ELSEVIER

Journal of Molecular Catalysis A: Chemical 174 (2001) 231–238

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

# Preparation and properties of an electrode with platinum microcrystals dispersed in films of poly(allyl ether *p*-benzeneammonium derivatives) Electrocatalytic hydrogenation of organic substrates

R.C.Z. Lofrano, J.V. Queiroz, J.R. Romero*

*Departamento de Química, FFCL, Ribeirão Preto, Universidade de São Paulo, Av. Bandeirantes 3900, 14040-091 Ribeirão Preto, S.P., Brazil*

Received 4 January 2001; received in revised form 6 April 2001; accepted 6 April 2001

**Abstract**

New modified electrodes were prepared containing platinum microcrystal dispersed in films of poly[allyl ether *p*-(2-ammoniumethylbenzene)] and poly(allyl ether *p*-ammoniumbenzene) coating carbon vitreous electrode. They can be used to generate hydrogen from an acid solution and hydrogenation of isosafrole to *n*-propyl-3,4-methylenedioxobenzene and benzaldehyde to benzylic alcohol with good yields. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Chemically modified electrode; Electrocatalytic hydrogenation; Platinum microcrystal

## 1. Introduction

Electrocatalytic hydrogenation and electrocatalytic reduction of organic compounds are different processes, although they frequently yield the same products. In the first case, hydrogen atoms adsorbed at transition metals are transferred to double bonds of unsaturated compounds also adsorbed. These hydrogen atoms come from the reduction of $H^+$ present in acidic solution [1]. Electrocatalytic reduction is processed by direct or indirect transfer of electrons from the cathode to the substrate that can occur even in the absence of a transition metal. In this case, an anion radical is formed which reacts with the $H^+$ present in solution ([2], p. 343). Commonly the negative potential needed for the reduction of $H^+$ is lower than that needed for electron transfer and, in this case, the intermediates formed are more reactive and can yield different products from those expected for electrocatalytic hydrogenation ([2], p. 350).

Electrocatalytic hydrogenation is advantageous compared to catalytic hydrogenation, the method commonly used for organic reduction, because it does not require hydrogen gas manipulation. In both cases, however, a highly partitioned transition metal with a very extended active surface is needed. Microparticles of palladium, platinum, nickel and rhodium can cover or to be dispersed in films covering the electrodes. These modified electrodes have been extensively studied and several recent reviews are available in [3–7].

The most common films are polypyrrole and derivatives, polypyridine and polythiophene [4,5], viologen [5] and Nafion [8]. The current methodology used to disperse these metal particles is ion exchange

* Corresponding author. Tel. +55-16-16-6023689; fax: +55-16-16-6338151.
*E-mail address:* jrromero@ffclrp.usp.br (J.R. Romero).

1381-1169/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(01)00179-0

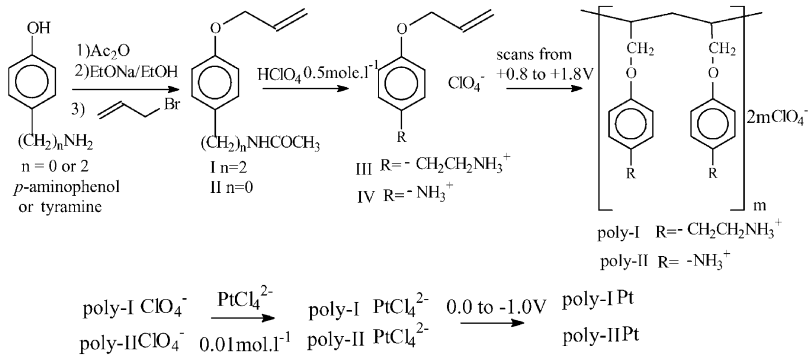


Fig. 1. Schematic presentation of the preparation of poly-I Pt and poly-II Pt.

involving their metal salts, which are further electrochemically reduced to zero valence.

We have recently studied in our laboratories a modified electrode covered with a film obtained from allyl ether *p*-substituted benzene electrooxidation that shows good mechanical and chemical resistance and is easy to prepare [9].

