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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

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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 LiPF6/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.
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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.
# TABLE OF CONTENTS

| Section                                                      | Page |
|--------------------------------------------------------------|------|
| Abstract                                                     | ii   |
| Acknowledgments                                             | iii  |
| Preface                                                     | iv   |
| Table of contents                                           | v    |
| List of tables                                              | vi   |
| List of figures                                             | vii  |
| List of figures                                             | ix   |
| Chapter 1. Introduction                                     | 1    |
| Background                                                  | 1    |
| Typical lithium ion battery                                 | 1    |
| Working mechanism of LIBs                                   | 2    |
| Electrolyte                                                 | 3    |
| Solid electrolyte interphase (SEI)                          | 5    |
| References                                                  | 6    |
| Chapter 2. Non-flammable electrolytes for lithium ion batteries | 10   |
| Introduction                                                | 11   |
| Experimental                                                | 12   |
| Results and discussion                                      | 15   |
| Conclusions                                                 | 24   |
| References                                                  | 26   |
| Chapter 3. Effect of added LiBOB on high voltage (LiNi_{0.5}Mn_{1.5}O_{4}) spinel cathodes | 46   |
# LIST OF TABLES

| TABLE | PAGE |
|-------|------|
| I. Chapter 1 | |
| Table 1-1. Structure and properties of solvents used in LIBs | 7 |
| II. Chapter 2 | |
| Table 2-1. Electrolyte solution compositions | 29 |
| Table 2-2. VTF Parameters ($A$, $B$ and $T_0$) and their Standard Deviations ($s[X]$) | 30 |
| Table 2-3. SET for the electrolyte solutions containing DMMP | 31 |
| Table 2-4. The concentration of C, O, F and P on the anode electrode surface | 32 |
| Table 2-5. The concentration of C, O, F, P and Ni on the cathode electrode surface | 33 |
| III. Chapter 3 | |
| Table 3-1. Elemental concentration on LNMS cathode surface | 55 |
| IV. Chapter 4 | |
| Table 4-1. Charge-discharge (formation) characteristics of experimental MCMB/ Li$_x$Ni$_y$Co$_{1-y}$O$_2$ lithium-ion cells containing methyl butyrate-based electrolytes and without various electrolyte additives | 87 |
| Table 4-2. Summary of the discharge characteristics experimental MCMB/ Li$_x$Ni$_y$Co$_{1-y}$O$_2$ lithium-ion cells containing various electrolytes over a wide temperature range (-50 to +23°C). Cells were charged at 20°C | 88 |
| Table 4-3. Elemental concentration on cycled and fresh anode surface | 89 |
| Table 4-4. Elemental concentration on cathode surface | 90 |
V. Chapter 5

Table 5-1. Electrolyte solution composition with and without additives .......121

Table 5-2. Elemental concentration on fresh and cycled silicon electrodes ....122
LIST OF FIGURES

I. Chapter 1

Figure 1-1. Typical LIB showing charging (left) and discharging (right) ........8

Figure 1-2. Voltage (vs Li/Li$^+$) vs capacity graph of graphite anode after first charge and discharge .................................................................9

II. Chapter 2

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) ........................................34

Figure 2-2. $^{19}$F, $^{31}$P and $^{11}$B NMR spectra of DMMP containing electrolyte before (a) and after thermal storage (b) ..............................................35

Figure 2-3. Cycle Voltommmagram of 1M LiPF$_6$ with 5% (wt.%) LiBOB in EC:EMC:DMMP (2:2:1, vol.) at glass carbon electrode, scan rate 10 mV/s.................................................................36

Figure 2-4. Cycling performances of the MCMB/Li half-cells containing different DMMP concentrations .................................................................37

Figure 2-5. Cycling performance of Li/LiNi$_{0.8}$Co$_{0.2}$O$_2$ half-cells with baseline electrolyte and 20% DMMP containing ........................................38

Figure 2-6. Cycling performance of LiNi$_{0.8}$Co$_{0.2}$O$_2$/MCMB cells with baseline (Electrolyte 1), 15% DMMP with (Electrolyte 5) and without LiBOB (Electrolyte 4) ..................................................................................39
Figure 2-7. SEM of cycled anodes .................................................40

Figure 2-8. SEM of cycled cathodes .............................................41

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) .......................42

Figure 2-10. FTIR spectra of LiNi$_{0.8}$Co$_{0.2}$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 .......................43

