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TUNABLE COMPOSITE MEMBRANES
FOR GAS SEPARATIONS

Progress Report

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During the past quarter of project DE-FG22-94PC222 we have made significant progress in the synthesis and characterization of conducting polymer composite membranes for gas separations. Highlights from this funding period include:

- The electrochemical cell has been modified to improve the system leak rate and the residual gas analyzer has been programed to monitor the low and high pressure gas streams during a permeation experiment. The RGA data can also be recorded in table form (selecting specific AMU's) or in an analogue form (a range of AMU's from 1 to 200).
- Zeolite/polyalkylthiophene composite membranes have now been prepared and characterized for zeolite NaY with both poly(3-dodecylthiophene) and poly(3-octylthiophene) at molecular sieve loadings of 20, 30 and 40% by weight.
- We have previously reported the synthesis and fabrication of membranes based on poly-3-(1,4,7-trioctylthiophene) and now we have prepared poly-3-(3,6,9-dioxy-tetradecylthiophene) which also incorporates the solid polymer electrolyte side chain.
- Membrane fabrication in laminar flow hood.

To date, all membranes have been cast in a laminar flow hood located in the clean room of an adjacent building. To facilitate membrane fabrication, a laminar flow hood was recently installed in the Musselman laboratory in Berkner. A membrane was cast in this hood and its thickness map acquired to demonstrate that membrane quality was preserved when changing the location of membrane fabrication. The average thickness in the central 3.5 cm of the membrane cast in the laminar flow hood was $35.0 \pm 4.0 \mu\text{m}$ (11% nonuniformity). This value compares favorably with that obtained in the clean room, $33.0 \pm 4.0 \mu\text{m}$ (12% nonuniformity). See Table 1.

TABLE 1. MEMBRANE FABRICATION

	Laminar Flow Hood Musselman Lab/Berkner	Laminar Flow Hood Clean Room/Eng. Bldg.
Width (cm)	from 0.6 to 3.6 cm 3.0 cm	from 0.5 to 3.4 cm 2.9 cm
Length (cm)	from 3.0 to 6.75 cm 3.75 cm	from 2.9 to 6.75 cm 3.85 cm
Area (cm ²)	11.25	11.02
Average Thickness (μm)	35.0 ± 4.0	33.0 ± 4.0
% error	11	12

- Nanometer-scale raised features on oxidized random PDDT membranes.

We previously reported that raised features 10 to 20 nm in height appeared on the surface of poly(3-n-dodecylthiophene) (PDDT) membranes when they were subjected to oxidation for 1 hr in a 1% w/w solution of NOBF₄ in dry acetonitrile. A similar structure has been observed for vapor deposited polythiophene films subjected to alternate oxidation chemistry.¹ Possible contributions to these features include the presence of residual oxidant at the surface or physical changes to the polymer surface. X-ray photoelectron spectroscopy (XPS) revealed the presence of C, S, O and F at the surface. The fluorine chemistry is consistent with the presence of oxidizing agent, however, it is expected that the BF₄⁻ anion is distributed uniformly through the oxidized membrane to maintain charge neutrality. Angle-resolved XPS spectra were acquired at 90° (analysis depth ~10-15 nm), 45° (analysis depth ~5-6 nm) and 25° (analysis depth ~3 nm) to determine whether the atomic concentration of F varied with depth. A higher F concentration at the shallowest depth (e.g. ~3 nm) would favor the presence of residual oxidant. As illustrated by Table 2 and Figure 1, the fluorine concentration was constant with depth indicating that the raised features are the result of a morphological change to the polymer surface.

TABLE 2. ARXPS OF OXIDIZED PDDT MEMBRANE

Theta	Sine Theta	~Depth (nm)	C 1s, At%	S 2p, At%	F 1s, At%
90	1	10-15	82.740	3.660	1.620
45	0.707	5-6	83.660	3.420	1.290
25	0.423	3	83.690	3.020	1.210

FIGURE 1

- Permeability/Microstructure of Neutral/Oxidized/Reduced Membrane Series.

A. Permeability Measurements

A series of three polymer films were cast to study the permeability and microscopy of PDDT membranes in the neutral, oxidized, and reduced states. The membranes were oxidized using a 3% w/w solution of SbCl_5 in dry acetonitrile. It was anticipated that the resulting anion would be distributed uniformly through the oxidized membrane to maintain charge neutrality. The membrane was reduced using a 1% w/w solution of H_2NNH_2 in water. Each film was subjected to permeability measurements, light microscopy (LM), scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX), and TappingMode™ atomic force microscopy (TMAFM) studies. Permeability and selectivity values for N_2 , O_2 and CO_2 are presented in Table 3. Additional experiments are currently being conducted to verify these results.

TABLE 3: PERMEABILITY AND SELECTIVITY FOR NEUTRAL, OXIDIZED AND REDUCED PDDT MEMBRANES CAST AS A SERIES

	Neutral	Oxidized	Reduced
P^{N_2}	8.8 ± 0.05	9.7 ± 0.01	10.3 ± 0.1
P^{O_2}	11.0 ± 0.3	13.0 ± 0.1	12.4 ± 0.3
P^{CO_2}	95.9 ± 0.4	121.9 ± 8.0	101.2 ± 1.3
$\alpha \text{ O}_2/\text{N}_2$	1.3	1.3	1.2
$\alpha \text{ CO}_2/\text{N}_2$	11.0	12.5	9.8

B. Scanning Electron Microscope Images

Cross-sections of the neutral, oxidized and reduced membranes, imaged by SEM, are presented in Figure 2. The neutral film cross-section was primarily smooth and dense (Figure 2a). A change in morphology was observed within the cross-sections of the oxidized and reduced films. The oxidized cross-section was significantly more rough throughout the entire cross-section (Figure 2b). An image of the reduced film cross-section revealed a "sandwich" structure (Figure 2c) where the interior of the membrane cross-section revealed a smooth morphology similar to that of the neutral membrane. In contrast, both edges (~8

μm in width) exhibited a rough texture similar to that of the oxidized membrane cross section.

FIGURE 2. RANDOM PDDT CROSS SECTIONS

C. Energy Dispersive X-ray Analysis (EDX)

Energy dispersive x-ray (EDX) spectra were acquired at 4 μm intervals across the thickness of the oxidized and reduced membrane cross sections to assess the uniformity of oxidation and reduction. The EDX spectra were obtained in the spot mode in which the electron beam dwells in one location exciting a volume of approximately 1 μm^3 . The Sb/S ratio was determined using the integrated counts for the Sb L α and S K α x-ray lines of each x-ray spectrum. Although local differences were observed for the Sb/S ratio across the thickness of the oxidized membrane (Figure 3a), the presence of Sb suggests that some degree of oxidation has occurred for the entire film. For the reduced membrane (Figure 3b), the Sb/S ratio is greatly reduced in the center as would be expected, however, it remains high at the edges indicating that Sb remains at both membrane surfaces. This observation suggests that either a portion of the membrane remains oxidized or that the SbCl_x^- anion was not completely washed out of the membrane upon reduction. Interestingly, the regions of high and low Sb correspond to the rough and smooth features, respectively, observed in the SEM image of the reduced "sandwich" structure (Figure 2c). Additional spectroscopy experiments (e.g. IR) are currently being carried out to resolve this issue.

FIGURE 3A

EDX of Oxidized PDDT Cross Section

FIGURE 3B:

¹ T. R. Dillingham, D. M. Cornelison, S. W. Townsend, 42nd National Symposium of the American Vacuum Society, Minneapolis, MN, October 16-20, 1995, poster presentation.

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