

Supplementary Information

Characterizing the hydrophobic-to-hydrophilic transition of electrolyte structuring in proton exchange membrane mimicking surfaces

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1. Preparation and characterization of the surfaces

Table S1 Preparation of the Au-substrates

Au-substrate	Methods	Purposes
Annealed Au (40)/Mica	A 40 nm Au layer was sputtered coated on Mica and was subsequently cleaned with piranha solution (volumetric ratio of H ₂ O ₂ and H ₂ SO ₄ = 1:3), rinsed with MilliQ water, and dried with N ₂ gas. The Au(40)/Mica substrates were flame annealed to make an atomically flat surface.	Static contact angle
Roughened Au/glass	200 nm Au was deposited onto a clean cleavage Mica sheet via physical vapor deposition (PVD). The Au(200)/Mica was roughened under electrochemical condition, where 0.1 M KCl solution was used and a linear potential sweep oxidation-reduction cycle (ORC) was applied to the substrates. 25 ORC cycles were applied for roughening the Au surface. ¹	Surface enhanced Raman scattering spectroscopy
Au/glue/glass	100 nm Au was deposited onto a freshly cleaved, clean Mica sheet via physical vapor deposition (PVD). A glass slide was subsequently cleaned with concentrated sulfuric acid, rinsed with MilliQ H ₂ O, and then rinsed with pure ethanol (Analytical standard, SIGMA-ALDRICH Chemie GmbH) following by drying with N ₂ gas. The cleaned glass slide was glued onto the Au (100)/Mica using UV-active glue (Norland Optical Adhesive 81, Norland Products). The glass/glue/Au(100)/Mica was left under UV-light for 12 h for curing the glue. The Mica was subsequently peeled off the glass/glue/Au(100)/Mica in order to expose an atomically smooth surface. ²	XPS; Atomic force microscopy (AFM)

Static contact angle

The macroscale hydrophobicity of the surface was characterized using static contact angle measurement, where 4 μL sessile (MilliQ H_2O) drop the SAM and the drop shape was analyzed using the analysis system DSA 10. The contact angles were obtained by fitting the drop contour with the Young-Laplace equation. The contact angle decreases with increasing X indicating that increasing the mole ratio of R-SO₃Na in the thiol-ethanol solutions results in increasing numbers of hydrophilic sulfonic acid groups on the surface.

2. X-ray photoelectron spectroscopy (XPS)

XPS was used to determine the thickness of self-assembled monolayer (SAM) on the Au-substrate. We used a PHI Quantera II instrument at a passing energy of 16 eV with a 24 W power. With a typical attenuation length λ of ~ 2 nm for electron attenuation in an organic matrix, the thickness T_{SAM} of a SAM with sulfonic acid headgroups can be estimated directly from the sulfur signals according to:

$$I=I_0 e^{-\frac{T_{\text{SAM}}}{\lambda \sin\theta}}$$

where I is the sulfur intensity of the sulfonic acid, which is located at the outer layer of the SAM, and I_0 is the reference intensity measured for sulfur that is bound to the gold below the SAM; θ is the incident angle of X-ray. Based on this approach, the thickness of the SAM can be estimated at ~ 6.2 Å.

3. The extended DLVO model

We used a so-called extended DLVO model to reconstruct the total force F_{tot} . The model is described as:³

$$F_{\text{tot}} = -\frac{R}{6} A_{\text{H}}(D_r) + \frac{4\pi\lambda_D\sigma^2R}{\epsilon\epsilon_0} \left(e^{-\frac{D_r}{\lambda_D}} + e^{-\frac{2D_r}{\lambda_D}} \right) - 4\pi\gamma R H y e^{-\frac{D_r}{\lambda_{\text{Hy}}}}$$

where $A_{\text{H}}(D_r) = \frac{A_0}{D_r^2} - 2 \frac{\sqrt{A_0 A_1}}{(D_r + T_{\text{SAM}})^2} + \frac{A_1}{(D_r + 2T_{\text{SAM}})^2}$, $A_0 = 4.5 \times 10^{-21}$ J quantifies the interaction between hydrocarbons and $A_1 = 400 \times 10^{-21}$ J quantifies the interaction between Au-tip/Au-substrate across the hydrocarbon layers;³ T_{SAM} is the thickness of SAM and the value in this work has been determined by the XPS results in the preceding text; R is the radius of the tip and has been restricted to a variation range between 8 nm to 40 nm; $\gamma = 45$ mJ/m² is the hydrophobic tension;³ σ is the surface charge density, whose value has been deduced from the fit; D_r is the distance between the tip and surface, Hydra Hy and Hydra decay length λ_{Hy}

