

Electronic Supplementary Information

Designing Electronic/Ionic Conducting Membranes for Artificial Photosynthesis

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Calculations

Minimum conductivity needed per unit membrane thickness

Estimating the current density, J , passing through a membrane, assuming a solar flux of $4.0 \text{ mmol-s}^{-1}\text{-m}^{-2}$ and assuming that one charge carrier traverses the membrane for every two incident photons absorbed by the photoelectrodes.

$$\begin{aligned} \text{Current density } J &= (4.0 \times 10^{-7} \text{ mol-sec}^{-1}\text{-cm}^{-2})(6.022 \times 10^{23} \text{ e}^{-}\text{mol}^{-1})(1 \text{ C}/6.24 \times 10^{18} \text{ e}^{-})/2 \\ &= 0.019 \text{ A-cm}^{-2}, \text{ or } \sim 20 \text{ mA-cm}^{-2} \end{aligned}$$

Theoretical membrane area resistance, R_A , given a solar-flux-generated current density of 20 mA-cm^{-2} and a maximum allowable iR loss, ΔV , of 10 mV . The 10 mV iR loss is roughly 1% of the theoretical driving force for splitting water (1.23 eV).¹

$R_A = \Delta V/IA$, where I = current in Amps and A = exposed membrane area

$$R_A = \Delta V/J = 10 \text{ mV}/20 \text{ mA-cm}^{-2} = 0.5 \text{ } \Omega\text{-cm}^2$$

Theoretical membrane conductivity, given $R_A = 0.5 \text{ } \Omega\text{-cm}^2$. Membrane thickness, L , is given in cm.

$$\sigma = (1/R_A)(L) = (1/0.5 \text{ } \Omega\text{-cm}^2)(L) = (2 \text{ } \Omega^{-1}\text{-cm}^2)(L)$$

$$\text{Given } L = 1 \text{ } \mu\text{m} \text{ or } 0.0001 \text{ cm, then } \sigma = 2 \text{ } \Omega^{-1}\text{-cm}^2 (0.0001 \text{ cm}) = 0.0002 \text{ } \Omega^{-1}\text{-cm}^{-1}$$

$$0.0002 \text{ } \Omega^{-1}\text{-cm}^{-1} = 0.0002 \text{ S-cm}^{-1} = 0.2 \text{ mS-cm}^{-1}$$

Hence, every $1 \text{ } \mu\text{m}$ increase in membrane thickness requires a corresponding increase in membrane conductivity of 0.2 mS-cm^{-1}

If one has a membrane that is $40 \text{ } \mu\text{m}$ thick, i.e. $L = 0.004 \text{ cm}$, then the minimum conductivity required to support a loss $\leq 1 \%$ would be $= 2 \text{ } \Omega^{-1}\text{-cm}^2(0.004 \text{ cm}) = 0.008 \text{ S-cm}^{-1}$, i.e. 8 mS-cm^{-1}

Experimental ionic conductivity with 4-electrode cell

$$R_{\text{mem}} = R_{\text{cell+mem}} - R_{\text{cell}}$$

R_{cell} = resistance of cell with membrane removed

$R_{\text{cell+mem}}$ = resistance of cell with membrane

$$R_A = R_{\text{mem}} \times A$$

R_A = area resistance and A = area of solution exposed to membrane = 0.967 cm²

$\sigma = (1/R_A)(L)$ L = wet membrane thickness determined with a Fowler Universal Micrometer

The calculation below is for a 12 % PEDOT-PSS/Nafion membrane through which 25 mA is passed and the resulting voltage drop, 0.0008 V in this case, being measured.

$$R_{\text{cell}} = 0.0008 \text{ V} / 0.025 \text{ A} = 0.03 \Omega$$

$$R_{\text{cell+mem}} = 0.0016 \text{ V} / 0.025 \text{ A} = 0.064 \Omega$$

$$R_{\text{mem}} = 0.064 - 0.03 = 0.034 \Omega$$

$$R_A = 0.034 \Omega \times 0.967 \text{ cm}^2 = 0.033 \Omega\text{-cm}^2$$

$$\sigma = 0.0040 \text{ cm} / 0.033 \Omega\text{-cm}^2 = 0.12 \text{ S-cm}^{-1}$$

Losses due to oxygen crossover

Losses due to oxygen crossover were determined from the calculated flux based on the experimentally determined diffusion coefficient of oxygen, and the solubility of oxygen in Nafion in contact with an oxygen-saturated aqueous solution (Haug and White)². The crossover was converted to the current density that would be lost from the expected solar flux, assuming the transfer of 4 electrons per oxygen crossover

$$J_O = I/A = nFm_oC^*$$

Where J_O is current density in $A\text{-cm}^{-2}$ passing through the membrane in contact with the solution, n is the number of electrons consumed per crossover, F is Faraday's constant ($F = 96485.34\text{ C}\cdot\text{mol}^{-1}$), m_o is the mass transfer coefficient, which was obtained by dividing the diffusion coefficient of oxygen, $D_{\text{oxygen}} = 0.62 \times 10^{-6}\text{ cm}^2\text{s}^{-1}$ by the membrane thickness, $L = 0.004\text{ cm}$ or $40\text{ }\mu\text{m}$, and C^* is the bulk concentration in the membrane ($C^* = 15.6 \times 10^{-6}\text{ mol}\cdot\text{cm}^{-3}$) in contact with an oxygen-saturated solution.

