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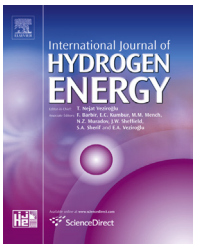

Proton conducting hollow graphene oxide cylinder as molecular fuel barrier for tubular H_2-air fuel cell

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ABSTRACT

If proton exchange membrane fuel cells (PEMFC) are ever to succeed in sustainable energy landscape as a potential zero emission technology, it is inevitable to reduce electricity production cost associated mainly with its MEAs, cell hardware and gas storage units. We demonstrate a diverse strategy for achieving this target with a concomitant amplification of its specific energy and power, by rolling a thin graphene oxide (GO) based MEA *alone* into a tubular and air breathing architecture with internal fuel storage. The unique properties of GO being a barrier for molecular fuels and proton conducting to construct a GO based cylindrical MEA. This makes the tubular PEMFC ~75 times lighter, featuring ~37 and ~92 times respectively, the power and energy per overall weight, making it a potential candidate for portable applications. The intrinsic electrochemical kinetics at the three-phase boundary are somewhat affected by the bending of the MEA, albeit at overall reduction in power production cost.

Introduction

Proton exchange membrane fuel cells (PEMFC) are at the heart of sustainable energy production because the H_2 and O_2 produced during artificial photosynthesis can be converted to electricity directly at the desired locations with higher efficiency and zero emission [1–5]. It is projected as the promising technology for portable and mobile applications because of its low temperature, quick start up and higher current density [6–8]. However as of now the electricity produced for a PEMFC is expensive than internal combustion engines, mainly because of the expensive nature of the Pt electrocatalysts, polymer electrolyte membrane and the requirement of robust, heavier and carefully machined cell hardware components (serpentine channels carefully machined on high density carbon, backing plates, gaskets etc.,) [9–13]. Though the race of nanotechnology have remarkably reduced the amount of Pt electrocatalysts to remarkably low levels (50 μg/cm^2), the latter two aspects still require substantial reduction in their cost for this technology to be commercially viable [14–17].

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Here we show a flexible and extremely lightweight PEMFC configuration based on inexpensive and therefore scalable graphene oxide (GO) membrane, just by rolling a thin GO based MEA alone into a tubular and air breathing configuration, equipping its three phase boundary with in-built gas storage unit while obliterating the use of any expensive and heavier cell hardware components [9–13]. Differing from the existing cylindrical configuration, the proposed tubular configuration consisting of just a GO based MEA alone encompassing all salient traits of a conventional PEMFC, which in turn is 75 times lighter than conventional planar configuration, allowing the fuel cell limiting parameters to be accessed in a single window, thereby reducing the overall cost of electricity production. We demonstrate that the tubular configuration can be extended to the benchmark Nafion based MEAs as well, indicating that proposed configuration can be generalized throughout the low temperature fuel cells. The proposed tubular configuration, improve the power and energy output per overall weight of the fuel cell by ~36 and ~74 times respectively albeit in the absence of separate H_2 and oxygen storage units as the former can be directly stored in the inner part of tube and the latter can be accessed directly from air since it is an air breathing configuration, making it suitable for portable applications.

