

Novel Non-Carbonate Based Electrolytes for Silicon Anodes

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OBJECTIVES

The objective of this project is to develop non-carbonate electrolytes that form a stable solid electrolyte interphase (SEI) on silicon alloy anodes, enabling substantial improvements in energy density and cost relative to current lithium ion batteries (LIBs). These improvements are vital for mass market adoption of electric vehicles. At present, commercial vehicle batteries employ cells based on LiMO_2 (M = Mn, Ni, Co), LiMn_2O_4 , and/or LiFePO_4 coupled with graphite anodes. Next generation cathode candidates include materials with higher specific capacity or higher operating voltage, with a goal of improving overall cell energy density. However, to achieve substantial increases in cell energy density, a higher energy density anode material is also required. Silicon anodes demonstrate very high specific capacities, with a theoretical limit of 4200 mAh/g and state-of-the-art electrodes exhibiting capacities greater than 1000 mAh/g. While these types of anodes can help achieve target energy densities, their current cycle life is inadequate for automotive applications. In graphite anodes, carbonate electrolyte formulations reductively decompose during the first cycle lithiation, forming a passivation layer that allows lithium transport, yet is electrically insulating to prevent further reduction of bulk electrolyte. However, the volumetric changes in silicon upon cycling are substantially larger than graphite, requiring a much more mechanically robust SEI film.

TECHNICAL BARRIERS

- In order for EVs to achieve mass adoption and make a significant dent in U.S and global CO_2 production, the key problems of driving range per charge and cost per kWh must be addressed.
Barriers addressed:
 - Performance: Low Wh/kg & Wh/L
 - Life: Poor cycle life
 - Cost: High \$/kWh

TECHNICAL TARGETS

Development of non-carbonate electrolyte formulations that

- form stable SEIs on 3M silicon alloy anode, enabling coulombic efficiency > 99.9% and cycle life > 500 cycles (80% capacity) with NMC cathodes;
- have comparable ionic conductivity to carbonate formulations, enabling high power at room temperature and low temperature;
- are oxidatively stable to 4.6V, enabling the use of high energy NMC cathodes in the future; and
- do not increase cell costs over today's carbonate formulations.

INTRODUCTION

Silicon-based anodes suffer from major disadvantages relative to graphite. First, during cycling, silicon exhibits a volume change of up to 300% (vs. 5-10% for graphite), causing severe mechanical stress and electrical disconnection of particles. This mechanical stress can be managed by careful control of particle size/morphology, including nanoparticles, nanowires, and nano-pillared materials. Such nanostructured materials have high surface areas (*e.g.*, >10 m²/g) and often require a composite matrix to prevent electrochemical sintering. Second, carbonate-based electrolyte formulations do not form a stable SEI on silicon, with subsequent high irreversible capacity losses and poor cycle life (typically >15% and <100 cycles, respectively).

3M has developed several prospective silicon alloy anodes that provide a 100% increase in the composite electrode energy density compared to graphite coatings. In 18650 test cells using a fluorinated ethylene carbonate (FEC)-based electrolyte, 3M has demonstrated a full cell energy increase of 15% to 20% against a standard NMC cathode, with charge depleting cycling for 500+ cycles resulting in 67% capacity retention at a C/2 charge/discharge rate from 2.8V to 4.35V. Catastrophic failure still occurs under long term cycling due to parasitic reactions consuming the electrolyte. This project focuses on the development of formulations that provide stable SEIs using additives in a non-carbonate formulation. Linear and cyclic carbonate solvents do not yield suitably stable SEIs on silicon. In order to avoid simultaneous reduction with the new SEI additives, carbonates need replacement.

APPROACH

Wildcat is using a three stage approach to the development of noncarbonate electrolytes for silicon anodes (Figure 1). In the first, an additive package was developed in a propylene carbonate (PC) based system. PC does not form a stable SEI on the anode, so the effect of additive(s) on the resulting SEI will be measureable. Once a promising additive package was identified, new solvent candidates were enabled. Therefore, the second stage consisted of identification of novel solvents that provide high ionic conductivity, good low temperature performance, improved thermal stability/safety, and adequate oxidative stability. The development of an effective additive package to form an SEI practically enables electrolyte solvents that might not otherwise be considered, and substantially increases the number of potential candidates. Finally, optimization of the electrolyte is necessary in the final stage of the project to ensure that the final solution can meet all of the PHEV/EV cell level goals, including ionic conductivity and oxidative stability to 4.6V.

In the design and development of novel SEI additives, several factors were taken into consideration, as shown in Table 1. The concept uses molecular design concepts to create an SEI with improved mechanical and electrochemical performance, enabling longer cycle life on silicon anodes.

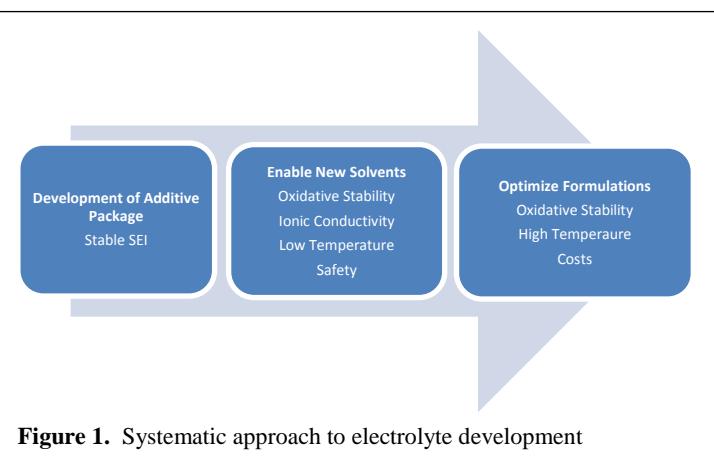


Figure 1. Systematic approach to electrolyte development

Table 1. Molecular design approach for anode SEI additives

Approach	Factor
Control SEI thickness	Influenced by the relative amount of polymer additive relative to surface area of anode, and the reduction potential of the additive
Control SEI modulus and/or glass transition temperature (T _g)	Property of polymer influenced by 1) average molecular weight and distribution, 2) chemical composition, 3) effective crosslink density, 4) degree of swelling by solvent.

