Influence of Anions on Propylene Carbonate Oxidative Decomposition Pathways from DFT Calculations

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Lithium salts dissolved in non-aqueous organic electrolytes have been widely used in commercial lithium ion batteries. Understanding the electrolyte stability and decomposition pathways is important for battery design and optimization processes, particularly for high voltage cathodes. However, the influence of the salt anion chemistry and involvement of anion in the electrolyte oxidation decomposition are still controversial.2-4

In this work, we build upon previous studies of the oxidation decomposition mechanism of isolated organic solvents and investigate the influence of two anions (PF6− and ClO4−) on the decomposition pathways of propylene carbonate (PC) using density functional molecular orbital theory (DFT).5 The results from our calculation indicate that the presence of PF6− and ClO4− anions significantly reduce the oxidative stability of PC, stabilize the PC-anion oxidation decomposition products and change the order of the oxidation decomposition paths, as shown in Figure 1. We also found PC-ClO4− oxidative decomposition to be more intense than PC-PF6− oxidative decomposition due to lower oxidative potential and a barrier the CO2 and acetone formation reaction. This has been proved by the study of Arakawa et al.6, they reported that the gas volume generated during PC-Li salt electrolyte oxidation to follow the order LiClO4− > LiBF4 > LiAsF6 > LiPF6.

The primary oxidative decomposition products of PC-PF6− and PC-ClO4− are CO2 and acetone radical that polymerize into poly(ethylene carbonate), which are in good agreement with the conclusion from experiment studies.7,8

References