To normalize for the effect of membrane thickness on the observed flux, one can multiply both sides by L , leading to

$$J_O L = n F D C^*$$

where the actual flux for any given membrane thickness can be determined by dividing $J_O L$ by the desired/measured membrane thickness L .

$$J_O L = (4)(96485.34\text{ C}\cdot\text{mol}^{-1})(0.62 \times 10^{-6}\text{ cm}^2\text{s}^{-1})(15.6 \times 10^{-6}\text{ mol}\cdot\text{cm}^{-3}) = 3.7 \times 10^{-6}\text{ A}\cdot\text{cm}^{-1}$$

The parameter $3.7 \times 10^{-6}\text{ A}\cdot\text{cm}^{-1}$ is useful because dividing this number by the membrane thickness L yields the actual flux of oxygen in terms of the current density through the membrane.

For a film in which $L = 0.004\text{ cm}$ or $40\text{ }\mu\text{m}$, the corresponding current density, J_O , lost due to oxygen crossover is $0.93\text{ mA}\cdot\text{cm}^{-2}$.

Dividing this loss by the $20\text{ mA}\cdot\text{cm}^{-2}$ of current passing through the system while under illumination, and multiplying by 100, results in a loss due to oxygen crossover of 4.7 %.

Losses due to hydrogen crossover

Losses due to hydrogen crossover were determined from the calculated flux based on the experimentally determined diffusion coefficient of hydrogen and the solubility of hydrogen in Nafion in contact with a hydrogen-saturated aqueous solution (Jiang et al.)³. The crossover was converted to the current density that would be lost from the expected solar flux, assuming the transfer of 2 electrons per hydrogen crossover.

$$J_{\text{H}}L = (2)(96485.34 \text{ C}\cdot\text{mol}^{-1})(7.6\times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1})(0.51\times 10^{-6} \text{ mol}\cdot\text{cm}^{-3}) = 0.75\times 10^{-6} \text{ A}\cdot\text{cm}^{-1}$$

This parameter $0.75\times 10^{-6} \text{ A}\cdot\text{cm}^{-1}$ is useful because dividing by the membrane thickness yields the actual flux of hydrogen in terms of the current density through the membrane.

For a film in which $L = 0.004 \text{ cm}$ or $40 \mu\text{m}$, the corresponding current density, J_{H} , lost due to hydrogen crossover is $0.19 \text{ mA}\cdot\text{cm}^{-2}$.

Dividing this loss by the $20 \text{ mA}\cdot\text{cm}^{-2}$ of current passing through the system while under illumination, and multiplying by 100, results in a loss due to hydrogen crossover of 0.94 %.

Total losses due to combined oxygen and hydrogen crossover

$$J_{\text{O}}L + J_{\text{H}}L = J_{\text{tot}}L = (3.7\times 10^{-6} \text{ A}\cdot\text{cm}^{-1} + 0.75\times 10^{-6} \text{ A}\cdot\text{cm}^{-1}) = 4.5\times 10^{-6} \text{ A}\cdot\text{cm}^{-1}$$

For a 0.004 cm or $40 \mu\text{m}$ thick film, this corresponds to

$$J_{\text{tot}} = 1.1 \text{ mA}\cdot\text{cm}^{-2}$$

or 5.6 % of the $20 \text{ mA}\cdot\text{cm}^{-2}$ current passing through the system while under illumination.

Losses due to absorption

Losses due to the absorption of light must also be considered. The absorptivity of light by the membrane will only influence a portion of the incident photons (i.e., approximately half will be absorbed by the micro-rods before getting to the membrane). However, if the membrane absorbs a significant fraction of the photons, such absorption would ultimately control product production, because both sides of the system are mutually coupled. Assuming an average absorptivity of $0.002 \mu\text{m}^{-1}\text{-wt}\%^{-1}$ in the 400-700 nm region, a 12 % by weight membrane will have an absorptivity of $\sim 0.025 \mu\text{m}^{-1}$ and will transmit $T = 10^{-0.025L}$, where L is the thickness in μm .

This will result in approximately 95 % transmittance, or a 5 % loss for a 1 μm thick membrane. However, this loss will increase rapidly with increased thickness.

Combined losses due to oxygen/hydrogen crossover and light absorption

There is clearly a decrease in the loss associated with crossover as the thickness of the membrane is increased. In contrast, there is an increase in loss associated with light absorption with increased membrane thickness. Figure SI-1 illustrates the contributions (a) and the total loss (b) associated with both mechanisms, for a series of membranes having different weight percentages of PEDOT-PSS.

