Cross-linked PEEK-WC proton exchange membrane for fuel cell

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ABSTRACT

The low cost proton exchange membrane was prepared by cross-linking water soluble sulfonated-sulfinated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (SsPEEK-WC). The prepared cross-linked membrane became insoluble in water, and exhibited high proton conductivity, 2.9×10^{-2} S/cm at room temperature. The proton conductivity was comparable with that of Nafion[®] 117 membrane (6.2×10^{-2} S/cm). The methanol permeability of the cross-linked membrane was 1.6×10^{-7} cm^2/s, much lower than that of Nafion[®] 117 membrane.

Keywords: proton conductivity; proton exchange membrane; cross-linked; water uptake; fuel cell; PEEK-WC

INTRODUCTION

A fuel cell is a device that generates electricity by direct electrochemical conversion of a fuel and an oxidant. Fuel cell technology is expected to become one of the key technologies of the 21st century both for stationary and for portable applications [1]. The proton exchange membrane is one of key components of proton exchange membrane fuel cell (PEMFC), which has double roles of conducting protons and separating the fuel from oxidant. DuPont's Nafion[®] is a perfluorinated sulfonic acid polymer based membrane. Because of its high proton conductivity and good chemical stability, it has been widely used as the proton exchange membrane in PEMFC [2]. However, the high cost of fluorinated polymers limits the large-scale commercialization of PEMFC [3]. Another shortcoming of Nafion[®], high methanol permeability drastically reduces the performance of direct methanol fuel cell (DMFC) [4] (a subcategory of PEMFC). In the last decade, the preparation of inexpensive membranes based on nonfluorinated polymers as alternative to Nafion[®] has received much attention [5-6].

Poly(oxa-*p*-phenylene-3,3-phtalido-*p*-phenylene-oxa-*p*-phenilene-oxy-phenylene) (PEEK-WC) is cheap and chemically inert polymer. The sulfonated PEEK-WC (SPEEK-WC) was used to prepare the proton exchange membranes for possible fuel cell applications [7-10]. The membranes based on SPEEK-WC show a good chemical and mechanical stability, high proton conductivity, and both reduced methanol permeability and a lower cost with respect to those of the Nafion[®] membrane. The physical and chemical properties such as proton conductivity are affected by degree of sulfonation of PEEK-WC. However, for membrane with higher degree of sulfonation, the extremely high water uptake limits the mechanical stability for fuel cell because it may cause mechanical membrane failure during operation [9].

In this work, the novel proton exchange membranes were prepared by cross-linking the sulfonated-sulfinated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenyleneoxy-

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phenylene) (SsPEEK-WC) via simple route. The properties of the cross-linked membrane, such as water uptake, proton conductivity, methanol permeability and thermal stability were investigated.

EXPERIMENTAL

Chemicals

PEEK-WC was supplied by Chang Chung Institute of Applied Chemistry. Chlorosulfonic acid (97.0 % Synthesis Grade), N-Methyl-2-pyrrolidinone (NMP), Sodium hydroxide and diiodomethane were purchased from Sigma-Aldrich. All chemicals were used without further purification.

Preparation of sulfonated-sulfinated PEEK-WC

PEEK-WC was modified with chlorosulfonic acid. 10 g of PEEK-WC powder was slowly added into 100 ml of chlorosulforic acid. The mixture was magnetically stirred for 10 h at room temperature. The mixture was precipitated in the ice-water, and then washed with distilled water to neutral. Thereafter, it was dried in a vacuum oven at 70 $^{\circ}$C. The sodium sulfite solution was added into the modified PEEK-WC as the reducing agent for 10 h at 80 °C and then washed with icy deionized water. The resulting sulfonated-sulfinated (SsPEEK) was dried at 60 °C in a vacuum oven.

Preparation of cross-linked PEEK-WC membrane

The cross-linker diiodomethane was added to the 15 wt% of SsPEEK-WC solution in NMP with magnetic stir. The solution was cast on a glass Petri dish. The solvent was then removed in a vacuum oven at 130 °C. The membrane was peeled off from the Petri dish. Thereafter, the membrane was treated in 10 wt% of sodium hydroxide solution at 90 °C for 24 h, then in 10 wt% H_2SO_4 at 90 °C for 24 h and finally in water for 24 h at 90 °C. An uncross-linked membrane was also prepared, but was soluble in water.

FT-IR spectroscopy

Fourier Transform Infrared (FT-IR) spectra were obtained in a scanning range of 400-4000 cm^{-1} on a PerkinElmer Spectrum™ 100 FT-IR spectrometer.

