

Organosilicon-based electrolytes with enhanced thermal and electrochemical stability to enable high energy lithium ion batteries

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Organosilicon (OS) electrolytes have been developed as a viable alternative to conventional carbonate electrolytes for lithium ion batteries^{1,2}. This novel organosilicon chemistry involves the merging of a silane with a lithium coordinating functionality, such as polyethylene oxide units. This combination results in solvents comprised of low molecular-weight molecules and having unique properties including high thermal stability, high flash point, low vapor pressure and relatively low viscosities.

Mechanistic studies of the reactivity of “Gen-1” original compounds³ in lithium ion battery geometries has led to the development of a new series of compounds, including more stable “Gen-1” compounds (e.g., 1ND2) and new “Gen-2” compounds (e.g., F1S3M2) whose thermal, chemical, and electrochemical properties surpass those of the initial suite of OS compounds. Specific examples of performance improvement include improved thermal stability, improved voltage stability at both the cathodic and anodic extremes, and higher flash point; in many cases exceeding 100°C when formulated into electrolytes with LiPF₆.

The primary structural difference between our “Gen-1” and “Gen-2” families of compounds concerns the substituents on the Si atom. There is a very broad set of applications for organosilanes and thus many possibilities to finely tune the properties that need to be enhanced in a molecule. Our 1st generation OS compounds, including 1NM3, are characterized by a Si-O bond, which is responsible for the excellent thermal stability of silicone polymers and enabled the production of OS electrolytes with high thermal stability. Encouraged by the successful results for “Gen-1” compounds, Silatronix performed mechanistic studies that identified “Gen-2” structural variants that provide even greater stability under more aggressive conditions. “Gen-2” OS solvents have thermal, chemical, and electrochemical properties that surpass those of the original compounds by introducing a less polar (i.e., more stable) Si-C bond, which is less susceptible to attack by fluorinated species, (e.g., HF and PF₅). For example, the onset temperature for decomposition of “Gen-2” molecules with LiPF₆ is increased by at least 50°C compared to “Gen-1”, with significantly lower reaction rates.

In this work, we focus on a series of fluorinated “Gen-2” compounds. Among the many substituents that can be placed on the silicon atom, fluorine could impart higher electrochemical stability to the molecule, because the Si-F bond is the strongest of all single bonds formed by silicon. For this we prepared a series of fluoro-organosilanes (FOS) using different synthesis methods

and we have evaluated their physical properties (e.g., conductivity, viscosity, flash point), thermal and electrochemical stability, and performance in coin cells.

For example, the thermal stability of OS-based electrolytes was evaluated using a real-time headspace analysis apparatus that integrates a mass spectrometer with a temperature-controlled cell to detect the evolution of gas-phase decomposition products at specific temperatures, shown in Figure 1. ¹H and ¹⁹F NMR was conducted on the remaining liquid to quantify the extent of decomposition of the OS material. Figure 2 summarizes this data for two OS electrolytes containing a “Gen-1” OS solvent (1ND2) or a “Gen-2” OS solvent (F1S3M2). This data clearly shows the enhanced thermal stability of the F1S3M2 structural variant.

*RJH and RW have a financial interest in the outcome of this work.

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Custom Temperature Controlled Atmospheric Mass Spectrometer Setup

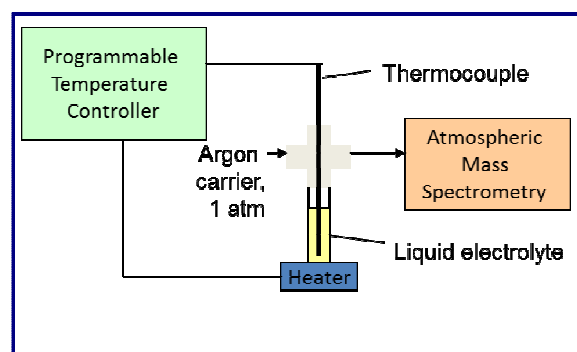


Figure 1: Custom apparatus for the real-time analysis of gas-phase decomposition of liquid electrolyte.

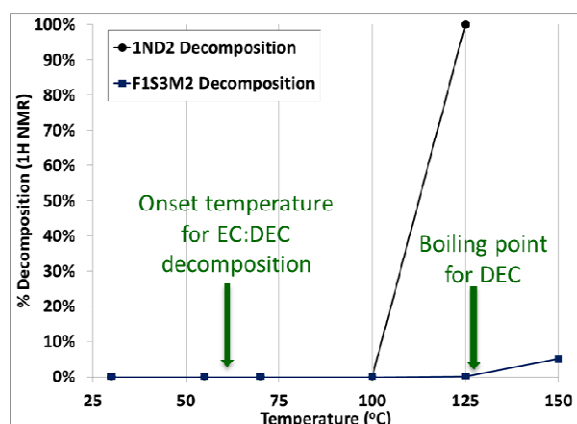


Figure 2: Extent of thermal decomposition for OS-based electrolytes with LiPF₆.