DESIGN OF MOLECULAR CONFIGURATION OF POLYIMIDE NANOCOMPOSITE MEMBRANE FOR CO_2/N_2 SEPARATION

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by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

6FDA	4,4′-(hexafluoroisopropylidene)diphthalic anhydride
6FpDA	4,4′-(hexafluoroisopropylidene)dianiline
APTES	(3-aminopropyl)triethoxysilane
APTMS	(3-aminopropyl)trimethoxysilane
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
BAFM	α,α-bis(4-amino-3,5-dimethylphenyl)-1-(4′-fluorophenyl)methane
BAPAF	2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane
BAPM	α,α-bis(4-amino-3,5-dimethylphenyl)-1-phenylmethane
BATFM	α,α-bis(4-amino-3,5-dimethylphenyl)-1-(3′,4′,5′-trifluorophenyl)methane
BDA	Benzidine
BDC	1,4-benzenedicarboxylate
BET	Brunauer-Emmett-Teller
BisP	4,4′-(1,4-phenylenediisopropylidene) bisaniline
BTC	Benzene-1,3,5-tricarboxylate
BTDA	Benzophenone-3,3′,4,4′-tetracarboxylic dianhydride
CFC	Chlorofluorocarbon
CNT	Carbon nanotube
COMPASS	Condensed-phase optimized molecular potentials for atomistic simulation studies
CVFF	Consistent-valence forcefield
DABA	3,5-diaminobenzoic acid
DAM	2,4,6-trimethyl-*m*-phenylenediamine
DAP	2,4-diaminophenol dihydrochloride
DLS	Dynamic light scattering

DMMDA	3,3′-dimethyl-4,4′-diaminodiphenylmethane
DPPD	3,8-diphenylpyrene-1,2,6,7-tetracarboxylic dianhydride
DPt	3,8-di(4-tert-butylphenyl)pyrene-1,2,6,7-tetracarboxylic dianhydride
EDX	Energy dispersive X-ray
EMT	Hexagonal Faujasite
FAU	Cubic Faujasite
FESEM	Field emission scanning electron microscopy
FFV	Fractional free volume
GC	Gas chromatograph
GCMC	Grand canonical Monte Carlo
GDP	Gross domestic product
GHG	Greenhouse gases
GONRs	Graphene oxide nanoribbons
GPC	Gel permeation chromatography
HBD	Hydrogen bond donation
Hmim	2-methylimidazole
IR	Infrared
MD	Molecular dynamics
MFC	Mass flow controller
m-HAB	4,4′-dihydroxybiphenyl-3,3′-diaminobiphenyl
MOF	Metal organic framework
MSD	Mean square displacement
m-TDA	2,4-toluenediamine
MWCNT	Multi-walled carbon nanotube
NMP	1-methyl-2-pyrrolidinone
NPT	Constant number of particles, pressure and temperature

NVT	Constant number of particles, volume and temperature
o-BAT	1,4-bis(2-aminophenoxy)triptycene
ODA	4,4′-oxydianiline
ODPA	4,4′-oxydiphthalic anhydride
PAA	Polyamic acid
p-BAT	1,4-bis(4-aminophenoxy)triptycene
PCFF	Polymer-consistent forcefield
PDI	Polydispersity index
p-DMPD	2,5-dimethyl-1,4-phenylenediamine
PEBA	Polyether-block-amide
PEBA 1657	Poly(amide-6-b-ethylene oxide)
PES	Polyethersulfone
PFDAB	2-(perfluorohexyl)ethyl-3,5-diaminobenzoate
p-HAB	3,3′-dihydroxy-4,4′-diaminobiphenyl
PI	Polyimide
PIM	Polymers of intrinsic microporosity
PMDA	Pyromellitic dianhydride
p-PDA	1,4-phenylenediamine
PSf	Polysulfone
SO_3H-MCM-41	Sulfonic acid functionalized ordered mesoporous silica spheres
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilica
THF	Tetrahydrofuran
UiO-66	Universitet i Oslo-66
XRD	X-ray diffraction
ZIF	Zeolitic imidazolate framework

