



High Durable Polymer Electrolyte Membrane for Fuel-Cell Applications

Asuman C. Küçük¹, Jun Matsui², Takuji Miyashita³

Abstract

Phosphonic-acid-containing double-decker-shaped polyhedral silsesquioxanes (2-PHOS-DDSQ and PHOS-DDSQ) were synthesized and the proton conductivity of the PHOS-DDSQ cast film was studied under humid and non-humid conditions. Two-armed and four-armed DDSQ functionalized with di(ethylene glycol) (DEG) (2DEG-DDSQ, 4DEG-DDSQ) were used as initial materials. Esterification reaction of phosphate was carried out using POCl₃ through the hydroxyl-terminated groups attached to 2DEG-DDSQ, 4DEG-DDSQ to synthesize 2PHOS-DDSQ and PHOS-DDSQ. However, it has been found that 2PHOS-DDSQ is not sustainable against to the water, thus proton conductivity measurements carried out with PHOS-DDSQ. A uniform film of PHOS-DDSQ was fabricated by drop casting. The cast film showed high proton conductivity (0.12 S cm⁻¹) under humid conditions. Moreover, the cast film offered good proton conductivity under non-humid conditions (3.6 10⁻⁴ S cm⁻¹ at 170 °C). The conductivity and thermal stability indicate that PHOS-DDSQ is a good candidate for use as a proton-conductive membrane in hydrated type fuel cells as well as fuel cells operated at intermediate temperatures (100–200 °C) under non-humid conditions.

Keywords: Silsesquioxane, Proton Conducting Electrolyte, Intermediate Temperature, Fuel-Cell

Introduction

Polymer electrolyte fuel cells (PEMFC) have clearly become an important research area. Mass productions on vehicles equipped with fuel cells have been already started. Perfluorosulfonic acid, which is known as Nafion, is widely used as polymer electrolyte membrane (PEM) in fuel cells [1]. It is chemically stable and its proton conductivity is very high up to 100 °C at high humidity level [2]. At low temperatures, the cell performance decreases with time due to the catalyst poisoning. Conversely, up to 120 °C, the catalyst poisoning remarkably decreases and there is no need to use highly pure hydrogen fuel. Thus, gas consumption of fuel cell greatly reduces. In addition to that, higher temperatures lead to faster electrode reactions and H₂/O₂ diffusion that increase the fuel cell performance [3]. However, the large scale-up of polymer fuel cells are still limited by their incompatibility with operating conditions of the automotive applications and required high cost [4]. Polyhedral silsesquioxanes (POSS) are organic–inorganic hybrid materials composed of an inorganic SiO_{1.5} core with organic coronae [5]. The SiO_{1.5} core provides good thermal and mechanical stability, whereas organic coronae provide compatibility with polymer materials [6]. Up to now, silsesquioxanes have been used as a nanofiller to improve the thermal and structural stability of polymer electrolytes. It has been reported that incorporation of sulfonated POSS into Nafion not only improves thermal and mechanical properties, but also increases the proton conductivity under non-humid conditions [7]. This new generation materials may be used in PEMFC as electrolytes and may have potential to increase the range of the operation region of electrolytes.

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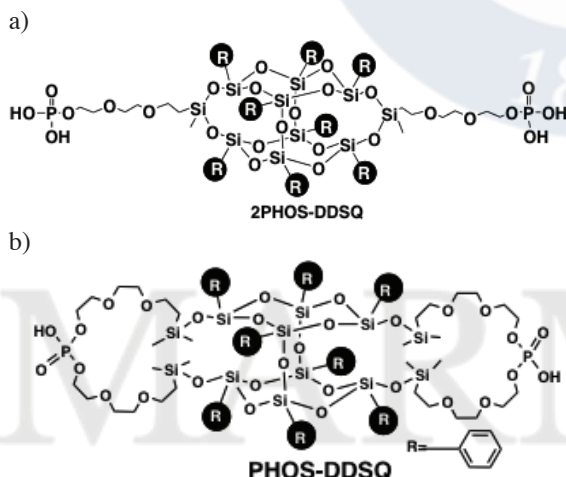
Results and Discussion

We earlier reported synthesizing process of core–coronae” type hybrid amphiphiles consist of double-decker-shaped polyhedral silsesquioxanes (DDSQ) as a hydrophobic core and DEG units as a hydrophilic coronae [8]. We used two kinds of hydrophobic cores, which are two-armed, and four-armed DDSQ. These hydrophobic cores were functionalized with DEG and 2DEG-DDSQ, 4DEG-DDSQ were obtained respectively. Furthermore, we studied the assembly ability of these structures at the air–water interface using Langmuir–Blodgett technique [9–11]. It is concluded that the self-assembled structure of “core–coronae” type amphiphile can be controlled by the chemical structure of the hydrophilic end groups as well as the number of hydrophilic chains [11].

