Promises and Challenges of Lithium- and Manganese-Rich Transition-Metal Layered-Oxide Cathodes

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Project ID# ES177

Overview

Timeline

- Start: October 2012
- Finish: September 2013

Barriers

- Development of a PHEV and EV batteries that meet or exceed DOE/USABC goals.
  - Calculating total battery mass, volume, & cost from individual components
  - Predicting methods & materials that enable manufacturers to reach goals

Budget

- Total project funding
  - 100% DOE
- FY2013: $115K (Voltage Fade)

Partners (Collaborators)

- ANL Voltage Fade Team
- ANL Cell Fabrication Facility

Project Objectives - Relevance

- Quantify materials level performance requirements of Li- and Mn-rich layered transition metal oxide cathodes (LMR-NMC) necessary to significantly improve upon existing Li-ion cathodes (pack level cost and energy density)
- Document barriers that need to be overcome to achieve the higher level of performance

Milestones

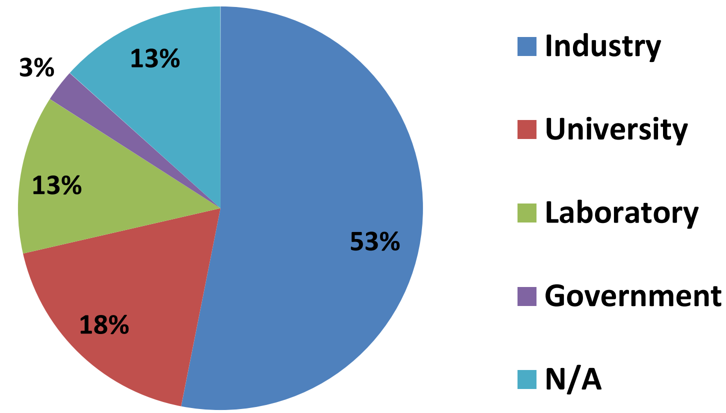
- Map out performance and cost space for generic chemistries (Dec 2012) **complete**
- Initial assessment of LMR-NMC capacity and average voltage to outperform existing materials(Dec 2012) **complete**
- Finalize LMR-NMC material level properties required to meet DOE PHEV40 and EV goals (July 2013) **on target**
- Document state-of-the-art performance and barriers still remaining to overcome for LMR-NMC (Sept 2013) **on target**

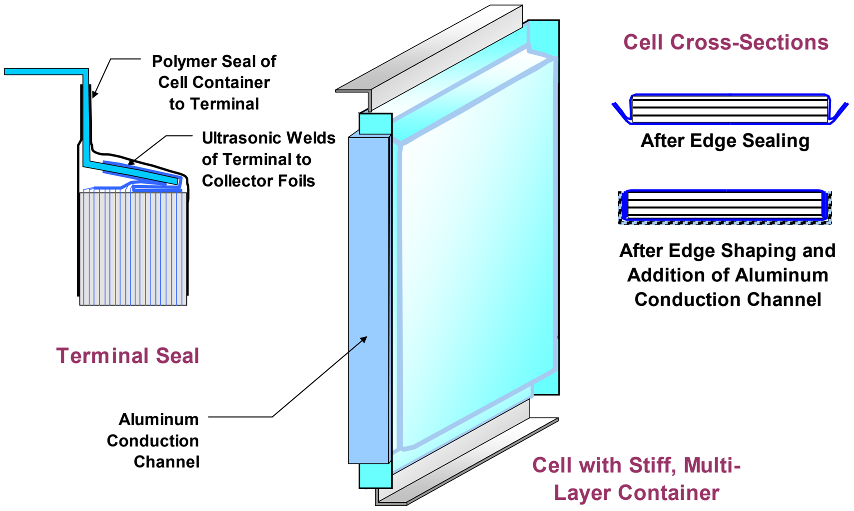
Approach

- Utilize BatPaC: peer-reviewed, transparent, publicly available bottom-up Li-ion performance and cost model
  - Map out performance and cost space
  - Sensitivity of material properties
  - Quantified targets for material
- Leverage Argonne Voltage Fade team and published literature for state-of-the-art understanding of LMR-NMC materials
- Interact with OEMs and cell suppliers to understand their view of barriers at materials, cell, and system level

