Semi-Interpenetrating 구조를 도입한 Poly(ethylene oxide) 기반 Solid Polymer Electrolyte의 성능 개선

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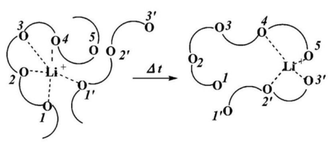
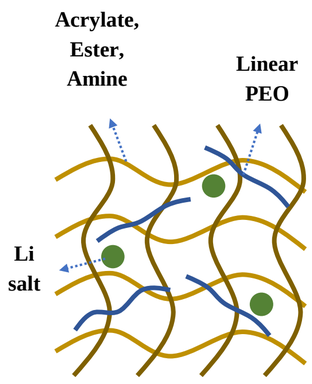
Introduction



Mechanism of Li^+ ion transport in PEO matrix [1]

▸ PEO-based polymer film

- PEO is a promising polymer for LIBs due to its strong affinity for lithium ions, but its low melting point and dissolution in electrolytes pose challenges.
- This study aims to improve its suitability for LIBs by forming a semi-IPN polymer network using high molecular weight PEO and functional monomers.



Semi-Interpenetrating polymer network

◆ Development Process of SPE

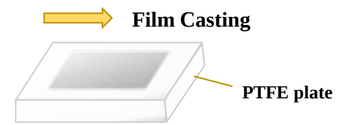
Pre-SPE Solution → Film Formation → Solubility in Liq. Electrolyte / Mechanical Strength → Ionic Conductivity → Cell Performance

Experimental

◆ Materials

- Main matrix polymer: Polyethylene oxide
- Interpenetrating polymers: Amine, Ester, Acrylate, Succinimidyl Glutarate
- Reaction solvent : Acetonitrile
- Initiator: BPO 0.5 wt.% of Acrylate monomer
- Li salt: LiTFSI

◆ Process



- PEO600K 7 wt.% of ACN, 12 hr, 40 ℃ stirring
- ICEMA and DEGDMA 10 wt.% of ACN, SG and AM 2 wt.% of ACN
- Casting pre-SPE solution on PTFE plate, and drying to evaporate acetonitrile.

◆ DSC

10℃/min, 1st cycle 30℃ to 80℃, 80℃ to -50 ℃ (to remove thermal history), using 2nd cycle data

◆ Pre-SPE solution

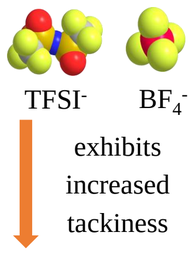
High concentration of polymer → Rapid reaction leads to extensive gelation, making production impossible if it reaches a solid state.
Up to 1 wt.% SG/AM compared to ACN.

Results and Discussion

▸ Film Formation

- Effect of Li salt on SPE

PEO 600K	LiTFSI	$LiBF_4$
	24:1	24:1
	18:1	18:1
	12:1	12:1
	6:1	6:1



exhibits increased tackiness

- Lithium salt ↑ → Film-forming ability ↓
- $TFSI^-$ has a greater impact on the decrease in film-forming ability compared to BF_4^- due to its larger and more flexible structure.
- A film with 20-30 wt.% acrylate relative to PEO is insoluble in liquid electrolyte.
- EGDMA content ↑ → Expansion rate ↓

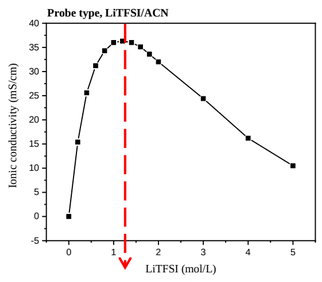
- Effect of acrylate monomer content on SPE formation

PEO/Acrylate (=ICEMA+EGDMA)	9:1	8:2				7:3				6:4	5:5
ICEMA/EGDMA	10:0	10:0	9:1	8:2	7:3	**10:0**	9:1	8:2	7:3	10:0	10:0
Expansion Rate (Area %)	-	302	269	261	Gel	**190**	185	183	Gel	Excess Fluidity	
Film Presence	Manufacturable				X	Manufacturable			X		
Electrolyte Solubility	Soluble	Insoluble							Soluble		

Film formation X **Unable to maintain shape in liq electrolyte** **Insoluble in liq electrolyte**

