

Special Theme Research Article

Enhancement of PEMFC performance by using carbon nanotubes supported Pt–Co alloy catalysts

Madhu Sudan Saha, Yougui Chen, Ruying Li and Xueliang Sun*

Department of Mechanical and Materials Engineering, The University of Western Ontario, London, Ontario, Canada

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ABSTRACT: Carbon nanotube-based Pt–Co (Pt–Co/CNT) alloy electrocatalysts for the oxygen reduction reaction were prepared by the silane-assisted deposition method. The transmission electron microscopy (TEM) reveals that the prepared Pt–Co alloy nanoparticles are uniformly dispersed on the surface of the CNTs support with narrow particle size distribution. As compared to Pt/CNTs catalyst, the bimetallic Pt–Co/CNTs catalyst exhibits an improved performance as cathode material in a H₂/O₂ fuel cell. © 2008 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: carbon nanotubes; Pt–Co nanoparticles; electrocatalysis; oxygen reduction reaction; proton exchange membrane fuel cells

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are thought to be efficient and clean energy sources for automotive and portable as well as stationary applications.^[1] To make commercially viable PEMFCs technology for automotive applications, there are several challenges to be addressed. One of the main obstacles is low performance of the oxygen reduction reaction (ORR) at the cathode.^[2] Therefore, it is very important to find highly active electrocatalysts that can effectively enhance the electrode kinetics of ORR. In the last several years, considerable efforts have been made to find new electrocatalysts for the ORR.^[3–5] Many studies have demonstrated that the alloying of Pt with nonprecious-metals such as Co,^[6,7] Cr,^[8,9] Ni,^[6,8] Fe,^[4] Mn,^[10] and V^[11] shows higher activity than Pt alone. The improvement in the ORR electrocatalysis has been ascribed to different factors such as a decrease in the Pt–Pt distance and therefore a more favorable adsorption of O₂,^[7] the lowering of the Pt oxidation state,^[12] the suppression of Pt oxide formation,^[12,13] the formation of a new electronic structure with 5d-orbital vacancies,^[6,7] and the formation of a catalytic and thin Pt skin on the surface of the alloy.^[6,14,15] Among the several possibilities of using binary alloys, the Pt–Co alloy has shown the most promising performance for the ORR.^[16–19] A recent study on the catalytic activity and stability of supported Pt–Co alloys with well-defined

structures by Watanabe *et al.*^[16] demonstrated that both Co and Pt dissolve out preferentially from small-size alloy particles and Pt redeposits on the surfaces of large-size ones in hot H₃PO₄. As seen above, the effect of the morphological or crystallographic changes and of the electronic structural change brought about by alloying on the electrocatalysis of the ORR still remains elusive.

In almost all cases, carbon blacks, particularly Vulcan XC-72 have been widely used as a support of the metal nanoparticles. Despite a high surface area and low electrical resistance of the carbon black support, current fuel cell electrocatalyst still suffers from low Pt utilization, limited mass transport capability, and limited electrochemical stability because of corrosion and the electrode structure of carbon black-based support.^[11] Therefore, it is of interest to explore the behavior of Pt-based catalysts prepared on supports different from those most frequently used.

Recently, carbon nanotubes (CNTs) appeared to be promising catalyst supports for PEMFCs and direct methanol fuel cells (DMFCs) because of their unique structure and properties such as high surface area, good electronic conductivity, strong mechanical properties, and high chemical stability.^[20,21] The deposition of Pt, Ru, and Pt–Ru on CNTs has been reported and the resulting supported catalysts can increase the performance of PEMFCs^[22–28] and DMFCs^[29–31] compared to those using commercial carbon black as support. In addition, several research groups have reported that CNTs are more resistant to electrochemical oxidation than carbon black with and without Pt on them.^[32–34] However, to our knowledge, there has been no report

*Correspondence to: Xueliang Sun, Department of Mechanical and Materials Engineering, The University of Western Ontario, London, Ontario, N6A 5B9, Canada. E-mail: xsun@eng.uwo.ca

of CNT-based Pt–Co alloy catalysts for the ORR in PEMFCs.

The aim of the present work is to report the preparation and characterization of Pt–Co-supported CNT catalysts and their implication on ORR. The Pt–Co nanoparticles supported CNT catalysts were characterized using scanning electron microscope (SEM) and transmission electron microscopy (TEM). Their performance in a single PEMFC was also evaluated.

