

## Poly(*N*-methylpyrrole) Films Doped with Iron-substituted Heteropolytungstates: A New Sensitive Layer for the Amperometric Detection of Nitrite Ions

Bruno Fabre,\* Gérard Bidan and Mieczyslaw Lapkowski

Laboratoire d'Electrochimie Moléculaire, CEA/DRFMC/SESAM, Centre d'Etudes Nucléaires de Grenoble, BP 85X, F-38041 Grenoble, France

The immobilisation of iron-substituted heteropolytungstates  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{XW}_{11}\text{O}_{39}]^{n-}$  ( $\text{X} = \text{P}$ ,  $n = 4$ ;  $\text{X} = \text{Si}$ ,  $n = 5$ ) in poly(*N*-methylpyrrole) films deposited on an electrode surface provides a sensitive assembly for the electrochemical detection of nitrite.

Nitrite ions interfere in our environment and are widely involved in food preserving. Moreover, they are highly toxic because of their possible carcinogenic effects.<sup>1</sup> The elaboration of sensors sensitive to  $\text{NO}_2^-$  is an important challenge for medical and environmental applications.

Toth and Anson demonstrated the catalytic utility and robustness of iron-substituted heteropolytungstates (HPTs)  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{XW}_{11}\text{O}_{39}]^{n-}$  ( $\text{X} = \text{P}$ ,  $n = 4$ ;  $\text{X} = \text{Si}$ ,  $n = 5$ ) for the electrocatalytic reduction of nitrite ions in homogeneous aqueous solution.<sup>2</sup> The presence of the iron centre is essential for the catalysis because nitrite has no effect on the voltammetry of the unsubstituted derivative  $[\text{XW}_{11}\text{O}_{39}]^{p-}$  ( $\text{X} = \text{P}$ ,  $p = 7$ ;  $\text{X} = \text{Si}$ ,  $p = 8$ ). Electrically conductive polymer films proved to be useful and efficient conductive matrices for immobilising anions of this series or more generally heteropolyanions at the surface of an electrode.<sup>3-7</sup> Even scattered in the polymer films, these molecules retain their electrocatalytic activities. The incorporation of  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{SiW}_{11}\text{O}_{39}]^{5-}$  in polypyrrole has already been realized but the modified electrode appeared to be degraded and the catalytic anion was lost when employed for the catalytic reduction of  $\text{H}_2\text{O}_2$ .<sup>8</sup> This result raised the problem of the choice of matrix and as a result, several conductive polymers have been synthesized on glassy carbon by electropolymerization using the salts of HPTs as electrolytes (the HPT is the doping agent of the polymer). These depositions were performed either by potential sweep or controlled-potential electrolysis. Depending on the polymer nature, the synthesized films do not display the same electrochemical properties and consequently, have different electrocatalytic activities. Indeed, the electropolymerization of thiophene or 3-methylthiophene in the presence of HPT gives an insulating film which passivates the working electrode. Because of the weak acidity of the nitrite ion solution (pH 4.6), the polyaniline film is electroinactive. The polypyrrole film displays a limited catalytic activity for the reduction of nitrite. Only the modified electrode obtained from poly(*N*-methylpyrrole) will be discussed here because it displays the most important electrochemical stability and catalytic activity. We can note that the results obtained with the immobilized anion  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{PW}_{11}\text{O}_{39}]^{4-}$  are very similar to those obtained with  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{SiW}_{11}\text{O}_{39}]^{5-}$ .

Because of the insolubility of the monomer in water, the poly(*N*-methylpyrrole) synthesis in the presence of HPT was performed in acetonitrile. Using this solvent, we obtained good electroactive polymer thin films. The synthesis solution contains the tetrabutylammonium salt of HPT ( $0.05 \text{ mol dm}^{-3}$ ) synthesized and purified as described previously<sup>9</sup> and *N*-methylpyrrole ( $0.01 \text{ mol dm}^{-3}$ ). The film was prepared by applying a potential at  $0.60 \text{ V}$  [vs.  $\text{Ag}-\text{Ag}^+$  ( $0.01 \text{ mol dm}^{-3}$ )],  $0.22 \text{ V}$  vs. SCE and its growth was monitored by chronoamperometry. The  $I-t$  transients show a typical profile of film growth on an electrode and have a similar shape to those observed by Pletcher and coworkers<sup>10</sup> (oligomer formation, precipitation, nucleation and growth). The deposit is composed of 0.07 catalyst molecules per monomer unit (as deduced from elemental analysis†) and the surface concentration of the immobilized catalyst varies in the range of  $4 \times 10^{-9}$  to  $6 \times 10^{-8} \text{ mol cm}^{-2}$  of the electrode (measured by integrating the charge under the  $\text{Fe}^{\text{III}}-\text{Fe}^{\text{II}}$  wave).

