

Short communication

Effect of electrolyte additives in improving the cycle and calendar life of graphite/Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ Li-ion cells[☆]

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Abstract

Lithium-rich layered metal oxide Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ was investigated as a potential positive electrode material for high-power batteries for hybrid electric vehicle (HEV) applications. In order to evaluate the power and life characteristics of the graphite/Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ cell chemistry, hybrid pulse power characterization (HPPC) and accelerated calendar life tests were conducted on several pouch cells containing electrolytes with and without additives. The data show that the cells containing 0.5 wt% lithium bis(oxalate)borate (LiBOB) or vinyl ethyl carbonate (VEC) additives, or the novel lithium difluoro(oxalato)borate (LiDFOB) additive, have much improved cycle and calendar life performance.

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Keywords: Li-ion battery; Additive; Cycle life; Calendar life; HEV

1. Introduction

Rechargeable lithium-ion batteries with high-energy densities and high-power capabilities have become an important power source for portable electronic devices such as cellular phones and laptop computers. Recently, they have attracted the attention of the automotive industry for applications in hybrid electric vehicles (HEV) [1–6]. Li-ion batteries were actually investigated for HEV applications in the mid-1990s under the partnership for a new generation of vehicles (PNGV) program. Under the auspices of that program, the Li-ion battery power showed very good promise for use in HEV applications. However, three major barriers were identified that presented a real challenge toward implementing this technology in HEVs. These barriers are (1) 15-year calendar life, (2) \$20/kW cost, and (3)

acceptable abuse tolerance to meet basic automotive safety standards.

Over the past 5 years, a significant amount of work has been carried out to improve the performance characteristics of the lithium ion batteries using either graphite/LiNi_{0.8}Co_{0.2}O₂ [1,2] or graphite/LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ [3–6] cells. Recently, we found that the Li_{1+x}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{1-x}O₂ material could be a very promising cathode material for high-power applications. This material has several advantages compared with the (LiNi_{0.8}Co_{0.2}O₂) and (LiNi_{0.8}Co_{0.15}Al_{0.05}O₂) electrodes. The Li_{1+x}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{1-x}O₂ material was found to have higher power and better safety characteristics than other lithium nickel oxide-based systems. From a fundamental viewpoint, the amount of active nickel ions in this material is small and the oxidation of all the available divalent nickel to the tetravalent state takes place at 4.6 V [7,8], which is higher than the cell upper operating voltage (4.0 V) for HEVs. As a result, the oxidation of the electrolyte with the unstable tetravalent nickel does not take place at 4.0 V and thus there is very limited interfacial impedance rise during cycling. In addition, Mn⁴⁺ ions in the material play an important role by stabilizing the oxygen in the structure and preventing any material decomposition during extensive cycling at high temperatures. In this paper, we present the most recent developments of some electrolyte functional additives and their impact on the power and calendar life of the graphite/Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ Li-ion battery system.

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2. Experimental

The positive electrode used in this study was coated on an Al foil and has a composition of 84% active $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$, 8% carbon, and 8% PVDF binder. The negative electrode was a mix of 90 wt% graphite (MCMB 1028), 2% carbon fiber, and 8% PVDF binder. Pouch-type cells were fabricated using $5\text{ cm} \times 5\text{ cm}$ electrodes and were used to perform the cycle life tests at room temperature and at 55°C . The capacity retention of the cells was calculated relative to the discharge capacity of the first cycle. The cells were cycled between 3.0 and 4.0 V. The baseline electrolyte was 1.2 M LiPF_6 in EC:PC:DMC (1:1:3, by weight). Lithium bis(oxalato)borate (LiBOB), vinyl ethyl carbonate (VEC), and Lithium difluoro(oxalato)borate (LiDFOB) were added to the baseline electrolyte as additives in very small quantities and their effect on cell performance was investigated.

Hybrid pulse power cell characteristics were obtained using the HPPC test in accordance with the FreedomCAR test manual [9]. The test is intended to establish the cell's area specific impedance (ASI) for 18 s discharge pulse and for the 2 s regenerative charge pulse as a function of the depth of discharge of the cell (%DOD).

Accelerated aging or calendar life tests [9] were carried out on the graphite/ $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ pouch cells with and without additives. The cells were charged up to 4.0 V and kept in an oven at 55°C . The area specific impedances (ASI) of the cells were monitored during the period of storage.

