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A consideration of electrolyte additives for $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ Lithium-Ion batteries

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Introduction

The oxidation of electrolyte is considered to be a key problem for $LiNi_{0.5}Mn_{1.5}O_4$. The use of electrolyte additives may be one approach to improve the stability of the electrolyte. Cresce et al. and Abouimrane et al. have reported several effective additives for LNMO/Li cells showing improved cycling performance [1, 2]. Dedryvere et al. found that electrode-electrode interactions in LNMO/LTO cells can significantly influence their electrochemical performance and lead to the capacity degradation [3].

In this paper, the function of additives for LNMO/LTO cells is studied while considering the impact of electrode-electrode interactions.

Experimental

Commercial LNMO and LTO electrodes were used with an active material loading of 84% and 88% respectively. The capacities of the LNMO and LTO electrodes were around 2.1 and 2.2 mAh to fabricate LNMO-limited LNMO/LTO cells. 2325-size coin cells were assembled. 1M $LiPF_6$ in 3:7 EC/DMC was used as the control electrolyte. 1% Lithium Perfluoro-tert-butoxide (LPTB) (by weight) was used as an additive in the control electrolyte. Other additives were also tested.

The LTO/LNMO cells were cycled at 30ºC with currents corresponding to C/20. Automated storage experiments were carried out at 30ºC on a precision 40 channel cycling/storage system at Dalhousie University [4].

Results and discussion

Figure 1 shows the capacity and coulombic efficiency vs cycle number for LNMO-limited LNMO/LTO Li-ion cells with control electrolyte and with electrolyte containing 1% LPTB. The cell with electrolyte additive shows an improved cycling performance but with decreased coulombic efficiency.

Figure 2 shows voltage vs capacity for cells with control electrolyte and cells having electrolyte with 1% LPTB. The cell with the additive shows increased capacity endpoint slippage compared to the control cell.

Figure 3 shows the normalized discharge curves D_0 (before storage), D_1 (immediately after storage) and D_2 (after charge after storage) of LNMO/LTO cells. The capacity D_0 has been set to 100% and the other capacities scaled by the same factor. For all the cells, discharge D_1 shows the smallest capacity and begins at the lowest potential due to the self-discharge during storage. Discharge D_2 has a smaller capacity than discharge D_0 due to irreversible capacity loss. The cell with electrolyte additive has smaller D_1 than the control cell indicating more self-discharge. The recovery of discharge D_2 is due to the increased slippage of the LNMO and LTO electrodes with the additive. The rapid self-discharge shows that the additive is actually poor and could not be used in practical LNMO/LTO cells although the cycling performance is "improved".

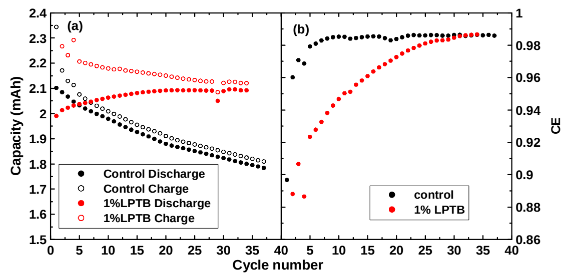

Fig. 1 (a) Capacity and (b) coulombic efficiency vs cycle number for LNMO-limited Li-ion cells in 1M $LiPF_6$ EC/DMC electrolyte with or without 1% LPTB.

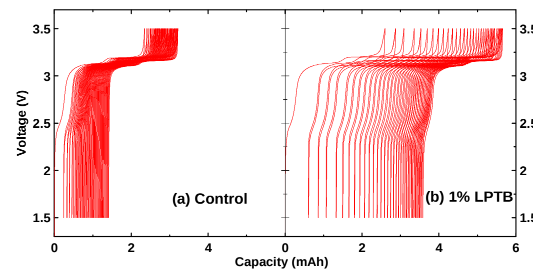

Fig. 2 Voltage vs capacity for LNMO-limited Li-ion cells in control electrolyte (a) and electrolyte with 1% LPTB (b).

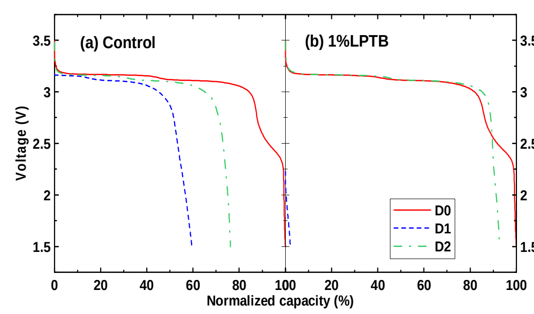

Fig. 3 Voltage versus normalized capacity (setting D_0=100%) for LNMO limited Li-ion cells in control electrolyte (a) and electrolyte with 1% LPTB (b). D_o before storage, D_1 after storage and D_2 after charging after storage.

Comprehensive studies of additives will be presented at the meeting in the form of cycling performance, coulombic efficiency, capacity endpoint slippage and self-discharge during storage. Studies of other additives such as PFBP-III, $Al(PFB)_3$ and $Al(HFiP)_3$ will be presented as well. These results allow researchers to get an overall evaluation of electrolyte additives.

References

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