

## **Electrolytes with Improved Safety Developed for High Specific Energy Li-ion Cells with Si-Based Anodes**

M. C. Smart<sup>1</sup>, F. C. Krause<sup>2</sup>, C. Hwang<sup>1</sup>, J. Soler<sup>1</sup>, W. C. West<sup>1</sup>,  
B. V. Ratnakumar<sup>1</sup>, and G. K. S. Prakash<sup>2</sup>

<sup>1</sup> Jet Propulsion Laboratory, California Institute of Technology,  
Pasadena, California 91109-8099, USA

<sup>2</sup> Loker Hydrocarbon Research Institute  
University of Southern California  
837 Bloom Walk, Los Angeles, California 91003, USA

A number of electrolyte formulations that have improved safety characteristics have been developed for use with high capacity silicon-based anodes. To improve the compatibility with Si-based anodes, a number of technical approaches have been employed, including: (1) the use of mono-fluoroethylene carbonate (FEC) in conjunction with, or in lieu of, ethylene carbonate (EC), (2) the use of high proportions of fluorinated co-solvents, (3) the use of vinylene carbonate (VC) to stabilize the Si/C electrode, and (4) the use of lithium bis(oxalato)borate (LiBOB) to improve the compatibility of the electrolyte when Si/C electrodes are used in conjunction with high voltage cathodes. Candidate electrolytes were studied in Li/Si-C and Si-C/ Li(MnNiCo)O<sub>2</sub> (NMC) coin cells, as well as in larger Si-C/NMC three-electrode cells equipped with lithium reference electrodes. In summary, many electrolytes that contain triphenyl phosphate (TPP), which is used as a flame retardant additive up to concentrations of 15 volume percent, and possess FEC as a co-solvent have been demonstrated to outperform the all-carbonate baseline electrolytes when evaluated in Si-C/ Li(MnNiCo)O<sub>2</sub> cells.

### **Introduction**

NASA requires high specific energy rechargeable batteries that possess enhanced safety for a number of “human-rated” applications. Lithium-ion technology has been identified as being the most promising energy storage device for near term applications, and extensive effort has been devoted to developing advanced anode and cathode materials to improve the energy density. With these new electrode chemistries, there is a strong desire to improve the safety characteristics, for both aerospace and terrestrial applications, including for hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEV). In our previous work,<sup>1,2</sup> a number of electrolytes with reduced flammability have been developed and demonstrated to be compatible with carbon based anodes and a range of cathode materials, including LiNiCoO<sub>2</sub>, LiNiCoAlO<sub>2</sub>, and LiMnNiCoO<sub>2</sub>. Some of the electrolytes identified and previously described perform well

when coupled with silicon-based anode materials, however, there is a desire to obtain further improved electrolytes that result in long life, while still providing enhanced safety.

Silicon-based alloy anode materials are especially attractive alternatives to the traditionally used carbon-based anodes, offering nearly three times more specific capacity. However, due to dramatic volume changes during cycling which results in mechanical disintegration, the materials are generally observed to have rapid capacity fading. Some groups have attempted to modify the electrolyte solution used in these systems with the intent of stabilizing the electrode-electrolyte interface, with the prospect of enhanced life. Nguyen and coworkers have described using an ionic liquid electrolyte which was observed to provide improved cycle life of Si-Cu film electrodes compared to a baseline carbonate-based electrolyte, being attributed to desirable solid electrolyte interphase (SEI) formation.<sup>3</sup> Researchers from Sony Corporation have reported that the use of mono-fluoroethylene carbonate (FEC) results in improved cycle life of Si electrodes, due to the formation of a stable SEI consisting of lithium fluoride and a polyene-compound.<sup>4</sup> Li et al. have described a system consisting of 0.5M LiBOB + 0.38M LiPF<sub>6</sub> in EC+dimethyl carbonate (DMC)+ethyl methyl carbonate (EMC) (1:1:1 v/v %) + 2% VC and report improved cycling life with Si thin-film electrodes when testing with a lithium counter electrode.<sup>5</sup> Other approaches involving the use of electrolyte additives include (a) the use of tris(pentafluorophenyl) borane (2-5 wt%) in LiClO<sub>4</sub> in EC+ diethyl carbonate (DEC) (1:1 v/v) electrolytes<sup>6</sup> (b) the use of succinic anhydride (3 wt%) in LiPF<sub>6</sub> in EC+DEC (1:1 v/v) electrolytes,<sup>7</sup> and (c) the use of vinylene carbonate (1 wt%) in LiPF<sub>6</sub> in EC+DMC (1:1 v/v) electrolytes.<sup>8</sup> Although these approaches resulted in improved performance, most of these systems were not designed to possess low flammability or provide improved safety. In addition, the majority of studies have been performed with lithium metal counter electrodes and the performance with high voltage cathodes was not addressed.

