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Krytox-Silica–Nafion® composite membrane: A hybrid system for maintaining proton conductivity in a wide range of operating temperatures

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Abstract

A homogeneous Krytox-Si–Nafion® hybrid membrane is proposed. The hybrid material is successfully prepared using Krytox 157 FSL whose structure is similar to that of Nafion®. Krytox 157 FSL is coupled onto a silica surface via a silane coupling agent to obtain the Krytox-Si. Krytox-Si–Nafion® hybrid membranes show improvement in water retention and an increase in degradation temperature as identified by thermogravimetry analysis. Scanning electron micrographs reveal good dispersion of silica through the membrane. The fully hydrated Krytox-Si–Nafion® hybrid membranes maintain their proton conductivity in a wide range of high temperatures (80–130 °C) in ambient condition of a closed system (without additional moisture feeding) as clarified by the plot of conductivity versus temperature.
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1. Introduction

For decades, the proton exchange membrane fuel cell (PEMFCs) has been developed as a compact-sized environmental friendly energy resource with high power density and energy conversion efficiency without polluting the environment [1]. One concern is about the sensitivity to CO tolerance of the electrodes. It is known that at only 10 ppm of CO in the H_2 feed gas, the Pt electrocatalyst is deactivated. The problem can primarily be solved by increasing the operating temperature over 100 °C or using a CO tolerable electrocatalyst, such as PtRu [2–4]. Not only is the CO tolerance improved when PEMFCs operate at high temperature, but also the reaction rates in both electrodes and the proton exchanging rate in the membrane are enhanced. PEMFC with an operating temperature above 100 °C is an alternative way to solve the above problem [5].

PEMFCs, however, work ideally in a high moisture atmosphere when the Nafion® membrane is used. DuPont's Nafion® (perfluorosulfonic acid polymer) and other perfluorinated sulfonic acid-based polymers (e.g. Aciplex from Asahi Chemicals) [6] are accepted as effective polymer electrolyte membranes functioning for PEMFCs due to their high proton conductivity, 10^{-2} to 10^{-1} S/cm in the hydrated state, excellent chemical and electrochemical stability, low reactant permeability, and retention of mechanical stability. The membranes have a specific multi-phase structure of the hydrophobic alkyl chain region together with a hydrophilic sulfonic acid part. Proton conductivity is satisfied by water molecules transferring among the sulfonic acid groups in the hydrophilic region [7]. Generally, at temperature above the boiling point of water, the hydrated membranes show water removal with a significant decrease in proton conductivity. Membranes functioning at high temperature is, thus, a worthy theme to be addressed.

The approaches to apply the proton exchange membrane at high operation temperature (> 100 °C) mainly use heterocyclic-structured and/or composite membranes. The former is achieved by replacing water with a high boiling point protonic

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molecules, such as liquid imidazole ($T_b \sim 257$ °C) and the latter is known as an organic-inorganic hybrid structure to promote water retention at high temperature.

It is important to note that a composite membrane can be prepared via either the sol-gel or the blending process. Preliminary investigation has shown that polymer–inorganic composites improve proton conductivity, water retention, operating temperature and they reduce the permeability of molecular species [8]. Recently, phosphotungstic acid (PWA) doped with organic polymer (polyethylene oxide, PEO; polypropylene oxide, PPO; polytetramethylene oxide, PTMO) prepared via the sol–gel process was reported by Honma et al. [9]. In the sol–gel process, alkoxysilane was used as a precursor and monophenyltriethoxysilane as an inorganic network. The hybrid membrane was stabilized up to 250 °C and had proton conductivity of 10^{-4} S/cm at 160 °C. However, the fact that the sol–gel process requires a high quantity of alkoxysilane and that the reaction condition is severe, practical application are limited.

For the blending process, Nafion® with silicon oxide and Nafion® with silicon oxide doped with phosphorictungstic acid (PWA) composite membranes were a good example reported by Shao et al. [10]. It was found that silicon oxide and PWA improved the crystallinity and degradation temperature of Nafion® 115 membrane while the proton conductivity (about 10^{-2} S/cm) was similar to that of Nafion® 115 membrane at high temperature in 100% relative humidity (RH). Nevertheless, the SEM photograph showed significant organic–inorganic phase separation.

