

# Increasing the three-phase boundary by a novel three-dimensional electrode

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## Abstract

A novel three-dimensional electrode has been fabricated using polypyrrole (Ppy) coated polystyrene spheres (PS) covered by a platinum catalyst. This new type of porous structured electrode allows liquid alcohol to penetrate the catalyst layer quite easily thereby reducing the liquid sealing effect. The chosen approach results in an increased active surface area for electrochemical reactions. Preliminary studies show an improved performance for methanol oxidation on a three-dimensional electrode compared to a conventionally prepared electrode with the same platinum loading.

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*Keywords:* Direct alcohol fuel cell; Three-dimensional electrode; Polystyrene spheres; Polypyrrole

## 1. Introduction

Direct alcohol fuel cells (DAFCs) have been the subject of considerable technological interest since the last decade mainly due to their promising applications as power sources for energy efficiency, non-polluting electric vehicles and portable electronics. Compared with PEMFC direct alcohol fuel cells have some advantages. DAFCs have a good theoretical energy density close to that of hydrocarbons and gasoline. The reversible energy efficiency of DAFCs is much better than that of a H<sub>2</sub>/O<sub>2</sub> fuel cell [1]. In addition, it is much safer in operation using liquid fuels [2–7] and more convenient in fuel storage and transportation.

In contrast to those promising thermodynamic data, the kinetics of alcohol oxidation is more difficult, leading to a high anodic overpotential [1]. Moreover, the crossover of liquid alcohol through the polymer electrolyte membrane into the cathodic compartment results in the decrease in the efficiency of the system [2]. One way to increase the anodic

activity is to look for more active electrocatalysts [8,9], or to increase the operating temperature [1]. New membranes [10,11] or modified ion exchange membranes [12,13] have been used for reducing the undesired crossover of liquid alcohol. We are concerned another important problem in DAFCs that affects the electrode kinetics [14], that is, the mass transportation of reactants and products in the catalyst layer. Gas diffusion electrodes (GDEs) are commonly used to increase the three-phase interface for electrode reactions of gaseous fuels [15–19]. However, the present GDE structure makes the liquid alcohol hardly get into the catalyst layer due to the sealing effect. The liquid sealing effect reduces the three-phase interface (or active surface area) and decreases the electrode kinetics. Some researchers made appropriate changes to the GDE by adding a range of suitable proprietary pore-forming additives into the catalyst layer to increase the pore volume [20,21].

In this paper, we report the fabrication of a novel three-dimensional electrode structure with large and small pores in micrometer scale instead of the conventional gas diffusion electrode in order to reduce the sealing effect in liquid fuel cells.

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## 2. Experimental

### 2.1. Preparation of three-dimensional electrode

The three-dimensional electrodes were prepared by following procedures: the synthesis of structure building blocks. Polystyrene spheres (PS) were used as structure building blocks in this study. Polystyrene spheres were widely used as the template to prepare metal oxide or metal nanomaterials [22–24]. The second step is the modification of PS spheres by conducting polymers such as polypyrrole (Ppy), polyaniline (Pani) and poly(3,4-ethylenedioxythio-phenylene) [25–27] on the surface to form continuous conducting shell since the electrocatalyst in fuel cells must be electrically conducting for performing the electrochemical reactions. Finally, the catalyst deposits on the surface of the conducting polymer layer.

Monodisperse PS with different diameters was obtained by emulsifier-free dispersion polymerization of styrene [28]. The polymerization of pre-treated styrene was conducted under nitrogen atmosphere with potassium persulphate as the initiator. The obtained latex (after 24 h polymerization) was dialysed against distilled water for 10 days using Visking dialysis tubing in order to remove unreacted monomer and potassium persulphate. Polypyrrole has been used to modify the non-conducting materials [29] and the conductivities of pure polypyrrole films were ranging from 10.28 to 127 S cm<sup>-1</sup> [30]. In order to make PS electrically conducting polypyrrole (Ppy) was coated on the surface of PS by in situ polymerization of pyrrole with FeCl<sub>3</sub> as the adulterant. The as-prepared polystyrene latex (solid content: 20 mg ml<sup>-1</sup>) mixed with FeCl<sub>3</sub> under magnetic stirring and a certain quantity of pyrrole was then added via syringe. The mixture was then stirred at room temperature for another 24 h prior to centrifugation at 4000 rpm. The polymerization time was optimized by checking the electrochemical activity of Ppy-coated PS electrode. Finally the conducting surface was modified by catalyst via an in situ reduction of precious metal salts [31]. The deposition of catalyst on the Ppy-coated PS surface was performed by the following procedure. H<sub>2</sub>PtCl<sub>6</sub> and Ppy-coated PS were mixed in an ethanol/water solvent (6/4, v/v) and the solution was then refluxed at 90 °C in a water bath. The mixture was boiled over night before separating the spheres from the mixture by centrifugation (4000 rpm).

