

The Reduction Resistant Electrolyte An MO Study

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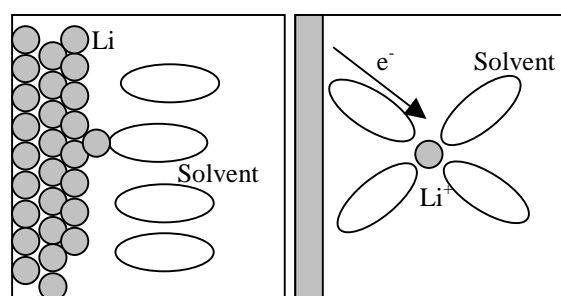
For the Li-ion batteries, the decomposition reaction of an electrolyte at a negative electrode is the first step for the formation of a solid electrolyte interphase (SEI). This reduction reaction mechanism has been studied experimentally and theoretically, but it is not clearly understood.¹⁾ We have studied the reduction reaction of the electrolyte by using *ab initio* molecular orbital methods.

Fig. 1 shows the two possible decomposition schemes which we have investigated for the reduction. The scheme A is that a solvent molecule is decomposed on the electrode, while the scheme B is that the solvent molecule is decomposed in the electrolyte. In the former scheme, the solvent molecule, which solvates a Li⁺ ion in the electrolyte, decomposes on the electrode surface after the Li⁺ ion is transferred to the electrode as Li atom. The latter scheme means the decomposition occurs just at the moment when the Li-solvent complex accepts one electron from the electrode. Here we will report the study of the Scheme A together with previous results of the Scheme B.

Fig. 2 shows the conformational change for the solvated Li⁺ cation which accepts one electron. The solvent is 1,3-dioxolane (DOL). The Li⁺ is coordinated by four DOL molecules, on the other hand, the neutral Li atom is coordinated by three molecules with a pyramidal structure. The excess DOL molecule seems to be removed without any energy barrier along the approximate reaction path. A schematic energy diagram is shown in Fig.3. The solvation energy for Li⁺ with DOL is about 130 kcal/mol, and the electron affinity energy of this complex is about 18 kcal/mol. The neutral Li atom in the electrolyte is stabilized by 35 kcal/mol with the solvent molecules, but the heat of vaporization of Li metal is 35 kcal/mol, so that the Li metal formation seems to be very smooth. The scheme B above mentioned is corresponding to the another branch from the middle of Fig. 3.

Fig. 4 shows the reaction path after the Li formation. In this calculation, the electrode is simulated by 15 Li atoms cluster with one negative charge, and tetrahydrofuran (THF) is used as a solvent which resists against the reduction. The activation barrier from the initial adduct to the transition state is rather high (63 kcal/mol). Our previous calculation for ethylene carbonate (EC) indicates much lower barrier height (9 kcal/mol). This suggests slow reaction rate for the reduction of THF at the negative electrode.

1) Y. Wan, S. Nakamura, M. Ue, and P. B. Balubuena,
J. Am. Chem. Soc., **123**, 11708 (2002).



Scheme A
Decomposition
on the electrode

Scheme B
Decomposition
in the electrolyte

Fig. 1 Hypothetical decomposition scheme
of the solvent molecule.

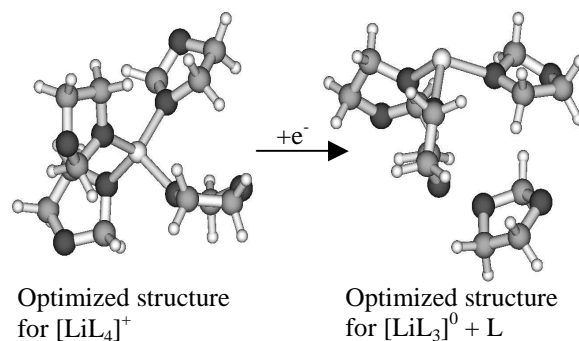


Fig. 2 Conformational change for solvated Li⁺
cation upon reduction (HF/6-31G).

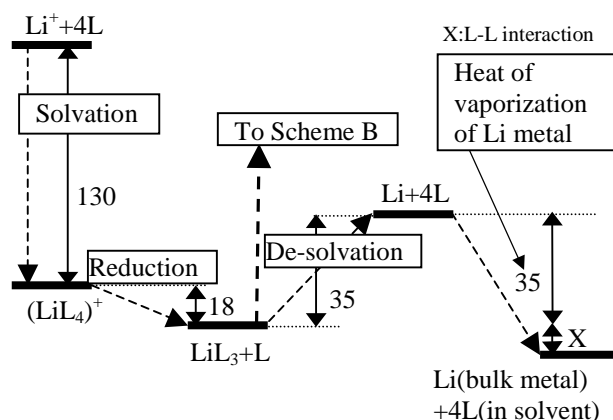


Fig. 3 Schematic energy diagram for Li-solvent
complex (kcal/mol)

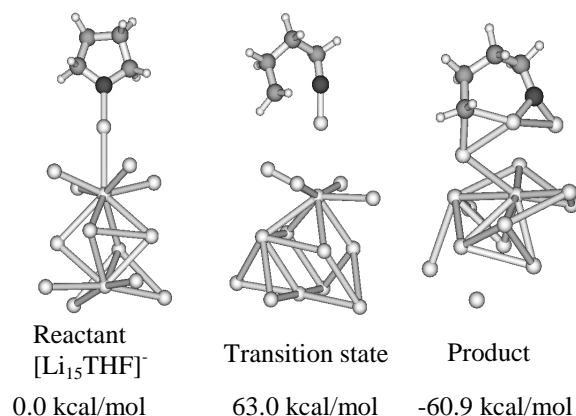


Fig. 4 Calculated reaction path of Li₁₅-THF cluster
(HF/6-31G)