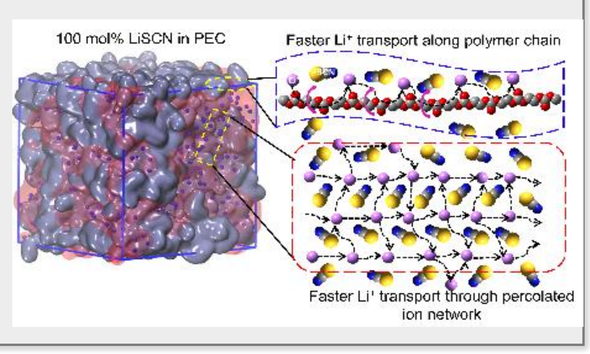
Enhanced Charge Transport Through Ion Networks in Highly Concentrated LiSCN-polyethylene Carbonate Solid Polymer Electrolytes

Kajal Kumbhakar,[a],† Sourav Palchowdhury,[a],† Thuy Duong Pham,[b] Seoeun Shin,[a] So Yeon Chun,[a] Joong Won Shim,[a],[c] Kyung-Koo Lee,[d],* Minhaeng Cho,[a],[c],* Kyungwon Kwak[a],[c],*

[a]Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Seoul 02841, Republic of Korea
[b]Faculty of Biotechnology, Chemistry and Environmental Engineering, Phenikaa University, Hanoi 10000, Vietnam
[c] Department of Chemistry, Korea University, Seoul 02841, Republic of Korea
[d] Department of Chemistry, Kunsan National University, Gunsan, Jeonbuk 54150, Republic of Korea
† Equally contributed to this work.

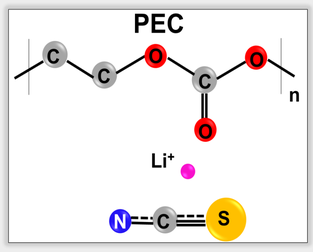
Abstract

Challenging the preference for bulky anions due to low binding energy with Li^+ ion, the lithium thiocyanate-polyethylene carbonate (LiSCN-PEC) solid polymer electrolyte (SPE) demonstrates higher ionic conductivities (3.16×10^{-5} S cm^{-1}) at polymer-in-salt concentration (100 mol%) compared to those with lithium bis(fluorosulfonyl)imide (LiFSI, 1.01×10^{-5} S cm^{-1}) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1.72×10^{-7} S cm^{-1}). Through the careful selection of PEC and LiSCN as components of SPE, the carbonyl stretching of PEC and the SCN^- stretching band as vibrational reporters provide detailed structural insights into the Li^+ ion transport channel. Spectroscopic investigations reveal that enhanced ion aggregation alters the solvation structure around the Li^+ and diminishes the interaction between Li^+ and polymer (PEC) with increasing LiSCN concentrations, promoting faster segmental motion as a major transport mechanism. However, the transition observed from subionic to superionic behavior in the Walden plot indicates the onset of segmental motion decoupled charge transport pathway. The SCN^- vibrational spectrum elucidates the evolution from a Li--SCN--Li type chain-like structure to a Li_2>SCN<Li_2 type extended ion network with increasing LiSCN concentration, revealing that the ion network provides an alternative channel for Li^+ ion transfer at higher concentrations, enhancing conductivity.



Materials and Methods

Polyethylene carbonate (PEC)
Lithium thiocyanate (LiSCN). LiSCN concentration ranges from 10 to 100 mol% (x mol%, $x = \frac{[\text{LiSCN}]}{[\text{EC unit}]} \text{x}100$).
For instance, 10 mol% LiSCN means that Li/carbonate molar ratio equals 1/10.

