

# Equilibrium Dynamics in Electrolytes of Li-Ion Battery Studied by Two-Dimensional IR Spectroscopy

Kyung-Koo Lee<sup>a</sup>, Kwanhee Park<sup>b</sup>, Kyungwon Kwak<sup>b\*</sup> and Minhaeng Cho<sup>b</sup>

<sup>a</sup>Department of Chemistry, Kunsan National University, Gunsan, Jeonbuk 573-701, Korea

<sup>b</sup>Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS) and Department of Chemistry, Korea University, Seoul 136-713, Korea, \*kkwak@korea.ac.kr

The solvation structures and dynamics of Li ions in liquid electrolyte play an essential role to Li-based battery performance. To mimic commercial electrolyte, Li<sup>+</sup> were dissolved in diethylcarbonate and its solvation behavior was observed with time-resolved IR spectroscopies. 2D-IR experiments show that there is fast equilibrium solvation dynamics around Li-ion.

Electrolytes are ubiquitous and indispensable in all electrochemical devices including electrolytic cells, capacitors, fuel cells, or batteries. Moreover, their function is the same in devices for serving as the medium for the ion transport between electrodes. The electrolyte determines how fast the energy could be released by controlling the rate of mass flow within the battery. After making solid electrolyte interphase on the carbonaceous anode, there is no decomposition in electrolyte and Li ion transport occurs through electrolyte. Thus, it has been suggested that the solvation structures and dynamics of Li ions in liquid electrolyte play an essential role to Li-based battery performance. To mimic commercial electrolyte composition composed of carbonates, Li ion were dissolved in diethylcarbonate (DEC) and its solvation behavior was observed with IR spectroscopy as well as time-resolved IR spectroscopies including IR pump-probe and 2D-IR experiments. IR spectroscopic results combined with DFT study reveals the possible solvation structure and major interaction site for Li ion. Subsequent 2D-IR experiments show that there is fast equilibrium solvation dynamics around Li-ion, which might give some clues about the molecular mechanism of Li ion transport through electrolyte. [1-3].

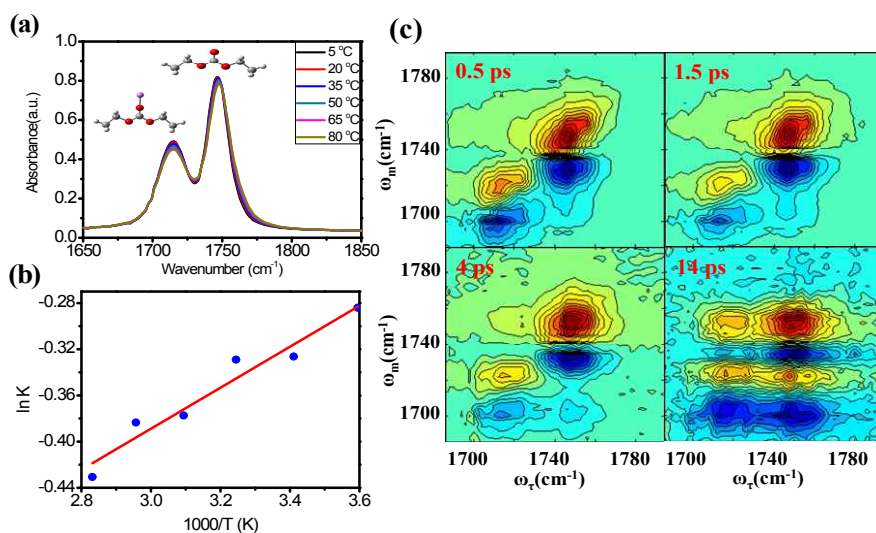


Fig.1 (a) The temperature-dependent linear absorption spectra of C=O stretching band of diethylcarbonate (DEC) dissolving LiPF<sub>6</sub> and (b) van't Hoff plot to get the enthalpy and entropy of formation. (c) 2D-IR spectra at several waiting times show that there is fast solvation shell exchange around Li<sup>+</sup> ion.

[1] K. Xu., Chem. Rev. **114**, 11503 (2014).

[2] X. Bogle, JPCL. **4**, 1664 (2013).

[3] K. M. Abraham, JPCL. **6**, 830 (2015)