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Xu, M., Zhou, L., Dong, Y., Tottempudi, U., Demeaux, J., Garsuch, A., & Lucht, B. L. (2015). Improved Performance of High Voltage Graphite/LiNi_{0.5}Mn_{1.5}O₄ Batteries with Added Lithium Tetramethyl Borate. *ECS Electrochem. Lett.* 4(8), A83-A86. doi: 10.1149/2.0021508eel

Available at: <http://dx.doi.org/10.1149/2.0021508eel>

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Improved Performance of High Voltage Graphite/LiNi_{0.5}Mn_{1.5}O₄ Batteries with Added Lithium Tetramethyl Borate

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Lithium tetramethyl borate (LTMB, LiB(OCH₃)₄) has been prepared and investigated as a novel cathode film forming additive to improve the performance of LiNi_{0.5}Mn_{1.5}O₄ cathodes cycled to high potential (4.25–4.8 V). Addition of LTMB to 1.2 M LiPF₆ in EC/EMC (3/7, v/v) improves the capacity retention of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells cycled at 55°C. The added LTMB is sacrificially oxidized on the surface of the cathode during the first charging cycle. Ex-situ surface analysis of the LiNi_{0.5}Mn_{1.5}O₄ by X-ray photoelectron spectroscopy (XPS) reveals the presence of a borate based passivating layer which appears to inhibit electrolyte oxidation on the cathode surface.

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Manuscript submitted March 29, 2015; revised manuscript received May 14, 2015. Published May 29, 2015. This was Paper 531 presented at the Cancun, Mexico, Meeting of the Society, October 5–9, 2014.

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. 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 which typically operate at ~4.0 V vs. Li/Li⁺.³ Cathode materials with a potential over 4.2 V have been developed, including LiMnPO₄,^{4–6} LiNiPO₄,^{5,7–9} and LiCoPO₄,^{10–12} and LiNi_{0.5}Mn_{1.5}O₄.^{13–16} Among these promising new cathodes, LiNi_{0.5}Mn_{1.5}O₄ has attracted much attention in recent years because of the high intercalation/deintercalation potential of 4.8 V and excellent rate performance. However, a major difficulty in using these high-voltage materials is the instability of the standard electrolyte, LiPF₆, in organic carbonate solvents at operating potentials over 4.5 V.^{17–19} The failure mechanisms of LiNi_{0.5}Mn_{1.5}O₄ cells at high voltage and elevated temperature has been recently investigated.^{20,21} Electrolyte decomposition, electrode/electrolyte interface degradation, 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, such as Al₂O₃, ZnO, and Bi₂O₃, on the cathode materials have been reported to improve performance at high potential.^{13,14,22,23} Alternatively there have been several investigations of the incorporation of cathode film forming additives which are sacrificially oxidized on the cathode surface to generate a cathode passivation layer similar in nature to the anode SEI.^{24–32} Among these additives, lithium bis(oxalato)borate (LiBOB) has been extensively investigated and provides multiple benefits in the battery system. However, the oxidation of LiBOB on the charged LiNi_{0.5}Mn_{1.5}O₄ surface at high voltages (>4.5 V, vs. Li/Li⁺) is accompanied by CO₂ gas evolution,³³ which limits application. Thus it is important to develop novel cathode film forming additives to improve the performance of high voltage LiNi_{0.5}Mn_{1.5}O₄ cathodes.

In the present report, a novel lithium salt, lithium tetramethyl borate (LTMB, LiB(OCH₃)₄), has been prepared and investigated as a cathode film-forming additive, to stabilize the LiNi_{0.5}Mn_{1.5}O₄. The use of related lithium tetraalkyl borates as functional group delivery agents has been recently disclosed.³⁴ Electrochemical methods and

ex-situ analysis have been used to understand the role of LTMB in the enhanced performance of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells.

Experimental

Synthesis and characterization.— A flask was charged with 2.1 g of trimethyl borate (98%, STREM CHEMICALS) in an excess of diethyl ether (anhydrous, ACRÖS). To this solution was added 9 ml of lithium methoxide solution (2.2 M in methanol, pure, ACRÖS). The mixture was stirred for an hour and the solid was separated by filtration. The solid lithium tetramethyl borate (LTMB, LiB(OCH₃)₄) was washed with diethyl ether and dimethyl carbonate and isolated by filtration. The residual solvent was removed by vacuum. The product was characterized by ¹H, ¹³C and ¹¹B nuclear magnetic resonance (NMR, Bruker) spectroscopy.