are free-fitting parameters that characterize the hydrophobicity of the surface, and the values for both of them were deduced from the fit; $\lambda_D = 9.6133 \times 10^{-10}$ m is the Debye length for the given ionic force; $\epsilon = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum; and $\epsilon_0 = 78.3$ F/m is the dielectric constant of water.

In the extended DLVO model, the total force was represented with the sum of the Van der Waals force ($-\frac{R}{6} A_H(D_r)$), the hydration ($-4\pi\gamma RHy e^{-\frac{D_r}{\lambda_{Hy}}}$) force and the electric double layer force ($\frac{4\pi\lambda_D\sigma^2R}{\epsilon\epsilon_0} (e^{-\frac{D_r}{\lambda_D}} + e^{-\frac{2D_r}{\lambda_D}})$). All force–distance curves in Figure 1 were fit to the model with Hy , λ_{Hy} and σ as free parameters.

4. Estimation of the surface charge density in Nafion[®] membranes

We estimated the charge surface density of the ionic water channels in commercial Nafion[®] membranes as explained below.⁶ Commercial Nafion[®] membranes are characterized by an equivalent weight (EW), which is the dry weight of Nafion[®] that contains 1 mole of $-\text{SO}_3\text{H}$ groups. For two industry standard membranes, Nafion[®] 212 and Nafion[®] 117, the EW = 1100 g).⁷ As is commonly believed, we assume the $-\text{SO}_3$ groups are distributed within cylindrical ionic water channels in Nafion[®],^{6a} and the surface density C_N [$\#/m^2$] of $-\text{SO}_3\text{H}$ groups can be written as $C_N = \#(\text{SO}_3\text{H})/A$, where A is the surface area of the cylindrical channel. A is given as $2 \times V \times (1/L + 1/r)$, where V is the volume of all water channels, L is the total length of all the water channels, and r is the radius of the water channels. Assuming $L \gg r$, we obtained $A \approx 2 \times V \times (1/r)$. Then, the surface density of $-\text{SO}_3\text{H}$ in the ionic channel of a Nafion[®] membrane is given by:

$$C_N \approx \frac{\#(\text{SO}_3\text{H})}{2 \times V \times \frac{1}{r}}$$

It has been reported that a dry Nafion[®] membrane with EW 1100 g/mol absorbs approximately 26 wt% when fully hydrated in liquid water.⁸ In other words, 1 g of the dry Nafion[®] membrane takes up 0.26 g of water when the membrane is fully hydrated. Therefore, the volume of water in the fully hydrated membrane is calculated as $0.26 \text{ g}/\rho_{\text{H}_2\text{O}}$, where $\rho_{\text{H}_2\text{O}}$ is the density of water in the membrane. For simplicity, we assume that $\rho_{\text{H}_2\text{O}}$ equals that of bulk water ($10^3 \text{ kg}/m^3$). Assuming all water in Nafion[®] resides in the channels, the channel volume channel equals water volume. Thus $V = 0.26 \text{ g}/\rho_{\text{H}_2\text{O}}$. The $\#(\text{SO}_3\text{H})$ in 1 g of Nafion[®] is given as $1/1100 [\text{mol}] \times N_A [\text{mol}^{-1}]$ for 1 g of dry Nafion[®] membrane. The average radius r

of the ionic channels in Nafion[®] 212 and Nafion[®] 117 is ~ 2.3 nm.⁹ Therefore, we obtained $C_N \sim 2.3 \times 10^{18} \text{ m}^{-2}$. As the $-\text{SO}_3\text{H}$ groups have been reported to be all deprotonated in the fully hydrated Nafion[®] membranes,¹⁰ we obtained the surface charge density C_s for Nafion[®] as $2.3 \times 10^{18} \text{ m}^{-2}/\text{m}^2$ respectively.

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