2011

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**ANALYSIS OF INTERPHASE FORMED ON THE ELECTRODES OF
LITHIUM ION BATTERIES**

BY

SWAPNIL DALAVI

**A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF**

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

UNIVERSITY OF RHODE ISLAND

2011

DOCTOR OF PHILOSOPHY DISSERTATION
OF
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DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
2009

ABSTRACT

Lithium-ion batteries (LIBs) are one of the most widely used energy sources, especially for portable electronics. However, the development of lithium ion batteries for Electric Vehicle (EV) and Plug-in Hybrid Electric Vehicle (PHEV) requires the research and development of improved electrolytes. The development of electrolytes which allow LIBs to perform over a wide temperature range and operating potential are of significant current interest. The interphase formed on the surface of the electrodes generally governs kinetics of charging and discharging and is an important factor in life of LIBs. Favorable electrode interphases can be generated by altering the composition of the electrolyte.

Commercially available LIBs have a normal discharge voltage around 3.7V where the electrolyte oxidation on the surface of cathodes is not a significant problem. Recent research in high voltage cathode materials (>4.5 V vs Li/Li^+) to increase the power and energy density of LIBs for EV applications has raised concerns about the stability of LiPF_6 /carbonate based electrolyte to oxidation. Furthermore, the flammability of organic electrolyte hinders LIBs' application in the EV market. Detailed investigations of improved electrolyte systems which can address the above issues will be presented. Components of the interphase are detected using various surface analysis techniques such as XPS, FTIR and SEM.

ACKNOWLEDGMENTS

First and foremost I would like to thank my mentor and research supervisor Prof. Brett L. Lucht for his guidance, patience and providing me with excellent atmosphere for doing research. It was an honor to work for Prof. Lucht and learn from his knowledge and countless skillful experience. I appreciate all the help provided by Prof. William Euler as Chemistry Department Chair and his numerous inputs during our research discussions. I thank Prof. Richard Brown, Prof. Sze Yang and Prof. Arijit Bose for reviewing my dissertation. My deepest gratitude is for University of Rhode Island for giving me the opportunity to pursue my graduate studies at the chemistry department.

I would like to thank Dr. Boris Ravdel at Yardney Technical Products for providing technical support during research. I thank Mr. Mike Platek for his guidance and help during surface analysis.

I thank my parents, sister and my friend Nilesh for their continual support and believing in me all the time. Their words always gave me motivation. My special thanks to my best friend and wife Sandhya for always cheering me.

I thank Dr. Li Yang for being a wonderful colleague. I thank my friends from Lucht group, especially Dr. Mengqing Xu, Dinesh, Liu and Dr. Tippawan Markmaitree for their help and effective discussion during research.

PREFACE

This dissertation is written in manuscript format. The first chapter provides information about lithium ion batteries. The second chapter is a manuscript published in The Journal of Electrochemical Society. The third chapter is a manuscript published in Electrochemical and Solid-State Letters. The fourth chapter is a manuscript that will be submitted to The Journal of Electrochemical Society. The fifth chapter is a manuscript that will be submitted to The Journal of Electrochemical Society.

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Chapter 1. Introduction

Background

Lithium ion batteries (LIBs) are the most popular and widely used rechargeable batteries for portable electronic devices as they fulfill most of the requirements for these applications. Diminishing fossil fuels have aroused interest in rechargeable Li-ion batteries for electric vehicles (EV).^{1,2} Lithium has attracted so much attention due to the combination following three properties (1) it is the metal with lightest atomic weight which provides highest theoretical capacity of 3860 mAh/g. (2) lowest density of lithium as a metal allows it to have highest gravimetric density. (3) Lithium has most negative electrochemical potential (-3.10V vs SHE) which allows it to have wide operating voltage window. Safety concerns arising from the use of lithium metal anodes gave birth to investigation of materials which can reversibly intercalate and de-intercalate lithium ions into host lattice.³

Typical lithium ion battery

Typical LIB (Fig.1) consists of anode and cathode separated by a thin separator made up of polyethylene or polypropylene which allows ionic conductance through electrolyte but prevents electrons to pass through. So the separator prevents direct electrical contact between anode and cathode. Anode is a thin graphite sheet deposited on a copper current collector which allows reversible Li^+ ion intercalation at very low potentials vs. Li/Li^+ . Fully lithiated carbon can provide theoretical specific capacity of 372 mAh/g. Quest for high capacity materials has led to silicon and tin-based anodes which can

form alloys with lithium and provide capacity as much as 4200 and 990 mAh/g.^{4,5} Cathode materials are generally lithium transition metal oxides such as LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, LiMn_2O_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ or phosphates such as LiFePO_4 coated on a aluminum current collector. Electrolytes are made up of a lithium salt (most commonly lithium hexafluorophosphate) dissolved in a mixture of organic solvents like ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) or ethyl methyl carbonate (EMC). Polymer electrolytes and ionic liquid electrolytes are other classes of electrolytes currently under investigation.⁶

Working mechanism of LIBs

Lithium ion batteries are assembled in the discharged state with all the lithium in cathode host. Fig. 1 shows charging (left) and discharging (right) process of typical LIB. During charging lithium ions leave cathode and travel through the electrolyte and separator to get intercalated in graphite sheets. Electrons move in the external circuit at the same time. The reverse process happens during discharging. Scheme 1 indicates reactions occurring in LIB.

Scheme 1

As shown in scheme 1 the reactions happening at anode and cathode are reversible.

Ideally one would want only these reactions to occur inside the battery so that battery can run forever. But there are other side reactions causing electrolyte decomposition and slow electrode material wear and tear which eventually result in capacity fade and battery failure. For EV applications LIBs must have long cycle life of up to 15 years. Mostly the research has been directed towards cycle life improvement of LIBs by development of new electrode materials and electrolytes. Our research group has targeted electrolyte development by incorporation of various additives and novel lithium salts to improve performance, reduced capacity fade and ultimately improves cycle life.

Electrolyte

Commonly used electrolyte in LIBs has lithium hexafluorophosphate (LiPF_6) salt dissolved in mixture of organic solvents. Typically used solvents and their physical properties are shown in Table 1.⁶ Solvents chosen for LIBs should possess following properties.

- (1) It should dissolve salt to sufficient concentration (high dielectric constant, ϵ).
- (2) It should have low viscosity, η and high conductivity.
- (3) It should not corrode or react with other cell components such as electrodes, current collector and battery pack. Chapter 5 in this thesis discusses use of various liquid and solid additives for use in batteries with silicon anode. These additives sacrificially form a protective surface film on anode surface and prevent it from further reaction with electrolyte components.

- (4) It should have low melting point and high boiling point so that it can be operated in wide temperature range. Chapter 4 in this thesis describe incorporation of low melting point (-84°C) solvent methyl butyrate (MB) in electrolyte so that battery can be operated at very low temperature.
- (5) It should be safe, non-toxic and inexpensive. Chapter 2 in this thesis describes incorporation of flame retarding solvent dimethyl methylphosphonate to the electrolyte which makes it non-flammable.
- (6) It should be electrochemically stable over operating voltage window of battery. Chapter 3 in this thesis describe use of lithium bis(oxalato)borate as an additive for high voltage (5V) LIB.

During charging and discharging of battery salt and solvents from the electrolyte react on electrode surface reversibly and irreversibly to form various products which are shown in scheme 2.^{7, 8, 9} These lithium alkyl carbonates, lithium alkoxides and lithium fluoride are key components of SEI.

Scheme 2

Solid electrolyte interphase (SEI)

Fig. 2 shows capacity upon first charge and discharge of graphite anode vs lithium metal. Voltage plateaus below 0.2V are indicative of lithium intercalation inside graphite host. Graphite forms various lithiated stages such as LiC_{36} , LiC_{12} and finally LiC_6 . The lost capacity seen on first cycle is related to the irreversible chemical reactions occurring on the anode surface during first cycle. Electrolyte reduction occurs in the voltage range of $\sim 0.8\text{--}0.2\text{V}$. These reactions result from irreversible reduction of electrolyte which forms a thin protective passivating layer on anode surface which is called as solid electrolyte interphase (SEI). Formation of SEI continues till its thickness exceeds tunneling of electrons. Traditionally the film formed on the anode surface is called SEI. Similar kind of protective film is also observed on cathode surface as well.^{11, 12} Composition of SEI determines kinetics of Li^+ transfer and thickness of SEI affects further electrolyte reduction. So SEI actually determines reversibility of lithium ion cells and cycle life of battery. Due to this careful analysis of SEI and tailoring of SEI by using favorable additives becomes an important part in LIB research.

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Solvent	Structure	Melting point (°C)	Boiling point (°C)	Dielectric constant (25 °C)	Viscosity (25 °C)
EC		36.4	248	89.78	1.90 (40 °C)
DMC		4.6	91	3.107	0.59
DEC		-74.3	126	2.805	0.75
EMC		-53	110	2.958	0.65

Table 1-1. Structure and properties of solvents used in LIBs.

Fig.1-1. Typical LIB showing charging (left) and discharging (right)

Figure 1-2. Voltage (vs Li/Li^+) vs capacity graph of graphite anode after first charge and discharge.

MANUSCRIPT – I

Published in The Journal of Electrochemical Society, Vol. 157, A1113, 2010

**Nonflammable Electrolytes for Lithium-Ion Batteries Containing Dimethyl
Methylphosphonate.**

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Chapter 2. Non-flammable electrolytes for Lithium-ion Batteries

Introduction

While commercial lithium-ion batteries (LIBs) perform well for most home electronic applications, currently available LIB technology does not satisfy some of the performance goals for aerospace applications or plug-in hybrid electric vehicles because of potential safety concerns. The electrolytes used in commercial LIBs are composed of LiPF_6 dissolved in organic carbonates or esters.^{1,2} The organic solvents present in lithium-ion battery electrolytes are volatile and flammable. Battery abuse can initiate numerous highly exothermic reactions of the electrolyte with the electrode materials potentially resulting in fire or explosion.³ These reactions create significant safety concerns for lithium ion batteries especially for large-scale battery applications. One area of interest is the replacement of liquid electrolytes with solid electrolytes. Many polymer and polymer-gel electrolytes have been investigated and have improved flame resistance.⁴ However, the improvements were accompanied with problems including significantly lower conductivity, especially at low temperature. Due to the inherent low conductivity of solid electrolytes they are not practical for many applications where high power and low temperature performance are required.

Recent efforts to address this problem have focused on developing flame retardants (FR) as electrolyte additives or co-solvents. Initial investigations into FR additives for lithium-ion batteries have focused on organophosphorus compounds, which suppress flame propagation and thermal runaway. So far, investigators have focused on trialkylphosphates such as trimethyl phosphate,⁵ triethyl phosphate,⁶ triphenyl

phosphate,⁷ tris (2,2,2-trifluoroethyl) phosphate,⁸ and bis (2,2,2-trifluoroethyl) methylphosphate,⁹ and phosphoramides including hexamethylphosphoramide,¹⁰ and phosphonates including dimethylmethyl phosphonate (DMMP).^{11,12,13} However, none of these materials have functioned ideally. Improved safety of electrolytes containing FRs is almost always accompanied by deterioration in the performance including low capacity utilization, high rate of capacity fade, or poor low temperature performance. Many of these performance losses have been attributed to disruption of the solid electrolyte interphase (SEI) formation process by the presence of the flame retardant. In order to develop flame retardant electrolytes capable of obtaining desirable performance goals, flame retardant electrolytes must be developed which generate stable anode SEIs.

The structure and stability of the anode SEI in lithium ion batteries is critical for cyclability of LIBs.^{14,15,16} While the SEI structure and formation mechanisms are still poorly understood, the presence of ethylene carbonate (EC) is typically required for the formation of a stable anode SEI. Alternative investigations have probed the use of additives or alternative salts for the formation of stable anode SEIs. However, there have been relatively few investigations on the incorporation of different salts or additives with flame retarding additives.^{12,13} Herein, we have conducted a thorough investigation of novel flame retardant electrolyte via combination of salt, solvents and additives to develop a flame retardant electrolyte with comparable performance to common flammable carbonate electrolytes.

Experimental

Battery-grade EC, dimethyl carbonate (DMC), diethyl carbonate (DEC), and

ethylmethyl carbonate (EMC) purchased from Novolyte Technologies, battery-grade lithium hexafluorophosphate (LiPF_6) obtained from Hashimoto Chemical Corporation, and lithium bisoxalatoborate (LiBOB) provided by Chemetal, Germany were used without further purification. Dimethylmethyl phosphonate (DMMP) was purchased from Aldrich and purified by repeated distillation under vacuum (1 –3 mm Hg) followed by drying with sodium hydride and 4 Å molecule sieves before use. The purity was analyzed by ^1H , ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectroscopy and gas chromatography with mass selective detection. The moisture content was determined by Karl Fischer coulometric titration. The electrolytes (Table 1) were initially trialed for conductivity, calorimetry, self extinguishing time (SET) measurement, and cyclic voltammetry (CVA). Lithium metal coin cells (half cells) were prepared using electrolyte compositions 2 and 3 in Table 1 whereas lithium-ion cells (full cells) were filled with electrolytes of compositions 4 and 5. Compositions 4 and 5 were utilized to maintain a constant concentration of EC compared to the baseline.

