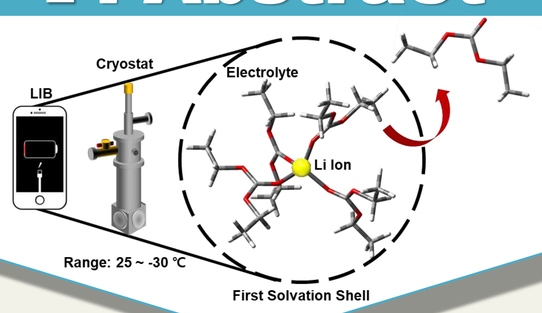
Lithium-Ion Battery Solvation Structure study at low temperature with Cryostat

Youngseok Chai[1,2], Kyungwon Kwak[1,2]*, Minhaeng Cho[1,2]*

[1] Center of Molecular Spectroscopy and Dynamics, Institute for Basic Science(IBS)

[2] Department of Chemistry, Korea University

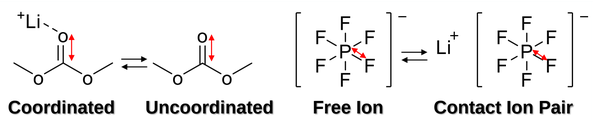
Ⅰ. Abstract

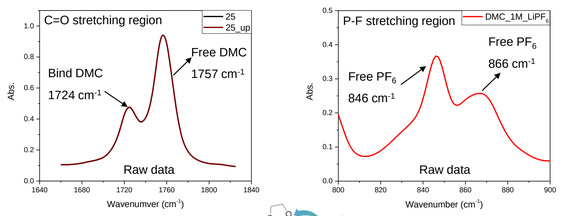


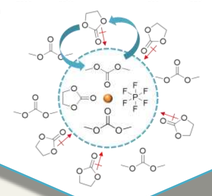
Lithium-ion battery has received much attention due to the high power density and good rechargeability. However, the application of the battery is limited at a low temperature, in that it shows poor performance in the unexpected cold due to the increasing impedance of charge transfer. To break through the current state, we are trying to get information about the change of the solvation structure of LIB at low temperature with a cryostat.

We observed that the number of coordinated electrolytes (DMC, DEC, PC) increases and the concentration of contact ion pair ($LiPF_6$) decreases as the temperature decreases. The number of coordinated electrolytes was calculated through analyzing C=O stretching of them and the trend of the CIP′s concentration was confirmed by investigating the P-F stretching of $LiPF_6$ (salt). We believe that the temperature dependence of the number of charge carriers has less effect on the temperature dependence of the conductivity than the mobility of charge carriers.

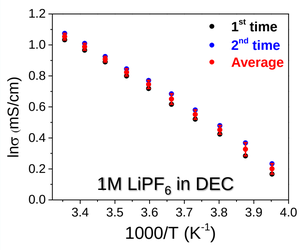
Ⅱ. Problem & Design







A. Ionic Conductivity at Low temperatures



Arrhenius Behavior

1. Zhang, S. S., **Xu, K., & Jow, T. R. (2003)**. Low-temperature performance of Li-ion cells with a LiBF4-based electrolyte. ***Journal of Solid State Electrochemistry***

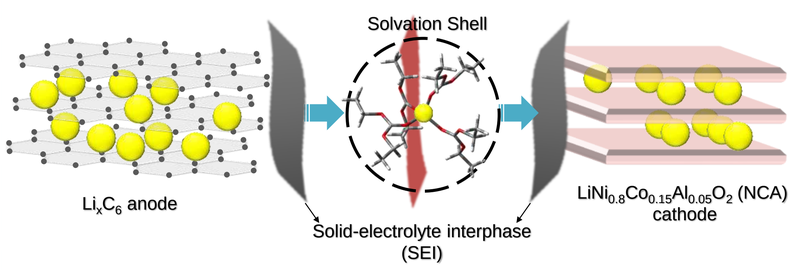
2. **Hayamizu, K. (2012).** Temperature dependence of self-diffusion coefficients of ions and solvents in ethylene carbonate, propylene carbonate, and diethyl carbonate single solutions and ethylene carbonate + diethyl carbonate binary solutions of LiPF 6 studied by NMR. ***Journal of Chemical and Engineering Data***