After synthesis, the modified electrode was washed in acetonitrile and water, and introduced into deaerated aqueous solution containing acetic acid ( $0.1 \text{ mol dm}^{-3}$ ) and sodium acetate ( $0.1 \text{ mol dm}^{-3}$ ) (pH = 4.6). This buffer is chosen because the immobilized HPT is stable between pH 2 and 8 but also in order to avoid complications associated with the possible disproportionation of nitrous acid.<sup>2</sup> It is established by cyclic voltammetry between  $-1.20$  and  $+0.05 \text{ V}$  that the HPT is immobilized in the polymer and does not exchange with acetate anions [Fig. 1(a)]. This redox system generally exhibits a stabilized electrochemical response after five cycles. It becomes unstable toward oxidative scanning. Five cycles in this buffer between  $-1.20$  and  $+0.60 \text{ V}$  result in a progressive degradation of the polymer matrix. We note that the polymer film formed by potential sweep (between  $-0.50$  and  $+0.70 \text{ V}$ ) displays the same electrochemical response to that formed by controlled-potential electrolysis. Moreover, the stability towards electrochemical cycling is comparable, so the two electrosynthetic pathways appear equivalent. The  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  couple is clearly observed at  $E_{1/2} -0.33 \text{ V}$  and the pair of two-electron waves at  $E'_{1/2} -0.95$  and  $E''_{1/2} -1.09 \text{ V}$  are assigned to the reduction of tungsten centres in the polyoxometalate framework.<sup>11</sup> For films containing up to  $2 \times 10^{-8} \text{ mole of the catalyst cm}^{-2}$ , the  $i_{\text{pa}}$  and  $i_{\text{pc}}$  values corresponding to the  $\text{Fe}^{\text{III}}-\text{Fe}^{\text{II}}$  couple vary linearly with sweep rates  $\nu$  between 2 and  $40 \text{ mV s}^{-1}$  as expected for the reaction of surface-localized material ( $i_{\text{pa}} = |i_{\text{pc}}|$ ). Moreover, in this range of sweep rates the peak-to-peak separation is independent of  $\nu$  ( $\Delta E_p$ ,  $30 \text{ mV}$ ), confirming the reversible nature of this charge transfer. For films containing more than  $2 \times 10^{-8} \text{ mole of the catalyst cm}^{-2}$ ,

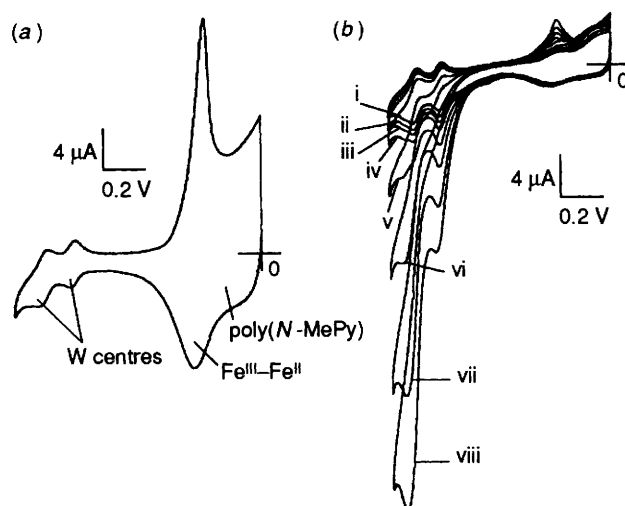
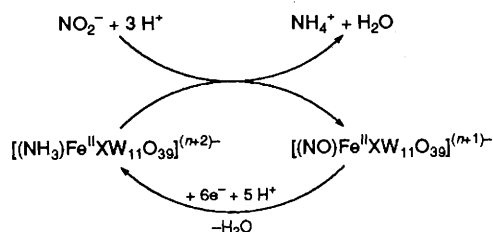
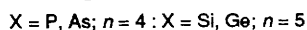
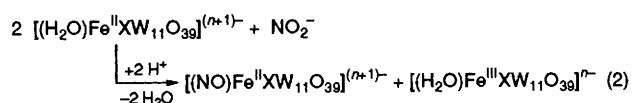
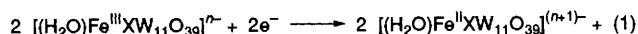


