

## Characterization and investigation of the electrocatalytic properties of poly-*p*-phenylene modified electrodes

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### Abstract

Poly-*p*-phenylene was polymerized electrochemically on the surface of platinum and glassy carbon electrodes. The polymer film differs both in morphology and in effects of modification when a comparison is made between the modified platinum and modified glassy carbon surfaces. The modified electrodes are shown to decrease the overpotential for oxidation of such biologically important compounds as NADH, acetaminophen, catechol, *p*-aminophenol, and ascorbic acid. In addition to the decrease in overpotential, there is also an increase in the current for the oxidative process. The electrodes are stable chemically and electrochemically both in aqueous solution and in mixtures containing methanol, making them excellent candidates for sensing and/or electrocatalytic applications.

**Keywords:** Sensing; Polyphenylene; Polymer; Catechols; Electrocatalysis

### 1. Introduction

The electroanalytical applications of various polymer-modified electrodes have been explored by a number of research groups over the last several years [1–3]. The applications have included detection of gas phase alcohols based on conductivity changes in the polymer film [4], analysis of metals by deposition and stripping [5], anion sensing based on exchange of dopant anions [6–8], biosensors based on enzyme and/or mediator incorporation in the films [9,10], and production of surfaces with novel electrocatalytic properties [11–14]. We report here work directed at the last of these applications.

We have produced and characterized quantitatively platinum and glassy carbon electrodes modified with poly-*p*-phenylene (PPP). These electrodes are capable of decreasing the overpotential and/or improving the reversibility of electrochemical processes for such compounds as catechol, norepinephrine, ascorbate and

NADH. Because of its thermal and chemical stability, PPP in the solid form has been characterized extensively over the last 40 years [15–17]. Electrosynthesis of PPP from its monomer benzene is possible in  $\text{AlCl}_3 + N$ -butylpyridinium chloride (a liquid at room temperature) [18] or in  $\text{CH}_3\text{CN} + (\text{Bu})_4\text{NPF}_6$  [19]. Long chains are favored, since the oligomeric products oxidize at less positive potentials than benzene itself [19]. Polyphenylene has an electrochemical potential window, in which the film electrode maintains its reversible electroactive properties, extending from about +1.0 V to about –2.0 V vs. SCE [15]. Although applications for battery design were explored in the early 1980s [20], PPP has not been widely investigated for electrode modification or its electroanalytical applications.

### 2. Experimental

#### 2.1. Procedure and apparatus

Electrochemical polymerization onto either platinum (Bioanalytical Systems-BAS-MF2013) or glassy carbon (BAS, MF2012) was carried out at +1.8 V vs.

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Ag|AgCl|KCl<sub>(sat)</sub> in a cell containing deaerated 0.1 M tetrabutylammonium hexafluorophosphate and 1.0 mM benzene in deaerated acetonitrile. The reference electrode (BASREF-1) provides a porous glass interface between the solution of interest and the reference cell. Cyclic voltammetric experiments were carried out using a Bioanalytical Systems CV-1B equipped with a Houston Instruments Omnigraphic 100 X-Y recorder. A platinum wire auxiliary electrode and an Ag|AgCl|KCl<sub>sat</sub> reference electrode were used with the modified platinum or glassy carbon working electrode (BAS).

Scanning electron micrographs were obtained using a Cambridge Stereoscan 600 scanning electron microscope.

## 2.2. Reagents

Tetrabutylammonium hexafluorophosphate (Fluka), NADH, norepinephrine (Sigma), benzene, ascorbic acid, acetaminophen, catechol, and *p*-aminophenol (Fisher) were used as received. Acetonitrile (Fisher HPLC grade) was stored over 3 Å molecular sieve (Fisher) for at least 24 h before use. Aqueous solutions were prepared with distilled water which had been further purified using a NanoPure II (Barnstead) manifold before use.

## 3. Results and discussion

Polyphenylene-modified electrodes have been found to be capable of decreasing the overpotential and/or improving the electrochemical reversibility of the redox processes for *o*-catechol, norepinephrine, ascorbic acid, dopamine and acetaminophen. A decrease in the overpotential required for oxidation of compounds such as these means that there is less background current and interference from other dissolved species. The improvement in electrochemical reversibility is reflected in sharper peaks and in prevention of electrode fouling from oxidation products. Both of these factors are important in obtaining lower detection limits for amperometric detection.

