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COMMUNICATION

Super Proton / Electron Mixed Conduction in Graphene Oxide Hybrids by Intercalating Sulfate Ions

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We successfully developed an efficient proton / electron mixed conductor composed of a single phase material that functions at room temperature by introducing sulfate ions into graphene oxide interlayers. The promising properties of this material would allow for their wide uses in fuel cells, supercapacitors, and gas separation membranes.

Mixed conducting materials with high electrical and protonic conductivities enable various applications such as fuel cells, supercapacitors and gas separation membranes.¹⁻⁵ Perovskite-type oxides such as BaCeO₃, LaYbO₃ and La₆WO₁₂ doped with foreign cations are most commonly used as mixed conductors.⁴⁻⁶ However, these materials only function at higher temperatures (> 650 °C). In addition, BaCeO₃ undergo severe chemical degradation in air containing water and CO₂. To overcome these drawbacks, heterogeneous mixing of electron and proton conductors has been reported to produce mixed conductors that function at room temperature.^{7, 8} A Nafion based membrane hybridized with carbon showed proton and electron conductivities of ~10⁻⁶-10⁻⁴ S cm⁻¹ and ~10⁻³ S cm⁻¹, respectively, at room temperature. However, in such a heterogeneous mixed conductor, carrier transport is limited by phase boundaries, making it substantially difficult to obtain high mixed conductivities. Poor mechanical properties of such composite thin films are also problematic. Thus, it is desirable to develop single phase mixed conducting materials where diffusion paths of charged carriers are interconnected in the molecular scale.

Graphene oxide (GO) has recently emerged as a

multifunctional material because of its good physicochemical properties such as high hydrophilicity,⁹ large surface area,¹⁰ and protonic conductivity.¹¹⁻¹⁴ Moreover, these properties of GO are tunable by control of the surface conditions; removal or attachment of surface oxygen functional groups drastically changes these properties. Another advantage of GO films is their good flexibility because they are made of a single phase material, graphene sheets. Previously, we reported that the proton and electron conductivities of GO can be controlled by reduction with thermal or light energies. We discovered that photo or thermally reduced GO (r-GO) films act as a good proton / electron mixed conductor at room temperature.¹⁵ The electrical conductivity increased with a decreasing oxygen content of r-GO, while the proton conductivity decreased concomitant with removal of oxygen surface groups, particularly epoxide groups. In addition, the proton conduction was strongly affected by the layer distance of r-GO films. We also reported that it was possible to increase the interlayer distance of GO films and thus enhance the proton conductivity by introducing sulfate ions into GO interlayers.¹⁶ Therefore, we prognosticated that the proton / electron mixed conduction in r-GO can be further improved by introducing sulfate ions into interlayer, as schematically modeled in Fig. 1.

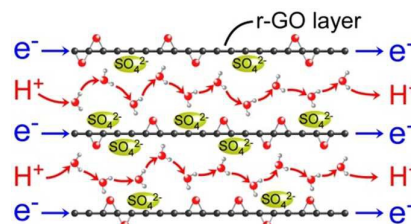


Fig. 1 Schematic model of proton / electron mixed conduction in a r-sGO film. Protons diffuse in the interlayer between each r-sGO layer with the Grotthuss mechanism where proton hopping sites are epoxide groups on GO and intercalated SO₄²⁻. Electrons transfer through GO planes with carbon sites without oxygen groups.

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On the basis of the above model, we measured proton and electron conductivities of r-GO with sulfate ions (r-sGO) films to demonstrate the validity of our methodology for improving the performance of a GO-based mixed conductor. Electrical- and ionic-conductivities were measured at 25 °C by the AC and DC measurement techniques. We studied the effects of photo and thermal reduction on oxygen contents in GO and its conductivities. The amounts of oxygen functional groups and layer distances of GO and r-sGO films were analyzed by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), respectively.

