Silatronix® High-performance organosilicon compounds for energy storage

New Advanced Stable Electrolytes for High-voltage Electrochemical Energy Storage

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Project ID: bat271

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Overview

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Timeline

- Project start date: 10/01/2015
- Project end date: 02/28/2018
- Percent complete: 100%

Budget

- Total project funding: $ 1,665 K
  - DOE (Silatronix): $897 K
  - Contractor share: $333 K
  - DOE (Subcontractor): $435K
- DOE (Silatronix) for FY17: $425 K
- DOE (Silatronix) for FY18: $2 K

Barriers

- Electrolyte development for
  - High voltage stability
  - Good thermal stability
  - Stable SEI layer to improve cycle life

Partners

- US Army Research Laboratory
- Argonne National Laboratory

Objective and Relevance

Project Objective: Develop an electrolyte system stable at high voltage (≥ 5V) to enable the development of high energy density Li-ion batteries required by the automotive industry.

Relevance: This technology, if successful, will have a significant impact on the enablement of high voltage cathode materials in Li-ion batteries. In turn, this will provide a significant pathway for the development of higher energy density electrochemical storage devices, which is critical to expanding the electrification of the US vehicle fleet.

Specific Technical Metrics:

- Oxidative Stability
  - Breakdown voltage > 6 V (vs. Li/Li^+)
  - Parasitic current < 0.02 mA/cm^2 (at 6 V and 50°C)
- High Voltage System Performance
  - Initial capacity ≥ carbonate control electrolyte (e.g. 5V LNMO system)
  - > 80% initial capacity remaining after 300 cycles at ≥ 55°C

Project Milestones

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Milestones for FY2018:

Milestones and Go/No-Go Decision	Milestone Verification Process	Date	Status
Manufacture multilayer pouch cells for large pouch cell builds	LMNO/graphite multilayer pouch cells manufactured at ANL	Oct. 2017	Complete
Performance Testing of Final Pouch Cell Build: Cycle stability at 30°C and Pouch swelling at 30°C	Top formulations: cycle stability (capacity loss %, mAh/g), pouch swelling (thickness %, ml) at ANL	Jan. 2018	Complete

Approach: LNMO/Graphite Pouch Cell Tests at ANL

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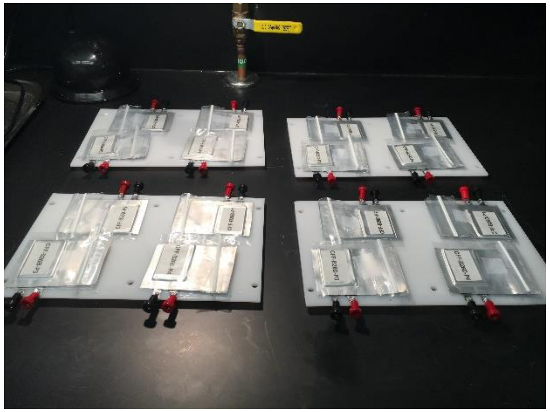
ELECTROCHEMICAL STUDY (4 Cells per formulation: Cut-off voltage dropped from 4.9 V to 4.7 V to reduce gassing)

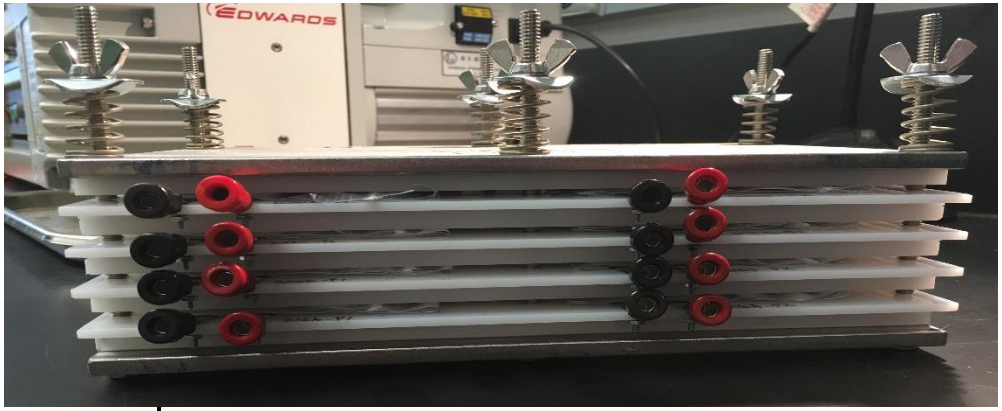
- Formation (5 cycles in test)
  - 1.5V Tap and hold for 15 min
  - **3.5-4.7V (1st round 4.9V):**
    - 3 cycles at C/10 and 2 cycles at C/3
- De-gas Pouch Cells and Reseal in Dry Room
- Rate Study (17 cycles in test)
  - **3.5-4.7V (1st round 4.9V):**
    - Cycles with discharge rates at C/20, C/10,C/5,C/2, 1C,2C.
- De-gas Pouch Cells and Reseal in Dry Room