EXPERIMENTAL

Growth of carbon nanotubes on carbon paper

The CNTs were synthesized in a Chemical vapor deposition (CVD) reactor by decomposing a hydrocarbon gas on catalytic Co–Ni particles deposited on the fibers of carbon paper. This has been described in detail elsewhere.^[35] Briefly, in the reactor, a small piece of carbon paper (E-TEK Division, PEMEAS Fuel Cell Technologies, Somerset, NJ) was loaded with the catalyst. The carbon paper was then fixed across a section of the inner quartz tube and connected to two electrodes. All gases fed into the inner quartz tube were forced to go through a 2.5 cm × 2.5 cm section of the carbon paper before exiting the reactor. Under the applied potential, the carbon paper was heated within seconds by the Joules effect up to a temperature high enough to decompose the gas used to grow nanotubes. The deposition of Co–Ni nanoparticles was carried out by the silane-assisted method.^[32] Prior to Co–Ni deposition, the carbon paper was pretreated with methanol for 30 min in order to improve the homogeneity of the Co–Ni particle sizes and their distribution on the carbon paper. The growth of CNTs was then carried out at 800 °C for 10 min in a mixture of 90% Ar, 5% H₂, and 5% C₂H₄. Finally, the system was cooled under an Ar atmosphere. In the following discussion, the CNTs grown on carbon paper were denoted as CNTs/carbon paper.

Deposition of Pt and Pt–Co nanoparticles on CNTs

CNT-supported Pt–Co alloy electrocatalysts in the nominal Pt : Co atomic ratio 75 : 25 were prepared by the silane-assisted deposition method.^[35] The silane used here was 2(4-chlorosulphophenyl) ethyl trichlorosilane, 50 vol% in dichloromethane purchased from Gelest Inc., Morrisville, PA. The solution was prepared by mixing 23 ml of Dimethyl Sulfoxide (DMSO), 0.5 ml of 2(4-chlorosulphophenyl) ethyl trichlorosilane, and 1.5 ml of deionized water. After hydrolysis of the solution, by stirring for 2 h at room temperature, PtCl₄ and CoCl₂

precursors were added into the solution to give a combined metal ion concentration of 0.08 M. After further stirring for 30 min, the CNTs grown on carbon paper were immersed in the solution for 24 h. Then the samples were picked out from the solution, washed with ethanol, and dried at 80 °C under vacuum over 8 h. Once the precursors of Pt–Co particles were adsorbed on the surface of CNTs, the Pt–Co salts were reduced to Pt–Co alloy metal nanoparticles at 500 °C for 30 min in an atmosphere of H₂ (125 sccm). Pure Pt nanoparticles supported CNT catalysts were prepared by the same procedure. The morphologies of the CNTs/carbon paper before and after the deposition of Pt or Pt–Co nanoparticles were examined using an SEM (Hitachi S-2600 N) and a TEM (Philips CM10). X-ray diffraction (XRD) analysis was carried out with an X-ray diffractometer (Rigaku-MiniFlex) using Cu K α radiation at 30 kV.

Electrochemical measurements

The electrochemical measurements were carried out by using an Autolab potentiostat/galvanostat (Model, PGSTAT-30, Ecochemie, Brinkman Instruments) in a three-electrode, two-compartment configuration cell. A Pt wire served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. All potentials in this paper are quoted against SCE. Purified Ar (99.9998%) and O₂ (99.5%) gases were purchased from Praxair Canada Inc. For the measurement of hydrogen electrosorption curves, the potential was cycled between –0.25 and +1.2 V at 50 mV s^{–1} to obtain the voltammograms of hydrogen adsorption in Ar-purged 0.5 M H₂SO₄ aqueous solution. All experiments were carried out at room temperature (25 °C).

Preparation and characterization of membrane electrode assembly (MEA)

A gas diffusion layer was applied on one side of the CNT-supported Pt or Pt–Co alloy catalysts. The gas diffusion ink was prepared by ultrasonically dispersing the required quantity of carbon black (Vulcan XC-72, Cabot) and polytetrafluoroethylene (PTFE) solution in a mixture of isopropanol and deionized water (80 : 20 volume ratio) for 30 min followed by magnetic stirring for about 1 h.^[36] The carbon loading was approximately 3.5 mg cm^{–2} and PTFE content was 30 wt%. The gas diffusion layer was sintered at 350 °C in Ar for 1 h.