This report presents two new modified electrodes (MEs) covered by poly[allyl ether *p*-(2-ammoniumethyl)benzene] and poly-(allyl ether *p*-ammoniumbenzene) with dispersed platinum microcrystals, poly-I Pt and poly-II Pt, which show activity in hydrogen generation from an acidic solution and hydrogenate some organic substrates. Fig. 1 shows a schematic illustration of the preparation of these MEs. The presence of a methylene chain in poly-I permitted a comparative

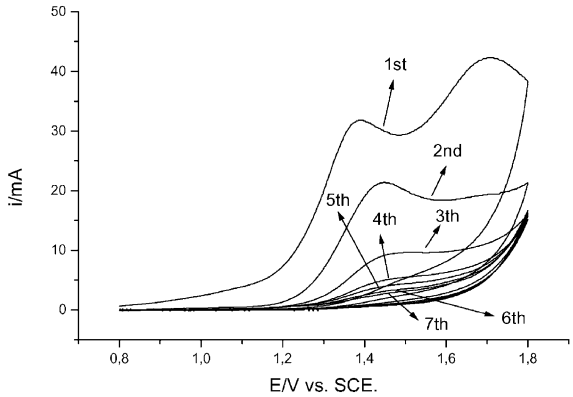


Fig. 2. Cyclic voltammograms for poly-I preparation. Scan intervals from +0.8 to +1.8 V, scan rate 10 mV $s^{-1}$ and $HClO_4$ 0.5 mol $l^{-1}$ solution.

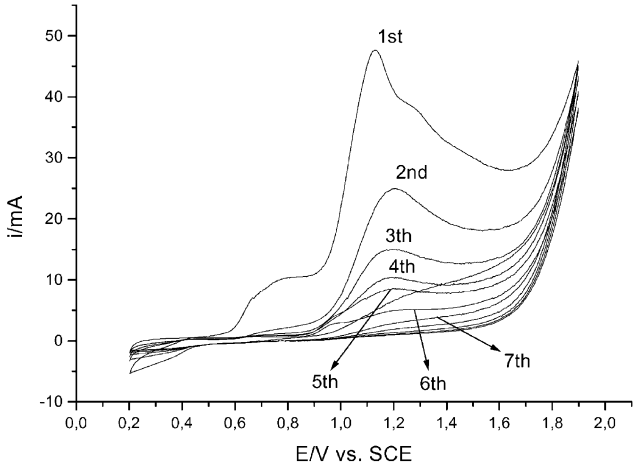


Fig. 3. Cyclic voltammograms for poly-II preparation. Scan intervals from +0.2 to +1.8 V, scan rate 10 mV $s^{-1}$ and $HClO_4$ 0.5 mol $l^{-1}$ solution.

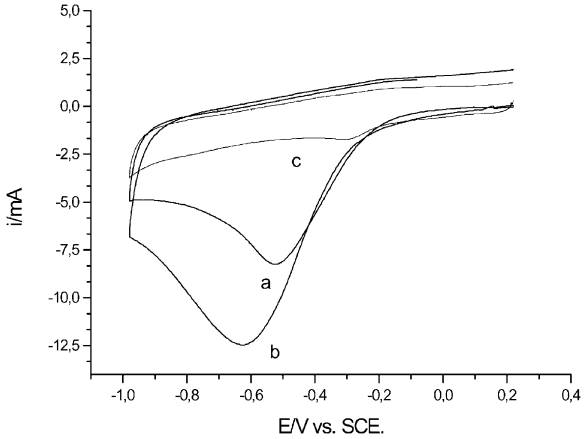


Fig. 4. Cyclic voltammograms for poly-I Pt preparation. Scan intervals from +0.2 to −1.0 V, scan rate 10 mV $s^{-1}$ and KCl 0.1 mol $l^{-1}$ solution: (a) film without platinum; (b) and (c) reduction of $PtCl_4{}^{2-}$.

study of the difference between the two films. We may assume that a larger distance between the ion exchange group and the polymeric chain in poly-I allows more efficient ion exchange and better dispersion of the metal microcrystals and renders the polymeric structure more permeable to the substrate molecules to be hydrogenated.

