

Advanced Electrolyte Solvents to Enable High Ni NMC Lithium Ion Batteries

Tobias O. Johnson, Monica L. Usrey, Peng Du, Sarah Guillot, and Brian Kerber

Koura Global, Inc. 3587 Anderson Street, Suite 108, Madison WI 53704

tobias.johnson@kouraglobal.com 1-608-661-1961

Abstract: Traditional commercial electrolytes based on carbonate solvents limit the long-term cycling stability, high voltage stability, and thermal stability of lithium-ion batteries (LIB) with high-Nickel NMC cathodes. Thus, there is significant research in the battery field towards developing electrolyte solvents and additives with improved electrochemical and thermal stability. To rationally design next generation electrolytes, a fundamental understanding of how these molecules function in the battery including mechanisms of solvation, surface interaction, and bulk reactivity and how the structure of the molecule contributes to its properties and behavior is required.

Silatronix has developed a series of organosilicon (OS) materials over several years through molecular design to target specific Li-ion battery performance-related characteristics. This design process included selection of specific ion coordinating functional groups, degree of fluorination, and structure optimization to balance molecular polarity, ionic conductivity, and viscosity. The inclusion of Si in the molecule has proved to be essential for maintaining improved thermal and electrochemical stability.

In addition, Silatronix has developed an optimized suite of tools and best practices that pair a commercially relevant comprehensive performance evaluation with the fundamental electrolyte understanding required to guide additional molecular design and optimization. This process elucidates structure-property relationships to optimize electrolyte formulation for high Ni NMC/graphite Li-ion cells. OS materials applied at only 0.5% to 3% of electrolyte composition have demonstrated improved high-temperature performance, including higher capacity retention, with significantly reduced gas generation and reduced impedance growth. In this paper, we discuss the cell-level performance benefits conferred by OS materials with nitrile-functionality for Li-ion cells with high-nickel cathode materials.

Keywords:

Electrolyte; Lithium Ion; solvent; organosilicon; OS; OS3[®]; LIB; Li, high nickel; thermal stability; oxidation; reduction; impedance; safety; solvation; LiPF₆; SEI; solid electrolyte interphase; energy storage; DSC; ONR; NMC; graphite; gassing; Office of Naval Research; DOD; battery; cell; molecule; electrochemistry; fluorine; Si, Silicon, anode; cathode; NMC811

Introduction

Silatronix[®] has developed a series of organosilicon (OS) materials using targeted molecular design to provide functional characteristics desirable for LIB applications.

Design of unique organosilicon molecules includes selection of specific ion coordinating functional groups, degree of fluorination, and structure optimization to balance molecular polarity, ionic conductivity, and viscosity (Figure 1).

The inclusion of Si in the molecule has proven to be essential for maintaining improved thermal and electrochemical stability. Multiple OS materials developed via this process have demonstrated excellent performance in LIB systems.

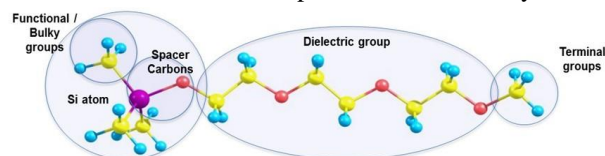


Figure 1. Organosilicon (OS) molecular design

Performance of OS3[®]

OS3[®] is an OS-nitrile solvent that is currently used in commercial Silicon-based anode cells. OS3[®] is also in advanced trials for use in next generation cell designs with partners in the USA, Europe, and Asia. The most comprehensive performance benefits have been observed at < 5 wt % OS3[®] in the electrolyte which fits comfortably within the additive market space of the LIB industry.

Properties of OS3[®]: The OS3[®] structure is balanced to provide excellent high voltage stability, thermal stability, low reactivity, low viscosity, high conductivity, high flash point / boiling point, and low vapor pressure (**Error! Reference source not found.**).

Table 1. Physical Characteristics of OS3[®]

Dielectric Constant	16.8
Flash Point	82 °C
Boiling Point	202 °C
Freezing Point	-57 °C
Density	0.93 g/cc
Viscosity	2 cP

Stabilizing of LiPF₆ salt:

OS3[®] is a strong coordinator of Li salts in electrolytes and prevents both decomposition of LiPF₆ and catalytic production of HF. Figure 2 demonstrates how addition of as little as 2% OS3[®] to a carbonate electrolyte with LiPF₆ results in removal of all initial HF and suppression of additional HF formation. Eliminating LiPF₆ decomposition reactions is critical to enabling high energy LIB systems with long calendar life and excellent high temperature performance. This OS3[®] mechanism protects all components in LIB cells which improves stability and reduces long-term impedance growth.

