

Fluorinated Battery Electrolytes for High Silicon Anodes and High Voltage Cell designs

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Abstract: Lithium-ion cells with high Si-content anodes encounter myriad challenges in delivering long term cycling stability due to anode pulverization, impedance growth, low efficiency, Lithium loss, and gassing. These factors are compounded when paired with high energy density cathodes (e.g., high-nickel, high-voltage lithium cobalt oxide - LCO). These high energy density designs (>400 Wh/kg) require finely balanced electrolyte formulations which often employ fluorinated solvents, blended Lithium salts, and various anode SEI and cathode CEI additives to stabilize the highly reactive surfaces.

Although Li-ion technology has advanced significantly over the last decade, traditional electrolytes can rapidly decompose in the high energy density systems at the highly reactive electrode surface interfaces. New advanced electrolytes must be integrated into the cell design to increase energy density, increase charge voltage, improve performance, reliability, and safety of Li-ion batteries.

We have commercialized an advanced organosilane (OS) solvent "OS3[®]" that prevents LiPF₆ decomposition, reduces solvent decomposition, passivates the cathode surface, scavenges HF, and enables fluorinated solvents like FEC to function more effectively. Due to these properties, OS3[®] has demonstrated performance improvements in high Si cells such as extended cycling stability with reduced cell gassing and impedance growth associated with FEC.

This paper discusses insight into the mechanistic origins of the OS3[®] material benefits in high energy Si anode cells. XPS surface analysis demonstrated that high temperature (HT) storage and cycling have significant impacts on the anode and cathode surfaces in 4.35V LCO/Si multi-layer pouch cells. The amount of silicon detected on anode surfaces was very low, indicating that a thick surface layer forms that attenuates the underlying silicon signal. SEM images showed reduced surface cracking with OS3[®] after RT cycling. XPS cathode analysis shows that OS3[®] affects the cathode surface layer composition (increase in %Si, %S, and %C-H along with decrease in %C-O and %C=O).

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Keywords: electrolyte; Lithium Ion; solvent; organosilicon; OS; OS3[®]; LIB; high voltage; high temperature; thermal stability; oxidation; reduction; impedance; safety; solvation; LiPF₆; Lithium; SEI; solid electrolyte interphase; energy storage; ONR; LCO; Silicon; Si; SiO; gassing; ONR; Office of Naval Research; Navy; DOD; battery; cell; molecule; electrochemical; electrochemistry; fluorine; anode; cathode; cycling

Introduction

Silatronix, now operating as the Madison Technology Center within Koura Global, has developed organosilicon (OS) materials using targeted molecular design to provide desirable electrochemical characteristics for Li-ion applications. The 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. The inclusion of Si and F in the molecule is critical to the thermal and electrochemical stability. Multiple OS materials have demonstrated excellent performance in Lithium Ion Battery (LIB) systems.

The commercial solvent "OS3[®]" provides exceptional thermal, and electrochemical stability in LIB systems up to 4.5V with current commercially available electrode materials; and fundamental oxidation stability up to 7V in a platinum reference cell. OS3[®] has low viscosity, good ionic conductivity, a high flash point (>80°C), and low freezing point (<-55°C) as shown in Table 1. The most comprehensive performance benefits are observed at < 5% OS3[®], which fits comfortably within the additive market space of the LIB industry.

Table 1. Physical Characteristics of OS3[®]

Dielectric	Flash	BP	FP	SG	Visc.
16.8	82°C	202°C	-57°C	0.93	2.0cP

OS3[®] is a strong coordinator of Li salts in the electrolyte solution preventing both LiPF₆ decomposition and catalytic HF production. Elimination of these reactions is critical to enabling high energy LIB systems with long calendar life and stable high temperature performance. OS3 reduces long-term impedance growth. OS3[®] also significantly reduces gas generation by stabilizing the cathode / electrolyte interface of high energy cathodes that can initiate oxidative decomposition, as illustrated in Figure 1.

