Voltammetric Response of Dopamine at an Overoxidised Polypyrrole–Dodecyl Sulfate Film Coated Electrode

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Overoxidised polypyrrole–dodecyl sulfate film coated glassy carbon electrode shows improved voltammetric sensitivity and selectivity toward dopamine.

Electrochemical determination of dopamine (DA) *in vivo* is of increasing interest in order to provide qualitative and quantitative information about neurotransmission processes. The major problem associated with measuring levels of dopamine *in vivo* is the very low dopamine concentration and the large excesses of interfering anions *e.g.* ascorbic acid (AA).[1] At most solid electrodes AA is oxidised at potentials similar to those of DA resulting in an overlapped voltammogram and hence complicating the interpretation of the data. The ability to distinguish between DA and AA *in vivo* has been a major goal in electroanalytical research for some time. Coating the electrode with permselective polymer films has been developed for separating the voltammetric responses of DA and AA.[2] Undoubtedly, new polymeric coatings with attractive permselective properties are desirable for further development of voltammetric sensors for *in vivo* electrochemistry.

In the present work, voltammetry of DA at an overoxidised polypyrrole–dodecyl sulfate (PPy–DS) film coated glassy carbon electrode has been studied. A noticeable enhancement of voltammetric sensitivity for DA oxidation and a remarkable improvement in selectivity against AA were observed at the coated electrode. The permselectivity of this film arises from charge discrimination and analyte accumulation. The most attractive feature of the overoxidised PPy film is the adjustable permeability through the precise control of the film thickness.

PPy–DS film prepared galvanostatically (current density 1–2 mA cm^{-2}) in a deaerated 0.1 mol dm^{-3} pyrrole–0.1 mol dm^{-3} sodium dodecyl sulfate solution. The working electrode was a glassy carbon disk electrode (5 mm diameter). The film

thickness was controlled by measuring the charge passed during electropolymerization.[3] The electrode was then rinsed thoroughly with water and transferred to a 0.1 mol dm^{-3} NaOH solution for potential cycling between 0.4 and −1.0 V. The potential scan rate used was in the range of 20–50 mV s^{-1}. After the overoxidation was completed, usually 20 min for 0.3 μm PPy film, the electrode was rinsed thoroughly with water and transferred into an electrolyte solution for further studies.

Fig. 1 shows linear sweep voltammograms (LSVs) of DA and AA at both bare and coated glassy carbon electrodes. As can be seen in Fig. 1(a) the anodic current of DA at the coated electrode was over 40 times higher than that at the bare electrode. Meanwhile, the voltammetric response of AA was significantly suppressed, only 8.9% of the oxidation current maintained at a 0.3 μm PPy–DS film coated electrode [Fig. 1(b)]. Moreover, the anodic peak potentials of AA and DA remained practically unchanged at both electrodes, which suggests that the oxidation of the solutes occurs at the substrate electrode rather than within the film or at the film–solution interface. This is highly reasonable because upon potential cycling in NaOH solution the polymer film is overoxidised by the nucleophilic attack of OH$^-$ on the pyrrole units and the hydroxy groups are then oxidised to carbonyls,[4] which results in the loss of conductivity and the conversion of the polymer from an electronic/ionic conductor into a non-electronic but purely ionic conductor.[4,5] The presence of carbonyl groups on pyrrole units has been confirmed by FTIR spectra of the polymers.[4] The cationic species in the solution are, therefore, accumulated into the film through ion-exchange equilibria.[6] The voltammetric response of DA at the bare glassy carbon electrode gave a typical diffusion controlled anodic peak in the concentrations studied. At the film coated electrode however DA gave a symmetric peak, no longer controlled primarily by the diffusion process in solution. An analysis of log v^n (scan rate) *vs.* log i_{pa} (anodic peak current) was done to determine the exponents (n) of potential scan rate as a function of the DA concentration and the film thickness. With decreasing DA concentration from mmol dm^{-3} to μmol dm^{-3} a shift of (n) values form 0.5 to 1 was observed, which is expected for a change from a diffusion-controlled process to a surface process.[7] The contribution of mass-transport process in solution is negligible at very low concentrations *e.g.* 0.1 μmol dm^{-3} and, therefore, the electrode process is entirely controlled by the accumulated analyte in the film. The voltammetry did not correspond to a totally surface process and some solution diffusion contribu-
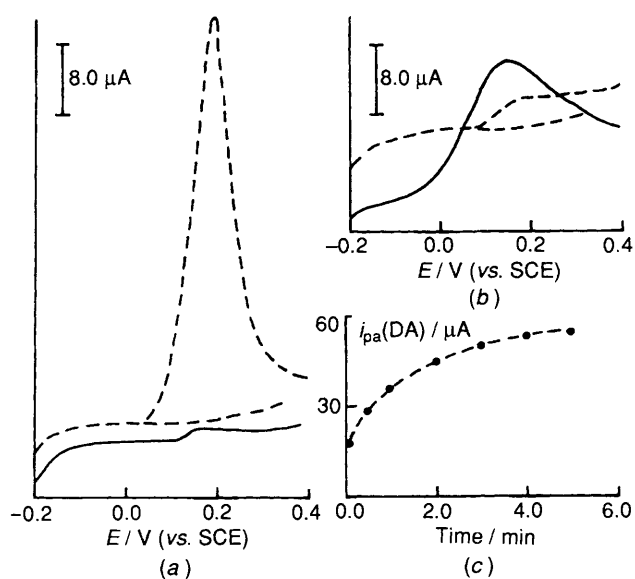

Fig. 1 LSVs of DA and AA at the bare and coated PPy–DS film coated electrodes. Film thickness 0.3 μm, 0.1 mol dm^{-3} phosphate buffer (pH 7.4), potential scan rate 40 mV s^{-1} exposure time before potential scan 120 s (open-circuit conditions).(a) 10 μmol dm^{-3} DA at the bare (—) and the coated electrode (— —). (b) 0.4 mmol dm^{-3} AA at the bare (—) and 1.0 mmol dm^{-3} AA at the coated electrode (— —); lower dashed traces are the background current at the film coated electrode. (c) The effect of exposure time before potential scan on the anodic peak current of DA; conditions are as for (a).