To fabricate MEA, the cathode was CNT/carbon paper composite while the standard E-TEK gas diffusion electrode (30 wt% Pt/C, 0.5 mg Pt cm^{–2}) was used as the anode. The electrode area was 1.0 cm² and typical loading of Nafion ionomer in all electrodes was

in the range of $0.9\text{--}1.0\text{ mg cm}^{-2}$. Nafion 112 (DuPont Inc., USA) was used as the polymer electrolyte membrane. Prior to MEA fabrication, the membrane was cleaned by immersing it in boiling 3% H_2O_2 for 1 h followed by boiling in $\text{M H}_2\text{SO}_4$ for the same duration with subsequent rinsing in boiling deionized water (1 h). This procedure was repeated at least twice to ensure complete removal of H_2SO_4 . The MEA was fabricated in-house via hot pressing at 130°C and 100 psi for 2 min. Polarization curve experiments were carried out at a single fuel cell test station (Fuel Cell Technologies, Inc., USA).

RESULTS AND DISCUSSION

Figure 1 shows the SEM and TEM micrographs of CNTs grown on carbon paper by CVD method. Before the growth of CNTs on carbon paper, the carbon paper substrate reveals many carbon fibers of about $5\text{--}10\ \mu\text{m}$ diameter crossing each other (inset, Fig. 1(a)). After the growth of CNTs, SEM image showed that a high density of nanotubes had been obtained (Fig. 1(a)). Further, TEM images show that the tubes are straight and clean. The diameters of the majority of the tubes range from 30 to 60 nm with a typical tube diameter of 50 nm shown in Fig. 1(b).

The effect of the catalyst composition on the particle size was investigated by TEM measurement. Figure 2 shows the TEM images together with particle size distribution histograms obtained from TEM images of the CNT-supported Pt and Pt–Co alloy electrocatalysts. Histograms of particle sizes were constructed using about 150 particles. It was found that Pt and Pt–Co alloy nanoparticles were uniformly dispersed on the surface of CNTs. The average sizes of Pt and Pt–Co particles were 2.75 and 3.62 nm, respectively.

The XRD analysis of Pt/CNT and Pt–Co/CNT catalysts reveals the presence of five main characteristic peaks of the face-centered cubic (fcc) crystalline Pt, namely, the planes (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) (not shown). These diffraction peaks for the Pt–Co/CNT alloy catalysts are slightly shifted to higher angles with respect to the corresponding peaks in the Pt/CNT catalyst, indicating a contraction of the lattice and alloy formation.

Figure 3 shows the cyclic voltammograms (CVs) of the Pt/CNT and the Pt–Co/CNT catalysts in Ar-saturated $0.5\text{ M H}_2\text{SO}_4$ at a scan rate of 50 mV s^{-1} . As shown in Fig. 3, the Pt–Co/CNT alloy catalyst has a hydrogen adsorption/desorption behavior similar to that of pure Pt owing to the presence of Pt skin layers on the alloy surface. The results with Pt–Co/CNT alloy catalyst in Fig. 3 are similar to those found by Salgado *et al.*^[19] for carbon supported Pt–Co/C alloy. The hydrogen adsorption/desorption peak current of the

