촉진수송 및 태양전지용 분리막

강 용 수 박사
(KIST)

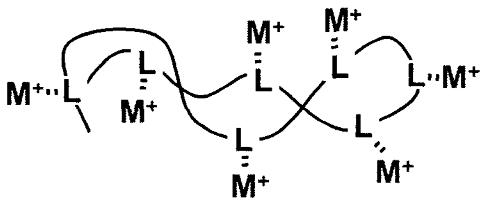
Polymer Electrolytes and their Applications to Solar Cells and Separation Membranes

강 용 수

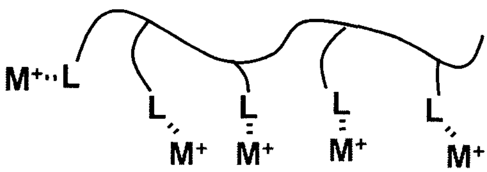
한국과학기술연구원 (KIST)
촉진수송분리막연구단

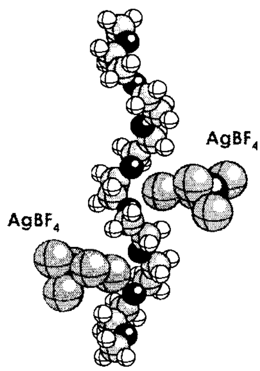
http://cftm.kist.re.kr

Metal Complexes in Macromolecules



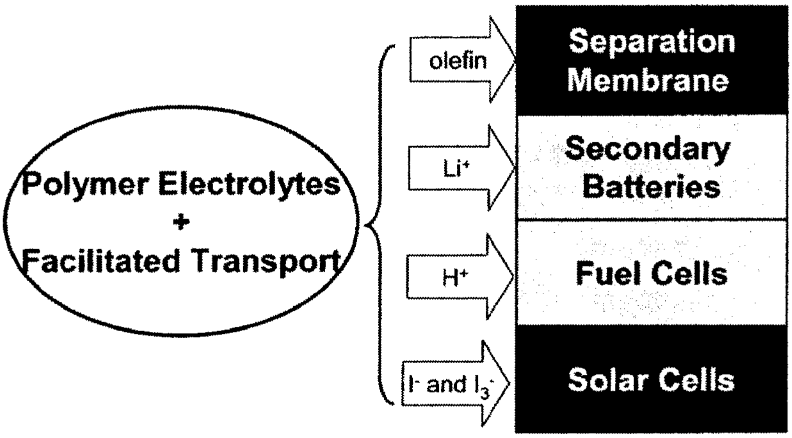
polymer electrolytes





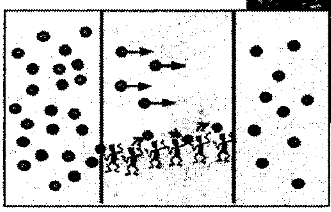
$AgBF_4$ in poly(ethylene oxide)

Applications of Polymer Electrolyte Membranes



Facilitated Transport in Solid State

Facilitated transport
=
bulk Fickian diffusion
(minor)
+
carrier-mediated transport
(dominant)



carrier for facilitated transport

Application to Dye-Sensitized Solar Cells

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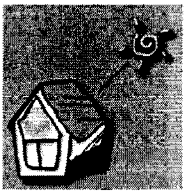
Solar Cells

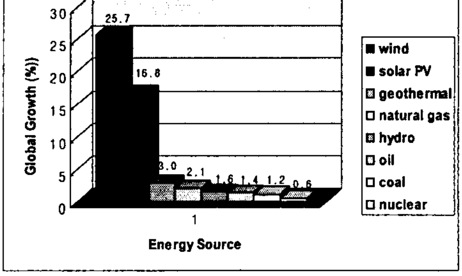
Annual market growth rate:

1992-1999: 20~30 %
1999~2000: 37 %

(IEEE power & energy magazine, Jan/Feb 2003, p.30)



Annual market growth rate: 1990-1998
(Source: REPP, Worldwatch 1998/99)



