soc* 105:4883 (and references therein)
- Andrieux CP, Dumas-Bouchiat JM, Saveant J-M (1982) *J Electroanal Chem* 131:1
- Andrieux CP, Saveant J-M (1982) *J Electroanal Chem* 142:1
- Andrieux CP, Saveant J-M (1992) Catalysis at redox polymer coated electrodes. In: Murray RW (ed) *Molecular design of electrode surfaces*. Techniques of chemistry, vol XXII, Chap V. Wiley, New York
- Schroder U, Scholz F (1997) *J Solid State Electrochem* 1:62
- Taniguchi I, Miyamoto S, Tomimura S, Hawkridge FM (1988) *J Electroanal Chem* 240:333
- Pelizzetti E, Mentasti E, Pramauro E (1978) *Inorg Chem* 17:1181
- Cunniff P (1999) Official methods of analysis of the AOAC, 16th edn, Chap 45. AOAC International, Maryland, MA, p 16
- Cai C-X, Xue K-H, Xu S-M (2000) *J Electroanal Chem* 486:111
- Ren J, Zhang H, Ren Q, Xia C, Wan J, Qiu Z (2001) *J Electroanal Chem* 504:59
- Furman NH, Miller CO (1950) *Inorg Synth* 3:160
- Thangamuthu R (2001) Ph.D. dissertation, Department of Physical Chemistry, University of Madras, India
- Brown AP, Anson FC (1977) *Anal Chem* 49:1589
- Lenhard JR, Murray RW (1978) *J Am Chem Soc* 100:7870
- Facci J, Murray RW (1982) *Anal Chem* 54:772
- Ilangovan G, Chandrasekara Pillai K (1997) *Langmuir* 13:566
- Senthil Kumar A, Chandrasekara Pillai K (2000) *J Solid State Electrochem* 4:408
- Ohasaka T, Okajima T, Oyama N (1986) *J Electroanal Chem* 215:191
- Jiang R, Anson FC (1991) *J Electroanal Chem* 305:171
- Yan SG, Hupp JT (1995) *J Electroanal Chem* 397:119
- Bonfranceschi A, Cordoba AP, Keunchkarian S, Zapata S, Tucceri R (1999) *J Electroanal Chem* 477:1 (and references therein)
- Karabinas P, Jannakoudakis D (1984) *J Electroanal Chem* 160:159
- Doherty AP, Foster RJ, Smyth MR, Vos JG (1991) *Anal Chim Acta* 255:45
- Kutnik MA, Hawkes WC, Schaus EE, Omage ST (1982) *Anal Biochem* 66:424
- Pachla LA, Reynolds DL, Kissinger PT (1985) *J Assoc Off Anal Chem* 68:1
- Zen J-M, Tsai D-M, Senthilkumar A, Dharuman V (2000) *Electrochem Commun* 2:782