## **Supplementary Material**

Material	Nb / $10^{10}$ cm <sup>-2</sup>
$D_2O$	6.25 <sup>a</sup>
H <sub>2</sub> O	-0.56 <sup>b</sup>
Au	4.49 <sup>a</sup>
Quartz	4.18 <sup>a</sup>
0.1 M NaClO <sub>4</sub> /H <sub>2</sub> O	-0.56 <sup>b</sup>
0.1 M NaClO <sub>4</sub> /D <sub>2</sub> O	6.25 <sup>a</sup>
1 M NaClO <sub>4</sub> /H <sub>2</sub> O	-0.30 <sup>b</sup>
1 M NaClO <sub>4</sub> /D <sub>2</sub> O	6.05 <sup>a</sup>
5 M NaClO <sub>4</sub> /H <sub>2</sub> O	0.648 <sup>b</sup>
5 M NaClO <sub>4</sub> /D <sub>2</sub> O	5.27 <sup>a</sup>

Supplementary Table 1. Scattering length density values used in model fitting routines.

<sup>a</sup> Experimentally measured values (recognizing the presence of  $H_2O$  in NaClO<sub>4</sub> and D<sub>2</sub>O, as supplied. <sup>b</sup> Values calculated from reference data and by measuring the amount of water required to make concentrated solutions of 1 M and 5 M NaClO<sub>4</sub>. To determine the Nb of 5 M NaClO<sub>4</sub>/D<sub>2</sub>O critical reflectivity was measured using a silicon block (Nb = 2.08 x 10<sup>10</sup> cm<sup>-2</sup>) immersed in the electrolyte solution.



Supplementary Fig. 1. Reflectivity profiles (dots and error bars) and fits (solid lines) obtained using a single layer for the PVF film A in the dry state (top curve, blue fit line), immersed in D<sub>2</sub>O (middle curve, red fit line) and immersed in H<sub>2</sub>O (bottom curve, green fit line). For clarity D<sub>2</sub>O and H<sub>2</sub>O profiles are divided by 100 and 1000 respectively. Asterisks indicate regions of visibly poorer fit compared to that obtained using more than one layer.  $\chi^2$ -values are 1.7, 1.9 and 1.4 (top to bottom).



Supplementary Fig. 2. Reflectivity profiles (dots and error bars) and fits (solid lines) using multiple layers for PVF film A immersed in 1 M NaClO<sub>4</sub> in either the reduced (profiles A and C) or oxidised (profiles B and D) state. Profile A, blue fit curve: reduced PVF in 1 M NaClO<sub>4</sub>/D<sub>2</sub>O; Profile C, red fit curve: reduced PVF in 1 M NaClO<sub>4</sub>/H<sub>2</sub>O; Profile B, green fit curve: oxidised PVF in 1 M NaClO<sub>4</sub>/D<sub>2</sub>O; Profile D, yellow fit curve: oxidised PVF in 1 M NaClO<sub>4</sub>/H<sub>2</sub>O. For clarity profiles B, C and D are divided by 10, 1000 and 100000 respectively.



Supplementary Fig. 3. Reflectivity profiles (dots and error bars) and fits (solid lines) obtained using a single layer for the PVF film A immersed in 0.1 M NaClO<sub>4</sub> in either the reduced (profiles A and C) or oxidised (profiles B and D) state. Profile A, blue fit curve: reduced PVF in 0.1 M NaClO<sub>4</sub>/D<sub>2</sub>O; Profile C, green fit curve: oxidised PVF in 0.1 M NaClO<sub>4</sub>/D<sub>2</sub>O; Profile B, red fit curve: reduced PVF in 0.1 M NaClO<sub>4</sub>/H<sub>2</sub>O; Profile D, yellow fit curve: oxidised PVF in 0.1 M NaClO<sub>4</sub>/H<sub>2</sub>O. For clarity profiles B, C and D are divided by 10, 10000 and 100000 respectively. Asterisks indicate regions of visibly poorer fit compared to that obtained using more than one layer.  $\chi^2$ -values are 2.0, 3.6, 1.4 and 1.7 (top to bottom).



Supplementary Fig. 4. Reflectivity profiles (dots and error bars) and fits (solid lines) obtained using a single layer for the PVF film A immersed in 1 M NaClO<sub>4</sub> in either the reduced (profiles A and C) or oxidised (profiles B and D) state. Profile A, blue fit curve: reduced PVF in 1 M NaClO<sub>4</sub>/D<sub>2</sub>O; Profile C, green fit curve: oxidised PVF in 1 M NaClO<sub>4</sub>/D<sub>2</sub>O; Profile B, red fit curve: reduced PVF in 1 M NaClO<sub>4</sub>/H<sub>2</sub>O. For clarity profiles B, C and D are divided by 10, 10000 and 100000 respectively. Asterisks indicate regions of visibly poorer fit compared to that obtained using more than one layer.  $\chi^2$ -squared values are 5.8, 3.9, 1.4 and 1.7 (top to bottom).



Supplementary Fig. 5. Reflectivity profiles (dots and error bars) and fits (solid lines) obtained using a single layer for the PVF film A immersed in 5 M NaClO<sub>4</sub> in either the reduced (profiles A and C) or oxidised (profiles B and D) state. Profile A, blue fit curve: reduced PVF in 5 M NaClO<sub>4</sub>/D<sub>2</sub>O; Profile C, green fit curve: oxidised PVF in 5 M NaClO<sub>4</sub>/D<sub>2</sub>O; Profile B, red fit curve: reduced PVF in 5 M NaClO<sub>4</sub>/H<sub>2</sub>O; Profile D, D fit curve: oxidised PVF in 5 M NaClO<sub>4</sub>/H<sub>2</sub>O. For clarity, profiles B, C and D are divided by 10, 10000 and 100000 respectively. Asterisks indicate regions of visibly poorer fit compared to that obtained using more than one layer.  $\chi^2$ -values are 3.4, 4.1, 1.0 and 1.0 (top to bottom).



Supplementary Fig. 6. Model scattering length densities obtained as best fits to reflectivity profiles for the PVF film of Figure 1 exposed to NaClO<sub>4</sub> solutions. Electrolyte concentration: (a) 0.1 M (model fit of Sup. Figure 2); (b) 1 M (model fit of Sup. Figure 3); (c) 5 M (model fit of Sup. Figure 4). Film oxidation state: reduced film, full line and dotted line; oxidised film, dashed and chained line. In each panel, upper (lower) two lines are for  $D_2O$  (H<sub>2</sub>O) as solvent.