The SET of the electrolytes was measured as described by Xu and co-workers.^{6,17} A cotton ball-wick (~1 cm diameter) soaked with 100 μL of the electrolyte was placed in a fume hood with the velocity of air flow of 100 ft/s and ignited. The burning time was measured by a stop watch. The SET was normalized by dividing the burning time by the electrolyte mass. For each sample, the experiment was repeated eight times to provide the average value.

The conductivity was measured as described earlier with a Metrohm 712 conductivity meter using Orion 018010 conductivity cells (the cell constant was about 1 cm^{-1} for

each cell).¹⁸ The conductivity cell was enclosed in an airtight Ace Glass-Thred® glass jacket by means of Ace-Thred® Teflon adapter and a FETFE O-ring. The cell contained 6-7 ml of the solution. This design of the conductivity cell made it possible to take it outside of the glove box and perform conductivity measurements without moisture contamination of the solutions. The temperature was controlled within $\pm 0.1^\circ\text{C}$ accuracy by means of a Tenney Environmental chamber.

Coin cells were employed to test the electrolytes containing the additives. The electrodes used $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as active cathode material, mesocarbon microbead (MCMB) as active anode material, and a polyethylene film separator. The negative electrodes were composed of 87% MCMB, 10% poly(vinylidene difluoride) (PVDF) binder and 3% conductive carbonaceous dilutant; the positive electrodes contain 89% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, 5% PVDF binder and 6% conductive carbonaceous dilutants. Each coin cell contained about 30 μL of electrolyte. Electrolytes preparation, filling the conductivity cell, and coin cells fabrication were conducted in glove box filled with high purity argon with moisture content less than 0.1 ppm.

The coin cells were cycled at room temperature at constant current-constant voltage charge and at constant current discharge using a BT4010 cycler (Arbin Instruments). The full cells were cycled between 4.1 and 3.0 V while the upper limit for cathode half cells was 4.2 V. The anode half cells were cycled at constant current charge and a constant current discharge between 1.3 V and 0.01 V. The half cells were cycled according to the schedule: 1st cycle at C/20, 2nd cycle at C/10 and remaining cycles at C/5. The full cells were cycled according to the schedule: 1st cycle at C/20, 2nd and 3rd

cycles at C/10, 4th, 5th and 6th cycles at C/5, 7th and 8th cycles at C/10 and remaining cycles at C/5. All cell types were prepared in duplicate or triplicate to confirm reproducibility of cycling behavior. Representative data sets are provided. After 30 cycles the full cells were disassembled in the glove box. The electrodes were rinsed with DMC to remove residual EC and LiPF₆ followed by overnight evacuation.

The XPS spectra were conducted with a PHI 5500 system using Al K α radiation ($h\nu=1486.6$ eV) under ultra high vacuum. The graphite peak at 284.3 eV was used as a reference for the final adjustment of the energy scale in the spectra. The spectra obtained were analyzed by Multipak 6.1A software and fitted using XPS peak software (version 4.1). A mixture of Lorentzian and Gaussian functions was used for the least-squares curves fitting procedure.

SEM was conducted on a JEOL-5900 SEM. FTIR spectra were acquired with a Thermo Nicolet IR iS10 spectrometer. Argon was purged during the acquisition process to avoid air exposure. The spectra were acquired in multiple locations on the electrodes in the ATR mode with 4 cm⁻¹ resolution with 128 total scans.

Results and Discussion

Conductivity measurement

Figure 1 shows the conductivity of the electrolyte solutions. There is no difference in the conductivity of the solutions containing 15 or 20% of DMMP. The conductivity of the baseline solution is slightly lower than the DMMP containing electrolytes at temperatures above ~25°C and the freezing point of both DMMP containing electrolytes is slightly higher than the baseline electrolyte, but otherwise the conductivities of the

different electrolytes are very similar. The specific conductivity (σ) over the temperature range of -40 to $+80^\circ\text{C}$ cannot be described by the activation mechanism mathematically expressed as the Arrhenius law for any of the solutions investigated:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

Where σ_0 is a constant, E_a is the activation energy for the ion's motion in solution, and R and T are the gas constant and absolute temperature, respectively.

It is not surprising that the motion of ions through mixed solvent of low dielectric constant does not follow Arrhenius behavior. Ions are extensively associated in organic electrolyte solutions of lithium salts and are frequently present as aggregates. The composition of the solvents in a mixed solvent system (i.e., the ratio solvent1 to solvent2) in the closest neighborhood of an ion most likely differs from the average composition of the mixture due to the formation of Li^+ solvates $[\text{Li}^+(\text{solvent1})_n(\text{solvent2})_{n-4}]$. This can be attributed to the different ion-complexing affinity of the different solvent molecules. Consequently, the moving ion may bring its solvation shell with it or form a new solvation shell during movement, or a combination of both. The result is that the composition of the solvent in the ion's solvent co-ordination sphere would change as it moves from one site to the next. In other words, the motion of the ions from one co-ordination site to another is assisted by the motion of the solvents. Thus, the solvent molecules are involved in the ionic transport process, and their mobility should affect the conductivity.

When ion transport is facilitated by the mobility of the solvent molecule, the

conductivity may obey the Vogel-Tammann-Fulcher (VTF) relation.^{19,20,21}

$$\sigma = AT^{1/2} \exp\left(-\frac{B}{T-T_0}\right) \quad (2)$$

Where A , B , and T_0 are constants. Although the exponential term looks similar to that in the Arrhenius equation (1), the B term of (2) does not have the same meaning of activation energy. B is related to the activation energy for the creation of critical free volume for ion transport, $B = E_{av,VTF}/R$. T_0 is the temperature at which the transport function ceases to exist or the solvent structural relaxation becomes zero. T_0 may be considered as the glass transition temperature or a temperature near it. To determine the parameters of the VTF equation a non-linear least squares analysis method was utilized.²² Figure 1 confirms that the agreement between experimental data (circles) and the VTF approximation (lines) is very good (the relative residual standard deviation was typically less than 1.5%). The VTF parameters are collected in Table 2.

From our previous conductivity studies,²³ the B parameter does not depend on the composition of the solutions of the pure salts LiPF_6 , LiBF_4 , $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, and their mixtures in blended solvents of various compositions of ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylmethyl carbonate (EMC). The value for B was reliably determined to be $401 \pm 14 \text{ K}$.²³ However the parameter of the solutions containing DMMP is noticeably higher. The result is consistent with the B parameter being characteristic of solvent. Thus, in a mixture of organic carbonates with different lithium salts B remains constant while the addition of a solvent component of different nature (e.g., DMMP) markedly shifts the value of B .

Thermal stability of the flame retardant electrolyte

The thermal stability of the electrolytes was investigated by multi-nuclear NMR spectroscopy. ^{11}B , ^{19}F , and ^{31}P NMR spectra of 1 M LiPF_6 with 5% LiBOB EC:EMC:DMMP (2:2:1) (Electrolyte 3, Table 1) before (b) and after storage at 85 °C for 1 week (c) are provided in Figure 2. Storage of Electrolyte 3 at 85 °C for 1 week results in the appearance of new species by NMR spectroscopy. Analyses of ^{19}F and ^{11}B NMR spectra are consistent with the generation of new species including $\text{LiBF}_2(\text{C}_2\text{O}_4)$ and LiBF_4 (Figure 2B and 2C), as previously reported.²⁴ In addition to the resonances characteristic of LiPF_6 , LiBF_4 , $\text{LiBF}_2(\text{C}_2\text{O}_4)$, there are resonances characteristic of $\text{OPF}_2(\text{OH})$ (^{19}F , d, 54.8 ppm; ^{31}P , t, -19.8 ppm), LiF/HF ~ -10 ppm, and a DMMP- PF_5 complex (^{19}F , d, 74 ppm and dd, 51 ppm). Complexes of PF_5 with good Lewis bases, such as DMMP, have been previously characterized.²⁵ Continued storage at 85 °C for 1 month results in only small changes to the spectra suggesting that the thermal decomposition reactions are inhibited. Previous investigation of LiPF_6 /carbonate electrolytes indicate nearly quantitative decomposition upon storage for several days at 85 °C, forming a number of by-products, including CO_2 , alkyl ethers (R_2O), alkylfluorides, phosphorus oxyfluoride (OPF_3), and fluorophosphates [OPF_2OR , $\text{OPF}(\text{OR})_2$].²⁶ Independent investigations of carbonate solutions of LiPF_6 with added LiBOB and LiPF_6 with added DMMP suggest that both additives can function as thermal stabilizing additives.^{24,25}

Self Extinguishing Time (SET)s

The flame-retarding effect of DMMP additive is summarized in Table 3. The baseline

electrolyte, 1 M LiPF₆ in EC/EMC (3:7, vol.) (Electrolyte 1, Table 1), is highly flammable with SET of 33.4 s. Upon addition of DMMP to the electrolyte, the SET significantly decreases to 1.8 s with 15% (vol.) DMMP and is further reduced to 0.8 s with 20% (vol.) DMMP. Previous investigations suggest that a decrease in the flammability of carbonate based electrolytes by 75% results in a reduced flammable electrolyte while a reduction of 90% results in a non-flammable electrolyte.^{6,17} Thus, addition of either 15 or 20 % of DMMP to carbonate electrolytes results in the generation of a non-flammable electrolyte.

Electrochemical Window Determination

Figure 3 presents a cyclic voltammogram of Electrolyte 1 (Table 1) on a glass carbon electrode. During the first cathodic potential sweep, a reduction peak is observed at 1.7 V, which is attributed to the reduction of oxalate-moieties present in the LiBOB salt.²⁷ On the second sweep, the reduction peak located at 1.7 V is not observed consistent with the formation of a stable oxalate-derived anode SEI during the first cycle. This suggests that the presence of DMMP does not interfere with SEI formation in electrolytes containing LiBOB.

Electrochemical performances of cells with DMMP

The electrochemical stability of DMMP on positive and negative electrodes of LIB was evaluated in lithium metal-MCMB (anode half-cell) and lithium metal-LNCO (cathode half-cell) during galvanostatic cycling. Figure 4 shows the cycling performance of anode half-cells with baseline electrolyte and electrolytes 2 and 3 (Table 1) after the first five formation cycles. The DMMP presence lowers the reversible capacity of the

cell (baseline, 4.3 mAh, 15% DMMP, 3.5 mAh, and 20% DMMP ,3.0 mAh) , which can be attributed to the presence of oxalate-related moieties in LiBOB and reduction of DMMP on the MCMB electrode. However, the cycling efficiencies of the cells with FR electrolyte are high and comparable to that of the cells with baseline electrolyte. After the first 22 cycles, the cells with baseline electrolyte and with the electrolyte containing 20% DMMP retained about 99% and 94%, respectively, of the initial reversible capacity. The majority of the capacity loss occurs during the first ten cycles. The cycling performance of cathode half-cells with baseline electrolyte and electrolytes 2 and 3 (Table 1) is provided in Figure 5. The cycling efficiencies of the initial cycles were calculated to be 95% and 97% for the baseline and 20 % DMMP electrolyte respectively. It is believed that that the irreversible capacity loss during the first cycle is attributed to the irreversible structural change of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ crystalline lattice and the formation of surface layer due to organic solvent oxidation.²⁸ Thus, it is reasonable to suppose that the electrochemical oxidation of DMMP is responsible for the reversibility decrease (97 vs. 95%). The capacity and coulombic efficiency on the sequential cycles were identical for the cells with both solvent's compositions (Figure 5). The trends in the discharge capacities of the full cells containing Electrolyte 1, Electrolyte 4 (without LiBOB), and Electrolyte 5 (with LiBOB) (Table 1) are provided in Figure 6. The addition of LiBOB to the DMMP containing electrolyte results in a dramatic increase the discharge capacity. The initial discharge capacity of the DMMP/LiBOB electrolyte after formation cycling (First eight cycles) is lower than the cells containing the baseline electrolyte. This capacity loss can be attributed to irreversible reduction of LiBOB on the surface of the electrode to generate an anode

SEI stable to the presence of DMMP. However the cells containing DMMP/LiBOB electrolyte have comparable coulombic efficiency to the cells containing baseline electrolyte upon further cycling. Surface analyses of electrodes extracted from cells with baseline electrolyte and DMMP containing electrolyte, as described below, provides insight into the source of the difference in capacity retention.

