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Supplementary Information

Cellulose Nanowhiskers to Regulate Microstructure of Perfluorosulfonate Ionomers for High-Performance Fuel Cell†

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1. Experimental

1.1. Materials

Nafion® 5%wt solution in water and low molecular weight alcohols and Nafion®117 membrane were acquired from E.I. DuPont de Nemours Company. The other chemicals were purchased from Merck. All chemicals were analytical grade and used without further purification. Deionized water (purified with Milipore™) was utilized in this work.

1.2. Preparation of cellulose whiskers

The whiskers used in the present study were prepared by sulfuric acid hydrolysis of commercial cotton fibers. At first, the cotton fibers were finely chopped, and passed through a 10-mesh sieve. Typically, 5.0 g of fibers were dispersed in 100 ml of 6.5 M sulfuric acid at 45°C and stirred vigorously for 45 min. Afterwards, 500 ml of cold distilled water was added to stop the reaction and dilute the suspension. Whiskers were collected after successive centrifugation and washing with distilled water to partially remove excess sulfuric acid. The fibers were then resuspended and the non-reactive sulfate groups were completely removed by following dialysis against distilled water. Finally, the suspension was ultrasonicated to achieve a stable colloidal suspension.

Cellulosic whiskers were characterized via CHNS elemental analysis (Perkin Elmer 2400 analyzer). The total content of Nitrogen, Carbon, Hydrogen and Sulphur was found to be 0.0754, 34.7532, 5.5951 and 2.8364%, respectively. Electrophoretic mobility of the aqueous whisker suspension was also measured with the Malvern Nanoseries Zetasizer instrument.

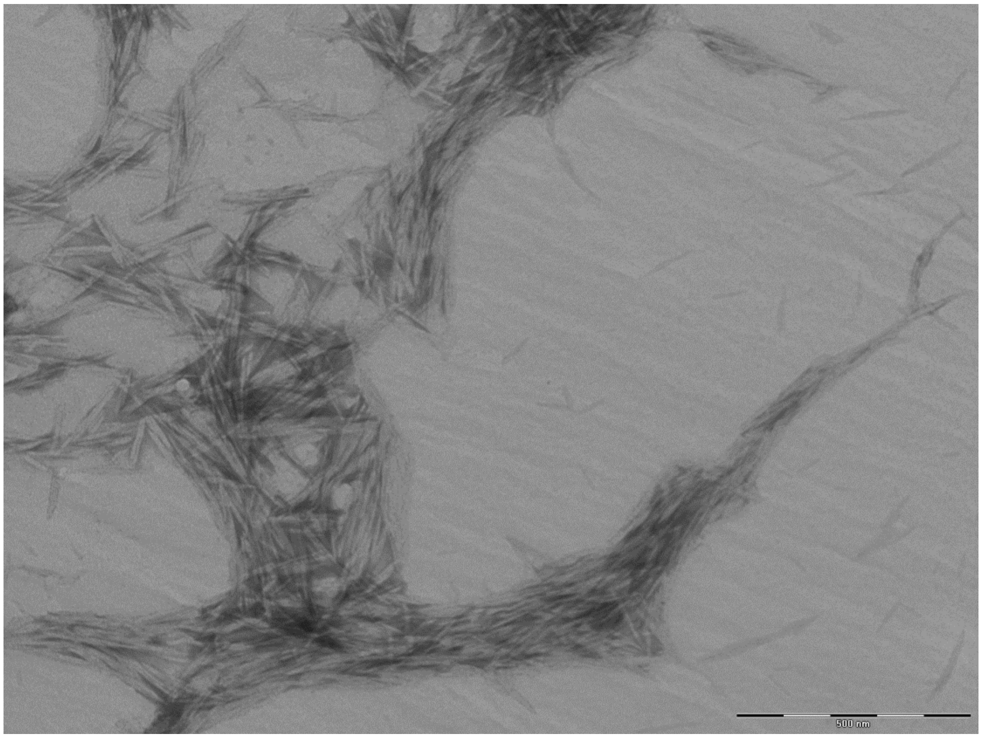
1.3. Membrane preparation

5 wt% CW (1 mg.ml^{-1} suspension) was added to Nafion® solution at room temperature and stirred for 2 h. The resultant mixture was ultrasonicated for two successive 5 min intervals, and then concentrated in rotary evaporator. The viscose solution was cast on Petri dishes, incubated overnight at room temperature, and subsequently dried at 70ºC for 8-10 h. Finally, newly fabricated membranes were annealed at 120ºC for 12 h. The pristine recast Nafion® membrane was also prepared and treated in the similar manner.

