

Synthesis and characterization of poly-(allylbenzene *p*-sulphonate) films incorporating electrolessly deposited Ni–P

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Abstract

The preparation of a novel electrode material is described. The ionic exchange properties of polymer films electrochemically prepared from the allyl ether of the *p*-benzenesulphonic acid monomer were explored with an incorporated ion of metallic crystallites in the polymeric matrix. The autocatalytic activity of the pristine and modified polymer for the electroless deposition of Ni–P from a hypophosphite containing solution was analyzed and conditions for the use of the deposition method to modify the nature and the size of the metal particles established. The performance of typical electrodes prepared by this route, e.g., polymer/Cu/Ni–P, towards the proton reduction reaction in buffer solution, when contrasted to polymer/Ni, revealed promising electrocatalytic activity. This behaviour, along with the simplicity of the preparation route makes these modified electrodes strong candidates to replace other systems for electrohydrogenation purposes.

1. Introduction

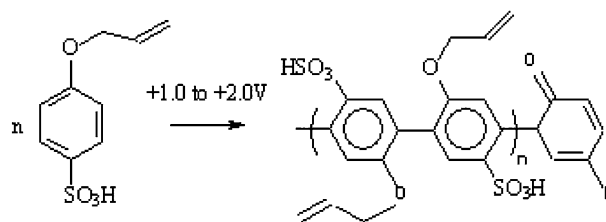
Polymer based modified electrodes bearing suitable dispersions of metal particles can be successfully used for the electrocatalytic hydrogenation of organic molecules. The ability of the metal to adsorb both the atomic hydrogen produced by proton reduction and the unsaturated organic substrate enables hydrogenation under mild conditions, i.e., avoiding the need for hydrogen gas production and the use of high temperatures and/or pressures. Polymeric matrices such as polythiophene [1], polypyrrolidone [2] and polypyrrole [3] have been described for this purpose.

Different routes can be used for the incorporation of metal particles. Polymers like polypyrrole or polyaniline can undergo spontaneous oxidation promoting the deposition of noble metals; this process has been described as electroless precipitation [4–6]. Specially designed monomers, with ionic exchange substituent groups have also been used to prepare the polymeric matrix [7–9]. After metallic ion exchange the system is subjected to an appropriate potential to reduce the metal ions to their lowest oxidation state [10, 11]. The deposited metals may have autocatalytic activity for electroless metal deposition which allows increasing the

size and/or changing the nature of the incorporated metal particles [12–15]. Also, the deposited metals may undergo displacement reactions that permit the deposition of fine dispersions of electrocatalytic metals such as Pt or Pd [16, 17].

For the preparation of the polymer films, particularly suitable monomers are the *p*-substituted allylbenzenes. Its anodic oxidation yields stable polymers and a variety of cationic and anionic exchange groups can be envisaged, such as $-\text{NH}_3^+$, $-\text{CH}_2\text{CH}_2\text{NH}_3^+$ or $-\text{SO}_3^-$, as represented in scheme 1.

Poly (*p*-substituted allylbenzene) have been employed in the preparation of modified electrodes, namely those allowing exchange with PtCl_4^{2-} or PdCl_4^{2-} , subsequently



Scheme 1. Polymerization of the allyl ether of the *p*-benzenesulphonic acid.

reduced to Pt^0 or Pd^0 [18, 19] and used for catalytic hydrogenation of unsaturated organic substrates [20–25].

New electrocatalytic modified electrodes based on poly (allyl ether of the *p*-benzenesulphonic acid), (scheme 1) have been developed in our laboratories. With cupric or nickel ions in the exchange step, the metallic nucleous produced by the subsequent cathodic reduction were coated by the electroless deposition of Ni–P. Using ferric ions in the ionic exchange, the reduced metal particle allows displacement reactions in order to observe platinum or palladium deposition. Both procedures give good metallic dispersion in the polymer film able to enhance its electrocatalytic activity.

