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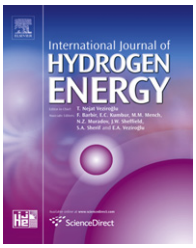

Graphene-multi walled carbon nanotube hybrid electrocatalyst support material for direct methanol fuel cell

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ABSTRACT

Nanostructured PtRu and Pt dispersed functionalized graphene–functionalized multi walled carbon nanotubes (PtRu/(*f*-G–*f*-MWNT)), (Pt/(*f*-G–*f*-MWNT)) nanocomposites have been prepared. Electrochemical studies have been performed for the methanol oxidation using cyclic voltammetry (CV) and chronoamperometry technique. Full cell measurements have been performed using PtRu nanoparticles dispersed on the mixture of functionalized graphene (*f*-G) and functionalized multi walled carbon nanotubes (*f*-MWNT) in different ratios as anode electrocatalyst for methanol oxidation and Pt/*f*-MWNT as cathode catalyst for oxygen reduction reaction in direct methanol fuel cell (DMFC). In addition, full cell measurements have been performed with PtRu/(50 wt% *f*-MWNT + 50 wt% *f*-G) and Pt/(50 wt% *f*-MWNT + 50 wt% *f*-G) as anode and cathode electrocatalyst respectively. With PtRu/(50 wt% *f*-MWNT + 50 wt% *f*-G) as anode electrocatalyst, a high power density of about 40 mW/cm^2 has been obtained, in accordance with cyclic voltammetry studies. Further enhancement in the power density of about 68 mW/cm^2 has been observed with PtRu/(50 wt% *f*-MWNT + 50 wt% *f*-G) and Pt/(50 wt% *f*-MWNT + 50 wt% *f*-G) as electrocatalyst at anode and cathode respectively. These results have been discussed based on the change in the morphology of the *f*-G sheets due to the addition of *f*-MWNT.

1. Introduction

Direct methanol fuel cell (DMFC) is attracting much attention and interest due to its potential application in portable and small devices. It has advantages like high power density, compact design and easy refueling [1,2]. Still there are some problems in commercialization of DMFC due to several reasons like slow reaction kinetics, methanol crossover and large electrode over voltage [3]. To reduce it, several factors need to be taken care of, from the catalytic activity like morphology and structure of catalyst layer to enhance catalyst utilization [4]. Several catalysts have been studied for methanol oxidation but till date PtRu is most efficient and widely studied, where Ru facilitates adsorption of dissociative water at low potential and promotes complete methanol oxidation on Pt surface [5]. Catalytic activity increases with the increase in reactive surface area of the catalyst particles which further depends on support material. Hence catalysts are supported on high surface area substrate having sufficient electrical conductivity which can also act as path for flow of electrons [6] with other properties like superb corrosion resistance and optimum pore size [7]. Variety of catalyst

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support has been studied in last decade ranging from vulcan carbon, black pearls, carbon black, fullerenes, carbon nanofiber and mesoporous carbon [8–12]. Researchers also reported the use of MWNT for catalyst application due to high electrochemical activity, high electrical conductivity and high mechanical strength [13–15]. Recently, platinum dispersed garphene catalysts using graphene oxide (GO) as a precursor for methanol oxidation has been discussed [16]. Besides, there are many research articles on DMFC about the use of nanotechnology as electrode materials [17,18].

Graphene, a single layer of carbon atoms arranged in honey comb structure has attracted tremendous attention in the recent years due to unique two dimensional structure, very high surface area and excellent transport properties [19,20]. It has been reported that graphene can be exfoliated by dispersing metal nanoparticles on its surface, which can be further used in catalysis, sensors, etc [21]. Xu et al. suggested the use of Pt coated graphene as catalyst support for DMFC [22]. However, the full use of graphene for DMFC applications has been unexplored till now. Graphene sheets prepared through the exfoliation of graphitic oxide leaves behind some defects and vacancies, and these defects can act as good anchoring sites for the deposition of metal nanoparticles which can be used for fuel cell applications, however, as-reduced graphene sheets tend to form irreversible agglomerates because of the van der Waals interactions and even restack to form graphite. In order to obtain graphene as individual sheets, attaching some molecules or polymers onto the sheets is an approach to reduce the aggregation. The attachment of inorganic particles, instead of organic materials, onto the graphene may not only prevent the restacking of these sheets during the chemical reduction process, but also lead to the formation of a new class of graphene-based nanocomposites. The restacking can be prevented by using metal nanoparticles (Pt, PtRu) and or CNTs as spacers which will result in the increase in the surface area thereby the enhancement in performance. It is anticipated that nanocrystalline PtRu and Pt dispersed graphene-carbon nanotube nanocomposites, which as a unique combination of 3D, 2D and 1D structure, have exceptionally high electrocatalytic activities toward methanol oxidation and oxygen reduction reaction in DMFC. In this paper, we describe the preparation of nanostructured Pt and PtRu dispersed functionalized graphene–functionalized multi walled carbon nanotubes (Pt/(*f*-G–*f*-MWNT) & PtRu/(*f*-G–*f*-MWNT)) nanocomposites and their performance as DMFC electrocatalysts. The main idea is to disperse PtRu nanoparticles on *f*-G and *f*-MWNT simultaneously with different ratios of *f*-G and *f*-MWNT and investigate their electrocatalytic activity under the direct methanol fuel cell operating conditions. The present work demonstrates the potential of 2D graphene – 1D carbon nanotube hybrid nanomaterials as catalyst support material for the dispersion of 3D nanocrystalline PtRu electrocatalysts for DMFC applications.

