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ORIGINAL PAPER

# Synthesis, characterization and catalytic properties of palladium-containing poly(allylbenzene *p*-sulphonic acid) films

**A. M. Fundo · F. L. S. Purgato · J. R. Romero ·
L. M. Abrantes**

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**Abstract** This work reports results achieved when a specially designed monomer, the allyl ether of *p*-benzenesulphonic acid, with a pendent anionic group, was used to prepare a polymeric matrix. Ion exchange with cupric ions followed by electrochemical reduction provided polymer films with highly dispersed $Cu^0$ particles. Immersion of the copper bearing modified electrode in a $PdCl_4^{2-}$ containing solution produced a displacement reaction causing the deposition of 50–200 nm sized Pd particles. The presence of Pd particles in the so-prepared films was confirmed by voltammetry, SEM/EDS and XRD. The behaviour of the submicron Pd particle/poly(allylbenzene *p*-sulphonic acid) modified electrode towards the HER was evaluated by recording polarization curves. The electrocatalytic activity reveals that the methodology is a promising approach for the preparation of cathodes for the electrohydrogenation of organic molecules.

**Keywords** Polymer film · Palladium submicron particles · Displacement reaction · Electrocatalytic activity · Hydrogen evolution reaction

## 1 Introduction

The incorporation of microparticles of noble metals in polymeric films has been the subject of intensive research due to the attractive characteristics of the so-modified electrodes for application in electrocatalytic hydrogenation (ECH) [1–5]. Polymer matrices are particularly suitable for hosting metallic clusters since their porous nature gives good dispersion of catalytic particles which, being electroactive, offer an effective route for the flow of charge, as observed in the most studied systems, polypyrrole and polyaniline [6–8].

The ability of bulk palladium to absorb hydrogen in large amounts has been a well-known difficulty for the characterization of the hydrogen adsorption process on this metal [9, 10]. To circumvent the problem several approaches have been reported such as the use of ultrathin Pd overlayers on single crystals [11] or deposited on neutral matrix [12], palladium clusters [13, 14] and mono-dispersed palladium nanoparticles [15].

Exhibiting different properties from the bulk material and displaying large surface-to-volume ratio, metal submicron particles are natural candidates for hydrogen electrosorption studies. The catalytic activity for the electrochemical hydrogen evolution reaction (HER) displayed by palladium particulates was found to be strongly dependent on the cluster size [14]; as reported recently [16], the growth conditions determine the shape and the morphology of Pd nanoparticles, features that are also expected to affect the electroactivity.

The incorporation of metal particles on polymer layers has been achieved by different routes: by electrochemical deposition [17, 18] either on a pre-formed films or during the electropolymerization process; by electroless precipitation, taking advantage of the spontaneous oxidation revealed by some systems, such as polyaniline and polypyrrole in acid solutions, which occurs at potentials particularly suitable for noble metals uptake [5, 19, 20]; and by using the ion exchange properties of pendent

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A. M. Fundo · L. M. Abrantes (✉)
CQB, Departamento de Química e Bioquímica,
Faculdade de Ciências da Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal
e-mail: luisa.abrantes@fc.ul.pt

F. L. S. Purgato · J. R. Romero
Departamento de Química, F. F. C. L. R. P. – U S P, Av.
Bandeirantes 3400, 14040-910 Ribeirao Preto, SP, Brazil

cationic or anionic groups in polymer backbones [21–23]. The authors have already reported the efficiency of poly (*p*-substituted allylbenzenes) as support for different metal particles [24, 25] and the catalytic activity of those systems bearing platinum [26].

In this work, the poly(allylbenzene *p*-sulphonate) matrix is employed to demonstrate the feasibility of dispersing submicron palladium particles. Instead of direct ion exchange with palladium species in solution, as reported elsewhere [2, 27], a two step procedure is followed. First, the polymer cation-exchange ability is used for incorporation of cupric ions, converted into metallic copper by appropriate electrochemical reduction. The so-modified layer is then immersed in a palladium ion containing solution to promote a displacement reaction.

Electrochemical characterization of the incorporated submicron palladium particle catalysts has been carried out focusing on the HER.

