JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 943–946

Polythiophene, polyaniline and polypyrrole electrodes modified by electrodeposition of Pt and Pt + Pb for formic acid electrooxidation

M. A. DEL VALLE*, F. R. DÍAZ, M. E. BODINI, T. PIZARRO, R. CÓRDOVA, H. GÓMEZ, R. SCHREBLER

Facultad de Química. Pontificia Universidad Católica de Chile, Casilla 306-Correo 22, Santiago, Chile

Received 7 February 1997; revised 26 November 1997

The electrosynthesis of polythiophene (PTh), polyaniline (PANI) and polypyrrole (PPy) films modified by dispersion of Pt or Pt + Pb and its employment in the electrocatalytic oxidation of HCOOH are studied and compared. The influence of parameters such as polymer film thickness, the number of dispersed Pt particles, the amount of Pb deposited and the presence of Pb^{2+} in the electrolyte on the electrooxidation of HCOOH is investigated. Electrode systems including the polymer and a mixture of Pt and Pb particles show a better electrocatalytic activity than electrodes having a polymer–Pt combination or bulk Pt electrodes. Furthermore, during the electrooxidation of HCOOH using polymer–(Pt + Pb) electrodes the presence of fewer poisoning species is observed, indicating that the role of Pb in these electrode systems is in agreement with the Pb adatom effect observed when bulk Pt electrodes are used. However, the presence of Pb(ɪɪ) in the electrolyte is not required for the PTh–(Pt + Pb) electrode system and, in addition, a better electrocatalytic effect is obtained in this case. With application of an appropriate *E*/*t* program the activity is unchanged over a long time.

Keywords: *polythiophene*, *polyaniline*, *polypyrrole*, *Pt modified polymer electrodes*, *bimetallic* (*Pt* + *Pb*)*-modified polymer electrodes*, *formic acid electrooxidation*

1. Introduction

Much attention has been focused on conducting polymers as a consequence of their diverse applications in areas such as electrocatalysis. Considering that polymeric systems do not have any intrinsic catalytic activity, they have been used as host matrices for metal particle incorporation, so that the polymeric system acquires catalytic functionality [1–13]. These studies have shown that the properties depend mainly on the film conductivity and the possibility of including the precursor chemical species for the emplacement of the catalytic active centres. In this regard, the electrocatalytic oxidation of some molecules by polymer dispersed metal systems indicate that the change in the nature of the working electrode promotes its catalytic properties, but generally this is not sufficient to prevent its decay with time. We have reported the preparation of bimetallic (Pt + Pb)-modified polythiophene electrodes [13]. Significant electrocatalytic activity for formic acid oxidation was observed. This activity remained unchanged for at least 36 h. This indicates that the role assumed by Pb in the polymeric matrix agrees with the Pb adatom effect observed in bulk Pt electrodes [14–16]. However, considering that polythiophene synthesis requires very thorough control of the working conditions, a study of analogous systems using polyaniline or polypyrrole as polymeric matrices has been proposed in order to take advantage of the ease of handling and good conductivity of these materials. This paper reports a comparative study of modified electrodes using these three types of polymeric matrices to determine their behaviour with respect to the oxidation of formic acid under optimized working conditions.

2. Experimental details

The electrochemical experiments were performed in a three-electrode two-compartment cell equipped with a platinum rotating disc of area about 0.07 cm^2 as the working electrode, a Pt coil as the auxiliary electrode (area 3 cm^2) and a Ag/AgCl reference electrode filled with an aqueous tetramethylammonium chloride solution. The potential of this electrode was 0.242 V vs NHE. All potentials reported are referred to this electrode.

For each experiment the working electrode was carefully polished with an alumina slurry (0.3 μm), sonicated for 10 min in deionized water and rinsed with acetonitrile prior to its introduction to the electrochemical cell.

All the reagents used were of analytical grade and the solutions were deaerated with high purity argon,

---

* Author to whom correspondence should be addressed.

0021-891X

both before and during the measurements. The experiments were performed at room temperature (20 °C).

Cyclic voltammetry (CV) and potential step (PS) experiments were performed using a Bioanalytical Systems (model CV-50W) voltammograph interfaced with a PC computer loaded with CV-50W Windows software (version 1.3).

