

## 가지형 공중합체/TiO<sub>2</sub> 나노복합 고분자 전해질막의 제조 및 분석

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### Preparation and Characterization of Graft Copolymer/TiO<sub>2</sub> Nanocomposite Polymer Electrolyte Membranes

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**요약:** 원자전달 라디칼 중합을 이용하여 poly(styrene sulfonic acid) 47 wt%를 가진 poly(vinylidene fluoride-co-chlorotrifluoroethylene)-g-poly(styrene sulfonic acid) (P(VDF-co-CTFE)-g-PSSA) 가지형 공중합체를 합성하였다. 티타늄 아이소프로폭사이드(TTIP)와 가지형 공중합체를 졸-겔 공정을 통하여 TiO<sub>2</sub>/가지형 공중합체 복합막을 제조하였다. TTIP는 가지형 공중합체의 친수성을 가진 PSSA 영역에만 선택적으로 결합하였으며, 그곳에 TiO<sub>2</sub> 나노 입자가 형성되어 성장하였다. 이와 같은 결과를 적외선과 자외선 분광학으로 확인할 수 있다. 함수량과 이온 교환 능력(IEC)은 TTIP의 함량에 따라 감소하였고 이것은 막이 가진 술폰산의 수가 감소하기 때문이었다. TTIP가 5 중량%일 때, 막의 기계적 강도는 증가하고 수소이온 전도도도 유지되었다.

**Abstract:** A graft copolymer, i.e. poly(vinylidene fluoride-co-chlorotrifluoroethylene)-g-poly(styrene sulfonic acid) (P(VDF-co-CTFE)-g-PSSA) with 47 wt% of PSSA was synthesized via atom transfer radical polymerization (ATRP). This copolymer was combined with titanium isopropoxide (TTIP) to produce graft copolymer/TiO<sub>2</sub> nanocomposite membranes via sol-gel process. TiO<sub>2</sub> precursor (TTIP) was selectively incorporated into the hydrophilic PSSA domains of the graft copolymer and grown to form TiO<sub>2</sub> nanoparticles, as confirmed by FT-IR and UV-visible spectroscopy. Water uptake and ion exchange capacity (IEC) decreased with TTIP contents due to the decrease in number of sulfonic acid in the membranes. At 5 wt% of TTIP, the mechanical properties of membranes increased while maintaining the proton conductivity.

**Keywords:** atom transfer radical polymerization (ATRP), graft copolymer, TiO<sub>2</sub>, proton conductivity, polymer electrolyte membrane

### 1. Introduction

A fuel cell is an electrochemical device which combines oxygen and hydrogen with the aid of electrocatalysts to generate electricity [1]. Among the types of fuel cells, the proton exchange membrane fuel cell, also known as polymer electrolyte membrane fuel cell

(PEMFC), is in the advanced stage of development. The PEMFC is a clean energy conversion device because the products are only water, heat and electricity. It has high efficiency (40~65%) and good reliability, low operating temperature (< 100°C), and high power density (0.8 W/cm<sup>2</sup>). As a result, PEMFC has been established as one of the most promising technology for many future applications such as portable electronics, distributed generation of energy, and vehicles [2].

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Polymer electrolyte membranes are promising candidates for the energetic electronic devices such as lithium battery, super capacitors, chemical sensors, fuel cells and etc. [3-6]. In spite of many advantages such as high performance, size, safety and environmental aspects, polymer membranes still suffer from some critical drawbacks that must be overcome for practical applications. One of the major drawbacks is high cost of polymer electrolyte membranes, e.g. Nafion. In addition, Nafion experiences some difficulties such as a drop in conductivity beyond 80°C, resulting in the reduction of cell performance [7,8]. These limitations have prompted research into alternative membranes such as composite membranes. Organic/inorganic composite materials constitute a remarkable family of isotropic, flexible, amorphous nanocomposite materials, which have been investigated extensively for materials for biomedical devices or fuel cells [9].

