Cross-linked PEO-based Polymer Electrolytes: Ionic Conductivity and Electrochemical Properties

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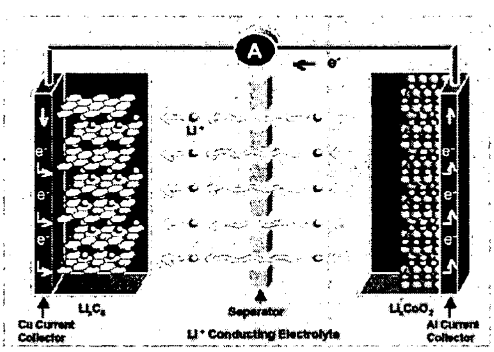
- ✓ **Lithium Batteries**
- ✓ **Polymer Electrolytes**
- ✓ **Recent Researches**
- ✓ **Synthesis and Electrochemical Properties of PEO-based Polymer Electrolytes**
- ✓ **Summary**

Comparison of Rechargeable Batteries

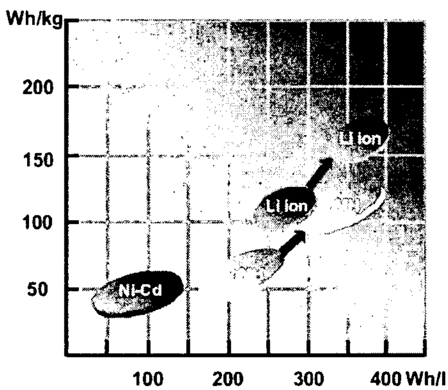
	Lead-Acid	Ni-Cd	Ni-MH	Li-ion	Li-Polymer
Positive Electrode	PbO_2	NiOOH	NiOOH	$LiCoO_2$	$LiCoO_2$ or $LiMn_2O_4$
Negative Electrode	Pb	Cd	MH	C(Li)	C(Li) or Li metal
Electrolyte	aqueous H_2SO_4	aqueous KOH	aqueous KOH	$LiPF_6$ in EC+DMC	Polymer Electrolyte
Avg. Voltage (Volts)	2.0	1.2	1.2	3.6	3.8
Capacity (Ah/kg)	15	48	58	34	27
Energy Density (Wh/kg)	30	58	70	100	100
Cycle Life	200	1000+	500	1000	1000
Operating Temp. Range	-20~50°C	-20~50°C	-20~40°C	-20~50°C	-20~50°C
Toxicity	Yes	Yes	Yes	No	No
Memory Effect	No	Yes	Y/N	No	No

Lithium Ion Battery



$$C + LiCoO_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_xC_6 + Li_{(1-x)}CoO_2$$

Anode Cathode Anode Cathode



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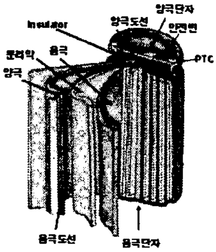
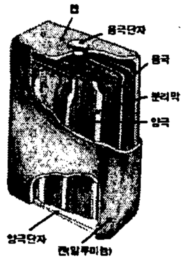
Lithium Polymer Battery

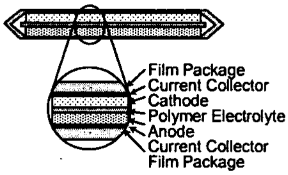
Lithium-ion Battery

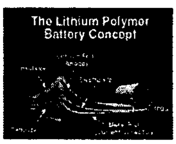


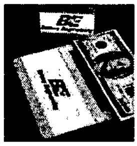


Cylindrical LIB cell Prismatic LIB cell

Lithium-Polymer Battery







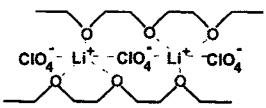
Advantages of the Lithium Polymer Battery

- Leak Free and Safe
- Simple Design
- High Energy Density
- Design Flexibility

Polymer Electrolytes for Lithium Battery

1. Intrinsic Polymer (Dry) Electrolytes

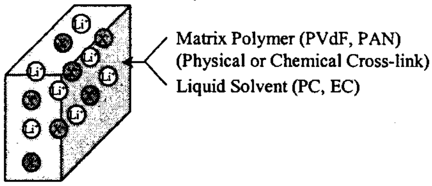
A salt is dissolved in a solvating polymer matrix
Conduction Mechanism : Local Segmental Motion of Polymer Chain



Poly(ethylene oxide)/$LiClO_4$

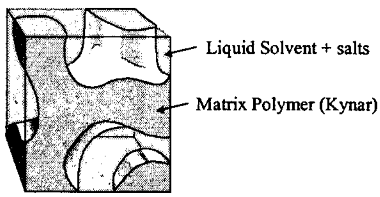
2. Hybrid (Gel) Polymer Electrolytes

Polymer Matrix is swollen with liquid solvent and salts
Conduction Mechanism : Mobility of the ionic species in the liquid phase



3. Porous Polymer Electrolytes

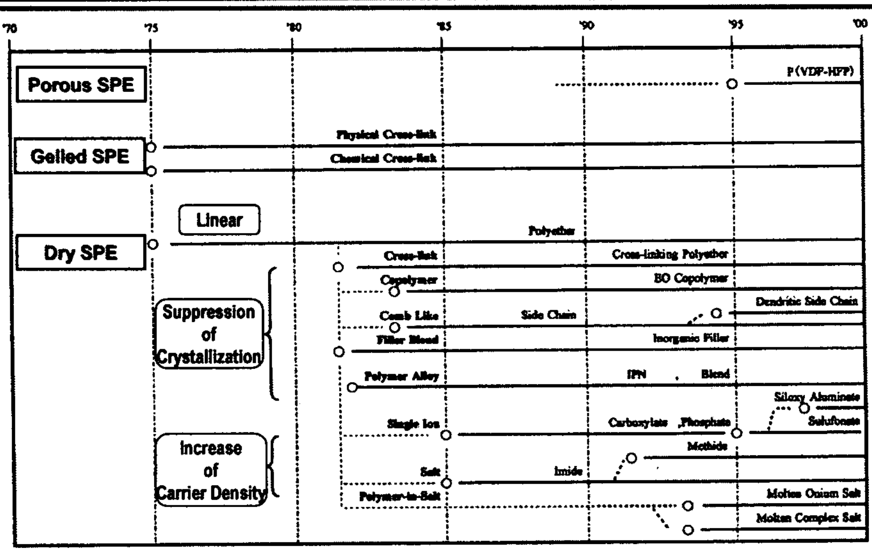
Liquid solvent is encapsulated in the porous polymer matrix
Conduction Mechanism : Mobility of the ionic species in the liquid phase



