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

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222th Meeting of the Electrochemical Society (ECS)
Honolulu, Hawaii
October 11, 2012

Outline

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- Experimental
- Approach and Methodology

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- Electrolytes developed for Si-C anodes
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  - Si-C/Toda $LiNiCoMnO_2$ Experimental Coin Cell Results
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Introduction

- NASA is actively pursuing the development of advanced electrochemical energy storage and conversion devices for future lunar and Mars missions.

- The Exploration Technology Development Program, Energy Storage Project is sponsoring the development of ***advanced Li-ion batteries*** and PEM fuel cell and regenerative fuel cell systems for the Altair Lunar Lander, Extravehicular Activities (EVA), and rovers and as the primary energy storage system for Lunar Surface Systems.

- At JPL, in collaboration with NASA-GRC, NASA-JSC and industry, we are actively developing advanced Li-ion batteries with improved specific energy, energy density and safety. One effort is focused upon developing Li-ion battery electrolytes with enhanced safety characteristics (i.e., low flammability) that are compatible with the next generation high voltage, high specific capacity mixed metal oxide cathode material.

- A number of commercial applications also require high specific energy density Li-ion batteries with enhanced safety, especially for automotive applications.

Exploration Technology Development Program
Energy Storage Project

Exploration Technology Development Program

Multiple focused projects to develop enabling technologies addressing high priority needs for Lunar exploration. Matures technologies to the level of demonstration in a relevant environment – TRL 6

Energy Storage Project –

Developing electrochemical systems to address Constellation energy storage needs

Altair - Lunar Lander

- **Primary fuel cells – descent stage**
- **Secondary batteries – ascent stage**

EVA

- **Secondary batteries for the Portable Life Support System (PLSS)**

Lunar Surface Systems (LSS)

- **Regenerative fuel cell systems for surface systems**
- **Secondary batteries for mobility systems**

➢ These applications will require high energy density Li-ion batteries with improved safety characteristics.

Desired Properties of Lithium-Ion Electrolytes

- ***Electrolyte Selection Criteria***
  - High conductivity over a wide range of temperatures
    - 1 mS cm-1 from –60 to 40^{o}C
  - Wide liquid range (low melting point)
    - -60 to 75^{o}C
  - Good electrochemical stability
    - Stability over wide voltage window (0 to 4.5V)
    - Minimal oxidative degradation of solvents/salts
  - Good chemical stability
  - Good compatibility with chosen electrode couple
    - Good SEI characteristics on electrode
    - Facile lithium intercalation/de-intercalation kinetics
  - Good thermal stability
  - Good low temperature performance throughout life of cell
    - Good resilience to high temperature exposure
    - Minimal impedance build-up with cycling and/or storage

- *In addition to meeting these criteria, the electrolyte solutions should be ideally have low flammability and be non-toxic !!*

Electrolyte Development Approaches to Stabilize the Performance of Silicon Anode Based Systems

- Fluoroethylene carbonate has been reported to stabilize silicon-based anodes.
  - Sony has reported that FEC leads to the formation of stable SEI consisting of LiF and a polyene-compound.[1] The researchers displayed improved performance with 1.0M LiPF6 in FEC +DEC (1:1).
  - Aurbach and co-workers[2] have reported the formation of a thin, low resistance SEI comprised of LiF and polycarbonates.
- Ionic liquids (i.e., LiTFSI/MPP-TFSI) have been observed to provide improved cycle life of Si-Cu film electrodes. [3]
- Vinylene carbontate (VC) has been investigated and reported to result in a desirable SEI layer (i.e., smooth, uniform morphology) and decreased impedance growth. [4]
- LiBOB in conjunction with VC has been reported to yield compact and stable SEI layers, resulting in improved cycle life. [5]
- Tris(pentafluorophenyl) borane[6] and succinic anhydride[7] have also been studied as electrolyte additives in silicon systems.

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2. V. Etacheri, O. Haik, Y. Goffer, G. A. Roberts, I. C. Stefan, R. Fasching, and D. Aurbach, Langmuit, 28(1), 965 (2012).
3. C. C. Nguyen, and S. –W. Song, *Electrochem. Commun.* , **12**, 1593-1595 (2010).
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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).
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Electrolytes for Advanced High Capacity Anode Systems

- **Technical approaches adopted in the development of electrolytes compatible with Si-based anodes and displaying improved safety for NASA applications.**
  - The initial effort was devoted to determining strategies to enable the use of flame retardant additives in the presence of Si-based anodes, which were investigated in Li/Si-C experimental cells.
  - Subsequent efforts were devoted to establishing the compatibility of these electrolytes with both the Si-based anodes and the high voltage NMC cathodes.
  - There is recent interest in also determining the compatibility of these electrolytes with the SiC/NCA system.

- **With the focus upon enabling these electrolytes with the high voltage NMC materials and the Si-based anodes, a number of technical approaches were pursued:**
  - The use of fluorinated solvents, especially mono-fluoroethylene carbonate (FEC)
  - Investigating the use of VC in high proportions
  - The use of other additives in conjunction with LiBOB
  - The use of high proportions of fluorinated solvents in conjunction with FEC

Flame Retardant Additives in Li-ion Cells for Improved Safety Characteristics

- Modification of electrolyte is one of the least invasive and cost effective ways to improve the safety characteristics of Li-ion cells. Common approaches include:
  - Use of Redox shuttles (to improve safety on overcharge)
  - Ionic liquids (have inherently low flammability, due to low vapor pressure)
  - Lithium salt modification
  - Flame retardant additives
  - Use of non-flammable solvents (i.e., halogenated solvents)
- Of these approaches, the use of flame retardant additives has been observed to possess the least impact upon cell performance.

Previous Work on Flame Retardant Additives in Li-ion Batteries

- Most flame retardant additives utilized contain phosphorus
  - Aromatic and alkyl phosphates most common
    - Tradeoff exists between flame retarding capabilities and electrochemical stability
  - Halogenated phosphate compounds
    - Tris (2,2,2-trifluoroethyl) phosphate reported to be one of the most promising FRAs examined to date - excellent performance characteristics[1]
  - Other potential FRAs include:
    - Phosphites[1]- P(III) oxidation state may lead to improve stability and act as Lewis acid scavenger
    - Phosphonates[3]
    - Phosphoramides
    - Phosphazenes[4]

1) K. Xu, S. Zhang, J. L. Allen, T. R. Jow *J. Electrochem. Soc.*, **2002**, *149*, A1079

2) (a) S. S. Zhang, K. Xu, and T. R. Jow, *Journal of Power Sources* 113 (1), 166-172 (2003), (b) Nam, T.-H., Shim, E.-G., Kim, J.-G., Kim, H.-S., Moon, S.-I., *Journal of Power Sources* 180 (1), 561-567 (2008).

3) J. K. Feng, X. P. Ai, Y. L. Cao, and H. X. Yang, J. Power Sources, 177, 194-198 (2008).

