Short communication

Inorganic additives for passivation of high voltage cathode materials

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ABSTRACT

The incorporation of additives designed to sacrificially react on the surface of cathode materials of lithium ion batteries has been investigated. Addition of low concentrations of inorganic additives including lithium bisoxalatoborate (LiBOB), lithium difluorooxalatoborate ($LiBF_2(C_2O_4)$), and tetramethoxy titanium (TMTi) to 1 M $LiPF_6$ in 1:1:1 EC/DEC/DMC improves the capacity retention of $Li/Li_{1.17}Mn_{0.58}Ni_{0.25}O_2$ cells cycled to 4.9 V vs. Li. Surface analysis of the cathode materials (XPS and IR) suggests that structure of the cathode surface film is modified by the presence of the additives resulting in a decrease in detrimental electrolyte oxidation reactions on the cathode surface.

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1. Introduction

The development of the next generation of lithium ion batteries for electric vehicles (EVs) requires the development of improved electrolytes [1]. The improvements in electrolytes could come from the development of novel salts, novel solvents, or novel additives that improve the properties of currently available salt/solvent combinations. $LiPF_6$/carbonate electrolytes are oxidatively stable above 4.5 V in the presence of non-active electrodes [1]. However, the active cathode materials ($LiCoO_2$, $LiMn_2O_4$, $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, $LiFePO_4$, and related materials) catalyze the oxidation of the electrolyte at lower potentials [2].

We have recently reported a class of cathode film forming additives based on organic molecules which can undergo cationic polymerization including 2,5-dihydrofuran (2,5-DHF) and gamma-buyrolactone (GBL) [3]. In the production of cathode materials such as $LiCoO_2$, $LiMn_2O_4$, $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, $LiFePO_4$, and related materials, various inorganic oxides including Al_2O_3, MgO, SiO_2 and TiO_2 have been used as surface coatings to improve electrochemical performance at voltages above 4.0 V vs. Li [4–6]. We report the use of inorganic small molecules as electrolyte additives for the in-situ generation of inorganic cathode surface films. The additives are designed to be preferentially oxidized, as suggested by computational investigations which provide estimates of the ionization potential and electron affinity, to form a cathode SEI and inhibit the oxidative reactions of the electrolyte in a similar fashion to the inhibition of the reduction of the electrolyte by the anode SEI. The

cathode SEI acts as a passivating layer preventing further oxidation of the electrolyte and allowing the cathodes to be cycled to higher voltages.

2. Experimental

Lithium hexafluorophosphate ($LiPF_6$) was obtained from Hashimoto Chemical Corporation. Battery-grade carbonate solvents, such as ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) were obtained from Novolyte Technologies. The standard electrolyte is 1 M $LiPF_6$ in 1:1:1 EC/DEC/DMC (wt). Lithium bisoxalatoborate (LiBOB) was donated by Chemetal, Germany, without further purification. Lithium difluorooxalatoborate, ($LiBF_2(C_2O_4)$) was synthesized as previously described [7]. Tetramethoxytitanium (TMTi, 99.9%) and tetraethoxysilane (TEOS, 99.9%) were purchased from Aldrich soaked in 3 Å molecular sieves prior to use. $Li_{1.17}Mn_{0.58}Ni_{0.25}O_2$ (LMNS) cathodes were received from collaborators at NASA JPL and contain PVDF binder and conductive carbon dilutant [8].

$Li_{1.17}Mn_{0.58}Ni_{0.25}O_2$/electrolyte/lithium half coin cells (NRC-ICPET, 23 mm in diameter) were fabricated for each electrolyte. The cells are cycled with the following schedule: 1 cycle of 1/20 C, 2 cycles of 1/10 C and 2 cycles of 1/5 C, followed by cycling the cells for ∼50 times at 1/5 C rate, from 2.0 to 4.9 V. Electrochemical impedance spectroscopy (EIS) analysis of the coin cells were performed using a 263A potentiostat/galvanostat (Princeton Applied Research), with ac perturbation amplitude was 10 mV, from 100 KHz to 0.1 Hz. The impedance of the cells was measured between 3.8 to 3.9 V.

Surface analysis of the cathodes was conducted after the cells finished cycling, ∼55 cycles. All the cathodes were washed with

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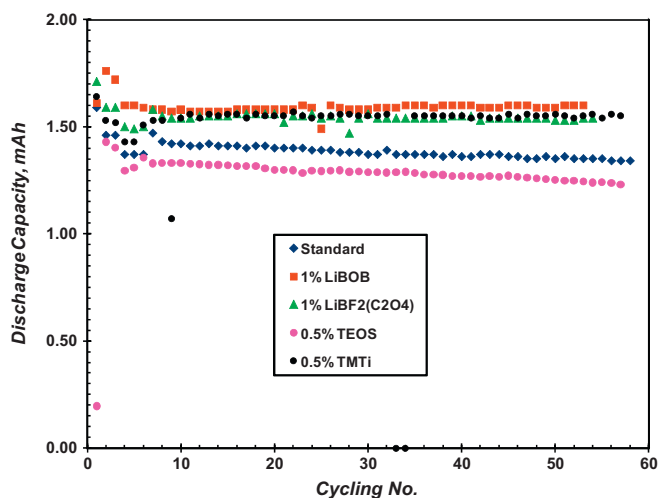
Fig. 1. Cycling performance of the electrolytes with and without additives.

