



Surfactant templated nanoporous carbon-Nafion hybrid membranes for direct methanol fuel cells with reduced methanol crossover



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ABSTRACT

In the path to improve the efficiency of direct methanol fuel cell (DMFC), development of an alternative membrane with reduced methanol cross over is the great deal of current interest. Herein, we configured a novel nanoporous carbon - Nafion hybrid membrane which reduces the methanol crossover by 50% compared to the pristine Nafion membrane. Firstly, nanoporous carbon (NPC) is synthesized through a surfactant template route using sodium dodecyl sulfate (SDS) which direct well-established pore geometry in the NPC during synthesis. NPC acts as effective filler to Nafion polymer matrix by restricting the methanol crossover in a hybrid membrane in return helps in enhancing DMFC output power density. Proton conductivity, methanol crossover, microscopic analysis along with durability in the cell mode is systematically studied to find potential application of derived hybrid membrane towards DMFC. The DMFC comprising Nafion-NPC hybrid membrane delivers the peak power density of 171 mW cm⁻² at 70 °C under ambient pressure which is about three folds higher than pristine Nafion membrane under identical operating conditions. Hence, the current investigation intended to find remarkable scope for the future DMFC technology development.

1. Introduction

Direct methanol fuel cells (DMFCs) are currently being investigated from several watts to near kilowatt size scales for various applications such as cell phones, laptops, residential application, etc., [1,2]. Dilute aqueous methanol is normally used as a fuel in a DMFC which has three major advantages viz. a very high energy density around 6000 Wh kg⁻¹, doesn't under goes storage issue like H₂ and a DMFC will have extended lifetime compared to the Li-ion batteries [3–6]. However, poor kinetics of methanol electro-oxidation at the anode and methanol crossover from anode to the cathode through the polymer electrolyte membrane (PEM) hinders the DMFC performance. Methanol crossover in a DMFC causes mixed potential at the cathode which reduces the cell performance and lowers the fuel efficiency. In order to maintain high DMFC efficiency, alternative membrane electrolyte restricting methanol crossover, superior methanol oxidation catalyst, and good methanol tolerant cathode catalysts need to be developed [7–10].

The Nafion, a perfluorosulfonic acid membrane with pendant hydrophilic sulfonic acid groups and Teflon hydrophobic back bone is widely used as polymer electrolyte membrane (PEM) for DMFC applications due to its excellent proton conductivity, thermal, chemical and mechanical stability [11,12]. However, tendency of methanol crossover

across the Nafion causes large drop in overall cell performance which restricts its widespread application in the DMFC [13,14]. In order to circumvent, inorganic filler materials, such as SiO₂ [15,16], TiO₂ [17,18], ZrO₂ [19,20], zirconium phosphate [21] and zeolites [22,23] are explored in embedding with Nafion and forming the hybrid membranes to reduce the methanol crossover. Recently, carbon materials like carbon nanotubes (CNTs), graphene etc., are also explored as potential filler materials to Nafion for constituting the hybrid membranes for DMFCs with lower methanol cross-over. Y. Choi et al. reported the application of a Nafion hybrid membrane containing sulfonated carbon spheres (SCS) in a H₂-O₂ fuel cell operation at low relative humidity. They claimed that the presence of SCS in Nafion polymer matrix increase the back diffusion of water molecules from the cathode to the anode which helps in maintaining the wettability at the anode catalyst layer and membrane interface which helps for easy proton movement [24]. Y.L. Liu et al. prepared the Nafion-functionalized MWCNT hybrid membrane for H₂-O₂polymer electrolyte membrane fuel cell (PEMFC) applications and showed that the addition of functionalized MWCNT increases the thermal and mechanical properties of the membrane [25]. Recently, mesoporous carbon derived by sol-gel route is explored as effective filler to prepare a Nafion hybrid membrane for PEMFCs applications operating under reduced relative humidity values [26]. Z.

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Chai et al. developed a Nafion-carbon hybrid membrane and claim that incorporation of carbon nano particles to the Nafion matrix suppresses methanol permeability in relation to pristine Nafion membrane [27]. Functionalized fullerene [28] and graphene [29] are also explored as potential fillers in Nafion and the hybrid membranes comprising these filler material when used in DMFCs selectively increase the proton transport over methanol and thus enhance the DMFC performance. The addition of inorganic fillers into Nafion led to restructured hydrophilic channels, composed of the pendant sulfonic acid groups of Nafion and the imbedded hydrophilic inorganic fillers improves the thermal and mechanical stability [15,30]. Moreover, the hygroscopic nature of inorganic fillers increases the water uptake capacity of the polymer and at the same time reduces the methanol permeability by increasing the tortuosity of diffusion path. However, the key challenge in preparing hybrid membranes is to achieve a uniform dispersion of the filler materials and its compatibility over the Nafion matrix.

Porous materials are attractive for various applications owing to the high specific surface area, pore geometry which leads to extraordinarily different physical behavior than the corresponding bulk materials. Inorganic porous materials with high surface area and distinctive pore structure helps increasing the physical interaction with Nafion and thus provide uniform dispersion over Nafion matrix. It was demonstrated that the incorporation of porous layered oxides with smaller pore size of a few angstroms in the Nafion matrix increases the barrier to methanol crossover without affecting the proton conductivity [31]. Moreover, the mesoporous titania – Nafion hybrid membranes allowed DMFC operation up to 145 °C with good electrochemical performance owing to larger specific surface area of mesoporous titania [32]. Nevertheless, synthesis of porous filler materials with varying pore structures and their interaction with the Nafion matrix need to be deeply understood while developing such hybrid membranes. The methanol cross-over and the real application towards DMFC in alleviating the performance need to be systematically studied for widespread commercial applications of this technology.

