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EXPLORATION OF ADDITIVES FOR IMPROVING PERFORMANCE OF HIGH
VOLTAGE LNi_{0.5}Mn_{1.5}O₄/GRAPHITE CELLS (APPLIED)

BY
YINGNAN DONG

A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF THE
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DOCTOR OF PHILOSOPHY DISSERTATION
OF
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UNIVERSITY OF RHODE ISLAND

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Abstract

Lithium ion batteries have been investigated extensively due to their widespread applications in portable electronic devices and electrical/hybrid vehicles. However, significant challenges still exist for an extended calendar life at a wide temperature range. Due to the intrinsic drawbacks of the commonly used LiPF_6 -carbonate electrolyte systems, such as insufficient thermal stability at elevated temperature and unavoidable HF contaminants, much effort has been paid to exploring novel additives. It is well known that the introduction of additives into electrolyte systems is one of the most effective and economic approaches to improve performance of lithium ion batteries.

In this dissertation, a novel class of borate compounds has been successfully synthesized and screened as additives for electrolyte of lithium ion battery. Nuclear magnetic resonance (NMR) spectroscopy was utilized to characterize compounds by dissolving additives into deuterated solvents. The cycling performance of these novel additives and other commercialized additives was compared by adding them into 1M LiPF_6 EC/EMC electrolyte, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /Graphite cells are cycled under both room temperature and elevated temperature up to 4.8V. Electrochemical impedance spectroscopy (EIS) and Linear sweep voltammetry (LSV) were used to investigate electrochemical activity of additives. The investigation of the interrelationship of cycling performance, additive structure, and electrode surface film structure has been conducted by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and FT-IR instruments. SEM and TEM images showed that novel additives can form uniform solid electrolyte interface (SEI) and cathode solid electrolyte interface (CEI). XPS and FT-IR spectra were acquired to

analyze main components of SEI and CEI, and they are beneficial for further understanding how addition of additives changed surface chemistry of electrodes. The surface reactions of both additives and electrolytes with the graphitic anode and lithium nickel manganese oxide cathode of lithium ion batteries have been speculated. New additives can not only form more uniform SEI on surface of anode, but also beneficial for forming uniform CEI on surface of cathode.

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Finally, I would like to thank my parents for giving me greatest support studying abroad. Thanks to everyone who have helped me, I wouldn't accomplish this achievement without any of you.

Preface

This dissertation is written in manuscript format. There are four chapters in this dissertation. Chapter 1 is an introduction of Lithium ion battery. Chapter 2 was already published in the Journal of the Electrochemical Society. Chapter 3 is written as a manuscript and will be submitted to the ACS Applied materials & interfaces. Chapter 4 is also written as a manuscript, will be submitted to the Journal of Power Sources in the future.

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Introduction

Background of Lithium Ion Battery

As we stepped into 21st century, technology evolved extremely fast, electronic devices such as cell phone, laptop, digital camera have been used more and more frequently in people's daily life. As power source of all these portable electronic devices, lithium ion batteries have been used widely with its unique advantages such as high energy density, longevity and no memory effects, many researchers are contributing their efforts to the development of lithium ion batteries [1-3]. Since "energy crisis" is becoming a very big challenge for human society, nowadays researchers also expect that lithium ion batteries can be developed further followed by extend its applications such as being used as main power supply for vehicles to substitute fuel based on non-renewable fossil energy.

Lithium ion battery research has been conducted for many years after the first release by the Sony company in early 1990s [4]. LIBs are usually composed of a cathode with an aluminum current collector, an anode with a copper current collector, a separator, and electrolyte. Lithium cobalt oxide (LCO) [5] is mostly used cathode material in commercial LiBs, and recent years, many other cathode materials such as lithium iron phosphate (LiFePO_4) [6], lithium nickel manganese oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) [7] and lithium nickel cobalt manganese oxide (NCM) [8] have drawn more and more attentions due to their own advantages. Most commercialized anode material is graphite because lithium ion can intercalate into/ deintercalate from layered graphite structure to store and release energy, silicon material is also explored to be using as anode material due to its high theoretical capacity (around ten times larger than graphite) in recent years. However,

its volume expansion during lithium ion intercalation process still limits its commercial application. The permeable polymeric separator is also a very important component of lithium ion battery, it can allow lithium ion passing through but inhibit the conduction of electrons to prevent short-circuit the battery [9]. Polyolefin film separator is mostly used separator in commercialized LIBs. After stacking cathode and anode materials with a separator, lithium ion battery is filled with electrolyte to make it work, the electrolyte plays a very important role in transporting lithium ions between cathode and anode. It is usually composed of lithium salt such as LiPF_6 , LiBF_4 , LiTFSI , and a combination of carbonate solvents including propylene carbonate, ethylene carbonate, ethyl methyl carbonate and so on. The typical lithium ion battery usually operates between 3.0 and 4.3 V with a working voltage around 3.7 V [10].

During charge process, lithium ion will be extracted from cathode material into electrolyte, then lithium ions will pass through separator, and intercalate into anode structure and neutralized with electrons from external power source, energy will be stored in lithium ion batteries. During discharge process, lithium ion will be deintercalated from anode and go back to the cathode structure, electrons will be released to external circuit. In an ideal situation, when lithium ions are fully intercalated into the anode, six carbons can accommodate one lithium. A typical chemical reaction in lithium ion batteries is described as following [10]:

It is generally believed that during initial charging process, a solid layer called solid electrolyte interface (SEI) which is usually composed of decomposition products of organic solvents will be formed on surface of anode electrodes [11], to prevent further decomposition of electrolyte after the second charge. In mostly used combination of linear and cyclic carbonates, ethylene carbon (EC) is decomposed at a relatively high voltage, 0.7 V vs. lithium, and forms a dense and stable interface [12]. SEI is a electrically insulating yet provides significant ionic conductivity.

Cathode Electrode Materials

Lithium ion batteries are becoming more and more important as they are more widely applied in electric vehicle field due to their high gravimetric and volumetric energy density [13, 14]. A large number of researchers have began to focus on exploring new cathode materials which can satisfy huge increasing demand of vehicle scale lithium ion batteries [15-17], because the mostly used cathode material-lithium cobalt oxide (LiCoO_2)-has many limitations such as low energy density, high cost, rare resource of cobalt [18, 19].

Recent years, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has drawn wide attention due to high intercalation/deintercalation potential of 4.8 V (vs. Li/Li^+), which can improve energy density significantly [20-23], whereas the traditional cathode materials such as layered LiCoO_2 [24, 25] and LiMn_2O_4 [26-28] can only be typically charged up to 4.0V vs. Li/Li^+ . However, a main challenge in manganese-containing cathodes is that HF generated from electrolyte decomposition can cause the dissolution of Mn^{2+} from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, leading to further structure collapse of cathode, and eventually result in the fast capacity fade [29-31].

A variety of methods have been proposed to solve these problems, such as coating inert surface on cathode [20, 32, 33]; using more stable solvents, including ionic liquid, sulfones and nitriles [34-36]; passivation film forming additive incorporation. Among these methods, additive incorporation is more attractive due to its less complexity and lower cost. A typical CEI-forming additive, lithium bis(oxalato)borate (LiBOB), has been extensively investigated and shows improved cycling performance. However, the oxidation of LiBOB on the charged $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface at high voltages (>4.5 V, vs. Li/Li^+) is accompanied by CO_2 gas evolution [37], which can cause potential safety issues such as explosion in lithium ion batteries. So exploring novel electrolyte additive, which can form robust and uniform solid electrolyte interface (SEI) on the surface of electrodes is becoming more and more important for achieving improved cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Graphite}$ cells.

Liquid Electrolyte Instability

Among all components of lithium ion battery, electrolyte plays a very important role in making lithium ion batteries recyclable.

Currently, most commercialized ion batteries use carbonate or based organic solvents as electrolyte solvent and LiPF_6 as

supporting electrolyte. However, at relatively high temperature (55°C), reactions between $\text{LiPF}_6/\text{electrolyte}$ occurred as following: $\text{LiPF}_6 \rightarrow \text{LiF(s)} + \text{PF}_5\text{(g)}$. Decomposition product PF_5 is strong Lewis acid, it will react with electrolyte solvent with the existence

of H₂O or small molecule alcohol impurities, leading to decomposition of the electrolyte [38, 39]. (Scheme 1)

As a result, the cycling performance of LIBs based on LiPF₆/ Carbonate electrolyte system at elevated temperature is relatively poor. In addition, since HF is generated by LiPF₆/carbonate electrolyte system [40], high energy density electrode materials LiNi_{0.5}Mn_{1.5}O₄ cannot match with LiPF₆/carbonate electrolyte system owing to the fact that deposition of metal atoms cause collision or distortion of electrode material structure and further cause the poor cycling ability. It is urgent to design suitable additives matching with LiPF₆/carbonate electrolyte system for researchers [41]. Moreover, for the first charge/discharge process, in order to form SEI on the electrolyte/electrode interface, ethylene carbonate which can function as SEI provider becomes essential component of electrolyte solvent. But the melting point of EC is relatively high (36.4°C), and restrict the application of Lithium ion batteries at low temperature, and further restrict its development as power source of electric vehicles [13].

Electrolyte Additives

For commercialized electrolyte formulation, several additives are usually incorporated into the electrolyte formula. Due to their different functions, additives are usually divided into these categories: (1) solid electrolyte interface (SEI) forming improver, (2) cathode protection agent, (3) LiPF₆ salt stabilizer, (4) safety protection agent, (5) Li deposition improver, and (6) other agents such as solvation enhancer, Al corrosion inhibitor, and wetting agent [42]. Among all kinds of additives, SEI and CEI forming additives have drawn much more attention than the other additives. Although SEI can be formed by organic solvents such as ethylene carbonate, incorporation of

specific additive can improve quality of SEI formed on the surface of anode, morphology can be more uniform and ionic conductivity can be improved by addition of more less resistant components of SEI form by additive. Vinylene carbonate (VC) is a well known SEI-forming additive that is widely used in lithium ion batteries [43-46]. Incorporation of VC into lithium ion batteries has been reported to improve cycling stability of graphite cells cycled at elevated temperature [47-50]. The improved stability is typically attributed to the generation of a stable polymer film on the graphite surface [48, 51]. Most current commercial lithium ion batteries contain VC as an additive. Recent years, a typical CEI-forming additive, lithium bis(oxalato)borate (LiBOB) has drawn many researchers' attention for its superior ability to form good passivation film on surface of cathode. It has been reported to be one of the better additives for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes [52, 53]. The related oxalato borate lithium difluorooxalato borate (LiDFOB) [54, 55] has also been reported to improve the properties of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ cathodes cycled to high potential [56]. In addition to the lithium oxalato borates [57, 58], we have recently reported on the beneficial effect of the incorporation of lithium tetralkylborates as Additives for Designed Surface Modification (ADSM) to function as functional group delivery agents to modify the cathode surface [59, 60].

LIB Problems and Solutions Presented in Thesis

Lithium ion batteries do have a lot advantages, to achieve higher energy density, high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /Graphite cells become very promising in the future. However, as we discussed above, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /Graphite cells do have a lot of problems need to be solved before it being commercialized. First of all, high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material has severe Mn dissolution issue due to HF generated by

electrolyte decomposition, especially when cycled at elevated temperature. Mn dissolution caused cathode structure collapse which is detrimental to the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Graphite}$ cells. Second, standard electrolyte is not stable when cycled at elevated temperature, more electrolyte consumption will cause faster capacity fade and also lower columbic efficiency of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Graphite}$ cells. To conquer these two main problems of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Graphite}$ cells, designing and screening novel electrolyte additives, which can form robust and uniform solid electrolyte interface (SEI) and protective cathode solid electrolyte interface (CEI) on the surface of electrodes become more and more important, beneficial passivation film on the surface of electrodes cannot only protect cathode and anode structure from collapsing by inhibiting Mn dissolution, but also inhibit further interaction between electrodes and electrolyte, and further improve cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Graphite}$ cells.