In this study, we consider the hybrid composite membrane under the concept of 'like dissolves like' of Nafion®–Silica hybrid material for the miscible blend system. Since Krytox 157 FSL (carboxylic acid terminated perfluoropolyether, Scheme 2) is a type of fluorocarbon polymer, we propose the immobilization of silica particles onto Krytox 157 FSL and blend with Nafion® as illustrated in Scheme 1.

2. Experimental

Five percent weight Nafion® in aliphatic alcohol solution was purchased from Aldrich, Germany. (3-Aminopropyl) triethoxysilane was obtained from Fluka, Switzerland. Krytox 157 FSL was provided from DuPont, USA. A water conjugating agent (WSC), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride 98%, was purchased from Acros, Belgium. Fumed silica was obtained from Degussa, Germany. All chemicals were used without further purification.
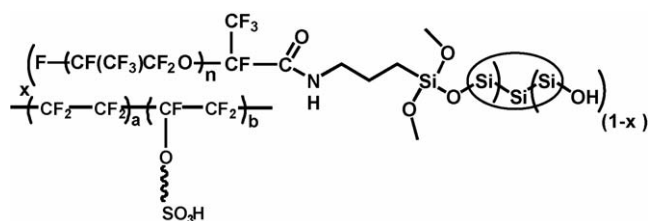
Scheme 1.

2.1. Preparation of the Krytox-Si–Nafion® hybrid materials (Scheme 2)

Fumed silica (Aerosil 380, surface area of 380 m² g⁻¹) was heated at 230 °C in a vacuum for 3 h before use. The hydrolyzed (3-aminopropyl) triethoxysilane, **1** (0.1427 g), was mixed with the pretreated silica (0.5107 g) in 100 ml of 90% ethanol. The mixture was stirred vigorously at 80 °C for 8 h and washed several times to obtain silica coupled with aminosilane, **2** (Eq. (2)). Compound **2** was stirred with WSC (0.13 g, 6.5×10^{-4} mol), in aqueous solution at room temperature for 6 h. Krytox 157 FSL (1.625 g) was added with the molar ratio of Krytox:silane:WSC 1:1:1. The mixture was stirred overnight at room temperature to obtain Krytox-Si, **3** (Eq. (3)). Nafion® 5 wt.% in aliphatic alcohol solution was mixed with various quantities of **3**, i.e., 1.5, 2.5 and 5 wt.%, in DMSO for 2 days and sonicated at ambient temperature for 1 h to obtain Krytox-Si–Nafion® hybrid solution, **4** (Eq. (4)).

2.2. Membrane preparation

All hybrid solutions of **4** (**4a**, **4b**, and **4c** with quantities of **3** for 1.5, 2.5, and 5 wt.%, respectively) for 4 ml were casted onto a teflon mold (3 cm × 3 cm × 3 cm) and isothermally treated at 160 °C for 3 h to obtain **4a**, **4b**, and **4c** membranes. The membranes were detached after overnight soaking in water. Five percent weight of Nafion® in aliphatic alcohol solution was casted by the same procedures to obtain **5**.

2.3. Structural analysis

The chemical structure of each product was identified by using a Thermo Nicolet Nexus 670 Fourier transform infrared (FT-IR) spectrometer. Elemental analysis (EA) was carried out by a PERKIN ELMER 2400 CHN. Anal. Calcd. for **2** ($H_2N(CH_2)_3Si(OH)_2$–O–Si (%): C, 21.95; H, 6.10; and N, 8.54. Found: (%) C, 7.17; H, 1.33; and N, 1.75: FT-IR (ZnSe, cm⁻¹): 3500–3400 (OH), 3350–3200 (NH), 2900–2800 (CH₂), and 1150–1050 (Si–O–Si).

FT-IR for **4** (ZnSe, cm⁻¹): 3500–3400 (OH), 3350–3200 (NH), 2900–2800 (CH₂), 1774 (C=O carboxylic acid), 1680 (C=O amide), and 1150–1050 (Si–O–Si).

