Fade Mechanisms of Lithium & Manganese Rich Layered-Oxide Li-ion Cells

$xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M=Ni, Co, Mn)

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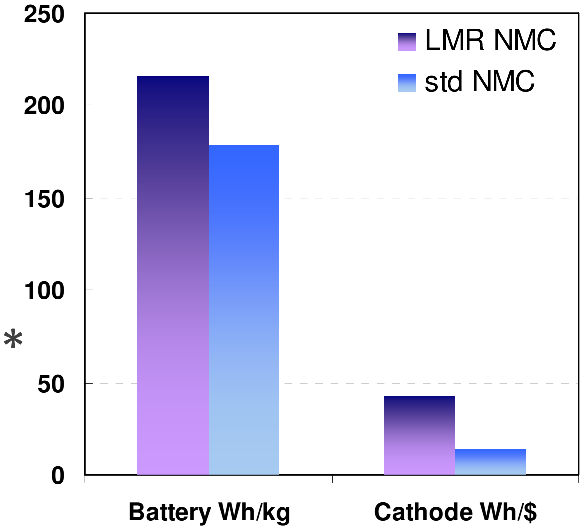
218th ECS Meeting – Las Vegas

Need for Higher Specific Energy Materials

- Improving the energy density for a PHEV-40 battery
- Standard NMC cathode: 150 mAh/g
  - Battery size: 50 L, 80 kg *
- Goal for Li & Mn rich oxides (LMR)

  LMR NMC: 285 mAh/g
  - Battery size: 44 L, 66 kg (313 Wh/L, 218 Wh/kg)*
  - ~ **14%** and **22%** increase in energy density

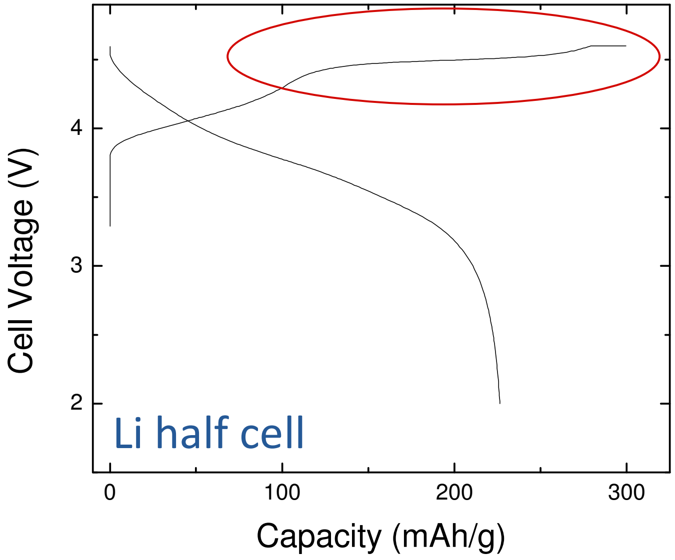


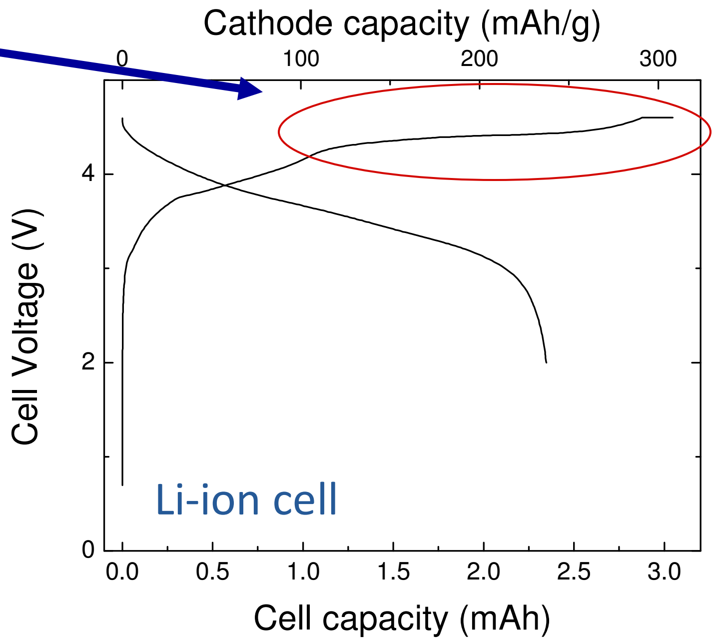
- LMR also reduces cost of active materials (less Co & Ni)
  - Standard NMC ~$40/kg; 3.8 Ah/$
  - LMR NMC ~$25/kg; 11.4 Ah/$
  - Reduce the cost of cathode material by 2/3

* Calculated using Argonne Battery Design Model

$xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M=Mn,Ni,Co)

- Structural feature
  - Integration and interconnection of $LiMO_2$-like (rhombohedral) and Li_2MnO_3 (monoclinic) structures at atomic level (Abs #987, Aurbach et al.)
- Electrochemical feature
  - Activation of Li_2MnO_3 at >4.4 V vs. Li/Li^+, leading to high capacity





Implementing LMR NMC into full-cells

- High-capacity ANL-NMC material[1]
  - Mildly fluorinated $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Mn_{0.31}Co_{0.25}O_2$
  - Alternatively, $Li_{1.2}(Mn_{0.524}Ni_{0.176}Co_{0.1})F_yO_{2-y}$ (y~0.05)

- Previous half cell performance
  - High capacity (250 mAh/g at 22 °C, 295 mAh/g at 55 °C)
  - Good cycle efficiency
  - Good capacity retention
  - Limited rate capability

- Full-cell performance (???)

