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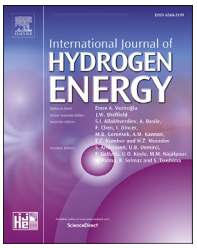

# Different interesting enhanced influence from polyaniline and poly(o-toluidine) on electrocatalytic activities of Pt on them toward electrooxidation of methanol

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ABSTRACT

Polyaniline (PANI) and poly(o-toluidine) (POT) with various film thickness were electropolymerized using potentiostatic method at the surface of GC electrode. The two conducting polymers were characterized by CV, *in situ* UV–vis spectroscopy and electrochemical impedance spectroscopy. Two composite catalysts (Pt/PANI/GC and Pt/POT/GC) with various film growth charge have been fabricated by the electro deposition of Pt on the PANI/GC and POT/GC at −0.1 V. then they were used for the electrooxidation of methanol in 0.5 M $H_2SO_4$ containing 1.0 M methanol. The properties of both the polymers change with the increase of film growth charge. As-formed composite catalysts were characterized by SEM and the electrochemical methods. The Pt nanoparticles deposited at −0.1 V exhibit thorns morphology and good dispersion on the POT with the film growth charge of 4.5 mC. The electrocatalytic activity for methanol oxidation of Pt/POT/GC is higher than Pt/PANI/GC for all the film charge, and they both exhibit the largest electrocatalytic activity at film charge of 4.5 mC. The present study shows that Pt/POT/GC would be a promising choice for methanol electrooxidation in comparison with Pt/PANI/GC.



## Introduction

Direct methanol fuel cells (DMFCs), as a kind of clean and renewable energy sources, have been attracted more and more attention in recent years, due to their high energy density, high electric efficiency, simple design, low operating temperature, convenient fuel storage and supply, and low pollutant emission which make them possible to be potential alternative energy sources for portable electronic devices [1–4]. However, three problems block the commercialization of DMFCs: (1) the poor oxidation kinetics of methanol [5] (2) the poisoning intermediates during the oxidation of methanol can be bound easily and strongly to Pt in acid media [6,7] (3) the higher loading of noble metal Pt catalysts. To date, much effort has been devoted to the development of catalysts by

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increasing catalytic activity, improving poisoning tolerance and reducing Pt loadings. One method is to change the supporting materials. Carbon, in particular Vulcan XC-72 [8,9], carbon nanotube [10,11], carbon blacks, graphene [12] and conducting polymers (CPs) [13–15] are common choices for supporting catalyst particles in fuel cells. In particular, the conducting polymers have been receiving special attention for the support of Pt nano particles because of their large surface area, high conductivity and pore structure.

As one of most important conducting polymers (CPs), polyaniline and its derivatives have been paid an increasing attention due to easy preparation, porous nanostructure, highly accessible surface area and high chemical stability [13–15] which are desirable to the support of electrocatalyst. In addition, the potential range of their electrochemical activity is also that of electro oxidation of methanol, so they have been investigated widely as a support for Pt nanoparticles in electro oxidation of methanol. Among numerous CPs, the studies of CPs as host material of Pt particles are centered on the polyaniline, poly(o-methoxyaniline), polypyrrole (PPy), polythiophene and their derivatives [2,16–20]. The effect of monomer concentration, film thickness of ploy (o-methoxyaniline) and electro-deposition method, deposition potential of Pt, $H_2PtCl_6$ concentration on the catalytic oxidation of methanol has been investigated in detail by Paulo Olivi et al. [16]. It was found that when the monomer concentration is 0.5 mol/L, the membrane charge is 77 mC/cm$^2$, the deposition potential of Pt was 0.3 V (RHE), the best electroactivity for electrooxidation of methanol was achieved. Lin Niu and Qiuhong Li et al. [21] have also studied the effect of film thickness of PANI, number of cycles, rate for Pt deposition and potential range on the oxidation of methanol. They found that the structure and film thickness of PANI have an important effect on the electroactivities of Pt nano particles. H. Razmi and E. Habibi et al. [22] deposited Pt nano particles into poly(o-phenylenediamine) (PoPD). Their results showed that PoPD significantly enhances the catalytic efficiency of platinum microparticles for oxidation of methanol in aqueous acid media, especially on a platinum substrate. From the above mentioned and the other concerned literatures, PANI and some its derivatives has been studied singly as support materials for dispersion of platinum particles. The properties of polyaniline and its derivatives, including conductivity, porosity, electrochemical activity and surface morphology, strongly depend on the type of monomers. Since their properties strongly affect the deposition of platinum nano particles on them and the electrooxidation of methanol on the composite of Pt and conducting polymers, the comparative studies on PANI and its derivatives as a support for Pt nano particles display the importance for understanding the nature of conducting polymers as a Pt support and their influence on electro oxidation of methanol.