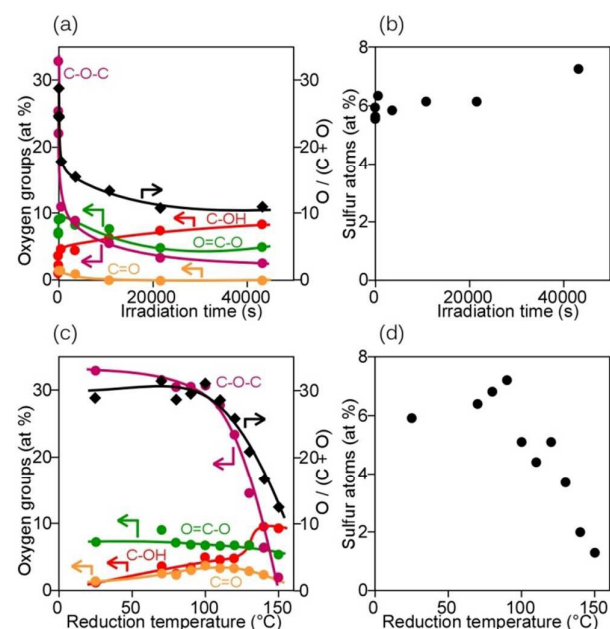


Fig. 2 (a) The percentages of oxygen functional groups and (b) sulfur atoms in sGO and r-sGO films as a function of light irradiation time. (c) The percentages of oxygen functional groups and (d) sulfur atoms in sGO and r-sGO films as a function of reduction temperature.

Fig. 2a presents the amounts of oxygen functional groups in sGO and r-sGO films treated with UV light from a Hg lamp (500 W), which were determined from the C 1s XPS spectra (Fig. S1a, ESI[†]) as a function of light irradiation time. The O atm % ($O / (C + O)$) was calculated using the calibration curve used in our previous report¹⁷ and is shown as a function of light irradiation time in Fig. 2a. The amount of epoxide groups (C-O-C) and the $O / (C + O)$ ratio both decreased with an increasing light irradiation time, while other oxygen functional groups were not significantly removed by the photoreduction. These results are in good agreement with those for usual GO films.¹⁵ Fig. 2b shows the percentages of sulfur atoms in sGO and r-sGO films as a function of light irradiation time, which were obtained by XPS measurements. The sulfur content almost remained intact even after photoreduction, indicating that sulfate ions strongly interact with the GO surface. We also examined the sulfur and oxygen contents in the films after thermal reduction. Fig. 2c shows the amounts of oxygen

functional groups and the $O / (C + O)$ ratio in the sGO and r-sGO films as a function of reduction temperature. These values were obtained from the C 1s XPS profiles of the films shown in Fig. S1b (ESI[†]). As seen in the photo reduction case, the epoxide content and the $O / (C + O)$ ratio drastically decreased with an increasing reduction temperature. The amounts of other oxygen functional groups little changed during thermal reduction. On the other hand, the sulfur content decreased after thermal reduction at higher than 100 °C, as shown in Fig. 2d. This trend is different from that for the photo reduction case. The results suggest that sulfate ions desorbed from the r-sGO interlayers together with water after thermal reduction at higher temperatures, probably due to thermally activated diffusion of water and sulfate ions.

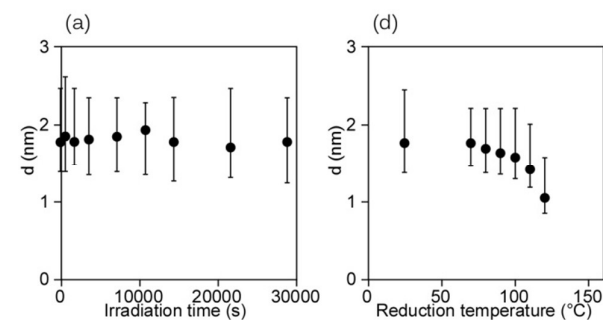


Fig. 3 The layer distances of sGO and r-sGO films as a function of (a) light irradiation time and (b) reduction temperature.

