INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 37 (2012) 14482−14491
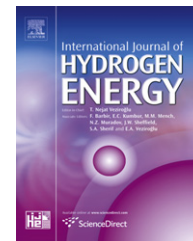
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Assimilation of highly porous sulfonated carbon nanospheres into Nafion® matrix as proton and water reservoirs

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ARTICLE INFO

Article history:
Received 18 April 2012
Received in revised form
22 July 2012
Accepted 24 July 2012
Available online 11 August 2012

Keywords:
Sulfonic acid
Porous nanocarbon particles
Composite membrane
PEM fuel cell
Crosslinking

ABSTRACT

A unique form of carbon nanospheres possessing an immense number of micropores and pendant surface sulfonic acid groups was synthesized and used as an effective filler to enhance proton transfer in Nafion® membrane at elevated temperatures. The synthesis of the filler involved the formation of polypyrrole nanoparticles and pyrolysis of them to generate carbon nanospheres (CN). Alkaline etching was then carried out to create the porous structure, and the resulting porous carbon nanospheres were then sulfonated to attain the sulfonated porous carbon nanospheres (sPCN, 1300 m^2/g, 6.9 mmol-SO_3H/g). Dispersion of a substantially small amount of sPCN in a Nafion matrix brought about a cross-adsorption between the hydrophilic side-chain of Nafion molecules and sPCN. This causes the formation of a cross-linking network with sPCN junctions. The scope of this network, however, decreased with the increase in the sPCN loading from 1 to 2 wt% due to a reduction in extent of the cross-adsorption. The sPCN loading of 1 wt% reached the highest crosslinking degree that displayed the maximum enhancement on proton transport. It can be attributed to the role of the sPCN crosslinking junctions in keeping moisture and supplying protons. The characterizations of glass transition behaviour, hydrophilic microenvironments, and proton conductivity under low humidity levels reflected the impact of crosslinking extent. In the single H_2-PEMFC test at 70 °C using dry H_2/O_2, 1 wt %-sPCN Nafion composite membrane manifested a power density of 571 mW/cm^2 as compared to the pristine Nafion membrane that showed uppermost value of 388 mW/cm^2.

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1. Introduction

A sulfonated perfluoropolymer membrane such as Nafion loses moisture under low humidity conditions when it is used in a proton exchange membrane fuel cell (PEM-FC) operated in the temperature range of 70−120 °C.

Dehydration in Nafion membrane results in low proton mobility and hence poorer fuel cell performance. To overcome this drawback, incorporation of inorganic nanoparticles such as SiO_2 or TiO_2 into the membrane offered a simple solution [1−4] relying on the physical interactions between Nafion polymer chains and filler particles. However,

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http://dx.doi.org/10.1016/j.ijhydene.2012.07.112

it is often difficult to disperse bare inorganic nanoparticles in Nafion matrix owing to thermodynamic incompatibility between matrix and filler. This causes aggregation of filler particles and consequently poorer mechanical properties and proton conductivity relative to that of the pristine membrane [5,6]. Development of the inorganic hybrid fillers with surface-attached organic functional groups has provided satisfactory solution to this problem [7—9]. In additional to hybrid inorganic particles, carbon nano fillers, namely carbon nanotubes, fullerene C60, graphene, carbon black, and modified carbon nanofibers, are also used to enhance PEM as long as these carbon particles do not form an electronic conducting network [10—13]. For instance, Chen et al. reported that surface-modified carbon nanotubes (CNT) in Nafion matrix improved its mechanical stability and proton conductivity [13—16]. Nevertheless, there is still a lack of detailed study on the physical chemistry aspects of the interaction between filler and Nafion molecules. It is clear that the generated filler-matrix interfacial characteristics are responsible to the changes in membrane structure, which in turn promotes proton conductivity and PEM fuel cell performance.

