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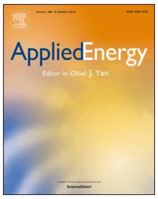

Effect of nano-size of functionalized silica on overall performance of swelling-filling modified Nafion membrane for direct methanol fuel cell application

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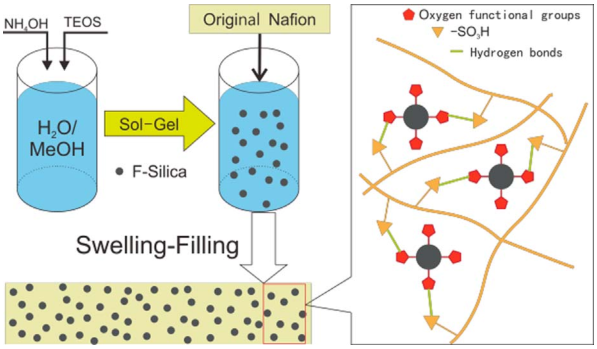
HIGHLIGHTS

- Non-destructively inserting of functionalized silica nano-particles in Nafion.
- F-silica tightly anchored with Nafion chains *via* hydrogen bonds.
- Selectivity was doubled compared to original Nafion.
- Mechanical and oxidative stabilities of Nafion were retained.
- DMFC power was enhanced by 30%.

GRAPHICAL ABSTRACT

Selectivity of Nafion for DMFC application is enhanced by 100% resulted from facile swelling-filling treatment of mono-dispersed functionalized silica nano-particles.



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ABSTRACT

A non-destructive swelling-filling (SF) strategy is applied for inorganic modification on Nafion by using functionalized silica (F-silica) nanoparticles as fillers. With the facilely prepared F-silica gel as SF treating agent, the mono-dispersed F-silica nanoparticles can *in*-situ insert into the Nafion membrane and tightly anchor on the Nafion chains through the hydrogen bonding interaction between the oxygen containing groups on F-silica fillers and $–SO_3H$ group on Nafion chains. The F-silica nanoparticles act as bi-functional fillers in the modified Nafion membrane to improve proton conductive and methanol-permeation resistive performances simultaneously. 100% enhanced proton/methanol selectivity therefore leads to a more than 30% improved direct methanol fuel cell (DMFC) performance in terms of power output. By considering the great mechanical, thermal and oxidative stabilities comprehensively, the F-silica-Nafion membranes exhibit promising application potential for high-energy DMFC application.

1. Introduction

Worldwide industrial development, population growth and environmental pollution have led to the global demand for sustainable energy supplies, e.g. solar energy [1] and wind energy [2], in recent decades [3]. However, uneven distribution of these sustainable energy

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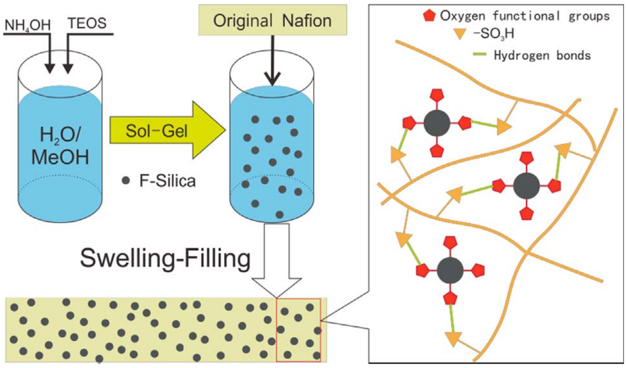
sources [2,4] is the most severe issue hinders their efficient application although efficient solar/wind energy conversion technologies have been developed [5]. Hydrogen energy was therefore considered as one of the most promising energy technologies to overcome uneven distribution issue of the sustainable energy application [6,7]. As a key segment in hydrogen energy chain, fuel cell technologies have been widely studied [8,9]. Among the currently available fuel cell technologies, direct methanol fuel cell (DMFC) technology [10,11] has shown promising application potential as direct power source for portable electronic devices due to the extraordinary high theoretical energy density of methanol [12,13]. Unfortunately, practical energy density of DMFC is almost 10 times smaller than the theoretical one due to the serve methanol crossover through the commercial perfluorosulfonic acid PEMs, represented by Nafion (DuPont), during DMFC operation [14,15]. Undesired mixed potential caused from the oxidation of permeated methanol in the cathode would lead to a reduction on power density [14,16]. Development of suitable methanol-permeation resistant proton exchange membrane (PEM) to replace Nafion membranes is hence one of the most urgent targets for the large-scale application of DMFC. In spite of numerous alternative methanol-permeation resistant PEMs were developed [10,17–21], methanol-permeation resistive modification on Nafion membrane is the most straightforward strategy to overcome the methanol crossover issue in DMFC. One or more species have to be employed for the Nafion modification *via* hybrid composition [22–25], surface coating [26,27] or other strategies [28,29]. Silica (SiO_2) was considered as one of the most efficient modifiers due to advantages represented by the great affinity with $–SO_3H$ groups on Nafion chains resulted from the hydrophilic property [30,31]. By compositing with silica, water retention capacity at low humidity and methanol permeation resistivity of Nafion can be remarkably improved [11,27,32–34]. Methanol permeability of the Nafion membrane was reduced to an undetectable level by coating it with sulfonated organic silica while the proton conductivity was also declined to 0.029 S/cm [27]. In another related study [34], a sulfonated-silica/Nafion hybrid membrane was prepared and exhibited enhanced proton conductivity and slightly lowered methanol permeability compared with the pristine Nafion membrane. Unfortunately, large-scale phase separation would occur between Nafion and silica during the re-casting process of the hybrid Nafion membrane and hence decay the mechanical stability of the Nafion membrane.