Table 1 The effect of film thickness on the voltammetric sensitivity and selectivity of DA against AA[a]

Thickness/μm	i_{pa}(DA)/μA	i_{pa}(AA)/μA	i_{pa}(DA)/i_{pa}(AA)[b]
0.0	1.1	33.8	3.25
0.1	24.5	7.2	340
0.3	45.2	3.0	1507
0.5	41.5	1.7	2441

[a] The concentrations for DA and AA are 10 μmol dm^{-3} and 1.0 mmol dm^{-3}, respectively, other conditions are as for Fig. 1(a). [b] i_{pa}(DA)/i_{pa}(AA) is calculated at the same concentration level; i_{pa}(AA) is estimated by assuming that a linear response exists at the film-coated electrode.

tions were undoubtedly present at high concentrations. However, a large part of the increased sensitivity seems clearly the result of DA accumulation. It must be mentioned that this only occurred with relatively thin films. On the other hand, (n) moves from 1 to 0.5 in 10 μmol dm^{-3} DA solution as the film thickness is increased from 0.1 to 1 μm, which indicates that the diffusion of DA within the film becomes predominant at thick film coated electrodes. As discussed above, the electron-exchange process occurs at the substrate electrode, any change of the film thickness will result in the change of diffusion pathway for DA. The diffusion process within the film becomes more and more important with increasing film thickness. Similar behaviour has been observed at Nafion-coated electrodes.[2a]

The sensitivity and selectivity were strongly dependent on the film thickness and the exposure time in the sample solution before potential scan. As illustrated in Table 1 the highest sensitivity was observed at a 0.3 μm film coated electrode for a 2 min exposure time in 10 μmol dm^{-3} DA solution. The film thickness required for reaching the highest sensitivity was reduced with decreasing the DA concentration. On the other hand, the selectivity was always increased by thickening the PPy–DS films. Better sensitivity and selectivity could be reached when prolonged exposure time was employed. This is not surprising since prolonged exposure allows a larger quantity of DA to partition into the film [Fig. 1(c)]. Renewal of the electrode following the voltammetric determination was accomplished by holding the electrode at 0.4 V for 60 s in a blank buffer solution.

The stability and reproducibility of a single film coated electrode were studied by ten parallel determinations in 0.1 mol dm^{-3} phosphate buffer solution (pH 7.4) containing 0.5 μmol dm^{-3} DA. For a 2 min exposure time at a 0.5 μm PPy–DS film, the mean anodic current was 2.1 μA with a range of 1.9–2.2 μA and a relative standard deviation of 6.7%. This is contrary to the observed fouling of the bare glassy carbon electrode by DA oxidation products, which results in anodic peak shifts and a decrease in anodic current.[8]

The anodic peak current at the 0.5 μm PPy–DS film coated electrode was directly proportional to the concentration of

DA in the range of 0.1 to 10 μmol dm^{-3} with a detection limit of 40 nmol dm^{-3} (2 min exposure time). Prolonged exposure time extended the low concentration end and shortened the linear response range. Whereas, increasing the film thickness reduced both current sensitivity and detection limit owing to the diffusion behaviour of the analyte within the film and the increase in background current.

In conclusion, the present communication has demonstrated the possibility of using the overoxidised conducting polymer film coated electrode for selective determination of DA. The overoxidised PPy–DS film shows excellent sensitivity, selectivity and anti-fouling properties. The high sensitivity and selectivity were proved to be mainly attributed to charge discrimination and analyte preconcentration.

References

1 R. N. Adams, *Anal. Chem.*, 1976, **48**, 1126A.
2 (*a*) G. Nagy, G. A. Gerhardt, A. F. Oke, M. E. Rice, R. N. Adams, R. B. Moore, III, M. N. Szentirmay and C. R. Martin, *J. Electroanal. Chem.*, 1985, **188**, 85; (*b*) C. D. Blaha and R. F. Lane, *Brain Res. Bull.*, 1983, **10**, 861; (*c*) J. Wang and M. S. Lin, *Electroanalysis*, 1990, **2**, 253; (*d*) L. A. Coury, Jr, E. W. Huber, E. M. Birch and W. R. Heinaman, *J. Electrochem. Soc.*, 1989, **136**, 1044.
3 A. F. Diaz and J. I. Castillo, *J. Chem. Soc., Chem. Commun.*, 1980, 397.
4 F. Beck, P. Braun and M. Oberst, *Ber. Bunsenges. Phys. Chem.*, 1987, **91**, 967.
5 *Handbook of Conducting Polymers*, ed. T. A. Skotheim, Marcel Dekker, New York, 1986.
6 R. W. Murray, A. G. Ewing and R. A. Durst, *Anal. Chem.*, 1987, **59**, 379A.
7 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.
8 M. D. Hawley, S. V. Tatawawadi, S. Piekarski and R. N. Adams, *J. Am. Chem. Soc.*, 1967, **89**, 447; A. W. Sterson, R. McCreery, B. Feinberg and R. N. Adams, *J. Electroanal. Chem.*, 1973, **46**, 313; R. F. Lane and A. T. Hubbard, *Anal. Chem.*, 1976, **48**, 1287.