To develop advanced electrolytes with improved safety for use with silicon anode-based systems, a number of approaches can be taken to reduce the flammability of electrolytes, including the use of phosphorus-based flame retardant additives.<sup>1,2</sup> Additional modification of the electrolyte is also required if it is to be used in conjunction with high voltage cathodes. Of the flame retardants that we have evaluated, triphenyl phosphate (TPP) was identified as being the most desirable, since it displays the best overall performance with a number of systems. It has been demonstrated that the flammability of the electrolyte can be reduced by approximately 60% with the incorporation of 10-15% TPP.<sup>9</sup> Based on our previous work with TPP-based electrolytes with LiBOB, a number of electrolytes were developed to be compatible with the Si-based anodes, which embodied a number of technical approaches, including: (1) the use of FEC in conjunction with or in lieu of EC, (2) the use of high proportions of fluorinated co-solvents, and (3) the use of vinylene carbonate (VC) to stabilize the Si/C electrode. The chemical structures of these electrolyte components that have been investigated are illustrated in Figure 1. To evaluate these electrolytes, they were assessed in coin cells consisting of (a) Si-C composite electrodes and lithium metal counter electrodes, and (b) Si-C composite anodes and Toda high voltage lithium excess layered-layered metal oxide cathodes (i.e., NMC 9100 Li(MnNiCo)O<sub>2</sub>). The Si-C composite electrodes were developed by Georgia Institute of Technology, who have reported anode materials that display high capacity and good cycle life characteristics by utilizing a number of techniques, including the coating of silicon nanopowders with carbon and using polyacrylic acid as a binder in preference to carboxymethylcellulose (CMC) and

poly(vinylidene difluoride) (PVDF).<sup>10-14</sup> In addition to evaluating these materials in coin cells, three-electrode cells were employed to investigate the lithium kinetics of the respective electrodes, utilizing a number of electrochemical techniques including Electrochemical Impedance Spectroscopy (EIS), Tafel polarization, and linear micro-polarization measurements. As described below, many TPP-containing electrolytes (up to 15%) that possess FEC as a co-solvent have been demonstrated to outperform the all carbonate baseline electrolytes when evaluated in Si-C/ Li(MnNiCo)O<sub>2</sub> cells.

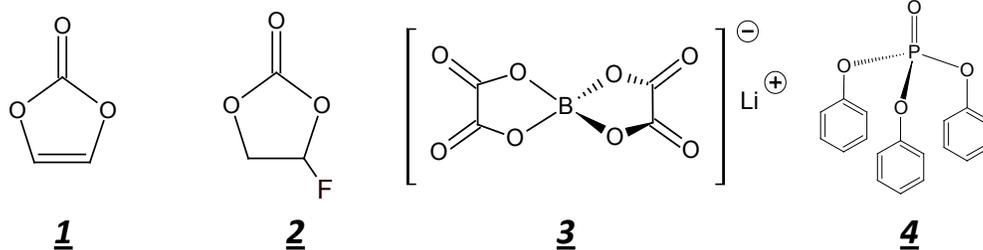


Figure 1. The chemical structures of various electrolyte components investigated in the development of electrolytes with improved safety and compatibility with silicon-based anodes, including vinylene carbonate (VC), 1, mono-fluoroethylene carbonate (FEC), 2, lithium bis(oxalato)borate, 3, and the flame retardant additive triphenyl phosphate (TPP) 4.

## Experimental

Initial coin-cell studies were performed with the Silicon-Carbon (Si-C) composite materials in Li/Si-C and Li/LiNiMnCoO<sub>2</sub> (NMC) systems by assembling them in stainless steel CR2032 coin cell hardware with Al clad stainless steel cases. Cell assembly was performed in an inert atmosphere glove box (water < 1 ppm). For more detailed electrical and electrochemical measurements, O-ring sealed, three-electrode, glass cells containing spiral rolls of Si-C anodes, Toda LiNiMnCoO<sub>2</sub> (NMC) cathodes, and lithium reference electrodes separated by two layers of porous polypropylene (Tonen-Setella) were used. The Si-C anode electrodes were coated with active material on both sides of the substrate and had an active material area of approximately 158.1 cm<sup>2</sup>, corresponding to ~ 3 mg/cm<sup>2</sup>. The NMC cathode electrodes were also double sided with an active material area of approximately 141.1 cm<sup>2</sup>, corresponding to ~ 19 mg/cm<sup>2</sup>. The carbonate-based solutions, EC and EMC containing LiPF<sub>6</sub> salt in the desired concentration, were purchased from Novolyte, Inc. and contained less than 50 ppm of water. Purified FEC, LiBOB, and additional LiPF<sub>6</sub> salt were also procured from Novolyte, Inc. and added to the stock solutions to produce the desired formulations. The TPP and VC used in the study was purchased from Aldrich Chem. Co. and Acros, Inc., respectively, and used as received.