Experimental

Functionalized graphene oxide and membrane preparation

Graphene oxide was prepared by modified Hummers method. The aryl diazonium salt was used for sulfonation of GO. 5 mL of NaOH (2%) and 0.05 g sulfanilic acid (SA) was mixed well in a beaker in warm water bath. To the above solution 0.02 g $NaNO_2$ was added at room temperature, and the mixed solution was added into 10 mL ice water and 1 mL of concentrated HCl under stirring and the temperature was kept at 0 °C for 15 min. The formed diazonium salt solution was added drop wise into 50 mL of graphene oxide (GO, 1 mg/mL) solution and the mixed solution was stirred well for 4 h in an ice water bath. After centrifuging and washing with water for several times, the obtained sulfonated GO (SGO) was dispersed in water. SGO membranes were made by solution casting method. Required amount of SGO was dispersed in water and casted on flat glass plate and dried in open air and peeled off. Recast Nafion membrane was prepared by dissolving precast Nafion membrane (320 mg; 5% Nafion solution in lower aliphatic alcohols, Sigma Aldrich) in (10 mL) dimethylacetamide and casted on glass plate and kept at 110 °C. After the formation of recast Nafion film, it was again kept in oven at 110 °C for 12 h to remove remaining solvent. Recast Nafion membrane was pretreated by boiling the membrane in 5% H_2O_2, then washed with deionized water, followed by boiling in 0.5 M H_2SO_4 and again washed with deionized water.

Characterization of the membrane

X-ray diffraction patterns of GO and SGO membranes were done using Bruker D8 Advance machine. Fourier transform infrared spectroscopy (FTIR) was measured on ATR-FT-IR using Bruker Alpha FTIR spectrometer system in the wave number between 4000 and 500 cm^{-1}. The thermo-gravimetric analysis of GO and SGO was carried out using a STA6000 machine over a temperature range of 25–600 °C with a scan rate of 5 °C min^{-1} under nitrogen flow (30 ml min^{-1}). The morphology of the membrane and membrane electrode assembly was investigated by a JSM-5300LV (Japan) scanning electron microscope (SEM) and TEM (Philips CM 100 Compustage (FEI)), and images are collected using an AMT CCD camera (Deben). Membranes were analyzed for Raman shift using HORIBA scientific. AC impedance measurements of tubular and planar MEAs in fuel cell mode was carried out between frequencies of 100 KHz and 10 mHz to understand MEAs ionic and electronic behavior with a PARSTAT potentiostat. The proton conductivity was measured with two equally spaced probes in contact with the measured material and from the Nyquist plot, the resistance was extracted from the high frequency intercept on the real axis and then calculated the proton conductivity using the following equations. The cell was operated with a variable temperature controller.

$$\sigma_{-IP} = L/R*A \quad (1)$$

Where σ-$_{IP}$ is the in-plane proton conductivity (S cm^{-1}), L is the distance between the Pt electrodes (0.5 cm), R is the resistance (ohms) and A is the area of the membrane (cm^2). Through plane proton conductivity was calculated using Equation (2).

$$\sigma_{-TP} = L/R*A \quad (2)$$

Where σ-$_{TP}$ is the through-plane proton conductivity (S cm^{-1}), L is the membrane thickness, R is the bulk resistance of the membrane and A is the area of the membrane (cm^2).

Tubular fuel cell assembly

The membrane electrode assembly was fabricated by coating Pt/C (0.05 mg/cm^2) ink made in 2-propanol and 15% ionomer (5% Nafion) on either side of the proton exchange membranes (SGO and Nafion 112). The catalyst coated membranes (CCM) were sandwiched between the carbon cloths and pressed at 60 kg cm^{-2} for 3 min. The SGO MEA was rolled into a tubular form having an inner diameter of ~1.5 cm^2. At either end of the MEA tube Teflon caps integrated with silicon tubes were attached with the help of double sided 3M foam tape. Adjustable screws were attached at the inlet and outlet of the silicon tubing to control the fuel flow, making it possible to store H_2 fuel directly in the MEA tube (Fig. S4 in the supporting information). Initially the tube was fed with N_2 to remove air and then filled with dry H_2 fuel. Gas leakage tests were done by using the Swagelok Snoop liquid leak detector. The fuel is stored directly in the MEA tube only at the atmospheric pressure, making the tubular fuel cell self-supported, obliterating the requirement of external hydrogen storage unit. All the fuel cell characterizations were made in air breathing mode with dry H_2 fuel at a flow rate of 100 cm^3/min unless and otherwise specified. Further the fuel cell was assembled in planar configuration by placing the MEA between two graphite blocks and stainless steel backing plates. The active electrode area formed by the

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