## 2 Experimental

Vitreous carbon plate was used as substrate (0.08 $cm^2$ exposed area), directly sealed into glass. The electrode was cleaned before each experiment by abrasion with successively finer grades of alumina (down to 0.05 μm) until a mirror finish was generated, followed by washing with Millipore water. Potentials were controlled with respect to a saturated calomel electrode (SCE) by a Wenking HP 96 High Power Potentiostat; a two-compartment electrochemical cell equipped with a Pt foil counter electrode was employed. The data were collected in an Omnigraphic-Houston Instrument 2000 X-Y-t Recorder.

All solutions were prepared from p.a. grade chemicals and Millipore water. The synthesis of the allyl ether of the *p*-benzenesulphonic acid has been reported elsewhere [25]; the electropolymerization was carried out potentiodynamically following the previously described procedure [28]. The topographic morphology of the poly(allylbenzene *p*-sulphonic acid) films was analysed by Atomic Force Microscopy (AFM), in tapping mode with a Nanoscope III Multimode from Digital Instruments.

The polymer film coated electrodes were immersed for 1 h in a saturated solution of $CuSO_4$ to accomplish the ion-exchange process (Cu(II) substitutes the hydrogen ion at the polymer sulphonate groups). After rinsing with Millipore water, the modified electrodes were polarized in KCl 0.5 mol $dm^{-3}$ solution, from the open circuit potential down to −900 mV, to promote the electrochemical reduction of metallic ions and to incorporate $Cu^0$ particles in the polymeric matrices.

The immersion of the copper bearing polymer modified electrodes in $PdCl_2$ 100 ppm of HCl 0.125 mol $dm^{-3}$ allowed observation of a displacement reaction; the deposition of Pd was followed by open circuit potential measurements and its presence confirmed electrochemically by cyclic voltammetry in $H_2SO_4$ 0.5 mol $dm^{-3}$ at $v = 10$ and 50 mV $s^{-1}$.

The modified electrode morphology was observed by Scanning Electronic Microscopy, SEM, (JEOL JSM-5200 LM). The composition was determined from quantitative Energy Dispersive X-ray Spectrometry (EDX—Rontec Edwin with 20 keV beam energy).

The film structure was analysed by X-ray diffraction (XRD), using a Philips diffractometer (X'Pert model), with $CuK_\alpha$ radiation, in grazing mode with an incidence angle of 2°.

The electrocatalytic activity of the modified electrodes was tested towards HER in 1.0 mol $dm^{-3}$ NaOH using slow linear voltammetry ($v = 1$ mV $s^{-1}$).

## 3 Results and discussion

The electropolymerization of *p*-substituted allyl benzenes has been previously reported by the authors [24, 25]. The allyl ether of the *p*-benzenesulphonic acid undergoes oxidation at potentials higher than 1,100 mV versus SCE (Fig. 1); three potential cycles carried out in the range from the open circuit potential to 1,900 mV caused full coverage of the substrate by a film. As recently described [28], deposit analysis shows that, besides carbon, it contains the proportions of sulphur and oxygen expected for the poly

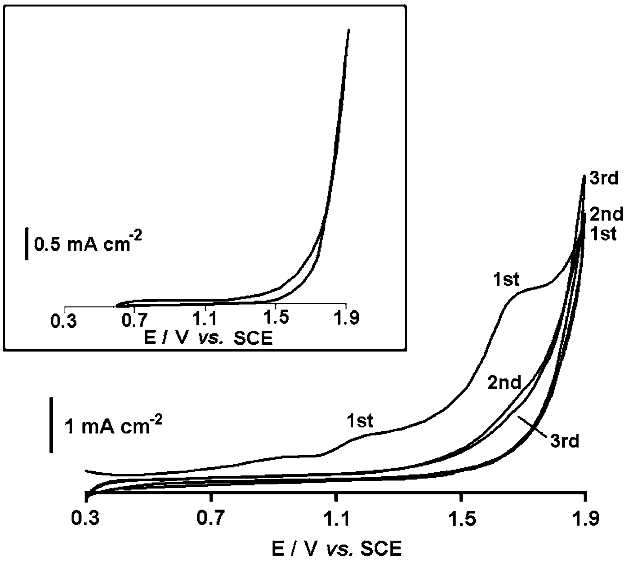

**Fig. 1** Potentiodynamic polymerization of the allyl ether of the *p*-benzenesulphonic acid, at vitreous carbon electrode, from 0.016 mol $dm^{-3}$ monomer in 0.5 mol $dm^{-3}$ $H_2SO_4$ solution; $v = 10$ mV $s^{-1}$. Inset: voltammogram of the vitreous carbon electrode in 0.5 mol $dm^{-3}$ $H_2SO_4$