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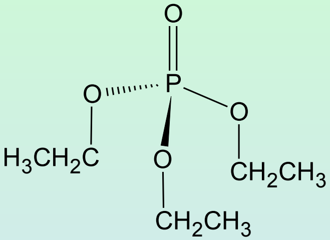
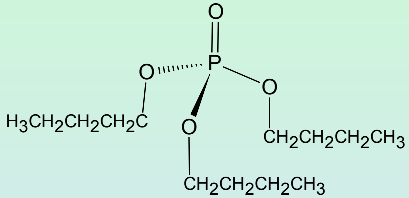
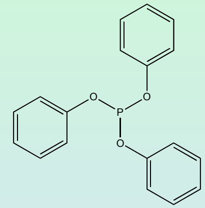
Development of Electrolytes Containing Flame Retardant Additives



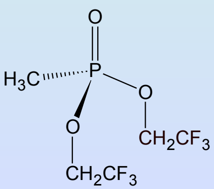
Triethyl phosphate (TEP)



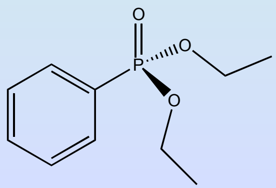
Tributyl phosphate (TBP)



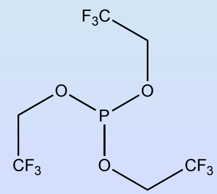
Triphenyl phosphite (TPPi)



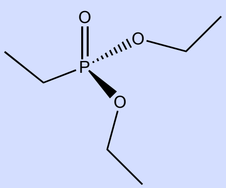
Bis-(2,2,2-trifluoroethyl)methyl phosphonate (BTFEMP)



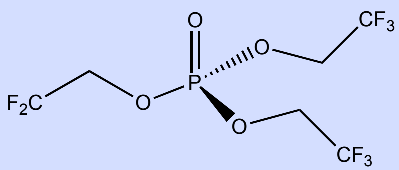
Diethyl phenylphosphonate (DPP)



Tris(2,2,2-trifluoroethyl) phosphite (TFPi)

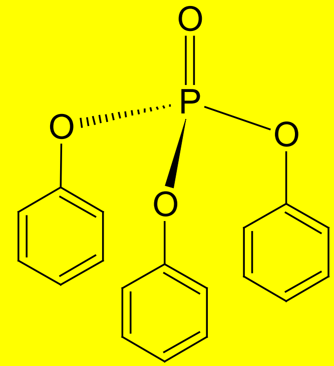


Diethyl ethylphosphonate (DEP)



Tris(2,2,2-trifluoroethyl) phosphate (TFPa)

TPP identified as being the most robust flame retardant additive



Triphenyl phosphate (TPP)

Electrolytes with the various additives were incorporated into three electrolyte cells with $LiNi_xCo_{1-x}O_2$ cathodes, MCMB anodes, and Li metal reference electrodes

1) Y. E. Hyung, D. R. Vissers, K. Amine
J. Power Sources, **2003**, *119-121*, 383

2) K. Xu, M. S. Ding, S. Zhang, J. L. Allen, T. R. Jow
J. Electrochem. Soc. **2002**, *149*, A622

Based on the favorable performance obtained with NCO, NCA, and NMC systems, TPP was investigated for Si-based anode systems.

Development of Electrolytes Containing Flame Retardant Additives

➢ Electrolytes and approaches investigated in NCA and NCO systems:

- 1.0M $LiPF_6$ EC+EMC+TPP (20:75:5 vol %)
- 1.0M $LiPF_6$ EC+EMC+TPP (20:70:10 vol %)
- 1.0M $LiPF_6$ EC+EMC+TPP (20:65:15 vol %)

← Varying Concentration of TPP

- 1.0M $LiPF_6$ EC+EMC+DTFEC+TPP (20:50:20:10 vol %)
- 1.0M $LiPF_6$ EC+EMC+DTFEC+TPP (20:30:40:10 vol %)
- 1.0M $LiPF_6$ EC+EMC+TFEMC+TPP (20:50:20:10 vol %)

← Use of Fluorinated Linear Carbonates

- 1.0M $LiPF_6$ FEC+EMC+TPP (20:70:10 vol %)
- 1.0M $LiPF_6$ FEC+EMC+TPP (20:65:15 vol %)
- 1.0M $LiPF_6$ FEC+EMC+TFEMC+TPP (20:50:20:10 vol %)

← Use of Fluorinated Ethylene Carbonate

- 1.0M $LiPF_6$ FEC+EMC+TFEMC+TPP (20:50:20:10 vol %) + 1.5% VC
- 1.0M $LiPF_6$ EC+EMC+TPP (20:75:5 vol %) + 1.5% VC
- 1.0M $LiPF_6$ EC+EMC+TPP (20:65:15 vol %) + 1.5% VC
- 1.0M $LiPF_6$ FEC+EMC+TPP (20:65:15 vol %) + 1.5% VC

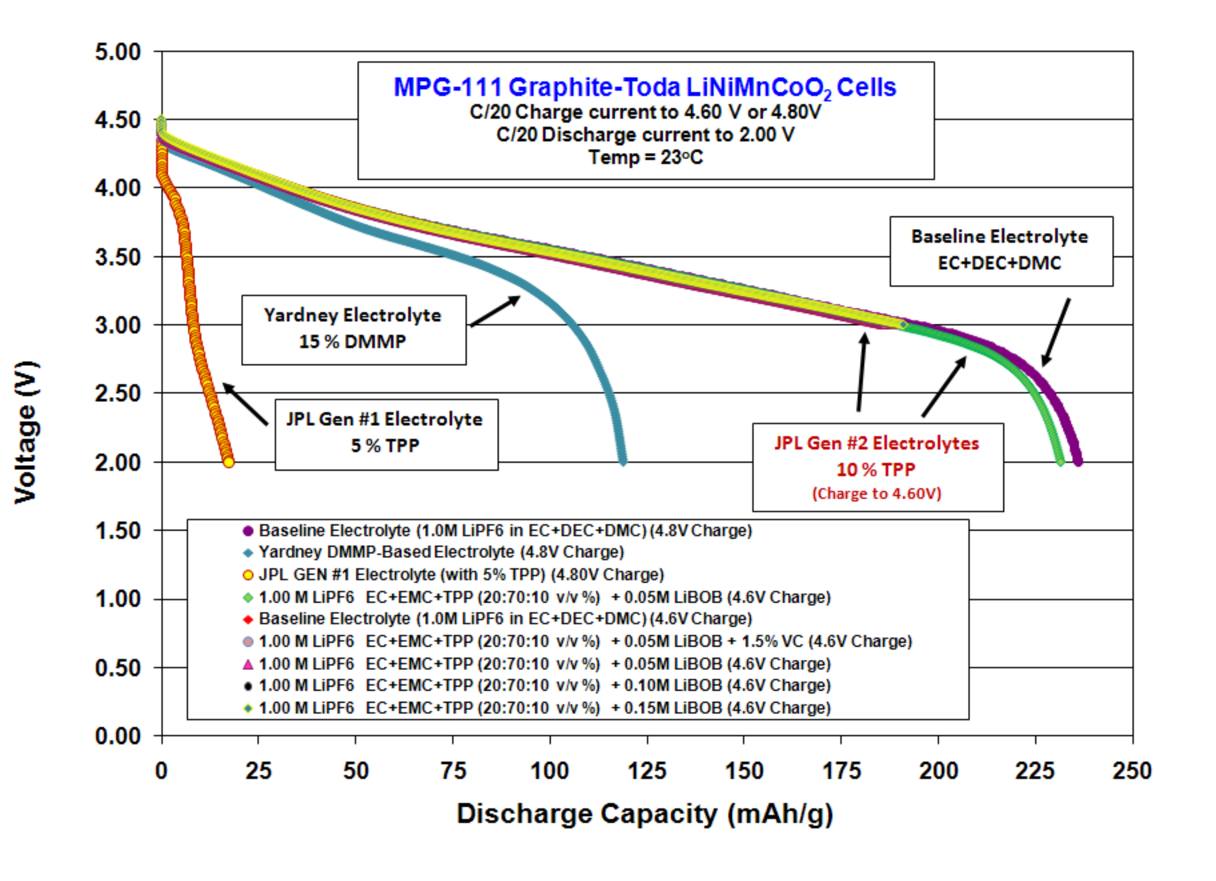
← Use of Additives (Vinylene Carbonate)