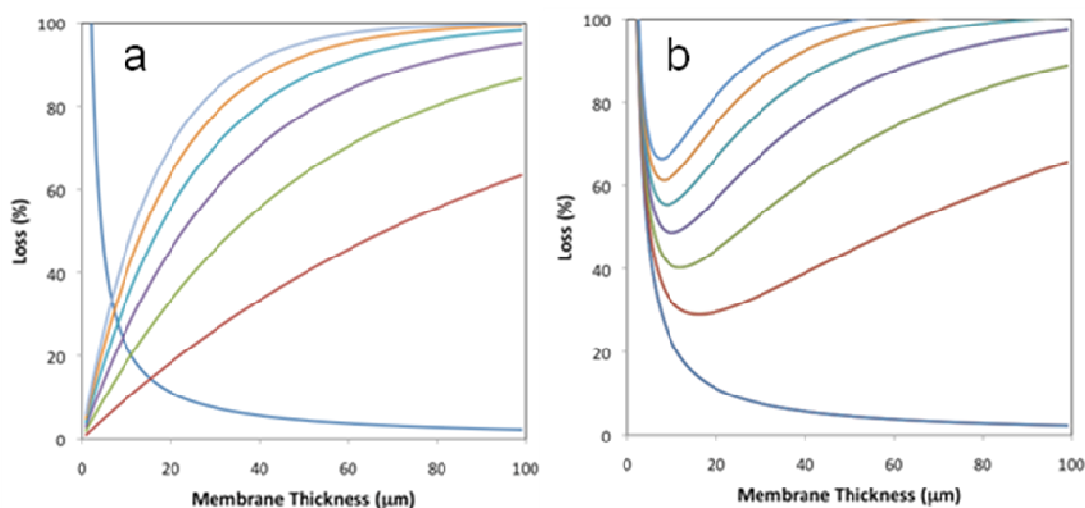


Figure SI-1. Loss (%) as a function of membrane thickness. (a) Loss (%) due to the sum of hydrogen and oxygen cross over increases exponentially in Nafion while the Loss (%) due to absorption increases on going from 2 to 12 % PEDOT-PSS in the composite. (b) Loss (%) resulting from the sum of losses due to hydrogen/oxygen crossover and losses due to increasing optical absorption on going from 2 to 12 % PEDOT-PSS in the composite.

Materials and Substrates

Nafion® perfluorinated ion-exchange resin, as a 10 wt% dispersion in water, high conductivity grade poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS), as a 2.2-2.6 wt% dispersion in water, acetonitrile, and isopropanol (IPA) were purchased from Aldrich, and were used without further purification. A PEDOT-PSS concentration of 2.4 wt% was assumed in all composite calculations. Precleaned Fisherbrand® microscope glass slides were purchased from Fischer Scientific. Glass substrates for membrane preparation, 75 mm x 50 mm x 2mm, were washed in an aqueous Fisherbrand® Sparkleen detergent solution, followed by rinsing in deionized water and then in isopropanol, before drying under a stream of N₂(g).

Membrane Fabrication (12.1 % PEDOT-PSS as a typical example)

2.5 mL of a 10 wt% dispersion of Nafion perfluorinated ion exchange resin in water, and 1.5 mL of a 2.2-2.6 wt% dispersion of high conductivity grade PEDOT-PSS, were mixed with a mechanical vortex for ~ 10 s. The composite dispersion was then carefully applied to a 75 mm x 50 mm x 2 mm glass substrate, and allowed to dry under ambient conditions for 16 h before placing in a vacuum oven at 110 °C for 90 min. The membrane was allowed to cool for ~ 10 min before being hydrated and removed from the glass substrate by soaking in ~ 250 mL of H₂O. The membrane was mechanically removed from the water and was then cut into various sizes for characterization.

Characterization.

UV-Vis-NIR spectra of the composite membranes were acquired under ambient conditions with a Varian Cary 5000 spectrophotometer, by taping the membranes in the optical path.

Four-point probe measurements were performed using a Signatone four-point probe apparatus attached to a Fluke 87 True RMS multimeter and constant-current source system (CHI-760 workstation controlled by a PC). The spring-loaded tungsten carbide probe contacts were spaced 0.1 cm apart. The electrical conductivity σ ($\Omega^{-1} \text{ cm}^{-1}$) was expressed as $\sigma = \ln 2(i)/\pi dV$, where d is the thickness of the films determined with an Alpha Step 500 general source profiler, i is the current that was passed through the outer probes, and V is the resulting voltage across the inner probes. Measurements were taken by carefully lowering the probes until they just made contact with the film surface, to prevent piercing of the soft material by the probe tips.

Scanning electron microscopy (SEM) images were collected using a Cambridge Instruments Stereoscan 120 SEM, equipped with a secondary electron (SE) detector, a four-quadrant semiconductor backscatter electron (SBE) detector, and an EDAX Genesis 4000 energy dispersive X-ray spectrometer (EDS) at an accelerating voltage of 20keV. No Au/carbon coating was deposited on the samples, unless otherwise specified.

AFM images were obtained on a Digital Instruments D3100 instrument in tapping mode.

XPS measurements were performed on a Kratos Axis Ultra DLD XPS system with a monochromated Al K α excitation source.

AES spectra were obtained on a JEOL JAMP-9500F Field Emission Scanning Auger Spectrometer at 10kV primary beam energy.