Figure 2-11. C1s, F1s, O1s and P2p spectrum 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) .........................................................44

Figure 2-12. C1s, F1s, O1s and P2p spectrum of LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode 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) .........................................................45

III. Chapter 3

Figure 3-1. Specific capacity and efficiency of cells containing standard electrolyte and electrolyte containing added LiBOB ............................56

Figure 3-2. EIS of cells containing standard electrolyte and electrolyte containing added LiBOB .......................................................57
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 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)

IV. Chapter 4

Figure 4-1. Discharge capacity (Ah) of experimental lithium-ion cells at –40°C (~ 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 (~ 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
.........................................................................................................................94

Figure 4-5. Electrochemical Impedance Spectroscopy (EIS) measurements at 23°C of LiNi_{x}Co_{1-x}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 prior to high temperature cycling
.........................................................................................................................95

Figure 4-6. Electrochemical Impedance Spectroscopy (EIS) measurements at 23°C of MCMB 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
.........................................................................................................................96

Figure 4-7. Electrochemical Impedance Spectroscopy (EIS) measurements at 23°C of LiNi_{x}Co_{1-x}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
.........................................................................................................................97

Figure 4-8. Tafel polarization measurements at 23°C of MCMB 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 ............98
Figure 4-9. Tafel polarization measurements at 23°C of LiNi$_x$Co$_{1-x}$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 ..........99

Figure 4-10. Tafel polarization measurements at -30°C of MCMB electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF$_6$ in EC+EMC+X (20:60:20 v/v %) (X = MP, EP, MB, EB, PB, and BB) .............100

Figure 4-11. Tafel polarization measurements -30°C of LiNi$_x$Co$_{1-x}$O$_2$ electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF$_6$ in EC+EMC+X (20:60:20 v/v %) (X = MP, EP, MB, EB, PB, and BB) .............101

Figure 4-12. C1s, F1s, O1s and P2p XPS spectra for cycled MCMB electrodes.................................................................102

Figure 4-13. B1s XPS spectrum for cycled MCMB electrodes containing LiBOB electrolyte .................................................................103

Figure 4-14. FTIR spectra of cycled MCMB electrodes .........................104

Figure 4-15. SEM images of cycled anodes ......................................105

Figure 4-16. C1s, F1s, O1s and P2p XPS spectra for cycled LiNi$_x$Co$_{1-x}$O$_2$ electrodes .................................................................106

Figure 4-17. B1s XPS spectrum for cycled LiNi$_x$Co$_{1-x}$O$_2$ electrode containing LiBOB electrolyte .....................................................107

Figure 4-18. FTIR of cycled LiNi$_{0.8}$Co$_{0.2}$O$_2$ electrodes ....................108

Figure 4-19. SEM images of cycled LiNi$_x$Co$_{1-x}$O$_2$ electrodes ..............109

V. Chapter 5
Figure 5-1. Discharge capacity (mAh/g) vs cycle number graph of Si/Li half cells with and without additives ..........................................................123
Figure 5-2. Cycling efficiency of Si/Li half cells with and without additives .124
Figure 5-3. C1s, F1s and O1s XPS spectra of cycled Si electrodes ...........125
Figure 5-4. FTIR spectra of cycled Si electrodes .................................126
Figure 5-5. SEM images of cycled Si electrodes .................................127
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).\textsuperscript{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.\textsuperscript{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.\textsuperscript{4,5}

Cathode materials are generally lithium transition metal oxides such as LiCoO\textsubscript{2}, LiNi\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{2}, LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4}, LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} or phosphates such as LiFePO\textsubscript{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.\textsuperscript{6}

\textbf{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.

\begin{align*}
\text{Cathode :-} & \quad \text{LiMO}_x & \xrightleftharpoons[\text{Discharging}]{\text{Charging}} & \text{Li}_{(1-y)}\text{MO}_x + y\text{Li}^+ + ye^- \\
\text{Anode :-} & \quad \text{C} + y\text{Li}^+ + ye^- & \xrightleftharpoons[\text{Discharging}]{\text{Charging}} & \text{Li}_y\text{C} \\
\text{Overall reaction:-} & \quad \text{LiMO}_x + \text{C} & \xrightleftharpoons[\text{Discharging}]{\text{Charging}} & \text{Li}_{(1-y)}\text{MO}_x + \text{Li}_y\text{C}
\end{align*}

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. Solvents chosen for LIBs should possess following properties.

