



Polymer electrolyte membranes containing titanate nanotubes for elevated temperature fuel cells under low relative humidity

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ABSTRACT

Nafion–titanate nanotubes composite membranes prepared through casting process have been investigated as electrolytes for polymer electrolyte membrane fuel cell applications under low relative humidity. The glass transition temperature and the decomposition temperature of composite membrane at dry state are higher than those of pristine Nafion membrane. Cracks have been observed in the membrane at the concentration of nanotubes above 5 wt.%. The maximum proton conductivity at 100 °C and 50% relative humidity is observed with the concentration of doped titanate nanotubes of 5 wt.%. Solid nuclear magnetic resonance spectrum is applied to qualitatively characterize the status of water inside the membrane at different temperatures. The power densities at 0.8 V for cell assembled from composite membrane containing 5 wt.% of titanate nanotubes are about 13% and 35% higher than that for plain Nafion cells under 50% relative humidity at 65 °C and 90 °C, respectively.

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1. Introduction

Polymer electrolyte membrane fuel cells operating at elevated temperature have been considered as the next generation of fuel cells as they could benefit from enhanced tolerance to fuels, simplified heat management, and possibly application of non-platinum catalysts as well [1,2]. One of the great technical barriers for elevated temperature fuel cells is the polymeric electrolytes that should maintain reasonable proton conductivity at elevated temperature and under reduced relative humidity of the fuels. The dramatic decrease in ionic conductivity for commonly used perfluorinated Nafion membrane produced by DuPont makes it unsuitable for fuel cell applications at elevated temperature and under low relative humidity. However, perfluorosulfonic acid polymeric membranes are still the most important choice for fuel cell applications because of their robust structure and excellent stability [3,4]. Thus, modification of perfluorinated Nafion membranes has attracted considerable attention for elevated temperature fuel cell applications.

One interesting approach for modification of Nafion membranes is to impregnate nanostructured hygroscopic metal oxides inside the perfluorinated Nafion membranes [5,6]. The motivation for the

addition of metal oxides in the membranes is to introduce surface hydroxyl groups for enhanced water retention ability, and accordingly to improve proton conductivity of membranes at elevated temperature [7]. Various hygroscopic metal oxide additives, including SiO₂, ZrO₂, and TiO₂, have been applied for inorganic–organic hybrid polymer electrolyte membranes [8–13]. For example, Jalani et al. [8] have investigated the water uptake and electrochemical properties of Nafion membranes incorporated with different metal oxide nanoparticles. It was found that the nanocomposite membranes exhibited higher water uptake and better electrochemical properties compared to plain Nafion membrane. It has been also observed by another research group that the Nafion–metal oxide nanoparticles composite membrane can bear the operating temperature of fuel cell up to 130 °C, whereas the commercial Nafion115 membrane was damaged at 120 °C within 1 h [10]. Although the exact role that metal oxide additives played is still unclear, metal oxide doped Nafion membranes are promising electrolytes for fuel cells operated at elevated temperature.

Among the nanostructured metal oxide additives for polymer electrolyte membrane applications, titanate nanotube is of interest because of its larger specific surface area and unique physicochemical properties [14,15]. Particularly, the high water retention ability induced by larger specific surface area and the moderate proton conductivity of the nanotubes make it suitable as additives in elevated temperature electrolytes for fuel cell applications [16–18]. Power density of about 0.72 W cm⁻² at 0.6 V has been observed at 130 °C with fully humidification of gas under a system pressure of 3 bar using the membrane containing 5 wt.% of nanotube.

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Although the water uptake of composite membrane increases with the increase in the content of the nanotube (from 0 to 15 wt.%), fuel cell using membrane containing 5 wt.% of nanotube as electrolytes showed the best performance in the whole measured temperature ranges [18]. The results were attributed to a competing effect between the increased water uptake induced by large specific surface area and the decreased proton conductivity with the increase of the content of the nanotube. Unfortunately, no proton conductivity data were presented in the paper for the membrane containing 5 wt.% of the nanotube.

We have recently observed [17] that the proton conductivity of Nafion membrane containing 5 wt.% of the nanotube is higher than that of pristine Nafion membrane in the whole measured temperature range under reduced relative humidity. For the membrane containing 10 wt.% of the nanotube, the proton conductivity without external humidification is lower than that of membrane containing 5 wt.% of the nanotube and is only higher than that of plain Nafion membrane at temperature above 90 °C. In this communication, we aim to understand why the composite membrane containing 5 wt.% of the nanotube exhibits best performance, how the relative humidity affects the performance of fuel cells at elevated temperature, and the thermal properties of formed composite membranes.