Fig. 2. EIS impedance of the LMNS cathodes.

anhydrous DMC three times to remove residual ethylene carbonate and $LiPF_6$ salt followed by vacuum drying overnight at room temperature. X-ray photoelectron spectroscopy analysis (XPS) and Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) analysis of the cathodes was conducted as previously described [3,9].

3. Results and discussion

3.1. Cycling performance

The capacity retention of LMNS/Li cells with and without additives is depicted in Fig. 1. The first cycle efficiency of the cells are 73% for standard, 59% for LiBOB, 73% for $LiBF_2(C_2O_4)$, 72% for TMTi, and 10% for TEOS. After formation cycles, the efficiency of all of the cells is comparable at approximately 98%. The capacity retention for cells containing 1% LiBOB, 1% $LiBF_2(C_2O_4)$, or 0.5% TMTi have better cycling performance than the cell containing the standard electrolyte. The cells containing LiBOB, $LiBF_2(C_2O_4)$, and TMTi have significantly lower capacity loss during formation cycling. The improved performance during formation cycling may be related to a decrease in oxygen evolution during formation [8]. After the initial formation cycles (first 5 cycles) the capacity of the cells containing the standard electrolyte decreases 15% over the next 50 cycles. Incorporation of the LiBOB, $LiBF_2(C_2O_4)$ and TMTi additives resulted in significantly lower capacity fade, 9.2%, 9.4% and 7.0% respectively. Unfortunately, the addition of 0.5% TEOS rendered worse cycling performance than the standard electrolyte.

3.2. Electrochemical impedance spectroscopy (EIS)

The EIS impedance of the half cells after 55 cycles is provided in Fig. 2. The half cells containing additives displayed lower impedance (smaller diameter of the half circle) when compared to the standard electrolyte. All of the additives result in a decrease in the impedance compared to the standard electrolyte. However, the smallest impedance was observed for cells containing LiBOB, $LiBF_2(C_2O_4)$, and TEOS.

3.3. X-ray photoelectron spectroscopy (XPS) of cycled cathodes

Fig. 3 contains XPS spectra of the fresh and cycled cathodes with and without additives. From the C1s spectra, one can observe that the fresh cathode surface is composed of PVDF ($\underline{C}$–F at 290.3 eV and
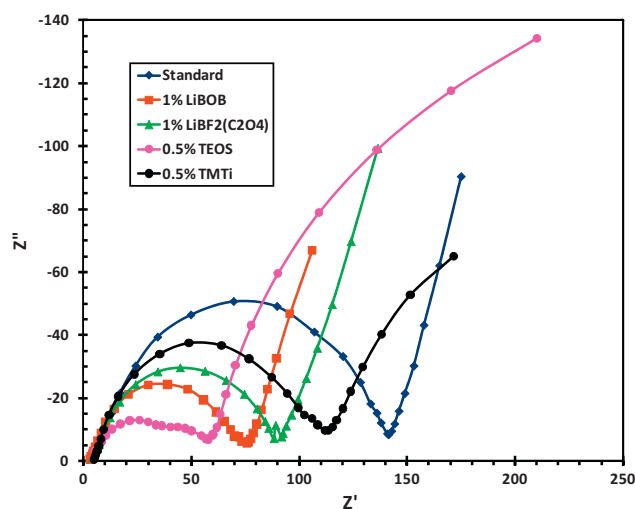
$\underline{C}$–H at 285.7 eV) and graphite [10]. Upon cycling the cells in the presence of the standard electrolyte, significant concentrations of polyethylene carbonate (PEC) (289 eV for $\underline{C}$=O and 286 for $\underline{C}$–O) are observed, as evidenced by the changes of the C1s spectra.

Differences were also observed in O1s spectra. The fresh cathode surface is mainly composed of metal oxide (529.5 eV) and Li_2CO_3 (531.5 eV) [9]. The cathode extracted from the cell cycled with the standard electrolyte contains a surface film which is primarily composed of PEC, as evidenced by the relative intensity of the C–$\underline{O}$ (533.5 eV) and C=$\underline{O}$ (531.8 eV) peaks [9]. The cathodes cycled with electrolytes containing added LiBOB and $LiBF_2(C_2O_4)$ retain higher concentrations of metal oxide (529.5 eV) suggesting a thinner surface film. The O1s spectrum of cathodes with added TMTi also retains more metal oxide (529.5 eV) and Li_2CO_3 (531.5 eV) consistent with a thinner surface film. The cathode with added TEOS has a similar O1s spectrum to the standard electrolyte consistent with a thicker surface film.