Four-electrode ionic conductivity measurements were performed with a glass cell shown below in Figure SI-5, similar to that described by Slade et al.⁴ The glass cell was designed to keep the Luggin capillaries flush when the two halves were mated. This allowed for the insertion of spacers that kept the Luggin capillary tips a fixed distance from each other. Each spacer was prepared by layering 20 pieces of packing tape resulting in a fixed distance of $\sim 850 \mu\text{m}$ between capillary tip and membrane face (i.e., the total distance between the capillaries was $\sim 1700 \mu\text{m}$ in the absence of a membrane). Pt auxiliary electrodes were controlled by a CH Instruments CHI-760 workstation potentiostat, with 25 to 200 mA of direct current applied between the platinum electrodes. Two Ag/AgCl reference electrodes were placed in the cell and were electrochemically connected to either side of the membrane via Luggin capillaries. The cell exhibited ohmic behavior over the range of applied currents. The electrolyte was 4.0 M H_2SO_4 . Proton conductivity measurements were made by carefully placing a wet membrane between two membrane spacers, and then clamping the whole assembly in the apparatus. The potential between the reference electrodes was measured with a Fluke 87 True RMS multimeter. The ionic conductivity values reported in the manuscript are the mean of three measurements on each membrane (See Table SI-1 for exact numerical values and their standard deviations). The cell and membrane assembly was disassembled and fresh 4 M H_2SO_4 added between each measurement.

Table SI-1. Wt% PEDOT-PSS, Mean Thickness, and Ionic Conductivity of PEDOT-PSS/Nafion Composite Membranes

Wt% PEDOT-PSS	Mean Thickness (μm)	Ionic Conductivity ($\text{mS}\cdot\text{cm}^{-1}$)
0	32	73 ± 6
6	37	94 ± 8
12	40	103 ± 4

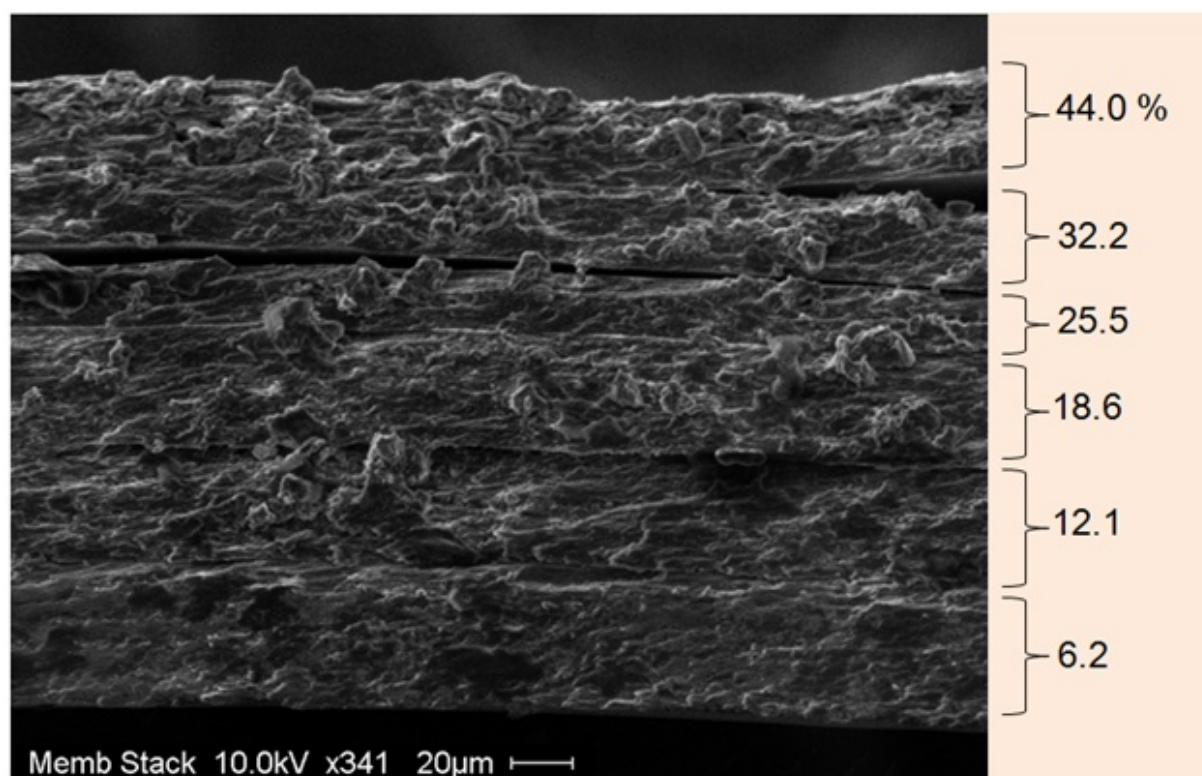


Figure SI-2. SEM micrograph of a stack of 6 membranes containing 6 to 44 weight percent PEDOT-PSS.

