# Supplementary Materials

**Materials and Methods**

**Preparation of Graphene Oxide.**

Graphite powder (1g, 300μm, Wako Ltd), $NaNO_3$ (fine mesh, 1.0 g) and $H_2SO_4$ (48 ml, 97%) was cooled to 0 °C by stirring in an ice bath for 15 min. 3.0 g finely meshed $KMnO_4$ powder was added slowly with vigorous stirring while keeping the temperature below 20 °C. After half an hour the mixture was warmed to 35±3 °C for 30 min. Then 180 ml water was added slowly, the temperature rose gradually and was kept in 95±3 °C for another 30 min. Then 400 ml water was added. Finally, $H_2O_2$ (30%, 12 mL) was added to convert the unreacted permanganate and manganese dioxide into soluble sulfates. The mixture was centrifuged (3000 rpm, 10 min.) and the precipitate was washed with 5% HCl solution (1 time) and water (3 times). It was then dispersed in water (0.9 mg / ml) by 2 hours sonication followed by discarding aggregated carbon through centrifugation at 4000 rpm for 1 hour.

**pH adjustment of GO dispersion.**

GO(n) (n = 2 – 11 corresponding to pH = 2 – 11) was adjusted to the required pH. 0.9 mg / mL of GO dispersion showed pH = 3. The dispersion was adjusted to pH = 2 by adding a few drops of dilute hydrochloric acid solution. On the other hand, neutral and basic GO dispersion was prepared by adding dilute aqueous ammonia solution. In order to prevent large concentration change of GO dispersion, pH adjustment liquid was used 2 ml or less.

**Fabrication of GO membranes.**

The pH-adjusted GO dispersion (0.9 mg / mL, 20 mL) was filtered under reduced pressure using a membrane filter with a pore size of 0.4 μm by followed by drying under ambient conditions. Each GO membrane was a uniform and homogeneous membrane with a thickness of 15 μm.

**Physical measurements.**

The structure and morphology of the samples were characterized by X-ray photoelectron spectroscopy (XPS, Theta Probe, Thermo Fisher Scientific), Fourier transform infrared spectroscopy (FT-IR, Spectrum two, Perkin Elmer) and Raman spectroscopy (NRS-3100 JASCO).

The nature of the conducting ionic species for the GO(3) and GO(11) nanosheets was determined by measuring the corresponding EMF in a water vapor concentration cell at 30 °C. This involved passing a humidified $O_2$ gas on one side of the cell and a dry $O_2$ gas stream on the other side (Figure 5a and 5b).[24] GO(3) and GO(11) membrane samples were sandwiched between a pair of stainless mesh electrodes. Electromotive forces were measured as open-circuit potentials or electrical voltages developed by charge separation across the membrane. The open circuit voltage was measured using the BAS electrochemical Analyzer 7002E.

An anion exchange membrane (AHA, ASTOMCo.) and a cation exchange membrane (Nafion 117; DuPont) were also used in a control experiment. The ion conductivities of the GO(3) and GO(11) membrane samples were measured by the four probe AC method using an impedance/gain phase analyzer (Solartron 1260, TOYO Corporation) over the frequency range 1Hz to 6 MHz under controlled temperature and humidity using an incubator (SH-221, ESPECF).[12] The impedance data were then employed to generate Nyquist plots, displayed as a compressed semicircle whose diameters represent the corresponding resistance (R) value. Ion conductivities ($\sigma$) were calculated according to $\sigma = (1/R) \times (d/A)$ where, d and A represent the distance between the Pt electrodes and the area of the Pt plate electrode, respectively.[15]