To the best of our knowledge, there are rarely reports about directly comparative studies of polyaniline and their derivatives as support materials of Pt nano particles for electrooxidation of methanol. In this work, under the same experimental condition, poly(o-toluidine) (POT) and polyaniline (PANI) with various thickness were electropolymerized on glass carbon substrate (GC) using potentiostatic method, and then the platinum nano particles were electrodeposited at the surface of POT and PANI, respectively, for electrooxidation of methanol. These two prepared composites, Pt/POT/GC and Pt/PANI/GC, were used to investigate systematically the effect of the film thickness of POT and PANI on the electrodeposition of Pt at POT and PANI, and their performance of electrooxidation of methanol. The different experimental results arising from Pt/POT/GC and PT/PANI/GC were analyzed comparatively using cyclic voltammetry, AC impedance spectra, SEM and in stiu UV–vis spectroelectrochemical method.

## Experimental

### *Reagents*

Aniline (≥99.5%, shanghai shangsi fine chemicals Co.,Ltd., China), o-toluidine (≥99%), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) (Shanghai Shiyi Chemicals Reagent Co., Ltd., China), methanol, $H_2SO_4$ are analytical grade and used as received without any purification. Doubly distilled water is used throughout the experiments and all the solutions in the experiment are prepared by 0.5 M $H_2SO_4$ solution. All the electrochemical experiments were carried out in a conventional three-electrode cell using a CHI660D electrochemical workstation (Shanghai Chenhua Instrument Plant, China). A glass carbon (GC) disc electrode with a surface area of 0.0707 cm$^2$ was used as the working electrode. A platinum foil and an Ag/AgCl, KCl(sat) were used as the counter electrode and the reference electrode, respectively. All the experiments were performed at room temperature.

### *Apparatus*

The CHI660D electrochemical workstation purchased from Shanghai Chenhua Instrument Plant, China was used for preparing and estimating the electroactivities of composite electrodes, and EIS measurements for the conducting polymeres film modified electrodes. The scanning electrode microscopy (SEM) (S-4800, Hitachi High Technologies Corporation, Japan) was used to characterize the morphology of as-prepared electrodes. Agilent 8453 UV–visible spectrophotometer (Agilent Technologies, USA) was used for some measurement of *in situ* Spectroelectrochemistry.

### In situ *spectroelectrochemical observation of electro-homopolymerization of aniline and o-toluidine*

*In situ* UV–visible spectra in spectroelectrochemical studies of polymers were recorded using Agilent 8453 UV–visible spectrophotometer (Agilent Technologies, USA) by the time course mode. All *in-situ* UV–vis spectroelectrochemical experiments were conducted in a quartz cuvette with a path length of 1 cm. An indium tin oxide (ITO) glass plates was used as the working electrode and a Pt wire, an Ag/AgCl, KCl(sat) were used as the counter electrode and reference electrode, respectively. Before each experiment, the ITO coated glass electrode was cleaned using acetone followed by double distilled water. In this work, all potential values are referred to the reference electrode of Ag/AgCl, KCl(sat).

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