Control amount of more brittle non-polymeric species	Influenced by other components of the electrolyte such as solvent, other additives, and salts
Control ionic conductivity of SEI	Influenced by polymer composition and other electrolyte components such as the salt

RESULTS

Phase 1: Identification of SEI Additives for EC-Free Electrolyte Formulations

Today's electrolyte formulations most often contain a blend of a high dielectric constant solvent and a low viscosity solvent. The most common high dielectric constant solvent is ethylene carbonate (EC), which solvates the Li^+ cations and also, fortuitously, participates in SEI formation on graphite anodes. Propylene carbonate (PC) is another commonly used high dielectric constant solvent. However, it cannot form effective SEI layers on graphite. However, EC (and many other high dielectric constant solvents) tend to have high viscosities, requiring dilution with a low viscosity solvent to work effectively in a battery. Linear carbonates such as ethyl methyl carbonate (EMC) are often used as the low viscosity solvents.

Today's common SEI additives, such as vinyline carbonate (VC) are used within electrolyte formulations that contain a blend of EC with various linear carbonate solvents. We, therefore, tested the electrochemical performance of hundreds of SEI additives in different chemical categories in the presence of EC, which participates in the SEI formation on graphite/silicon, and PC, which does not participate in SEI formation. This allows us to elucidate those additives that can form an effective SEI on their own vs. those that require co-reaction with EC to form an SEI. Figure 2 shows a subset of the data, including three categories of additives tested in two different base formulations. All additives were tested at two different concentrations (open and closed circles).

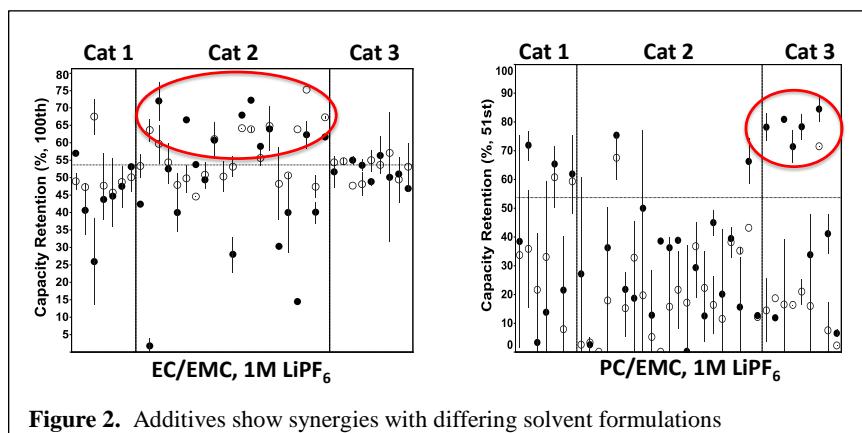


Figure 2. Additives show synergies with differing solvent formulations

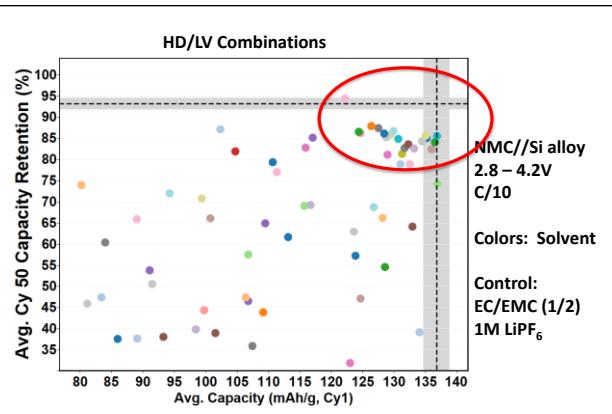
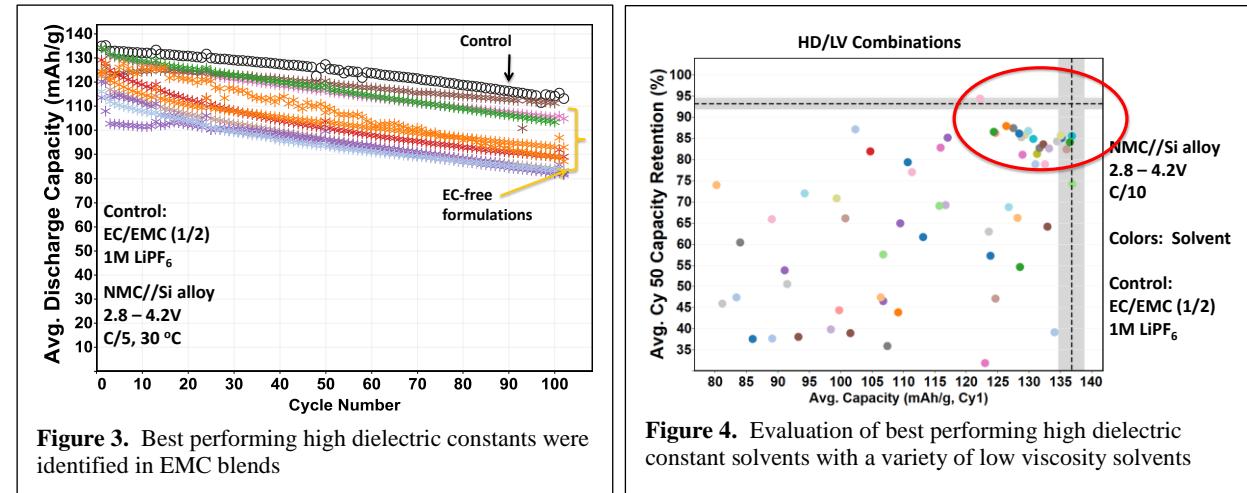
In EC-based formulations, Category 2 additives tended to show improved capacity retention relative to the baseline (dashed line). Yet these same additives showed detrimental performance relative to the baseline in PC based formulations. Instead, Category 3 additives improved the cycle life performance when used with PC. Category 2 additives were reactive monomer species, such as VC, which appear to form an SEI in a cooperative fashion with EC to form higher molecular weight species. In the absence of the EC, they are unable to create an effective SEI. Category 3 based additives are polymer/oligomeric in nature, providing the necessary higher molecular weight species to the SEI film. Several other promising categories of additives were also identified that resulted in improved cycle life in PC-based formulations.