2.4. Water uptake and thermal stability

The percent water uptake and degradation temperature of the membranes were clarified by using a TGA 2950 DuPont. The hybrid membranes were dried in a vacuum oven at 70 °C for 24 h and equilibrated in water vapor at 60 °C for 24 h before measuring the water uptake. The amount of water in the hybrid membrane was evaluated by the percent weight loss of water at 80–100 °C. Degradation temperatures were carried out at 25–700 °C with a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out using a DSC7 Perkin-Elmer. The membranes were heated to 500 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

2.5. Morphology and silica distribution

The morphology and silica distribution of the composite membranes were observed by a JEOL JSM-6400 scanning electron microscope. Silica-mapping mode using a Ling ISIS Series 300 was applied for evaluation of silica distribution.

2.6. Proton conductivity measurement

The membranes were soaked in 3% (v/v) of H_2O_2 at 80 °C for 1 h, distilled water at 100 °C for 1 h, 1 M H_2SO_4 at 80 °C for 1 h and distilled water at 100 °C for 15 min before measuring the proton conductivity. The membranes obtained were hydrated and placed in the test cell, where they were clamped between two platinum electrodes. Proton conductivity was measured by a Solartron 1260 impedance spectrometer over 10 Hz to 1 MHz at 20–140 °C in ambient condition of a closed system (without moisture feeding).

3. Results and discussion

3.1. Coupling reaction of silica and Krytox 157 FSL

Compound **1** shows the CH_2 peak at 2900–2800 cm^{-1}, OH peak at 3500–3400 cm^{-1} and NH peak at 3350–3200 cm^{-1} (Fig. 1(a)). This implies the successful hydrolyzation of (3-aminopropyl) triethoxysilane. In the case of **2**, the strong Si–O–Si peak at 1150–1050 cm^{-1} with most peaks similar to **1** informs that the coupling reaction of silica and silane coupling agent is satisfied (Fig. 1(b)). After conjugating **2** with Krytox 157 FSL, the obtained compound gives characteristic peaks at

Fig. 1. FT-IR spectra of **1** (a), **2** (b), **3** (c), and **4** (d).

1774 cm^{-1} (C=O of Krytox), at 1680 cm^{-1} (C=O of amide), and at 1100–1040 cm^{-1} (Si–O) (Fig. 1(d)) suggesting that Krytox 157 FSL is developed on the silica particles as shown in Eq. (4) (Scheme 2).

The content of aminosilane coupled onto silica particles was quantitatively analyzed as follows. Scheme 1 shows a simplified structure to calculate the coupling efficiency. Hence, the percentage C and N can be applied to calculate the x content based on the relationship below:

$$N\,(\%) = \frac{100 \times 14x}{45(1-x) + 164x} \quad \text{and}$$

$$C\,(\%) = \frac{100 \times 36x}{45(1-x) + 164x}$$

As the elemental analysis gives N and C for 1.75 and 7.17%, respectively, the x value is then equal to 0.1. The value of x implied that one-tenth of the aminosilane was successfully coupled onto silica surface.