The Pt/PTh, Pt/PTh–Pt and Pt/PTh–(Pt + Pb) electrodes were prepared as indicated previously [13]. The Pt/PTh electrode was prepared from 0.3 M thiophene + 0.1 M $TBAPF_6$ (TBA: tetrabutylammonium) solution in anhydrous acetonitrile. The PTh films were deposited by CV scanned from −0.20 to 1.90 V at 0.1 V s^{-1}. The number of cycles, *n*, was varied between 1 and 30, and hence the film thickness ranged from 0.0 to 7.1 μm [13]. After electropolymerization electrodes were rinsed with acetonitrile and transferred to cells containing 0.1 M $TBAPF_6$ in acetonitrile solution or the aqueous KPF_6 described later.

The Pt/PTh–Pt electrode was prepared by cycling the Pt/PTh electrode in a 10^{-3} M H_2PtCl_6 + 0.1 M KPF6 aqueous solution. The dispersion of Pt in the polymeric matrix was performed by a platinization cycle (PC) which consisted of a linear potential sweep from −0.5 to 1.5 V at a scan rate of 0.010 V s^{-1}, followed by a potential pulse of −0.5 V for 10 s. The amount of Pt included was varied by applying a repetitive PC and was estimated by integrating the charge of the *i*/*t* responses obtained during the potentiostatic step. These values were corrected by subtracting the respective dedoping charge of the polymer in a background electrolyte solution.

The Pt/PTh–(Pt + Pb) electrode was prepared by inmersing the Pt/PTh–Pt electrode in 0.3 M $Pb(NO_3)_2$ aqueous solution for a period varying from 1 to 30 min (t_i) and then immediately transferring it to a cell containing 0.1 M KPF_6 aqueous solution and applying a potential of −0.2 V for 5 s. The amount of Pb included was estimated in a similar way to that described above for Pt.

The Pt/PANI electrodes were prepared from a 0.1 M aniline + 0.5 M H_2SO_4 solution in water. PANI films were deposited by cyclic the potential between −0.2 to 0.76 V at a scan rate of 0.05 V s^{-1}. The Pt/PPy electrodes were prepared from a 0.1 M pyrrole + 0.1 M $KClO_4$ solution in a 1 : 1 acetonitrile : water solvent. The film thickness was varied by changing the number of potential scan cycles.

The Pt/PANI–Pt, Pt/PANI–(Pt + Pb), Pt/PPy–Pt and Pt/PPy–(Pt + Pb) electrodes were prepared as previously described for the analogous PTh modified electrodes. The preparation conditions for all the electrodes were previously optimized considering its behaviour toward the oxidation of HCOOH.

The electrocatalytic properties of these electrodes towards formic acid electrooxidation were determined in 0.1 M HCOOH + 0.1 M KPF_6 aqueous solution by successive potentiodynamic scans from −0.20 to 1.00 V at 0.1 V s^{-1} and by the *E*/*t* program shown in the inset of Fig. 5.

3. Results and discussion

The *j*/*E* profiles obtained for the aqueous KPF_6 and KPF_6–HCOOH solutions with each of the polymers studied show that, in the potential range between −0.2 V and + 1.0 V, no significant redox processes are observed. This is indicative that the polymeric matrices prepared show no electrocatalytic activity towards the electrooxidation of HCOOH, because these films significantly cover the platinum base electrode. This shows that the electrolytic solution does not contact the surface of the base Pt electrode. This observation is corroborated using carbon as base electrode. Under similar conditions the same kind of response was obtained.

From the above results, it can be concluded that modification of the polymeric matrices is necessary to attain electrocatalytic properties. As seen in Fig. 1, the dispersion of platinum on PTh, PANI or PPy produces an electrocatalytic activity higher than that shown by pure platinum. This confirms that platinum can be dispersed into all three types of the prepared polymers, exhibiting a lower degree of poisoning of the catalytic site caused by the fixation of intermediate species produced during HCOOH oxidation [17, 18]. In addition to the current maxima obtained as the result of this lower degree of poisoning, a negative shift of the oxidation potential or a significant increase in current as a function of potential is also observed in some instances, Fig. 1.

After a certain number of potentiodynamic scans a deactivation phenomenon is observed which is due either to poisoning of the platinum sites, which