In the following study, phosphoric acid groups were bonded covalently to 2DEG-DDSQ, 4DEG-DDSQ through DEG units. 2PHOS-DDSQ and PHOS-DDSQ were respectively obtained [12]. Then the proton-conductive abilities of 2PHOS-DDSQ and PHOS-DDSQ were investigated. Obtained hybrid materials (2PHOS-DDSQ and PHOS-DDSQ) (**Scheme 1**) were characterized using ^1H , ^{31}P -NMR, FT-IR, XPS and MALDI-TOF MS spectrometry. In the FT-IR spectrum of 2PHOS-DDSQ suggested that DDSQ core remained unchanged during the synthesis. Moreover, in the ^1H NMR spectrum of 2PHOS-DDSQ showed just shifting of methyl protons to a higher magnetic field.

Fig. 1 shows the ^{31}P NMR spectra of 2PHOS-DDSQ taken in CDCl_3 . After 2nd time washing of 2PHOS-DDSQ with water for purification, phosphor atom peak at 5.6 ppm disappeared (**Fig. 1**).

This result shows that ester bond in 2PHOS-DDSQ was hydrolyzed by several treatments with water and 2PHOS-DDSQ cannot be durable against to the water.



Scheme 1: Structure of 2PHOS-DDSQ (a), PHOS-DDSQ (b).

On the other hand, FT-IR and also ^1H NMR spectra show similar result with 2PHOS-DDSQ, Si-O-Si stretching of DDSQ core appears, suggesting that DDSQ core remained unchanged during the synthesis and just shifting of methyl protons to a higher magnetic field in ^1H NMR respectively. Conversely to 2PHOS-DDSQ, according to the ^{31}P NMR spectra of PHOS-DDSQ taken in CDCl_3 , even for 2nd time washing with water, one phosphor atom peak at -21.4 ppm, and its position or intensity did not change (**Fig. 2**). This result can be concluded that the phosphor atom is stable against to the water. Therefore, proton-conducting measurement carried out just for PHOS-DDSQ.

The amount of acid in one PHOS-DDSQ molecule was determined by titration measurement and found to be 1.82. Further characterization made by MALDI-TOF mass spectrum, which shows molecular ions at 2058.50 g mol^{-1} for $[\text{M}+\text{Ag}^+]$, calculated value 2060.27, that strongly supports successfully functionalization of 4DEG-DDSQ with phosphonic acid [MALDI-TOF MS =2058.50 ($\text{M} + \text{Ag}^+$, calculated value 2060.27)]. The results obtained from the spectra and titration measurements have proven that PHOS-DDSQ has crown-ether like structure.

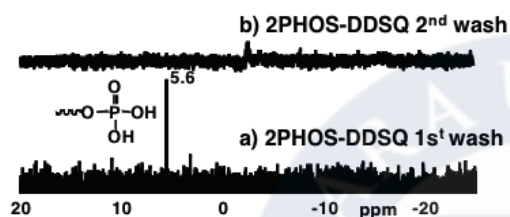
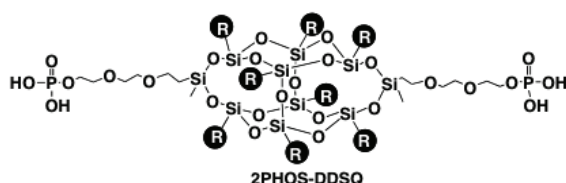


Fig. 1: ^{31}P NMR of 2PHOS-DDSQ in CDCl_3 after (a) 1st washing, (b) 2nd washing with water.

The temperature stability of PHOS-DDSQ was found to be $222\text{ }^\circ\text{C}$ that is beneficial for use as an intermediate proton-conductive polyelectrolyte application. Furthermore, amorphous phase transition belong to PHOS-DDSQ was also determined from DSC measurement (The glass transition temperatures is $-24\text{ }^\circ\text{C}$).

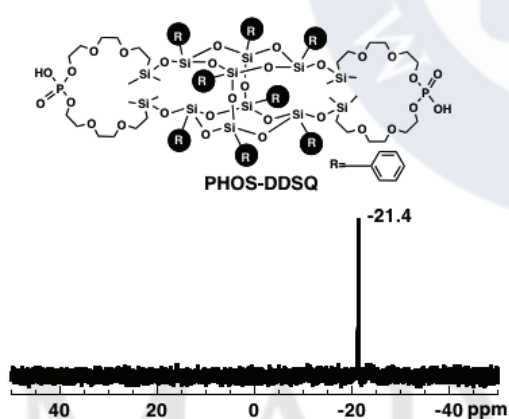


Fig. 2: ^{31}P NMR spectrum of PHOS-DDSQ.

