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Improvements to Disordered Rocksalt Li-Excess Cathode Materials

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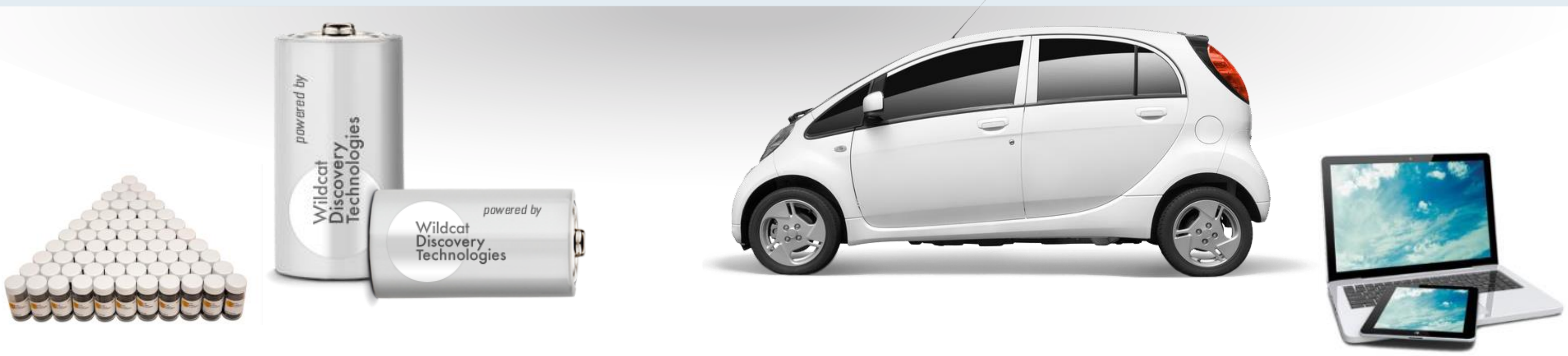
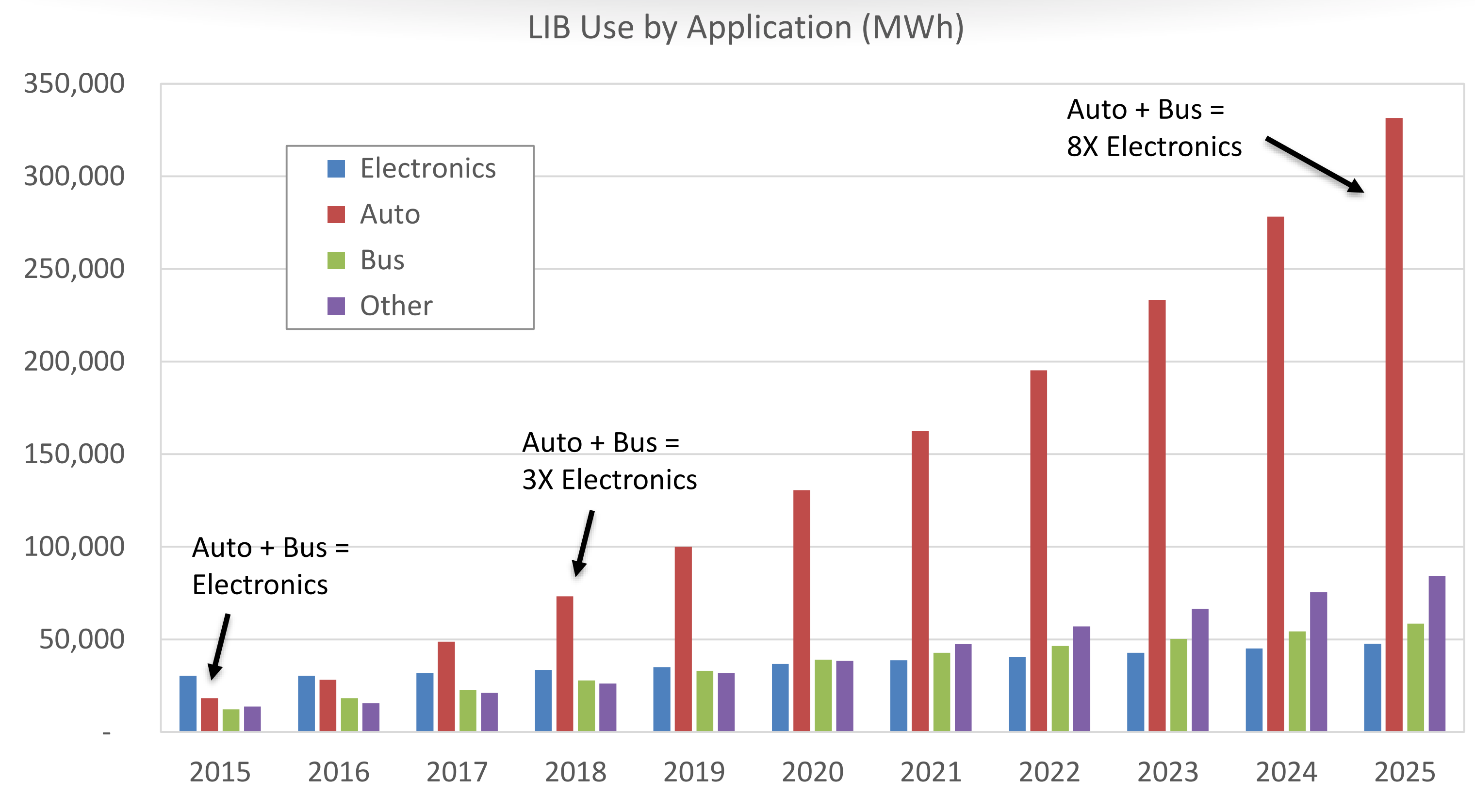