Scanning Electron Microscopy (SEM) of anodes and cathodes

SEM images of the anode and cathode are depicted in Figures 7 and 8, respectively. The appearance of the anodes extracted from cells cycled with the standard electrolyte and the DMMP/LiBOB electrolyte are very similar. The morphology of the primary and secondary particles is intact. However, the MCMB particles of the anode extracted from the cell cycled with the DMMP electrolyte without LiBOB appear to have significant damage to the MCMB particles, consistent with graphite exfoliation and the observed poor cycling performance. The SEM images of the cathodes extracted from cells cycled with the three different electrolytes are very similar suggesting that the bulk cathode particles are not altered by any of the electrolytes.

FTIR

The surfaces of the electrodes were also analyzed by FTIR-ATR spectroscopy. The IR spectra of the anodes and cathodes extracted from cycled full cells are provided in Figure 9 and 10, respectively. The IR spectra of the anodes extracted from cells containing different electrolytes are similar and are dominated by the absorptions characteristic of the PVDF binder (1400, 1271, 1170, 1070, 877, and 840 cm^{-1}). Li_2CO_3 is also observed in all the anodes and cathodes at $\sim 1500 \text{ cm}^{-1}$. Both the cathodes and

anodes extracted from cells containing the DMMP/LiBOB electrolyte contain additional peaks at 1630 cm^{-1} and 1760 cm^{-1} . These peaks are characteristic polycarbonate (1730 cm^{-1}) and oxalate (1630 cm^{-1}) species on surface. Irreversible reaction of LiBOB on the surface electrodes is most likely the source of the differences.

X-ray Photo Electron Spectroscopy (XPS) surface analyses.

In order to better understand the composition of the surface films on the electrodes extracted from cells cycled in baseline electrolyte and DMMP containing electrolyte, the electrodes were analyzed by XPS. Analysis of the anodes reveals significant differences in the surface species (Tables 4 and 5, Figures 11 and 12). XPS surface analyses of anodes suggest a decrease in concentrations of C and F and an increase in the concentrations of O and P on cycled anode surfaces as compared to fresh anode consistent with the generation of an anode SEI from electrolyte decomposition products and a covering of the graphite and PVDF binder. The anode extracted from the cells cycled with both DMMP containing electrolytes contain lower concentrations of F and P compared to the anode extracted from the cell containing the baseline electrolyte while the C concentration is higher for the anodes cycled with the DMMP containing electrolytes. The O concentration is comparable for all anodes. The anode extracted from the cell containing LiBOB also contains 5 % B on the surface.

The C1s spectra of the anodes cycled in different electrolytes (Figure 11) are dominated by peaks characteristic of graphite (284.3 eV) and PVDF (285.7 and 290.4 eV). Additional peaks characteristic of C-O (288 eV) and C=O (290 eV) bonds in ethers and carbonates are also observed. The cycled anode containing DMMP/LiBOB electrolyte

has more C-O and C=O containing species on its surface as compared to other two anodes, consistent with the presence of oxalate species on the surface.²⁷ The F1s spectrum contains peaks characteristic of LiF (684.5 eV), PVDF (687 eV), and a small peak at 688 eV attributed to $\text{Li}_x\text{PF}_y\text{O}_z$ or Li_xPF_y . The LiF concentration is lower on the anode surface containing DMMP/LiBOB electrolyte, as has been previously reported for LiBOB containing electrolytes.²⁷ The O1s spectrum contains a broad peak around 531-533 eV characteristic of a mixture of C-O, C=O and P-O bonds, in ethers, lithium alkyl carbonates, LiPF_yO_z , and Li_2CO_3 . An increase in the intensity of the shoulder at 532-533 eV for anodes with DMMP containing electrolyte is consistent with more carbonate and oxalate containing species on surface. The P2p spectrum includes a peak characteristic of $\text{Li}_x\text{PO}_y\text{F}_z$ at 134 eV on all three anodes. Anodes cycled in DMMP containing electrolyte shows an additional peak at 133 eV which is most likely due to the reduction products of DMMP on the surface. Anodes cycled with LiBOB contain a B 1s peak at 193 eV consistent with the formation of borate species from the reduction of LiBOB.²⁷

Elemental concentration on the surface of cycled cathodes is provided in Table 7. The surface of the fresh cathode is dominated by the PVDF binder, conductive carbon, and a surface coating of Li_2CO_3 on the cathode particles. After cycling the F concentration decreases and O concentration increases on the cathode surface, relative to the fresh cathode, for all of the electrolytes investigated suggesting deposition of electrolyte decomposition products on the surface covering the PVDF. The Ni concentration is very low on the surface of the fresh cathode and the cathode cycled with the baseline electrolyte consistent with little exposed metal oxide on the surface. Cathodes extracted

from cells cycled with DMMP containing electrolytes have higher Ni concentrations suggesting thinner surface films. Interestingly there is no boron present on the surface of the cathode.

The C1s spectra of all three cathodes are similar and dominated by PVDF (285.7 and 290.4 eV) and conductive carbon (284.3 eV). The F1s spectrum contains peaks for LiF (684.5 eV) and PVDF (687 eV). The relative intensity of the LiF peak is much lower for the cathodes cycled with DMMP/LiBOB electrolyte. The O1s spectrum contains a broad peak centered at 531.5 eV consistent with a mixture of Li_2CO_3 (531.5 eV) and lithium alkyl carbonates with shoulders at 529 eV for the metal oxide (529 eV) and C-O (533 eV) containing species including ethers and alkoxides. The intensity of the metal oxide peak roughly correlates with the observed concentrations of Ni discussed above. The P2p spectrum contains a peak characteristic of $\text{Li}_x\text{PO}_y\text{F}_z$ (134 eV) for all samples.

Conclusions

Non-Flammable electrolytes for lithium ion batteries can be prepared with LiPF_6 /carbonate electrolytes containing 15 % DMMP and 5 % (wt) LiBOB. The conductivity of the electrolyte is nearly identical to LiPF_6 in EC/EMC, but the thermal stability is dramatically improved. The addition of LiBOB significantly improves cycling performance of the electrolyte making it comparable to LiPF_6 in EC/EMC. However, a loss of approximately ~ 7 % of the initial capacity is observed. Ex-situ surface analysis suggests that the addition of LiBOB results in the generation of an anode SEI which is stable in the presence of DMMP allowing efficient reversible cycling without graphite exfoliation. Electrolytes with added DMMP and LiBOB may

be useful alternatives to standard LiPF_6 /carbonate electrolytes when non-flammability of the electrolyte is critical.

Acknowledgement

We thank NASA NRA Project No. 006637 for financial support of this research. M. X. acknowledges the China Scholarship Council (CSC) for financial support.

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	Sample	Composition
1	Baseline	1 M LiPF ₆ in EC/EMC=3:7
2	Flame retarding 15% DMMP	1 M LiPF ₆ +5% LiBOB in EC/EMC/DMMP (42.5/42.5/15)
3	Flame retarding 20% DMMP	1 M LiPF ₆ +5% LiBOB in EC/EMC/DMMP (2/2/1)
4	15% DMMP without LiBOB	1 M LiPF ₆ in EC/EMC/DMMP (3/5.5/1.5)
5	15% DMMP with LiBOB	1 M (95% LiPF ₆ +5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)

Table 2-1. Electrolyte solutions compositions

Electrolyte Solution	A	B (K)	T_0 (K)	$s[A]$	$s[B]$	$s[T_0]$
Baseline Electrolyte	2937	430	152.5	321	26	3.3
Flame retarding 15% DMMP	3677	454	153.7	142	10	1.4
Flame retarding 20% DMMP	3725	464	150.7	155	12	1.6

Table 2-2. VTF Parameters (A , B , and T_0) and their Standard Deviations ($s[X]$).

Electrolyte Solution	<i>SET, s</i>	<i>s[*], s</i>
Baseline Electrolyte	33.4	3.4
Flame retarding 15% DMMP	1.8	1.5
Flame retarding 20% DMMP	0.8	0.5
* standard deviation		

Table 2-3. SET for the electrolyte solutions containing DMMP.

	C1s	O1s	F1s	P2p
	(%)	(%)	(%)	(%)
Fresh Anode	62	3	35	-
1 M LiPF ₆ /EC :EMC/3 :7	26	37	31	6
1 M LiPF ₆ /EC:EMC:DMMP/3:5.5:1.5	32	38	28	2
1 M (95 % LiPF ₆ + 5% LiBOB) EC:EMC:DMMP/3:5.5:1.5	37	32	24	2

Table 2-4. The concentration of C, O, F and P on the anode electrode surface.

	C1s	O1s	F1s	P2p	Ni2p
	(%)	(%)	(%)	(%)	(%)
Fresh Cathode	50	7	40	-	3
1 M LiPF ₆ /EC :EMC/3 :7	55	23	17	2	3
1 M LiPF ₆ /EC:EMC:DMMP/3:5.5:1.5	40	12	38	2	8
1 M (95 % LiPF ₆ + 5% LiBOB) EC:EMC:DMMP/3:5.5:1.5	39	24	27	4	6

Table 2-5. The concentration of C, O, F, P and Ni on the cathode electrode surface.

Figure 2-1. The conductivity of the baseline and flame retardant additive containing electrolyte solutions (the circles are the experimental values, and the lines are the best fits to the VTF equation).

Figure 2-2. ^{19}F , ^{31}P and ^{11}B NMR spectra of DMMP containing electrolyte before (a) and after thermal storage (b).

Figure 2-3. Cycle Voltammogram of 1 M LiPF_6 with 5% (wt.%) LiBOB in EC:EMC:DMMP (2:2:1, vol.) at glass carbon electrode, scan rate 10 mV/s.

Figure 2-4. Cycling performances of the MCMB/Li half-cells containing different DMMP concentrations.

Figure 2-5. Cycling performance of Li/LiNi_{0.8}Co_{0.2}O₂ half-cells with baseline electrolyte and 20% DMMP containing.

Figure 2-6. Cycling performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2/\text{MCMB}$ cells with baseline (Electrolyte 1), 15% DMMP with (Electrolyte 5) and without LiBOB (Electrolyte 4).

EC/EMC (3/7) – 1M LiPF₆

EC/EMC/DMMP (3/5.5/1.5) – 1M LiPF₆

EC/EMC/DMMP (3/5/1.5) – 1M (95% LiPF₆ + 5% LiBOB)

Figure 2-7. SEM of cycled anodes.

EC/EMC (3/7) – 1M LiPF_6

EC/EMC/DMMP (3/5.5/1.5) – 1M LiPF_6

EC/EMC/DMMP (3/5/1.5) – 1M (95% LiPF_6 + 5% LiBOB)

Figure 2-8. SEM of cycled cathodes.

Figure 2-9. FTIR spectra of MCMB anode cycled in the electrolyte (a) 1M LiPF_6 in EC :EMC (3:7) (b) 1M LiPF_6 in EC:EMC:DMMP (3:5.5:1.5) and (c) 1M (95% LiPF_6 + 5% LiBOB) in EC:EMC:DMMP (3:5.5:1.5).

Figure 2-10. FTIR spectra of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ anode cycled in the electrolyte (a) 1M LiPF_6 in EC :EMC/3 :7 (b) 1M LiPF_6 in EC:EMC:DMMP/3:5.5:1.5 and (c) 1M (95% LiPF_6 + 5% LiBOB) in EC:EMC:DMMP/3:5.5:1.5.

Figure 2-11. C1s, F1s, O1s and P2p spectrum of MCMB anode cycled in the electrolyte (a) 1 M LiPF₆ in EC:EMC (3:7) (b) 1 M LiPF₆ in EC:EMC:DMMP (3:5.5:1.5) and (c) 1 M (95% LiPF₆ + 5% LiBOB) in EC:EMC:DMMP (3:5.5:1.5).

Figure 2-12. C1s, F1s, O1s and P2p spectrum of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode cycled in the electrolyte (a) 1 M LiPF_6 in EC:EMC (3:7) (b) 1 M LiPF_6 in EC:EMC:DMMP (3:5.5:1.5) and (c) 1 M (95% LiPF_6 + 5% LiBOB) in EC:EMC:DMMP (3:5.5:1.5).

MANUSCRIPT – II

Accepted for publication in Electrochemical and Solid state Letters.