Fig. 1 Cyclic voltammograms at  $10 \text{ mV s}^{-1}$  of glassy carbon electrode ( $S = 0.07 \text{ cm}^2$ ) modified with a poly(*N*-methylpyrrole) film doped with  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{PW}_{11}\text{O}_{39}]^{4-}$ . (a)  $5 \times 10^{-8} \text{ mol cm}^{-2}$  of  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{PW}_{11}\text{O}_{39}]^{4-}$  is incorporated into the polymer film (voltammogram after five cycles); (b)  $1.7 \times 10^{-8} \text{ mol cm}^{-2}$  of  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{PW}_{11}\text{O}_{39}]^{4-}$  is incorporated into the polymer film. In the absence of  $\text{NaNO}_2$  (i) and in the presence of  $5 \times 10^{-4}$  (ii),  $10^{-3}$  (iii),  $2 \times 10^{-3}$  (iv),  $5 \times 10^{-3}$  (v),  $10^{-2}$  (vi),  $2 \times 10^{-2}$  (vii),  $3 \times 10^{-2} \text{ mol dm}^{-3} \text{ NaNO}_2$  (viii).

the  $i_{pa}$  and  $i_{pc}$  values vary linearly with  $v$  between 2 and 20  $\text{mV s}^{-1}$  [ $i_{pa} \neq |i_{pc}|$ ] as shown in Fig. 1(a)]. We also observe an increased peak-to-peak separation which becomes dependent on  $v$  ( $\Delta E_p$  100 mV at 20  $\text{mV s}^{-1}$ ) consistent with slow, heterogeneous charge transfer. Both reductions of the W centres are reversible processes in solution and catalyst immobilization in the polymer film does not change this ( $\Delta E'_p = \Delta E''_p = 25 \text{ mV}$  at 20  $\text{mV s}^{-1}$ ). Also verified is that the ratio of charge for the first W-centres reduction wave to that for the  $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$  wave is *ca.* 2 for the thin films ( $\Gamma_{\text{Fe}} \leq 2 \times 10^{-8} \text{ mol cm}^{-2}$ ), taking into account the strong background current caused by the polymer. This result is consistent with two-electron (W-centres) and one-electron ( $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$  couple) reductions. For thicker films, this ratio is no longer 2. The origin of this difference is not well understood; it may be explained on the basis of a change in electrical wiring (redox accessibility).<sup>4,12</sup> As a matter of fact, the  $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$  couple lies at the conducting state of the poly(*N*-methylpyrrole) matrix, while the W centres lie at the insulating state of the polymer.

Once the redox system exhibits a stabilized electrochemical response, it was used for the amperometric detection of nitrite ions. Fig. 1(b) shows typical voltammograms at 10  $\text{mV s}^{-1}$  on a poly(*N*-methylpyrrole)-modified glassy carbon electrode (0.07  $\text{cm}^2$ ) doped with  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{PW}_{11}\text{O}_{39}]^{4-}$  with the



Scheme 1 Mechanism for the electrocatalytic reduction of nitrite ions

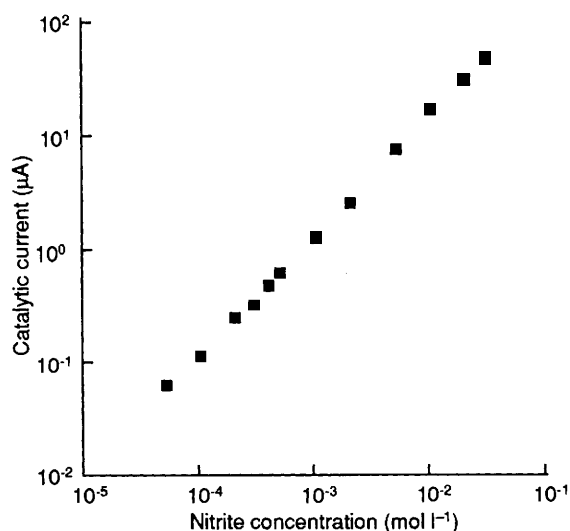


Fig. 2 Catalytic current  $I_{\text{cat}}$  vs. nitrite concentration, measured at  $-1.20 \text{ V}$  from cyclic voltammograms obtained with a modified electrode as in Fig. 1(b)