Next Generation Energy Source

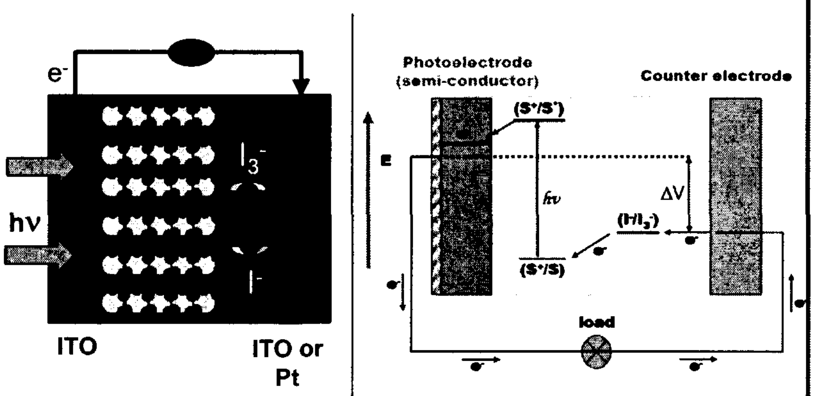
Why Dye-Sensitized Solar Cell?

Costs of Electricity Generation	
Resource	Generation Cost (¢/k Wh)
Coal	3.11 - 3.41
Gas turbine	2.53 - 3.41
Nuclear	3.31 - 5.74
Good Wind Site	5.84
Optimal Wind Site	3.89
Silicone Solar Cell	25 - 30
Organic Solar Cell	3 - 5 (?)

(Sources: International Atomic Energy Agency, ExternE, and Wind Power Monthly, The Wall Street Journal, 27 Aug. 2002.)

Cost for producing DSSCs is 1/5 of that for conventional silicone cells.
Science, **300**, 1219 (23 May 2003)

Configuration of Dye-Sensitized Solar Cells

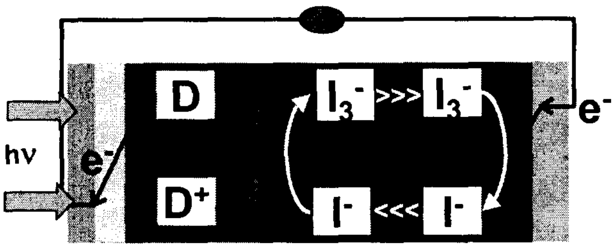


: semiconductor (TiO_2)

: dye (Ru dye)

: electrolyte ($M^+ + I^- + I_3^-$ in CH_3CN)

Transport in Dye-Sensitized Solar Cells



$D \xrightarrow{h\nu} D^+ + e^-$ $\quad 3I^- \rightarrow I_3^- + 2e^-$

$D^+ + e^- \rightarrow D$ $\quad I_3^- + 2e^- \rightarrow 3I^-$

I^- and I_3^- transport

Roles of Electrolytes in Solar Cells

Electrolytes:

- I^- and I_3^- conductor
- electron barrier or hole conductor
- electrochemical redox reaction media
- interfacial contactor for dye, TiO_2 and electrode
- mechanical separator

Issues in Electrolytes for Solar Cells

Liquid electrolyte: $M^+ + I^- + I_3^-$ in liquid solvent (CH_3CN)
(M^+: Li^+, Na^+, K^+, R_4N^+ or imidazolium ion)

- difficulty in preparation and maintenance
- solvent leakage
- poor mechanical strength

⇩ polymer solvent

Polymer electrolyte: $M^+ + I^- + I_3^-$ in polymer solvent

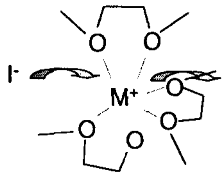
- low ionic conductivity
- poor contact

Improvement in ionic conductivity and interfacial contact

three different approaches

Facilitated transport to increase ionic conductivity

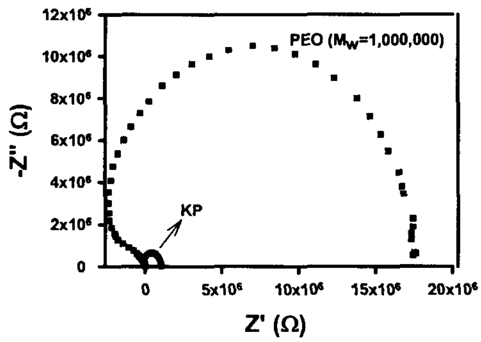
Facilitated transport of I^- and I_3^- ions



Electrostatic interaction of M^+ and I^- becomes weak because of coordination of oxygens to M^+, and becomes perhaps reversible.

Metal ion coordinated by neighboring oxygens can act as a carrier for iodide ions.