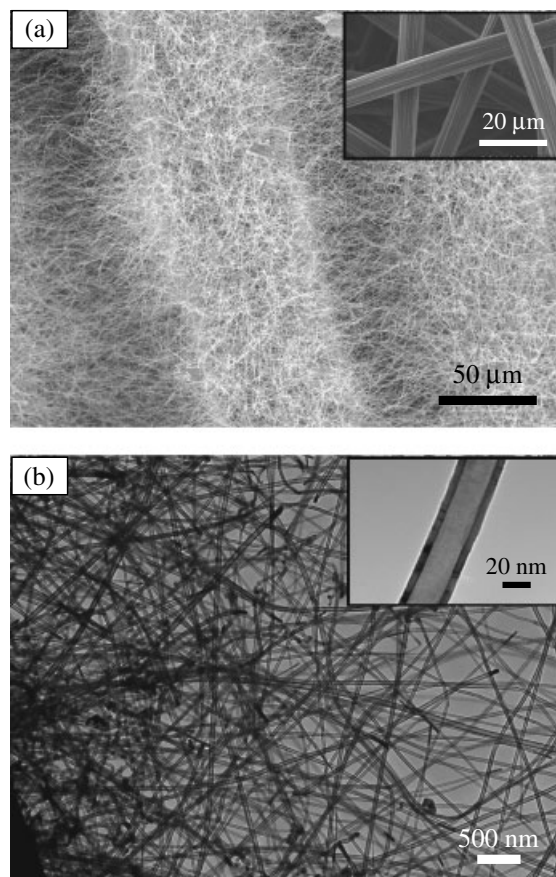


Figure 1. (a) SEM image of CNTs grown on the carbon fibers of a carbon paper by chemical vapor decomposition method (inset: bare carbon fibers). (b) TEM image of CNTs grown on the carbon fibers of a carbon paper (inset: single CNT showing diameter of the tube).

Pt–Co/CNT alloy catalyst is lower than that of the Pt/CNT catalyst. Moreover, the onset of oxide formation on Pt (accepted as Pt–OH) slightly shifted to more positive potentials for the Pt–Co/CNTs compared to Pt/CNTs. This observation demonstrates that alloying of Pt with transition metals inhibits the chemisorption of OH on the Pt sites at high potentials by the change in electronic effects and leads to an enhancement in the rate of ORR.^[10] The transition metals are believed to provide sites to bind and activate water.^[37] This means that alloying of Pt with a transition metal has significant effects on some changes in the way Pt atoms of Pt alloy catalysts interact with water. Murthi *et al.*^[38] have shown that the onset of OH formation shifts to higher potentials for Pt/C in 6 M trifluoromethane sulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$) or Pt–Co/C in 1 M $\text{CF}_3\text{SO}_3\text{H}$, as compared to Pt/C in 1 M $\text{CF}_3\text{SO}_3\text{H}$. They suggested that the onset of the oxide formation can be shifted by either alloying the Pt with a second metal that increases the 5d-band vacancies or by lowering the activity of the water.^[38] Reduction peak of Pt oxide for Pt–Co/CNTs is more

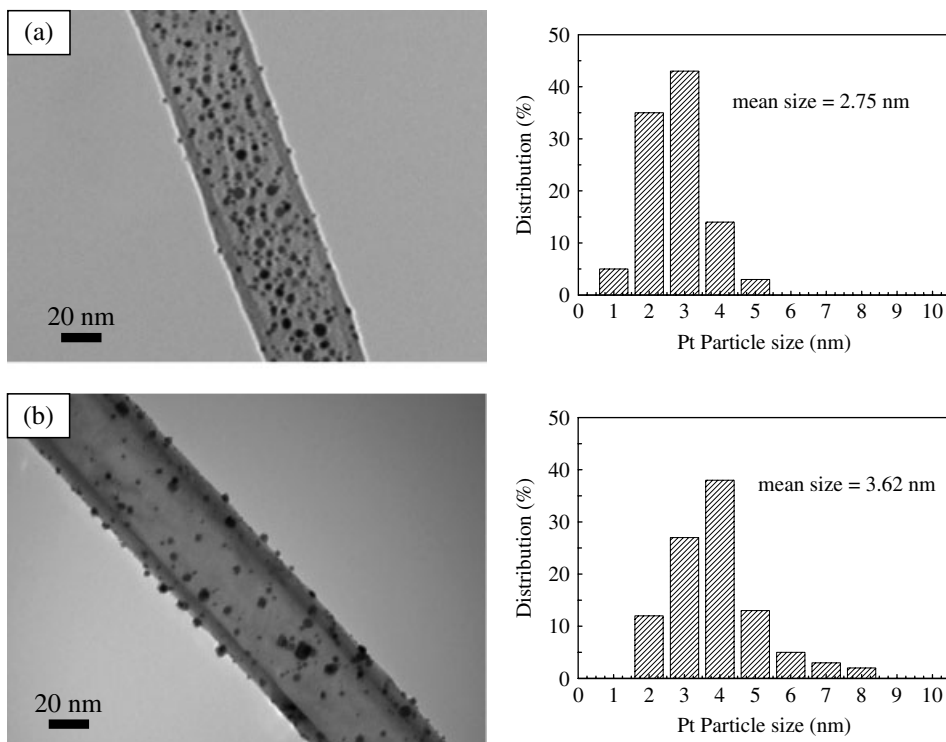


Figure 2. TEM images and particle size distribution histograms of Pt/CNTs (a) and Pt-Co (3:1)/CNTs (b) electrocatalysts prepared by silane-assisted deposition method.

negative than that for Pt/CNTs. This result might indicate that the Pt oxide on Pt-Co/CNT catalyst is hard to reduce compared to that on Pt/CNTs.