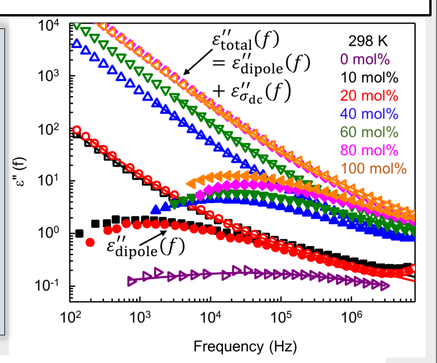


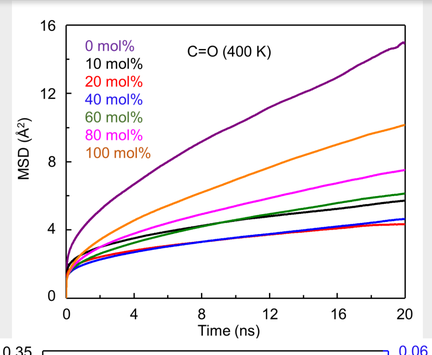
Experiment: Electrochemical impedance spectroscopy, dielectric relaxation spectroscopy, transmission FT-IR spectroscopy, pump-probe IR spectroscopy.

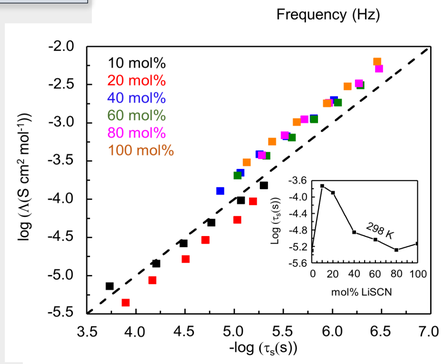
MD simulation: Classical molecular dynamics simulations, LAMMPS package, non-polarizable OPLS force field.
DFT level calculation using B3LYP/6-311++G(D,P) basis set.

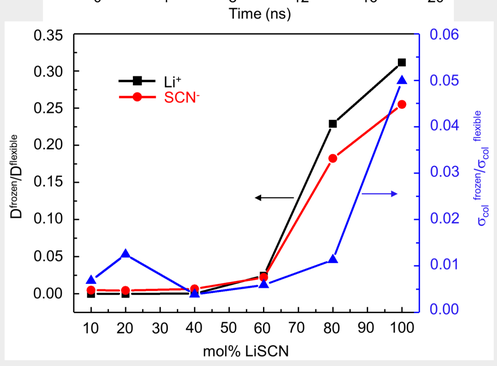
Faster Polymer Segmental Motion and Decoupled Conductivities with Increasing LiSCN Concentration

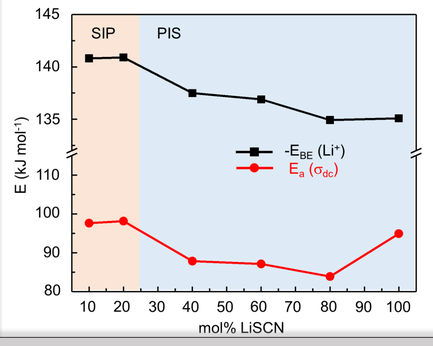
Complex dielectric constant, $\boldsymbol{\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f) = \frac{1}{2\pi i f Z^*(f) C_0}}$, the imaginary part $\boldsymbol{\varepsilon''(f) = \frac{Z'(f)}{2\pi f\left(Z'^2 + Z''^2\right)}}$, report dipolar relaxation times. Capacitance of the empty cell, $\boldsymbol{C_0 = \varepsilon_0 \frac{A_{SPE}}{d_{SPE}}}$, ε_0 = 8.854 x 10^{-12} F/m.
Fitting model: $\boldsymbol{\varepsilon^*(f) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1+(i2\pi f \tau_{HN})^\alpha]^\beta} + \frac{\sigma_{dc}}{2\pi i \varepsilon_0 f}}$









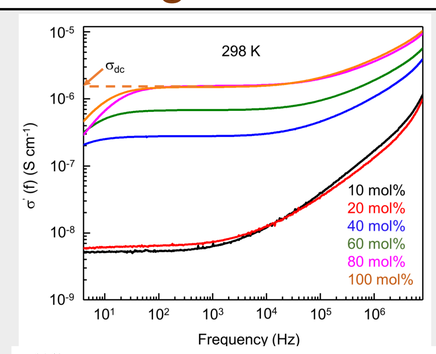


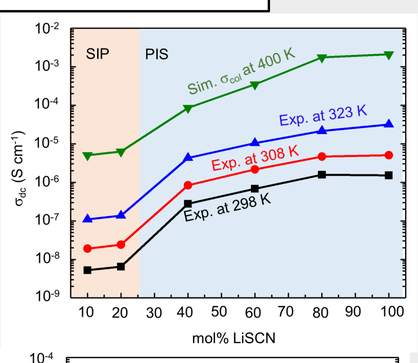
Faster polymer segmental relaxation time, τ_S with increase in LiSCN mol% is not the primary facotor in enhanicng lithium ion diffusion in the LiSCN-PEC SPEs.