A quantity of catalyst ink produced by mixing homemade catalyst and isopropanol was spread on Au substrate to form a three-dimensional electrode. Electrode prepared by 40% Pt/C E-Tek catalyst was used for the comparison.

### 2.2. Electrochemical and physical characterization

The electrochemical experiments were conducted on French VoltaLab 80 electrochemical workstation (Radiometer Analytical). A three-electrode cell with Pt foil as counter electrode and SCE as reference electrode was used for measurements in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 1 mol dm<sup>-3</sup>

methanol. All the tests were done at room temperature (about 25 °C).

The crystallinity of Pt deposited on Ppy-coated PSs was determined by X-ray diffraction (XRD). A X-ray diffractometer D/Max-III A (Rigaku Co., Japan, Cu K $\alpha$ 1 ( $\lambda = 1.54056 \text{ \AA}$ ) as radiation source was used). The morphologies of PS, Ppy-coated PS and Pt deposited on Ppy-coated PS were imaged with a scanning electron microscopy (SEM) (LEO 1530 VP, Germany).

## 3. Results and discussion

Fig. 1 shows the typical SEM images of PS spheres. Uniformly dispersed PS was prepared when the monomer concentration was 0.1 mol dm<sup>-3</sup>, the initiator concentration was  $2.76 \times 10^{-3}$  mol dm<sup>-3</sup> under violent stirring at 90 °C (Fig. 1a). The average diameter of the spheres is about 200 nm. The inset of Fig. 1a is the enlarged SEM micrograph of PS. The perfect spheres with the same size were

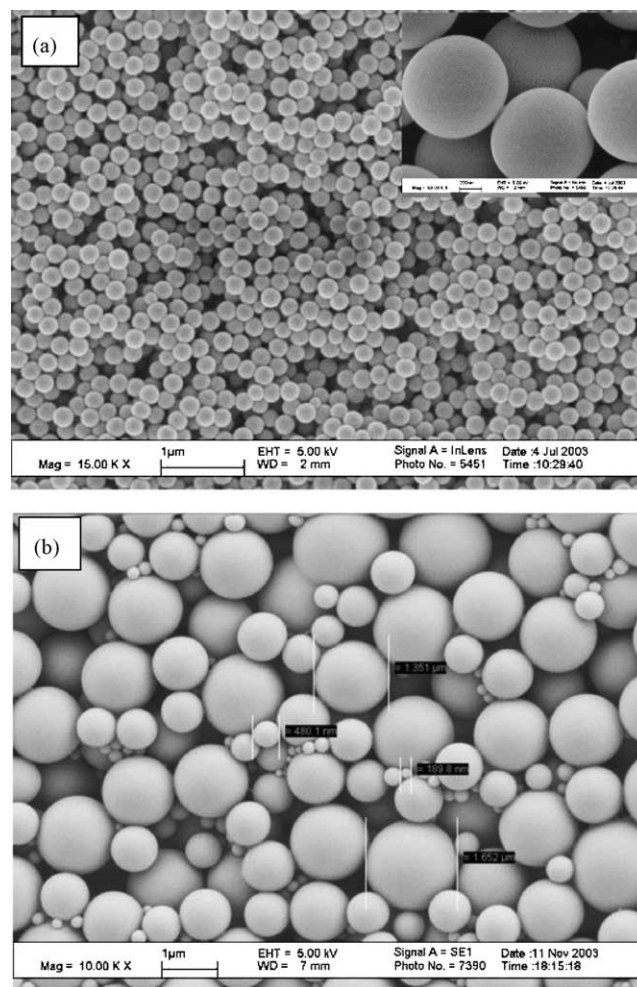


Fig. 1. SEM micrographs of PS under different polymerization conditions. (a) 0.1 mol l<sup>-1</sup> Monomer concentration, temperature: 90 °C, violent stirring; (b) 3 mol l<sup>-1</sup> monomer concentration, temperature: 80 °C.