3. Berhaut, C. L., Lemordant, D., Porion, P., Timperman, L., **Schmidt, G., & Anouti, M. (2019).** Ionic association analysis of LiTDI, LiFSI and $LiPF_6$ in EC/DMC for better Li-ion battery performances. ***RSC Advances***

B. Limiting Factor

ΔG(kcal/mol)

Smart, M. C., Ratnakumar, B. V., Whitcanack, L. D., Chin, K. B., Surampudi, S., Croft, H., ... **Staniewicz, R. (2003).** Improved low-temperature performance of lithium-ion cells with quaternary carbonate-based electrolytes. ***Journal of Power Sources***



1. Extraction from Li_xC_6 anode
2. Diffusion in the graphite interlayer
3. Across between the graphite electrode and the graphite SEI
4. Diffusion through the SEI layer of graphite
5. Solvation in electrolyte
6. Migration in electrolyte
7. **Desolvation from electrolyte at the SEI layer on NCA**
8. Diffusion through the CEI layer on NCA
9. Across between the NCA CEI and the NCA electrode
10. Diffusion in the interlayer of NCA
11. Appropriate site of the NCA lattice

C. Diffusion Coefficient

Hayamizu, K. (2012)
Journal of Chemical and Engineering Data,

1M $LiPF_6$ in DEC

T(℃)	DEC	PF_6^-	Li^+	R_{Li}
80	14.5	7.43	7.10	2.04
70	12.6	6.21	5.75	2.19
60	10.7	5.30	5.00	2.14
50	9.34	4.38	4.33	2.16
40	7.50	3.77	3.40	2.21
30	8.80	2.75	2.70	2.15
20	5.10	2.43	2.27	2.25
10	4.21	2.02	1.83	2.30
0	3.37	1.71	1.60	2.11
-10	2.54	1.17	1.06	2.40
-20	2.07	0.77	0.69	3.00
-30	1.47	0.52	0.48	3.06

$$D_{solv} = \frac{kT}{c\pi\eta r_s^{solv}} \quad D_{ion} = \frac{kT}{c\pi\eta r_s^{ion}}$$

$$R = \frac{D_{solv}}{D_{ion}} \propto \frac{r_s^{ion}}{r_s^{solv}}$$

Hydrodynamic Size increases!

at Low temperatures

D. Problem & Design

Ionic Conductivity decrease

↓

Major kinetic barrier

: **Desolvation** process

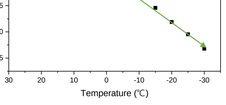
↓

(Solvation structure change)

