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Experimental Investigation of Proton Exchange Membrane Fuel Cells Operated with Nanofiber and Nanofiber/Nanoparticle

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Abstract**—**Nanofibers are defined as fibers with diameters less than 100 nanometers. In this study, behaviours of activated carbon nanofiber (ACNF), carbon nanofiber (CNF), polyacrylonitrile/ carbon nanotube (PAN/CNT), polyvinyl alcohol/nanosilver (PVA/Ag) in proton exchange membrane (PEM) fuel cells are investigated experimentally. This material was used as gas diffusion layer (GDL) in PEM fuel cells. In this study, the electrical conductivities of nanofiber and nanofiber/nanoparticles have been studied to understand their effects on PEM fuel cell performance. According to the experimental results, the maximum electrical conductivity performance of the fuel cell with nanofiber was found to be at PVA/Ag (at UConn condition). The electrical conductivities of CNF, ACNF, PAN/CNT are lower for PEM. The resistance of cell with PVA/Ag is lower than the resistance of cell with PAN/CNT, ACNF, CNF.

Keywords**—**Proton exchange membrane fuel cells, electrospinning, carbon nanofiber, activate carbon nanofiber, PVA fiber, pan fiber, carbon nanotube, nanoparticle, nanocomposites.

I. Introduction

PROTON exchange membrane fuel cell technology has advanced significantly in the last 20 years. Membranes based on (perfluorinated, sulfonic acid containing) PFSA ionomers are being used in systems for commercial applications such as portable and back-up power. These markets can be successful with today's *technology* while other markets such as stationary residential power, micro electronics applications, and automotive power systems will all require additional advances in membrane technology. Significant research is underway in many laboratories around the world to address the need for membranes with improved durability, higher conductivity, and the ability to operate at higher temperatures (>100°C) without the need for external humidification of the reactant gases. Some of the strategies being employed are based on improving existing PFSA technology by incorporating new side chain structures, stabilizing end groups, or incorporating reinforcements, while other approaches are based on the development of new membrane technology such as sulfonated hydrocarbon membranes, proton conducting additives, or polymers with acid groups other than sulfonic acids. For any of these approaches to be successful the membrane will have to meet the performance, cost, and durability targets for the desired application [1].

Reference [2] shows that nafion nanofibers can be used for new design of high power density PEM fuel cells. Reference [3] reported the porous structure allows polybenzimidazole (PBI) to achieve a higher doping level and enhanced proton conductivity. Reference [4] carried out a study on super capacitance from cellulose and carbon nanotube nanocomposite fibers. They noted that the incorporated multiwalled carbon nanotube (MWNTs) reduce the activation energy of the oxidative stabilization of cellulose from ~230 to ~180 kJ mol^{-1}. The nanotubes also increased the crystallite size, structural order and the electrical conductivity of the resultant the activated carbon nanofibers (ACNFs). The specific surface area of the ACNFs increased from ~870 to ~1120m^2 g^{-1} upon the addition of 6% of MWNTs due to a rougher surface. The ACNFs were activated in a steam/argon flow and used as the electrodes of a super capacitor. The specific capacitance has been found to be ~105 and ~145 F g^{-1} at a current density of 10 A g^{-1} for the pristine ACNF and the 6% MWNT/ACNF, respectively. The improvement in capacitance of the MWNT/ACNF compared to the pristine ACNF is thought to be due to the increased surface area and electrical conductivity. Reference [5] carried out a study on activated carbon nanofiber produced from electrospun polyacrylonitrile nanofiber as a highly efficient formaldehyde adsorbent. They observed the potential of the novel ACNFs in the practical application, that is, as a membrane filter in forced-air-circulation-system was proved.

In this study, performances of nanofiber and nanofiber/nanoparticles are investigated experimentally on PEM fuel cell. The performance of PEM fuel cell with the PVA/Ag is more higher.

II. Electrospinning Theory and Process

Electrospinning is a unique approach using electrostatic forces to produce fine fibers. Electrostatic precipitators and pesticide sprayers are some of the well known applications that work similarly to the electrospinning technique. Fiber

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production using electrostatic forces has invoked glare and attention due to its potential to form fine fibers. Electrospun fibers have small pore size and high surface area. There is also evidence of sizable static charges in electrospun fibers that could be effectively handled to produce three dimensional structures. Polymer solution or the melt that has to be spun is forced through a syringe pump to form a pendant drop of the polymer at the tip of the capillary. High voltage potential is applied to the polymer solution inside the syringe through an immersed electrode, thereby inducing free charges into the polymer solution. These charged ions move in response to the applied electric field towards the electrode of opposite polarity, thereby transferring tensile forces to the polymer liquid. At the tip of the capillary, the pendant hemispherical polymer drop takes a cone like projection in the presence of an electric field. And, when the applied potential reaches a critical value required to overcome the surface tension of the liquid, a jet of liquid is ejected from the cone tip [6]. Various polymers have been successfully electrospun into ultrafine fibers in recent years mostly in solvent solution and some in melt form. Potential applications based on such fibers specifically their use as reinforcement in nanocomposite development have been realized [7]. Schematic diagram of the electrospinning experimental setup is shown in Fig. 1 [8].