Presentation Outline

- The LIB Cathode Market
  - The Herd
  - The Opportunity
- Disordered Rocksalt
  - How it's Different
  - Performance Challenges
  - Development Progress
- Summary

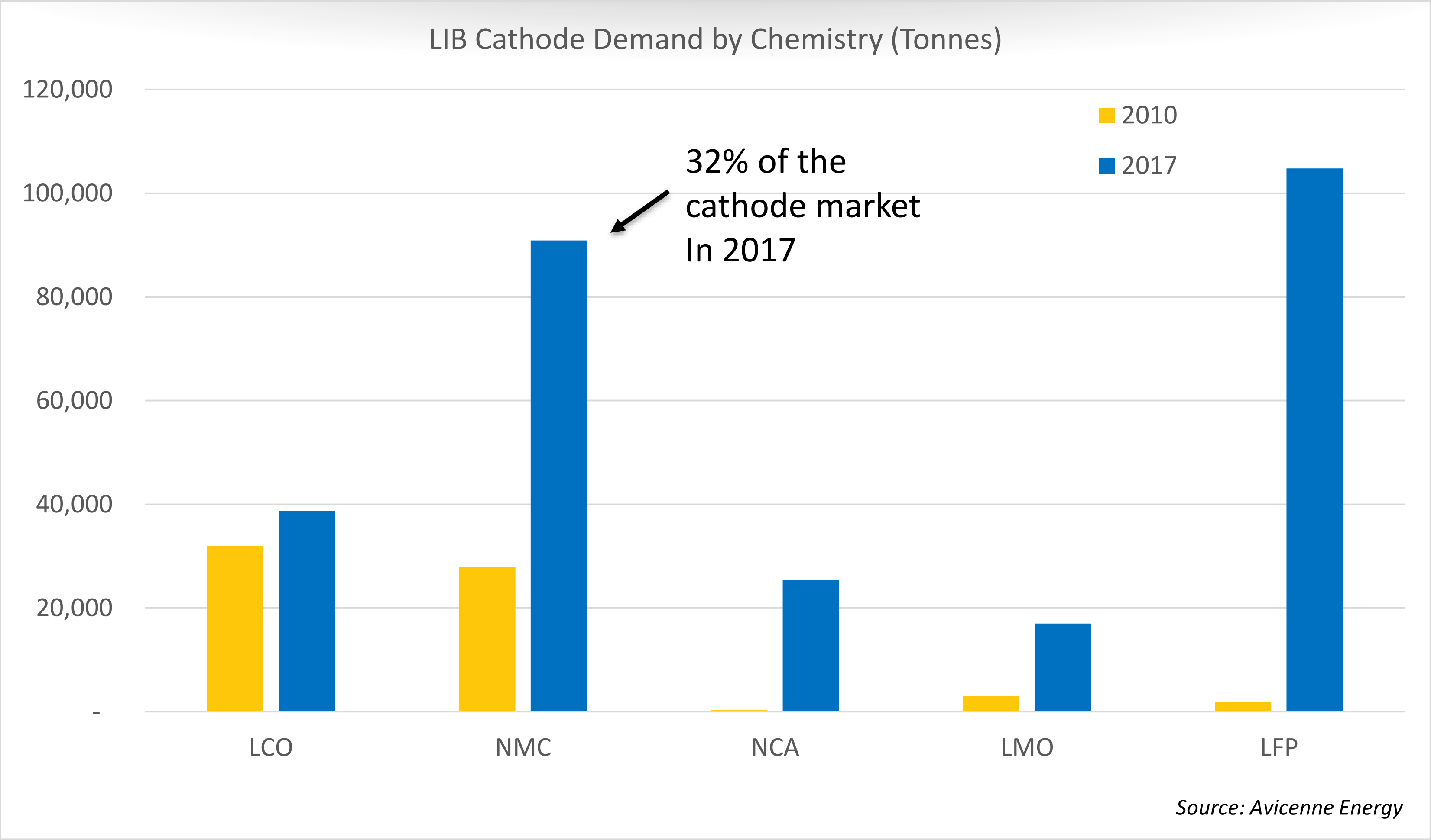
EV and E-Bus Markets are Growing Rapidly