3.2. Water content and thermal stability

Table 1 shows the water content and degradation temperature of **4a**, **4b**, **4c**, and **5**. Yang et al. [11] reported that the water content in the Nafion® 115 membrane at 80 °C was about 18%. In this work, **5** was used as a reference to compare with other membranes. The water content evaluated from 80–100 °C reveals that **5** retains a water content of 8% whereas **4c** shows the water content for 50%. For **4a** and **4b,** the water uptakes are 22 and 42, respectively (Table 1). This implies that inorganic content induces the water uptake in the membrane effectively. Kim et al. [5] demonstrated that the OH groups on the silica particles form the hydrogen bond with water molecules to maintain water in the membrane. Taking this to the consideration of **4a**–**4c** membranes, the high content of **3** might give the preferable condition to stabilize a greater amount of water in the membrane. Table 1 shows that the thermal degradation of **4a**, **4b**, **4c,** and **5** are at 333.8°, 336.2°, 347.4°, and 327 °C, respectively. Wilkie et al. [12] reported that the increase of degradation temperature, when an inorganic content was added into the Nafion® 115 membrane, might be due to the silica framework functioning as a heat-tolerant in the membrane. Here, the decompositions of **4a**–**4c** shifted to the higher temperature as compared to that of **5** reflect the role of silica content. The energy consumed for water evaporation from **4a**–**4c** and **5** was further studied by DSC. It was expected that when silica was hybridized in the membrane, the OH groups of silica might form the strong hydrogen bond with water molecules yielding the increase of the water evaporation enthalpy, ΔH_{water}. Table 1 shows ΔH_{water} for **4a**, **4b**, **4c**, and **5** membranes at 663.97, 685, 797.73, and 442.31 J/g, respectively. This supports the above speculation, or in other words, **3** might play an important role in water retention. Studies on other physical and mechanical properties of the membranes are in progress.
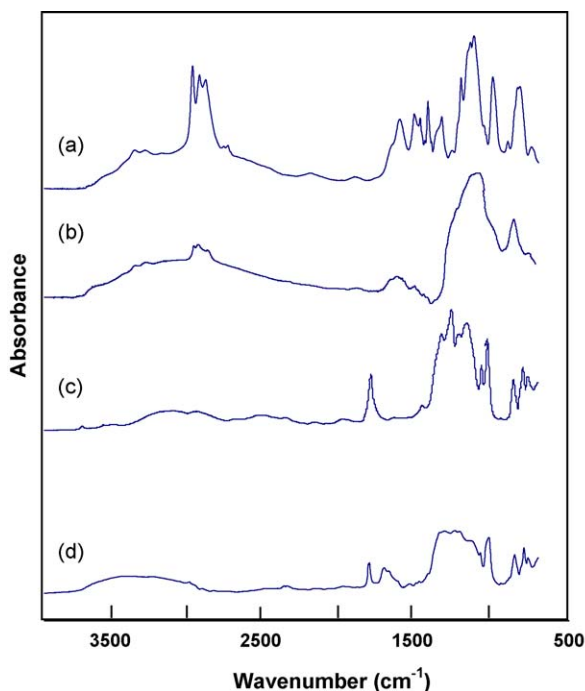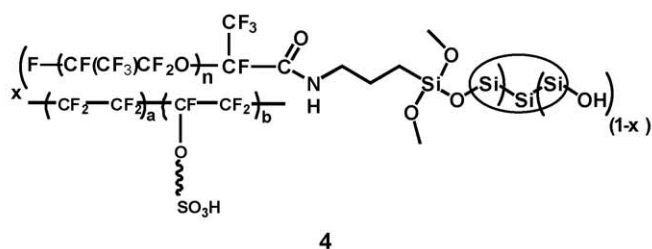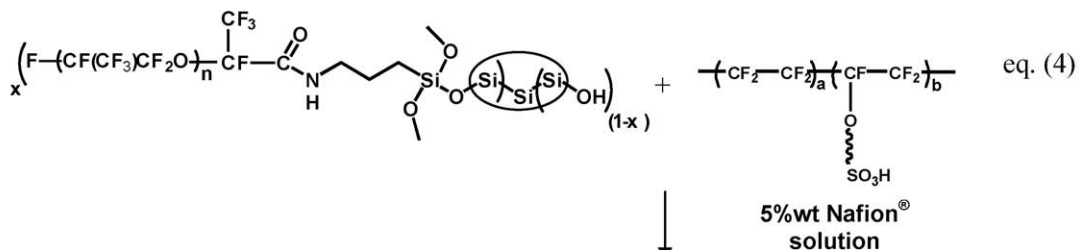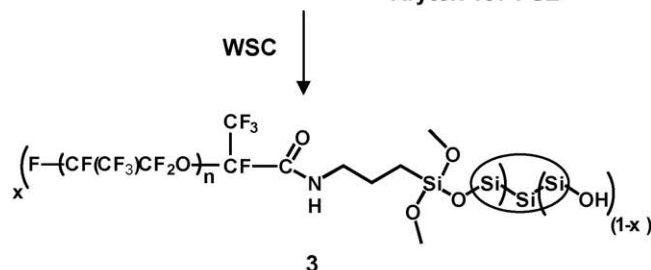
eq. (1)

eq. (2)

