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# Spatially electrodeposited platinum in polyaniline doped with poly(styrene sulfonic acid) for methanol oxidation

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**Abstract**

Polyaniline (PANI) can be doped with poly(styrene sulfonic acid) (PSS) via doping–dedoping–redoping process. The specific characteristics of PANI doped with PSS (PANI-PSS) were checked by UV–vis spectroscopy, cyclic voltammetry, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). PANI-PSS was found to have spatial structure with minimum degradation products. Platinum can be potentiostatically deposited in a spatial layer of the PANI-PSS as evidenced by electron dispersive element analysis (EDS) and Auger electron spectroscopy (AES). The electrochemical measurements demonstrated that PANI-PSS-Pt exhibited a much higher electrocatalytic activity for methanol oxidation than PANI-Pt.

*Keywords:* Polyaniline; Poly(styrene sulfonic acid); Pt particles; AES; Methanol oxidation

## 1. Introduction

Fuel cells are attractive sources of electrical power since they realize the direct conversion of chemical to electrical energy. One promising system is the direct methanol fuel cell (DMFC) [1–3]. Unfortunately, the expensive catalytic materials, such as platinum, and relatively low electrocatalytic efficiency for electrochemical reactions of the fuel are drawbacks. To date, efforts have focused on the development if techniques of produce Pt catalysts with a high surface area [4,5]. It has been proved that the support materials in electrocatalysts play an important role to the electrochemical performance [6]. Though improvement has been made in the catalytic activity and stability of the electrocatalyst by effectively dispersing Pt particles onto the electrically conducting supports, many efforts are still continuing.

In fact, the choice of a suitable supporting material is an important factor that may affect the performance of supported electrocatalysts owing to interactions and surface reactivity [7,8]. Pt supports can be separated as two categories. One is carbon supported, including traditional carbon support materials (XC-72), graphite nanofibers (GNFs) [9,10], carbon nanotubes [11,12] and mesocarbon microbeads (MCMB) [13,14]. However, the limitation of carbon in terms of performance is that the proton does not easily contact with catalyst. The other group is the conducting polymers, such as polyaniline (PANI) [15,16], and polypyrrole (PPY) [17,18]. Conducting polymer-stabilized metal nanoparticles or nanoclusters often act as an excellent homogeneous catalyst and show interesting properties [19–21]. They not only provide access to a large number of catalytic sites but also offer the possibility of synergetic effect between the polymer matrix and the metal nanoparticles. Another advantage of the polymer matrix might provide an efficient pathway for electron and preferably for protonic species for DMFC application.

Recently, new attempts have been focused on the modification of conducing supports with increasing Pt utilization and enhancing the electrocatalytic properties toward methanol oxidation. Peng and co-workers [8] reported that highly dispersed Pt nanoparticles supported in sulfonated carbon nanotubes (Pt/sulfonated-CNTs) with high electrocatalytic activity for DMFC. Huguenin and co-workers [22] showed a biodegradable chitosan and poly(vinyl sulfonic acid) (PVS) in layer-by-layer (LB) film serving as templates to yield metallic platinum. Bensebaa et al. [23] synthesized polypyrrole di(2-ethylhexyl) sulfosuccinate (PPYDEHS) stabilized PtRu catalysts for DMFC. Dong and co-workers [24] synthesized a stable

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electroactive conducting copolymer film of poly(aniline-*co-o*-aminobenzensulfonic acid) three-dimensional tubal networks on indium oxide glass (ITO) and the cytochrome *c* was immobilized on the matrix by the electrostatic interactions. The composite film showed direct electron transfer between protein and electrode surface with high electron transfer rate of 12.9 s.

Modification of electrode surfaces provides an attractive way of confining catalytic species to the effective spatial region and combines the experimental advantages of heterogeneous catalysts with the benefits of a three-dimensional distribution of active centers typically characteristic of homogeneous catalysts. Hence, the introduced sulfonic acid groups ($SO_3H$) might affect the properties of supporting materials and performance for its application in DMFC. This motivated us to investigate the feasibility of incorporating $SO_3H$ groups into conducting polymer as support for Pt. We employed a simple "doping–dedoping–redoping" method to introduce the $SO_3H$ groups (poly(styrene sulfonic acid), PSS) into PANI in the present study. PANI-PSS composite behaves as a good probe for the deposition Pt particles and increased the density of the active sites in the polymer film. The well-dispersed Pt particles inside such conducting composite support can lead to good Pt utilization and an improvement of the catalytic activity for methanol oxidation. In the work, we describe the synthesis and characterization of PANI-PSS composite film incorporated PSS into PANI matrix via doping–dedoping–redoping method. PANI-PSS composite film embedded Pt particles by electrodeposition technique shows higher electrocatalytic properties and stability for methanol oxidation than that of Pt deposited in PANI without PSS incorporated and is more promising for application in electrocatalyst.