Morphological characterization

The micrograph of the cross-section of the membrane has been realized using a Hitachi x650 scanning electron microscope (SEM) at an accelerating voltage of 25 kV.

Water uptake

The water uptake of the cross-linked membrane was determined by measuring the weight difference between the fully hydrated membrane and the dry membrane. The membrane was saturated with water until no further weight gain was observed. The water on the surface of the wet membrane was quickly removed using tissue paper, and immediately weighed. Subsequently, the membrane was dried in an oven at 100 °C and reweighed. The percentage weight gain with respect to the weight of a dried membrane was determined as a water uptake. The following formula was used:

$$Water uptake = \frac{G_w - G_d}{G_d} \times 100\% \qquad [1]$$

where G_w is the weight of the wet membrane, and G_d is the weight of the dry membrane.

Conductivity measurement

A schematic representation of the cell for proton conductivity measurements is shown on Figure 1.

The membrane was placed between two stainless steel electrodes with a contact area of 0.28 cm^2. Impedance measurements were conducted using a potentiostat/galvanostat (Autolab PGSTAT30, Netherlands) in combination with the computer controlled frequency response analyzer over the frequency range from 0.1 Hz to 100 kHz. The resistance was obtained from the Cole–Cole plot by extrapolating to high frequencies using Autolab's software. The proton conductivity σ was calculated, using the relationship:

$$\sigma = L/RS \qquad [2]$$

where L, R and S is the thickness (cm), resistance (Ohm) and contact area of the membrane (cm^2), respectively.

Methanol permeability

The methanol permeability (sometimes referred to as a cross-over) was examined by using a diaphragm diffusion cell. The cell has got two-compartments (A and B). Compartment A was filled with 1M methanol solution while compartment B was filled with deionized water. The membrane was clamped between the two compartments. The methanol concentration changes in time in compartment B were measured using gas chromatography (Hewlett Packard 5890) at 25 °C.

The methanol permeability P was calculated according to the following equation [11]:

$$P = \frac{L}{A} \times \frac{V_B}{C_A} \times \frac{\Delta C}{\Delta t} \qquad [3]$$

where, P is the methanol permeability, cm^2/s; *L* is the membrane thickness, cm; *A* is the membrane area available for crossover, cm^2; V_B is the volume of the receiving compartment (compartment B), M; C_A is the initial concentration, M;

Morphological characterization

The micrograph of the membrane has been acquired using a Hitachi x650 scanning electron microscope (SEM). To expose the membrane cross-section, the specimen for the SEM was prepared by freezing the dry membrane samples in liquid nitrogen and subsequently breaking the membrane into small pieces. Thereafter, the fragment of the fractured membrane was mounted on aluminum stubs and coated with a thin layer of gold by vacuum sputtering for three minutes.

Thermogravimetric analysis

The thermal stability of membrane was analyzed was analyzed in an argon atmosphere by using Thermal Analyzer STA 1500 (CCI-3, *Rheometric Scientific*) in a temperature range from 20 °C to 700 °C at a heating rate of 10 °C/min.

RESULTS AND DISCUSSIONS

FT-IR analysis

FT-IR spectra verified that the substitution of sulfonic group was successful and the cross-linking structure was existed in the membrane by sulfone –SO$_2$– structure (Figure 2).

The comparative FT-IR spectra of PEEK-WC and of cross-linked membrane are given in Figure 3. The peak at 1775 cm^{-1} is attributed to ketonic and esteric C=O stretching of the

PEEK-WC. The broad band at 3450 cm^{-1} in the membrane is assigned to O-H vibration from molecular water, which is adsorbed water due to interacting with sulfonic groups. In the membrane, the aromatic C–C band at 1500 cm^{-1} for PEEK-WC was split due to substitution of sulfonic group. The absorption bands at 1025 and 1085 cm^{-1} in the sample were assigned to symmetric and asymmetric stretching vibration O=S=O due to the introduction of sulfonic groups [12]. The absorption band at 1190 cm^{-1} was the characteristic band of S=O stretching vibration of sulfone $-SO_2-$ [13], which implied that sulfone $-SO_2-$ presented and formed cross-linking structure.