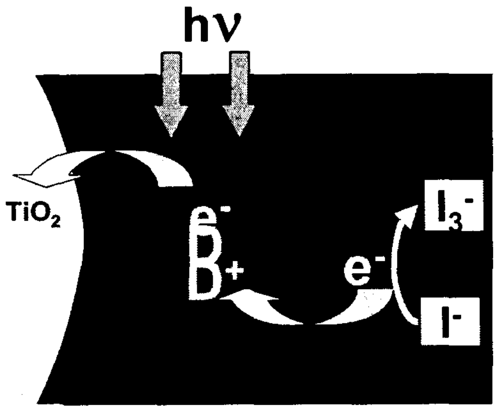
Increase in the ionic conductivity



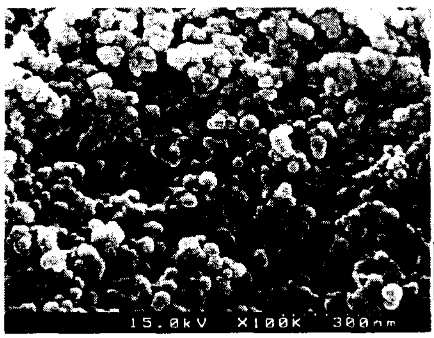
Ionic conductivity increase:
PEO : 1.66 x 10^{-6} (S cm^{-1})
KP : 24.77 x 10^{-6} (S cm^{-1})

Importance of Contacts in Solar Cells

Contacts of electrolyte with semiconductor and dye



SEM of TiO_2 coated with high Mw PEO

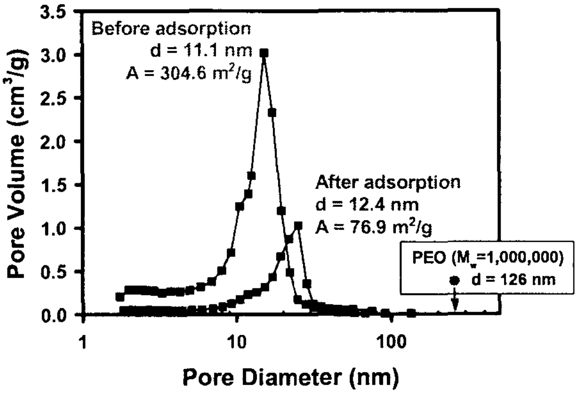


PEO (Mw=1,000K)

Poor contact

Low conversion efficiency
(η = 0.07 %)

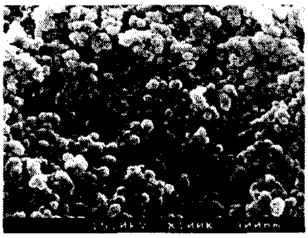
Pore size distribution in TiO_2 layer (BET/N_2)



R_g= c(Mw)$^{0.5}$ where c=0.063 (nm) for PEO in MeOH.
C. Vandermmiers, P. Damman and M. Dosiere, *Polymer*, **39**, 5627 (1998)

Contact of electrolytes with TiO_2 particles

Poor contact



PEO (η = 0.07 %)

Better contact

KP (η= 8.10 % at 10 mW/cm^2)

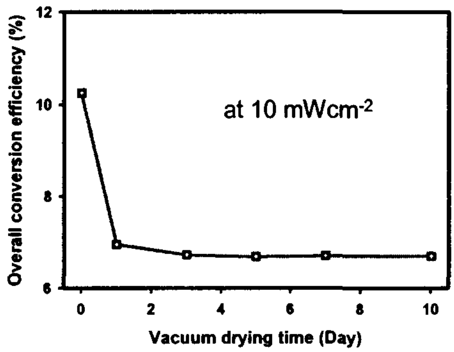
Properties for dye-sensitized solar cells

measured at10 mW/cm²

Electrolyte	$\sigma \times 10^6$ (S cm^{-1})	V_{OC} (V)	J_{SC} (mA cm^{-2})	*ff* (−)	η (%)
PEO/NaI/I_2	1.66	0.60	0.04	0.25	0.07
KP/NaI/I_2	24.77	0.67	1.36	0.73	8.10

Improvement in both ionic conductivity and interfacial contact induces the increase in the overall energy conversion efficiency mostly because of the increase in the current density