The GO dispersion begins to precipitate as GO-H hybrid at pH = 1 or lower while some of the negatively charged oxygenated sites in GO are neutralized by bonding with $H^+$. Therefore, in current work, is not possible to prepare the GO(1) or GO(0) membrane. However, in our previous study, a much lower proton conductivity was calculated as $10^{-7}$ to $10^{-5}$ S cm$^{-1}$ where GO-H powdered sample was compressed into pellets.[12] The associated lower conductivity of GO-H palate sample can be attributed to (i) some of the hydrophilic sites are blocked by $H^+$ and (ii) GO-H pellet sample shows a combination of the in-plane and through-plane conductivities.
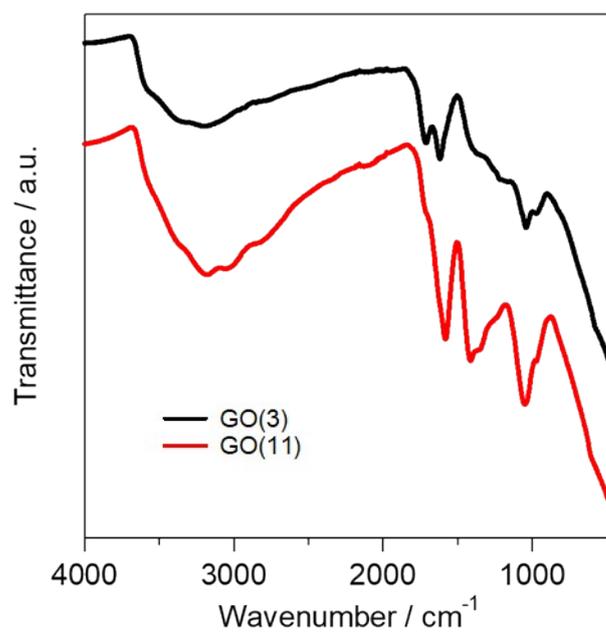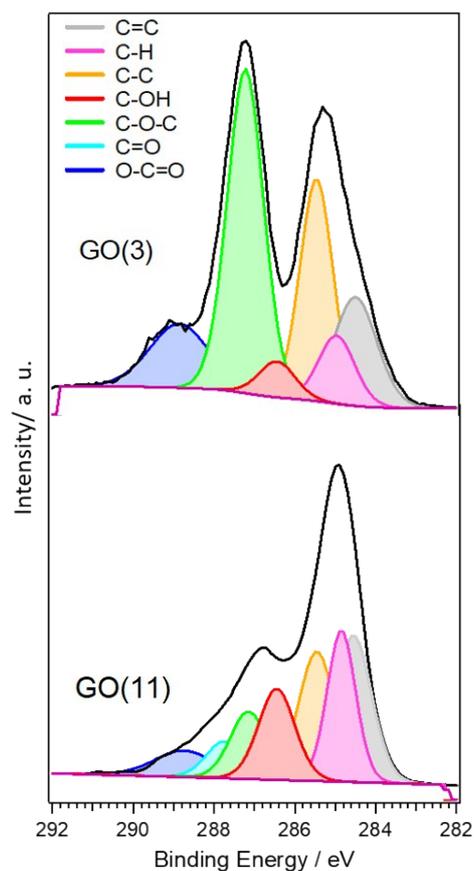
**Figure S1.** The color changes of the GO dispersions under acidic and basic conditions (pH = 2-11).
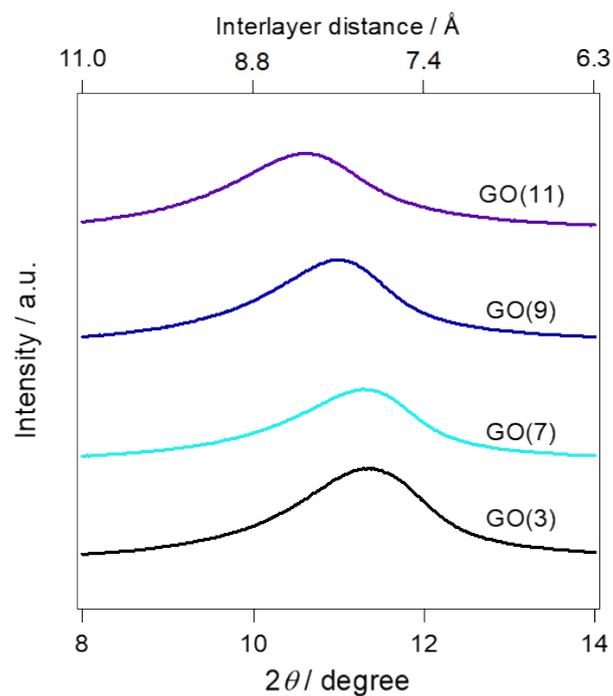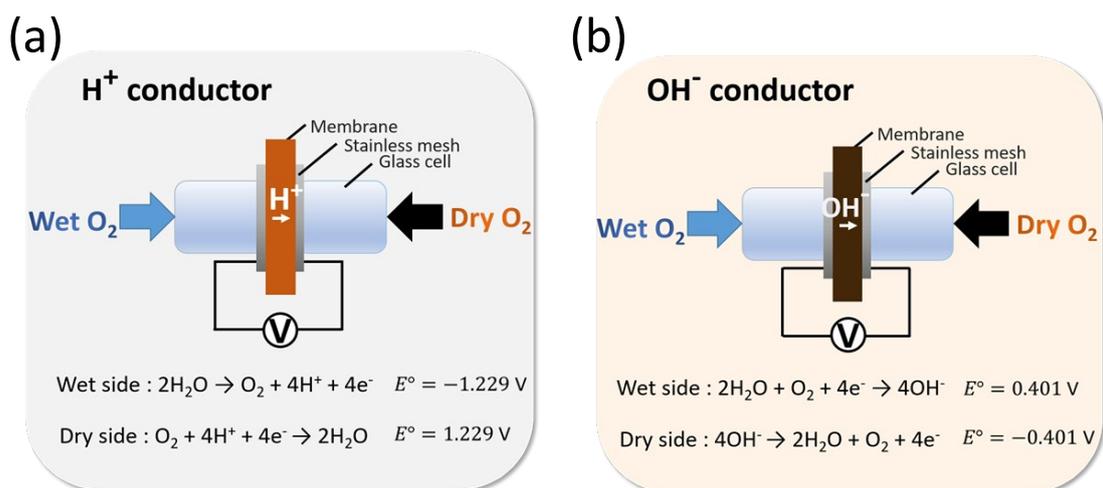
**Figure S2.** PXRD pattern of GO(3)-GO(11) and corresponding interlayer distance.
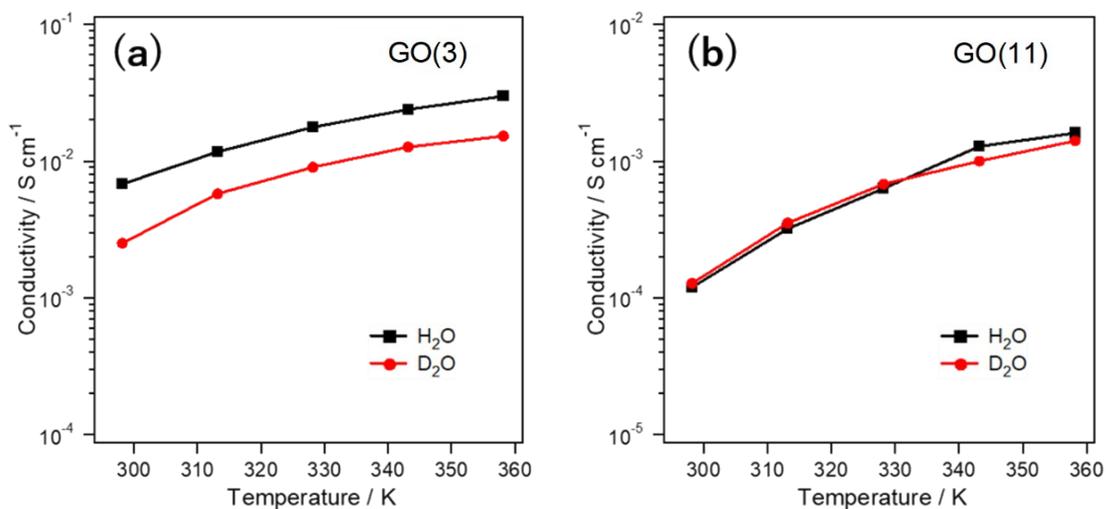


