Reach MAX - Reaching maximum volumetric energy density for high-voltage cathodes in lithium batteries

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Relevance:
Increasing volumetric energy density

>>> 30 - 40% energy density increase

Berg et al, JES, 162 A2468 (2015),
Why high-voltage cathode?
Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO)

$\sim 4.7 \text{ V (vs. Li/Li}^+\text{)}$ => Simpler pack design

![Graph showing voltage vs. capacity for LNMO and NMC/G](image)

NMC/G (3.7V) vs. LNMO/Li (4.7V)

$N=100$ $370\text{V}$ $N\approx80$
Goal: To understand the mechanisms of capacity fade in LNMO based cells

- Electrolyte oxidation at high potential
- Mn/Ni dissolution

- Interaction of oxidation products & Mn/Ni ions with anode: ‘cross-talk’

- Effect of electrolyte additives.

- Effect of temperature.

- Use of model cell design and high-precision test equipment.
Cell-balance drift

~50% State of Charge (SOC):

\[ t = 0 \]

\[ \text{Cathode} \]

\[ \text{Anode} \]

‘Lithium inventory’:
The total amount of lithium in cathode + anode at any arbitrary time

‘Lithium inventory’ = 100%
Conventional cell: 
*electrolyte reduction* results in <50% SOC

\[ t > 0 \]

Stable Cathode

‘Lithium inventory’ < 100%
Cell-balance drift

high-V cathode >>> electrolyte oxidation
State of charge: 50%

$t > 0$

'Cathode

'Stable anode: e.g. LTO

'Lithium inventory' > 100%
Cycling of whole cells with balance drift – a simulation

LNMO
4 mAh
- 
LTO
5 mAh

Side reactions only on LNMO

Side reactions only on LTO

Side reactions on LNMO & LTO

Cathode
Anode
Cathode
Anode
Cathode
Anode
A: Performance of 3-electrode LNMO-LTO cells

>> Increased fade with temperature

Fade mechanism: side reactions on anode surface!

>> decrease in Li inventory!
B: ‘back-to-back’ LNMO-LTO cells: Electrolyte isolation!

>>> Increased fade with temperature

Fade mechanism: side reactions on cathode surface

>>> increase in Li inventory
Intermediate conclusions:

- Electrolyte is oxidized on high-voltage cathode surface
- Oxidation products migrate to anode and are reduced.

= ‘Cross-talk’

Part II: Effect of electrolyte additives
Does FluoroEthylene Carbonate (FEC) additive work in high voltage cells?
LNMO – LTO whole cells: The effect of electrolyte additive (FEC) on power

Power Capability at RT

Low cycling rate:
>>Similar capacity

High cycling rate:
>>Lower capacity with FEC
The effect of FEC additive, temperature and ‘cross-talk’

C/5 cycling at RT > 55°C

>>> Fade more pronounced at 55 ºC.

LTO – XPS*

>>> Mn and Ni detected on anode already after 1 cycle
>>> ‘cross talk’

* X-ray Photoelectron Spectroscopy

- No beneficial effect of FEC additive was observed for LNMO.
- Dramatic increase of fading at high temperature, and cross talk due to Mn/Ni migration to anode.
Summary

**LNMO-LTO** whole cell model – a useful system to study high-voltage cathodes.

‘Cross-talk’ can play a critical role and dominate cycling behavior

Outlook

- Additives / protective coatings
- Novel electrolytes with high stability, e.g. Ionic liquids
- In-depth study of ‘cross-talk’, gas formation etc.