Analysis of the F1s spectra provides additional information. A strong signal for PVDF (687.7 eV) is observed for all of the samples. The concentration of Li$\underline{F}$ (685 eV) is low for the cathodes containing the standard electrolyte and cells with added LiBOB, $LiBF_2(C_2O_4)$, and TMTi while it is higher for the cathode containing electrolyte with added TEOS.

Analysis of the B1s XPS of the cathodes cycled with electrolytes containing LiBOB and $LiBF_2(C_2O_4)$ contain a broad trigonal-borate signal at 192 to 193 eV (not shown here) which supports the presence of borates [11]. The presence of borates on the surface of the cathodes supports oxidation of the LiBOB and $LiBF_2(C_2O_4)$ additives on the cathode surface which may provide a protective passivation layer preventing further oxidation of the electrolyte. Related reduction reactions of LiBOB and $LiBF_2(C_2O_4)$ on the anode have been reported [12,13]. Cathodes extracted from cells cycled with TEOS and TMTi contain weak Si2p and Ti2p peaks (not shown here) consistent with low concentrations of Si and Ti containing species on the surface related to SiO_2 and TiO_2.

Surface concentration of the elements (Table 1) indicate the cathode cycled with the standard electrolyte has a high concentration of C and O consistent with the presence of PEC on the surface. The addition of LiBOB and $LiBF_2(C_2O_4)$, results in the elemental concentrations having the greatest similarity to the fresh cathode, consistent with a thin surface film. The cathode containing TMTi has the highest concentration of O on the surface which is in accord with the large amount C–O on O1s XPS. Furthermore, all the cathodes with additives have greater Ni and Mn content than the standard
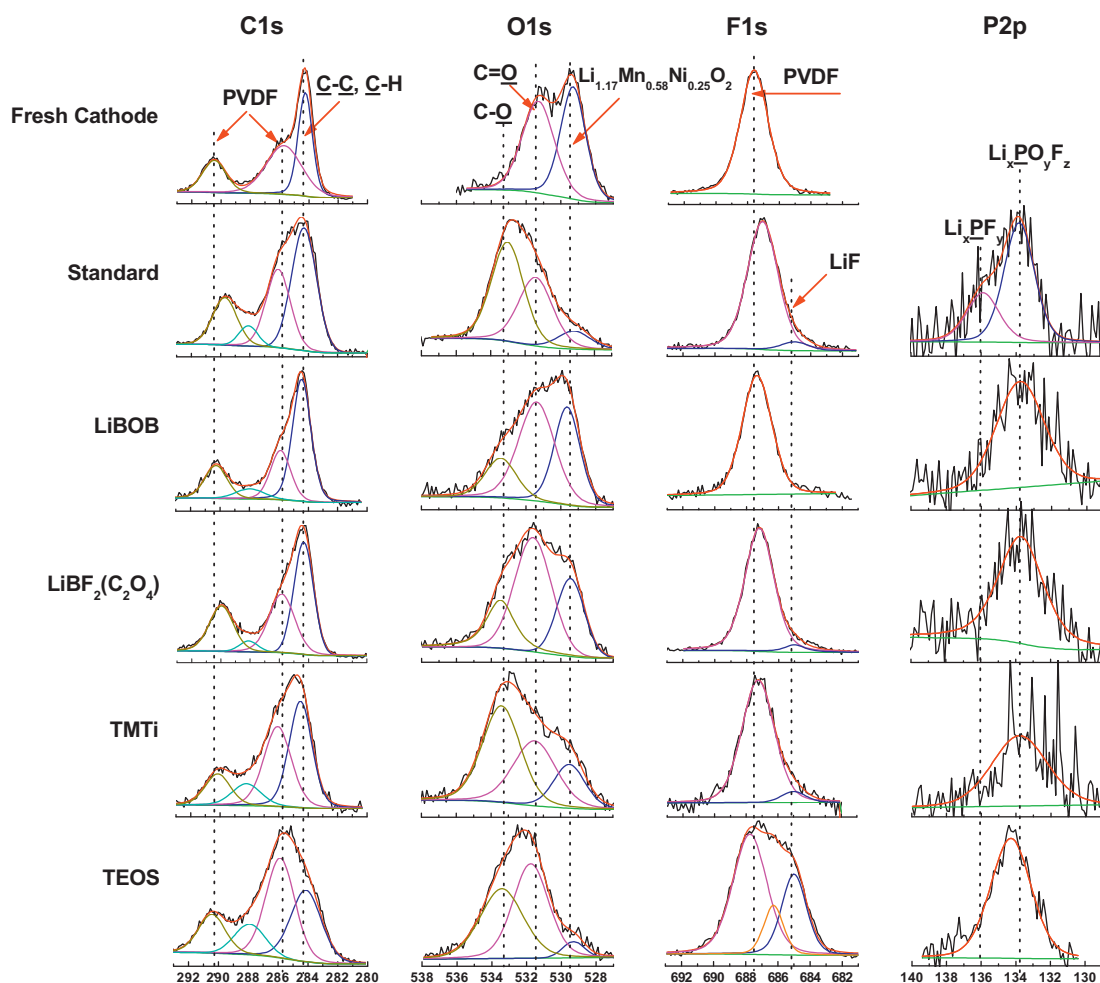
Fig. 3. XPS spectra of the fresh and cycled LMNS cathodes with/without additives.