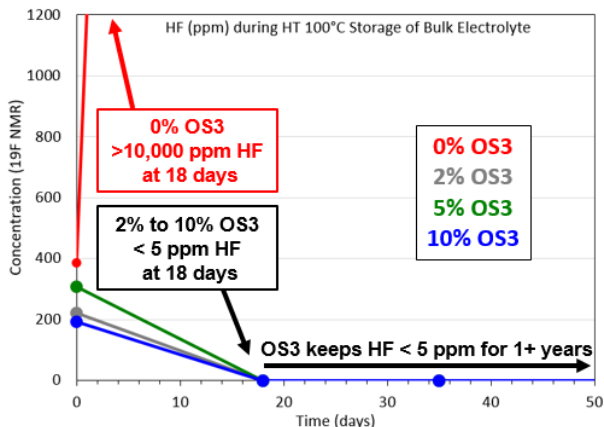


Figure 2. HF concentration in EC/DEC/LiPF₆/OS3[®] electrolytes during HT storage

Thermal stability enhancement:

OS materials have demonstrated the ability to reduce the thermal response of electrodes during differential scanning calorimetry (DSC). DSC testing of the high energy NMC622 cathode found lower peak heating rates and increased onset temperature (Figure 3) with 20% OS3[®]. In addition, several cell development partners have reported improved safety test results with low concentrations of OS3[®] (1% to 5%).

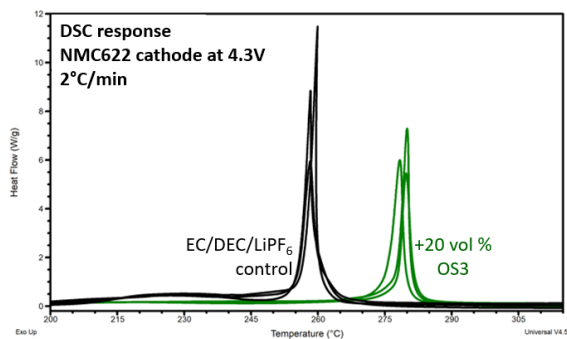


Figure 3. DSC response of OS materials with NMC cathode

Cell-level performance improvements:

Several commercial cell development partners in the US, Asia, and Europe have observed practical improvements to comprehensive battery cell performance; including excellent HT cycling stability, reduced impedance growth, improved calendar life rate capability, reduced gas generation, reduced pouch cell swelling, improved safety / abuse response, and improved low temperature rate capability. Benefits have been observed in various cathode and anode systems.

Full format cell level testing and fundamental research of OS technology has been completed with ONR funding on several programs, including both shipboard and NAVAIR targeted applications. OS3[®] has demonstrated improved HT stability, reduced gas generation, and reduced impedance

growth in multiple cell chemistries, including those utilizing high Ni NMC cathodes.

Molecular Engineering of OS Materials

As discussed above, the OS family of materials is quite versatile by design. As an example, several variations within the OS3[®] family (nitrile functionality) have been synthesized to target specific physical and electrochemical characteristics. Figure 4 shows the fundamental oxidation stability (on platinum electrodes) for several members of this family. The OS3[®]-family of materials offers improved oxidative stability compared to an EC/EMC baseline.

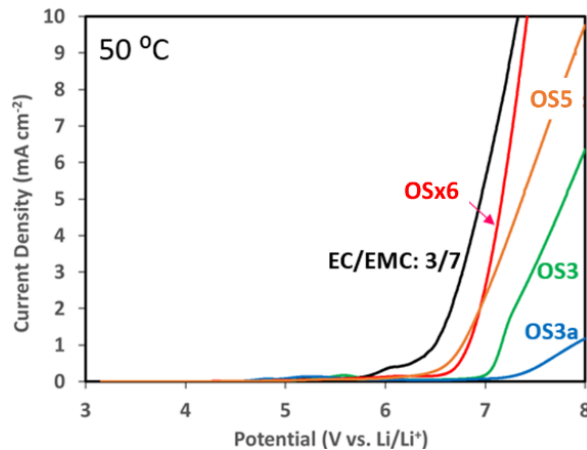


Figure 4. OS-nitrile solvent oxidative stability (Pt)

All members of the OS3[®] family of solvents share the same fundamental property benefits including strong solvation of Lithium salts, stabilization of Lithium salts, and increased oxidative stability (compared to carbonate control).