Charge-discharge measurements and cycling tests were performed with either an Arbin or a Maccor battery cycler. For the formation cycling of the Li/Si-C coin cells, the cells were discharged to 0.010V (with the voltage held at 0.010V until the current decayed to a C/50 rate) and charged to 1.0V using C/20 rates. For the cycling of the Si-C/NMC cells, the cells were generally charged to 4.600V (with the voltage held at 4.600V until the current decayed to a C/50 rate) and discharged to 2.00V (using C/20 rates for the formation and C/10 rates for cycle life testing). To maintain the cells at the desired temperature, they were placed in Tenney environmental chambers (+/- 1°C).

## Results and Discussion

As previously mentioned, one of the primary goals of this work is to develop electrolyte formulations that enable the use of the next generation of high specific energy materials, such as high capacity Si-C-based anodes and high voltage lithium excess mixed metal oxide cathodes, while providing improved safety compared with traditionally used all-carbonate blends. To accomplish improved capability with Si-C-based anodes, a number of approaches were initially investigated including: (i) the use of FEC in lieu of EC, (ii) the use of high proportions of fluorinated solvents (i.e., the use of 2,2,2-trifluoroethyl butyrate (TFEB) in conjunction with fluoroethylene carbonate) and (iii) the use of vinylene carbonate (VC) to stabilize the Si/C electrode. To improve the compatibility with LiNiMnCoO<sub>2</sub> (NMC) cathodes, LiBOB was adopted with the intent of producing a desirable cathode electrolyte interface (CEI), based on favorable results when used in conjunction with TPP in C/NMC systems.<sup>2</sup> More recent work has also focused upon developing electrolytes that are compatible with Si-C anodes when used in conjunction with more traditional lower voltage cathodes, such as LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>. The result of this work has led to the conclusion that LiBOB is not a beneficial additive in such systems, so formulations have been explored in which it is not present. To gauge the success of these approaches, an all-carbonate-based electrolyte was also investigated to serve as a baseline. In summary, the electrolytes investigated in Li/Si-C and Si-C/NMC cells include the following:

- 1.0 M LiPF<sub>6</sub> in EC+EMC +DMC (1:1:1 v/v %) (Baseline)
- 1.00M LiPF<sub>6</sub> + 0.15M LiBOB in EC+EMC+TPP (20:70:10 vol %)
- 1.00M LiPF<sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol %)
- 0.50M LiPF<sub>6</sub> + 0.10M LiBOB in FEC+TFEB+TPP (20:70:10 vol %)
- 1.00M LiPF<sub>6</sub> + 0.15M LiBOB in EC+EMC+TPP (20:70:10 vol %) + 5% VC
- 1.00M LiPF<sub>6</sub> in EC+EMC+TPP (20:70:10 vol %)
- 1.00M LiPF<sub>6</sub> in FEC+EMC+TPP (20:70:10 vol %)

Initial studies involved evaluating the formation characteristics, the discharge rate capability, and cycle life performance in Li/Si-C and Li/LiNiMnCoO<sub>2</sub> (NMC) coin cells. More detailed electrical and electrochemical assessment was performed in three-electrode, cylindrical cells consisting of Si-C anodes, LiNiMnCoO<sub>2</sub> (NMC) cathodes, and lithium reference electrodes. In addition to investigating their charge/discharge performance, both anodes and cathodes were subjected to a number of electrochemical measurements, including Electrochemical Impedance Spectroscopy (EIS), Tafel polarization, and linear micro-polarization measurements (discussion is not included in this manuscript, due to size limitations).

### Formation Characteristics of Li/Si-C Coin Cells.

As illustrated in Table 1, high reversible capacity was observed with a number of candidate electrolytes in Li/Si-C cells, with over 1700 mAh/g being delivered for all samples after completing the formation cycling, which consisted of discharging to 0.010V (with the voltage held at 0.010V until the current decayed to a C/50 rate) and charging to 1.0V using C/20 rates. It should be noted that the first cycle consisted of only partially discharging and charging the cell in an attempt to maintain the desired two-

phase microstructure of silicon (i.e., lithiated amorphous silicon and completely unlithiated crystalline silicon) and avoid the lithiation of the crystalline phase.<sup>15</sup>

Table 1. The formation characteristics of Li/SiC cells containing various electrolytes at 23°C using C/20 discharge rates to 0.010V and C/20 discharge rates to 1.00V.

