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NEW ADVANCED STABLE ELECTROLYTES FOR HIGH VOLTAGE ELECTROCHEMICAL ENERGY STORAGE

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New Advanced Stable Electrolytes for High-voltage Electrochemical Energy Storage

Executive Summary

To improve the performance, reliability, and safety of Li-ion batteries, new advanced materials need to be integrated into the cell design. Specifically, the DOE roadmap recognizes the importance in the automotive industry of the development of new electrolytes with improved electrochemical and thermal stability for advance cathodes with higher operating voltages, higher energy density, and reduced cost.

This program seeks to address this challenge by developing an advanced, stable, high-voltage (HV) electrolyte to meet the DOE goals for electrochemical energy storage in transportation systems. The project team leveraged expertise from industrial companies (Silatronix®) and government resources (Argonne National Lab (ANL) and US Army Research Lab (ARL)) to achieve the objective through a balanced electrolyte formulation approach. The scope included the development of a fundamental understanding of the failure mechanisms of Li-ion electrolytes as it relates to the oxidative breakdown in high voltage environments. This understanding will guide development of new materials which are engineered to mitigate the observed failure mechanisms of current electrolyte systems in HV environments, as well as develop synergistic behaviors between advanced electrolyte components. The HV system (5V $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) electrode system in this program) was evaluated at multiple levels of complexity from analyzing electrolyte/electrode interactions *ex situ* to evaluation of performance in coin cells to demonstration of improvement in large format pouch cells. Technical metrics related to voltage stability, thermal stability, surface interaction, Li^+ solvation properties and cycling performance were measured.

In this program, Silatronix® and ARL have synthesized and characterized HV electrolyte materials based upon rational molecular design to achieve the superior oxidative stability required for HV applications. Furthermore, the development of a fundamental understanding of the effect of individual electrolyte components and the identification of specific HV formulations for additional analysis in full cells have been performed at Silatronix® and ARL. From the testing results, most organosilicon (OS) solvents exhibit exceptional electrochemical stability and thermal stability under oxidizing conditions and meet fundamental electrolyte metrics (conductivity, viscosity). Furthermore, OS solvents maintain synergy with existing electrolyte components, as well as advanced electrolyte salts and additives developed under this program to provide reliable, long-lasting cells which operate at high-voltages (>5V). Superior OS electrolyte performance was demonstrated on the electrochemical and gas generation studies of the selected HV electrolytes in LNMO/graphite pouch cells at ANL; several OS formulations finished cycle life testing (422 cycles total) with ~70% capacity retention, which is superior to the carbonate control (~50% capacity retention after 222 cycles). One promising OS solvent (OS3d) not only showed the least swelling during pouch cell testing, it also provided the best cycling performance at only 2% formulation. Therefore, Silatronix® will apply the acquired knowledge from this program to the next-generation HV cathode materials.

Project Objectives:

- Synthesize, characterize, and integrate novel solvents and additives into electrolytes to create the conditions necessary for reliable, long-lasting cells which operate at high-voltages (> 5V).
    - Specific metric: oxidative stability in reference system (Pt electrode)
        - Provide oxidative breakdown voltage above 6 V.
        - Provide parasitic current below 0.02 mA/cm^2 after 10 hours above 6 V at 50°C.
- Investigate the fundamental mechanisms of complex behavior of new solvent and additive materials within formulations containing commercial electrolyte components (solvents, salts, additives).
- Demonstrate commercially viable performance characteristics using state-of-the-art high voltage electrodes from Argonne National Laboratory (ANL) and US Army Research Laboratory (ARL).
    - Specific metric: cycling performance in 5V LNMO full cells
        - Full cell initial capacity ≥ carbonate control
        - Over 80% initial capacity after 300 cycles at ≥55°C

Major Milestones:

- HV stability demonstrated in reference cells:
    - **Go/No-Go:** Linear scan voltammetry (>6 V); Parasitic current 4.5-6.5 V at 50°C (<0.02 mA/cm^2 at 6 V). (Complete June 2016)
- New HV materials synthesized at Silatronix® (4-6 OS compounds) and ARL (4-6 compounds). (Complete August 2016)
- Fundamental electrochemical evaluation (Complete September 2016) and cycling stability at 30°C and 55°C (Complete March 2017) of new materials.
- Performance testing of final pouch cell build: cycle stability at 30°C, pouch swelling at 30°C. (Complete January 2018)

Key Results and Accomplishments:

HV Material Synthesis and Evaluation

- OS3® solvent family shows excellent oxidative stability in Pt reference system with a wider electrochemical stability window and lower parasitic currents above 4.5V compared to the EC/EMC carbonate control.
    - 12 OS solvents have been synthesized and evaluated.
    - 4 OS solvents met the Go/No Go technical metric (see Objectives).
- Additive selection is an important factor in full cell cycling performance, especially for OS electrolytes. Army Research Laboratory (ARL) synthesized and screened 10 additives for performance improvement. Five additives were shipped to Silatronix® for evaluation.

Fundamental Studies for OS Containing Electrolytes

- DSC tests performed on de-lithiated LNMO cathodes showed that addition of OS3® reduces the magnitude of the main exothermic peak without a significant change in onset temperature.
- Surface analysis found that OS3® participates in cathode and anode surface layer formation.
- Solvation studies identified OS3® and OS3d as high-affinity Li^+ solvents based upon Electrospray Ionization-Mass Spectrometry (ESI-MS) and Nuclear Magnetic Resonance (NMR) spectroscopy measurements. Therefore, OS solvents could have an impact in SEI formation and other interfacial phenomena.

LNMO/Graphite Full Cell Performance

- Electrolytes with less than 5% OS solvent content show comparable or improved HT cycling stability compared to the EC/EMC carbonate control in coin cells.
    - Low OS content electrolytes were chosen for the pouch build at Argonne National Laboratory (ANL).
- All pouch cells with FEC in EC-free electrolytes demonstrate a gassing problem even at the reduced 4.7 V cut off voltage indicating FEC is a major gas generator at higher voltage.
- To further reduce gassing, the EC content was reduced from 30% to 10%, which is a key factor to improve cycle life.
- Pouch cells containing six HV electrolytes finished cycle life testing (422 cycles total) with ~70% capacity retention, which is superior to the carbonate control (~50% capacity retention after 222 cycles).
- OS3d is a promising OS solvent to reduce swelling during pouch cell testing, which also provides the best cycling performance at only 2% formulation.

Results and Discussion:

Approach:

Silatronix® and ARL synthesized new materials based upon rational molecular design to achieve the superior oxidative stability required for HV applications. The fundamental electrochemical behavior of these materials was studied in reference cells to determine the oxidative breakdown voltage and mechanism of breakdown to produce a library of materials with superior fundamental oxidative stability for evaluation.

The performance and safety of the new HV solvents and additives in formulated electrolytes was evaluated with the HV cathodes provided by ANL (5V LNMO). Surface analysis was conducted after cycling to identify underlying mechanisms of degradation (i.e., surface film formation, metal dissolution, cathode morphology changes). Differential scanning calorimetry (DSC) was conducted on de-lithiated cathode material to understand the safety impact of the new HV materials. Solvation studies, using ESI-MS and NMR spectroscopy, was conducted to understand the Li^+ solvation behavior of the new OS solvents. These studies expanded the understanding of the fundamental mechanistic behavior and included the relationship between the structure and properties of individual electrolyte components and the performance of a complete system. Top performing HV formulations identified were tested in 5V LNMO pouch cells (13 layers, 200-300 mAh) at ANL. The pouch cell analysis focused on cycling stability and pouch swelling.

Evaluation of Advanced OS Solvents in Pt Reference Cell

In this program, Silatronix® evaluated more than 12 organosilicon (OS) solvents, characterizing their physical properties and electrochemical behavior. Some of these OS solvents show promising results and their physical properties are listed in Table 1. These solvents include members of the high stability OS3® structural family and advanced OS4 family solvents which contain different functional groups than OS3®. Data for other solvents and blends tested in the program, including OS3® and the EC/EMC (3/7) control blend, is shown for comparison. All considered organosilicon solvents have flash points significantly higher than the EC/EMC control blend.

Table 1: Physical Properties of OS Solvents

OS	Neat Solvent Properties			Electrolyte Properties (w/1M $LiPF_6$) at 30 °C	
				No co-solvent	
	Dielectric	Flash Pt (°C)	Density (g/cc)	Conductivity (mS/cm)	Viscosity (cP)
EC/EMC (3/7)	22.1	<30	1.10	10	3.1
OS3	16.8	82	0.93	2.8	8.0
OS3a	18.2	78	1.09	3.5	7.9
OS3b	15.7	94	0.91	1.9	10.3
OS3c	17.9	98	1.03	2.3	11.5
OS3d	N/A	180	1.1	N/A	
OS4a	7.3	68	0.97	1.53	6.09
OS4b	6.6	76	1.11	0.43	7.92

Generally, superior oxidative stability was observed with these OS electrolytes in Pt reference cells by linear scanning voltammetry (LSV) and constant voltage floating tests at 30°C and 50°C. Figure 1 compares the parasitic currents for $LiPF_6$ electrolytes using EC/EMC (3/7, %v) and 100% OS3® at 30°C. The OS3® electrolyte showed superior stability compared to EC/EMC between +4.6 V and +6.5 V (vs. Li/Li^+) with the Pt working electrode with current at 6V less than 0.02 mA/cm^2.

