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Nitrogen containing carbon nanotubes as supports for Pt – Alternate anodes for fuel cell applications

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Abstract

Aligned nitrogen containing carbon nanotubes have been synthesized using Anodisc alumina membrane as template. Highly dispersed platinum nanoparticles have been supported on the nitrogen containing carbon nanotubes. Nitrogen containing carbon nanotubes as platinum catalyst supports were characterized by electron microscopic technique and electrochemical analysis. The EDX patterns show the presence of Pt and the micrograph of TEM shows that the Pt particles are uniformly distributed on the surface of the nitrogen containing carbon nanotube with an average particle size of 3 nm. Cyclic voltammetry studies revealed a higher catalytic activity of the nitrogen containing carbon nanotube supported Pt catalysts.

Keywords: Nitrogen containing carbon nanotubes; Template synthesis; Alumina template; Catalyst support; Methanol oxidation

1. Introduction

Since the last decade, fuel cells have been receiving an increased attention due to the depletion of fossil fuels and rising environmental pollution. Fuel cells have been demonstrated as interesting and very promising alternatives to solve the problem of clean electric power generation with high efficiency. Among the different types of fuel cells, direct methanol fuel cells (DMFCs) are excellent power sources for portable applications owing to its high energy density, ease of handling liquid fuel, low operating temperatures (60–100 °C) and quick start up [1,2]. Furthermore, methanol fuel cell seems to be highly promising for large-scale commercialization in contrast to hydrogen-fed cells, especially in transportation [3]. The limitation of methanol fuel cell system is due to low catalytic activity of the electrodes, especially the anodes and at present, there is no practical alternative to Pt based catalysts. High noble metal loadings on the electrode [4,5] and the use of perfluorosulfonic acid membranes significantly contribute to the cost of the devices. An efficient way to decrease the loadings of precious platinum metal catalysts and higher utilization of Pt particles is by better dispersion of the desired metal on the suitable support [6]. In general, small particle size and high dispersion of platinum on the support will result in high electrocatalytic activity. Carbon materials possess suitable properties for the design of electrodes in electrochemical devices. Carbon is an ideal material for supporting nano-sized metallic particles in the electrode for fuel cell applications. No other material except carbon material has the essential properties of electronic conductivity, corrosion resistance, surface properties, and the low cost required for the commercialization of fuel cells. In general, the conventional supports namely carbon black is used for the dispersion of Pt particles [7].

The appearance of novel carbon support materials, such as graphite nanofibers (GNFs) [8,9], carbon nanotubes (CNTs) [10–17], carbon nanohorns [18], and carbon nanocoils [19–22], provides new opportunities of

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carbon supports for fuel cell applications. Bessel et al. [8] and Steigerwalt et al. [9] used GNFs as supports for Pt and Pt–Ru alloy electrocatalysts and observed better activity for methanol oxidation. The high electronic conductivity of GNFs and the specific crystallographic orientation of the metal particles resulting from well-ordered GNF support were believed to be the important factors for the observed enhanced electrocatalytic activity. The morphology and the nature of the functional groups of the support influence the activity of fuel cell electrocatalyts [23–26]. Carbon with sulphur or nitrogen based functionality [25], can influence the activity of the catalyst.

The present report focuses on the efforts undertaken to develop unconventional supports based platinum catalysts for methanol oxidation. Nitrogen containing carbon nanotubes were used to disperse the platinum particles effectively without sintering and to increase the catalytic activity for methanol oxidation. The tubular morphology and the nitrogen functionality of the support have influence on the dispersion as well as the stability of the electrode. In this communication the preparation of highly dispersed platinum supported on nitrogen containing carbon nanotubes, the evaluation of the activity for the methanol oxidation of these electrodes and comparison with the activity of conventional electrodes are reported.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade. Polyvinyl pyrrolidone (Sisco Research Laboratories, India), dichloromethane and concentrated HF (both from Merck) were used. Hexachloroplatinic acid was obtained from Aldrich. 20 wt% Pt/Vulcan carbons were procured from E-TEK. Methanol and sulphuric acid were obtained from Fischer chemicals. The alumina template membranes (Anodisc 47) with 200 nm diameter pores were obtained from Whatman Corp. Nafion 5 wt% solution was obtained from Dupont and was used as received.

2.2. Synthesis of nitrogen containing carbon nanotubes

Pyrolysis of nitrogen containing polymers is a facile method for the preparation of carbon nanotube materials containing nitrogen substitution in the carbon framework. Nitrogen containing carbon nanotubes were synthesized by impregnating polyvinylpyrrolidone (PVP) inside the alumina membrane template and subsequent carbonization of the polymer [27]. Polyvinylpyrrolidone (PVP – 5 g) was dissolved in dichloromethane (20 ml) and impregnated directly in the pores of the alumina template by wetting method [28]. After complete solvent evaporation, the membrane was placed in a quartz tube (30 cm length, 3.0 cm diameter), kept in a tubular furnace and carbonized at 1173 K under Ar gas flow. After 3 h of carbonization, the quartz tube was cooled to room temperature. The resulting template with carbon–nitrogen composite was immersed in 48% HF at room temperature for 24 h to remove the alumina template and the nitrogen containing CNTs were obtained as an insoluble fraction. The nanotubes were then washed with distilled water to remove the residual HF and dried at 393 K.

2.3. Loading of Pt catalyst inside nanotube

Platinum nanoclusters were loaded inside the N-CNT as follows; the C/alumina composite obtained (before the dissolution of template membrane) was immersed in 73 mM H_2PtCl_6 (aq) for 12 h. After immersion, the membrane was dried in air and the ions were reduced to the corresponding metal(s) by a 3 h exposure to flowing H_2 gas at 823 K. The underlying alumina was then dissolved by immersing the composite in 48% HF for 24 h. This procedure resulted in the formation of Pt nanocluster loaded N-CNT and the complete removal of fluorine and aluminum was confirmed by EDX analysis.

2.4. Preparation of working electrode

Glassy carbon (GC) (Bas electrode, 0.07 cm^2) was polished to a mirror finish with 0.05 m alumina suspensions before each experiment and served as an underlying substrate of the working electrode. In order to prepare the composite electrode, the nanotubes were dispersed ultrasonically in water at a concentration of 1 mg ml^{-1} and 20 μl aliquot was transferred on to a polished glassy carbon substrate. After the evaporation of water, the resulting thin catalyst film was covered with 5 wt% Nafion solution. Then the electrode was dried at 353 K and used as the working electrode.

2.5. Characterization methods

The chemical composition of the nanotubes was determined by elemental analysis using Hereaus CHN analyzer after the removal of alumina template. The scanning electron micrographs were obtained using JEOL JSM-840 model, working at 15 keV. The nanotubes were sonicated in acetone for 20 min and then were dropped on the cleaned Si substrates. The AFM imaging was performed in air using the Nanoscope IIIA atomic force microscope (Digital Instruments, St. Barbara, CA) operated in contact mode. For transmission electron microscopic studies, the nanotubes dispersed in ethanol were placed on the copper grid and the