1. It should dissolve salt to sufficient concentration (high dielectric constant, $\varepsilon$).
2. It should have low viscosity, $\eta$ 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 retreading 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 alkoxydes and lithium fluoride are key components of SEI.

\[
\begin{align*}
&\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5 \\
2(\text{CH}_2\text{O})_2\text{CO} + 2\text{e}^- + 2\text{Li}^+ &\rightarrow (\text{CH}_2\text{OCO}_2\text{Li})_2 + \text{C}_2\text{H}_4 \\
(\text{CH}_2\text{O})_2\text{CO} + 2\text{e}^- + 2\text{Li}^+ &\rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 \\
\text{CH}_3\text{OCO}_2\text{CH}_3 + \text{e}^- + \text{Li}^+ &\rightarrow \text{CH}_2\text{OCO}_2\text{Li} + \text{CH}_3. \\
\text{CH}_3\text{OCO}_2\text{CH}_3 + \text{e}^- + \text{Li}^+ &\rightarrow \text{CH}_3\text{OLi} + \text{CH}_3\text{CO}_2. \\
\text{CH}_3\text{CH}_2\text{OCO}_2\text{CH}_2\text{CH}_3 + \text{e}^- + \text{Li}^+ &\rightarrow \text{CH}_2\text{CH}_2\text{OCO}_2\text{Li} + \text{CH}_3\text{CH}_2. \\
\text{CH}_3\text{CH}_2\text{OCO}_2\text{CH}_2\text{CH}_3 + \text{e}^- + \text{Li}^+ &\rightarrow \text{CH}_3\text{CH}_2\text{OLi} + \text{CH}_3\text{CH}_2\text{CO}_2. \\
\end{align*}
\]

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 $\text{LiC}_{36}$, $\text{LiC}_{12}$ and finally $\text{LiC}_6$. 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 ~0.8–0.2V. 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.\textsuperscript{11,12} Composition of SEI determines kinetics of $\text{Li}^+$ 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      | ![Structure](image1.png) | 36.4               | 248                | 89.78                       | 1.90 (40 °C)     |
| DMC     | ![Structure](image2.png) | 4.6                | 91                 | 3.107                       | 0.59             |
| DEC     | ![Structure](image3.png) | -74.3              | 126                | 2.805                       | 0.75             |
| EMC     | ![Structure](image4.png) | -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.
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 \( \text{LiPF}_6 \) 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, tris (2,2,2-trifluoroethyl) phosphate, and bis (2,2,2-trifluoroethyl) methylphosphate, and phosphoramides including hexamethylphosphoramide, and phosphonates including dimethylmethyl phosphonate (DMMP). 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. 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. 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 bisoxalalatoborate (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 $^1$H, $^{13}$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). 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 ±0.1°C accuracy by means of a Tenney Environmental chamber.

Coin cells were employed to test the electrolytes containing the additives. The electrodes used LiNi$_{0.8}$Co$_{0.2}$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% LiNi$_{0.8}$Co$_{0.2}$O$_2$, 5% PVDF binder and 6% conductive carbonaceous dilutants. Each coin cell contained about 30µL 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: 1$^{\text{st}}$ cycle at C/20, 2$^{\text{nd}}$ cycle at C/10 and remaining cycles at C/5. The full cells were cycled according to the schedule: 1$^{\text{st}}$ cycle at C/20, 2$^{\text{nd}}$ and 3$^{\text{rd}}$
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 Kα radiation (hv=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 ($\sigma$) over the temperature range of –40 to +80°C cannot be described by the activation mechanism mathematically expressed as the Arrhenius law for any of the solutions investigated:

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

Where $\sigma_0$ 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 [Li$^+$(solvent1)$_n$(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.\textsuperscript{19,20,21}

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

(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, $B = E_{a,VTF}/R$. $T_0$ 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.\textsuperscript{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 then 1.5%). The VTF parameters are collected in Table 2.