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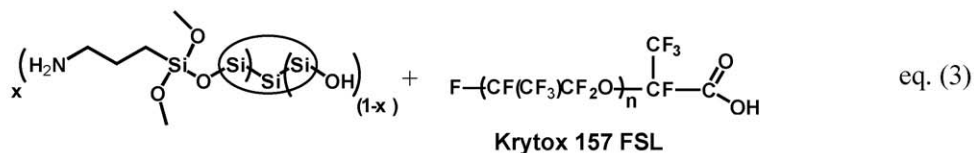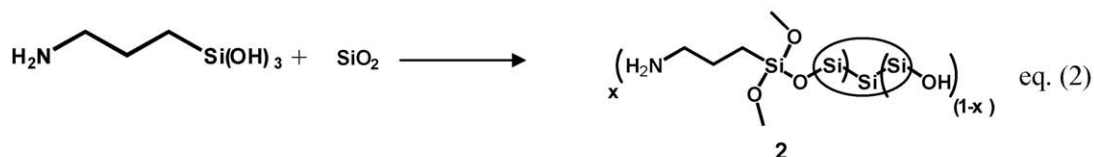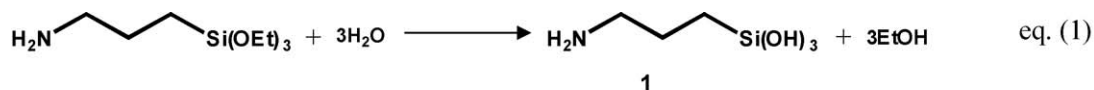
Scheme 2.

3.3. Membrane morphology and silica distribution

Shao et al. [10] reported the preparation of the Nafion® with silicon oxide composite membrane prepared via the blending process. However, the SEM photograph insisted the phase separation. In the present work, Krytox 157 FSL is focused so as to achieve miscibility between Nafion® and silica. It was found that silica particles are well-dispersed with good homogeneity between the organic part of Nafion® polymer and the inorganic part of silica particles. Fig. 2 shows the membrane morphology of **4c** to express cross-section and silica distrbution. Fig. 2a exhibits the good distribution of silica on the membrane surface. In order to confirm the existance of silica throughout the membrane, SEM mapping mode was carried out. Fig. 2b gives the information about the dispersion of silica on the membrane. Although there are some local aggregation of silica, over 85% of the membrane is occupied by silica. The cross-section observation suggests that Krytox-Si and Nafion® are in good miscibility and silica aggregation is hardly observed (Fig. 2c).
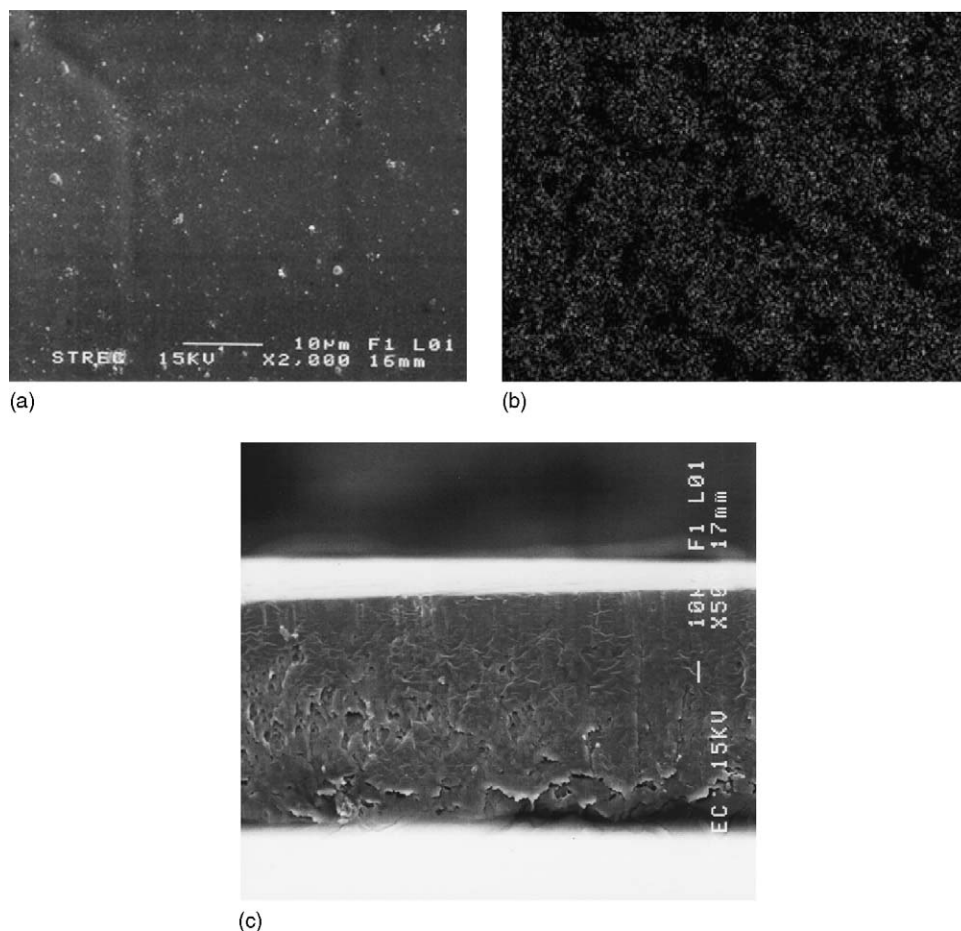
Table 1
Water uptake at 60 °C, degradation temperature (T_d), and enthalpy of water evaporation (ΔH_{water})