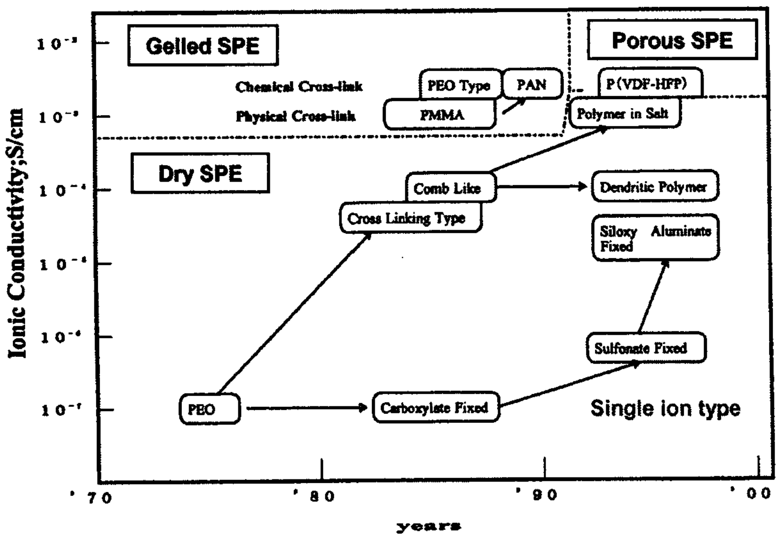
Requirements of Solid Polymer Electrolyte

- ✓ **High ionic conductivity at operating temperature**
  : $10^{-3} \sim 10^{-4}$ S/cm
- ✓ **Chemical and Electrochemical Stability**
  : Electrochemical window > 4.5V vs. Li
- ✓ **Compatibility with electrodes**
- ✓ **Mechanical properties**
- ✓ **Processability**

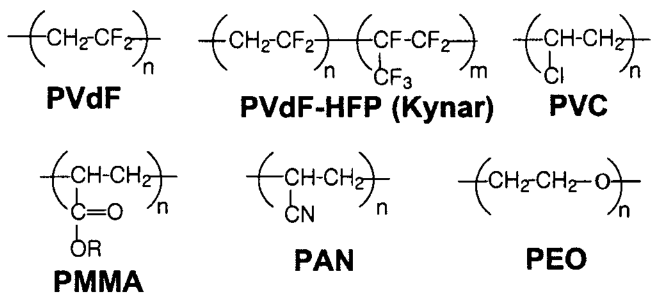
History of Solid Polymer Electrolyte Development



History of Ionic Conductivity Improvement



Gelled Solid Polymer Electrolytes



Advantages

- ✓ Polymer matrix Acting as Mechanical Supporter and separator
- ✓ High Conductivity at Room Temperature
- ✓ Well Known Chemistry and Electrochemistry

Disadvantages

- ✓ Containing Volatile Solvents
- ✓ Difficulties in Processing
- ✓ Limited Chemical and Electrochemical Stability
- ✓ Poor Mechanical Properties

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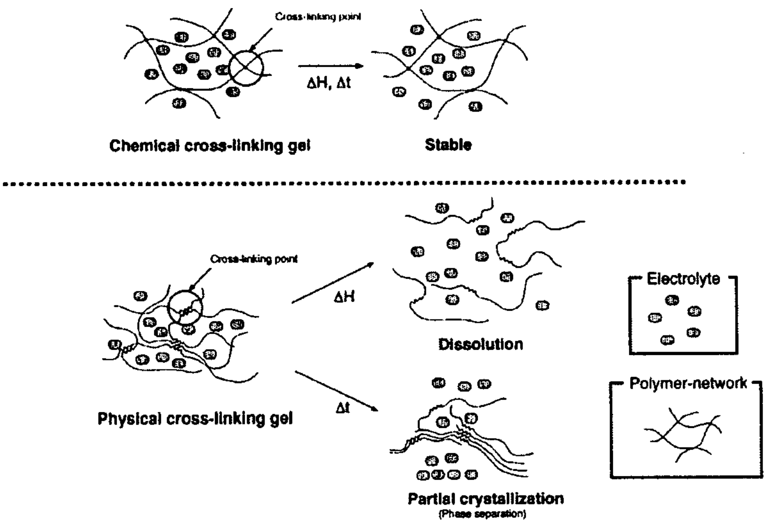
Gelled Solid Polymer Electrolyte Models



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Gelled Solid Polymer Electrolytes

Ionic conductivities of some gel polymer electrolytes and polymer composite electrolytes. Dimensionally stable gels consisting of PEG–PAN–PC–EC–$LiClO_4$ were prepared by Munichandraiah et al. [197]. Compared with gels PEO–PC–$LiClO_4$ and PAN–PC–EC–$LiClO_4$, the PEG containing gels showed lower room temperature conductivities, but higher mechanical stabilities

Polymer system	Polymer host	Polymer electrolyte	Conductivity (S cm^{-1}), 20°C
Plasticized			
Linear PEO	poly(ethylene oxide)	$(PEO)_8$-$LiClO_4$ (EC:PC, 20 mol%)	10^{-3}
Crosslinked PEO	poly(ethylene oxide)	$(PEO)_8$-$LiClO_4$ (PC, 50 wt.%)	8×10^{-4}
PVdF	poly(vinylidene fluoride)	PVdF-$LiN(CF_3SO_2)_2$ (EC:PC, 75 wt.%)	1.5×10^{-3}
PEGA	poly(ethylene glycol acrylate)	PEGA-($LiClO_4$:PO, 1 M)	10^{-3}
PEI	poly(ethylene imine)	PEI-$LiClO_4$	10^{-3}
PPTA	poly(*p*-phenylene terephthalamide)	PPTA-(PC:EC: $LiBF_4$, 25:25:0.8 mol%)	2.2×10^{-3}
Acrylates	ethylene glycol dimethacrylate (EGDMA)	EGDMA-($LiClO_4$:PC, 1M)	2×10^{-3}
PAN	poly(acrylonitrile)	PAN-(EC:PC:$LiClO_4$), 38-33:21:8 mol%	10^{-3}
Composites			
Glass polymer composites		$(0.564Li_2S - 0.19B_2S_3 - 0.25LiI)$-($(PEO)_6$-$LiN(CF_3SO_2)_2$) (18:13 vol.%)	10^{-4}
Gel polymer composites		PAN-(PC:EC:$LiAsF_6$)-zeolite	10^{-2}
Nanocomposites (ceramic composites)		$(PEO)_8$-$LiBF_4$-alumina (10%wt)	10^{-4}
Nanocomposites (ceramic composites)		PEG_{200}-$LiCF_3SO_3$-silica, 20%wt.	1.5×10^{-3}