2. Experimental part

Titanate nanotubes were prepared using alkaline hydrothermal process according to literature with minor modification [19]. Typically, 1 g TiO₂ powder (P25, Degussa) in 50 ml aqueous solution of 10 M NaOH was stirred at room temperature for 30 min. The suspension was then transferred into a Teflon-lined autoclave and heated for 24 h at 170 °C. After cooled down to room temperature, the mixture was centrifuged and washed with 0.1 M HCl and then with deionized water until a pH value of 7 was reached. Finally, the white product was dried at 85 °C under vacuum for 12 h.

Nafion membrane doped with titanate nanotubes was formed by a casting process. A commercial Nafion dispersion (5 wt.%, DuPont) was evaporated at 100 °C and re-dissolved in ethylene glycol (Aldrich) under vigorous stirring. After the desired amount of nanotubes was dispersed in water by ultrasonic bath, the dispersion was added to above Nafion solution. The pH value of the resulting suspension was adjusted to ~1.5 using 0.1 M HCl and the suspension was continuously stirred for 24 h. The membrane was cast by pouring the suspension in a Teflon dish, followed by heat-treatment at 80 °C for 10 h, 120 °C for 2 h, and 160 °C for 0.5 h, respectively. The so-formed membrane was cleaned by treatment in 3 wt.% H₂O₂, deionized water, 0.5 M H₂SO₄, and finally deionized water again at 80 °C for 30 min for each step. Unless otherwise stated, the content of the nanotubes inside composite membranes is about 5 wt.%.

The size and morphology of formed titanate nanotubes were examined using high resolution transmission electron microscopy (TEM, JEM-2010FEF). Samples for TEM measurements were prepared by directly placing a drop of the solution on a thin carbon film supported by a copper grid. X-ray diffraction (XRD) patterns for membranes were obtained on a D/MaxRB X-ray diffractometer (Rigaku, Japan) using Cu K α radiation operating at 40 kV and 30 mA. Surface area, pore volume, and pore size distribution of the formed titanate nanotubes were calculated from the adsorption–desorption isotherm of nitrogen at 77 K on JW-BK instrument (JWGB Sci & Tech Co., Ltd., China).

Surface morphology of formed membranes was examined using scanning electron microscopy (SEM, JEOL JSM-5610LV equipped with Energy Dispersive Spectrum Analyzer). The samples for cross-sectional SEM images were obtained by fracturing the samples in

liquid nitrogen. Differential thermo-gravimetric analysis (DTG) of the membranes was carried out using NETZSCH STA449C Simultaneous Thermal Analyzer with a conventional mode (dynamic heating) at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere were applied over the temperature range of 30–600 °C. Thermo-mechanical measurement (TMA) was carried out using a TMA-202 analyzer (NETZSCH, Germany) with 50 cm³ min⁻¹ of nitrogen purge gas. The sample size was 12.0 mm × 4.0 mm. Experiments were run from 30 to 200 °C with a temperature ramp rate of 20 °C min⁻¹. Mechanical strength of membranes was measured using an Electromechanical Universal Testing Machine (WDW-1C) based on Chinese Standard QB-13022-91. The membranes were cut into stripes of 6 mm × 40 mm. The samples were measured at a strain rate of 50 mm min⁻¹. The pulling stress was slowly increased and the strain with different stresses was recorded. Three repetitions of the measurements were made for each sample. The proton conductivity of membranes was calculated from impedance spectroscopy measured by an impedance analyzer (Autolab PG30/FRA, Eco Chemie, Netherland) in a homemade testing cell with controllable temperature and relative humidity. Electrochemical impedance spectra (EIS) were recorded in the frequency range of 1 Hz and 105 kHz and the signal amplitude of 10 mV. Measurements were carried out from lower temperature to higher temperature and data were recorded after stable EIS was investigated. ¹H nuclear magnetic resonance (NMR) was applied to investigate the status of water inside the membrane at different temperature. The ¹H NMR measurements were performed on a Varian UNITYINOVA 600 MHz spectrometer operating at a proton frequency of 599.186 MHz. Hydrogen signals were observed through the NANO probe with a relatively low spinning rate of 2 kHz to reduce the phase-separation effects of the centrifugal force caused by sample spinning. Background spectrum of NMR tubes was subtracted from all the spectra to eliminate the background signal.

The membrane electrode assemblies were fabricated using catalyst coated membrane (CCM) method as reported previously [20]. Loading of Pt electrocatalyst (Hispec™ 9100, Johnson Matthey) on both cathode and anode was 0.2 mg cm⁻². Carbon paper (TGP-060, Toray) treated with PTFE was used as gas diffusion layer and hot pressed on CCM. The active area of the formed membrane electrode assembly was 25 cm². The performance of assembled single cells was measured on a G50 Fuel Cell Test Station (GreenLight, Canada) using H₂ as fuel and air as oxidant without back pressure. H₂ and air flow rates were 300 and 2000 sccm, respectively. The humidity of H₂ and air was kept at the same level controlled by dew point. Prior to the measurement, cells were activated by polarization at a constant current until stable performance was achieved. The polarization curve was recorded until the performance reached a stable state at each testing point.