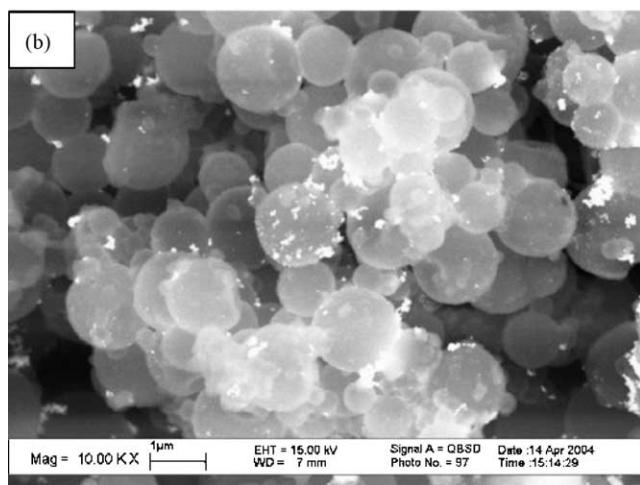
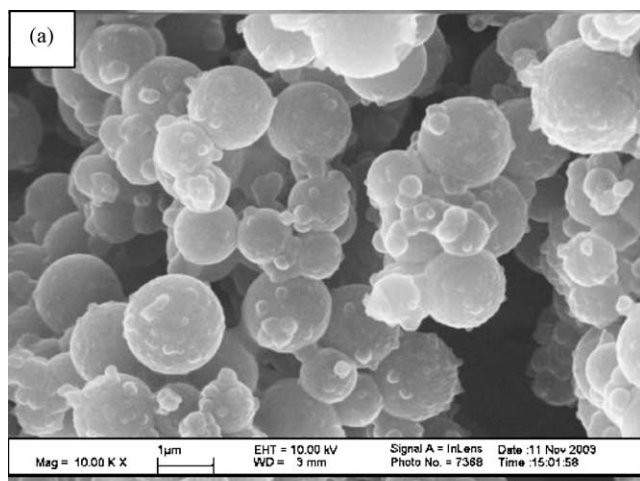


Fig. 2. SEM micrographs of (a) PS covered by Ppy and (b) after Pt deposition on the top of conducting layer (back scattering).

formed by this method. However, different sizes of PS coexisted when the condition of the monomer concentration was  $0.876 \text{ mol dm}^{-3}$  at  $70^\circ\text{C}$  (Fig. 1b). The results indicated that changing the experimental conditions the PS size could be easily controlled. PS spheres ranging from several hundred nanometers to several micrometers can be prepared with the monomer concentration from  $0.1$  to  $3 \text{ mol dm}^{-3}$ .

Fig. 2a is the SEM micrograph of Ppy-coated PS spheres. Gold sputtering was not needed indicating the good conductivity of the coated polystyrene. Fig. 2b shows the morphology of the Pt catalyst on Ppy-coated PS surface. The picture was taken as back scattering mode to show distribution of Pt on the conducting surface. The bright dots are the Pt clusters. X-ray diffraction confirmed the existent of Pt on the surface showing the typical reflections of fcc Pt (Fig. 3b). A commercially available carbon-supported 40% Pt catalyst (E-Tek Inc.) was used for comparison (Fig. 3a). The average size of the particles was calculated by Debye–Scherrer equation, the crystal size of E-Tek Pt/C and Pt/Ppy/PS are 3.8 and 3.6 nm, respectively.

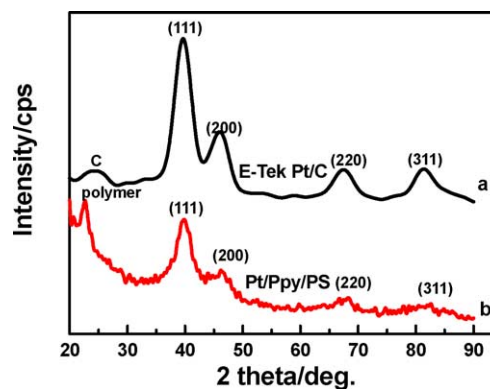


Fig. 3. The X-ray diffraction patterns of E-Tek Pt/C (a) and Pt on Ppy-coated PS (b).