↓

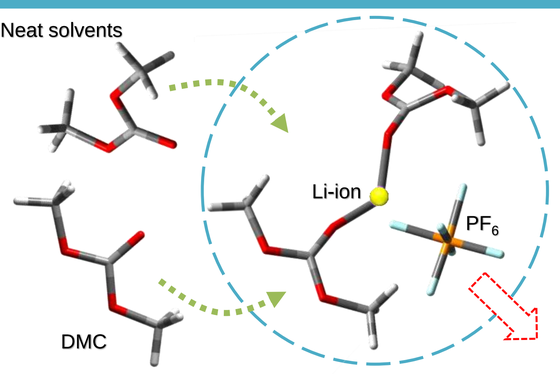
Size of solvation shell

increase

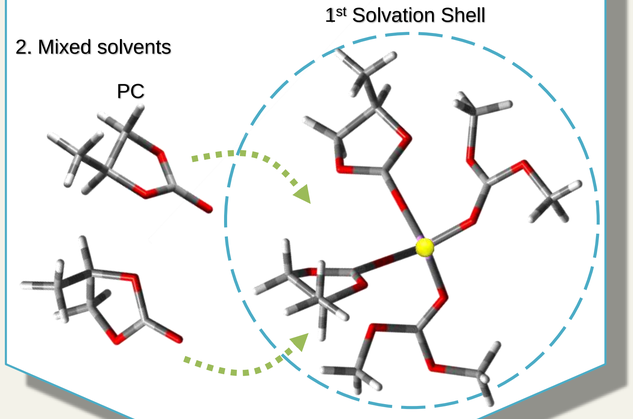


Ⅲ. Experiment Result

1. Neat solvents

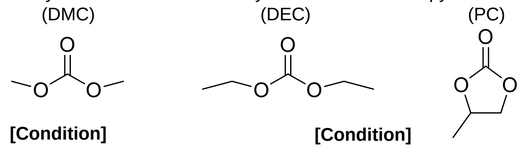


2. Mixed solvents



1. Neat Solvents (electrolytes)

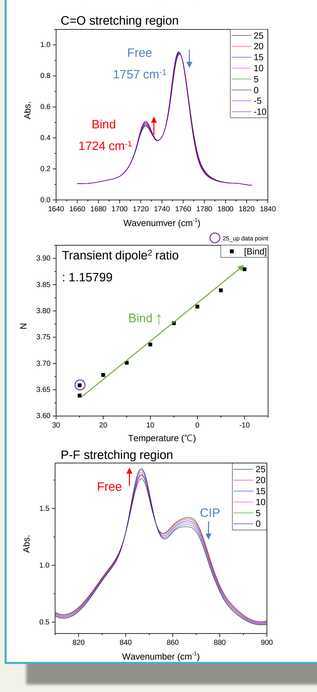
Dimethyl Carbonate (DMC) | Diethyl Carbonate (DEC) | Propylene Carbonate (PC)



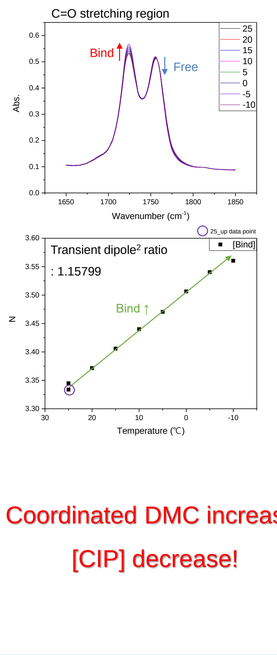
Solvation Number N

$$N = \frac{I_{Bind}}{I_{Free} + I_{Bind}} \frac{\#\ of\ tot\ Solvent}{C_{LiPF_6}}$$

[Condition]
Sample : DMC 1M $LiPF_6$
Temperature (5 ℃) : 25 ↔ -10



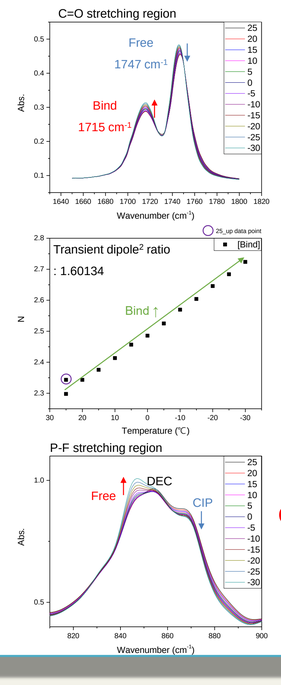
[Condition]
Sample : DMC 2M $LiPF_6$
Temperature (5 ℃) : 25 ↔ -10



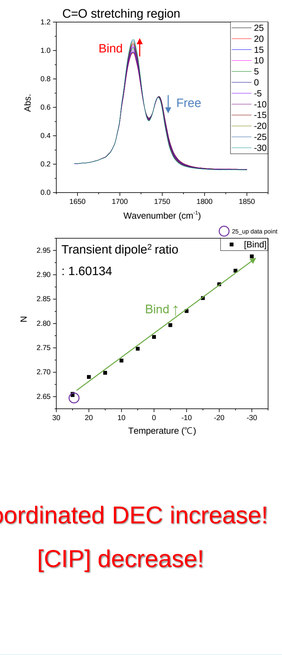
Coordinated DMC increase!

[CIP] decrease!