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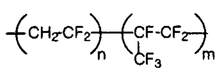
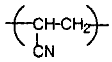
Porous Polymer Electrolytes

Preparation



PVdF-HFP (Kynar)



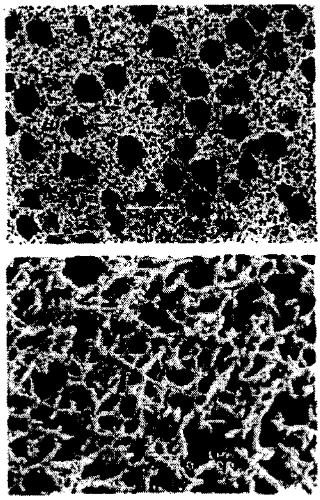
PAN

1) Film Preparation
   - Solvent Casting

2) Pore Generation
   - Extraction (Bell-Core Process)
   - Phase Inversion

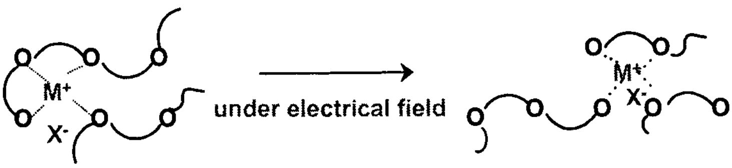
3) Electrolyte Preparation
   - Immersion

Structure



Intrinsic (PEO-based) Solid Polymer Electrolytes

A salt is dissolved in a solvating polymer matrix
Conduction Mechanism : Local segmental motion of polymer chain



First suggestion by M. B. Armand (Saint-Martin d'Heres, France)

Advantages

- ✓ Solvent Free Polymer Electrolyte
- ✓ High Chemical and Electrochemical Stability
- ✓ Minimizing Lithium Dendrite
- ✓ Good Mechanical Properties

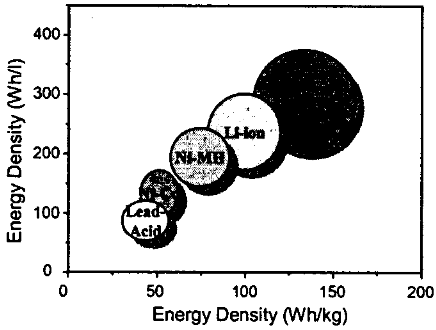
Disadvantages

- ✓ Relatively Low Conductivity
- ✓ Polymer Electrolyte Electrode Interface
- ✓ Need to Synthesize Amorphous Polymer

Why Lithium Metal Electrode?

High Energy Density

Anode Materials	Capacity (weight, mAh/g)	Capacity (Volume, mAh/ℓ)
C_6(Coke)	186	372
C_6(Graphite)	372	515
Li Metal (25%)	965	837
Li Metal (100%)	3861	2062

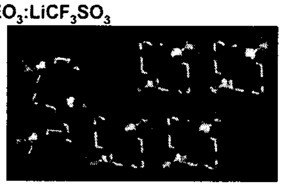


Structure of Poly(ethylene oxide)

T_m = 65 °C T_g = -60 °C ε ~ 5-8

Crystalline PEO

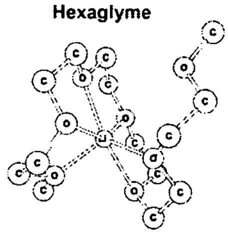
$PEO_3:LiCF_3SO_3$

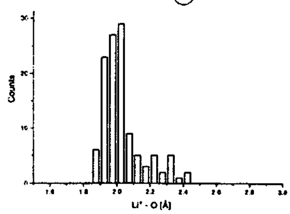


$PEO_6:LiAsF_5$

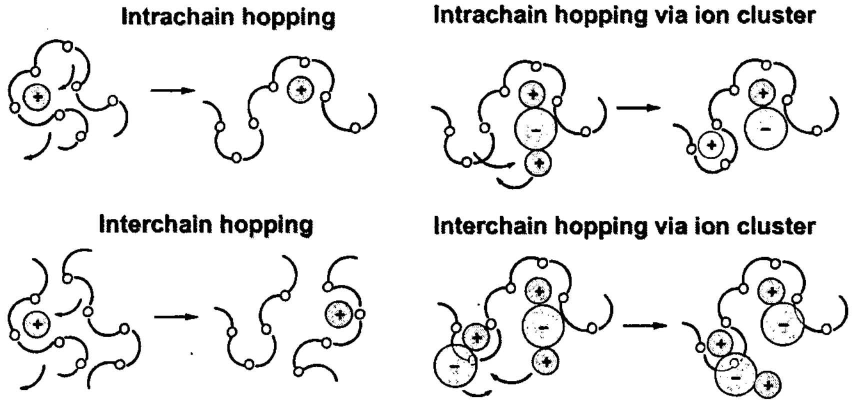
Amorphous PEO

Hexaglyme





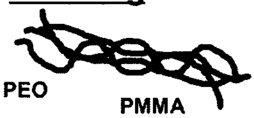
Ion Transport Mechanism



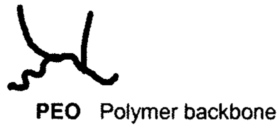
Suppression of Poly(ethylene oxide) Crystallization

- High Mw PEO : High Crystallinity at Room Temp
- Low Mw : PEO : Poor Mechanical Strength