3. Results and discussion

The titanate nanotubes were synthesized according to the reported process [19]. The synthesized titanate nanotubes have the inner diameter of 5 nm, wall thickness of about 1.4 nm, and the length of 50–140 nm, as indicated by transmission electron microscopic images (Fig. 1a). The size distribution peak at around 100 nm detected by dynamic light scattering (data not shown) confirmed the size of the formed nanotubes. The X-ray diffraction (XRD) pattern of the synthesized nanotubes was shown in Fig. 1b. The peaks at 2 θ of 10.46°, 24.27°, and 48.38° are corresponded to the hydrogen titanate (H₂Ti₃O₇) structure [18], indicating that large amount hydroxyl groups at surfaces of the formed nanotubes. Surface area of the formed nanotubes was calculated as about 321 m² g⁻¹ from the thermal adsorption curves (Fig. 1c). The calculated pore size (inset in Fig. 1c) of the synthesized nanotubes from

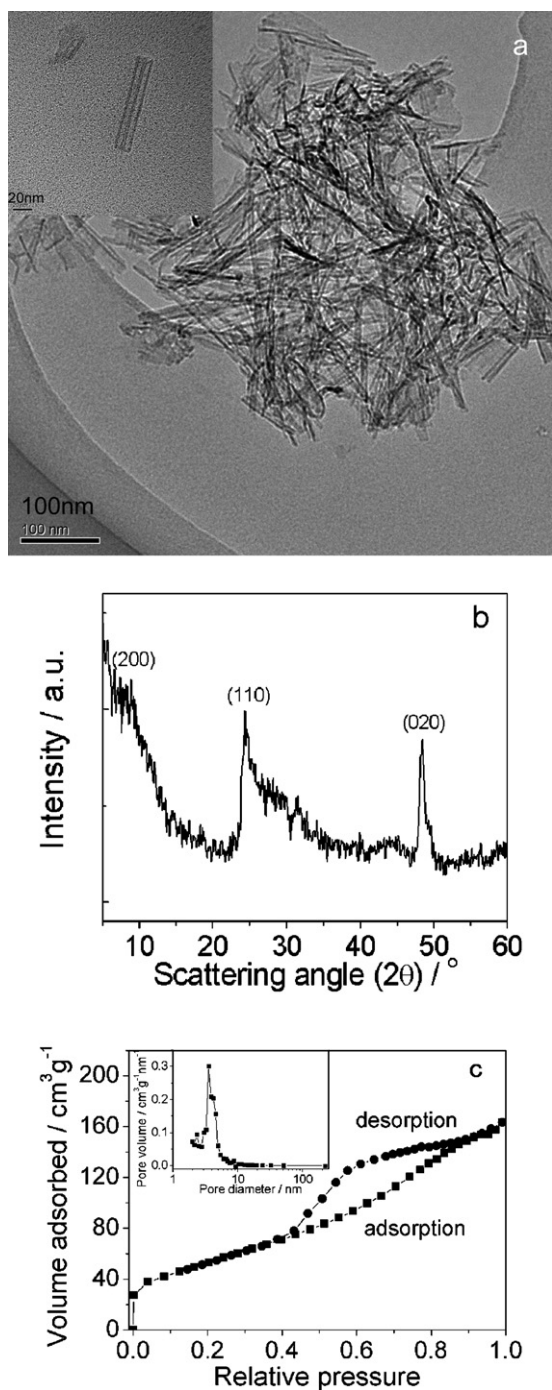


Fig. 1. (a) Transmission electron microscopic image of the formed titanate nanotubes. The inset is higher magnification TEM image of a nanotube. (b) X-ray diffraction pattern for the formed titanate nanotubes. The identified peaks correspond to the hydrogenated titanate. (c) Pore volume and pore size distribution of the formed titanate nanotubes calculated from the adsorption–desorption isotherm.

thermal adsorption–desorption curves is about 4 nm, that agrees well with the TEM observation.

Since Nafion/titanate nanotubes composite membrane with 5 wt.% of nanotubes showed the best cell performance and the highest proton transporting properties as observed in literature [17,18], we first investigated the morphology of composite membranes with various content of titanate nanotubes in the membrane using scanning electron microscope, as shown in Fig. 2. Relatively smooth surfaces were observed for composite membranes with the nanotube content below 5 wt.%. The proton transportation inside the

membrane can be enhanced because of the increased water uptake with the increase of the nanotube content up to 5 wt.%. While the nanotube content further increased to 7 wt.% in the membrane, small cracks with the width of about 40 nm appeared on the surface (Fig. 2c). With further increase in nanotube content to 10 wt.% in the membrane, large cracks were clearly observed on the surface with the width of about 70 nm (Fig. 2d). The generated several tens nanometer sized cracks during membrane formation process were attributed to the incompatibility between the polymer and the incorporated inorganic materials and the formed cracks can cut/block the pathway of protons in the membrane, leading to decreased proton transporting ability. Accordingly, the proton conductivity and cell performance decreased.

