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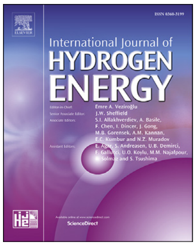

Proactive role of carbon nanotube-polyaniline conjugate support for Pt nano-particles toward electro-catalysis of ethanol in fuel cell

Abhishek De, Rajib Adhikary, Jayati Datta[*]

Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Howrah 711103, India

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ABSTRACT

Uniformly dispersed Pt over CNT-Pani hybrid support, shows considerable proficiency in energy conversion for ethanol electro-oxidation in acid medium. Thermal stability of the configuration was studied by thermo gravimetry while the functional moieties within the close packed composite structure were identified through FTIR spectroscopy. The size, shape and distribution of Pt NPs over the polymer modified CNT support were investigated through XRD and TEM analysis and the morphology was obtained from FESEM studies. The much improved functional property of Pt decorated CNT-Pani composite with respect to Pt over bare CNT, for direct ethanol fuel cell (DEFC), is attributable to the simultaneous effect of several promoting factors like creation of active electrochemical centers, charge tunneling and proton gliding within the composite structure, ensuring faster reaction kinetics and propagation of the reaction to considerable extent.

Introduction

Amongst the category of low temperature fuel cell, the direct ethanol fuel cell (DEFC) has emerged as one of the promising energy conversion devices that match with the existing fuel delivery infrastructure. DEFC is not only attractive for the ease of fuel feeding but at the same time, ethanol can be produced in abundance from the fermentation of biomass [1,2] as well as from the greenhouse gas like CO_2, as reported recently [3]. Pt is an automatic choice for the oxidation of the anodic fuel like H_2 and small organic molecules like methanol and ethanol due to the reasonably high oxidation exchange current densities and stability in acidic as well as in alkaline medium. Usually Pt nanoparticles (NPs) are decorated over carbon support for their use as fuel cell catalysts. However in course of comprehensive studies on electro-catalysis, the main constraints identified for carbon support relates to poor corrosion resistance, insufficient proton conductivity, agglomerated growth of NPs and exfoliation of the metallites at highly polarized conditions [4,5]. Particularly during the durability studies with the Pt based catalysts operating in polymer electrolyte membrane fuel cell (PEMFC), stability of support materials possess to be a major challenge in acid/alkali media.

Such impending situation has resulted in the upsurge of interest in investigating a variety of support materials like carbon nanotubes, ceramic/transition metal oxides, graphene, graphene oxides and also polymeric materials [16,41,42,47]. Carbon nanotubes (CNT) are no doubt attractive

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[*] *Corresponding author.*
E-mail address: jayati_datta@rediffmail.com (J. Datta).

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substrates in terms of their inherent pro-catalytic features like high conductivity, narrow distribution of metal NPs on the surface, creating extensive reaction centers, expanding the reaction zone for better electrode-electrolyte interactions and so on. Various efforts are made to develop potential electro-catalyst for alcohol oxidation by decorating metal NPs over CNT or modified CNT supports [6–11].

In this respect the polymeric materials like polyaniline (Pani), polypyrrole (Ppy) are known to stabilize the CNT matrix by forming a wrap-over, as well as act as capping agent for the metal NPs [12]. In fact the conducting polymers with conjugate structure, function as charge transfer channel in between the support materials and deposited metal NPs on the surface [13]. The growth of the Pt NPs is directly dependent on the geometry and chemical nature of the support materials as has been reported earlier [14,15]. Further, Pt–polymer interactions [16] have been reported for the study of poison tolerance in the fuel cell reactions. Polyaniline, in particular, has been reported as support materials for its promising stability, reversible acid doping/de-doping feature along with charge tunneling properties [42–44]. Polymer modified electrodes are also characterized for their stability towards electrode kinetics as reported in alcohol oxidation [17–19,33].

In view of the application potential of Pani and CNT as proactive support materials for electro-catalysis by their individual capacity, this investigation aims at the combinatorial approach for designing a hybrid structure of Pt NPs deposited CNT-Pani composite (CNT-Pani/Pt) to act as the energy efficient materials for DEFC. It may be noted that CNT-Pani composite material has been reported for sensor, supercapacitor applications as well as electrode material for microbial fuel cell [20–22]. In the present study Pt decorated CNT-Pani composite is used for the study of ethanol electro-oxidation. Few studies have been made on methanol and formic acid electro-oxidation using Pt deposited and Pani decorated CNT support [6,13,15,23–26]. However till date ethanol electro-oxidation has not been reported on such materials.