Water uptake

Water uptake is an important attribute of all proton exchange membrane for fuel cell, as it is related to mechanical strength and dimensional stability. The prepared membrane without cross-linking is water soluble. However, the water solubility is not tolerable for practical application in fuel cells. No doubt, a water soluble membrane can not be used in fuel cell. After cross-linking, the membrane became water insoluble. This is particularly important for PEEK-WC, which has high proton conductivity with high degrees of sulfonation. The water uptake of the cross-linked PEEK-WC membrane is 44 % at room temperature. The cross-linked membrane is also insoluble in strong solvents. There was no weight loss detected in N,N-Dimethylacetamide and N-Methyl-2-pyrrolidinone after 1 week.

The cross-linkages between the polymer chains in the membrane form a three-dimensional network as illustrated in Figure 4, and prevent the polymer from swelling to infinity, in other words from dissolving. This is due to the elastic retraction forces of the network which decreases the entropy of the chains as they become more dense after cross-linking [14].

Proton conductivity

The proton conductivity is one of the most important properties of the proton exchange membrane for PEMFC application. The proton conductivities of the cross-linked membrane were determined in a fully hydrated condition at temperatures ranging from 20 °C to 80 °C. The proton conductivity of cross-linked membrane was 2.9×10^{-2} S/cm at 20 °C. It is comparable with that of Nafion$^{®}$ 117 membrane (6.2×10^{-2} S/cm). The proton conductivity of the cross-linked membrane is shown as a function of temperature in Figure 5. It was found that no water loss and drop of conductivity until 80 °C for cross-linked membrane increases continuously with increasing temperature. The proton conductivity of the cross-linked membrane reached to 5.4×10^{-2} S/cm at 80 °C.

The structure of proton exchange membrane has been extensively studied by many researchers, and it is well known that protons transfer between ionic clusters consisting of polar groups such as sulfonic groups [15-17]. The number of ionic clusters increases with the increase of the number of sulfonic groups and water content in membrane [18-19]. The mechanical strength of the membrane and reduced the water uptake of the membrane can be improved by cross-linking.

Methanol permeability

The perfluorinated sulfonic acid membrane, Nafion$^{®}$ is widely used as proton exchange membrane due to its excellent chemical and thermal stability and excellent proton conductivity. However, it has been found that over 40 wt% of the methanol can be wasted in DMFCs across the membrane due to high methanol permeability [20]. In order to achieve improved high overall efficiency of DMFC, two major obstacles, namely, low activity of the methanol electro-oxidation catalysts and permeability of methanol through the membrane have to be overcome [21]. The methanol permeability from anode to cathode lowers the fuel utilization, affects the oxygen cathode activity and causes the excess thermal load in the cell.

It was found that the methanol permeability of the cross-linked membrane was 1.6×10^{-7} cm^2/s, much lower than that of Nafion[®] 117 membrane (1.4×10^{-6} cm^2/s). This result recommended that the cross-linked membrane is a promising possibility for DMFC applications. Although, the proton conductivity of the cross-linked membrane is still lower than that of Nafion[®] 117, the resistance of the cross-linked membrane can be reduced by reducing the thickness due to its low methanol permeability.

The SEM cross-section image of the cross-linked membrane is shown in Figure 6, demonstrates the dense structure of the cross-linked membrane, and no obvious micro pores are presented. It might be a reason for the low methanol permeability.

Thermostability

The thermal stability of membrane was analyzed by TGA. Three subsequent steps of weight loss are observed in Figure 7. The absorbed water in the membrane causes the first weight loss from 20 to 150 °C. The second weight loss from 250 to 400 °C can be associated to the decomposing of the sulfonic groups from the main chain of PEEK [22-23]. The third weight loss is attributed to the decomposition of the membrane from 400 °C. The cross-linked membrane is thermally stable up to 250 °C. This is enough for DMFC application.

CONCLUSIONS

The novel cross-linked PEEK-WC membrane was prepared by cross-linking highly sulfonated and sulfinated PEEK-WC. The cross-linked membrane is low cost due to its use of non-expensive chemical and simple synthesis procedure. The low cost, suitable water uptake and high proton conductivity of the cross-linked membrane suggested that it is a promising candidate for PEMFC applications, especially for DMFC due to its low methanol crossover.

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Figure captions

Figure 1. Schematic representation of proton conductivity cell.

Figure 2. Structural formula of cross-linked PEEK-WC

Figure 3. FT-IR of PEEK-WC and cross-linked PEE-WC membrane

Figure 4. A schematic diagram of cross-linked membrane.

Figure 5. Proton conductivity as a function of temperature.

Figure 6. SEM cross-section image of cross-linked PEEK-WC membrane.

