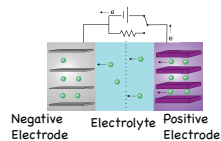


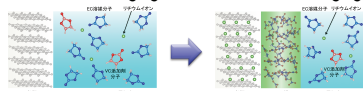
Introduction

Lithium Ion Battery (LIB) is a central target to resolve current energy issues.



Before first charging

After first charging



Solid Electrolyte Interphase (SEI)



©NTSB
Thermal runaway

- "Solid Electrolyte Interface (SEI)" is formed at the first charging
- SEI plays a role of electronic insulator but transporting Li⁺ ions.
- Quality of SEI controls capacity, power & safety, cycle life of LIB.
- Characterisation & control of SEI is crucial for future development of LIB with high performance & high safety.

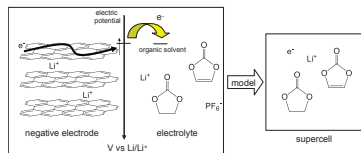
Our target:

- Thermodynamics & kinetics of the reductive decomposition and the subsequent oligomerisation of the electrolyte molecules toward SEI formation on the atomic scale.
- Most typical case: ethylene carbonate (EC) solvent & vinylene carbonate (VC) additive.

Methods

Reduction condition model

(Low potential model: V ~ 0 V vs. Li/Li⁺
Constant number of electrons.)



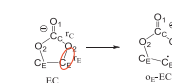
DFT Car-Parrinello MD

EC system (32EC) &
EC/VC system (31EC/VC)
with/without Li⁺ ion.



- + Periodic boundary condition (PBC)
- + Cubic supercell with a=15.24 Å
- + Plane wave basis with 90 Ry cutoff
- + PBE functional
- + T=353K (Nose thermostat)
- + Δt=5 a.u. (~0.12 fs)
- + Several initial configurations
- % supplemental cluster BC calc. with B3LYP

Blue-moon ensemble for free energy profile



Constrained MD w.r.t.
reaction coordinate

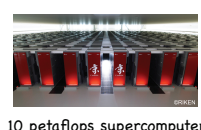
$$\frac{dA}{dx} = \frac{(Z^{-1/2}[-\lambda + kT G])_{x'}}{(Z^{-1/2})_{x'}}$$

Potential of mean force

$$A(x_b) - A(x_a) = \int_{x_a}^{x_b} dx' \frac{dA}{dx'}$$

Free energy profile

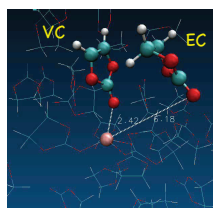
Tuned CPMD for K computer



10 petaflops supercomputer

- + Hybrid parallel calc. (Tuning achieved a rather high efficiency)
- + Parallel Blue-moon ensemble (statCPMD@NIMS)
- + Parallel I/O (statCPMD@NIMS)

Solvation & Reduction



Before reduction

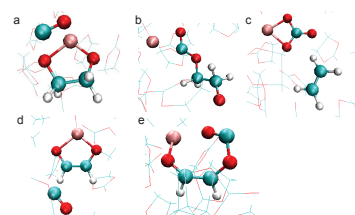
Li⁺-4EC < Li⁺-3ECVC by 9.6 kcal/mol
VC is not coordinating to Li⁺.

After reduction

Li⁺-3ECVC < Li⁺-3ECEC < VC⁻ < EC⁻
Electron first goes to VC (not coordinating to Li⁺)
→ Transfer to EC coordinating to Li⁺
→ VC⁻ is migrating into the solvation shell

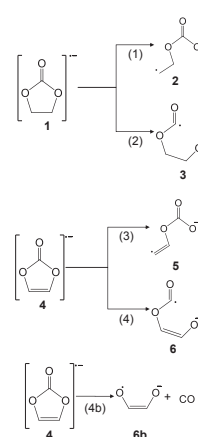
EC can be reduced even in the presence of VC.

