

A study of the interactions between positive and negative electrodes: Charge and discharge slippage in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ Li-ion full cell

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Introduction

The LNMO/LTO system has been promoted for Li-ion batteries over the years. Xiang et al. [1] and Wu et al. [2] found LTO-limited LNMO/LTO cells showed more stable cycling performance than LNMO-limited LTO/LNMO Li-ion cells. The reason why LTO-limited cells performed better was not explained and is surprising upon reflection. Besides, an extremely interesting electrode-electrode interaction was found in LNMO/LTO cells by Dedryvere et al. [3] which can significantly influence electrochemical performance and lead to capacity degradation.

In this paper, we use some very simple illustrative examples to prove that electrode-electrode interactions exist.

Experimental

LNMO was prepared from a co-precipitated hydroxide precursor as described in our previous work [4]. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes were made with a 92:4:4 weight ratio of active material, carbon black and PVDF binder. Commercial LTO electrodes were made with an active material loading of 88%. The LTO electrode has a capacity around 2.0 mAh. The capacity of LNMO electrodes were around 1.0 mAh and 5.8 mAh to fabricate LNMO-limited and LTO-limited Li-ion cells. 2325-size coin cells were assembled with LTO as the negative electrode and LNMO as the positive electrode. 1M LiPF_6 in 3:7 EC/DMC was used as the electrolyte.

Results and discussion

Figures 1a, b, e and f show the voltage curves of LNMO/Li and LTO/Li cells for simulated LNMO-limited and LTO-limited Li-ion cells. The LNMO electrode shows capacity endpoint slippage in the half cell while the LTO electrode does not. The expected voltage curves for LNMO-limited and LTO-limited Li-ion cells are shown in Figures 1c and g. The expected LNMO-limited Li-ion cell should show a stable cycling performance while the LTO-limited Li-ion cell should show capacity loss as expected in Figures 1d and h.

Figure 2 shows the cycling performance and voltage curves for actual LNMO-limited and LTO-limited Li-ion cells. The actual LNMO-limited Li-ion cell shows a rapid capacity fading while the LTO-limited Li-ion cell shows no capacity loss with cycle number.

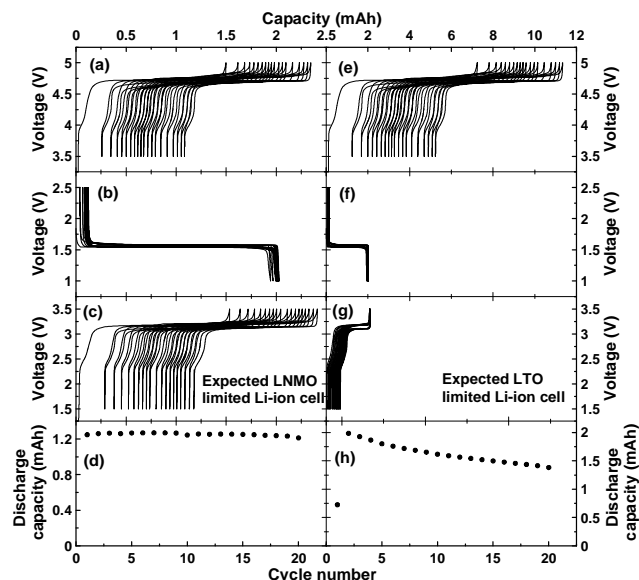


Figure 1. Voltage vs capacity of LNMO/Li (a, e) and LTO/Li cells (b, f) for simulated LNMO-limited and LTO-limited Li-ion cells. Voltage vs capacity for expected LNMO-limited (c) and LTO-limited Li-ion cells (g). Discharge capacity vs cycle number for expected LNMO-limited (d) and LTO-limited (h) Li-ion cells.

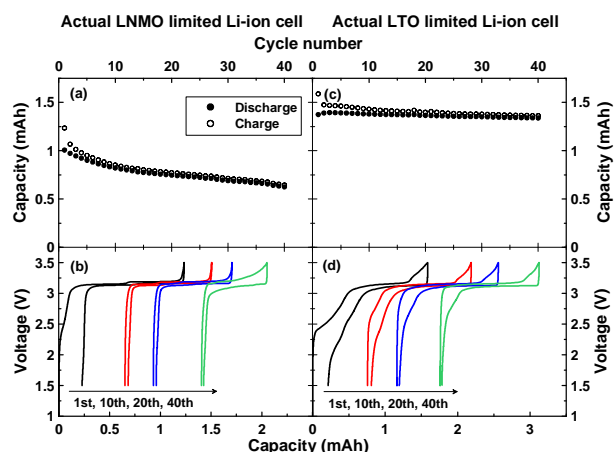


Figure 2. Charge and discharge capacity vs cycle number for actual LNMO-limited (a) and LTO-limited (c) Li-ion cells. 1st, 10th, 20th, 40th voltage curves for actual LNMO-limited (b) and LTO-limited (d) Li-ion cells.

When LNMO and LTO electrodes are present within the same cell, electrolyte oxidation products at the LNMO electrode migrate to the LTO electrode causing the LTO electrode to undergo capacity endpoint slippage. The measured slippages of the LNMO and LTO electrodes inside the actual LNMO limited and LTO limited Li-ion cells will be presented at the meeting. Understanding such electrode-electrode interactions is critical in making long-lived Li-ion batteries and also for understanding the function of electrolyte additives.

References

1. H.F. Xiang, X. Zhang, Q.Y. Jin, C.P. Zhang, C.H. Chen, X.W. Ge, *J. Power Sources*, 183, (2008) 355.
2. H.M. Wu, I. Belharouak, H. Deng, A. Abouimrane, Y.-K. Sun, K. Amine, *J. Electrochem. Soc.*, 156, (2009) A1047.
3. R. Dedryvere, D. Foix, S. Franger, S. Patoux, L. Daniel, D. Gonbeau, *J. Phys. Chem. C*, 114 (2010) 10999.
4. F. Zhou, X. Zhao, A.V. Bommel, X. Xia, J.R. Dahn, *J. Electrochem. Soc.*, 158, (2011) A187.