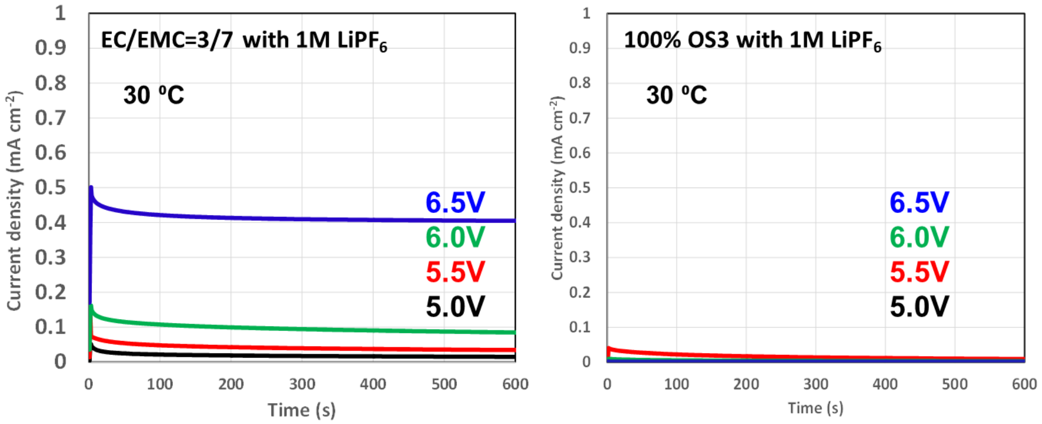


Figure 1. Parasitic current results for $LiPF_6$-based electrolytes in a 3-electrode cell (Pt: WE, Li/Li^+: CE, RE)

During the first year of this program, four OS3® family solvents with $LiPF_6$ salt satisfied the Go/No-Go Metric #1 (breakdown potentials > 6V at 30°C, shown in Figure 2a) and were identified as good candidates for HV systems. Figure 2b summarizes the parasitic currents of these OS3® family electrolytes, which showed superior stability and satisfied Go/No-Go Metric #2 (50°C parasitic current <0.02 mAh/cm^2 at 6V).

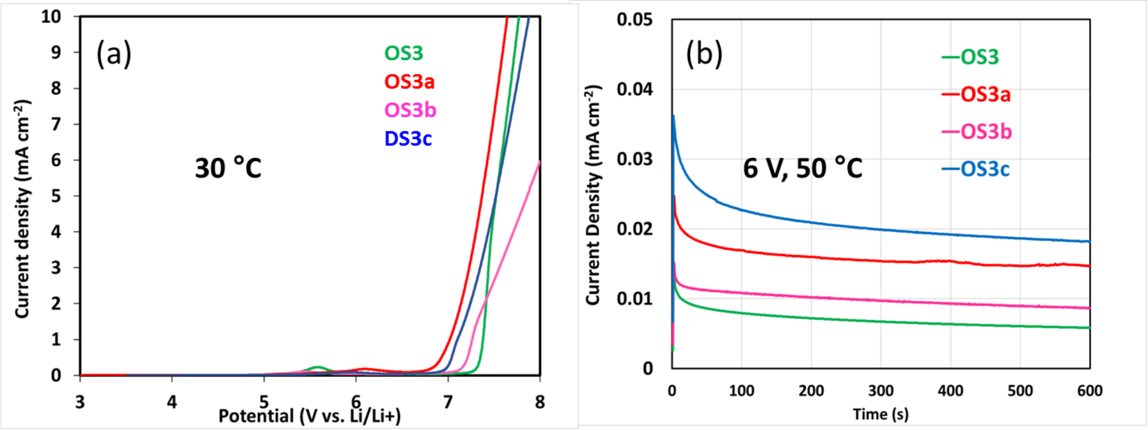


Figure 2: a. Oxidative stability comparison at 30°C; b. parasitic current results at 6 V and 50°C of OS3® family electrolytes.

The oxidative stability of one more OS3® family solvent (OS3d) and two additional OS4 family solvents were evaluated in Pt reference cells using the same methods. Figure 3 summarizes the oxidative stability (vs. Li/Li$^+$) measured at 80°C for OS3d and OS3® and measured at 50°C for the carbonate control (EC/EMC, 3/7 %v). All electrolytes contain 1M $LiPF_6$.

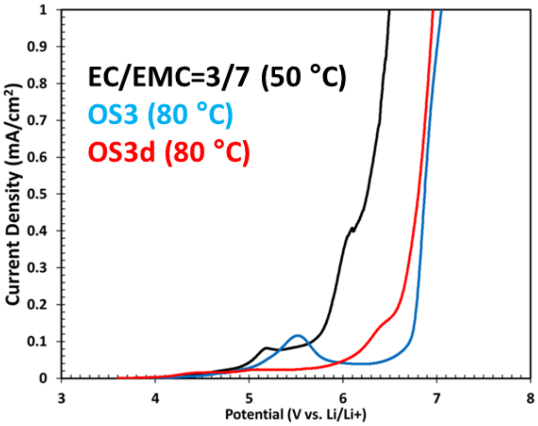


Figure 3: Oxidative stability comparison at high temperature of OS3d vs OS3® vs carbonate control electrolyte.

OS3d showed excellent oxidative stability between 5 and 6V. The measurement was conducted at elevated temperature as OS3d is a solid and does not dissolve $LiPF_6$ at room temperature. Figure 4 shows the parasitic current behavior at 80°C for OS3d and OS3® with $LiPF_6$ in a 3-electrode cell (Pt: WE, Li/Li$^+$: CE, RE). Overall, the behavior at 5.0 and 5.5V was similar for OS3® and OS3d. Neither showed a significant current increase at these voltage levels. At 6.0V, OS3® does not show an increase in parasitic current while OS3d does (< 0.01 vs. 0.04 mA/cm^2). At 6.5V, both OS3® and OS3d show higher parasitic currents but OS3d has a significantly lower current density (0.06 vs. 0.16 mA/cm^2). Therefore, OS3d was identified as a good candidate for the >5 V HV system.

In addition, OS4a and OS4b (OS4 family solvents) demonstrate a higher breakdown voltage than the EC/EMC carbonate control and OS3®, and were evaluated in the 5V LNMO full cell.

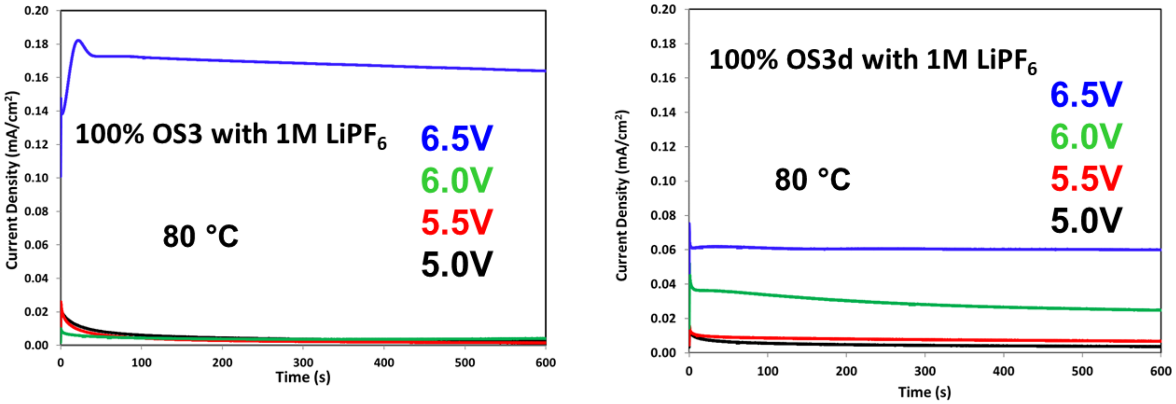


Figure 4: Parasitic current results for LiPF$_6$-based electrolytes in a 3-electrode cell (Pt: WE, Li/Li$^+$: CE, RE).

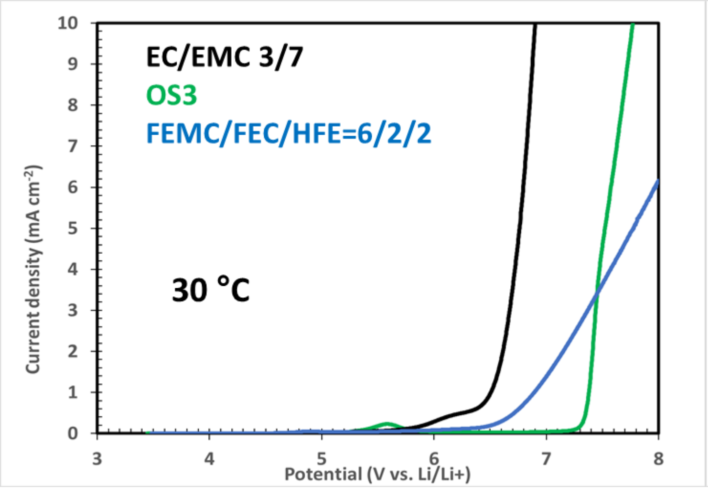


Figure 5: Oxidative stability comparison at 30°C of OS3® vs carbonate control vs fluorinated electrolyte.