- Life Cycle (200 cycles in test)
  - **3.5-4.7V (1st round 4.9V):**
    - 1 cycle: C/20; 47 cycles: C/2; 1 cycle: 1C
    - HPPC (9 pulses of 5C discharge, 3.75C charge)
  - Above Process repeats 4x
  - Life cycle testing procedure is restarted on cells that retain discharge capacity retention > ~80%

GAS FORMATION STUDY (Archimedes Measurement)

- **Pre** Formation
- **After** Formation/Rate (Pre & Post De-Gas Measurements)
- **After** Life Cycle





Pouch Cell (LNMO/Graphite) – First Round Test at 3.5-4.9 V (Gassing: Failed after rate test)

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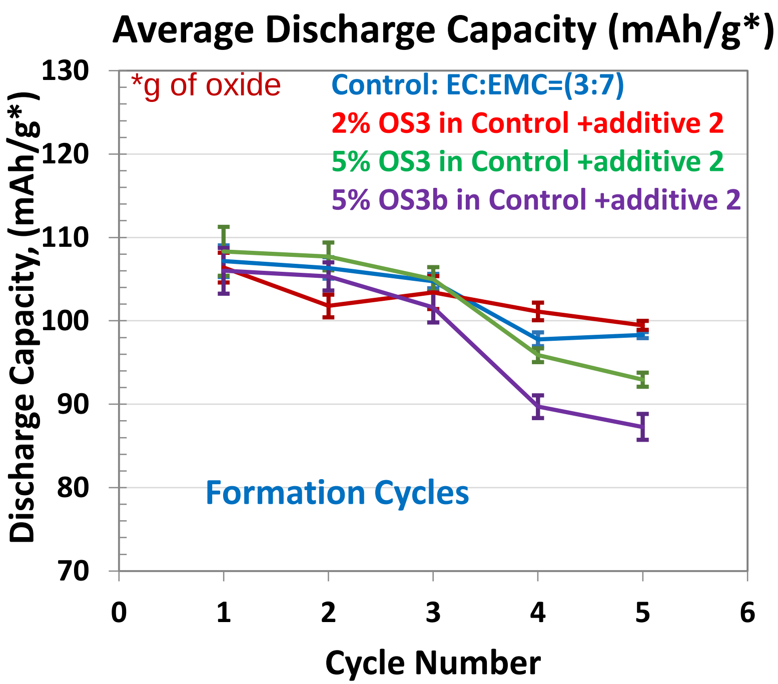
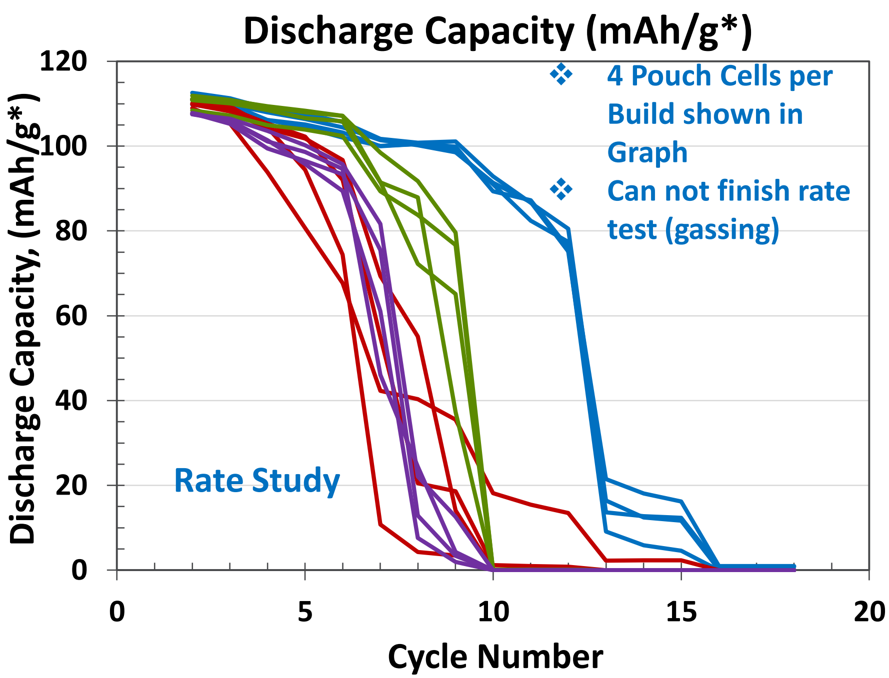
Electrolyte	FORMATION DATA (Averaged)				RATE STUDY DATA (Averaged)			
	1st Charge Capacity (mAh/g)	Reversible Discharge Capacity (mAh/g)	Irreversible Capacity Loss (mAh/g)	1st Cycle Efficiency (%)	C/10 (mAh/g)	C/2 (mAh/g)	1C (mAh/g)	2C (mAh/g)
Control: EMC:EC=(7:3) by vol	141	106	35	76	103	82	65	48
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