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Chapter 2

Investigation of the effect of added Methylene Ethylene Carbonate (MEC) and Vinylene Carbonate (VC) on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /Graphite cell performance

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Abstract

Cycling performance of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells cycled up to 4.8 V (vs LiC₆/C₆) with added methylene ethylene carbonate (MEC, 0.5% wt.) and vinylene carbonate (VC, 0.5% wt.) in 1.2 M LiPF₆ in EC/EMC (3/7, v/v, STD electrolyte) has been investigated at 25 °C and 45 °C. Addition of VC to the STD electrolyte results in a decrease the cell cycling performance, especially at 45 °C, while addition of MEC to the standard electrolyte does not decrease performance. After 50 cycles at 45 °C, the cells with added MEC retain 79% of the original capacity, while the cells with added VC retain only 68% of the initial cell capacity. While improved performance can be obtained with MEC compared with VC, however, neither additive provides significant improvement over the STD electrolyte. Ex-situ surface analysis of the electrodes conducted by XPS and FT-IR supports the presence of a uniform passivation layer on the cathode surface with added MEC. The modification of the cathode solid electrolyte interphase (CEI) is consistent with the improved performance for cells with added MEC at 45 °C, compared to cells with added VC.

1. Introduction

Li-ion batteries (LiBs) are widely used for portable consumer electronics and have recently been incorporated into electric vehicles (EVs) [1,2]. The performance requirements for EV applications are much more stringent than portable electronics applications. These requirements include longer cycle life and long term stability upon exposure to moderately elevated temperature (45 °C). Many of these performance limitations are due to the electrochemical and thermal instability of the electrolyte [3,4].

One of the primary methods to improve the high temperature stability of lithium ion batteries is the incorporation of electrolyte additives, which generate a more stable solid electrolyte interphase (SEI) on the anode [5]. Vinylene carbonate (VC) is a well known SEI-forming additive that is widely used in lithium ion batteries [6-9]. Incorporation of VC into lithium ion batteries has been reported to improve cycling stability of graphite cells cycled at elevated temperature [10-13]. The improved stability is typically attributed to the generation of a stable polymer film on the graphite surface [11, 14]. Most current commercial lithium ion batteries contain VC as an additive. Thus, cathode materials which are incompatible with electrolytes containing VC are problematic.

Methylene ethylene carbonate (MEC) has also been reported to be a good additive for lithium ion batteries for similar reasons [15, 16]. While many anode film forming additives have been investigated with graphite anodes and LiCoO_2 or related layered metal oxides with operating potentials around 4.1-4.2 V vs Li/Li^+ . There have been no reports on the comparative performance of VC and MEC as anode film forming additives (VC or MEC) with the graphite anode and the high voltage spinel (~4.8 V)

LiNi_{0.5}Mn_{1.5}O₄ cathode. In this manuscript, the cycling performance of LiNi_{0.5}Mn_{1.5}O₄/graphite cells with MEC and VC as electrolyte additives are compared.

2. Experimental

2.1 Electrochemical test and characterization

Electrolytes consisting of 1.2 M LiPF₆ in a EC/EMC (3/7 v/v) (STD electrolyte) with 0.5% (wt.) MEC (MEC electrolyte) or 0.5% (wt.) VC (VC electrolyte) additives were prepared in an argon-filled glove box, in which the oxygen and water content were less than 1 ppm. The STD electrolyte and additives (MEC and VC) were provided by BASF as battery grade materials. The composite cathode and anode electrodes were also obtained from BASF. The composite LiNi_{0.5}Mn_{1.5}O₄ electrode with diameter of 14.7 mm is composed of active material (92%), conductive carbon (4%) and PVDF binder (4%). The composite anode electrode with diameter of 15 mm is composed of graphite (ConocoPhillips, 95.7%) along with conductive carbon (0.5%) and Carboxymethyl Cellulose (CMC) & Styrene-Butadiene Rubber (SBR) binder (3.8%). The loading of cathode was wt.(total) 15.9 mg/cm² and loading of anode was wt.(total) 7.1 mg/cm². The balancing of the cells was 1.25. LiNi_{0.5}Mn_{1.5}O₄/graphite. 2032-type coin cells were constructed in an Argon-filled glove box with a trilayer polypropylene/polyethylene (PP/PE/PP) separator (d = 19 mm, Celgard) and one layer of glass fiber separator (d = 16 mm, thickness= 0.67 mm, Whatman) and 100 μL of electrolyte. Cells were cycled on an Arbin Instruments battery cycler and the temperature was controlled with a Fisher Scientific Isotemp Incubator. Carbon black electrode (Super C65, d = 15 mm, BASF) half-cells were built with a trilayer polypropylene/polyethylene (PP/PE/PP) separator (d = 19 mm, Celgard) and one layer of glass fiber separator (d = 16 mm,

thickness= 0.67 mm, Whatman) and 100 μ L of electrolyte. Cells were scanned from the open circuit potential (OCV) to 6.5 V (high potential) and 0.01 V (low potential) vs. Li/Li⁺ at a rate of 0.1 mV s⁻¹ with Bio-Logic Instrument and at a controlled temperature of 25.0 °C.

The LiNi_{0.5}Mn_{1.5}O₄/graphite cells were initially cycled at room temperature with the following cycling protocol: C/20 D/20 for the first cycle; C/10 D/10 for the second and third cycle; and then C/5 D/5 for the remaining cycles at 25 °C. After the initial cycling at 25 °C, the temperature was increased to 45 °C and the cells underwent 50 cycles at C/5 D/5 rate. The LiNi_{0.5}Mn_{1.5}O₄/graphite cells were charged using a CC-CV mode, constant current charge (CC) to 4.8 V, followed by a constant voltage (CV) charge step at 4.8 V vs. LiC₆/C₆ until the current decreased to 10% of the applied charging current for a maximum duration of 1 hour. The cells were discharged to 3.30 V at the same CC. Cells were built in triplicate and cell to cell variation was approximately 3%. A representative data set is provided. Electrochemical impedance spectroscopy (EIS) was performed on a Bio-Logic Instrument after formation cycles, 25 °C and 45 °C cycling at 100 % SOC. Perturbation is 10 mV with the frequency range 1000 kHz-20 mHz.

The cycled cells were disassembled (~3.3 V) in argon glove-box, and the cycled anodes/cathodes were harvested and rinsed with anhydrous dimethyl carbonate (DMC, Sigma, extra dry 99%) 3 times (3 x 500 μ L) to remove residual electrolyte, followed by vacuum drying overnight at room temperature.

XPS measurements were carried out using a ThermoFisher K-Alpha spectrometer, under a focused monochromatised Al K α radiation (ν =1486.6 eV). An air-free transfer

vessel (ThermoFisher) was used to avoid any contact with air/moisture. Peaks were recorded with constant pass energy of 50 eV with energy resolution of 50 meV and charge neutralization. Peak positions and areas were optimized by a weighted least squares fitting method using 70% Gaussian, 30% Lorentzian line shapes using Advantage (ThermoFisher) software.

FTIR spectra were acquired on Bruker Tensor 27 with Attenuated Total Reflectance (ATR) accessory with Germanium crystal, 512 scans with a resolution of 4 cm^{-1} . The IR spectrometer is inside of a N_2 filled glove box.

3. Results and Discussion

3.1. Electrochemical stability of the electrolytes

Electrochemical stability of the STD and VC or MEC containing electrolytes is evaluated on carbon black electrodes (Super C65) with linear sweep voltammetry at high and low potential.

Anodic linear sweep voltammetry of Super C65/Li cells is presented in Figure 2-. Additive oxidation is clearly observed in the 4.5-5.1 V vs. Li/Li^+ with the appearance of an anodic peak for MEC and VC at 4.55 V and 4.7 V vs. Li/Li^+ , respectively. After oxidation of the additives, the cells containing the VC and MEC electrolytes have increased current at high potential compared to the STD electrolyte consistent with greater electrolyte oxidation. The increased current for the VC electrolyte is observed between 5.1-5.5 V vs. Li/Li^+ while the increased current is observed between 4.7-5.5 V vs. Li/Li^+ for the MEC electrolyte. This suggests that during the first anodic scan, more oxidation reactions occur with the MEC electrolyte than are observed for the VC

electrolyte. The increased reaction may lead to additional surface film formation on the cathode as discussed below.

Cathodic linear sweep voltammetry of Super C65/Li cells is presented in Figure. For the three electrolytes, STD, MEC, and VC, EC reduction is observed at 0.65 V vs. Li/Li⁺. The intensity of the EC reduction peak varies as a function of the additive. Addition of VC increases the intensity of the EC reduction peak slightly, while addition of MEC diminishes the intensity of the same peak. Despite the fact that both VC and MEC are reduced at a similar potential (~1.5 V vs. Li/Li⁺), the nature of passivation layers that are deposited at low potential are likely different due to the structural differences of the additives.

3.2. Cycling performance

Charge and discharge curves of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells using the STD electrolyte, with 0.5% MEC and 0.5% VC are provided in Figure 3. The initial charge capacity of the cells with the MEC electrolyte are 184.3 mAh.g⁻¹, which is about 30 mAh.g⁻¹ higher than the cells using the STD electrolyte. The charge/discharge efficiency of the cells with the MEC electrolyte (75.2% for the 1st cycle and 96.2% for the 2nd cycle) are lower than the cell with the STD electrolyte (87.2% for the 1st cycle and 98.1% for the 2nd cycle). Poor efficiency of LiNi_{0.5}Mn_{1.5}O₄ cathodes with STD electrolyte has been previously reported [17]. The cell with VC electrolyte has a charge capacity of 174.2 mAh.g⁻¹ and initial charge/discharge efficiency of 80.7%, but much lower charge/discharge efficiency of 90.4% for the 2nd cycle. This suggests that the VC electrolyte continues to be consumed after the first cycle. The additional charge capacity

and lower initial efficiency of the cell with MEC electrolyte suggest more reaction of MEC than STD electrolyte and VC electrolyte [18]. The lower initial coulombic efficiency of cells with the MEC electrolyte suggests that more electrolyte is consumed during the first cycle. However, despite the differences in efficiencies, the discharge capacities are comparable. The efficiencies and discharge capacities suggest that some of the electrochemical reactions occurring during the first cycle do not result in loss of active lithium.

The cycling performance of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite cells with the electrolytes under investigation is presented in Figure 4. The cycling performance of the cells differs for the different electrolyte formulations. The cyclability of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite cells containing the MEC electrolyte is better than the VC electrolyte. The discharge capacities of the cells using the electrolytes with the STD electrolyte, MEC electrolyte and VC electrolyte at the 70th cycle are 99.5, 100.3 and 84.6 mAh.g^{-1} , respectively, and the corresponding capacity retentions after 50 cycles at elevated temperature is 77.2%, 78.7%, and 67.8%, respectively. Addition of 0.5% MEC can improve the efficiency and capacity retention of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite cells compared to the VC electrolyte.

Initial coulombic efficiency of cells containing the VC electrolyte are higher than cells containing the MEC electrolyte (Figure 4b). However, upon room temperature and elevated temperature cycling, the coulombic efficiency of the cell with 0.5 wt.% VC is much lower than the other electrolytes. This suggests that more electrolyte is continuously consumed during cycling with the VC electrolyte.