Where DTFEC = di-2,2,2-trifluoroethyl carbonate
TFEMC = 2,2,2-trifluoroethyl methyl carbonate
FEC = mono-fluoroethylene carbonate
TPP = triphenyl phosphate

Flammability tests have been performed on select samples by Prof. Lucht at Univ. Rhode Island

Results from Second Batch of Electrolytes Evaluated in the MPG-111-Toda System

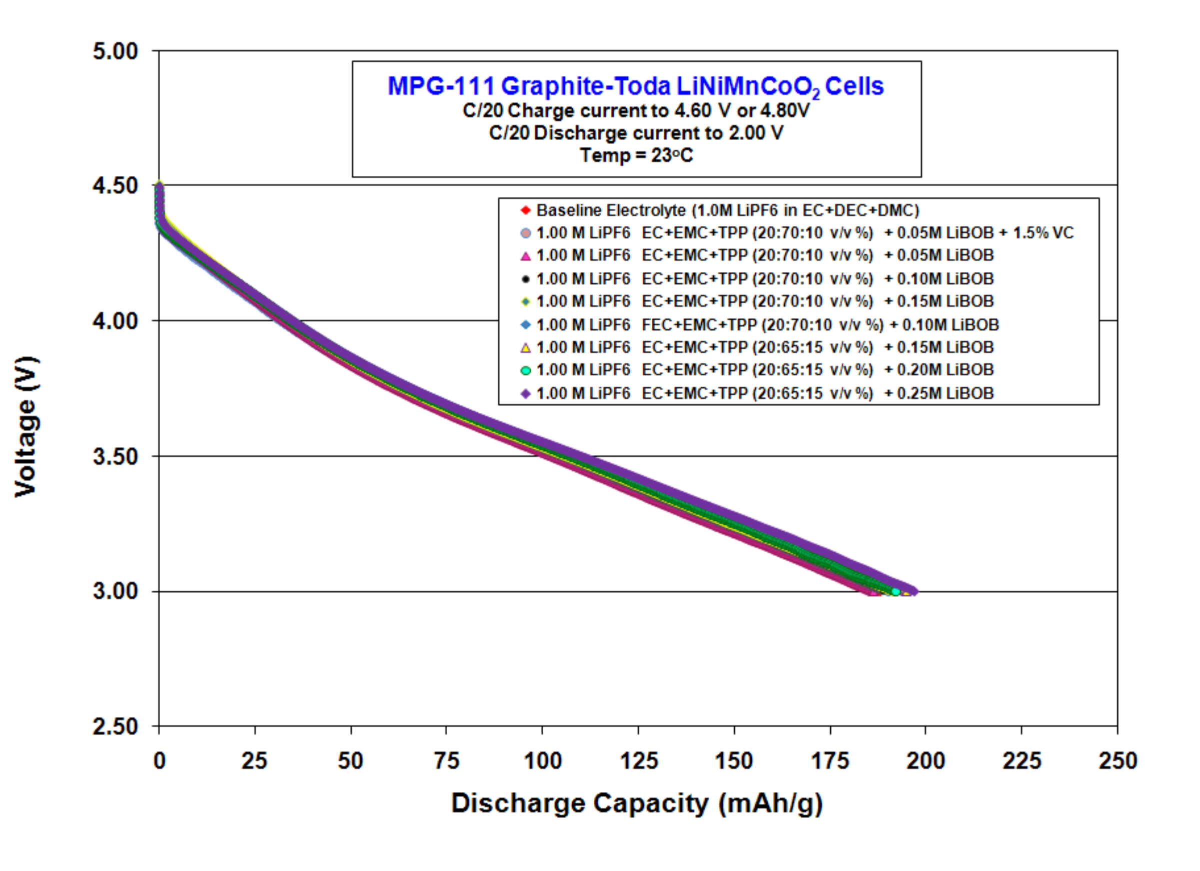
Comparison of Electrolyte Types (After Formation)



- *Comparable performance was obtained with the JPL Gen #2 electrolytes (containing LiBOB) compared with the baseline solution.*
- *There is no observed capacity (or voltage) benefit observed with charging to 4.80V*

Results of Electrolytes Evaluated in the MPG-111-Toda System

Comparison of Electrolyte Types (After Formation)

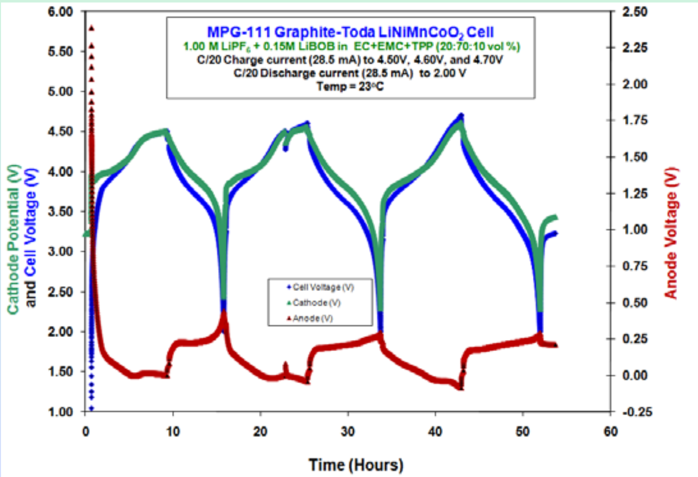


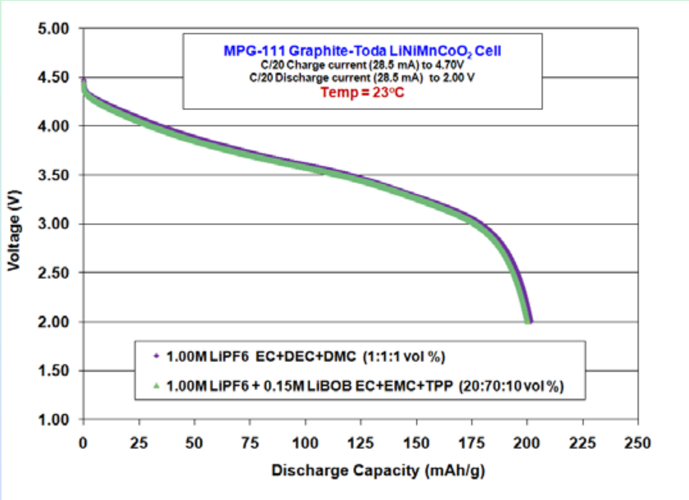
On-going work to identify further improvements (i.e., increasing TPP content and varying LiBOB concentrations)

- *A number of electrolytes displayed comparable performance with the the baseline solution, including the JPL Gen #2 electrolyte as well as newer iterations with increased TPP content (15%) and an FEC-containing blend.*
- *Cell cycled over the voltage range of 3.00 to 4.60V.*

Formation Characteristics of MPG-111-Toda Experimental Cells

Discharge Capacity





- Nearly identical reversible capacity was obtained with both electrolytes types.
- The discharge voltage profiles are very similar also.