Battery grade carbonate solvents, ethylene carbonate (EC) and ethyl (methyl) carbonate (EMC) were provided by BASF. Lithium hexafluorophosphate (LiPF₆) was provided by BASF. The baseline electrolyte is 1.2 M LiPF₆ EC/EMC (3/7, v/v). Composite LiNi_{0.5}Mn_{1.5}O₄ cathodes provided by BASF contained active material (85%), conductive carbon (Super P 6%, graphite 3%) and PVDF binder (6%). The composite anodes provided by BASF consist of graphite (Conoco Philips, 91%) along with super P carbon and PVDF binder. Graphite/LiNi_{0.5}Mn_{1.5}O₄ 2025 coin cells with trilayer polypropylene/polyethylene (PP/PE/PP) separator (Celgard) were assembled in argon glove-box for electrochemical measurements.

The graphite/LiNi_{0.5}Mn_{1.5}O₄ cells were cycled at room temperature initially with the following cycling protocol, C/20 for the first cycle; C/10 for the second and third cycle; C/5 for the remaining 16 cycles at room temperature (RT, 25°C). After RT cycling, the cells were transferred to elevated temperature (ET, 55°C) with C/5 (29 mA/g) cycling rate for 30 cycles. The cells were charged with CC-CV mode (4.25–4.8 V), constant current charge to 4.8 V followed by a constant voltage charge (V = 4.8 V, vs. Li/Li⁺) until the current decreased to 10% of the applied charging current (CV mode), and then the cells were discharged to 4.25 V with the same constant current (CC mode). Cells were built in triplicate. Cell to cell variation was approximately 5%. Representative cycling data is provided.

The cycled cells were disassembled in an argon glove-box, and the cycled anodes/cathodes were harvested and rinsed with anhydrous dimethyl carbonate (DMC) 3 times to remove residual LiPF₆ or EC, followed by vacuum drying overnight at room temperature. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5500 system using Al Kα radiation (hν = 1486.6 eV) under ultrahigh vacuum conditions as previously described.^{21,35}

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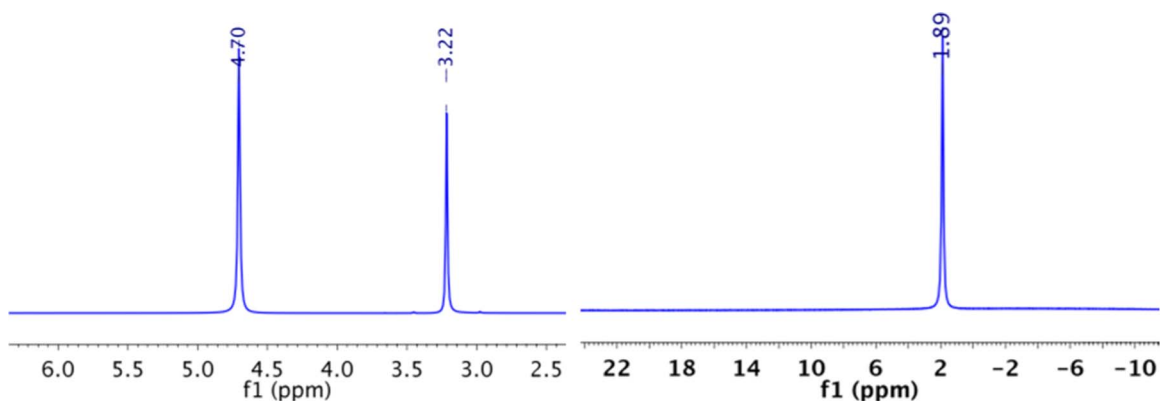


Figure 1. ^1H (left) and ^{11}B (right) NMR spectra of lithium tetramethyl borate (LTMB) in D_2O .

Results and Discussion

NMR characterization.— The ^1H and ^{11}B NMR spectra of LTMB dissolved in D_2O are depicted in Figure 1. The ^1H spectrum contains two peaks. The singlet at 3.20 ppm is characteristic of LTMB while the singlet at 4.70 ppm is from the residual H in D_2O . The boron peak characteristic of the product appears at 1.90 ppm. The chemical shift of the resonances, lack of coupling, and absence of any additional peaks corresponding to impurities confirm the structure and high purity of LTMB.