Effect of added LiBOB on high voltage ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) spinel cathodes

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Chapter 3. Effect of added LiBOB on high voltage ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) spinel cathodes

Introduction

While lithium ion batteries have been widely utilized in portable electronic devices for over a decade, recent interest in developing lithium ion batteries for electric vehicle (EV) applications has spurred research into novel battery materials.¹ One direction of significant current interest is in the development of higher voltage cathode materials including $\text{Li}_{1.17}\text{Mn}_{0.58}\text{Ni}_{0.25}\text{O}_2$ ² and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.^{3,4} However, as interest in these materials has grown, so have concerns about the stability of the state-of-art electrolyte (LiPF_6 in a mixture of carbonate solvents) when cycled to high voltage (> 4.5 V vs Li).⁵⁻⁹ Researchers have employed two primary techniques to improve the performance of high voltage cathode materials in the presence of electrolyte. First, cathode particles have been coated with "inert" metal oxides such as Al_2O_3 , SiO_2 , and TiO_2 .¹⁰⁻¹² The cathode surface coatings have been reported to inhibit the reaction of the electrolyte with the cathode surface at high voltage and improve cycling performance. Second, electrolyte additives have been incorporated to sacrificially react with the cathode surface to generate a cathode passivation film similar in nature to the anode solid electrolyte interface (SEI).¹³⁻¹⁵

We have recently reported the use of cathode film forming additives for high voltage $\text{Li}_{1.17}\text{Mn}_{0.58}\text{Ni}_{0.25}\text{O}_2$ cathodes.^{13,14} We have now expanded this investigation to include the investigation of cathode film forming additive on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes. While there have been previous reports on the investigation of LiBOB based electrolytes cycling to high voltage with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and related cathode materials,¹⁶⁻¹⁸ we

currently report and investigation of the effect of the addition of low concentrations of lithium bis(oxalato)borate (LiBOB) to LiPF_6 /carbonate electrolytes on the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ cells.²⁰ Electrochemical impedance spectroscopy and ex-situ surface analysis of cycled cells suggest that the addition of LiBOB inhibits the growth of a cathode surface film and improved cell performance.

Experimental

1.1 M Lithium hexafluorophosphate (LiPF_6) dissolved in 1:2 Ethylene carbonate (EC)/diethylene carbonate (DEC) (vol. %) (standard electrolyte) was obtained from Daikin America, Inc. and was used without further purification. Lithium bis(oxalato)borate (LiBOB) was provided by Novolyte Technologies and was used without further purification. LiBOB was added to baseline electrolyte in 1.0 and 0.25 % (wt.) quantity and was allowed to dissolve overnight. Coin cells were prepared using lithium metal/electrolyte/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMS, Shanshan, China). The electrodes contain 89% active material, 6% conductive carbon, and 5% PVDF binder. The average weight loading of the cathode is 12.6 mg/sq.cm. The cells were built in triplicate and were cycled as follows: 1 cycle at C/20, 2 cycles at C/10 and 12 cycles at C/5 rate from 3.0 V to 4.9 V. Electrochemical impedance spectroscopy (EIS) analysis of the coin cells were performed using a 263A potentiostat/galvanostat (Princeton Applied Research), with the ac perturbation amplitude was 10 mV, from 100 KHz to 0.1 Hz. After cycling, the cells were disassembled in a glove box filled with high purity Argon. The LNMS electrodes were washed with anhydrous DMC to remove residual LiPF_6 salt and EC from the electrode surface and dried overnight under vacuum. X-ray photoelectron spectroscopy (XPS) was conducted with a PHI 5500 system using Al $K\alpha$ ($h\nu=1486.6$

eV) radiation under ultrahigh vacuum. The graphite peak at 284.3 eV was used to check the binding energy scale and charging effect. The spectra obtained were analyzed by Multipak 6.1A software. Line syntheses of elemental spectra were conducted using Gaussian–Lorentzian (70:30) curve fit with Shirley background subtraction. Element concentration was calculated based on the equation: $C_x = (I_x/S_x)/(\sum I_i/S_i)$, where I_x is the intensity of the relative element, and S_i is the sensitivity number of the element, acquired from the Multipak 6.1A software. Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) analysis of the cathodes was carried out with Thermo Nicolet iS10 IR spectrometer which has a smart performer accessory with a Germanium crystal. For each sample, 128 scans were collected at two/three different locations, constantly purged with high purity Argon. SEM analyses were conducted on a JEOL-5900 environmental SEM.

Results and Discussion

Cycling performance

The discharge capacity of Li/LiNi_{0.5}Mn_{1.5}O₄ cells containing LiPF₆/carbonate electrolyte with and without added LiBOB over the first fifteen cycles are depicted in Figure 1. Cells containing baseline electrolyte showed higher discharge capacity after the first cycle but gradual capacity fade is observed upon subsequent cycling consistent with previous reports.^{8,9} Cells containing LiBOB showed lower discharge capacity after first cycle but capacity retention was much improved in following cycles. Cells containing 0.25% LiBOB retained almost 93% of the initial discharge capacity as compared to 71% capacity retention for cells containing standard electrolyte. The cell

efficiency was also improved with added LiBOB. Cells containing the standard electrolyte have relative low efficiency (~94%). Incorporation of LiBOB significantly improves cell efficiency with efficiencies exceeding 99% for cell with 0.25% LiBOB (Figure 1).

Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectrum of the half cells and the equivalent circuit are shown in Fig. 2. The ac impedance was measured after 15 cycles and at 3.0 V. The EIS in the high to intermediate frequency range is typically attributed to the solid electrolyte interface SEI impedance with a small contribution from charge-transfer resistance.²⁰ The half cells containing LiBOB have lower impedance (smaller diameter of the semicircle) than the cells containing baseline electrolyte. The diameter of the semicircles decrease as the LiBOB concentration is decreased consistent with the improved capacity retention and efficiency at lower concentrations of LiBOB.

Elemental concentration on LNMS cathode surface

X-ray photoelectron spectroscopy (XPS) is useful for studying the surface films since the method analyzes the top ~ 5.0 nm of the surface, has good sensitivity for the elements of interest (B, C, O, F, and P), provides elemental concentrations, and allows determination of bonding energies (C-O, C=O, C-C, etc.). Elemental concentrations as determined by XPS suggest subtle changes to the cathode surface. The concentrations of oxygen and phosphorus are slightly increased and the concentration of fluorine is slightly decreased for all cycled cathodes. The carbon concentration was increased for

the cell cycled with the standard electrolyte, but decreased for the cells containing LiBOB. The changes to the surface of the cathodes is consistent with reaction of the electrolyte and generation of a cathode surface film.⁶⁻⁸ The cathode extracted from the cell containing the standard electrolyte has a lower concentration of manganese than the cathodes extracted from cells cycled with electrolyte containing added LiBOB suggesting a thicker cathode surface film for the standard electrolyte. Surprisingly, none of the cycled cathodes contain Ni on surface and the cells cycled with electrolyte containing added LiBOB contain no B on the surface.

X-ray photoelectron spectroscopy (XPS) of cycled cathodes

XPS spectra of fresh and cycled cathodes are provided in figure 3. The fresh cathode contains peaks characteristic of PVDF at 285.7 (C-H) and 290.4 eV (C-F) and graphite at 284.3 eV in the C1s spectrum. Related peaks characteristic of PVDF are observed in the F1s spectrum at 687.6 eV. The fresh cathode surface also contains O1s peaks characteristic of metal oxide at 529.5 eV along with residual Li_2CO_3 at 531.5 eV. The element spectra of the cathodes extracted from cycled cells reveal changes to the surface species. New peaks characteristic of C-O and C=O are observed at 286-287 and 288-289 eV in the C1s spectrum and 533.5 and 531.5 eV in the O1s spectrum for cathodes cycled with the standard electrolyte and electrolytes with added LiBOB. The intensity of the C-O and C=O peaks is greater for cells cycled with the standard electrolyte than cells cycled with electrolytes containing LiBOB. In addition, the peak characteristic of the metal oxide (529.5 eV) has weaker intensity for the cell cycled with the standard electrolyte than cells cycled with electrolytes containing LiBOB. The new peaks are

consistent with the presence of electrolyte decomposition products including poly(ethylene carbonate) (PEC), lithium alkyl carbonates, oxalates, and related electrolyte decomposition products.⁶⁻⁸ The stronger intensity of the C-O and C=O peaks and the weaker intensity of the metal oxide peak on cathodes extracted from cells cycled with the standard electrolyte is consistent with a thicker cathode surface film. The changes to the F1s spectra of cycled electrodes are smaller. The F1s spectrum of the cathode extracted from the cell containing standard electrolyte is nearly identical to the fresh cathode while the cathodes extracted from cells cycled with electrolytes containing LiBOB have small peaks characteristic of LiF at 685 eV. The P2p spectra has one peak at 134-135 eV which is characteristic of $\text{Li}_x\text{PO}_y\text{F}_z$. The corresponding F1s peak of $\text{Li}_x\text{PO}_y\text{F}_z$ has a similar bonding energy to PVDF and is not observed due to peak overlap and low intensity.

FTIR Analyses of LNMS Cathodes

FTIR-ATR spectra of fresh and cycled cathodes are displayed in figure 4. The spectra are dominated by PVDF peaks at 1400, 1271, 1170, 1070, 877, and 840 cm^{-1} . The cycled cathodes contain additional peaks at 1740 cm^{-1} and 1640 cm^{-1} characteristic of PEC and oxalate, respectively. The peak characteristic of PEC is strongest for the cell cycled with standard electrolyte while the intensity of the oxalate peak is strongest from the cells cycled with LiBOB.

SEM of cathodes

SEM images of fresh cathodes and cathodes that have been cycled with either standard electrolyte or electrolyte with added LiBOB are depicted in figure 5. There are no observable differences in the cathode particles suggesting that cycling in the presence of electrolyte with or without added LiBOB does not alter the bulk cathode particles.

Conclusion

The effect of low concentrations of LiBOB on the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes cycled to high voltage (4.9 V vs Li) was investigated. The incorporation of LiBOB improves the cycling efficiency and capacity retention of $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ coin cells and decreases cell impedance. Ex-situ surface analysis of the cathodes suggests the incorporation of LiBOB alters the surface chemistry of the electrode resulting in thinner cathode surface films containing oxalate species. Addition of low concentrations of LiBOB appears generate novel cathode surface films which improve the performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes cycled to high voltage. The performance enhancement is most likely due to one of two possible mechanisms. First, the oxidation of LiBOB on the cathode surface could generate a cathode passivation layer which inhibits further oxidation of the electrolyte. Second, the presence of LiBOB could inhibit the generation of acidic species in the electrolyte (HF or PF_5) from the decomposition of LiPF_6 which inhibits the dissolution of Mn from the cathode surface.²¹⁻²² Further investigations of the source of performance enhancements are in progress and will be reported in due course.

Acknowledgement

We thank the Batteries for Advanced Transportation Technologies (BATT) Program supported by the U.S. Department of Energy Office of Vehicles Technologies for financial support of this research work.

	Carbon	Fluorine	Oxygen	Phosphorus	Nickel	Manganese
Fresh	48.6	33.7	11.1	-	1.8	4.8
Standard	50.8	29.0	16.6	1.5	-	2.1
1% LiBOB	45.8	31.1	16.4	1.0	-	5.6
0.25% LiBOB	47.1	29.0	17.4	1.0	-	5.4

Table 3-1: Elemental concentration on LNMS cathode surface.

Figure 3-1. Specific capacity and efficiency of cells containing standard electrolyte and electrolyte containing added LiBOB.

Figure 3-2. EIS of cells containing standard electrolyte and electrolyte containing added LiBOB.

Figure 3-3. XPS spectra of LNMS cathodes extracted from cells after cycling.

Figure 3-4. FTIR-ATR spectra of LNMS cathodes extracted from cells after cycling.

Figure 3-5. SEM images of LNMS fresh (a), cycled with standard electrolyte (b), and cycled with 0.25 % added LiBOB (c).

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MANUSCRIPT – III

Prepared for submission to The Journal of Electrochemical Society

The Effect of Additives Upon The Performance of MCMB/ $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ Li-ion Cells Containing Methyl Butyrate-Based Wide Operating Temperature Range Electrolytes.

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Chapter 4. The effect of additives upon the performance of MCMB/ $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ Li-ion cells containing methyl butyrate-based wide operating temperature range electrolytes

Introduction

There is a continued desire to develop improved lithium-ion batteries that can operate efficiently over a wide temperature range, while still providing long life characteristics. The narrow operating range of the state of art systems has been identified by the Department of Energy (DoE) as one of the technical barriers associated with their use in PHEVs, along with, limited cycle and calendar life, and poor abuse tolerance.¹ For this reason, they have interest in the development of advanced electrolytes which will improve the performance over a wide range of temperatures (-30 to +60°C) and lead to long life characteristics (5,000 cycles over a 10-year life span). In addition, there is a desire for these candidate electrolyte systems to operate well at high voltages, (i.e., 5V) to take advantage of the new class of high specific energy cathode materials. From a space applications perspective, some future NASA missions aimed at exploring Mars, the Moon, and the outer planets also require such rechargeable batteries that can operate over a wide temperature range (i.e., -60° to +60°C) and provide good life characteristics to satisfy various applications, such as landers, rovers, and penetrators.² The state of art lithium-ion systems have been demonstrated to operate over a reasonably wide range of temperatures (-40° to +40°C), however, the high temperature resilience is generally very poor and as well, the power densities at low temperatures aren't satisfactory.

