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Title: Highly Mesoporous Carbon Aerogel as Catalyst Support in Proton Exchange Membrane Fuel Cells
Category: Energy: Sustainable Materials & Design

Proton exchange membrane fuel cells (PEMFC) have recently seen interest as a prospective new energy conversion system [1]. The development of alternative energy sources has been of focus to decrease the emission of greenhouse gases from the burning of fossil fuels [2-4]. The fuel cell's applications are diverse, ranging from transport, stationery, medical, and more [5-6]. PEMFCs can be utilized as efficient chemical converters especially in transport vehicles, which is largely attributed to their high efficiency, high power density, and low operating temperature [7-10]. The cell's primary component is the MEA, which includes a membrane and electrodes, which facilitates the chemical process of the oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR) [11]. Some challenges need to be addressed to further enhance the fuel cell's potential in the scientific community, though, including its lower durability and higher cost compared to their combustion engine counterparts. One method of mitigating these issues is to utilize supported catalysts with lower noble metal loadings.

Carbon materials possess unique structural and electrical properties which make it suitable for use as a catalyst support in PEMFC. A high mesopore volume is desirable in catalyst support to ensure contact between the catalyst metal and the electrolyte. A number of carbon supports have been investigated, such as carbon black, carbon nanotubes, graphenes, and carbon aerogels. Carbon black, in particular, is a widely used catalyst support due to its cheap cost of production and wide availability. However, its high micropore volume, disorganized mechanical structure, and low conductivity all contribute to poor performance in PEMFC by limiting the diffusion of reactants and products. Thus, carbon black does not make efficient use of the precious metal catalyst and negates its cheaper price. Carbon nanotubes and graphenes have better electrical conductivity but are not suitable for commercialization due to their high manufacturing costs. Difficulty in platinum impregnation has also been observed in these materials. Carbon aerogels have been proposed as efficient catalyst supports due to its high electrical conductivity, high surface area, and tunable mechanical structure.

One of the challenges with commercializing hydrogen fuel cell cars is the price. On average, a fuel cell car costs $60,000, and within the fuel cell, 50% of the cost is dedicated to the platinum catalyst material. High performance and low-cost PEMFC that reduces the use of platinum will bring down the price of the hydrogen car dramatically, making it more accessible to the public.

According to the United States Environmental Protection Agency, motor vehicles cause 75% of carbon monoxide pollution and 27% of greenhouse gas emissions in the US. In contrast to a normal gasoline car that creates pollution, a hydrogen car simply outputs water. By bringing down the price of hydrogen cars and making it more accessible to the public, hydrogen cars will replace gasoline cars, ultimately removing a major source of pollution and moving us a step towards a greener earth.

Activated carbon aerogel based catalysts are novel methods used in applications in hydrogen fuel cells. Several papers have documented its use in supercapacitors and microbial fuel cells. However, the microporous properties of the activated carbon aerogels make them unsuitable for use in PEMFC. A new synthesis method is thus engineered to help further increase mesopore volume, a parameter deemed significant for PEMFC catalyst improvement supported by previous research.

Synthesis of carbon aerogel has four major steps: gelation, aging, drying, and carbonization. The conventional drying method utilizes supercritical fluid drying to maintain the pore structure and

mesoporosity while removing the solvent. However, supercritical drying requires the use of several expensive components which drives up the cost of production. Alternative drying methods have been observed such as freeze-drying and template-based method. Yet, these methods involve numerous chemical processing techniques and result in high density, microporous carbon aerogels. Furthermore, previous research has shown that these methods also yield low electrochemically active surface areas, resulting in low support conductivity and fuel cell performance.

In this research, an efficient yet inexpensive synthesis method of carbon aerogel and activated carbon aerogel as catalyst support for PEMFC will be devised using ambient drying to reduce the costs as an alternative to the traditional supercritical-drying process.

3.08 g of resorcinol and 0.016 g of sodium carbonate is dissolved in 50.4 mL of water. The mixture is magnetically stirred for 20 minutes. 0.51 mL of 37% wt formaldehyde solution is added to the mixture and stirred for an additional 5 minutes. Similar batches of resorcinol-formaldehyde gels are created at a resorcinol/catalyst ratio of 100, 200 and 300. The mixture is heated in a sealed container at 50 °C for 24 h and 85 °C for 48 h. The R-F gel is washed with excess amounts of acetone, solvent exchanging every 24 h. The gel is then dried in a vacuum oven at 100 °C.

The organic gel is carbonized and activated in a Lindberg Blue M Tube Furnace. Equal amounts of organic R-F aerogel are loaded into two ceramic boats. Both boats are carbonized under an N_2 atmosphere at 800 °C for 2 h at a heating ramp of 10 °C/min. After pyrolysis, the furnace is allowed to cool to 300 °C. The three batches of different R/C ratio carbon aerogels are compared to find the highest mesopore volume. The most optimal batch of carbon aerogel is further activated under CO_2 atmosphere at 900 °C for 2 h at a heating ramp of 10 °C/min.