[1] S.-H. Kang, K. Amine, *JPS* **146** (2005) 654–657

Experimental details

- Cell configurations
  - Cathode: ANL-NMC
  - Anode: metallic lithium or graphite (MCMB 10-28 or Mag-10)
  - 1.2 M $LiPF_6$ in EC/EMC (3:7 wt), no additives
  - 2032 coin cell
  - All cycling data at least in duplicate

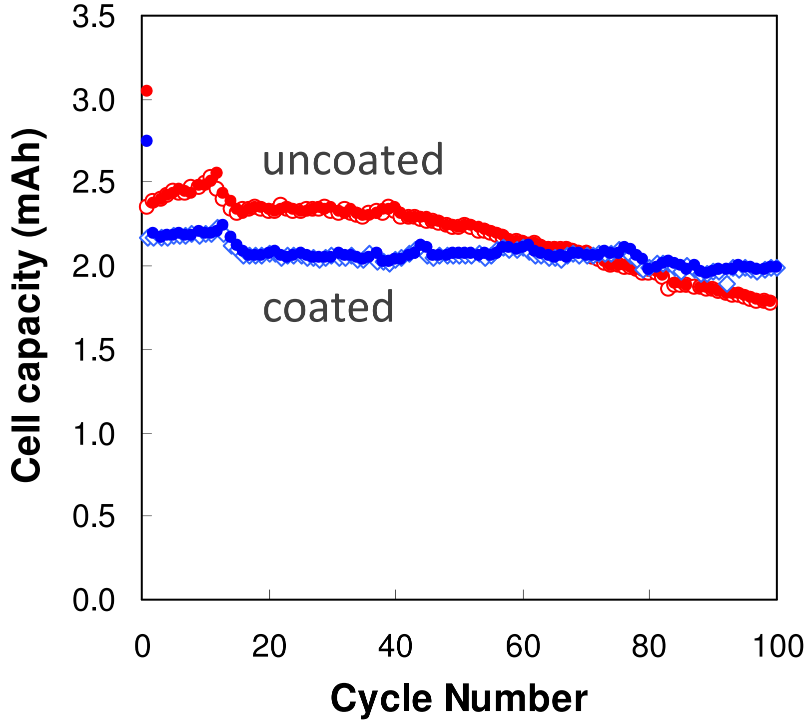
- Reference electrode studies use a “fixture cell” 32 cm^2 area

- Compare pristine to Li-Ni-PO_4 coating[2]
  - Sol-gel method, 5 mol %
  - Better rate capability (200 mAh/g at 1C)
  - Improved cycling efficiency

2) S.-H. Kang, M.M. Thackeray, *Electrochem Comm* **11** (2009) 748-751

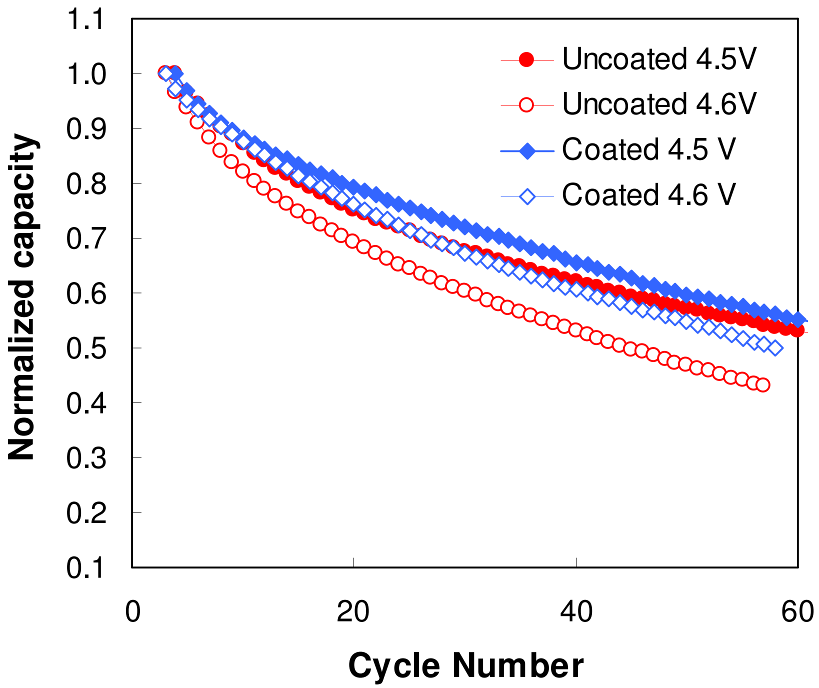
Room temperature full-cell cycling

- 2-4.6V @ C/15, 3hr CV
- Coated ANL-NMC shows less capacity fade with cycling
- Uncoated ANL-NMC shows unacceptable fade



