

Electrochemical and Thermal Stability of Organosilicon
Electrolytes for Lithium Ion Batteries

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Organosilicon (OS) electrolytes are promising substitutes for commercial carbonate-based electrolytes because of their low flammability and high electrochemical and thermal stability. In order to understand the factors that ultimately control the stability of these compounds in formulated electrolytes and operational lithium ion batteries, we have undertaken a comprehensive analysis that integrates analysis of the gas-phase and surface products with computational studies of molecular electronic structure. A real-time headspace analysis apparatus that integrates a mass spectrometer with a temperature-controlled electrochemical cell can be used to detect the evolution of gas-phase decomposition products at specific temperatures during thermal cycling or at specific potentials during electrochemical measurements. XPS analysis of the electrodes provides complementary analysis of the surfaces. Finally, density functional calculations have been used to understand the relationships between OS molecular structure and stability.

In this work we report studies using the molecule 1NM3 as a model OS compound, investigating its stability and decomposition pathways with LiPF₆ salt at high temperatures and high potentials. We show that PF₅ species (and not F⁻) from LiPF₆ decomposition fluorinate 1NM3 molecules and facilitate the 1NM3 hydrolysis reaction at high temperature above 100 °C or at extreme potentials. In the absence of additional additives or blends, anode SEI layers are formed by fragmentation of the Si-O bond, leaving the SEI layer comprised largely of ethylene glycol fragments combined with LiF. The formation of the SEI layer can be manipulated through alternation of the molecular structure or through incorporation of SEI-forming additives such as vinyl carbonate. Ultimately this integrated approach provides fundamental insights into the factors controlling the chemical and electrochemical stability of OS compounds and leads to a systematic pathway toward the design of electrolytes with enhanced electrochemical performance. *RJH and RW have a financial interest in the outcome of this work.