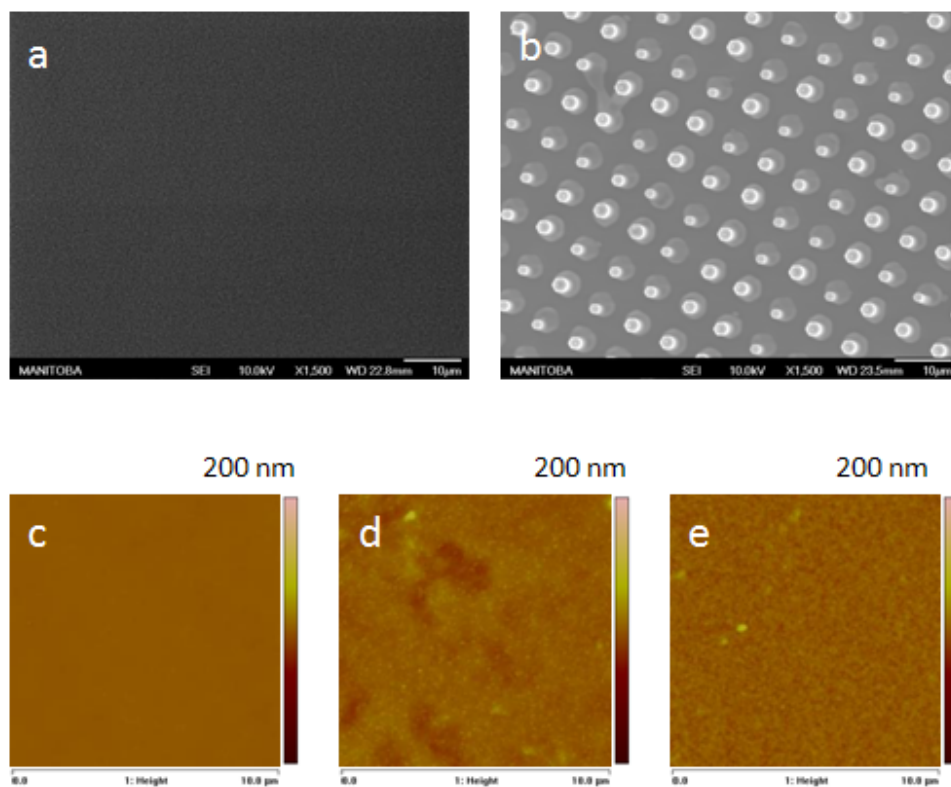


Figure SI-3. SEM and AFM images of PEDOT-PSS/Nafion composites. (a) SEM of a 12 weight percent PEDOT-PSS/Nafion film. (b) with microrods overlayed. (c) AFM image of a Nafion film (d) 12 weight percent PEDOT-PSS/Nafion composite (e) a PEDOT-PSS film

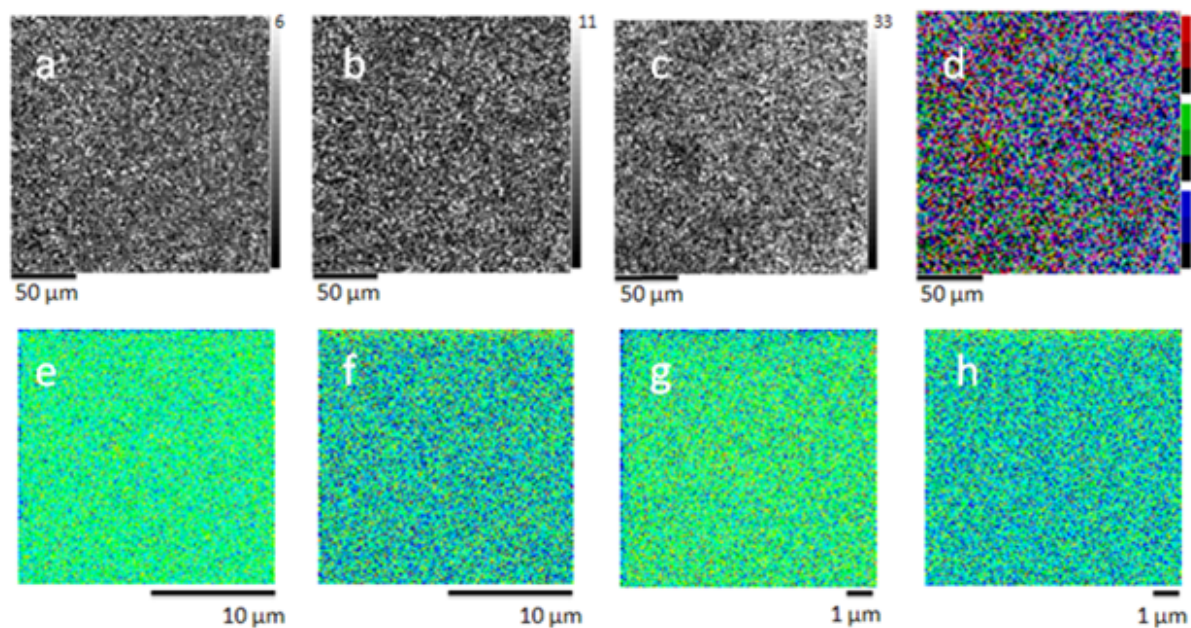


Figure SI-4. XPS and AES images of 12 wt % PEDOT-PSS/Nafion membranes. (a) XPS image of C_{Ar} 1s (BE = 283.3 eV). (b) C_F 1s (BE = 290.1 eV). (c) F 1s (BE = 687.3 eV). (d) Combined image of C_{Ar} (red), C_F (green) and F (blue). (e, g) AES images of C KLL (KE = 258 eV). (f, h) F KLL (KE = 652 eV).