1.4. Characterization

Electron microscopy

Transmission electron microscopy (TEM; CM200-FEG-Philips) was used to characterize the morphology of whiskers. A dilute suspension of whiskers was deposited onto the Cu grid that supported a carbon film. TEM operated at 200 kV accelerating voltage.



Supplementary Figure S1. *Transmission electron micrograph of the Cellulosic whiskers.*

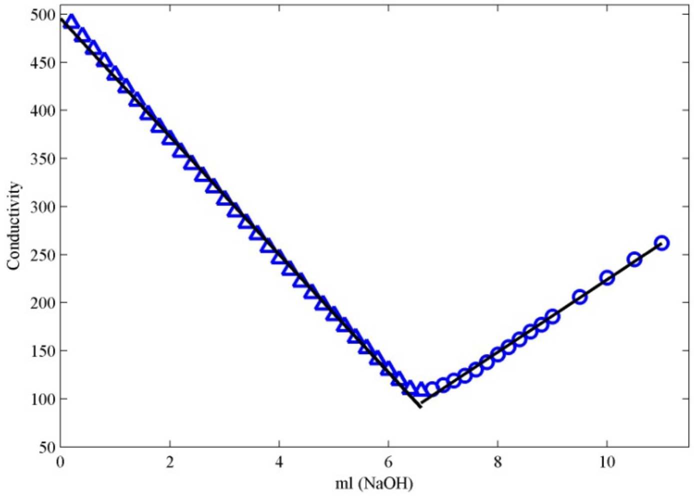
It should be noticed that just one type of cellulose whisker was used in this study. Rod-like crystalline CWs were extracted from semi-crystalline cellulosic fibers through hydrolysis with sulfuric acid. The controlled hydrolysis of the cellulose fibers with sulfuric acid leads to stable aqueous suspension of nanocrystallites, which neither precipitate nor flocculate.

Here we explain a procedure base on conductometric titration for rough estimation of SO_3^- functional groups on the surface of cellulose nanowhiskers. In brief, an aliquot of 10 ml from nanowhiskers suspension with concentration of 1g per 100 ml was titrated with NaOH solution (1 M). The following reaction could be considered for neutralization of the cellulosic nanoparticles: $-SO_3^- + NaOH \rightarrow -SO_3Na + OH^-$

The conductivity variation of the nanowhiskers suspension against volume of the added NaOH solution has been shown below. As seen in **Figure S2**, addition of 6.6 ml of the sodium hydroxide solution has resulted in neutralization of the nanoparticles.

$$6.6^{cc} \times \frac{1mol\,NaOH}{1000^{cc}} \times \frac{1mol - SO_3^-}{1mol\,NaOH} = 6.6 \times 10^{-3} mol - SO_3^-$$

Considering the density of 1.58 g/cm^3 for the cellulosic nanoparticles, total volume of the nanoparticles in the suspension is obtained as 0.6×10^{20} nm^3. The average volume of a single cellulosic nanoparticle based on a cylindrical geometry (121 nm length and 10 nm width) could be also calculated to be 9503 nm^3. Accordingly, the average number of SO_3^- groups per cellulose nanowhiskers is obtained as 6.3×10^5.



***Supplementary Figure S2**. Conductometric titration of cellulose whisker with NaOH solution (1 M).*

Atomic force microscopy (AFM)

The morphology of the composite structures and dispersion of CWs were characterized using a Bruker's Dimension FastScan AFM.

Water and methanol uptake

To study the swelling behavior of the membranes, the dry samples were first soaked in deionized water at room temperature for a day, and then quickly weighed at different time intervals after carefully removing the excess water or methanol with filter paper, and then immersed back. This process was repeated several times until no further weight gain was observed. Finally, the water uptake (WU) was calculated using the following equation: $WU = (W_{sw} - W_{dry})/ W_{dry} \times 100$, wherein W_{sw} and W_{dry} are the weights of membranes in the swollen and dried states, respectively. The same method was used to calculate the methanol uptake of the samples.

The ratio of the mole number of water molecules to the fixed-charged sulfonate groups, denoted as lambda (λ), was calculated from Eq. (1):

(1)

where WU, IEC and M_{water} are the water uptake, ion exchange capacity and molecular weight of water (18 g mol^{-1}), respectively. In fact, the average number of water molecules per ionic groups (λ) shows how many water molecules could be bound to the ionic groups of polyelectrolyte. The hydration of polyelectrolytes and the proton conduction across the membranes is often explained with λ.