In this paper, we highlight and discuss the performance of OS3[®], OS5[™], OSx6 in LIB cells, including improved capacity retention, reduced impedance growth, and reduced gas generation. Performance of these materials in pouch cells with high-Ni cathodes and graphite anodes is summarized.

Results and Discussion

OS solvents have demonstrated comprehensive performance improvements in several LIB cell systems. The most significant improvements occur in high energy density applications which tend to apply more oxidative stress on the electrolyte on highly reactive active material surfaces. Observed benefits include HT and/or fast charge cycling stability, reduced impedance growth, reduced gas generation, and improved safety / abuse response.

45°C Cycling Performance Improvement

Performance of OS3[®] and OS5[™]

The nitrile-family of OS materials significantly improves the 45°C cycling stability of several high Ni NMC chemistries, including 4.35V Gr/NMC622 and 4.3V Gr/NMC811 cells. Addition of 3% OS3[®] or OS5[™] to a carbonate control

increased the capacity retention from 75% to 90% after 45°C cycling in ~230 mAh pouch cells with single-crystal NMC811 cathode and graphite anode cycled between 2.75V and 4.3V (Figure 5). The capacity retention benefit was accompanied by a significant reduction in cell gassing ($\geq 70\%$) and impedance growth, especially with OS5™.

XPS surface analysis on the NMC811 cathodes after 45°C cycling (Figure 6) shows the surface layer with OS3® is thicker (lower substrate signal), more inorganic (less C-O, C=O; more LiF and P), and primarily formed from decomposition of the LiPF₆ salt, not the carbonate solvents.

The presence of Si and N on the surface demonstrates that OS3® participates in surface layer formation, although its primary function is as a solvent that does not undergo significant consumption during cell operation. Overall, this higher inorganic content cathode layer formed by OS3® results in more stable HT cycling, reduced impedance, and reduced gas generation with high Ni NMC cathodes.

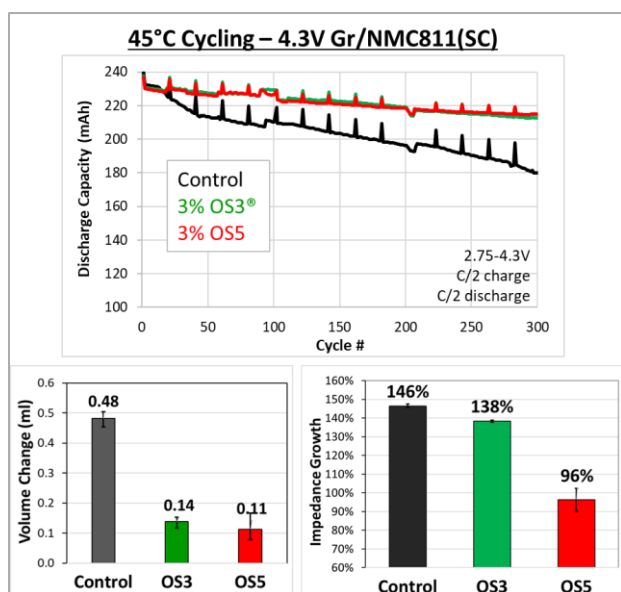


Figure 5. 45°C Cycling in 4.3V Gr/NMC/11(SC) cells.

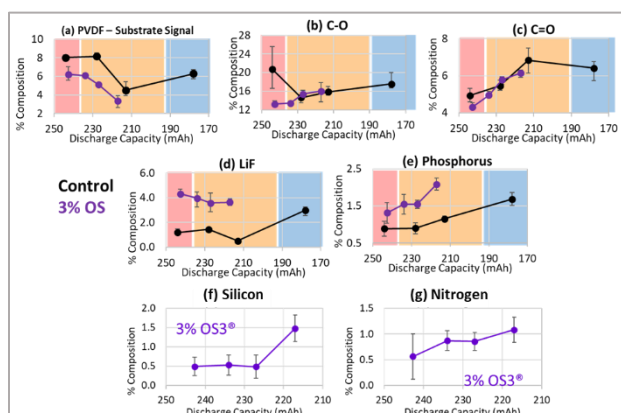


Figure 6. XPS surface analysis of NMC cathodes after 45°C cycling in 4.3V Gr/NMC811(Single Crystal) cells.