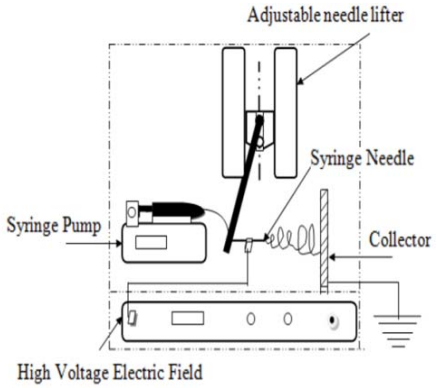


Fig. 1 Schematic diagram of the electrospinning experimental setup

III. Electrical Conductivity Measurements

It is well known that one of the subatomic particles of an atom is the electron. The electrons carry a negative electrostatic charge and under certain conditions can move from atom to atom. The direction of movement between atoms is random unless a force causes the electrons to move in one direction. This directional movement of electrons due to an electromotive force is what is known as electricity. Electrical conductivity is a measure of how well a material accommodates the movement of an electric charge. It is the ratio of the current density to the electric field strength. Electrical conductivity is a very useful property since values are affected by such things as a substances chemical composition and the stress state of crystalline structures [9]. In this study, the electrical conductivity testing was performed by using the Florida Solar Energy Center procedure and the electrical conductivity value was calculated using (1):

$$\sigma = \frac{d}{RA}\ (S/cm) \tag{1}$$

where d is the sample thickness, A is the area of electrode and R is the resistance offered by the sample, which is estimated from the I–V data [10].

In this study, the electrical conductivity of one layer CNF, the electrical conductivity of one layer ACNF, the electrical conductivity of PAN/CNT and the electrical conductivity of PVA/Ag are shown in Table I. The maximum electrical conductivity value is obtained 2.19×10^{-5} Scm^{-1}.

TABLE I
Electrical Conductivity (at UConn Condition)

Material name	Electrical Conductivity, Scm^{-1}
ACNF	1.22×10^{-10}
CNF	7.73×10^{-10}
PAN/CNT	2.16×10^{-10}
PVA/Ag	2.19×10^{-5}

IV. Experimental Study

The present study on experimental investigation of proton exchange membrane fuel cell operated with nanofiber and nanofiber/nanoparticle is carried out for the best performance. In this study, nanofibers and nanofibers/nanoparticles have been used as GDL. GDLs are in four different features have been prepared. These are presented below.

Cell # 1

- Anode GDL : Carbon paper Toray+ACNF
- Cathde GDL : Freudenberg C4

Cell # 2

- Anode GDL : Freudenberg C4+CNF
- Cathode GDL : Freudenberg C4

Cell # 3

- Anode GDL : 10 BC+ PAN/CNT
- Cathode GDL : Freudenberg C4

Cell # 4

- Anode GDL : 10 BC+ PVA/Ag
- Cathode GDL : Freudenberg C4

A. Equipment (Fuel Cell Assembly for 25 cm^2)

The preparation of experimental systems and the fuel cell testing is performed by using the University of Connecticut School of Engineering Center for Clean Energy Engineering procedures [11]. Expanded view of PEM fuel cell hardware is shown in Fig. 2.

A catalyst coated membrane (CCM) (Gore PRIMEA) consisting of:

- A piece of membrane
- A cathode catalyst layer, active area of 50-cm^2
- An anode catalyst layer, active area of 50-cm^2.
- Teflon films for protection as a gasket
- Anode and cathode end plates
- Anode and current collectors
- Single serpentine 25 cm^2 graphite bipolar flow field plate (anode side)

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- Triple serpentine 25 cm^2 graphite bipolar flow field plate (cathode side)
- 8 bolts for the connection of anode and cathode end plates
- Krytox (Dupont performance lubricants, Teflon Grease)
- Deionized water and ethanol for washing.