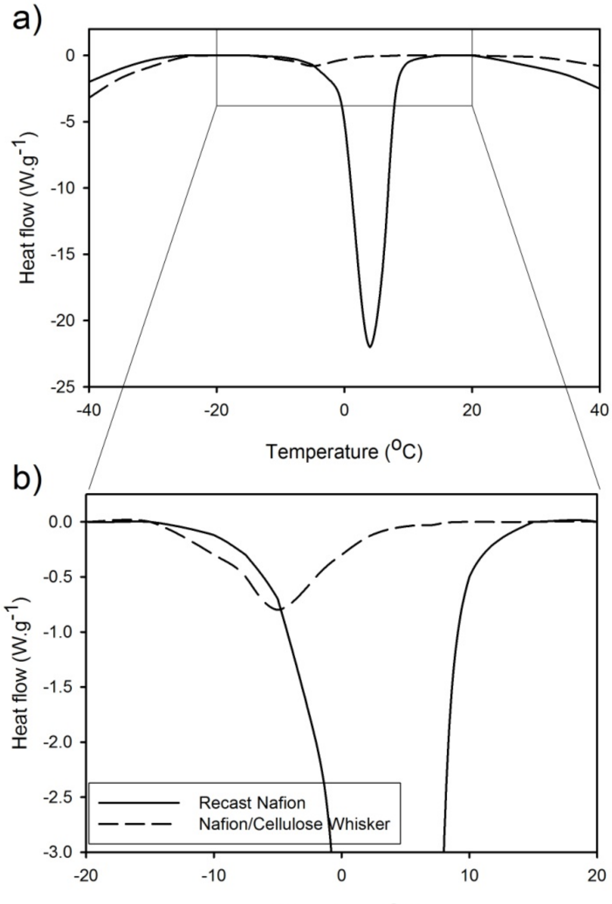
Differential scanning calorimetry (DSC)

Two types of water, freezing (free) and nonfreezing (bound) water molecules, in the membranes were detected by melting transitions in differential scanning calorimetry (DSC; Perkin-Elmer) with a liquid nitrogen-cooled heating element. The temperature scale of the calorimeter was calibrated with indium. All of the samples were weighed (5 ± 0.2 mg) and enclosed in an aluminum pan. An empty aluminum pan was used as the reference. Each sample was first cooled from 25°C to -40 °C and then heated to 40°C at a heating rate of 5 °C/min. The reported data at **Figure S3**, are the average of three determinations.

The amount of bulk water in the samples was calculated by integrating the peak area of the endotherm melting. The degree of crystallinity for water that is obtained from the heat of fusion of pure ice was used as the standard. The weight fraction of free water (ω_f) to the fully-hydrated membranes can be estimated from the total melting enthalpy (ΔH_m) that is obtained by integration of the transition heat capacity (ΔC_P) over the broad melting temperature interval. The weight fraction of free water (ω_f) was calculated based on Eq. 2:

$$\omega_f = \frac{\Delta H_m}{Q_{melting}} = \frac{\int \Delta C_p dT}{Q_{melting}} \tag{2}$$

where $Q_{melting}$ is the heat of fusion of bulk ice (334 J/g). The weight fraction of bound water (ω_b) is calculated by subtracting the amount of freezing water (ω_f) from the total water uptake (ω_t). The bound water degree (χ) is also defined as a ratio of the amount of bound water to the total water uptake.[S1]



Supplementary Figure S3. *The DSC* thermograms *of Nafion and Nafion/ Cellulose whisker 5 wt% membranes.*

Supplementary Table S1. *Physical state of water molecules in CW-filled Nafion nanocomposite and corresponding pristine membranes compared with commercial Nafion®117 membrane.*

Sample	Water Uptake (%)	Ion Exchange Capacity (meq/gr)	λ (H_2O/SO_3)	$\lambda_{\text{free water}}$ (H_2O/SO_3)	$\lambda_{\text{bond water}}$ (H_2O/SO_3)	% of bound water
Nafion 117	32	0.89	20	11.5	8.5	42.4
Nafion/Whisker -5wt%	28.5	1.04	15.2	1.46	13.76	90.5

λ: The number of water molecules per sulfonated groups.