Figure 5 summarize the oxidative stability (vs. Li/Li$^+$) of OS3®, the carbonate control (EC/EMC, 3/7 %v) and the fluorinated control electrolyte (FEMC/FEC/HFE, 6/2/2, %v) with LiPF$_6$ at 30°C.

Figure 6 shows the parasitic current behavior at 30°C for the fluorinated control electrolyte and OS3® with LiPF$_6$ in a 3-electrode cell (Pt: WE, Li/Li$^+$: CE, RE). The data show that OS3® has the highest voltage stability. The fluorinated control electrolyte displays a wider window of electrochemical stability than the EC/EMC control. As a result, FEMC and FEC were investigated as replacements for the non-fluorinated EC and EMC solvents in the program.

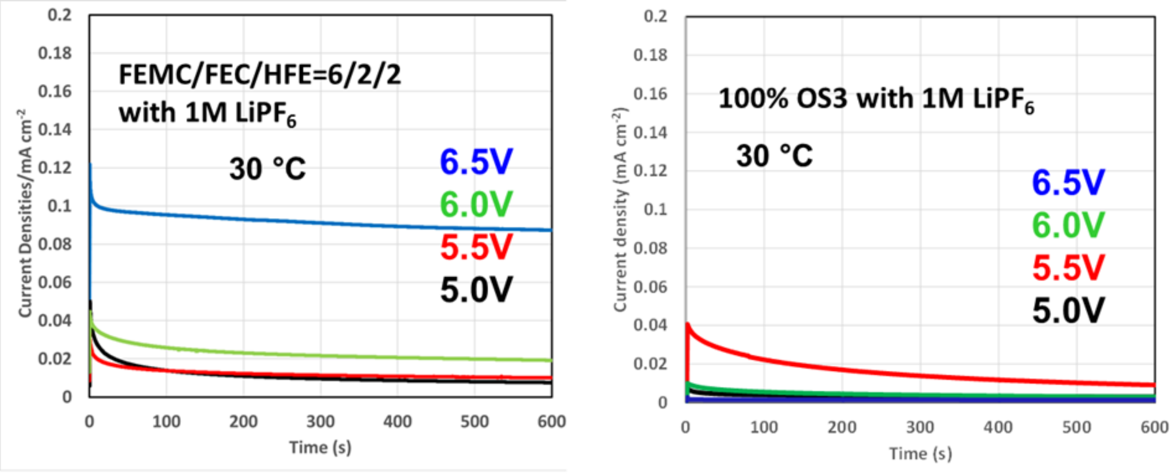


Figure 6. Parasitic current results for LiPF$_6$-based electrolytes in a 3-electrode cell (Pt: WE, Li/Li$^+$: CE, RE)

ARL synthesized 10 new additives with bifunctional groups for protection of both anode and cathode. Most have been characterized with electrochemical characterization and half-cell tests at ARL and the structures are shown in Figure 7. Figure 8 summarizes the calculated HOMO-LUMO values to demonstrate their potential for HV applications. Five of those additives were provided for testing at Silatronix®. To date, no performance benefit has been observed using these additives.

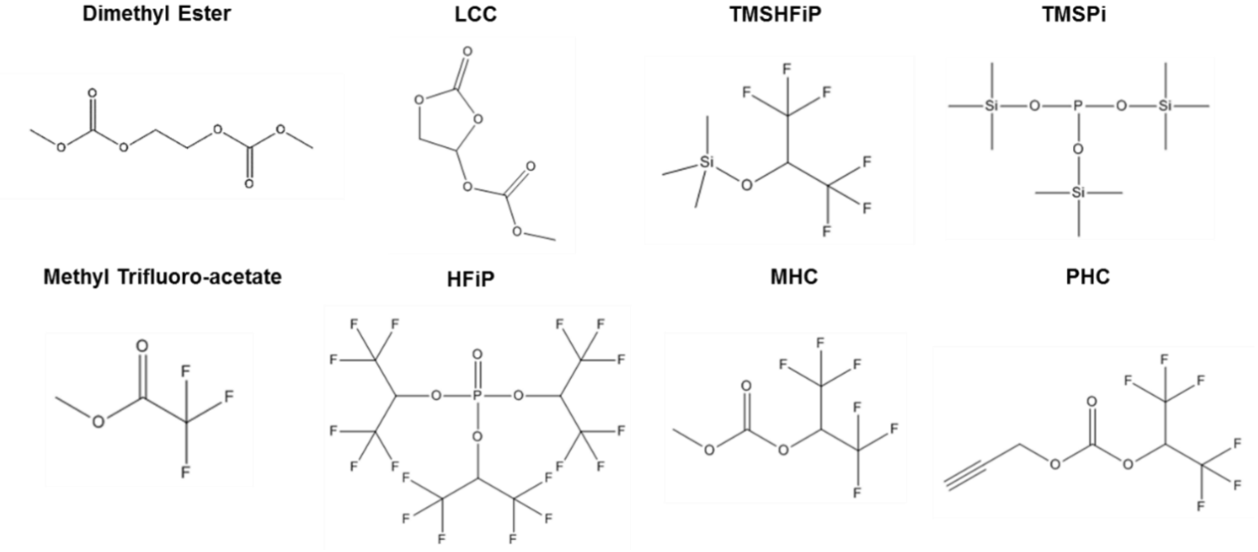


Figure 7: Chemical structures for HV additives evaluated at ARL.

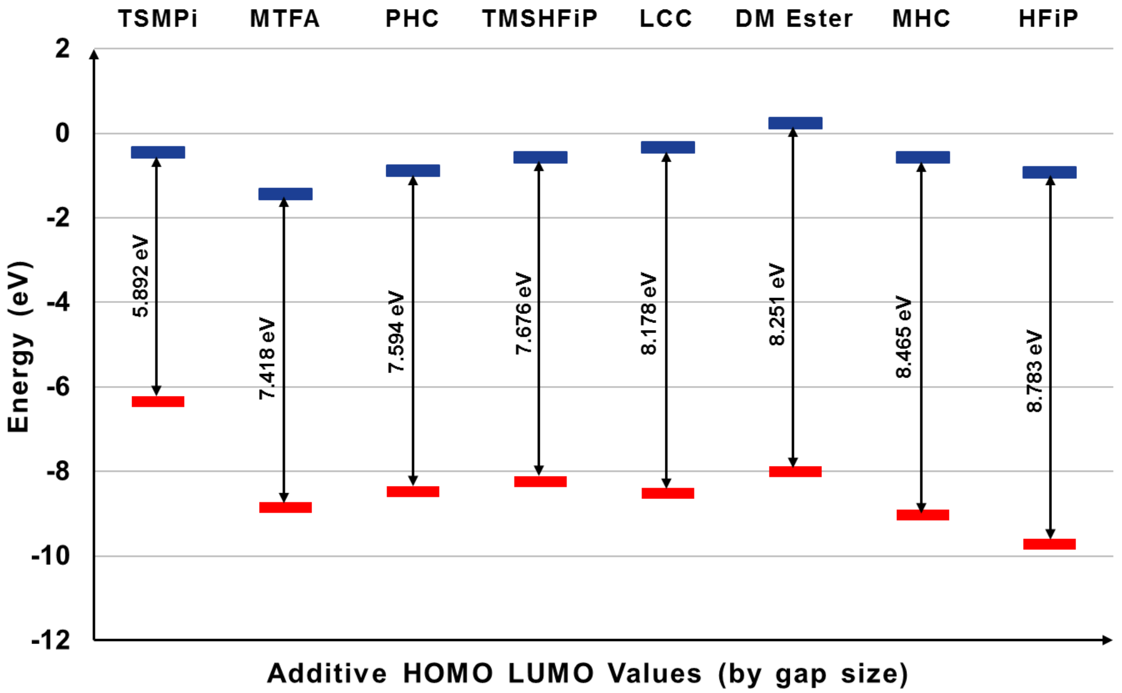


Figure 8: Theoretical calculation of HOMO-LUMO values for ARL HV additives.

Fundamental Studies for OS Containing Electrolytes

The effect of OS3® concentration on the safety profile of the charged LNMO cathode was investigated using differential scanning calorimetry (DSC), as shown in Figure 9. No additives were included in the tested formulations to isolate the effect of OS3®.