LIST OF SYMBOLS

A	Area of membrane sample	cm^2
a	Slope of mean square displacement versus time plot	$Å^2/ps$
$\alpha_{a/b,B}$	Binary gas selectivity	dimensionless
$\alpha_{a/b,I}$	Ideal selectivity	dimensionless
C	Concentration of ZIF-8 units	mol/cm^3
C_i	Gas concentration in polymer matrix	$cm^3(STP)/cm^3$ polymer
C_o	Equilibrium concentration of ZIF-8 units	mol/cm^3
D	Gas diffusivity	cm^2/s
D_o	Pre-factor of diffusivity	cm^2/s
D_s	Diffusion coefficient of solid particle	m^2/s
dp/dt	Permeation rate	cmHg/s
ΔE	Binding energy of membrane system	kcal/mol
ΔG_v	Gibbs free energy per unit volume	J/m^3
Δp	Differential pressure	cmHg
E_a	Electron affinity	dimensionless
$E_{complex}$	Total energy of a membrane system comprising of different components	kcal/mol
E_d	Diffusion activation energy	kcal/mol
$E_{individual}$	Energy of individual component present in a particular membrane system	kcal/mol
k	Boltzmann constant	J/K
l	Membrane thickness	cm
l_c	Initial membrane casting thickness	µm
M	Mass of membrane or polyimide chain	g
M_w	Molecular weight	g/mol

N	Number of diffusing molecules	dimensionless
η	Viscosity	Pa·s
Ω	Atomic volume	m^3
P_a	Pure gas permeability of gas *a*	Barrer
P_b	Pure gas permeability of gas *b*	Barrer
P_{bf}	Pure gas permeability obtained from bubble flow permeation method	Barrer
P_{br}	Pure gas permeability obtained from barometric permeation method	Barrer
P/P_o	Relative pressure	dimensionless
$\mathcal{P}$	Gas permeance	GPU
$\mathcal{P}_a$	Permeance of gas *a*	$cm^3(STP)/(cm^2 \cdot s \cdot cmHg)$
p	Operating pressure	bar
p_d	Downstream pressure	Pa
p_i	Sorbent pressure	cmHg
ρ	Membrane density	g/cm^3
R	Universal gas constant	$cm^3 \cdot cmHg/mol \cdot K$
r	Radius of diffusing particle	m
r^*	Minimum size to form a stable ZIF-8 nucleus	m
$r(0)$	Initial position vector of gas molecule	Å
$r(t)$	Final position vector of gas molecule over time interval *t*.	Å
S_i	Solubility of gas *i*	$cm^3(STP)/(cm^3 \cdot cmHg)$
σ	Supersaturation	dimensionless
T	Temperature	°C or K
T_g	Glass transition temperature	°C
t	Simulation run time	ps
μ	Dipole moment	D

μ_x	Dipole moment in *x* direction	D
μ_y	Dipole moment in *y* direction	D
μ_z	Dipole moment in *z* direction	D
V	Downstream reservoir volume	cm^3
V_{ds}	Volume of dope solution	mL
V_e	Specific volume of sample	cm^3/g
V_o	Volume occupied by polymer chains	cm^3/g
V_T	Total membrane volume	μm^3
V_w	Van der Waals volume	cm^3/g
$\dot{V}$	Permeate flow rate	cm^3/s
x_a	Mole fraction of gas *a* in feed stream	dimensionless
x_b	Mole fraction of gas *b* in feed stream	dimensionless
y_a	Mole fraction of gas *a* in permeate stream	dimensionless
y_b	Mole fraction of gas *b* in permeate stream	dimensionless
γ	Surface energy of ZIF-8 formed	J/m^2

