

NANOCATALYSTS IMPREGNATED POLYTHIOPHENE ELECTRODES FOR THE ELECTROOXIDATION OF FORMIC ACID

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Abstract

Conductive and porous polythiophene (PTh) films, which are used as host matrices for Pt and Pt/Pd nanoparticles, are synthesized electrochemically. PTh films containing nanometre-sized Pt and Pt/Pd bimetallic particles are electro synthesized on an indium tin oxide (ITO) glass plate by voltammetric cycling between -0.1 to $+1V$ (Vs Ag/AgCl / 2M NaCl). The ensuing PTh electrode, modified with nanoparticles, was probed for its catalytic activity towards the electrooxidation of formic acid, an industrially important material. The modified electrode exhibits significant electrocatalytic activity for oxidation of formic acid and this may be attributed to (a) the uniform dispersion of nanoparticles in the PTh film and (b) the synergistic effect of the highly dispersed metal particles and the PTh film reducing the electrode poisoning by adsorbed CO species. Monometallic (Pt) and bimetallic (Pt/Pd) nanoparticles are found to be uniformly dispersed in PTh matrixes as confirmed from analytical data using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Energy dispersive X-ray analysis (EDAX) is used to characterize the composition of metal present in the nanoparticles modified electrodes.

Keywords: Electrocatalytic oxidation; Polythiophene; Platinum and Pt/Pd, nanoparticles; Formic acid; Fuel cells.

1. Introduction

Conducting polymers (CPs) have attracted considerable attention and several publications related to its general features have been reported [1-4]. Some potential

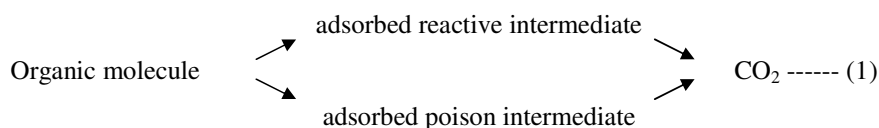
applications for CPs have already been found, including electrochromic and electronic devices, electrical energy storage in rechargeable batteries [5], and electrochemical sensors [6,7] *etc.*. Since the polymeric systems do not have any intrinsic electrocatalytic activity, they have been used as host matrixes for different chemical species *viz.* metal particles [6-12], complex ions [12,14], and enzymes [15] through which the polymeric systems acquire catalytic functionality. Among the various CPs, polypyrrole (Ppy), polyaniline (PANI) and polythiophene (PTh) have certain advantages over other candidates, such as simplicity and rapidity of preparation of the polymer by chemical and electrochemical methods, chemical durability against aerial oxidation, possibility of being formed in aqueous electrolytic solutions, and stability in such media [16]. CPs also fulfil a vital role in electrochemistry as supporting materials for electrocatalysts for a number of reactions involved in the process of energy conversion in fuel cells. Most catalytic reactions of this type are controlled by an adsorption process whose rate strongly depends on the nature and structure of the catalytic centres. Electrodes formed from PANI, Ppy, or PTh, following modification by electrodeposition of Pt or Pd particles, have been proposed for the oxidation of small molecules such as hydrogen, formic acid, formaldehyde and methanol [6-12].

The rate of electrocatalytic reactions using classical electrocatalysts is often disfavoured and needs to be modified. The improvements and modifications are mainly required for two reasons (i) the need to reduce reliance upon the use of precious metals and (ii) the formulation of new electrocatalysts with more than one metal. The prime objective has implications for technologies involving applications such as generators for electric vehicles and for electronic devices. The amount of precious metals (*e.g.* platinum) influences not only the formulation of bimetallic electrocatalysts, but enhances the catalytic activity as well as eliminating the difficulties encountered with the monometallic catalyst system used for electrochemical reactions. Reductions in the consumption of catalyst can be achieved by the use of smaller catalyst particles of greater surface area as this leads to a more efficient use of the catalysts; only metallic atoms present on the surface can be involved in the different adsorption steps which are always a part of the electrocatalytic process.