(allyl ether of *p*-benzenesulphonic acid). Within the considered potential domain, the polymer shows no electroactivity, as indicated by the near-zero current monitored throughout the reverse potential sweeps. Also, the decrease in current due to monomer oxidation, observed for the second and subsequent potential cycles, denotes the poor conductivity nature of the deposited film.

In spite of these properties, the poly (allyl ether of *p*-benzenesulphonic acid) layers are highly effective ion-exchange matrices for the incorporation of a variety of metallic cations [26].

Information on the film morphology was obtained by ex-situ AFM imaging. As observed in Fig. 2, the polymer layer has small globular features in a fairly uniform arrangement, giving a rather smooth surface. The images shown in Fig. 2 are representative of the whole sample area.

The facile loading of the polymer pendent sulphonated groups with metallic ions (the sulphonic acid group permits exchange of $H^+$ by ions such as $Fe^{2+}$, $Ni^{2+}$ or $Cu^{2+}$ (unpublished work)) can be achieved by simple immersion of the polymer in a metallic ion containing solution and confirmed by subsequent electroreduction of the respective metallic species [26]. For the purpose of the present study the ion-exchanging groups in the polymer backbone were used to incorporate copper.

As reported by the authors in preceding papers [26, 28], the film impregnation by $Cu^{2+}$ can be achieved through polymer modified electrode immersion in a saturated $CuSO_4$ solution for 1 h. The electrochemical reduction of the embedded copper ions, carried out in KCl 0.5 mol $dm^{-3}$ solution, by scanning the potential from 450 mV (open circuit) down to −900 mV and holding the potential until zero current is observed, provides a 5 μg $cm^2$ loading of copper particles in the polymer film.

Once the polymer is bearing copper, the metal can be used to produce catalytic centres. It is well known [29, 30] that spontaneous deposition of metals may occur by a displacement reaction between solutions of more noble metal salts ($M_1$) and easily reduced immersed metals ($M_2$) as described by

$$M_1{}^{n+} + n/m\, M_2 \rightarrow M_1 + n/m\, M_2{}^{m+}.$$

The standard equilibrium potentials

$$PdCl_4{}^{2-} + 2e \rightarrow Pd + 4Cl^- \quad E^0 = +915\ \text{mV}$$

$$Cu^{2+} + 2e \rightarrow Cu \quad E^0 = +340\ \text{mV}$$

indicate that Pd can be deposited when poly (allylbenzene *p*-sulphonate) films, with embedded copper metal particles, are immersed in $PdCl_4{}^{2-}$ containing solutions.

Figure 3 shows the open circuit potential, $E_{ocp}$, of the poly(allylbenzene *p*-sulphonate)/Cu, $P(H^+POBS^-)/Cu$, coated electrodes in contact with 100 ppm $PdCl_2$ in 0.125 mol $dm^{-3}$ HCl solution as a function of time. For comparison, the data recorded for the pristine and copper bearing polymers in palladium free acid media are also shown. The electrode potential