In this work the successful preparation of modified electrodes incorporating electrolessly deposited Ni–P is described and their catalytic properties towards the HER illustrated. Another paper will be devoted to polymer film modification by the inclusion of noble metals through displacement reactions.

2. Experimental

Electrochemical experiments were carried out with a vitreous carbon plate (0.08 cm^2 geometrical area) placed in a two-compartment cell equipped with a Pt foil counter electrode. For each experiment a fresh mirror-finishing surface was generated by hand polishing the working electrode with an aqueous suspension of successively fine grades of alumina (down to $0.05 \mu\text{m}$). All potentials were controlled with respect to the saturated calomel electrode (SCE) using a Wenking HP 96 High Power Potentiostat. The data was collected in an Omnigraphic-Houston Instrument 2000 X-Y-t Recorder.

The synthesis of the allyl ether of the *p*-benzenesulphonic acid is described elsewhere [23]. The electropolymerization from a solution containing the monomer (0.16 mol l^{-1}) in H_2SO_4 0.5 mol l^{-1} was carried out by multiple potential cycling, typically 3 cycles, at 10 mV s^{-1} , between the open circuit potential and 1900 mV vs. SCE .

Surface analysis of the coated vitreous carbon plates were carried out by scanning electron microscopy (SEM) employing a LEO model 440 Instrument coupled to a energy dispersive X-ray (EDX – model 7060).

The polymer film was rinsed with Millipore water and subjected to the ion-exchange process by dipping the coated vitreous carbon electrode into saturated solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, or NiSO_4 for 60 min.

After careful washing with Millipore water, the modified electrodes were polarized in KCl 0.5 mol l^{-1} solution, from the open circuit potential until -900 mV , to reduce the incorporated ions to the metallic state. The respective amounts of deposited metals were estimated through the evaluation of the involved charges.

Up to this stage all experiments were carried out at room temperature.

The copper or nickel modified electrodes were immersed in $0.20 \text{ mol l}^{-1} \text{ NaH}_2\text{PO}_2$, $0.10 \text{ mol l}^{-1} \text{ NiSO}_4$ and $0.15 \text{ mol l}^{-1} \text{ NaO}_2\text{CCH}_3$ aqueous solutions at pH 4.8 (adjusted with CH_3COOH), for a period of 15 min and at $60.0 \pm 0.1 \text{ }^\circ\text{C}$. This allowed observation of the deposition of Ni–P, after induction of the process [26] by applying a potential pulse of -800 mV vs. SCE . Under these conditions, previously reported data have shown that the Ni–P deposit contains ca. 14% at P and reaches approximately $2 \mu\text{m}$ [27].

The electrocatalytic activity of the so-modified electrodes towards the HER was evaluated by performing slow linear voltammetry, ($v = 1 \text{ mV s}^{-1}$) in $1 \text{ mol l}^{-1} \text{ NaOH}$.

3. Results and discussion

The potentiodynamic polymerization of the allyl ether of the *p*-benzenesulphonic acid illustrated in Figure 1 shows that the monomer oxidation occurs at about 1600 mV . The polymer produced by the chain reaction does not display electroactivity in the potential domain considered and the decrease in current during the subsequent potential cycles reveals its poor conductivity. The surface morphology of the so-modified vitreous carbon plate, observed by scanning electron microscopy, is shown in Figure 2(a). The coupled EDX analysis (Figure 2(b)) indicates the presence of sulphur and oxygen in the expected proportions (as well as carbon).

As expected the polymer voltammogram is featureless (Figure 3(a)). However, after the ion exchange step (the sulphonic acid group permits the exchange of H^+ by