3. Results and discussion

Fig. 1 shows the ASIs of the MCMB-1028/ $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ lithium-ion cell as a function of the depth of discharge (DOD) during the HPPC test. The electrolyte used was 1.2 M LiPF_6 in EC/PC/DMC (1:1:3, by weight) as baseline electrolyte. One pair of high-rate discharge/charge pulses was applied to the cells at every 10% of DOD. For the HPPC test mentioned in this work, the discharge pulse was applied at a 10C rate for 18 s and the charge pulse was applied at a 7.5C rate for 2 s. The area specific impedance (ASI) of the cell was then calculated from the voltage changes during pulses.

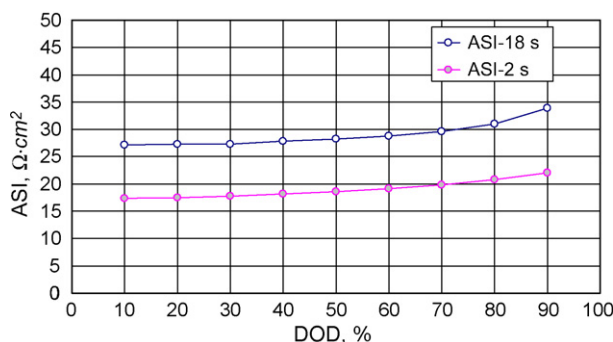


Fig. 1. ASIs of MCMB-1028/ $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ lithium-ion cell during HPPC test at different DOD.

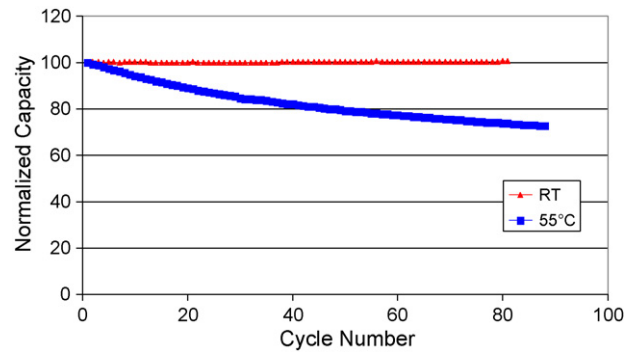


Fig. 2. Capacity retention of MCMB-1028/ $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ lithium-ion cells cycled at room temperature and 55°C .

Fig. 1 shows that the MCMB-1028/ $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ lithium-ion cell had a low ASI of about $28\ \Omega\text{ cm}^2$ for 18 s pulse discharge and about $17\ \Omega\text{ cm}^2$ for 2 s pulse charge. The cell ASIs for both charge and discharge are lower than the required minimum values set by FreedomCAR to meet the power requirement for HEVs. These minimum required values are $35\ \Omega\text{ cm}^2$ for 18 s pulse discharge and $25\ \Omega\text{ cm}^2$ for the 2 s pulse charge. Fig. 2 shows the capacity retention during cycling of MCMB-1028/ $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ lithium-ion cells at room temperature and 55°C . The electrolyte used in both cells was 1.2 M LiPF_6 in EC/PC/DMC (1:1:3, by weight). When cycled at room temperature, the cell showed excellent cycling performance without capacity fade. However, the cell that was subjected to high-temperature cycling shows rapid capacity fade with 28% loss in the capacity after only 90 cycles. The capacity fade is very likely caused by the instability of the conventional solid electrolyte interface (SEI) layer at the carbon surface caused by the reduction of the electrolyte during the initial formation process. Therefore, we believed that using new functional electrolyte additives that either reduces or polymerized at the surface of carbon electrode to form a robust solid electrolyte interface could be a good way to improve the capacity retention of MCMB/ $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ lithium-ion cells at elevated temperatures.

Fig. 3 shows the differential capacity profiles of MCMB-1028/ $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ lithium-ion cells during initial charge. The baseline electrolyte used was 1.2 M LiPF_6 in EC/PC/DMC (1:1:3, by weight), and the additives investigated were vinyl ethylene carbonate (VEC), lithium bis(oxalato)borate (LiBOB), and lithium difluoro(oxalato)borate (LiDFOB). The VEC, LiBOB, and LiDFOB compounds were added into the baseline electrolyte in concentrations of 0.5, 0.5 and 5 wt%, respectively. Fig. 3 clearly shows extra peaks corresponding to the reduction of VEC [10], LiBOB [11], and LiDFOB [12], respectively. Hence, there was an interest in investigating the impact of the new SEI based on these additives on cycling performance and cell impedance while aging the cells.