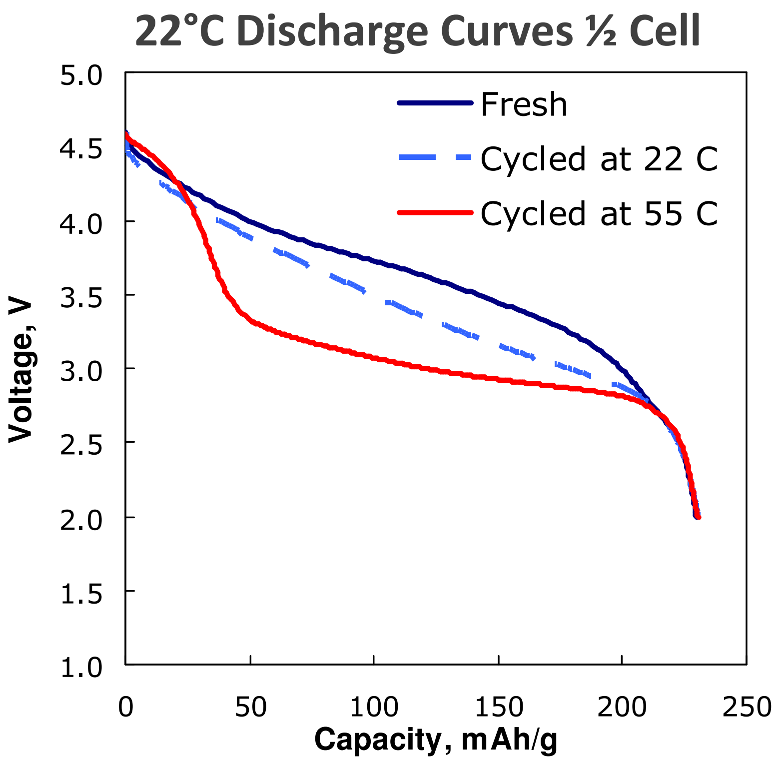
55 °C full-cell cycling

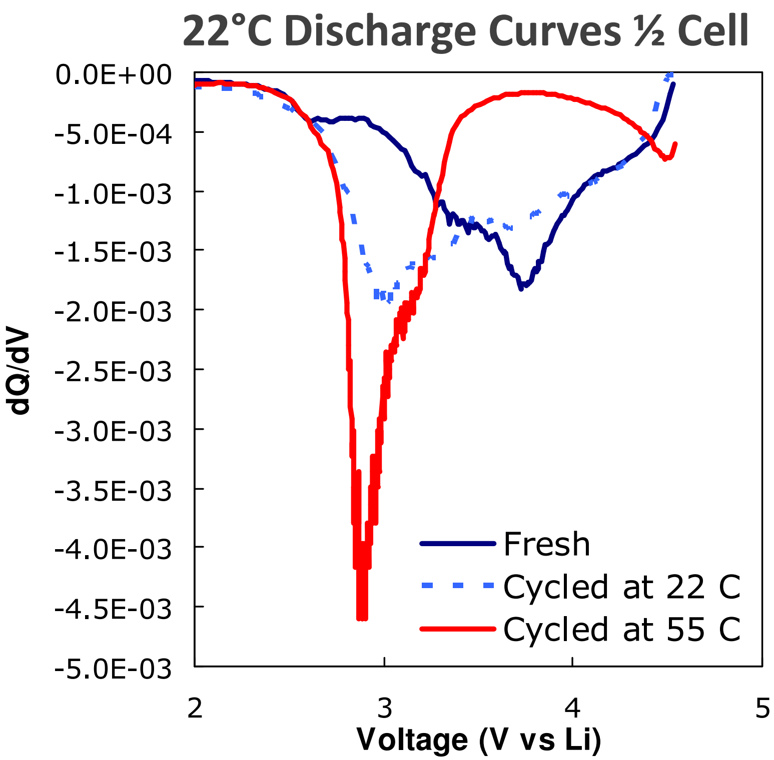
- Potential windows
  - 2-4.6V @ C/15, 3hr CV
  - 2-4.5V @ C/15
- Coated ANL-NMC shows less capacity fade with cycling
- Lowering high potential reduces fade for uncoated material



Change in voltage profile after cycling

- Electrode harvested from aged 55°C full cell
- Rebuilt in a half cell and tested at 22°C





