Electrochemical Composite Membranes based on Intrinsically Conducting Polymers

Synthesis and Characterization

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Abstract

Membranes based on intrinsically conducting polymers (ICPs) have been employed in various membrane processes such as gas separation, pervaporation, nanofiltration and electrodialysis. The change in the membrane morphology, hydrophilicity, and ion exchange behaviour based on the oxidation state and doping levels of ICP have been used to enhance permeability and selectivity. In this thesis, a highly permeable membrane with high selectivity was developed by depositing polyaniline (PANI) on the pore walls of a microporous base membrane without blocking the pores. The layering of positively charged polyaniline originates electrolyte polarisation in the pores and permselectivity is achieved by the electrostatic screening of permeating ions through the membrane.

Polyaniline (PANI) was deposited on mixed-cellulose ester (ME) microporous membranes by using various in situ chemical oxidative polymerization techniques. These include solution-phase polymerization, vapour-phase polymerization and diaphragmatic polymerization in a two-compartment cell. The composite membranes were characterized by scanning electron microscopy (SEM), gravimetric PANI content measurement, Fourier-transform infrared (FTIR-ATR) spectroscopy and x-ray photoelectron spectroscopy (XPS). The solution-phase and vapour-phase polymerizations yielded PANI layering on the surface of the base membrane whereas PANI was deposited on the pore walls of the membrane by using the two-compartment cell technique. FTIR and XPS results showed PANI deposition in its emeraldine salt state and Cl^- doping was polymerization time dependent. XPS quantified the extent of PANI layering at the surface that was polymerization time dependent. The solution-phase polymerization yielded an incomplete surface layering as compared to the vapour-phase polymerization. Surface and trans-membrane electrical conductivities were measured by using four-point micro probe and two- point probe techniques, respectively. These conductivities showed dependence on PANI deposition site and extent in the membranes.

Electrochemical characterization of the composite membranes was conducted by using electrochemical impedance spectroscopy (EIS) and transport numbers measurements. EIS data were analysed by using equivalent circuit modelling technique. The results showed the dependence of charge transport resistance of the membranes on PANI deposition site, extent and doping levels. In-pore PANI deposition in the membranes showed several orders of magnitude lower levels of resistance and higher capacitance due to the polarisation of pore electrolyte. In addition, the low values of diffusional resistance and high capacitance indicate

anion-coupled charge transport in the membrane through PANI polaron/bipolaron transitions. The composite membranes with PANI layering only at the surface or undoped PANI showed higher diffusional resistance and low capacitance due to slow electronic/ionic diffusion inside the bulk membrane.

Transport numbers of counter-ions in the composite membranes showed high anion selectivity at low pH (in HCl) as compared to the membranes at high pH (~12). The transport numbers showed the weak dependence on PANI deposition site and levels.

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$\hat{V}$, $\hat{I}$	phasor representation of voltage and current, respectively.
A^-	doping anion
a	activity coefficient
A	area
A^o	angstrom
ac	alternating current
APS	ammonium persulphate
asym.	asymmetric
At.	Atomic
BE	binding energy
c	concentration
C	capacitance
CA	cellulose acetate
C_d	double layer capacitance
cm	centimetre
CPE	constant phase element
CPS	counts per second
CSA	camphursulphonic acid
D	diffusion coefficient
d	distance
DBSA	dodecylbenzesulphonic acid
dc	direct current
DMF	dimethylformamide
DMFC	direct methanol fuel cell
e^-	electron

EDS	electron-dispersive-spectroscopy
EIS	electrochemical impedance spectroscopy
EMI	electromagnetic interference
E^o	standard electrode potential
eV	electron volts
f	linear frequency
F	Faraday
FTIT-ATR	fourier -transform infrared-attenuated total reflectance
g	gram
g_{ct}	frequency-dependent charge transfer resistance
h	hour
HIPS	high-impact polystyrene
I	current
i	current
ICP	intrinsically conducting polymer
Im	imaginary
I_o	current amplitude
j	$\sqrt{-1}$
k	conductivity
m-	meta
m	meter
m	milli (10^{-3})
M	mole
ME	mixed-ester membrane
MF	microfiltration
min	minutes
min	minutes
MWCO	molecular weight cut off
NC	nitrocellulose

NF	nanofiltration
NHE	neutral hydrogen electrode
nm	nanometer
NMP	N-methylpyrrolidone
o-	ortho
OSN	organic solvent nanofiltration
p-	para
P	permeability
P(%)	percentage permselectivity
PAAc	polyacrylic acid
PAc	polyaceytelene
PANI	polyaniline
PCB	printed circuit board
PE	polyethylene
PEEK	polyether-ether ketone
PEMFC	polymer-electrolyte-membrane-fuel cell
Ph	phenyl
PPY	polypyrrole
PTFE	polytetraflouroethene
pTSA	p-toluenesulphonic acid
PV	pervaporation
PVA	polyvinyl acetate
PVDF	polyvinyldiflouride
PVTMS	polyvinyl trimethylsilane
q	charge
R	resistance
R_{ct}	charge transfer resistance
Re	real
Redox	reduction-oxidation

r.m.s	root-mean-squared
RO	reverse osmosis
s	seconds
S	siemen
S	solubility
SDS	sodium dodecylsulphate
SEM	scanning electron microscopy
SPEEK	sulphonated polyether-ether ketone
SPEEKK	sulphonated polyether-ether ketone ketone
sym.	symmetric
t	thickness
T	transmittance
t_{coun}, t_{co},	transport number of counter- and co-ion, respectively.
TCPB	three-component polymer blend
THF	tetra-hydrofurane
UF	ultrafiltration
V	volts
V_o	voltage amplitude (volts)
vs.	versus
W	Warburg impedance
wt	weight
X_c	reactance
XPS	x-ray photoelectron spectroscopy
Z	impedance
Z', Z''	real and imaginary component of impedance, respectively.
α	dispersion index
λ	wave length
Ω	resistance
ρ	resistivity

υ	wave number
ϕ	phase angle
φ	potential
ω	angular frequency
χ^2	“chi-square value” for EIS model fitting