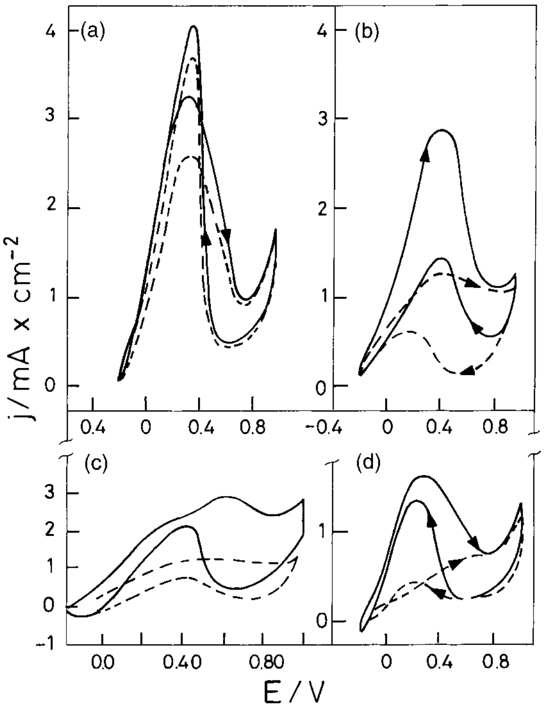

Fig. 1. *j*/*E* profiles of a 0.1 M KPF_6 + 0.1 M HCOOH aqueous solution (v = 0.1 V s^{-1}). Curves corresponds to (a) Pt/PTh–Pt electrode, (b) Pt/PANI–Pt electrode, (c) Pt/PPy–Pt electrode and (d) bulk Pt electrode. In all the cases (— — —) corresponds to the 1st cycle and (——) to the 30th cycle.

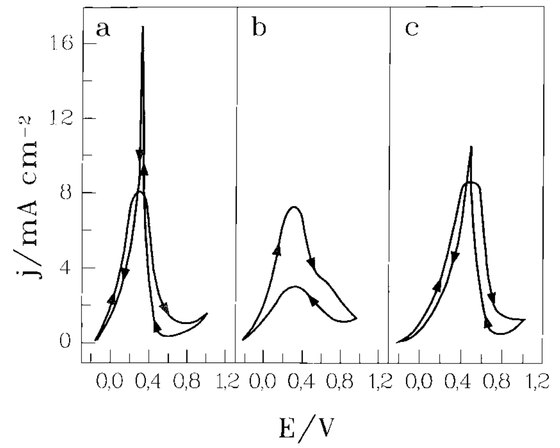

Fig. 2. j/E profiles of a 0.1 M KPF_6 + 0.1 M HCOOH aqueous solution (v = 0.1 V s^{-1}) after the first cycle. Curves corresponds to (a) Pt/PTh–(Pt + Pb) electrode, (b) Pt/PANI–(Pt + Pb) electrode and (c) Pt/PPy–(Pt + Pb) electrode.

cannot be avoided despite the presence of the metallic dispersion, or to a progressive decrease in the surface area of Pt caused by the electrochemical sintering that takes place during successive potentiodynamic cycles.

Therefore, to obtain a more stable response with time, the addition of Pb represents a good alternative. Figure 2 shows that the electrocatalytic activity towards the oxidation of HCOOH of the bimetallic-doped electrode is higher than that of each electrode containing only dispersed platinum. This confirms that the presence of lead precludes the fixation of poisoning intermediate species on platinum.

The optimal conditions of preparation to attain the best response of each electrode are listed in Table 1. These data show that the optimal film thickness using a PTh matrix is much smaller than that for the other two studied matrices. In addition, only two platinization cycles are required to disperse the optimal amount of metal in this matrix.

In the case of PANI and PPy a much higher number of potentiodynamic sweeps are required to obtain the most favourable film thickness and a higher number of platinization cycles are necessary to obtain an adequate amount of dispersed platinum. This effect can be ascribed to the different degree of porosity of these polymers and, particularly, to a hindrance of the ion exchange process responsible for the inclusion of $PtCl_6^{2-}$ in the matrix.

Table 1. Optimum preparation conditions of modified electrodes

Electrode [Pt/polymer]	n*	$PC^{\dagger}$	$t_i^{\ddagger}$/min
Pt/PTh	5	2	10
Pt/PANI	25	180	25
Pt/PPy	25	3	5

* Number of voltammetric cycles for the polymer deposition on the Pt electrode.

† Number of cycles in an aqueous solution of $PtCl_6^{2-}$, to disperse platinum in the polymeric matrix.

‡ Immersion time in an aqueous solution of $Pb(NO_3)_3$, to deposit Pb in the Pt/polymer–Pt electrode.