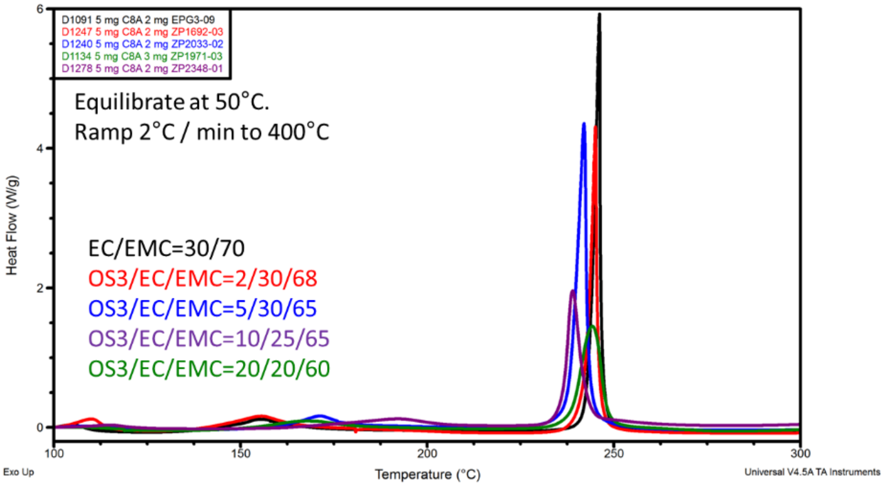


Figure 9: Differential scanning calorimetry (DSC) test results for de-lithiated LNMO cathodes formed with various HV electrolyte formulations: Carbonate control (black), 2% OS3® (red), 5% OS3® (blue), 10% OS3® (purple), and 20% OS3® (green).

The carbonate control (black data - EC/EMC – 3/7 %v) shows a sharp exothermic peak near 250°C with minor features near 150°C. By comparison, addition of 2% OS3® (red data) or 5% OS3® (blue data) decreases the overall magnitude of this main exothermic peak with little to no shift in the onset temperature. Increasing the OS3® concentration to 10% (purple) or 20% (green) results in over a 60% reduction in the peak magnitude with no onset temperature reduction. The data shown in Figure 9 shows that including OS3® in the HV electrolyte formulation improves the safety and stability of the de-lithiated LNMO cathode.

In addition, post-test degradation analysis was conducted, including XAS measurements at Argonne National Laboratory's Advanced Photon Source (beamline BM20) and SEM and XPS measurements at the University of Wisconsin–Madison. This analysis serves to identify the composition of and evaluate the stability of the SEI layer and the bulk structure of the cathode active material.

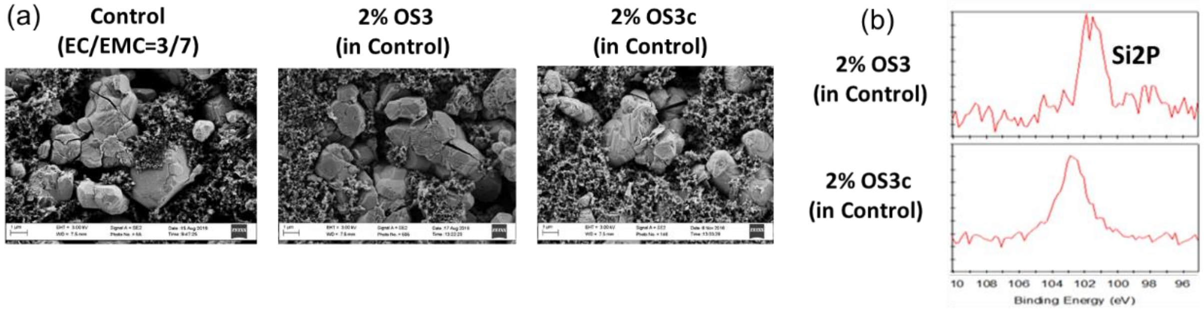


Figure 10: (a) SEM images and (b) XPS surface composition data for the de-lithiated LNMO cathode after cycling (50 cycles at C/2 between 3.5 and 4.9 V at 55°C) with control carbonate and 2% OS3®, and 2% OS3c formulations. All electrolytes contain 1M $LiPF_6$.

Figure 10 summarizes surface analysis data for 5V LNMO cathodes recovered from cells cycled with 2% OS3®, 2% OS3c and the carbonate control. The morphology of the electrode surfaces at 50% SOC was examined using scanning electron microscopy (SEM) to evaluate the SEI layer morphology and mechanical integrity. In Figure 10a, the surface morphology of the cathodes is similar regardless of the specific electrolyte formulation.

Therefore, the addition of 2% OS3® or 2% OS3c does not significantly affect the thickness and morphology of any surface layers formed on the LNMO cathode. Information regarding the composition of any surface layers formed on the LNMO cathode was obtained using X-ray photoelectron spectroscopy (XPS). Figure 10b shows data from the Si(2p) regions for the cathode surface layers formed with 2% OS3® and 2% OS3c formulations. XPS surface analysis showed silicon present on cathode samples after cycling with 2% OS3® and OS3c electrolytes, indicating that OS solvents are involved in cathode film formation. Similar results were obtained for anode samples after 50 cycles at 55°C, which means OS solvents also participate in anode SEI formation.

Post cell analysis using X-ray absorption spectroscopy (XANES) was performed to identify the stability of the bulk structure of the cathode active material. XANES spectra show more shifts are present in the Ni K-edge data compared with Mn K-edge data, which indicates the oxidation of Ni(III) to Ni(IV) is the major contributor for the LNMO cathode, and the Li^+ lost during cycling is more related to Ni-bonded Li^+ rather than Mn-bonded Li^+. Among different electrolyte formulations, little to no change in the crystal structure is observed with or without OS molecules.

This trend does not agree with the cycling performance differences observed and suggests the cathode/anode SEI layers lay a major role in cycling performance.

ESI-MS experiments were performed at ARL to investigate the Li^+ solvation behavior of OS3® containing electrolytes. Initial results are shown in Figure 11. The role of OS3® in the fluorinated electrolyte system is shown in Figure 11a. Without OS3® FEC is the strongest Li^+ solvator of the three fluorinated solvents. When OS3®is added, it dominates all fluorinated solvents. The role of OS3®in the EC/EMC control system is shown in Figure 11b. The ESI-MS data demonstrate that OS3® is a strong competitor for EC in Li^+ solvation.

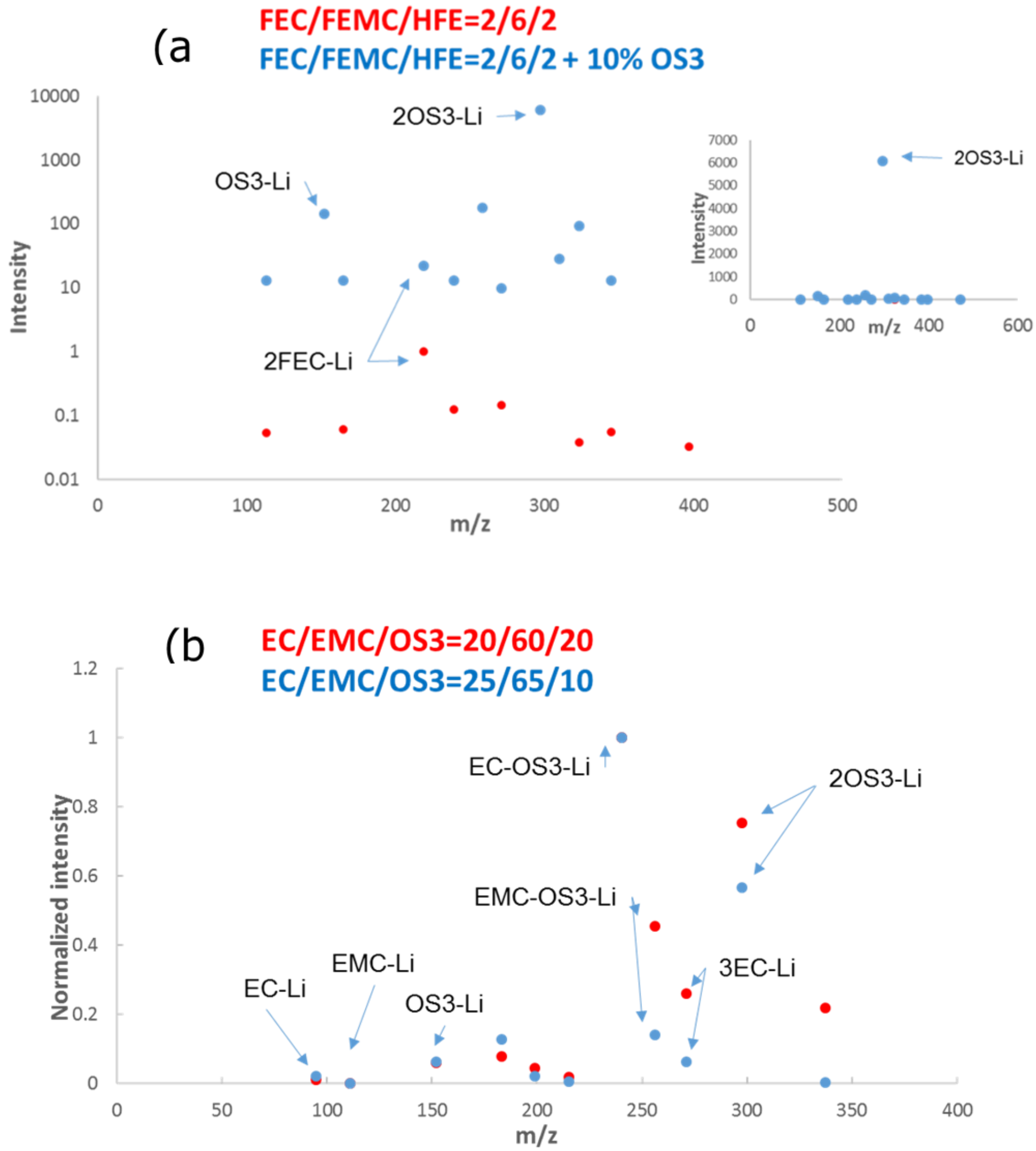
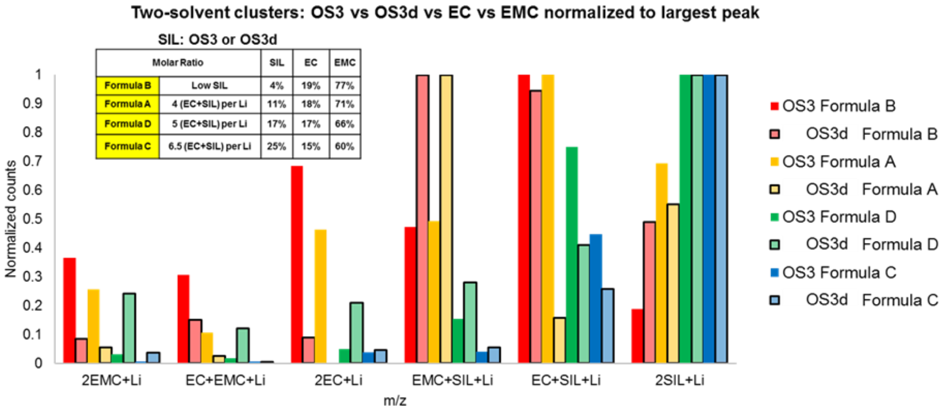