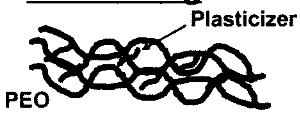
Blending



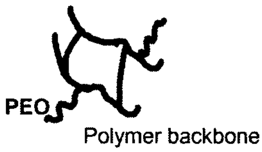
Grafting



Plasticizing



Cross-linking



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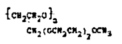
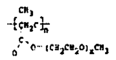
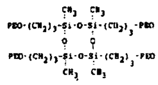
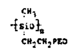
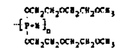
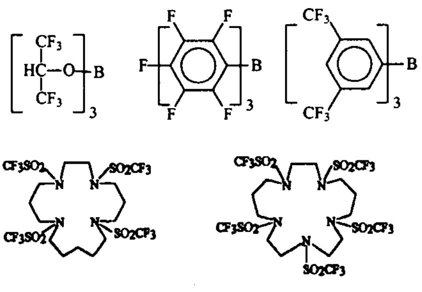
Polymer System	Polymer Host	Repeat Unit	Polymer Electrolyte (example)	Conductivity (Scm^{-1}), 20°C.
LINEAR				
PEO	Poly(ethylene oxide)	$-[CH_2CH_2O]_n-$	$(PEO)_8$-$LiClO_4$	10^{-8}
POM	Poly(oxymethylene)	$[CH_2O]_n$	(POM) - $LiClO_4$	10^{-8}
PPO	Poly(propylene oxide)	$-[(CH_3)CH_2CH_2O]_n-$	$(PPO)_8$-$LiClO_4$	10^{-8}
POO	Poly(oxymethylene-oligo-oxyethylene)	$-[(CH_2O)(CH_2CH_2O)]_n-$	$(POO)_{25}$-$LiCF_3SO_3$	3×10^{-5}
Polysiloxane	Poly(dimethyl siloxane) (DMS)	$-[(CH_3)_2SiO]_n-$	DMS-$LiClO_4$	10^{-4}
Unsaturated Polymers (UP)	Unsaturated ethylene oxide-segmented	$-[HC=CH(CH_2)_4O(CH_2CH_2O)_n(CH_2)_4]_x-$ n = 3-5	UP-$LiClO_4$ (EO:Li^+ = 32:1)	10^{-5}
BRANCHED				
Comb branched ethers	Poly[(2-methoxy)ethyl glycidyl ether) (PMEGE)		$(PMEGE)_8$-$LiClO_4$	10^{-5}
Comb-branched methacrylates (PMG_x)	Poly(methoxy poly(ethylene glycol) methacrylate		PMG_{22}-$LiCF_3SO_3$ (EO:Li+ = 18:1)	3×10^{-5}
Block copolymers (cross-linked polymer networks)	(PEO-PPO-PEO)-SC SC=siloxane crosslinked		(PEO-PPO-PEO)-SC-$LiClO_4$ (4:1 molar)	1-5×10^{-5}
Polysiloxanes	PEO-grafted polysiloxane (PGPS)		PGPS-$LiClO_4$	10^{-4}
Polyphosphazenes $(R_2P{=}N)_n$	Poly[bis-2-(2-methoxyethoxy)ethoxy)) phosphazene] (MEEP)		$(MEEP)_4$-$LiBF_4$ $(MEEP)_4$-$LiN(CF_3SO_2)_2$ $(MEEP)_4$-$LiC(CF_3SO_2)_3$	2×10^{-5} 5×10^{-5} 10^{-4}

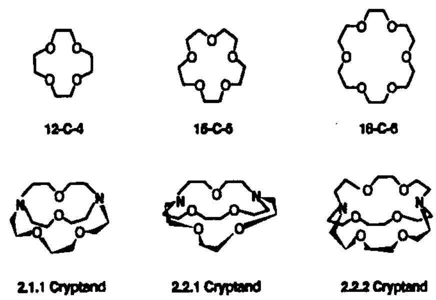
New Approaches for PEO-based SPE (I)

1) Anion Receptors



J. McBreen et al, J. Electrochem. Soc., 146 (2000), 9

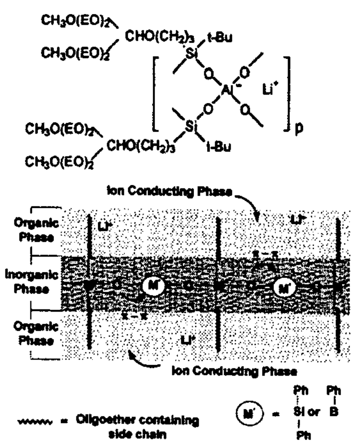
2) Cation Receptors



R.E.A. Dillon, Chem. Mater., 11(1999) 3296

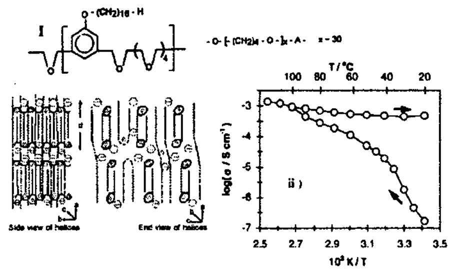
New Approaches for PEO-based SPE (II)

3) Organic-inorganic Hybrid



T. Fujinami et al, Electrochim. Acta, 45 (2000), 1181

4) Self-Organized SPE



Y. Zheng et al, J. Power Sources 97-98 (2001), 641

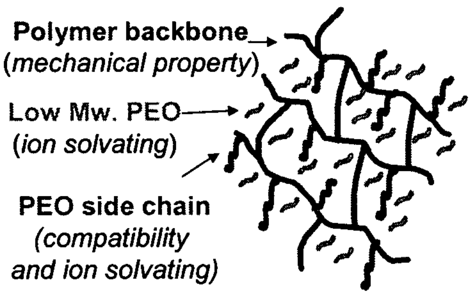
5) Ferroelectric inorganic composite

$BaTiO_3$, $PbTiO_3$, $LiNbO_3$

H.Y. Sun et al., J. Electrochem. Soc., 146(1999) 2672

Our Approach to the PEO-based Polymer Electrolyte

Low Mw. PEO incorporated network polymer electrolyte



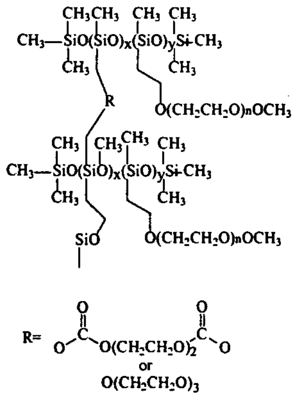
PVdF-HFP

*K. M. Abrahamet al., , Chem. Mat., **9**, 1978 (1997); J. Electrochem. Soc., **144**, L136 (1997).*