Figure 7. TGA of cross-linked PEEK-WC membrane.

Figure1
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Stainless Electrodes

Membrane

Connect to Potentiostat
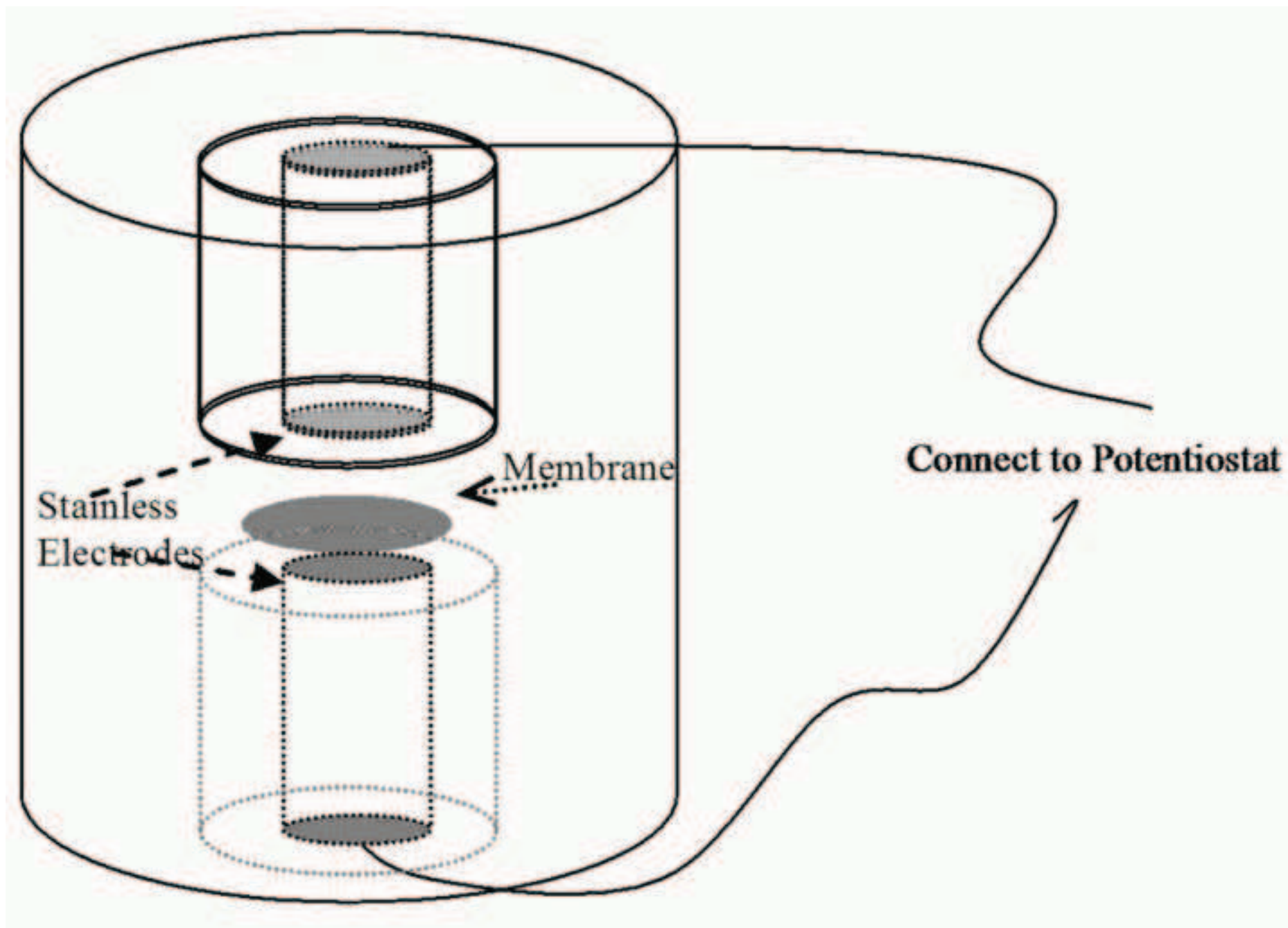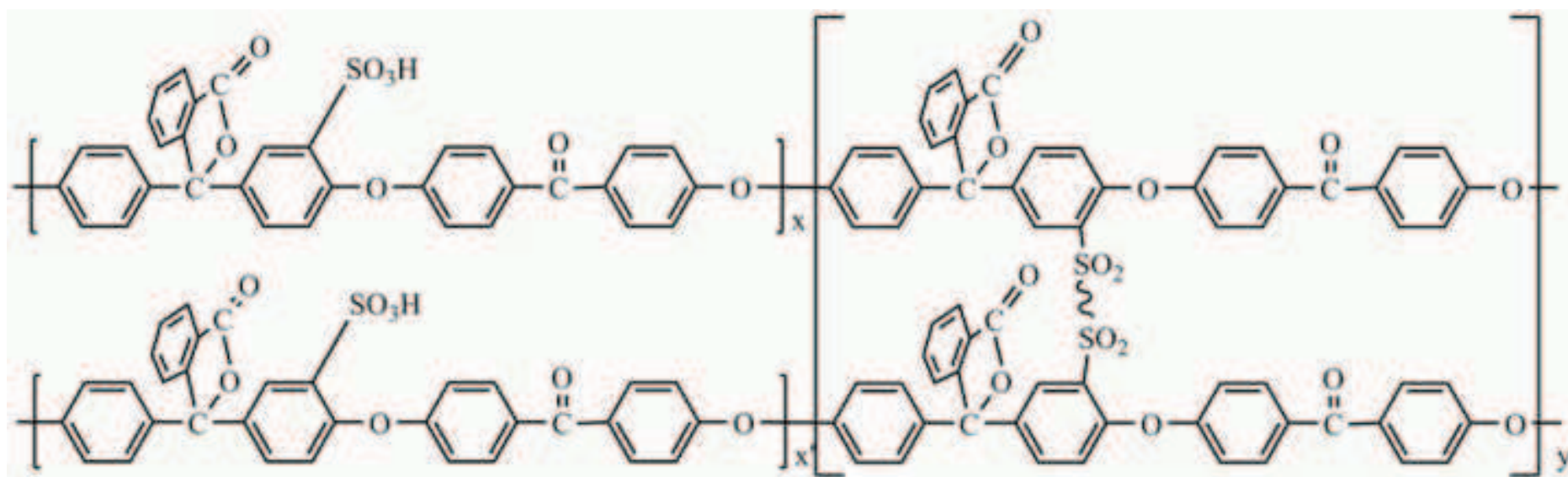
Figure2