Cell failed after rate tests.





Pouch Cell (LNMO/Graphite) – Second Round Test at 3.5-4.7 V

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Formation & Rate Data (2nd round pouch cell tests at 4.7 V cut-off voltage)

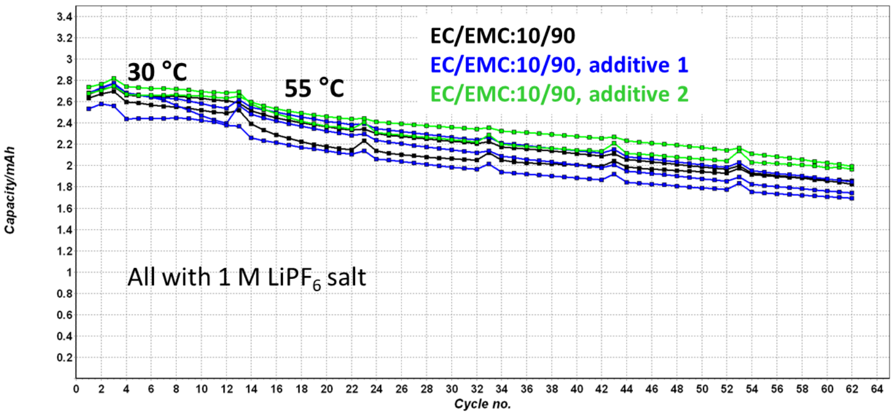
Electrolyte	FORMATION DATA (Averaged)				RATE STUDY DATA (Averaged)			
	1st Charge Capacity (mAh/g)	Reversible Discharge Capacity (mAh/g)	Irreversible Capacity Loss (mAh/g)	1st Cycle Efficiency (%)	C/10 (mAh/g)	C/2 (mAh/g)	1C (mAh/g)	2C (mAh/g)
1. Control: EMC:EC=(7:3) by vol	122	92	30	76 %	98	92	85	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

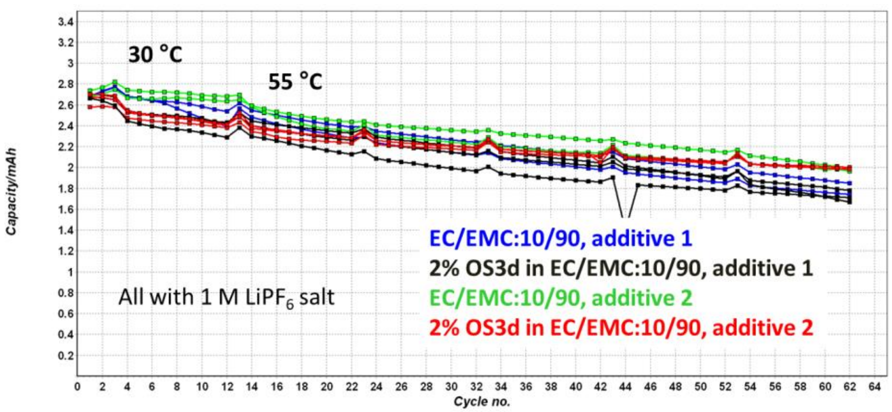
Cell failed after rate tests.