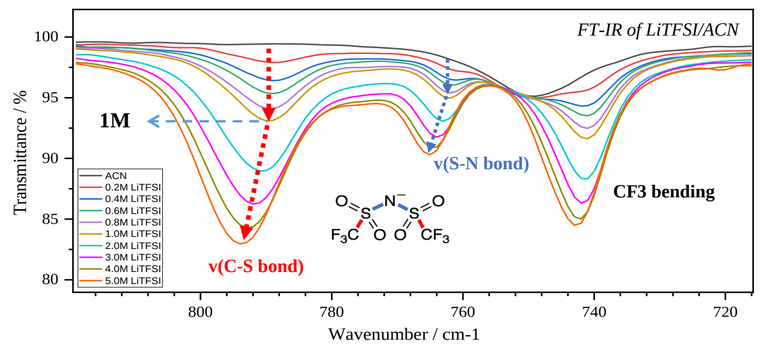
▸ LiTFSI Solvation

- Ionic conductivity of LiTFSI/ACN

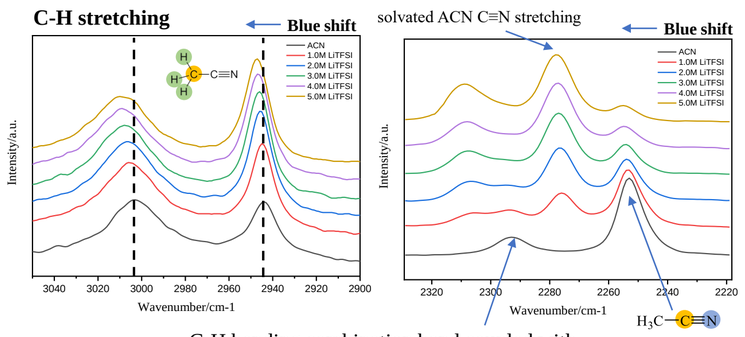


Maximum ionic conductivity around 1 mol/L

Low concentration: Free TFSI- ↑, minimal shifts in vibrational peaks
High concentration: Li+ ion pair, ion cluster
→ More constrained bond vibrations, blue shifts



- FT-IR of LiTFSI/ACN

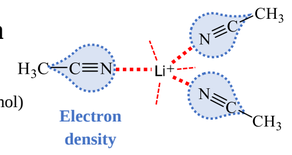


C-H bending combination band coupled with C≡N stretching through Fermi resonance

Free ACN C≡N stretching

- Li-ion solvation

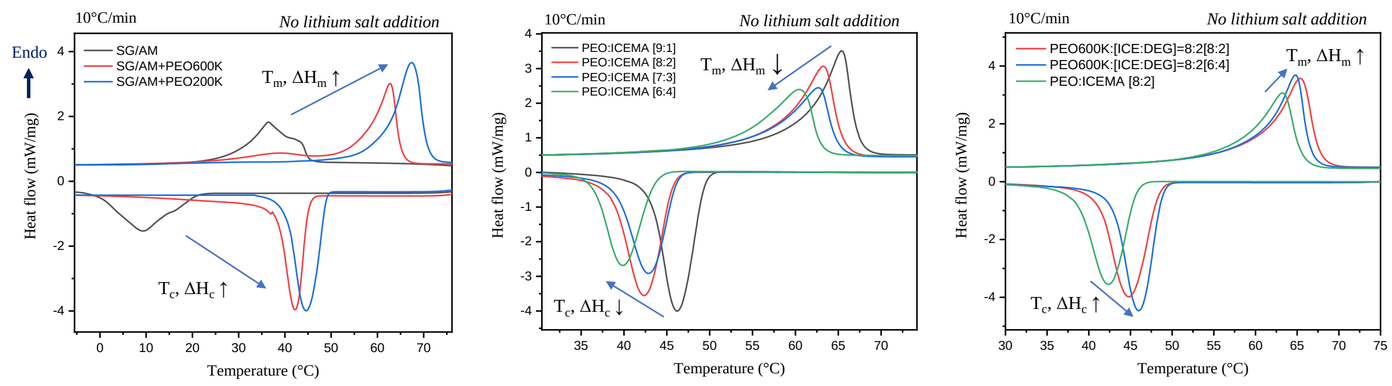
1 mol/L
→ ACN : LiTFSI = 19 : 1 (mol)



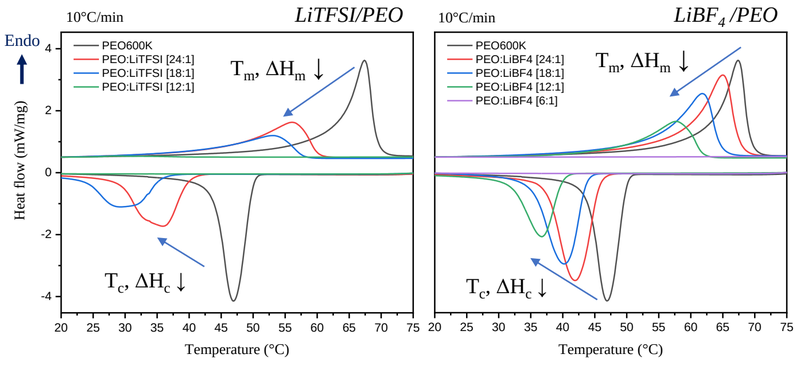
- Li salt ↑ → Solvation ↑, π interaction → Electron density of the C≡N, C-H ↓ → C≡N, C-H stretching energy ↑
- Changes in the peak occur at concentrations around 1M.