[Condition]
Sample : DEC 1M $LiPF_6$
Temperature (5 ℃) : 25 ↔ -30



[Condition]
Sample : DEC 1M $LiPF_6$
Temperature (5 ℃) : 25 ↔ -30

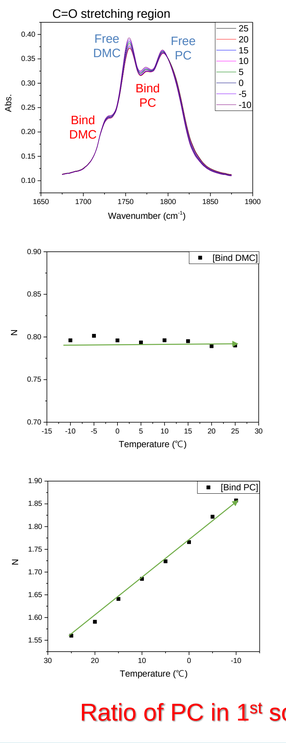


Coordinated DEC increase!

[CIP] decrease!

2. Mixed Solvents (electrolytes)

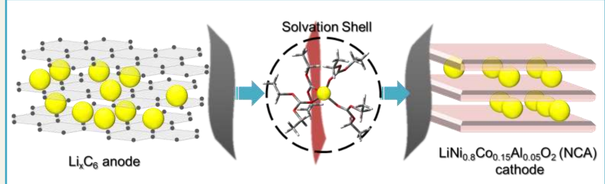
[Condition]
Sample : DMCPC(v/v 1:1)
1.5 M $LiPF_6$
Temperature (5 ℃) : 25 ↔ -10



[Condition]
Sample : DECPC(v/v 1:1)
1.5 M $LiPF_6$
Temperature (5 ℃) : 25 ↔ -30

Ratio of PC in 1st solvation shell increase!

Ⅳ. Conclusion



Temperature decrease

↓

Size of Solvation Shell increase

↓

Mobility of Charge carrier decrease

of Charge carrier ~~decrease~~ increase

↓

Conductivity decrease

1. Conclusion

Ionic Conductivity decrease

↓

Major kinetic barrier

: **Desolvation** process

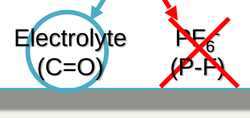
↓

(Solvation structure change)

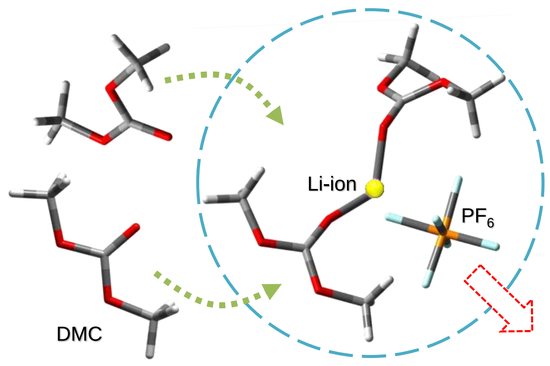
↓

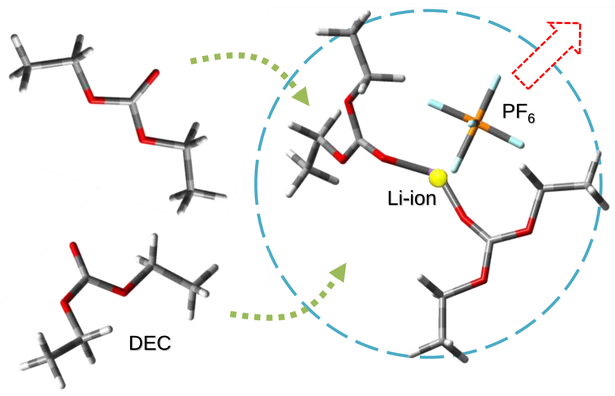
Size of solvation shell

increase



2. Future Work





❖ The quantitative analysis of [CIP] in the P-F stretching region.

❖ Confirm the equilibrium states by calculating the exchange ratio between electrolytes and PF_6^-.