In this work, we synthesized highly porous carbon nanospheres with pendant sulfonic acid groups (sPCN) and investigated how sPCN associate with Nafion molecules and affect proton transport under different relative humidity levels. sPCN possess high surface area ($\sim$1300 m^2/g), readily accessible interior space (micro-pores, $\sim$0.8 ml/g), and prevailing hydrophilicity. These porous features enable sPCN to act effectively as the proton transport promoter in the Nafion matrix in which they are uniformly distributed. It was observed that Nafion molecules underwent cross adsorption with sPCNs, leading to a physical crosslinking network. The sPCN themselves were the reservoir of both moisture and protons besides serving as the crosslinking junctions. The loading of sPCN in the Nafion matrix significantly affect the chain packing of Nafion molecules. With a loading greater than 1% by weight, the cross adsorption structure turned to the self-adsorption structure that caused sPCN-Nafion core—shell like structure. This structural transition in the composite membranes was identified through the microscopic and thermal analyses. The analytical results were also in line with the evaluations of proton transport properties under different conditions. The loading of 1% sPCN in the Nafion matrix initiated the strongest crosslinking network of the composite membrane formulated, and thus gave rise to the highest magnitudes of water uptake, ion exchange capacity (IEC) and proton conductivity. In contrast to the pristine Nafion membrane matrix that was made by solution coasting and thus possesses the submicron domain-boundary morphology, the inclusion of 1% sPCN in this matrix stimulated interconnected hydrophilic spots due to clustering of the sulfonic acid groups of Nafion with the uniformly distributed sPCN. As a result, the composite membrane sustained a power-density output 50% higher than that the pristine membrane could hold in a single PEM fuel cell using dry H$_2$/O$_2$ feeds at 70 °C. This is proposed to be due to the radiations of proton conducting channels from individual sPCN sites and their moisture retaining capability.

2. Experimental

2.1. Preparation of sulfonated porous carbon nanospheres (sPCN)

The porous carbon nanospheres (CN) were synthesized using the method previously reported by Su et al. [17]. In a typical run, a mixture containing 2 ml 1-decanol (>99.5%, Fluka) and 60 ml deionized water was stirred at 0 °C for 20 min in a flask. 2.4 ml dodecyltrimethylammonium bromide (DTAB) (99%, Aldrich) was then introduced to the mixture under stirring for another 20 min. Subsequently, 1.6 g pyrrole (98%, Aldrich) was added dropwise in the resultant emulsion, which was then ultrasonicated for 5 min. After that, 4 g FeCl$_3$ powder (anhydrous, 98%, Sigma—Aldrich) was added into the flask and the mixture was further ultrasonicated for 1 h. The generated polypyrrole nanospheres (PyN) was separated from the mixture by filtration. It was washed several times with ethanol and water, and dried in a vacuum oven overnight at 60 °C. The PyN were then pyrolyzed under N$_2$ at 800 °C for 2 h (heating rate 2 °C/min) to obtain carbon nanospheres (CN). After that, the CN powder was blended with a certain amount of KOH in the presence of a small amount of water under gentle blending at 60 °C in a plastic beaker for 2 h before drying at 100 °C. The dried powder was then heated at 900 °C for 1 h using a heating rate of 5 °C/min under N$_2$ for the etching treatment. This treated CN was then washed in 1 M HCl solution and water and dried at 100 °C to obtain a powder consisting of highly porous carbon nanospheres (PCN). The final sulphonation step was carried out by mixing 0.1 g PCN in 20 ml concentrated H$_2$SO$_4$ (ACS reagent, 95—98%, Aldrich) at 150 °C for 4 h. After cooling, the solution was dropped into copious cold ethanol to precipitate the sulfonated carbon powder (sPCN), which was purified through repeatedly water rinse and filtration before drying at 60 °C.

2.2. Preparation of the Nafion-Carbon composite membranes

As a typical procedure, Nafion solution (5 wt% in a mixture of low aliphatic alcohols/H$_2$O (20%), EW 1100) was mixed with a given amount of sPCN (0.5%—2% by weight on the basis of dry Nafion resin). The suspension was ultrasonicated until a homogeneous sol was obtained. The sol was casted onto a petri dish and dried at 80 °C for 12 h. The membrane obtained was soaked in 1 M H$_2$SO$_4$ for at least 24 h before use. Nafion-x% sPCN (x = 0.5, 1, 1.5 or 2) are used to denote the composite membranes prepared in the following sections. A pristine Nafion membrane was also prepared by the same procedure as control. The thickness of membranes was fixed at about 50 μm.

2.3. Structural characterizations

The porous features of the carbon spheres were determined by the nitrogen isotherms obtained from Brunauer—Emmett—-Teller (BET) surface area measurement (Autosorb-1, Quantachrome instruments). Before each measurement, the samples were degassed at 300 °C for 6 h. The nano structure of