introduction of successive amounts of nitrite. The two-electron reduction waves of the  $[(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{PW}_{11}\text{O}_{39}]^{5-}$  anion are significantly enhanced by the addition of nitrite. Thus, it seems clear that the reduced forms of the immobilized HPT react with the added substrate. The response arising from the  $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$  couple is much diminished because the  $\text{Fe}^{\text{II}}$  site reacts with nitrite to form an iron-nitrosyl complex  $[(\text{NO})\text{Fe}^{\text{II}}\text{PW}_{11}\text{O}_{39}]^{5-}$  [eqn. (2) of Scheme 1] which produces a positive shift in its oxidation potential. Nevertheless the extension of the potential scan to more positive potentials (up to 0.60 V) only reveals polymer electroactivity which may mask the oxidation of this complex. The *in situ* spectroelectrochemical study of the modified electrode in the presence of nitrite enables detection of the complex at  $463 \pm 3 \text{ nm}$  when the  $\text{Fe}^{\text{III}}$  site is reduced to the  $\text{Fe}^{\text{II}}$ . We note that the immobilized complex and that prepared in solution appear spectrally identical. On adjusting the potential to  $-1.20 \text{ V}$ , the complex was reduced and  $\text{NH}_4^+$  cations were generated. The efficiency of the catalytic electroreduction of  $\text{NO}_2^-$  to  $\text{NH}_4^+$  is examined by conducting an electrolysis at  $-1.20 \text{ V}$  of a film deposited on carbon felt. With 4 h electrolysis, it was possible to reduce 10% of the initial  $\text{NO}_2^-$  (via the reaction  $\text{NO}_2^- + 8 \text{ H}^+ + 6e^- \rightarrow \text{NH}_4^+ + 2\text{H}_2\text{O}$ ) and the concentration of generated  $\text{NH}_4^+$  (as determined by an ion-selective electrode) varied linearly with the electrolysis time. The turn-over is *ca.* 270 (mole of generated  $\text{NH}_4^+$ /mole of the immobilized catalyst) and the coulombic efficiency is 70%, this value being higher than that obtained with the catalyst in solution.<sup>2</sup> The great similarity between this mediated catalysis and the corresponding process in solution lead us to propose the reduction mechanism given in Scheme 1 which is also similar to that obtained for an iron porphyrin.<sup>13</sup>

From the voltammograms of Fig. 1(b), we can determine the catalytic currents  $I_{\text{cat}}$  (difference between peak currents in the presence and in the absence of substrate) at  $-1.20 \text{ V}$ . At this potential, a linear relationship is served between  $I_{\text{cat}}$  and nitrite concentration in the range  $5 \times 10^{-5}$  to  $3 \times 10^{-2} \text{ mol dm}^{-3}$  (Fig. 2), and shows non-interference of nitrate (up to  $3 \times 10^{-2} \text{ mol dm}^{-3}$ ) over the time-scale of the experiment. The electrochemical and catalytic responses of this sensor do not change over extended periods if stored in acetic acid-sodium acetate buffer. Moreover, immersion does not lead to swelling of the deposit, contrary to a nitrite sensor based on an osmium polymer reported by Doherty and Vos.<sup>14</sup> With most catalysts used in the electroreduction of nitrite, hydroxylamine is either the major product or a significant side product.<sup>13,15-17</sup> In this study, the quantity of hydroxylamine was not determined but the HPTs accomplish the reduction in solution without the formation of this product.<sup>2</sup> It seems unlikely that the presence of the conductive polymer modifies this behaviour since the key of the selectivity towards  $\text{NO}_2^-$  is the formation of the nitrosyl complex.

The effect of interfering ions which may accompany nitrite and the nature of the mediation process were not examined here and will be the subject of a future paper.

In conclusion, the specific association of poly(*N*-methylpyrrole) with the HPT allows the synthesis in a one-step electrochemical deposition of a layer sensitive to  $\text{NO}_2^-$  without interference by  $\text{NO}_3^-$ . The electrocatalytic transformation of  $\text{NO}_2^-$  anions into  $\text{NH}_4^+$  cations without by-products allows a stoichiometric redox reaction and may explain the excellent proportionality of the catalytic current with substrate concentration over more than 3 orders of magnitude.

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**Footnote**

† In our case, it is not possible to deduce the composition of the film by comparing the charge under the poly(*N*-methylpyrrole) response and under the HPT one. Indeed, in aqueous solution the polymer electroactivity is lowered.

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