Long-term stability

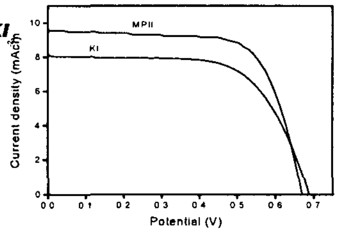


Variation in the overall energy conversion efficiencies of DSSCs employing KP with KI/ I_2 with the vacuum drying time

Solar Cell Performance-2

nanocomposite electrolyte

- *Ionic conductivity is ~ 10^{-3} S/cm at RT*
- *MPII shows higher ionic conductivity than KI*



	P (mW/cm²)	V_{oc} (V)	J_{sc} (mA/cm²)	FF	Efficiency (%)
MPII	100	0.67	9.58	0.70	4.5
	10	0.59	2.19	0.74	8.1
KI	100	0.69	8.10	0.64	3.6
	10	0.61	1.80	0.71	6.7

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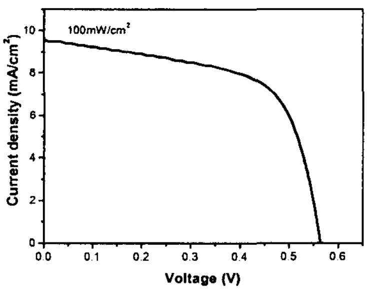
Solar Cell Performance-3

DSSC employing supramolecular electrolytes



- σ = 2.5 x 10^{-5} S/cm
- V_{oc} = 0.57 V
- J_{sc} = 9.53 mA/cm²
- η = 3.34 %
- FF = 62.0 %

Active area = 0.126 cm²
Light intensity = 100 mW/cm²

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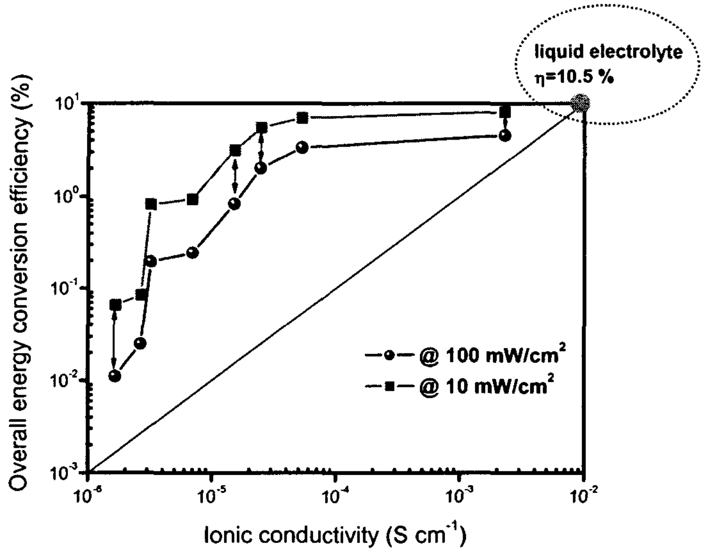
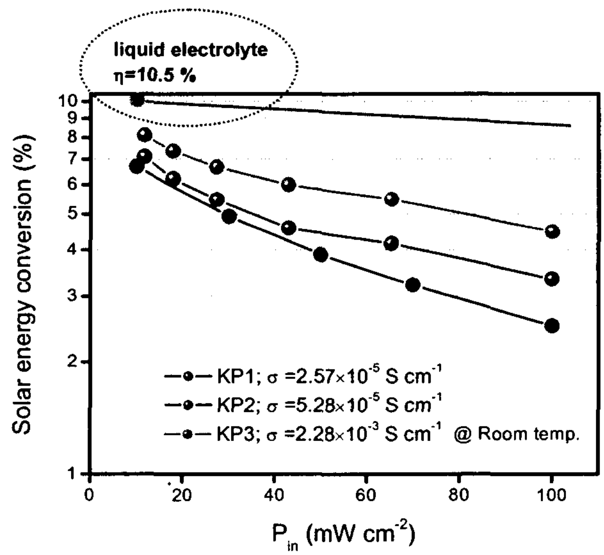
Solar Cell Performance vs Ionic Conductivity



Solar Cell Performance vs Solar Intensity



Conclusions

Novel solid polymer electrolytes provide high ionic conductivity as well as good interfacial contact between electrolyte and dye-adsorbed nanocrystalline TiO_2 layer.

The cell performance are
8.1 % at 10 mW/cm^2 (ex. 2.6%) and
4.5 % at 100 mW/cm^2 (ex. 1.6%).