Electrolyte	1st Discharge (lithium intercalation) (mAh)	1st Charge (lithium intercalation) (mAh)	2nd Discharge (lithium intercalation) (mAh)	2nd Charge (lithium intercalation) (mAh)	5th Discharge (lithium intercalation) (mAh)	5th Charge (lithium intercalation) (mAh)	Cumulative Irreversible Capacity Loss (mAh/g)	5th Charge, (lithium intercalation) (mAh/g)
1.00M LiPF <sub>6</sub> in EC+DEC+DMC (1:1:1 vol%)	0.4780	0.3081	2.4561	2.2484	1.8325	1.8895	242.159	2222.94
1.00M LiPF <sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%)	0.5260	0.2772	2.5103	2.1722	1.8043	1.8563	488.414	1985.35
1.00M LiPF <sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%)	0.5260	0.2743	2.4673	2.0767	1.7648	1.7688	713.694	1891.76
0.50M LiPF <sub>6</sub> + 0.10M LiBOB in FEC+TFEB+TPP (20:70:10 vol%)	0.5260	0.2828	2.3215	1.9439	1.6564	1.6572	692.037	1772.41
1.00M LiPF <sub>6</sub> + 0.15M LiBOB in EC+EMC+TPP (20:70:10 vol%) + 5% VC	0.5260	0.2701	2.6297	2.2005	1.8990	1.9189	731.175	2052.30

Of the electrolytes investigated, the Li/Si-C cell containing the baseline all-carbonate-based formulation delivered the highest reversible capacity (i.e., approximately 2200 mAh/g) and the lowest cumulative irreversible capacity over the five cycles (i.e., approximately 242 mAh/g). When the solutions containing TPP are compared, the cell containing the 1.0M LiPF<sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 v/v %) displayed the best overall performance with 1985 mAh/g and 488 mAh/g being displayed for the reversible and irreversible capacity, respectively. All of the cells displayed good (charge, or delithiation) rate capability, being able to support C/2 discharge rates with over 90% of the C/20 capacity being delivered in most cases.

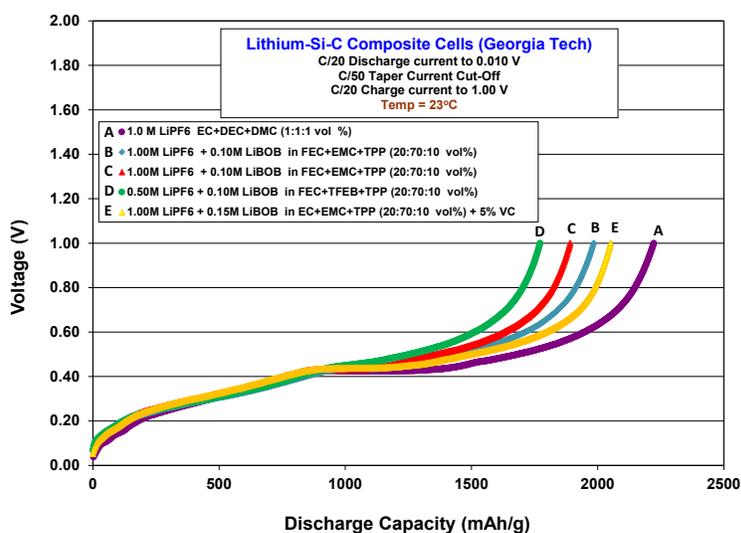


Figure 2. Fifth charge (delithiation) of Li/Si-C cells containing various TPP-containing electrolytes at 23°C. Cells were discharged to 0.010V (with the voltage held at 0.010V until the current decayed to a C/50 rate) and charged to 1.0V using C/20 rates.

After completing the formation cycles and limited rate characterization studies, the cell were subjected to full depth of discharge (0.010V to 1.00V) cycle life testing. In general, good cycle life performance was observed with all of the TPP-containing electrolytes outperforming the baseline electrolyte, as shown in Figure 3, with the cell containing 1.00M LiPF<sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%) displaying the best performance. Although good cycle life has been observed with high specific capacity being delivered when cycled in this cell orientation (i.e., Li/Si-C cells), it should be noted that these results are generated under conditions of lithium being present in excess. Given that relatively high irreversible capacity is observed for the Si-C-based electrodes, the performance of these materials anticipated is to be poorer when coupled with mixed metal oxide cathodes, since there is a limited amount of lithium available. In light of this, the reduction of the irreversible capacity of these materials continues to be a main technical challenge.