We also studied the interlayer structure by XRD analysis. Fig. 3a shows the layer distances of the sGO and r-sGO films as a function of light irradiation time. The spacing between layers was calculated from the XRD diffraction peaks around 5 degrees of the films shown in Fig. S2a (ESI[†]). The layer distance of the sGO film before reduction was ~1.6 nm, which value was larger than that of as-synthesized GO films (1.0 nm).¹⁸ The larger layer distance indicates that bulky sulfate ions were successfully introduced into the interlayer. Surprisingly, this large layer distance of sGO film was not strongly influenced by photo reduction, in contrast to the case for as-synthesized GO films whose layer distances decreased with an increasing light irradiation time.¹⁵ This anomalous feature of the sGO films should result from the presence of stable sulfate ions in the interlayers (Fig. 2b). The constant layer distances of the sGO and r-sGO films were also seen in the initial stage of thermal reduction (< 100 °C) in Fig. 3b. However, the layer distance decreased after thermal reduction at higher than 100 °C. The decrease in the layer distance can be interpreted in terms of desorption of sulfate ions, as discussed above (Fig. 2c). Notably, the diffraction peaks of the sGO and r-sGO films gradually became weak and broad after photo- and thermal- reduction for longer time and at higher temperatures, respectively. The XRD peaks finally disappeared, as shown in Fig. S2 (ESI[†]), suggesting the collapse of the layer structure probably due to significant void formation in the graphene sheets by removal of surface oxygen groups.

Electron and proton conductivities of the sGO and r-sGO films as a function of the irradiation time are shown in Fig. 4a. The electron conductivities were calculated from I - V curves (Fig. S3, ESI[†]) obtained by two-probe DC measurements. The proton conductivities were obtained by subtracting the electron conductivities from the total conductivities estimated from Nyquist plots shown in Fig. S4 (ESI[†]). The detailed method for determination of electron and proton conductivities is described in supplementary information and was also noted in our previous report.¹⁵ The sGO film showed a high proton conductivity, reaching $7.9 \times 10^{-2} \text{ S cm}^{-1}$ at 90% RH before reduction. This high conductivity was not deteriorated by reduction; a high value of $2.9 \times 10^{-2} \text{ S cm}^{-1}$ was obtained even after 14 h photo reduction. However, by decreasing the humidity to 40% RH, the proton conductivities decreased, exhibiting a typical behavior of proton conductors that work according to the Grotthuss mechanism. As revealed by the elemental analysis, sulfate ions were stably incorporated in the interlayer. Thus, the presence of sulfate ions should keep the layer distance large (Fig. 2b, 3a), resulting in a small change in the proton conductivity at high RH even after photo reduction. We previously reported that sulfate ions contributed to the proton transportation at high RH, while epoxide groups act as proton hopping sites at low RH.¹⁶ Thus, the removal of epoxide groups by the photo reduction process (Fig. 2a) caused the decrease in the proton conductivity at low RH. On the other hand, the electrical conductivities rapidly increased with an increasing light irradiation time and were not influenced by humidity. The appearance of the electron conduction is due to the formation oxygen free carbon sites, as supported by the decrease in the oxygen content of O / (C + O) shown in Fig. 2. The next shows the thermal reduction case. Fig. 4b exhibits the electron and proton conductivities of the sGO and r-sGO films as a function of reduction temperature. Proton and electron conductivity values were almost the same as those for the photo reduction case. One difference is that the proton conductivity sharply decreased and disappeared after thermal reduction at more than 100 °C. The desorption of sulfate ions from the interlayer at higher temperatures should decrease the proton conductivity, as explained above in terms of collapse of the layer structure (Fig. 2b, 3b).⁶

By optimizing reduction conditions, we achieved significantly high proton conductivities of $\sim 3 \times 10^{-2} \text{ S cm}^{-1}$ and $\sim 2 \times 10^{-2} \text{ S cm}^{-1}$ at 90% RH, for photo and thermally reduced r-sGO films, respectively. These values were ~ 2 - 3 order magnitudes higher than those for r-GO films. On the other hand, the electron conductivities were $\sim 1 \times 10^{-3} \text{ S cm}^{-1}$ and $\sim 2 \times 10^{-2} \text{ S cm}^{-1}$ for photo and thermally reduced r-sGO films, respectively. So far, a total conductivity (electron and ionic) of $\sim 10^{-5}$ - $10^{-2} \text{ S cm}^{-1}$ was reported for perovskite-type oxides such as $\text{Nd}_{5.5}\text{WO}_{11.25-8}$ and $\text{La}_6\text{WO}_{12}$ at higher temperatures than 250 °C.^{3,4} For a composite of Nafion and carbon nanotubes, the electrical and proton conductivities of $\sim 10^{-6}$ - $10^{-4} \text{ S cm}^{-1}$ and $\sim 10^{-3} \text{ S cm}^{-1}$, respectively, were reported.⁷ Thus, the obtained proton and electron conductivities are extremely high as compared with those for other mixed conductors.