Cell TM01
Baseline Electrolyte

Cycle #	Charge (Ah)	Discharge Capacity (Ah)	Irreversible Capacity (Ah)	Efficiency (%)	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)
1	0.28674	0.20135	0.085	70.22	162.38	68.86
2	0.25745	0.23368	0.024	90.77	188.45	19.17
3	0.25257	0.24971	0.003	98.86	201.38	2.31

Cumulative Irreversible Capcity Loss = 0.1120 Ah

Cumulative Irreversible Capcity Loss = 90.34 mAh/g

Cell TM02
JPL Generation II Electrolyte

Cycle #	Charge (Ah)	Discharge Capacity (Ah)	Irreversible Capacity (Ah)	Efficiency (%)	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)
1	0.24729	0.17637	0.071	71.32	142.35	57.19
2	0.26617	0.22849	0.038	85.84	184.41	30.39
3	0.25655	0.24780	0.009	96.59	200.00	7.06

Cumulative Irreversible Capcity Loss = 0.11735 Ah

Cumulative Irreversible Capcity Loss = 94.64 mAh/g

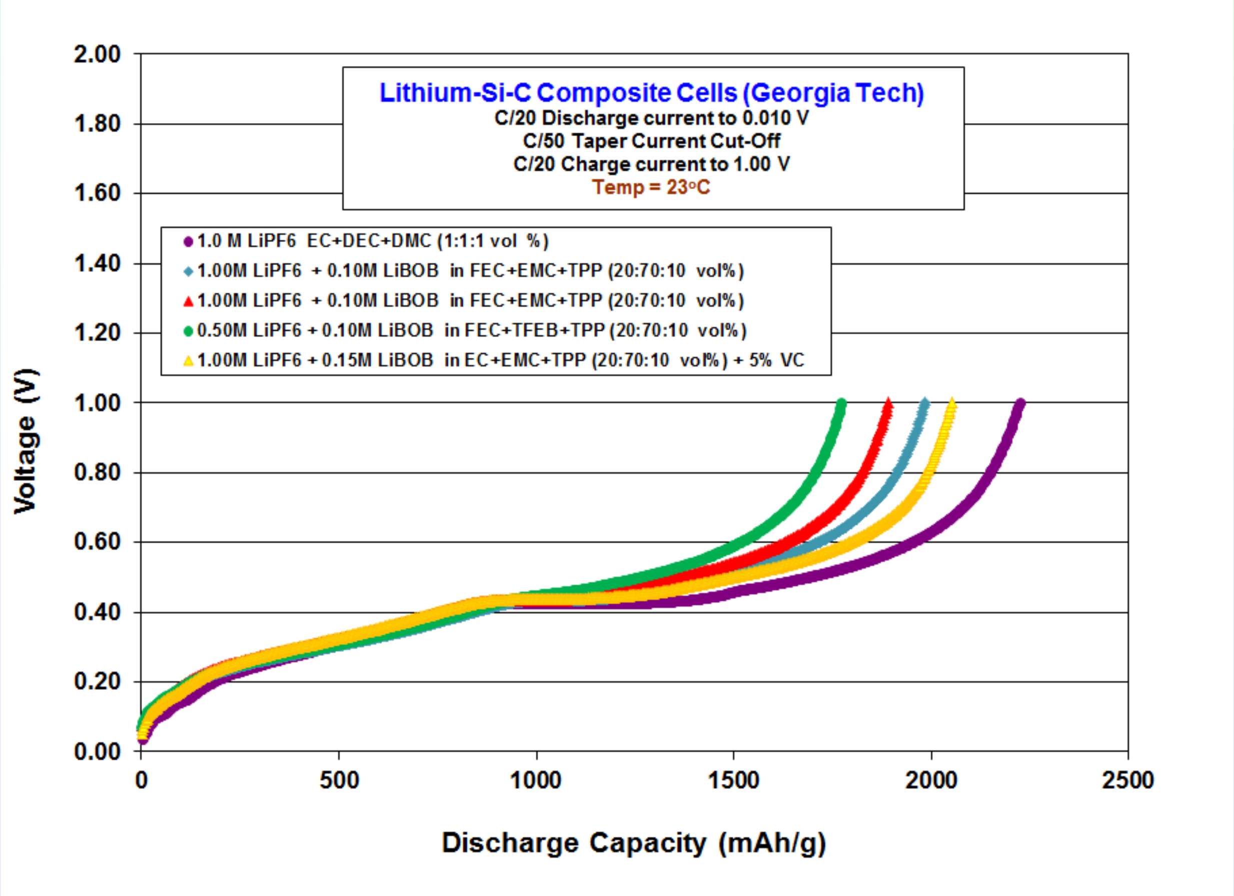
High Capacity Silicon Carbon Composite Anodes Developed by Georgia Tech

- Yushin and coworkers at Georgia Tech have developed high capacity silicon-carbon composite anode materials that display high capacity and good cycle life characteristics. [1,2,3,4,5]
  - Carbon coated silicon nanopowders have been demonstrated to deliver stable performance.
  - Polyacylic acid has been demonstrated to have improved performance over carboxymethylcellulose (CMC) and poly(vinylidene difluoride)(PVDF) binders. [3]
- In support of the NASA Space Power Systems (SPS) program (NASA-GRC led), Georgia Tech has developed multiple generations of Si-C composite electrodes which have been evaluated in various systems (i.e., NCM and NCA).
- In support of the this program, our efforts have been focused upon developing electrolyte formulations that provide improved safety while being compatible with the high capacity Si-based anodes. Challenges include (i) reducing irreversible capacity loss, (ii) improving coulombic efficiency, (iii) demonstrating compatibility with high voltage cathodes, and (iv) demonstrating good cycle life performance.

1. A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala, G. Yushin, *Nature Materials*, **9 (4)**, 353-358 (2010).
2. B. Hertzberg, A. Alexeev, and G. Yushin, *J. Amer. Chem. Soc*., **132(25)**, 8548-8549 (2010).
3. 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).
4. K. Evanoff, A. Magasinski, J. Yang, and G. Yushin, *Adv. Energy Mat.,* **1** (4) 495-498 (2011).
5. 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).

Formation Characteristics of Li-Si/C Coin Cells

Summary of Formation Characteristics (5th Cycle Comparison)

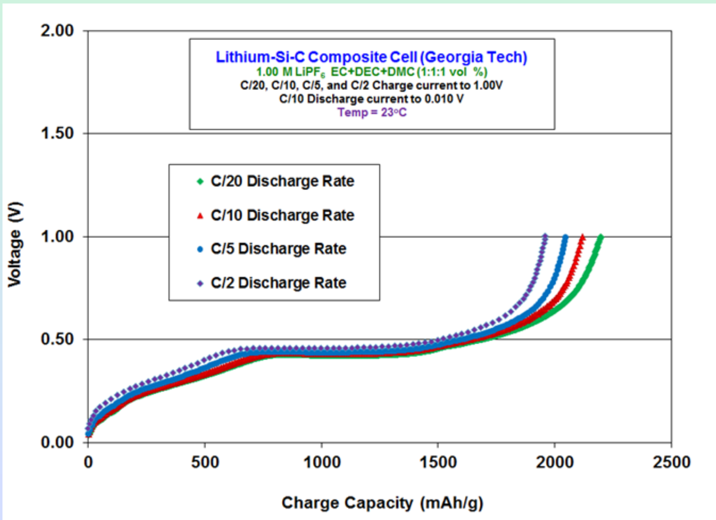


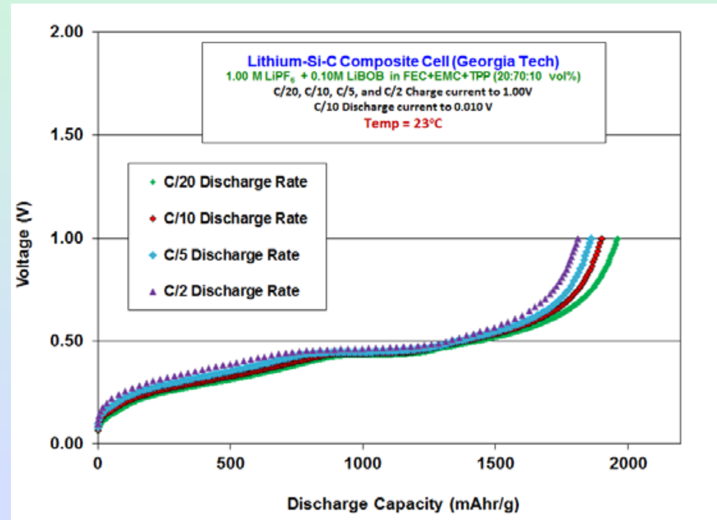
- Initial efforts focused on formulations incorporating FEC, LiBOB, fluorinated esters, TPP and VC in high concentration.
- Generally decreased reversible capacity was observed in contrast to the baseline electrolyte.