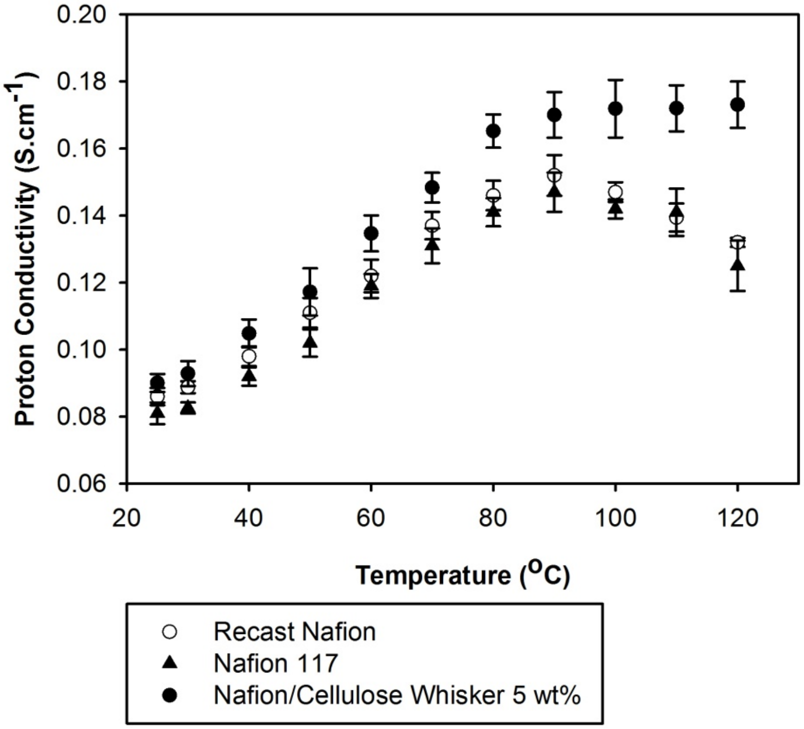
λ_f: The number of bound water molecules per sulfonated groups.

λ_b: The number of free water molecules per sulfonated groups.

Small angle X-ray scattering (SAXS)

Small angle X-ray scattering (SAXS) analysis of the membranes was carried out by using a diffractometer equipped with Cu K source and Kratky SAXS apparatus. The water swelled samples was incubated in a sealed sample holder at 25°C. The intensity of the X-ray scattering is plotted versus the scattering vector, q, defined as $q = (4\pi/\lambda) \sin \theta$, where λ is the X-ray wavelength and 2θ is the scattering angle.

Proton Conductivity. The proton conductivity of the fully hydrated membranes was measured at temperature range of 25-120°C via the AC electrochemical impedance spectroscopy method, using a Solartron Interface 1260 gain phase analyzer over the frequency range of 1-10^6 Hz. The conductivity values were calculated from the $\sigma = L.R^{-1}.A_e^{-1}$ formula, where L is the membrane thickness, A_e is the cross-sectional area of the membrane and R is the resistance. A Four-point probe apparatus (Bekktech Conductivity Cell) has been used to measure the bulk conductivity of membranes. For conductivity measurements, the samples were immersed in water to reach at equilibrium hydrated state, and then put in the conductivity cell. The conductivity measurement also performed as a function of relative humidity using humidity control chamber. The data obtained are reported as the average of at least three samples (Supplementary **Figure S4**).