The carbon is ground to obtain a fine powder. 100 mg of carbon powder is dispersed into 80 mL of DI water. The mixture is then stirred for 20 minutes and further sonicated for another 20 minutes. 2.6 mL of 0.1 M H_2PtCl_6 is added to the solution drop by drop under continuous magnetic stirring. The mixture is sonicated for 20 minutes. A stoichiometric excess of 0.6 M $NaBH_4$ is dispersed drop-wise as the reducing agent and sonicated for 1 h. The solution is finally filtered using a Buüchner funnel and washed several times with DI water. Desired Pt powder is obtained after heating at 80 °C overnight. 50 mg of catalyst powder is mixed with 222 mg of 15% Nafion solution, 0.53 mL of DI water, and 2.5 mL of IPA. The solution is mixed overnight to form the catalyst ink.

The ink is applied onto the 5 cm^2 papers of Sigracet 29 BC carbon paper using a spray gun. The papers are placed onto a heating plate to keep the surface temperature of the paper at 85 °C to evaporate the excess liquid. Finally, electrodes with the desired Pt loading of 0.1 mg/cm^2 are obtained for both cathode and anode sides. The membrane electrode assembly is prepared by putting the current collector, electrodes, and a 5 cm^2 Nafion 117 membrane together.

Carbon aerogel and activated carbon aerogel is expected to have large increases in mesopore volume, translating to high performance in the fuel cell.

Nitrogen adsorption and desorption measurements are carried out with the NOVAtouch LX^2. EDXRF elemental analysis is conducted using a Rigaku NEX DE. The analysis is conducted in a helium atmosphere. TEM imaging is conducted using a JEOL JEM 1400 Transmission Electron Microscope. The prepared MEA is tested in a fuel cell test station from Fuel Cell Technologies, Inc. Electrochemical tests are conducted in four different environments: 60 °C H_2/air, 60 °C H_2/O_2, 80 °C H_2/air, and 80 °C H_2/O_2. A standard accelerated stress test is conducted on all the MEAs for 10,000 cycles to assess the durability of

the MEA: H_2 atmosphere for the anode and N_2 atmosphere for the cathode at 80 °C. The protocol consists in jumping between two potentials, 2 seconds at 0.6 V and 2 seconds at 0.96 V.

The nitrogen adsorption data is analyzed using NLDFT modelling on SAEIUS. The data is then plotted using MATLAB to see the visual characteristics of the graph. The EDXRF data is plotted using the Rigaku NEX DE software, then extrapolated. The pore sizes of the TEM imaging is extracted using ImageJ, and the data from ImageJ is plotted on a histogram using MATLAB. The fuel cell results and accelerated stress test data are graphed using MATLAB.

The risk assessment of the project is done with a Qualified Scientist, Dr. Miriam Rafailovich, by filling out the Risk Assessment Form before experimentation. The form is reviewed and approved by the same Qualified Scientist.

Resorcinol can cause acute toxicity, skin irritation, and serious eye damage. Chloroplatinic acid hexahydrate can cause severe skin burns & eye damage and may cause allergy or asthma symptoms if inhaled. Formaldehyde is flammable, carcinogenic; it can cause skin irritation and serious eye damage. Sodium Carbonate causes serious eye irritation. Sodium borohydride is toxic; it can ignite spontaneously in contact with water, cause severe skin burns & eye damage, and damage fertility or the unborn child. Prolonged contact with the 5% Nafion solution can cause skin irritation. IPA is flammable and can cause eye irritation. Keep away from heat, and keep the container closed. Due to the high voltages in the tube furnace to generate high temperatures, there is a risk of electrocution, fire, and severe burns.

To reduce risks, when using resorcinol, chloroplatinic acid, formaldehyde, sodium carbonate, sodium borohydride, Nafion solution, or IPA, wear personal protective equipment such as gloves, goggles, and lab coats, avoid eating or drinking when using chemicals, and wash skin thoroughly after use of the chemical. Chemicals will be kept in safe temperature conditions. Operations on all chemicals will be performed in a fume hood. It is important that Sodium borohydride is handled under inert gas, protected from moisture, and prevented from contacting water. The tube furnace must be grounded with no loose wires, and protective clothing is required. During fuel cell testing, H2 and CO detectors will be used to monitor the levels of gas. In the case of hazardous H2 and CO concentrations, alarms will sound, and occupants will leave the room until it is deemed to be safe to return.

Sharps will be disposed of in a cardboard container to prevent possible damage and risk. General hazardous chemicals will be sent to a licensed professional waste disposal service or burned in a chemical incinerator with an afterburner and scrubber. Materials related to nanoparticles will be put into plastic bags for disposal to prevent contamination and inhalation of toxic chemicals.

NO ADDENDUMS EXIST

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