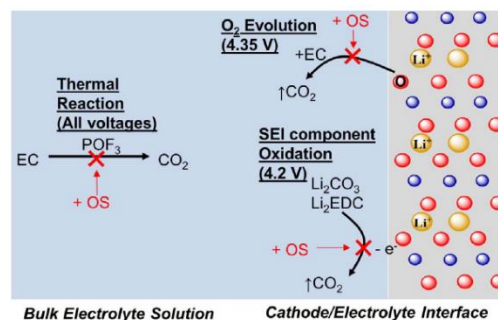


Figure 1. Mechanisms for OS nitrile gas reduction.

Several commercial cell development partners in the US, Asia, and Europe have observed practical improvements to comprehensive cell performance in multiple LIB systems, including excellent HT cycling stability, reduced impedance growth, improved calendar life rate capability, reduced gas generation, improved safety, and improved low temperature rate capability. Benefits have been observed with a variety of cell chemistries but there is a specific synergy between Si anodes and OS3[®] that improves cycling stability, lowers impedance, and protects the Si anode structure.

This paper summarizes the benefits of OS3[®] for high-Si content anodes / LCO cathodes. Analysis of the anode and cathode surfaces following cycle life testing provides insights into the mechanism by which OS3[®] improves cell performance. Full format cell testing and fundamental research of OS technology has been completed with ONR funding, including development efforts on contract N00014-20-C-1053 with collaboration with cell development partner Amprius Technologies. Amprius has developed a 100% Si nanowire anode technology which is paired with a high voltage LCO cathode to produce the highest energy density commercial cell design currently on the market.

Results and Discussion

Reduced gassing in Si nanowire / HV LCO pouch cells

Amprius provided ~ 200 mAh pouch cells with 2-sided Si nanowire anodes sandwiched between 2 single sided LCO cathodes for testing at Silatronix[®].

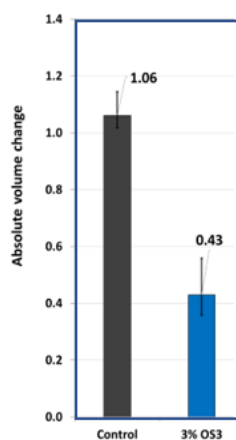


Figure 2: Cell gassing after RT cycling

Electrolyte optimization was conducted to improve the 30°C cycling performance (C/2 rate, 2.75V-4.35V) of a control electrolyte that was a blend of EC, EMC, FEC (<10v%), 1M LiPF₆, plus multiple additives at <5% combined concentration (VC, succinonitrile, and adiponitrile). Addition of OS3[®] (3%v) resulted in the significant reduction of gas generation (i.e., 60% lower cell swelling) after 220 cycles at 30°C in the high energy density Amprius cells (Figure 2).

Surface Morphology Analysis using SEM

After 30°C cycling, surface analysis was conducted on Si anodes recovered from the high energy density Si/LCO Amprius cells to investigate the impact of OS3[®] addition on the morphology and topography of the Si anodes. Cells were disassembled at 50% SOC in an Argon glove box to prevent exposure to oxygen and moisture. Figure 3 shows the images

collected for the control (top) and 3% OS3[®] (bottom) electrolyte formulations.

All anodes showed two distinct areas across the surface of the Si anodes. These are labeled “lighter” and “darker” based on the SEM images. The morphology of the Si anodes in the “darker” areas are very similar for both electrolyte formulations, as the silicon nanowires are clearly visible. However, the SEM images of the “lighter” areas show significant differences. The anode cycled with the OS3[®] electrolyte displays significantly reduced cracking compared to the control and any observed cracks were significantly smaller than those in the control.

This imaging suggests that the surface layer formed by the OS3[®] electrolyte is more flexible and stable than that formed by the control electrolyte and results in a more robust surface chemistry that is less prone to cracking during the volume expansion associated with Si anode cycling.