Electrochemical impedance spectra of cells at full state of discharge (100 % SOD, ca. 3.3 V) are measured at different stages upon cycling. The corresponding EIS Nyquist plots are depicted in Figure 5. After 20 cycles at 25 °C (Figure 5a), the impedance of the cell with the VC or MEC electrolytes is found to be similar to the cell containing the STD electrolyte. However, significant changes in EIS spectrum shape are observed upon cycling at 45 °C (Figure 5b). Impedance of the cell with the STD electrolyte is the lowest among the three cells under investigation. The cells containing the MEC electrolyte have higher impedance than the cells with VC electrolyte due to a significant increase of the charge transfer resistance in the medium frequency range[19]. Nevertheless, important differences in the EIS spectra of the VC and MEC cells can be observed in the high frequency range. Indeed, first semi-circle of the EIS spectrum of the cells containing MEC are smaller than that observed for the VC electrolyte, suggesting that the surface films formed by MEC decomposition are more conductive (and less dense) than the surface films formed by the decomposition products of VC. Despite of reduced SEI resistance, the increased reactivity of MEC, especially at high potential, generates thicker surface films, which limits charge transfer. The presence of the vinyl group at different positions changes both the reactivity of the additive and the conductivity of the resulting surface films. Incorporation of MEC, compared to VC, results in a thicker but less dense and more conductive surface film (Figure 6) [8, 20]. In addition, the initially generated polymers may be reductively or oxidatively unstable on the electrode surfaces leading to further decomposition reactions. Differences in these subsequent decomposition reactions could contribute to the observed differences in performance [21, 22]. Ex-situ

analysis of the cycled electrodes has been conducted to better understand the differences in electrochemical performance.

3.3. Ex-situ Surface analysis

XPS spectra of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and graphite electrodes extracted from cells cycled at 45 °C have been acquired to develop a better understanding of the effects of MEC and VC on electrode surface chemistry. The C1s and O1s XPS spectra of the cycle cathode with/without additive are provided in Fig 7.

The C1s spectrum of the fresh cathode contains peaks characteristic of the Super P conductive carbon at 284.3 eV and PVDF binder at 286.5 eV ($-\text{CH}_2-$) and 290.7 eV (C-F) (Figure 7a) [23, 24]. The corresponding O1s core spectrum contains the metal oxide peak of the LNMO crystal lattice at 529 eV (Figure 7a). Another O1s peak is observed at 531.5 eV characteristic of residual Li_2CO_3 on the surface of the cathode particles [25].

The C1s spectrum of cathode cycled with the STD electrolyte contains peaks characteristic of the PVDF binder at 290.7 eV and 286.5 eV and conductive carbon at 284.3 eV (Figure 7b). In addition, new peaks resulting from EC oxidation are observed at 286.5 eV (C-O), 287.7 eV (C=O), and 289.9 eV (O-C=O) characteristic of a Cathode Electrolyte Interface (CEI) composed of poly(ethylene carbonate) and other decomposition products of the electrolyte [26,27]. The corresponding O1s spectrum contains a strong peak for the bulk metal oxide at 529 eV, along with new contributions of surface species at 531.5 eV, 533.0 eV, and 534.3 eV characteristic of poly(ethylene carbonate).

Analysis of the cathode surface reveals differences when LNMO is cycled with the VC and MEC electrolytes. The intensity of the peaks characteristic of C-O, C=O, and O-C=O is increased in the C1s spectrum suggesting that the CEI is thicker when VC is added to the STD electrolyte. The C1s spectrum of the cathode cycled with the MEC electrolyte also has increased intensity of the C-O, C=O, and O-C=O peaks, consistent with the generation of a thicker CEI and the results of the anodic linear sweep voltammetry described earlier (Fig 1), where increased current at high voltage was observed. . The O1s spectra provide further support. The intensity of the O-M peak at 529 eV has weaker intensity for the electrode cycled with the VC electrolyte compared to the STD electrolyte, consistent with a thicker film for the VC electrolyte. The change is greater for the cathode cycled with the MEC electrolyte. The O-M contribution is hardly visible from the spectrum, suggesting thicker coverage of metal oxide particles by CEI deposition. Although the addition of MEC did not appear to negatively influence the limited cycle life testing performed, it seems apparent that cell resistance is higher which may adversely affect the rate capability. Alternatively, VC reacts on the surface of the cathode to generate a similar, but thinner surface film. Oddly, the film derived for VC is detrimental to the performance of the cell. The difference is likely related to the difference in polymer structure and packing in the surface film (Figure 6).

The C1s spectrum of the anode cycled with the STD electrolyte (Figure 8) contains peaks characteristic of C-O bonds containing species (286-287 eV) and C=O bonds (288-290 eV) characteristic of lithium alkyl carbonates and lithium carbonate from carbonate solvent reduction [26,27]. The O 1s spectrum of the fresh graphite electrode contains O 1s peaks of the CMC binder, along with the Auger peak of sodium at 536 eV.

The O 1s spectrum of the graphite electrode cycled with the STD electrolyte contains peaks characteristic of electrolyte decomposition products in the SEI such as lithium alkyl carbonates and lithium carbonate: 531.2 eV, 532.5 eV, and 533.2 eV. The XPS spectra of the graphite anodes cycled with either VC or MEC are very similar. Since XPS has a shallow depth of penetration (~5 nm) the outer SEI is similar for all electrolytes investigated and is composed primarily of lithium alkyl carbonates and Li_2CO_3 .

3. 4. FT-IR

FT-IR/ATR spectroscopy has been conducted on LNMO cathodes and graphite anodes extracted from cells cycled at 45 °C with different electrolytes.

The IR spectra of the fresh cathodes are dominated by peaks from the PVDF binder at 1400, 1170, 1070, 877, and 840 cm^{-1} (Figure 9a). The cathodes extracted from cells containing the STD electrolyte have only small changes to the IR absorptions, suggesting minimal electrolyte decomposition, consistent with the XPS observations. However, the cathodes extracted from cells cycled with the MEC electrolyte contain an additional strong peak at 1800 cm^{-1} , consistent with the presence of Poly(MEC) [16]. A similar peak, characteristic of poly(VC) is observed for the cathode cycled with the VC electrolyte, although the intensity is weaker for the VC electrolyte compared to the MEC electrolyte. The IR spectra suggest that the CEI is thickest for the MEC electrolyte, which is in agreement with the XPS results.

The C=O region of the IR spectrum of the graphite anode cycled with the standard electrolyte is dominated by peaks associated with lithium alkyl carbonates (~1640 cm^{-1})

and Li_2CO_3 (1450 cm^{-1}). The intensity of the peaks associated with lithium alkyl carbonates and Li_2CO_3 are diminished for the electrodes cycled with either the VC electrolyte or the MEC electrolyte. New absorptions are observed between 1750 and 1800 cm^{-1} consistent with the presence of poly(VC), poly(MEC), or polycarbonate (Figure 9b). Since the IR has a greater depth of penetration than XPS, the poly(VC) and poly(MEC) are predominantly in the inner SEI. The results are consistent with previous reports utilizing VC or MEC as additives to improve the stability of the anode SEI via the generation of polymeric species [11, 14-16].

4. Conclusions

The effect of MEC and VC addition to the EC/EMC 1.2 M LiPF_6 electrolyte upon the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite cells has been investigated. Interestingly, the incorporation of VC results in a significant decrease in the capacity retention of graphite / $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells cycled at 45°C in contrast to that reported for graphite/ LiCoO_2 cells. Alternatively, similar capacity retention and cycling efficiency are obtained upon incorporation of MEC despite its inherent initial instability at high potential. Ex-situ surface analysis conducted by XPS and FT-IR of the electrodes supports similar anode SEI for both MEC and VC. The inner SEI contains poly(VC) or poly(MEC) while the outer SEI is dominated by lithium alkyl carbonates and Li_2CO_3 . The incorporation of additives also significantly modifies the surface of the cathode. The poly(MEC) surface film on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode is thicker than the poly(VC) surface film on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. The thicker surface film in the presence of MEC may contribute to the improved performance of MEC compared to VC, together with a different polymerization pattern that favors conductivity of the organic layers.

Although improved performance is observed with MEC compared with VC, neither additive provides significant improvement over the STD electrolyte. Unfortunately, at this time the source of the performance decreases in the presence of VC are also unclear.

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Figure 2-1. Anodic linear sweep voltammetry at 25 °C of SC65/Li cells (sweep rate of 0.1 mV.s⁻¹) using (in black) the EC/EMC (3/7) 1.2 M LiPF₆, (in red) EC/EMC (3/7) 1.2 M LiPF₆ + 0.5 % MEC, and (in blue) EC/EMC (3/7) 1.2 M LiPF₆ + 0.5 % VC electrolytes.

Figure 2-2. Cathodic linear sweep voltammetry at 25 °C of SC65/Li cells (sweep rate of 0.1 $\text{mV}\cdot\text{s}^{-1}$) using (in black) the EC/EMC (3/7) 1.2 M LiPF_6 , (in red) EC/EMC (3/7) 1.2 M LiPF_6 + 0.5 % MEC, and (in blue) EC/EMC (3/7) 1.2 M LiPF_6 + 0.5 % VC electrolytes.

Figure 2-3. First charge and discharge curve of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells (C/20 D/20, cutoff potentials at 25 °C and 45 °C: 4.80 V-3.3 V vs. LiC₆/C₆) using the STD electrolyte, with 0.5% MEC and 0.5% VC.

Figure 2-4. (a) Cycling retention and (b) coulombic efficiency of LiNi_{0.5}Mn_{1.5}O₄/Graphite cells (C/5 D/5, cutoff potentials at 25 °C and 45 °C: 4.80 V-3.3 V vs. LiC₆/C₆) using the STD electrolyte, with 0.5% MEC and 0.5% VC.

Figure 2-5. EIS spectra at full state of discharge (3.3 V vs. LiC_6/C_6) of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}_x\text{C}_6$ cells using the (in black) STD, (in red) STD + 0.5 % MEC, and (in blue) STD + 0.5% VC electrolytes after (a) 20 cycles at 25 °C and (b) 30 additional cycles at 45 °C.

Figure 2-6. (a) Reduction of VC already proposed in the literature and possible reduction of MEC; (b) Possible formation pattern of the poly(VC) and poly(MEC) polymers after first oxidation at high potential of the VC and MEC molecules that combines to other VC and MEC molecules to form the polymer.

Figure 2-7. (On the left) C 1s and (on the right) O 1s core spectra of (a) the fresh $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes cycled with the (b) STD, (c) STD + 0.5% VC, and (d) STD + 0.5% MEC electrolytes at 45 °C for 50 cycles.

Figure 2-8. (On the left) C 1s and (on the right) O 1s core spectra of (a) the fresh graphite electrode and graphite anodes cycled with the (b) STD, (c) STD + 0.5% VC, and (d) STD + 0.5% MEC electrolytes at 45 °C for 50 cycles.

Figure 2-9. FT-IR spectra of (a) LiNi_{0.5}Mn_{1.5}O₄ and (b) graphite electrodes taken from cells cycled at 45 °C in the STD, STD + 0.5% (wt.) VC, and STD + 0.5% (wt.) MEC electrolytes.

Chapter 3

Improving the Performance at Elevated Temperature of High Voltage Graphite/LiNi_{0.5}Mn_{1.5}O₄ Cells with Added Lithium Catechol Dimethyl Borate

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Abstract

Performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite cells cycled to 4.8 V at 55 °C with the 1.2 M LiPF_6 in EC/EMC (3/7, STD electrolyte) with and without added lithium catechol dimethyl borate (LiCDMB) has been investigated. The incorporation of 0.5 wt % LiCDMB to the STD electrolyte results in improved capacity retention and coulombic efficiency upon cycling at 55 °C. Ex-situ analysis of the electrode surfaces via a combination of SEM, TEM, and XPS reveals that oxidation of LiCDMB at high potential results in the deposition of a passivation layer on the electrode surface, preventing transition metal ion dissolution from the cathode and subsequent deposition on the anode. NMR investigations of the bulk electrolyte stored at 85 °C reveals that added LiCDMB prevents the thermal decomposition of LiPF_6 .

Graphical abstract

1. Introduction

Lithium-ion batteries are widely used for portable electronics and are currently being incorporated into electric vehicles due to their high energy density (1, 2). However, there is significant interest in further increasing the energy density of lithium-ion batteries (3). One method to achieve higher energy density is increasing the operating potential of the cathode material. Most commercial lithium-ion batteries contain a lithiated transition metal oxide cathode that typically operates at ~ 4.0 V vs. Li/Li^+ (3, 4). Several novel cathode materials with an operating potentials over 4.0 V are currently under investigation, including LiNiPO_4 , (5) and LiCoPO_4 , (5, 6), and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. While the high operating potential of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel cathode (4.8 V vs. Li/Li^+) offers high energy density, commercialization has been hampered by severe capacity fade and poor efficiency (7). The capacity fade is particularly pronounced at moderately elevated temperatures (> 45 °C) and in full cells employing a graphite anode (7). The failure mechanisms of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells at high voltage and elevated temperature have been recently investigated (8-12). Electrolyte decomposition, electrode/electrolyte interface degradation, and transition metal dissolution are the leading factors reported for performance fade. One effective method for improving the performance of high voltage cathodes involves the incorporation of film-forming electrolyte additives that are sacrificially oxidized on the surface of electrodes to generate a passivation film which inhibits transition metal dissolution and further electrolyte oxidation.