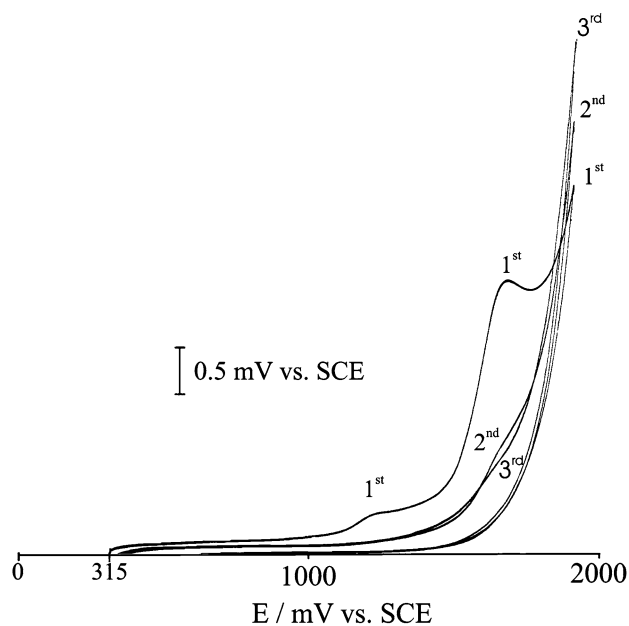


Fig. 1. Potentiodynamic polymerization of the allyl ether of the *p*-benzenesulphonic acid, at vitreous carbon electrode from 0.16 mol l^{-1} monomer in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ solution; potential scan rate 10 mV s^{-1} .

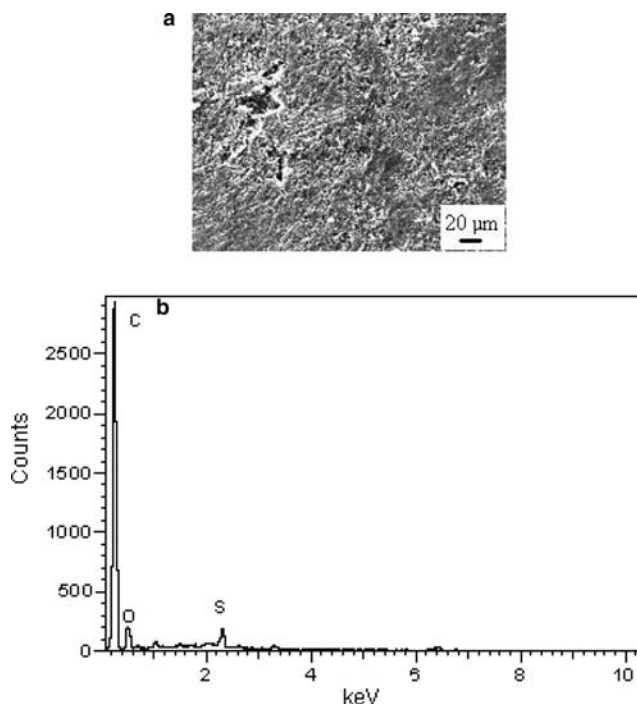


Fig. 2. SEM image of poly(allyl ether of the *p*-benzenesulphonic acid) (a) and corresponding EDX analysis (b).

Ni^{2+} or Cu^{2+} ions), the reduction of the incorporated metallic ions is evident in the cathodic potential sweep (Figure 3(b, c)). As can be seen in Figure 3(b), cupric ion reduction starts at about 250 mV and, under the used conditions, the estimated amount of deposited copper is $5 \mu\text{g cm}^{-2}$. The presence of metal is further evidenced by the two typical oxidation waves [28] observed during the anodic potential scan (Figure 3(d)). For the modified polymer after ion exchange with Ni^{2+} , the increase in the cathodic current after 0 mV also indicates metallic ion reduction.

The modified electrode (ME) autocatalytic activity towards the electroless metal deposition (EMD) from a sodium hypophosphite containing solution was evaluated by open circuit potential evolution when the electrodes were immersed in the nickel electroless bath. As can be seen in Figure 4, the open circuit potential of the pristine polymer remains slightly positive showing its inability to promote the EMD. Furthermore, the usual procedure to induce the electroless deposition [26, 27, 29, 30] by applying short potential pulses, e.g. -800 mV for 10 s (curve a), is ineffective since the open circuit potential value where the hypophosphite adsorption and hydrogen bond cleavage should occur (about -600 mV under the conditions used [26, 30]) is not observed, even enlarging the pulse width to 20 s (curve b) or to 40 s (curve c). Instead, the electrode open circuit potential is shifted from its initial value denoting the alteration due, very likely, to Ni electrodeposition. The same type of behaviour was evidenced, at room temperature, by the polymer bearing metallic copper modified electrode (Figure 5(a)) whereas condi-