- Decreasing the voltage to 4.7V resulted in reduced gassing for the EC/EMC control (Formulation 1) and the 5% OS3 EC/EMC electrolyte (Formulation 2).
- 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.

Technical Accomplishment: Cycling Tests of OS Electrolytes (LNMO/Graphite Coin Cell)

C/20 for 2 cycles and C/2 for 10 cycles at 30°C, then 50 cycles at 55°C with C/2.
Voltage Window: 3.5-4.9 V.





The 1st round of pouch cell tests comparing the EC/EMC control and 3 OS formulations showed a large amount of gassing and could not complete the cycling evaluation. FEC showed as a gas generator during 2nd round test even at 4.7 V.

The composition of the final formulations was optimized at Silatronix to reduce gassing and also improve capacity retention testing.

- To further reduce gassing, the EC content was reduced in the carbonate controls.
- OS formulations (e.g. 2% OS3d) with different additives show similar capacity retention compared to the corresponding carbonate controls.
- 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.

Technical Accomplishment: LNMO/Graphite Pouch Cell Tests in Optimized Electrolytes at ANL

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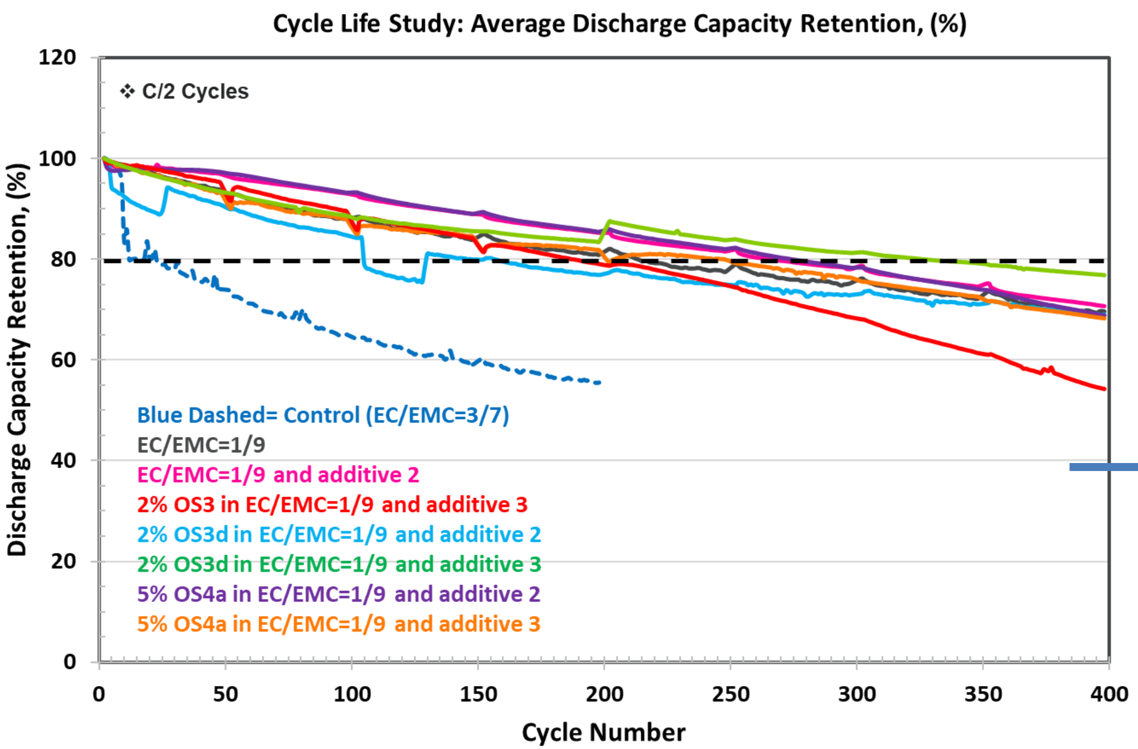
- After the 2nd round of pouch cell tests at 4.7 V, 8 optimized OS electrolytes and carbonate controls (without FEC) went through the same test protocol.
  - Formation, rate, cycle life testing and gas generation studies.
- Seven HV electrolytes (2 carbonates and 5 OS electrolytes) completed the initial cycle life testing with >~ 80% capacity retention. These cells were restarted for a second cycle life test (422 cycles total).



