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Electrochemical Composite Membranes based on Intrinsically Conducting Polymers

Synthesis and Characterization

Asif Ali Qaiser

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.
Acknowledgements

I would like to express my special gratitude to Associate Professor Margaret Hyland, my main supervisor, for her guidance, support and encouragement during my PhD studies at the University. In fact, she always has been accommodative to me in spite of her busy schedules and facilitated my work and living here in every aspect. I am also thankful to Dr. Darrell Patterson, my co-supervisor for his time-to-time discussions and evaluation of my work. His appreciation always remained a source of encouragement to me. I am also thankful to Associate Professor Allen Easteal and Neil Edmonds for providing me the electrochemical testing facilities at the Tamaki campus. The discussions with Allen Easteal also contributed towards my better understanding of the conducting polymers.

I want to thank Michael Wadsworth (Chemistry) and his team for the fabrication of the two-compartment permeation cells. Many thanks go to Catherine Hobbis for her help in SEM, Dr. Colin Doyle for XPS analysis and Michel Nieuwoudt (Chemistry) for FTIR spectroscopy. I would like to specially acknowledge the help of Stephen Cawley (CACM) in the electrochemical characterizations of the membranes.

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List of Abbreviations and Symbols

\( \hat{V}, \hat{I} \) phasor representation of voltage and current, respectively.
A\(^-\) doping anion
a activity coefficient
A area
A\(^\circ\) 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
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>EDS</td>
<td>electron-dispersive-spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EMI</td>
<td>electromagnetic interference</td>
</tr>
<tr>
<td>$E^0$</td>
<td>standard electrode potential</td>
</tr>
<tr>
<td>eV</td>
<td>electron volts</td>
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<tr>
<td>f</td>
<td>linear frequency</td>
</tr>
<tr>
<td>F</td>
<td>Faraday</td>
</tr>
<tr>
<td>FTIT-ATR</td>
<td>fourier-transform infrared-attenuated total reflectance</td>
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<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>$g_{ct}$</td>
<td>frequency-dependent charge transfer resistance</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
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<tr>
<td>HIPS</td>
<td>high-impact polystyrene</td>
</tr>
<tr>
<td>I</td>
<td>current</td>
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<tr>
<td>i</td>
<td>current</td>
</tr>
<tr>
<td>ICP</td>
<td>intrinsically conducting polymer</td>
</tr>
<tr>
<td>Im</td>
<td>imaginary</td>
</tr>
<tr>
<td>$I_0$</td>
<td>current amplitude</td>
</tr>
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<td>j</td>
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<tr>
<td>k</td>
<td>conductivity</td>
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<tr>
<td>m-</td>
<td>meta</td>
</tr>
<tr>
<td>m</td>
<td>meter</td>
</tr>
<tr>
<td>m</td>
<td>milli ($10^{-3}$)</td>
</tr>
<tr>
<td>M</td>
<td>mole</td>
</tr>
<tr>
<td>ME</td>
<td>mixed-ester membrane</td>
</tr>
<tr>
<td>MF</td>
<td>microfiltration</td>
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<tr>
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</tr>
<tr>
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<td>minutes</td>
</tr>
<tr>
<td>MWCO</td>
<td>molecular weight cut off</td>
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<td>NC</td>
<td>nitrocellulose</td>
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<tr>
<td>NF</td>
<td>nanofiltration</td>
</tr>
<tr>
<td>NHE</td>
<td>neutral hydrogen electrode</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methylpyrrolidone</td>
</tr>
<tr>
<td>o-</td>
<td>ortho</td>
</tr>
<tr>
<td>OSN</td>
<td>organic solvent nanofiltration</td>
</tr>
<tr>
<td>p-</td>
<td>para</td>
</tr>
<tr>
<td>P</td>
<td>permeability</td>
</tr>
<tr>
<td>P(%)</td>
<td>percentage permselectivity</td>
</tr>
<tr>
<td>PAAC</td>
<td>polyacrylic acid</td>
</tr>
<tr>
<td>PAc</td>
<td>polyacetelene</td>
</tr>
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<td>PANI</td>
<td>polyaniline</td>
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<tr>
<td>PCB</td>
<td>printed circuit board</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>PEEK</td>
<td>polyether-ether ketone</td>
</tr>
<tr>
<td>PEMFC</td>
<td>polymer-electrolyte-membrane-fuel cell</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>PPY</td>
<td>polypyrrole</td>
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<tr>
<td>PTFE</td>
<td>polytetraflouroethene</td>
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<tr>
<td>pTSA</td>
<td>p-toluenesulphonic acid</td>
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<tr>
<td>PV</td>
<td>pervaporation</td>
</tr>
<tr>
<td>PVA</td>
<td>polyvinyl acetate</td>
</tr>
<tr>
<td>PVDF</td>
<td>polyvinylidifluoride</td>
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<tr>
<td>PVTMS</td>
<td>polyvinyl trimethylsilane</td>
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<td>q</td>
<td>charge</td>
</tr>
<tr>
<td>R</td>
<td>resistance</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>charge transfer resistance</td>
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<td>real</td>
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<tr>
<td>Redox</td>
<td>reduction-oxidation</td>
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List of Abbreviations and Symbols

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_{co, t_{co}}  transport number of counter- and co-ion, respectively.
TCPB  three-component polymer blend
THF  tetra-hydrofurane
UF  ultrafiltration
V  volts
V_0  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
List of Abbreviations and Symbols

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<thead>
<tr>
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<tbody>
<tr>
<td>υ</td>
<td>wave number</td>
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<tr>
<td>φ</td>
<td>phase angle</td>
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<td>φ</td>
<td>potential</td>
</tr>
<tr>
<td>ω</td>
<td>angular frequency</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>“chi-square value” for EIS model fitting</td>
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