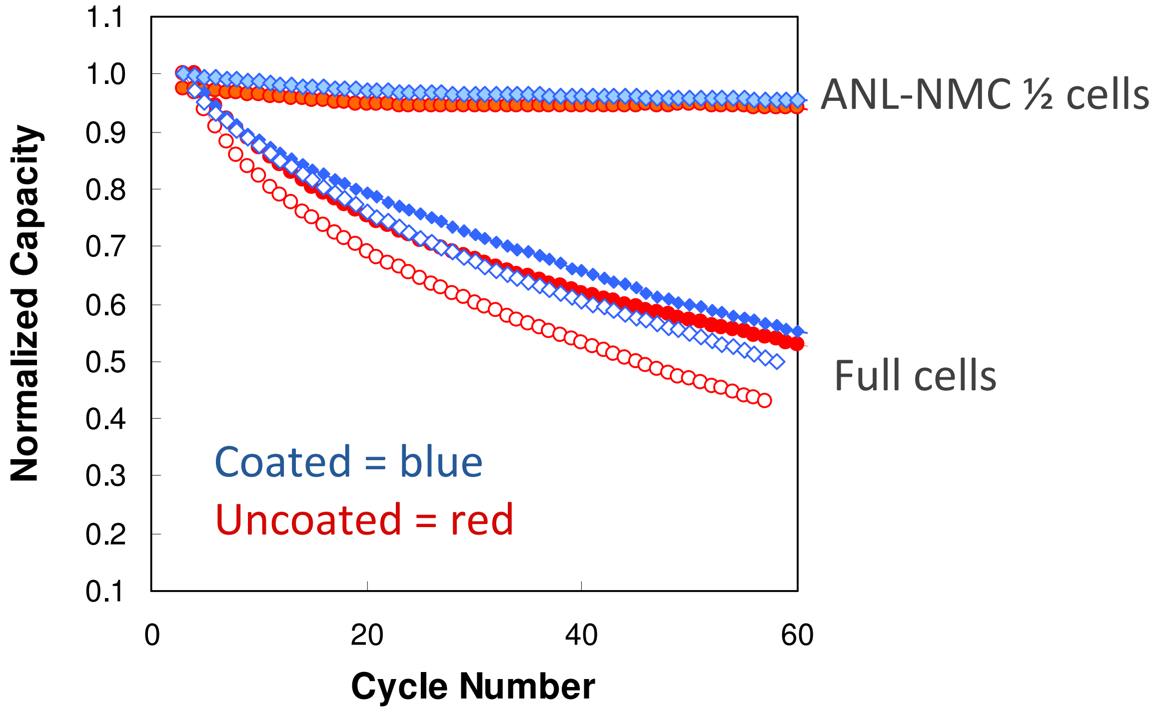
$LiNiPO_4$ coated ANL-NMC after 65 cycles at 55 °C
Or 50 cycles at 22 °C

Challenges indentified

- Capacity fade
  - Role of coating
  - Impact of high potential
  - Mechanism
- Power fade
  - Initial analysis of large impedance of ANL-NMC
- Voltage profile change
  - Source of change
  - Sources of acceleration
  - Mechanism

Origin of capacity fade

- Graphite electrode is likely candidate
- Verified by high temperature cycling of ANL-NMC half cells
- Both (un)coated ANL-NMC shows little capacity fade in ½ cell

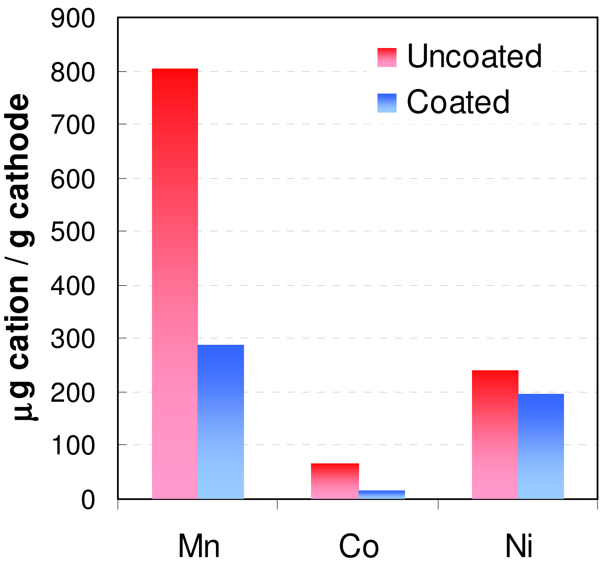


2-4.6V @ C/15, 3hr CV at 55°C

Negative electrode capacity fade

- ICP/MS reveals difference in cation levels at harvested graphite
- Mn and Co dissolution is reduced by ~70 % for coated ANL-NMC

- Ion dissolution will be a challenge for ANL-NMC as it is with other Mn rich systems