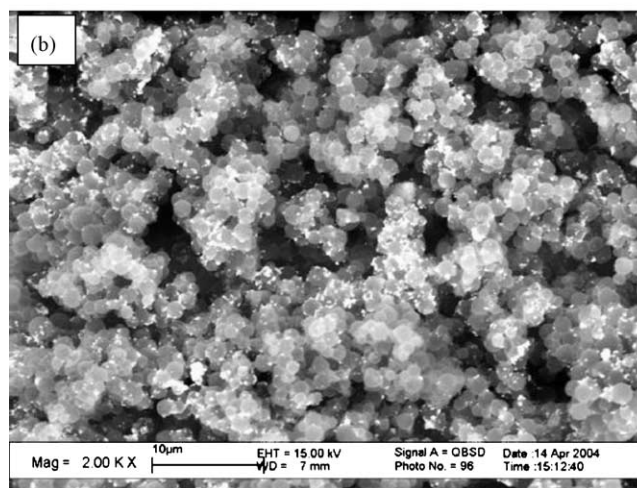
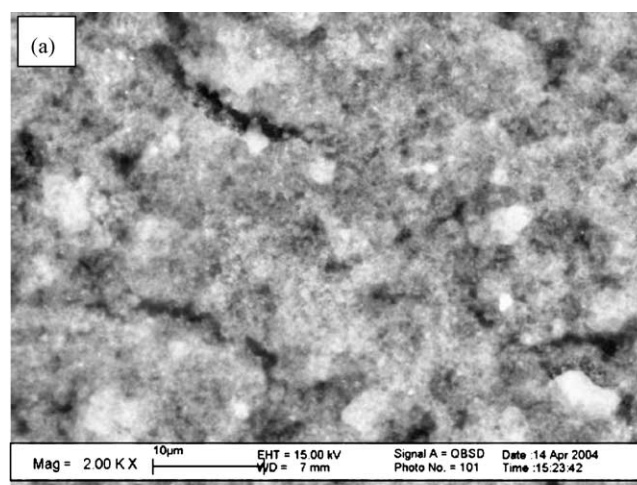


Fig. 4. SEM micrographs of (a) the E-Tek Pt/C electrode and (b) Pt/Ppy/PS electrode (back scattering).

Fig. 4 presents the SEM images both prepared electrodes with the same Pt loading ( $0.2 \text{ mg cm}^{-2}$ ), the one with the commercial catalyst and home-made three-dimensional electrode. Porous structured morphology with large and small pores was formed for the Pt/Ppy/PS electrode (Fig. 4b),

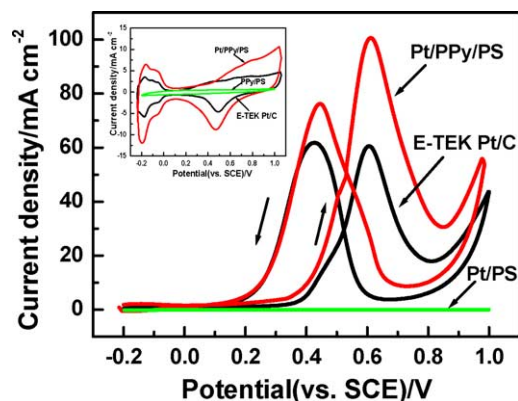


Fig. 5. Cyclic voltammograms of methanol oxidation on Pt/PPy/PS, Pt/C and Pt/PS respectively in  $1 \text{ mol dm}^{-3} \text{ CH}_3\text{OH}/0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  solution at  $20 \text{ mV s}^{-1}$ , room temperature. Inset: CVs of Pt/PPy/PS, Pt/C and PPy/PS in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  solution at  $20 \text{ mV s}^{-1}$ . The PS used for preparing the three-dimensional electrode was fabricated under the condition of  $3 \text{ mol dm}^{-3}$  monomer at  $80^\circ\text{C}$ .