High ionic conductivity, good chemical, thermal and mechanical stability, and low price are the favorable characteristics of polymer electrolyte membranes. These prerequisites of polymer electrolyte membranes can be obtained by combining an organic polymer and inorganic nanomaterials. For example, Adjemian *et al.* proposed a sol-gel approach of adding metal oxide to a Nafion membrane that might provide superior performance to particles, because the sol-gel produced nanoparticles are homogeneously dispersed on the angstrom scale versus submicrometer-length scales for the particle composites [10]. Thus, the organic-inorganic hybrid materials can possess enhanced properties compared to the pure materials [11]. In this paper, a graft copolymer, i. e. poly(vinylidene fluoride-co-chlorotrifluoroethylene)-g-poly(styrene sulfonic acid) (P(VDF-co-CTFE)-g-PSSA) was synthesized via atom transfer radical polymerization (ATRP) and combined with titanium isopropoxide (TTIP) to produce graft copolymer/TiO<sub>2</sub> nanocomposite membranes via sol-gel process. These nanocomposite membranes were characterized in terms of proton conductivity, water uptake, ion exchange capacity (IEC) and mechanical property.

## 2. Experimental

### 2.1. Materials

P(VDF-co-CTFE) (PVDF SOLEF® 31508/1001) was kindly provided by Solvay. Titanium isopropoxide (TTIP, 98%), dimethylsulfoxide (DMSO), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), 4-styrene sulfonic acid (SSA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper(I) chloride (CuCl, 99%), phenolphthalein (C<sub>20</sub>H<sub>14</sub>O<sub>4</sub>, 0.5 wt% solution in 50 wt% ethanol) were purchased from Aldrich and used as received without further purification.

### 2.2. Synthesis of Graft Copolymers

1.0 g of P(VDF-co-CTFE) was dissolved in 25 mL NMP in a round flask at 80°C. Separately, 6.0 g of SSA were dissolved in 20 mL DMSO at 80°C and added to P(VDF-co-CTFE) solution. After producing homogeneous solution, 0.08 g of CuCl and 0.2 mL of HMTETA were added and the reaction flask was sealed with a rubber septum. After N<sub>2</sub> purging for 30 min, the reaction vessel was immersed in an oil bath at 120°C. The reaction was allowed to proceed for 24 h. After polymerization, the resultant polymer was diluted with DMSO. After passing the solution through a column with activated Al<sub>2</sub>O<sub>3</sub> to remove the catalyst, it was precipitated in methanol. The polymer was purified by redissolving in DMSO and reprecipitating in methanol. Finally, the polymer was dried in a vacuum oven overnight at room temperature.

### 2.3. Preparation of Nanocomposite Membranes

The nanocomposite membranes containing TiO<sub>2</sub> in various weight ratios were prepared using sol-gel method. First, the as-synthesized P(VDF-co-CTFE)-g-PSSA graft copolymer was soaked in methanol at 40°C for 1 h. Then it was soaked in 0.5 N H<sub>2</sub>SO<sub>4</sub> at room temperature for 15 h. The proton-exchanged graft copolymer was thoroughly washed with deionized water. It was then dried in a vacuum oven at room temperature for 24 h. The acidic graft copolymer and the de-

sired amounts of TTIP with 0~20 wt% were dissolved in DMSO together to form a transparent solution. After complete dissolution, the solutions were cast onto a Teflon-coated glass dish. The solutions were dried in a convection oven at 80°C for 48 h, and then in a vacuum oven at 100°C for 24 h.

#### 2.4. Water Uptake

Water uptake was determined by weighing vacuum dried membrane and fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with an absorbent paper to remove the excess of water adhering to it and the sample was then weighed. The water uptake of membranes was determined from equation (1), where  $W_w$  and  $W_d$  are the weights of wet and dried membranes, respectively [12].

$$\text{water uptake (wt\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

#### 2.5. Ion Exchange Capacity (IEC)

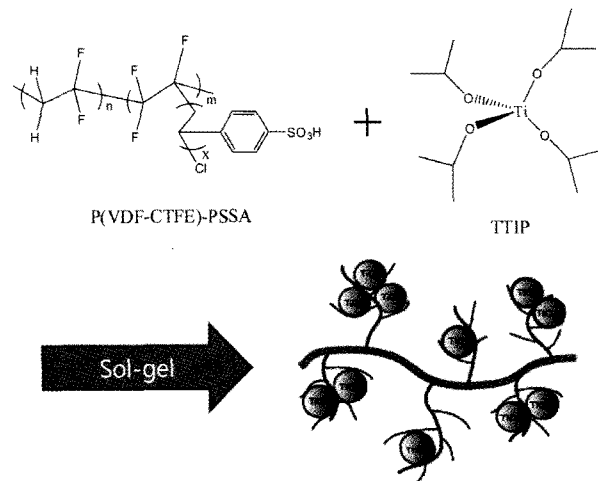
The IEC values of membranes were measured by the classical titration method. The membranes were soaked in 1.0 M NaCl solution for 24 h before measuring IEC. The protons released due to the exchange reaction with Na ions were titrated against 0.01 M standardized NaOH solution, using phenolphthalein indicator. The IEC of the graft copolymer membranes was calculated using the following equation [12,13]:

$$\text{IEC (meq/g)} = \frac{X \times N_{\text{NaOH}}}{\text{Weight (polymer)}} \quad (2)$$

where  $X$  is the volume of NaOH consumed and  $N_{\text{NaOH}}$  is the normality of NaOH.

