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Graphene Oxide: A New Platform for High-Performance Gas- and Liquid-Separation Membranes**

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In recent times, graphene and graphene oxide have been of intense interest for a broad spectrum of applications, including field-effect transistors, paper-like materials, polymer nanocomposites, capacitors, batteries, and separation membranes for gas and water purification.[1–4] Regarding the last two applications, graphene oxide (GO) is the focus of two very recent studies by Joshi et al.[4] and Kim et al.,[3] who reported breakthrough discoveries in the small-molecule permeation properties of GO. Kim et al. reported highly permeable and selective GO membranes for separating mixtures of gases of industrial relevance, whereas Joshi et al. described the permeation of aqueous solutions of ions and neutral molecules through GO, reporting "ultrafast" transport properties.

GO has a long history, dating back to at least 1859, when Brodie reported its synthesis.[1] Despite this history, the structure of GO is still under debate. A popular structural model, shown in Figure 1, was proposed by Lerf and Klinowski.[5] As indicated in this figure, GO is largely comprised of carbon and oxygen in atomically thin, plate-like structures. GO is prepared by oxidizing graphite through one of several mechanisms.[1] The method used by Yoshi et al. and Kim et al. is the so-called Hummers method, which uses a combination of potassium permanganate and sulfuric acid to oxidize graphite. The resulting GO structures are atomically thin sheets or flakes that are stacked into a laminate structure. Membranes were prepared by sonicating GO in aqueous solutions to disperse the GO flakes, and this solution was filtered through a porous membrane with pores smaller than the lateral dimensions of the GO to deposit a layer of GO on the surface of the porous membrane. Aside from this method, Kim et al. also used a spin-casting method to prepare GO membranes. In both studies, the GO sheets were believed to be impermeable, with transport occurring through defect regions or around the boundaries of GO sheets. The lateral dimensions of the GO sheets were estimated by Joshi et al. to be on the order of 1 μm.[4] The thickness of a GO sheet was estimated as 3.4 Å,[4] so GO sheets form large, thin barrier layers (i.e., with a high aspect ratio) that, depending on how they are assembled into stacks, leave atomic-scale defects and pathways that permit molecular transport.

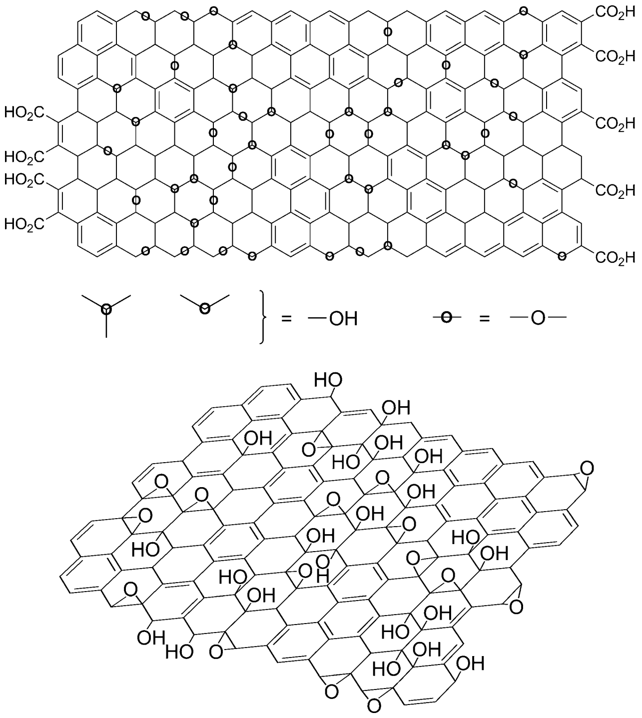

Figure 1. Variations of the Lerf–Klinowski model of GO. The top model shows carboxylic acids at the periphery of the GO sheet, whereas the bottom model does not. Reprinted with permission from Ref. [1].

Joshi et al. focused on the transport of ions (e.g., NaCl, $MgCl_2$, and $K_3[Fe(CN)_6]$) as well as water-soluble neutral molecules (e.g., glycerol and sucrose).[4] They used classic diffusion cell studies to monitor permeation of these species from a donor solution, which was rich in the solute of interest, to a receiver solution, which initially contained only deionized water. By monitoring the solute concentration in the receiver chamber, they were able to observe which species permeated through GO membranes and which did not.

Two examples of their results are shown in Figure 2. First, Joshi et al. observed a remarkably sharp cutoff in the

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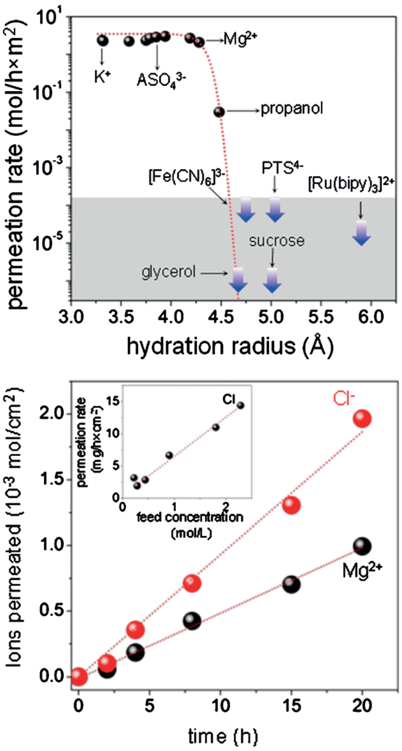

Figure 2. Permeation rates of small molecules through a 5 μm thick GO membrane separating two aqueous phases. Top: No permeation could be detected for the solutes in the grey area, despite experiments lasting at least ten days. bipy = 2,2′-bipyridine, PTS^{4-} = pyrenetetra-sulfonic acid. Reprinted and modified with permission from Ref. [4].