## 2. Experimental

### *2.1. Preparation of PANI-PSS and PANI-PSS-Pt composite films*

PANI film was prepared by the electrochemical polymerization (at a constant potential of 0.8 V) of aniline (Merck) in 0.5 M $H_2SO_4$ aqueous solution as described elsewhere [25]. Emeraldine base form (EB) of PANI was obtained by treating the PANI film in ammonium hydroxide (Aldrich), and then the EB film was redoped by poly(styrene sulfonic acid) (PSS) ($M_w = 75{,}000$, Aldrich). PANI doped with PSS is denoted as PANI-PSS.

Pt particles were deposited onto the ITO/PANI-PSS from a solution of $H_2PtCl_6$. For a comparative purpose, Pt particles were deposited onto PANI matrix under otherwise similar conditions to the deposition of Pt particles onto ITO/PANI-PSS. Typically, a plating solution consisting of 5 mM $H_2PtCl_6 \cdot 6H_2O$, 0.01 M HCl, and 0.1 M KCl was used. The reduction of Pt particles was accomplished at −0.2 V for the charge passed of 0.1 C. After Pt particles incorporation, the electrodes were rinsed with double distilled water for 5 min then dried at 100 °C for 3 min. Pt electrodeposited in PANI and PANI-PSS denoted as PANI-Pt and PANI-PSS-Pt.

### *2.2. Physical and electrochemical characterizations*

The surface morphologies of PANI-PSS and PANI-PSS-Pt were observed with a scanning electron microscopy (Philips X1-40 FEG). The X-ray photoelectron spectroscopy (XPS) measurement was performed with ESCA210 and MICROLAB 310 D (VG Scientific Ltd., U.K.) spectrometers. XPS spectra were recorded with Mg Kα($h\nu = 1256.6$ eV) irradiation as photon source with a primary tension of 12 kV and an emission center of 20 mA. The pressure of the analysis chamber scans was kept approximately at $10^{-10}$ mbar during the scan. Auger electron spectroscopy (AES) depth profiles were performed with Microlab 310 D (VG Scientific Ltd.) spectrometer at an emission current of 0.1 and 8 mA with gun tension of 10 (electron) and 3 kV (ion), respectively.

Electrochemical characterizations of composite electrodes were performed using PGSTAT20 electrochemical analyzer, AUTOLAB Electrochemical Instrument (The Netherlands). All experiments were carried out in a three-component cell. An Ag/AgCl electrode (in 3 M KCl), Pt wire and composite electrode (1 $cm^2$ area) were used as reference, counter and working electrodes, respectively. A Luggin capillary, whose tip was set at a distance of 1–2 mm from the surface of the working electrode, was used to minimize errors due to *iR* drop in the electrolytes.

### *2.3. Methanol electrooxidation on PANI-PSS-Pt composite electrode*

Methanol electrooxidation on PANI-Pt and PANI-PSS-Pt was examined by CV at 10 mV $s^{-1}$ ranged from −0.2 to 1.0 V and potential–time curves at 0.02 mA $cm^{-2}$ in 0.1 M $CH_3OH$ + 0.5 M $H_2SO_4$ solution. All the electrochemical experiments were carried out at room temperature.

## 3. Results and discussion

### *3.1. Electrochemical characterization of PANI and PANI-PSS*

The incorporation of PSS into PANI has been achieved by "doping–dedoping–redoping" process, being evidenced by UV–vis spectroscopy. Fig. 1 shows UV–vis spectra for PANI doped form (electrochemical polymerization of PANI in $H_2SO_4$ medium), dedoped form and redoped form with PSS. The doped form of PANI (doped with $H_2SO_4$, curve a) possesses three peaks at ca. 356, 434 and 780 nm (free carrier tail). These peaks correspond to electron transition from valance band to polaronic band characteristic of the doped emeraldine oxidation state of PANI [25]. Dipping the emeraldine salt of PANI with ammonium hydroxide yields the dedoped form of PANI. The corresponding UV–vis spectrum (curve b) exhibits two absorption maxima at 326 and 598 nm, representing the $\pi$–$\pi^*$ transition and charge transfer excitation-like transition bands of the emeraldine base form of PANI [26]. After immersing the dedoped form of PANI in PSS solution, three characteristic peaks can be observed in UV–vis spectrum (curve c) and similar to that of the PANI doped form. It indicates that PANI can be doped with