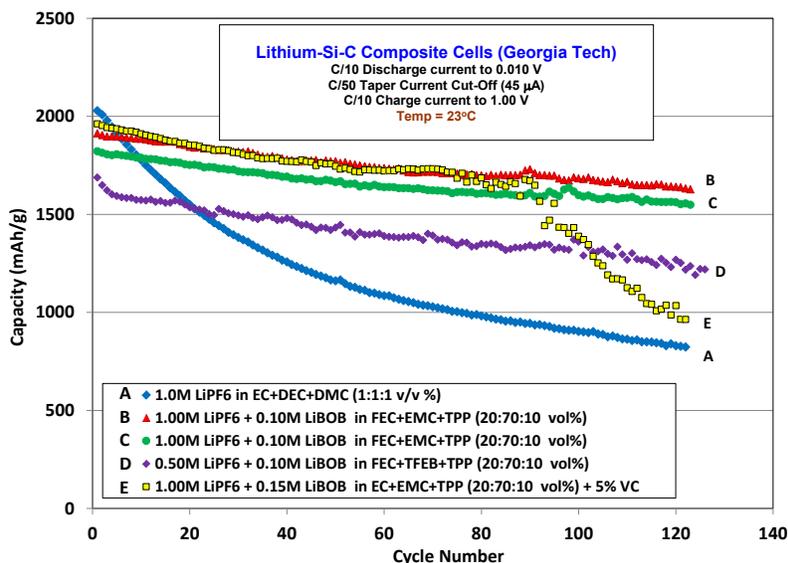


Figure 3. Cycle life performance of Li/Si-C cells containing various TPP-containing electrolytes at 23°C. Cells were discharged to 0.010V (with the voltage held at 0.010V until the current decayed to a C/50 rate) and charged to 1.0V using C/20 rates.

#### Formation Characteristics of Si-C/ LiNiMnCoO<sub>2</sub> (NMC) Coin Cells.

A number of electrolytes have also been evaluated in coin cells which consisted of Si-C anodes and Toda high voltage lithium excess LiNiMnCoO<sub>2</sub> (NMC) cathodes. For the formation cycling, the Si-C/NMC cells were charged to 4.60V (with the voltage held at 4.60V until the current decayed to a C/50 rate) and discharged to 2.50V. As illustrated in Table 2, comparable performance was observed for all of the electrolytes after completing the five formation cycles as expressed in terms of the cathode specific capacity (the limiting electrode), with the baseline electrolyte (i.e., 1.0M LiPF<sub>6</sub> in EC+DEC+DMC (1:1:1 v/v %)) delivering the best performance, as shown in Figure 4. During the course of our studies, much higher reversible capacities were generally observed (based on the limiting cathode electrodes) with cells possessing heavier loading Si-based anodes compared to cells which contain the light loading Si-based anodes, the former enabling more complete utilization of the cathode material over the voltage range investigated. In addition to evaluating a number of TPP-containing solutions, a wide

operating temperature range electrolyte containing an ester co-solvent (i.e., methyl butyrate (MB)) was also investigated to determine the compatibility in the system. More specifically, the electrolyte consisting of 1.0M LiPF<sub>6</sub> + 0.10M LiBOB in EC+EMC+MB (20:20:60 v/v %) was evaluated, which has been demonstrated to have good performance over a wide temperature range in traditional systems.<sup>16</sup>

Table 2. The formation characteristics of Si-C/NMC cells containing various electrolytes at 23°C using C/20 discharge rates to 4.600V (with C/50 taper current cut-off) and C/20 discharge rates to 2.00V.

