

Supporting Information for

Functionalized High Performance Polymer Membranes for Separation of Carbon Dioxide and Methane

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Experimental Section

Materials and Chemicals

Aniline hydrochloride and ammonium peroxydisulfate (APS) were obtained from Alfa Aesar (Ward Hill, MA, USA). Pyrrole, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 1,4-dioxane, t-butyl alcohol, hydrochloric acid, and 2-2'-(ethylenedioxy) bis (ethylamine) were obtained from Aldrich (St. Louis, MO, USA). Microporous polypropylene film Celgard 2400 with a thickness of 25 μm and an average pore size of 43 nm was kindly supplied by Celgard, Inc. (Charlotte, NC, USA).

Film Fabrication

Composite membranes combining polyaniline (PANI) and polypyrrole (PPy) as an active layer were prepared using an *in situ* deposition technique. The polymerization reaction was carried out with aqueous solutions of aniline hydrochloride or pyrrole (0.2 mol/L) and ammonium peroxydisulfate (0.25 mol/L). The reaction mixture was prepared by combining the monomer and oxidant solutions at 5 °C for PANI film and at 20 °C for PPy film, and poured onto the surface of the porous polypropylene film support with a pore size of 43 nm (Celgard

Inc., Charlotte, NC, USA) pre-wetted with methanol and placed in a simple device described elsewhere.^[S1] After 2h, the supports coated with PANI and PPy film were rinsed with 0.2 mol/L aqueous hydrochloric acid to remove the adhering precipitate, and then dried in air. Protonated PANI was converted into an Emeraldine base by treatment with an excess of 0.1 mol/L ammonium hydroxide.

PANI and PPy modification

The surface of both types of membranes was modified using a photografting described previously.^[S2] The PANI and PPy layers were wetted with a photografting mixture consisting of glycidyl methacrylate (25 wt%), 2-hydroxyethyl methacrylate (25 wt%), and 3:1 v/v t-butyl alcohol-water mixture (50 wt%) and placed between two quartz plates with which the surface was fluorinated to avoid sticking. The quartz plates were fixed with clamps and positioned under a deep UV lamp at 360 nm (Hg/Xe 500W short-arc lamp UXM-501MA, Ushio America) at a distance of 23 cm for 15 min. After completion of the UV exposure, the quartz plates were carefully removed and the membrane was immediately immersed in 1,4-dioxane for about 1 h to dissolve all soluble polymers, then washed with methanol, and dried. The PANI and PPy layers, photografted with poly(glycidyl methacrylate-co-2-hydroxyethyl methacrylate), were further modified at room temperature by immersing them in a 2 mol/L aqueous solution of 2-2'-(ethylenedioxy)bis(ethylamine) for 3 h, then washed with methanol, and dried.

Instrumentation

Atomic force microscopy images were obtained in semicontact mode using SmartSPM instrument (AIST-NT, Inc., Novato CA, USA). A *PHI 5400 ESCA* system (*PerkinElmer, Waltham, MA, USA*) including an *Al anode* (primary photon energy of 1486.6 eV) and a *X-ray*

source with a *power* of 150 W (15 kV at 10 mA) was used for XPS measurements. Sputtering of an area of 2×2 mm² was performed with an Ar⁺ ion gun (Beam Voltage 3000 V, Emission Current 25 mA). Membranes were dried prior these measurements at 100° C for 24 h.

An Easy Drop Goniometer (Krüss GmbH, Germany) was used to determine the contact angle for water using droplet with a volume of 2 μL. The PEG deposition was achieved using a *spincoater* P6700 (Specialty Coating System, Inc. IN, PH, USA).

Mixed-gas permeability coefficients were measured using a constant pressure/variable volume system equipped with a gas chromatograph.^[S2] Helium was used as a sweep gas and was passed over the permeate side of the membrane. After introduction of the feed, the system was allowed to reach a steady state. All mixed gas tests were performed at room temperature. The total operating gas pressure was approximately 128 kPa for the feed and less than 100 kPa for the permeate.

When steady state transmembrane flux was reached, and the feed flow rate was much greater than the gas flux through the polymer film (i.e. stage cut < 1%), the permeability coefficient of individual components in the gas mixture passing through the membrane was obtained by using equation 1:

$$P_{\text{CO}_2} = x_{\text{CO}_2}^{\text{P}} S l / x_{\text{He}}^{\text{P}} A \Delta p_{\text{CO}_2} \quad (1)$$

where P_{CO_2} is the permeability of carbon dioxide, $x_{\text{CO}_2}^{\text{P}}$ is the molar fraction of carbon dioxide in the permeate stream, S is the helium sweep gas flow rate (2 cm³/min), l is the thickness of selective layer, x_{He}^{P} is the molar fraction of helium in the permeate stream, A is the area of the membrane (2.01 cm²), and Δp_{CO_2} is the partial pressure difference of carbon dioxide across the membrane.

The separation factor α is given by equation 2:

$$\alpha_{CO_2/CH_4} = (y_{CO_2}/y_{CH_4}) / (x_{CO_2}/x_{CH_4}) \quad (2)$$

where x is the molar fraction of each gas on the feed side and y the molar fraction of each gas on the permeate side determined from gas chromatography measurements. The value in denominator $x_{CO_2}/x_{CH_4} = 0.11$ remained constant in all experiments.

References

[S1] N. V. Blinova, F. Svec, *J. Membr. Sci.* 2012, **423**, 514.

[S2] N. V. Blinova, J. Stejskal, J. M. J. Fréchet, F. Svec, *J. Polym. Sci., Polym. Chem.* 2012, **50**, 3077.