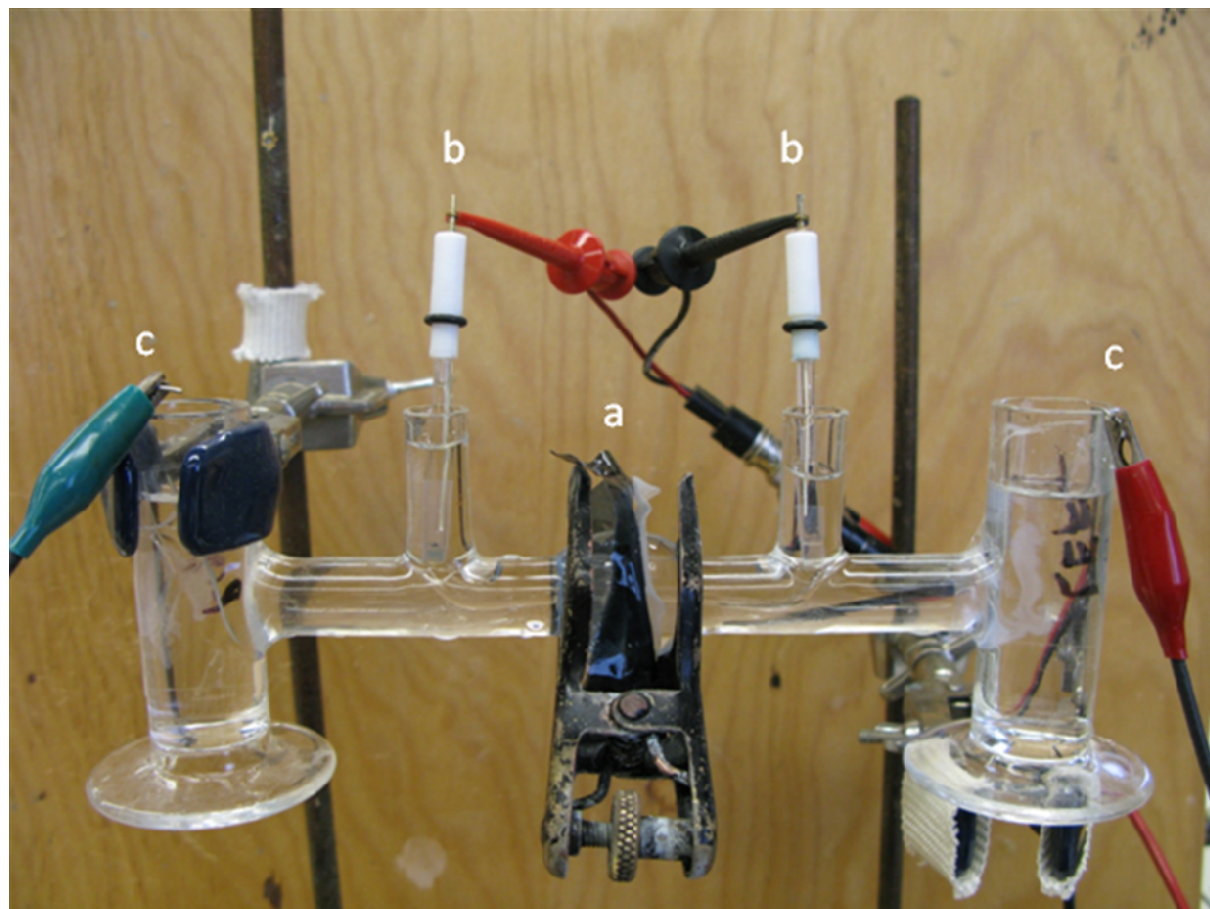


Figure SI-5. Photograph of the four-electrode glass cell used for proton conductivity measurements. (a) Composite membrane and 2 spacers. (b) Two Ag/AgCl reference electrodes connected to a Fluke 87 True RMS multimeter. (c) Two current-carrying Pt electrodes connected to a CHI Instruments CHI-760 workstation potentiostat.