### 3.1. Effect of deposition time on cyclic voltammetric behavior at PPP-modified electrodes

Films of PPP were deposited electrochemically onto platinum and glassy carbon electrodes for several different time periods ranging from 15 to 250 s on platinum and 15 to 500 s on glassy carbon electrodes. Diagnostic cyclic voltammetry was then carried out after each deposition time for 5 mM *o*-catechol in 0.1 M H<sub>2</sub>SO<sub>4</sub> at these modified surfaces. Fig. 2 illustrates the variations in the electrocatalytic nature of the polymer-modified electrode as the PPP layer thickens.

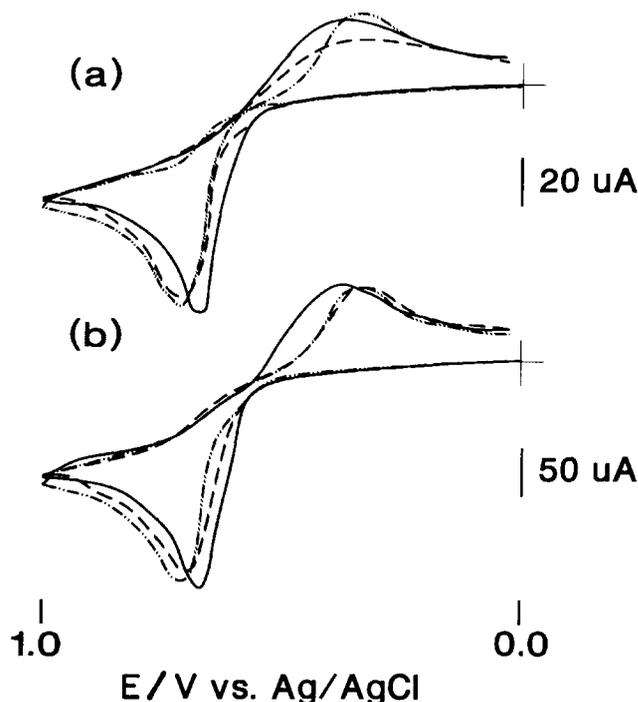


Fig. 1. Comparison of catechol behavior at bare (---), polarized (—) and modified (—) electrodes. (a) Platinum, (b) Glassy carbon.

There is not only a marked decrease in the overpotential for oxidation but also in  $\Delta E_p$  for the oxidation–reduction process. This behavior occurs for both platinum and glassy carbon surfaces modified with PPP. As Fig. 3 indicates, at longer deposition times the peak currents increase and the peak current ratio approaches that expected for a reversible system. Both  $I_{p,a}$  and  $I_{p,c}$  seem to reach maximum values at PPP-modified platinum (PPP|Pt) at deposition times of about 100–120 s, then  $I_{p,c}$  declines. At PPP-modified glassy carbon (PPP|GC), the current enhancement effect is maximized at shorter deposition times (50–70 s) and does not decrease for either process at longer deposition times. A comparison of the behavior of *o*-catechol at the PPP-modified surfaces with that at platinum, glassy carbon, and some other polymer-modified surfaces is shown in Table 1. It is of interest to note that the oxidation potential shown in Table 1 is different for the PPP|Pt and PPP|GC surfaces. This is in contrast to the behavior found for the other polymer-modified surfaces where the electrode substrate had no effect [13]. This difference in behavior is postulated to be due to the absence of a heteroatom in the polymer, the apparent site of electron transfer for the other modified surfaces [21].

To confirm that the decrease in overpotential was not due simply to holding the platinum or glassy carbon at +1.8 V, a comparison was made between catechol behavior at electrodes held for 2 min at +1.8