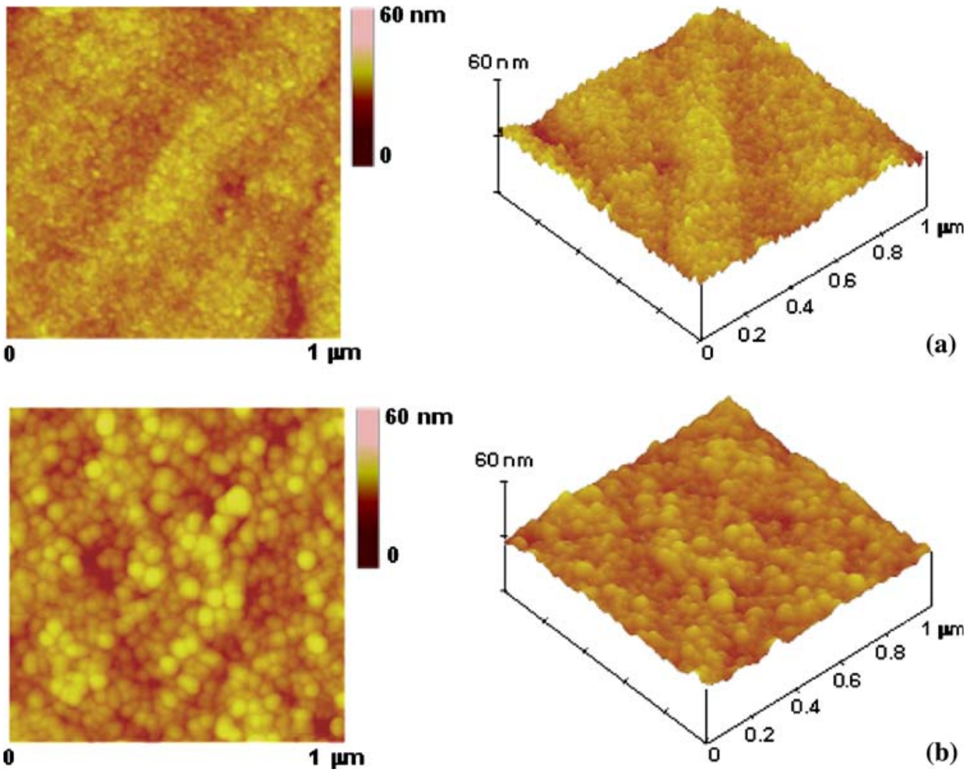

**Fig. 2** Ex-situ AFM images (tapping mode) in air of the polished vitreous carbon (**a**) and modified with poly(allylbenzene *p*-sulphonic acid) (**b**)

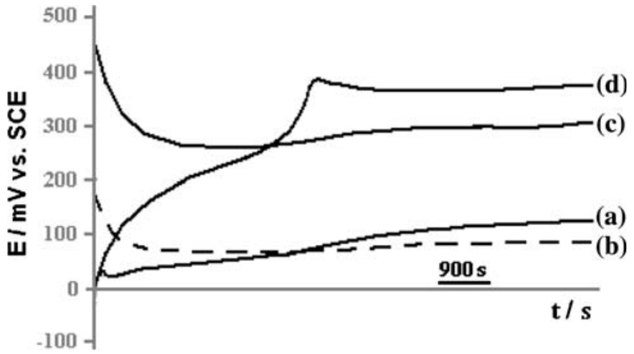

**Fig. 3** Open circuit potential evolution. Polymer (a) and polymer with Cu particles (b) in 0.125 mol $dm^{-3}$ HCl; polymer (c) and polymer with Cu particles (d) in $PdCl_2$ 100 ppm in 0.125 mol $dm^{-3}$ HCl solution

changes positively from around −210 to +360 mV indicating Pd deposition through the displacement reaction,

$$\mathrm{Pd(II)} + \mathrm{Cu(0)} \rightarrow \mathrm{Pd(0)} + \mathrm{Cu(II)}.$$

The time dependence of $E_{ocp}$ reveals that the palladium loading increases with immersion time. While initially (up to 900 s) there is a rapid uptake of the noble metal, for reaction completion about 90 min is required for the contact time of $P(H^+POBS^-)/Cu$ with the anionic chloropalladium complex solution. Although the film is relatively thin and the cementation reaction starts at the film surface, time must be given to allow for maximum penetration of the metal complex into the polymeric matrix. After removal of the electrode from the solution, the successful incorporation of Pd particles in the film could be seen (by naked eye) by the surface metallic brightness. In fact, assuming that all immobilized copper is used in the displacement reaction, as much as 8.4 μg $cm^2$ Pd might have been cemented.

Figure 4 presents SEM photomicrographs of the electrode surfaces after 2 h galvanic displacement. The images clearly show that a regular distribution of spherical Pd particles with a generally consistent size of the order of 50–200 nm is obtained.