▸ Analysis of DSC Data

- Effect of crosslinked structure changes on polymer film



- Effect of Li salt on PEO polymer electrolyte



$$X_c(\%) = \frac{\Delta H_{measured}}{\Delta H_{100\%\ crystalline}} \times 100,\ \Delta H_{100\%\ crystalline\ PEO} = 197 J/g$$

PEO600K: Li salt (mol)	LiTFSI			LiBF4		
	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)
24:1	89	-90	45	127	-130	65
18:1	69	-70	35	116	-117	59
12:1				72	-78	39

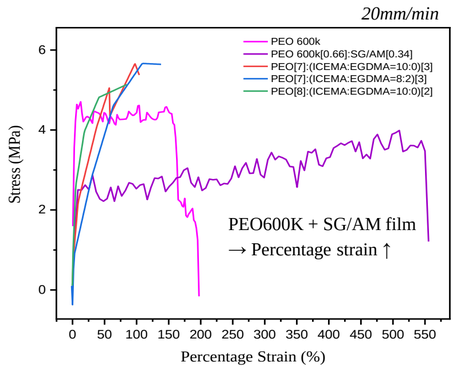
Xc ↓

- The polymer film should ideally not show T_m or Tc within the operating range (-20 ℃ to 80 ℃).
- ICEMA ↑ or Li salt ↑ → Crystallinity of PEO film ↓

▸ Analysis of UTM data

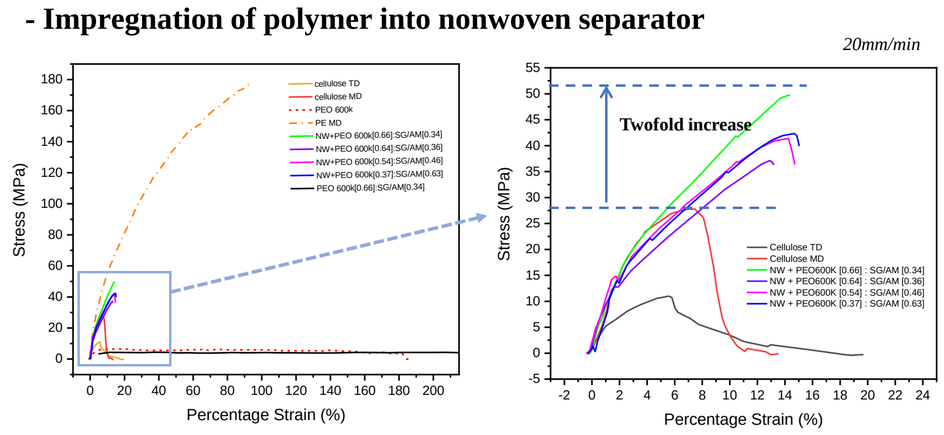
- Polymer film without Li salt

MD: Machine direction
TD: Transverse direction



- The separator's mechanical strength varies with MD and TD.
- Impregnation of the cellulose separator with a pre-SPE solution reduces high strain and doubles the tensile strength.
- Optimal condition: Impregnation for 1.5 hours, PEO:SG/AM = 66:34 (wt.%)

- Impregnation of polymer into nonwoven separator



Conclusions & Future Works

▸ Conclusions

- Higher lithium salt content in PEO film decreases crystallinity.
- Larger anion size (LiTFSI > LiBF4) has a greater impact on reducing crystallinity.
- Blue shift of the peak is observed at LiTFSI concentrations above 1 mol/L.
- Nonwoven separator impregnated with PEO600K + SG/AM solution shows up to twofold tensile strength increase and reduced strain.

▸ Future works

- Improve the ionic conductivity of the SPE film.
- Identify methods to maintain an amorphous structure of the film within the operating temperature range of LIBs.
- Improve the tensile strength up to half that of the PE separator.

Acknowledgement

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References

[1] Zhao, W., Yi, J., He, P., & Zhou, H. (2019). Solid-State Electrolytes for Lithium-Ion Batteries: Fundamentals, Challenges, and Perspectives. Electrochemical Energy Reviews, 2, 574–605. Published August 12, 2019.
[2] Rassmus Andersson, Guiomar Hernández, and Jonas Mindemark, "Quantifying the ion coordination strength in polymer electrolytes," Phys. Chem. Chem. Phys., 2022, 24, 16343–16352, DOI: 10.1039/d2cp01904c.
[3] Young-il Shin, et al. Improving the performance of high-concentration acrylate-based gel polymer electrolytes, 2023 Korean Battery Society