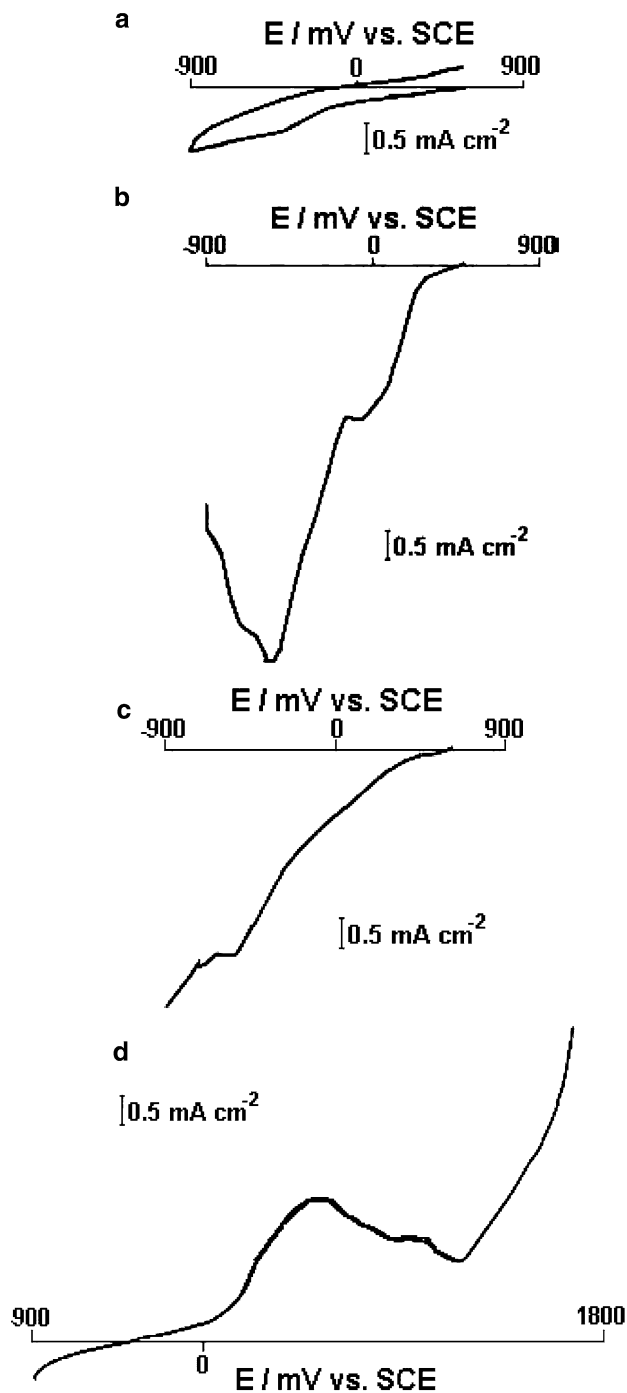


Fig. 3. Voltammograms of the pristine polymer (a) and of the modified polymer after ion exchange with Cu^{2+} ions (b), Ni^{2+} ions (c) and the polymer bearing dispersed metallic copper ($5 \mu\text{g cm}^{-2}$) (d) in $\text{KCl } 0.5 \text{ mol l}^{-1}$ solutions; potential scan rate: 10 mV s^{-1} .

tions for the occurrence of nickel-phosphorous autocatalytic deposition were achieved when the system temperature was raised to $60 \text{ }^\circ\text{C}$, as illustrated by the data in Figure 5(b).

As expected, for the polymer containing metallic nickel modified electrodes a similar procedure is required, e.g., potential pulse -800 mV height and 3 s width, electroless solution at $50 \text{ }^\circ\text{C}$, to observe the electroless deposition of Ni-P.