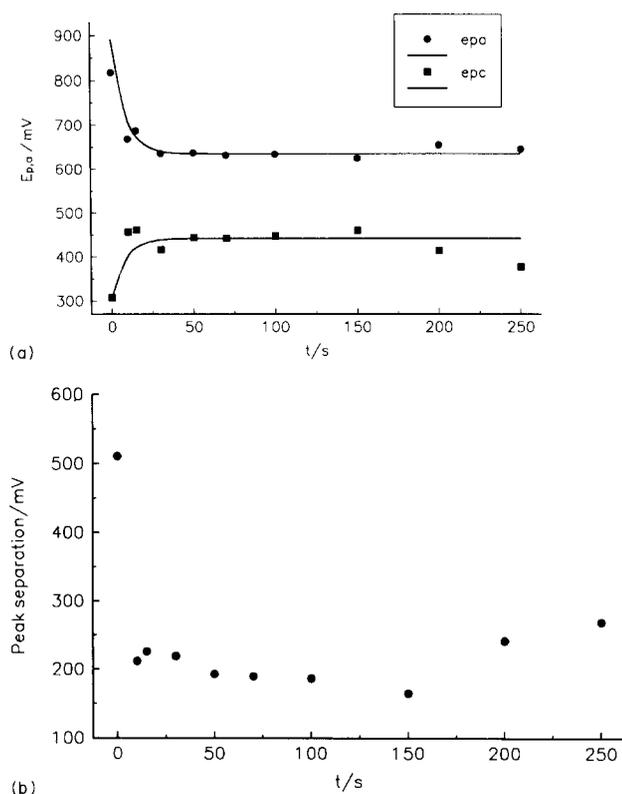


Fig. 2. Peak potentials vs. Ag|AgCl for oxidation and reduction of catechol at PPP|Pt as a function of deposition time (5 mM catechol in 0.10 M  $H_2SO_4$ , 50 mV/s): (a) peak potentials, (b) peak separation.

V vs. Ag|AgCl in 0.1 M tetrabutylammonium hexafluorophosphate +  $CH_3CN$  (i.e. no benzene) and at electrodes where the solution also contained benzene (Fig. 1). Although there was an improvement in the behavior of catechol at the unmodified electrodes, there were greater decreases in overvoltage and in  $\Delta E$  for the PPP-modified platinum and glassy carbon electrodes.

### 3.2. Other compounds of biological interest

A film deposition time of 120 s was used to investigate the cyclic voltammetric behavior of nore-

Table 1  
Catechol oxidation on polymeric electrodes

	$E_{p,a}$ /mV (vs. Ag AgCl)	Peak separation /mV
GC-PPP	560	90
Pt-PPP	650	160
P3MT <sup>a</sup>	560	69
PNMP <sup>a</sup>	587	122
PA <sup>a</sup>	556	67
PF <sup>a</sup>	643	183
Pt	820	510
GC	740	450

GC glassy carbon, Pt platinum disk, P3MT poly-3-methylthiophene, PA polyaniline, PNMP poly-N-methylpyrrole, PF polyfuran.

<sup>a</sup> Ref.[13].

Table 2

Comparison of oxidation potentials for bare and modified Pt and glassy carbon,  $E$ /mV (Ag|AgCl)

	Bare Pt	Pt-PPP	Bare GC	GC-PPP ( $H_2SO_4$ )	GC-PPP (NaCl)
Catechol	820	650	740	560	520
Acetaminophen	600	740	904	660	650
<i>p</i> -Aminophenol	620	570	900	780	–
Ascorbic acid	860	580	NR	600	–
NADH	NR	NR	NR	530	650

Background electrolytes 0.1 M, scan rate 50 mV s<sup>-1</sup>.

pinephrine, acetaminophen, NADH and ascorbic acid in aqueous solution (10 mM in 0.1 M  $H_2SO_4$  background electrolyte). These conditions were chosen so that the results could be compared with those reported for poly-3-methylthiophene, polyaniline and polyfuran.

As seen in Table 2, with the exception of acetaminophen, oxidation occurs at potentials which are on the order of 100–300 mV less positive on the PPP-modified surfaces than at bare platinum or bare glassy carbon. This decrease in overpotential and the differences in the oxidation potentials seen could provide the basis for electrochemical detection of these compounds in the presence of acetaminophen. As shown in Fig. 4, in NaCl the oxidation potential is moved to less positive potentials. (The increase in reversibility is due more probably to the change in pH.)

### 3.3. Scanning electron microscopy of PPP-modified electrodes

Scanning electron microscopy was performed on PPP|Pt and PPP|GC electrode surfaces. As shown in Fig. 5(a), at high magnification, the films on platinum appear to be composed of long, randomly oriented, fibrous deposits. The films on glassy carbon (Fig. 5(b)) are much more uniform in the areas where deposition has taken place, but there are large dark areas where the glassy carbon surface is exposed. (The areas that look like water smears are due to electrolyte salts which have been left behind after pumping off any remaining deposition solution.) The differences in morphology of the the modified surfaces could explain the difference in electrocatalytic activity between the two types of electrodes.