Figure 11: ESI-MS test results for OS3® containing electrolytes at ARL. (a) OS3® in fluorinated electrolyte (b) OS3® in EC/EMC carbonate control.

The Li^+ solvation behavior of OS3®/EC/EMC and OS3d/EC/EMC electrolytes was investigated. Electrolyte formulations were designed to understand the competing solvation between EC and OS solvents. Formulation A contains 11% OS by mole and contains 4 moles of EC and OS per Li^+. Formulation B contains 4% OS by mole and contains only 3 moles of EC and OS per Li^+. Formulation C contains 25% OS by mole and contains 4 moles of OS per Li^+ and 6.5 moles of EC and OS per Li^+. Formulation D contains 17% OS by mole and represents equal competition between OS and EC.



Molar Ratio		SIL	EC	EMC
Formula B	Low SIL	4%	19%	77%
Formula A	4 (EC+SIL) per Li	11%	18%	71%
Formula D	5 (EC+SIL) per Li	17%	17%	66%
Formula C	6.5 (EC+SIL) per Li	25%	15%	60%

Figure 12. Normalized ESI-MS counts as a function of cluster for OS/EC/EMC electrolyte formulations.

A summary of the results is shown in Figures 12 and 13. Both OS3® and OS3d consistently coordinate with Li^+ more strongly than EC or EMC. Clusters of Li^+ with two solvents were the best represented in ESI-MS data. The role of OS3® in the carbonate electrolyte system can be seen in the relative magnitude of the EC/OS3® and 2OS3® clusters in the low OS3® content electrolytes (A – orange, B – red) compared to the high OS3® content electrolytes (C – blue, D – green). This trend shows that as OS3® concentration increases in the electrolyte, the number of 2OS3® clusters grows compared to the EC/OS3® cluster. This ESI-MS data demonstrates that OS3® is a strong competitor for EC in Li^+ solvation. OS3d has a larger population of OS3d+EMC clusters than OS3d+EC, which is the most common OS3®/carbonate cluster. OS3d also shows lower populations of all non-OS3d clusters in general.

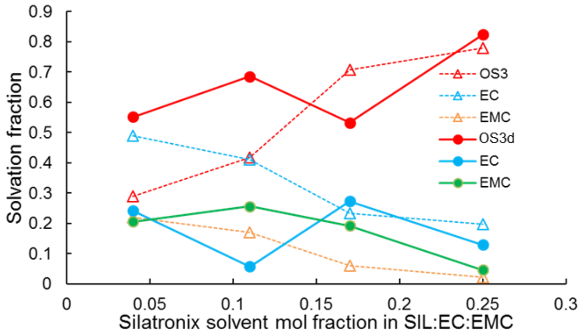


Figure 13. Calculated fraction of bulk solvents participating in solvation based upon ESI-MS results in Figure 12.

Figure 13 shows the fraction of solvent participating in solvation, based upon the relative prevalence of the clusters from Figure 12 compared to the bulk composition, for OS3®, EC, and EMC solvents as a function of OS3® concentration. This data shows that OS3® participates in solvation at all concentration levels with >50% OS3® participating in the high OS3® concentration electrolytes. Figure 12 shows that OS3d is a stronger Li^+ solvator than OS3®, displacing carbonate solvents from the Li^+ solvation sheath to a greater extent than OS3®.

Since the analysis of Li^+ solvation in HV electrolytes using an ESI-MS technique demonstrates that OS3® or OS3d compete well with EC for solvation of Li^+ and may contribute to the formation of SEI layers, Silatronix® performed Li^+ solvation studies using ^{13}C and ^{15}N NMR spectroscopy to evaluate Li^+ solvation behavior in the bulk solution.

Table 2: $^{13}C/^{15}N$ NMR Li^+ solvation results for carbonate/OS3® blends with 1M $LiPF_6$.

	Ternary Mixtures	Solvent per Li			EC		EMC	OS3	
		OS3	EC	EMC	CO3	CH2	CO3	CN	15N CN
B	Low OS3	0.5	2.5	10	2.3	2.6	0.9	0.7	0.6
A	4 (EC + OS3)	1.5	2.5	10	2.3	2.7	1.1	0.7	0.6
D	Equal OS3	2.5	2.5	10	2.3	2.7	1.3	0.7	0.6
C	Excess OS3	4	2.5	9.7	2.4	2.8	1.5	0.7	0.7

The NMR measurements examines Li^+ solvation behavior for individual solvents, but unlike the ESI-MS data does not directly measure the solvents present in the Li^+ coordination sheath. Results are summarized in Table 2. In Table 2, the normalized chemical shift difference for the primary Li^+ coordinating group for each solvent is shown for each formulation. Overall, as observed in the binary mixtures, EC shows the same coordination strength in all ternary mixtures as expected due to the constant EC/Li^+ ratio. The OS3® coordination does not vary significantly with OS3® concentration. EMC coordination increases with increasing OS3® concentration showing a greater participation.

Table 3: $^{13}C/^{15}N$ NMR Li^+ solvation results for FEMC/EC/OS3® blends with 1M $LiPF_6$.

7/2/1 (vol)	FEMC (5.8M)	EC (3M)	OS3 (0.64M)	
	CO_3	CO_3	CN	15N CN
S	0.7	2.9	0.8	0.9
6/2/2 (vol)	FEMC (5.0M)	EC (3M)	OS3 (1.3M)	
	CO_3	CO_3	CN	15N CN
S	0.7	2.8	0.7	0.8
4/2/4 (vol)	FEMC (3.3M)	EC (3M)	OS3 (2.6M)	
	CO_3	CO_3	CN	15N CN
S	0.5	2.0	0.4	0.5

Table 3 summarizes Li^+ solvation data for ternary blends containing EC, OS3®, and FEMC. This data was collected to understand the effect of replacing EMC with FEMC in HV electrolytes. The EC concentration was held constant at 20% by volume with FEMC varied from 40-70% to mimic actual electrolytes tested. At a constant EC concentration (3M), increasing OS3® content (0.64M to 2.6M) decreases EC coordination (decreasing $\Delta\delta$). This shows that OS3® is successfully competing with EC for Li^+ solvation. The OS3® and FEMC behavior is similar in the 70% and 60% FEMC electrolytes with reduced coordination observed for both in the 40% blends.

Table 4: $^{13}C/^{15}N$ NMR Li^+ solvation results for FEMC/FEC/OS3® blends with 1M $LiPF_6$.

