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Supporting Information

Retarded O_2 transport in Co^{2+}-coordinated supramolecular polymer networks for membrane CO_2/O_2 separations

Taliehsadat Alebrahim, Narjes Esmaeili, Gengyi Zhang, and Haiqing Lin

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA

* Corresponding author: Email: haiqingl@buffalo.edu

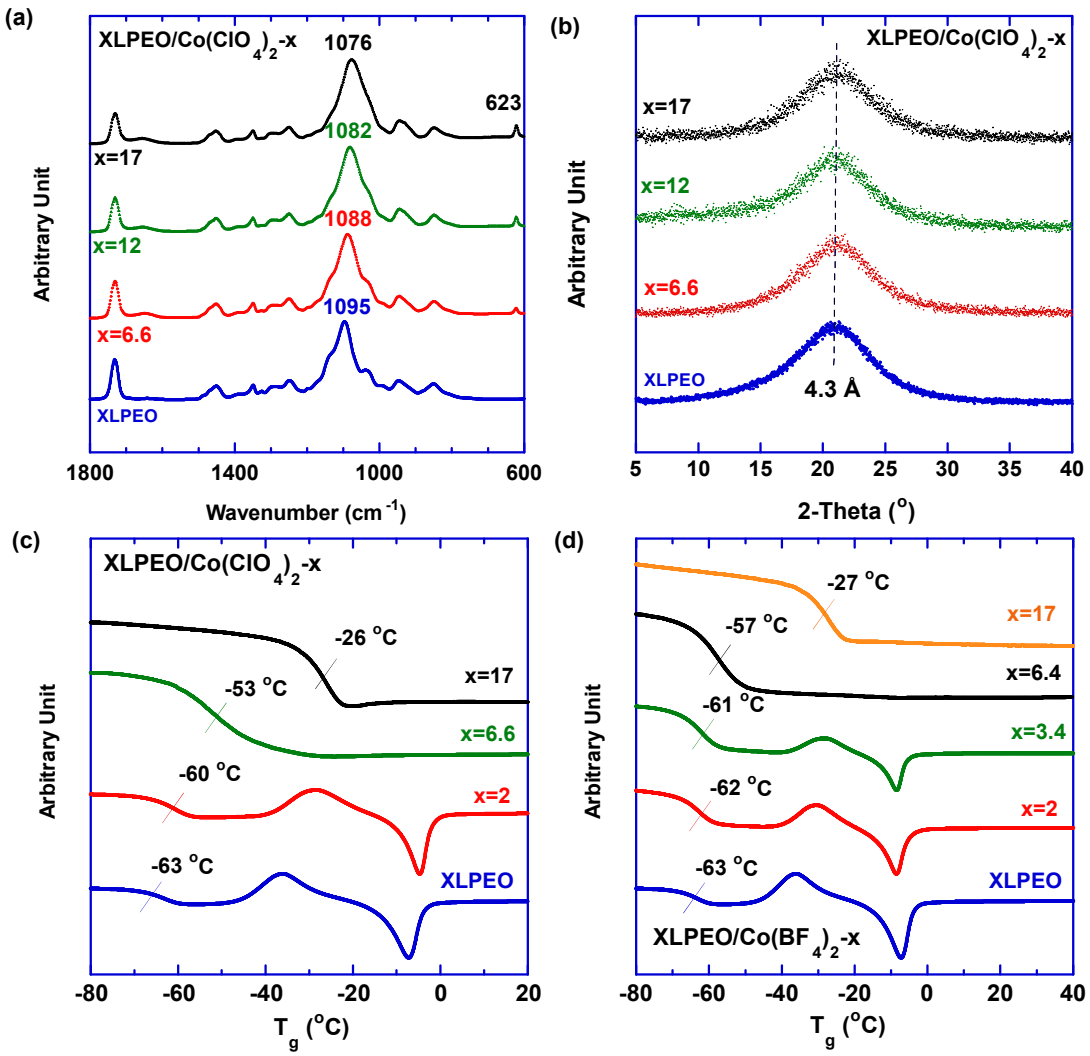

Fig. S1. (a) FTIR spectra, (b) XRD patterns, and (c) DSC thermograms of XLPEO/$Co(ClO_4)_2$ SPNs. (d) DSC thermograms of XLPEO/$Co(BF_4)_2$ SPNs.