This article involves formulation of CNT-Pani combined structure by polymerization of aniline on the functionalized carbon nanotubes (FCNT) by chemical method at low temperature. Pt NPs are grown on the surface of CNT-Pani composite by borohydride reduction method. Subsequently the CNT-Pani/Pt composite matrix was subjected to physico-chemical characterizations, electron microscopy and a series of electrochemical techniques in order to validate their electro-catalytic activities toward the anodic reaction in DEFC. The extent of ethanol oxidation, vis-a-vis the catalytic performance was determined by quantifying the ethanolic intermediates formed during the reaction through ion chromatographic analysis.

Experimental

Synthesis of catalyst

Multiwalled CNT was functionalized with $-CO_2H$ group by refluxing with the 1:1 mixture of H_2SO_4 and HNO_3 for 4 hrs at 120° C and then centrifuged several times with distilled water to maintain the pH of the medium nearly neutral and finally dried at 100° C. The CNT-Pani composite was subsequently prepared by taking appropriate amount of the FCNT and the aniline monomer in acidic solution followed by oxidation with ammonium persulfate for 5 hrs, maintaining the temperature at 0–5 °C. After the completion of polymerization reaction, the precipitate is washed several times with distilled water and the dried at 60 °C. The Pt metallites were grown onto the CNT-Pani by $NaBH_4$ reduction of the Pt precursor salt as described in our earlier articles [16,27,28]. For comparative study Pt NPs were also deposited on mesoporous carbon and bare CNT and CNT-Pani by similar reduction procedure. The Pt catalyst loading was maintained around 40% on each of the support materials.

Materials characterization

The morphology of the catalyst matrices was studied by scanning electron microscopy (SEM) with a JEOL JSM-6700F FESEM microscope. X-ray diffraction (XRD) patterns were obtained with the help of SEIFERT 2000 diffractometer operating under CuK_α radiation ($\lambda = 0.1540$ nm) generated at 35 kV and 30 mA with the scans at 1^0 min^{-1} for 2θ values between 20 and 90°. Further the average particle size and distributions were determined through TEM analysis using JEOL JEM 2010 operated at an accelerating voltage of 200 kV. The catalyst matrices were subjected to FTIR spectroscopy by the help of a JASCO FT/IR-460 Plaus spectrophotometer operated with 4 cm^{-1} resolution in the range 4000 to 600 cm^{-1}. Thermogravimetric analysis (TGA) was carried out in ambient condition with the help of Netzsch STA 449C (Germany) within room temperature and 1000 °C at the heating rate of 5 °C/min. Electrochemical measurements were conducted using a computer controlled potentiostat/galvanostat with PG STAT 12 and FRA modules of Metrohm, Netherlands. A catalyst ink was prepared using 5 wt% Nafion solution and isopropanol to fabricate the electrode component. The working solutions containing 1 mol L^{-1} ethanol (EtOH) (AR grade, Merck, Germany) & 0.5 mol L^{-1} H_2SO_4 were purged with nitrogen gas (XL grade, BOC India Ltd.) for 30 min before starting each of the electrochemical experiments and the geometrical area of the electro-catalysts exposed to the solution was maintained at 0.65 cm^2.

Result & discussion

Fig. 1 shows series of SEM images of bare CNT, CNT/Pt and CNT-Pani/Pt catalysts at different resolutions. Fig. 1a shows the morphology of FCNT while Fig. 1b and c displays the low and high resolution images of Pt NPs deposited on CNT. In Fig. 1b, Pt NPs appears to be agglomerated in several regions. The morphological changes over the CNT surface after Pani enwrapping is clearly visible from Fig. 1e and f where Pt NPs are found to be more uniformly decorated over CNT-Pani composite than on the bare CNT support. Dimension of CNT before and after functionalization remains almost the same as shown in Fig. S1 in Supplementary Information. Fig. 2a represents TEM images of CNT/Pt catalyst, where clusters of Pt NPs are found to grow over the CNT surface while the

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