Supporting Material

High Flux Ethanol Dehydration using Nanofibrous Membranes Containing Graphene Oxide Barrier Layer

Tsung-Ming Yeh[1], Zhe Wang[3], Devinder Mahajan[1, 2], Benjamin S. Hsiao[3],

and Benjamin Chu[1, 3]

[1] *Materials Science and Engineering Department,*

Stony Brook University, Stony Brook, NY

11793-3400

[2] *Sustainable Energy Technologies Department, Brookhaven National Laboratory,*

Upton, NY, 11793

[3] *Chemistry Department, Stony Brook University, Stony Brook, NY, 11794-3400*

Pervaporation Performance Evaluation:

When characterizing the pervaporation performance, two important parameters were evaluated: the permeate flux (J) and the separation factor (SF) defined as below,

$$J = \frac{Q}{A\Delta t} \qquad (1)$$

$$SF = \frac{Y_W/Y_E}{X_W/X_E}) \qquad (2)$$

where Q is the weight of permeate collected over a time interval Δt; A is the effective membrane area; X and Y are the mass fractions in the feed and permeate, respectively; the subscripts W and E represent water and ethanol, respectively.

Membrane Preparation:

The tested GO-based TFNC membranes were prepared by using the following procedures. The GO dispersion solution (Graphene Supermarket inc.), containing flakes in the size range of 0.5~5 microns, was first treated by the Hummer method. [1] Varying concentration of GO solutions were prepared and sonicated to disperse the GO sheets/particulates before casting. The resulting GO solutions were cast on the chosen three-layered TFNC membrane using either spin-coating or vacuum filtration method to prepare the GO barrier layer of different thicknesses. A representative experimental GO/TFNC membrane was shown in Fig. 1c (the membrane diameter was 3.8 cm). This membrane possessed a water contact angle of 68 ± 3° and an ethanol contact angle of 8 ± 3°. We believe that the low ethanol contact angle value does not mean the surface of GO membrane was ethanol-philic. Instead, it was probably due to the low surface tension force of ethanol itself. For other hydrophilic dense membranes, such as typical RO and NF membranes, they tend to have a smaller alcohol contact angle than water contact angle.

With the higher GO concentration, a longer curing time was needed to produce a thicker GO layer thickness. However, in a prolonged process, some defects could occur, including the uneven aggregation of GO flakes. On the other side, the lower GO concentration could lead to voids or cracks. Hence, the operating parameters in the casting procedure, which were strongly dependent on the properties of the chosen TFNC membrane (e.g. hydrophilicity and average pore size of the cellulose layer), should be carefully optimized in order to prepare a thin and uniform barrier layer consisting of GO.

Table S1 Sample preparation schemes for various GO-based TFNC membranes, and their corresponding GO layer thickness and pervaporation results.

Sample	GO Casting Method	Aqueous GO Concentration [a] [mg/L]	GO Layer Thickness [nm]	Permeate [b] Water conc.[c] [wt %]	Permeate [b] Total Flux [kg/m^{2}hr]
GO_1	Spin coating	2500	N/A	97.8	2.4
GO_2	Spin coating	5000	N/A	97.2	1.2
GO_3	Vacuum filtration	0.5	93	98.7	2.2
GO_4	Vacuum filtration	1.0	187	98.7	1.7
GO_5	Vacuum filtration	2.0	300	98.8	1.3
GO_6	Vacuum filtration	4.0	618	99.0	0.9
TFNC Membrane		N/A	100 (Cellulose)	19.9	27.6
Sulzer 1210 (PVA based)		N/A	1.81μm (PVA)	95.9	1.1

[a] The designated concentration of GO solution used for casting of the top barrier layer

[b] Permeate data were measured by pervaporation experiment with a feed solution containing 80 wt% ethanol and water at 70 °C

[c] The concentration was quantitatively analyzed by using gas chromatograph (Hewlett-Packard GC5890) with a flame ionization detector and a Carbowax-20M column (Agilent)

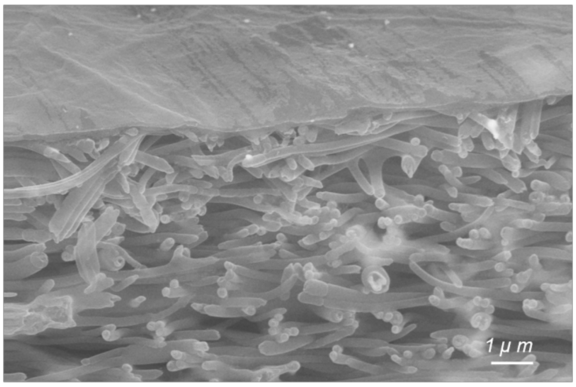

Fig. S1 SEM image of a cross-sectioned TFNC membrane with a GO barrier, which reveals the real morphology without the waviness effect as seen in Figure 2b.

Reference

[1] J. William, S. Hummers, R. E. Offeman, J. Am. Chem. Soc. **1958**, 80, 1339.