Two electron (2e) reductive decomposition

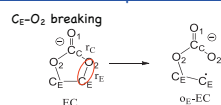


- # a,b: Reactant = undecomposed EC-CO evolution
- # c: Reactant = O₂-EC⁻
C₂H₄ and CO₃²⁻ evolution
consistent with experiments
- # d,e: Reactant = undecomposed VC
CO evolution
similar to 1e reductive decomposition

One electron (1e) reductive decomposition



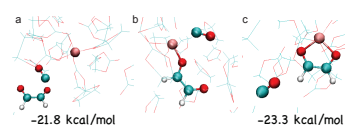
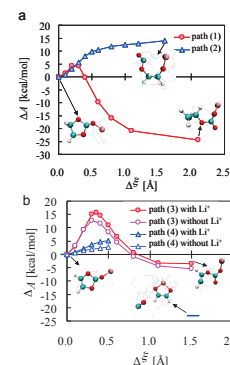
Reductive decomposition of EC



C_E-O₂ : ΔA[#] = 4.8, ΔA = -24.5 (kcal/mol)
→ Li⁺ - O₁O₂C₂O₂C₂H₄

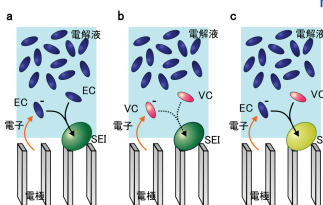
Reductive decomposition of VC

C_C-O₂ : ΔA[#] ~ 5, ΔE = -21 ~ -23 (kcal/mol)
→ CO evolution
% Conventional = C_E-O₂



Conclusion

Summary of the reductive decomposition reactions of EC and EC/VC systems.



- (a) EC only case: EC radical oligomerisation following 2e reduction will be the source of SEI.
- (b) A conventional pathway for the EC/VC system, namely oligomerisation of VC anion radical sacrificially reduced.
- (c) A new mechanism with 1e reduction only for the EC/VC system, proposed in this work. VC passivates the EC anion radical.

Because the present VC mechanism is realized via 1e reduction, the irreversible capacity at the SEI formation will decrease, consistent with the experiments.

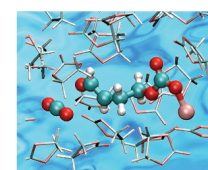
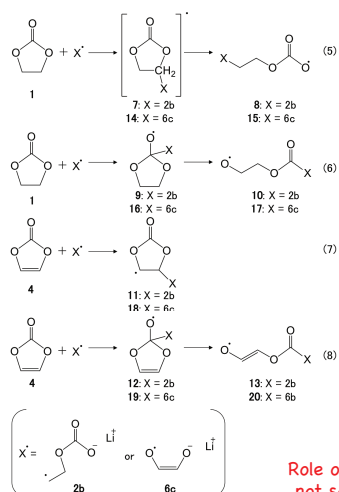
These results not only reveal the primary role of the VC additive in the EC solvent, but also provide a new fundamental perspective for the reductive decomposition of carbonate-based electrolyte near the negative electrode.

Future computational design of novel electrolytes (solvents & additives) with higher performance as well as higher safety.

Acknowledgements

K.S. and Y.T. were partly supported by KAKENHI (# 23340089). This work also supported by the Strategic Programs for Innovative Research (SPIRE), MEXT, and the Computational Materials Science Initiative (CMSI), Japan. The calculations in this work were carried out on the K computer at the RIKEN AICS through the HPCI Systems Research Projects (Proposal Numbers hp120181 and hp130021), the Fujitsu PRIMEHPC FX10 System in the Information Technology Center, The University of Tokyo, and the supercomputer center of NIMS.

Radical attack under 1e condition



VC radical + intact EC: endothermic
EC radical + intact VC: exothermic
ΔA[#] = 9.7, ΔA = -16.2 (kcal/mol)

Role of VC additive is to passivate the EC anion radical, not sacrificial reductive decomposition & oligomerisation.