**Figure S3.** A comparison of the FT-IR spectra for the various functional groups of GO(3) and GO(11).
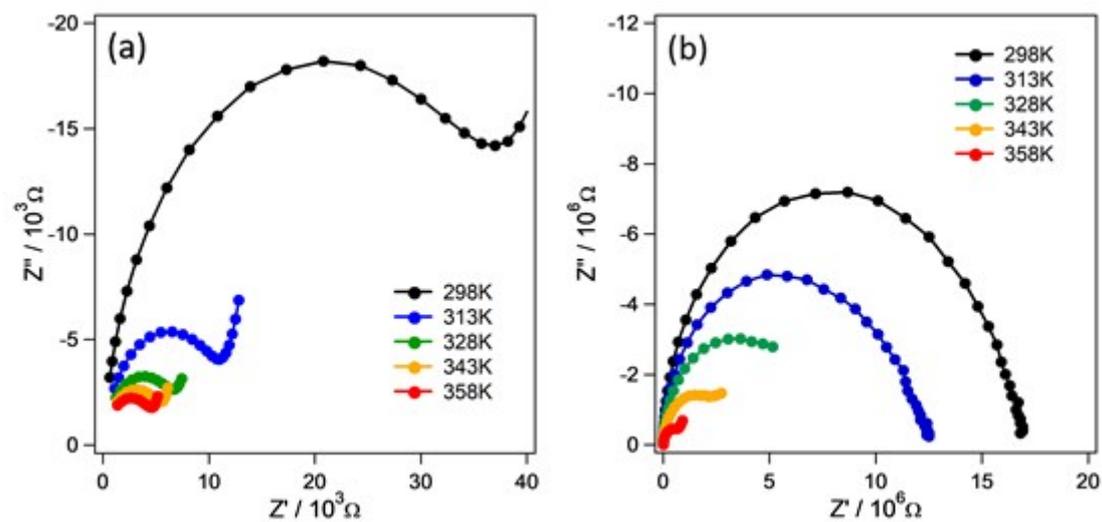
**Figure S4.** The C1s XPS spectra for GO(3) and GO(11).