Membrane Separation for Olefin/Paraffin Mixtures

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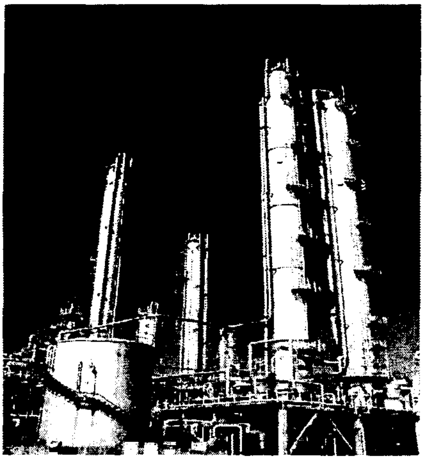
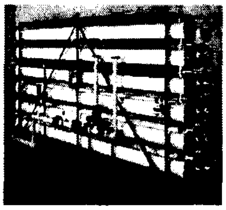
Issues on separation of olefin/paraffin mixtures

- ethylene and propylene :
  1st and 3rd in production
- cryogenic distillation:
  high operation cost
  # of theoretical plates > 100
- large initial capital investment
  50 m high x 2



< Distillation towers >



< Membrane skid >

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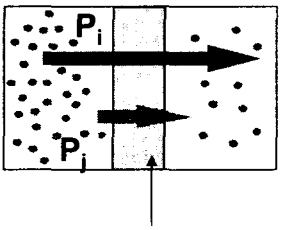
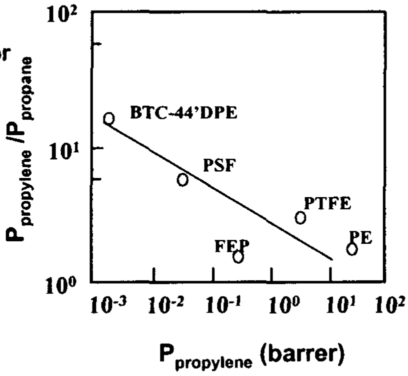
Propylene/Propane Separation Performance of Polymeric Membranes

$P_i = D_i S_i$: permeability

$\alpha_{ij} = P_i/P_j$: ideal separation factor (selectivity)





Trade-off behavior!!!

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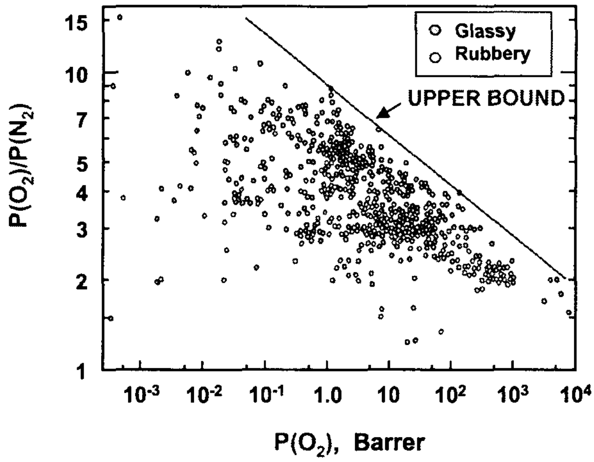
Oxygen/Nitrogen Separation Performance of Polymeric Membranes

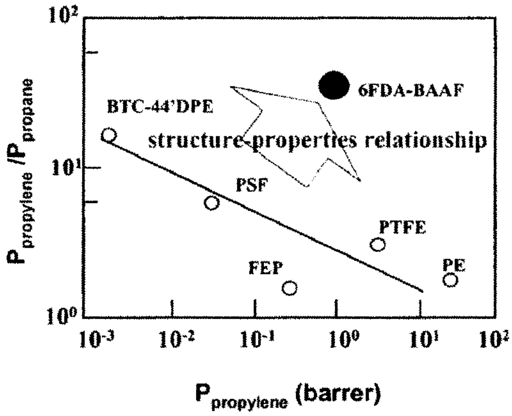


L. M. Robeson, J. Memb. Sci., 62, 65-185 (1991)

How to Overcome the Trade-Off Behavior

- **structure-properties relationship**
- **molecular sieve membranes**
- **facilitated transport in solid state**