Allyl oxidation of III and IV yields polymeric films that recover the carbon vitreous electrode and turns it electrically isolated [9] (Figs. 2 and 3). The $ClO_4{}^-$ ions of poly-I and poly-II are exchanged with $PtCl_4{}^{2-}$ by immersion of the electrode in a solution of $K_2PtCl_4$. These incorporated ions turn the electrode electroactive and they are then reduced to $Pt^0$ by scanning at a negative potential (Figs. 4 and 5). When an adequate potential is applied in an HCl solution, poly-I Pt and poly-II Pt generate hydrogen much more efficiently than when the same potential is applied to a platinum bulk electrode (Figs. 6 and 7 and Table 1). These MEs were also used to hydrogenate a carbonyl compound, benzaldehyde, and an olefin, isosafrole, providing very good yields of the products benzyl alcohol and *n*-propyl-3,4-methylenedioxobenzene.

## 2. Experimental

### 2.1. Equipment

Film preparation was carried out in a 50 ml one-compartment cell with a 2.6 cm × 4.5 cm (0.15 cm of thickness) carbon vitreous plate as working electrode, a saturated calomel electrode (SCE) as reference and a platinum gauze with a 0.1 cm thick, 1.0 cm high and 80 cm long wire as an auxiliary electrode. This platinum gauze was rolled into a cylinder and the carbon plate was fixed inside it in a symmetrical fashion. The working and auxiliary electrodes were connected to system by platinum wire.

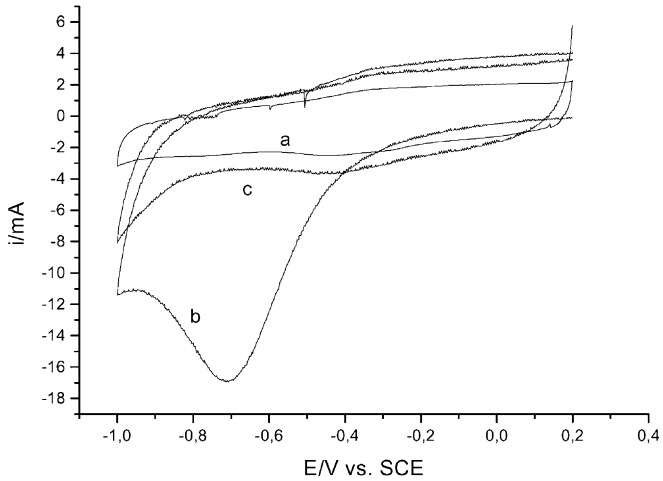


Fig. 5. Cyclic voltammograms for poly-II Pt preparation. Scan intervals from +0.2 to −1.0 V, scan rate 10 mV $s^{-1}$ and KCl 0.1 mol $l^{-1}$ solution: (a) film without platinum; (b) and (c) reduction of $PtCl_4{}^{2-}$.

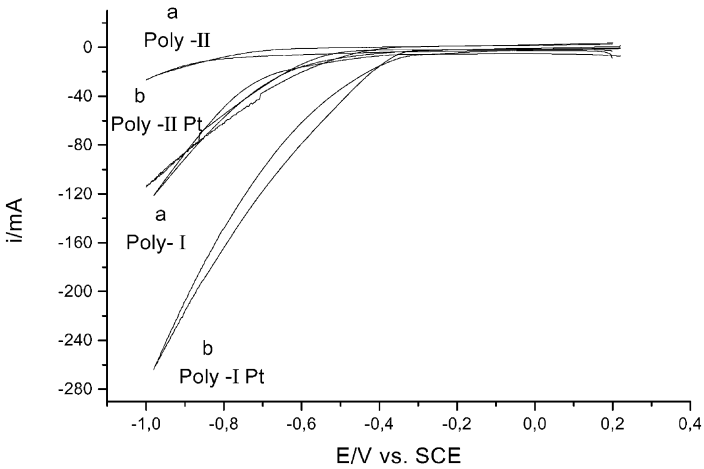


Fig. 6. Cyclic voltammograms for hydrogen generation. Scan intervals from +0.2 to −1.0 V, scan rate 10 mV $s^{-1}$ and HCl 0.1 mol $l^{-1}$ solution: (a) film without platinum; (b) film with platinum microcrystal.

The other electrochemical procedures were carried out in a conventional 50 ml one-compartment cell with the MEs as working electrodes, SCE as reference and a platinum wire inside a sintered glass tube as auxiliary electrode.

