SHORT COMMUNICATION

Electrocatalytic oxidation of hydrogen, formic acid and methanol on platinum modified copolymer (pyrrole-dithiophene) electrodes

H. LABORDE, J.-M. LEGER, C. LAMY
Laboratoire de Chimie 1, 'Electrochimie et Interactions', URA CNRS D0350, Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers, Cedex, France

F. GARNIER, A. YASSAR
Laboratoire des Matériaux Moléculaires, ER 241, CNRS, 2 rue Henry Dunant, 94320 Thiais, Cedex, France

Received 17 May 1989

1. Introduction

Numerous studies have been devoted to the investigation of electronic conducting organic polymers. The study of these materials is growing since the number of new conducting polymers synthesized is continuously increasing. Among them, three types appear to be particularly important for potential applications: polyaniline [1–2], polypyrrole [3] and polythiophene [4]. The possibility of incorporating catalytic metal particles inside the polymer matrix [5] opens up new fields of application, particularly in electrocatalysis [6–8].

The aim of the present work is to investigate the electrocatalytic properties of a conducting polymer modified by the inclusion of a small amount of dispersed platinum. Three electrocatalytic reactions will be taken as typical examples: the electrooxidation of hydrogen, of formic acid and of methanol.

All conducting polymers have a defined domain of electroactivity and although polythiophene appears promising, owing to its excellent chemical and electrochemical stability, its electroactivity potential range, from 0.5 to 1 V/SCE does not fit with these electrooxidation reactions. Thus, in order to extend this working range, a copolymer poly (pyrrole-thiophene) has been used as a conducting matrix; this has been shown to be electroactive between 0 and 1 V/SCE [9].

2. Experimental details

Copolymerisation of pyrrole and thiophene was carried out electrochemically on a gold sheet (1 cm^2 geometrical area) under galvanostatic conditions from a solution containing 0.1 M pyrrole and 0.1 M dithiophene in acetonitrile with 0.05 M NBu_4ClO_4. Platinum particles were then incorporated by electrodeposition from a solution of 10^{-3} M K_2PtCl_4 in 0.05 M KCl with pulses of potential (pulses of 20 ms between -0.1 and -0.5 V/SCE). The thickness of the copolymer layer was around 2 μm and the amount of incorporated platinum was 0.1 mg cm^{-2}.

For the electrocatalytic tests, electrolytic solutions were prepared from ultrapure water (Millipore Milli Q system) and Merck reagents (p.a. for formic acid and methanol and 'suprapur' for $HClO_4$); hydrogen was U quality from l'Air Liquide. All experiments were performed at 25°C under a nitrogen atmosphere. The reference electrode was a mercury/mercurous sulphate electrode (MSE), but the electrode potentials are given on the reversible hydrogen electrode (RHE) scale.

Voltammograms were recorded using standard equipment (a wemking PSG 77 potentiostat, a PAR 175 universal programmer and a Linseis LY 17000–xy recorder).

3. Results

The electroactivity of the copolymer electrode, modified with 0.1 mg cm^{-2} of platinum, was investigated by observing the electrooxidation of three model molecules: hydrogen, formic acid and methanol.

Figures 1, 2 and 3 show the voltammograms of the Pt-modified copolymer electrode for the oxidation of hydrogen, formic acid and methanol, respectively. These curves were recorded at a sweep rate of 5 mV s^{-1} in a solution saturated by bubbling H_2 or in solutions containing 0.1 M HCOOH or 0.1 M CH_3OH. The supporting electrolyte was 0.1 M $HClO_4$.

In each figure, the curve corresponding to the supporting electrolyte alone is also given. The upper potential limit is limited to about 0.95 V/RHE in order to avoid any destruction of the copolymer film. The voltammograms recorded in the supporting electrolyte (the dashed curve of Figs 1, 2 and 3) do not show any well-defined peaks corresponding to the adsorption-desorption region of hydrogen on platinum. This observation confirms that the copolymer electrode contains a small amount of platinum and that a very good dispersion of platinum is achieved, since there are no platinum islands which should have the adsorption properties of the bulk metal.