The presence of Pd was confirmed by energy dispersive emission analysis of X-rays (EDX) attached to SEM (Fig. 5). The peak position corresponding to palladium is well defined, whereas no copper atoms appear to be present in the sample. Taking into account the small thickness of the polymer film and that the EDS information concerns not only surface but near-surface information, this result also points to complete removal of Cu by Pd in the 2 h galvanic displacement step.

This result is different from that observed after the immersion of a copper electrode in a solution containing Pd ions, where the formation of a Cu–Pd alloy has been reported [31, 32]. This difference is likely due to the very small amount of Cu incorporated in the polymer which is completely consumed to originate Pd deposition, whereas when a massive sheet of Cu or a deposited layer of Cu is employed, the displacement reaction will stop when a thin compact layer of palladium covers the Cu, or is delayed (porous deposited Pd layer) so that conditions for the alloy formation can occur.

X-ray analysis of the prepared samples (Fig. 6) provided independent confirmation of the presence of Pd. Within the $2\theta$ range = 30–90°, the X-ray diffractogram of the bare $P(H^+POBS^-)$ film (Fig. 6a) exhibits low intensity, broad and ill-defined peaks, whereas the identification and assignment of the reflection traces observed for the modified polymer (Fig. 6b) reveal the crystalline nature of the embedded Pd particles. The pattern indicates a face centred cubic lattice, with a lattice parameter $a = 3.88$ nm, very close to the theoretical value given by JCDS 5-0681 [33] ($a = 3.89$ nm).

Figure 7 details the voltammetric responses of the $P(H^+POBS^-)/Pd$ modified electrode in 0.5 mol $dm^{-3}$ $H_2SO_4$, at scan rates of 50 and 10 mV $s^{-1}$; the initial scan proceeded cathodically starting from the open circuit potential. The behaviour is similar to those reported for palladium thin films deposited on gold [34, 35] and vitreous carbon [35]. The reversible process characteristic of the atomic hydrogen adsorption/desorption is clearly detected by the cathodic and anodic current peaks denoted by A (at

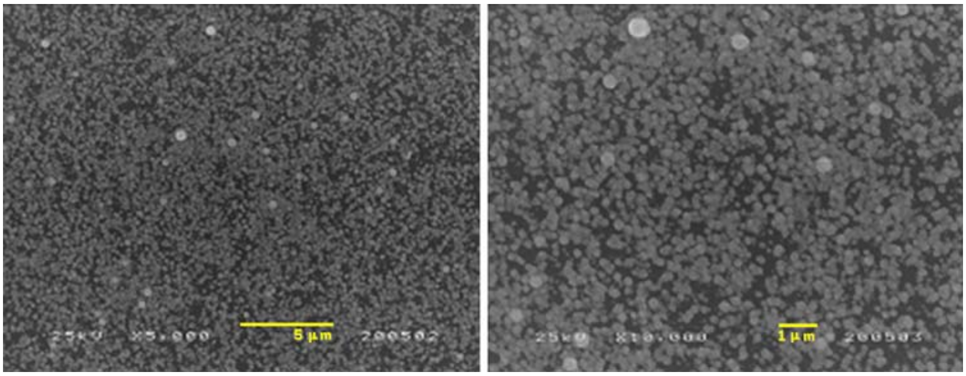

**Fig. 4** Scanning electron microscopy images of the polymer modified electrode after 2 h cementation of Pd particles by displacement reaction with Cu

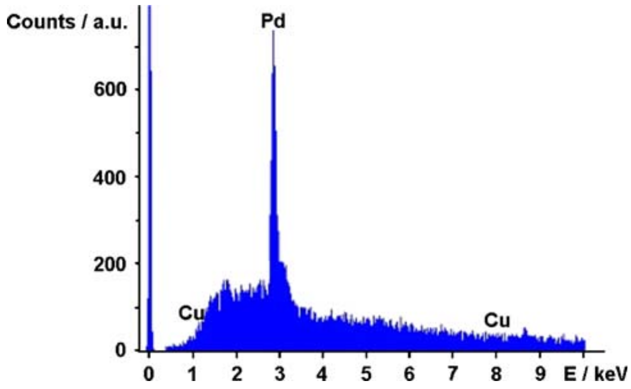

**Fig. 5** Energy-dispersive X-ray spectrum of the polymer modified electrode after 2 h cementation of Pd particles by displacement reaction with Cu. The X-ray emission energies which would identify copper are also shown