A PAR 273 Potentiostat/Galvanostat run by an Electrochemical Analysis Software Model 270 and a Potentiostat MQPG-01 coupled to the Model 270 Electrochemical Analysis Software MQPG were utilized in the experiments.

Spectroscopic measurements were made in a 3.0 ml quartz cell using a 8453 HP spectrophotometer coupled to an HP 89090A Peltier temperature control.

## 2.2. Reagents

All reagents and solvents were of analytical grade and were purified when necessary. Some substrates were synthesised according to methods described [10].

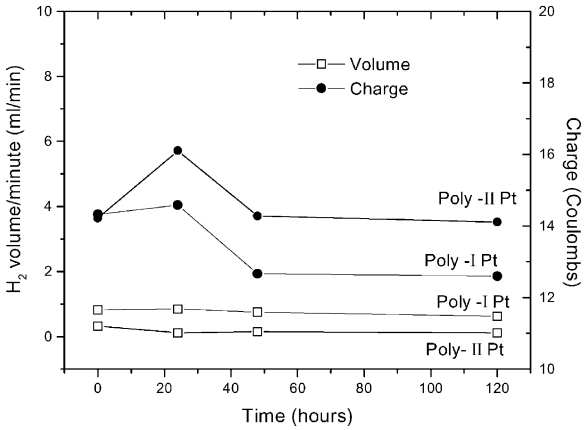


Fig. 7. Volume and number of Coulombs per min for hydrogen generation by poly-I Pt and poly-II Pt.

Table 1
Hydrogen generation efficiency for poly-I Pt and poly-II Pt

| Electrodes | Surface ($cm^2$) | Mass Pt (g) | Current at −1.0 V vs. SCE (mA) | Current density (mA $cm^{-2}$) | Current/mass of Pt (mA $g^{-1}$) |
|---|---|---|---|---|---|
| Pt gauze | 164.0 | 18.2 | 1303.0 | 7.9 | 71.6 |
| Poly-I Pt | 18.4 | $8.2 \times 10^{-5}$ | 372.7 | 20.3[a] | $4.5 \times 10^{6}$ |
| Poly-II Pt | 15.8 | $6.7 \times 10^{-5}$ | 170.2 | 10.8[a] | $2.5 \times 10^{6}$ |

[a] Film surface used for calculation.

The films were removed from the carbon vitreous electrodes and the electrodes were cleaned using a PK-4 polishing kit from Bioanalytical Systems Inc. (BAS).

### 2.3. Analysis

Gas–liquid chromatographies were performed with an Intralab 3300 chromatograph equipped with an OV-17 column, an ionisation flame detector and an Intralab 4290 recorder. Proton nuclear magnetic resonance ($^1$H NMR) spectra were obtained with a Brüker AC-80 (80 MHz) spectrometer.

### 2.4. Preparation of I and II monomers

#### 2.4.1. p-Aminophenol and tyramine acetylation

*p*-Aminophenol or tyramine (0.05 mol) was suspended in 15 ml of water and 5.4 ml (0.057 mol) of acetic anhydride were added. This mixture was warmed under vigorous stirring until dissolution of the solid material. The solution was cooled to room temperature and the precipitated solid was filtered and recrystallised in hot water. The yield of the acetyl derivative of *p*-aminophenol was 67% (mp 165–166°) and the yield of the tyramine derivative was 73.6% (mp 128–130°) ([10], p. 1273).

#### 2.4.2. Allyl ethers preparation

Sodium (0.33 mol) was dissolved in 30 ml of anhydrous ethanol under an inert atmosphere, 0.03 mol of the acetyl derivatives prepared below were added and 0.05 mol of allyl bromide were dropped into this solution. The solution was refluxed by 1.5 h and then cooled to room temperature. Water was added in an amount just sufficient to dissolve the NaBr precipitated and the solution was kept in a refrigerator overnight at 0°C. The solution was then rewarmed to room temperature and the solid precipitated was filtered and dried. The yield of the acetyl derivative of the allyl ether *p*-aminophenol (II) was 77% (mp 69–71°, $^1$H NMR ($CDCl_3$), $\delta$ (ppm) = 2.2 (3H, s), 4.55 (2H, d), 5.30 (2H dd), 6.05 (1H, m), 6.85 (2H, d), 7.45 (2H, d), 9.8 (1H, s)) and the yield of the acetyl derivative of the allyl ether tyramine (I) was 49.4% (mp 82–84°, $^1$H NMR ($CDCl_3$), $\delta$ (ppm) = 1.90 (3H, s), 2.75 (2H, t), 3.50 (2H, dt), 4.50 (2H, d), 5.30 (2H, dd), 6.05 (1H, m), 6.80 (2H, d), 7.10 (2H, d), 7.26 (1H, s) ([10], p. 584).