Electrolytes for Advanced High Capacity Anode Systems

Discharge Rate Capability of Li-Si/C Coin Cells

Rate Performance at 23°C





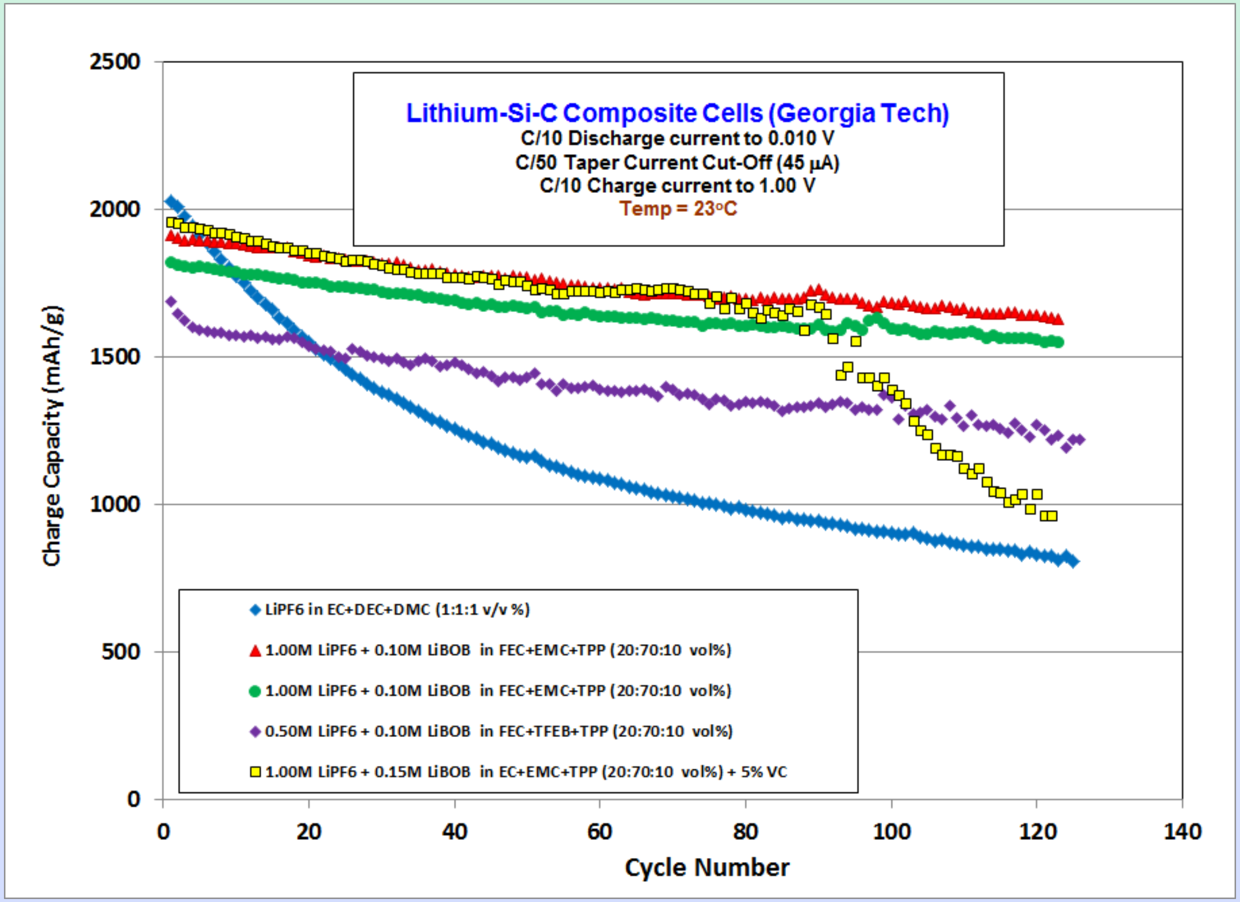
	1.00M $LiPF_6$ in EC+DEC+DMC (1:1:1 vol%)			1.00M LiPF^6 + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%)			1.00M LiPF6 + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%)			0.50M LiPF6 + 0.10M LiBOB in FEC+TFEB+TPP (20:70:10 vol%)			1.00M $LiPF_6$ + 0.15M LiBOB in EC+EMC+TPP (20:70:10 vol%) + 5% VC		
	Cell GT11			Cell GT13			Cell GT14			Cell GT15			Cell GT16		
Discharge Rate	mAh	mAh/g	% of C/20 Capacity (mAh/g)	mAh	mAh/g	% of C/20 Capacity (mAh/g)	mAh	mAh/g	% of C/20 Capacity (mAh/g)	mAh	mAh/g	% of C/20 Capacity (mAh/g)	mAh	mAh/g	% of C/20 Capacity (mAh/g)
C/20	1.8669	2196.35	100	1.8342	1961.71	100	1.7403	1861.28	100	1.6168	1729.20	100	1.9018	2034.01	100
C/10	1.8000	2117.65	96.42	1.7786	1902.25	96.97	1.6955	1813.37	97.43	1.5712	1680.43	97.18	1.8407	1968.66	96.79
C/5	1.7379	2044.59	93.09	1.7402	1861.18	94.88	1.6648	1780.53	95.66	1.5490	1656.68	95.81	1.7915	1916.04	94.20
C/2	1.6651	1958.94	89.19	1.6939	1811.66	92.35	1.6219	1734.65	93.20	1.5016	1605.99	92.87	1.7249	1844.81	90.70

However, a number of these formulations display good rate performance compared to the baseline while still providing enhanced safety.

