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Catalytic performance of non-platinum-based hybrid carbon hetero-structure for oxygen reduction and hydrogen oxidation reactions in proton exchange membrane fuel cell

Priji Chandran, Sundara Ramaprabhu*

Alternative Energy and Nanotechnology Laboratory (AENL), Nano-Functional Materials and Technology Centre (NFMTC), Department of Physics, Indian Institute of Technology Madras, Chennai, Tamil Nadu, 600036, India

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ABSTRACT

The present work describes the potential of a hybrid carbon hetero-structure having the unique properties of one-dimensional carbon nanotubes and two-dimensional graphene as a catalyst support material for platinum-free electrocatalysts in polymer electrolyte membrane fuel cell (PEMFC) for hydrogen oxidation reaction (HOR) or oxygen reduction reaction (ORR). Partially exfoliated carbon nanotubes (PCNT), which have the synergistic effect of good electrical conductivity and high surface area, have been used as the support material for Pd₃Co alloy catalysts. This provides more active sites for the dispersion of catalyst particles along with quick electron transport through the carbon structure. This unique characteristic increases the catalytic activity of the electrocatalysts. The electrochemical half-cell studies confirm that, ORR on Pd₃Co/PCNT proceeds via a four-electron process. The single cell measurements were carried out by preparing a membrane electrode assembly (MEA) using Pd₃Co/PCNT at the anode, cathode separately as well as simultaneously at both the anode and cathode. A maximum power density of 327 mW cm⁻², 240 mW cm⁻² and 96 mW cm⁻² is attained from the use of Pd₃Co/PCNT nanocomposite at anode, cathode and at both electrodes simultaneously in a PEMFC at 60 °C, respectively.

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Introduction

Compared to the different types of fuel cells, polymer electrolyte membrane fuel cells (PEMFC) have the advantage of fast start-up time, less pollution, low operating temperature, simple maintenance and high efficiency [1]. In general, a PEMFC consists of two electrodes, an anode and a cathode

separated by a polymer electrolyte membrane. At the anode, in the presence of catalysts, hydrogen oxidation reaction (HOR) takes place, whereas at the cathode oxygen reduction reaction (ORR) takes place. In order to achieve good HOR and ORR activity, the development of better electrocatalysts material is a necessity. Vast research has been carried out to develop better electrode materials, which facilitate good interaction between the support material and the catalyst

* Corresponding author.

E-mail address: ramp@iitm.ac.in (S. Ramaprabhu).

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nanoparticles [2–5]. The prominent direction of research has been towards the development of efficient catalyst support materials, which enable the maximum utilization of catalyst particles for fuel cell reaction. The catalyst support material plays a key role in the fuel cell, because it determines the degree of dispersion of catalyst particles, thereby making it available for the HOR and ORR. The characteristics of a good support material include high surface area, good chemical tolerance and high electrical conductivity [6]. Carbon black is the common catalyst support material used in fuel cell due to its low cost, but its weak interaction with the catalyst particles leads to the agglomeration of catalyst nanoparticles, thereby reducing the electrochemical surface area [7]. Other widely used carbon support materials in the fuel cell are two-dimensional graphene and one-dimensional carbon nanotubes due to their high surface area and good electrical conductivity. But one of the demerits of the graphene nanosheets is the restacking of the graphene layers which leads to reduction in the available surface area [8]. To prevent the restacking, use of different spacers in between the graphene layers has been reported by several groups [9–11]. Among the different spacers used, carbon nanotubes have proved to be good as they facilitate the electron transfer between the graphene nanosheets, though they have lesser surface area compared to graphene [12,13]. Recent studies have proved that compared to the performance of only graphene and carbon nanotubes, the combined 1D-2D hybrid structure has the advantage of both high surface area and good electrical conductivity. Aravind et al. [2] showed an enhanced fuel cell performance by using Pt decorated on carbon nanotube-graphene composite as catalyst support material in PEMFC. Sahoo et al. [14] showed significant improvement in fuel cell performance using partially exfoliated nanotubes as catalyst support material for Pt nanoparticles. Similarly, Long et al. [15] proved that Pt decorated on partially unzipped outer walls of carbon nanotubes is responsible for the high catalytic activity of the electrocatalysts.