BatPaC v2.1 available from www.cse.anl.gov/batpac

Over 600 unique user downloads

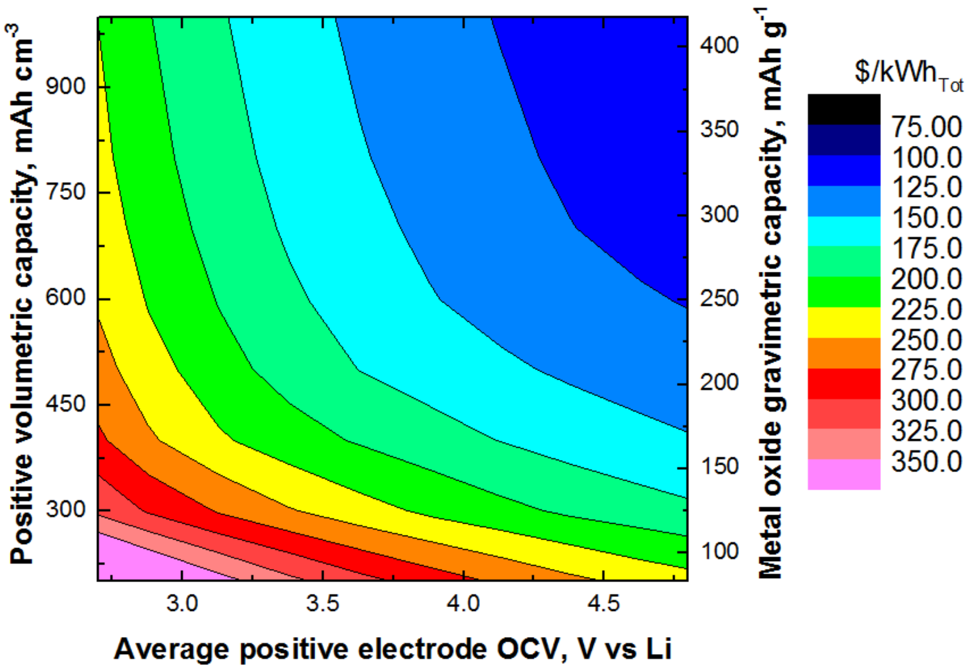




Major Accomplishments and Technical Progress

- Mapped out performance and cost space
- Created first draft of positive electrode material level targets
- Detailed barriers impeding implementation

40 kWh$_{Tot}$, 100 kW 360V, Adv Si negative



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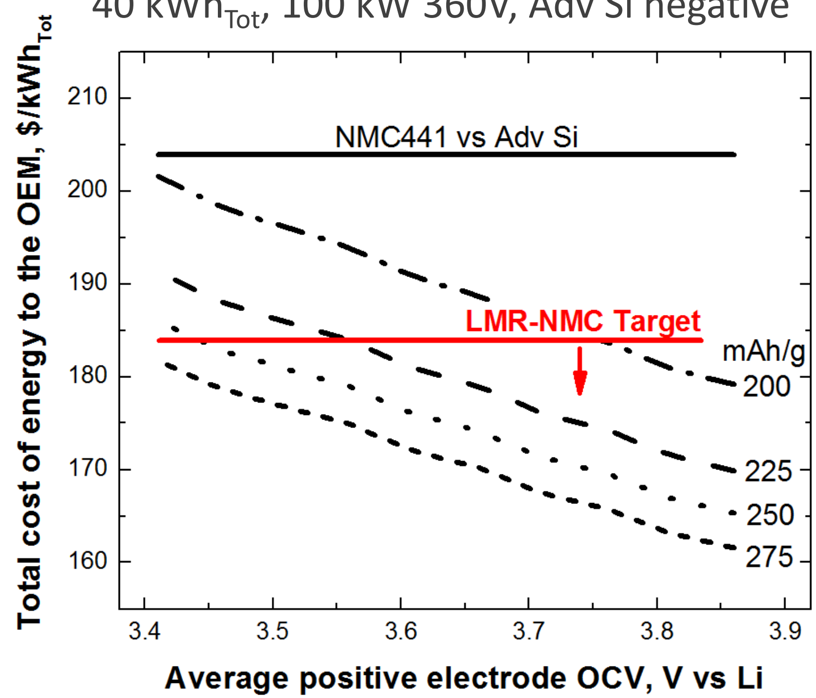


BatPaC approach to understanding cost & energy

- Designs Li-ion battery and required manufacturing facility based on user defined performance specifications for an assumed cell, module, and pack format
  - Power, energy, efficiency, cell chemistry, production volume
- Calculates the total cost to original equipment manufacturer (OEM) for the battery pack produced in the year 2020
  - Not modeling the cost of today's batteries but those produced by successful companies operating in 2020
  - Some advances have been assumed while most processes are similar to well-established high-volume manufacturing practices
- Efficient calculations completed in fractions of a second