Cross-sectional microscopic images of composite membranes were shown in Fig. 3. Similar to the observation on morphology of membranes, no cracks or defects was found for the membrane containing 5 wt.% of the formed nanotubes, whereas apparent cracks appeared for the membrane with 10 wt.% of nanotubes. Fig. 4 shows energy dispersive spectrum of Ti-atom at cross-sectional direction of the formed membrane with 5 wt.% nanotubes (corresponding to Fig. 3a). It can be concluded that the incorporated nanotubes were well-distributed in the membrane.

The motivation of the formation of Nafion/titanate nanotubes composite membrane is to seek suitable electrolytes for elevated temperature fuel cell applications. The glass transition temperature (T_g) and thermal-stability of membranes are of importance for elevated temperature applications. Thermal-mechanical analysis curves of composite membranes with different content of titanate nanotubes were plotted in Fig. 5a. It can be seen that the T_g of composite membranes at dry state increases with the increase in the content of the nanotubes. For the membrane with 5 wt.% of nanotubes, the T_g is about 150 °C that is about 15 °C higher than that of pristine Nafion membrane at dry state. Fig. 5b shows differential thermo-gravimetric curves of the formed membranes with different content of titanate nanotubes. The decomposition temperature of sulfonic acid groups on the side chain of Nafion increases with the increase in the content of nanotubes as well, from about 280 °C for plain membrane to about 290 °C and 320 °C for membranes containing 5 wt.% and 10 wt.% of titanate nanotubes, respectively. The increased decomposition temperature and glass transition temperature indicate that the formed composite membranes containing titanate nanotubes are thermally more stable than pristine Nafion membrane. The enhanced thermal stability of the formed composite membrane was attributed to the interaction between hydroxyl groups at nanotube surface and the sulfonic acid groups on side chains of Nafion.

One of very important properties that a qualified fuel cell membrane should have is mechanical strength of the membrane as it can strongly affect its practical applications in a fuel cell. Fig. 6 shows the tensile strength of formed composite membranes containing different amount of the formed titanate nanotubes with 5% elongation at both fully hydrated and dry states. As comparison, the tensile strength of recast Nafion membrane was recorded in the same figure. It is evident, that the tensile strength for composite membranes with the nanotube content below 5 wt.% is slightly lower than that of recast Nafion membrane at both dry and fully hydrated states. However, the tensile strength drops quickly with further increase in the titanate nanotube content and the membrane even becomes brittle with the nanotube concentration of 10 wt.%. The decrease in tensile strength is probably attributed to the increased interfacial energy of Nafion and titanate nanotubes caused by the incompatibility of the resin and the nanotubes.

Since the fuel cell performance strongly depends on the proton transport properties and the formed Nafion/titanate nanotubes composite membrane is supposed to be suitable for elevated temperature fuel cell applications, proton conductivity of the formed