Commonly, Platinum (Pt) and its alloys have been used as the catalyst in a fuel cell at both the anode and cathode due to its high stability and better electrocatalytic activity in a fuel cell operating environment compared to other catalysts [16–19]. Thus, major contribution to the total cost of a fuel cell is due to the electrocatalysts. Vast amount of research has been going on to find a best alternative for Pt, without compromising on the electrocatalytic performance. Exploring non-platinum based electrocatalysts with similar electrocatalytic property to Pt is one of the major challenges of PEMFC. Many research groups have recently investigated the feasibility of replacing Pt with other platinum-group metals like Pd which is more abundant and cheap compared to Pt [20–22]. The cost of Pd is less compared to Pt, but the catalytic activity of pure Pd is five times less than Pt [23,24]. Therefore, researchers have tried to improve the catalytic activity of Pd by incorporating different transition metals like Co [23], Fe [25], Ni [26], Cu [27], Mo [28], Bi [29], Ir [30], W [31] into Pd. In particular, Pd–Co alloy based electrocatalysts have proved to be an efficient electrocatalyst for PEMFC [32–34]. For instance, Savadogo et al. [33] showed better ORR performance of Pd–Co alloy nanocomposite compared to Pd–Cr alloy. Wei et al. [35] demonstrated the enhancement in ORR activity due to the

synergistic effect of Co alloying and surface oxidation of Pd catalyst. Similarly, Rahul et al. [34] showed that the catalytic activity of Pd₃Co alloy catalyst is good compared to alloys of different composition ratios of Pd and Co.

In the present study, partially exfoliated carbon nanotubes (PCNT) were synthesized by controlled oxidation of multiwalled carbon nanotubes and used as a catalyst support material for Pd₃Co alloy catalyst nanoparticles. The use of PCNT as a support material provides high accessible surface area and good electronic conductivity due to the strong interaction of exfoliated graphene layers and intact inner tubes of partially exfoliated carbon nanotubes. The physical and electrochemical characterizations were carried out for as-synthesized Pd₃Co/PCNT and it was used as the anode and cathode electrocatalysts separately as well as simultaneously at both the anode and cathode side in PEMFC.

Experimental section

Materials

Palladium (II) chloride (PdCl₂), Sulphuric acid (H₂SO₄), Hydrogen peroxide (H₂O₂) were purchased from Rankem Chemicals. Ethylene glycol (EG), Sodium hydroxide (NaOH), Potassium permanganate (KMnO₄), Sodium nitrate (NaNO₃) and Cobalt (II) chloride hexahydrate (CoCl₂·6H₂O) were procured from Merck. High pure de-ionized (DI) water was used in all experiments.

Synthesis of PCNT and Pd₃Co/PCNT

Catalytic chemical vapor deposition (CCVD) technique was used to synthesize the multiwalled carbon nanotubes (MWNTs) using MmNi₃ (Mm = Misch metal) alloy hydride as catalyst at 700 °C in a tubular furnace [36]. The as-grown MWNTs were purified by air oxidation and acid treatment to remove amorphous carbon and unutilized catalytic impurities, respectively. The purified MWNTs (CNT) were used to prepare partially oxidized carbon nanotubes (POCNT) and PCNT by modifying the Hummers method [37] as reported earlier by our group [38].

The polyol reduction method was used for the decoration of Pd₃Co alloy nanoparticles over PCNT. Briefly, the PCNT was dispersed in a mixture containing EG and DI water taken in 2:1 ratio (EG: water). The calculated amount of PdCl₂ and CoCl₂·6H₂O was added to the solution followed by the addition of NaOH to adjust the pH of the solution to 11 and refluxed at 130 °C for 6 h. The obtained solution was filtered and vacuum dried at 60 °C to obtain Pd₃Co/PCNT. For comparison, Pd₃Co alloy nanoparticles decorated on CNT (Pd₃Co/CNT) was prepared using the same procedure mentioned above.

Physical characterizations

The powder X-ray diffraction (XRD) patterns were recorded using Rigaku X-ray diffractometer with X-ray source of wavelength $\lambda = 0.15406$ nm. The scan was performed for the

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