3.1. *Electrooxidation of hydrogen*

Figure 1 represents the electrooxidation of hydrogen dissolved at saturation in perchloric acid solution. The oxidation starts at 0.0 V/RHE, which is normal for an active catalytic electrode, the hydrogen overpotential being small for such electrodes. The current density reaches a limiting value resulting from kinetic control of the overall process by diffusion of the electroactive species. Under these conditions of stirring

0021-891X/90 $03.00 + .12

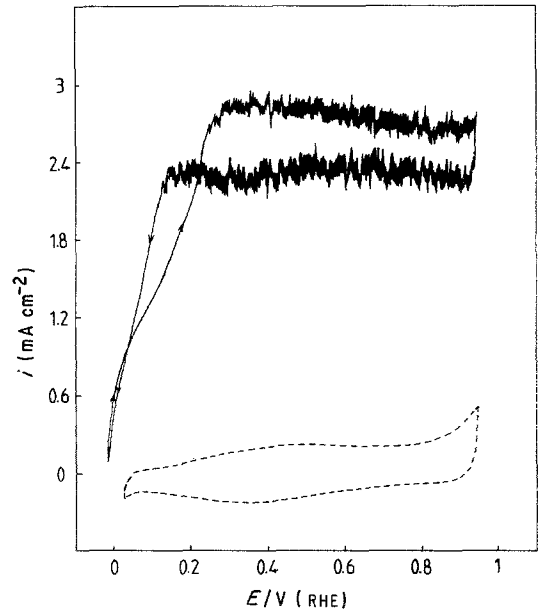

Fig. 1. Voltammograms of a copolymer (polypyrrole-polydithiophene) electrode modified with $0.1\,\mathrm{mg\,cm^{-2}}$ of platinum, in 0.1 M $HClO_4$; 25°C; $5\,\mathrm{mV\,s^{-1}}$. (- - -) without H_2; (——) in an H_2 saturated solution.

(magnetic stirrer), this limiting current is around $2.5\,\mathrm{mA\,cm^{-2}}$. The general shape of the curve confirms that the Pt-modified copolymer electrode is conducting at lower potentials, in contrast with the case of polymer electrodes without Pt particles.

3.2. *Electrooxidation of formic acid.*

The electrooxidation of formic acid is shown in figure 2 for 0.1 M HCOOH in 0.1 M $HClO_4$. The oxidation starts at around 0.1 V/RHE and reaches a maximum of about $9\,\mathrm{mA\,cm^{-2}}$ at 0.85 V. During the reverse sweep, the curve is practically superimposed on that obtained during the positive sweep. No significant poisoning of the electrode active sites is thus detected.

3.3. *Methanol electrooxidation*

Figure 3 shows the voltammogram for the electrooxidation of 0.1 M methanol at a Pt-modified copolymer electrode. Methanol oxidation starts at 0.55 V/RHE and the maximum of the current density ($i_m \approx 1\,\mathrm{mA\,cm^{-2}}$) is observed at 0.9 V/RHE. The potentials at which oxidation occurs during the two sweeps are quite similar. This fact confirms the observation made previously with a Pt-modified polyaniline electrode [8], namely, that poisoning, which leads to a potential shift between the two sweeps, is very weak with dispersed platinum electrodes. However, the maximum current densities for methanol oxidation obtained with the polypyrrole-dithiophene copolymer electrode are smaller than those obtained with a Pt-modified polyaniline electrode containing the same amount of platinum.