PHOS-DDSQ formed an amorphous film by drop casting. Then the proton conductivities of the cast film under humid and non-humid conditions were studied using impedance spectra measurements. The conductivity of PHOS-DDSQ are reasonable at $75\text{ }^\circ\text{C}$ in the present measurement relative humidity conditions: $1.2 \times 10^{-3}\text{ S cm}^{-1}$ at 55% RH, $1.3 \times 10^{-2}\text{ S cm}^{-1}$ at 75% RH, and $1.2 \times 10^{-1}\text{ S cm}^{-1}$ at 95% RH respectively (Fig. 3).

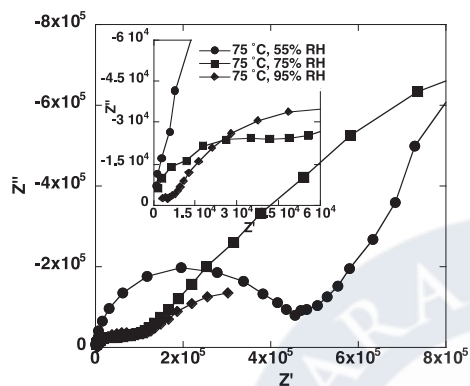


Fig. 3: Impedance response of the PHOS-DDSQ cast film at different RH at 75 °C.

In the humid condition, the proton transport mechanism of the film occurs via both “forming–breaking–forming” hydrogen bonding process and diffusion of water. The activation energy of PHOS-DDSQ was calculated to be 40 kJ mol^{-1} at 95% RH (Fig. 4).

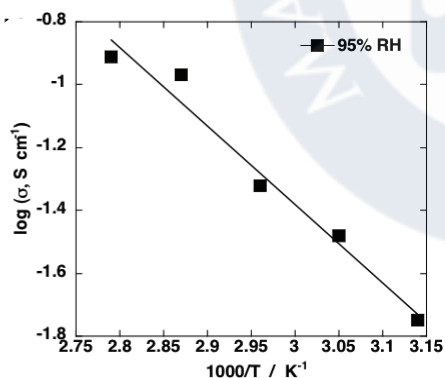


Fig. 4: Arrhenius plots of proton-conductivities of the PHOS-DDSQ cast film measured at 95% RH condition.

The non-humid proton conductivity of PHOS-DDSQ film was measured by increasing the temperature in the chamber. The highest conductivity value has been reached the value of $3.6 \times 10^{-4} \text{ S cm}^{-1}$ at 170 °C with the increasing temperature, then it drops to a low conductive value (Fig. 5). Up to 170 °C, the conductivity started to decrease due to the self-condensation of phosphonic acid units.

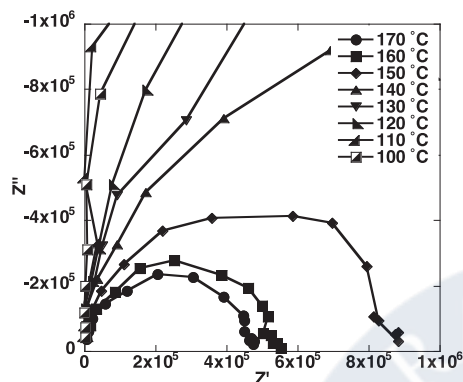


Fig. 5: Arrhenius plot of proton-conductivities of the PHOS-DDSQ cast film measured in non-humid conditions.

Proton transportation mechanism occurred via hydrogen-bond breaking and forming processes among phosphonic acids and between phosphonic acid and ether oxygen of DEG groups. The conductivity followed the Arrhenius relation in the range of 100–165 °C. The activation energy was calculated as 70 kJ mol⁻¹ (**Fig. 6**).

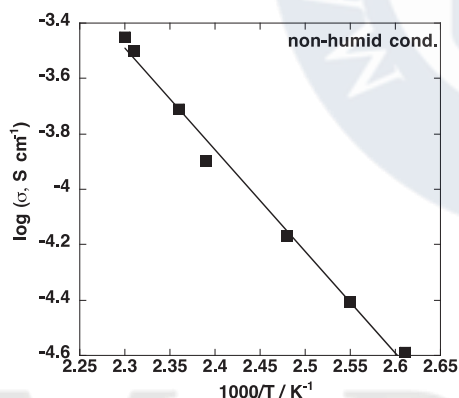


Fig. 6: Arrhenius plot of proton-conductivities of the PHOS-DDSQ cast film measured in non-humid conditions.

Conclusions

Phosphonic acid groups were attached to the DDSQ through DEG units. The spectra and titration measurements prove that PHOS-DDSQ has a crown-ether-like structure. Additionally, PHOS-DDSQ is stable against to the water and reaches proton conductivity of 0.12 S cm⁻¹ in humid conditions, as well as maximum conductivity of 3.6×10^{-4} S cm⁻¹ in non-humid conditions. The prepared material exhibits high proton conductivity in humid conditions and moderate proton conductivity in non-humid conditions. Considering acceptable proton conductivity either humid or non-humid conditions as well as the high thermal stability, this material, PHOS-DDSQ, may be powerful candidate for fuel cell applications.



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1883

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