Membrane	Water uptake at 60 °C (%)	T_d (°C)	ΔH_{water} (J/g)
4a	22	333.8	663.97
4b	42	336.2	685
4c	51.5	347.4	797.73
5	8	327	442.31

Fig. 2. SEM micrographs of: membrane surface (a), silica mapping mode (b), and cross-section (c) of **4**c.

3.4. Proton conductivity

In order to evaluate the electrical properties of composite membranes fabricated from polymer matrices and silica particles, the complex impedances were measured by applying alternating current with various frequencies. Fig. 3 shows the typical impedance response (Z'–Z'' plot) of **4b** at various temperatures of 40, 60, 80, 100, and 130 °C. The plot on Fig. 3 was obtained by varying the frequency to observe Z' and Z''. The impedance plot is known as indirect information about the membrane homogineity and conductivity. Fig. 3 confirms that the complex impedance of each temperature is gradually increased to give the Z'–Z'' a curve continuous increment through all frequencies. This result implies that there was no ionic capacity in the composite membrane. In other words, it can be expected that all protons might diffuse thoroughly in the homogeneous membrane. Xie et al. [13] reported that the Z'–Z'' plot gives a semicircle to evaluate the charge transfer in the membrane; however, the relationship might be interrupted by the noises at low frequency. In our case it was found that the noises were so significant that the evaluation was difficult. Here, the proton conductivity, σ, was calculated from the complex impedance values at various temperatures based on $\sigma = L/RA$, where L and A are the thickness and surface area of the membrane, respectively.

Membranes **4a**, **4b**, **4c**, and **5** showed the thickness for an average of 0.105 mm. The bulk resistance, R, of the sample was obtained from the intersection of Z' axis [14]. From
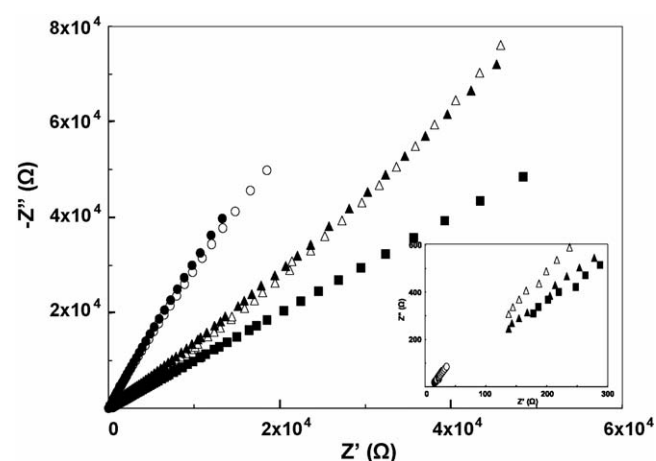

Fig. 3. Complex impedance of **4**b at 40 °C (●), 60 °C (○), 80 °C (△), 100 °C (▲), and 130 °C (■).

Table 2
Proton conductivity of **4b**

Temperature (°C)	Bulk resistance (Ω)	Proton conductivity (S/cm)
40	15.457	1.97×10^{-3}
60	17.801	1.71×10^{-3}
80	137.40	2.22×10^{-4}
100	137.41	2.22×10^{-4}
130	177.74	1.72×10^{-4}
25 (Nafion® 117)	n/a	10^{-2}