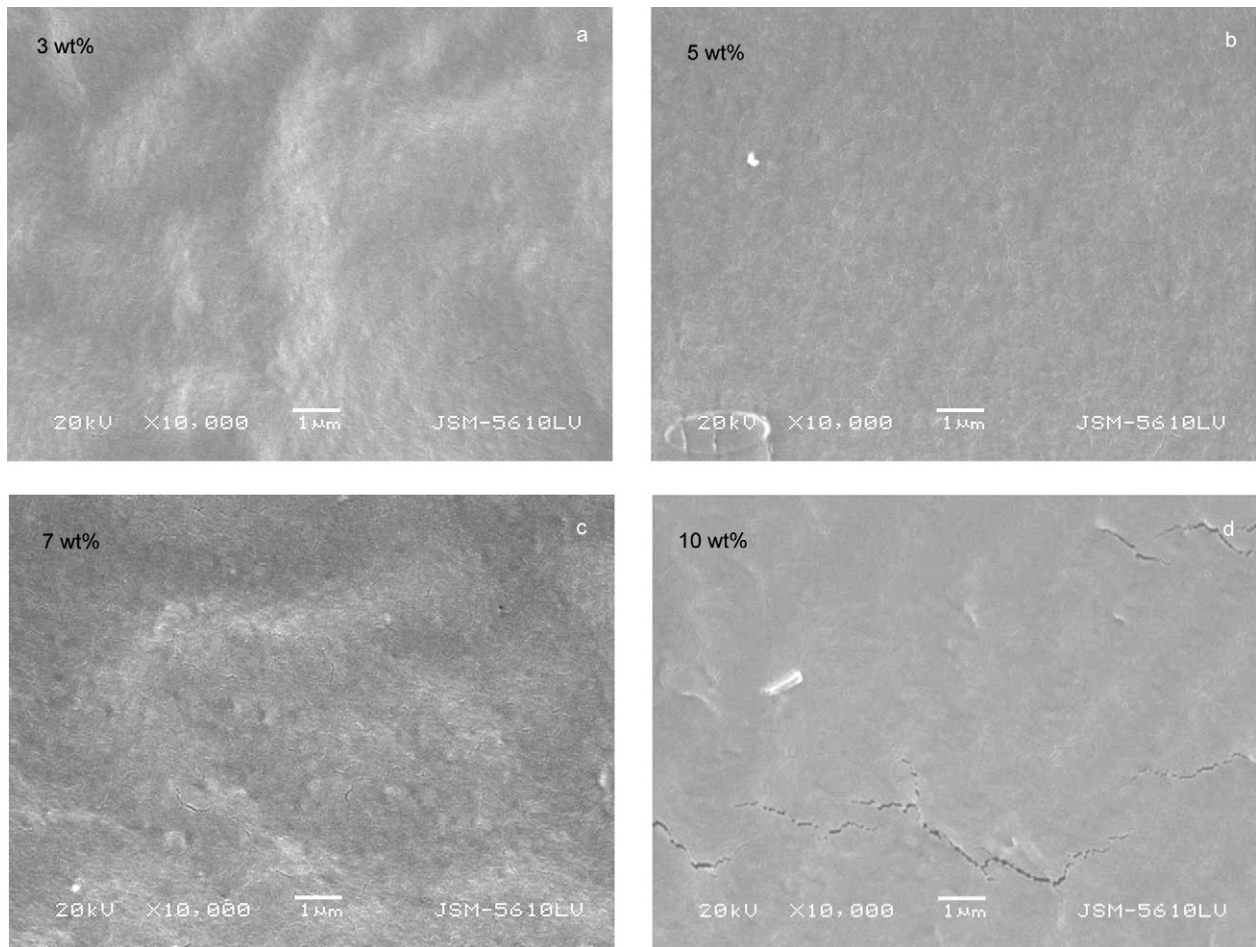


Fig. 2. Scanning electron microscopic images of Nafion/titanate nanotubes composite membranes with different concentration of nanotubes as indicated on the images.

membranes was first investigated as a function of the concentration of the doped nanotubes at 100 °C, as shown in Fig. 7. At fully hydrated state, the proton conductivity of the formed membranes decreases with the increase in the concentration of doped nanotubes since the doped titanate nanotubes is much less proton conductive [16]. However, within the experimental ranges, a maximum proton conductivity at reduced relative humidity of 50% was observed at the concentration of titanate nanotubes of 5 wt.%, reaching 0.016 S cm^{-1} . In our previous work [17] and the

work carried out by Santiago and co-workers [18], the increase in water uptake with the concentration of doped titanate nanotubes and enhanced water retention ability of composite membranes were observed. As water is proton transport medium inside the membrane, the enhanced water retention ability could improve the proton transportation, leading to enhanced proton conductivity. However, the proton conductivity at reduced relative humidity decreases with the increase in the concentration of doped titanate nanotubes above 5 wt.%. This probably results from the incompat-

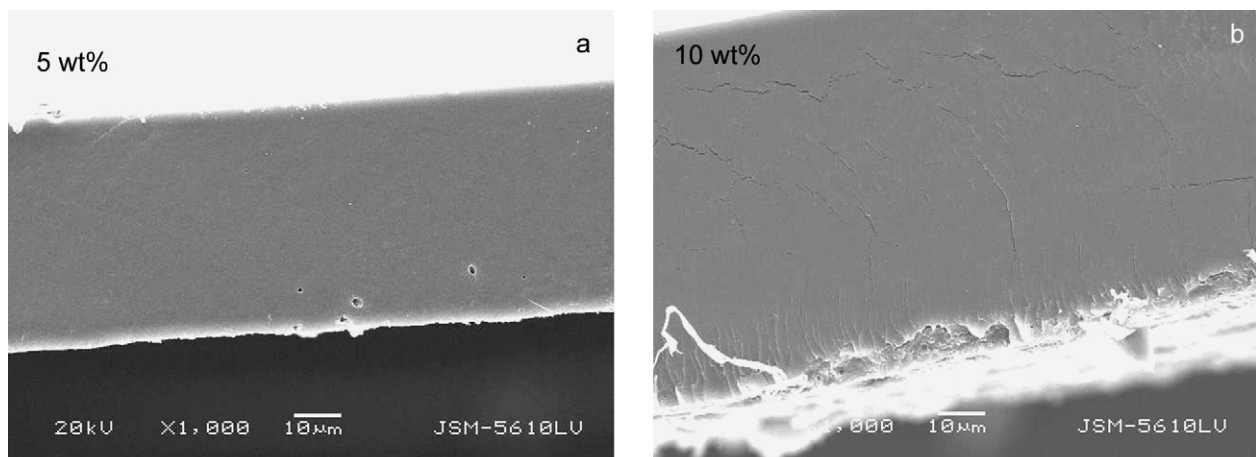


Fig. 3. Cross-sectional images of the formed composite membranes with the concentration of titanate nanotubes of 5 wt.% (a) and 10 wt.% (b).

