

Fabrication of Graphite/PTFE Based Electrodes for Proton Exchange Membrane Fuel Cell

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ABSTRACT

Fuel cells are a promising energy source on account of their high efficiency and low emissions. Proton exchange membrane fuel cells (PEMFC) are clean and environmental-friendly power sources, which can become future energy solutions especially for transport vehicles. They exhibit good energy efficiency and high power density per volume. Working at low temperatures ($<90^{\circ}\text{C}$), hydrogen fuelled proton exchange membrane fuel cells (PEMFCs) are identified as promising alternatives for powering autos, houses and electronics. At the middle of the proton exchange membrane (PEM) fuel cell is the membrane electrode assembly (MEA). The MEA consists of a proton exchange membrane, catalyst layers, and gas diffusion layers (GDL). However, most of the researchers have already mentioned that PEMFC are not competitive enough to rechargeable lithium ion battery with respect to price because of the rare metal used such as platinum in it. Presence of platinum in PEM fuel cells is one of the reasons why fuel cells are excluded from commercialization. Therefore, reducing the amount of platinum used in fuel cells is very important for their commercialization. The catalyst layer of a PEM fuel cell is a porous mixture of polymer, carbon, and platinum. The characteristics of the catalyst layer play a critical role in determining the performance of the PEM fuel cell. In this work, we develop modified Graphite/ polytetrafluoroethylene (PTFE) based electrodes for PEMFC. Graphite owing to its conductivity, corrosion resistance and easy machinability, is the preferred material in the system. For adherence of the graphite powder on the electrode we use N-methyl pyrrolidone medium. Then PTFE dispersion are heated to 80°C and added with chemically treated graphite powder and this paste is coated on the electrode. Carbon-fluorine (C-F) bonding in Teflon (PTFE) is very strong as compared to the other organic bonds; therefore it is quite difficult to break. Also, smaller size of fluorine atom makes it difficult to exchange the electrons for the formation of multiple bonds. This property of PTFE is used to enhance the overall functionality of the fuel cell and hence decrease the amount of platinum catalyst used.

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INTRODUCTION

There is a need for secure, reliable and affordable energy supplies for global economic stability and growth. Future energy demand and supplies are subjected to numerous uncertainties, most of which are difficult to predict such as energy prices, global economic growth rate, demographic changes, technological advances, government policies and consumer behavior. Regular consumption of petrol based fuels has not only caused pollution but has also harmed the environment to a great extent [1]. Looking at the current scenario of energy consumption it is vital to focus towards the use of renewable source of energy like fuel cell, solar energy etc. [2]

There has been an increasing interest in fuel cells as they are cleaner sources of energy [3]. Amongst the various types of fuel cells, Proton exchange membrane fuel cells are considered as promising alternatives especially for application in transport sector [4]. However, these are considered to be

environment friendly energy source as the end product is water but on the other hand high cost of fuel cell is a very important issue. Fuel cell stacks costs from 2500-5000 \$/KW as compared to 25-50 \$/KW for the present internal combustion engines [5]. Major challenges at present are to bring the overall cost of fuel cell down to limits so that it can become commercially viable. Nafion membrane and platinum catalyst are the main culprits for making the fuel cell expensive [6]. It is believed that in the forthcoming future fuel cell will have a high impact on the developing nations and global balance of power as these nations may directly move to non-polluting hydrogen economies instead of the oil application phase.

PEMFC uses hydrogen and oxygen as its fuels [7]. The Nafion membrane used is sulfonated tetrafluoroethylene based fluoropolymer-copolymer whose unique proton conducting abilities are key success for functioning of the fuel cell. The MEA is at the heart of the fuel cell which comprises of the Nafion membrane sandwiched between two electrodes which

can be of carbon cloth or carbon paper [8]. Carbon paper is preferred over carbon cloth due to water management problem associated with it. Choice of the appropriate fuel cell components is very crucial as it affects the overall performance. Both these gas diffusion layers offer different porosity, conductivity, hydrophobicity and mass transport properties but carbon paper is brittle and should be handled carefully. In addition to this they also require higher compression forces. The carbon cloth on the other hand is thicker and more compressible which affects the stack size of a fuel cell and therefore these parameters should be kept in mind before choosing the suitable gas diffusion layer [9, 10, 11]. The fabrication cost of membrane electrode assemblies can be reduced by [12]:

- 1). Reducing the amount of platinum loadings on gas diffusion layers.
- 2). Using any other alternative catalyst.
- 3). Using high temperature membranes like polybenzimidazole (PBI).

In the present investigation an attempt has been made to reduce the amount of platinum loading in order to bring down the overall cost. The gas diffusion layers are coated with PTFE and the modified graphite. As we know that graphite is an allotrope of carbon which is known for its multi layered sp^2 hybridized carbon sheet. Single atomic layer of graphite layer is known as graphene and it can be prepared by various techniques like chemical method, thermal reduction or electrochemical method [13]. Carbon-fluorine (C-F) bonding in Teflon (PTFE) is very strong as compared to the other organic bonds therefore it is quiet difficult to break. Also, due to smaller size of the fluorine atom, it is difficult to gain or lose electron so as to form multiple bonds. This property of PTFE is used to enhance the overall functionality of the fuel cell and hence decrease the amount of platinum catalyst used [14, 15, 16, 17, 18].

EXPERIMENTAL

1. Objectives and Experimental Setup

The following objectives were set for the present work:

- Fabrication of the membrane electrode assembly by using commercially available platinum black (Adams catalyst) as the catalyst.
- Decrease the amount of platinum loading on the gas diffusion electrode by coating it with modified graphite and polytetrafluoroethylene (PTFE) without compromising in performance
- To bring down the cost of a fuel cell unit

1.1. Experimental Setup

The experimental setup used for the current investigation consisted of High precision water bath, Convective heater, Centrifuge etc. All the apparatus used were first calibrated and then used for the fabrication.