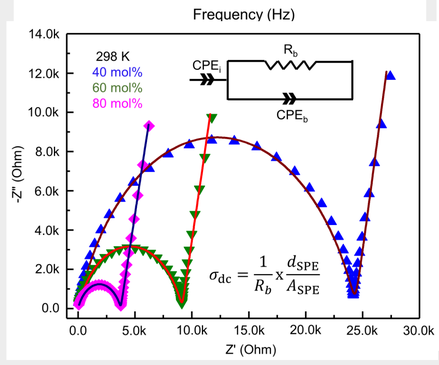
Enhanced Ionic Conductivity of PEC-based SPEs with Increasing LiSCN Concentration

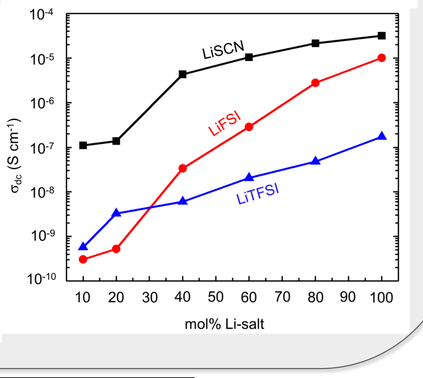
Frequency-dependent complex impedance spectra, $\boldsymbol{Z^*(f) = Z'(f) + iZ''(f)}$, Real component, Z' and imaginary part, Z''.
Complex conductivity $\boldsymbol{\sigma^*(f)}$= $\boldsymbol{\sigma'(f) + i\sigma''(f) = \frac{1}{Z^*(f)} \text{x} \frac{d_{SPE}}{A_{SPE}}}$. d_{SPE} and A_{SPE} are thickness and area of SPE. σ_{dc} is the extrapolation of the frequency-independent plateau regime to $f \rightarrow 0$ of the $\sigma'(f)$.

σ_{dc} enhances with LISCN mol%, report a transition of conductivity at > 20 mol%, emerges mainly from switching the SIP regime to PIS. Our newly developed LiSCN-PEC SPEs yield higher ionic conductivity than that with LiTFSI-and LiFSI.