Phase 2: Identification of Promising Solvents for Noncarbonate or EC-Free Electrolyte Formulations

Solvent Selection

Using the additives identified in Phase 1 of the project, we evaluated the performance of large numbers of solvent combinations in full cells containing NMC and 3M silicon alloy anode. Approximate 25 high dielectric (HD) constant solvents and 25 low viscosity (LV) solvents were selected that met criteria of

electrochemical stability, physical properties, salt solubility, *etc.* for use as lithium ion battery electrolytes. Initial screening consisted of blending all the HD solvents with a linear carbonate, EMC, and evaluating with 1M LiPF₆ and one of five different SEI additives. Cycle life results for the best performing formulations are shown in Figure 3.



The most promising HD solvents were then blended with all LV solvents, 1M LiPF₆, and a single SEI additive for evaluation in full cells. The first cycle discharge capacity and capacity retention of these formulations are shown in a correlation plot in Figure 4. In this graph, the baseline performance for both metrics is shown as the gray band (vertical and horizontal). The data points in different colors represent varying combinations of HD and LV solvents. A number of combinations showed performance similar to the standard carbonate control formulation, which are circled in red.

These formulations provided the basis for further iteration and optimization. These best noncarbonate or EC-free formulations were then improved by optimization of solvent ratios, salts (concentration and combinations), and additives (concentrations and combinations).

Salt Optimization

While a wide variety of solvents were evaluated as described above, other formulation variables were kept constant. For example, all formulations contained 1M LiPF₆. However, there was no reason to expect that this salt or this concentration would be optimal for entirely new solvent systems. Therefore, optimization was required. Results for an example of the initial salt optimization experiments are summarized in Table 2. In the experimental design, each of the best combinations of HD solvents and LV solvents is tested with five different salts. For example, LV solvent A is blended with HD solvents 1, 2, and 3; LV solvent B is blended with HD solvents 1, 2, and 4; etc.

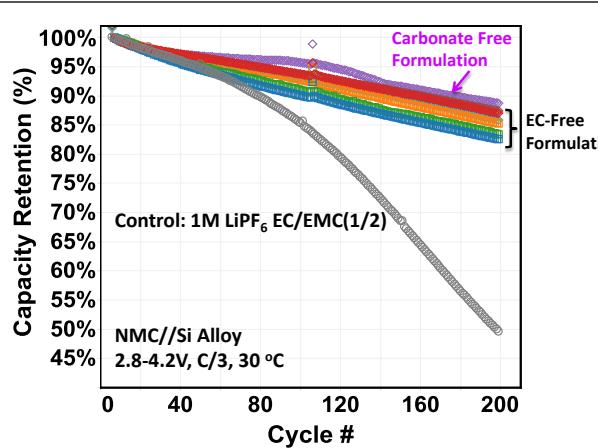
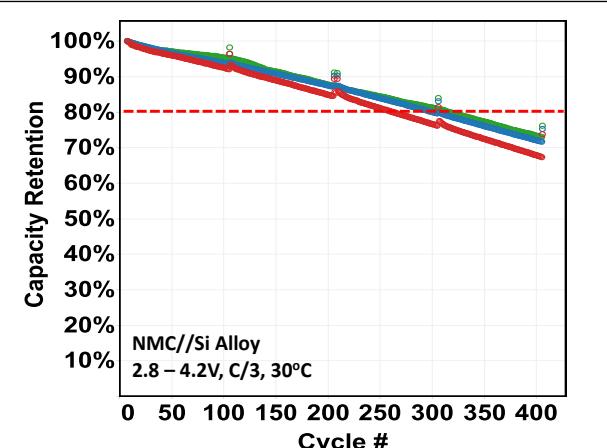
For each formulation, the cycle 1 capacity and cycle 100 capacity retention is determined. Results are visualized by color coding the box green if the performance is improved relative to the control, gray if the results are unchanged from the control, and red if the results are worse than the control. In this way, it is easy to see that, for example, Salt 5 tends to be beneficial to LV solvent B blended with HD solvents 1, 2, and 4. These results are the basis for further optimization of salt composition, concentration, and salt combinations to further improve full cell cycle life.

Table 2. Salt efficacy is very solvent dependent

		LiPF6		Salt 1		Salt 2		Salt 3		Salt 4		Salt 5	
LV	HD	Cy1 Capa. mAh/g	Capa. Reten (%)										
	Control	134.2	83.6	134.2	83.6	134.2	83.6	134.2	83.6	134.2	83.6	134.2	83.6
A	1	132.4	72.0	122.4	30.3	129.4	21.7	133.1	0.47	129.1	92.1	123.8	82.4
	2	134.1	80.2	122.6	33.0	131.6	33.9	132.7	0.34	129.8	93.3	123.2	80.1
	3	122.9	71.8	80.3	41.5	131.4	53.3	128.7	1.9	125.9	89.0	122.4	82.3
B	1	124.5	78.4	31.1	59.4	125.9	26.3	134.5	76.7	127.3	15.1	131.3	88.2
	2	131.6	75.7	116.6	62.5	131.9	73.9	131.5	84.6	102.3	6.9	127.2	89.6
	4	123.1	86.9	126.1	54.2	131.1	76.0	134.0	79.8	131.9	43.0	132.9	86.3
C	5	133.8	80.8	90.6	54.5	121.6	0.1	137.7	0.1	103.6	1.2	131.8	87.7
	6	131.7		-	-	118.6		135.7		120.4		129.2	
	7	136.5		-	-	118.5		135.1		133.7		129.5	
D	3	134.0	86.9	122.1	66.2	121.2	90.4	135.7	88.8	133.9	81.7	130.4	88.4
E	2	135.5		-	-	130.6		127.3		134.3		125.4	

Capacity Retention @ 100 cycles

Example cycle life results for optimized salts in the novel solvent formulations are shown in Figure 5, where cycle life of the noncarbonatd or EC-free formulations exceed that of the control. Cycle life results after further optimization are shown in Figure 6, where 300 cycles are achieved to 80% capacity retention in carbonate-free formulations. Thus far, all of the formulations contain only a single SEI additive - leaving much headroom for optimization of additives, additive concentrations, and combinations of additives.

**Figure 5.** Carbonate-free formulations exceed performance of control electrolyte**Figure 6.** Carbonate-free formulations achieve 300 cycles to 80% capacity retention

In parallel to the optimization experiments in novel solvent formulations, we continued to screen additional SEI additives in both EC and PC based formulations. These experiments provided additional options to include new additives in combination with those previously identified. Throughput multiple rounds of high throughput screening, Wildcat achieved further improvement in cycle life while building knowledge on structure property relationships as we expand upon promising additives by structural modifications.