BatPaC calculation overview

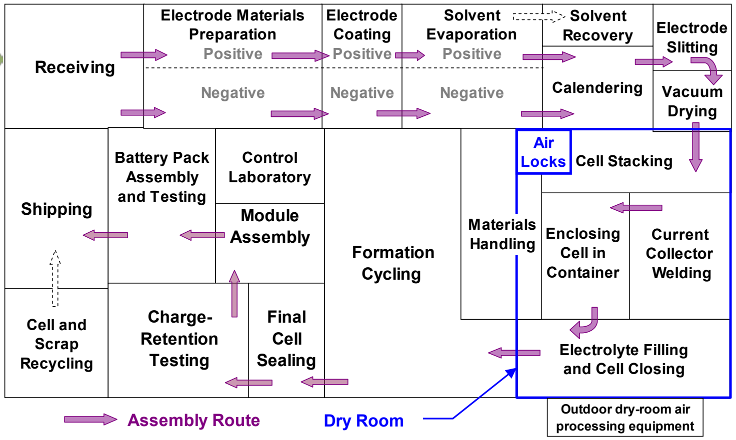
Iterate Over Governing Eqs. & Key Design Constraints

- Cell, module, & pack format
- Maximum electrode thickness
- Fraction of OCV at rated power

Battery Pack Components

- Volume
- Mass
- Materials
- Heat generation

$$\text{Process cost} = \text{Baseline cost} \cdot \left(\frac{\text{Processing rate}}{\text{Baseline processing rate}} \right)^{p}$$



- **Pack specifications**
  - Power and energy (range)
  - Number of cells
- **Cell Chemistry**
  - Area-specific impedance (ASI)
  - Reversible capacity C/3
  - OCV as function of SOC
  - Physical properties

Governing Equations

$$E = N \cdot C \cdot \left(U_E - \frac{C}{3} \frac{ASI_E}{A} \right)$$

$$L = \frac{C}{Q \cdot \rho \cdot \varepsilon \cdot A}$$

$$I = \frac{P}{A \cdot N \cdot U_P \left[\frac{V}{U} \right]}$$

$$A = \frac{ASI_P \cdot P}{N \cdot (U_P)^2 \left[\frac{V}{U} \right] \left(1 - \left[\frac{V}{U} \right] \right)}$$

$$ASI = \frac{\alpha + f(I)}{L} + \beta$$

Total Cost to OEM

- Materials & purchased items
- Individual process steps
- Overhead, depreciation, etc.
- Warranty