Fig. 4 shows the normalized discharge capacity of MCMB-1028/ $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ lithium-ion cells using different electrolyte additives. The cells were cycled between 3.0 and 4.0 V at 55°C with a constant current of $C/2$. The cell with-

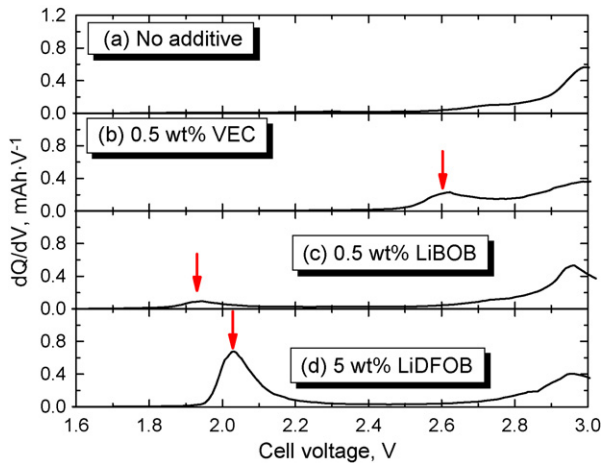


Fig. 3. Differential capacity profiles of MCMB-1028/Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ lithium-ion cells during initial charge, showing the impact of the electrolyte additives.

out any additive lost about 23% of its initial capacity after 100 cycles; however, the capacity retention of the cells was greatly improved when the electrolyte additives were added. The trend is that the cell with 5 wt% LiDFOB had better capacity retention than that with 0.5 wt% LiBOB. Only 5% capacity loss was observed when LiDFOB was used as additive in the electrolyte. The cell with 0.5 wt% VEC had the smallest improvement of the three additives reported. It can be reasonably extrapolated that better capacity retention for VEC and LiBOB can be achieved by adding a higher concentration of additive, as in the case of LiDFOB (5 wt%). However, if we add high concentrations of VEC additive, the initial cell impedance significantly increases and can have a negative effect on the power capability of the cell, as shown in Fig. 5. The addition of only 2% VEC to the cell increased cell initial impedance to several times higher than that of the cell without additive. The resulting high cell impedance makes it difficult to meet the power requirements for HEV applications even though better capacity retention can be expected by

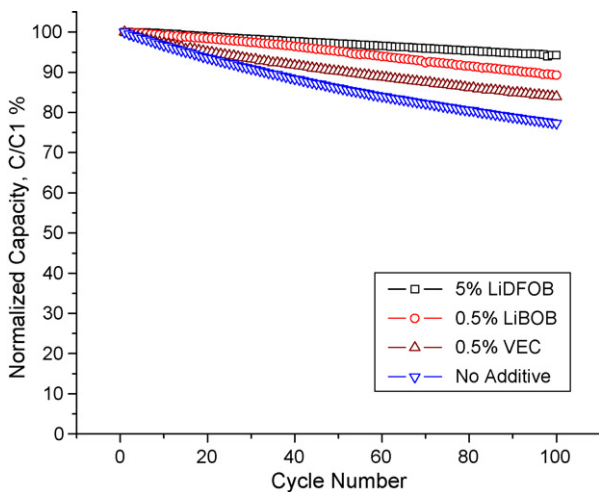


Fig. 4. Capacity retention of MCMB-1028/Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ lithium-ion cells showing the positive impact of electrolyte additives on the capacity retention. The cells were cycled at 55 °C.

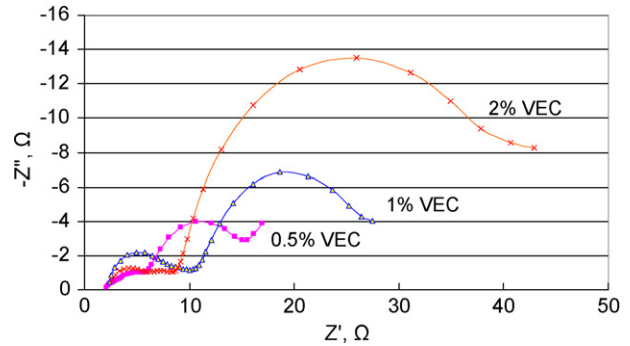


Fig. 5. AC impedance (at 100% SOC) of MCMB-1028/Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ lithium-ion cells, showing the impact of VEC concentration in the electrolyte on cell impedance.

adding up to 2 wt% VEC. The same trend was obtained for the LiBOB additive.

