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Supporting Information

Tuning and Understanding the Solvent Ratios of Localized Saturated Electrolytes for Lithium-metal Batteries

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Figure S1. SEM images of calcined LNO cathode secondary particles: (a) a single secondary particle and (b) multiple secondary particles.



Figure S2. Evolution of the Coulombic efficiencies of LNO half cells cycled in the various electrolytes of interest.



Figure S3. Average charge and discharge voltages over the course of long-term cycling in LNO half cells cycled in the various electrolytes of interest.



Figure S4. Cycling performances of LNO coin half cells paired with thin Li-plated Cu foil in LP57 and D5 LSE under lean-electrolyte conditions.



Figure S5. EIS plots of LNO half cells charged to 3.8 V in the various electrolytes of interest after (a) three C/10 formation cycles and after (b) 30 cycles comprised of C/2 charge and 1C discharge steps.



Figure S6. (a) LSV scans of Li | Al half cells in several electrolytes of interest charged up to 5 V with a scan rate of 0.05 mV s⁻¹. (b) Inset in (a) focusing on the four LSEs in D1 – D7. The M47 LHCE consists of LiFSI : DME : TTE in a 1 : 1.2 : 3 molar ratio.



Figure S7. EIS plots of (a) LNO|LNO and (b) Li|Li symmetric cells that were harvested after 50 cycles from LNO|Li half cells in LP57 and D5 LSE. The half cells were charged to 3.9 V following the 50 cycles and then were disassembled to make the symmetric cells.

Figure S6a shows the EIS plots for the LNO|LNO symmetric cells in LP57 and D5 electrolytes. For both curves, two semicircles are visible, more prominently on the LP57 cell. The first semicircle in the high-medium frequency region is ascribed to both surface-film resistance from the growth of the electrode-electrolyte interphases over cycling as well as contact resistance stemming from poor conductive contact between the current collector and electrode.^{1,2} The second

semicircle in the low-frequency region is typically attributed to the charge-transfer resistance across particle-to-particle and particle-to-electrolyte interfaces.³ It can be seen that both semicircle impedances are much smaller for the D5 symmetric cell than that of the LP57 symmetric cell, indicating a lower overall resistance growth for the former. This also suggests that a less-resistive CEI is formed on the LNO cycled in D5 LSE. Figure S6b correspondingly shows the EIS plots of the Li|Li symmetric cells. Only one semicircle is present for the Li|Li symmetric cells, but appears to have two smaller semicircles merged into one, as seen with the oblong nature of the overall semicircle. This suggests that the individual impedance contributions are further convoluted together for the Li|Li symmetric cell shows a smaller overall impedance growth compared to the LP57 cell, which implies that the SEI formed over the course of cycling for the D5 LSE cell is less resistive to Li⁺ de-/intercalation. The overall EIS plots for both LNO|LNO and Li|Li cells indicate the growth of a more resistive CEI and SEI on LNO and Li-metal anode that were cycled with the LP57 electrolyte compared to those cycled in the D5 LSE and help explain the better long-term cyclability observed for the D5 LSE in half cells.



Figure S8. Full view of the Coulombic efficiency cycling of various electrolytes in Li|Cu cells seen in Figure 5a.



Figure S9. ⁷Li NMR spectra of the various electrolytes tested. Note that the D1 - D7 samples were analyzed without the addition of TTE.



Figure S10. First screening test of electrolytes in this study by comparing the cycling performance of LNO in Li-metal coin half cells with the various electrolytes of interest under C/2 charge and 1C discharge rates.



Figure S11. Images of LSEs tested in this study displayed from increasing FEC/EMC ratios starting from LSE EMC containing only saturated EMC as the solvent to LSE FEC containing only saturated FEC as the solvent. The red arrows on the LSE FEC image indicate the two phase separation between the saturated FEC solution and TTE. The bottom image is a magnified view of the LSE FEC to better showcase the separation layer between the saturated FEC and TTE.



Figure S12. FTIR spectra of the (a) saturated electrolytes along with pure FEC and EMC solvents and (b) LSEs along with pure TTE from 800 to 900 cm⁻¹ to study the PF_6^- coordination.

Electrolyte	Conductivity (mS cm ⁻¹)	
LP57	8.80	
D1	1.46	
D3	1.77	
D5	1.98	
D7	2.19	

Table S1. Ionic conductivities of the various electrolytes used in this study

LNO Cathode							
Atomic %	<u>C</u>	<u>0</u>		<u>F</u>			
		O lattice	Rest of O species	LiF	Rest of F species		
LP57	57.43	1.37	17.47	4.43	25.08		
D1	52.65	1.29	11.82	6.82	33.09		
D3	51.64	1.1	12.46	7.18	35.91		
D5	53.91	1.27	12.05	7.99	34.05		
D7	52.65	0.18	18.25	6.55	29.11		

Table S2. Tabulated atomic compositions of the main elements present in the LNO CEI from XPS data after 30 cycles of the half cells in the various electrolytes tested

Li-metal Anode						
<u>Atomic %</u>	<u>C</u>	<u>0</u>	F			
			LiF, Li _x PO _y F _z	Rest of F species		
LP57	47.91	23.4	11.69	17.02		
D1	39.82	25.41	21.89	12.87		
D3	43.85	26.6	17.02	12.53		
D5	42.45	27.96	22.51	7.09		
D7	41.81	29.21	20.05	8.93		

Table S3. Tabulated atomic compositions of the main elements present in the Li-metal SEI from XPS data after 30 cycles of the half cells in the various electrolytes tested

Table S4. Average CE of Li|Cu half cells in various electrolytes based on Figures 5a and S6 and the corresponding cycle number range the average was calculated with. The ranges were determined based on the parts of the cycling that had the least fluctuation in CE to determine a more accurate average. Initial cycling CE values from 1 - 50, for example, were omitted for the average calculation as the cells still showed increasing CE during that range for plating and stripping formation onto the Cu anode. The ranges also omitted the final cycling numbers where the cells begin to rapidly drop in CE. The average CE calculation was only carried out for D3, D5, and D7 cells, as the LP57 and D1 cells had no stable cycling regions where an accurate average could be determined.

Average	<u>e CE (%)</u>	Cycle Number Range for Avg.	
LP57	N/A	N/A	
D1	N/A	N/A	
D3	97.49%	50 - 100	
D5	97.97%	50 - 125	
D7	96.94%	50 - 125	

References

1 Y. Chen, W. Zhao, Q. Zhang, G. Yang, J. Zheng, W. Tang, Q. Xu, C. Lai, J. Yang and C. Peng, *Adv Funct Mater*, 2020, 30, 2000396.

2 D. Pritzl, A. E. Bumberger, M. Wetjen, J. Landesfeind, S. Solchenbach and H. A. Gasteiger, *J Electrochem Soc*, 2019, 166, A582–A590.

3 Y. Li, M. Bettge, B. Polzin, Y. Zhu, M. Balasubramanian and D. P. Abraham, *J Electrochem Soc*, 2013, 160, A3006–A3019.