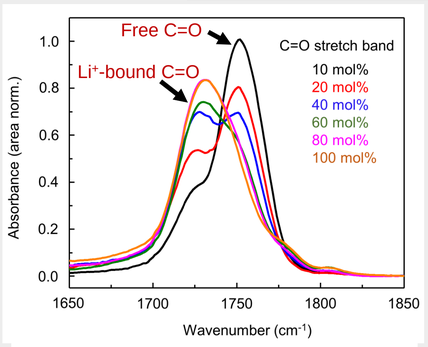


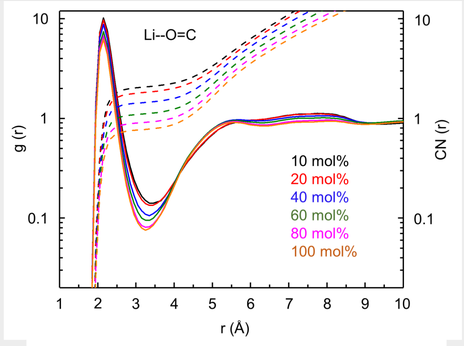


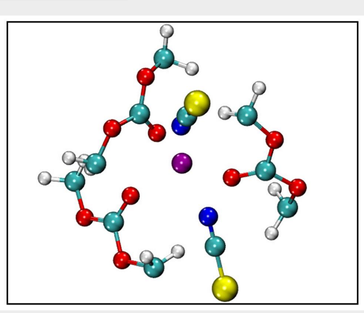


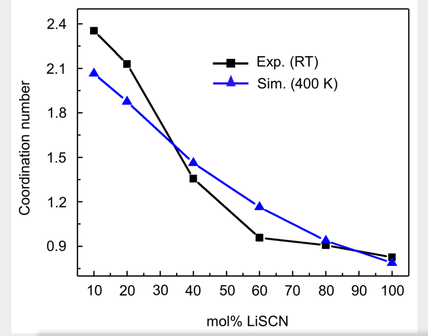


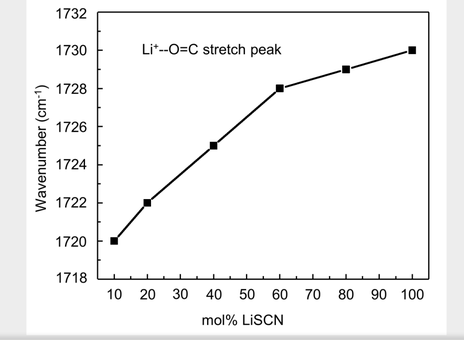
Li⁺-polymer Interaction Becomes Weaker with Increasing LiSCN Concentrations

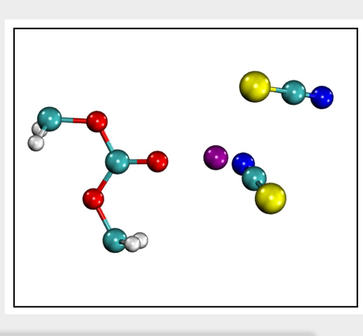






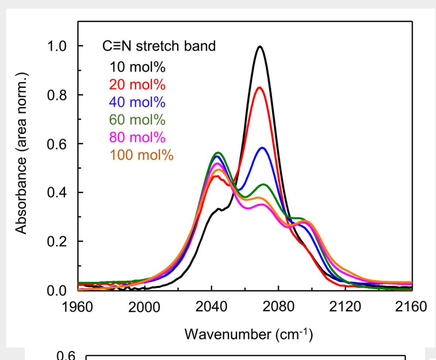


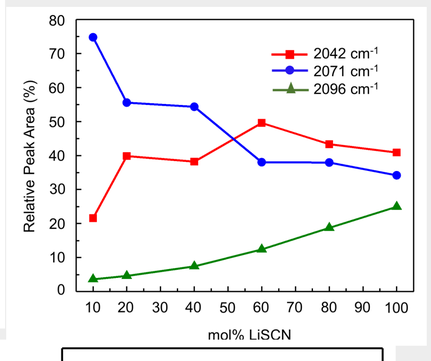


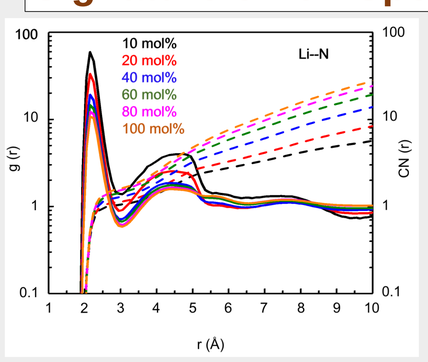


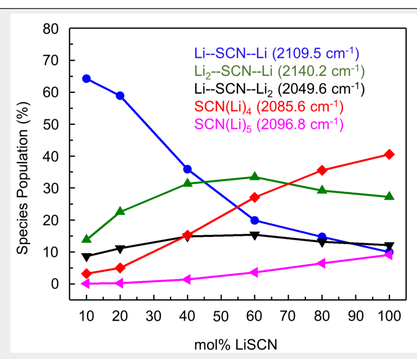
With increasing LiSCN mol%, a 10 cm^{-1} blue shift (from 1720 to 1730 cm^{-1}) observed for the Li^+-bound carbonyl peak manifests the gradual weakening of Li^+-carbonate interaction as reflected in faster PEC segmental motion, and a decrease in $E_{BE}^{Li^+}$ with increasing LiSCN concentration.

