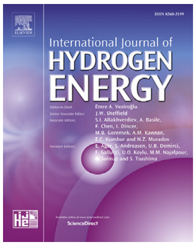
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



3-D structured Pt/rGO-polyethyleneimine-functionalized MWCNTs prepared with different mass ratio of rGO and MWCNT for proton exchange membrane fuel cell

H.N. Yang [1,2], Y.D. Ko [2], W.J. Kim *

Department of Materials Chemistry and Engineering, College of Engineering, Konkuk University, 120 Neungdong-ro,
Gwangjin-gu, Seoul, 05029, South Korea

ARTICLE INFO

Article history:
Received 8 November 2017
Received in revised form
4 December 2017
Accepted 25 December 2017
Available online xxx

Keywords:
3D-structure
Reduced graphene oxide
Carbon nanotube
Hybridization
Durabilty
PEMFC

ABSTRACT

Various 3-D structured Pt/xrGO-yPolyethyleneimine-functionalized MWCNTs (PMWCNT) were successfully prepared by the hybridization of rGO and PMWCNT. The FE-SEM and TEM images confirm the 3-D structure of hybridized Pt/rGO-PMWCNT catalyst and dispersion of Pt nanoparticles. In case of Pt/PMWCNT, Pt nanoparticles are preferentially deposited onto the external surface of PMWCNT but upon hybridization, the preferential deposit of Pt nanoparticles onto PMWCNT is not expected due to high affinity of rGO toward Pt nanoparticles. The Pt content deposited onto the hybridized supporting materials tends to be increased with rGO content. It is noteworthy that the BET surface area is increased with PMWCNT content due to the formation of the 3-D structure. The electrochemical active surface area (ECSA) and durability based on ECSA is also affected by the mass ratio of rGO and PMWCNT, exhibiting the highest ECSA of 32.5 m^2/g and the least reduction of ECSA after 1200 cycle by Pt/1rGO-1PMWCNT. The cell performance is enhanced by the hybridization with the best cell performance by Pt/1rGO-1PMWCNT. It is, therefore, desirable to choose the appropriate mass ratio of rGO and PMWCNT to maximize the electrochemical properties.

Introduction

Carbon nanomaterials have been extensively used as the supporting materials in electrochemical catalyst because of their cost competitiveness, high electrical conductivity, excellent durability and thermal stability. In particular, carbon nanomaterials have great potential in the field of fuel cells and hydrogen storage [1–5]. Fuel cells have received much attention as an eco-friendly alternative energy source. Among various fuel cells, the proton exchange membrane fuel cell (PEMFC) has been widely studied due to several advantages such as low operating temperature, high power density, and high energy conversion efficiency [6–9].

In PEMFC, platinum is most widely used as an electrochemical catalyst although it is expensive and highly

---

* *Corresponding author.*
E-mail address: whajungk@konkuk.ac.kr (W.J. Kim).

[1] Current address: Laboratory of Materials for Renewable Energy (LMER), Institute of Chemical Sciences and Engineering (ISIC), École polytechnique fédérale de Lausanne, EPFL Valais/Wallis, 1951, Sion, Switzerland.

[2] Co-first authors

https://doi.org/10.1016/j.ijhydene.2017.12.135
0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Please cite this article in press as: Yang HN, et al., 3-D structured Pt/rGO-polyethyleneimine-functionalized MWCNTs prepared with different mass ratio of rGO and MWCNT for proton exchange membrane fuel cell, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2017.12.135

vulnerable to CO at low operating temperature. The durability of catalyst is also an important issue in the economic point of view. Therefore, the catalyst supporting materials have become of importance in the aspect of the durability and catalytic activity. Carbon black (CB) has been most widely used as the platinum support materials [10,11] because it has a high electrical conductivity with hydrophobic property which is advantageous of discharging water generated from the oxygen reduction reaction (ORR) at cathode. However, its relatively low surface area has been pointed out in the aspect of catalytic activity and Pt utilization. More importantly, high vulnerability to oxidative corrosion during the operating condition could cause the Pt loss [12,13]. Due to these disadvantages of CB, many carbon materials such as carbon nanotubes (CNT) [14], fullerene [15], carbon molecular sieve (CMS) [16], and graphene [17] have received a spotlight as an alternative supporting material. Among them, CNT has high specific surface area, excellent electrical conductivity, durability and mass transfer ability [18,19]. However, CNT generally has a disadvantage of low catalyst loading rate due to surface inertness. Therefore, a proper surface functionalization is required to support the catalyst [20]. One of the other carbon materials, graphene has the advantages of having high catalyst loading due to its extraordinarily high surface area as well as excellent electrical conductivity [21]. However, graphene has the disadvantage of irreversible restacking due to van del Waals forces, which causes catalyst agglomeration and results in reducing catalytic activity [22–24]. Our previous work [25] demonstrated that carbon black was used as a spacer to prevent the restacking of graphene and to enhance the cell performance. To obtain the synergistic effect of graphene and CNT, several attempts have been tried for transparent conductors [26], electrode materials for lithium batteries [27] and supercapacitors [28]. Aravind et al. [29] demonstrated the facile synthesis of graphene/CNT composites by chemical vapor deposition for energy and sensing applications. More recently, Wang et al. [30] reported that the introduction of 1-D CNT into 2-D graphene sheet enhanced the electrochemical properties and methanol oxidation.