Electrolyte	1st Charge (mAh)	1st Discharge (mAh)	2nd Charge (mAh)	2nd Discharge (mAh)	5th Charge (mAh)	5th Discharge (mAh)	Cumulative Irreversible Capacity Loss (%)	5th Discharge, (lithium intercalation) (mAh/g)
1.00M LiPF <sub>6</sub> in EC+DEC+DMC (1:1:1 vol%)	7.25406	5.38150	5.47585	5.40649	5.64741	5.50117	38.213	239.27
1.00M LiPF <sub>6</sub> in EC+DEC+DMC (1:1:1 vol%)	7.32056	5.42738	5.51313	5.44854	5.64373	5.54549	37.554	237.77
1.00M LiPF <sub>6</sub> + 0.15M LiBOB in EC+EMC+TPP (20:70:10 vol%)	7.13459	5.29832	5.41529	5.38823	5.51317	5.44595	36.175	235.17
1.00M LiPF <sub>6</sub> + 0.15M LiBOB in EC+EMC+TPP (20:70:10 vol%)	7.45697	5.50086	5.61126	5.57724	5.62636	5.58262	38.976	228.00
1.00M LiPF <sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%)	7.33505	5.36848	5.45783	5.40215	5.51062	5.51745	38.542	229.23
1.00M LiPF <sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%)	7.37415	5.35470	5.46803	5.42113	5.55874	5.58851	38.084	229.80
1.00M LiPF <sub>6</sub> + 0.15M LiBOB in EC+EMC+MB (20:20:60 vol%)	7.45469	5.54502	5.62334	5.57973	5.68610	5.61854	37.417	231.83
1.00M LiPF <sub>6</sub> + 0.05M LiBOB in EC+EMC+TPP (20:70:10 vol%) + 1.5% VC	7.36253	5.38552	5.48852	5.44557	5.53153	5.50008	39.280	224.63
1.00M LiPF <sub>6</sub> + 0.05M LiBOB in EC+EMC+TPP (20:70:10 vol%) + 1.5% VC	7.36032	5.45098	5.55390	5.52799	5.62229	5.60441	36.039	232.84

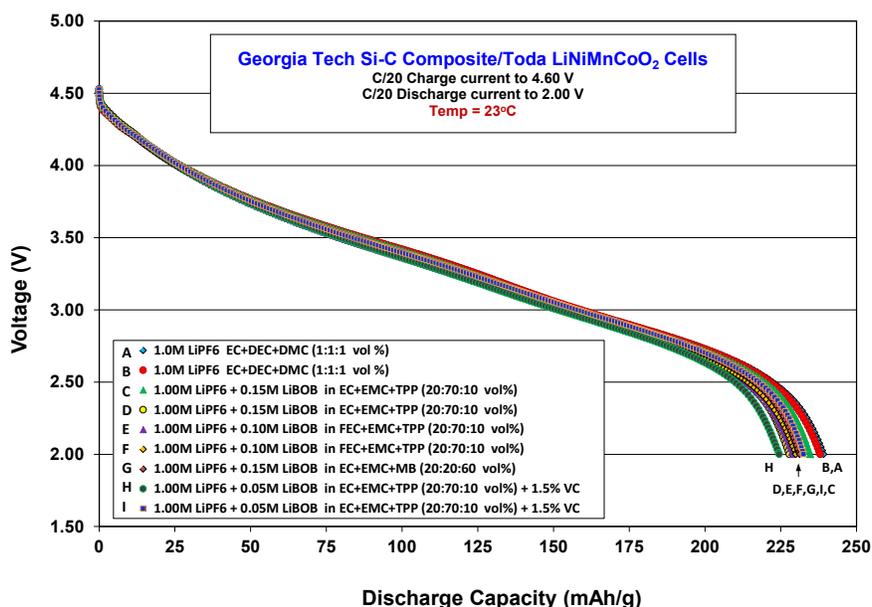


Figure 4. Fifth discharge of Si-C/NCM cells containing various TPP- and MB-containing electrolytes at 23°C. Cells were charged to 4.60V (with the voltage held at 4.60V until the current decayed to a C/50 rate) and discharged to 2.0V using C/20 rates.

When full depth of discharge cycling was performed on the Si-C/NCM cell (after completing the formation and limited rate characterization), comparable trends were observed with respect to the electrolyte type compared to the Li/Si-C cells, as illustrated in Figure 5. However, much greater capacity fade was exhibited, which has been attributed to (a) there being a limited source of lithium present, (b) the inherent capacity fade associated with the high voltage NCM material, and (c) an un-optimized cathode/anode ratio in the cell design. The best cycle life performance was delivered with the cells containing the 1.00M LiPF<sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%) electrolyte. The improved performance that this electrolyte exhibited compared to the other candidates investigated is rationalized as being due to the presence of FEC (resulting in the formation of a stable solid electrolyte interphase, SEI, layer on the Si-C anode) and LiBOB (which results in the formation a desirable cathode electrolyte interface, or CEI, on the NMC electrode).