A good electrode material has to have good mechanical, chemical and electrochemical stability especially in contact with aggressive media such as strong acids or bases [21]. A possibility for such applications may be the use of a CP as a host matrix for electrocatalytic properties, provided that the polymer is stable under different experimental conditions, is porous, conductive and has large effective area. Among the various conducting polymer substrates, PTh is one of the most attractive polymers due to its stability and processability at ambient conditions, making it potentially an ideal matrix, which is well suitable for such electrocatalytic reactions. Furthermore, there is much interest in this polymer, due to its range of electrochemical activity and the control that can be exerted on its morphology and electrical properties, either by controlling the electrosynthesis conditions [17] or by structural modifications [18-20]. The electroformation of a polymer with an open morphology and adequate conductivity allows the incorporation of metal particles and easy accessibility to the substrate, and this can be achieved using PTh. A number of relevant studies have been conducted in this area. Schrebler *et al.* prepared PTh modified by electrodepositing Pt and Pt supported lead for the electrooxidation of formic acid and has found that the activity of the electrode was maintained over 36 h without any variation [22]. Swathirajan and Mikhail have probed methanol oxidation using Pt-Sn catalysts dispersed poly(3-methyl)thiophene electrodes[23], while Yassar *et al.* have electrodeposited Pd particles of different sizes in PTh and found that the activity of Pd/PTh electrode for oxygen reduction varies with particle size [24]. Balaraman *et al.* have also studied the use of platinum dispersed PTh films for the electroreduction of oxygen [25].

Fuel cells constitute one of the most promising sources of alternative energy by providing high energy output and in theory emitting no harmful by products. The oxidation of small organic molecules such as formaldehyde, methanol and formic acid on Pt and other noble metal electrodes has been the subject to a number of investigations in the past few decades [26], as these compounds offer the potential as fuel for the new devices. The oxidation reactions are generally complex and involve the formation of reactive intermediates which may become adsorbed on the electrode's surface and can serve to poison the catalyst. This 'self-poisoning effect' is a serious problem in the electrocatalytic oxidation of organic fuels on noble metal electrodes. Formic acid, which

is known to be an intermediate product in the electrooxidation of methanol, is a potential liquid fuel for the direct formic acid fuel cell (DFAFC) application due to its high theoretical open circuit potential [27]. Recently, DFAFCs have been shown to possess excellent characteristics for powering portable electronic devices and microelectromechanical systems (MEMS) [28], as formic acid displays a crossover flux through a nafion membrane that is some two orders of magnitude smaller than methanol; allowing the use of highly concentrated fuel solutions in DFAFCs [29,30]. Formic acid also has a higher theoretical electromotive force (EMF) in a fuel cell, as calculated from the Gibbs free energy, than either hydrogen or direct methanol fuel cells (DMFCs). The reaction mechanism, commonly known in the literature [26,31-33] as the ‘dual path’ reaction mechanism, can be presented in the general form given below:



Nanotechnology imparts a well developed surface chemistry [34,35], a controllable geometry [36], rigidity, chemical stability [37] and offers an excellent tool to evaluate the contribution of conformational entropy in polyvalent binding, as elucidated by Whitesides *et al.*, [38,39]. The improvement of catalysis in the nanoscale domain is mainly necessary for economic reasons: the metals in the form of nanoparticles are expected to play an important role in electrocatalysis reactions. With this in mind, the present work was undertaken to investigate the catalytic activity of an electrochemically-synthesized PTh film modified, with mono- and bi-metallic nanoparticles, towards the electro oxidation of formic acid. Three electrodes were fabricated *viz.*, ITO modified with PTh, PTh-Pt(0), PTh-Pt/Pd(0) and the surface morphology of these were characterized using SEM and AFM, while the presence of metallic particles was confirmed from EDAX analysis. The modified electrodes were subsequently used for the investigation of formic acid oxidation.

2. Experimental

2.1 Materials

Hexachloroplatinic acid (99.9%), Palladium (99%), Thiophene (99%) and *n*-tetrabutyl ammonium tetrafluoroborate (99%) were obtained from Aldrich, while trisodium citrate (99%) was received from Merck. All solvents were distilled prior to use and the solutions were prepared with Millipore water.

2.2 Equipment and Methods

All electrochemical measurements were carried out under nitrogen atmosphere at room temperature. Electropolymerisation of thiophene was studied using an ITO (1cm²) glass plate as the working electrode in 0.3M *n*-tetrabutyl ammonium tetrafluoroborate, (TBABF₄) as the electrolyte. A Ag/AgCl (3M NaCl) and Pt electrode served as the reference electrode and the counter electrode respectively. All potentials in this work are presented in the Ag/AgCl scale. The electrochemical measurements were carried out using CHI600B instrument and surface analysis (SEM) was carried out using an LEO-stereoscan 440 microscope. The presence of metal nanoparticles in the polymer matrix was probed using energy dispersive X-ray analysis with a INCA200 instrument. A NANOSCOPE IIIa, Digital AFM instrument, with a 90µm scan range, was used to view the surface morphology of the polymer electrodes (images were obtained by scanning at a rate of 1.5 Hz using contact mode technique) where bright colours indicate the higher regions while the darker regions show the lower regions of the samples. UV-Visible spectroscopy was performed on a Perkin-Elmer LAMBDA 25 to study the optical properties of metal nanoparticles and their sizes were confirmed using TEM (TECHNIE 10) with an accelerating voltage of 80 kV.