### 3.4. Stability of PPP-modified electrodes

In 5 mM *o*-catechol in 0.1 M  $H_2SO_4$ , cyclic linear scans between 0 and 1.0 V vs. Ag|AgCl over a period of 15 h resulted in an increase in  $\Delta E_p$  for catechol at a PPP|GC electrode from about 70 mV to about 150 mV, still far below the 500 mV separation for a bare platinum electrode. The peak current decreased about 15% during the first hour, but then 14 h were required

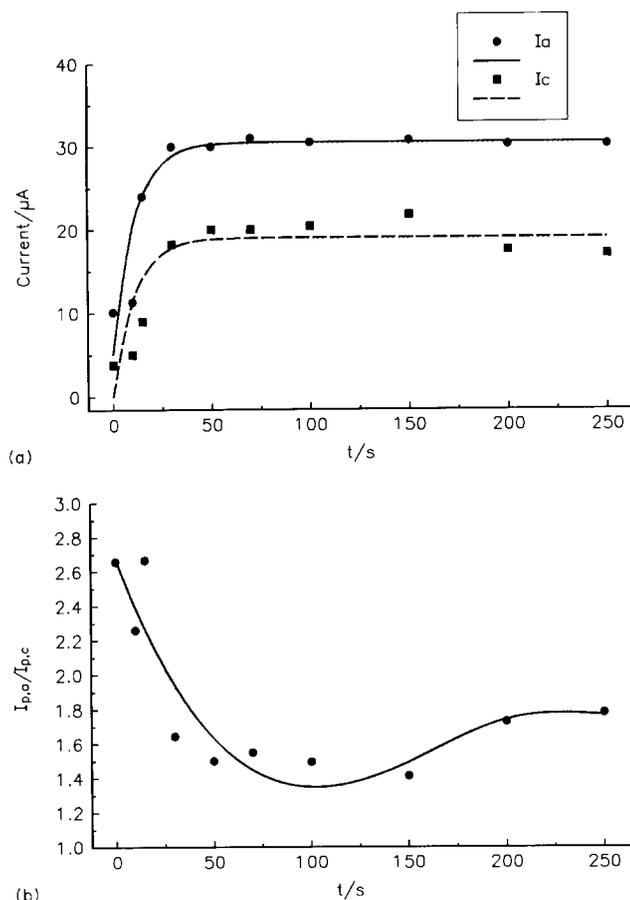


Fig. 3. Peak currents and ratios for oxidation and reduction of catechol at PPP|Pt as a function of deposition time (5 mM catechol in 0.10 M H<sub>2</sub>SO<sub>4</sub>, 50 mV/s). (a) I<sub>a</sub> and I<sub>c</sub>, (b) I<sub>a</sub>/I<sub>c</sub>.

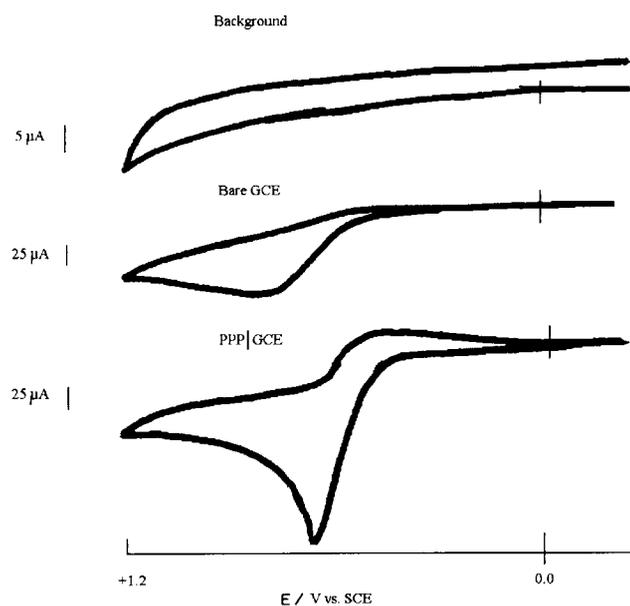


Fig. 4. Cyclic voltammograms of acetaminophen on GCE|PPP and (b) PPP|GCE (10 mM in 0.1 M NaCl, 50 mV/s).

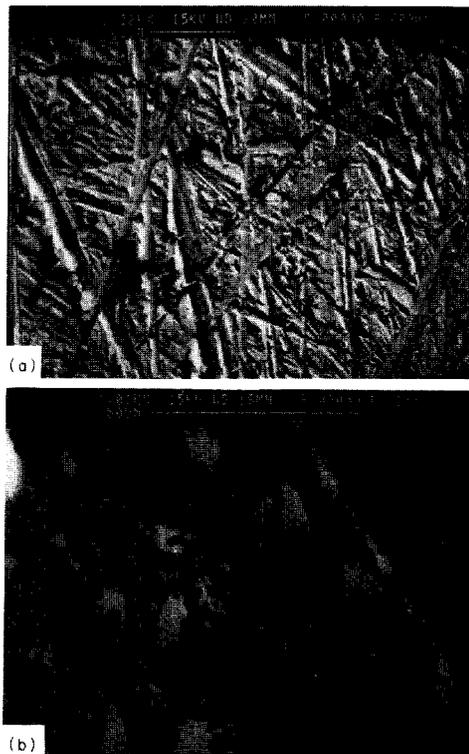


Fig. 5. Scanning electron micrographs of PPP films on platinum and glassy carbon, deposition time 180 s: (a) platinum substrate, (b) glassy carbon substrate.

to produce an additional 15% decrease. At a PPP|Pt electrode, there was a 7% loss in peak current over a period of 5 h, with only a relatively small (less than 5%) increase in peak separation.