Source: Avicenne Energy

The transportation market is driving enormous LIB demand

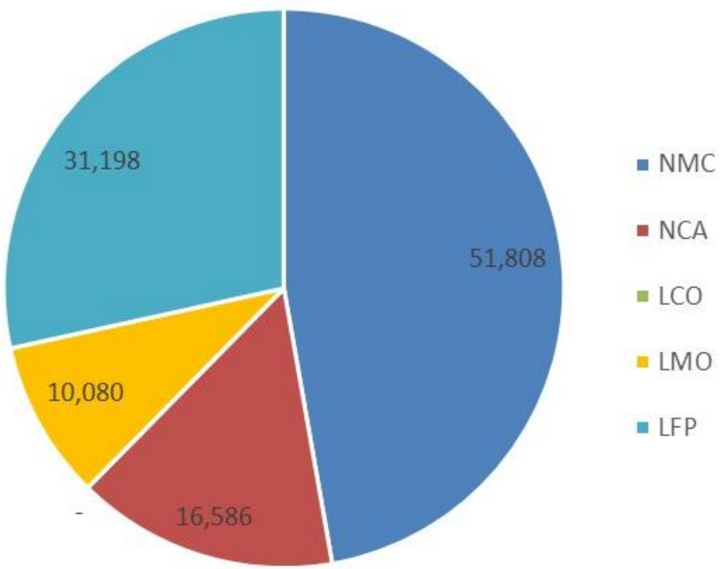
Lithium-Ion Cathode Demand – 2010 vs. 2017



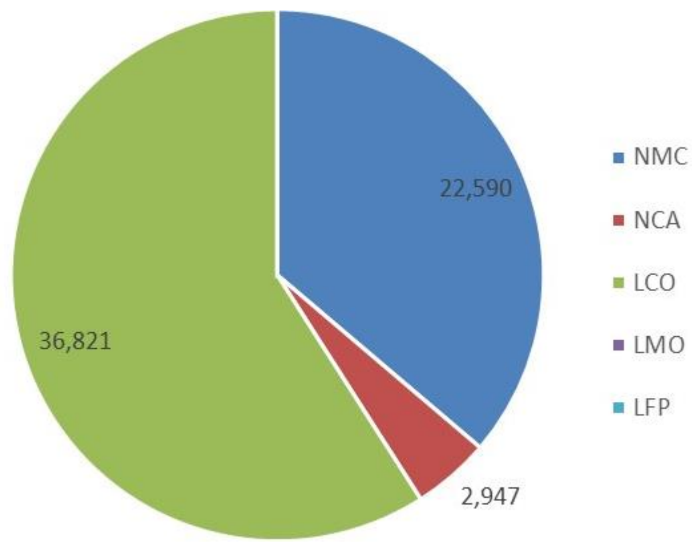
NMC and LFP use have grown dramatically since 2010