From our previous conductivity studies,\textsuperscript{23} the $B$ parameter does not depend on the composition of the solutions of the pure salts LiPF$_6$, LiBF$_4$, LiN(SO$_2$C$_2$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 ± 14 K.\textsuperscript{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. $^{11}\text{B}$, $^{19}\text{F}$, and $^{31}\text{P}$ 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 $^{19}\text{F}$ and $^{11}\text{B}$ NMR spectra are consistent with the generation of new species including LiBF$_2$(C$_2$O$_4$) and LiBF$_4$ (Figure 2B and 2C), as previously reported.$^{24}$ In addition to the resonances characteristic of LiPF$_6$, LiBF$_4$, LiBF$_2$(C$_2$O$_4$), there are resonances characteristic of OPF$_2$(OH) ($^{19}\text{F}$, d, 54.8 ppm; $^{31}\text{P}$, t, -19.8 ppm), LiF/HF ~ -10 ppm, and a DMMP-PF$_5$ complex ($^{19}\text{F}$, 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$_2$O), alkylfluorides, phosphorus oxyfluoride (OPF$_3$), and fluorophosphates [OPF$_2$OR, OPF(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 LiPF$_6$ 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.\textsuperscript{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$_2$CO$_3$ is also observed in all the anodes and cathodes at ~ 1500 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. The F1s spectrum contains peaks characteristic of LiF (684.5 eV), PVDF (687 eV), and a small peak at 688 eV attributed to Li$_x$PF$_y$O$_z$ or Li$_x$PF$_y$. The LiF concentration is lower on the anode surface containing DMMP/LiBOB electrolyte, as has been previously reported for LiBOB containing electrolytes. 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$_y$O$_z$, and Li$_2$CO$_3$. 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 Li$_x$PO$_y$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.

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$_2$CO$_3$ 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 cycles with DMMP/LiBOB electrolyte. The O1s spectrum contains a broad peak centered at 531.5 eV consistent with a mixture of Li$_2$CO$_3$ (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 LixPOyFz (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.

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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          | $A$ (K) | $B$ (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                  | $SET, \ s$ | $s^*, \ s$ |
|--------------------------------------|------------|------------|
| 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.
|                        | C\text{1s} | O\text{1s} | F\text{1s} | P\text{2p} |
|------------------------|------------|------------|------------|------------|
| 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) | 37       | 32         | 24         | 2          |
| EC:EMC:DMMP/3:5.5:1.5  |            |            |            |            |

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) | 39      | 24      | 27      | 4       | 6        |
| EC:EMC:DMMP/3:5.5:1.5 |         |         |         |         |          |

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 Voltomgram of 1 M LiPF₆ 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$_{0.2}$O$_2$ half-cells with baseline electrolyte and 20% DMMP containing.
Figure 2-6. Cycling performance of LiNi$_{0.8}$Co$_{0.2}$O$_2$/MCMB cells with baseline (Electrolyte 1), 15% DMMP with (Electrolyte 5) and without LiBOB (Electrolyte 4).
Figure 2-7. SEM of cycled anodes.
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 LiNi_{0.8}Co_{0.2}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 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).
Figure 2-12. C1s, F1s, O1s and P2p spectrum of LiNi_{0.8}Co_{0.2}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).
Effect of added LiBOB on high voltage (LiNi_{0.5}Mn_{1.5}O_4) spinel cathodes

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Chapter 3. Effect of added LiBOB on high voltage (LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>) 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 Li<sub>1.17</sub>Mn<sub>0.58</sub>Ni<sub>0.25</sub>O<sub>2</sub>\(^2\) and LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>.\(^3,4\) However, as interest in these materials has grown, so have concerns about the stability of the state-of-art electrolyte (LiPF<sub>6</sub> 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<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and TiO<sub>2</sub>.\(^10-12\) 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 Li<sub>1.17</sub>Mn<sub>0.58</sub>Ni<sub>0.25</sub>O<sub>2</sub> cathodes.\(^13,14\) We have now expanded this investigation to include the investigation of cathode film forming additive on LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathodes. While there have been previous reports on the investigation of LiBOB based electrolytes cycling to high voltage with LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> 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 LiPF₆/carbonate electrolytes on the cycling performance of LiNi₀.₅Mn₁.₅O₄/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 (LiPF₆) 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/LiNi₀.₅Mn₁.₅O₄ (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 LiPF₆ 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 Kα (hυ=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: \( C_x = \frac{I_x}{S_x} \cdot \frac{\sum S_i}{I_i} \), 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\(_{1.5}\)O\(_4\) cells containing LiPF\(_6\)/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. 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.\textsuperscript{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$_2$CO$_3$ 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.\textsuperscript{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 Li\textsubscript{x}PO\textsubscript{y}F\textsubscript{z}. The corresponding F1s peak of Li\textsubscript{x}PO\textsubscript{y}F\textsubscript{z} has a similar bonding energy to PVDF and is not observed due to peak overlap and low intensity.

