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Surface tailored single walled carbon nanotubes as catalyst support for direct methanol fuel cell

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HIGHLIGHTS

- Effect of Surface functionalization of the catalyst support on ORR and MOR.
- Hydrophilic groups support MOR, whereas hydrophobicity improves ORR.
- Hydrophobic catalyst support also proves to show methanol tolerance.

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ABSTRACT

A strategy for tuning the surface property of Single Walled Carbon Nanotubes (SWNTs) for enhanced methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) along with methanol tolerance is presented. The surface functionality is tailored using controlled acid and base treatment. Acid treatment leads to the attachment of carboxylic carbon (CC) fragments to SWNT making it hydrophilic (P3-SWNT). Base treatment of P3-SWNT with 0.05 M NaOH reduces the CCs and makes it hydrophobic (P33-SWNT). Pt catalyst supported on the P3-SWNT possesses enhanced MOR whereas that supported on P33-SWNT not only enhances ORR kinetics but also possess good tolerance towards methanol oxidation as verified by the electrochemical technique.

1. Introduction

DMFC is a promising energy source for both automotive applications and small portable electronic devices due to the high energy density of methanol (6100 Wh/Kg). It has received considerable and persistent attention, due to the ease of liquid fuel transportation, compactness and low working temperature. The few challenges in the commercialization of DMFC is slow methanol oxidation reaction (MOR) kinetics at anode along with slow oxygen reduction reaction (ORR) at cathode. Another major hindrance is the methanol cross over from anode to cathode due to the diffusion of methanol through polymer electrolyte membrane [1]. This leads to fuel loss at anode and parasitic MOR at cathode, which creates mixed potential and reduces the overall fuel cell efficiency. There has been considerable interest by the scientific community recently to overcome these limitations. Methanol crossover can be mitigated by modifying the electrolyte membrane in such a way that it reduces its crossover from anode to cathode. Another viable option is to synthesize effective and efficient ORR electrocatalyst, which is also methanol tolerant [2,3]. Hence, the requirement for high performance DMFC is highly active anode electrocatalyst for MOR and highly active ORR electrocatalyst with methanol tolerant properties at cathode.

In the recent past much effort has been put in developing the binary, ternary and quaternary methanol tolerant catalyst [4–6]. Platinum based bimetallic electrocatalyst have shown considerable methanol tolerance [7,8]. Gao et al. developed methanol-tolerant Pt/$CoSe_2$ nanobelt as efficient cathode catalyst with improved ORR activity and methanol tolerance [9]. Carbon supported Pt-TiO_2 is another developed methanol tolerant catalyst, which possess good ORR activity [10]. Quaternary catalyst is a class of methanol tolerant catalyst developed by Jeon et al. [6]. Recently Wang et al. reported the use of platinum nanoparticles embedded in pyrolyzed

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nitrogen-containing cobalt complexes for high methanol-tolerant oxygen reduction activity [11]. Pt/Fe core shell-SWNT has been reported to be effective electrocatalyst with high methanol tolerance [12]. Much effort has been paid towards the development of methanol tolerant ORR catalyst but to the best of our knowledge, this is the first report towards the development of catalyst support where the same catalyst support is tuned for its efficient and improved performance at both the electrodes appropriately in direct methanol fuel cell (DMFC).

It has been understood that catalyst support plays an important role in the electrocatalyst development along with the catalyst. SWNT is an efficient catalyst support for methanol oxidation and oxygen reduction in DMFC and PEMFC respectively compared to fullerene nanostructures, multiwalled carbon nanotubes (MWNT) and commercially used carbon black [13,14]. High efficiency of SWNT as catalyst support has been largely understood due to its unique properties like high conductivity and mesoporous film network morphology. However its effectiveness for different reactions like ORR and MOR depends on its surface functionalities. Surface property of the support depends on the specific properties of the functional groups present on its outer surface. DMFC has the requirement of high MOR kinetics at anode and high ORR kinetics at cathode. To overcome the limitation, which arises due to methanol crossover from anode to cathode, highly durable methanol tolerant electrocatalyst with high ORR is the prime necessity at cathode. Same support can be employed for ORR, MOR along with high methanol tolerance depending on the surface property of the support. In the present work, we report the use of HNO_3 purified SWNT (P3-SWNT), which contains carboxylated carbon fragments, as an efficient electrocatalyst for MOR. After the treatment of P3-SWNT with NaOH (P33-SWNT), carboxylic content is reduced and it also leads the support its hydrophobic nature [15]. This catalyst support developed has improved ORR kinetics and also possess the property of high methanol tolerance. The full cell DMFC framework is presented in Fig. 1.