2.3 Preparation of colloidal reagents

The Pt colloid was prepared using a standard protocol method [40]: H₂PtCl₆ (4 cm³ of 5% w/w aqueous solution) was added to freshly distilled water (340 cm³) and heated to 80 °C with efficient stirring. Sodium citrate (60 cm³ of a 1% w/w aqueous solution) was added and heating was continued for about 4 hours. The resultant Pt colloid (which was stable for months) was transparent, having a weak absorption tail stretching across the UV region, but no absorption at $\lambda > 200$ nm. Colloidal suspensions of Pt/Pd bimetallic nanoparticles were prepared using a modified procedure based on the

reports described earlier [41]]. PdCl_2 ($9.3 \times 10^{-4} \text{ M}$, 50 cm^3) formed from 0.016 g in 1N HCl (2 cm^3) and made up to 100 cm^3) and tri-sodium citrate ($3.4 \times 10^{-2} \text{ M}$, 100 cm^3) were placed in a round bottom flask and stirred for 15 minutes. To the vessel were added chloroplatinic acid ($1.4 \times 10^{-3} \text{ M}$, 212.5 cm^3) and tri-sodium citrate ($3.4 \times 10^{-2} \text{ M}$, 37.5 cm^3), which was further diluted to 100 cm^3 and refluxed to $90 \text{ }^\circ\text{C}$ under stirring for six hours until a brown colour observed, which was then filtered and stored for further use.

3. Results and Discussion

3.1 Mono and Bimetallic Nanoparticles

The UV-visible spectra for the platinum (Pt) and Pt/Pd (0) nanoparticles are shown in Figures 1a and 1b. Initially, absorptions at 260 and 425 nm were observed, which can be attributed to ligand to metal charge transfer transitions of $[\text{PtCl}_6]^{2-}$ and $[\text{PdCl}_4]^{2-}$ ions. The absorption peaks due to platinum and palladium ions completely disappear after the solutions are refluxed, which indicates that the complete reduction of precursor metal ions has occurred. This is also further confirmed using TEM analysis [Figures 1c and 1d], which shows an average size of *ca.* 5-6 and *ca.* 9-10 nm for monometallic and bimetallic nanoparticles respectively.

3.2 Fabrication of Polythiophene Films on ITO Electrodes

For the fabrication of PTh films, the working electrodes were typically cycled between +1.4 V and -0.2 V *versus* Ag/AgCl at 100 mV/s in order to effect polymerization. Oxidative electrochemical polymerization of thiophene on ITO has been accomplished from monomer solution containing electrolyte in acetonitrile (0.3 M *n*-tetrabutyl ammonium tetrafluoroborate and 0.1MHB₄) for continuous 10 cycles. Representative data for the electropolymerisation of thiophene containing 0.3M TBABF₄ on ITO are shown in Figure 2a. It was observed that the redox current increases with increasing cycles and a current loop is formed, indicating the nucleation and growth process of PTh on ITO electrodes. The increase in the redox currents with the appearance of an adherent polymeric film of metallic red colour on the electrode indicates monomer oxidation and corresponds to the main process for the film growth.

Once polymerization had been accomplished, the PTh coated electrode was removed from the cell, rinsed copiously with acetone and deionized water. The electrode was then characterized by cyclic voltammetry in the same range at a scan rate of 100 mV/s in an aqueous monomer free 0.3M TBABF₄ solution. The voltammogram for the PTh films exhibits fairly well defined oxidation and reduction peaks (Figure 3a), while the presence of acid such as HBF₄ stabilizes the electrochemically produced cation radicals.

3.3 Pt & Pt/Pd(0) incorporated Polythiophene Electrodes

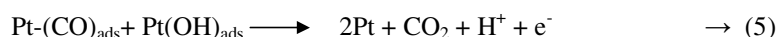
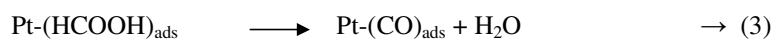
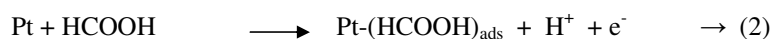
PTh electrodes containing dispersed nanoparticles were fabricated by electrodepositing the latter during the course of electropolymerization. The electrooxidation of the PTh electrode modified in this manner shows a high electroactive response that might be due to the oxidation of thiophene moiety on the nanoparticles' surfaces. A further increase in redox currents is observed in the case of the PTh electrodes modified with bimetallic nanoparticles, since the catalytic activity was found to be greater in the case of bimetallic nanoparticles rather than monometallic nanoparticles [25-27]. Thus, the nanoparticulate Pt/Pd(0) catalyst effectively promotes the rate of polymerization of thiophene as observed from the higher redox current. The corresponding data obtained in aqueous electrolyte solution for PTh electrodes modified with both monometallic and bimetallic nanoparticles are shown in Figures 2b and 2c respectively.