Performance of OSx6

Recent 45°C cycling experiments in ~230 mAh 4.3V Gr/NMC811 cells show that 1% OSx6 provides superior cycling stability to a control without any SEI layer forming additives (Figure 8) and outperforms 1% VC, a standard commercial additive for graphite LIB systems. Cells were cycled between 2.75V and 4.3V at C/2 charge and discharge.

To understand the source of performance improvement, modeling of the full cell impedance to estimate the anode and cathode contributions was conducted (Figure 7 – inset). The addition of OSx6 or VC significantly reduces the anode impedance after 45°C cycling with OSx6 providing the lowest anode contribution. The cathode impedance is reduced by both OSx6 and VC similarly and is likely not the source of the performance difference between these additives. This data shows that OSx6 can replace VC and provide a more stable anode/electrolyte interface.

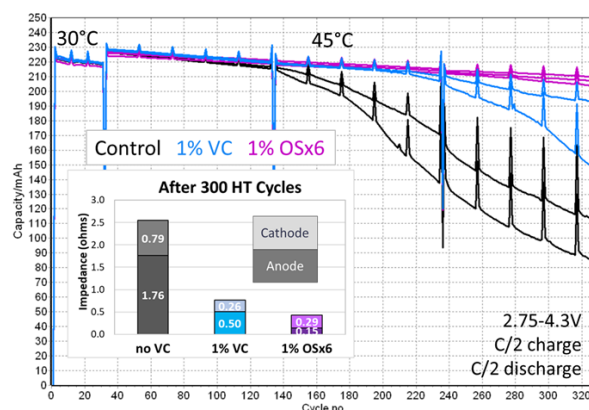


Figure 7. 45°C Cycling in 4.3V Gr/NMC/11(SC) cells.

45°C Fast Charge Cycling Performance Improvement

The comprehensive benefits provided by OS materials can enable operation under multiple extreme operating conditions. For example, both OS3® and OS5™ significantly improve 45°C fast charge cycling stability and reduce cell resistance in ~230 mAh 4.35V Gr/NMC622 cells at low concentration (3%) in a commercial carbonate electrolyte (Figure 8). Cells were cycled between 2.75V and 4.35V at 2C charge C/2 and discharge.

Visual analysis of the graphite anodes after fast charge cycling shows a significant reduction in Li plating with OS addition resulting in a 20-25% improvement in capacity loss depending on the specific OS material.

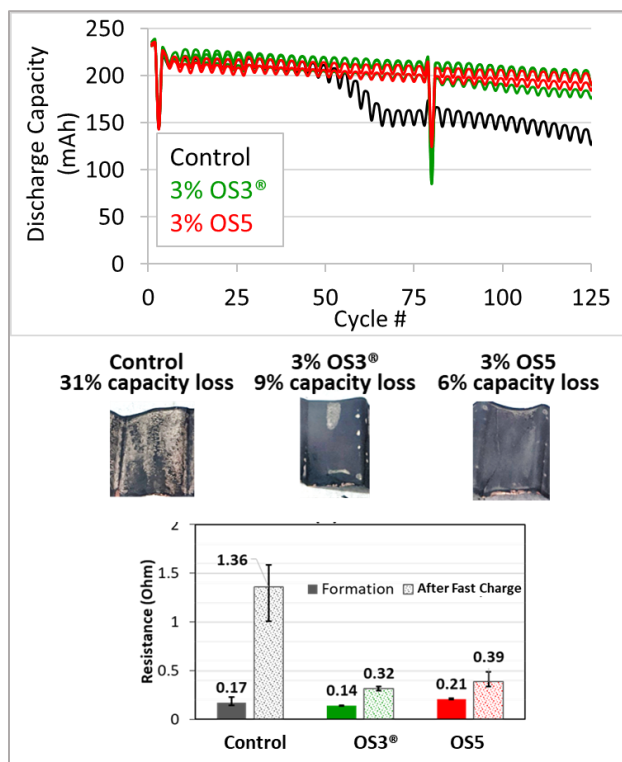


Figure 8. 45°C Fast Charge in 4.35V Gr/NMC622 cells.