We have already reported that a fuel cell using a GO solid electrolyte showed a good performance comparable to that of Nafion-based cells.¹⁹ Therefore, our sGO membrane with controlled oxygen contents would also be applied to fuel cells and achieve higher performance because of its improved proton conductivity. However, it is definitely an issue for applications that the through-plane proton conductivity of GO with the two-dimensional structure is 1-2 times smaller than the in-plane conductivity. To tackle this problem, a number of approaches has been proposed. One way is to use nano-size GO sheets to fabricate GO membranes with more proton conduction channels in vertical direction of the membrane by increasing the number of grain boundaries that provide diffusion paths at the sheet periphery. We also showed that such membranes composed of nano GO sheets exhibited an approximately 2 times larger current density than the one using micrometer size GO sheets.¹⁹ Another way is to introduce many tiny pinholes in a membrane using highly ozonated GO, which led to significantly improved proton conductivity probably because the pinholes acted as proton conduction channels.¹⁴

We believe that the promising properties of the r-sGO films, including high mixed conductivity, room temperature operability, and good flexibility, would allow for their wide uses in fuel cells, supercapacitors, and gas separation membranes.

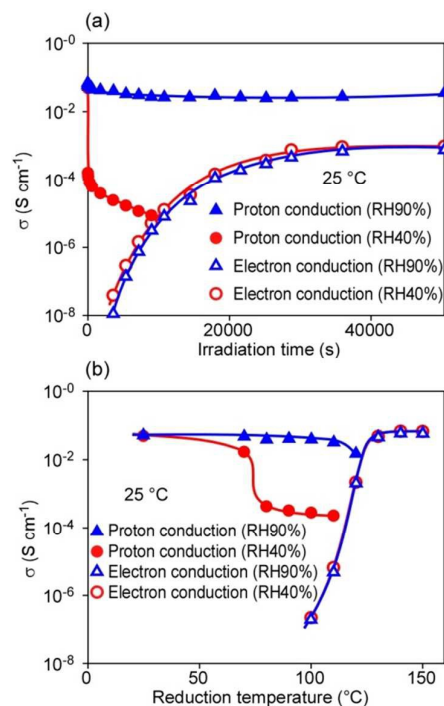


Fig. 4 Proton and electron conductivities of sGO and r-sGO films as a function of (a) light irradiation time and (b) reduction temperature at 40% and 90% RH.

Conclusions

In conclusion, we successfully developed an efficient proton / electron mixed conductor composed of a single phase material that functions at room temperature by introducing sulfate ions into GO interlayers. Because of sulfate ions intercalated, the large layer distance of GO films were kept almost constant even after the photo and thermal reduction treatments. Accordingly, the films showed high proton conductivities before and after reduction. Among mixed conductors reported, the developed GO films exhibited the best performance at room temperature, demonstrating their feasibility for various applications such as fuel cells, supercapacitors and gas separation membranes. Our methodology using sulfate ions would be applicable to interlayer modification of other layered materials to develop proton conductors.

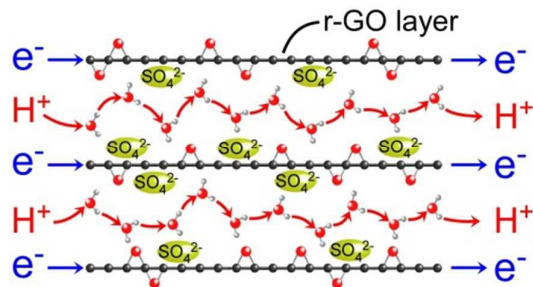
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