$Li_{1.2}(Mn_{0.524}Ni_{0.176}Co_{0.1})F_yO_{2-y}$

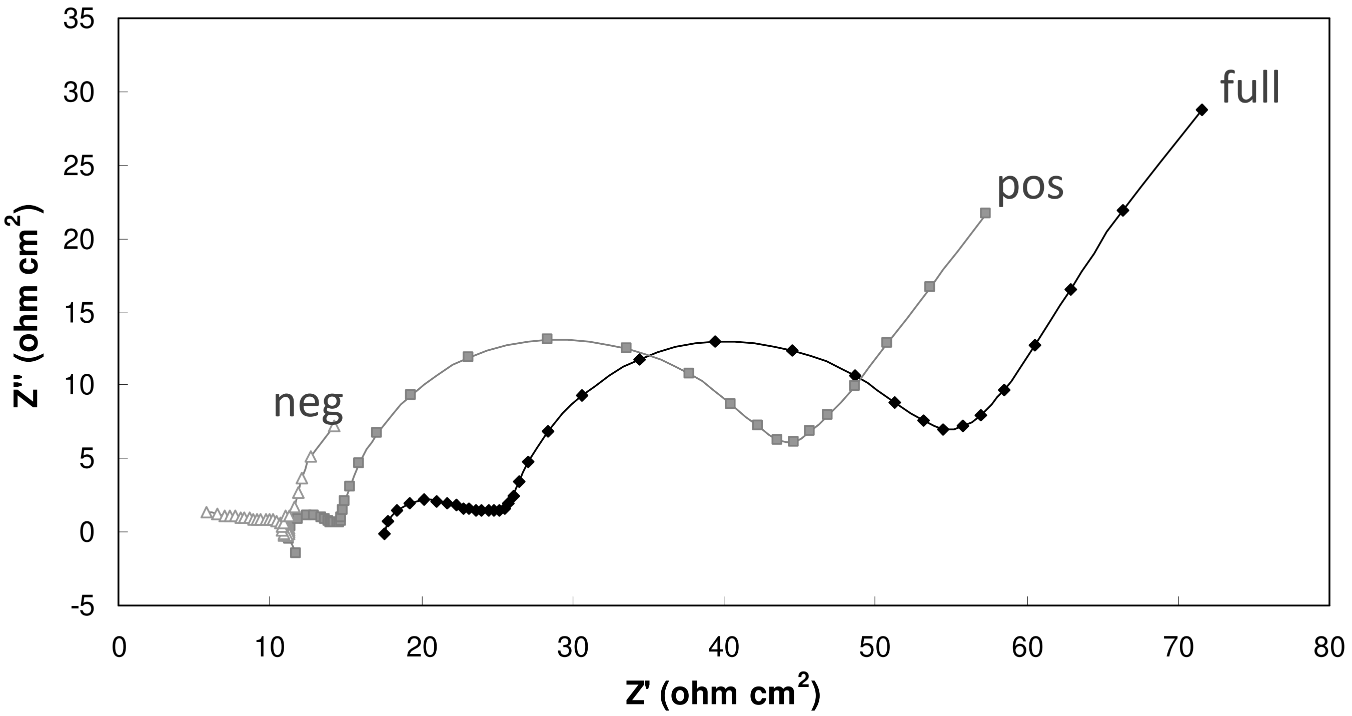
µg_cation / g_cathode

	Mn	Co	Ni
Uncoated	804	65	241
Coated	288	17	195

2-4.5 V @ C/15, at 55 °C

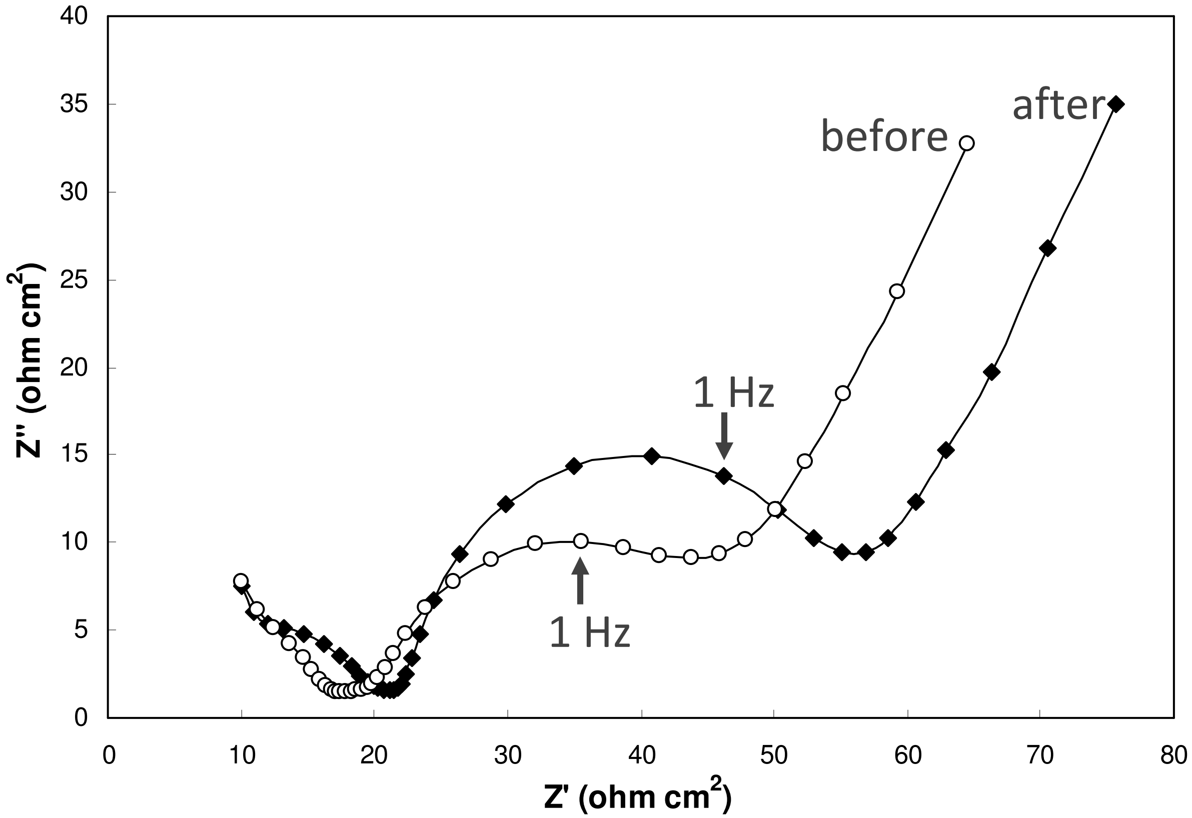
Initial impedance study

- Uncoated ANL-NMC dominates full-cell impedance
  - After activation 2-4.6V @ C/15, 3hr CV at 30 °C
  - Reference electrode cell, 100kHz - 0.01Hz @ 3.75 V
- Frequency response suggests sluggish interfacial properties



