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The factor of ion permeation through graphene oxide membrane

Graphene oxide (GO), the oxidised form of graphene, can be synthesized by easy method at low cost. GO possesses excellent mechanical strength, flexibility and high surface area.[1] Therefore, researcher worldwide are trying to adopt GO for various applications. Recently, the peculiar permeation of gases, liquids and ions through GO films has been actively studied.[2] GO thin films with a thickness less than 20 nm show good gas separation properties for H_2 and CO_2 sieving because of the presence of defects in the nanosheets. On the other hand, due to the presence of interlayer water, GO films with a submicrometer thickness completely block gases including helium, although some liquids and ions can easily permeate through it. Consequently, many types of separation membranes using GO have been reported, and the separation performance of some GO membranes exceed that of commercial membranes. Among these separation membranes using GO, ion-sieving membranes have attracted many attentions. Ion-sieving techniques are important from industrial and environmental points of view because they can be introduced into wide fields such as water purification, artificial dialysis and membrane concentration. Therefore, it is necessary to develop the ion permeation properties of GO membranes. Changing the interlayer spacing of GO membranes is considered a feasible approach for the next step. Some studies have proved that the interlayer spacing between neighbouring GO nanosheets is significantly important in their unique ion permeation properties because ions must pass through the interlayer spacing of GO layers to reach the other side. Therefore, scientists have tried to control the ion permeation properties of GO using techniques such as intercalation chemistry and chemical modification. Only recently, tunable ion permeation was reported by Nair *et al*.,[3] however, a complex process is required for tuning ion permeation rates. Therefore, a simpler method for tuning the interlayer spacing is anticipated. Previously, we have closely studied the proton conductivity of GO membranes and found that there is a linear relationship between the proton conductivity and the interlayer spacing of the GO membrane.[4] In this case, the interlayer spacing of GO membranes was tuned by simple reduction processes, which allowed a precise comparative analysis of the interlayer spacing and proton conductivity. We also reported that the interlayer spacing of GO membranes can be expanded by introducing sulfate ions.[5] Accordingly, we expect that it is possible to easily tune the interlayer spacing of GO membranes and ion permeation rate using similar techniques. Meanwhile, the existence of oxygen functional groups in GO requires consideration because some reports suggested that the interactions between ions and oxygen functional groups and/or aromatic π-electrons in GO sheets are responsible for ion permeation. Therefore, a detailed study of the effect of oxygen functional groups is necessary to develop ion-sieving membranes using GO. With this background, herein, we measured the Cu^{2+} ion permeation rate through GO membranes with tuned interlayer spacing. Cu^{2+} ions are one of the most popular and commonly used ions in many fields, and the results obtained for Cu^{2+} are applicable to many other ionic species. The permeation tests were performed using a U-shaped glass cell separated into two blocks by a GO membrane (Figure 1a). The interlayer spacing of GO membranes was tuned by either thermal reduction or by introduction of sulfate ions. The thermal reduction was performed at temperature of 100, 120, 140 and 160 °C. Two types of GO membranes with different amounts of H_2SO_4 (sGO), sGO-0.1 and sGO-0.15, were prepared by mixing 2 mL of GO solution (0.5 g L^{-1}) with 0.1 mL and 0.15 mL of H_2SO_4 solution (0.36 mol L^{-1}),

respectively. The amounts of oxygen functional groups and interlayer spacing of GO membranes were analysed by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. The effect of oxygen functional groups on ion permeation was also investigated by correlating the ion permeation rate with the amounts of oxygen functional groups. The permeation rates as a function of reduction temperature and the amount of mixed H_2SO_4 are shown in Figure 1b and 1c, respectively. The pristine GO membrane showed a permeation rate of ~1 mol h^{-1} m^{-2}. The permeation rate decreased with increasing reduction temperature and finally became undetectable after thermal reduction at 160 °C. On the other hand, the permeation accelerated in the case of sGO membranes and its rates increased with increasing the amount of mixed H_2SO_4. The sGO-0.15 membrane showed a permeation rate of ~2 mol h^{-1} m^{-2}, which is about two times higher than that of the pristine GO membrane. Moreover, we found that there is a linear relationship between the ion permeation rate and interlayer spacing, all the way from reduced GO (rGO) to sGO membranes (Figure 1d). This result indicates that the interlayer spacing in GO membranes is very important for the permeation properties. In contrast, the other plots, for instance the plot of Cu^{2+} permeation rate vs. oxygen content, showed a disjointed behaviour. This result reveals that the oxygen functional group does not affect ion permeation rates. In view of these facts, we suggest that there is a high possibility that the interlayer spacing is the only factor that determines ion permeation through GO membranes.

References

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Figures

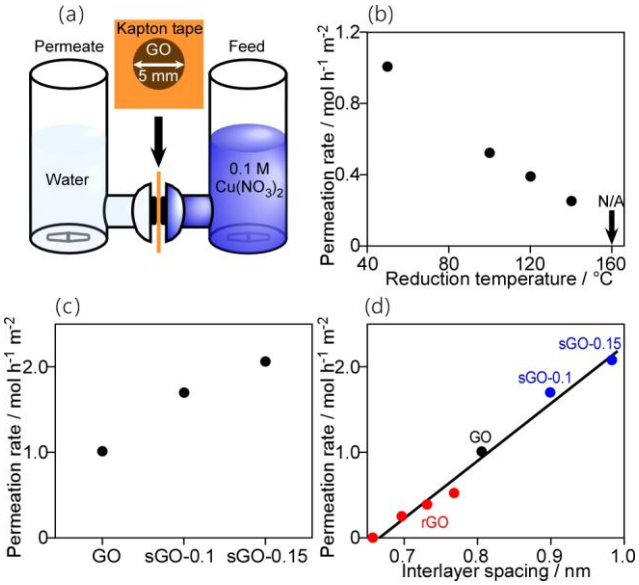

Figure 1: (a) Schematic of our permeation test cell. (b) Permeation rates as a function of reduction temperature. (c) Permeation rates of GO and sGO membranes. (d) Permeation rates as a function of the interlayer spacing of GO, rGO and sGO membranes.