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Figure 4

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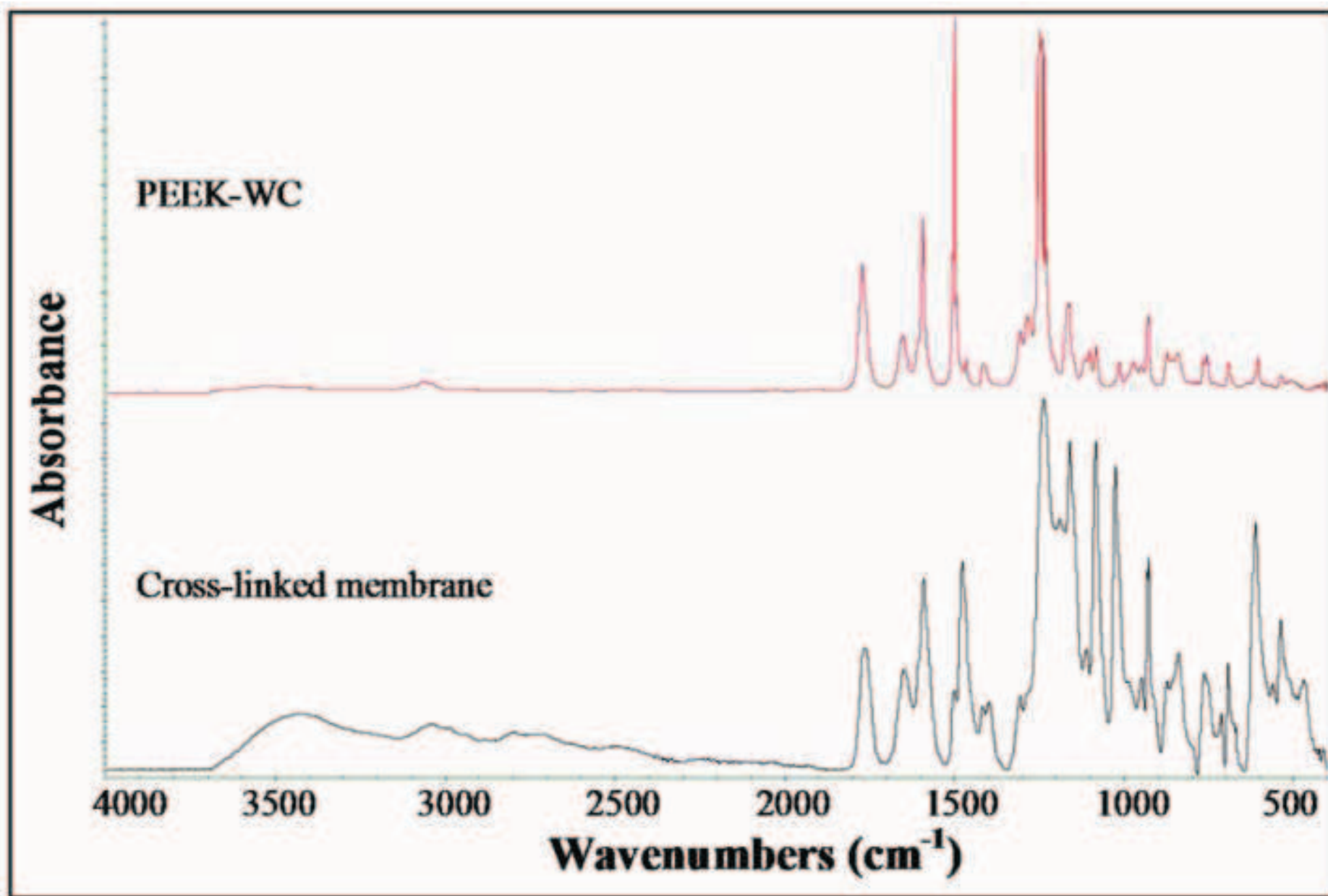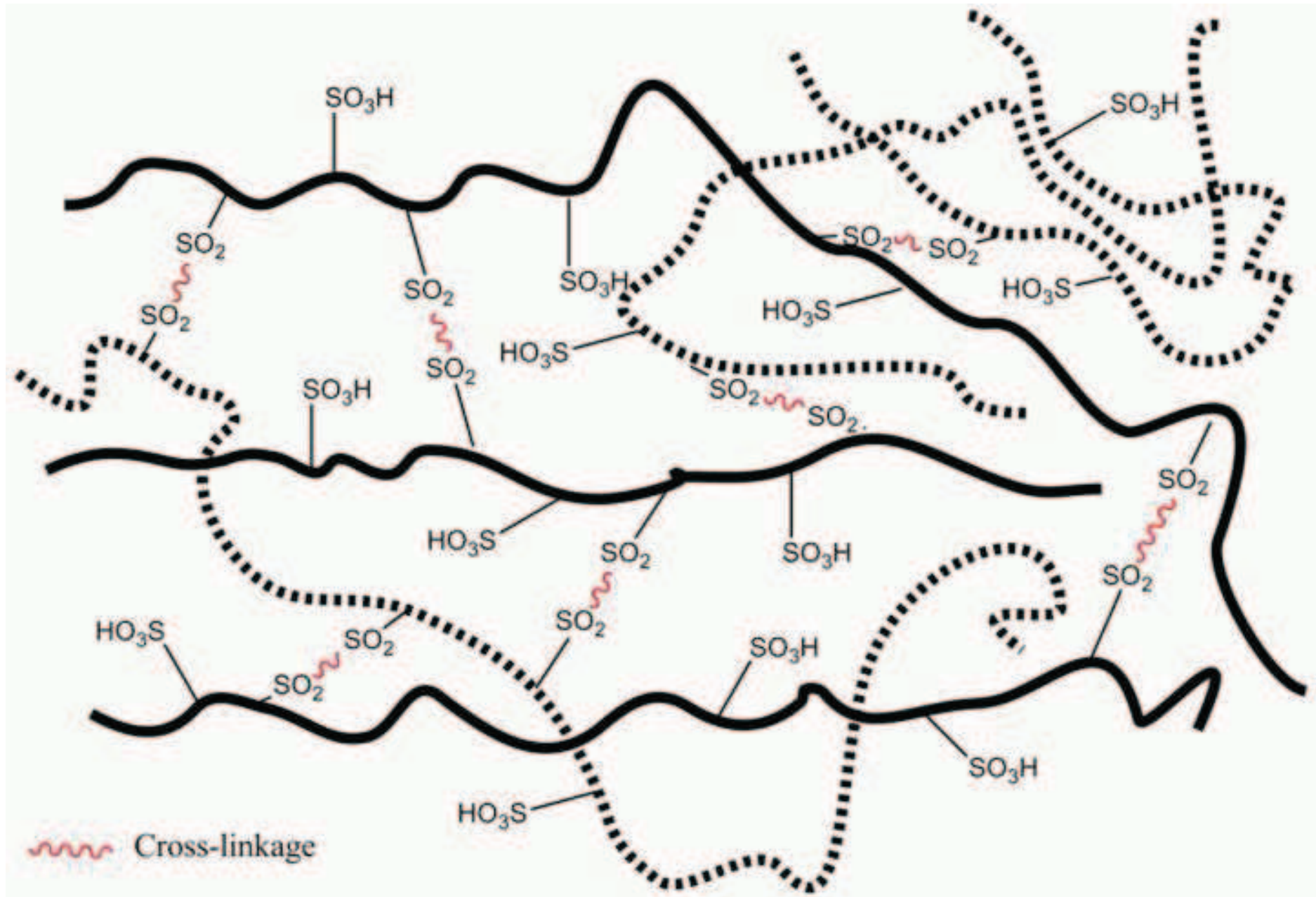