2. MATERIALS

Graphite powder was used as a precursor for modified graphite, phosphoric acid, sulphuric acid, hydrogen peroxide, dichloromethane, acetic anhydride; Platinum black catalyst was purchased from Aldrich and was used without any further purification. PTFE dispersion was obtained from DuPont. Double distilled water was used during the processing. Other materials include screws, 5% Nafion solution in methanol, Stainless Steel (SS) sheet, graphite plates, NRE-212-10 Nafion rolls, carbon cloth.

3. PROCEDURE

3.1. Treatment of Nafion Membrane

Five units of Nafion of 5*5 cm were cut down from 30*30 cm sheet. All Nafion-212 membranes were first cleaned with distilled water in a water bath at 80-90°C (Fig 1), followed by heating in 5% H_2O_2 for 1 hour at 70-80°C (Fig 2) to remove organic impurities. It was then heated in 0.5 M H_2SO_4 for 1 hour at 70-80°C. The H_2SO_4 was removed by repeated washing in boiled water. The membrane was stored overnight in the dark in distilled water. Membranes were scooped out of the beaker and allowed to cool on clean glass plate. During the entire above mentioned procedure no metallic object was allowed to come in contact with any one of the prepared solutions.



Fig 1. Hot water bath treatment



Fig 2. Treatment of Nafion membrane using peroxide bath

3.2. Treatment of Carbon Cloth

Twenty pieces of carbon cloth 3*3cm were treated in a manner as stated below:

1. Sulphonised graphite powder, water, isopropyl alcohol, Nafion dispersion were mixed using magnetic stirrer for 30 minutes.
2. Dispersion was made which had the same composition as above but isopropyl alcohol/water was replaced by N-methyl pyrrolidone.

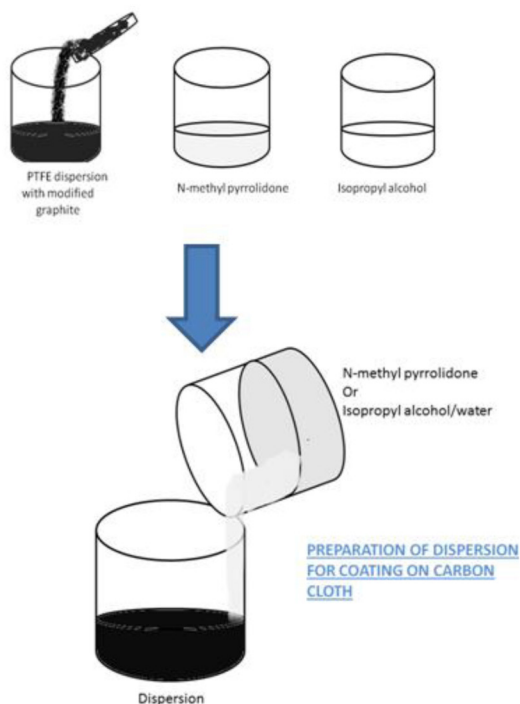


Fig 3. Preparation of dispersion for coating

Although they are used for the same purpose but the key difference is regarding the stability of the dispersion which was observed in the latter one. The viscous mixtures were coated on the carbon cloth using brush coating method and then dried for one day. The modified graphite preparation is described below in 3.2.1.

The membranes once completely dried were stored in a plastic zip pouch to prevent from contamination. The GDL was then further modified using platinum catalyst. The catalyst loading opted was 0.25 mg/cm² for cathode while it was 0.15mg/cm² anode. Nafion solution and iso-propyl alcohol and PTFE were mixed (Fig 3), then addition of platinum catalyst was done to the solution and coated on to the diffusion layer with the help of non-metallic brush and was dried in an oven at 80°C to remove water and iso-propyl alcohol.

Preparation of Sulphonized Graphite

Preparation of Graphite Oxide

An aqueous suspension of graphite oxide was synthesized from natural graphite powder using improved Hummer's method. In this process, the natural graphite powder (3 gm) was dispersed in a 13:3 mixture ratio of concentrated H₂SO₄/H₃PO₄ (325:75 ml) at room temperature and the mixture was kept in an ice bath. Initially, the system was set to a temperature below 15°C. Then, KMnO₄ (40 gm) was added very slowly so that the temperature of the mixture does not reach beyond 30°C. Keeping the temperature low, the suspension was stirred for 30 hours. Distilled water (100 ml) was added very gradually, maintaining the temperature below 50°C. The mixture was stirred for 1 hour by the addition of a large amount of de-ionized water (500 ml). Subsequently, addition of 30% H₂O₂ solution (20 ml) to the above mixture caused violent effervescence and temperature was increased to 50°C, after which the color of the suspension changed from dark brown to bright yellow. The graphite oxide (GO) suspension was centrifuged (4000rpm, 50min) and the supernatant was decanted away. The remaining solid material was then washed twice in succession with 200 ml of water, 200 ml of 30% HCl, and 200 ml of ethanol in order to remove metal ions. For each wash, the mixture was centrifuged (4000 rpm for 50 min) and the supernatant decanted away. The paste collected was dried at 80±5°C in a vacuum oven [19, 20, 21, 22, 23].

Graphite oxide to sulphonized graphite

Acetyl sulphate solution was prepared first. This solution was prepared by mixing dichloromethane and acetic anhydride under inert atmosphere (N₂). The solution was cooled to 0°C and 95-97% sulphuric acid was carefully added. This reaction mixture was stirred until a homogeneous and clear solution was obtained at room temperature. The acetyl sulphate was freshly prepared prior to each sulphonation reaction [24, 25, 26, 27].