There have been several reports where electrolyte additives have improved the performance of cathodes cycled to high potential (13-16,21). Lithium bis(oxalate borate) (LiBOB) has been reported to be one of the better additives for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes

(14, 15, 21, 50). The related oxalato borate lithium difluorooxalato borate (LiDFOB) (25-29) has also been reported to improve the properties of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ cathodes cycled to high potential (17) In addition to the lithium oxalato borates (24, 30), we have recently reported on the beneficial effect of the incorporation of lithium tetralkylborates as Additives for Designed Surface Modification (ADSM) to function as functional group delivery agents to modify the cathode surface (8, 9).

In this manuscript, a new asymmetric lithium borate, lithium catechol dimethyl borate (LiCDMB) is synthesized via a simple two-step reaction. Incorporation of LiCDMB into a standard lithium ion battery electrolyte improves the electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ / Graphite cells cycle to high potential (4.8 V vs. LiC_6/C_6) (Figure 6). Ex-situ surface analysis of the cycled electrodes was conducted to better understand the source of performance enhancement.

2. Experimental

2.1. Synthesis and characterization

Scheme 1

2.75 g of catechol (99 %, Aldrich) was dissolved in 100 mL of ether. 30 mL of n-butyl lithium (1.6 M in hexanes, ACRÖS) was added to the solution drop by drop. The reaction mixture was stirred for 24 hours the product precipitated and collected via filtration in a N_2 -filled glove-box. The salt obtained was subsequently washed with small

amount of ether and stored under vacuum overnight to remove solvent. The product was characterized as lithium catechol by ^1H NMR. 1.25 g of lithium catechol was suspended in 50 mL of ether, and 2.5 mL of trimethyl borate was added to the suspension. A slurry mixture was obtained. After solution was stirred for 24 hours, the mixture that composed of lithium tetramethyl borate and lithium catechol dimethyl borate was filtered in the N_2 -filled glove box. The mixture obtained was separated by adding excess dimethyl carbonate to dissolve lithium catechol dimethyl borate (lithium tetramethyl borate has poor solubility in DMC). The filtrate was collected and the DMC was removed under vacuum, lithium catechol dimethyl borate (LiCDMB, Scheme 1) was obtained as a white crystal. The product was characterized by ^1H and ^{11}B nuclear magnetic resonance (NMR) spectroscopy.

2.2. Electrochemical test and characterization

Battery grade of carbonate solvents, lithium hexafluorophosphate (LiPF_6) and 1.2 M LiPF_6 in EC/EMC (3/7 v/v) (STD electrolyte) were obtained from BASF. The additive was added as weight percent of the total mass of electrolyte.

Lithium catechol dimethyl borate (LiCDMB) was synthesized and added as 0.5 % (wt.) to the STD electrolyte. The composite cathode and anode electrodes were obtained from BASF. The composite $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode is composed of active material (92%), conductive carbon (4%) and PVDF binder (4%). The composite anode electrode is composed of graphite (ConocoPhilips, 95.7%) along with conductive carbon (0.5%) and CMC & SBR binder (3.8%). The cathode loading is 15.9 mg/cm^2 and loading of anode is 7.1 mg/cm^2 . 2032-type coin cells were built with cathode ($d = 14.7 \text{ mm}$) and

graphite anode ($d = 15.0$ mm), a Setela E20MM ($d = 19$ mm) separator, and 40 μ L of electrolyte in each cell in an Argon-filled glove box with a water content less than 0.1 ppm. Carbon black electrode (Super C65, $d = 15$ mm, BASF) half-cells were built with 100 μ L of electrolyte, a glass fiber (Whatman, $d = 15.6$ mm) separator and a Setela E20MM ($d = 19$ mm) separator. Cells were cycled on an Arbin Instruments battery cycler and the temperature was controlled with Fisher Scientific Isotemp Incubators.

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite cells were cycled at 25 $^{\circ}\text{C}$ initially with the following cycling protocol: C/20 D/20 for the first cycle; C/10 D/10 for the second and third cycles; and then C/5 D/5 for the remaining cycles at 25 $^{\circ}\text{C}$. After cycling at 25 $^{\circ}\text{C}$, cells were transferred to 55 $^{\circ}\text{C}$ and C/5 D/5 cycling was continued for an additional 30 cycles. Cells were charged with a CC-CV mode, constant current charge to 4.8 V followed with a constant voltage charge step at 4.8 V vs. LiC_6/C_6 until the current decreased to 10 % of the applied charging current. The cells were discharged to 4.25 V vs. LiC_6/C_6 at same constant current (CC mode). Coin cells were sealed with epoxy resin prior to 55 $^{\circ}\text{C}$ cycling and there was no evidence for cell leakage after cycling at 55 $^{\circ}\text{C}$. Cells were built in triplicate. Cell to cell variation was approximately 1%. Electrochemical impedance spectroscopy (EIS) was performed on a Bio-Logic Instrument after formation, 25 $^{\circ}\text{C}$ and 55 $^{\circ}\text{C}$ cycling at 100 % SOC. The perturbation is 10 mV with the frequency range 100 kHz-20 mHz. Cycled cells were disassembled in an argon glove-box, and cycled anodes/cathodes were harvested and rinsed with anhydrous dimethyl carbonate (DMC, Sigma, extra dry 99 %) 3 times to remove residual electrolyte, followed by vacuum drying overnight at room temperature.

Ex-situ surface analysis of the discharged electrodes was conducted. XPS measurements were carried out using a ThermoFisher K-Alpha spectrometer, under a focused monochromatised Al K α radiation ($\nu = 1486.6$ eV). Cells were disassembled in the glove box and electrode samples were rinsed 3 times with DMC and dried under vacuum at room temperature for 10 minutes. Samples were then sealed in a vial under controlled atmosphere of the glove box and stored for 24 hours. A transfer case (ThermoFisher) was used to avoid any contact with air/moisture. Peaks were recorded with constant pass energy of 50 eV with an energy resolution of 50 meV and charge neutralization. Peak positions and areas were optimized by a weighted least squares fitting method using 70% Gaussian, 30% Lorentzian line shapes using the Advantage (ThermoFisher) software.

The discharged electrodes were briefly (15 s) exposed to air during transfer to the SEM and TEM vacuum chamber. Surface morphology of the cycled electrodes was characterized by scanning electron microscopy (SEM, JEOL5900). The cycled electrodes were exposed to ultrasound in DMC solvent for 3 h to allow homogenous dispersion of the active materials in the solution, and then the dispersed solution was cast on a copper TEM grid (500 mesh) and dried overnight in a vacuum oven. The TEM grids were quickly transferred into the TEM chamber. Imaging was conducted using a JEOL JEM-2100F TEM (Peabody, MA) at 160 eV. The diameter of the beam was 5 nm, and low-dose imaging was employed to minimize electron-beam-induced changes to organic components in the surface layer.

2.3. Thermal stability

Samples for NMR spectroscopy were prepared in a glove box filled with high purity Ar followed by flame sealing under reduced pressure. Sealed samples were heated in a silicon oil bath at 85 °C. Samples were weighed before and after storage to confirm seal. NMR analyses were conducted on a Bruker 300 MHz NMR spectrometer. ^{19}F NMR spectra were referenced to LiPF_6 at 65.00 ppm and ^{31}P NMR spectra were referenced to LiPF_6 at -145.0 ppm, as described previously (31-33).

3. Results and Discussion

3.1. Characterization of Lithium catechol dimethyl borate (LiCDMB)

The as-synthesized product is purified via crystallizations, and characterized by NMR spectroscopy in D_2O (^1H , ^{11}B). The corresponding ^1H and ^{11}B NMR spectra are depicted in Figure 2. The singlet peak at 3.3 ppm is characteristic of the methoxyl group ($-\text{OCH}_3$) of the product, a small peak characteristic of residual wash solvent (DMC) can be observed at 3.8 ppm, and the peak ascribed to the residual H in D_2O is observed at 4.8 ppm. The singlet peak observed at 6.7 ppm is attributed to the aromatic protons of the product. The integrated ratio of methyl protons to aromatic protons is 4:6, which matches the structure of LiCDMB. A single peak characteristic of the product at 7.7 ppm is observed in the ^{11}B NMR spectrum, ^{11}B chemical shift of boric acid located between -20-0 ppm as a function of pH [49], suggesting LiCDMB doesn't decompose into boric acid in D_2O . The ^1H and ^{11}B NMR spectra support the isolation of a pure compound.

3.2. Thermal stability

The ^{19}F and ^{31}P NMR spectra of the STD electrolyte and STD with 0.5 % added LiCDMB before and after storage for 8-days at 85 °C are presented in Figure 3. The spectra are consistent with the addition of LiCDMB inhibiting the thermal decomposition of the LiPF_6 electrolyte. In both cases, the fresh electrolytes contain a single set of peaks in the ^{19}F and ^{31}P NMR spectra characteristic of LiPF_6 (33). The ^{19}F spectrum of the STD electrolyte after 8 days of storage at 85 °C reveals new peaks around -85 ppm characteristic of fluorophosphates ($\text{OPF}_x(\text{OR})_y$), in addition a small peak for LiF is observed at -155 ppm. After 8 days of storage at 85 °C the ^{19}F NMR spectrum of the electrolyte with added LiCDMB has a much lower concentration of peaks characteristic of $\text{OPF}_x(\text{OR})_y$, consistent with an inhibition of LiPF_6 decomposition (Figure 3a). The ^{31}P spectra further support the inhibition of electrolyte decomposition with added LiCDMB. The ^{31}P spectrum of the STD electrolyte stored at 85 °C for 8 days contains new peaks around 25 ppm characteristic of $\text{O=PF}_x(\text{OR})_y$. While the same peaks are present in the samples containing added LiCDMB, the intensity of the peaks is significantly diminished consistent with inhibition of the thermal decomposition of LiPF_6 (34, 35).

3.3. Electrochemical stability

Electrochemical stability of both the STD and the LiCDMB electrolyte have been evaluated on carbon black electrodes with linear sweep voltammetry at high and low potential (10, 34).

Anodic linear sweep voltammetry of Super C65/Li cells is presented in Figure 4. Additive oxidation is clearly observed above 3.5 V vs. Li/Li^+ as increased current,

compared to the STD electrolyte. Additional oxidation peaks are observed at 4.0 V vs. Li/Li⁺ and 4.4 V vs. Li/Li⁺ for the borate-containing electrolyte. Increased current is observed for the LiCDMB electrolyte up to 5.6 V vs. Li/Li⁺.

Cathodic linear sweep voltammetry of Super C65/Li cells is presented in Figure 5. For the STD electrolyte, the reduction peak of EC at 0.65 V vs. Li/Li⁺ can be clearly observed (35). For the electrolyte containing LiCDMB, the reduction peak for EC is observed at similar potential and intensity. This suggests that the presence of the LiCDMB additive does not affect EC reduction at low potential. There is no evidence for reduction of additive in the 3.0 V-0.7 V vs. Li/Li⁺ potential range.

Investigation of the electrochemical stability at both high and low potentials of the LiCDMB electrolyte suggests reactivity high potential. Additive oxidation is observed above 3.5 V vs. Li/Li⁺, before the first redox couple of the high voltage spinel situated at 4.3 V vs. Li/Li⁺ (Mn^{+III}/Mn^{+IV}). This reactivity may result in the generation of a cathode passivation layer which inhibits Mn²⁺ dissolution and further electrolyte oxidation.