\textbf{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\textsuperscript{-1}. The cycled cathodes contain additional peaks at 1740 cm\textsuperscript{-1} and 1640 cm\textsuperscript{-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.

\textbf{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 LiNi$_{0.5}$Mn$_{1.5}$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 Li/LiNi$_{0.5}$Mn$_{1.5}$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 LiNi$_{0.5}$Mn$_{1.5}$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.

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|             | 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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The Effect of Additives Upon The Performance of MCMB/ LiNi\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{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/ LiNi$_x$Co$_{1-x}$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.\textsuperscript{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.\textsuperscript{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, vinylenecarbonate (VC) has been shown to be an effective additive in improving the high temperature cycle life and storage characteristics.\textsuperscript{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.\textsuperscript{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\textdegree{}C.\textsuperscript{8,9} Lucht and coworkers have investigated Lewis base electrolyte additives\textsuperscript{10-12}, namely dimethyl acetamide (DMAC) and N-methyl pyrrolidone (NMP), as stabilizing agents which have been found to reversibly bind with PF\textsubscript{5}, preventing LiPF\textsubscript{6} and carbonate solvents from decomposition at high temperature. In collaboration with URI, we have also demonstrated good performance of 1.0 M LiPF\textsubscript{6} EC+DEC+DMC (1:1:1 v/v %) solutions with these additives upon high temperature storage.\textsuperscript{7} In a similar fashion, lithium oxalate was envisioned to complex any free PF\textsubscript{5} generated from the decomposition of LiPF\textsubscript{6} much in the same manner as LiBOB has been reported to stabilize LiPF\textsubscript{6}-based solutions.\textsuperscript{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).\textsuperscript{15} In a similar type of study, FEC was added to LiClO\textsubscript{4} dissolved in PC and the lithium deposition characteristics were investigated.\textsuperscript{16} FEC has also been studied in 1.30M LiPF\textsubscript{6} solutions of EC+DEC (30:70) to improve the efficiency of Li/Si thin-film cells.\textsuperscript{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,\textsuperscript{18-20} as well as finding from other groups\textsuperscript{21-24}, 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 LiPF\textsubscript{6} 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\textsubscript{x}Ni\textsubscript{y}Co\textsubscript{1-y}O\textsubscript{2} 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, LiNi$_{0.80}$Co$_{0.2}$O$_2$ cathodes, and lithium reference electrodes separated by two layers of porous polypropylene (Tonen-Setella) were employed. The carbon electrodes (~ 114 µM in thickness) were coated with active material on both sides of the substrate, and had an active material area of approximately 158.1 cm$^2$, corresponding to an electrode loading of ~ 16 mg/cm$^2$. The NCO electrodes (~ 114 µM in thickness) were also double sided with an active material area of approximately 141.1 cm$^2$, corresponding to a loading of ~ 19 mg/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 mA/cm$^2$ (~ C/16 rate) and 0.50 mA/cm$^2$ (~ 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 Kα (hν=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: \( C_x = \frac{(I_x/S_x)}{(\sum I_i/S_i)} \), 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 LiNi_{0.8}Co_{0.2}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 LiNi_{0.8}Co_{0.2}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 ~ 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. 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 anode.\(^{25-29}\) 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 LiNi\(_{0.80}\)Co\(_{0.2}\)O\(_2\) and MCMB electrodes (prior to cycling)**
In most lithium-ion cells, including the MCMB/ LiNi$_{0.80}$Co$_{0.2}$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 LiNi$_{0.80}$Co$_{0.2}$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 LiNi_{0.80}Co_{0.2}O_{2} and MCMB electrodes (after cycling)**

When EIS measurements 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 LiNi_{0.80}Co_{0.2}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$_x$Ni$_y$Co$_{1-x}$O$_2$ 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 LiNiCoO$_2$ 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 LiNiCoO$_2$ 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 Li$_2$C$_2$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 Li$_2$C$_2$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 bread peak centered at ~532 eV is consistent with the presence of C-O (532 eV) and C=O (533 eV) containing species. 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 Li$_x$PO$_y$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 Li$_x$PF$_y$O$_z$ (686-687 eV, F1s; 134 eV, P2p) are much stronger. Similar increases in the intensity of peaks associated with Li$_x$PF$_y$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 Li$_2$C$_2$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 Li$_2$C$_2$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 LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\) electrodes**

**Elemental concentration on the LiNi\(_{0.8}\)Co\(_{0.2}\)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 Li\(_2\)C\(_2\)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$_2$CO$_3$ 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 Li$_x$PF$_y$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 LiNi$_{0.8}$Co$_{0.2}$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 840 cm$^{-1}$.$^{36}$ Additional weak peaks characteristic of oxalate at $\sim$1600 cm$^{-1}$ and polycarbonate at $\sim$1740 cm$^{-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 1830 cm$^{-1}$. 
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$_x$Ni$_y$Co$_{1-y}$O$_2$ 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$_x$Ni$_y$Co$_{1-y}$O$_2$ 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.