In this study, the reduced graphene oxide (rGO)-polyethyleneimine (PEI)-functionalized multiwall carbon nanotube (PMWCNT) composite materials with different mass ratio of rGO and PMWCNT were first hybridized using graphene oxide (GO) and PMWCNT to prevent the restacking of rGO. The Pt nanoparticles were then deposited on the 3-D structured rGO-PMWCNT composite material. The prepared Pt/xrGO-yPMWCNTs are applied to the PEMFC as an electrochemical catalyst. The electrochemical properties are investigated and the cell performance of the membrane electrode assembly (MEA) fabricated with these catalysts is evaluated and discussed.

Experimental

Synthesis of GO

GO is the intermediate step material; it was synthesized by modified Hummers method [10,11]. 4 g of graphite powder, 5 g of $K_2S_2O_8$ (99.0%, Sigma—Aldrich, USA), and 5 g of P_2O_5 (98.0%, Sigma—Aldrich, USA) were mixed with 80 ml of concentrated H_2SO_4 (95%, Samchun Chem. Co, Korea). This mixture was stirred at 80 °C for 2 h. Next, the mixture was cooled to room temperature for 12 h. Then, the mixture was diluted with 500 ml of deionized (D.I.) water and filtered 3 times, followed by overnight dry at 80 °C. This pre-oxidized graphite was reoxidized through one more oxidation process: that is, the treated graphite powder was first added to 100 ml of concentrated H_2SO_4. Then, 12 g of $KMnO_4$ (97%, Sigma—Aldrich, USA) was added to the mixture very slowly with stirring. This step was kept below 4 °C in ice-bath for 30 min until the color of mixture became dark blue. Subsequently, the mixture was stirred for 30 min at 40 °C, and then diluted with 100 ml of D.I. water. Then, the mixture was stirred for another 30 min at 80 °C. Finally, the reaction was terminated by the sequential addition of 600 ml of D.I. water, 20 ml of 30 wt% H_2O_2 (34.5% Samchun Chemical Co, Korea) solution and 100 ml HCl solution (5%, Samchun Chemical Co, Korea). The color of the mixture was then changed to brilliant yellow and sonicated for 4h at room temperature. GO was finally obtained by high-speed centrifugation and the mixture was neutralized by D.I. water and dried in vacuum oven at 60 °C for 12 h [25].

Functionalization of MWCNT by polyethyleneimine (PEI)

MWCNT (95.0%, Plasmachem, USA) was functionalized by PEI (Sigma—Aldrich, USA). MWCNT was dispersed in 0.4 wt% PEI aqueous solution and stirred for 24 h at 60 °C. Upon completion of stirring for 24 h, the solution was filtered and washed using D.I. water and finally dried at 60 °C in vacuum (hereinafter PEI-MWCNT is denoted as PMWCNT).

Preparation of 3-D catalyst support using GO and PMWCNT

Different amounts of as-synthesized GO and PMWCNT (GO/PMWCNT mass ratio = 1/3, 1/1 and 3/1) were dispersed in 10 mL D.I water for 3 h, respectively. The dispersed PMWCNT and GO were then mixed with a little 0.1 M HCl solution (35%, Samchun, Korea) and 200 mg vitamin C (99.9%, Sigma—Aldrich, USA) and the mixture was sonicated for 4 h. The mixture was stirred in oil bath for 12 h at 50 °C [31]. Finally the mixture was obtained and referred as GO-PMWCNT.

Pt deposition on rGO and PMWCNT support (Pt/rGO-PMWCNT)

Pt was deposited on GO-MWCNT by microwave treatment [32–35]. 100 mg of GO-PMWCNT was dispersed into the mixture of 48 ml EG (Samchun Chemical Co, Korea) and 12 ml isopropyl alcohol (IPA, Samchun Chemical Co., Korea) under 3 h sonication for complete dispersion. 160 mg of H_2PtCl_6 (Aldrich Co.) as the Pt precursor was added to 4 ml of EG solution and stirred for 3 h, which was then added to GO-PMWCNT dispersed solution and sonicated for 2 h to ensure perfect mixing. 1 M NaOH solution was added dropwise to the mixture to adjust pH to 12. The mixture was then irradiated in a household microwave oven (Samsung, RE-C21AW, operating frequency: 2450 MHz) at an output power of 700 W for 3 min.

Please cite this article in press as: Yang HN, et al., 3-D structured Pt/rGO-polyethyleneimine-functionalized MWCNTs prepared with different mass ratio of rGO and MWCNT for proton exchange membrane fuel cell, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2017.12.135