60°C Storage Performance

The OS³ family of solvents also significantly reduce gas generation during HT/HV storage in high Ni NMC cells. Figure 9 shows that increasing gas reduction is observed with increasing OS³ concentration in 4.35V Gr/NMC622 cells. Composition analysis via GC-TCD shows the gas reduction is due to a reduction in all observed gas products, but primarily CO₂. For the control electrolyte, CO₂ is the majority decomposition species attributed to oxidation of carbonate solvents (e.g., EC) at the NMC811 surface.

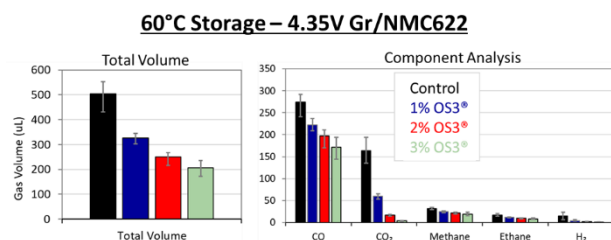


Figure 9: 60°C storage in 4.35V Gr/NMC622 cells.

60°C storage in 4.3V Gr/NMC811 cells with ¹³C-labeled EC in the electrolyte was conducted to understand the source of the CO₂ generation and elucidate the mechanism of OS³ gas reduction. This data (Figure 10) clearly shows that although EC is a significant source of CO₂, over 60% of the CO₂ generated is from “non-EC” sources. OS materials reduce CO₂ from all sources indicating that the OS gas reduction benefit is not limited to EC protection (Case 1) but is a surface effect (Case 2) or bulk effect (Case 3) or both (Cases 2 and 3) that provides more universal gas reduction.

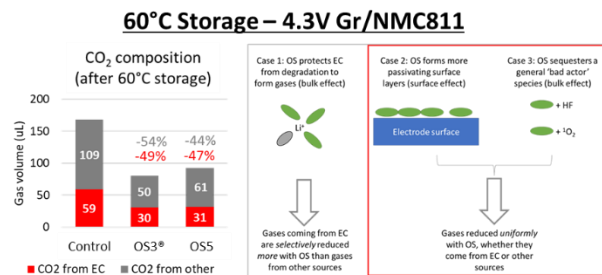


Figure 10: 60°C storage in 4.3V Gr/NMC811 cells with ¹³C-labeled EC for mechanistic studies.

Conclusions

Organosilicon (OS) solvents have demonstrated excellent performance in high Ni NMC cathode Lithium Ion Battery (LIB) systems. Silatronix[®] commercial product “OS3[®]” provides exceptional thermal and electrochemical stability. OS³ is a strong coordinator of Li salts and prevents LiPF₆ salt decomposition and catalytic production of HF, which is critical to enablement of high energy LIB systems with long calendar life and excellent high temperature performance.

Comprehensive LIB cell performance benefits have been observed with multiple OS family materials, including excellent HT cycling stability, reduced impedance growth, improved calendar life rate capability, reduced gas generation, reduced pouch cell swelling, and improved safety. Mechanistic studies indicate that the benefits provided by OS family solvents are due to a combination of bulk effects (e.g., LiPF₆ salt stabilization and HF removal) and surface effects (e.g., reduced charge transfer resistance, formation of stable surface layers).

Acknowledgements

The authors thank the Office of Naval Research (ONR), and the Department of Energy (DOE) for funding to advance organosilicon technology. These include ONR contracts N00014-15-C-0031, N00014-16-C-2025, N00014-17-C-2031, N00014-19-C-1009, N00014-21-C-1075; and DOE contract DE-EE0007232. Thanks to UW-Madison, Argonne National Lab, Army Research Laboratory, and NSWC Carderock for their collaboration.

References

- Guillot, S.L.; Usrey, M.; Peña-Hueso, A.; Kerber, B.; Zhou, L.; Du, P.; Johnson, T., Reduced Gassing In Lithium Ion Batteries With Organosilicon Additives. *Journal of the Electrochemical Society* 2021, 168, 030533.