Electrolytes for Advanced High Capacity Anode Systems

Cycling Characteristics of Li-Si/C Coin Cells

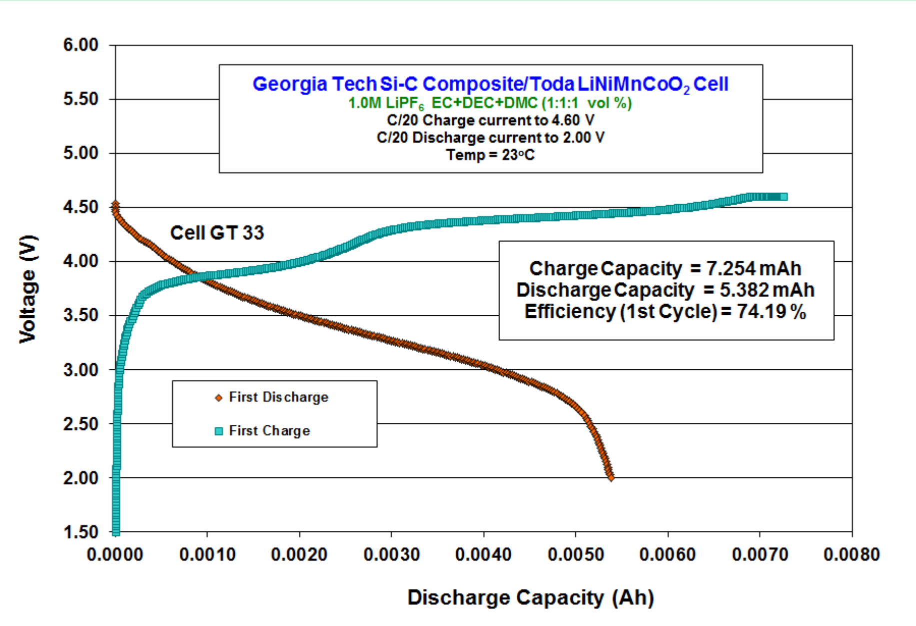
100% DOD Cycle Life at 23°C

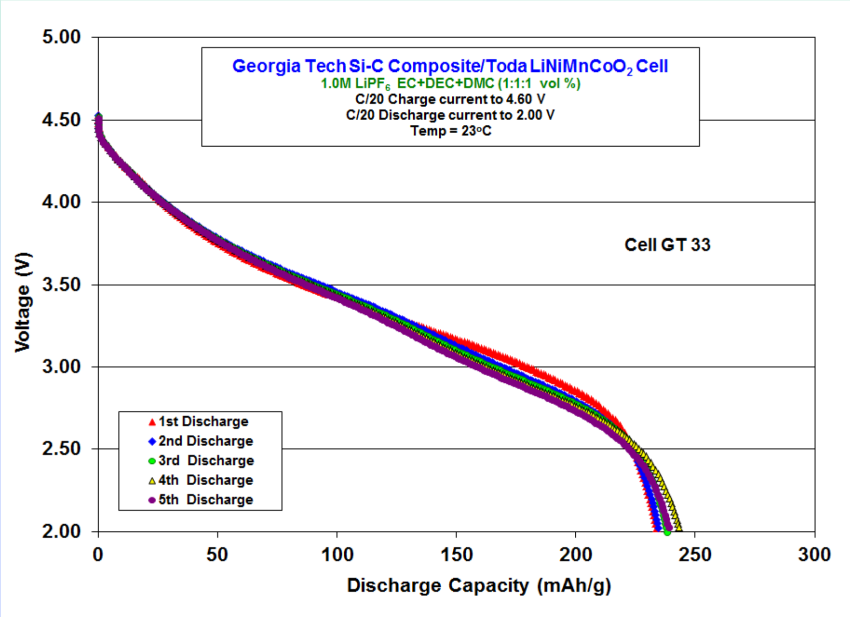


Many of these formulations display improved cycle life performance compared to the baseline while still providing enhanced safety.

Georgia Tech Si-C Composite/Toda ($LiNiCoMnO_2$) Coin Cells

1.0M $LiPF_6$ in EC+DEC+DMC (1:1:1 vol%)



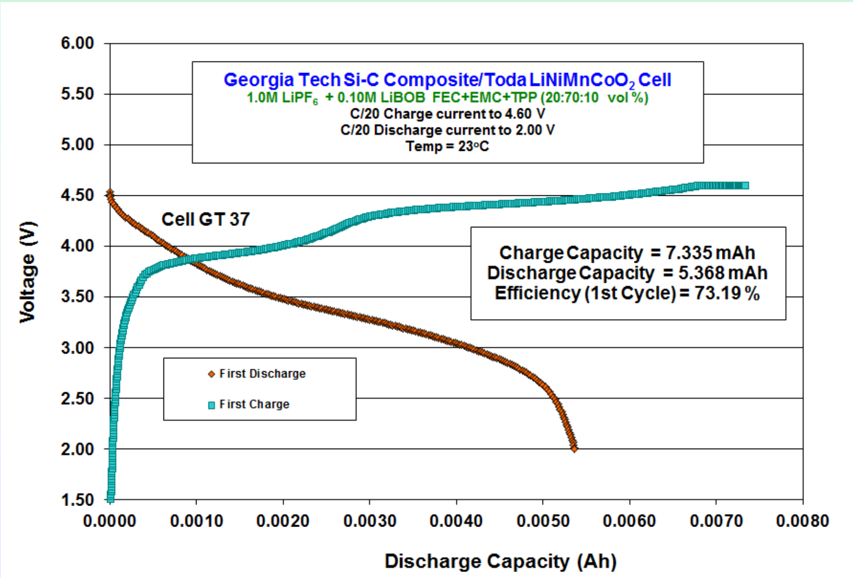


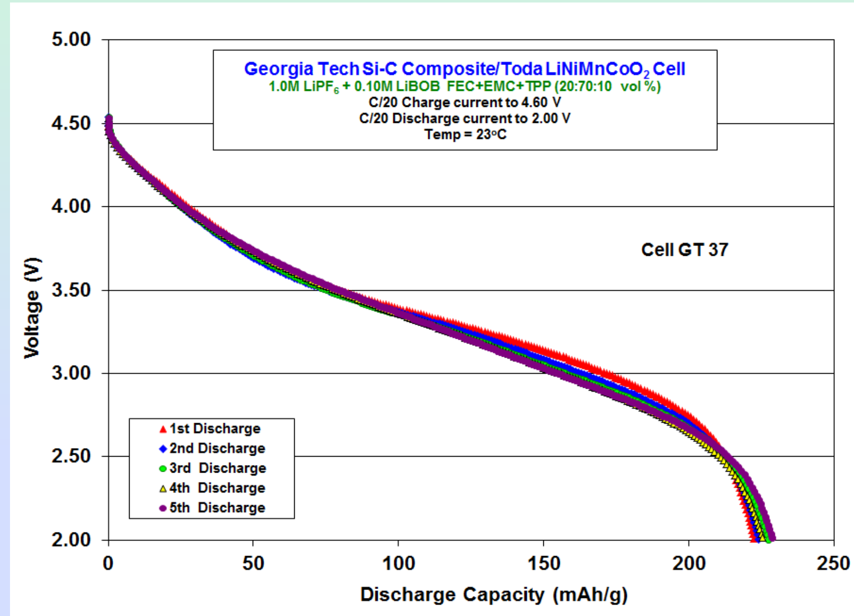
Cycle #	Charge (Ah)	Discharge (Ah)	Irreversible Capacity (Ah)	Efficiency (%)
1	0.007254	0.005382	0.001873	74.19
2	0.005476	0.005406	0.000069	98.73
3	0.005482	0.005479	0.000004	99.93
4	0.005618	0.005607	0.000010	99.82
5	0.005647	0.005501	0.000146	97.41

- The baseline electrolyte (LiPF6 in EC+DEC+DMC) generally displayed good *initial* performance when evaluated in a high voltage system (i.e., NCM).
- However, poor cycle life was delivered characterized by poor coulombic efficiency.