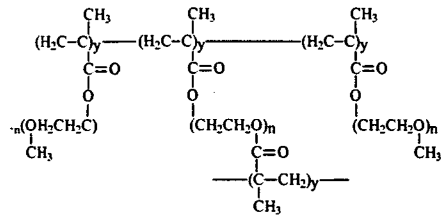
Maximum Conductivity : ~ 2 × 10^{-4} S/cm

SPE Polymer Backbone

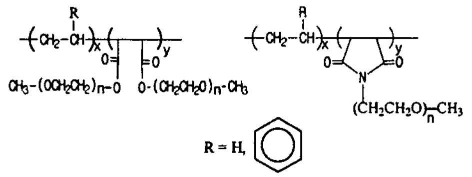
Crossed-linked Polysiloxane



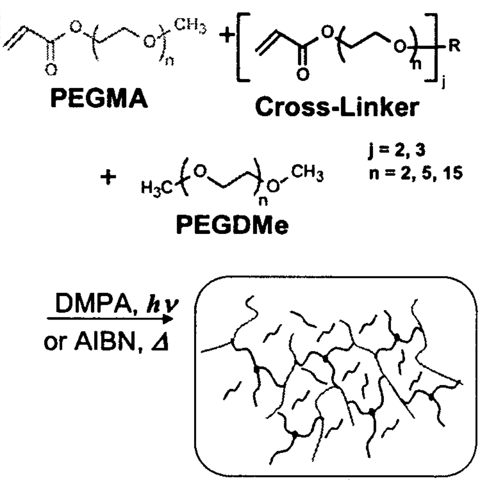
Cross-linked Polyacrylate



Branched Styrene-Maleic Anhydride Copolymer



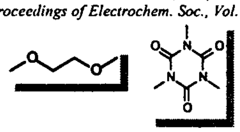
Preparation of Highly Branched PEO Network Polymer



Previous Studies

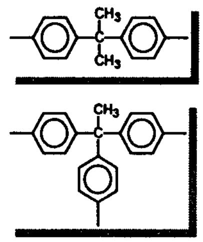
Y. Kang, et. al, J. Power Sources, 92, 255 (2001).
Y. Kang, et al Proceedings of Electrochem. Soc., Vol. 99-25, 534 (1999).

R =



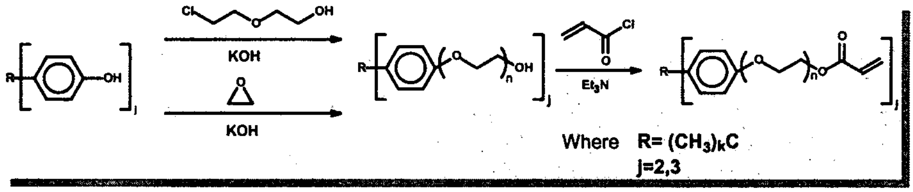
- ***High conductivity : 0.8mS/cm***
- ***Poor Mechanical Stability***

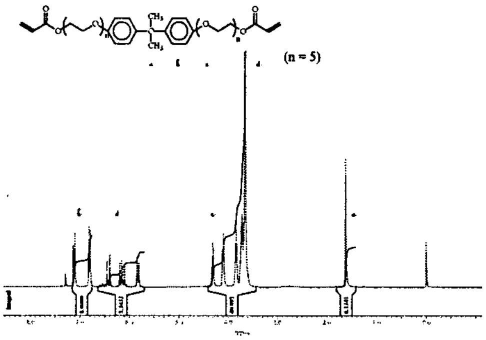
This Study

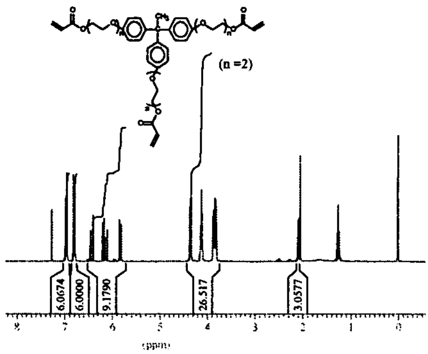


- ***to improve mechanical Stability***
- ***to sustain high conductivity.***

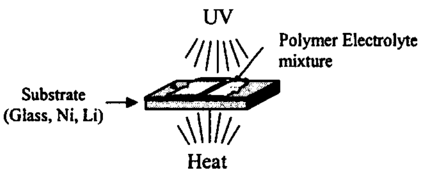
Synthesis of Cross-linker



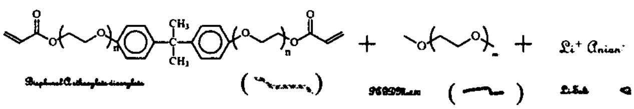


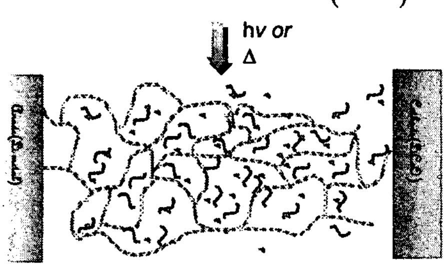


Preparation of Polymer Electrolyte

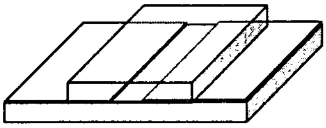


Advantages
- Simple and In-Situ Process
- Free or reduced solvent emission
- High quality end products





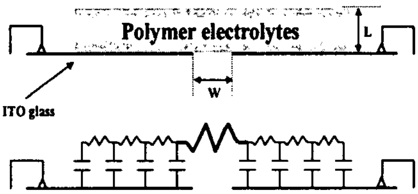
Conductivity Measurement



$$\frac{1}{R}=\frac{\sigma b}{\pi}\ln\left[1+\frac{\sqrt{1+(w/2L)^2}}{w/2L}\right]$$