Herein, we report the synthesis of nanoporous carbon (NPC) from phloroglucinol-formaldehyde resin by adopting sodium dodecyl sulfate (SDS) as a structure directing agent and evolve a Nafion hybrid membrane suitable for DMFC applications. SDS, a hydrocarbon tail with a pendant sulfate group attached has amphiphilic properties that allow to form micelles, and so as to create the porous structure. The effective interaction of NPC with Nafion matrix in the hybrid membrane and its methanol crossover across the membrane is studied in detail with DMFC performance evaluation. The optimized minimal loading of high surface area NPC reduces the negative effect on proton conduction and mitigates the methanol cross-over by more than 50% in relation to the pristine Nafion membrane. A peak power density of 171 mW cm⁻² is achieved for a DMFC comprising Nafion-NPC hybrid membrane at 70 °C and ambient pressure which out performs the performance of pristine Nafion membrane under identical operating conditions.

2. Experimental

2.1. Materials

Sodium dodecyl sulfate (SDS) was procured from Acros Organics, India. Ethanol and formaldehyde solution (37–41%) were obtained from Merck, Germany. Nafion ionomer 5 wt% was procured from DuPont. Pt/C (40 wt% Pt on Vulcan XC-72R carbon) and Pt-Ru/C (40 wt % Pt and 20 wt% Ru on Vulcan XC-72R carbon) was obtained from Alfa Aesar (Johnson Matthey) Ltd. The commercial Gas diffusion layers (Sigracet DC-35) were obtained from SGL group, Germany. All the chemicals were used without further purification and de-ionized water (18 mΩ) is used in all the experiments.

2.2. Synthesis of nanoporous carbon (NPC) and fabrication of hybrid membrane

Nanoporous carbon (NPC) was synthesized by sol-gel route using SDS as structure directing agent similar to the process described elsewhere [33]. In brief, 2.5 g of phloroglucinol and 2.5 g of SDS were dissolved in to 18 g of 10:9 weight ratio of ethanol and water mixture under magnetic stirring at room temperature. To this admixture, 0.2 g of HCl was added as catalyst. The solution is stirred at room temperature till a light pink color appeared. Followed this, 2.6 g of formaldehyde is added to the above solution and continued the stirring process. With the polymerization reaction, the solution separated into two layers after 30 min. The upper layer mainly consists of water and ethanol mixture, while the lower layer was a clear polymer solution. The polymer solution stirred overnight to form elastic but non-sticky monolith that was further cured at 100 °C overnight and followed by calcination at 850 °C for 2 h in a tubular furnace under nitrogen atmosphere. The material was then collected and ground to fine powders.

The required amount of NPC with respect to dry Nafion membrane weight is added to the 5 wt% Nafion ionomer and ultra-sonicated for 1 h followed by mechanical stirring for 12 h. The resultant admixture is transferred to a flat glass Petri dish and dried at 80 °C for 6 h. The hybrid membranes thus formed were detached by adding water. Prior to further characterizations, membranes were pretreated with 0.5 M sulfuric acid (H₂SO₄) at 80 °C for 1 h followed by washing with de-ionized water until the pH of the washing water reaches neutral. The thickness of all the finished membranes was about 160 μm. Pristine Nafion membrane of identical thickness was also prepared without any filler content for the comparison.

2.3. Physicochemical characterization

Nanoporous carbon was characterized by powder X-ray diffraction (XRD), Philips Pan Analytical X-ray diffractometer using Cu-Kα (λ = 1.5 Å) radiation and also with Raman spectroscopy (RFS27, Bruker) employing Nd:YAG laser of wavelength 1064 nm. The morphology of synthesized NPC was studied by high resolution scanning electron microscope (F E I Quanta 200 FEG) and transmission electron microscopy (TEM) (Tecnai 20 G2). Nitrogen adsorption and desorption isotherms were evaluated by N₂ physisorption at 77 K using a Micromeritics ASAP 2020. Total surface area and pore volumes were determined using the Brunauer–Emmett–Teller (BET) equation and the single point method, respectively. Pore size distribution (PSD) curves were obtained by the Barrett–Joyner–Halenda (BJH) method and the position of the maximum of the PSD was used as the average pore diameter. The thermal stability of Nafion-NPC hybrid membranes were studied using NETZSCH STA 449TG-DSC instrument in the temperature range between 30 and 900 °C at a heating rate of 5 °C min⁻¹ under nitrogen atmosphere. Morphological evolution of Nafion-NPC hybrid membranes in comparison with pristine recast Nafion was observed by atomic force microscopy (AFM) (AFM, Pico SPM-Picoscan 2100, Molecular Imaging, USA). The imaging was performed in tapping mode with a diamond-like carbon coated ultra-sharp silicon tip. For quantitative and qualitative observations, topological and phase images were also analyzed along with line profile which gives the height variation at a certain cross-section on membrane surface. The mechanical strength for pristine Nafion and hybrid membranes was evaluated from the stress-strain test on a Shimadzu universal testing instrument Autograph AGS-J10kN at 30 °C. The membranes were placed in a sample holder and pulled at a cross head speed of 1 mm min⁻¹.

2.4. Proton conductivity

Through-plane proton conductivity of hybrid and pristine Nafion membranes were measured by electrochemical impedance spectroscopy (EIS) measurements using potentiostat (Autolab PGSTAT 30) with built-

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