In this study, silica nanoparticles are employed into the Nafion membrane framework *via* the non-destructive swelling-filling (SF) modification strategy previously developed [29,35] by taking the advantage that silica can be functionalized with oxygen-containing groups during the sol–gel synthesis. Compared to the polymeric fillers we previously used for SF modification on the Nafion membranes, [29,35] the inorganic filler silica is more chemical stable and the potential harm of filler on oxidative stability of the Nafion membrane can be avoided. As demonstrated in Scheme 1, functionalized silica (F-silica) can be tightly anchored with Nafion chains *via* hydrogen bonds between the oxygen functional groups on F-silica surface and $–SO_3H$ group on Nafion chains [30,31] in the F-silica SF modified Nafion (F-silica-Nafion) membrane. Both proton conductivity and methanol-permeation resistivity of the Nafion membrane were therefore remarkably improved. At the same time, dependence of proton conductivity, methanol permeability and mechanical stability of the F-silica-Nafion membrane was investigated to optimize the size of F-silica nanoparticles. With optimal nano-size of F-silica, almost all the key performance of the Nafion membrane for DMFC application can be remarkably improved due to matchup of the F-silica with the nano pores in the Nafion membrane during the non-destructive SF modification.



Scheme 1. Schematic diagram of *in*-situ SF modification of Nafion membrane in the freshly prepared F-silica solution.

2. Experimental

2.1. F-silica gel synthesis

A typical sol–gel process was used for the mono-dispersed F-silica preparation [36]. The process involves hydrolysis and condensation of tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$) in the presence of NH_3 as catalyst in water/methanol solution. 100 mL TEOS water/methanol solutions (0.5 M) with different water/methanol volume ratios (1:2, 1:1 and 2:1) were firstly prepared. 10 mL 5 M NH_3 aqueous solution was then added into the TEOS/water/methanol mixture dropwisely. After 5 h aging under stirring at room temperature, mono-dispersed silica gels can be obtained. By adjusting the water/methanol volume ratio, average size of F-silica nanoparticles in the mono-dispersed F-silica gels can be controlled to be 45 nm, 110 nm and 220 nm as shown in the scanning electron microscopy (SEM) images of the F-silica nanoparticles in Fig. 1.

2.2. F-silica-Nafion membrane preparation

F-silica-Nafion membranes were prepared through the SF strategy with the mono-dispersed F-silica gels as SF treating agents. Before the SF treating, Nafion 212 membrane (DuPont) pieces were pretreated sequentially by boiling in 5% H_2O_2 solution, 1 M H_2SO_4 solution and deionized water for 1 h. Subsequently, the pretreated Nafion membranes were directly soaked in the prepared mono-dispersed 45 nm, 110 nm and 220 nm silica gels, respectively, to gain F-silica-Nafion-1, F-silica-Nafion-2 and F-silica-Nafion-3 membranes. During the swelling process of Nafion membrane, F-silica nanoparticles were *in*-situ inserted into the Nafion framework together with the solvent. The solvent was removed from the Nafion membrane afterward by heating at 80 °C under vacuum for 12 h to obtain the F-silica-Nafion membranes.

2.3. Characterizations

2.3.1. Water uptake and volume swelling

Water uptake and volume swelling ratio measurements of the original Nafion 212 membrane and the F-silica-Nafion membranes were conducted as follows: the membrane was first equilibrated in deionized water at room temperature for 24 h and wet weight (W_{wet}) and volume (V_{wet}) were immediately measured after removing the surface water; the dried weight (W_{dry}) and volume (V_{dry}) of the membrane were quickly measured after during the membrane at 80 °C for 12 h; membrane volumes at different states were calculated *via* $l \times w \times \delta$ (l is length, w is width and δ is thickness of the membrane); water uptake (WU) and volume swelling ratio (VS) of the membrane were obtained according to the following equations:

$$WU = (W_{wet} - W_{dry})/W_{dry} \qquad (1)$$

$$VS = (V_{wet} - V_{dry})/V_{dry} \qquad (2)$$