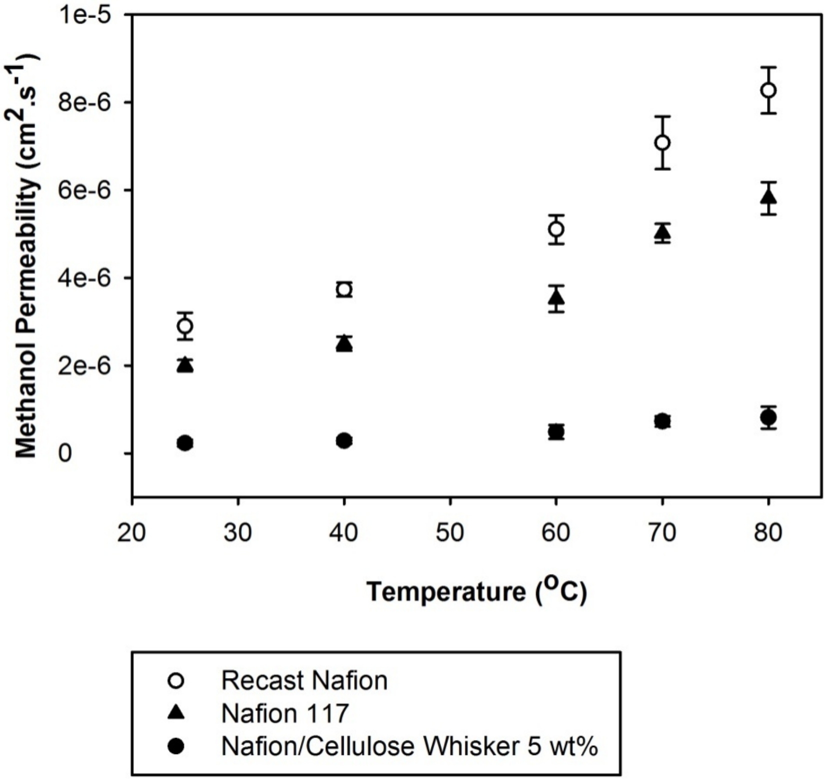


Supplementary Figure S4. *Proton conductivity of Nafion/Cellulose Whisker-5wt% nanocomposite membrane as a function of temperature in comparison with corresponding pristine Nafion® and Nafion®117 membranes.*

Methanol Permeability. The methanol permeability was determined by means of a two-compartment glass diffusion cell. Prior to testing, the membranes were equilibrated in deionized water for 24 h. Methanol solution was poured into one side of the diffusion cell (cell A) and the other side (cell B) contained pure water. The solution in each compartment was stirred continuously to ensure the homogeneity. The concentration of the methanol in cell B was measured via the gas chromatography method. The methanol permeability was determined using the following equation (Eq. 3),

$$P = \frac{1}{C_A}\left(\frac{\Delta C_{B(t)}}{\Delta t}\right)\left(\frac{L.V_B}{A}\right) \tag{3}$$

where, P is the methanol permeability of the membrane (cm^2 s^{-1}), C_A is the methanol concentration in cell A (mol L^{-1}), $\Delta C_B/\Delta t$ is the slope of the molar concentration variation of methanol in the cell B as a function of time (mol L^{-1} s^{-1}), V_B is the volume of each diffusion reservoir (cm^3), A is the membrane area (cm^2) and L is the membrane thickness (cm). The surface area of the membrane samples for permeability measurements was 2.5 cm^2, and a 2M methanol solution was used for methanol permeability measurements. Methanol permeability measurements were performed on at least three multiple samples, and results have been reported as the average with standard deviation (S.D.) (Supplementary **Figure S5**).



Supplementary Figure S5. *Methanol permeability of prepared Nafion®/Cellulose Whisker-5wt% nanocomposite membranes as a function of temperature in comparison with corresponding pristine Nafion and Nafion117membranes.*

Membrane Selectivity. The membrane selectivity (ratio of proton conductivity to methanol permeability) of the nanocomposite membranes as well as for Nafion®117 were calculated and shown in **Figure 5**. As shown, modification of microstructure of Nafion® membrane with cellulosic nanorods has led to considerable improvement of membrane selectivity at the whole temperature range.

Performance Tests for a Single Cell Fuel Cell.

The DMFC single cell was composed of stainless steel as the end plates and flow fields, two carbon papers as the gas diffusion layers (GDL, TGP-H-120 Toray), silicon rubber sheets as the sealants and a membrane electrode assembly (MEA). MEAs were prepared via the catalyst painting technique as reported previously. [S2,S3] In brief, Pt and Pt/Ru-black were used as catalysts for the anode and cathode, respectively. The catalysts were mixed with Nafion® solution and several drops of glycerol. The suspension was brushed directly (4 mg.cm^{-2}) onto the membranes, and hot-pressed to increase the contact area between the catalysts and membranes. The area of the tested membranes was 3×3 cm^2 and MEAs were fabricated using a 200 kg.cm^{-2} hot-press at 120°C for 90 second for each side of membranes.

The performance of the single cell was evaluated at two methanol concentrations (1 and 5 M) and or air flow rates into the anode and cathode sides at 70°C. The cell temperature as well as the temperature of anode and cathode sides was fixed at 70°C, which was controlled by preheating the fuels (air and methanol solution). The relative humidity (RH) was fixed at 70% RH. Methanol was fed to the anode side at 20 psi back pressure for one hour and air was introduced to the cathode side with gradual pressure increase to 20 psi, and the cell was allowed to run for half an hour before collecting the polarization curves data.[S2-S4] All single cell performance tests were performed on multiple samples and the results are presented as the mean values. For methanol crossover measurements, humidified nitrogen was fed to cathode side at 70°C, and the fuel cell was performed until a limiting current occurs. The limiting current at the open circuit condition indicates the oxidation current of methanol crossover from anode to cathode.

References

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S4. Protocol on Fuel Cell Component Testing, *US Fuel Cell Council*, Document: USFCC 04-003 **2004,** 12-17.