permeation properties as a function of the hydration size of the permeating solute. Small hydrated ions, ranging in size from K^+ to Mg^{2+}, had similar permeation properties, whereas larger species were essentially prohibited from permeating through the GO membrane. They estimated that their membrane was essentially impermeable to molecules with a hydration radius larger than approximately 4.5 Å and rationalized the sharp cutoff in size of the species that could permeate through a GO laminate using a mechanism that assumes that water present between adjacent sheets of GO plays an essential role in the observed transport properties. The effective thickness of each GO sheet was 3.4 Å, and laminates of GO soaked in water had an interlayer separation of approximately 13 Å, which could accommodate a few layers of water, yielding an effective pore size of approximately 9 Å, which would account for the observed cutoff in permeation for molecules with a hydration radius greater that is greater than about 4.5 Å.

Interestingly, the authors found no evidence for differentiation in transport rates based on solute charge, with ions such as AsO_4^{3-} permeating at approximately the same rate as Na^+ or Cl^- ions. From the data in the bottom plot of Figure 2, one may estimate a permeability coefficient for $MgCl_2$ using the conventional definition of permeability, $P = Nl/\Delta c$, where N is the steady-state flux of ions, l is the membrane thickness (5 μm in this case), and Δc is the external salt concentration difference across the membrane (0.2 M in this case). These membranes have a salt flux of approximately $5 \times 10^{-5}\,\mathrm{mol\,cm^{-2}\,h^{-1}}$, or $1.4 \times 10^{-8}\,\mathrm{mol\,cm^{-2}\,s^{-1}}$ (Figure 2, bottom). Inserting this flux value into the definition of the permeability yields a salt permeability coefficient of $3.5 \times 10^{-8}\,\mathrm{cm^2\,s^{-1}}$. For comparison, the diffusion coefficient of $MgCl_2$ in water at 20–25 °C is approximately $1 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$,[6,7] so a hypothetical membrane that is composed of pure water would have a $MgCl_2$ permeability coefficient of $1 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$. Therefore, the GO membrane transports salt at a rate that is about 300 times slower than the rate at which the salt would be transported through water. In this sense, the GO membrane salt transport result is reasonable, as one would expect the GO laminate structure to impede the transport of salt. The authors argued that the salt must be migrating rapidly through the space between the GO sheets, as the diffusion pathway through the GO laminate must be far greater than the thickness of the GO membrane. Joshi et al. also reported very high partition coefficients for salts with GO membranes, suggesting values for the salt partition coefficient, K (the ratio of the salt concentration in the GO membrane to that in the external solution), as high as ten or more. Such values are extraordinary, given that in typical polymers, which are widely used for desalination and other applications involving salt transport, K values of less than one are usually reported.[8–10] If these findings are true, the fundamental basis for such large salt partition coefficients should be the subject of intense future investigations to understand its molecular origins.

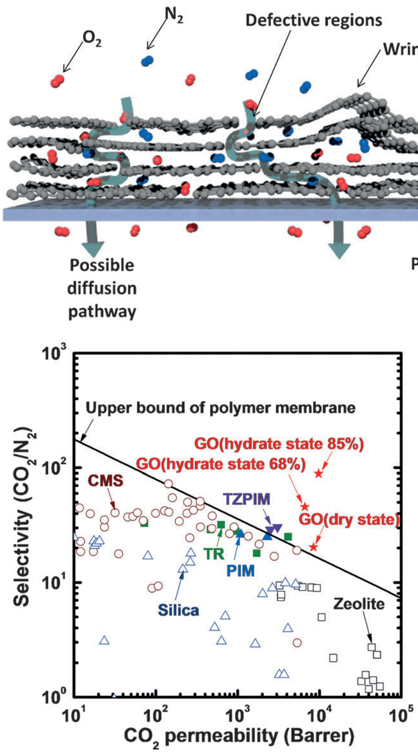

Figure 3. Permeation of gas molecules through laminates of GO membranes. Top: permeation of gases through defect regions. Bottom: performance of GO membranes relative to other high-performance polymeric (TR = thermally rearranged polymer, TZPIM = tetrazole functional polymer of intrinsic microporosity, PIM = polymer of intrinsic microporosity) and inorganic (CMS = carbon molecular sieve, zeolite, silica) membranes. Reprinted with permission from Ref. [3].

Kim et al. focused on the gas-transport properties of thin (i.e., few-layered) defective graphene and GO membranes. They reported that graphene itself displays outstanding gas-separation properties, with O_2/N_2 separation properties above the so-called upper bound, which defines the best combination of gas permeability and selectivity for polymers, the materials most commonly used today for gas separation membranes.[11] Further studies on GO showed outstanding properties in terms of CO_2 separation from N_2 (a key separation process for post-combustion carbon capture; Figure 3). Apparently, the preparation methods of either vacuum filtration or spin casting produce defect regions in the graphene or GO laminates of an appropriate size for molecular sieving, as shown in Figure 3. Consequently, the authors reported that the gas-transport properties are quite sensitive to the preparation method and the presence of, for example, water in the GO structures, as these variables change the organization of the laminate structure, thereby changing the shapes and sizes of the openings available for gas transport.

In summary, graphene oxide membranes are the subject of intense interest for a wide variety of applications. These two recent publications demonstrate the potential of GO membranes for small-molecule separation under aqueous conditions or for the purification of gaseous mixtures. Many fundamental studies remain to be carried out to fully understand the performance of this new platform of materials and ultimately determine their potential for practical separation applications.

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