Phase 3: Formulation Optimization

The final optimization was completed and these formulations were sent for large format (18650 cell testing). The optimization consisted of combinations of additives and co-solvents in both noncarbonate and carbonate solvents to give a good balance of performance across multiple metrics. Thus, the formulations with the absolute best cycle life were not necessarily the ones selected for 18650 cell testing – as they may have had a severe shortfall that could not be corrected with additional additives. A total of four final formulations were identified for testing in 18640 cells (2-5) compared to a baseline formulation containing EC/EMC (1:2 by volume) + 10 wt. % FEC, as summarized in Table 3.

Table 3. Summary of final formulations for 18650 cells

Formulation	Solvents	Additives
Control	EC/EMC (1:2 by volume)	10% FEC
2	EC/EMC (1:2 by volume)	2% LiBOB, 2% WDT-2317
3	EC/EMC (1:2 by volume)	2% WDT-2320
4	Noncarbonate combination	2% VC, 0.5% WDT-2094
5	Noncarbonate combination	2% WDT-2320, 2% WDT-2094
6	Noncarbonate combination	2% VC, 2% WDT-2093

Room Temperature Cycle Life

Figure 7 shows the room temperature cycle life of these formulations 2-6 compared to the control electrolyte.

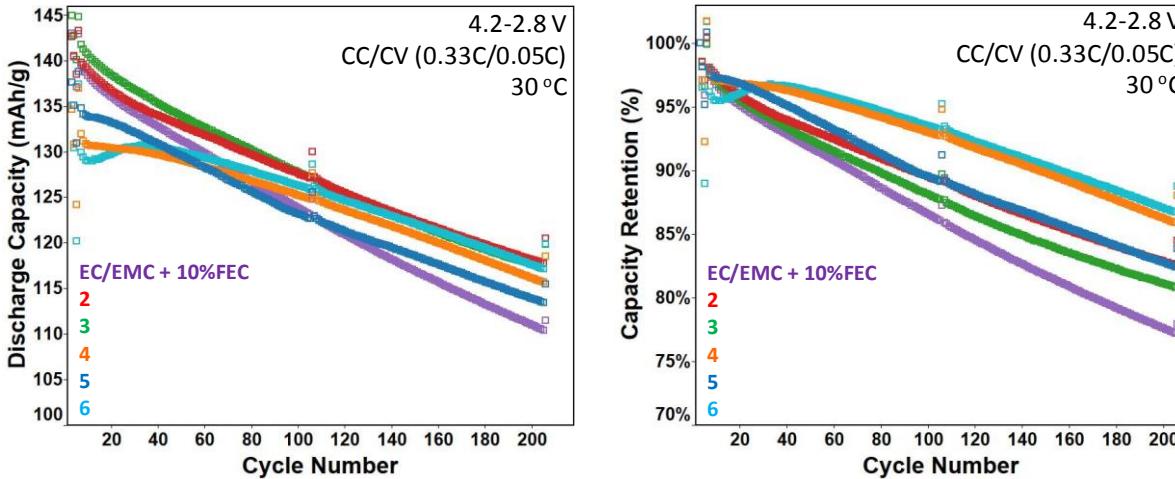


Figure 7. Room temperature cycle life improved with Wildcat formulations

All of the formulations identified by Wildcat improved capacity retention relative to the control. However, the two noncarbonate formulations (4, 5) had lower initial capacity. The best performing electrolyte in terms of capacity retention extrapolates to approximately double the cycle life of the control – 320 cycles. While the project goal was 500 cycles, our post-mortem work suggests that electrode failure mechanisms occurred that were unrelated to true lithium loss due to SEI formation (reported in last quarterly report). If active material

utilization decreases due to electrical isolation of particles or delamination from current collector, these problems cannot be affected by electrolyte improvements. Addressing these types of failure mechanisms was outside the scope of this project, but suggests that future efforts must address multiple failure mechanisms in parallel. Nevertheless, the new formulations show improved cycle life in full cells without the use of FEC.

Wildcat conducted a shelf life study of formulations 2-5, and found that formulation 4 was not stable over the course of weeks. Therefore, formulation 6 was substituted for formulation 4 in the 18650 cell testing. Formulation 6 showed similar room temperature performance.

High Temperature Cycle Life

The high temperature cycle life of formulations 2-5 is shown in Figure 8.

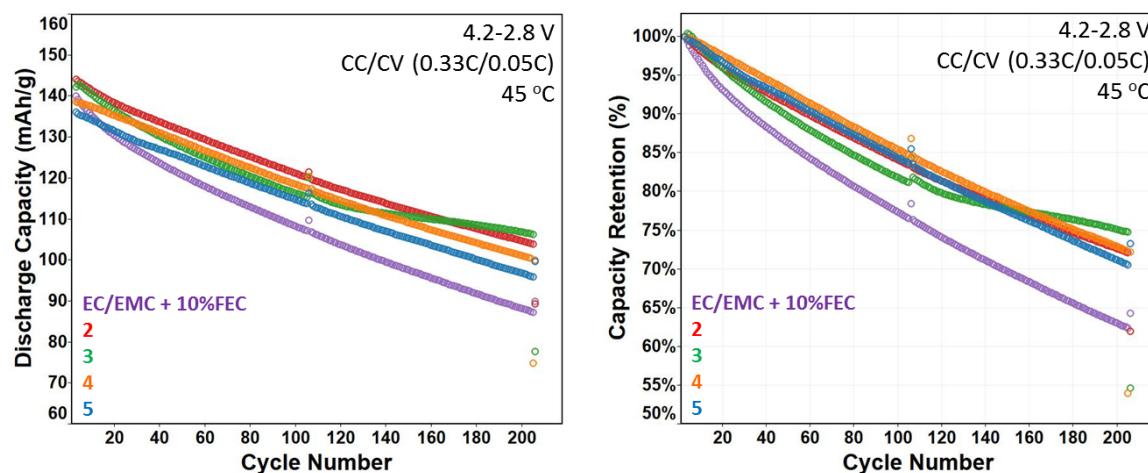
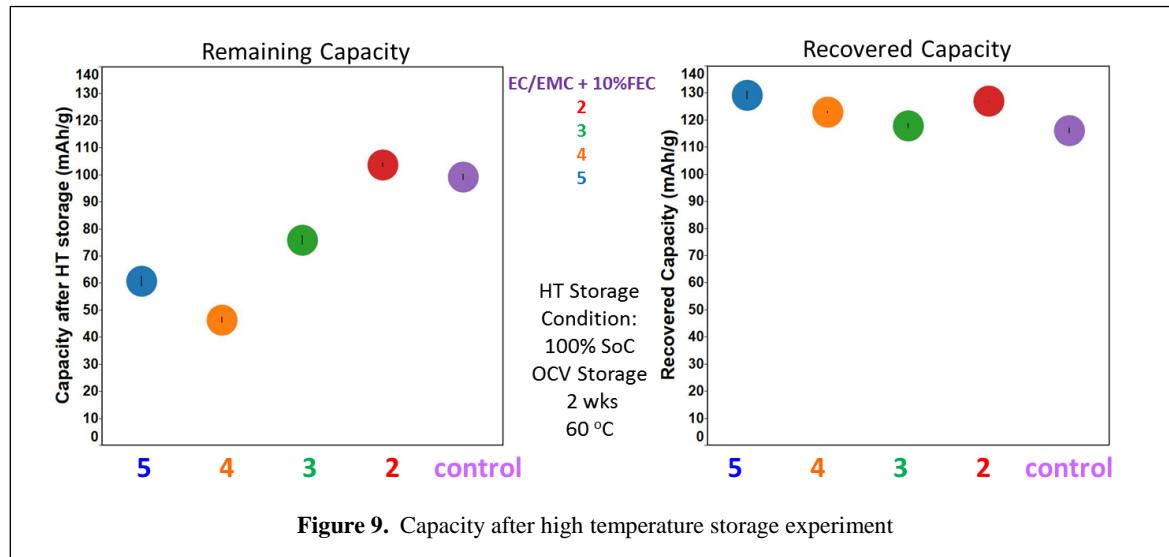