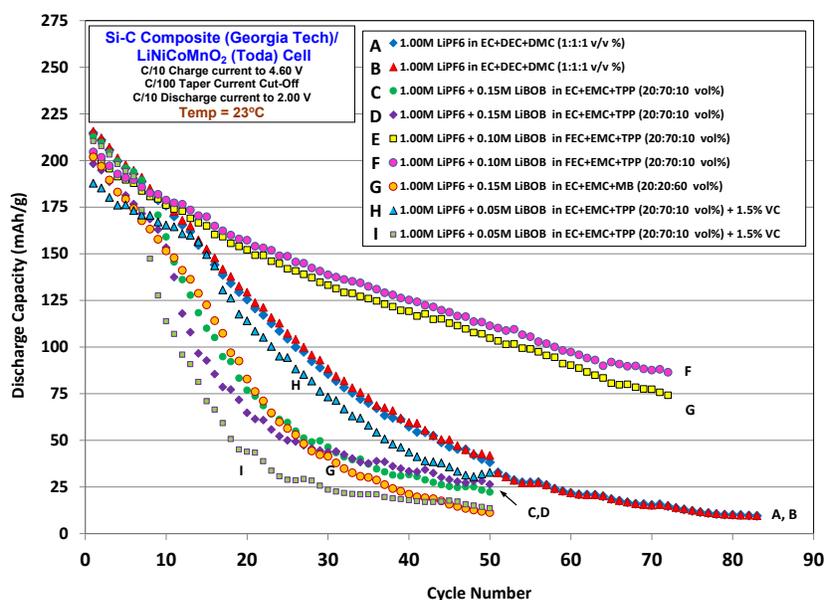


Figure 5. Cycle life testing of Si-C/NCM cells containing various TPP- and MB-containing electrolytes at 23°C. Cells were charged to 4.60V (with the voltage held at 4.60V until the current decayed to a C/50 rate) and discharged to 2.0V using C/10 rates.

### Performance Characteristics of Si-C/ LiCoAlO<sub>2</sub> (NMC) Coin Cells.

In addition to investigating the use of the high capacity Si-C for use in conjunction with high voltage cathode materials, effort was also devoted to developing electrolytes that are compatibility the Si-C/LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) system. Based on the favorable results obtained with the Si-C/NCM system, an electrolyte containing both FEC and LiBOB was evaluated. As illustrated in Figure 6A, improved performance was obtained with 1.00M LiPF<sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%) electrolyte compared with the baseline all-carbonate electrolyte. However, further improvement of the cycle life performance was obtained upon removal of LiBOB, suggesting that its presence is much more beneficial when used with high voltage NMC-based materials in contrast to systems with NCA cathodes. These cells were cycled over

a somewhat narrow voltage range (3.0V to 4.0V) with the intent of limiting the utilization of the anode to preserve the life. In summary, the cell that delivered the best cycle life performance consisted of 1.0M LiPF<sub>6</sub> in FEC+EMC+TPP (20:65:15 v/v %). In addition, all of the candidate electrolytes investigated displayed higher coulombic efficiency compared to the cell with the baseline formation, as shown in Figure 6, suggesting that the irreversible capacity loss (and the continual formation of the SEI layer) can be strongly influenced by electrolyte type. It should be noted that further decreased capacity fade is anticipated (with all electrolyte types) if a more desirable cell design is utilized (i.e., lower cathode to anode ratio).

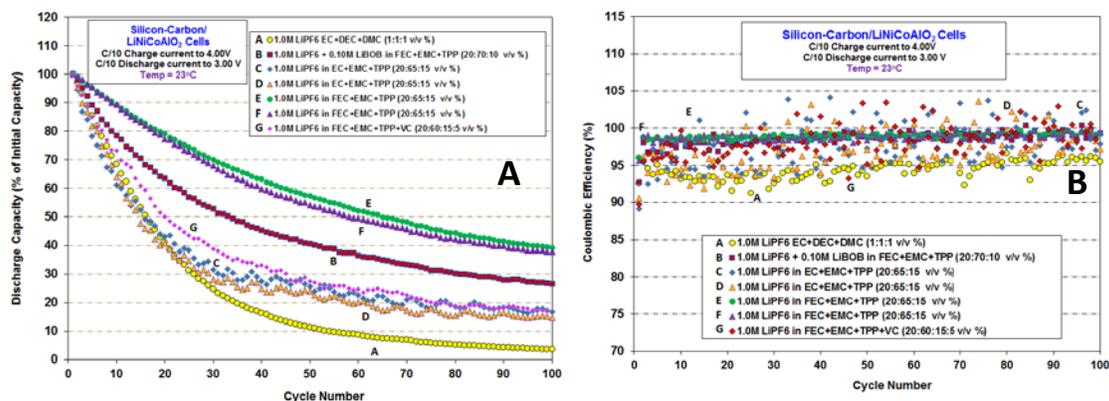


Figure 5. Cycle life testing of Si-C/NCA cells containing various TPP- -containing electrolytes at 23°C. Cells were charged to 4.00V (with the voltage held at 4.00V until the current decayed to a C/50 rate) and discharged to 3.0V using C/10 rates.