3.4. Cycling performance

Cycling performance at 25 °C and 55 °C of LiNi_{0.5}Mn_{1.5}O₄/Graphite cells using the STD and LiCDMB electrolytes is presented in Figure 6. Additive concentration of 0.5 % (wt.) is found to be optimal for improved performance of high voltage cells. As seen from Figure 6a, the cell with the borate additive shows better capacity retention than the standard cell after 30 cycles at 55 °C. After 30 cycles at 55 °C, retention of 76 % of the original capacity is observed with added LiCDMB, while the cell with the STD electrolyte retains only 60 % of its original capacity.

Coulombic efficiencies of the cells with the STD and LiCDMB electrolytes are presented in Figure 6b. The first cycle efficiency at C/20 D/20 is higher for the cell containing the STD electrolyte than the cell containing the LiCDMB electrolyte. The difference may be due to additive oxidation at high potential (Figure. 4). However, after formation cycling the efficiency of cells containing the LiCDMB electrolyte is better than the cells containing the STD electrolyte, supporting a beneficial effect of the borate additive upon cycling. Upon cycling at 55 °C, the differences in coulombic efficiency are enhanced and the cell containing the LiCDMB electrolyte has 3 % higher efficiency than the cell containing the STD electrolyte. Despite a small decrease in the first cycle discharge capacity and efficiency, the long term cycling performance at 25 °C and 55 °C is significantly improved with the LiCDMB electrolyte.

3.5. Electrochemical impedance spectroscopy

Electrochemical impedance spectra of cells at a full state of charge (100 % SOC, 4.8 V) are measured at different stages upon cycling. The corresponding EIS Nyquist plots are depicted in Figure 7. After formation cycling, the impedance of the cell with STD electrolyte is found to be similar to the cell containing the LiCDMB electrolyte (Figure 7a) (39). After 20 cycles at 25 °C, the EIS of the cell with the STD electrolyte and the cell with the LiCDMB electrolyte remain very similar (Figure 7b), consistent with similar specific capacity (Figure 6). However, a significant change in EIS is observed upon cycling at 55 °C (Figure 7c). Impedance of the cell with the STD electrolyte is almost twice as large as the cell with the LiCDMB electrolyte. While additional electrolyte oxidation is observed for cells containing LiCDMB electrolyte

during formation cycling, the presence of the oxidation products of LiCDMB result in better capacity retention, efficiency, and lower impedance.

3.6. SEM/TEM imaging of electrodes

SEM imaging of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and graphite electrodes after cycling at 55 °C has been conducted in order to investigate electrode surface morphology. SEM micrographs of the fresh $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes and cathodes cycled with and without added LiCDMB are depicted in Figure 8. The fresh electrode consists of secondary spherical particles of ca. 8 μm . These spherical particles are composed of a primary rod structure several hundred nanometers in length. The fresh cathode particle surface is clean and smooth. After cycling with the STD electrolyte at 55 °C, the structure of the cathode particles is severely damaged. The particle damage likely results in increased impedance and reduced capacity retention of cells, as discussed above. For the cells cycled with the LiCDMB electrolyte, the original secondary and primary structure of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles is maintained after cycling at 55 °C. The surface of the primary particle is covered by a thick CEI. Maintenance of the original structure of the cathode and formation of a passivating CEI contributes to enhanced cycling performance of the cells at 55 °C.

SEM micrographs of the fresh graphite electrode and graphite anodes cycled with or without added LiCDMB are depicted in Figure 9. The surfaces of the fresh graphite electrode particles have sharp edges, and are primarily composed of flake-like structures. After cycling with the STD electrolyte, the graphite surface becomes very rough and non-uniform with many small particles due to the deposition of electrolyte decomposition

products on the surface of the graphite. Upon cycling with the LiCDMB electrolyte, a more uniform smooth layer is observed on the graphite surface.

Electrodes extracted from graphite / $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells cycled at 55 °C have been analyzed by TEM (Figure 10). Both fresh $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and graphite electrodes have sharp edges. After cycling with the STD electrolyte, inhomogeneous coverage of the cathode surface is observed. Alternatively, the surface of the cathode cycled with the LiCDMB electrolyte has a more uniform surface film (Figure 4). TEM images of the graphite electrode cycled with the STD electrolyte reveal significant concentrations of electrolyte decomposition products. The SEI is grainy and uneven, as observed by SEM above. The graphite anode cycled with the LiCDMB electrolyte has a thinner but more continuous surface layer. Thus, TEM images are in agreement with SEM images: addition of LiCDMB results in a thicker CEI on the high voltage cathode, and a thinner but more uniform SEI on the graphite anode.

3.7. XPS

3.7.1. Relative atomic concentrations

In order to corroborate cycling performance of graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells with surface chemistries of the electrodes, XPS has been conducted on both $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and graphite electrodes fresh and after cycling. Relative atomic concentrations of elements detected on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes fresh and cycled at 55 °C in both the STD and LCDMB electrolytes are presented in Figure 11. The cathode cycled with the STD electrolyte has a reduced concentration of C 1s and inorganic O 1s (metal oxide) due to the deposition of organic components of the CEI. Increased concentration of

organic O 1s (C-O, C=O) confirms the generation of a new cathode-electrolyte interface. Relative atomic concentrations of elements detected on the cathode cycled with the LCDMB electrolyte indicates that the amount of organic species deposited on the surface is further increased compared to the cathode cycled with the STD electrolyte. A significant increase of organic O 1s along with decrease of the Mn 2p and inorganic O 1s suggest significant coverage of the electrode surface. Therefore, addition of the LiCDMB additive to the STD electrolyte allows the deposition of a thicker passivating CEI, likely due to the oxidation of LiCDMB at high potentials (Figure 4).

Relative atomic concentrations of elements detected on the graphite anode cycled at 55 °C with both the STD and LCDMB electrolytes are compared in Figure 12 to the fresh graphite electrode. The graphite electrode cycled with the STD electrolyte has a decrease in the concentration of C, and increases in the concentrations of O, F, P, and Mn consistent with the generation of an SEI. A high concentration of Mn is detected on the graphite electrode cycled with the STD electrolyte, consistent with manganese dissolution from the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ during cycling at 55 °C and deposition at low potential on the anode. The graphite anode cycled with the LiCDMB electrolyte shows increased concentrations of O 1s, and F 1s ($\text{LiF} + \text{Li}_x\text{PO}_y\text{F}_z$) due to the generation of the SEI. The decreased concentration of Mn 2p is significant, consistent with the LiCDMB electrolyte inhibiting Mn dissolution from the high voltage spinel (Figure 11).

3.7.2. XPS element spectra

The O 1s and C 1s core spectra of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes are depicted in Figure 13. The O 1s spectrum of the fresh cathode is dominated by the metal oxide at

529.0 eV (37, 38). The cathode cycled with STD electrolyte contains the same O-M (M=Mn, Ni) peak at 529.0 eV, along with new peaks at higher binding energy which correspond to electrolyte decomposition products on the cathode surface characteristic of C=O, C-O, and **O**-C=O bonds respectively at 531.2 eV, 532.5 eV, and 533.0 eV (37, 38, 42). The differences are greater for the cathode cycled with LiCDMB electrolyte (Figure 10). The peak characteristic of the metal oxide at 529.0 eV is very weak while the peaks characteristic of electrolyte decomposition products have high intensity. In addition, a new small peak is observed at ~535 eV which results from the oxidation of LiCDMB and is likely the result of shake up satellites from the presence of aromatic species on the cathode surface (37, 39-41, 47, 48). This suggests greater coverage of the cathode surface in the presence of added LiCDMB (Figure 4).

The C 1s core spectra of the cathodes reveal significant differences in the electrode surfaces for the different electrolytes. The fresh electrode contains C 1s peaks characteristic of C-C (284.3 eV) and C-H (285.6 eV), along with peaks of the PVdF binder at 286.5 eV (-CH₂-) and 290.7 eV (-CF₂-) (37-39, 42). The C 1s spectrum of the cathode cycled with the STD electrolyte shows the deposition of organic species that comprise the CH₂ (285.6 eV), C-O (286.5 eV), C=O (ca. 288 eV), and O-C=O (289.9 eV) groups (37, 39, 42, 43). The low intensity of the PVdF peaks at 290.7 eV (-CF₂-) and at 286.5 eV (-CH₂-) suggests that the active material is mostly covered by the constituents of the CEI. The XPS spectra of the cathode cycled with the LiCBMD electrolyte has a thicker surface film since the peaks associated with PVdF are no longer visible in the C 1s spectrum which confirms coverage of the cathode material. Functional groups of the

CEI at 284.3 eV (C-C), 285.6 eV (C-H), 286.5 eV (C-O), ca. 288 eV (C=O), and 289.9 eV (O-C=O) are observed in the C 1s spectra.

The C 1s and O 1s XPS spectra of the graphite electrodes are depicted in Figure 14. The C 1s spectrum of the fresh graphite shows high intensity of the C-C peak at 284.3 eV, along with CO_x peaks of the CMC binder (40). The anode cycled with the STD electrolyte contains C 1s peaks characteristic of lithium alkyl carbonates and lithium carbonate from carbonate solvent reduction as expected from SEI formation (40, 41). Similar peaks are also observed in the C 1s spectrum of the anode cycled with the LiCDMB electrolyte. An additional C 1s aromatic shake-up satellite, is observed at 291.5 eV (40, 41).

The O 1s spectrum of the fresh graphite electrode contains O 1s peaks of the CMC binder, along with the Auger peak of sodium at 536 eV (38). The O 1s spectrum of the graphite electrode cycled with the STD electrolyte contains peaks characteristic of electrolyte decomposition products in the SEI such as lithium alkyl carbonates and lithium carbonate: 531.2 eV, 532.5 eV, and 533.2 eV (37, 39-41). The O 1s spectrum of the graphite electrode cycled with the LiCDMB electrolyte contain similar O 1s peaks. Nevertheless, a fourth peak is observed at 535.2 eV, consistent with shake up satellites from the presence of aromatic species and correlates with the C 1s peak at 291.5 eV (40, 41). The addition of LiCDMB results in the deposition aromatic borates on the graphite anode which are not present on the electrode cycled with the STD electrolyte.

The Li 1s, Mn 3p, and Ni 3p spectra of the graphite anodes cycled in electrolytes with and without added LiCDMB are presented in Figure 15. The Li 1s, Mn 3p, and

Ni 3p spectra of the anode cycled with the STD electrolyte contain peaks at 49 eV (Mn^{+IV}) and 48 eV (Mn^{+III}), 69 eV (Ni^{+IV}) (44), and LiF at 56 eV (Figure 15b). This indicates that transition metal dissolution from the cathode surface is occurring followed by deposition on the anode damaging the SEI (Figure 13b) (45, 46). Much weaker intensity XPS peaks associated with Ni and Mn are observed on the graphite anode cycled with the LiCDMB electrolyte (Figure 15c). The reduced concentration of Ni and Mn on the anode likely results from the generation of a cathode passivation layer composed of the oxidation products of LiCDMB which inhibits Mn and Ni dissolution. While the concentration of B is surprisingly low, the B concentration is unfortunately difficult to determine due to overlap of the B1s peak with the P2s peak.

An XPS investigation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and graphite electrodes cycled with STD electrolyte with or without added LiCDMB indicates that incorporation of LiCDMB results in the generation of a surface film on the high voltage cathode. The presence of the novel surface film inhibits Mn and Ni dissolution and subsequent deposition on the graphitic anode. The presence of the cathode passivation layer results in enhanced cycling performance of the graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells.