2017 Cathode Demand (Tonnes) by Market

Auto



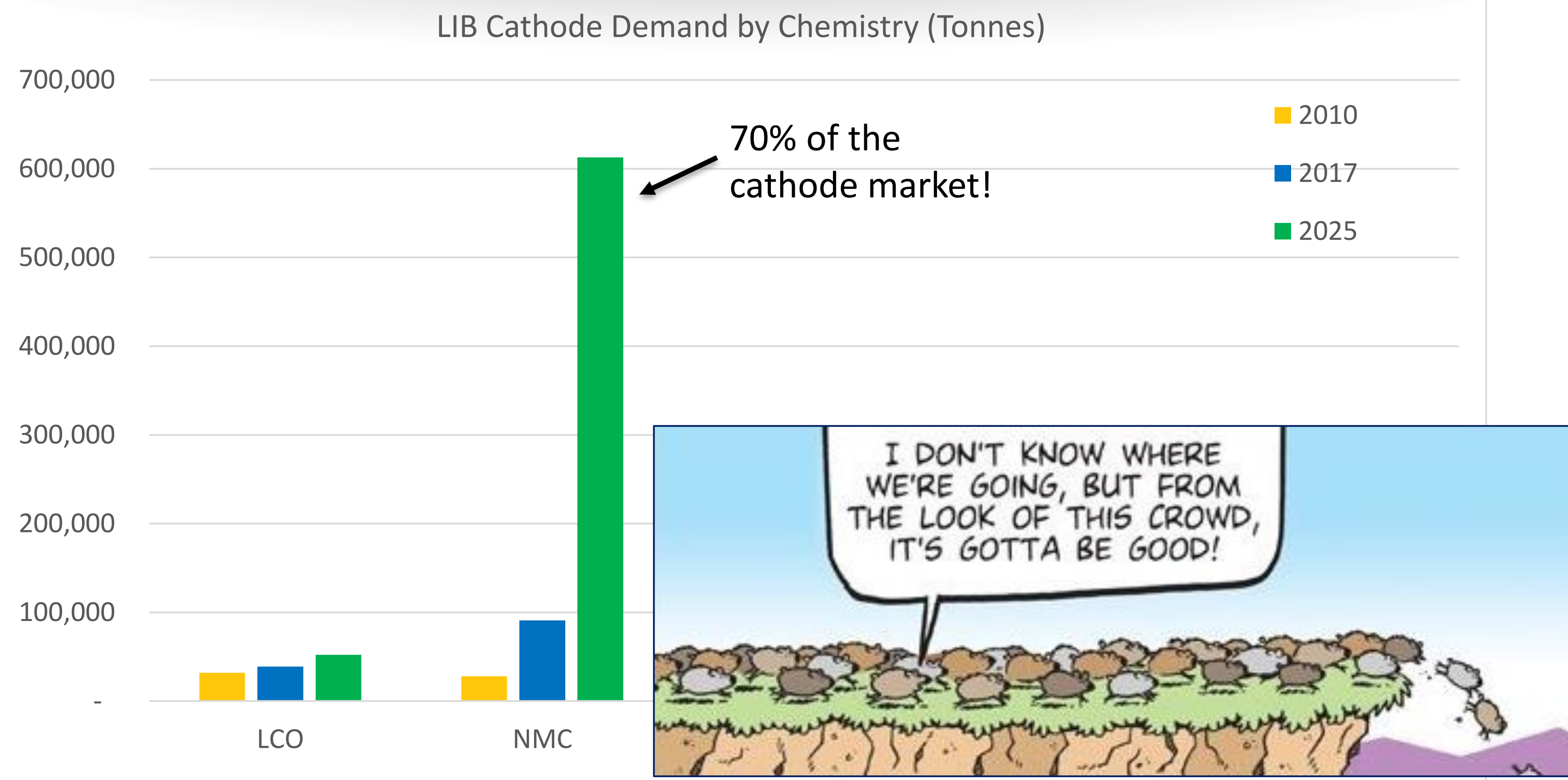
Consumer Electronics



Source: Avicenne Energy

NMC is the heavy favorite for automotive applications

Lithium-Ion Cathode Demand – 2010 vs. 2025



Source: Avicenne Energy

NMC is forecast to take over 70% of the global market by 2025

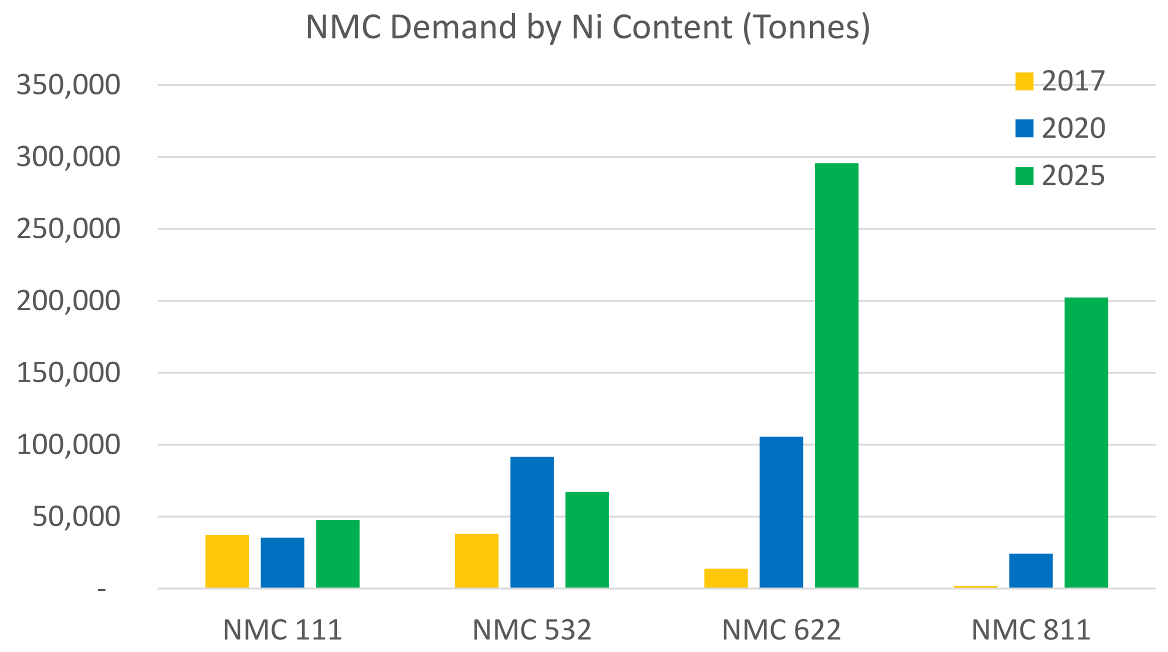
Cobalt Concerns

What can be done to reduce our reliance on cobalt?

The Move to Higher Nickel NMC's

More nickel, less cobalt

- Strong move toward higher nickel content NMC's
- Reduction of Co content from 33% to less than 10%
- And even higher nickel versions are being considered (>90%)