## Summary and Conclusions

A number of electrolytes designed to have improved safety has been demonstrated to have good compatibility with silicon-carbon composite-based materials. These electrolytes incorporate triphenyl phosphate (TPP) as a flame retardant additive, which has recently been shown to have promise in more traditional Li-ion systems. A number of approaches have been adopted to enhance the compatibility with the Si-C-based system, including: (1) the use of FEC in conjunction with or in lieu of EC, (2) the use of high proportions of fluorinated co-solvents, (3) the use of vinylene carbonate (VC) to stabilize the Si-C electrode, and (4) the use of LiBOB to improve the compatibility of the electrolyte when Si/C electrode are used in conjunction with high voltage cathodes. When coupled with NCM cathode materials, cell possessing 1.00M LiPF<sub>6</sub> + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%) displayed the best overall performance (outperforming the baseline), which has been attributed to the presence of FEC and LiBOB leading to the formation of desirable SEI and CEI on the anode and cathode electrodes, respectively. Improved performance of Si-NCA was also observed with this electrolyte formulation; however, even further enhancement was realized upon the removal of LiBOB, suggesting that its manner of interacting at the cathode interface is different in the two systems.

## Acknowledgments

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA) and under sponsorship of the Game Changing Technologies Development Program from the NASA-Office of Chief Technology.

## References

1. K. A. Smith, M. C. Smart, G. K. S. Prakash, and B. V. Ratnakumar, *ECS Trans*, **16 (35)**, 33 (2009).
2. M. C. Smart, F. C. Krause, W. C. West, J. Soler, G. K. S. Prakash, B. V. Ratnakumar, *ECS Trans*, **35 (13)**, 1 (2011).
3. C. C. Nguyen, and S. -W. Song, *Electrochem. Comm.*, **12**, 1593-1595 (2010).
4. H. Nakai, T. Kubota, A. Kita, and A. Kawashima, *J. Electrochem. Soc.*, **158 (7)**, A798-A810 (2011).
5. M. -Q. Li, M. -Z. Qu, X. -Y. He and Z. -L. Yu, *J. Electrochem. Soc.*, **156 (4)**, A294-A298 (2009).
6. G. -B. Han, J. -N. Lee, J. W. Choi, and J. -K. Park, *Electrochim. Acta*, **56**, 8997-9003 (2011).
7. G. -B. Han, M. -H. Ryou, K. Y. Cho, Y. M. Lee, and J. -K. Park, *J. Power Sources*, **195**, 3709-3714 (2010).
8. L. Chen, K. Wang, X. Xie, and J. Xie, *Electrochem. Solid State Lett.*, **9 (11)**, A512-A515 (2006).
9. R. P. Dunn, J. Kafle, F. C. Krause, C. Hwang, B. V. Ratankumar, M. C. Smart, and B. L. Lucht, *J. Electrochem. Soc.*, **159 (12)**, A2100-A2108 (2012).
10. A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala, G. Yushin, *Nature Materials*, **9 (4)**, 353-358 (2010).
11. B. Hertzberg, A. Alexeev, and G. Yushin, *J. Amer. Chem. Soc.*, **132(25)**, 8548-8549 (2010).
12. A. Magasincki, B. Zdyrko, I. Kovalenko, B. Hertzber, R. Burtovyy, C. F. Heubner, T. F. Fuller, I. Luzinov, and G. Yusin, *ACS Applied Materials and Interfaces*, **2 (11)**, 3004-3010 (2010).
13. K. Evanoff, A. Magasinski, J. Yang, and G. Yushin, *Adv. Energy Mat.*, **1 (4)** 495-498 (2011).
14. K. Evanoff, J. Khan, A. A. Balandin, A. Magasinski, W. J. Ready, T. F. Fuller, and G. Yushin, *Adv. Mater.*, **24 (4)**, 533-537 (2012).
15. M. N. Obrovac, and L. J. Krause, *J. Electrochem. Soc.*, **154 (2)**, A103-A108 (2007).
16. M. C. Smart, B. L. Lucht, S. Dalavi, F. C. Krause, and B. V. Ratnakumar, *J. Electrochem. Soc.*, **159 (6)**, A739-A751 (2012).