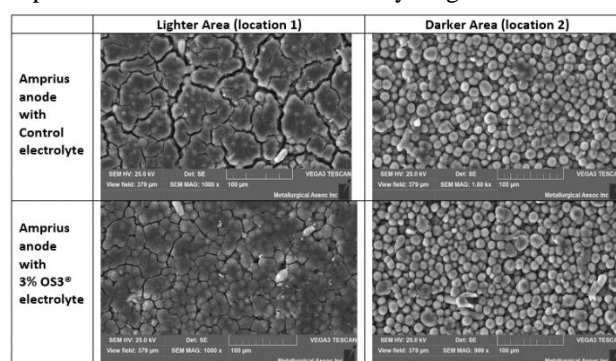


Figure 3: SEM images of Amprius Si anodes after 30°C cycling with control and OS3[®] electrolytes.

Surface Composition Analysis after Formation (XPS)

After formation of the Amprius 2-layer Si nanowire/LCO pouches, XPS surface analysis was conducted to understand differences in the SEI layer composition depending on electrolyte formulation. Formulations shown Table 2 include additions of OS3[®] and other OS family molecules with higher degrees of fluorination. OS3[®], OS5, and OS6 are all fluorinated organosilicon nitrile molecules. OS3[®] has the lowest fluorination. OS6 has the greatest fluorination. The concentration of higher fluorinated molecules was adjusted based on previous results that show better performance at lower concentrations.

Table 2: Electrolyte formulations for surface analysis

Formulation Description (vol.%)	Solvents (vol.%)				Additives (vol. %)		
	EC	DEC	EMC	FEC	OS3	OS3-X	VC
Control	30	30	29	10	-	-	1
3% OS3	29	29	28	10	3	-	1
1% OS5	30	29	29	10	-	1	1
0.5% OS6	30	29.5	29	10	-	0.5	1

Figure 4 shows the elemental composition of the Si anode surface layer after formation for the 4 electrolyte formulations shown in Table 2. This data shows that each OS material changes the surface layer in a unique way. While the different concentrations of the added OS may be

a factor in the chemical diversity of their anode SEIs, each OS material appears to have a distinct mechanism.

With 3% OS3[®], the effect on composition is decreased carbon, oxygen, and cobalt, and increased fluorine and lithium. There is no significant increase in silicon or nitrogen. This suggests that 3% OS3[®] reduces carbonate decomposition (C, O) and increases salt decomposition (Li, F) while not significantly decomposing itself.

1% OS5 decreases oxygen and increases fluorine (similar to OS3[®]) but does not impact carbon or lithium. Therefore, OS5 likely affects salt decomposition (F) but not in the exact manner as OS3[®]. The OS5 surface layer has significant signal from silicon and nitrogen, which indicates that OS5 is forming part of the SEI layer.

Finally, 0.5% OS6 is similar in composition to the control anode for all major elements, while showing increased phosphorus and decreased silicon and cobalt. The lack of silicon and nitrogen signal indicates a lack of direct participation in SEI layer formation.

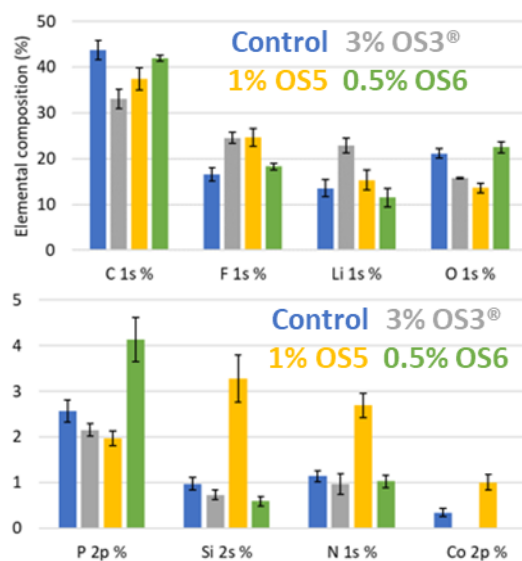


Figure 4: Elemental composition after formation (Si anode).