Figure 8. New formulations outperform control with 10% FEC

All the final formulations outperform the control electrolyte containing 10% FEC. High temperature performance of FEC is known to be problematic. Wildcat formulations offer significant value at high temperature due to replacement of FEC with other additives.

High Temperature Storage

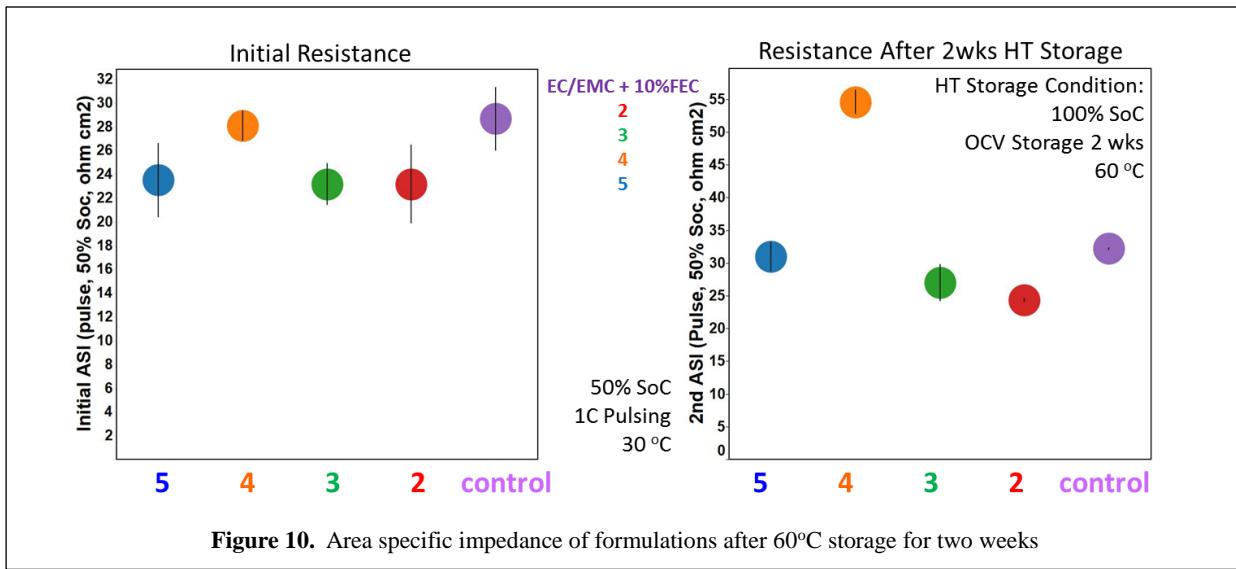
High temperature storage (60°C) experiments for two weeks were performed. The capacities remaining after the high temperature storage, as well as the recovered capacities are shown in Figure 9. Both the remaining capacities and recovered capacities were measured at 30°C at C/10 discharge rate. Several of the new electrolytes (3, 4, and 5) showed lower capacities after high temperature storage than the control. This self discharge could probably be minimized with further optimization of the formulations. All formulations showed similar or better recovered capacities to the control formulation containing 10% FEC.