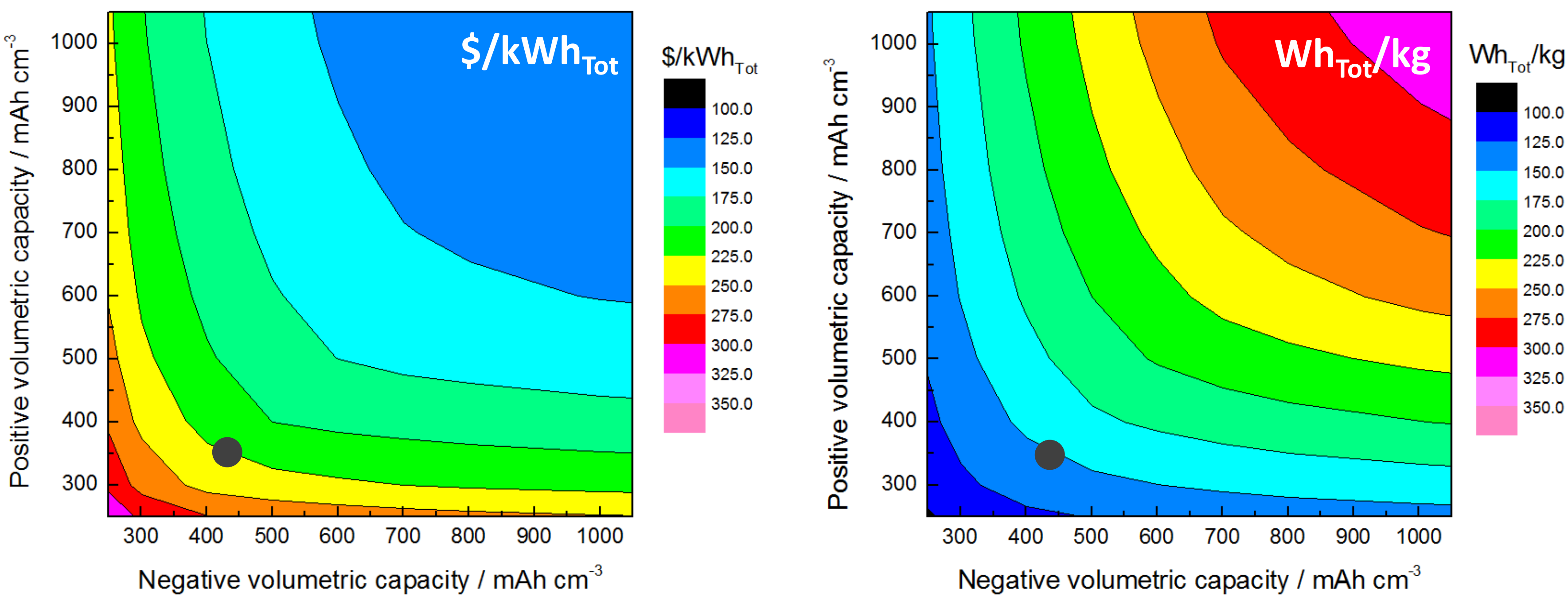
Mapping out performance and cost space

- Use EV150 battery, lower P/E ratio is less sensitive to ASI
  - Results will be more broadly applicable to other chemistries
  - 40 kWh_{Tot}, 100 kW, 360 V @ 100k/yr
- Materials properties default to NMC333/Gr when not overridden
  - Density, electrode porosity, ASI, etc
- Active material costs assumed in contour plots:
  - Positive $30/kg; Negative $20/kg
- Advanced Si composite anode assumed for capacity-voltage plots
  - 50% electrolyte volume fraction in discharged state
  - 1300 mAh/g; 80:10:10 active:carbon:binder
  - Prelithiated to achieve 85% 1^{st} cycle efficiency

Constant voltage and ASI contour plots

- Steepest decent by increasing both electrode capacities
- Volumetric drives energy density (but active materials are $/kg)
  - $mAh/cm^3 = \rho \cdot \varepsilon \cdot Q$ [$g/cm^3_{act} \cdot cm^3_{act}/cm^3_{elect} \cdot mAh/g$]

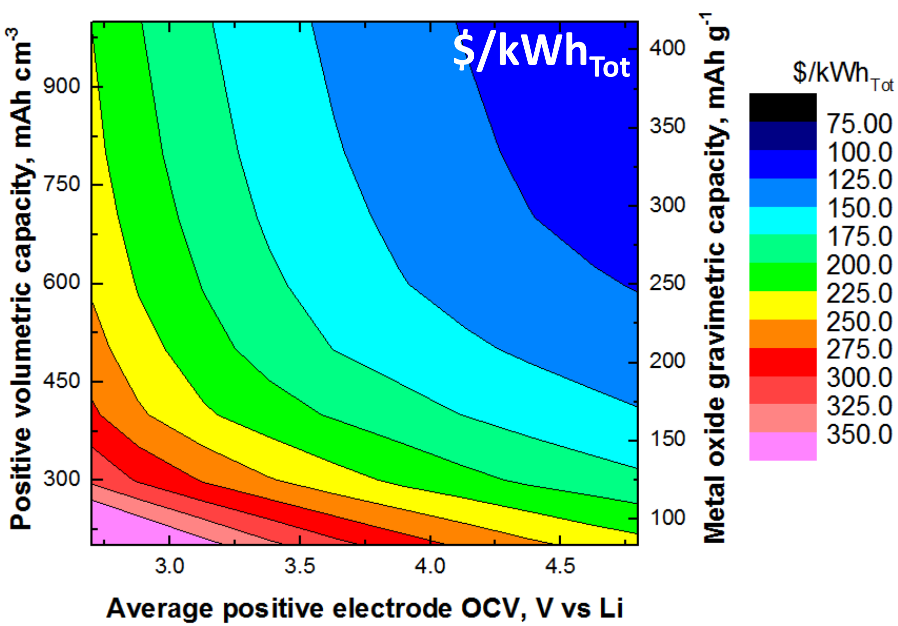
3.5 V_{cell} for 40 kWh_{Tot}, 100 kW 360V