To improve the temperature range of operation of lithium-ion cells, many research groups have attempted to modify the electrolyte formulation, either through the use of (a) optimized solvents blends, (b) use of novel co-solvents, (c) use of novel electrolyte salts, or (d) the use of electrolyte additives, to achieve improved cell resilience to warm temperature exposures. Relative to the electrolyte additives, vinylene carbonate (VC) has been shown to be an effective additive in improving the high temperature cycle life and storage characteristics.³⁻⁵ It is generally held that VC sacrificially polymerizes on the electrode surfaces, producing protective films preventing further electrolyte reaction at the interface. Although the bulk of the studies have focused upon its effect during the formation process upon the SEI of the carbon electrode, it is acknowledged that VC influences the SEI on the cathode also.⁵⁻⁷ Amine and coworkers have also described electrolyte formulations based on the use of similar additive, vinyl ethylene carbonate with propylene carbonate-based electrolytes and demonstrated their resilience to temperatures as high as 50°C.^{8,9} Lucht and coworkers have investigated Lewis base electrolyte additives¹⁰⁻¹², namely dimethyl acetamide (DMAC) and N-methyl pyrrolidone (NMP), as stabilizing agents which have been found to reversibly bind with PF₅, preventing LiPF₆ and carbonate solvents from decomposition at high temperature. In collaboration with URI, we have also demonstrated good performance of 1.0 M LiPF₆ EC+DEC+DMC (1:1:1 v/v %) solutions with these additives upon high temperature storage.⁷ In a similar fashion, lithium oxalate was envisioned to complex any free PF₅ generated from the decomposition of LiPF₆ much in the same manner as LiBOB has been reported to stabilize LiPF₆-based solutions.^{13,14} Mono-fluoroethylene carbonate has also been

investigated in electrolyte solutions consisting of FEC+EC+PC (1:3.5:3.5) primarily to prevent the exfoliation of graphite anode electrodes when used in the presence of propylene carbonate (PC).¹⁵ In a similar type of study, FEC was added to LiClO₄ dissolved in PC and the lithium deposition characteristics were investigated.¹⁶ FEC has also been studied in 1.30M LiPF₆ solutions of EC+DEC (30:70) to improve the efficiency of Li/Si thin-film cells.¹⁷ In short, many of these electrolyte additives including mono-fluoroethylene carbonate (FEC), vinylene carbonate (VC), and lithium bis(oxalatoborate) (LiBOB), have been shown in the past to result in improved high temperature resilience of all carbonate-based electrolytes. Based upon the improved low temperature performance of lithium-ion cells that we have observed with the use of ester containing electrolytes,¹⁸⁻²⁰ as well as finding from other groups²¹⁻²⁴, we sought to further this general approach with the use of electrolyte additives to improve the high temperature resilience and life characteristics.

In the present work, we describe a number of electrolyte formulations that incorporate selective or specific electrolyte additives, that are anticipated to improve the high temperature resilience, low temperature power capability, and life characteristics of methyl butyrate-based electrolyte solutions, i.e., 1.00M LiPF₆ in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + methyl butyrate (MB) (20:20:60 v/v %). Several of these electrolyte formulations were investigated in experimental three electrode MCMB/ Li_xNi_yCo_{1-y}O₂ lithium-ion cells, to study the charge and discharge behavior of the cells, as well as to understand the interfacial effects on the intercalation kinetics, using a number of electrochemical techniques, including Electrochemical Impedance Spectroscopy (EIS), Tafel polarization and linear polarization to understand

the interfacial effects on the intercalation kinetics. The electrochemical observations were further corroborated by ex-situ analytical techniques to understand the nature of surface films.

Experimental

For detailed electrical and electrochemical measurements, three-electrode, O-ring sealed, glass cells containing spiral rolls of MCMB (1028)-carbon anodes, $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$ cathodes, and lithium reference electrodes separated by two layers of porous polypropylene (Tonen-Setella) were employed. The carbon electrodes ($\sim 114\ \mu\text{m}$ in thickness) were coated with active material on both sides of the substrate, and had an active material area of approximately $158.1\ \text{cm}^2$, corresponding to an electrode loading of $\sim 16\ \text{mg}/\text{cm}^2$. The NCO electrodes ($\sim 114\ \mu\text{m}$ in thickness) were also double sided with an active material area of approximately $141.1\ \text{cm}^2$, corresponding to a loading of $\sim 19\ \text{mg}/\text{cm}^2$. The carbonate-based solvents, ethylene carbonate (EC) and ethyl methyl carbonate (EMC), containing LiPF_6 salt in the desired concentration (1.0M), and methyl butyrate were purchased from Mitsubishi Chemicals (battery grade) or Novolyte Industries, Inc. with less than 50 ppm of water.

Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat (273A) interfaced with an IBM PC, using Softcorr 352 for DC measurements. A Solartron 1255 Frequency Response Analyzer was used with this potentiostat for impedance measurements, with M388 software. Charge-discharge measurements and cycling tests were performed with an Arbin battery cycler. The cycling tests were done at current densities of $0.25\ \text{mA}/\text{cm}^2$ ($\sim \text{C}/16$ rate) and $0.50\ \text{mA}/\text{cm}^2$ ($\sim \text{C}/8$ rate) for

charge and discharge, respectively. The cells were charged to 4.10V, followed by a tapered charge period at constant potential for three hours, and discharged to 2.75V, with 15 minutes of interval between the charge/discharge steps. For the low temperature discharge rate characterization of the experimental cells, after charging at room temperature, the cells were allowed to dwell at the desired temperature for at least 5 hours prior to discharging to 2.00V. To maintain the cells at the desired temperature, they were placed in Tenney environmental chambers (+/- 1°C).

After completing the low temperature discharge characterization, high temperature cycling, and post-cycling electrochemical characterization were carried out. The electrodes were subsequently harvested from the cells for ex-situ analysis, which carried out at the University of Rhode Island. The electrodes were washed with anhydrous DMC three times to remove residual carbonate solvents and LiPF₆ salt followed by vacuum drying overnight at room temperature prior to such measurements. X-ray photoelectron spectroscopy analysis (XPS) was conducted with a PHI 5500 system using Al K α (h ν =1486.6 eV) radiation under ultrahigh vacuum. The graphite peak at 284.3 eV in the electrodes was used to check the binding energy scale and charging effects. The spectra obtained were analyzed by Multipak 6.1A software. Line syntheses of elemental spectra were conducted using Gaussian–Lorentzian (70:30) curve fit with Shirley background subtraction. Element concentration was calculated based on the equation: $C_x = (I_x/S_x)/(\sum I_i/S_i)$, where I_x is the intensity of the relative element, and S_i is the sensitivity number of the element, acquired from the Multipak 6.1A software. Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) analysis of the cathodes was carried out with Thermo Nicolet iS10 IR spectrometer, which has a smart

performer accessory with a Germanium crystal. For each sample, 128 scans were collected at two/three different locations, while constantly purging with high purity Argon. SEM analyses were conducted on a JEOL-5900 environmental SEM.

Results and discussion

A number of experimental lithium-ion test cells, consisting of MCMB carbon anodes and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes, have been fabricated to study the electrolytes described. These cells serve to verify and demonstrate the reversibility, low temperature performance, and electrochemical aspects of each electrode as determined from a number of electrochemical characterization techniques. The electrolytes selected for evaluation include a number of methyl butyrate-containing electrolytes, which contain various additives, as listed below.

- 1) 1.0 M LiPF_6 EC+EMC+MB (20:20:60 v/v %) (where MB=methyl butyrate)
- 2) 1.0 M LiPF_6 EC+EMC+MB (20:20:60 v/v %) + 2% FEC
- 3) 1.0 M LiPF_6 EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 4) 1.4 M LiPF_6 EC+EMC+MB (20:20:60 v/v %) + lithium oxalate
- 5) 1.0 M LiPF_6 EC+EMC+MB (20:20:60 v/v %) + 2% VC
- 6) 1.0 M LiPF_6 EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB

Various electrochemical methods were used to evaluate these electrolytes, to ascertain the kinetics of lithium intercalation and de-intercalation, and to determine the charge-discharge capacities all as a function of temperatures. In addition, the relative interfacial stability of the candidate electrolyte with the MCMB-carbon anodes and the $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$ cathodes were studied by performing EIS measurements, as described in

the following sections.

Experimental Cell Results

Formation Characteristics

As illustrated in Table 1, good performance characteristics were obtained with the cells containing the methyl butyrate-based electrolytes with and without the use of electrolyte additives, as judged from the coulombic efficiency in the first cycle (being an indication of the inherent stability and the electrode film forming) and the cumulative irreversible capacity losses. The cell containing the mono-fluoroethylene carbonate additive was observed to have notably low irreversible capacity loss over the first five cycles and much high coulombic efficiency in the first cycle. These results suggest that very desirable solid electrolyte interphase (SEI) layers are being formed on the electrode (especially on the carbon anode). The high coulombic efficiency and comparable irreversible capacity losses are indirectly related to the overall stability and suggest good cycle life characteristics can be obtained. It should be noted that the observed trends cannot be entirely attributed to electrolyte effects, and that some small differences in reversible capacity can be partly attributed to cell to cell variability (i.e., <5% variation in electrode weights).

Discharge Characteristics.

After performing the formation cycling, the cells were subjected to systematic discharge rate characterization testing over a wide temperature range. These tests consisted of charging the cells at ambient temperature and then discharging at the desired

temperatures after soaking the cells for at least four hours prior to discharge and the results are summarized in Table 2.

Given the rationale of adding the electrolyte additives was to improve the high temperature resilience, it is significant that the discharge rate capability is somewhat comparable for all of the formulations investigated. This suggests that the electrolyte additives are not having a negative impact upon the cell impedance of the cell, which would limit the low temperature performance. For example, as displayed in Fig. 1, when the cells were discharged at $\sim C/16$ discharge rate at -40°C , very comparable performance was obtained in all cases with approximately 75% of the room temperature capacity being delivered.

In contrast, in many cases, the cells containing the electrolyte additives actually deliver better performance than the baseline formulation under many conditions. As shown in Fig. 2, more differentiation of the cells can be observed under high rate conditions at low temperatures (i.e., using a $C/4$ discharge rate at -40°C). As illustrated, the cells containing the LiBOB, VC, FEC, and lithium oxalate all outperformed the baseline solution without any additive. These results suggest that the lithium intercalation/de-intercalation kinetics are more favorable with the cells containing the electrolyte additives, presumably due to preferable SEI characteristics. In order to decipher the influence of the electrolyte additives upon the kinetics of the respective electrodes, detailed electrochemical characterization of the cells was performed, as described in the section below.

High Temperature Cycling

After performing the rate characterization testing, cycling tests at high temperatures were performed on the cells to determine their high temperature resilience. This consisted of performing 20 cycles at 60°C, followed by electrochemical characterization, which was in turn followed by performing an additional 20 cycles at 80°C. As illustrated in Fig. 3, the cells containing the VC and lithium oxalate additives displayed the best capacity retention after being subjected to cycling at 60°C. This trend followed for the most part even after cycling at 80°C, with the cell containing the VC additive displaying the best performance. It is, however, likely that the underlying capacity fade mechanisms may be different at these two temperatures, and for the various electrolyte formulations (i.e., the performance characteristics of the anode and cathode may degrade at different rates depending upon the electrolyte type) to account for the observed trends in the high temperature resilience.

Electrochemical characteristics

Based on previous work, it is believed that the improved rate capability at low temperatures of Li-ion cells that utilized these ester-based solutions is primarily attributed to a combination of improved mass transfer characteristics in the electrolyte (higher ionic conductivity) and facile kinetics of lithium intercalation/de-intercalation at the interface due to favorable film formation behavior at the electrode surfaces.^{18,20} To enhance this understanding on the impact that the electrolyte additives have upon these factors as well as any benefit they may have to increase the high temperature resilience, we have assessed the electrochemical characteristics of the systems using a number of techniques, including Tafel polarization measurements, Electrochemical Impedance

Spectroscopy (EIS), and linear micro-polarization measurements.

