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

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<th>Au-substrate</th>
<th>Methods</th>
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<td>Annealed Au(40)/Mica</td>
<td>A 40 nm Au layer was sputter 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.</td>
<td>Static contact angle</td>
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<td>Roughened Au/glass</td>
<td>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.$^1$</td>
<td>Surface enhanced Raman scattering spectroscopy</td>
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<tr>
<td>Au/glue/glass</td>
<td>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.$^2$</td>
<td>XPS; Atomic force microscopy (AFM)</td>
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Static contact angle

The macroscale hydrophobicity of the surface was characterized using static contact angle measurement, where 4 μL sessile (MilliQ H₂O) 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 \( \lambda \) of ~2 nm for electron attenuation in an organic matrix, the thickness \( T_{\text{SAM}} \) of a SAM with sulfonic acid headgroups can be estimated directly from the sulfur signals according to:

\[
I = I_0 e^{-\frac{T_{\text{SAM}}}{\lambda}}
\]

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; \( \theta \) 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 \( F_{\text{tot}} \). The model is described as: ³

\[
F_{\text{tot}} = -\frac{R}{6} A_H(D_r)^4 \frac{4\pi \lambda_D \sigma^2 R}{\varepsilon \varepsilon_0} \left( e^{\frac{D_t}{\varepsilon_0}} + e^{-\frac{2D_t}{\varepsilon_0}} \right) - 4\pi \gamma H y e^{-\frac{D_t}{\lambda_H y}}
\]

where

\[
A_H(D_r) = \frac{\lambda_0}{D_r^2} \cdot 2 \cdot \frac{\sqrt{A_0 A_1}}{(D_r + T_{\text{SAM}})^2} + \frac{A_1}{(D_r + 2T_{\text{SAM}})^2}
\]

\( \lambda_0 = 4.5 \times 10^{-21} \) 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; \( T_{\text{SAM}} \) 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; \( \sigma \) is the surface charge density, whose value has been deduced from the fit; \( D_r \) is the distance between the tip and surface, Hydra \( H y \) and Hydra decay length \( \lambda_H y \)
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; \( \varepsilon = 8.85 \times 10^{-12} \) F/m is the permittivity of vacuum; and \( \varepsilon_0 = 78.3 \) 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 \((-4\pi R H \gamma e^{-H_D})\) force and the electric double layer force \(\left(\frac{4n\lambda_D^2}{\varepsilon_0} \frac{D_r}{2D} \frac{D_r}{2D} e^{-\lambda_D D} + e^{-\lambda_D D}\right)\). All force–distance curves in Figure 1 were fit to the model with \( H_D, \lambda_D \) and \( \sigma \) 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. 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. As is commonly believed, we assume the \(-\text{SO}_3\text{H}\) groups are distributed within cylindrical ionic water channels in Nafion®, and the surface density \( C_N \) [#/m^2] of \(-\text{SO}_3\text{H}\) groups can be written as \( C_N = \frac{#(\text{SO}_3\text{H})}{A} \), 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 \( L >> r \), 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. 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 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 kg/m^3). Assuming all water in Nafion® resides in the channels, the channel volume channel equals water volume. Thus \( V = 0.26 \ g/\rho_{\text{H}_2\text{O}} \). The #(SO_3H) 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 
\[ C_N \approx 2.3 \times 10^{18} \text{ m}^{-2}. \]
As the –SO\(_3\)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 \[ 2.3 \times 10^{18} \text{ m}^{-2}/\text{m}^2 \text{ respectively}. \]
References