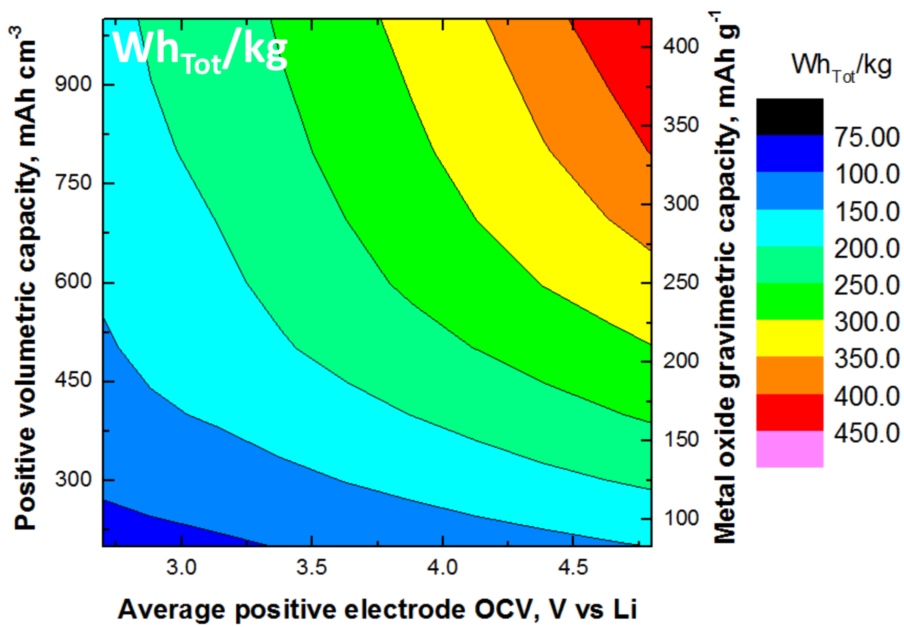


● NMC333/Gr volumetric capacities

Positive voltage and capacity contour vs Si anode

- Diminishing returns for improving a single electrode capacity
- Increasing cell voltage key to improve performance and cost
- Contour plot shows transition between two regions
  - < 500 mAh/cm^3 (~210 mAh/g): capacity has stronger sensitivity
  - > 600 mAh/cm^3 (~250 mAh/g): voltage has stronger sensitivity





DOE-EERE Vehicle Technologies Program – BatPaC available from www.cse.anl.gov/batpac

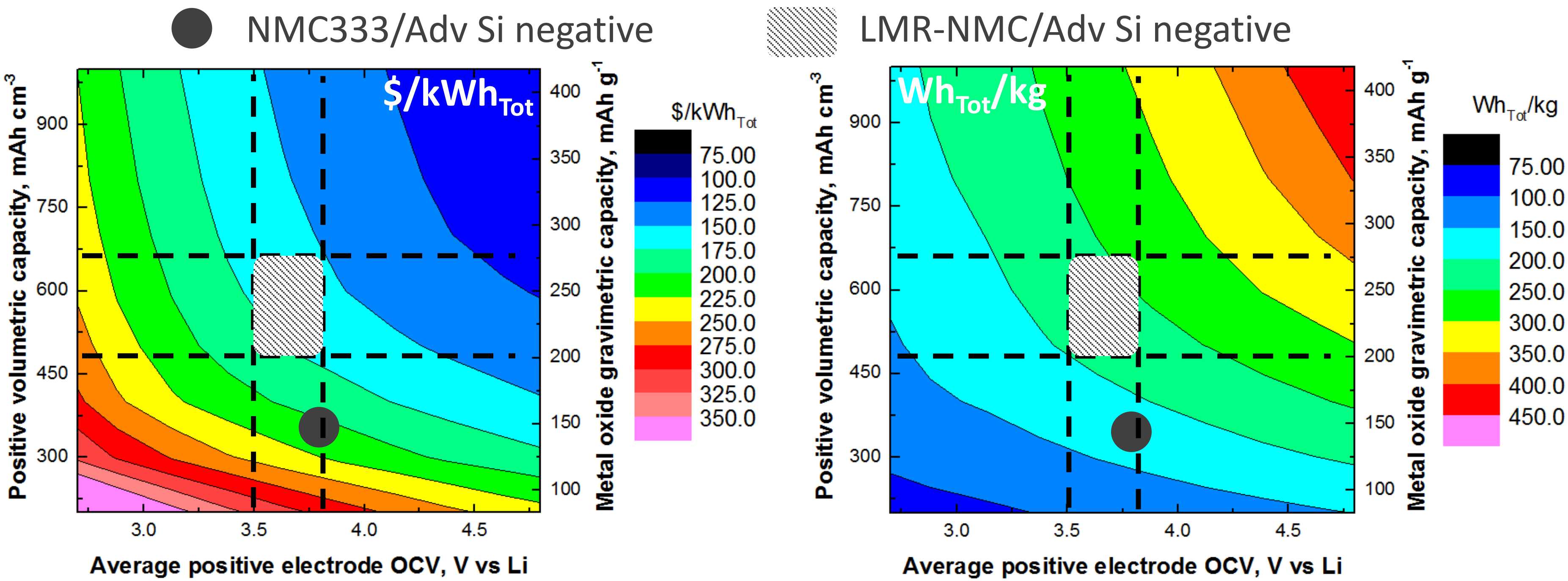
40 kWh$_{Tot}$, 100 kW 360V, Adv Si negative
Positive properties similar to metal oxide