Georgia Tech Si-C Composite/Toda ($LiNiCoMnO_2$) Coin Cells

1.0M $LiPF_6$ + 0.10M LiBOB in FEC+EMC+TPP (20:70:10 vol%)





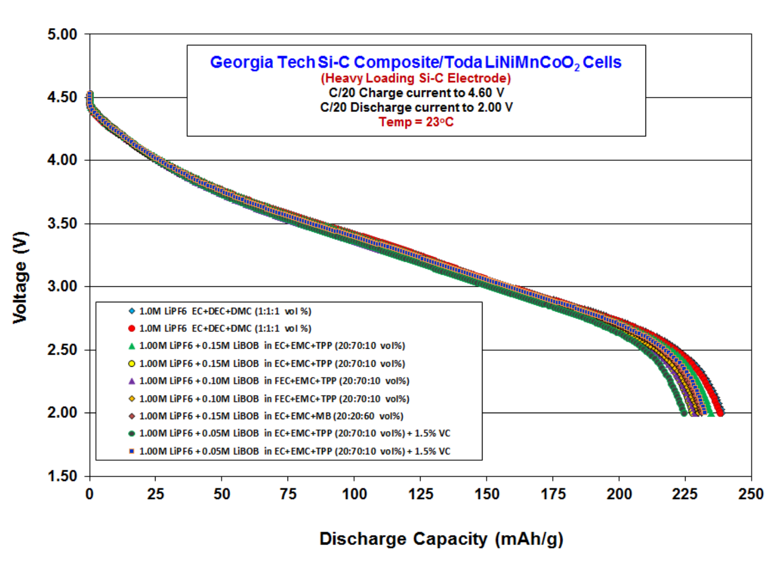
Cycle #	Charge (Ah)	Discharge (Ah)	Irreversible Capacity (Ah)	Efficiency (%)
1	0.007335	0.005368	0.001967	73.19
2	0.005458	0.005402	0.000056	98.98
3	0.005510	0.005484	0.000026	99.53
4	0.005524	0.005439	0.000085	98.46
5	0.005511	0.005517	0.0000	100.12

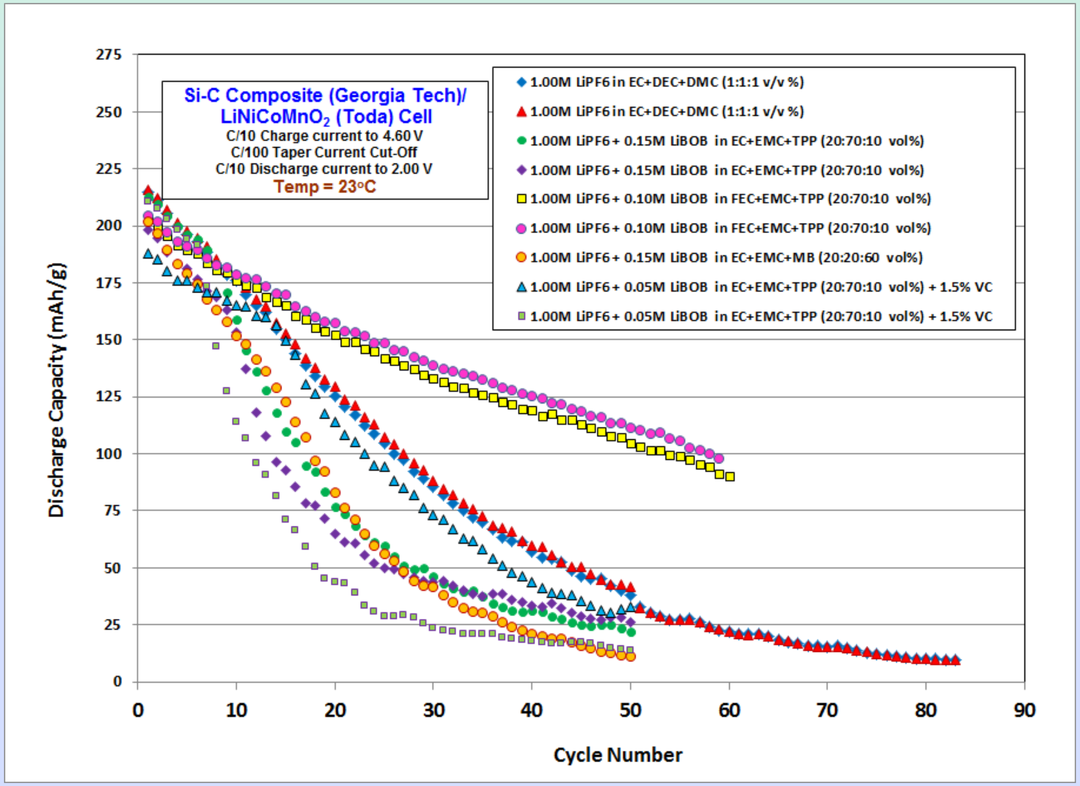
- An electrolyte containing 10% TPP (for safety), LiBOB (for high voltage compatibility) and FEC (for improved compatibility with Si) also displayed good performance when evaluated in a high voltage system (i.e., NCM).
- It was anticipated that this electrolyte would provide improved life characteristics.

Electrolytes for Advanced High Capacity Anode Systems

Georgia Tech Si-C Composite/Toda ($LiNiCoMnO_2$) Coin Cells

(Formation Characteristics-5TH Discharge Comparison)



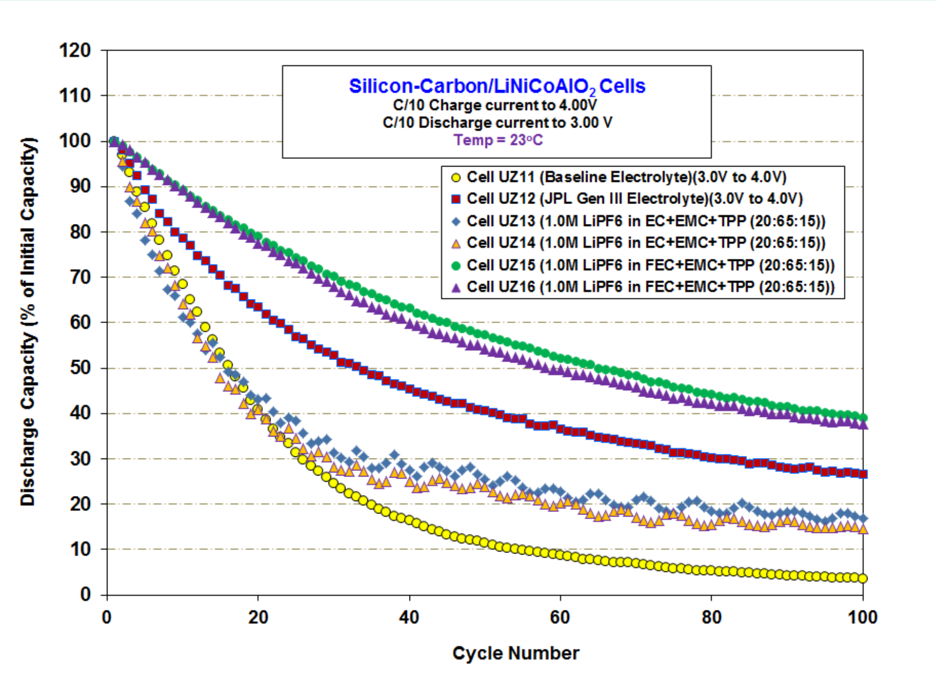


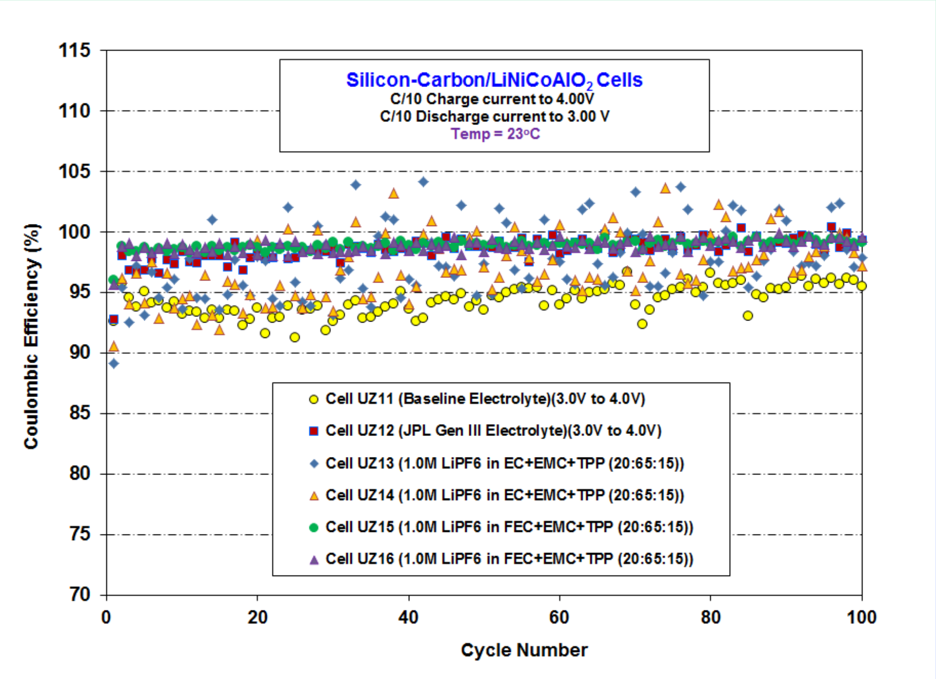
- The electrolyte containing 10% TPP, LiBOB and FEC delivered superior cycle life performance compared to the baseline electrolyte when evaluated in a high voltage system (i.e., NCM).