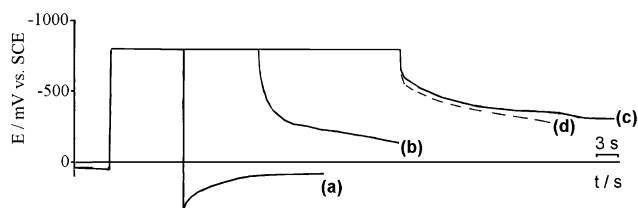


Fig. 4. Open-circuit potential evolution of the polymer modified electrode after being subjected to potential pulses (-800 mV height, 10 s (a), 20 s (b) and 40 s (c) width) in the nickel electroless solution at room temperature and 40 s at 60 °C (d).

Since the pristine polymer remains non-catalytic for EMD, even when the temperature is increased, (Figure 4(d)), the above mentioned conditions could be used to enlarge the size of the metal particles incorporated in the polymer whilst maintaining good dispersion. Thus, Ni-P deposition was carried out for 30 min in order to obtain new modified electrodes: polymer/Cu (or Ni)/Ni-P. The surface morphology was analysed by SEM as shown in Figure 6 which also allowed estimation of the average size of the dispersed crystallites: $1 \mu\text{m}$. The presence of Ni-P was further confirmed by the voltammetric responses of the MEs in KOH solution, where one finds the known features of Ni-P oxidation and reduction [27]. It is also clear that there is no significant influence of inducing the electroless nickel process in the alloy deposition behaviour.

The improvement in the electrocatalytic activity towards the hydrogen evolution reaction (HER) achieved, can be evaluated by analysis of the current responses of the MEs within the potential domain where proton reduction takes place, as shown in Figure 7.

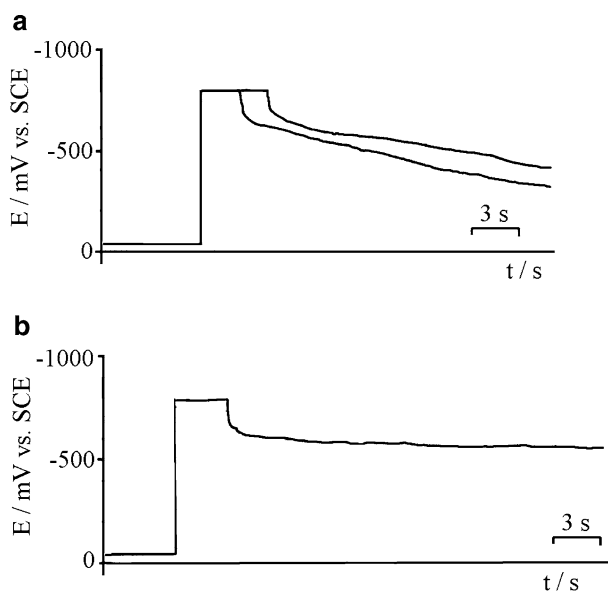


Fig. 5. Open-circuit potential evolution of Polymer/Cu after being subjected to potential pulses in the nickel electroless solution at room temperature (a) and at 60 °C (b).

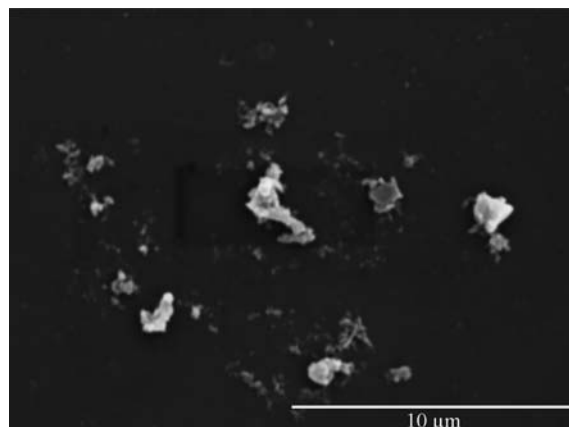


Fig. 6. SEM image of Poly-(allylbenzene *p*-sulphonic acid) bearing dispersed Ni-P particles.