Examination of the carbon components comprising the overall carbon signal provides more specific information of the impact of OS addition on SEI layer formation (Figure 5). Component analysis shows that all OS materials reduce the most highly oxidized CO₃ component which indicates that OS3[®], OS5, and OS6 all impact decomposition of the carbonate solvents. However, 3% OS3[®] is the only OS that also reduces the C-H and C-O components. This shows that OS3[®] has the strongest overall impact on carbonate solvent decomposition by impacting multiple mechanisms.

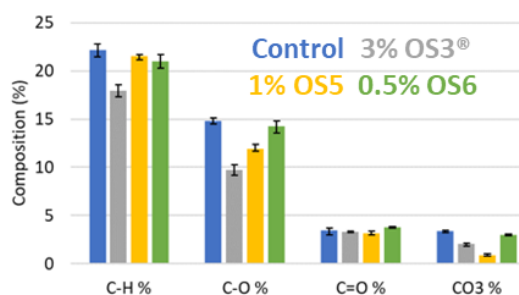


Figure 5: Carbon components after formation (Si anode).

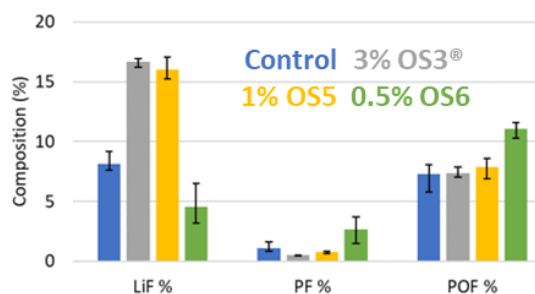


Figure 6: Fluorine components after formation (Si anode).

The impact of OS addition on LiPF₆ salt-related SEI layer formation mechanisms was studied by examination of the fluorine components comprising the overall fluorine signal (Figure 5). Similar to the carbon component analysis, different OS molecules show different behavior. Both OS3[®] and OS5 have significantly increased LiF content compared to the control or OS6. In contrast, OS6 has reduced LiF content compared to the control but higher PF and POF species which is consistent with the higher total phosphorus observed in Figure 4. This indicates that all OS impact LiPF₆ salt decomposition; however, there is a significant difference in mechanism with highest OS fluorination (OS6).

Overall, Figures 4, 5, and 6 clearly show that OS addition in the EC/DEC/EMC/FEC control formulation impacts SEI layer formation on the Si anode. While all OS show impacts on both carbonate solvent and LiPF₆ salt decomposition mechanisms, each OS demonstrates distinct behavior.

Surface Composition Analysis after HT testing (XPS)

The effect of HT cell testing on the electrode surface layers in the Amprius LCO/Si cells was studied using XPS after formation, after 100 cycles at 50°C, and after storage at 50°C for three weeks. For these tests, the electrolyte used was EC/EMC 3/7 v% + 1M LiPF₆ + 10% FEC + 1% ADN + 2% SN + 1% VC + 3% OS3[®].

The cathode surface layer thickness can be estimated by the attenuation of the signal from the bulk electrode (typically PVDF binder). After 50°C storage or 50°C cycling, the cathode surface layer thickness increases (+3.5 nm), with no significant difference between storage or cycling (Figure 7). This indicates that decomposition products formed in the electrolyte are building up on the LCO cathode.

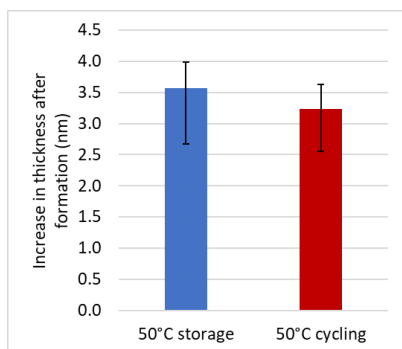


Figure 7: Cathode surface layer thickness estimate after storage or cycling relative to after formation (~1 nm).

