

High Precision Studies on a Family of Borate Electrolyte Additives

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Introduction

The use of electrolyte additives is one of the most effective ways to improve Li-ion battery performance. Burns et al. [1] studied the impact of several additives, including VC, on commercial wound Li-ion cells with LiCoO_2 as the positive electrode and either graphite or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as the negative electrode using high precision coulometry. It was shown that improved coulombic efficiency directly correlated to longer cell lifetime. Boron-based electrolyte additive such as LiBOB and TMOBX have been studied extensively for Li-ion battery applications. However there are very few studies on alkyl borate electrolyte additives such as trimethyl borate (TMB), triethyl borate (TEB), trimethyl silyl borate (TMSB), etc. in Li-ion battery applications. Chang et al. [2] claim that the addition of TMB improves high temperature performance of LiFePO_4 cells. TMSB is claimed to have improved high temperature and high voltage performance for LiFePO_4 and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2/\text{graphite}$ cells. [3, 4]

In this presentation, of the impact of alkyl borate electrolyte additives with and without the addition of VC in $\text{LiCoO}_2/\text{graphite}$ pouch cells was studied.

Experimental

Dry 402030-size 200 mAh LCO/graphite pouch cells were received from a reputable manufacturer. Duplicate cells for most groups were made for cycling in the Ultra High Precision Charger (UHPC) built at Dalhousie University. The required number of cells was filled with control electrolyte and with electrolytes containing the other electrolyte additives in the study. Additives were added at 1 wt% to the control electrolyte 1 M LiPF_6 electrolyte in EC:EMC (3:7). After assembly, cells were held at 1.5 V for 24 hours at 40°C for complete wetting. The formation cycle was conducted in two steps. First, 10 hours of charge at 2 mA (C/100), then charge to 4.2V at 15 mA and discharge to 3.8 V at 15 mA. After degassing, cells were connected back to UHPC for cycling. The UHPC can measure coulombic efficiency to an accuracy of $\pm 0.003\%$. During these experiments, cells were located in thermostats set to $40.0 \pm 0.1^\circ\text{C}$. Electrochemical impedance spectra were measured after UHPC cycling at 10 and 30°C.

Results and discussion

Figure 1 shows the first 1% of the formation charge for all the additives.

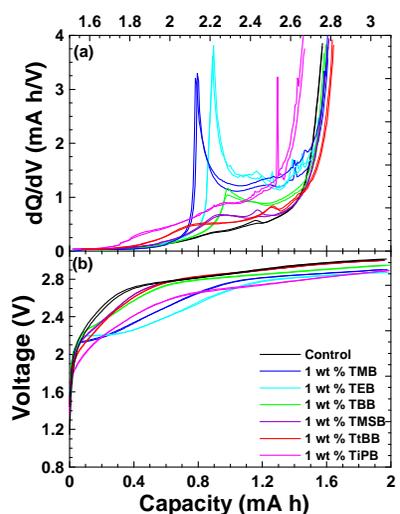


Figure 1: Voltage versus cell capacity (b) and the differential capacity versus voltage (a) during the first 1% of the formation cycle on the UHPC at 40 °C.

The borate electrolyte additives apparently get reduced on the graphite surface around a cell voltage of 2.1 to 2.4

V (corresponds to approx 1.7 V vs Li/Li^+). TMB, TEB and TBB show a sharp reduction peak around a cell terminal voltage of 2.1 to 2.4 V, and the peak shifts to higher terminal voltage with increasing alkyl chain length. However, the bulky alkyl borates TtPB, TtTB and TMSB have very little impact during formation. The formation data of VC and VC containing borate electrolyte additive will be shown in the meeting.

Figure 2 shows data collected from the UHPC during cycling. It is difficult to distinguish cell performance by only looking at the capacity loss during these cycles (Figure 2b).

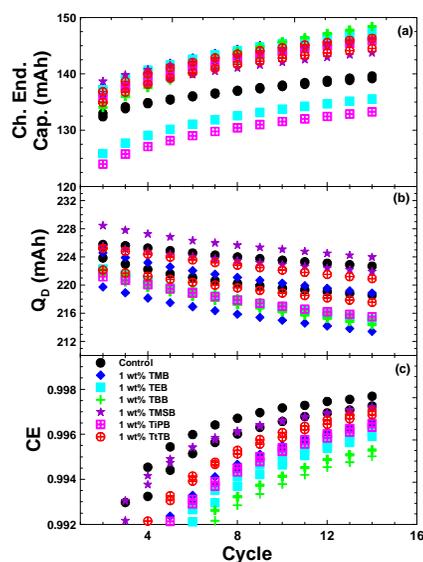


Figure 2: The charge end point capacity (a), discharge capacity (b) and coulombic efficiency (c) versus cycle number for all cells cycled on the HPC at 40 °C.

This is why the coulombic efficiency (Figure 2a) and capacity end point positions (Figure 2c) must be accurately measured with equipment such as the UHPC. A shift of the coulombic efficiency (CE) closer to 1.0000 and a decrease in charge end point slippage (slope of charge end point capacity versus cycle number) are indications of a reduction in parasitic reactions which normally correlates with longer lifetime. TMSB is the only electrolyte that shows similar CE as the control electrolyte. All other electrolytes with borate additives have smaller CE than control. The charge slippage of all the cells was higher than than the control electrolyte. The addition of both VC and borate-based electrolyte additives increases the CE, reduces the charge slippage and the short term fade (to be discussed in the meeting) compared to the borate only electrolytes but not these parameters are not better than when VC alone is used.

TMSB is the only electrolyte shown to have similar performance to the control electrolyte. However, the impedance (to be discussed in meeting) of the TMSB containing cells was lower than control electrolyte. It is possible that TMSB might be useful as an impedance reducing additive in cells that also contain VC.

References

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