Charge Selective Ion Transport through Graphene Oxide Based Membranes

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Graphene, as a new type of two-dimensional nanomaterial, has been regarded as an efficient barrier material due to its impermeability to all gases and liquids in its pristine state.¹ It has also been investigated as an ideal material for next generation membranes with high selectivity and permeability based on the size selective transport through the nanopores in its lattice.²⁻⁵ While graphene has been mostly explored as the barrier materials¹, gas separation membranes^{2, 3, 5}, and water transport membranes⁴, graphene oxide (GO) has been recently reported to show selective ion transport through the nanocapillaries formed between GO laminates due to the different coordination chemistry between various cations with oxygen functionalities on the GO surface.⁶ GO also has a great potential as ion exchange membranes due to its potential ability to discriminate charges on the individual ions. GO has considerable amount of oxygen functionalities on its surface and known to assume negative charges in its pristine state due to presence of the negatively charged carboxylic groups predominantly on the edges.⁷ In principle, therefore, electrostatic charge selection could be possible with the pristine GO membranes. Moreover, chemical modification can enhance or invert the surface charges on the GO surfaces which enable both cation and anion selective ion exchange membranes based on GO.

Herein, we report the charge selective ion transport through the graphene oxide (GO) membrane. Freestanding GO films have been fabricated by vacuum filtration methods. Aqueous GO colloids prepared by modified Hummer's method were used for the film formation processes. The resulting films with thickness of between $2\sim5$ µm showed wrinkled a surface morphology (Figure 1(b)) and a clear layered structure (Figure 1(c)).



Figure 1. (a) A photograph of a free-standing GO film, (b) a tilted SEM image of a GO film, and (c) cross-sectional SEM images of GO films.

The fabricated free-standing GO films have been tested as ion exchange membranes for charge selective ion transport. To assess the ion selectivity, membrane potentials were measured across the membrane with 0.1 M KCl(aq.) vs. 0.5 M KCl(aq.) solutions. As-made free-standing GO membranes with thickness between $2\sim5$ µm showed cation selectivity with permselectivity α =0.91

(Figure 2). This cation selectivity is comparable to those the state-of-the art ion exchange membranes. With further modification for better selectivity and possible thickness optimization for higher flux along with the known mechanical strength of graphene-based materials, GO ion exchange membranes could achieve high flux without compromising selectivity which is a great challenge in the conventional membrane technologies.



Figure 2. Permselectivity of the cation selective pristine GO film .

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