The elemental composition of the cathode surface layer after formation, after 50°C storage, and after 50°C cycling is shown in Figure 8.

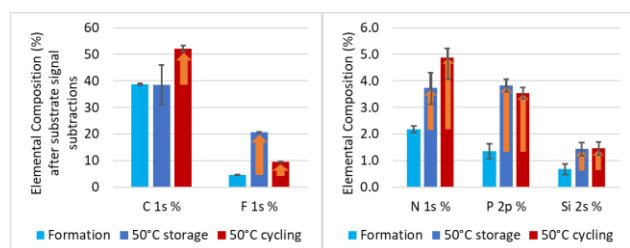


Figure 8: Elemental composition after formation, 50°C storage, and 50°C cycling (LCO cathode).

After 50°C storage, there are significant increases in LiPF₆ decomposition (increased fluorine and phosphorus) and evidence of OS3[®] participation in cathode layer formation (increased silicon and nitrogen). After 50°C cycling, all components increase which shows a similar impact as storage (increased LiPF₆ decomposition, OS3[®] participation) with additional solvent and/or additive decomposition (increased carbon).

The elemental composition of the anode surface layer after formation, after 50°C storage, and after 50°C cycling is shown in Figure 9. The orange line represents the average increase in %Li and is shown directly compared to % differences in other elements and components.

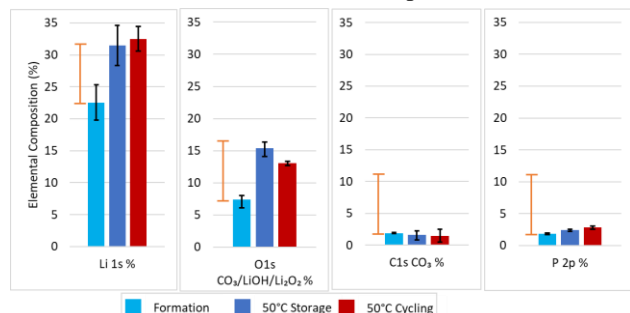


Figure 9: Elemental composition after formation, 50°C storage, and 50°C cycling (Si anode).

The anode surface layer demonstrates increases primarily in lithium and phosphorus after 50°C storage or 50°C cycling relative to after formation. This indicates significant LiPF₆ salt decomposition occurs during aging with incorporation of products into the anode SEI throughout cycling and storage. The magnitude of the increase in lithium is significantly greater than that of phosphorus but is matched by the increase in the CO₃/LiOH/Li₂O₂ components of the oxygen peak, indicating that on the anode the impact of both cycling and storage is to add lithium oxides to the SEI layer.

Overall, high temperature storage and cycling have significant impacts on both the anode and the cathode surface layers with the EC/EMC 3/7 v% + 1M LiPF₆ + 10% FEC + 1% ADN + 2% SN + 1% VC + 3% OS3[®] electrolyte in Amprius' LCO/Si cells. Visible effects include increasing LiPF₆ salt decomposition and increasing solvent and/or additive decomposition (including OS3[®]).

Conclusions

Organosilicon (OS) solvents have demonstrated excellent performance in Lithium Ion Battery (LIB) systems with Si containing anodes. OS3[®] functions synergistically with FEC and Si anodes to extend cycling stability while also reducing cell gassing and impedance growth that often accompanies FEC addition. XPS analysis demonstrated that high temperature (HT) storage and cycling have significant impacts on both the anode and the cathode surface in 4.35V LCO/Si multi-layer pouch cells. The amount of silicon detected on anode surfaces was very low, indicating that after formation a thick surface layer has formed that attenuates the underlying silicon signal. Anode SEM images showed less surface cracking with OS3[®] electrolyte variation after RT cycling. XPS cathode analysis also indicated that OS3[®] electrolyte affected cathode surface layer composition.

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