Electrochemical impedance spectroscopy (EIS)

To interpret the impedance patterns from Li-ion cell electrodes an equivalent circuit is typically used which consists of two relaxation loops and is comprised of a series resistance, R_s , which represents an algebraic sum of the electronic resistance from both the electrodes, leads and the electrolyte ionic resistance, a parallel resistor-capacitor network (C_f and R_f) in series for the high frequency relaxation loop associated with surface film between the electrolyte and the electrodes, another resistor-capacitor parallel network in series for the low frequency relaxation loop (C_{dl} and R_{ct}) and a Warburg impedance (w), to represent a slow solid state diffusion of lithium inside the cathode or anode²⁵⁻²⁹ A schematic of the equivalent circuit used in the analysis in the present study is provided in our previous publications.³⁰ In the event that more than two relaxation loops are observed, the addition of resistor-capacitor networks in series were added to represent the multi-layer lamina formed parallel to the surface.³¹ The capacitors are replaced with constant-phase elements (CPE) to represent their non-ideal characteristics, whenever needed. For cathode measurements, an inductor was appropriately added to account for the magnetic properties attributable to the aluminum substrate. The impedance data were analyzed, using the above equivalent circuit and ZSimWin CNLS modeling software from Princeton Applied Research.

EIS measurements of $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$ and MCMB electrodes (prior to cycling)

In most lithium-ion cells, including the MCMB/ $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$ electrochemical couple studied in this work, the interfacial impedance of the cathode dominates that of the anode in contributing to the overall cell resistance. When EIS measurements were performed on the MCMB electrodes after formation, but prior to cycling and high temperature exposure, in general all of the cells displayed comparable results, as illustrated in Fig. 4. Of the permutations studied, the cell containing the electrolyte with FEC as an additive displayed the lowest film and charge transfer resistances of the MCMB anodes, being noticeably lower than that of the baseline cells which contains no additives. In contrast, the cells containing LiBOB or VC displayed much higher film resistances. It should be noted that significant differences in the series resistances were observed, which is likely due to the differing nature of the porous composite-type solid electrolyte interphase (SEI) films formed in the presence of the varying electrolytes. Although no capacitance is expected, these films are anticipated to add resistance which is reflected in the series resistance. Of course, a significant contribution to the series resistance comes from the electrolyte conductivity; however, this alone cannot explain the observed trends since the ionic conductivity of the formulations studied do not vary significantly, due to the low concentration of the additives employed.

When EIS measurements of the $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$ electrodes were performed after formation, but prior to cycling and high temperature exposure, most of the cells containing the additives displayed comparable behavior to the baseline, with the exception of the cell containing LiBOB, as shown in Fig. 5, which exhibited dramatically higher series resistance. In a similar fashion to the MCMB anodes, the LiBOB is likely changing the nature of the cathode electrolyte interphase film, such that

it displays increased resistance.

EIS measurements of $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$ and MCMB electrodes (after cycling)

When EIS measurement were performed on the MCMB electrodes after cycling and high temperature exposure, all of the cells containing the electrolyte additive displayed lower film and charge transfer resistances, as shown in Fig. 6. This suggests that all of the electrolyte additives contribute positively to producing desirable, protective surface films on the MCMB electrodes, resulting in decreased SEI growth compared with the baseline. Of all the samples, the cell containing VC displayed the lowest film and charge transfer resistances, suggesting that the presence of poly(vinylene carbonate) is especially suited in inhibiting further electrolyte reduction.

In contrast to the results obtained prior to cycling, when the EIS measurements were performed on the $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$ electrodes after cycling, much more differentiation between responses was observed in Fig.7, being much more dependent upon the electrolyte type. The most favorable results were obtained with the cell containing lithium oxalate as an electrolyte additive, suggesting that it may have prevented excessive electrolyte decomposition due to the complexation of PF_5 generated. The largest film resistance was observed with the cell containing the FEC additive, suggesting that this additive displays some reactivity at the cathode possibly leading to the formation of poly(fluoroethylene carbonate) by a similar mechanism reported for the polymerization of EC.

Tafel polarization measurements

The lithiation/de-lithiation kinetics were determined for the anodes and the cathodes by conducting Tafel polarization measurements of the MCMB-Li_xNi_yCo_{1-y}O₂ cells in contact with the various electrolytes. The measurements were conducted on fully charged cells (i.e., cells were charged at room temperature and the open circuit potential was above 4.08V) and allowed to equilibrate at the desired temperatures for at least two hour prior to performing the tests. These measurements were performed under potentiodynamic conditions, using slow scan rates (0.2mV/sec), approximating steady-state conditions. In all of these Tafel plots, there are distinct charge-transfer controlled regimes, where the overpotential increases linearly with log (I). The effect of mass transfer seems to be relatively insignificant, such that kinetic parameters, i.e., exchange current and transfer coefficients can be obtained. In cases, where there is mass transfer interference, proper correction was applied in the data analysis. These rate parameters, i.e., the exchange currents and transfer coefficients, for the intercalation/de-intercalation of lithium were determined from the intercept and the slope of the mass-transfer corrected plots (i.e., generated by plotting the logarithm of $I/(1-I/I_{lim})$ against the electrode potential).

As illustrated in Fig. 8, with the exception of the cell containing the LiBOB, improved lithium de-intercalation kinetics (i.e. higher limiting currents) were observed for the anodes in contact with the electrolytes possessing the electrolytes additives compared to the baseline solutions, suggesting that desirable surface films have formed in these cases.

As illustrated in Fig. 9, in which the Tafel polarization measurements have been performed on the LiNiCoO₂ cathodes at room temperature, the cell containing the VC and lithium oxalate electrolyte additives displayed enhanced lithium kinetics (i.e., higher limiting current densities) compared to the baseline system that does not contain the additive. This observation, namely that VC has a beneficial effect upon the nature of the SEI layer on the cathode and the corresponding lithium kinetics, has been previously found in our previous studies involving different solvent mixtures.

Generally, the trends with regard to the observed lithium kinetics and how they depend upon electrolyte type tend to track well with temperature. For example, when the Tafel measurements were performed on the MCMB anodes at low temperature, as displayed in Fig. 10, the cells containing the FEC and lithium oxalate additives delivered somewhat improved performance over the baseline solution. However, when the LiNiCoO₂ cathodes were measured at -30°C, as shown in Fig. 11, a different trend was observed compared to that displayed at 20°C, with the cell containing the LiBOB delivering significantly better performance.

Ex-Situ analysis of harvested electrodes

XPS of MCMB electrodes

Elemental concentration on the MCMB anode surface

The fresh MCMB composite electrode has high concentrations of C and F due to the presence of PVDF binder. There is also a low concentration of O due to the presence of oxygenated surface impurities. After cycling with the baseline MB containing

electrolyte, the concentration of C is significantly decreased while the concentrations of O and P are increased while the concentration of F is slightly decreased. The changes in the atomic concentrations are consistent with the formation of an anode solid electrolyte interphase (SEI) as previously reported. The incorporation of additives clearly affect the elemental concentrations of the surface species. Addition of FEC results in a greater decrease in the concentration of C and F and a greater increase in the concentrations of O and P. Similar changes in the elemental concentrations are observed for cells containing LiBOB, although the concentration of B is also very high (15 %). Incorporation of $\text{Li}_2\text{C}_2\text{O}_4$ results in only small changes to the elemental concentrations of C, F, O, and P, compared to the baseline electrolyte suggesting that the surface films may be similar in the presence of $\text{Li}_2\text{C}_2\text{O}_4$. The addition of VC results in the highest concentrations of F and the lowest concentrations of C, O, and P on the surface of the electrode.

The XPS element spectra of the cycled anodes provide additional insight into the differences in structure of the anode SEI in the presence of different additives. The C1s XPS spectrum of the anode extracted from the cell containing the baseline electrolyte contains a broad peak centered at ~285 eV consistent with the presence of C-C (284.3 eV), C-H (285.7 eV), and C-O (286-287 eV) containing species. The C1s spectrum also contains a higher energy shoulder centered at ~ 289 eV consistent with the presence of C=O (288-289 eV) and C-F (290.4 eV) containing species. The presence of C-O and C=O containing species was further supported by the O1s spectrum. A broad peak centered at ~532 eV is consistent with the presence of C-O (532 eV) and C=O (533 eV) containing species.³² The F1s spectrum contains a primary peak at 685 eV

characteristic of LiF and a shoulder at ~687 eV, which is likely a combination of PVDF binder (687.6 eV) and $\text{Li}_x\text{PO}_y\text{F}_z$ (686-687 eV). The XPS element spectra of the anode extracted from the cell cycled with FEC is similar to the element spectra for the baseline electrolyte. However, the peaks associated with $\text{Li}_x\text{PF}_y\text{O}_z$ (686-687 eV, F1s; 134 eV, P2p) are much stronger. Similar increases in the intensity of peaks associated with $\text{Li}_x\text{PF}_y\text{O}_z$ are observed on anodes extracted from cells cycled with lithium oxalate. However, an additional decrease in the intensity of peaks characteristic of C=O bonds (~289 eV) is observed. The XPS element spectra for anodes cycled with LiBOB containing electrolyte are very similar to the element spectra for anodes cycled with $\text{Li}_2\text{C}_2\text{O}_4$, except they contain an additional B1s peak at 192 eV for borates generated from the reduction of LiBOB on anode surface.³³ The anodes extracted from the cells containing VC have similar element spectra, except that the intensity of the peak characteristic of LiF is much greater than for any of the other samples.

FTIR and SEM of cycled MCMB electrodes

The IR spectra of all of the anodes extracted from cells after cycling are dominated by the peaks associated with the PVDF binder at 1400, 1271, 1170, 1070, 877, and 840 cm^{-1} . All the anodes contain a broad peak at ~ 1600 cm^{-1} corresponding to C=O stretch from oxalate containing species.³⁴ The anodes cycled with the baseline electrolyte and the baseline with FEC have a strong absorption at 1730 cm^{-1} characteristic of poly(ethylene carbonate).³⁵ The anodes cycled with $\text{Li}_2\text{C}_2\text{O}_4$ and LiBOB also contain the peak at 1730 cm^{-1} although with weaker intensity. The anode from the VC

containing electrolyte shows additional small peak at 1778 cm^{-1} which is due to the presence of poly(VC).

SEM images of cycled anodes indicate that the bulk MCMB particles are covered with a thin film of electrolyte decomposition products characteristic of the SEI. However, the bulk spherical MCMB particles are intact and the surface coverage is similar for anodes cycled with all electrolytes.

XPS of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrodes

Elemental concentration on the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ surface

The fresh cathodes contain high concentrations of C and F due to the presence of PVDF binder and conductive carbon and low concentrations of O and Ni. The electrodes extracted from cells cycled with the baseline electrolyte have a slight decrease in the concentration of C and Ni and slight increases in the concentrations of O and P consistent with the generation of a thin cathode surface film. The addition of either FEC or VC containing electrolytes results in slight increases in the concentrations of C, O, and P and decreases in the concentration of F and Ni, supporting a thin cathode surface film, but with a different elemental composition than generated with the baseline electrolyte. Cathodes cycled with electrolytes containing $\text{Li}_2\text{C}_2\text{O}_4$ or LiBOB have decreases in the concentration of C, F, and Ni and increases in the concentrations of O and P. In addition, the sample cycle with LiBOB containing electrolyte has 7 % B on the surface. The incorporation of different additives appears to alter the surface chemistry of the cathode particles.

The C1s and F1s XPS spectra of the fresh cycled cathodes are dominated by the presence of PVDF binder at 285.7 eV and 290.4 eV (C1s) and 687.6 eV (F1s). The O1s spectrum contains a peak characteristic of metal oxide at 529 eV and residual surface Li_2CO_3 at 531 eV. Upon cycling with the baseline electrolyte, the XPS element spectra of the cathode surface are altered. New peaks are observed in the C1s spectrum consistent with the formation of C-O and C=O containing species on the surface. In the O1s spectrum the peak characteristic of the metal oxide (529 eV, O1s) is decreased in relative intensity and new peaks characteristic of C-O and C=O containing species are observed. A small new peak is observed in the F1s spectrum at 685 eV consistent with the presence of LiF. Finally, a new peak is observed in the P2p spectrum consistent with the presence of $\text{Li}_x\text{PF}_y\text{O}_z$ at 134-135 eV. The B1s element spectrum of the cathode extracted from the cell cycled with LiBOB contains a peak for borate species formed from the decomposition of LiBOB.

FTIR and SEM of cycled $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrodes

The IR spectrum of the fresh cathode is dominated by the peaks of the PVDF binder at 1400, 1271, 1170, 1070, 877 and 840cm^{-1} .³⁶ Additional weak peaks characteristic of oxalate at $\sim 1600\text{ cm}^{-1}$ and polycarbonate at $\sim 1740\text{ cm}^{-1}$ are observed on all cycled cathodes. The IR spectra of the cathodes cycled with the baseline electrolyte and electrolytes containing additives are similar except for the cathode extracted from the cell cycled with electrolyte containing VC which contains a small absorption characteristic of poly(VC) at 1830cm^{-1} .

