Supporting Information

Optimization of Proton Conductivity in Graphene Oxide by Filling Sulfate Ion

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Experimental Section

Graphite oxide was prepared through modified Hummers' method using graphite powder, $NaNO_3$, H_2SO_4, $KMnO_4$ and H_2O_2 solutions.[1] The graphite oxide was suspended in distilled water by ultrasonication for 2 h. 200 nm thick GO film on comb electrode was prepared from 0.15 μL GO dispersion (0.6 g L^{-1}) by drop-cast method. The sGO films were prepared by mixing GO (10 mL, 0.6 g L^{-1}) and H_2SO_4 solutions (0.12, 0.24 and 0.60 mL; 0.19 mol L^{-1}) and were dropped on comb electrodes followed by drying under vacuum. Other electrolytes were also loaded by similar method. GO and sGO papers (18 μm) were prepared by filtering 2 mL of the GO (4 g L^{-1}) and 10 mL of sGO (S / C = 0.08) solutions using a membrane filter (0.4 μm pore size, Merck Millipore) under reduced pressure and successive vacuum drying. The morphology and thickness of the samples on the comb electrodes were evaluated by AFM (Bruker, Digital Instruments Nanoscope V). Interlayer distances within the films were measured by a Rigaku RINT 2500 powder X ray diffractometer, using Cu Kα (λ = 0.154 nm) radiation. SEM images were recorded by a field-emission SEM (Hitachi High-Tech, SU-8000). EDS analysis were performed on an attached EDAX (coupled with Hitachi High-Tech SU-8000) spectrometer. The elemental compositions and assignments of carbon peaks of the samples were analyzed by an XPS analyzer (Thermo Scientific, Sigma Probe). TGA curves were generated in a thermal analyzer (Seiko Instruments, EXSTAR 6000) at scan rate 10 °C min^{-1}. The proton conductivities of the films were measured by an impedance/gain phase analyzer (Solartron 1260) in the frequency range from 1 MHz to 1 Hz with a perturbation voltage amplitude of 50 mV. The measured resistance of bare comb electrode was very high (> 10^8 Ω), which confirmed the absence of any parasitic impedance contribution. The dominance of ionic conductivity was confirmed from isotope effect where conductivity of D_2O humidified samples were lower than H_2O humidified samples. The σ and E_a values were calculated according to the methods described in our previous paper. The proton conductivity of GO paper was measured by a four-probe DC method using a potentiostat with a function generator (IVIUM TECHNOLOGIES, CompactStat).

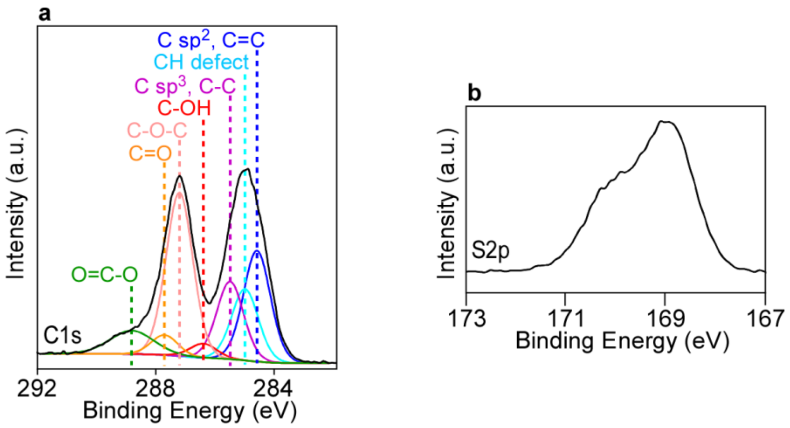

Fig. S1 XPS spectra of C1s and S2p of the sGO film (S / C = 0.08). The peak around 169 eV corresponds to sulfate ion[2].

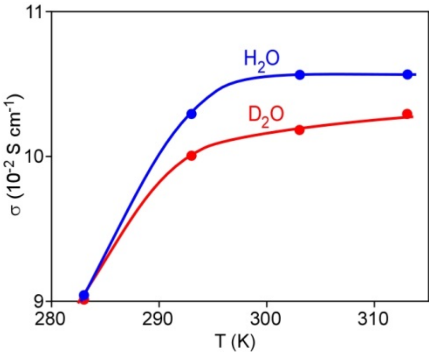

Fig. S2 Temperature dependent conductivities of sGO (S/C = 0.41, 75 nm) humidified by H_2O and D_2O by 90%.

Reference

1 M. R. Karim, H. Shinoda, M. Nakai, K. Hatakeyama, H. Kamihata, T. Matsui, T. Taniguchi, M. Koinuma, K. Kuroiwa, M. Kurmoo, Y. Matsumoto and S. Hayami, *Adv.Funct.Mater.*, 2013, **23**, 323-332.

2 M. Y. Smirnov, A. V. Kalinkin, A. V. Pashis, A. M. Sorokin, A. S. Noskov, K. C. Kharas and V. I. Bukhtiyarov, *J. Phys. Chem. B*, 2005, **109**, 11712-11719.