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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 | Cumulative Irreversible Capacity (1st-5th Cycle) | Coulombic Efficiency (5th Cycle) |
|------------------|-------------------------------|----------------------------------|---------------------------------|-------------------------------|-------------------------------|----------------------------------|-----------------------------------------------|-------------------------------|
| 1.2 M LiPF$_6$ 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 LiPF$_6$ 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 LiPF$_6$ 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 LiPF$_6$ 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 LiPF$_6$ 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$_2$Ni$_{x}$Co$_{1-x}$O$_2$ lithium-ion cells containing methyl butyrate-based electrolytes and without various electrolyte additives.
| Temperature | Current (mA) | 1.2 M LiPF6 EC+EMC+MB (20:20:60 v/v %) | 1.2 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 4% FEC | 1.2 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 2% lithium oxalate | 1.2 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB |
|-------------|--------------|---------------------------------------|-----------------------------------------------|------------------------------------------------|------------------------------------------------|
| 23°C        | 25 mA        | 0.3973 100.00                         | 0.3825 100.00                                 | 0.3850 100.00                                 | 0.3969 102.62                                 |
|             | 50 mA        | 0.3514 88.46                          | 0.3355 87.71                                  | 0.3431 89.12                                  | 0.3549 89.40                                  |
|             | 100 mA       | 0.3376 84.99                          | 0.3177 83.06                                  | 0.3269 84.91                                  | 0.3409 85.87                                  |
|             | 150 mA       | 0.3269 82.27                          | 0.3048 79.70                                  | 0.3178 82.55                                  | 0.3296 83.03                                  |
| -20°C       | 25 mA        | 0.3438 86.53                          | 0.3236 84.60                                  | 0.3299 85.70                                  | 0.3484 88.23                                  |
|             | 50 mA        | 0.3226 81.19                          | 0.3022 79.01                                  | 0.3104 80.64                                  | 0.3268 82.32                                  |
|             | 100 mA       | 0.3051 76.79                          | 0.2842 74.30                                  | 0.2967 77.05                                  | 0.3140 79.32                                  |
|             | 150 mA       | 0.2906 73.14                          | 0.2714 70.96                                  | 0.2863 74.36                                  | 0.3011 75.97                                  |
| -30°C       | 25 mA        | 0.3179 80.01                          | 0.3001 78.46                                  | 0.3030 78.71                                  | 0.3230 82.86                                  |
|             | 50 mA        | 0.2990 75.27                          | 0.2808 73.43                                  | 0.2930 76.11                                  | 0.3090 78.44                                  |
|             | 100 mA       | 0.2704 68.07                          | 0.2535 66.28                                  | 0.2730 70.91                                  | 0.2873 74.29                                  |
|             | 150 mA       | 0.2233 56.20                          | 0.2095 54.78                                  | 0.2502 65.00                                  | 0.2642 68.31                                  |
| -40°C       | 25 mA        | 0.2938 73.95                          | 0.2792 73.00                                  | 0.2861 74.32                                  | 0.2956 76.43                                  |
|             | 50 mA        | 0.2348 59.10                          | 0.2355 61.57                                  | 0.2530 65.71                                  | 0.2634 68.09                                  |
|             | 100 mA       | 0.0823 20.71                          | 0.1690 44.18                                  | 0.1709 44.39                                  | 0.2068 53.48                                  |
|             | 150 mA       | 0.0501 12.60                          | 0.0388 10.14                                  | 0.0606 15.74                                  | 0.1104 28.54                                  |
| -50°C       | 25 mA        | 0.0709 17.83                          | 0.0497 12.99                                  | 0.0939 24.40                                  | 0.1031 26.66                                  |
|             | 50 mA        | 0.0463 11.64                          | 0.0310 8.11                                   | 0.0532 13.83                                  | 0.0450 11.63                                  |
|             | 100 mA       | 0.0203 5.12                           | 0.0104 2.72                                   | 0.0285 7.41                                   | 0.0107 2.76                                   |