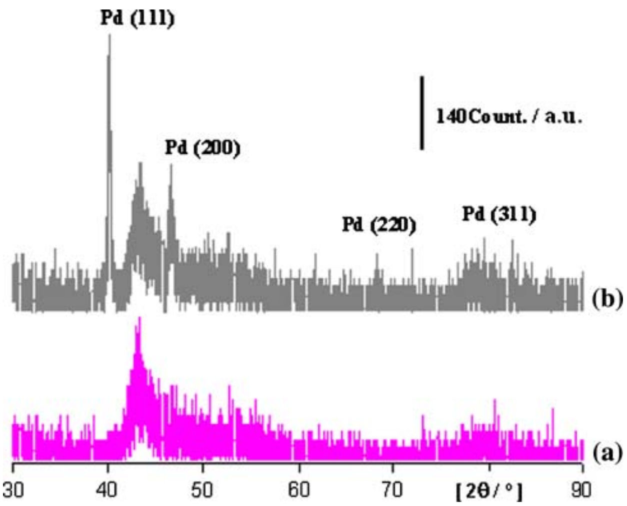

**Fig. 6** X-ray diffractogram of the bare polymer film (**a**) and of the modified electrode (**b**) after 2 h cementation of Pd particles by displacement reaction with Cu

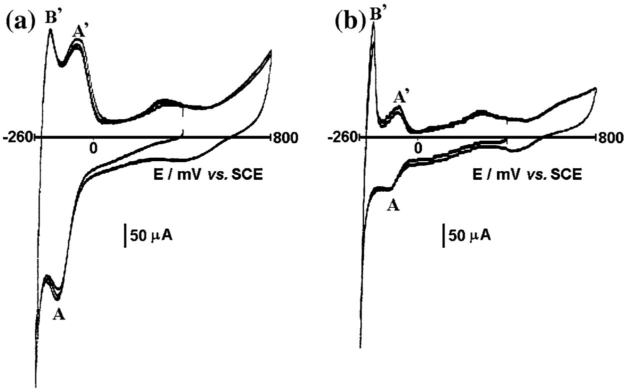

**Fig. 7** Cyclic voltammograms of the poly(allylbenzene *p*-sulphonic acid) film incorporating Pd particles at 50 mV $s^{-1}$ (**a**) and 10 mV $s^{-1}$ (**b**)

about −150 mV) and A′ (at −70 mV). Hydrogen absorption is likely masked by the hydrogen evolution reaction, but during the anodic potential sweep the desorption peak B (at −195 mV) is well defined in both cases.

The influence of sweep rate on the hydrogen desorption mechanism, namely the relative contribution of the two simultaneous reactions occurring at the electrode surface (the electrooxidation of sorbed hydrogen, $H_{sorb} \rightarrow H^+ + e^-$, and the hydrogen desorption via non-electrochemical recombination process and $H_2$ diffusion into the solution, $2H_{sorb} \rightarrow H_2$) can be analysed through the electric charges of the above mentioned current peaks, after subtracting the response of a Pd free polymer modified electrode. Within the hydrogen desorption region, 1,180 and 984 μC have been estimated, respectively, for 50 and 10 mV $s^{-1}$ sweep rates. Although the charges involved in process B′ are similar (500 and 490 μC), the values for peak A′ are much larger for the highest sweep rate, i.e. 680 μC while just 485 μC is recorded for 10 mV $s^{-1}$. Thus, in this case it is plausible to assume that the absorption and the amount of $H_2$ generated by the recombination process are more significant. This trend is in agreement with the model postulated by Czerwinski et al. [36] for hydrogen desorption from a palladium limited volume electrode.

For palladium electrodes, according to Woods [37], an estimate of the real area of highly dispersed surfaces can be achieved considering the potential region where processes involving oxygen occur. From measurements of charge corresponding to the oxygen coverage at low potentials, e.g. 0.8 and 1.2 V versus SCE, the computed real surface area of the palladium particles immobilized in the polymer film is 1.1 $cm^2$. The well known plot of oxygen coverage as a function of potential, in 1.0 mol $dm^{-3}$ $H_2SO_4$, at 25 °C [37] (where the widely accepted specific charge of 0.424 mC $cm^{-2}$ is assumed) has been used.