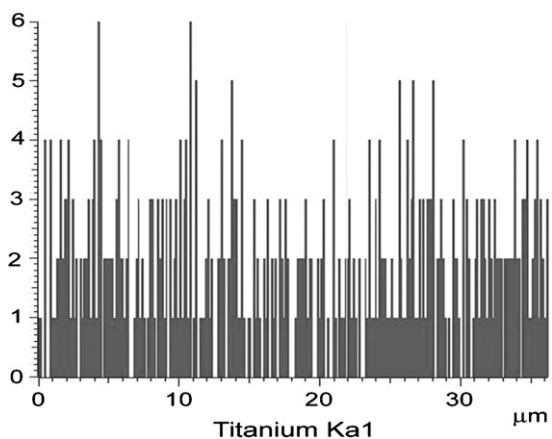


Fig. 4. Energy dispersive spectrum of Ti atoms at the cross-sectional direction for the formed composite membrane with the concentration of nanotubes of 5 wt.%.

ibility of Nafion and titanate nanotubes as observed by scanning electron microscopy.

Nuclear magnetic resonance (NMR) was applied to qualitatively investigate the status of water at different temperatures in the composite membrane with the concentration of the doped nanotubes of 5 wt.% (Fig. 8). In ^1H NMR spectra, the peak around 10 ppm was assigned to hydrogen-bonded water clusters associated with protons which plays important role for proton transportation inside the membrane and the peak 4 ppm was assigned to physically adsorbed water molecules according to literature [21,22]. With the increase in temperature, the intensity of both peaks at around 10 ppm and 4 ppm decreases, indicating that the amount of water molecules (physisorbed and proton-associated) decreases because of evaporation. In addition, the peak for proton-associated water molecules shifted to downfield and the line width has no significant change with the increase in temperature, indicating the improved mobility of proton-associated water molecules. This observation is contrast to that in pristine Nafion membrane investigated in literature [22,23] where the resonance peak for proton-associated water molecules shifted to upfield and the line width became broad with the increase in temperature, indicating that proton transportation inside the pristine membrane became difficult. The quantitative analysis of ^1H NMR with controllable conditions (temperature and relative humidity) is still under investigation. Nevertheless, this qualitative result implies that the titanate nanotube doped Nafion membrane is potential candidate electrolyte for polymer electrolyte membrane fuel cell applications.

Since the formed Nafion/titanate nanotubes composite membranes show relatively strong incompatibility between polymeric

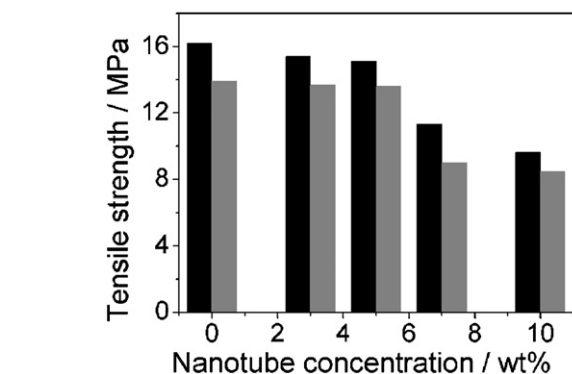
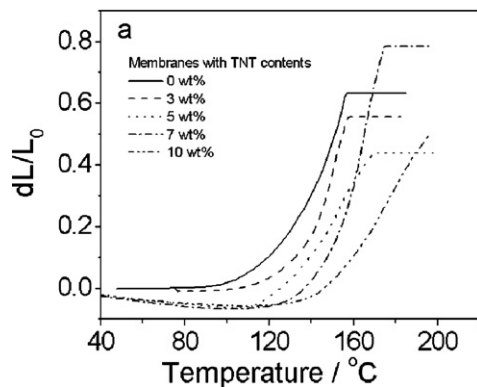


Fig. 6. Tensile strength of formed membranes containing different amount of titanate nanotubes with 5% elongation at fully hydrated state (black) and dry state (gray).