Cycling performance of the graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cell with LTMB.— The cycling performance of graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells at 25 and 55°C containing baseline electrolyte (1.2 M LiPF_6 in 3:7 EC/EMC (3/7, v/v)) with and without added LTMB are depicted in Fig. 2. Upon cycling at room temperature, the cycling performance of the cells with and without LTMB is comparable, showing slight capacity fading after 20 cycles, which is ~7% of the fourth discharge cycle. A significant difference is observed when the cells are cycled at elevated temperature. After 30 cycles at 55°C, the cells with baseline electrolyte suffer severe capacity loss, only delivering 33.3 mAh g^{-1} , or 39% capacity retention. The cycling stability of the cell was dramatically enhanced with 1.0% (wt) of lithium tetramethyl borate incorporation, 60.1% capacity retention. In addition, the cells with LTMB added electrolyte have slightly higher coulombic efficiency than the cells with baseline electrolyte upon cycling at elevated temperature.

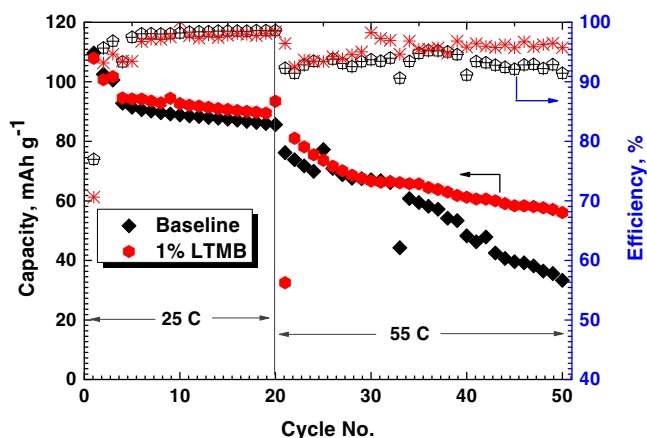


Figure 2. Cycling performance of graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells at 25 and 55°C containing baseline electrolyte (1.2 M LiPF_6 in 3:7 EC/EMC (3/7, v/v)) with and without lithium tetramethyl borate (LTMB).

$\text{Li/LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells with various concentrations of lithium tetramethyl borate (LTMB) were constructed to investigate the electrochemical behaviors on the cathode electrode. The dQ/dV vs. voltage profiles are depicted in Figs. 3a and 3b. Two pairs of reversible peaks are observed during the charge/discharge processes at the potential range of 4.6~4.8 V, Fig. 3a, corresponding to the redox reactions of $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$, accompanying with extraction/removal and insertion/intercalation of lithium cations from and into the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode.^{33,36–39} A slight potential shift is observed as well for the cells with LTMB added electrolyte, which can be ascribed to the modified interfacial chemistry on the cathode electrode. A significant difference is observed at the potential of 4.45 V during the charging processes, as shown in the zoomed profile in Fig. 3b. An irreversible oxidative peak is present for cells containing LTMB. In addition, the intensity of the oxidation peak is increased upon increasing the concentration of LTMB, which suggests that the irreversible oxidation peak at 4.5 V during the first charging process corresponds to the oxidative decomposition of LTMB on the cathode surface. LTMB participates in the surface layer formation process by modifying the structure and chemistry of the surface layer formed on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ leading to the enhanced cycling performance.

Ex-situ surface analysis with X-ray photoelectron spectroscopy (XPS).— Changes to the surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes cycled to high voltage with baseline electrolyte and the electrolyte containing 1% LTMB were monitored by XPS. XPS spectra of the fresh cathode and cathodes extracted from graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells after cycling at elevated temperature are depicted in Fig. 4. The C 1s spectrum of the fresh $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode contains three peaks, 284.3, 285.7, and 290.4 eV, corresponding to the conductive carbon, and PVDF binder (C-H and C-F), respectively. The corresponding peak for PVDF is observed in the F 1s spectrum at 687.6 eV. The O 1s spectrum of the fresh $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode is dominated by transition metal oxide (~529.5 eV), and contains a low concentration of Li_2CO_3 (531.5 eV), which is frequently present on fresh cathode particles.⁴⁰

After cycling, new peaks are observed in the C 1s, O 1s, F 1s, P 2p, and B 1s spectra characteristic of electrolyte decomposition products. The C 1s and O 1s spectra are similar for the baseline electrolyte and the electrolyte with 1% LTMB and are characteristic of C-O and C=O in lithium alkyl carbonates and polycarbonates.^{21,28,33} In addition, the intensity of the transition metal oxide (O-M, O 1s) decreased after cycling consistent with the presence of a surface film on the cathode. However, the intensity of the metal oxide peak is greater for the cell cycled with electrolyte containing LTMB consistent with the inhibition of electrolyte oxidation. In addition, a single peak is observed at 191 eV in the B 1s spectrum of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode cycled with the electrolyte with 1% LTMB, suggesting that LTMB is involved in the cathode film forming process, as supported