#### 2.6. Proton Conductivity

A four-point probe method was used to measure the proton conductivity of the membranes using home-made conductivity cell. Before the measurement of proton conductivity, the prepared membranes were equilibrated with deionized water. Complex impedance measure-



**Scheme 1.** Preparation of proton conducting nanocomposite membranes consisting of P(VDF-CTFE)-PSSA graft copolymer and TTIP.

ments were carried out in the frequency range 1 Hz~8 MHz at 25°C using a ZAHNER IM-6 impedance analyzer. The impedance spectra of membranes can be used to generate Nyquist plots, and the proton conductivity was calculated from the plots. The impedance of each sample was measured five-times to ensure good data reproducibility. The average estimated error was  $\pm 5\%$  [12].

#### 2.7. Characterization

FT-IR spectra of samples were collected for the frequency range of 4,000 to 600  $\text{cm}^{-1}$  using an Excalibur Series FTIR instrument (DIGLAB Co.). UV-visible spectroscopy was measured with spectrophotometer (Hewlett Packard) in the range of 200 to 800 nm. The mechanical properties of membranes were measured with universal tensile machine (UTM, Mecnesin, Multi test 1-i) between the stress range of 2.0 to 0.0 MPa,

### 3. Result and Discussion

Schematic preparation method of proton conducting nanocomposite membranes consisting of P(VDF-CTFE)-PSSA graft copolymer and TTIP is illustrated in Scheme 1. The synthesized graft copolymer is in acidic form, which may help proceed sol-gel reaction of TTIP

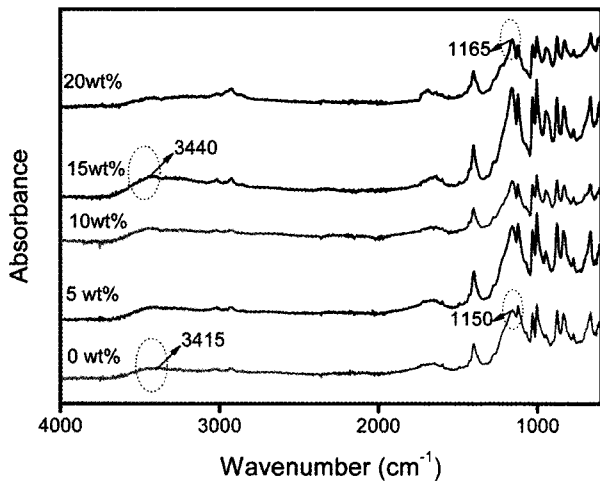


Fig. 1. FT-IR spectra of P(VDF-CTFE)-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP.

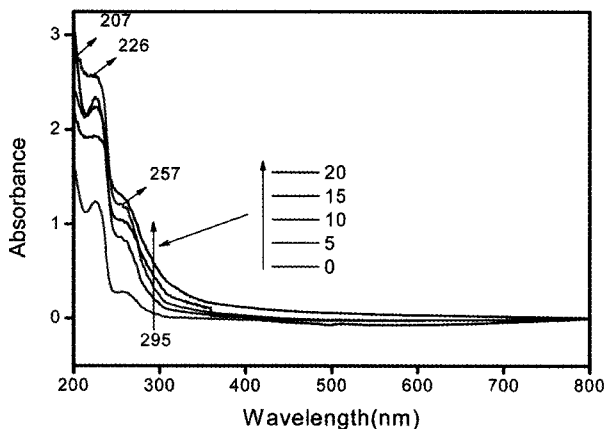


Fig. 2. UV spectra of P(VDF-CTFE)-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP.