Table S1. Physical properties, including r (molar ratio of ether oxygens to cations), ρ_{PE}, T_g, and pure-gas permeability and selectivity at 35 ℃ in XLPEO/$Co(ClO_4)_2$-x.

x (mass%)	r	ρ_{PE} (g/cm^3)	T_g (℃)	P_A (Barrer)			Selectivity		
				N_2	O_2	CO_2	CO_2/N_2	CO_2/O_2	O_2/N_2
0	0	1.149	-63	10	26	510	51	20	2.6
2	273	1.167	-60	8.1	11	140	17	13	1.4
6.6	83	1.207	-53	1.9	2.3	29	15	13	1.2
17	34	1.304	-26	0.38	0.43	18	46	37	1.1

Table S2. Comparison of a values for various polymer/salt networks.

Salts in SPNs	a (10^{-4} m^3 kmol^{-1} K^{-1})	Ref.
Co salts	8.1	This work
$LiClO_4$	2.6	[1]
$Ni(BF_4)_2$	9.3	[1]
$Cu(BF_4)_2$	3.2	[1]

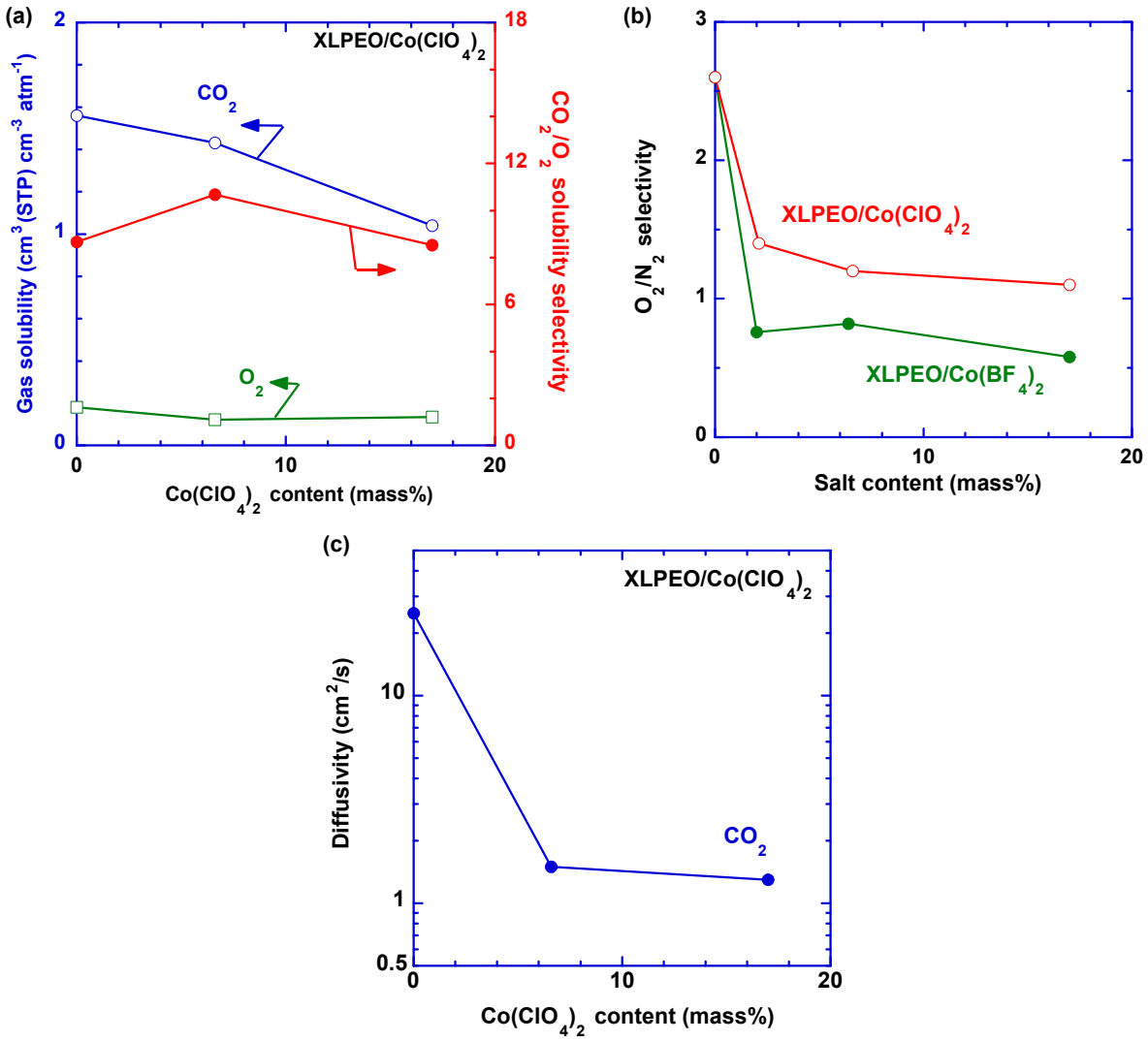

Fig. S2. (a) Effect of the $Co(ClO_4)_2$ and $Co(BF_4)_2$ content in XLPEO on O_2/N_2 selectivity at 35 °C and 50 psig. (b) CO_2 and O_2 solubility and CO_2/O_2 solubility selectivity and (c) CO_2 diffusivity as a function of $Co(ClO_4)_2$ loading. Gas solubility (S_A, cm^3 (STP) cm^{-3} atm^{-1}) at any equilibrium pressure (p_A, atm) is calculated by $S_A=C_A/p_A$, where C_A is the gas concentration in the polymer (cm^3 (STP) cm^{-3}).

