



Improved performance of PEM fuel cell using carbon paper electrode prepared with CNT coated carbon fibers

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ARTICLE INFO

Article history:

Received 1 July 2009

Received in revised form 30 July 2009

Accepted 30 July 2009

Available online 7 August 2009

Keywords:

Carbon fiber

Fuel cell

Power density

Polarization

Porosity

ABSTRACT

Porous conducting carbon paper has been identified as the most suitable material to be used as a backing material for the fuel cell electrode. The surface of carbon fiber, the major constituent of the carbon paper was modified by: (1) removing the functional groups by heat cleaning process and (2) coating the non-functionalized carbon fiber with multi-walled carbon nanotubes (MWCNTs). This has a marked influence on the fiber–matrix interactions during later stages of processing of carbon paper that helped in controlling its various characteristic properties. Using the carbon paper formed with CNT coated carbon fiber as electrode, the maximum power density achieved from a unit fuel cell was found to be 783 mW/cm² as compared to 630 mW/cm² when the paper was formed with normal fiber.

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1. Introduction

Fuel cells have gained attention in the last few years not only due to depleting energy resources but also due to growing concern about urban air pollution and consequent environmental problems. These are electrochemical cells that use hydrogen and oxygen/air as the fuel and oxidant respectively, generating energy and water as the only by-products. Because of their capability of directly converting chemical energy into electrical energy, they have high efficiency [1,2].

Among all the fuel cells PEM fuel cell is much preferred because of its high power density, favorable stability of cell voltage during lifetime, absence of corrosive liquid electrolyte, favorable efficiency and low operating temperature.

The electrode substrate also known as gas diffusion layer provides mechanical support for the electrocatalysts. It allows diffusion of gaseous reactants from the bulk flow streams to the reaction site within the catalyst layer and removal of the product water from the reaction site to the bulk flow streams. It transfers heat and electrons through the cells and maintains a uniform contact pressure between the catalyst layer and the matrix containing the electrolyte. Because of its critical role in fuel cell performance, much effort has been guided towards optimizing its properties [3–10]. Porous conducting carbon paper has been identified as the

most promising material as a GDL, not only because of its high conductivity that allows easy flow of electrons but also because of its fine porosity that allows uniform distribution of the reactant gases over its surface. The high mechanical strength of the carbon paper provides mechanical integrity to the MEA.

In their previous studies the authors have reported the process of making porous conducting carbon paper by first making carbon fiber preform by paper making technology followed by its subsequent impregnation with resin, compression molding and carbonization [9]. Because of the strong fiber matrix interaction during the curing and carbonization cycles (with the commercially available fibers), large volume shrinkage occurred along the thickness of the sample which not only resulted in the decrease in the porosity of the samples but also in a non-uniform pore size distribution (PSD). In the present study we report two different approaches of controlling the fiber–matrix interactions (and hence the porosity and pore size distribution) by modifying the surface of carbon fibers. In the first case by using surface cleaned carbon fibers along with the neat fibers (as received commercial fibers) in varying proportions, while in the second case the surface of the carbon fiber has been further modified by MWCNTs coating. References have been cited whereby CNTs have been effectively used as a catalyst support for better utilization of the later, which in turn leads to increased performance [11–15] and durability [16] of fuel cell. We report here significant improvement in the physical and electrical properties of the carbon paper (produced by this new technique), which in turn contributes to the enhanced performance of the fuel cell.

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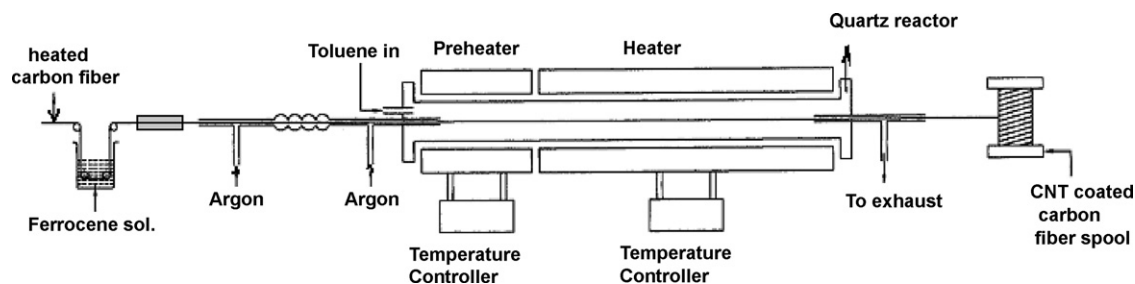


Fig. 1. Schematic of the experimental set up for the growth of MWCNT on carbon fiber surface by CVD technique.

2. Experimental

2.1. Preparation of carbon paper

PAN based T 300 carbon fiber chopped in 10 mm length was used as the starting material. The commercially available fiber is normally functionalized to make bonds with the resin and surface coated with thin layer of resin (0.1%) for better handling and wetting with any resin system. Different steps were taken at the initial stage to modify the fiber surface so as to influence the properties of the resulting carbon paper. Thus carbon fiber performs were prepared [9] with

- As received carbon fiber (commercially available), type A.
- Desized and heat treated carbon fiber, type B.
- Type B fiber coated with CNT, type C.