4. Conclusions

Performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /Graphite cells cycled up to 4.8 V at 55 °C with 1.2 M LiPF_6 in EC/EMC (3/7 v/v, STD electrolyte) with and without 0.5 % (wt.) lithium catechol dimethyl borate (LiCDMB) has been investigated. Upon cycling at 55 °C, cells with 0.5 % LiCDMB have improved capacity retention and better cycling efficiency. After cycling the electrodes were extracted from the cells and ex-situ surface analysis

was conducted via a combination of SEM, TEM, and XPS. Analysis of the cathode reveals the presence of LiCDMB reaction products which generates a thick passivation layer on the high voltage spinel. The novel cathode electrolyte interface (CEI) prevents the dissolution of transition metal ions and subsequent migration and deposition on the graphite anode. Analysis of the anodes reveals that incorporation of LiCDMB results in the formation of a thin but continuous SEI which a much lower concentration of Mn than observed on anodes cycled with the STD electrolyte. Incorporation of LiCDMB has also shown to inhibit the thermal decomposition of the STD electrolyte at 85 °C. The incorporation of the novel additive, LiCDMB, results in improved performance and changes to the electrode surface chemistry for graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells cycled to high potential.

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Figure 3-1. Chemical structure of lithium salt anions: (a) $\text{B}(\text{O}(\text{CO}_2)_2\text{O})_2^-$ (BOB⁻), (b) $\text{BF}_2(\text{O}(\text{CO}_2)_2\text{O})^-$ (DFOB⁻), and (c) a new non-fluorinated anion $\text{B}(\text{OMe})_2(\text{O}(\text{C}_6\text{H}_4)\text{O})^-$ (CDMB⁻).

Figure 3-2. (Top) ¹H and (bottom) ¹¹B NMR spectra of lithium catechol dimethyl borate (LiCBMD) in D₂O.

Figure 3-3. (a) ^{19}F (a) and (b) ^{31}P NMR spectra of electrolytes before storage and after a 8-day storage at 85 °C: (in black) the STD and (in red) the STD + 0.5 % LiCDMB electrolytic solutions.

Figure 3-4. Anodic linear sweep voltammetry at 25 °C of Super C65/Li cells (sweep rate of 0.1 mV.s⁻¹) using (in black) the EC/EMC (3/7) 1.2 M LiPF₆ and (in red) EC/EMC (3/7) 1.2 M LiPF₆ + 0.5 % LiCDMB electrolytes.

Figure 3-5. Cathodic linear sweep voltammetry at 25°C of Super C65/Li cells (sweep rate of 0.1 mV.s^{-1}) using (in black) the EC/EMC (3/7) 1.2 M LiPF_6 and (in red) EC/EMC (3/7) 1.2 M LiPF_6 + 0.5 % LiCDMB electrolytes.

Figure 3-6. (a) Cycling retention and (b) coulombic efficiency of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Graphite}$ cells (C/5 D/5, cutoff potentials at 25 °C and 55 °C: 4.80 V-4.25 V vs. LiC_6/C_6) using the STD electrolyte with (in red) or without (in black) added LiCDMB.

Figure 3-7. EIS spectra at full state of charge (4.8 V vs. LiC_6/C_6) of $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}_x\text{C}_6$ cells using the (in black) STD and (in red) STD + 0.5 % LiCDMB electrolyte after (a) formation cycling, (b) 20 cycles at 25 °C, and (c) 30 additional cycles at 55 °C.

Figure 3-8. SEM micrographs of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes harvested from cells after overall cycling at 25 °C and 55 °C using the STD and STD + 0.5 % LiCDMB electrolytes.

Figure 3-9. SEM micrographs of the graphite electrode and graphite anodes harvested from cells after overall cycling at 25 °C and 55 °C using the STD and STD + 0.5 % LiCDB electrolytes.

Figure 3-10. TEM images of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and graphite electrodes harvested from cells after 50 cycles at 25 °C and 45 °C using the STD and STD + 0.5 % LICDMB electrolytes.

Figure 3-11. Relative atomic concentrations of elements present on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes after overall cycling at 25 °C and 55 °C in the STD and STD + 0.5 % LCDMB electrolytes.

Figure 3-12. Relative atomic concentrations of elements present on the graphite electrode and graphite anodes after overall cycling at 25 °C and 55 °C in the STD and STD + 0.5 % LCDMB electrolytes.

Figure 3-13. (On the left) O 1s and (on the right) C 1s core spectra of (a) the fresh $LiNi_{0.5}Mn_{1.5}O_4$ electrode and $LiNi_{0.5}Mn_{1.5}O_4$ cathodes cycled at 55 °C with the (b) STD and (c) STD + 0.5 % LiCDBM electrolytes.

Figure 3-14. (On the left) C 1s and (on the right) O 1s core spectra of (a) the fresh graphite electrode and graphite anodes cycled at 55 °C with the (b) STD and (c) STD + 0.5 % LiCDMB electrolytes.

Figure 3-15. Li 1s, Mn 3p, and Ni 3p core spectra of (a) the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode and graphite anodes cycled in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Gr}$ cells with (b) the STD and (c) STD + 0.5 % LiCDMB electrolytes.

Chapter 4

Improving the Performance of Graphite/LiNi_{0.5}Mn_{1.5}O₄ Cells with Added N,N-dimethylformamide Sulfur Trioxide Complex

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Abstract

N,N-dimethylformamide sulfur trioxide complex (DMF-SO₃) is attempted to improve performance of LiNi_{0.5}Mn_{1.5}O₄/graphite cells cycled up to 4.8 V at 25 °C and 45 °C with the 1.2 M LiPF₆ in EC/EMC (3/7, v/v) baseline electrolyte. When 0.1 % DMF-SO₃ is added into the standard electrolyte, capacity retention and coulombic efficiency of LiNi_{0.5}Mn_{1.5}O₄/graphite cells are significantly enhanced, after 20 cycles at 25 °C, as well as after 50 cycles at 45 °C. Ex-situ characterizations using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) demonstrate that a uniform interfacial film is formed on the LiNi_{0.5}Mn_{1.5}O₄ surface, which contains decomposition products of DMF-SO₃.

1. Introduction

Lithium ion batteries are widely used for portable electronics and are currently being incorporated into electric vehicles due to the high energy density (1, 2). However, there is significant interest in increasing the energy density of lithium-ion batteries (3). One method to achieve higher energy density is increasing the operating potential of the cathode material. Most commercial lithium-ion batteries contain a lithiated transition metal oxide cathode that typically operates at 4.0 V vs. Li/Li⁺ (3, 4). Cathode materials with a potential over 4.0 V have been developed, including LiMnPO₄ (4.1 V vs. Li/Li⁺) (5-7), LiNiPO₄ (6, 8) and LiCoPO₄ (4.8 V vs. Li/Li⁺) (8, 9), and LiNi_{0.5}Mn_{1.5}O₄. Although the high operating voltage (4.7 V vs. Li/Li⁺) of the LiNi_{0.5}Mn_{1.5}O₄ spinel cathode offers high power capability, its commercialization has been hampered by severe capacity fade (10). The capacity deterioration is particularly pronounced at elevated

temperatures and in full cells employing a graphite anode (10). The failure mechanisms of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells at high voltage and elevated temperature have been recently investigated (11-15). Electrolyte decomposition, electrode/electrolyte interface degradation, gassing, and transition metal dissolution are the leading factors reported for performance fade.

Various methods have been proposed to inhibit the detrimental reactions on high voltage cathode materials. Inert surface coatings on the cathode materials, such as ZnO (16), Al_2O_3 (17), BiOF (18), Bi_2O_3 (19), SiO_2 (20), ZrO_2 (21) and phosphates like FePO_4 (22), AlPO_4 (23), Li_3PO_4 (24), $\text{Li}_4\text{P}_2\text{O}_7$ (25) have been reported to improve performance at high potential and elevated temperature. Alternatively there have been several investigations of the incorporation of cathode film forming additives that are sacrificially oxidized and/or reduced on the cathode surface to generate a cathode passivation layer (12, 26, 27). Among these additives, lithium bis(oxalate)borate (LiBOB) has been extensively investigated and provides multiple beneficial effects in the battery system (28). However, oxidation of LiBOB on the delithiated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface at high potential ($> 4.5 \text{ V vs. Li/Li}^+$) is accompanied by CO_2 gas generation, which limits its practical application (29). Thus it is important to develop novel cathode film forming additives to improve the performance of high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes.

An alternative class of sulfur-based compounds has been investigated in the past literature to have a favorable impact on the SEI of graphite such as higher diffusion of Li^+ ions (30, 31). Their anodic instability presents the potential to form passive layers on high voltage cathodes (32). These include SO_2 (33, 34), CS_2 (35), polysulfides S_x^{2-} (30, 36), cyclic alkyl sulfites, such as ethylene sulfite (37), propylene sulfite (38), and aryl sulfites

(38), propane sultone (39), butyl sultone (40), functionalized sulfones (41), and sulfates (42).

In the present report, a novel sulfonate additive, N,N-dimethylformamide Sulfur Trioxide Complex (DMF-SO₃), is investigated as a cathode film forming additive in order to stabilize the LiNi_{0.5}Mn_{1.5}O₄ interface, along with a favorable impact of sulfur on the SEI of graphite. Experimental investigations by SEM, TEM, XPS, and FT-IR are conducted to understand the contribution of added DMF-SO₃ to improve interfacial stability of both the LiNi_{0.5}Mn_{1.5}O₄/electrolyte and graphite/electrolyte interfaces.

2. Experimental

The baseline electrolyte is 1.2 M LiPF₆ in EC/EMC (3/7 by vol). Battery grade of carbonates solvents and lithium hexafluorophosphate (LiPF₆) were obtained from BASF. Additive was added in weight percentage based on the total mass of electrolyte.

The additive, DMF-SO₃ (99%), was purchased from Sigma Aldrich, and used as is without further purification. 2032-type cells were built with Elexcel cathode (d = 14.7 mm) and Elexcel graphite anode (d = 15.0 mm), a piece of Setela E20MM (d = 16 mm) separator, and 100 μ L of electrolyte in each cell in an Argon-filled glove box in which the water content is smaller than 0.1 ppm. The cells were cycled on an Arbin cycler with the temperature controlled by Fisher Scientific Isotemp incubators.

LiNi_{0.5}Mn_{1.5}O₄/graphite cells were cycled at 25 $^{\circ}$ C initially with the following cycling protocol: C/20, D/20 for the first cycle; C/10, D/10 for the second and third cycles; and then C/5, D/5 for the next 17 cycles. After cycling at 25 $^{\circ}$ C, cells were transferred to 45 $^{\circ}$ C to perform C/5 D/5 cycling for 50 cycles. Cells were charged

following a CC-CV procedure, a constant current charge to 4.8 V followed by a constant voltage charge at 4.8 V vs. LiC_6/C_6 until the current decreased to 10 % of the applied charging current. Then, cells were discharged to 4.25 V vs. LiC_6/C_6 at same constant current (CC mode).

Electrochemical impedance spectroscopy (EIS) was performed on a Bio-Logic instrument after both cycling at 25 °C and 45 °C at OCV after discharge down to 4.25 V. Perturbation was 10 mV and the frequency range was 100 kHz-10 mHz. Cycled cells were disassembled in an argon glove-box, and cycled anodes/cathodes were harvested and rinsed with anhydrous dimethyl carbonate (DMC, Sigma, extra dry 99%) 3 times to remove residual electrolyte, followed by vacuum drying overnight at room temperature. The discharged electrodes were briefly (15 s) exposed to air during transfer to the SEM and TEM vacuum chamber. Surface morphology of the cycled electrodes was characterized by scanning electron microscopy (Zeiss Sigma FE-SEM). The cycled electrodes were exposed to ultrasound in DMC solvent for 3 h to allow homogenous dispersion of the active materials in the solution, and then the dispersed solution was cast on a copper TEM grid (500 mesh) and dried overnight in a vacuum oven. The TEM grids were quickly transferred into the TEM chamber. Imaging was conducted using a JEOL 2100 transmission electron microscope at 160 eV.

XPS measurements were carried out using a ThermoFisher K-Alpha spectrometer, under a focused monochromatised Al $\text{K}\alpha$ radiation ($\nu = 1486.6 \text{ eV}$). Cells were disassembled in the argon glove box and the electrodes were rinsed 3 times with DMC (3 x 500 L) and dried under vacuum at room temperature for 10 minutes. Samples were then sealed in a vial under controlled atmosphere of the glove box and stored for 24 hours.