Table S3. Pure-gas solubility and diffusivity in XLPEO/Co salts at 35 ℃.

SPNs	S_A		S_{CO_2}/S_{O_2}	D_A (10^{-7} cm^2/s)		D_{CO_2}/D_{O_2}
	CO_2	O_2		CO_2	O_2	
XLPEO	1.5	0.19	8.2	26	11	2.5
XLPEO/$Co(BF_4)_2$-6.4	1.3	6.7	0.20	0.83	0.0048	173
XLPEO/$Co(BF_4)_2$-17	0.93	10	0.090	0.69	0.0011	650
XLPEO/$Co(ClO_4)_2$-6.6	1.4	0.12	11	1.5	1.5	1.0
XLPEO/$Co(ClO_4)_2$-17	1.0	0.14	8.5	1.3	0.23	5.7

S_A: cm^3(STP) cm^{-3} atm^{-1}.

Table S4. Pure-gas permeability in XLPEO/$Co(BF_4)_2$-5 at 35 ℃ during a continuous test. The film had a thickness of ~300 μm, and it was kept under vacuum for ~4 months before the test. The films were tested with CO_2 at 50 psig and O_2 at 100 psig alternatively. The films were exposed to a vacuum for at least 8 h during the gas change.

	CO_2 Day 1	O_2 Day 2	CO_2		O_2 Day 8
			Day 3	Day 6	
CO_2 permeability (Barrer)	75		15	12	
O_2 permeability (Barrer)		0.74			0.25
CO_2/O_2 selectivity		100			48

Reference

1. T. Alebrahim, A. Chakraborty, L. Hu, S. Patil, S. Cheng, D. Acharya, C. M. Doherty, A. J. Hill, T. R. Cook and H. Lin, *J. Membr. Sci.*, 2022, **644**, 120063.