7/2/1 (vol)	FEMC (5.8M)	FEC (2.7M)	OS3 (0.64M)	
	CO_3	CO_3	CN	15N CN
S	1.0	1.8	1.0	1.2
6/2/2 (vol)	FEMC (5.0M)	FEC (2.7M)	OS3 (1.3M)	
	CO_3	CO_3	CN	15N CN
S	1.0	1.7	0.9	1.2
4/2/4 (vol)	FEMC (3.3M)	FEC (2.7M)	OS3 (2.6M)	
	CO_3	CO_3	CN	15N CN
S	1.0	1.5	0.8	1.1

Table 4 summarizes Li^+ solvation data for blends containing FEC, OS3®, and FEMC. This data was collected to understand the effect of using only fluorinated carbonate solvents. Overall, the Li^+ solvation for the individual solvents in these blends is more similar as a function of concentration compared to Table 3. FEMC shows no variation with composition. FEC shows reduced Li^+ coordination strength as the OS3® content increases (0.64M to 2.6M). This shows that OS3® is successfully competing with EC for Li^+ solvation. The OS3® and FEMC behavior is similar in the 70% and 60% FEMC electrolytes with reduced coordination observed for both in the 40% blends.

The competition between other OS3® family solvents and commercial carbonate solvents (EMC, EC) was also investigated in binary mixtures. Results show that OS molecules participate in Li^+ coordination in all electrolytes tested and certain modification of the functional group on the silicon can enhance or impede competition with EC and EMC.

Full Cell Cycling and Stability Performance

ANL delivered single side coated 5V LNMO and MCMB electrodes to Silatronix® and ARL for the evaluation of advanced HV electrolyte materials. Initial screening of OS electrolytes was completed using both 5V LNMO half cells and full cells. Cycling in LNMO half cells and full cells confirmed the importance of additives, especially in electrolyte formulations with higher OS concentration, which showed a lower parasitic current at voltages above 5V compared to carbonate control electrolytes in LNMO cells.

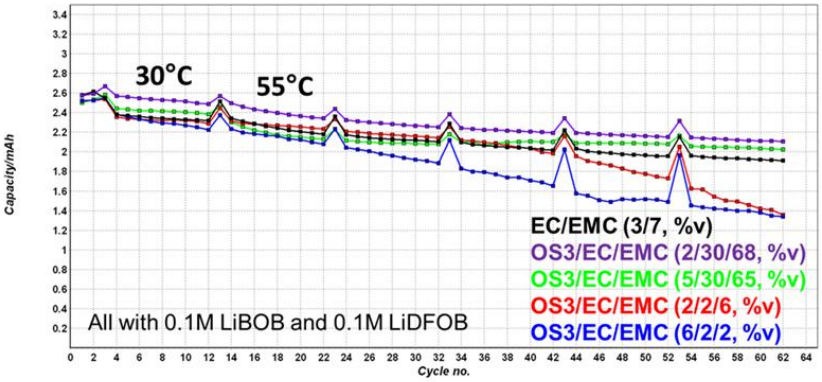


Figure 14: Comparison of LNMO full cell performance with control carbonate electrolyte and OS3® containing electrolytes (all with 1M $LiPF_6$). Cells are cycled at C/10 for 2 formation cycles and at C/2 for 10 cycles at 30°C, then continued 50 cycles at C/2 between 3.5 and 4.9 V at 55°C.

The effect of OS3® concentration on full cell cycling performance was examined in coin cells previously in this program. Formulations containing 2%, 5%, 20%, and 60% OS3® were tested in EC/EMC electrolytes. The EC content was held at 30% for low OS3® concentrations (2%, 5% OS3®) and at 20% for high OS3® concentrations (20%, 60% OS3®). Figure 14 summarizes the 30°C and 55°C cycling data for the OS3® formulations and carbonate control. All electrolytes contain 1M $LiPF_6$ and 0.1M LiBOB and 0.1M LiDFOB additives. Representative data is shown for each formulation. The low OS3® concentration electrolytes (2% - purple, 5% - green) show greater capacity retention compared to the carbonate control after 50 cycles at 55°C. Higher OS3® concentrations (20% - red, 60% - blue) result in greater capacity degradation.

Based upon this cycling data, three top performing HV formulations with 2% or 5% OS as the first round were tested in 5V LNMO pouch cells (13 layers, 200-300 mAh) at ANL. The pouch cell analysis is focused on cycling stability and pouch swelling. Each pouch cell undergoes formation (including de-gassing) followed by a rate test, HPPC test, and cycle life testing. All testing occurs at 30 °C with a 3.5 to 4.9V voltage window.

Since the performance improvement in coin cells was observed for 2% OS3**®** and 5% OS3**®**, similar formulations were tested for OS3d, OS4a and OS4b. Figure 15 summarizes the full cell cycling results for these OS structures tested at the 2% concentration level. Both OS4 family molecules (OS4a – purple data, OS4b– green data) show improved capacity retention compared to the carbonate control. The enhanced stability OS3d (blue data) shows similar performance to the carbonate control blend. These OS molecules were also selected for pouch cell testing.

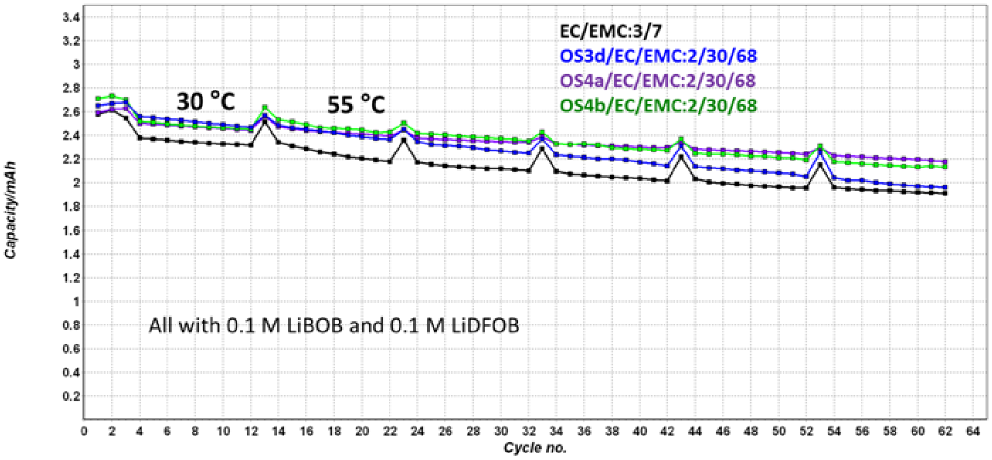
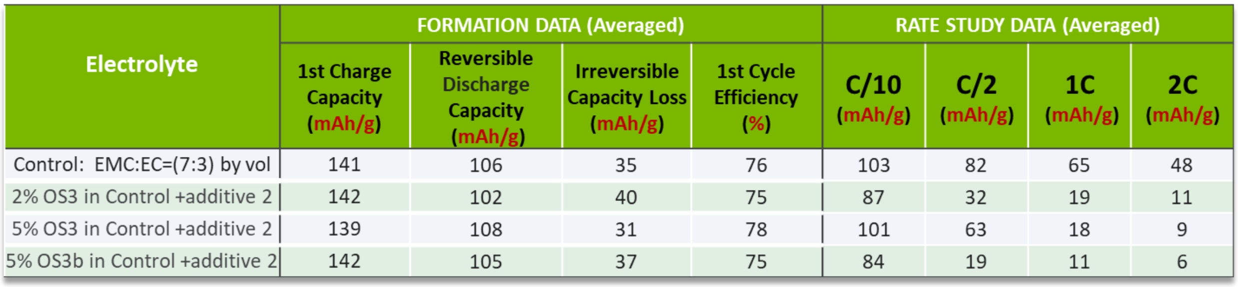


Figure 15. Comparison of LNMO full cell performance with control carbonate electrolyte and 2% OS formulations (all with 1M $LiPF_6$). Cells are cycled at C/10 for 2 formation cycles and at C/2 for 10 cycles at 30°C, then 50 cycles at C/2 between 3.5 and 4.9 V at 55°C.

During the first round of testing, all pouch cells exhibited a large amount of gassing and the initial rate test could not be completed. After another de-gas step, the cells were transferred to the HPPC and cycle life tests. However, gassing continued and all cells failed quickly. The test results are summarized in Table 5. In addition, higher irreversible capacity loss has been observed in this LNMO system, which can be attributed to the cathode stability and electrolyte decomposition at higher voltage.