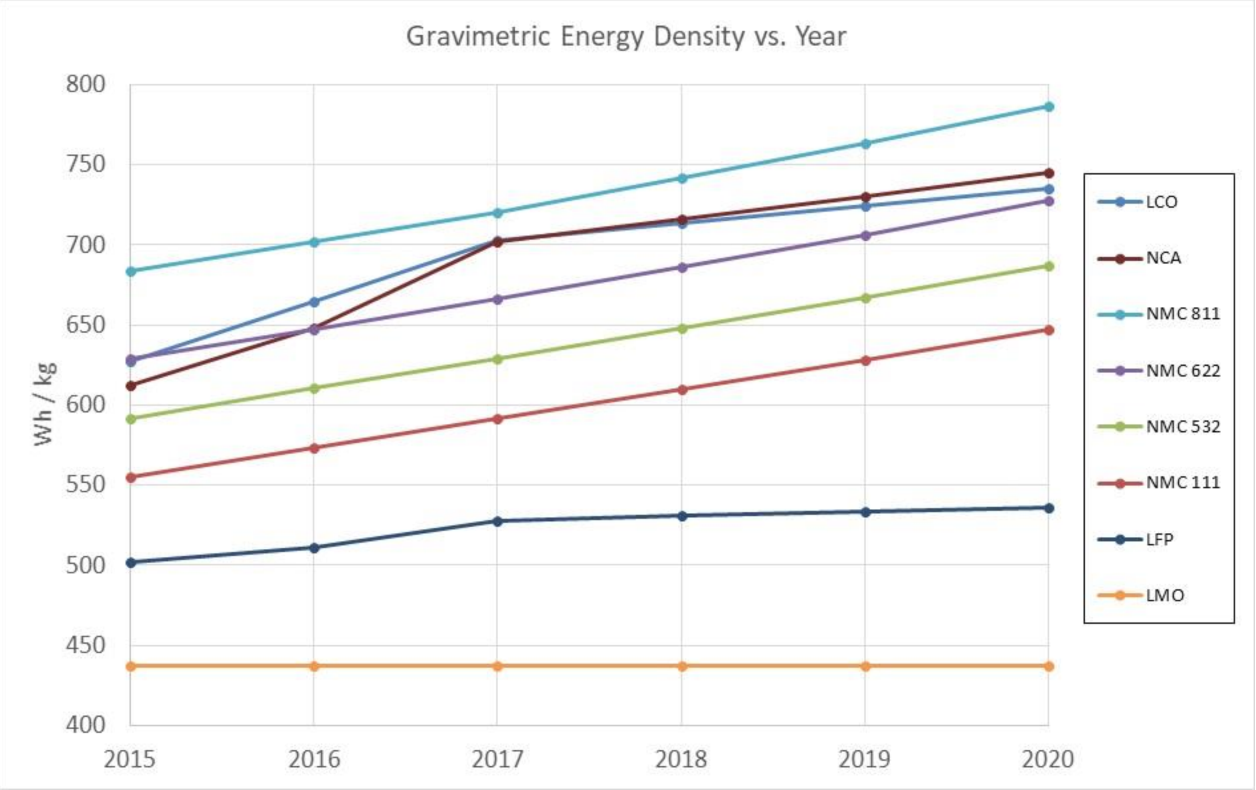
Source: Avicenne Energy

NMC 811 is one of the world's most popular near-term R&D targets

Energy Improvements are Possible, but Modest

Increase energy

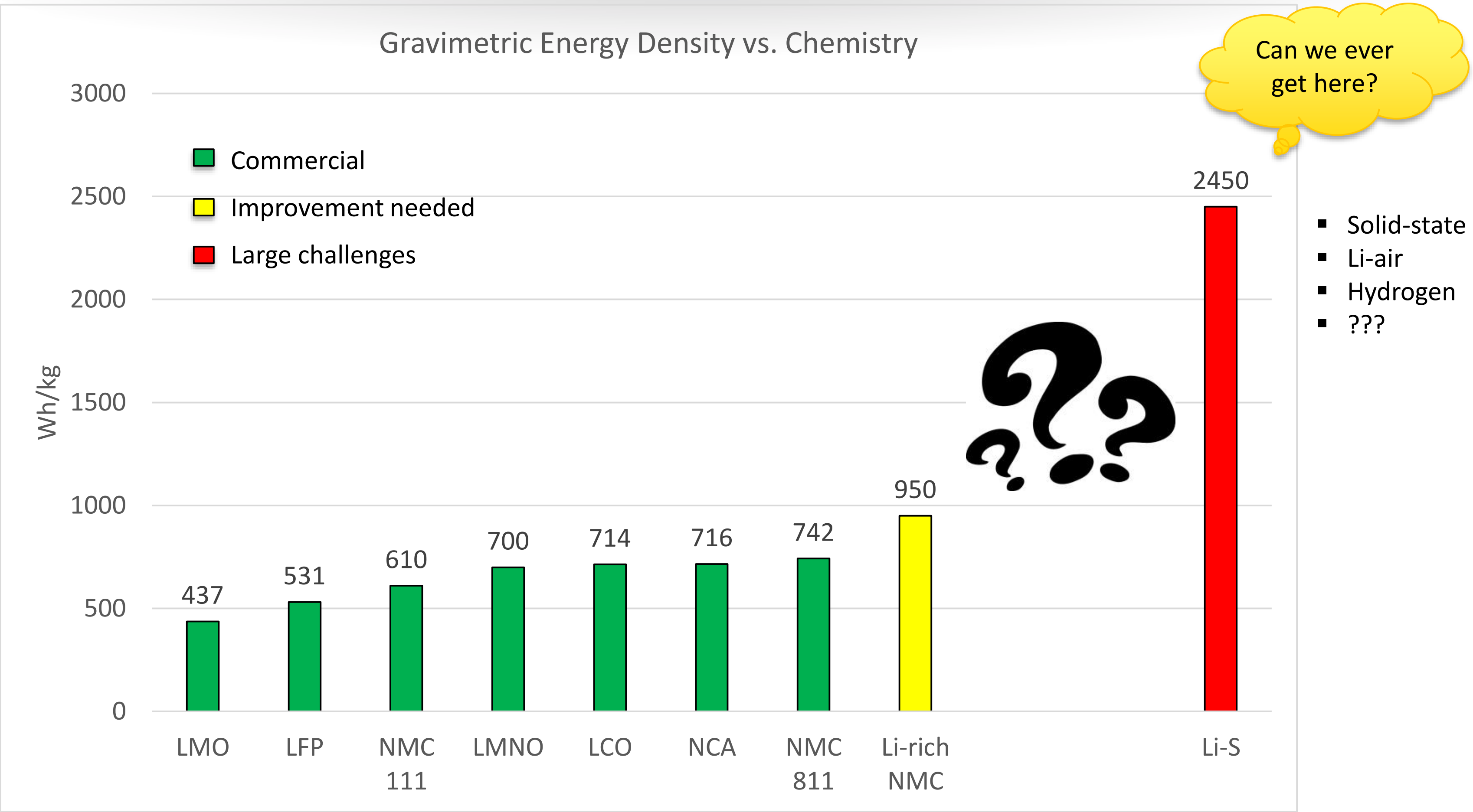
- Cell energies have increased 3% per year, but are near cathode theoretical limits
- Increased voltage leads to higher energies…
- …but introduces electrolyte stability and gas generation challenges



Source: Avicenne Energy

Are there alternatives to NMC…with higher energy and no Cobalt?