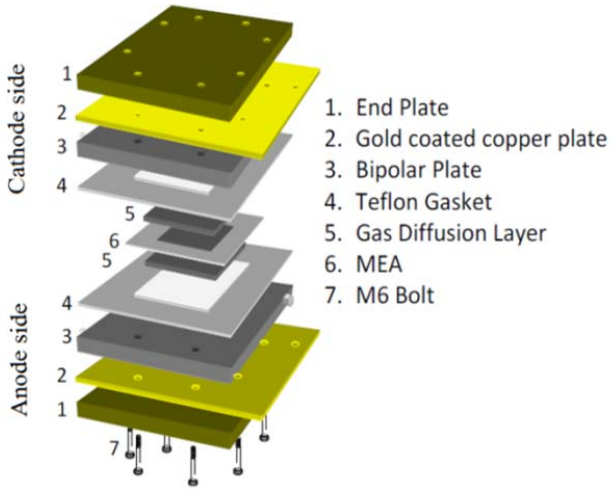


Fig. 2 Expanded view of PEM fuel cell hardware [11]

B. Cell Test

The experimental setup used in this study is shown in Fig. 3. The details of experimental study are presented below.

- Set Purging Flow Rate

For 25 cm^2 active area fuel cells, set flow rates at 250/250 sccm for anode/cathode with nitrogen

- Set Temperature
  - Set cell temperature at 40°C
  - Set anode and cathode gas lines at 60°C
  - After gas lines temperature reaches the setting point, set anode and cathode humidifier temperature at 50°C
  - Change set points to the Cell/Anode Humidifier/Cathode Humidifier to 80/80/73°C:
- Set cell temperature at 80°C
- Set anode and cathode gas lines at 90°C
- On the test panel, set anode humidifier controllers at 80°C (100% R.H.)
- On the test panel, set cathode humidifier controllers at 73°C (75% R.H.)
- After the temperatures reach the set points, switch the anode gas valve to H_2 and switch the cathode gas valve to nitrogen (or make sure the cathode supplying gas is nitrogen). Then press the button in the software "Apply Fuel"
- Wet up the cell
- Set Flow Rates
  - Set Working Flow Rates at:
  - Anode : Minimum Flow: 200sccm
  - Load based flow: 0 sccm /A/cell +13.95 sccm/A/cell(for 2 stoichiometry of H_2)
  - Cathode: Minimum Flow: 200 sccm
  - Load based flow: 0 sccm/A/cell+ 33.2 sccm/A/cell (for 2 stoichiometry of air)
- Switch the anode gas valve to H_2 and switch the cathode gas valve to air. Wait until the cell voltage (which is the open circuit voltage at this point) stabilizes. (~ 3 minutes). Then record the exact open circuit voltage.

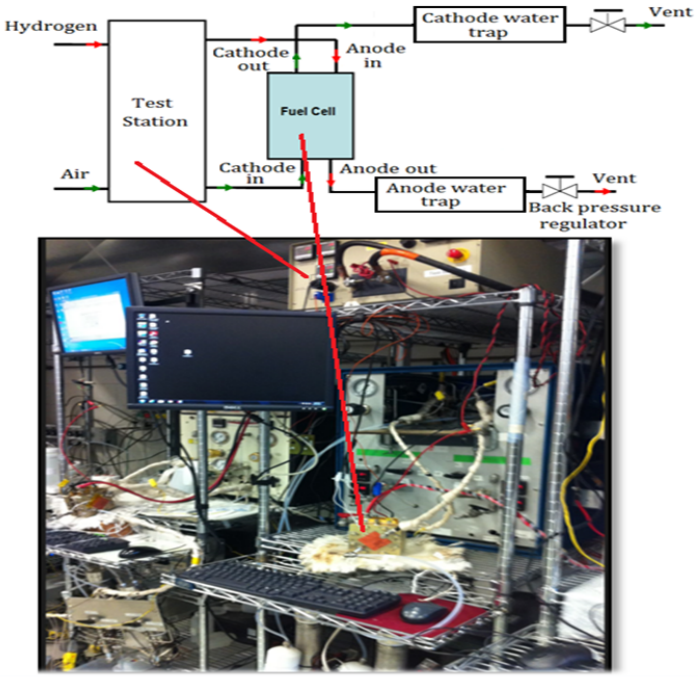


Fig. 3 The experimental setup

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V. Conclusions and Comments

In this study, performance of PEM fuel cell was experimentally investigated. The parameter of performance is current. The maximum current value was obtained 10 A for Cell # 4 (Table II). SEM images of nanoparticle-nanofibers (PVA/Ag) were taken in SEM device (Fig. 4). The electrochemical oxidation has increased when the effect of increasing voltage was taken into account for PVA/Ag (Fig. 5).