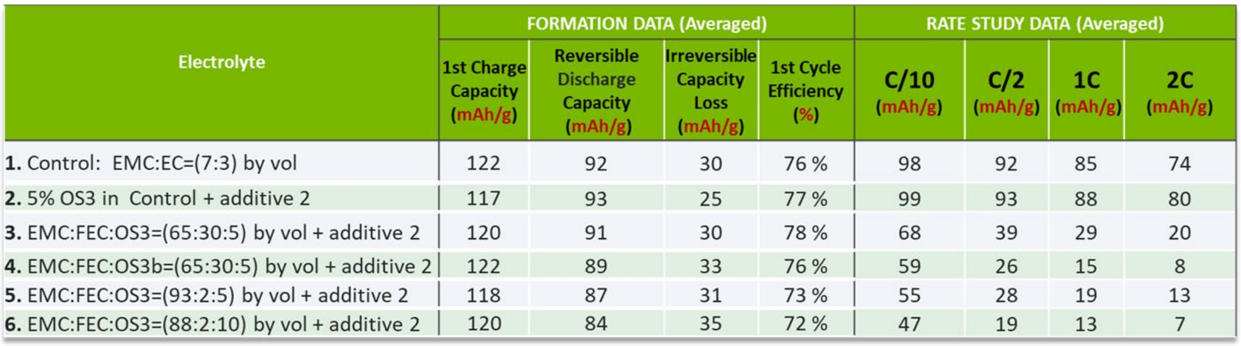
Table 5: Formation & Rate Data (1st round pouch cell tests at 4.9 V cut-off voltage; additive 2: borate additives)



Electrolyte	FORMATION DATA (Averaged)				RATE STUDY DATA (Averaged)			
	1st Charge Capacity (mAh/g)	Reversible Discharge Capacity (mAh/g)	Irreversible Capacity Loss (mAh/g)	1st Cycle Efficiency (%)	C/10 (mAh/g)	C/2 (mAh/g)	1C (mAh/g)	2C (mAh/g)
Control: EMC:EC=(7:3) by vol	141	106	35	76	103	82	65	48
2% OS3 in Control +additive 2	142	102	40	75	87	32	19	11
5% OS3 in Control +additive 2	139	108	31	78	101	63	18	9
5% OS3b in Control +additive 2	142	105	37	75	84	19	11	6

Due to the gassing issue observed in the 1st pouch cell build, the 2nd pouch cell build at ANL focused on electrolytes with higher EMC content (lower EC content) and other OS solvents (e.g, OS3d and OS4b). In addition, the pouch cell testing plan was revised to run the same test steps (Formation, Rate Study, HPPC and Cycle Life) with the new voltage window of 3.5-4.7V to further reduce gassing.

Table 6: Formation & Rate Data (2nd round pouch cell tests at 4.7 V cut-off voltage; additive 2: borate additives)



Electrolyte	FORMATION DATA (Averaged)				RATE STUDY DATA (Averaged)			
	1st Charge Capacity (mAh/g)	Reversible Discharge Capacity (mAh/g)	Irreversible Capacity Loss (mAh/g)	1st Cycle Efficiency (%)	C/10 (mAh/g)	C/2 (mAh/g)	1C (mAh/g)	2C (mAh/g)
1. Control: EMC:EC=(7:3) by vol	122	92	30	76 %	98	92	85	74
2. 5% OS3 in Control + additive 2	117	93	25	77 %	99	93	88	80
3. EMC:FEC:OS3=(65:30:5) by vol + additive 2	120	91	30	78 %	68	39	29	20
4. EMC:FEC:OS3b=(65:30:5) by vol + additive 2	122	89	33	76 %	59	26	15	8
5. EMC:FEC:OS3=(93:2:5) by vol + additive 2	118	87	31	73 %	55	28	19	13
6. EMC:FEC:OS3=(88:2:10) by vol + additive 2	120	84	35	72 %	47	19	13	7

To further reduce gassing, a series of "EC-free" electrolyte formulations containing FEC/EMC/OS3 were tested in pouch cells during the 2nd round at ANL. Details for the electrolytes formulations are listed in Table 6. Solvent compositions are listed by volume. Each pouch cell undergoes formation (including de-gassing) followed by a rate test, HPPC test, and cycle life testing. Decreasing the upper cutoff voltage to 4.7V resulted in reduced gassing for the EC/EMC control (Formulation 1) and the 5% OS3® EC/EMC electrolyte (Formulation 2). In the previous pouch cell build, these formulations failed due to high gassing. However, these formulations still exhibit gassing (albeit at lower levels). All pouch cells with FEC (Formulations 3-6), which were included as EC-free electrolytes to reduce gassing, still exhibited a large amount of gassing even with the reduced charging voltage of 4.7 V. These cells were opened to confirm sufficient electrolyte was present in the cells. After another de-gas step, the cells were transferred to the

HPPC and cycle life tests. However, the gassing continued and all cells failed quickly. We attribute this failure to the presence of FEC, which is a major gas generator at higher voltage.

Since the FEC containing electrolytes also showed gassing, we switched to lower EC content formulations instead of “EC-free” electrolytes. Additive optimization has focused on HFIP (additive 1) or borate additives (additive 2: e.g. LiBOB, LiDFOB).

To reduce gassing, the EC content was reduced to 10%. Full cell performance with HFIP (blue) or borate (green) additives were evaluated for the new carbonate control. Figure 16 summarizes the 30°C and 55°C cycling data for the 10% EC formulations with and without additives. Formulations containing the borate additives show slightly improved capacity retention compared to formulations with no additive or HFIP containing electrolyte.

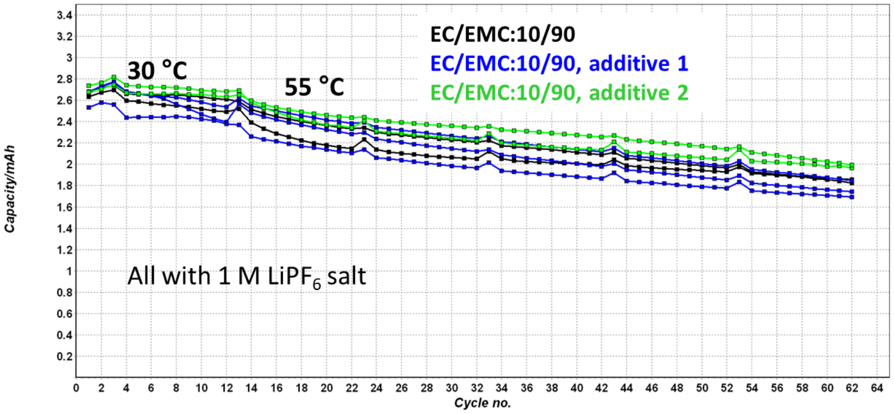


Figure 16: Comparison of LNMO full cell performance for low EC content carbonate electrolytes: no additive, additive 1 (HFIP), and additive 2 (borate additives) (all with 1M LiPF$_6$). Cells are cycled at C/10 for 2 formation cycles and at C/2 for 10 cycles at 30°C, then continued 50 cycles at C/2 between 3.5 and 4.9 V at 55°C

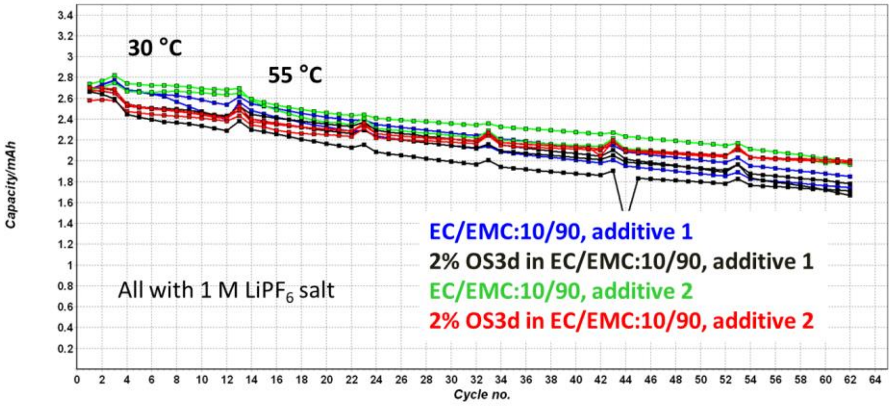


Figure 17: Comparison of LNMO full cell performance with lower EC content carbonate electrolytes and 2% OS3d electrolytes (all with 1M LiPF$_6$). Cells are cycled at C/10 for 2 formation cycles and at C/2 for 10 cycles at 30°C, then continued 50 cycles at C/2 between 3.5 and 4.9 V at 55°C.

OS formulations (e.g. 2% OS3d, shown in Figure 17) with different additives provided similar capacity retention compared to the corresponding carbonate controls. Therefore, the three 10% EC controls and 8 optimized OS formulations (2 OS3®, 1 OS3b, 2 OS3d and 3 OS4a containing electrolytes) with different additive package in the 10% EC system were selected for the final pouch cell build.

ARL continued electrolyte optimization in higher EMC content formulation (2~5% OS contents without EC) using different HV additive packages. The results demonstrate that despite initial improvement in 30°C cycling capacity by all additives, the OS3®/EMC formulations with LiBOB still exhibit the best cycling performance compared to other OS molecules. For 55 °C cycling, only the HFIP additive reliably improves high temperature cycling performance.