2. Experimental details

MWNT was prepared by the pyrolysis of acetylene over YNi_3 alloy hydride catalyst at the temperature of 700 °C. As-grown MWNT was purified by air oxidation and acid treatment for the removal of amorphous carbon and catalytic impurities respectively [14]. It was further functionalized to get hydrophilicity, for nanoparticles attachment by sonicating in conc. HNO_3 [23]. For the synthesis of graphene, graphitic oxide was first prepared by treating graphite with an oxidizing solution of sulfuric acid and nitric acid for 4 days and drying at 80 °C for 6 h. Thermal exfoliation of graphitic oxide was done in quartz tube at 1050 °C for 30 s [24]. Functionalization of graphene was done by sonicating graphene with a solution of conc. sulfuric acid and conc. nitric acid for 30 min. The functionalized MWNT and functionalized graphene are labeled as *f*-MWNT and *f*-G respectively. Pt and PtRu alloy nanoparticle dispersion on *f*-MWNT was done using the similar chemical reduction technique as explained in our earlier work [14]. For the synthesis of PtRu/(25 wt% *f*-MWNT + 75 wt% *f*-G), PtRu/(50 wt % *f*-G + 50 wt% *f*-MWNT) and PtRu/(75 wt% *f*-MWNT + 25 wt% *f*-G), about 1 g of the mixture of *f*-MWNT and *f*-G in the required ratio (1:3; 1:1; 3:1) was ultra sonicated in de-ionized water for 40 min and then magnetically stirred for 12 h. Required amount of 1% solution of $H_2PtCl_6.6H_2O$ and $RuCl_3$ was added to get 40 wt% PtRu loading. The Pt and Ru salts were reduced by slowly adding a reducing solution, which is a solution of 0.1 M $NaBH_4$ in 1 M NaOH. After completion of the reaction, the solution was washed, filtered and dried at 80 °C for 3 h. Dispersion of Pt and PtRu on the mixture of *f*-MWNT and *f*-G were done first by sonicatng the hybrid mixture for 40 min followed by magnetic stirring for nearly 12 h. Graphene sheets have the natural tendency of agglomeration due to van der Waals interaction, this treatment helps in reducing restacking [22]. PtRu were dispersed on this hybrid nanocomposite by adding precursor salts, namely mixture of $H_2PtCl_6.6H_2O$ and $RuCl_3$. Hsieh et al. [25] reported high performance of electrocatalyst PtRu in the atomic ratio of 1:1, hence salts for the dispersion of alloy catalysts are added to maintain the same atomic ratio. Pt/(50 wt% *f*-MWNT + 50 wt% *f*-G) was also prepared by the same procedure as mentioned above but $H_2PtCl_6.6H_2O$ alone was used instead of mixture of $H_2PtCl_6.6H_2O$ and $RuCl_3$. The above synthesized electrocatalysts were characterized by X-ray diffractometer (XRD), Transmission electron microscopy (TEM) and Energy dispersive X-ray Analysis (EDX).

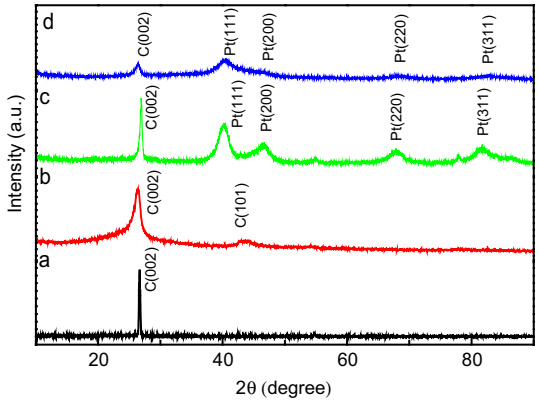

Fig. 1 – X-Ray diffractograms of (a) Graphene (b) MWNT (c) Pt/(50 wt% MWNT + 50 wt% graphene) and (d) PtRu/(50 wt % MWNT + 50 wt% graphene).