resulting in larger three-phase interface for the electrochemical reactions. Such structure can provide more channels for the reactants transfer into and products out the catalyst layer. Hydrogen adsorption/desorption measurements confirmed that the surface area of Pt/PPy/PS electrode is larger than that of conventional electrode (see the inset of Fig. 5). The morphology of conventional electrode was flat and dense, leading to a reduced porosity and subsequently decreased the activity. Electrochemical measurements were carried out in  $1 \text{ mol dm}^{-3}$  methanol and  $0.5 \text{ mol dm}^{-3}$  sulfuric acid solutions using the half-cell method. The performance of methanol oxidation on three-dimensional electrode is shown in Fig. 5. The PS used for preparing the three-dimensional electrode was fabricated under the condition of  $3 \text{ mol dm}^{-3}$  monomer at  $80^\circ\text{C}$ . The conducting treatment of the PS is very important. The CV curve of Pt/PS electrode without the modification of Ppy in Fig. 5 shows that it is hardly active for the oxidation of methanol due to the limited Pt particles and the poor conductivity of the electrode. The methanol oxidation starts at lower potential on Pt/PPy/PS electrode. The anodic peak current density of methanol oxidation on the three-dimensional electrode is nearly doubled compared with that of on the E-Tek catalyst at the same Pt loading ( $0.2 \text{ mg/cm}^2$ ). The inset in the Fig. 5 is the CVs in background solution. Well-defined CVs were observed both for Pt/PPy/PS electrode and electrode made by E-Tek catalyst, indicating the surface of the electrode is clean. No signal of the Ppy is seen on the curves since its redox current is very small. The area of adsorption or desorption of atomic hydrogen on the curve of the cyclic voltammogram has been frequently used to estimate the surface area of catalysts [32,33]. The cathodic and the anodic peaks appearing between  $-0.2$  and  $0.2 \text{ V}$  versus SCE originated from H-adsorption and H-desorption in acidic media. By using the charge passed for H-adsorption  $Q_H$ , Electrochemical

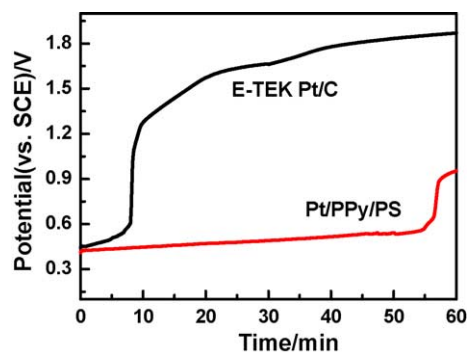


Fig. 6. Potential/time plots of Pt/PPy/PS and Pt/C in  $1 \text{ mol dm}^{-3} \text{ CH}_3\text{OH}/0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  solution at  $5 \text{ mA cm}^{-2}$ .

active surface (EAS) of platinum can be estimated:

$$\text{EAS} = \frac{Q_H}{0.21 \times [\text{Pt}]}$$

where [Pt] represents the platinum loading ( $\text{mg cm}^{-2}$ ) in the electrode,  $Q_H$  is the charge for hydrogen adsorption ( $\text{mC cm}^{-2}$ ) and  $0.21$  ( $\text{mC cm}^{-2}$ ) represents the charge required to oxidize a monolayer of  $\text{H}_2$  on bright Pt. The electrochemical active areas of platinum in Pt/PPy/PS electrode and E-Tek Pt/C electrode calculated by the above equation are  $44.5$  and  $23.6 \text{ cm}^2 \text{ g}^{-1}$ , respectively, indicating a larger EAS for the three-dimensional electrode.

The performance of the Pt/PPy/PS electrode for methanol oxidation was further characterized by constant current density polarization. Fig. 6 shows the results. It can be seen that the Pt/PPy/PS electrode can be operated at a lower overpotential and last a longer time to be poisoned at the same current density.

The better performance of the three-dimensional electrode towards methanol oxidation might be attributed to the co-existent of large and small pores or channels in the catalyst layer that can provide disparity of pressure. The disparity of pressure in the electrode makes the liquid reactants diffuse into the catalyst layer easily, resulting in the reduction of liquid sealing effect greatly. The reduction of liquid sealing effect in turn increases the active surface area for electrochemical reactions. The preliminary results are far from satisfaction and further optimization is in progress. However, it is exciting that the electrochemical performance of alcohol oxidation could be greatly improved by the built up of three-dimensional structured electrode.

#### 4. Conclusions

The three-dimensional electrode was fabricated by four steps: the preparation of building blocks (PS in this study, Carbon spheres (CS), silica spheres and various oxide foams can be used as structure building blocks as well.), the in situ polymerization of conducting polymer on the surface of the building blocks, the deposition of catalyst on the top layer and

the fabrication of three-dimensional electrode by coating the catalyst ink on the conducting substrate. Such structure permits liquid alcohol to diffuse into the catalyst layer easily and forms larger three-phase interface, resulting in the reduction of liquid sealing effect and a better performance. The three-dimensional electrode prepared by present method showed superior properties for methanol oxidation comparing with the conventional electrode made by commercially available E-Tek catalyst. The new type of electrode will lead to the applications in liquid fuel cells.

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