From the practical point of view, the single-cell test is the ultimate evaluation criterion for novel electrocatalyst materials. Therefore, the performance of the membrane electrode assembly (MEA) in PEMFC using the Pt/CNTs and Pt-Co/CNTs as cathodes, and commercial Pt/C (30 wt% Pt on carbon) obtained from E-TEK as the anodes were evaluated in a single-cell PEMFC at 80 °C.

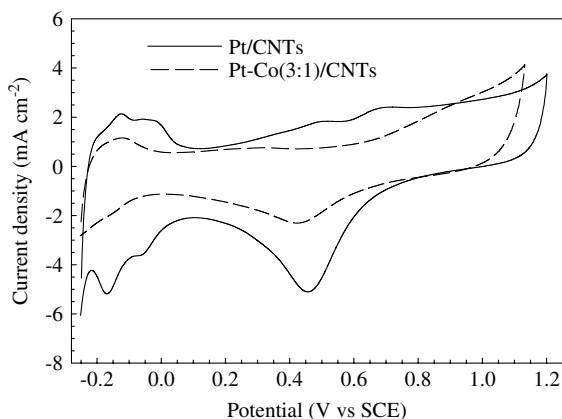


Figure 3. CVs of Pt/CNT/carbon paper and Pt-Co/CNT/carbon paper composites prepared by silane-assisted deposition method in Ar-saturated 0.5 M H₂SO₄ at scan rate of 50 mV s⁻¹.

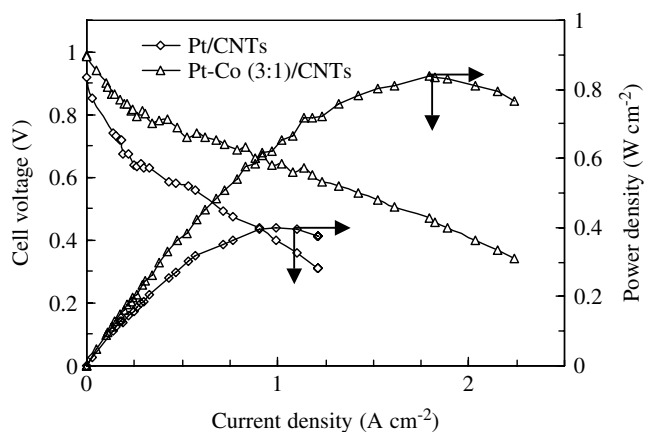


Figure 4. Polarization curves and power density curves in single-cell PEMFC with Pt/CNTs and Pt-Co/CNTs as cathodes for H₂/O₂ at 80 °C, Nafion 112 membrane, 25/30 psig anode and cathode back pressure, respectively. Anode electrodes were E-TEK GDE with 0.5 mg Pt cm⁻².

The comparison polarization curves and power density curves were shown in Fig. 4. As shown in Fig. 4, the Pt-Co/CNTs alloy cathode catalysts show much better performance than pure Pt/CNTs cathode. At a fixed cell voltage of 0.6 V, the current density of Pt-Co/CNT alloy catalyst is 1.18 A cm⁻² which is higher by a factor of 2.6 relative to that of Pt/CNT catalyst (0.45 A cm⁻²).

The maximum power density of Pt–Co/CNT alloy catalyst was 0.83 W cm^{-2} while the corresponding power density for the Pt/CNT catalyst was 0.40 W cm^{-2} , thus showing an increase in power density of about 0.43 W cm^{-2} for the former case.

CONCLUSIONS

Pt–Co alloy nanoparticles have successfully been deposited on the CNTs grown directly on carbon paper by the silane-assisted deposition method. TEM images indicate that the Pt–Co alloy catalysts prepared by this method have nanometer size particles with an average size of 3.62 nm, and were well dispersed on the surface of the CNTs support. Electrocatalytic activity of the Pt–Co/CNT alloy catalysts was investigated with regard to the ORR as cathode in a single-cell PEMFC. It was found that the Pt–Co/CNT alloy catalysts possessed enhanced oxygen-reduction activity compared to Pt/CNTs. The results of this work will contribute to the development of cheaper active cathode catalysts for PEMFCs.

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