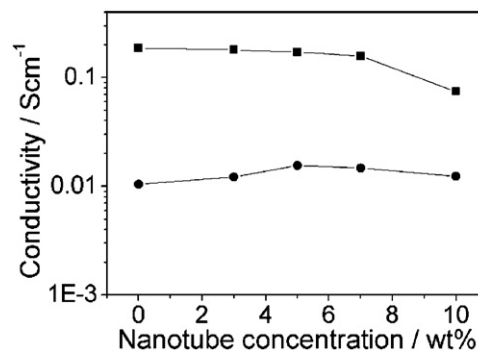


Fig. 7. Proton conductivity of formed composite membranes as a function of the concentration of titanate nanotubes at 100 °C under different relative humidity: 100% (squares) and 50% (circles). Lines are guide to eyes.

resin and incorporated inorganic materials with the nanotube concentration above 5 wt.%, composite membrane with the nanotube concentration of 5 wt.% was applied for membrane electrode assembly (MEA) with standard Pt/C electrodes. For comparison, recast pristine Nafion membrane with similar thickness was also applied for MEA formation. Polarization curves of the resulting single cells at 65 °C and 90 °C under different relative humidity were shown in Fig. 9. The performance for single cells using both pristine Nafion membrane and composite membrane is humidity-dependant. At low relative humidity (<50%), the decreased amount of water leads to an increased resistance of membranes. As a result, the decreased cell performance was observed because of the large ohmic drops at low relative humidity. For the composite mem-

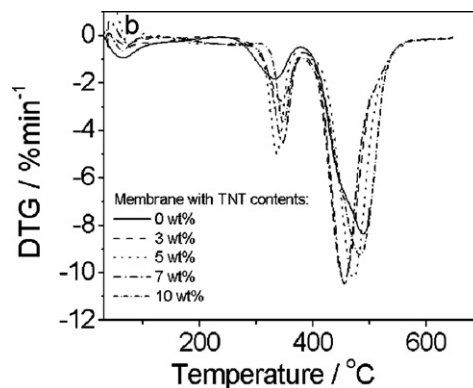


Fig. 5. Thermal-mechanical analysis curves (a) and differential thermo-gravimetric analysis curves (b) of composite membranes with different concentration of titanate nanotubes as indicated on the images.

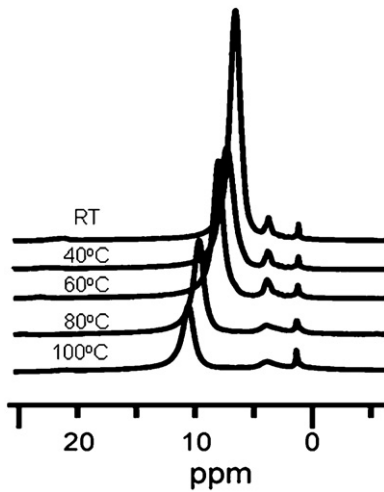


Fig. 8. ^1H NMR spectra of the formed composite membrane with the concentration of doped nanotubes of 5 wt.% at different temperatures.

brane, the performance of the assembled cell is similar to that of the cell using pristine Nafion membrane as electrolyte at high relative humidity (>80%). However, with the decrease in relative humidity to below 50%, the enhanced performance of the assembled cell using Nafion/titanate nanotubes composite membrane was clearly observed in comparison to the cell using pristine Nafion membrane as electrolyte. The enhancement of the cell performance using composite membrane as electrolyte was even more pronounced at higher operating temperature. As shown in Fig. 10, the power density at 0.8 V for cells using composite membrane as electrolyte was observed as 0.44 W cm^{-2} at 90°C under 50% relative humidity, which is about 35% higher than that obtained from single cells using plain Nafion membrane as electrolyte operated at the same conditions. For cell using composite membrane as electrolyte operated at 65°C , only about 13% higher power density at 0.8 V under 50% relative humidity was obtained while compared to the cell using plain Nafion membrane as electrolyte.

The enhancement of the cell performance using composite membrane as electrolyte at operating temperature above under fully hydrated state was observed in the literature as well [18]. To have a better understanding on this phenomenon, proton conductivity of the formed composite membrane with the concentration of nanotubes of 5 wt.% and recast pristine Nafion membrane was investigated as a function of temperature and relative humidity, as shown in Fig. 11. At fully hydrated state (100% relative humidity), enough water molecules exist in both membranes for proton transportation. As the doped nanotubes can occupy the pathway for

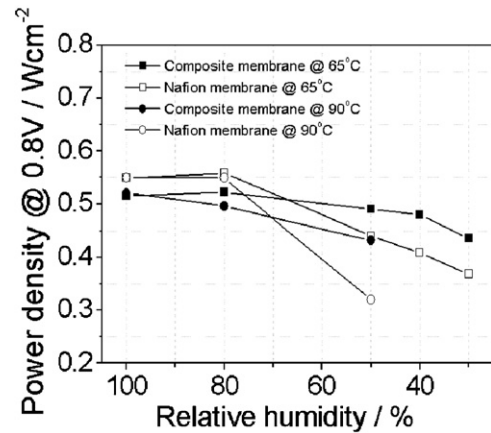


Fig. 10. Power density at 0.8 V for membrane electrode assemblies using plain Nafion membrane (open symbols) and composite membrane with the concentration of titanate nanotubes of 5 wt.% (solid symbols) as a function of relative humidity at 65°C (squares) and 90°C (circles).