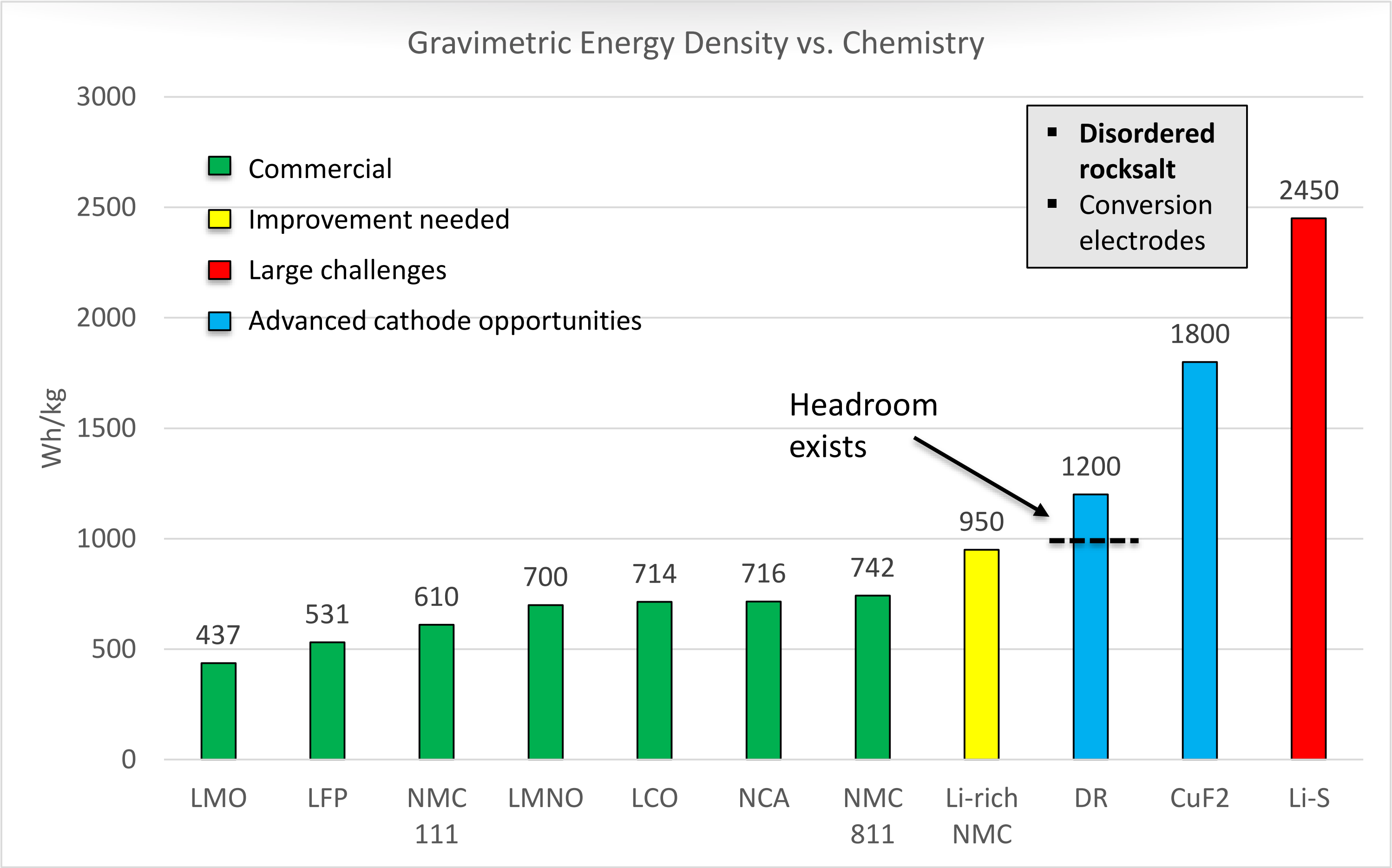
Cathode Material Energy



- Solid-state
- Li-air
- Hydrogen
- ???