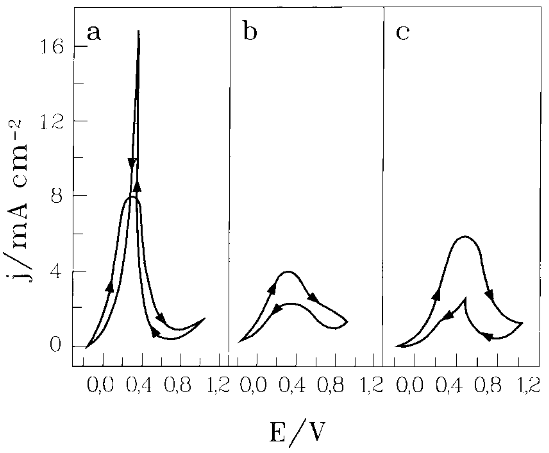

Fig. 3. j/E profiles of a 0.1 M KPF_6 + 0.1 M HCOOH aqueous solution (v = 0.1 V s^{-1}) after the 50th (n) cycle. Curves corresponds to (a) Pt/PTh–(Pt + Pb) electrode, (b) Pt/PANI–(Pt + Pb) electrode, (c) Pt/PPy–(Pt + Pb) electrode.

Only the best Pt/polymer–Pt electrodes obtained above were used for the preparation of the bimetallic Pt/polymer–(Pt + Pb) systems. The time of immersion of these electrodes in a Pb(II) solution has little influence in their behaviour as catalysts and all are efficient catalysts of the HCOOH oxidation. Electrodes formed by the PTh polymeric matrix, on the other hand, show higher current densities and the electrocatalytic activity is more stable towards successive potentiodynamic cycles, Fig. 3. Furthermore, no difference was observed in the behaviour of this electrode upon addition of Pb(II) to the electrolyte.

Figure 4 shows a model of the behaviour of a platinum and lead polymeric matrix electrode. In this case a sponge structure is assumed to retain Pb(II) ions. Under condition I of this figure, the polymeric

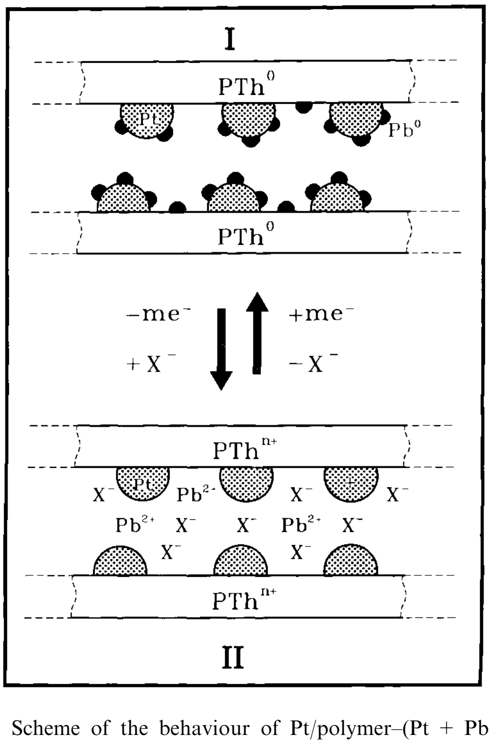

Fig. 4. Scheme of the behaviour of Pt/polymer–(Pt + Pb) electrodes.

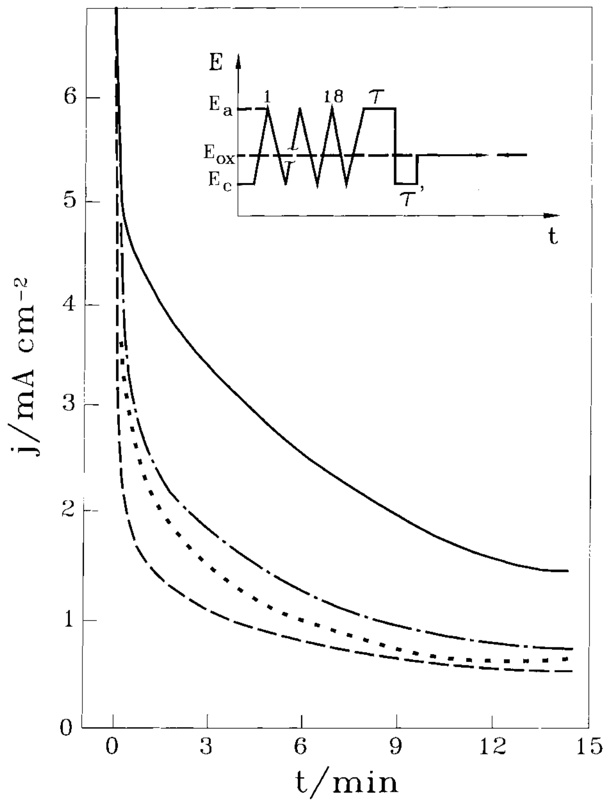

Fig. 5. *j*/*t* transients of different electrodes subjected to the *E*/*t* program shown in the inset ($E_c = -0.2\,V$; $E_a = 1.0\,V$; $E_{ox} = 0.4\,V$; $t = t' = 20\,s$) in aqueous 0.1 M HCOOH + 0.1 M KPF_6: (———): Pt/PTh–(Pt + Pb); (– · – · –): Pt/PANI–(Pt + Pb); (– – –): Pt/PPy–(Pt + Pb).