After the 2nd round of pouch cell tests at 4.7V, 8 optimized OS electrolytes and 4 carbonate controls (without FEC) were included for the final round of pouch cell tests. All of the cells went through formation, rate study and the cycle life testing protocols with the 3.5-4.7V voltage window. Several promising HV electrolytes (2 10% EC carbonate controls and 5 OS containing electrolytes) provided greater than 80% capacity retention after the initial cycle life test (222 cycles). These cells were restarted for an additional 200 cycle life testing. The gas generation study for this round of 12 electrolytes and EC/EMC (3/7) reference control was completed. The Archimedes method has been utilized to measure the volume changes after 222 cycles, including analysis after formation, after the rate study, and after cycle life testing.

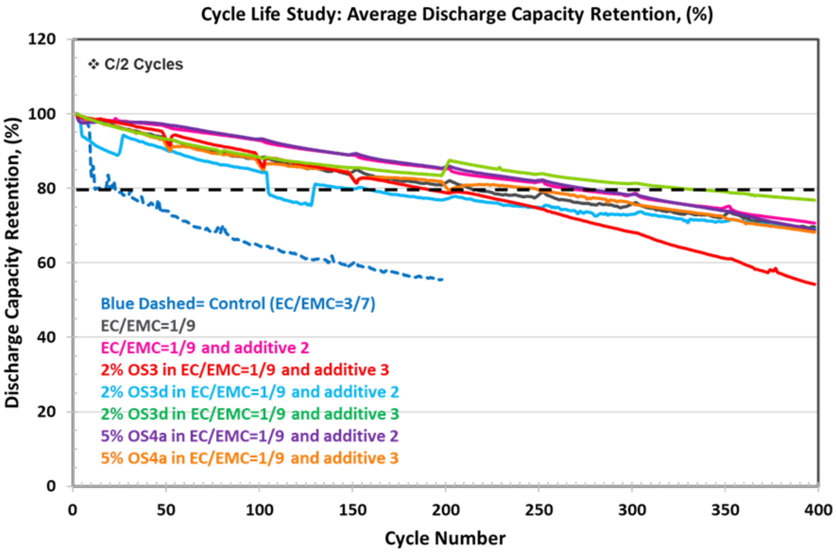
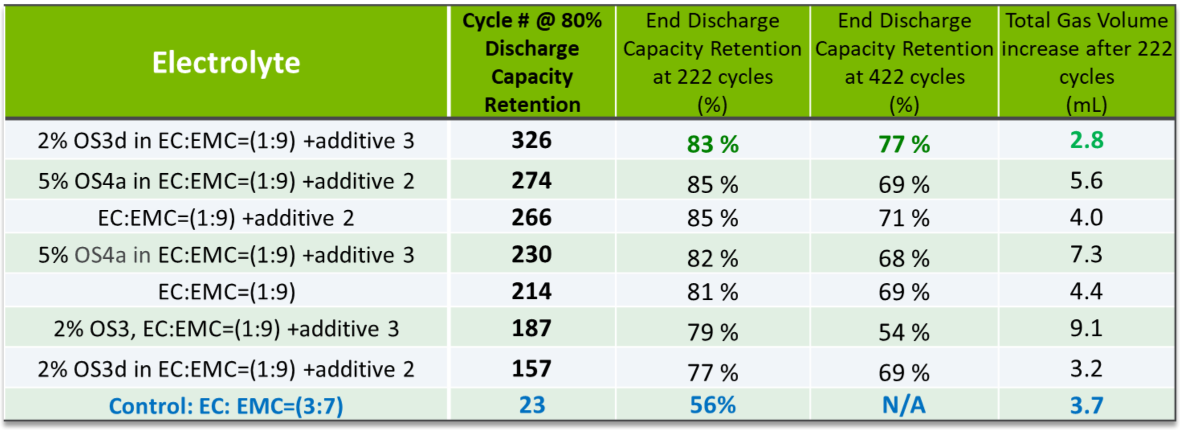


Figure 18: Average normalized discharge capacity (mAh/g) of top HV electrolyte formulations vs. carbonate controls.

For the final cycle life testing, data from all pouch cell chemistries was averaged (Figure 18). These formulations demonstrate much better cycling performance compared to the EC:EMC (3/7, %v) carbonate control (blue data - dashed) The control completed the initial cycle life testing (222 cycles) with no additional cycle life testing due to low discharge capacity retention. The 2% OS3d and 5% OS4a electrolytes show similar or improved capacity retention compared to their 10% EC corresponding carbonate controls.

Table 7: Cycle # @ 80% Discharge Capacity Retention and Gas Generation Results



Electrolyte	Cycle # @ 80% Discharge Capacity Retention	End Discharge Capacity Retention at 222 cycles (%)	End Discharge Capacity Retention at 422 cycles (%)	Total Gas Volume increase after 222 cycles (mL)
2% OS3d in EC:EMC=(1:9) +additive 3	**326**	**83 %**	**77 %**	**2.8**
5% OS4a in EC:EMC=(1:9) +additive 2	**274**	85 %	69 %	5.6
EC:EMC=(1:9) +additive 2	**266**	85 %	71 %	4.0
5% OS4a in EC:EMC=(1:9) +additive 3	**230**	82 %	68 %	7.3
EC:EMC=(1:9)	**214**	81 %	69 %	4.4
2% OS3, EC:EMC=(1:9) +additive 3	**187**	79 %	54 %	9.1
2% OS3d in EC:EMC=(1:9) +additive 2	**157**	77 %	69 %	3.2
Control: EC: EMC=(3:7)	**23**	**56%**	**N/A**	**3.7**

Table 7 summarizes the cycle life testing and the gas generation results for the electrolytes shown in Figure 18. Six HV electrolytes finished cycle life testing (422 cycles total) with ~70% capacity retention, which is superior to the carbonate control (~50% capacity retention after 222 cycles). By further analyzing the performance of the top 6 formulations, we can conclude that reducing the EC content from 30% to 10% significantly improves cycle performance in LNMO/graphite pouch cells. Also, low OS3d and OS4b concentration electrolytes show improved capacity retention compared to the carbonate control. 2% OS3d formulation not only demonstrates the lowest gassing after cycling it also provides the best cycling performance with appropriate additives.

Remaining Challenges and Barriers:

- The reliable source of cathode materials (> 5V) that are stable during high temperature tests is still a challenge in this Li-ion battery system.
- To address the gassing phenomenon at higher voltage, the role of both OS and carbonate solvents in gas generation needs to be identified. This will give a guidance for OS electrolyte optimization in the HV system.
- Additional optimization of the additive package could increase compatibility between electrode materials and OS solvents, which may allow the increase of OS content in electrolyte to provide better voltage and thermally stability in the HV system.

Conclusions:

The focus of this program was the fundamental evaluation of high stability OS solvents and performance of OS-containing high voltage (HV) electrolyte formulations in 5V LNMO full cells. All OS molecules evaluated in this program demonstrate similar properties as previously tested OS molecules, including higher flash points than the carbonate control (EC/EMC, 3/7 %v). Superior oxidative stability (above 6V) is observed for OS molecules in reference cells (Pt) by linear scanning voltammetry (LSV) and floating current testing.

DSC tests performed on de-lithiated LNMO cathodes showed that addition of OS3® to the EC/EMC electrolyte reduced the magnitude of the main exothermic peak (near 250°C) without a significant change to the onset temperature. ARL performed the analysis of Li^+ solvation in HV electrolytes using ESI-MS, which demonstrates that both OS3® and OS3d consistently coordinate Li^+ more strongly than EC or EMC. Clusters of Li^+ with two OS are the best represented in ESI-MS data. Therefore, OS molecules may contribute to the formation of SEI layers. Silatronix® performed the analysis of Li^+ solvation in HV electrolytes by NMR spectroscopy. Results show all OS solvents participate in Li^+ solvation in EC and EMC binary mixtures at all tested concentrations. Surface analysis found evidence that OS3® participates in cathode and anode surface layer formation. XANES spectra found little or no change in the crystal structure of the LNMO cathode based upon electrolyte formulations (with or without OS). This suggests that the cathode and anode SEI layers, not the underlying electrode structures, are a key factor for cell performance.

Initial full cell testing found that the addition of 2% OS3®, OS3d, OS4a and OS4b improves the 55°C cycling performance by reducing capacity degradation across 50 cycles compared to the EC/EMC (3/7, %v) control. Due to the gassing issue observed in the 1st pouch cell build, full cell testing focused on electrolytes with higher EMC/lower EC content, lower OS solvent concentration, and a reduced voltage window (4.7 vs 4.9V). The final pouch cell test results indicate the reduction of EC content from 30% to 10% significantly improves cycle performance in LNMO/graphite pouch cells and 2% OS3d formulation demonstrates the lowest gassing after cycling and also provides the best cycling performance with appropriate additives.

Glossary of Terms:

- EC: Ethylene carbonate
- EMC: Ethyl methyl carbonate
- FEC: Fluoroethylene carbonate
- FEMC: 2-Fluoroethyl methyl carbonate
- HFE: 1,1,2,2-Difluoropropyl-1',1',2',2'-difluoroethyl ether
- LNMO: $LiNi_{0.5}Mn_{1.5}O_4$
- MCMB: MesoCarbon MicroBeads graphite
- SEI: Solid-electrolyte interphase