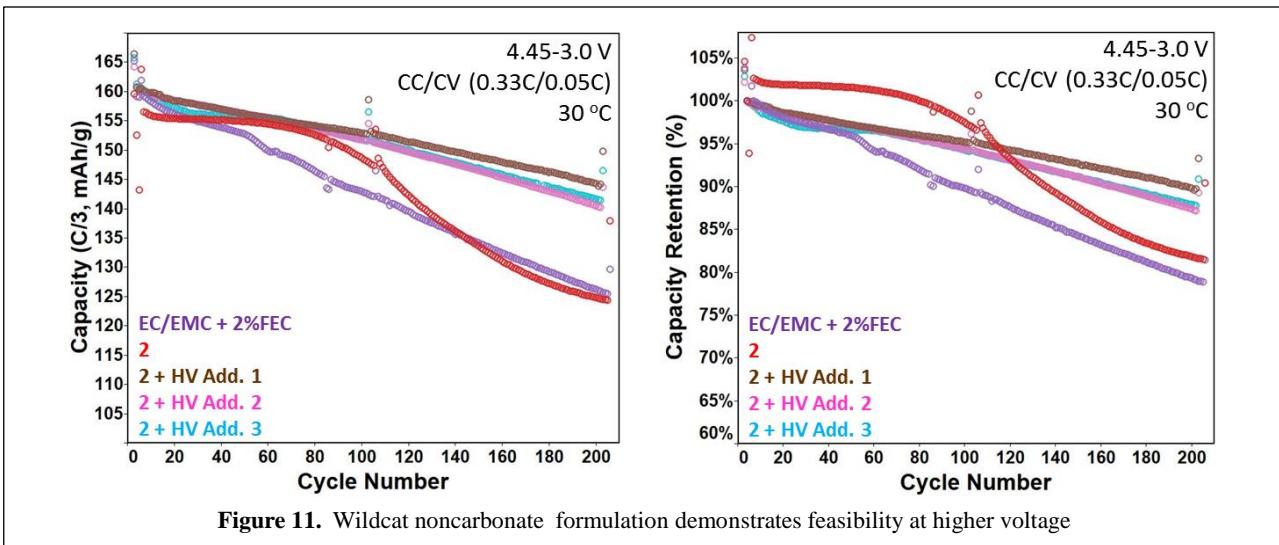


The cell impedance growth after high temperature storage (60°C) for two weeks was also measured for these formulations. Figure 10 shows that the initial impedance of the four final (non-carbonate and carbonate-based) formulations is similar or lower to that of the control electrolyte with 10% FEC. After high temperature storage, three of four formulations maintain similar area specific impedances.

High Voltage Cycle Life

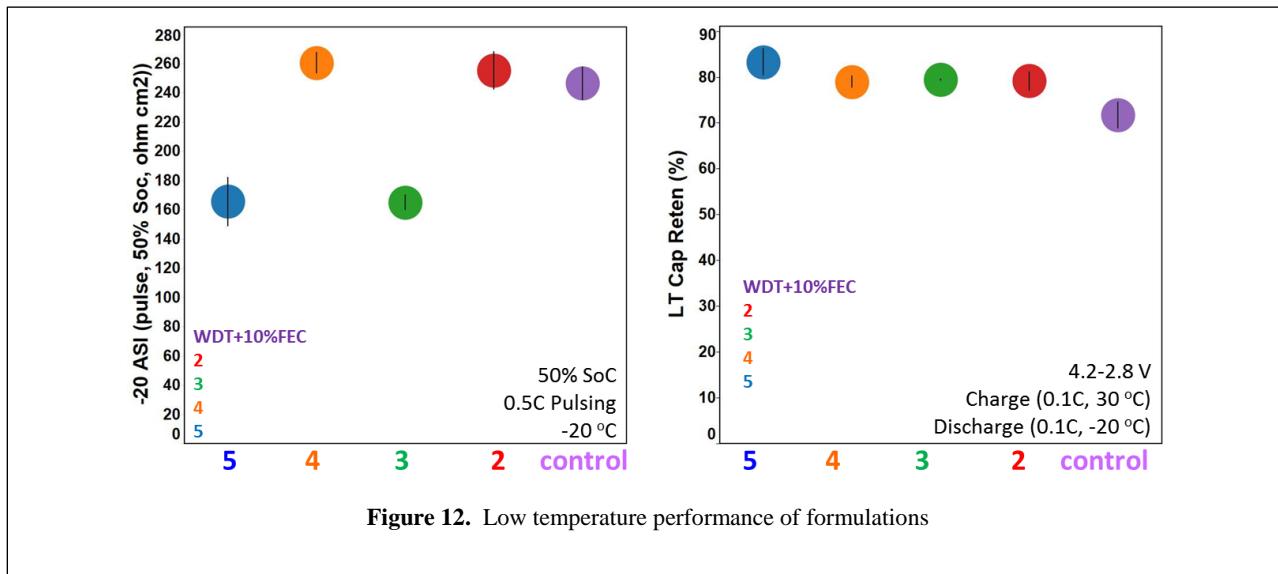
The new formulations would be expected to have similar performance at high voltage as standard carbonate formulations, but benefit from elimination of the FEC. One of the new formulations were tested and optimized with high voltage additives to demonstrate their feasibility at higher voltages, as shown in Figure 11. In this case, the FEC content in the control electrolyte was reduced to 2% as we know this additive does not perform well at high voltage. The formulations could not be tested above 4.45V, as we did not have electrodes balanced for higher voltages. However, the results at 4.45V show that with the addition of high voltage additives, this new formulation can cycle better than the control.





Low Temperature Performance

The low temperature (-20°C) area specific impedance (ASI) and capacity retention on C/10 discharge were also measured for the formulations. As shown in Figure 12, the new formulations all showed similar or lower ASI and similar or higher discharge capacity (C/10) at -20°C compared to the 10% FEC control electrolyte.



Ionic Conductivity

Ionic conductivity results for the formulations are summarized in Table 4. While the room temperature ionic conductivity is less for the noncarbonate formulations (4,5,6), the low temperature ionic conductivity is similar. In general, silicon anodes cannot be cycled at high rates, so room temperature ionic conductivity can tolerate some decrease. However, in order to pass low temperature cold crank tests, it is important not to significantly decrease the low temperature ionic conductivity.

Table 4. Room temperature and low temperature ionic conductivities of formulations

Formulation	25°C Ionic Conductivity (mS/cm)	-30°C Ionic Conductivity (mS/cm)
Control (10% FEC)	8.5	1.8
Control (2% FEC)	7.5	1.4
2	9.1	1.7
3	9.2	1.8
4	5.4	1.6
5	5.0	1.4
6	5.8	1.7

Pouch Cell Testing

In an effort to help ensure translation of results from Wildcat small format cells to larger format cells (such as 18650), we prepared single layer pouch cells using the same NMC//Si alloy electrodes. Variables such as the electrolyte amount and stack pressure were varied to determine the effect on cell performance for a selection of electrolytes. Samples of the results are shown in Figures 13 and 14.