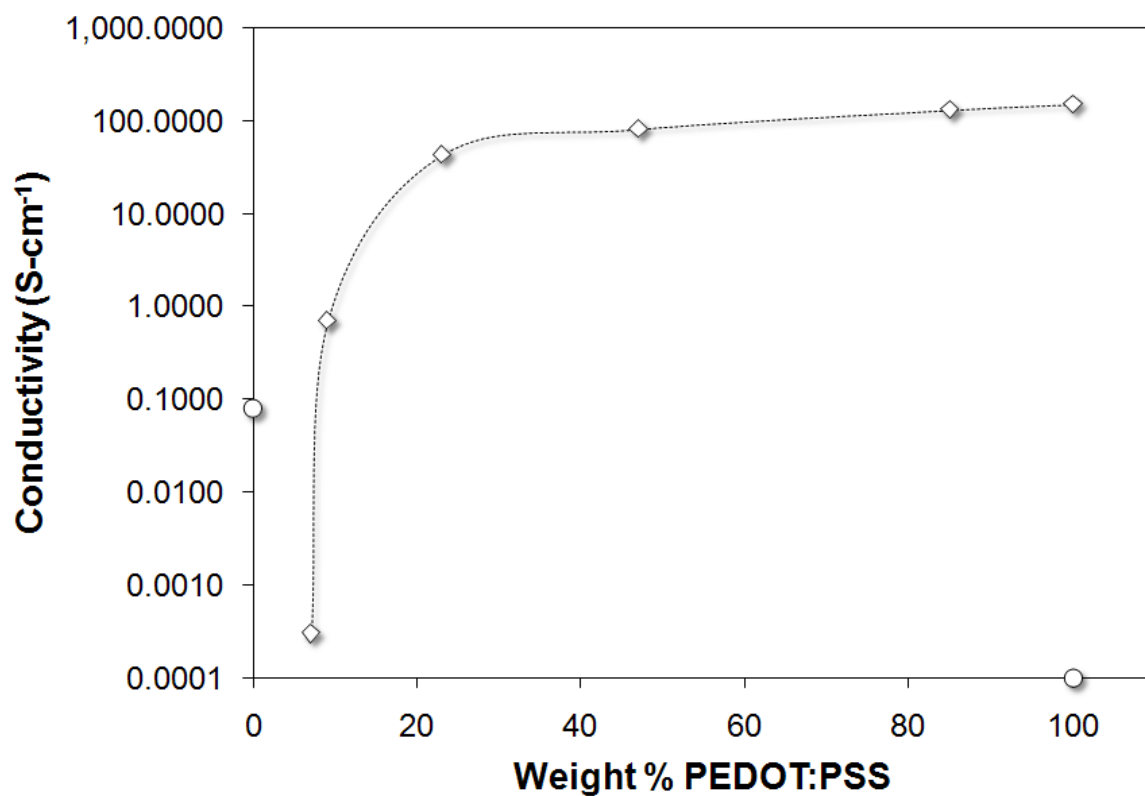


Figure SI-6. Electron conductivity of PEDOT-PSS/Nafion composites prepared using alcohol-based composites as a function of the weight percent PEDOT-PSS. Conductivities were measured by the 4-point probe technique.