**Figure S5.** Schematic presentation of the water vapor concentration cell associated with the determination of the sign of the EMF in the membrane sample. (a) For H+ conductor. (b) For OH- conductor.
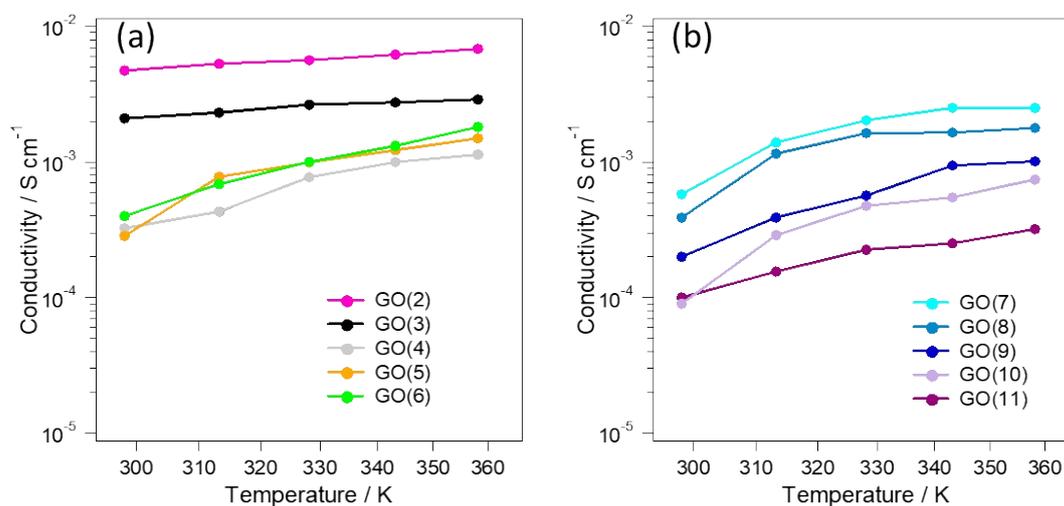
**Figure S6**. The temperature-dependent conductivities of (a) GO(3) and (b) GO(11) humidified by $H_2O$ and $D_2O$ at 90% RH.



**Figure S7.** The traces formed by the real (Z′) and imaginary parts (Z″) of the impedance as the frequency was varied at 90% RH. (a) GO(3) (b) GO(11)
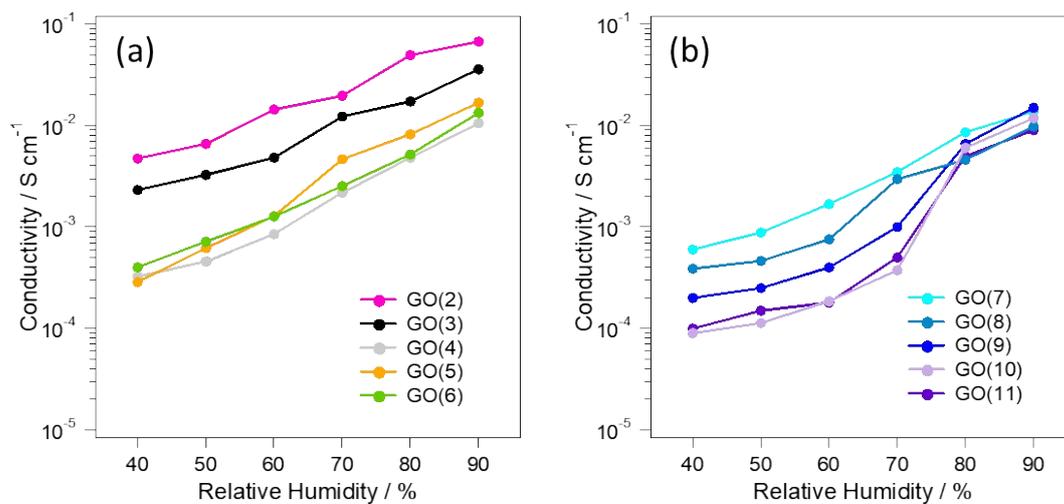
**Figure S8.** Relative humidity-dependent ion conductivity at 298K. (a) GO (2)-GO(6). (b) GO (7)-GO(11).



**Figure S9.** Temperature-dependent ion conductivity at 40% RH. (a) GO (2)-GO(6). (b) GO (7)-GO(11).