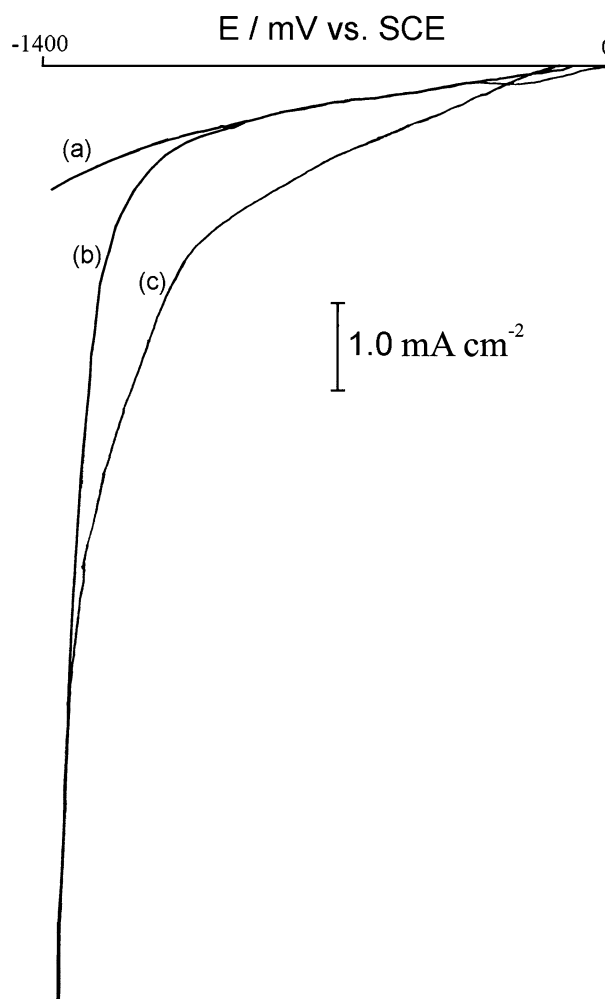


Fig. 7. Hydrogen generation obtained with prepared ME: polymer (a) polymer/Ni (b) and polymer/ Cu/ Ni-P (c) in NaOH 1 mol l^{-1} ; potential scan rate: 1 mV s^{-1} .

Although the enlargement in the active area for the reduction of H^+ must be taken into account in analyzing the significant increase in the current observed for the modified electrode incorporating Ni-P, the data

support interest in this type of ME for electrocatalysis purposes, namely for hydrogenations. Indeed, the marked deviations in the slopes which can be defined in the different potential domains, namely the difference current observed in -0.2 and -1.1 V vs. SCE, strongly suggests that the formation/adsorption of H, occurring at relatively lower potential values, is easier at the alloy surface than at Ni particles. Moreover atomic hydrogen recombination and subsequent H_2 evolution occurs later when the modified electrode with dispersed alloy particles is used. Thus, atomic hydrogen adsorption at the electrode surface, a requirement for electrohydrogenation reactions, seems to be favoured by the presence of the Ni–P crystallites.

4. Conclusions

Homogeneous polymer coating of a glassy carbon electrode has been obtained by the electropolymerization of the allyl ether of the *p*-benzenesulphonic acid. Ion exchange properties of the polymer permit the inclusion of metallic ions which, in turn, were easily reduced. One of the advantages of this modified electrode is that the metal is well dispersed over the whole area of the electrode.

To change the nature and enlarge the amount of the incorporated metal, the Ni–P electroless deposition method was successfully used. This provides an alternative route for the preparation of new modified electrodes.

The modified electrode containing nickel or copper electrolessly coated with Ni–P showed promising electrocatalytic activity towards proton reduction. Using this methodology we expect to produce long-life cathodes for the hydrogenation of organic molecules.

Acknowledgements

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