Fig. 6 shows the AC impedance of MCMB-1028/Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ lithium-ion cells using 1.2 M LiPF₆ and 1.0 M LiDFOB in EC/PC/DMC (1:1:3, by weight). The AC impedance was measured after the cells were charged to 60% state of charge (SOC). In this case, the impedance of the cell with a large concentration of LiDFOB (about 1 M) was similar to that of a cell with 1.2 M LiPF₆ in EC/PC/DMC (1:1:3, by weight) without any additive. This result clearly shows that adding a high concentration of LiDFOB does not cause a significant initial cell impedance increase. Hence, it is possible to add a high concentration of LiDFOB to maximize the cell capacity retention while maintaining low cell impedance for better power capabilities.

Fig. 7 shows the ASIs during the aging process at 55 °C and 50% DOD of MCMB-1028/Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ cells with different electrolyte additives. The electrolyte for the control cell was 1.2 M LiPF₆ in EC/PC/DMC (1:1:3, by weight), and for the other cells 0.5 wt% VEC, 0.5 wt% LiBOB, and 5 wt% LiDFOB. Before and after every 4 weeks of aging, the cells were cooled to 25 °C and an HPPC test was performed to mea-

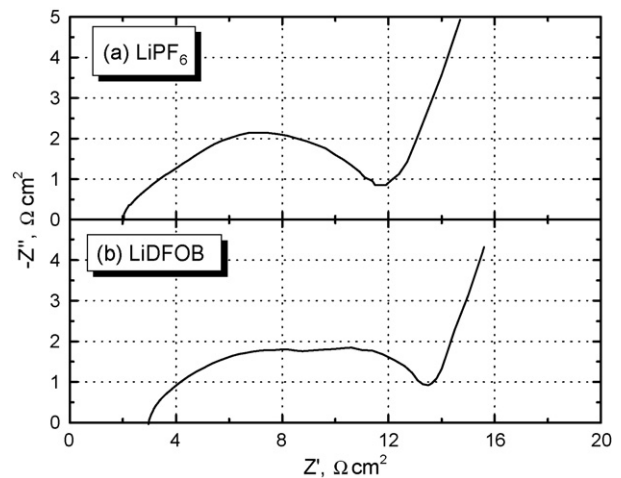


Fig. 6. AC impedance (at 60% SOC) of MCMB-1028/Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O₂ lithium-ion cells using (a) 1.2 M LiPF₆ and (b) 1.0 M LiDFOB in EC/PC/DMC (1:1:3, by weight).

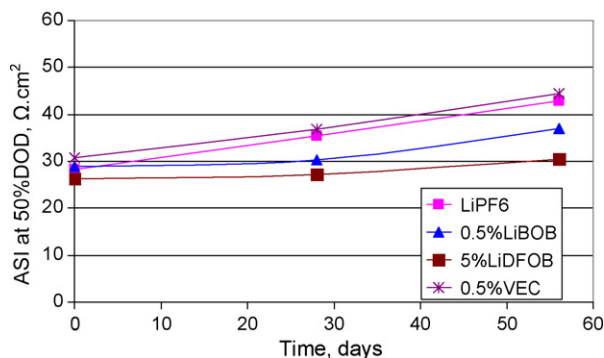


Fig. 7. ASIs during the aging process at 55 °C and 50% DOD of cells with and without electrolyte additives.

sure the ASI of the cells as a function of aging time. The cell with 0.5 wt% VEC had the highest initial ASI and the highest degree of ASI growth together with the cell having the baseline electrolyte without any additives. Although the addition of VEC can suppress the capacity fade of lithium-ion cells, it does not help in suppressing the cell power fade. The initial ASI of the cell with 0.5 wt% LiBOB was slightly higher than the cell using the baseline electrolyte, but had a slower ASI increase during the aging of the cell. The most promising cell is the one with 5 wt% LiDFOB that had a lower initial ASI and the smallest ASI increase of all the cells. This result clearly shows that selecting an additive that stabilizes the SEI without increasing initial cell impedance is the right approach in addressing the calendar life problems of lithium batteries for HEV applications.

4. Conclusion

A lithium-ion cell comprising a MCMB negative electrode and a $\text{Li}_{1.1}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]_{0.9}\text{O}_2$ positive electrode has excellent power capability and is a promising candidate to meet the power requirements for HEV applications. However, the self-discharge reactions of the lithiated graphite at elevated temperatures can significantly shorten the life of the batteries because of the instability of the SEI film at the negative

electrode surface. By using electrolyte additives such as VEC, LiBOB, or LiDFOB, one can provide an improved SEI film to suppress the degradation of the graphite negative electrodes, and to improve the capacity retention of the cells during the cycling and aging processes at elevated temperature. LiDFOB, however, is the most promising additive to improve the capacity retention, for it is unique in that it does not affect the cell's initial impedance and power.

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