Fig. 3, the proton conductivities of **4b** at various temperatures were calculated and summarized in Table 2. Although the bulk resistance increases at elevated temperature, it is only an order of magnitude of conductivity reduction occuring for temperature changing from 60° to 80 °C. This might be due to the evaporation of some water molecules in the inorganic part, i.e., silica particles. Compared to the conductivity at room temperature and 100% relative humidity of Nafion® 117 (10^{-2} S/cm) [15], our membrane reveals lower proton conductive efficiency. It is important to note that the conductivity of our membrane is maintained at 10^{-4} S/cm, even though the temperature was up to 130 °C. Although it is difficult to compare the conductivity of **4a**, **4b**, and **4c** to that of Nafion® 117 due to the differences in experimental condition, the conductivity of Nafion® 117 shown in Table 2 is raised as a guideline to discuss how the membranes (**4a**, **4b**, and **4c**) show their potential application. Subsequently, the measurements of the temperature dependent complex impedance of other membranes were investigated and calculated resulting in the plot of proton conductivity versus temperature. It should be pointed out that as our instrument has the limitation in controlling the humidity, all tests were run in ambient condition. Here, the hybrid membranes were fully hydrated in advance and it was assumed that the absorbed water molecules in the membrane might play an important role in the proton conductivity as reported by Vona et al. [16]. Fig. 4 shows that the proton conductivity of **5** is 10^{-2} S/cm when the temperature is lower than 80 °C and decreases gradually to

5×10^{-6} S/cm at temperatures above 80 °C. In the case of **4a**, the proton conductivity is decreased above 80 °C, similar to that of **5**. It should be noted that the conductivity of **4b** and **4c** are found to be retained at 10^{-3} and 5×10^{-4} S/cm, respectively, eventhough the temperature was up to 130 °C. The results indicated that the proton conductivity at temperatures above 100 °C was improved when the Krytox-Si content was increased. Previously, Miyake et al. reported that the proton conductivity of the polymer membrane was strongly dependent on the water content of the membrane [17]. Moreover, the water content was increased with the silica content [18]. Taking this into consideration, we suspect that the improvement in proton conductivity at temperatures above 100 °C might result from the functions of silica particles and their homogeneous distribution on the Nafion® matrices.

4. Conclusions

(3-Aminopropyl) triethoxysilane was used as a coupling agent to incorporate Krytox 157 FSL onto a silica surface. Krytox 157 FSL was applied as a polymer chain to offer miscibility with Nafion® based on their similar structure. The surface of silica was successfully functionalized with Krytox 157 FSL by using the carbodiimide conjugating agent to obtain Krytox-Si. The composite membranes obtained from casting the mixing solutions of Krytox-Si and Nafion® demonstrated a homogeneous phase with a good dispersion of silica as observed by SEM photographs. The water retention and degradation temperature were increased when the Krytox-Si content was increased. The continuous impedance responses indicated that the bulk Nafion® phase was rarely interrupted by the silica inorganic phase. When the Krytox-Si was as high as 5 wt.%, the proton conductive studies in ambient condition showed that the composite membranes maintained their conductivity at 10^{-3} S/cm even the temperature was up to 130 °C.

Fig. 4. Proton conductivity of **5** (●), **4a** (○), **4b** (▲), and **4c** (Δ) at 20–140 °C with no moisture conditioning.

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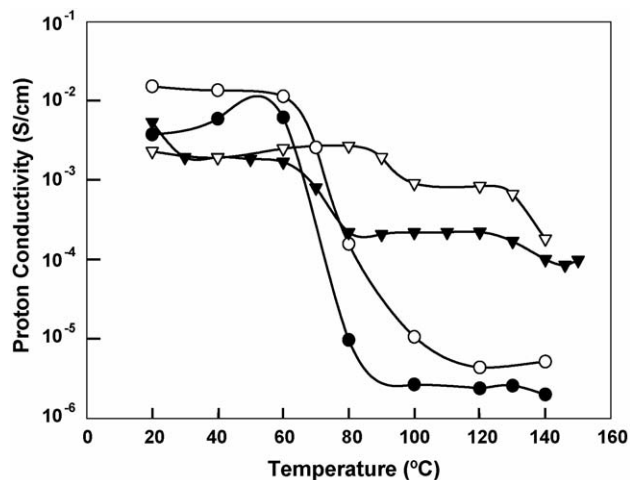[4] R. Ianniello, V.M. Schmidt, U. Stimming, J. Stumper, A. Wallau, Electrochim. Acta 39 (1994) 1863.

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