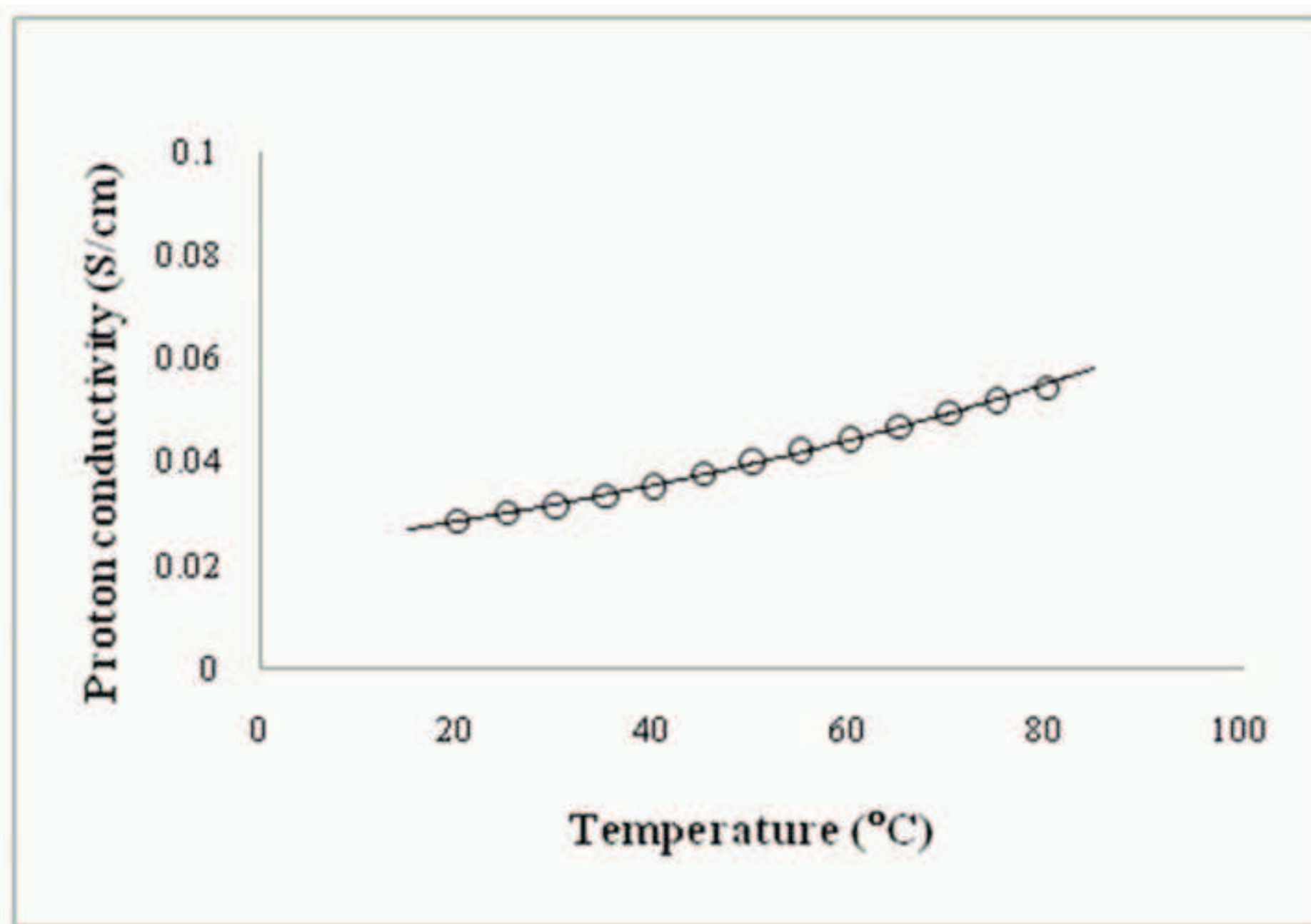**Click here to download high resolution image**