3.4 Nanoparticles modified Electrodes for oxidation of Formic acid

Figure 3b presents the voltammetric profile for formic acid oxidation on a PTh modified ITO electrode (ITO/PTh): no oxidation current was observed for formic acid oxidation. Prior to studying the effects of Pt/Pd bimetallic nanoparticles on formic acid oxidation, it is interesting to probe the effect of Pt(0) modified PTh electrodes towards the electrooxidation of formic acid. Figure 5a presents the voltammetric profile for formic acid oxidation on Pt(0) modified PTh films and the cyclic voltammetric response for the PTh electrodes modified with nanoparticles in the absence of formic acid is shown for comparison (Figure 4). With the addition of formic acid, the profile at the

ITO/PTh/Pt(0) electrode is well established with the onset potential on anodic sweep at 0.38V. It is well documented that the electrooxidation of formic acid (HCOOH) on Pt results in the formation of the poisonous (CO)_{ads} species as the overwhelmingly predominant stable intermediate on the electrode surface, since Pt is highly susceptible to (CO)_{ads} formation (step 3), and yields CO₂ as the final product.. Formic acid oxidation on the ITO/PTh/Pt(0) electrode is characterized by the presence of a broad anodic current peak from 0.38V to 1.20V. Traditional Pt-based catalysts are thought to follow a dual pathway mechanism, which involves the formation and adsorption of poison intermediate on the electrode surface.

Dual Pathway Mechanism

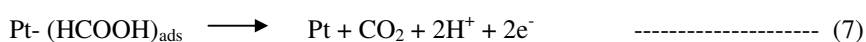


The only way to remove the poisonous (CO)_{ads} intermediate is to oxidize it by reacting with OH_{ads} formed by the dissociation of water molecules on Pt surface (steps 4 and 5). A high potential of 0.6V is needed for water activation process on Pt electrode surface as CO becomes oxidized only at higher potentials. Because of this disadvantage, the electrode poison “CO” remains on the electrode surface for a longer time occupying active catalyst sites of Pt thereby lowering the overall activity towards formic acid oxidation.

Formic acid oxidation on the ITO/PTh-Pt/Pd (0) electrode was characterized by the presence of broad current peak from 0.32V to 7.2V. The addition of a second metallic nanoparticle species to the system has a remarkable effect on formic acid oxidation. For instance, when bimetallic Pt/Pd nanoparticles were incorporated into PTh electrodes, a higher and enhanced oxidation rate towards the electrooxidation of HCOOH was noted in the cyclic voltammograms (Figure 5b), due to the fact that Pd can increase the rate of formic acid oxidation *via* a direct CO₂ pathway at a lower potential and Pt is active for CO_{ads} oxidation at a higher potential [26]. This suggests that the reaction

mechanism now proceeds *via* a direct pathway where HCOOH is oxidized directly to CO₂ without any poison intermediate.

Direct Pathway



The absence of “CO” poisoning means that the activity of Pd catalysts can be much higher than that of using platinum alone. An alternative explanation for the diminution of CO or the dramatic drop of affinity of CO for bimetallic systems may be due to a consequence of its structure. “CO” becomes bound between the 3-D lattice sites of Pt. In the case of Pt-Pd(0) system, the Pt-Pt distance increases and, owing to this expansion, the poisonous intermediate species cannot bind in the three fold or hollow site configurations of Pt, because each CO moiety requires atleast three neighbouring Pt sites to become adsorbed. With the decrease in Pt-Pt interatomic distance, the CO becomes reduced directly to CO₂ without adsorption and hence the rate of electrode poisoning is reduced, thus enhancing the rate of oxidation of oleic acid and consequently the overall formic acid oxidation is enhanced. Thus, the Pd additive may act as promoter which modifies the Pt assemble by a selective site blocking and impedes “CO” chemisorption. As evidenced from Table 1, the onset potential for formic acid oxidation shifts to a more negative potential in the case of nanoparticles dispersed polymer films that were found to be applicable in the fuel cell applications.