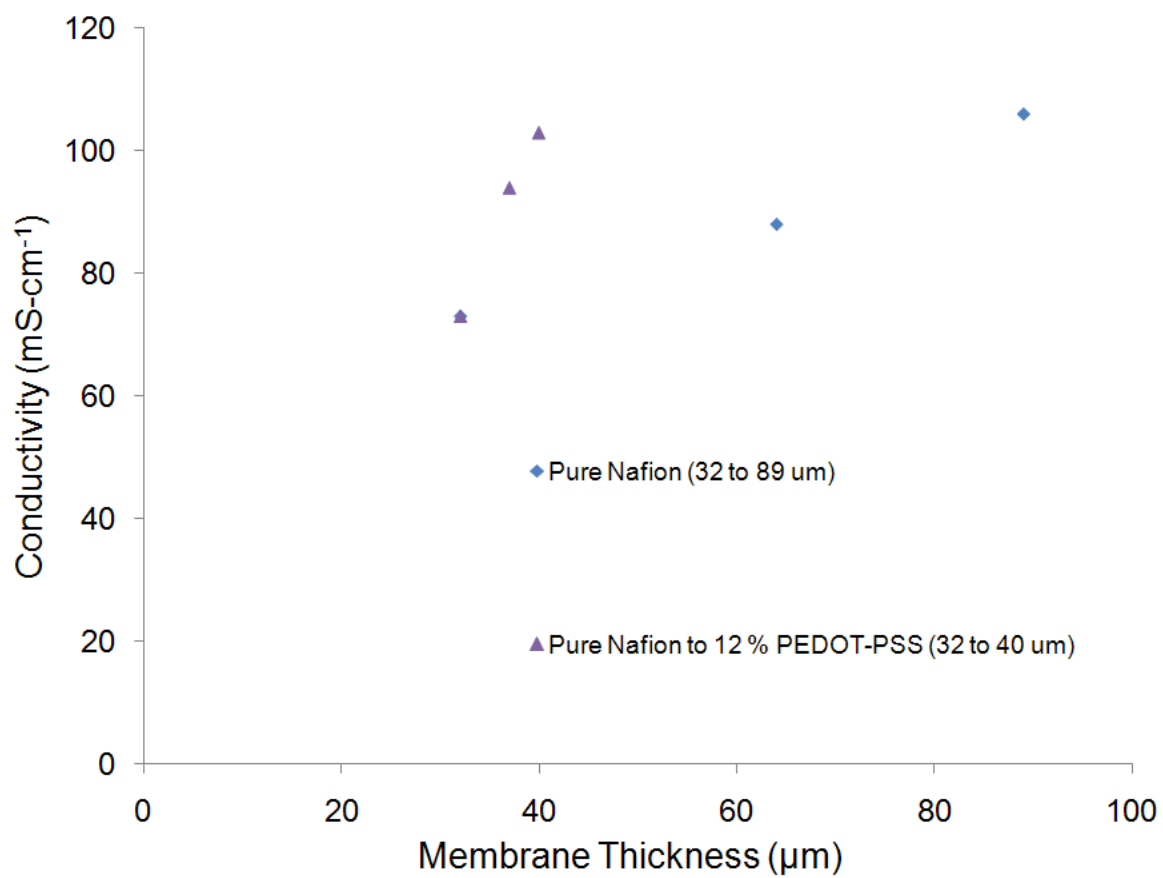


Figure SI-7. Conductivity as a function of membrane thickness (blue squares) and as a combined function of membrane thickness and composite composition (purple triangles).

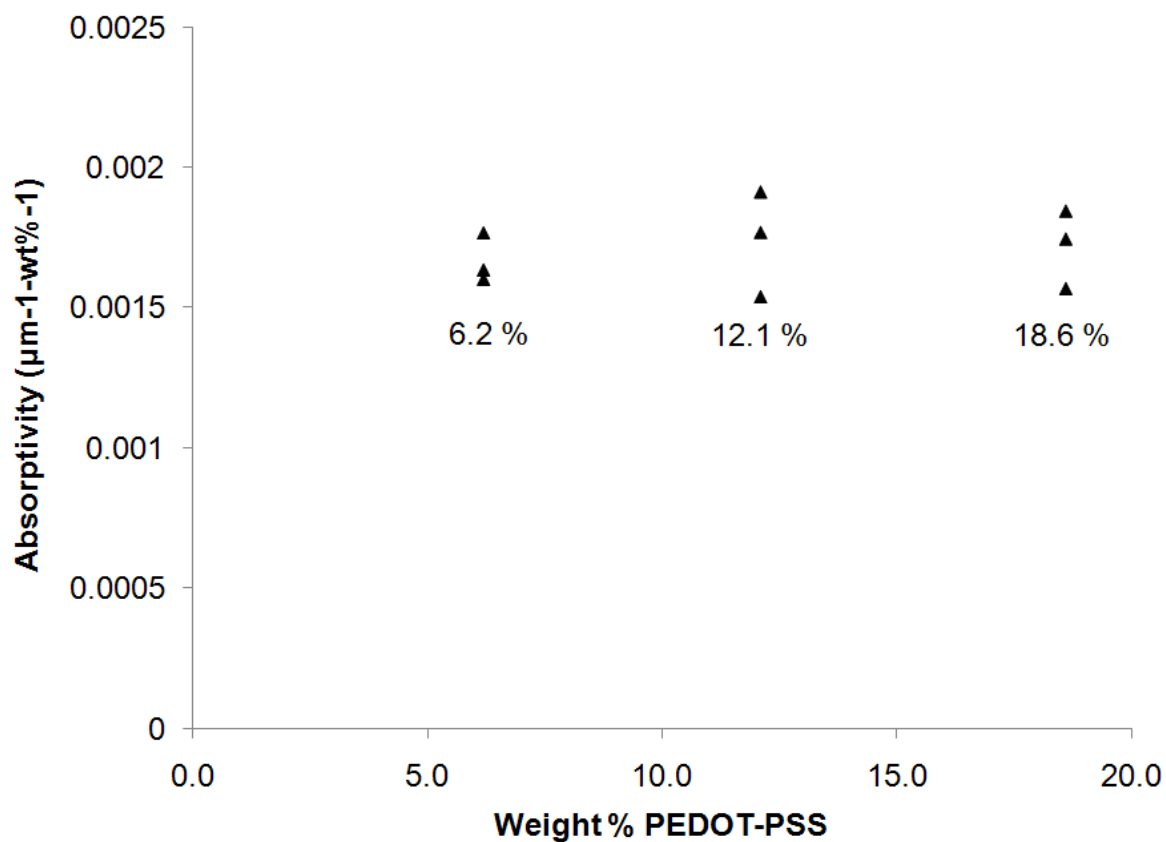


Figure SI-8. Absorptivity of composite membranes as a function of the weight percent PEDOT-PSS. Three samples were cut from each membrane. The thickness was estimated from the SEM micrograph in Figure SI-2.

- (1) Z. G. Zou, J. H. Ye, K. Sayama and H. Arakawa, *Nature*, 2001, **414**, 625.
- (2) A. T. Haug and R. E. J. White, *J. Electrochem. Soc.*, 2000, **147**, 980.
- (3) J. H. Jiang and A. J. Kucernak, *J. Electroanal. Chem.*, 2004, **567**, 123.
- (4) S. Slade, S. A. Campbell, T. R. Ralph and F. C. Walsh, *J. Electrochem. Soc.*, 2002, **149**, A1556.