1) w<<L

$$\sigma=\frac{\pi}{Rb\ln\left[1+\frac{\sqrt{1+(w/2L)^2}}{w/2L}\right]}=\frac{\pi}{Rb\ln\left(\frac{2}{w/2L}\right)}=\frac{\pi}{Rb\ln\left(\frac{4L}{w}\right)}$$



Transmission line approximation

2) w>>L

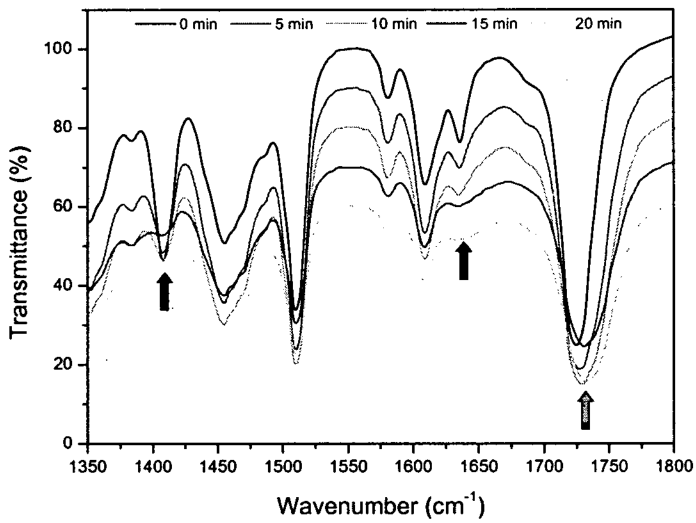
$$\frac{1}{R}=\frac{\sigma b}{\pi}\ln\left[\frac{1+w/2L}{w/2L}\right]=\frac{\sigma b}{\pi}\ln\left(\frac{1+x}{x}\right)=\frac{\sigma b}{\pi}\ln\left(1+\frac{1}{x}\right)$$

$$=\frac{\sigma b}{\pi}\left(\frac{1}{x}+\frac{1}{2!}\left(\frac{1}{x^2}\right)+\frac{1}{3!}\left(\frac{1}{x^3}\right)+.....\right)$$

$$=\frac{\sigma b}{\pi}\left(\frac{2L}{w}\right)$$

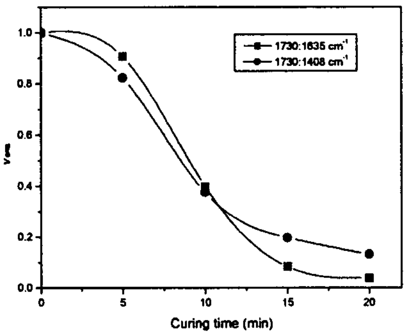
$$\therefore\sigma=\frac{\pi w}{2bRL}=\frac{\pi}{2}\left(\frac{w}{bRL}\right)$$

Curing Kinetics - IR Studies



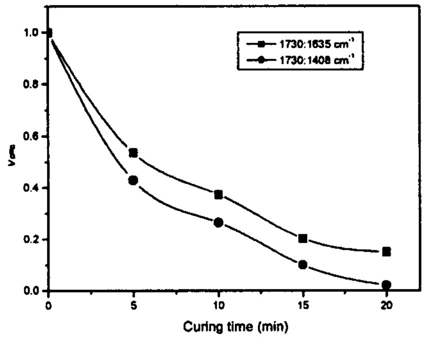
Curing Behaviors of Electrolyte

Thermal curing



* BisA4 + BPO + PEGDME (MW=500, 30 wt%)
(Temp.$_{cure}$: 80℃)

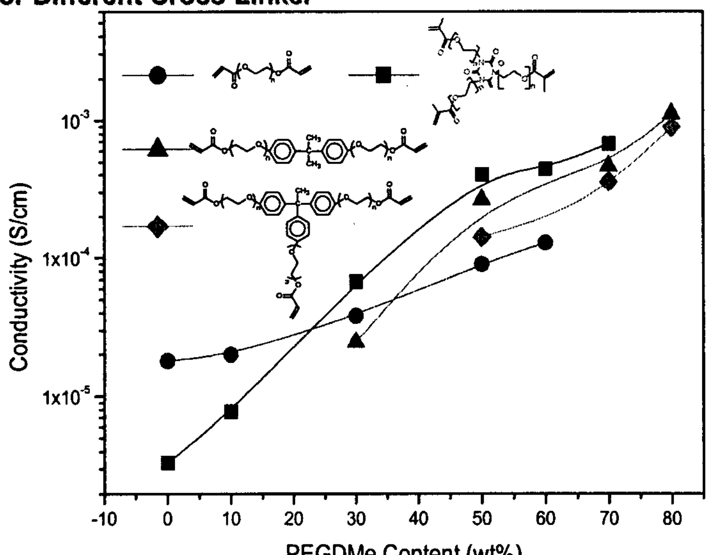
UV curing



* BisA4 + DMPA + PEGDME (MW=500 30 wt%)
(UV:365nm)

PEGDMe Content Dependence of Conductivity

For Different Cross-Linker



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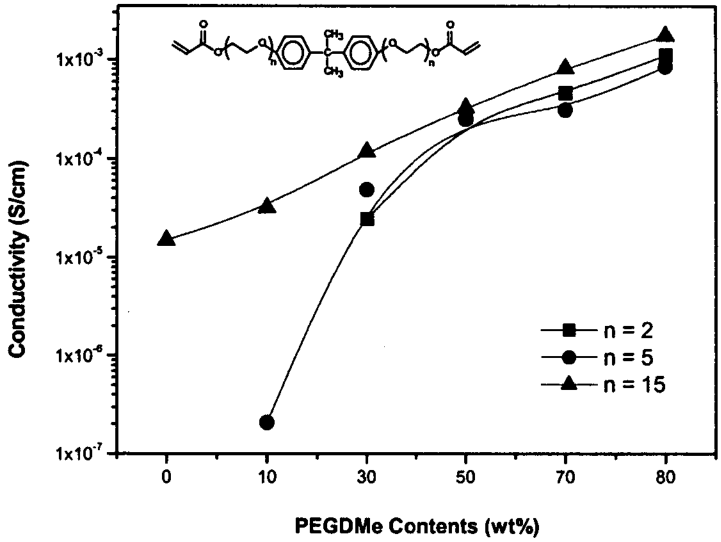
Effects on the Chain Length of Cross-Linker