SEM images of cycled cathodes indicate that the bulk cathode particles are not damaged upon cycling. Difference between the SEM images of cathodes cycled with different additives are small and thus the changes are limited to the surface.

Conclusions

In this study, a number of cells MCMB/Li_xNi_yCo_{1-y}O₂ lithium-ion cells containing methyl butyrate-containing electrolytes designed for operation over a wide temperature range were characterized in terms of their charge/discharge characteristics, and lithium intercalation kinetics as a function of temperature. With the intent of improving the high temperature resilience of these cells, a number of electrolyte additives were investigated in methyl butyrate containing electrolytes, including mono-fluoroethylene carbonate (FEC), lithium oxalate, vinylene carbonate (VC), and lithium bis(oxalato borate) (LiBOB). The electrolyte formulations investigated contained low EC content (20%) and high MB content (60%), with and without additives, making them especially suited for improved low temperature performance. The low temperature discharge rate capability was improved with the incorporation of the additives, suggesting that the lithium intercalation/de-intercalation kinetics are more favorable with the cells containing the electrolyte additives, presumably due to preferable SEI characteristics. This contention is supported by Tafel polarization measurements in which much higher limiting currents were observed on the Li_xNi_yCo_{1-y}O₂ electrodes from the cells containing LiBOB and VC and also modestly high limiting currents on MCMB anodes with the cells containing FEC and lithium oxalate. With regard to the high temperature

resilience, the cells containing VC and LiBOB displayed the best performance, retaining a greater proportion of the initial capacity. Post mortem analysis of the electrodes has indicated that incorporation of additives clearly affect the elemental concentrations of the surface species on MCMB anodes. Furthermore, it was observed that the incorporation of different additives appears to alter the surface chemistry of the cathode particles as well.

Acknowledgements

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 NASA-Exploration Systems Mission Directorate (ESRT) and the Department of Energy (BATT Program-LBNL).

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Electrolyte Type	Charge Capacity (Ah) 1st Cycle	Discharge Capacity (Ah) 1st Cycle	Irreversible Capacity (1st Cycle)	Coulombic Efficiency (1st Cycle)	Charge Capacity (Ah) 5th Cycle	Reversible Capacity (Ah) 5th Cycle	Cummulative Irreversible Capacity (1st- 5th Cycle)	Coulombic Efficiency (5th Cycle)
1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %)	0.4791	0.4071	0.072	84.96	0.4104	0.3973	0.1326	96.80
1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 4% FEC	0.4619	0.3998	0.062	86.55	0.3831	0.3825	0.0726	99.83
1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + lithium oxalate	0.4571	0.3935	0.064	86.10	0.3927	0.3850	0.1011	98.05
1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 2% VC	0.4711	0.3938	0.077	83.59	0.3939	0.3868	0.1153	98.20
1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB	0.3856	0.3196	0.066	82.87	0.4054	0.3969	0.1123	97.92

Table 4-1. Charge-discharge (formation) characteristics of experimental MCMB/Li_xNi_yCo_{1-y}O₂ lithium-ion cells containing methyl butyrate-based electrolytes and without various electrolyte additives.

Electrolyte Type		1.2 M LiPF ₆ EC+EMC+MB (20:20:60 v/v %)		1.2 M LiPF ₆ EC+EMC+MB (20:20:60 v/v %) + + 4% FEC		1.2 M LiPF ₆ EC+EMC+MB (20:20:60 v/v %) + 2% lithium oxalate		1.2 M LiPF ₆ EC+EMC+MB (20:20:60 v/v %) + 2% VC		1.2 M LiPF ₆ EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB	
Temperature	Current (mA)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)
23°C	25 mA	0.3973	100.00	0.3825	100.00	0.3850	100.00	0.3868	100.00	0.3969	102.62
0°C	25 mA	0.3514	88.46	0.3355	87.71	0.3431	89.12	0.3558	91.98	0.3549	89.40
	50 mA	0.3484	87.70	0.3300	86.29	0.3384	87.90	0.3534	91.37	0.3503	88.26
	100 mA	0.3376	84.99	0.3177	83.06	0.3269	84.91	0.3432	88.72	0.3409	85.87
	150 mA	0.3269	82.27	0.3048	79.70	0.3178	82.55	0.3329	86.06	0.3296	83.03
- 20°C	25 mA	0.3438	86.53	0.3236	84.60	0.3299	85.70	0.3484	90.06	0.3502	88.23
	50 mA	0.3226	81.19	0.3022	79.01	0.3104	80.64	0.3285	84.92	0.3268	82.32
	100 mA	0.3051	76.79	0.2842	74.30	0.2967	77.05	0.3140	81.19	0.3149	79.32
	150 mA	0.2906	73.14	0.2714	70.96	0.2863	74.36	0.3011	77.84	0.3016	75.97
- 30°C	25 mA	0.3179	80.01	0.3001	78.46	0.3030	78.71	0.3230	83.51	0.3289	82.86
	50 mA	0.2990	75.27	0.2808	73.43	0.2930	76.11	0.3090	79.88	0.3113	78.44
	100 mA	0.2704	68.07	0.2535	66.28	0.2730	70.91	0.2873	74.29	0.2879	72.52
	150 mA	0.2233	56.20	0.2095	54.78	0.2502	65.00	0.2642	68.31	0.2604	65.60
- 40°C	25 mA	0.2938	73.95	0.2792	73.00	0.2861	74.32	0.2956	76.43	0.3038	76.53
	50 mA	0.2348	59.10	0.2355	61.57	0.2530	65.71	0.2634	68.09	0.2660	67.01
	100 mA	0.0823	20.71	0.1690	44.18	0.1709	44.39	0.2068	53.48	0.2106	53.04
	150 mA	0.0501	12.60	0.0388	10.14	0.0606	15.74	0.1104	28.54	0.0705	17.76
- 50°C	25 mA	0.0709	17.83	0.0497	12.99	0.0939	24.40	0.1031	26.66	0.1694	42.69
	50 mA	0.0463	11.64	0.0310	8.11	0.0532	13.83	0.0450	11.63	0.0396	9.97
	100 mA	0.0203	5.12	0.0104	2.72	0.0285	7.41	0.0107	2.76	0.0167	4.21

Table 4-2. Summary of the discharge characteristics experimental MCMB/ Li_xNi_yCo_{1-y}O₂ lithium-ion cells containing various electrolytes over a wide temperature range (-50 to +23°C). Cells were charged at 20°C.

	Carbon (%)	Fluorine (%)	Oxygen (%)	Phosphorus (%)
Fresh	63.8	33.9	2.3	-
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %)	35.7	30.1	29.9	4.3
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %) + 2% FEC	28.2	22.8	40.0	9.0
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %) + Li ₂ C ₂ O ₄	36.5	25.3	32.0	6.2
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %) + 2% VC	24.6	51.5	20.5	3.4
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %) + 0.10M LiBOB	27.8	28.1	36.7	7.4

Table 4-3. Elemental concentration on cycled and fresh anode surface.

	Carbon (%)	Fluorine (%)	Oxygen (%)	Phosphorus (%)	Nickel (%)
Fresh	46.4	37.8	11.1		4.7
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %)	40.8	37.5	16.0	2.1	3.6
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %) + 2% FEC	50.7	27.6	17.1	1.5	3.1
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %) + Li ₂ C ₂ O ₄	44.5	32.8	17.1	2.6	3.0
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %) + 2% VC	50.8	25.8	19.3	1.5	2.6
1.20M LiPF ₆ in EC+EMC+MB (20:20:60 vol %) + 0.10M LiBOB	39.2	30.8	23.3	3.6	3.1

Table 4-4. Elemental concentration on cathode surface.

Figure 4-1. Discharge capacity (Ah) of experimental lithium-ion cells at -40°C ($\sim \text{C}/16$ rate) containing electrolytes consisting of 1.0M LiPF₆ EC+EMC+MB (20:20:60 v/v %) with and without different additives.

Figure 4-2. Discharge capacity (Ah) of experimental lithium-ion cells at -40°C ($\sim \text{C}/4$ rate) containing electrolytes consisting of 1.0M LiPF₆ EC+EMC+MB (20:20:60 v/v %) with and without different additives.

Figure 4-3. The cycling characteristics of experimental MCMB-LiNiCoO₂ lithium-ion cells containing electrolytes consisting of 1.0M LiPF₆ EC+EMC+MB (20:20:60 v/v %) with and without different additives at high temperatures (60° and 80°C).

Figure 4-4. Electrochemical Impedance Spectroscopy (EIS) measurements at 23°C of MCMB electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF₆ EC+EMC+MB (20:20:60 v/v %) with and without different additives. Measurements performed prior to high temperature cycling.

Figure 4-5. Electrochemical Impedance Spectroscopy (EIS) measurements at 23°C of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF₆ EC+EMC+MB (20:20:60 v/v %) with and without different additives. Measurements performed prior to high temperature cycling.

Figure 4-6. Electrochemical Impedance Spectroscopy (EIS) measurements at 23°C of MCMB electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF₆ EC+EMC+MB (20:20:60 v/v %) with and without different additives. Measurements performed after high temperature cycling.

Figure 4-7. Electrochemical Impedance Spectroscopy (EIS) measurements at 23°C of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF_6 EC+EMC+MB (20:20:60 v/v %) with and without different additives. Measurements performed after high temperature cycling.

Figure 4-8. Tafel polarization measurements at 23°C of MCMB electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF₆ EC+EMC+MB (20:20:60 v/v %) with and without different additives.

Figure 4-9. Tafel polarization measurements at 23°C of LiNi_xCo_{1-x}O₂ electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF₆ EC+EMC+MB (20:20:60 v/v %) with and without different additives.

Figure 4-10. Tafel polarization measurements at - 30°C of MCMB electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF₆ in EC+EMC+X (20:60:20 v/v %) (X = MP, EP, MB, EB, PB, and BB).

Figure 4-11. Tafel polarization measurements - 30°C of LiNi_xCo_{1-x}O₂ electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF₆ in EC+EMC+X (20:60:20 v/v %) (X = MP, EP, MB, EB, PB, and BB).

Figure 4-12. C1s, F1s, O1s and P2p XPS spectra for cycled MCMB electrodes.

Figure 4-13. B1s XPS spectrum for cycled MCMB electrodes containing LiBOB electrolyte.

Figure 4-14. FTIR spectra of cycled MCMB electrodes.

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %)

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %) + 2 % FEC

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %) + lithium oxalate

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %) + 2 % VC

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB

Figure 4-15. SEM images of cycled anodes.

Figure 4-16. C1s, F1s, O1s and P2p XPS spectra for cycled $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ electrodes.

Figure 4-17. B1s XPS spectrum for cycled $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ electrode containing LiBOB electrolyte.

Figure 4-18. FTIR of cycled LiNi_{0.8}Co_{0.2}O₂ electrodes.

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %)

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %) + 2% FEC

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %) + lithium oxalate

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %) + 2% VC

1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB

Figure 4-19. SEM images of cycled LiNi_xCo_{1-x}O₂ electrodes.

MANUSCRIPT – IV

Submitted for publication in The Journal of Electrochemical Society.

**Performance Enhancing Electrolyte Additives for Lithium Ion Batteries with
Silicon Anodes.**

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Chapter 5. Additives for thin film silicon anode half cells

Introduction

Lithium ion batteries are very promising and attractive energy storage devices due to their high volumetric and gravimetric energy density.¹⁻³ While current lithium ion battery technology is adequate for portable electronic applications, the increased power demand of electric vehicle applications require development of anode and cathode materials with higher energy density. Silicon is one of the most promising anode materials due to the very high theoretical capacity of the fully lithiated phase $\text{Li}_{4.4}\text{Si}$ (4212 mAh/g)¹⁴ compared to graphite (372 mAh/g).⁴ One of the primary obstacles for the use of silicon as an anode material is the large volume expansion (200-300%) during lithiation.⁵ This results in large irreversible capacity during first cycle and poor cycle life.⁶ To overcome this problem researchers have employed nano-structured silicon particles, thin film silicon and amorphous silicon anodes.⁷⁻⁹ While this has improved capacity retention, the large changes in surface area consume additional electrolyte via the generation of a new solid electrolyte interphase (SEI) during each cycle. The development of a stable surface film on the silicon electrode surface is critical for long cycle life. Development of new electrolytes or incorporation of electrolyte additives is one method to generate a stable SEI and improve the cycle life of silicon anodes. Kim and co-workers have investigated the effect of added fluorethylene carbonate (FEC) to LiPF_6 electrolytes and lithium bis(oxalato)borate based electrolytes on the cycling performance of thin film silicon anodes.^{10,11} The effect of low concentrations of succinic anhydride and vinylene carbonate (VC) have also been reported.^{12,13} However, there has not been a direct comparative study of multiple electrolytes for Si thin film anodes. We

are reporting a detailed investigation of the effect of different additives on cycling performance and SEI structure for silicon thin film anodes.