Electrolytes for Advanced High Capacity Anode Systems

Georgia Tech Si-C Composite/NCA Coin Cells

Cycle Life Characteristics



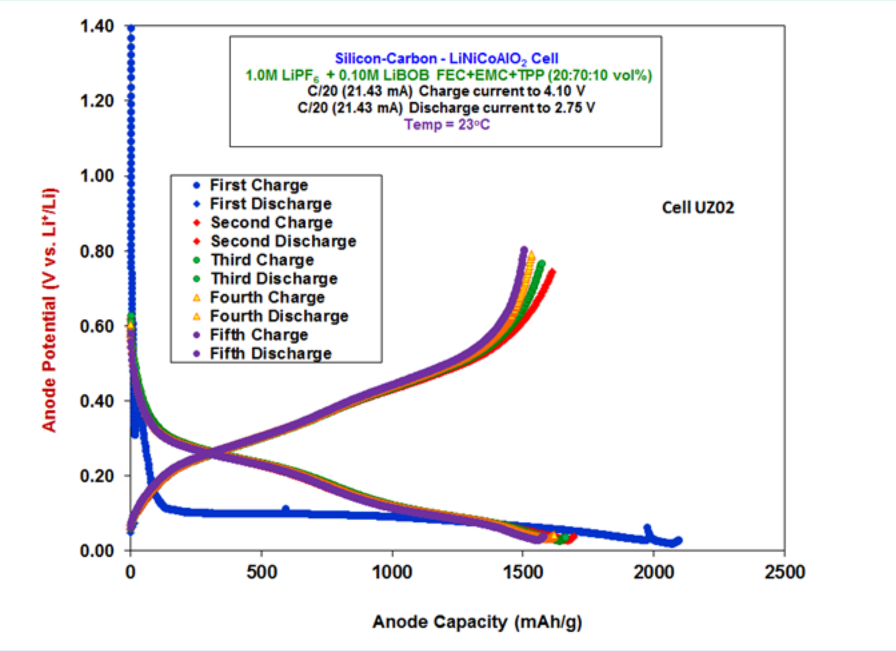


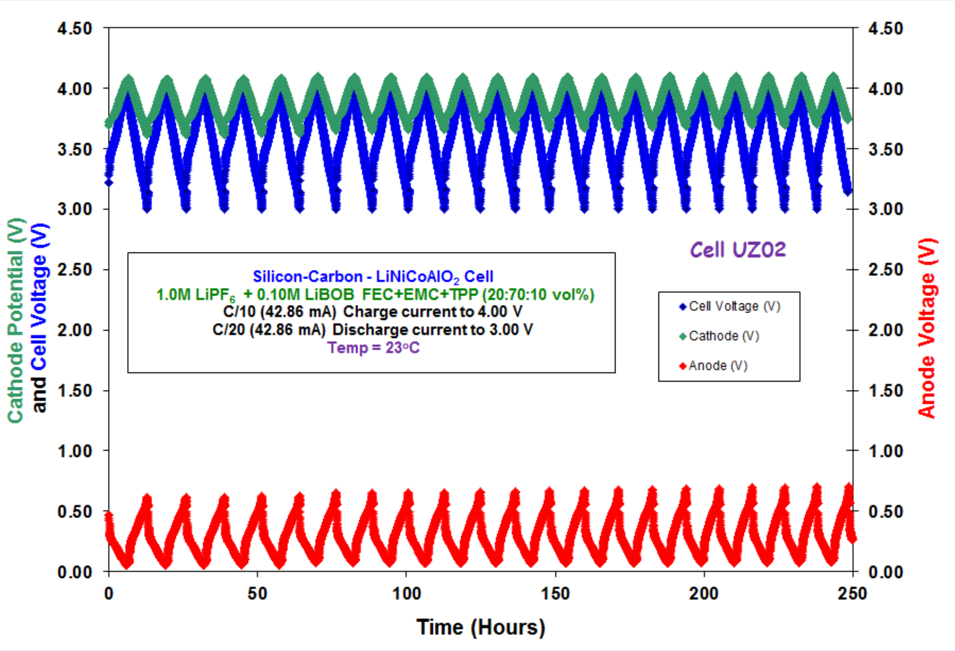
- In NCA-based systems, TPP and FEC containing electrolytes performed much better without the addition of LiBOB, suggesting that it is not a preferred additive for Si-based anodes.
- An electrolyte containing 15% TPP, and 20% FEC delivered superior cycle life performance compared to the baseline electrolyte when evaluated in a low voltage system (i.e., NCA).
- Further improvement in the cycle life performance is anticipated with an optimized C/A ratio and voltage range of operation to limit lithiation/de-lithiation of silicon.

Electrolytes for Advanced High Capacity Anode Systems

Georgia Tech Si-C Composite/NCA Three-Electrode Cells

Cycle Life Characteristics





- In larger three electrode cells, the anode and cathode potential were monitored during the course of formation and cycling.
- The generally poor cycle life performance is attributed to over-utilizing the silicon anode in the current cell design (i.e., anode lean).
- Current efforts are devoted to optimizing the cell design utilize a more conservative anode capacity to minimize undesirable morphological changes.

SUMMARY and CONCLUSIONS

- ***Performance in Li/Si-C Coin Cells***
  - *Initial efforts focused on formulations incorporating FEC, LiBOB, fluorinated esters, TPP and VC in high concentration.*
  - *Many of these formulations display improved cycle life performance compared to the baseline while still providing enhanced safety.*
  - *The electrolyte consisting of 1.0M $LiPF_6$ + 0.10M LiBOB in FEC+EMC+TPP (20:70:10) displayed the best overall performance.*
- ***Performance in Si-C/NCM Coin Cells***
  - *An electrolyte containing 10% TPP (for safety), LiBOB (for high voltage compatibility) and FEC (for improved compatibility with Si) displayed good performance when evaluated in a high voltage system (i.e., NCM).*
- ***Performance in Si-C/NCA Coin Cells***
  - *In NCA-based systems, TPP and FEC containing electrolytes performed much better without the addition of LiBOB, suggesting that it is not beneficial for Si-based anodes when coupled with lower voltage systems.*
  - *An electrolyte containing 15% TPP, and 20% FEC delivered superior cycle life performance compared to the baseline electrolyte.*
- ***Performance in Si-C/NCA Three Electrode Cells***
  - *The generally poor cycle life performance is attributed to over-utilizing the silicon anode in the current cell design (i.e., anode lean).*

➢ ***Further improvements in the electrolyte formulation is desired to increase the coulombic efficiency when Si is coupled with mixed metal oxide cathodes.***

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), in support of the NASA Space Power Systems (SPS) program.