3.5 Surface Features of Nanoparticles Incorporated Polythiophene Films

The morphologies of the PTh films modified with nanoparticles were studied using scanning electron microscopy [Figures 6a and 6b] and the corresponding EDAX images for the modified PTh electrodes are shown in Figures 6c and 6d), which indicate the presence of Pt and Pd in the system. Polymer morphologies were probed using contact mode atomic force microscopy (AFM) and AFM images for the modified films show a homogeneous coverage of metal nanoparticles. The platinum and Pt/Pd nanoparticles are clearly seen embedded in the PTh matrix with an average size of *ca.* 6 nm and *ca.* 10 nm respectively [Figure 7(a &b)]. An AFM image for the unmodified PTh film is given for comparison [Figure 7a]. The polymer film gains in both height and width during deposition of metal nanoparticles on the PTh electrode.

4. Conclusion

Polythiophene (PTh), a conducting polymer matrix, is found to be an ideal material for the incorporation of monometallic (Pt) and bimetallic (Pt/Pd) nanoparticles. Modified PTh films containing nanoparticles show better electrocatalytic activity than the unmodified polymers towards formic acid oxidation and this may be due to the stabilization of nanoparticles in the polymeric matrix. Furthermore, it has been shown that the electrocatalytic oxidation of formic acid was more effective in the case of the bimetallic system than the corresponding PTh film containing monometallic nanoparticles. This is due to the rate of decrease of electrode poisoning by CO species resulting from dehydrogenation mechanism. PTh films incorporating monometallic (Pt) or bimetallic (Pt/Pd) nanoparticles show electrooxidation that is superior to thin PTh film on ITO glass plate. The dispersion of metallic nanoparticles was confirmed from EDAX techniques and the enhanced electrocatalytic activity may be due to the uniform dispersion of nanoparticles in PTh films as evidenced by SEM and AFM analysis.

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Table 1: Comparison of Formic acid Oxidation Activity on Pt and Pt/Pd(0) Incorporated Polymer Matrixes

Electrode	Onset potential for HCOOH oxidation Vs Ag/AgCl in Volts	Oxidation Current ($1a \times 10^{-4} A.cm^{-2}$)
ITO/PTh-Pt(0)	0.3854	0.9105
ITO/PTh-Pt/Pd(0)	0.3288	1.9497

Figure Captions

Figure 1: UV-Visible Spectrum of citrate stabilized (a) platinum (b) Pt/Pd bimetallic nanoparticles and transmission electron microscopic images of citrate stabilized (c) Platinum (d) Pt/Pd bimetallic nanoparticles

Figure 2a: Cyclic voltammograms during the electropolymerization of thiophene in 0.3M thiophene + 0.3M TBABF₄/ 0.1M HBF₄ on ITO glass plate at 100mVs⁻¹

Figure 2b: Cyclic voltammograms during the electropolymerization of thiophene in 0.3M thiophene + 0.3M TBABF₄/ 0.1M HBF₄ + Pt nanoparticles on ITO glass plate at 100mVs⁻¹.

Figure 2c: Cyclic voltammograms during the electropolymerization of thiophene in 0.3M thiophene + 0.3M TBABF₄/ 0.1M HBF₄ + Pt/Pd bimetallic nanoparticles on ITO glass plate at 100mVs⁻¹.

Figure 3: Cyclic voltammograms of unmodified PTh electrodes in (a) 0.5M H₂SO₄ and (b) 0.5M H₂SO₄ + 0.5M HCOOH.

Figure 4: Cyclic voltammograms of (a) Pt(0) and (b) Pt/Pd(0) modified PTh electrodes in 0.5M H₂SO₄.

Figure 5a: Cyclic voltammograms of Pt(0) modified PTh electrodes in 0.5M H₂SO₄ + 0.5 M HCOOH.

Figure 5b: Cyclic voltammograms of Pt/Pd(0) modified PTh electrodes in 0.5M H₂SO₄ + 0.5 M HCOOH.

Figure 6: Scanning electron microscopic images of (a) Pt(0) and (b) Pt/Pd(0) modified PTh electrodes and the corresponding EDAX spectrum of (c) Pt(0) and (d) Pt/Pd(0) modified PTh electrodes.

Figure 7a: Contact mode atomic force micrographic images of surface morphology of PTh films fabricated electrochemically on ITO electrodes.

Figure 7b: Contact mode atomic force micrographic images of surface morphology of Pt(0) impregnated PTh films fabricated electrochemically on ITO electrodes.

Figure 7c: Contact mode atomic force micrographic images of surface morphology of Pt/Pd(0) impregnated PTh films fabricated electrochemically on ITO electrodes.