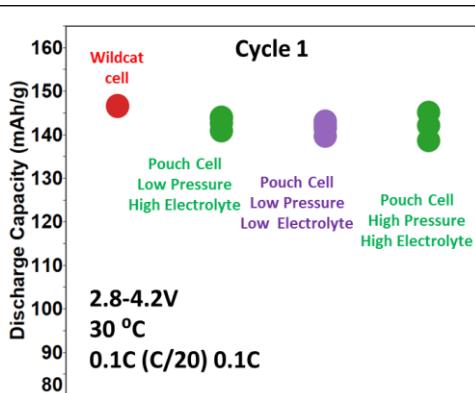


Figure 13. Wildcat pouch cells perform similar to high throughput cells on Cycle 1

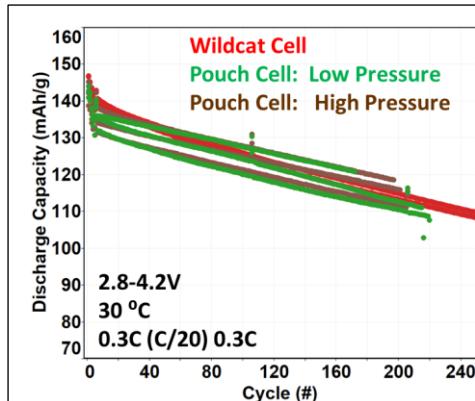


Figure 14. Cycle life in Wildcat pouch cells is similar to high throughput cells

Post-Mortem Testing

From the cycled pouch cells, we defined electrochemical experiments to determine if the failure mechanism of the cell has changed at the longer cycle life. In general, the anodes show visual flaws and delaminations after cycling (Figure 15).

The cycled cathodes and anodes were harvested, washed, and re-tested in half cells, with results shown in Figures 16 and 17. With essentially infinite lithium supply in the half cell testing, loss of capacity on either electrode indicates a reduction in access of the active material.

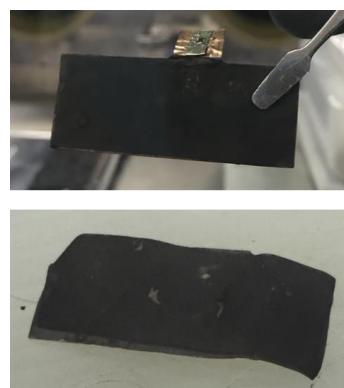
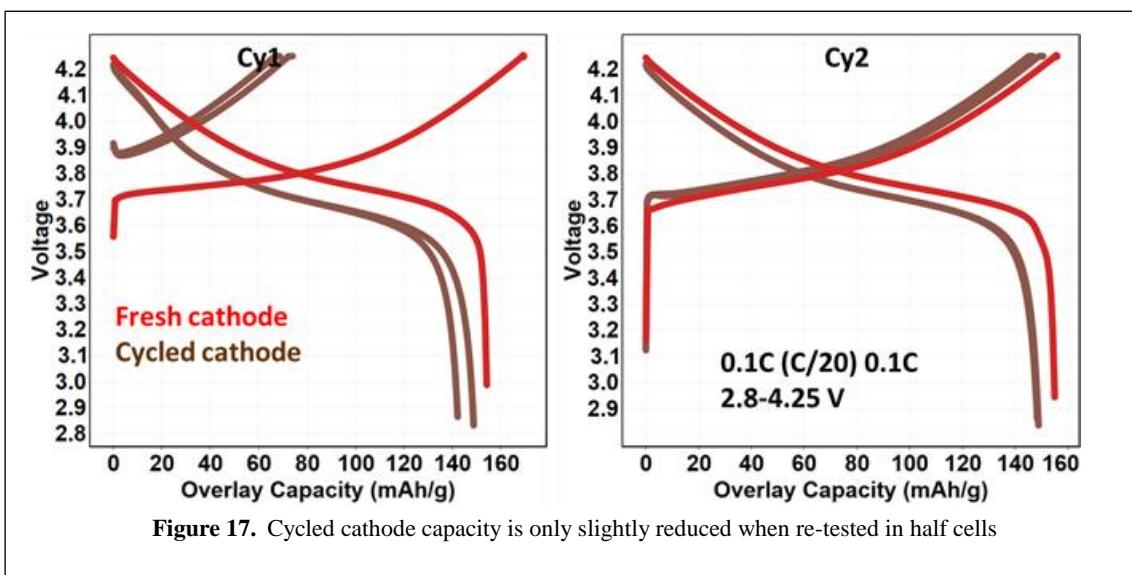
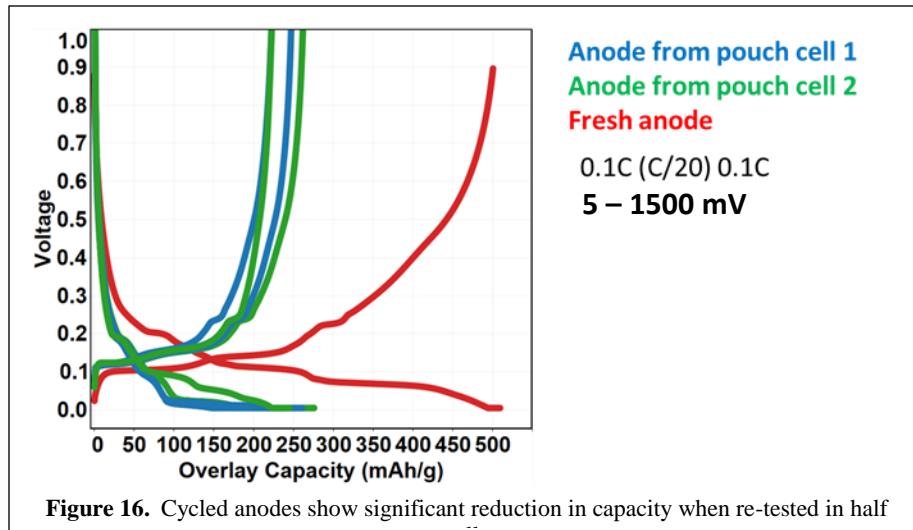


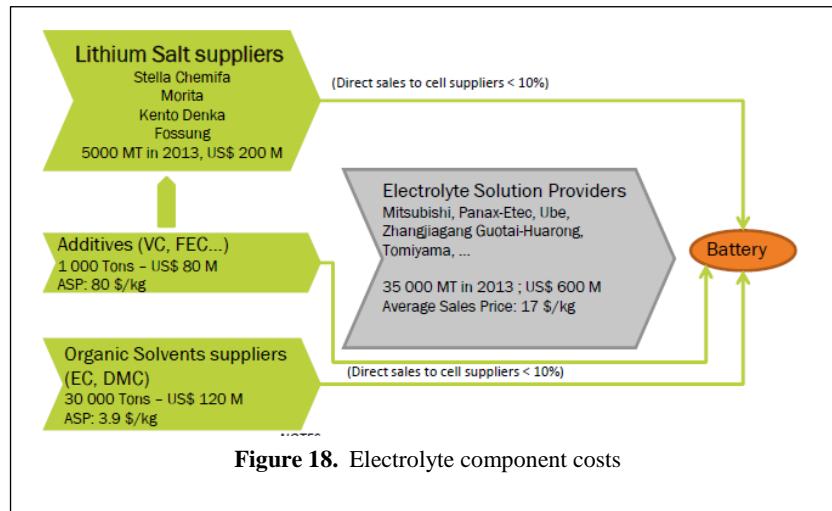
Figure 15. Anode delamination is observed after cycling



Significant capacity loss was observed on the anode relative to the cathode. The large loss on the anode can be due either to a large impedance growth on the cycled anode or to actual loss of active material in the electrode. The data were obtained at a fairly low c-rate (C/10), which would indicate active material loss is a big contributor.

