Determination of the components of the hydrated regions.

To estimate $b_{\text{hydra}}$, we have to know the components of hydrated regions. We think about three possible cases for the hydrated region as illustrated in Figure S1: case 1) the entire graft chains (both imidazole and styrene segments are included) and water, as shown in the inset of Figure 6 as well; case 2) the imidazole segments on the graft chains (styrene segments are excluded) and water; and case 3) water. In these three cases, we plot $I(q)$ as a function of $(b_{\text{cry\_ETFE}} - b_{\text{amo}})^2$ separately to see which case gives a linear relationship as shown in Figure 6, Figure S2 and S3.

Case 1. In this case, the hydrated regions are composed of the entire graft chains and water. Thus $b_{\text{hydra}}$ is given by the averaged SLD of all the components in the region as

$$b_{\text{hydra}} = \frac{\phi_{\text{im}} b_{\text{im}} + \phi_{\text{st}} b_{\text{st}} + \phi_{\text{w}} b_{\text{w}}}{\phi_{\text{graft}} + \phi_{\text{w}}}$$  \hspace{1cm} (S1)

at $m_1$ ($f_{\text{D2O}} = 55\%$), $b_{\text{hydra}}$ is estimated to be $2.23 \times 10^{10}$ cm$^{-2}$ by eq. (S1). Thus $b_{\text{cry\_ETFE}}$ is determined to be $2.23 \times 10^{10}$ cm$^{-2}$. $(b_{\text{cry\_ETFE}} - b_{\text{amo}})^2$ in eq. (5) can be calculated in terms of eq. (6) as a function of $f_{\text{D2O}}$. We plot $I(q)$ versus $(b_{\text{cry\_ETFE}} - b_{\text{amo}})^2$ in Figure 6, and a good linear relationship is obtained, verifying not only the correctness of $b_{\text{cry\_ETFE}}$ but the components of the hydrated regions.

IV-1.2 Case 2. In this case, the hydrated regions are composed of the partial of the graft chains-imidazole segments, and water. Thus $b_{\text{hydra}}$ is given by

$$b_{\text{hydra}} = \frac{\phi_{\text{im}} b_{\text{im}} + \phi_{\text{w}} b_{\text{w}}}{\phi_{\text{im}} + \phi_{\text{w}}}$$  \hspace{1cm} (S2)

at $m_1$, $b_{\text{hydra}}$ is calculated to be $2.4 \times 10^{10}$ cm$^{-2}$ by eq. (S2). Consequently, $b_{\text{cry\_ETFE}}$ is...
estimated to be $2.4 \times 10^{10}$ cm$^{-2}$. In eq. (5) can be calculated in the same way as in case 1. Figure S2 shows the plot $I(q_i)$ versus $(b_{c_{r_y,ETFE}} - b_{amo})^2$, and the datapoints are scattered, indicating the incorrect assumptions of $b_{cry, ETFE}$ and the components of the hydrated regions.

**IV-1.3 Case 3.** In this case, the hydrated regions are only composed of water, which is the characteristic pattern in Nafion.$^{43,44}$ Thus $b_{hydra}$ is simply given by

$$b_{hydra} = b_{w} \quad \text{(S3)}$$

at $m_1$, $b_{hydra}$ is estimated to be $3.235 \times 10^{10}$ cm$^{-2}$ by eq. (S3). Thus $b_{cry, ETFE} \sim 3.235 \times 10^{10}$ cm$^{-2}$. The plot between $I(q_i)$ versus $(b_{c_{r_y,ETFE}} - b_{amo})^2$ on the base of case 3 is shown in Figure S3, and an even more scattered dataset is observed, revealing the assumption of case 3 is wrong.

According to the discussions above, we conclude that the hydrated regions are composed of the entire graft chains and water, and SLD of the crystalline ETFE domains ($b_{cry, ETFE}$) is $2.23 \times 10^{10}$ cm$^{-2}$, the value of which is listed in Table 1.

**Verification of contrast factors $A$ and $B$ in eq. (10).** $A$ is the contrast factor, proportional to the contrast square between crystalline region ($b_{cry, ETFE}$) and the entire amorphous region ($b_{amo}$), given by

$$A \sim (b_{c_{r_y,ETFE}} - b_{amo})^2 \quad \text{(S4)}$$

where $b_{cry, ETFE}$ is estimated to be $2.23 \times 10^{10}$ cm$^{-2}$ in section IV-1 in the text. $b_{amo}$ can be calculated by eq. (6) in the text. We plot $A$ versus $(b_{c_{r_y,ETFE}} - b_{amo})^2$ for all the
profiles at $f_{D2O} > 55\%$ in Figure S4. A good linear relationship is clearly observed, evidencing the correctness of $A$.

$B$ is the contrast factor, proportional to the contrast square between amorphous ETFE ($b_{amo\_ETFE}$) and all the rest components in the sample ($b_{rest}$), given by

$$B \sim (b_{amo\_ETFE} - b_{rest})^2 \quad (S5)$$

where $b_{amo\_ETFE}$ is $\sim 2.0 \times 10^{10}$ cm$^{-2}$, which was listed in Table 1 in the text. $b_{rest}$ can be calculated by eq. (S6) below

$$b_{rest} = \frac{\phi_{cry\_ETFE} b_{cry\_ETFE} + \phi_{im} b_{im} + \phi_{st} b_{st} + \phi_{w} b_{w}}{\phi_{cry\_ETFE} + \phi_{graft} + \phi_{w}} \quad (S6)$$

where all parameters have been explained in the text and listed in Table 1. We plot $B$ versus $(b_{amo\_ETFE} - b_{rest})^2$ for all the profiles at $f_{D2O} > 55\%$ in Figure S5. A good linear relationship is clearly observed, evidencing the correctness of $B$.

**SANS profiles for grafted-ETFE membranes and the corresponding AEMs with different GDs.** SANS profiles for grafted-ETFE membranes with GD of 30, 46 and 120% and the corresponding AEMs with IECs of 0.95, 1.26 and 2.15 mmol/g are shown in Figure S6. To avoid overlapping, the profiles were vertically shifted.
Figure S1

Case 1

Case 2

Case 3

Hydrated regions

Figure S2

\[ I(q_1) \text{ (cm}^{-1}) \]

\[ (b_{\text{cry}_{\text{ETFE}}} - b_{\text{amo}})^2 \]
Figure S3

Figure S4
Figure S5

![Graph showing a linear relationship between $B$ and $(b_{\text{amo ETFE}} - b_{\text{rest}})^2$.](image_url)
Figure S6