Contour plots takeaways

- Specific energy and cost strongly inversely correlated
- Diminishing returns for improving a single electrode capacity
- Increasing cell voltage key to improve performance and cost
- Volumetric capacity is a driver
  - Volume fraction and density of active material are important
  - Related to tap/tapped density (not a rigorous correlation)
- Inflection point from capacity to voltage impact is driven by electrode thickness limitation (100 microns in BatPaC)
  - Tortuous Li^+ transport in electrolyte
  - Life and cold temperature performance
  - Manufacturing reliability and quality
  - All complex phenomena not well understood!
- *We are limited to the materials that we have: e.g. LMR-NMC*

LMR-NMC electrodes promise to lower cost

- Initial LMR-NMC analysis from contour plots
- Ranges for predicted LMR-NMC capacity and OCVs
- Ignore difference in active material price
  - NMC333 vs LMR-NMC: \$30-40/kg vs \$20-25/kg



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Promise of LMR-NMC positive electrodes

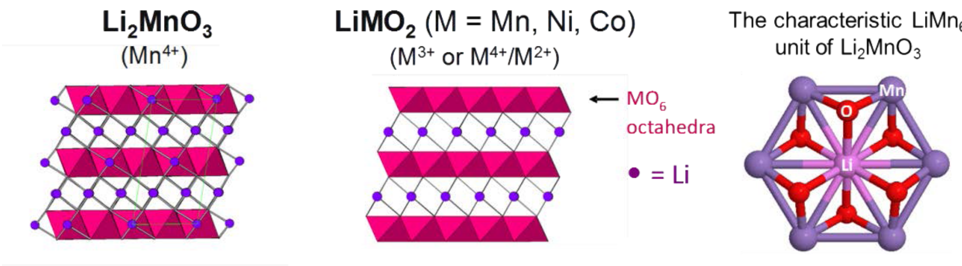
- $xLi_2MnO_3 \cdot (1\text{-}x)LiMO_2$ materials are under development worldwide to increase energy density and lower cost
  - Hypothesis: Li_2MnO_3 increases the stability of the layered structure
  - Thus, allowing access to higher reversible capacities
- High capacity shows synergy with advanced Li-ion negative
- Rich in manganese lowering $/kg
- High in energy lowering $/kWh
- Safety performance may be similar to NMC333*

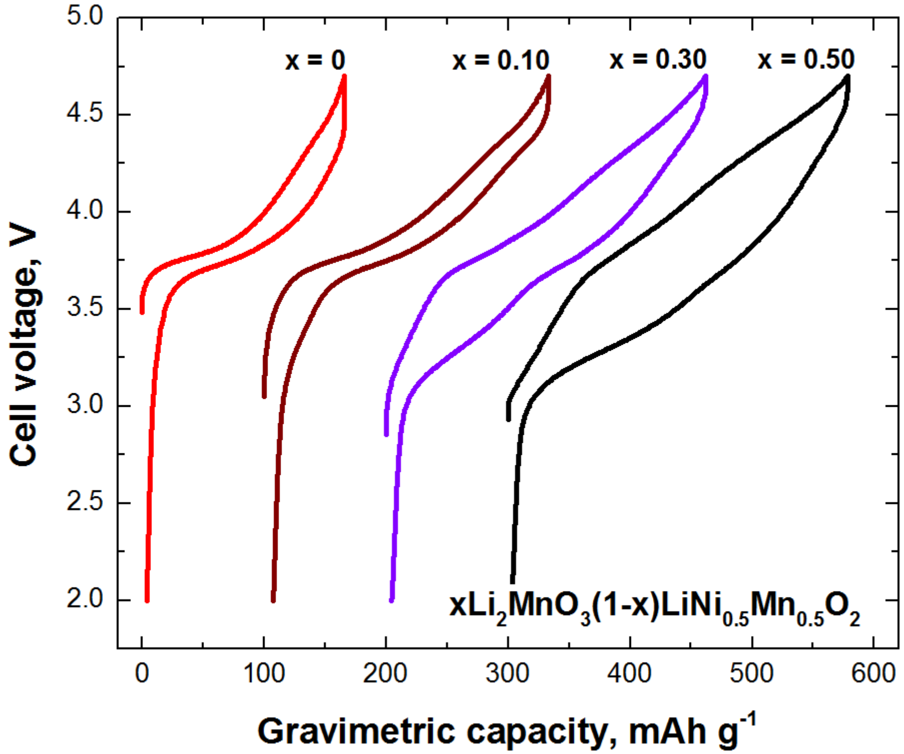
*Zonghai Chen et al. (Argonne) Poster ES035

- Some laboratory and industrial developers have demonstrated exciting progress to date

