Supplementary Information

Dielectric response and proton transport in water confined in graphene oxide

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Fig. S1 Thickness measurement of graphene oxide membrane using optical profilometry.

The thickness of GO membranes supported on substrates was measured using optical profilometry. The presence of wrinkles caused the measured thickness to be a little larger than the actual one. Here the smallest step size was taken as the thickness of the membrane which matches very well with the thickness obtained through the cross-sectional FESEM image.
SII
Custom-made set-up for impedance measurements under variable relative humidity

Fig. S2 Schematic of the setup for measuring impedance at variable humidity conditions. Here V1-V4 are ball valves. MFC denotes Mass Flow Controller.
SIII

Flake size measurement

Fig. S3 (a) SEM image of a graphene oxide flakes on SiO\textsubscript{2}/Si substrate cast from a highly diluted solution (scale bar is 10 μm). (b) Flake size distribution obtained from the FESEM image of flakes (Here the counts are based on numbers, not on the area).
Fig. S4 Raman spectrum of graphene oxide.

The Raman spectrum of graphene oxide was taken with a 632.81 nm He-Ne laser. The position of the D peak and G peak were found to be at 1339.8 cm$^{-1}$ and 1580.7 cm$^{-1}$ respectively with the area integrated ratio $I_D/I_G = 2.48$. 
Fig. S5 XPS survey spectrum of graphene oxide showing Os1 and Cs1 peaks.

The total area under O1s curve is 13437 units, while the total area under the C1s curve is 10390 units. The sensitivity factor ratio of oxygen and carbon is 2.93:1. From this, it follows that the C:O elemental ratio is 2.27:1.
SVI

Water adsorption by graphene oxide membrane

Fig. S6 Dynamic vapor sorption data of water uptake by a GO membrane at different RH%.
SVII

Increase in the interlayer spacing with RH

Fig. S7 (a) XRD of graphene oxide in the ambient environment (~ 50% RH) (b) Change in position of (001) peak with RH%.

The calculated interlayer spacing of GO in the ambient environment is 8.4 Angstroms. The estimated mean crystallite size based on the Scherrer equation was 10 nm.
Impedance of graphene oxide at different humidities

Fig. S8 Nyquist plot of graphene oxide at (a) 2% RH, (b) 15% RH, (c) 25% RH, (d) 45% RH, (e) 60% RH and (f) 80% RH in the frequency range 10 Hz to 500 kHz.
### Fitting parameters

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<th>R3 Ω</th>
<th>Q1 Sn1/Ω</th>
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<th>Q2 Sn2/Ω</th>
<th>n2</th>
<th>W Sn5/Ω</th>
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Calculating the bulk resistance and capacitance of GO at different RH%.

The value of resistance and capacitance of graphene oxide at different RH% can be calculated from R2 and Q1. The bulk resistance equals R2, and the capacitance is calculated from constant phase element (CPE) Q1.

The impedance of CPE is given by

$$Z(\text{CPE}) = Y_0^{-1} (j\omega)^{-n}$$

Here $Y_0 = 1/Q$. The value of capacitance is calculated from the formula [1].

$$C = Y_0 (\omega_m'')^{n-1}$$

Here, $\omega_m''$ is the frequency where the semicircle portion has the maximum value for the imaginary part of Z.
SIX

Dispersion in R and C values

In the above circuit, R1 varies from 17 Ω to 33 Ω for the samples studied in this work.

Fig. S9 (a) Dispersion of capacitance value of graphene oxide with the frequency of the applied bias frequency. (b) Dispersion in resistance values with the frequency of applied voltage bias.
Comparison: Capacitance and loss: full frequency versus high-frequency fit

Fig. S10 (a) Comparison of the dielectric value of GO calculated from high-frequency fit (hf) and full-frequency fit (ff) (10 Hz to 500 kHz). (b) Comparison of the conductivity of GO calculated from high-frequency fit and full frequency fit (10 Hz to 500 kHz).

Calculation of lower bound of water dielectric

From the effective-medium approach [2], the dielectric constant of a composite ($\varepsilon_{\text{eff}}$) will be in the limits

$$\frac{1}{\left[(\theta/\varepsilon_{1}) + (1- \theta)/\varepsilon_{2}\right]} \leq \varepsilon_{\text{eff}} \leq \theta \varepsilon_{1} + (1- \theta)\varepsilon_{2}$$

$\theta$ is the vol. fraction of the inclusion
$\varepsilon_{1}$ is the dielectric constant of the inclusion (water)
$\varepsilon_{2}$ is the dielectric constant of the host matrix (Unhydrated GO)

$\varepsilon_{\text{eff}}$ is known from the experimental data (Fig. 3(b) of main text). The value of $\theta$ can be obtained from the water weight, the density of GO (1.8 g/cc) and the density of water inside GO (taken to be 1 g/cc). The dielectric value of unhydrated GO is taken from Yoshio et al. [3].
References