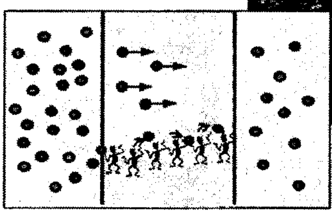
Structure-Property Relationship



A. Shimazu, T. Miyazaki, M. Maeda, O. Tozawa and K. Ikeda, SEN'I GAKKAISHI (纖維와 工業), vol. 56, p 85 (2000)

Facilitated Transport in Solid State

Facilitated transport
=
bulk Fickian diffusion
(minor)
+
carrier-mediated transport
(dominant)



carrier for facilitated transport

Carrier Properties for Facilitated Transport

A carrier (B) is a compound which *reversibly* and *specifically* reacts with a solute (A)

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB \qquad K = k_1/k_2$$

Concentration fluctuation model for facilitated transport:

$$\bar{P}_f \propto k_2 C_B \ln(1 + Kp_0)$$

where P_f, C_B and Kp_o are permeability, carrier concentration and driving force, respectively.

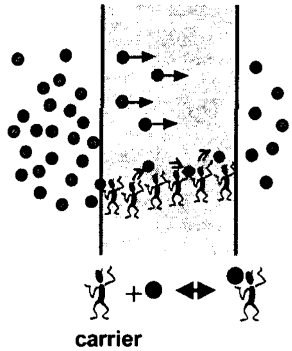
Facilitated Transport

What happens if K is large but k_2 is small?

No facilitated transport!!!!

The backward reaction rate constant k_2 **is more important than the equilibrium constant K in determining facilitated transport.**

Facilitated Transport in Solid State



⇨ Fickian transport

\+

⇨ Carrier-mediated transport

||

Facilitated transport

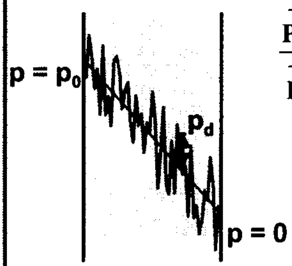
silver polymer electrolyte

Carrier Properties

A carrier (B) is a compound which *reversibly* and *specifically* reacts with a solute (A)

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB \qquad K = k_1/k_2$$

Concentration Fluctuation Model



$$\frac{\bar{P}_f}{\bar{P}} = 1 + \left(\frac{p_d}{p_0}\right)\left(n^2 + \left[\frac{2\pi k_2 L^2 C_B}{\bar{P}}\frac{\ln(1+Kp_0)}{p_0}\right]^2\right)^{1/2}$$

where $n = N_A C_B(\pi r_s^2 L)$

$\bar{P}_f$ & $\bar{P}$:	permeabilities in facilitated transport membranes & pure matrix
p_d & p_0:	pressure fluctuation & applied pressure
k_2 & K:	backward reaction rate & equilibrium constants
C_B & L:	carrier concentration & membrane thickness

$$\bar{P}_f \propto k_2 C_B \ln(1+Kp_o)$$

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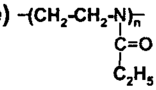
Olefin Carriers

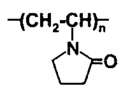
Liquid-free Solid Polymer Electrolyte System

$AgBF_4$ **poly(2-ethyl 2-oxazoline)**



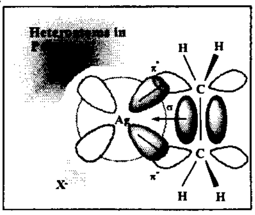
POZ

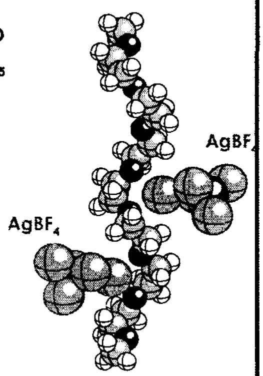
$AgCF_3SO_3$ **poly(*N*-vinyl pyrrolidone)**



PVP

carrier *polymer solvent*

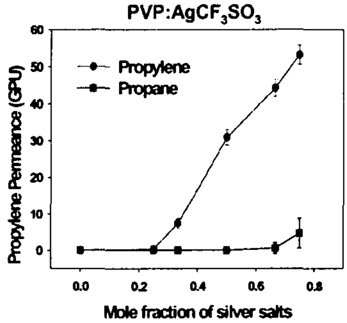


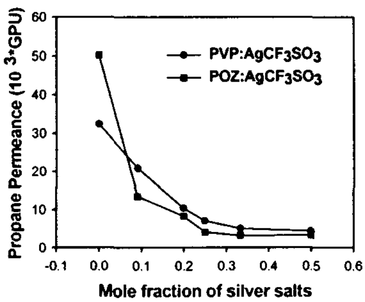


Separation Performance: Concentration

Facilitated transport of olefin through polymer electrolyte membranes

PVP:$AgCF_3SO_3$





$P_{propylene}$: 0.05 ⇨ 55, $P_{propane}$: 0.05 ⇨ 0.003 with increasing silver salts