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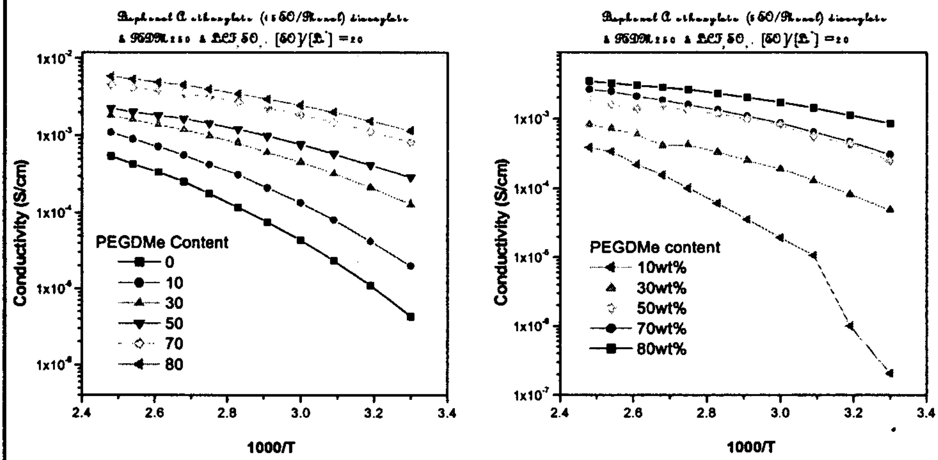
Effects on the Temperature



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Effects on the Temperature

VTF Equation

$$\sigma = AT^{-1/2} \mathrm{Exp}[-E_a/R(T-T_o)]$$

A: No. of Charge carrier E_a: Pseudo activation energy
R: Gas constant T_o: T_g − 50 °C

PEGDMe Content (wt%)	n = 2 A (S K$^{0.5}$/cm)	n = 2 E_a (kJ/mole)	n = 2 T_o (°C)	n = 5 A (S K$^{0.5}$/cm)	n = 5 E_a (kJ/mole)	n = 5 T_o (°C)	n =15 A (S K$^{0.5}$/cm)	n =15 E_a (kJ/mole)	n =15 T_o (°C)
0							3.09	9.78	-31.7
10							7	11.14	-56.9
30	3.74	12.03	-80.3	0.91	7.88	-57.9	3.01	9.21	-76.4
50	0.73	6.69	-79.6	1.07	7.13	-83.5	-		-
70	0.89	6.31	-81.4	2.01	7.68	-78.2	1.93	6.47	-81.2
80	0.78	4.90	-82.4	1.03	5.76	-89.1	2.2	6.31	-83.6

E_a of pure PEO : 9 ~ 13kJ/mole

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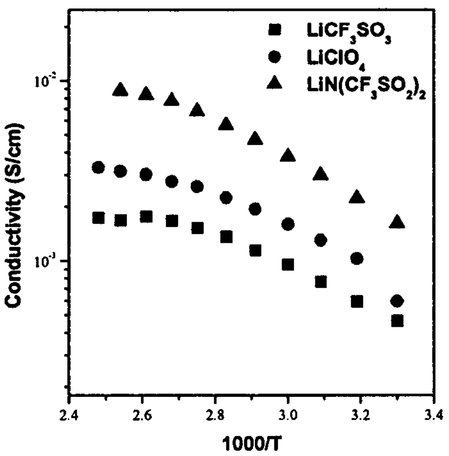
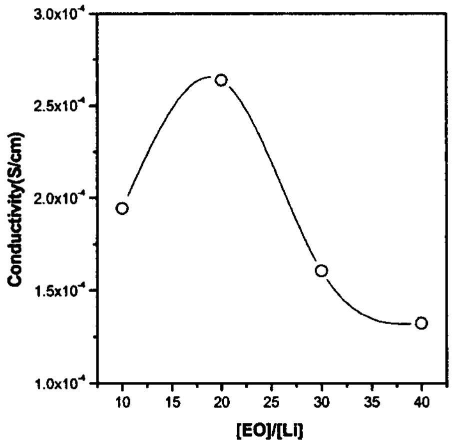
Effects on the Lithium Salts

For Different Lithium Salts



For Salt Concentration



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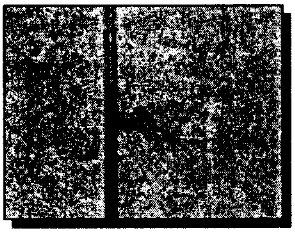
Mechanical Properties

Tensile Strength

Cross-Linker	PEGDMe Contents (wt%)	Tensile Strength (Mpa)	Percent Strain (%)
Tris(4-hydroxyphenyl)ethane ethoxylate triacrylate (n=2)	50	4.49	35.2
Bisphenol A ethoxylate diacrylate (n=2)	30	5.32	34.48
	50	2.40	38.62
Bisphenol A ethoxylate diacrylate (n=5)	30	1.54	34.44
	50	0.59	35.12
Bisphenol A ethoxylate diacrylate (n=15)	30	0.61	56.78
	50	0.42	42.15

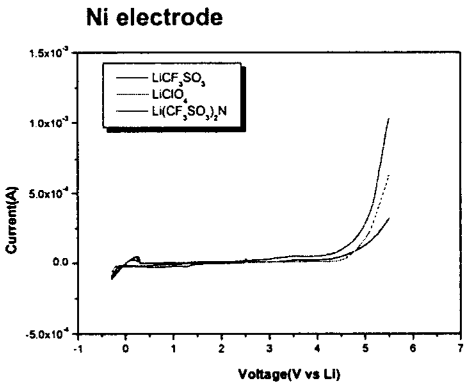


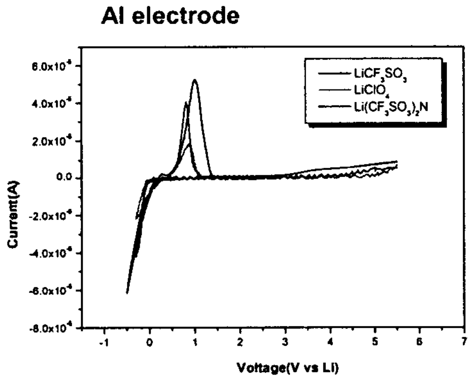
bending 180° against 3mm rod

Bending Test

Cross-Linker	PEGDMe Contents (wt%)	Flexibility	
		90°	180°
Tris(4-hydroxyphenyl)ethane ethoxylate triacrylate (n=2)	50	O	△
Bisphenol A ethoxylate diacrylate (n=2)	30	O	△
	50	O	O
Bisphenol A ethoxylate diacrylate (n=5)	30	O	△
	50	O	O
Bisphenol A ethoxylate diacrylate (n=15)	30	O	O
	50	O	O