### 2.5. Preparation of the poly-I and poly-II films covering carbon vitreous electrodes

An amount of 1 mmol (0.02 mol l$^{-1}$) of the acetamide derivatives I and II was hydrolysed in a 50 ml perchloric acid solution 0.5 mol l$^{-1}$ (to dissolve I, it was necessary to use *tert*-butanol as co-solvent at a proportion of 3:7) at 60–85°, under stirring for 1 or 2 h. Hydrolysis was monitored by the disappearance of the 225 or 245 nm UV band corresponding to amide function. The perchlorate ammonium salts III and IV, thus obtained in the perchlorate acid solution of appropriate concentration were transferred to the electrochemical cell where at least seven scans were performed at +0.8 to +1.8 V intervals versus SCE and scan rate of 10 mV s$^{-1}$, to yield the poly-I and poly-II deep blue films covering the electrode.

### 2.6. Tetrachloroplatinate ion incorporation into the film and its reduction; preparation of the MEs poly-I Pt and poly-II Pt

The carbon vitreous plates covered with the poly-I and poly-II films were initially dipped in a KCl solution 0.5 mol l$^{-1}$, and then in a potassium tetrachloroplatinate solution 0.01 mol l$^{-1}$, for 30 min in both cases. These electrodes were transferred to a conventional electrolytic cell with KCl, 0.1 mol l$^{-1}$, and three scans were performed at +0.2 to −1.0 V intervals versus SCE and scan rate of 10 mV s$^{-1}$.

### 2.7. Hydrogen generation from HCl solution

The MEs poly-I Pt and poly-II Pt were connected to a conventional electrolytic cell containing an HCl solution, 0.1 mol l$^{-1}$, and scans were performed at +0.2 to −1.0 V intervals versus SCE and scan rate of 10 mV s$^{-1}$.

### 2.8. Comparative study on hydrogen generation from poly-I Pt and poly-II Pt

#### 2.8.1. Reduction current method

The $H^+$ reduction current generated by the MEs was compared with the reduction current generated in the same solution of HCl (0.1 mol l$^{-1}$) by a platinum gauze with a surface of 164 cm$^2$ and a weight of 18.2 g

used as working electrode. The mass of platinum microcrystals incorporated in the films was calculated based in the number of Coulombs consumed by the reduction of the tetrachloroplatinate ions to metallic platinum (two electrons), with care taken to deduct those Coulombs generated by the film without the platinum microcrystals. These Coulombs were compared to the theoretical Coulombs needed to reduce all tetrachloroplatinate in the solution whose concentration was known. Table 1 shows these results.

*2.8.2. $H_2$ volume method*

The conventional electrochemical cell was modified by connecting it to a graduated U-tube containing water to measure the gas exit. The sintered compartment for auxiliary electrode was kept out and all three electrodes were sealed with a tight-fitting glass stopper. A three-way plug was also connected to the cell to equalise the pressure during the experiment. A −0.9 V potential was applied to electrodes dipped in an HCl solution, 0.2 mol $l^{-1}$, for a determined period of time. The volume of gas generated was measured in the U-tube. Chlorine gas generation was observed in the counter-electrode and was measured together with hydrogen. This did not represent a problem, since chlorine gas generation is always proportional to hydrogen generation and the purpose of the procedure was to compare gas generation between the two types of MEs. Fig. 7 shows these results.