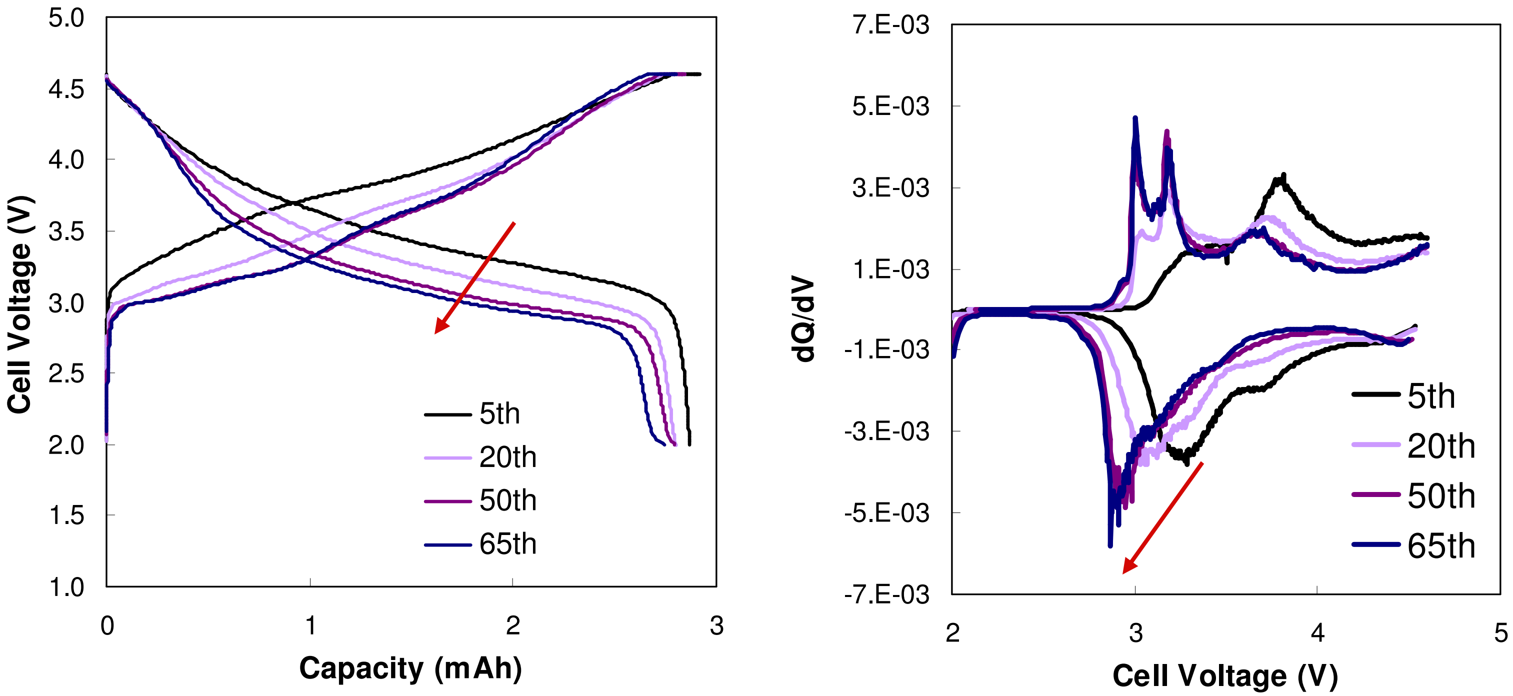
Initial impedance study

- Impedance before and after activation process
  - Uncoated ANL-NMC in Full cell @ 4.0 V, 100kHz-0.01Hz
  - Largest change in interfacial regime



Voltage profile change during aging

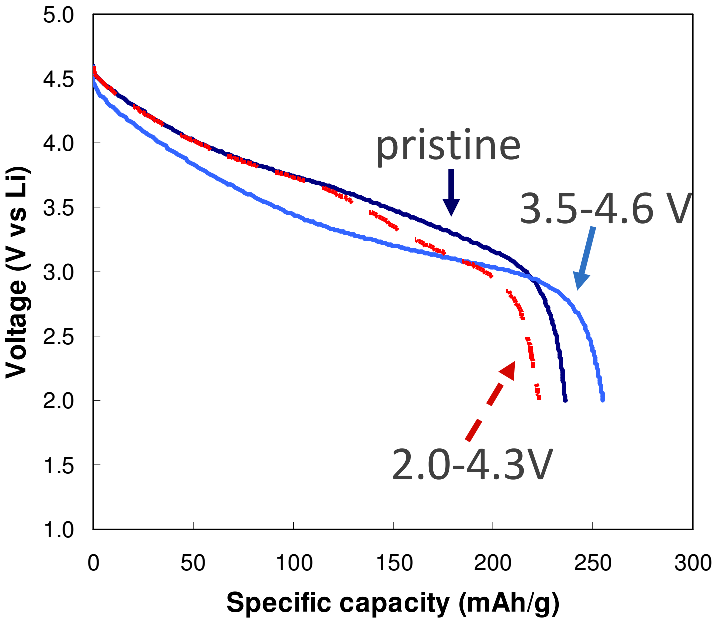
- Voltage profile change
  - Maximum peak in dQ/dV discharge shifts from 3.2 to 2.9 V
  - Distinct changes in charge dQ/dV as well