Table 4-2. Summary of the discharge characteristics experimental MCMB/ Li$_2$Ni$_{x}$Co$_{1-x}$O$_2$ 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 %) + 0.10M LiBOB | 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            | 4.7        |
| **1.20M LiPF₆ in EC+EMC+MB**    | 40.8       | 37.5         | 16.0       | 2.1            | 3.6        |
| (20:20:60 vol %)               |            |              |            |                |            |
| **+ 2% FEC**                   | 50.7       | 27.6         | 17.1       | 1.5            | 3.1        |
| **1.20M LiPF₆ in EC+EMC+MB**    | 44.5       | 32.8         | 17.1       | 2.6            | 3.0        |
| (20:20:60 vol %)               |            |              |            |                |            |
| **+ Li₂C₂O₄**                  | 50.8       | 25.8         | 19.3       | 1.5            | 2.6        |
| **1.20M LiPF₆ in EC+EMC+MB**    | 39.2       | 30.8         | 23.3       | 3.6            | 3.1        |
| (20:20:60 vol %)               |            |              |            |                |            |
| **+ 0.10M LiBOB**              |            |              |            |                |            |

Table 4-4. Elemental concentration on cathode surface.
Figure 4-1. Discharge capacity (Ah) of experimental lithium-ion cells at –40°C (~ C/16 rate) containing electrolytes consisting of 1.0M LiPF$_6$ 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 (~ C/4 rate) containing electrolytes consisting of 1.0M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %) with and without different additives.
Figure 4-3. The cycling characteristics of experimental MCMB-LiNiCoO$_2$ lithium-ion cells containing electrolytes consisting of 1.0M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %) with and without different additives at high temperatures (60$^\circ$ and 80$^\circ$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 LiPF$_6$ 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 LiNi$_{x}$Co$_{1-x}$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 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 LiPF$_6$ 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 LiNi$_x$Co$_{1-x}$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 LiPF$_6$ EC+EMC+MB (20:20:60 v/v %) with and without different additives.
Figure 4-9. Tafel polarization measurements at 23°C of LiNi$_{x}$Co$_{1-x}$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.
Figure 4-10. Tafel polarization measurements at -30°C of MCMB electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF$_6$ 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$_{x}$Co$_{1-x}$O$_2$ electrodes from lithium-ion cells containing electrolytes consisting of 1.0M LiPF$_6$ 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.
Figure 4-15. SEM images of cycled anodes.
Figure 4-16. C1s, F1s, O1s and P2p XPS spectra for cycled LiNi$_x$Co$_{1-x}$O$_2$ electrodes.
Figure 4-17. B1s XPS spectrum for cycled LiNi$_x$Co$_{1-x}$O$_2$ electrode containing LiBOB electrolyte.
Figure 4-18. FTIR of cycled LiNi_{0.8}Co_{0.2}O_{2} electrodes.
Figure 4-19. SEM images of cycled LiNi$_x$Co$_{1-x}$O$_2$ electrodes.
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.\(^1\) 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 Li\(_{4.4}\)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(oxalate)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$^{-2}$ (~C/20), second and third cycle at 5.6 μAcm$^{-2}$ (~C/10) and next 52 cycles at 11.2 μAcm$^{-2}$ (~C/5). The cells were cycled using BT2000 cycler (Arbin Instruments) at 16 °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 Kα (hv=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:

\[ C_x = \frac{I_x}{S_x} / \left( \sum \frac{I_i}{S_i} \right), \]

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 initial 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 Li$_x$PF$_y$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$_2$CO$_3$ 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)). 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). 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 Li$_x$PF$_y$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$_2$CO$_3$ and the broad peak centered around 1000 cm$^{-1}$ is characteristic of C-O peaks in ethers and Li$_x$PF$_y$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 ~1800cm$^{-1}$ 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 (< 1µm). The surface of the electrode extracted from electrolyte containing LiBOB is smooth with medium irregular cracks (2-3 µm). 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 nm).

**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$_2$CO$_3$. 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 Li$_x$PF$_y$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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|   | Electrolyte solution composition with and without additives. |
|---|-------------------------------------------------------------|
| 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. %)                   |
|                        | 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.
Figure 5-5. SEM images of cycled Si electrodes