2. Experimental details

2.1. Synthesis of Pt-P3-SWNT and Pt-P33-SWNTs

P3-SWNTs and P33-SWNTs were procured from Carbon Solutions Inc. Riverside, CA. The synthesis detail of P3 and P33 SWNTs are given in supporting information. The NIR-RP of these SWNT materials were calculated as reported in earlier publications [17,18]. Thermogravimetric analysis (TGA) of SWNTs were carried out in air atmosphere at the heating rate of 5 °C/min using a Perkin-Elmer Pyris 1 Thermal Analyzer, after the samples were held at 120 °C for 30 min in order to eliminate moisture. The ash content was obtained by holding the SWNT sample at 900 °C for 30 min in order to completely remove the carbon content of the sample. The SWNT samples were outgassed at 150 °C for 2 h before the measurements. The adsorption isotherms were obtained using nitrogen at 77 K from relative pressure (P/P_0) 0.05 to 0.3.

Platinum nanoparticles were loaded on SWNTs using the following procedure: briefly, 228 mg of SWNTs were sonicated in 40 mL of ethylene glycol (EG) in a round bottom flask till uniformly dispersed suspension is formed and then 263 mg of H_2PtCl_6 was added to that suspension. The pH of the suspension was adjusted to 11–12 using NaOH and the temperature was increased to 135 °C. The suspension was then stirred for 3 h at 135 °C. After the reaction, the pH of the slurry was decreased to 2 using HCl and washed with excess water three times using a centrifugation/decantation process to remove excess EG and finally water was exchanged with ethanol using centrifugation/decantation to obtain an ethanol dispersion of concentration 1–2 mg/mL. This dispersion was sonicated overnight and diluted to 0.1 mg/mL dispersion with ethanol. The sonication was carried out using Dakshin (5.5L-150H model) bath sonicator with a power of 150 W. Metal loading of Pt-P3-SWNT and Pt-P33-SWNT was determined by TGA after subtracting the residual weight for P3-SWNT and P33-SWNT respectively.

2.2. Electrochemical measurements

Electrochemical performance of the Pt supported on SWNTs was measured by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) using a Potentiostat/Galvanostat (Metrohm μAutolab). A three electrode one compartment electrochemical cell was used for the measurement with catalyst coated glassy carbon (GC) disk as working electrode, Ag/AgCl (3 M KCl) as reference electrode and Pt foil as counter electrode. The glassy carbon electrode was polished using alumina slurry and washed thoroughly with de-ionized water prior to use. 5 mg of Pt loaded SWNTs were sonicated in 1.05 mL of ethanol containing 50 μL of 5 wt % nafion solution (in ethanol) for 30 min followed by drop casting the suspension of 1 μL over GC electrode (Area - 0.0314 cm^2) using a micropipette. The electrochemical cell containing 0.5 M H_2SO_4 electrolyte was purged with Ar or O_2 prior to experiments and all the measurements were performed at room temperature. LSV was recorded using a rotating disk electrode with the same electrode prepared for CV but with a rotation of 1500 rpm. CV and LSV measurements were also recorded in the presence of 1 M methanol in 0.5 M H_2SO_4 for activity check in methanol atmosphere.

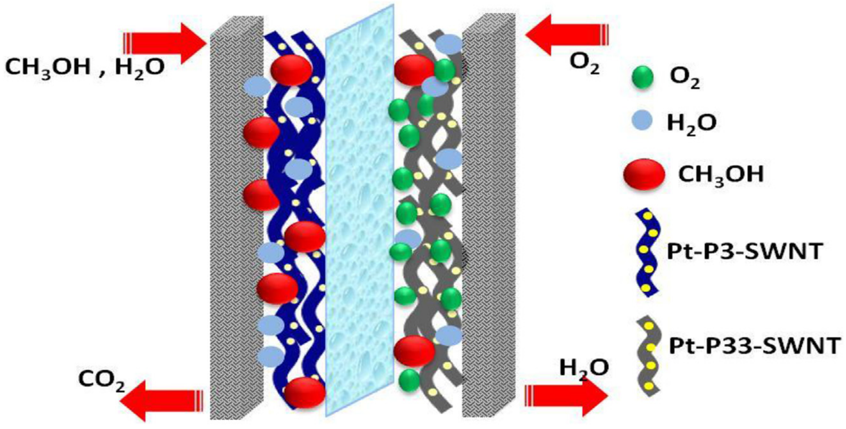

Fig. 1. Schematic of the direct methanol fuel cell.