*2.9. Isosafrole and benzaldehyde electrocatalytic hydrogenation using poly-I Pt and poly-II Pt*

An amount of 1 mmol of isosafrole or benzaldehyde was added to the conventional electrocatalytic cell with 50 ml of a 0.2 mol $l^{-1}$ HCl solution (1:1 ethanol as co-solvent/HCl solution was used for isosafrole). A −0.9 V potential was applied under stirring for 24 h. Hydrogen gas formation in the working electrode was noticeable. The current was kept constant by eventual addition of concentrated HCl. Aliquots were withdraw and their UV–VIS absorbances were recorded (decay in 284 nm for benzaldehyde and 304 nm for isosafrole). After the experiment, the solution was neutralised with a saturated solution of $NaHCO_3$, the product was extracted with ethyl ether and the organic phase was dried and evaporated. Gas chromatography showed a clean product without started material that was analysed by conventional spectroscopic methods. Benzaldehyde yielded benzylic alcohol (93.8%) and isosafrole yielded *n*-propyl-3,4-methylenedioxobenzene (82.7%, $^1$H NMR (DMSO-D6), $\delta$ (ppm) = 0.85 (3H, t), 1.5 (2H, m), 2.4 (2H, m), 5.9 (2H, s), 6.6 (1H, m) and 6.75 (2H, m).

## 3. Results and discussion

Both I and II were prepared by well-known methods [10]. Acetamide groups were necessary to protect the amino groups in the *O*-alkylation step. Their hydrolysis gave unstable amino groups derivatives that were difficult to purify. However, their ammonium salts proved to be stable in acid solution. Hydrolysis was then carried out directly in the perchloric acid solution used in the next step. Thus, the ammonium perchlorates solution obtained was scanned at anodic potential, a more efficient procedure than constant potential application [9]. Figs. 2 and 3 show electric isolation of the electrodes after these scans with decay to residual values of the discharges corresponding to an allylic function [9] close to +1.4 V for I and between +1.0 and +1.2 V for II. The bluish films obtained covering the electrode had a surface varying between 15 and 18 $cm^2$ and proved to be highly resistant to chemicals and to mechanical handling and could be stored in a 0.1 mol $l^{-1}$ KCl solution for an indeterminate period of time.

The ion exchange of perchlorate with chloride before the incorporation of the tetrachloroplatinate ions increased the current reduction to $Pt^0$ of the latter. Figs. 4 and 5 demonstrate that only one scan was sufficient to reduce tetrachloroplatinate to $Pt^0$, since (b) shows the reduction current at −0.6 to −0.7 V and (c) shows that the current collapse to residual values.

Fig. 6 compares the $H^+$ reduction discharges from HCl solution to $H_2$ for electrodes only covered with poly-I and poly-II films and for electrodes with dispersed platinum microcrystals poly-I Pt and poly-II Pt. A considerable increase in the reduction discharge close to −1.0 V can be seen for the latter. The increase was more marked for poly-I Pt than for poly-II Pt. The $H_2$ generation at this potential for poly-I and poly-II films, without the presence of the transition metal, do not reduce organic substrates.

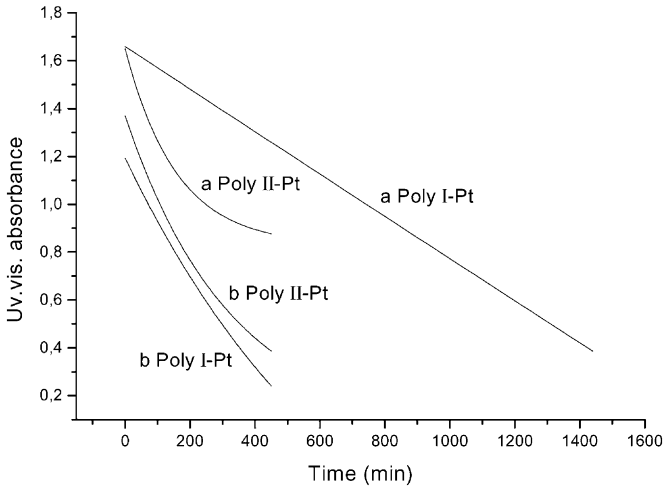


Fig. 8. Absorbance decay curves for (a) isosafrole ($k$ for poly-I Pt, $8.9 \times 10^{-4}\,s^{-1}$ and for poly-II Pt, $1.7 \times 10^{-3}\,s^{-1}$) and (b) benzaldehyde ($k$ for poly-I Pt, $2.1 \times 10^{-3}\,s^{-1}$and for poly-II Pt, $2.26 \times 10^{-3}\,s^{-1}$).