electrode system is in the reduced state and the lead atoms are deposited on the surface of the platinum granules and on the polymeric matrix. The electroadsorption of HCOOH takes place on the Pt active sites (not shown in the figure) and the polymer eliminates anions through the undoping process. Under condition II the following processes take place:

(i) Direct oxidation of HCOOH
(ii) Partial oxidation of the polymer with subsequent anionic doping
(iii) Total oxidation of the Pb atoms

However, the electrocatalytic activity of the electrodes using PANI or PPy as the polymeric matrix decreases very rapidly with time because lead is transferred to the solution as the oxidation proceeds. This effect can be observed very clearly in Fig. 3, where the 50th potentiodynamic cycle is shown for each of these electrodes.

The loss of lead in these systems can be explained considering that in the oxidation process Pb(II) is not fixed in the polymer. This effect is not observed when the polymeric matrix is PTh because, in this case, a greater affinity holds between the cation and the sulphur atoms of the thiophene rings. Consequently, the Pt/PTh–(Pt + Pb) electrodic system does not require the presence of Pb^{2+} ion in the electrolytic solution to produce a long-lasting electrocatalytic effect. Therefore, this system appears attractive as an electrocatalyst in fuel cells and in electrochemical sensors, considering that, upon application of the adequate *E*/*t* program, the activity is unchanged for a long time, as indicated in Fig. 5. At longer times, the rate of current decrease is much larger for PANI or PPy matrices, while a steady value is reached for PTh.

It has been shown in this work that this polymeric matrix is the most suitable, despite the fact that the preparation of PTh films is far more cumbersome and must be done in totally anhydrous solvent in order to obtain good reproducibility. The loss of Pb(II) from PANI or PPy indicates that in looking for suitable new materials to prepare these catalysts it is very important to consider the chemical affinity between the metal to be included in the polymer and the groups present as substituents in the original monomer.

Acknowledgements

Financial support by Fondecyt (Fondo Nacional de Investigación Científica y Tecnológica) through grant 8 970 011 is gratefully acknowledged.

References

[1] G. Tourillon and F. Garnier, *J. Phys. Chem.* **88** (1984) 5281.
[2] F. T. A. Vork, L. J. J. Janssen and E. Barendrecht, *Electrochim. Acta* **31** (1986) 1569.
[3] L. Coche and J-C. Moutet, *J. Amer. Chem. Soc.* (1987) 109.
[4] A. Yassar, J. Roncali and F. Garnier, *J. Electroanal. Chem.* **255** (1988) 53.
[5] S. Holdcroft and B. L. Funt, *Synth. Met.* **28** (1989) c121.
[6] M. Gholamian and A. Q. Contractor, *J. Electroanal. Chem.* **289** (1990) 69.
[7] T. N. S. Kumar and A. Q. Contractor, *Bull. Electrochem.* **6** (1990) 333.
[8] V. Tsakova and A. Milchev, *Electrochim. Acta* **36** (1991) 1151.
[9] C. S. C. Bose and K. Rajeshwar, *J. Electroanal. Chem.* **333** (1992) 235.
[10] A. Leone, W. Marino and B. R. Sharifker, *J. Electrochem. Soc.* **139** (1992) 235.
[11] C. Cheu, C. S. C. Bose and K. Rajeshwar, *J. Electroanal. Chem.* **161** (1993) 350.
[12] H. Laborde, J. M. Léger and C. Lamy, *J. Appl. Electrochem.* **24** (1994) 1019.
[13] R. Schrebler, M. A. del Valle, H. Gómez, C. Veas and R. Córdova, *J. Electroanal. Chem.* **219** (1995) 380.
[14] R. R. Adzić, D. N. Simić, D. M. Drazić and A. R. Despić, *ibid.* **61** (1975) 117.
[15] R. R. Adzić, D. N. Simić, D. M. Drazić and A. R. Despić, ibid. **65** (1975) 587.
[16] R. R. Adzić, D. N. Simić, A. R. Despić and D. M. Drazić, *ibid.* **81** (1977) 80.
[17] A. Capon and R. Parsons, *ibid.* **98** (1979) 189.
[18] R. Schrebler, H. Gómez and R. Córdova, *Electrochim. Acta* **34** (1989) 1405.