Electrode stability in the methanol + water mixture was probed by obtaining a cyclic voltammogram of *o*-catechol just after polymer deposition, then after various times in the stirred mixture. After times as short as 30 s, a double peak is seen for the reduction process. At longer times, the current for the reduction peak continues to shift into the peak closer to 0.0 V. The oxidation peak current, however, does not decrease appreciably (less than 5%) and there is no shift in the oxidation peak out to the very positive potentials seen for bare Pt. Since reversibility is not a requirement for amperometric sensing applications, the modified electrodes might still be more useful than platinum for the polar organic + aqueous mixtures commonly used as mobile phases for HPLC.

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## References

- [1] A. Ivaska, *Electroanalysis*, 3 (1991) 247.
- [2] A.R. Hillman, in R.G. Linford (ed.), *Electrochemical Science and Technology of Polymers-1*, Elsevier, New York, (1987) 241.
- [3] P.R. Coulet and G. Bardeletti, *Biochem. Soc. Trans.*, 19 (1991) 1.
- [4] M. Josowicz and J. Janata, *Anal. Chem.*, 58 (1986) 514.
- [5] G.G. Wallace and Y.P. Lin, *J. Electroanal. Chem.*, 247 (1987) 145.
- [6] Y. Ikariyama and W.R. Heineman, *Anal. Chem.*, 58 (1986) 1803.
- [7] Z. Lu, Z. Sun and S. Dong, *Electroanalysis*, 1 (1989) 271.
- [8] J. Ye and R.P. Baldwin, *Anal. Chem.*, 60 (1988) 1979.
- [9] I. Katakis and A. Heller, *Anal. Chem.*, 64 (1992) 1008.
- [10] C.J. Chen, C.C. Liu and R.F. Savinell, *J. Electroanal. Chem.*, 348 (1993) 317.
- [11] M.E.G. Lyons, W. Breen and J. Cassidy, *J. Chem Soc. Faraday Trans.*, 87 (1991) 115.
- [12] R.A. Saraceno, J.G. Pack and A.G. Ewing, *J. Electroanal. Chem.*, 197 (1986) 265.
- [13] N.F. Atta, A. Galal, E. Karagozler, H. Zimmer, H.B. Mark, Jr., and J.F. Rubinson, *Chem. Commun.*, (1990) 1347.  
N.F. Atta, A. Galal, E. Karagozler, G. Russell, H. Zimmer, H.B. Mark, Jr., and J.F. Rubinson, *Anal. Lett.*, 26 (1993) 1361.
- [14] J. Wang and R. Li, *Anal. Chem.*, 61 (1989) 2809.
- [15] J.-L. Bredas, in T.A. Skotheim (ed.), *Handbook of Conducting Polymers*, Vol. 2, Marcel Dekker, New York, 1986, p. 859.
- [16] R.L. Elsenbaumer and L.W. Shacklette, in T.A. Skotheim (ed.), *Handbook of Conducting Polymers*, Vol. 1, Marcel Dekker, New York, 1986, p. 213.
- [17] G.K. Chandler and D. Pletcher, in D. Pletcher (ed.), *Electrochemistry*, Vol. 10, Royal Society of Chemistry, London, 1985, p. 117.
- [18] V.M. Kobryanskii and S.A. Arnautov, *Makromol. Chem.*, 193 (1992) 455.
- [19] T. Osa, A. Yildiz and T. Kuwana, *J. Am. Chem. Soc.*, 91 (1969) 3994.
- [20] L.W. Shacklette, R.L. Eisenbaumer, R.R. Chance, J.M. Sowa, D.M. Ivory, G.G. Miller and R.H. Baughman, *J. Chem. Soc.*, (1992) 361.
- [21] H.B. Mark, Jr., N. Atta, Y.L. Ma, K.L. Petticrew, H. Zimmer, Y. Shi, S.K. Lunsford, J.F. Rubinson and A. Galal, *Bioelectrochem. Bioenerg.*, in press.