

Theoretical study of the solvation effect on the reductive reaction of vinylene carbonate in Lithium-ion Batteries

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The reductive reactions in the organic electrolyte solutions of Lithium ion batteries (LIBs) play important roles to the safety, power, capability, and cycle life of LIBs.¹ Since the reaction intermediates are anionic radicals and strong electrostatic interaction with the other solvent molecules occurs, a crucial key to understand the reactions in LIBs is the solvation effects. In the present study, we focused on the CO generation reaction of vinylene carbonate (VC) shown in Fig. 1, and evaluated the solvation effects on this process using RISM-SCF-SEDD method.² RISM-SCF-SEDD method is a hybrid methodology of quantum chemistry and statistical mechanics for molecular liquids. Thanks to the inherent of RISM theory, solvation free energy can be computed in the analytical fashion, together with molecular level information of solvent distribution.

Geometry optimizations were carried out by DFT(B3LYP) with cc-pVDZ (hydrogen) and aug-cc-pVDZ (carbon and oxygen) basis sets. All the energy was then evaluated with the ROCCSD method using the same basis set both in the gas phase as well as in the solutions. Computations in pure ethylene carbonate (EC) and in 1.0 M LiClO₄/EC at 323 K were then carried out with the RISM-SCF-SEDD method. The RISM integral equation was solved with the Kovalenko-Hirata closure.

At the neutral state (**1**), VC has planar structure. After the ionization (**1'**), the structure hardly changes and both **1** and **1'** are C_{2v} symmetries. From **1'** to **2'**, the structure around C_{v1} is changed from planar to tetrahedral via the transition state (TS_{1'2}). Then the dissociation of C_{v1}-O_{v3} bond occurs and finally CO is produced by the dissociation of C_{v1}-O_{v2} bond. Fig. 2 shows the free energy changes along the CO generation pathway. In the solutions, all anionic species are stabilized compared with those in the gas phase and the profile is largely changed. After the ionization, the free energy barriers in the entire reaction in EC and in 1.0 M LiClO₄/EC are 11.08, and 19.46 kcal mol⁻¹, respectively. Hence, the Lithium salt suppress the CO generation after the ionization of VC.

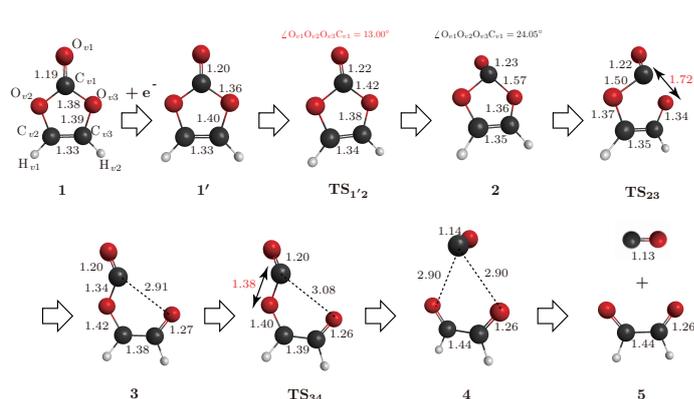


Fig. 1: CO generation pathway of VC in the gas phase. Species **5** is defined as the sum of products at infinite separation.

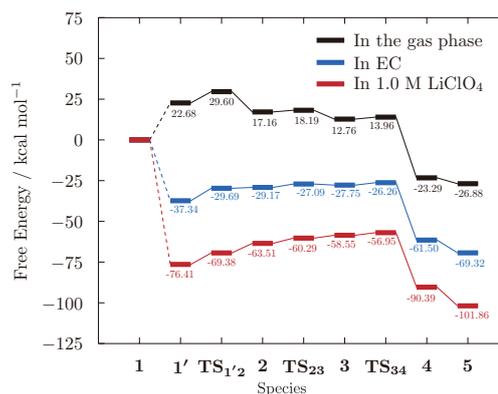


Fig. 2: The free energy changes along the CO generation pathway in the gas phase, EC and 1.0 M LiClO₄/EC solutions.

¹P. B. Balbuena et al., *Lithium-ion batteries Solid-Electrolyte Interphase*, Imperial College Press (2004).

²D. Yokogawa et al., *J. Chem. Phys.*, **126**, 244504 (2007).