cathode consistent with a thinner surface film than the standard cathode.

3.4. FTIR-ATR of cycled cathodes

FTIR-ATR spectra of the fresh and cycled cathodes are provided in Fig. 4. The absorptions characteristic of the PVDF binder (1400, 1271, 1170, 1070, 877, and 840 cm^{-1}) dominate the spectra for all cathodes. The cathode cycled with the standard electrolyte has the strongest PEC absorption at 1740 cm^{-1} [9]. Cathodes cycled with added LiBOB and LiBF$_2$(C$_2$O$_4$) display very little PEC content and, interestingly, no evidence for lithium oxalate on the cathode surface. This is presumably due to the oxidation of LiBOB and LiBF$_2$(C$_2$O$_4$) to form borates [11] on the cathode surface which suppresses EC oxidation. The addition of TEOS and TMTi also reduce the oxidation of EC, although low concentrations of PEC can still be detected.
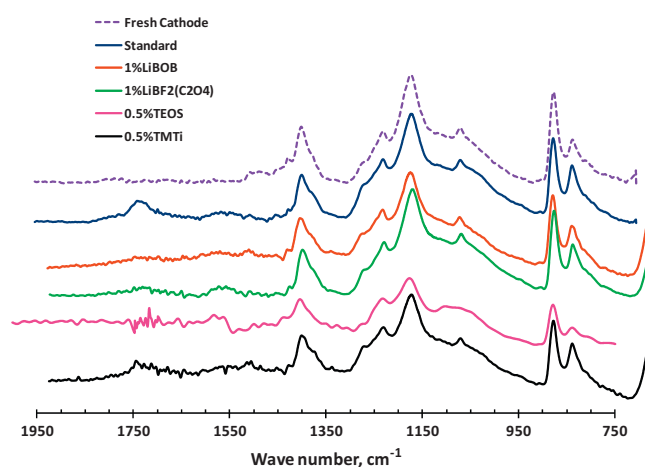

Fig. 4. FTIR-ATR spectra of the cycled LMNS cathodes.

4. Conclusions

Inorganic additives including LiBOB, LiBF$_2$(C$_2$O$_4$), TEOS and TMTi were investigated as cathode film forming additives to improve the performance of the Li/Li$_{1.17}$Mn$_{0.58}$Ni$_{0.25}$O$_2$ cells charged to 4.9 V vs. Li. The cycling performances indicate that all of the additives except TEOS enhancing the cycling performance. Electrochemical impedance spectroscopy indicates that

Table 1
Surface concentration of different elements on LMNS cathodes.

	C	O	F	P	Ni	Mn	
Fresh	56.4	14.0	21.7	0	3.3	4.6	
Std	53.7	21.6	17.9	1.3	2.6	3.0	
LiBOB	48.1	15.9	19.3	2.2	4.0	5.1	B: 5.3
LiBF$_2$(C$_2$O$_4$)	45.5	17.5	21.9	1.5	4.3	4.8	B: 4.4
TMTi	48.9	26.8	12.9	2.5	4.0	4.5	Ti: 0.5
TEOS	40.6	16.4	33.6	2.1	4.2	2.2	Si: 0.9

cells containing additives have smaller impedance than the standard cell. Surface analysis of the $Li_{1.17}Mn_{0.58}Ni_{0.25}O_2$ cathodes after cycling by XPS and FTIR-ATR suggest that LiBOB and $LiBF_2(C_2O_4)$ are oxidized to form borates on the surface of the cathodes which suppress the decomposition of EC to form PEC. Cathodes cycled in the presence of TEOS and TMTi contain lower concentrations of PEC on the cathode surface than cathodes cycled with the standard electrolyte and have evidence for the presence of TiO_2 or SiO_2 on the surface. The presence of electrolyte additives leads to cathode passivation which inhibits further electrolyte oxidation and PEC formation leading to improved capacity retention.

Acknowledgements

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