Cost Analysis

A cost comparison of the electrolytes was also performed. According to Avicenne Energy (4/2015, 24th Edition), carbonate solvents for battery use have an average selling price of \$3.9/kg (2013 data, Figure 8). Common additives such as FEC have an average selling price of \$80/kg. Most electrolytes used with silicon anodes today contain high concentrations (10 – 30 weight %) of FEC, resulting in significant cost increases.



Wildcat developed both carbonate and non-carbonate based formulations with improved performance over the course of this project. The carbonate-based formulations use typical carbonate solvents expected to match the average selling price of \$3.9/kg. Formulations 2 and 3 (carbonate) shown in preceding graphs contained no FEC, and contained much lower additive quantities. Formulation 2 contains 4 weight % total additive concentration, and formulation 3 contains 2 weight %. The specific additive packages used are combinations of common additives used today and newly discovered Wildcat additives. The common additives (used at 2 weight % or less) would compare in cost to those in Avicenne report, so should not impart a cost increase in the new formulations relative to a standard carbonate formulation. Prices for the new additives can be found on line for small volumes on the order of \$5-10/kg, well under the average selling price of \$80/kg. The new additives are also used at typical concentrations of 2 weight % or less.

Similar additives are used in the noncarbonate formulations, so the cost comparison will depend upon the relative costs of the solvents. Online prices for higher volume high purity anhydrous solvents used for the new formulations were on the order of \$3-5/kg (\$3000-\$5000/metric ton). Of course, the actual cost comparison will depend upon many factors including purity of the starting components and any purification that might be required. Materials used in this project were used as received and were not subjected to further purification.

In summary, the high level cost analysis of Wildcat new formulations do not show any obvious cost increases over today's state of the art silicon electrolyte formulations – which contain high levels (10-30 weight %) of expensive FEC.

CONCLUSIONS AND FUTURE DIRECTIONS

We have made dramatic progress in the identification of noncarbonate solvents for use with silicon anodes in lithium ion batteries. The current cycle life of 350 cycles to 80% capacity retention outperforms the control electrolyte containing significant quantities of expensive FEC. It should be pointed out that further improvements could be made to the carbonate based control electrolyte – which may make it a better selection in the long run. However, this project will result in alternatives to carbonates that may provide other advantages such as high voltage stability, lower volatility, etc. Furthermore, the electrolyte additives being discovered may be valuable across a range of solvent systems.

PROJECT PUBLICATIONS/PRESENTATIONS

1. Strand, D.A., Caldwell, M., DOE Annual Merit Review poster (Jun., 2014, Washington, DC)
2. Strand, D.A., Zhu, Y., Cheng, G., Caldwell, M., "Development of Novel Electrolytes for Silicon Anodes," The Battery Show, (Sept., 2014, Novi, MI)
3. Strand, D.A., Zhu, Y., Cheng, G., Caldwell, M., "Review: Development of Novel Electrolytes for Silicon Anodes," BATT Review, (Jan., 2015, Berkeley, CA)
4. Strand, D.A., Zhu, Y., Cheng, G., Caldwell, M., "Novel Noncarbonate Electrolytes for Silicon Anodes," 32nd International Battery Conference, (Mar., 2015, Ft. Lauderdale, FL)
5. Li, B., Strand, D.A., Zhu, Y., Cheng, G., Caldwell, M., "Novel Noncarbonate Electrolytes for Silicon Anodes," 2nd International Forum on Cathode & Anode Materials for Advanced Batteries, (Apr., 2015, Hangzhou, China)
6. Zhu, Y., Strand, D.A., Cheng, G., "Development of Novel Lithium Ion Battery Electrolytes for Silicon Anodes," 227th ECS Meeting, (May, 2015, Chicago, IL)
7. Strand, D.A., Zhu, Y., Cheng, G., Caldwell, M., "Novel Noncarbonate Electrolytes for Silicon Anodes," DOE AMR, (Jun., 2015, Washington, D.C.)
8. Cheng, G., Zhu, Y., Strand, D.A., "Development of Novel Electrolytes for Silicon Anodes," 4th China LIB Electrolytes Conference 2015, (Jun., 2015, Hangzhou, China)
9. Cheng, G., Zhu, Y., Strand, D.A., "Novel Noncarbonate Electrolytes for Silicon Anodes," AABC USA 2015, (Jun., 2015, Troy, MI)
10. Strand, D.A., Zhu, Y., Cheng, G., "Development of Novel Electrolytes for Silicon Anodes," ABAA8, September/2015, Bilbao, Spain.
11. Strand, D.A., Zhu, Y., Cheng, G., "Development of Novel Electrolytes for Silicon Anodes," Batteries 2015, October/2015, Nice, France.
12. Li, B., Zhu, Y., Strand, D., Cheng, G., "Development of Electrolytes for Silicon Anodes," 12th China International Battery Fair (CIBF), May, 2016, Shenzhen, China.
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14. Zhu, Y., Strand, D., "Development of Electrolytes for Silicon Anodes," IMLB (June, 2016, Chicago, IL).
15. Strand, D., Caldwell, M., Cheng, G., "Electrolyte Formulations with Improved Cycle Life on Silicon Anodes," PCT/US15/045902.
16. Cheng, G., Strand, D., Zhu, Y., Caldwell, M., "Electrolyte Formulations with Improved Cycle Life on Silicon Anodes," US15/045902.
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18. Zhu, Y., Cheng, G., Strand, D., Yang, J., "Electrolyte Formulations with Improved Cycle Life on Silicon Anodes," US15/251755.
19. Zhu, Y., Cheng, G., Strand, D., Yang, J., "Electrolyte Formulations with Improved Cycle Life on Silicon Anodes," US15/251763.
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