REKA BENTUK KONFIGURASI MOLEKUL MEMBRAN NANOKOMPOSIT POLIIMIDA UNTUK PEMISAHAN CO_2/N_2

ABSTRAK

Aplikasi luas membran poliimida (PI) untuk pemisahan CO_2 perindustrian telah dihadkan oleh keseimbangan intrinsik antara kebolehtelapan dan kememilihan. Sehubungan itu, kajian ini menerokai reka bentuk molekul polimer PI dan pembangunan membran nanokomposit PI/partikel kerangka imidazolat zeolitik-8 (ZIF-8) untuk meningkatkan prestasi pemisahan gas. Secara prinsipnya, berat molekul asid poliamik (PAA) dan PI yang sepadan sangat bergantung pada kereaktifan monomer yang dikawal oleh halangan sterik gantian monomer tetapi bukan sifat electroniknya. Ia juga didapati bahawa perilaku reologi dan berat molekul PAA boleh bertindak sebagai garis panduan untuk menyaring protokol sintesis membran yang sesuai untuk struktur PI tertentu. Khususnya, PAA dengan kelikatan yang tinggi (> 81 cP) dan berat molekul yang tinggi (≥ 5.39 Mg/mol) adalah prasyarat untuk membentuk membran PI tanpa kecacatan melalui penuangan larutan PI yang diimidai secara kimia. Ia juga mendapati bahawa kesan kesekerjaan antara konfigurasi atom dan kekutuban monomer harus dipertimbangkan dalam menganalisa pecahan isipadu bebas (FFV) membran PI. Suatu monomer dengan struktur tak sesatah dan kekutuban yang rendah adalah lebih baik untuk mencapai membran PI dengan FFV yang tinggi. Membran 4,4′-(heksafluoroisoproilidena)diftalik anhidrida (6FDA)-2,4,6-trimetil-*m*-fenilen diamina (DAM):asid 3,5-diaminobenzoik (DABA) (3:2) yang menpunyai FFV tinggi pada 0.212 telah menunjukkan prestasi pemisahan yang terbaik antara struktur PI yang dikaji. Ia mempunyai kebolehtelapan CO_2 sebanyak 63 Barrer (0.60 GPU) dan kememilihan CO_2/N_2 setinggi 57 dalam ujian penelapan pada 3 bar. Simulasi dinamika molekul (MD) juga dijalankan untuk meramalkan kelakuan pengangkutan gas membran PI. Sesungguhnya, kebolehharapan model PI yang dibina menggunakan *Materials Studio* telah disahkan kerana kebolehtelapan CO_2 dan N_2 yang diramalkan hanya berbeza daripada keputusan ujikaji dengan faktor 1.86 dan 1.76 masing-masing. Kemudian, ZIF-8 telah diletakkan di atas membran PI yang disokong oleh alumina melalui penyalutan celup untuk menghasilkan membran nanokomposit PI/ZIF-8. Keberkesanan (3-aminopropil)trietoksisilan (APTES) untuk meningkatkan keserasian antara alumina-PI-ZIF-8 telah diramal dengan menggunakan simulasi molekul berdasarkan pengiraan tenaga pengikat. Hasil simulasi juga disahkan selanjutnya dengan ujikaji. Dalam pemisahan gas perduaan, telapan CO_2 dan kememilihan CO_2/N_2 yang optimum adalah 93.47 GPU dan 7.50 dengan penyalutan celup ZIF-8 sebanyak 5 kali. Secara keseluruhan, kajian ini memberikan gambaran asasi tentang peranan reka bentuk molekul dan membran nanokomposit PI/ZIF-8 dalam penyesuaian prestasi pemisahan gas membran. Kajian pada masa hadapan boleh ditumpukan kepada pengubahsuaian permukaan ZIF-8 untuk mengurangkan kecenderungan penggumpalan ZIF-8 dan seterusnya menambahbaik prestasi pemisahan gas membran nanokomposit PI/ZIF-8.