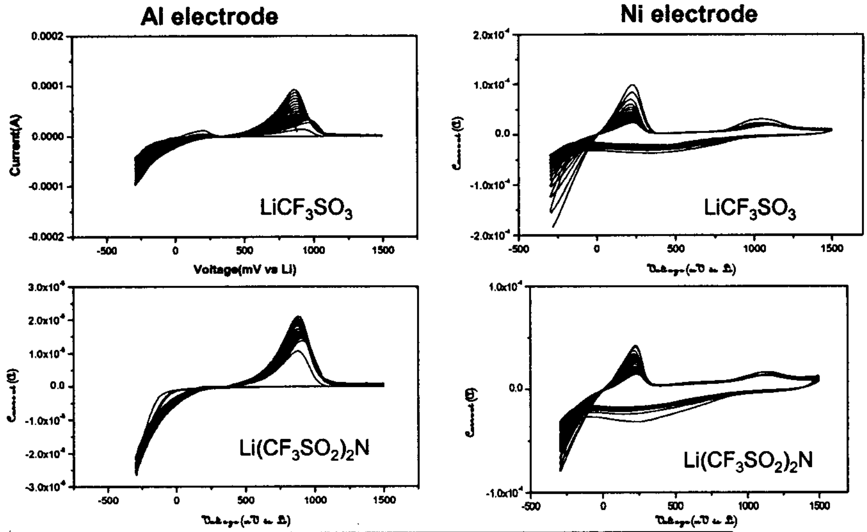
Electrochemical Stability





Bisphenol A ethoxylate diacrylate, PEGDMe250 (70wt%). $LiCF_3SO_3$, $LiClO_4$, $Li(CF_3SO_2)_2N$ (EO/Li = 20) at 30°C. Li/SPE/Ni&Al, 5mV/s

Lithium Plating/Stripping



Bisphnol A ethoxylate diacrylate, PEGDMe250 (70 wt%),
$LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, (EO/Li = 20) at 30℃, Li/SPE/Al, and Ni: 5mV/s

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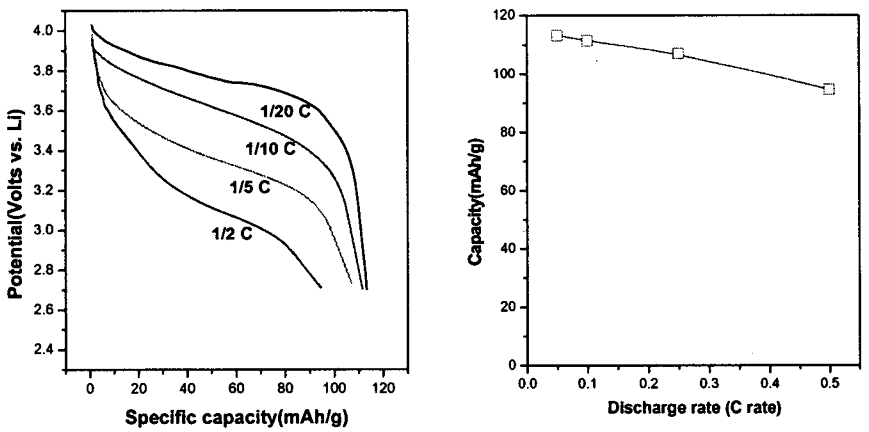
Cell Performance at Various Discharge Rate



Anode :	Li metal
Cathode:	$LiCoO_2$, PEO600,000 composite electrode
SPE ,	Bisphnol A ethoxylate diacrylate, PEGDMe250 (70 wt%)
	$LiCF_3SO_3$, (EO/Li = 20) at 30℃

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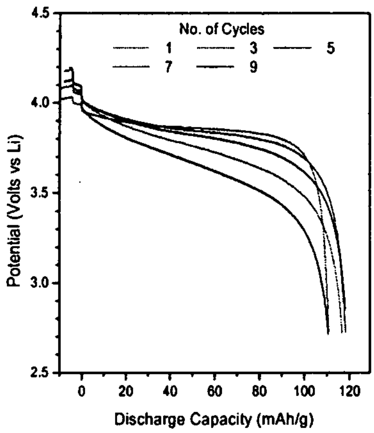
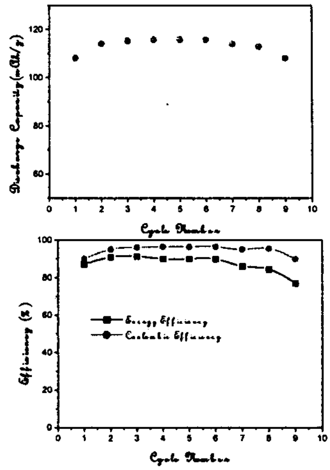
Cycle Characteristic of Test Cell





Anode : Li metal
Cathode : $LiCoO_2$, PEO600,000 composite electrode
SPE : Bisphenol A ethoxylate diacrylate, PEGDMe250 (70wt%)
$LiCF_3SO_3$ (EO/Li = 20) at 30℃

Summary

- PEO-based SPE incorporated low molecular weight PEGDMe was prepared by UV radiation curing method.
- Good mechanical Stability : tensile strength : 0.5 ~ 5MPa.
- Conductivity increases as increasing PEGDMe content up to 80wt%.
- Maximum conductivity is measured to be 1.0 x 10^{-3} S/cm at 30°C.
- Electrochemical window : > 4.5V (vs. Li).
- Reversible electrochemical plating/stripping of lithium.
- Battery Performance at 30°C
  - capacity : 115.mAh/g
  - Coulombic efficiency : > 95%
  - Power efficiency : > 90%