in the membranes. Fig. 1 presents the FT-IR spectra of P(VDF-co-CTFE)-g-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP. Pristine graft copolymer exhibited strong absorption at 1,150 cm<sup>-1</sup>, attributed to SO<sub>3</sub>H stretching vibrations of PSSA. Upon the incorporation of TiO<sub>2</sub> via sol-gel process, the absorption of SO<sub>3</sub>H at 1,150 cm<sup>-1</sup> gradually shifted to a higher wavenumber of 1,165 cm<sup>-1</sup>. It is presumably related to the variation of interaction strength of SO<sub>3</sub>H groups with TiO<sub>2</sub> contents. A broad absorption band of -OH at 3,415 cm<sup>-1</sup> shifted to a higher wavenumber of 3,440 cm<sup>-1</sup>, resulting from the different interaction strength of hydrogen bonding between graft copolymer and nano-

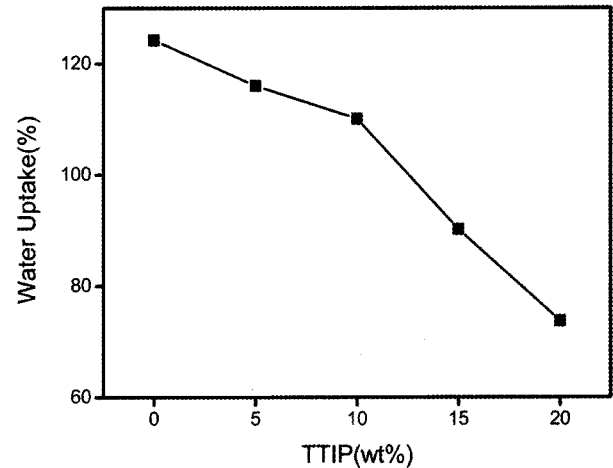


Fig. 3. Water uptake of P(VDF-CTFE)-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP.

composites [14].

UV-visible absorption spectra are known to be quite effective in monitoring the formation of titania nanoparticle [15,16]. Fig. 2 shows the UV-visible spectra of pristine graft copolymer and the nanocomposite membranes with different amounts of TTIP. Pristine P(VDF-co-CTFE)-g-PSSA film exhibited UV absorption peaks at a wavelength of 226 and 257 nm due to aromatic ring of styrene units [17]. Upon the incorporation of TiO<sub>2</sub> via sol-gel process, another UV absorption at 295 nm gradually grew up, which is assigned to the typical absorption edge of TiO<sub>2</sub> [18-20]. These FT-IR and UV-visible spectroscopic results support successful formation of nanocomposite membranes.

Water uptake of membranes plays an important role in determining the proton conductivity and the mechanical properties of membranes. It is because the proton exchanging reaction requires a significant amount of water to coordinate with proton as it moves through the membranes. Fig. 3 presents water uptake of P(VDF-co-CTFE)-g-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP. As seen, the water uptake continuously decreased with increasing TTIP concentration. The water uptake of 124% was observed for pristine P(VDF-co-CTFE)-g-PSSA graft copolymer, which is roughly three times higher than that of Nafion [21]. When 20 wt% of TTIP was introduced, the water

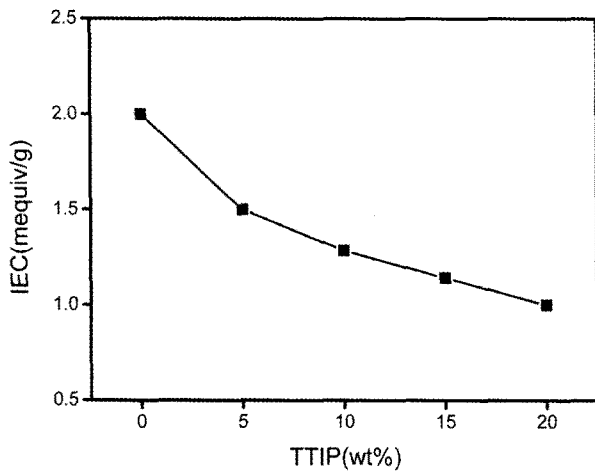


Fig. 4. IEC of P(VDF-CTFE)-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP.

uptake of membrane reduced to 73%. The reduced water uptake is attributed to the decrease in number of sulfonic acid as water absorption sites resulting from the strong hydrogen bonding interaction between the sulfonic acid and the TiO<sub>2</sub> nanoparticles [22,23].