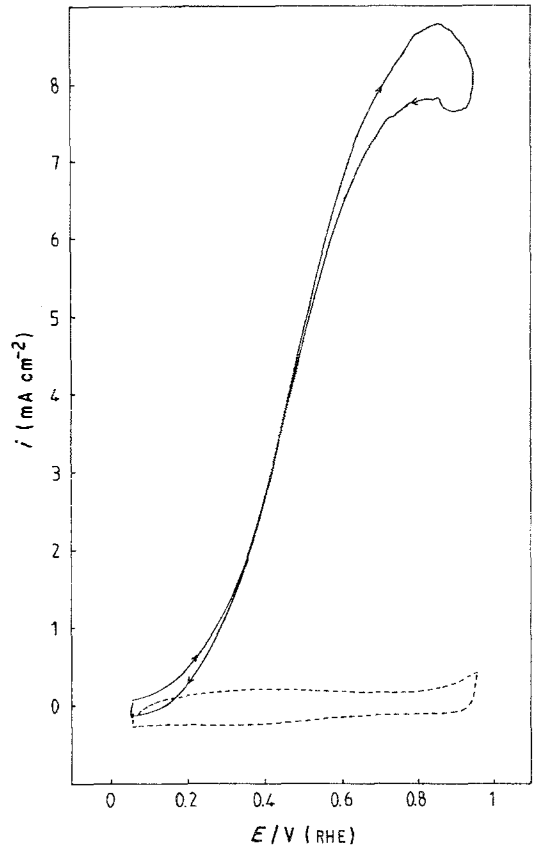

Fig. 2. Voltammograms of a copolymer (polypyrrole-polydithiophene) electrode modified with $0.1\,\mathrm{mg\,cm^{-2}}$ of platinum, in 0.1 M $HClO_4$; 25° C; $5\,\mathrm{mV\,s^{-1}}$. (- - -) without HCOOH; (——) with 0.1 M HCOOH.

4. Conclusion

These preliminary measurements clearly show the possibility of making an active electrode with a small amount of platinum ($0.1\,\mathrm{mg\,cm^{-2}}$) dispersed into a conducting polymer matrix. The electroactivity of such an electrode towards the oxidation of hydrogen, formic acid or methanol is very encouraging, showing the possibility of attaining good electrocatalytic anodes for fuel cells. The main point concerns the

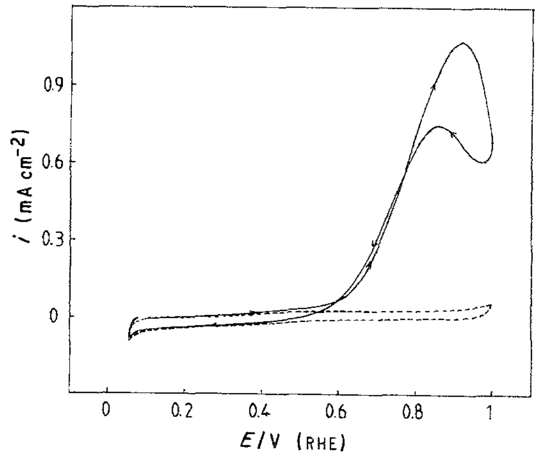

Fig. 3. Voltammograms of a copolymer (polypyrrole-polydithiophene) electrode modified with $0.1\,\mathrm{mg\,cm^{-2}}$ of platinum, in 0.1 M $HClO_4$; 25° C; $5\,\mathrm{mV\,s^{-1}}$. (- - -) without CH_3OH; (——) with 0.1 M CH_3OH.

reduction of poisoning phenomena, in contrast with the behaviour of massive platinum electrodes, on which poisoning species are easily formed during the tion of organic molecules such as formic acid or methanol [10].

Acknowledgements

Part of this work was supported by 'Agence Française pour la Maîtrise de l'Energie' under contract no. 8.03.00001.

References

[1] J. C. Chiang and A.G. McDiarmid, *Synth Met.* **13** (1986) 193.

[2] E. Genies and C. Tsintavis, *J. Electroanal. Chem.* **195** (1985) 109.

[3] A.F. Diaz and K.K. Kanazawa, in 'Extended Linear Chain Compounds', (edited by G. S. Miller), Plenum Press, New York (1982) p. 3.

[4] G. Tourillon and F. Garnier, *J. Electroanal. Chem.* **135** (1982) 173.

[5] G. Tourillon and F. Garnier, *J. Phys. Chem.* **88** (1984) 5281.

[6] F. T. A. Vork, L. J. J. Janssen and E. Barendrecht, *Electrochim. Acta* **31** (1986) 1569.

[7] M. Gholmian, J. Sundaram and A. Q. Contractor, *Langmuir* **3** (1987) 741.

[8] P. Ocon-Esteban, J.-M Léger, C. Lamy and E. Genies, *J. Appl. Electrochem.* **19** (1989) 462.

[9] D. Gningue, G. Horowitz and F. Garnier, *J. Electrochem. Soc.* **135** (1988) 1695.

[10] C. Lamy, *Electrochim. Acta* **29** (1984) 1581.