Abstract #1133, 224th ECS Meeting, © 2013 The Electrochemical Society

Understanding Li^+-Carbonate Interaction in Electrolytes with ^{17}O-NMR

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To understand how Li^+ interacts with individual carbonate molecules in nonaqueous electrolytes, we conducted natural abundance ^{17}O NMR measurements on electrolyte solutions of 1 M $LiPF_6$ in a series of binary solvent mixtures of ethylene carbonate (EC) and dimethyl carbonate (DMC).

It was observed that the largest changes in ^{17}O chemical shift occurred at the carbonyl oxygens of EC, firmly establishing that Li^+ strongly prefers EC over DMC in typical nonaqueous electrolytes, while mainly coordinating with carbonyl rather than ethereal oxygens. Further quantitative analysis of the displacements in ^{17}O chemical shifts renders a detailed Li^+-solvation structure in these electrolyte solutions, revealing that maximum six EC molecules can coexist in the Li^+-solvation sheath, while DMC association with Li^+ is more "noncommittal" but simultaneously prevalent. This discovery, while aligning well with previous fragmental knowledge about Li^+-solvation, reveals for the first time a complete picture of Li^+ solvation structure in nonaqueous electrolytes.

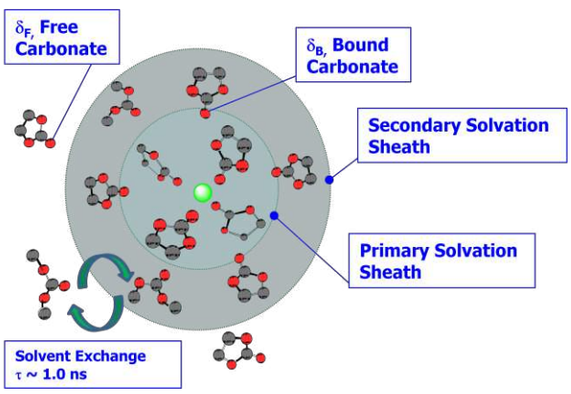

Fig. 1 Schematic drawing of Li^+-solvation sheath structure and the corresponding ^{17}O-NMR chemical shifts.

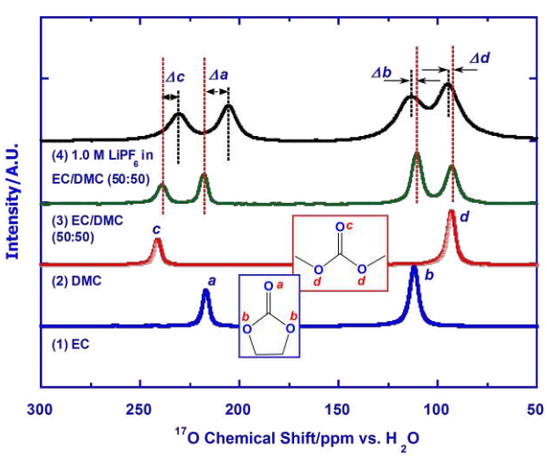

Fig. 2 ^{17}O-NMR chemical shifts as function of solvent mixing and Li-salt addition.

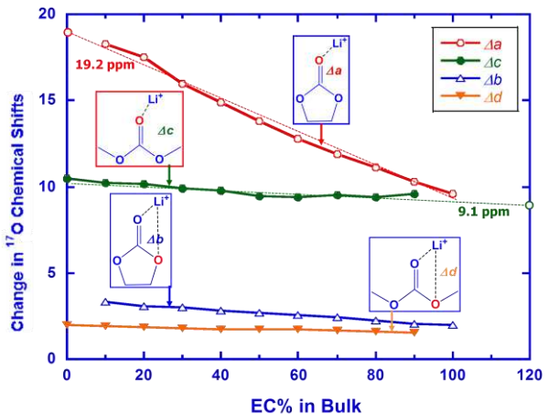

Fig. 3 ^{17}O-NMR chemical shifts of carbonyl- and ethereal-oxygens in cyclic and acyclic carbonates as the result of Li^+-induction.

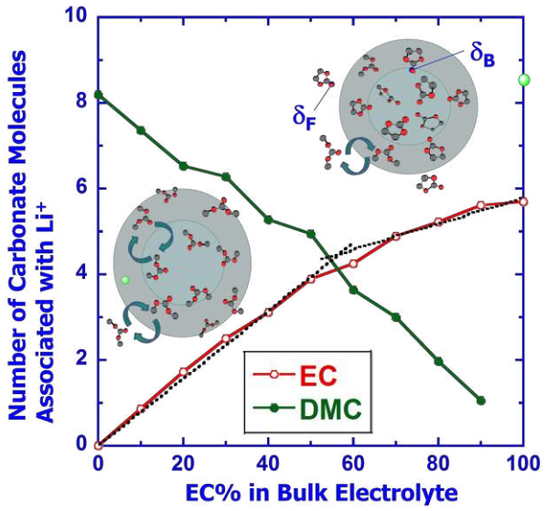

Fig. 4 Detailed structure Li^+-solvation with primary- and secondary spheres.

Reference:

1. X. Bogle, R. Vazquez, S. Greenbaum, A. v. Cresce, and Kang Xu, J. Chem. Phys. Lett., **2013**, 4, 1664