Experimental

Battery grade solvents ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), fluoroethylene carbonate (FEC) and battery grade lithium bis(oxalato)borate (LiBOB) were obtained from Novolyte Technologies (U.S.) and used without further purification. Battery grade propylene carbonate (PC) and lithium hexafluorophosphate (LiPF_6) were obtained from Yardney Technical Products and was used without further purification. Vinylene carbonate (VC) was purchased from Aldrich and was purified by vacuum distillation before using. Lithium difluoro(oxalato)borate (LiFOB) was synthesized and purified as described previously. 1.0M LiPF_6 dissolved in EC/DMC/DEC (1/1/1, vol. %) was used as a baseline electrolyte. Table 1 show different electrolytes prepared using various concentrations of additives. To study effect of PC on Si anode an electrolyte was prepared by replacing EC from baseline electrolyte by PC.

A 50 nm silicon film deposited on 0.08 cm copper disc (1.5 cm diameter) was used as an anode. 2032 type Si/Li coin cells containing 30 μL electrolytes were prepared in a glove box filled with high purity argon. Electrodes were separated by a polypropylene separator. The cells were cycled using constant current discharge and constant current charge between 0.005 V to 1.3 V according to following schedule: first cycle at 2.8 μAcm^{-2} ($\sim\text{C}/20$), second and third cycle at 5.6 μAcm^{-2} ($\sim\text{C}/10$) and next 52 cycles at 11.2 μAcm^{-2} ($\sim\text{C}/5$). The cells were cycled using BT2000 cycler (Arbin Instruments) at 16 $^\circ\text{C}$. After cycling, the cells were opened in a high purity argon glove box. The Si

thin film electrodes were rinsed with anhydrous DMC to remove residual electrolyte from the electrode surface and dried overnight under vacuum. X-ray photoelectron spectroscopy (XPS) was conducted with a PHI 5500 system using Al K α (h ν =1486.6 eV) radiation under ultrahigh vacuum. Universal hydrocarbon contamination peak at 285 eV was used to check the binding energy scale and charging effect. The spectra obtained were analyzed by Multipak 6.1A software. Line syntheses of elemental spectra were conducted using Gaussian–Lorentzian (70:30) curve fit with Shirley background subtraction. Element concentration was calculated based on the equation: $C_x = (I_x/S_x)/(\sum I_i/S_i)$, where I_x is the intensity of the relative element, and S_i is the sensitivity number of the element, acquired from the Multipak 6.1A software. Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) analysis of the cathodes was carried out with a Thermo Nicolet iS10 IR spectrometer which has a smart performer accessory with a Germanium crystal. For each sample, 128 scans were collected at two/three different locations, constantly purged with high purity Argon. SEM analyses were conducted on a JEOL-5900 environmental SEM.

Results and Discussion

Electrochemical performance of Si/Li cells

All of the cells show a first cycledischarge capacity >3200 mAh/g. A high discharge capacity (>2800 mAh/g) is retained for all cells during the first ten cycles. Cells without film forming additives have rapid capacity fade after the first ten cycles. The cell containing PC retains only 21% of initial discharge capacity while the baseline electrolyte, containg EC, retains only 59% of intial discharge capacity after the first 55

cycles. The incorporation of additives improve capacity retention of Si anode cell by about 12 – 24% over the baseline electrolyte. The initial discharge capacity is best with the cells containing VC and LiFOB. While the capacity retention is best with cells containing VC and FEC.

Cycling efficiency of Si/Li half cells is displayed in fig.2. All the cells have low first cycle efficiencies, 36 – 63 %. Cells from electrolyte containing PC and FEC showed best first cycle efficiency (62-63%) while cells containing LiFOB had the worst first cycle efficiency (36 %). The cycling efficiencies for most cells stabilize at >95% after the first five cycles. Cells containing VC, LiFOB and FEC have cycling efficiencies >99% for cycles 10-55 cycles. Cycling efficiency with baseline and LiBOB containing electrolyte are maintained at ~95% and ~97%, respectively. Efficiency decreases gradually for PC based electrolyte after the first 10 cycles consistent with the poor cycling performance depicted in Figure 1.

Surface analysis of Si electrodes

Elemental concentration on electrode surface

XPS spectra of cycled Si electrodes extracted from cells after 55 cycles supports changes in the composition of the anode SEI due to changes in electrolyte composition (Figure 3, Table 2). The elemental concentration of the fresh electrode contains 39 % oxygen and 37 % silicon, a carbon peak is observed associated with universal carbon contamination. After cycling with all EC containing electrolytes, Si is no longer observable on the surface of the electrodes consistent with the generation of a thick SEI. A low concentration of Si is observed on the surface of the cell cycled with PC based

electrolyte consistent with a thin SEI. The thin SEI and very poor cycling performance suggest that the reduction products of PC do not passivate the surface and may be soluble in the electrolyte. Electrodes from cells containing EC and PC based electrolyte have the lowest concentrations of C and highest concentrations of F further supporting that EC and PC based electrolytes do not effectively passivate the anode surface leading to continuous decomposition of the LiPF_6 salt. Electrodes from cells having electrolytes containing additives, especially VC, have much higher concentrations of C and O and lower concentrations of F. All of the electrodes contain low concentrations of P consistent with trace $\text{Li}_x\text{PF}_y\text{O}_z$.

XPS of Si electrodes

The fresh electrodes contain a Si peaks at 99.6 and 102.3eV consistent with pure silicon and surface silicon oxide respectively (not shown in Figure 3). The XPS spectrum of the electrode cycled with baseline electrolyte contains a large peak in the C1s spectrum at 285 eV consistent with the presence of alkane products and very small peaks at 286-287 and 288-289 eV consistent with the presence of C-O and C=O containing species, respectively. The low concentration of C-O and C=O species is surprising and supportive of a lack of passivation of the anode surface. A single broad peak is observed in the O1s spectrum consistent with the presence of C-O and C=O containing species at 533-534 and 532-533 eV and Li_2CO_3 at 533-534 eV. A large single peak at 685 eV is observed in the F1s spectrum consistent with the presence of LiF, which is observed for all extracted anodes. The element spectra of the cells containing additives are different that the baseline electrolyte. The C1s spectrum of the cell containing FEC contains a

large C-H peak at 285 eV and small C-O and C=O peaks at 286-287 and 288-289 eV, respectively. A related broad O1s peak consistent with the presence of C-O and C=O species is present at ~532 eV. The F1s spectrum contains a peak for LiF. There are no peaks in the C1s, O1s, or F1s spectra consistent with the presence of C-F bond or poly(vinylene carbonate) (poly(VC)).¹⁵ The surface of the Si electrode cycled with electrolyte containing FEC is covered with a passivation layer composed of lithium alkyl carbonates, polycarbonates, and oxalates. The C1s of the electrode cycled with VC containing electrolyte contains a peak at 291 eV which is due to poly(VC).¹⁵ The corresponding poly(VC) peak is observed in the O1s spectrum at 534.3 eV. The other C1s and O1s peaks observed support the presence of C-O and C=O containing species. The element spectra of the anodes extracted from LiBOB and LiFOB are similar. The C1s spectrum contains a large peak at ~290 eV characteristic of oxalates. The O1s peak at 531-532 eV is also consistent with the presence of oxalates. Interestingly, the F1s spectra of the anodes extracted from cells containing LiBOB and LiFOB contain significant concentrations of $\text{Li}_x\text{PF}_y\text{O}_z$. The element spectra for the anode cycled with PC electrolyte is similar to the anode cycled with the baseline electrolyte except the peaks characteristic of C-O and C=O species have greater intensity.

FTIR analysis

The IR spectrum of the anode extracted from the cell containing the baseline electrolyte contains peaks at 1640, 1420, 1330, 1070 and 840 cm^{-1} (Figure 4). The peaks at 1600-1700 cm^{-1} and 1300-1350 cm^{-1} are consistent with the presence of lithium alkyl carbonates and lithium oxalate, the peak centered at ~1420 cm^{-1} is characteristic of

Li_2CO_3 and the broad peak centered around 1000 cm^{-1} is characteristic of C-O peaks in ethers and $\text{Li}_x\text{PF}_y\text{O}_z$.¹⁶ The IR spectra of the anodes extracted from cells cycled with additives are similar to the spectra of the baseline samples with a few important differences. The sample with VC contains a weak peak at $\sim 1800\text{ cm}^{-1}$ due to poly(VC). The samples with FEC, LiBOB and LiFOB have moderate peaks 1320 cm^{-1} characteristic of oxalates. The anode extracted from cells containing PC based electrolyte has similar IR absorption to the baseline (EC) electrolyte.

SEM analysis of Si electrodes

SEM of fresh electrode depicts a very smooth surface. SEM images of cycled anodes reveal changes to the surface. Electrodes cycled with baseline electrolyte have evidence for the formation of an inconsistent rough surface film. Electrode cycled in FEC has retained much of the surface smoothness but there are tubular shaped species on the surface. Electrode cycled with electrolyte containing VC has a consistent mottled film with few small cracks ($< 1\mu\text{m}$). The surface of the electrode extracted from electrolyte containing LiBOB is smooth with medium irregular cracks ($2\text{--}3\text{ }\mu\text{m}$). Electrode cycled with LiFOB electrolyte has a rough surface film with irregular round shapes. The electrode cycled with PC based electrolyte shows the most surface damage with long wide cracks ($5\text{ }\mu\text{m}$).

Conclusions

The cycling performance of Si anodes in the presence of LiPF_6 carbonate electrolytes with and without film forming additives has been investigated. The incorporation of

film forming additives improves the capacity retention and cycling efficiency and alters the structure of the anode SEI. The baseline electrolyte does not passivate the electrode surface effectively leading to poor cycling performance and surface films dominated by LiF with low concentrations of lithium alkyl carbonates and Li_2CO_3 . Addition of FEC results in the presence of a greater concentration of oxalates and lower concentrations of LiF on the surface, improving the cycling performance. Incorporation of VC results in the generation of poly(VC) on the anode surface reducing the LiF concentration and providing the best cycling performance. The addition of LiBOB and LiFOB generate surface films with high concentrations of oxalates and $\text{Li}_x\text{PF}_y\text{O}_z$ while reducing the LiF content and providing a modest improvement in cycling performance. The use of PC based electrolytes provides the worst cycling performance and generates surface films with high concentrations of LiF and low concentrations of organic species which provide little passivation of the anode.

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1	1.0M LiPF ₆ EC/DMC/DEC (1/1/1, vol. %)
2	1.0M LiPF ₆ EC/DMC/DEC (1/1/1, vol. %) + FEC (3%, wt. %)
3	1.0M LiPF ₆ EC/DMC/DEC (1/1/1, vol. %) + VC (5%, wt. %)
4	1.0M LiPF ₆ EC/DMC/DEC (1/1/1, vol. %) + LiBOB (5%, wt. %)
5	1.0M LiPF ₆ EC/DMC/DEC (1/1/1, vol. %) + LiFOB (1%, wt.%)
6	1.0M LiPF ₆ PC/DMC/DEC (1/1/1, vol. %)

Table 5-1. Electrolyte solution composition with and without additives.

	Carbon (%)	Fluorine (%)	Oxygen (%)	Silicon (%)	Phosphorus (%)
Fresh	24.3	-	39.2	36.5	-
Baseline electrolyte	37.2	49.4	12.3	0.0	0.1
Fluoroethylene carbonate	47.1	14.7	37.5	0.0	0.5
Vinylene carbonate	56.8	4.0	38.5	0.0	0.7
Lithium bisoxalatoborate	43.8	9.3	45.6	0.0	1.2
Lithium difluorobisoxalatoborate	47.6	12.7	38.7	0.0	1.0
Propylene carbonate	29.7	41.4	25.8	2.3	0.7

Table 5-2. Elemental concentration on fresh and cycled silicon electrodes.

Figure 5-1. Discharge capacity (mAh/g) vs cycle number graph of Si/Li half cells with and without additives.

Figure 5-2. Cycling efficiency of Si/Li half cells with and without additives.

Figure 5-3. C1s, F1s and O1s XPS spectra of cycled Si electrodes.

Figure 5-4. FTIR spectra of cycled Si electrodes.

Fresh

Baseline electrolyte

Fluoroethylene carbonate

Vinylene carbonate

Lithium bis(oxalato)borate

Lithium difluoro(oxalato)borate

Propylene carbonate

Figure 5-5. SEM images of cycled Si electrodes