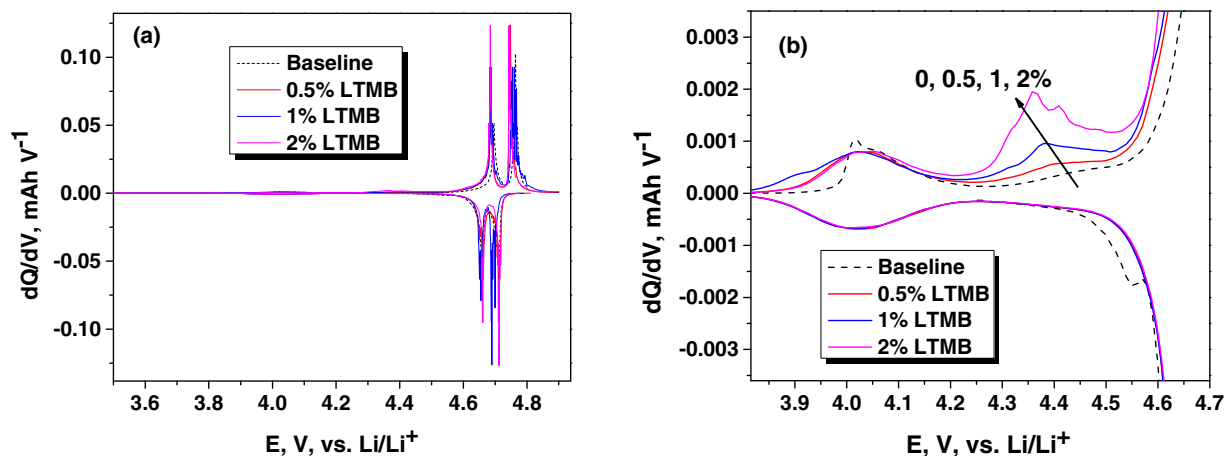


Figure 3. dQ/dV vs. E curves of $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells with various concentrations of lithium tetramethyl borate added, 0, 0.5, 1.0, and 2.0%, full potential range (a), and the zoomed in potential range of interest (3.8~4.6 V, b).

by the dQ/dV plots. Additional weak peaks characteristic of LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ are observed in the F1s and P2p spectra (not shown) and are similar for both electrodes.

Conclusions

A novel electrolyte additive lithium tetramethyl borate (LTMB, $\text{LiB}(\text{OCH}_3)_4$) has been prepared and investigated as a cathode film forming additive to improve the performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes cycled to high potential (4.8 V). Addition of LTMB to graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells improves capacity retention upon cycling at 55°C . Electrochemical analysis suggests that the LTMB is oxidized on the surface of the cathode during the first charging cycle. Ex-situ surface analysis of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode reveals inhibition of electrolyte oxidation on the cathode surface and the presence of a borate based passivating layer which is likely responsible for the improved performance.

Acknowledgment

The authors thank BASF SE Electrochemistry Research Network for financial support.

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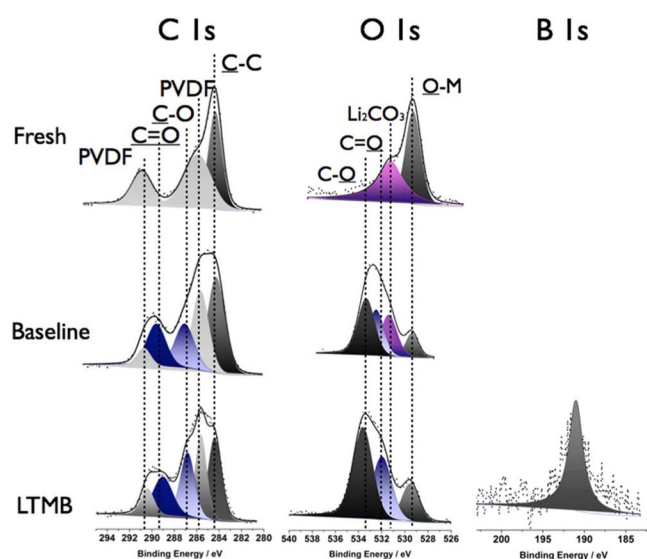


Figure 4. C 1s, O 1s, and B 1s XPS spectra of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode, fresh, and after cycling at elevated temperature with baseline electrolyte and electrolyte with 1% LTMB.

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