$P_{propylene}$ / $P_{propane}$ is higher than 10,000

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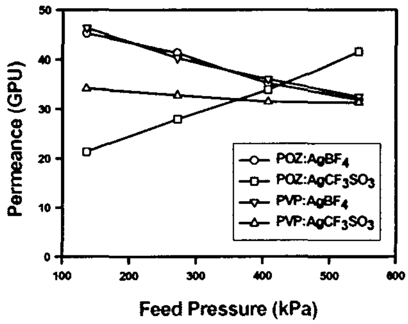
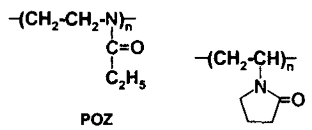
Separation Performance: Pressure

Olefin carrier : silver polymer electrolytes



silver salt : $AgBF_4$, $AgCF_3SO_3$
polymer solvent : POZ, PVP



POZ
poly(2-ethyl 2-oxazoline)

PVP
poly(*N*-vinyl pyrrolidone)

propylene permeance: 0.05 ➡ 45
propane permeance: 0.05 ➡ 0.003

high permeance as well as **high selectivity** at high pressures

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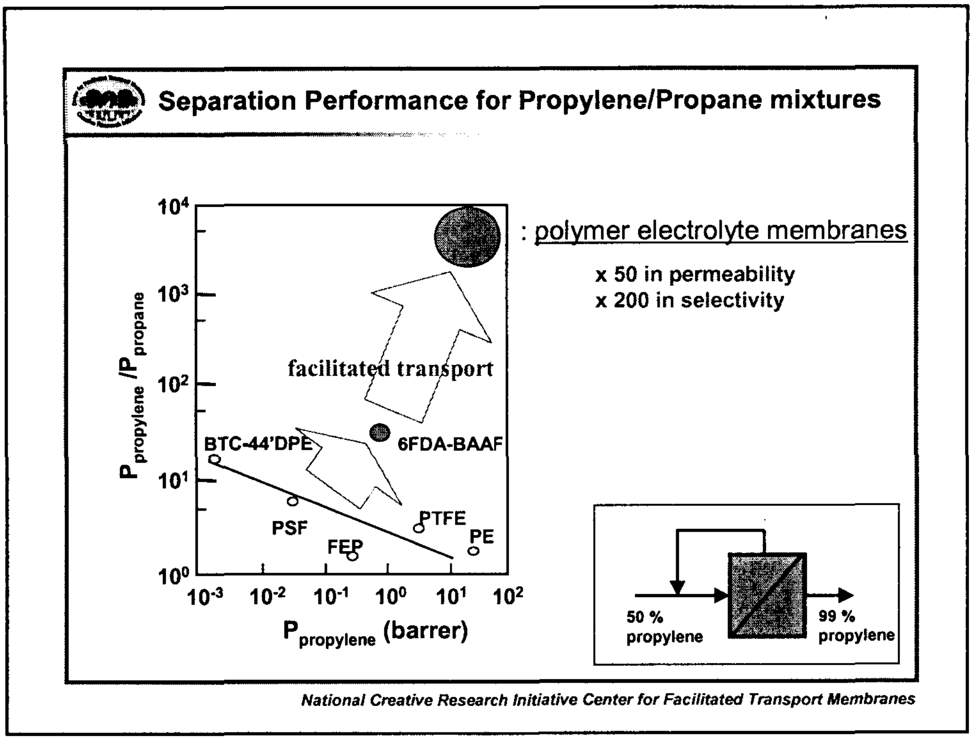
Separation Performance for Propylene/Propane mixtures
: polymer electrolyte membranes
x 50 in permeability
x 200 in selectivity
facilitated transport
BTC-44'DPE
6FDA-BAAF
PSF
FEP
PTFE
PE
P propylene /P propane
P propylene (barrer)
50 % propylene
99 % propylene
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