The poly-I Pt modified electrode is more efficient than poly-II Pt one for the generation of hydrogen. Table 1 shows that an 8–10 times smaller electrode surface for the MEs and a platinum mass incorporated about $2.3 \times 10^4$ times less produce a current per gram of platinum about $2 \times 10^7$ times greater when compared with the bulk platinum gauze. The poly-I Pt that contains the methylene chain generates $H^+$ reduction current twice higher than poly-II Pt with the same amount of incorporated platinum.

The indirect calculation of platinum mass incorporated to MEs motivated us to perform experiments in which the production of hydrogen by the electrode could be directly measured. The volumes of hydrogen plus chlorine from poly-I Pt and poly-II Pt indicate the efficiency of the electrodes. Fig. 7 presents the volume and the number of Coulombs per minute for the two electrodes determined on several occasions over a period of 5 days. The MEs were preserved in a $0.1\,mol\,l^{-1}$ KCl solution. Again, poly-I Pt proved to be more efficient and both were stable with a minimum loss of activity during that time.

The spacing of the micro-crystals in poly-I Pt due to the methylene chain allowing to greater ion and molecule mobility in the polymer mesh, can be deduced from the above results giving a more efficient generation of hydrogen by this ME.

The double bonds of benzaldehyde and isosafrole were reduced with very good yields when the substrates were added to the cell containing HCl and submitted to catalytic hydrogenation by the MEs. There was no noticeable difference in yield and first order speed between the two electrodes for both substrates, as shown in Fig. 8 (isosafrole: $k$ for poly-I Pt, $8.9 \times 10^{-4}\,s^{-1}$ and for poly-II Pt, $1.7 \times 10^{-3}\,s^{-1}$ and benzaldehyde: $k$ for poly-I Pt, $2.1 \times 10^{-3}\,s^{-1}$and for poly-II Pt, $2.26 \times 10^{-3}\,s^{-1}$). This close reactivity must be due to a copious gas evolution on the surface of the electrode indicating that this amount of hydrogen is fully sufficient for the hydrogenation of the substrates. The hydrogen is adsorbed at a concentration far higher than that of the substrate adsorbed (this permits to establish a substrate kinetics of pseudo first order). It is also possible that some hydrogen does not adsorb to the surface of the microcrystals but evolves directly as gas.

## 4. Conclusion

Carbon vitreous electrodes modified by poly[allyl ether $p$-(2-ammoniumethylbenzene)] and poly(allyl

ether *p*-ammoniumbenzene) films having platinum microcrystals, poly-I Pt and poly-II Pt, were easily produced from stabilised monomers and proved to be chemically and mechanically stable. They can be used to generate hydrogen from an acid solution and to hydrogenate double bonds of olefin and aldehyde with good yields and close reactivity. Poly-I Pt proved to be more efficient than poly-II Pt in the generation of hydrogen and both showed to be stable with a minimum loss of activity during a long time.

## Acknowledgements

The authors thank CAPES, CNPq and FAPESP for the grants received.

## References

[1] S.J.C. Cleghorn, D. Pletcher, Electrochim. Acta 38 (1993) 425.
[2] H. Lund, M.M. Baizer (Eds.), Organic Electrochemistry, 3rd Edition, Marcel Dekker, New York, 1991, pages 343 and 350.
[3] A. Mertz, Top. Curr. Chem. 152 (1990) 50.
[4] J-C. Moutet, Org. Prep. Proc. Int. 24 (1992) 309.
[5] A. Deronzier, J-C. Moutet, Coord. Chem. Rev. 147 (1996) 339.
[6] J.-C. Moutet, Actual. Chim. 8-9 (1998) 63.
[7] A. Malinauskas, Synth. Met. 107 (1999) 75.
[8] W. Na, J.K. Hong, P.N. Pintauro, J. Appl. Electrochem. 29 (1998) 94.
[9] R.C.Z. Lofrano, J.M. Madurro, J.R. Romero, J. Mol. Catal. A: Chem. 153 (2000) 237.
[10] Vogel's, Textbook of Practical Organic Chemistry, 5th Edition, Longman, UK, 1989, pages 584 and 1273.