  - No difference seen between coated and uncoated

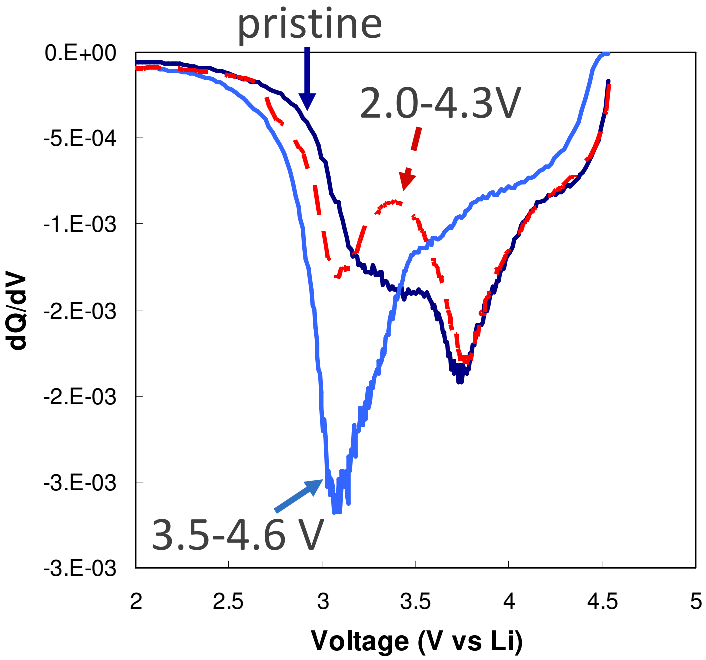


2-4.6 V @ C/15, 3 hr CV at 55 °C w/ uncoated ANL-NMC

Cycling in different voltage windows

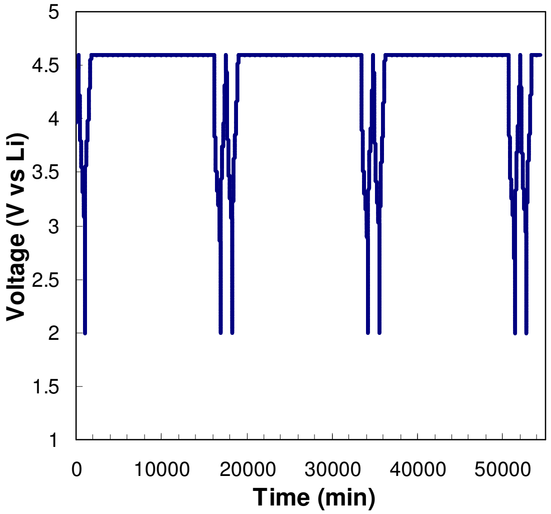
- Test cycling potential ranges (windows) of uncoated ANL-NMC
  - 5 cycles at 22°C, 2-4.6V, 3hr CV
  - 40 cycles at 55°C, 3.5-4.6 V or 2-4.3 V
  - 3 cycles at 22°C, 2-4.6V, 3hr CV
- Higher potential and temperature accelerate profile change