Figure6
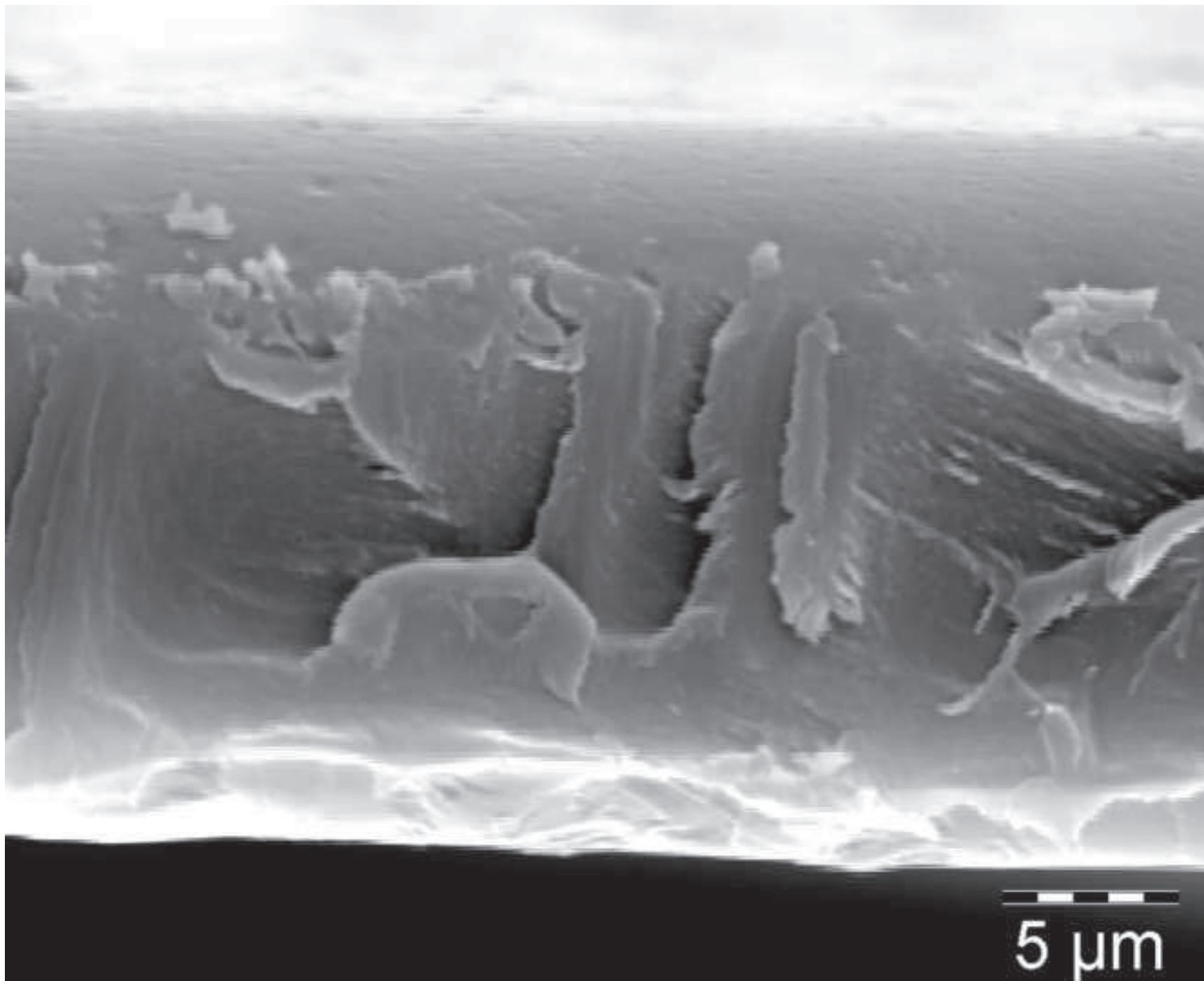**Click here to download high resolution image**

5 µm

Figure7
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