Tailor Li_2MnO_3 content to optimize Wh/kg

- $xLi_2MnO_3 \cdot (1-x)LiNi_{0.5}Mn_{0.5}O_2$
  - x = 0
    - 160 mAh/g, 3.78 U_{ave} vs Li
    - **605 Wh/kg vs Li**
  - x= 0.10
    - 225 mAh/g, 3.81 U_{ave} vs Li
    - **857 Wh/kg vs Li**
  - x= 0.30
    - 260 mAh/g, 3.67 U_{ave} vs Li
    - **954 Wh/kg vs Li**
  - x= 0.50
    - 275 mAh/g, 3.58 U_{ave} vs Li
    - **985 Wh/kg vs Li**
- Capacity and voltage tradeoff
  - **xLi_2MnO_3 between 0.1 to 0.4 may be best**

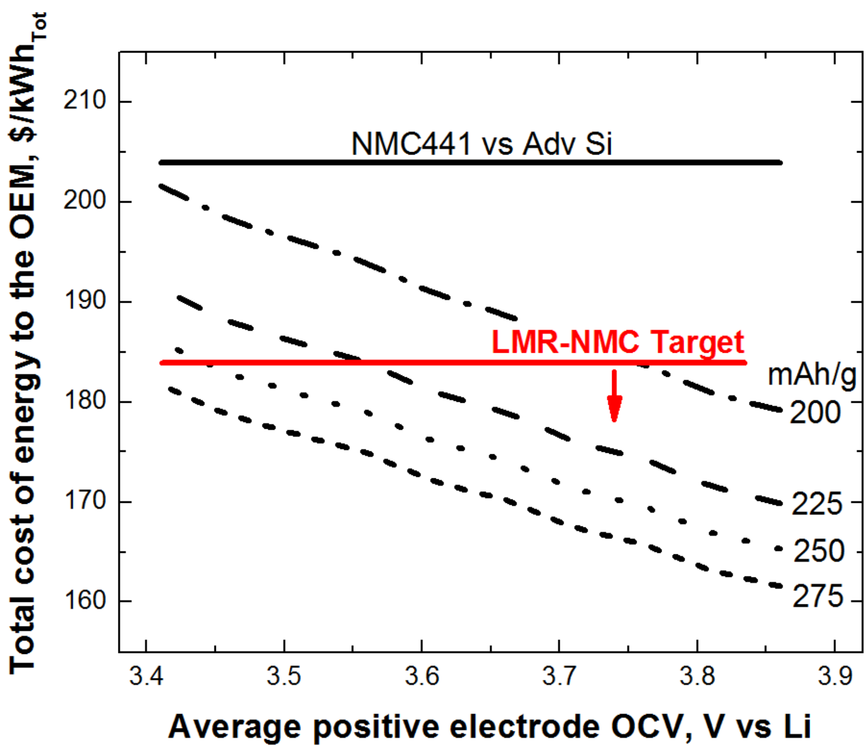




Lithium half cells
2nd cycle 30°C @ 5 mA/g
Jason Croy et al (Argonne)

Materials metrics for LMR-NMC: capacity vs voltage

- LMR-NMC must outperform the next best available material
- Assume this is a high performance NMC441*
  - $Li_{1.05}(Ni_{4/9}Mn_{4/9}Co_{1/9})_{0.95}O_2$ or $0.1Li_2MnO_3 \cdot 0.9LiNi_{0.497}Mn_{0.397}Co_{0.124}O_2$
  - Peak charge of 4.4 V vs Li, 175 mAh/g at C/3, U_{ave} = 3.90 V vs Li
  - Estimated price of positive active material
    - $25-30/kg for NMC 441
    - $20-25/kg for LMR-NMC
- C/3 Capacity and OCV targets:
  - 225 mAh/g and U_{avg} > 3.55 V vs Li
  - 250 mAh/g and U_{avg} > 3.45 V vs Li
  - 275 mAh/g and U_{avg} > 3.35 V vs Li
- 100 mV ≈ 25 mAh/g
- Average OCVs should be considered end of life values to account for voltage fade