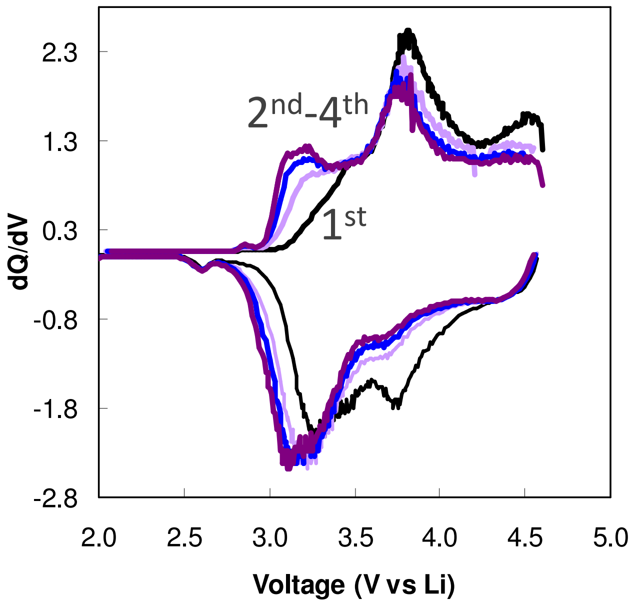




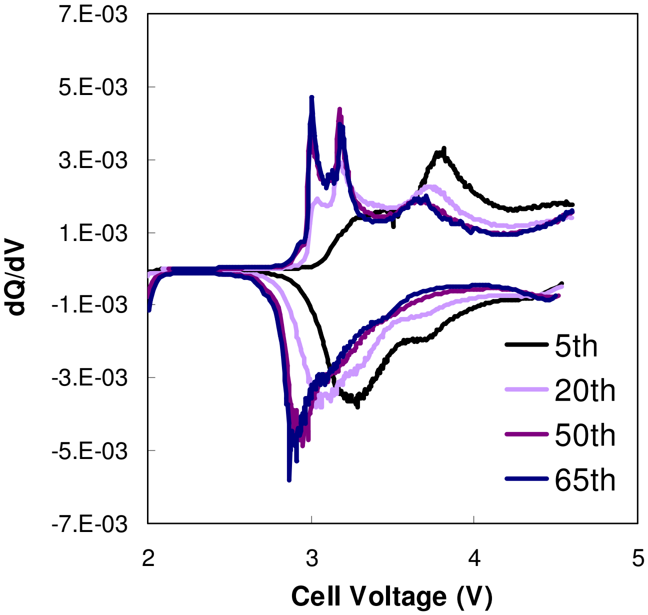
High potential hold

- 10 day 4.6 V hold, 2 cycles
  - Promote side reaction with electrolyte
  - Promote activation of Li_2MnO_3
- Change is not as significant as cycling





dQ/dV at 55 °C in ½ cell, uncoated



Continuous cycles at 55 ˚C in ½ cell, uncoated

Shown previously on slide 14

Acceleration of voltage profile change

- Cycling induces profile change
  - Shuffling a deck of cards?
- Profile change accelerated by
  - Temperature
  - High potential cycling (low lithium concentrations in cathode)
- Change in crystallography is undetermined
  - XRD is not sensitive enough, XAS studies needed
  - What phase(s) are being formed?
  - What is the mechanism?

Summary

- Capacity fade
  - Ion dissolution from ANL-NMC aggravates graphite SEI growth
- Role of coating
  - Reduce dissolution of cations
    - Reduce side reaction with electrolyte
    - Stabilize Mn^{4+} ions with the presence of $Ni^{4+/2+}$ in coating
  - Improves rate capability
- Voltage profile change
  - Accelerated by temperature and high potential cycling
  - Most likely not a side reaction with electrolyte
  - More fundamental analysis needed (**XAS**, etc)

Acknowledgements

- Support for this work is from DOE-EERE, Office of Vehicle Tech.
  - David Howell
  - Peter Faguy
- Dennis Dees, ANL
- Daniel Abraham, ANL

- The presentation has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory (“Argonne”). Argonne, a U.S. Department of Energy Office of Science Laboratory, is operated under Contract No. DE-AC02-06CH11357.