A transfer case (ThermoFisher) was used to avoid any contact with air/moisture. Peaks were recorded with constant pass energy of 50 eV with an energy resolution of 50 meV and charge neutralization. Peak positions and areas were optimized by a weighted least squares fitting method using 70% Gaussian, 30% Lorentzian line shapes using the Advantage (ThermoFisher) software.

FTIR spectra were acquired on Bruker Tensor 27 with Attenuated Total Reflectance (ATR) accessory with Germanium crystal, 512 scans with a resolution of 4 cm^{-1} .

3. Results and Discussion

3.1. Electrochemical windows of electrolytes

Electrochemical stability of electrolytes is evaluated at high and low potential using carbon black composite electrodes (13, 43). Anodic stability of the baseline electrolyte and the DMF-SO₃-based compositions is presented in Figure 1. The baseline formulation presents the best anodic stability with the lowest current values during the anodic scan. When 0.1% DMF-SO₃ is added to the standard formulation, increased current is observed at potentials starting from 4.8 V vs. Li/Li⁺, due to DMF-SO₃ oxidation. Increased content of DMF-SO₃, i.e. 1.0 %, show significant increase of the anodic current, along with new oxidation peaks at 4.7 V, 5.1 V, and 5.3 V vs. Li/Li⁺ that might be attributed to DMF-SO₃ decomposition. Similar current values in the 5.6 V-6.0 V potential range for the STD and 0.1% DMF-SO₃ electrolytes is likely due to PF₆⁻ insertion into the carbon black particles (44-46).

Cathodic scans of carbon black/Li cells with the same baseline and DMF-SO₃ electrolytes are presented in Figure 2. EC reduction is systematically observed at 0.65 V vs. Li/Li⁺ for the three electrolyte formulations (47). No other clear reduction peak is seen with the 0.1% DMF-SO₃ additive. When it comes to the 1.0% DMF-SO₃ electrolyte, additional reduction peaks of strong intensity are observed at 2.4 V and 1.0 V vs. Li/Li⁺. For the three electrolyte formulations, peak intensity of EC reduction is about the same, which suggests the DMF-SO₃ additive does not affect passivation of graphite by EC reduction during the first cathodic scan.

Electrochemical stability of the three electrolytes is checked in LiNi_{0.5}Mn_{1.5}O₄/C₆ full cells. Voltage profiles of such cells during the first cycle at C/20 D/20 are depicted in Figure 3. Charge capacity of 162.9 mAh.g⁻¹ is obtained by the baseline electrolyte while higher charge capacities of 166.7 mAh.g⁻¹ and 189.6 mAh.g⁻¹ are reached with the 0.1 % and 1.0 % DMF-SO₃ electrolytes, respectively. Extra capacity of LiNi_{0.5}Mn_{1.5}O₄/C₆ cells is likely due to electrolyte decomposition at both high (Figure 1) and low (Figure 2) potentials on the LiNi_{0.5}Mn_{1.5}O₄ and graphite interfaces. As more electrolyte oxidation and reduction is caused by DMF-SO₃ addition in the baseline electrolyte, more charge capacity is obtained during the first cycle.

Inset data graph of Figure 3 shows the residual current at 4.8 V measured during the constant voltage step at high potential. This shows that more electrolyte decomposition is obtained in presence of the DMF-SO₃ additive. Consequently, higher additive concentration causes higher residual current at 4.8 V, which means more electrolyte oxidation/reduction. Nevertheless, a different impact on discharge capacity of cells can be observed during the first cycle. A beneficial effect of DMF-SO₃

decomposition is obtained with the 0.1% concentration. Higher discharge capacity is obtained: 138.0 mAh.g⁻¹ instead of 135.2 mAh.g⁻¹. On the contrary, 1.0 % additive concentration is detrimental to LiNi_{0.5}Mn_{1.5}O₄/C₆ cells, with reduced discharge capacity of 120.7 mAh.g⁻¹.

Test of electrochemical windows of electrolytes with and without added DMF-SO₃ in carbon black half-cells and LiNi_{0.5}Mn_{1.5}O₄/C₆ full cells shows more electrolyte decomposition with the presence of the additive in the baseline solution. Addition of a high content of DMF-SO₃ causes both strong electrolyte oxidation and reduction that are detrimental to full cells. Addition of a reasonable amount of DMF-SO₃, i.e. 0.1%, causes slight increase of electrolyte decomposition. Nevertheless, this additional electrolyte decomposition is beneficial to LiNi_{0.5}Mn_{1.5}O₄/C₆ cells with a slight increase of discharge capacity during the first cycle at C/20 D/20.

3.2. Cycling performance

Cycling performance of LiNi_{0.5}Mn_{1.5}O₄/C₆ cells at 25 °C and 45 °C employing the sulfonate additive is presented in Figure 4.

Capacity and capacity retention of cells built with 0.1% DMF-SO₃ is increased as compared to the one employing the baseline electrolyte (Figure 4a). On the opposite, cells with 1.0 % additive show much lower capacity and much faster capacity fade (Figure 4a). This is likely due to much more electrolyte reduction and oxidation at both high (Figure 1) and low (Figure 2) interfaces. At 45 °C, capacity retention of cells with 0.1 % DMF-SO₃ is improved significantly. After 20 cycles at 25 °C and 50 cycles at 45 °C, 74 % of the original capacity can be retained while the baseline cell only retains

67.7 %. Coulombic efficiency of cell with 0.1 % DMF-SO₃ is about 1.0 % higher than that of standard cell (Figure 4b) showing that the addition of 0.1 % DMF-SO₃ improves the cycling performance of high voltage cells significantly. For the cell with 1.0 % DMF-SO₃, after cycling at 45 °C for 50 cycles, the capacity fades much faster than previous room temperature cycles, indicating major degradation of the cell chemistry (Figure 4b). Much lower coulombic efficiency of such cells, also with the diminution of this efficiency during cycling at 45 °C suggests the deposition of resistive passivation films on the electrode/electrolytes interfaces.

3.3. Electrochemical impedance spectroscopy

EIS Nyquist plots of cells after both cycling at 25 °C and 45 °C with the STD and 0.1 % DMF-SO₃ electrolytes are shown in Figure 5. After cycling at 25 °C, impedance spectra of Li_xNi_{0.5}Mn_{1.5}O₄/Li_xC₆ cells presents two semi-circles. The first semi-circle in high frequency range is attributed to the impedance contribution of passive layers, while the second one in the medium-low frequencies is ascribed to charge transfer impedance (48-50). Lower impedance of the DMF-SO₃ is measured after 25 °C cycling, with lower impedance for both the first and second semi-circle contributions. This means that passive layers on electrode/electrolyte interfaces are of reduced resistance with added DMF-SO₃. After cycling at 45 °C, impedance spectra of the STD and DMF-SO₃ cells have different shapes. The DMF-SO₃ cell conserves a two semi-circle spectrum. Impedance contribution of the first semi-circle is notably increased after high temperature cycling, while the second is barely increased. Impedance of the STD cell is significantly higher than the one of the DMF-SO₃ cell. The sulfonate additive is then able to prevent impedance rise of cells at both 25 °C and 45 °C. Reduced resistance of cells with DMF-

SO₃ enhances cycling retention and efficiency of high voltage cells. Nevertheless, addition of a higher amount of additive (not showed here) drastically increases cell impedance causing reduced capacity and poor capacity retention.

3.4. SEM/TEM imaging of electrodes

SEM imaging is conducted on the graphite and LiNi_{0.5}Mn_{1.5}O₄ electrodes cycled at 45 °C in order to investigate their surface morphology. The SEM micrographs of graphite electrodes of cells with and without the DMF-SO₃ additive are displayed in Figure 6. Fresh graphite surface is very smooth and it is composed of flake-like structure. For the STD graphite anode, the surface is very rough and grainy with many visible particles after cycling at 45 °C. On the contrary, the graphite anode cycled in the 0.1 % DMF-SO₃ electrolyte solution shows a uniform SEI formation. Interestingly, the surface of the anode cycling with 1.0 % DMF-SO₃ is strongly and deeply cracked. During cycling with such additive concentration, the integrity of the graphite electrode is no longer assured.

The damaging impact of DMF-SO₃ at 1.0 % additive concentration is also confirmed on the LiNi_{0.5}Mn_{1.5}O₄ cathode side (Figure 7). Many cracks are also observed, along with the collapse of the cathode grains material, which present much smaller particles, thicker surface film is also observed on the surface of cathode in higher magnification figure. This explains much larger impedance (not showed here) and capacity loss observed for cells with 1.0 % additive, especially at higher temperature. The cathode cycled with 0.1% DMF-SO₃ retains the initial structure of the fresh cathode material, and a very uniform CEI formed on the surface of cathode. Maintenance of the

integrity of the cathode material and well coverage of CEI is beneficial for cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{C}_6$ cells over cycling at 45 °C.

TEM is conducted on the same graphite and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes after cycling at 45 °C (Figure 8

Figure). TEM images reveal the presence of a surface layer that is deposited on both the anode and cathode particles after cycling. For both the anodes and cathodes cycled with the STD electrolyte, a rough surface with discontinuous deposition of SEI/CEI (*Cathode Electrolyte Interface*) material is observed. Quite uniform and thin surface films are deposited on the graphite and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface when 0.1 % DMF- SO_3 is employed as additive in the STD formulation, which contributes to better cycling retention of cells. Much greater differences in surface morphology are observed when it comes to the 1.0 % DMF- SO_3 electrodes. On the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode, a very thick layer of deposited material is observed on the metal oxide particle, and more discontinuous SEI is seen on the graphite material, as compared to 0.1 % DMF- SO_3 , which mostly consists in the formation of agglomerates. These types of SEI and CEI morphologies are then likely to cause important impedance growth and much larger capacity loss (Figure 5).

Study of surface morphologies of cycled graphite and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes conducted by SEM and TEM shows important difference depending on the presence of the DMF- SO_3 additive and its concentration. At 0.1 % DMF- SO_3 concentration, uniform passive layers of graphite are observed, while the integrity of the cathode oxide grains is maintained. Nevertheless, TEM imaging of the same electrode exhibits a thicker CEI than

in the case of the STD cathode material. Formation of a more covering then protective CEI could explain the better cycling retention of cells that employ the STD + 0.1 % DMF-SO₃ electrolyte. Higher concentration of DMF-SO₃ (i.e. 1.0 %) is detrimental to surface chemistries of both the cathode and anode, with extremely thick CEI deposition and sparse SEI, respectively.

3.5. XPS

In order to relate cycling performance of LiNi_{0.5}Mn_{1.5}O₄/C₆ cells with surface chemistries of the electrodes, XPS is conducted on both LiNi_{0.5}Mn_{1.5}O₄ and graphite electrodes that have been cycled at 25 °C and 45 °C.