Discharge Capacity Retention compares:

- 1st Full C/2 cycle in the Cycle Life testing (cycle 24)
- Last Full C/2 Cycle in Cycle Life Testing

2% OS3d and 5% OS4a electrolytes show similar or improved capacity retention compared to the 10% EC carbonate controls.

Technical Accomplishment: LNMO/Graphite Pouch Cell Tests in Optimized Electrolytes at ANL

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Cycle #@ 80% Discharge Capacity Retention Rankings (Listed in Order from Best to Worst)

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**

- Reduction of EC content from 30% to 10% significantly improves cycle performance in LNMO/graphite pouch cells.
- Low OS3d and OS4a concentration electrolytes show improved capacity retention compared to the carbonate control.
- 2% OS3d demonstrates lowest gassing after cycling, which also can provide best cycling performance with appropriate additives.

Response to Reviewers Comments

Comment #1: The reviewer inquired can OS3 be applied to general electrode to improve safety as well.
Response #1: We observed safety benefit from OS3 in different electrode systems. (e.g. NMC, NCA, LCO and LFP).

Comment #2: The reviewer commented that no data are given on low-temperature performance.
Response #2: We are using performance at high temperature as a metric to better provide differentiation in HV performance. We understand the importance of low-temperature performance for specific applications, however it is beyond the scope of this development program.

Comment #3: The reviewer noted that all pouch cells were showing a large amount of gassing and developing an electrolyte system stable at high voltage (>5V) was unlikely.
Response #3: Several methods have been applied to reduce gassing in this program. Based on what we learned from this program, lowering the EC content and optimizing the additive package has a significant impact on gassing. This may allow the application of higher OS concentrations or combinations of different OS solvents. We believe we can develop an electrolyte that is stable in HV (> 5V) system.

Collaboration and Coordination

Collaborators:

- U.S. Army Research Laboratory (Kang Xu, Project team member)
- Argonne National Laboratory (Bryant Polzin, Project team member)

Interactions:

- University of Wisconsin Madison (Facilities Use in Chemistry Department and UW Advanced Materials Consortium)
- APS Center at Argonne National Laboratory (XANES Experiment)

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.

Summary

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The focus of this year has been to optimize and evaluate HV electrolytes in pouch cells at Argonne National Laboratory (ANL).

- Over 20 HV electrolyte formulations have been evaluated at ANL this year. 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).
- All pouch cells with FEC in EC-free electrolytes demonstrate a gassing problem even at 4.7 V cut off voltage, and we believe 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.
- OS3d is a promising OS solvent to reduce swelling during pouch cell testing, which also provides the best cycling performance at only 2%.
- With appropriate additive packages, some OS solvents show cycling and swelling benefits for LNMO system, which may also be applied to other electrodes at higher voltage.

Technical Back-Up Slides

Pouch Cell Tests (Cycle at 3.5-4.7 V, Formation/Rate Data)

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HV electrolytes with 422 total cycle number vs. Control

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)
2% OS3d in EC:EMC=(1:9) +additive 3	137	110	27	79 %	110	107	106	104
5% OS4a in EC:EMC=(1:9) +additive 2	131	106	25	80 %	112	107	104	99
EC:EMC=(1:9) +additive 2	123	99	24	78 %	112	108	106	103
5% OS4a in EC:EMC=(1:9) +additive 3	128	101	27	78 %	108	104	101	97
EC:EMC=(1:9)	128	101	27	75 %	109	105	101	97
2% OS3, EC:EMC=(1:9) +additive 3	135	108	27	79 %	108	103	98	92
2% OS3d in EC:EMC=(1:9) +additive 2	127	99	28	76 %	107	103	98	93
Control (EC/EMC:3/7)	120	94	26	75 %	103	96	88	81

- All HV electrolytes show better rate performance than control.
- Some OS containing electrolytes show better initial capacity and 1st cycle efficiency than carbonate controls.