It has been well known that the IEC values directly depend on the content of sulfonic acid group incorporated into the polymer and thus they are indicative of the actual ion exchange sites available for proton conduction. In general, high value of IEC is desirable to achieve higher proton conductivity in membranes. However, the higher content of sulfonic acid group may result in the deterioration of mechanical properties in a membrane due to highly hydrophilic property of the membrane [24,25]. The IEC of P(VDF-co-CTFE)-g-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP is shown in Fig. 4. The IEC value continuously decreased with increasing TTIP concentration, which is attributed to the decrease in number of sulfonic acid as ion exchange site.

Fig. 5 shows the proton conductivity of P(VDF-co-CTFE)-g-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP at room temperature. As seen, the proton conductivities of membranes were changed depending on the TTIP concentrations. As TiO<sub>2</sub> is introduced, the concentration of SO<sub>3</sub><sup>-</sup> site decreases (or IEC decrease), leading to the decrease of proton con-

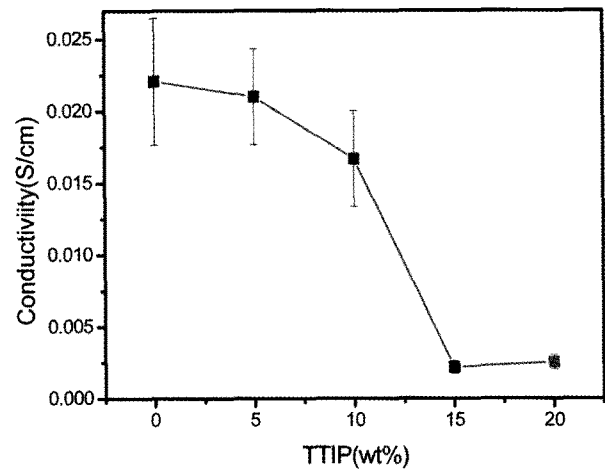


Fig. 5. Conductivity of P(VDF-CTFE)-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP.

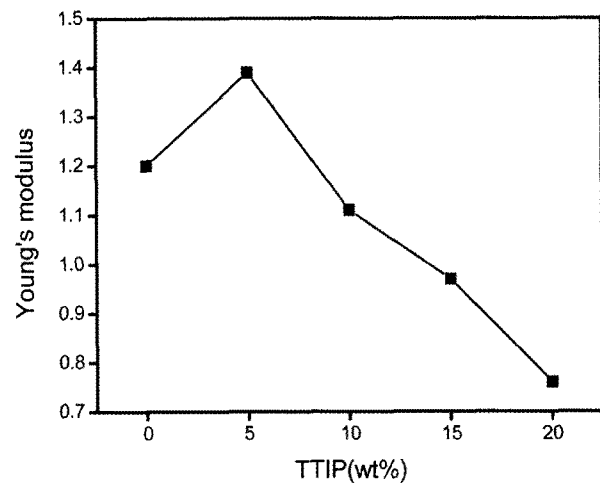


Fig. 6. Young's modulus of P(VDF-CTFE)-PSSA/TiO<sub>2</sub> nanocomposite membranes with different amounts of TTIP.

ductivity [26,27]. However, the proton conductivity of nanocomposite membranes with 5 wt% of TTIP (0.023 S/cm at room temperature) was not significantly different from that of pristine graft copolymer.

Fig. 6 presents the variation of mechanical properties (e.g. Young's modulus) in nanocomposite membranes as a function of TTIP concentration. The Young's modulus of membranes slightly increased up to 5 wt % of TTIP, above which it decreased continuously. The increase of mechanical properties results from nanocomposite formation by the strong interaction between SO<sub>3</sub>H of PSSA and OH of TiO<sub>2</sub>. The decrease above

5 wt% TTIP is presumably originated from the miscibility limit between organic polymeric chains and inorganic nanoparticles.

#### 4. Conclusion

A graft-type amphiphilic copolymer, P(VDF-co-CTFE)-g-PSSA was synthesized via ATRP. Proton conducting nanocomposite membranes consisting of graft copolymer and TiO<sub>2</sub> were prepared via sol-gel reaction, as confirmed by FT-IR and UV-visible spectroscopy. Water uptake and IEC were decreased with increasing contents of TTIP, due to the decrease in number of sulfonic acid as ion exchange site and water absorption sites. The proton conductivity decreased with increasing TTIP concentration. However, the proton conductivity of membranes was not significantly decreased upon the addition of 5 wt% of TTIP, at which the mechanical properties of membranes were the greatest.

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