The type B carbon fiber was produced by heating the carbon fiber “type A” at 750 °C for an hour in an inert atmosphere. This fiber was then coated with nanotubes in a continuous manner using chemical vapor deposition (CVD) process. Ferrocene was used as the source of Fe catalyst whereas toluene was used as hydrocarbon source. The type B carbon fiber (with all sizing and functional groups removed) tow was passed through 12 wt% ferrocene solution and squeezed through a hole of diameter 1 mm, so that it is uniformly coated with ferrocene, prior to its entry into the CVD reactor (Fig. 1). The liquid feed solution (Toluene) is injected into the reactor at the rate of 7 ml/h through the capillary tube and carried to the reaction zone by the steady flow of argon. The flow rate of argon was maintained at 2 l/min, and the furnace temperature at 750 °C. At the exit end the fiber was collected onto a spool which in turn was connected to a motor that pulls the fiber tow. The pulling speed was adjusted to control residence time of the fiber in the effective reaction zone which was nearly 5 min. The amount of CNT growth was thus controlled. The SEM picture of the type C fibers clearly shows a uniform coating of MWCNTs on the fiber surface (Fig. 2). The amount of MWCNTs grown on the fiber surface was determined through thermal gravimetric analysis of the samples as discussed later in the text.

In the first set of experiments carbon fiber performs were prepared [9] using different vol. ratios of type A (as received) and type B (heat treated) carbon fibers, whereas in the second set of experiments the carbon fiber performs were prepared using different vol. ratios of type A and type C (CNT coated) carbon fiber. Fig. 2 (inset) shows the SEM of the carbon fiber perform processed with type C carbon fiber, indicating a strong anchoring of CNTs even after the processing.

The carbon fiber performs thus prepared were impregnated with phenolic resin (obtained from ‘IVP India Ltd.’) such that the ratio of reinforcement and the resin is 1:1 by volume. The impregnated performs were then molded into sheets by compression molding technique. Following molding, a post-cure is performed at 150 °C for 2 h in air to ensure full curing and cross-linking of

the binder material before carbonization. The samples so obtained were known as green samples. These were further heated to 2200 °C in an inert atmosphere with a heating rate of 900 °C/h [9,10].

In the following text the carbon paper samples formed with type A, type B and type C carbon fibers are referred to as a, b, and c respectively. The samples formed with different proportions of type A and type B fiber (3:1, 1:1, 1:3) are termed as b1, b2, b3 and those formed with different proportions of type A and type C fiber (3:1, 1:1, 1:3) are termed as c1, c2, and c3 respectively.

2.2. Characterization of the carbon paper

The electrical resistivity of the paper was measured using the four probe technique. Keithley 224 programmable current source was used for providing current. The voltage drop was measured by Keithley 197 A auto-ranging microvolt DMM.

The Flexural strength and modulus of the carbon paper samples were measured on the INSTRON machine model—4411 according to ASTM: D 1184-69. The stress strain curves along with the flexural strength of the samples were directly recorded from the software provided with the machine. Fractured surfaces of the individual samples were observed under the SEM, model Leo S-440.

The porous network was determined using mercury porosimetry analyzer (model: Poremaster (33/60), P/N 05060) obtained from Quantachrome Instruments, USA. In this method, mercury (Hg) with its very high surface tension ($4.80 \times 10^{-5} \text{ J cm}^{-2}$) is forced into the pores of the sample. The amount of Hg uptake as a function of pressure allows one to calculate the total porosity as well as the pore size distribution.

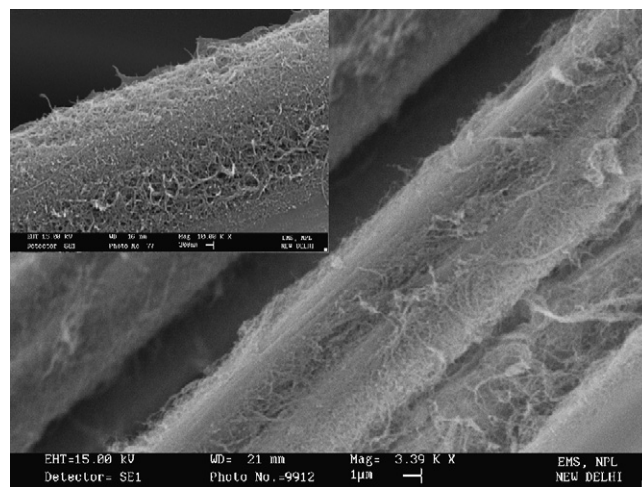


Fig. 2. SEM image of the surface of type C carbon fibers. Inset showing SEM image of the carbon fiber performs prepared with type C carbon fiber, indicating a strong anchoring of MWCNTs with the carbon fiber surface.

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