TABLE II
Cell Performances

Cell No	Cell # 1	Cell # 2	Cell # 3	Cell # 4
Current (A)	1	0.1	0.2	10

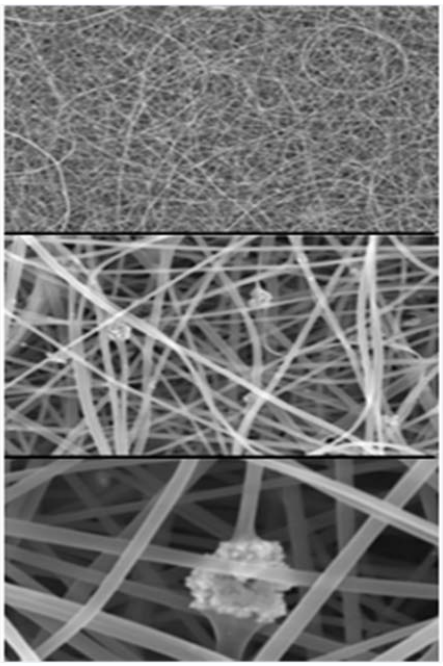


Fig. 4 SEM image of PVA/Ag

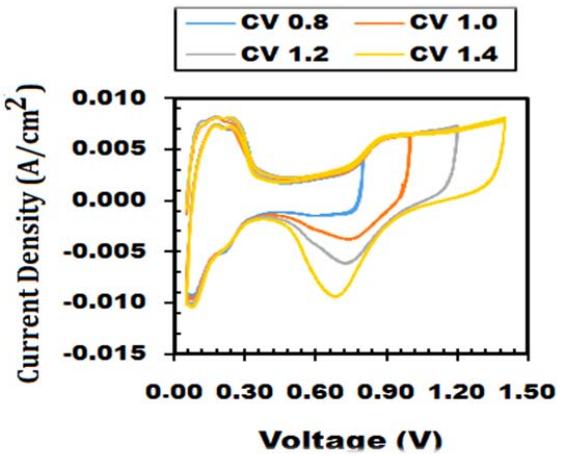


Fig. 5 Cyclic voltammetry (CV) for PVA/Ag: The scan rate and were 20 mV/s and 0.05-1.4 V, respectively

Micromeritics BET was used for adsorption of freudenberg C4, desorption of freudenberg C4, pore diameter of freudenberg C4, pore volume of freudenberg C4, pore area of freudenberg. Freudenberg C4 is GDL for cathode side. The results characterization of freudenberg C4 is as follows. The quantity absorbed has increased when the effect of increasing relative pressure was taken into account. According to the BET results, maximum value of quantity adsorbed is obtained as P/Po= 1.0 (Fig. 6).

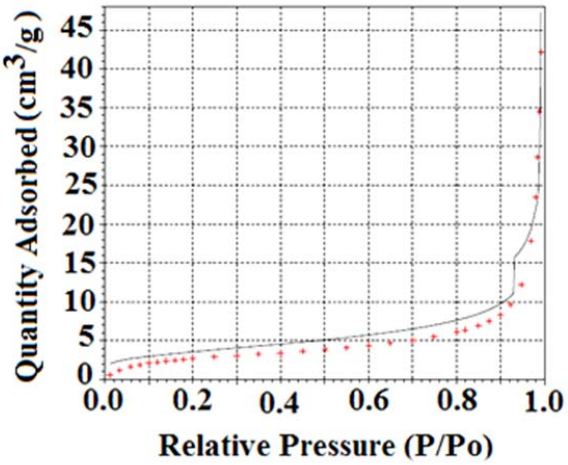


Fig. 6 Variation of quantity adsorbed performance of the freudenberg C4 with relative pressure

With this study, it was found that while the pore volume (PV) is at minimum value at PV=0.012 cm^3/g, it shifts to maximum value at pore diameter=1700 À (Fig. 7).

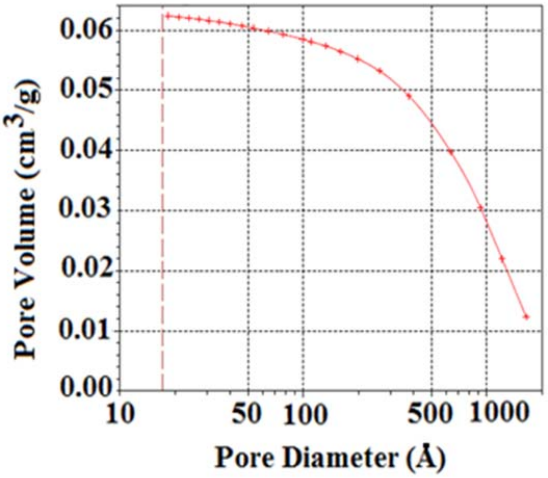


Fig. 7 Variation of pore volume performance of the freudenberg C4 with pore diameter

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