O 1s and C 1s core spectra of the LiNi_{0.5}Mn_{1.5}O₄ electrodes are presented in Figure 9. O 1s spectrum of the fresh cathode is dominated by the O²⁻ ions of the crystal lattice at 529.0 eV (48, 51, 52). The STD cathode presents the same O-M (M=Mn, Ni) peak at 529 eV, along with the apparition of new peaks at higher binding energy that correspond to organics species, constituents of the CEI (48, 51, 52). The O-M O 1s peak is diminished for the DMF-SO₃ cathodes, as compared to the ones of organic species, consistent with TEM imaging (Figure 8). This suggests higher coverage of the cathode material due to augmented electrolyte oxidation (Figure 1). Nevertheless, higher intensity of the O-M peak with 0.1 % DMF-SO₃ implies a thinner CEI deposition than the one with 1.0 % DMF-SO₃. For the later, this O-M peak is almost disappeared because of a complete coverage of the cathode material by surface species, consistent with TEM imaging (Figure 8). C 1s core spectra of the same cathodes shows important differences when cycled in the three electrolytes. The fresh cathode shows C 1s peaks of C-C

(284.3 eV), C-H (285.6 eV), along with peaks of the PVdF binder at 286.5 eV (CH₂) and 290.7 eV (CF₂) (48, 51-53). C 1s spectrum of the STD cathode shows the deposition of organic species that comprise the CH₂ (285.6 eV), C-O (286.5 eV), C=O (ca. 288 eV), and O-C=O (289.9 eV) groups (48, 51-53). PVdF peaks of CF₂ (290.7 eV) and CH₂ (286.5 eV) confirm that the active material is not fully covered by the constituents of the CEI (53). The fact that these two peaks of PVdF are no longer visible in the C 1s spectrum of the 0.1% DMF-SO₃ cathode evidences important coverage of the cathode. Functional groups of the CEI at 284.3 eV (C-C), 285.6 eV (C-H), 286.5 eV (C-O), ca. 288 eV (C=O), and 289.9 eV (O-C=O) are indeed the only peaks of the C 1s spectra. C 1s spectrum of the 1.0% DMF-SO₃ cathode shows interesting feature. Two peaks of the same intensity (290.7 eV and 286.5 eV), along with the one of C-C (284.3 eV) suggest that PVdF is the main constituent of the CEI despite the presence of the traditional functional groups (C-O, C=O, O-C=O) coming from carbonate oxidation on the cathode. This is likely due to the PVdF binder dissolution by the DMF-SO₃ additive when present at 1.0% concentration in the baseline electrolyte (54). Binder dissolution is then responsible for the thick and resistive CEI observed by TEM (Figure 8) and poor cycling performance at 25 °C and 45 °C (Figure 4).

Additive reactivity on the high voltage cathode is checked through the N 1s and S 2p spectra (Figure 10). N 1s spectra of the DMF-SO₃ cathodes show similar shape. N 1s signal is nevertheless low and only one component of the N 1s is identified at 401 eV (55, 56). S 2p spectra of the same cathodes are very similar and show decomposition of the initial -SO₃ group (168.3 eV) (57), into sulfites (RSO₂Li/Li₂SO₃,

166 eV) (55, 56, 58) and sulfides (163 eV) (57-61). S 2p signal is nevertheless stronger in the case of 1.0% DMF-SO₃ because of a higher additive content in the bulk electrolyte.

C 1s and O 1s core spectra of the graphite electrodes are presented in Figure 11. C 1s spectrum of the fresh graphite shows strong intensity of the C-C peak at 284.3 eV, along with CO_x peaks of the CMC binder. The STD anode shows C 1s traditional peaks of C-C (284.3 eV), C-H (285.6 eV), C-O (286.5 eV), C=O (ca. 288 eV), O-C=O (289.9 eV), corresponding to the deposition of the organic SEI issued from carbonate reduction (51, 62, 63). The same peaks are also seen for the C 1s spectra of the 0.1% DMF-SO₃ and 1.0% DMF-SO₃. Nevertheless, higher intensity of the C 1s signal suggests higher C 1s concentration on the surface and possibly thinner SEIs when the sulfonate additive is present in the baseline formulation. Consequently, the peak of partially lithiated graphite is observed at ca. 283 eV (61). This peak is even more intense with the 1.0% DMF-SO₃ anode, showing less coverage of the graphite electrode, consistent with the observation of agglomerates instead of a uniform and thin film by TEM (Figure 8). F 1s spectra of the anodes are quite similar for the STD and DMF-SO₃ graphite with two F 1s contributions of LiF (285 eV) and Li_xPF_y/Li_xPF_yO_z (287 eV) (51, 63). F 1s becomes much more intense for the 1.0 % DMF-SO₃ graphite, together with the apparition of a strong peak of LiF (685 eV).

Additive reactivity on the graphite anode is checked through the N 1s and S 2p spectra (Figure 12). N 1s spectra are of stronger intensities than that of the cathodes (Figure 10). N 1s spectra of the two DMF-SO₃ anodes evidence reduction of the additive with the apparition of new peaks. Original peak of the additive powder at ca. 401 eV is present for the two electrodes. Nevertheless, a new peak at ca. 400 eV appears for the 0.1%

DMF-SO₃ graphite that can be attributed to LiN(CH₃)₂CHO formed after the release of the -SO₃ group. More additive reduction is achieved at higher concentration with higher N 1s signal intensity and the apparition of a second reduction peak at ca 399 eV. Sulfur deposition is also observed on the graphite surface. Nevertheless, S 2p is hardly detected for the 0.1% DMF-SO₃ graphite, unlike the cathode surface. For the 1.0% DMF-SO₃ graphite, higher content of S 2p is detected. The original -SO₃ group (168.3 eV) (57) is reduced into sulfites (RSO₂Li/Li₂SO₃, 166 eV) (55, 56, 58) and sulfides (163 eV) (57-61).

XPS conducted on the LiNi_{0.5}Mn_{1.5}O₄ and graphite cycled at 45 °C in electrolytes with or without added DMF-SO₃ show major difference on the surface chemistry of the electrodes. The DMF-SO₃ additive is preferably reacting on the cathode surface where important coverage of the oxide particle is measured. Higher content of DMF-SO₃ tend to dissolve the PVdF binder. On the graphite electrode, DMF-SO₃ prevents electrolyte reduction. This results in the establishment of a thin SEI that contains sulfur and nitrogen. Surprisingly, reactivity of the -SO₃ group is similar on both the cathode and anode side, as identical S 2p peaks have been measured.

3.6. FTIR/ATR

FT-IR spectra of LiNi_{0.5}Mn_{1.5}O₄ and graphite electrodes cycled in the three electrolytes under study are presented in Figure 13. PVDF characteristic peaks mostly dominate the LiNi_{0.5}Mn_{1.5}O₄ cathode spectrum (1400 cm⁻¹, 1180 cm⁻¹, 890 cm⁻¹) (Figure 13a). After DMF-SO₃ addition, a small polycarbonate peak can be detected at 1800 cm⁻¹, and much more ester and oligomer species can be observed at 1740 cm⁻¹. These species contribute to most of the CEI composition.

For the anodes, the STD graphite is quite similar to the 0.1% DMF-SO₃ anode. As the concentration of DMF-SO₃ increased to 1.0 %, the anode spectrum shows less lithium alkyl carbonate (1600 cm⁻¹) and lithium carbonate (1430 cm⁻¹), suggesting that more complicated reactions occurred on the surface of anodes with excess additive. Strong peaks at 1300 cm⁻¹ and 1150 cm⁻¹ show that more C-N stretches can be detected, resulting from the decomposition products of DMF-SO₃ and consistent with significantly increased N 1s core spectrum intensity (Figure 12).

4. Conclusions

Electrochemical test shows more electrolyte decomposition with the presence of DMF-SO₃ in the baseline solution. Addition of a high content of DMF-SO₃ causes both strong electrolyte oxidation and reduction that are detrimental to full cells. Addition of a reasonable amount of 0.1% DMF-SO₃ is beneficial to LiNi_{0.5}Mn_{1.5}O₄/C₆ cells with a slight increase of discharge capacity during the first cycle at C/20 D/20, better capacity retention and higher coulombic efficiency during following cycles at 45 °C.

Study of surface morphologies of cycled graphite and LiNi_{0.5}Mn_{1.5}O₄ electrodes conducted by SEM, TEM, and XPS shows important difference depending on the presence of the DMF-SO₃ additive and its concentration. At 0.1 % DMF-SO₃ concentration, uniform passive layers of graphite are observed, while the integrity of the cathode oxide grains is maintained. Nevertheless, TEM and XPS conducted on the same electrode exhibits a thicker CEI than in the case of the STD cathode material. Formation of a more covering and conductive CEI explains the better cycling retention of cells that employ the 0.1 % DMF-SO₃ electrolyte. Higher concentration of 1.0% DMF-SO₃ is

detrimental to surface chemistries of both the cathode and anode, with extremely thick CEI deposition and sparse SEI, respectively

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Figure 4-1. Anodic linear sweep voltammetry at 25 °C of C/Li cells (sweep rate of 0.1 mV.s⁻¹) using (in black) the EC/EMC (3/7) 1.2 M LiPF₆, (in red) EC/EMC (3/7) 1.2 M LiPF₆ + 0.1% DMF-SO₃, and (in blue) EC/EMC (3/7) 1.2 M LiPF₆ + 1.0% DMF-SO₃ electrolytes.

Figure 4-2. Cathodic linear sweep voltammetry at 25 °C of C/Li cells (sweep rate of 0.1 mV.s⁻¹) using (in black) the EC/EMC (3/7) 1.2 M LiPF₆, (in red) EC/EMC (3/7) 1.2 M LiPF₆ + 0.1% DMF-SO₃, and (in blue) EC/EMC (3/7) 1.2 M LiPF₆ + 1.0% DMF-SO₃ electrolytes.

Figure 4-3. First cycle at 25 °C of LiNi_{0.5}Mn_{1.5}O₄/Gr cells (C/20 D/20, cutoff limits: 4.80 V-4.25 V vs. LiC₆/C₆) using the EC/EMC (3/7) 1.2M LiPF₆, EC/EMC (3/7), EC/EMC (3/7) 1.2 M LiPF₆ + 0.1% DMF-SO₃, and EC/EMC (3/7) 1.2 M LiPF₆ + 1.0% DMF-SO₃ electrolytes. Inset data graph represents residual current of cells maintained at 4.8 V during charge taper step (maximum duration of 1 hour) for the three electrolytes under investigation.

Figure 4-4. (a) Specific discharge capacity and (b) coulombic efficiency of LiNi_{0.5}Mn_{1.5}O₄/Graphite cells (C/5 D/5, cutoff potentials at 25 °C and 45 °C: 4.80 V-4.25 V vs. LiC₆/C₆) using the baseline electrolyte without (-□-) or with 0.1%(-○-) and 1% (-△-) added DMF-SO₃.

Figure 4-5. EIS spectra at 4.25 V after cycling at 25 °C and 45 °C of LiNi_{0.5}Mn_{1.5}O₄/C₆ cells with and without added 0.1 % DMF-SO₃.

Figure 4-6. SEM micrographs of fresh graphite and electrodes harvested from cells after 50 cycles at 45 °C using the STD, STD + 0.1 % DMF-SO₃, and STD + 1 % DMF-SO₃ electrolytes.

Figure 4-7. SEM micrographs of fresh $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and electrodes harvested from cells after 50 cycles at 45 °C using the STD, STD + 0.1 % DMF-SO₃, and STD + 1 % DMF-SO₃ electrolytes.

Figure 4-8. TEM images of electrodes harvested from cells after 50 cycles at 45 °C using the STD, STD + 0.1 % DMF-SO₃, and STD + 1 % DMF-SO₃ electrolytes.

Figure 4-9. (On the left) C 1s and (on the right) O 1s core spectra of (a) the fresh $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes cycled at 45 °C with the (b) STD, (c) STD + 0.1 % DMF-SO₃, and (d) STD + 1.0 % DMF-SO₃ electrolytes.

Figure 4-10. (On the left) N 1s and (on the right) S 2p core spectra of (a) the fresh DMF-SO₃ powder and LiNi_{0.5}Mn_{1.5}O₄ cathodes cycled at 45 °C with the (b) STD, (c) STD + 0.1% DMF-SO₃, and (d) STD + 1.0% DMF-SO₃ electrolytes.

Figure 4-11. (On the left) C 1s and (on the right) F 1s core spectra of (a) the fresh graphite electrode and graphite anodes cycled at 45 °C with the (b) STD, (c) STD + 0.1% DMF-SO₃, and (d) STD + 1% DMF-SO₃ electrolytes.

Figure 4-12. (On the left) N 1s and (on the right) S 2p core spectra of (a) the fresh DMF-SO₃ powder and graphite anodes cycled at 45 °C with the (b) STD + 0.1% DMF-SO₃, and (c) STD + 1% DMF-SO₃ electrolytes.

Figure 4-13. FT-IR spectra of (a) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes and (b) graphite anodes cycled at both 25 °C and 45 °C with the STD, STD + 0.1% DMF- SO_3 , and STD + 1.0% DMF- SO_3 electrolytes.