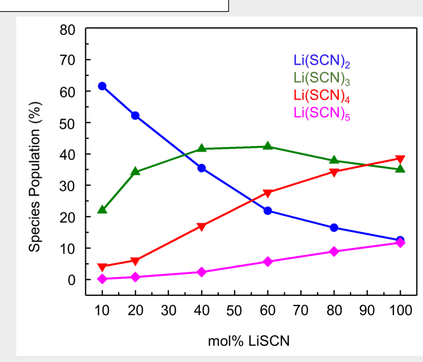
Signature of Ion Species and Ion Network Formation

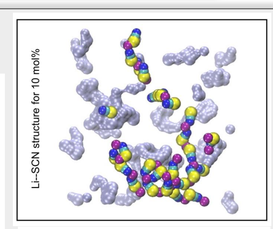


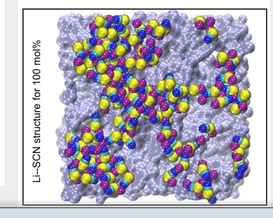


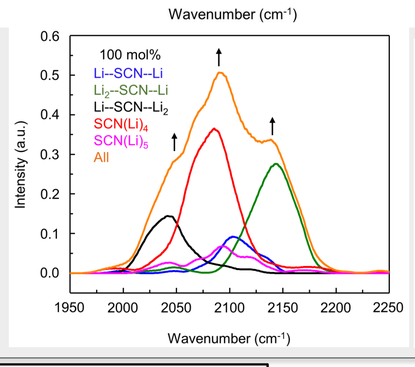


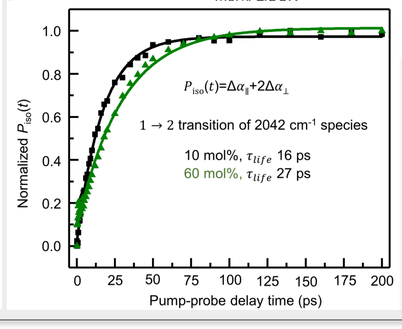












Three well separated peaks ~ 2042, 2071, and 2096 cm^{-1} in the C≡N stretch spectrum of the SCN^-.
With increasing LiSCN concentration, the 2071 cm^{-1} peak contribution diminishes, while the 2042 and 2096 cm^{-1} species increase significantly. Experiment supported by MD simulation and DFT calculations suggest that the experimentally observed center peak at 2071 cm^{-1} comes from a combination of Li--SCN--Li, Li_2>SCN<Li_2, and $SCN(Li)_5$. The band at 2042 cm^{-1} originates from a combination of Li--SCN<Li_2 and Li_2>SCN<Li_2, while the band at 2096 cm^{-1} is from Li_2--SCN--Li motifs. The concentration-dependent evolution of SCN^- stretch band is a key signature of ion network formation in LiSCN-PEC SPEs. The SCN^- stretch band reflects the structural transition from chain-like ion-cluster, Li--SCN--Li, to ion network structures, Li_2>SCN<Li_2.

Conclusion

We developed concentrated PEC-based SPEs with LiSCN salt, which provides higher ionic conductivity compared to other Li-salts with bulky anions like LiTFSI and LiFSI. By leveraging spectroscopic analysis and MD simulations, we offer an in-depth molecular understanding of the mechanisms driving enhanced ion conductivity with increasing LiSCN concentration. With increasing LiSCN concentration, the reduced Li^+--PEC interaction promotes faster polymer segmental motion and more efficient Li^+ ion transfer along the polymer backbone. Moreover, the strong tendency of SCN^- to form ion aggregates partitions more Li^+ ions into the ion network channels, thereby enhancing charge transport through this network. At higher LiSCN concentrations, a percolated ion network channel is formed, facilitating faster Li^+ diffusion. This conclusion, previously suggested through MD simulations alone, is now experimentally validated using vibrational spectroscopy. These insights suggest that the inherent limitations of SPEs in terms of ionic conductivity can be mitigated by creating additional fast Li^+ diffusion channels. This can be achieved not only through high concentrations of LiSCN but also potentially by incorporating multiple salts or inorganic additives into the electrolyte matrix.

Reference: ***Enhanced Charge Transport through Ion Networks in Highly Concentrated LiSCN-Polyethylene Carbonate Solid Polymer Electrolytes***, **Kajal Kumbhakar, Sourav Palchowdhury, Thuy Duong Pham, Seoeun Shin, So Yeon Chun, Joong Won Shim, Kyung-Koo Lee, Minhaeng Cho, Kyungwon Kwak,** ***Small Science 2025, 2400653 (1-9).***