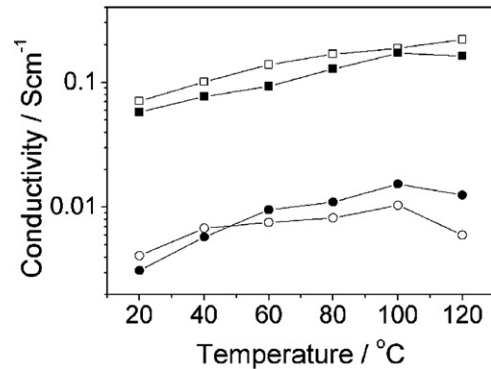


Fig. 11. Proton conductivity of composite membrane with the concentration of nanotubes of 5 wt.% (solid) and recast pristine Nafion membrane (open) as a function of temperature at different relative humidity: 100% (squares) and 50% (circles). Lines are guide to eyes.

proton transportation, the doped less proton conductive nanotubes have negative effects on that, showing that the proton conductivity of recast pristine Nafion membrane is higher than that of composite membranes under hydrated state at all the measured temperature range. Accordingly, the performance of fuel cell using composite membrane as electrolyte under fully hydrated state is higher than that using pristine Nafion membrane as electrolyte. At reduced hydration state (50% relative humidity here), the proton conductivity of composite membrane below 50°C is smaller than that of

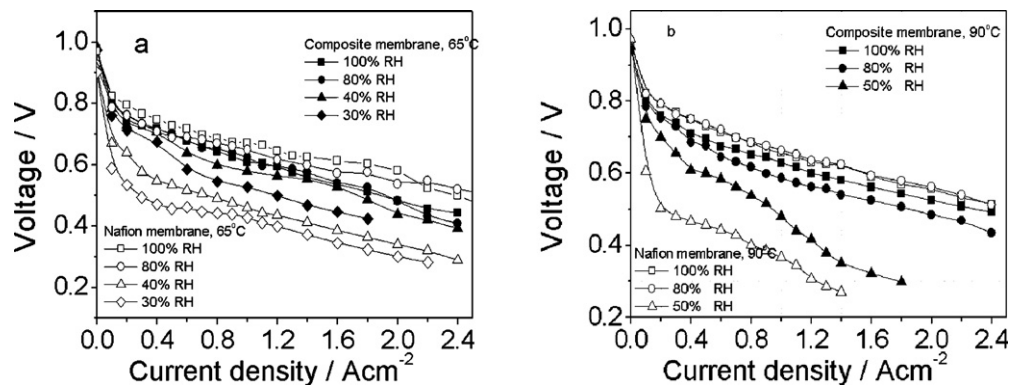


Fig. 9. Polarization curves of membrane electrode assemblies made from plain Nafion membrane (open symbols) and Nafion/titanate nanotubes composite membrane with the concentration of nanotubes of 5 wt.% (solid symbols) under various relative humidity at 65°C (a) and 90°C (b).

recast pristine Nafion membrane because of the less conductive of the doped nanotubes. With further increase in temperature, the composite membrane can trap more water molecules compared with pristine Nafion membrane as observed in NMR spectra, facilitating proton transportation in the membrane. Accordingly the performance of fuel cell can be enhanced with the introduction of titanate nanotubes to Nafion membrane at elevated temperature and reduced hydration state as water is proton transporting media in the membrane.

Although the increase in the concentration of incorporated titanate nanotubes leads to improved water uptake [18], the incompatibility between polymeric resin and inorganic titanate nanotubes leads to the cracks in the membrane at the concentration of the nanotubes above 5 wt.%, which could offset the benefit arisen from the improved water uptake. We are currently working on the surface modification of titanate nanotubes to improve the compatibility between Nafion and the nanotubes.

4. Conclusion

Proton exchange membranes comprised of Nafion and titanate nanotubes were developed using recast process. Because of the incompatibility between polymeric resin and the incorporated inorganic titanate nanotubes, cracks appeared in the formed composite membrane at relatively high concentration of titanate nanotubes (>5 wt.%), which strongly affect the physicochemical and electrochemical properties of the membrane. Compared to pristine Nafion membrane, Nafion/titanate nanotube composite membrane exhibits enhanced thermal properties, and improved proton conductivity at elevated temperature and reduced relative humidity, attributed to the interaction between hydroxyl groups on the surface of nanotubes and the sulfonic acid groups on the side chains of polymer. The performance of single cell assembled from composite membrane was improved at rather low relative humidity in comparison of plain Nafion membrane, attributed to the great water retention ability of composite membranes. The results presented here suggest that the Nafion/titanate nanotube composite membranes are suitable as electrolytes for fuel cell applications at elevated temperature under low relative humidity.

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