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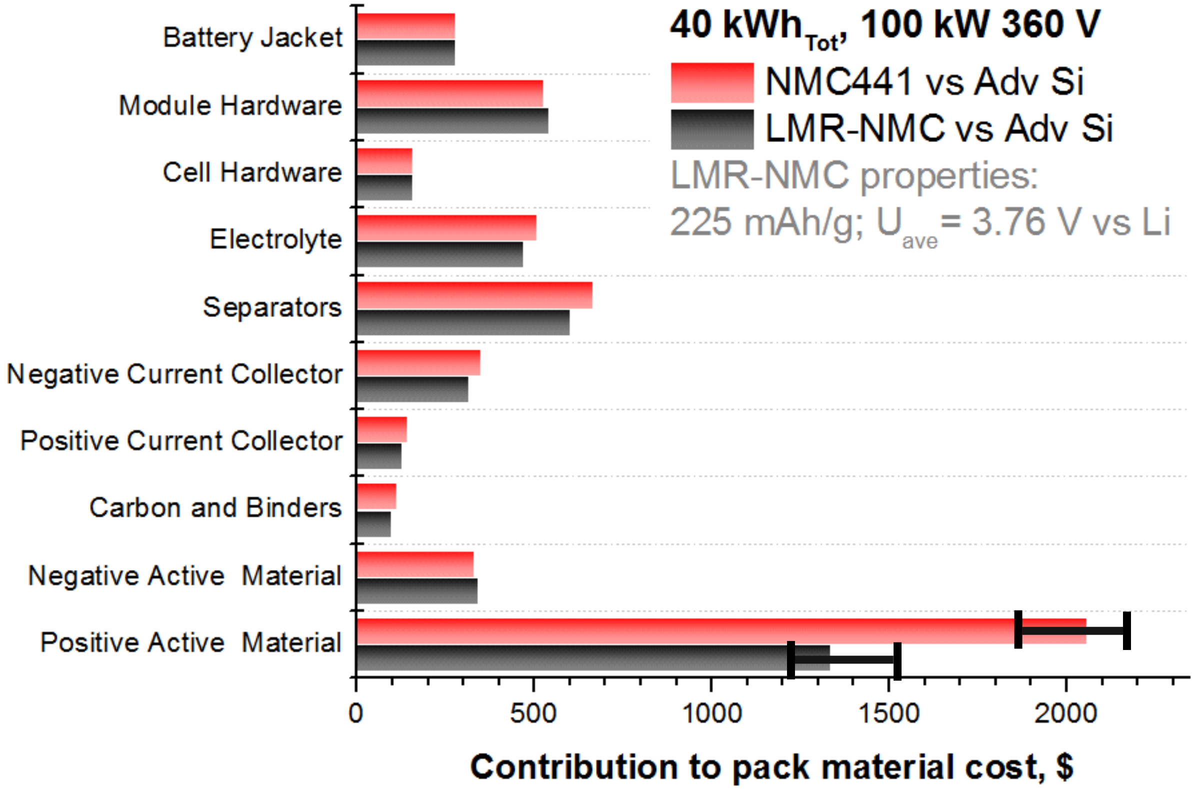
*S.-H. Kang et al. *J. Electrochem. Soc.* **158** (8) A936 (2011)

LMR-NMC reduces positive electrode cost, >$720

- Materials cost breakdown comparison
  - Assumes 225 mAh/g at C/3, 33% electrode porosity
  - Average LMR-NMC OCV, U_{ave}, of 3.76 V vs Li



Challenges for LMR-NMC positive electrodes

- Voltage fade and hysteresis
  - Structural change in bulk of material
  - Lowers energy density and complicates SOC management
- Oxide surface reactions during first charge
  - Possibly related to high ASI at low SOC and TM ion dissolution
  - Mitigation attempts with coatings and additives may help
- Low rate capability
  - Good enough for EVs, but challenging for low mile PHEVs (High P/E)
- Volumetric capacity
  - Lower tap density: higher Li content and need for smaller particle size

- Systems level concern: Wide voltage window, especially with Si, may require DC/DC convertor to boost voltage

Future Work

- Finalize LMR-NMC material levels properties
  - With and without an advanced negative electrode
  - EV case (new USABC goals this summer)
  - PHEV40 case: also quantify C/1 energy and ASI at rated power

- Document SOA performance and barriers that may prevent commercial acceptance
  - Initial performance
  - Life and safety performance
  - Low-temperature performance
  - System level SOC and power management issues

Summary of promise and challenges of LMR-NMC

- Intermediate Li_2MnO_3 content may prove best performers
  - Trade-off between voltage and capacity
  - Contour plots teach
    - < 500 mAh/cm^3 (~210 mAh/g): capacity has stronger sensitivity
    - > 600 mAh/cm^3 (~250 mAh/g): voltage has stronger sensitivity
- LMR-NMC positive electrodes must outperform the next best available material: high performance, low cobalt metal oxides
- Many barriers still exist:
  - Impedance and life issues see significant improvements
  - Voltage fade phenomenon is challenging
  - Achieving high volumetric capacity requires additional engineering

Acknowledgements & Collaborators

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  - **David Howell & Peter Faguy**

Collaborators:

- Argonne National Laboratory
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  - Cell fabrication facility
  - J. Croy, A. Burrell, M. Balasubramanian, M. Thackeray
  - D. Dees, P. Nelson, M. Bettge, D. Abraham, W. Lu
- Silent partners – cell suppliers and OEMs