This large value of active area (the substrate geometric area is 0.08 $cm^2$) reflects good dispersion of palladium particles. The voltammetric reproducibility also demonstrates that the modified polymer offers mechanical stability.

Considering that the ultimate goal of this study is the preparation of electrocatalytic materials for the ECH of organic molecules, a preliminary evaluation of the catalytic activity of the palladium-polymer electrodes towards the HER was carried out by slow scan (1 mV $s^{-1}$) linear sweep voltammetry in 1.0 mol $dm^{-3}$ NaOH solution. Figure 8 contrasts the response obtained for a bulk palladium electrode with the behaviour displayed by the modified electrode containing the Pd submicron particles. In the former, hydrogen adsorption, absorption and evolution currents overlap whereas in the signal recorded with the modified electrode the hydrogen adsorption process can be distinguished. The differences are very likely related to the

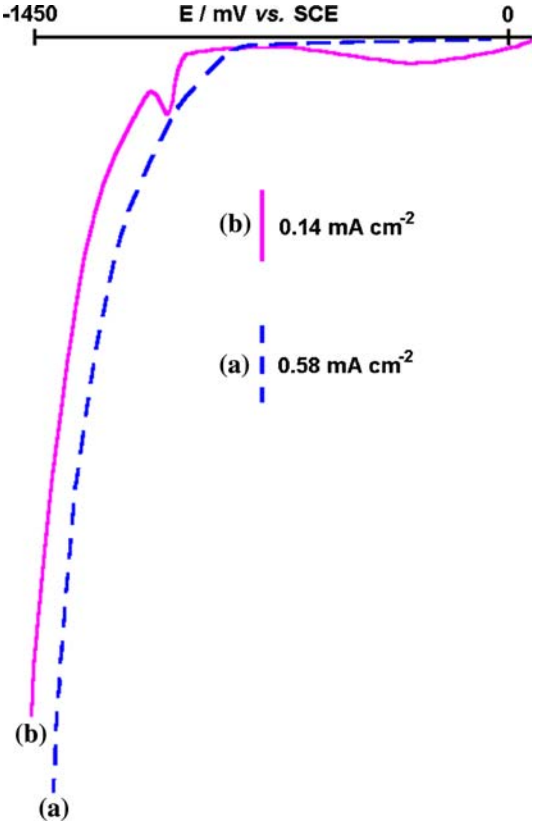

**Fig. 8** Steady state polarization curves for hydrogen evolution reaction obtained with bulk palladium (a) and the poly(allylbenzene *p*-sulphonic acid) film incorporating Pd particles modified electrode (b) in 1.0 mol dm$^{-3}$ NaOH; $v$ = 1 mV s$^{-1}$

significant influence of the crystallographic orientation on the hydrogen evolution mechanism [38]. In fact, as shown in the X-ray diffraction analysis (Fig. 6), the main crystallographic orientation observed for the Pd particles is (111) face; according to the literature, Pd (111) is the only surface which favour hydrogen adsorbed recombination reactions. Other orientations, present no adsorption sites and the H atom prefers to penetrate into the bulk than to diffuse on the surface. Although these considerations deserve further confirmation by other electrochemical methods, the results suggest that the modified electrodes are promising cathode materials.

## 4 Conclusions

The inclusion of submicron particles of catalytic metals such as palladium in coated electrodes can be easily achieved using poly(allylbenzene *p*-sulphonate) films.

The process involves the sulphonated group in the polymer backbone to promote the incorporation by ion-exchange of cations that can be easily reduced (e.g. Cu(II)). The ion-exchange procedure is followed by electrochemical reduction leaving the metal species in its lowest oxidation state and thus able to participate, once immersed in solution of more noble metal salts (e.g. $PdCl_2$) in a displacement reaction producing the deposition of Pd crystals. As revealed by SEM images, a homogenous dispersion of 50–200 nm sized Pd particles is obtained.

The modified electrodes are physically and electrochemically stable and favour hydrogen adsorption due to the preferential crystallographic orientation, Pd (111), obtained for the Pd submicron particles. Thus they are promising electrode materials for the ECH of organic molecules.

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