A gap exists between today's LIB energies and post-LIB technologies

Cathode Material Energy



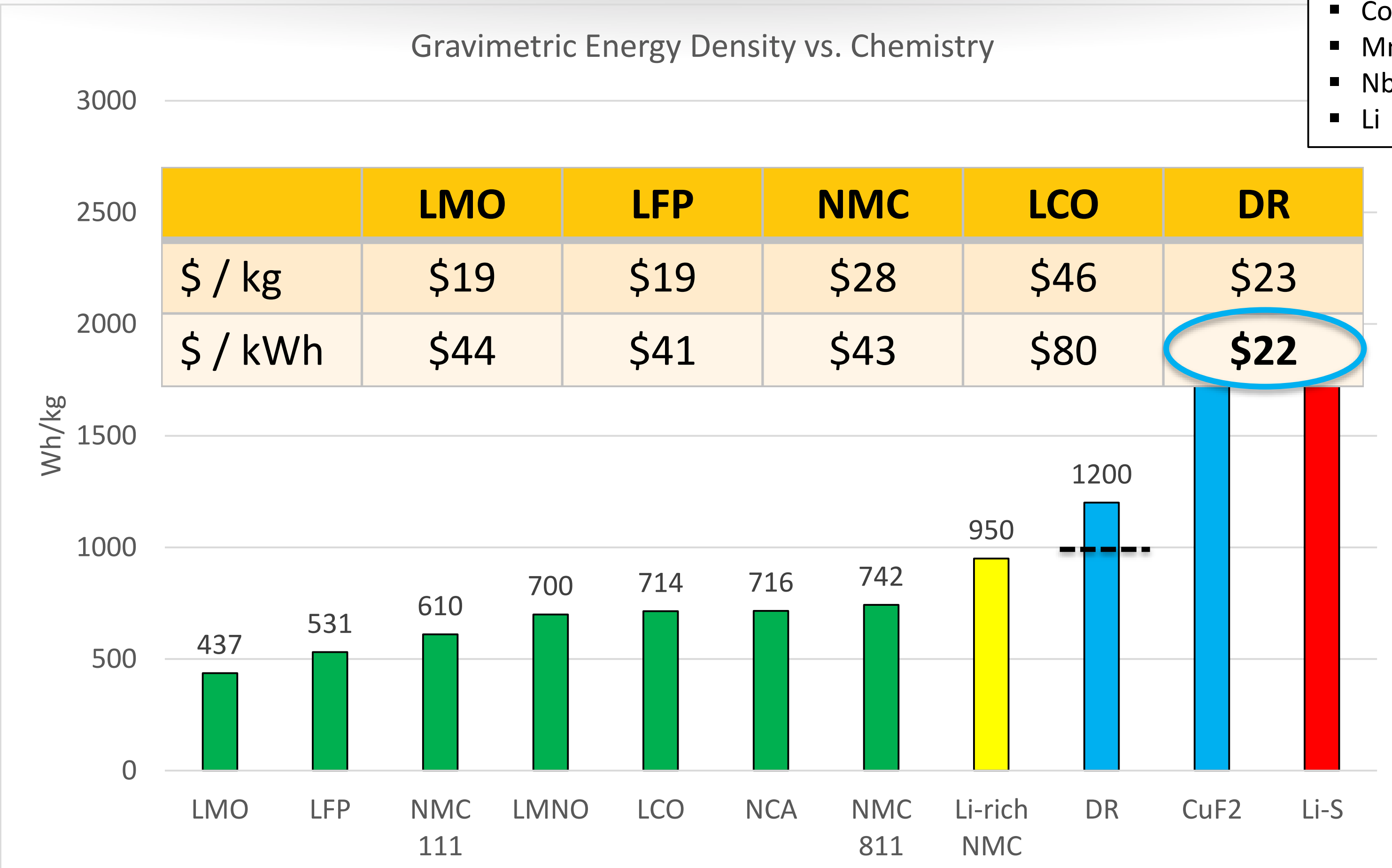
Disordered rocksalt is a Co-free alternative to NMC with ~40-60% more energy

Cathode Material Cost per kWh

- Ni $18/kg
- Co $60/kg
- Mn $4/kg
- Nb $41/kg
- Li $33/kg

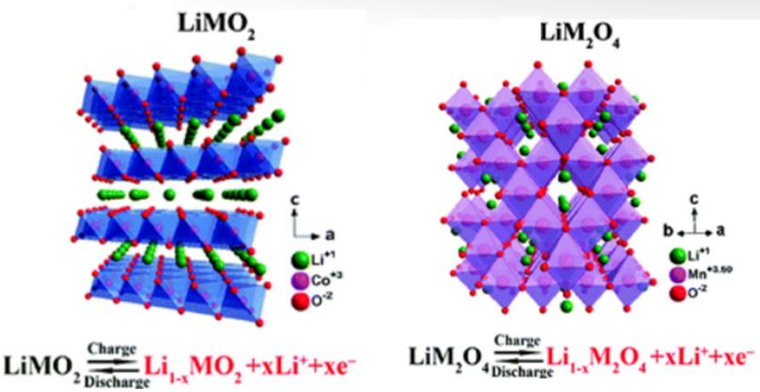
Source: LME

	LMO	LFP	NMC	LCO	DR
$ / kg	$19	$19	$28	$46	$23
$ / kWh	$44	$41	$43	$80	**$22**

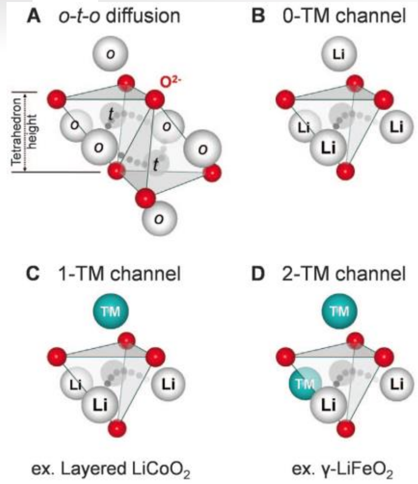


DR offers a tremendous $/kWh value proposition

Ordered vs. Disordered Structures



Chen, *Nanoscale Horiz.*, **1** (2016)



Ceder, *Science*, **343** (2014)

Today's cathodes are mostly ordered structures:

- Li sites and pathways separated from TM sublattice
- Provides stability (good cycle life)
- TM layers provide electron storage capacity

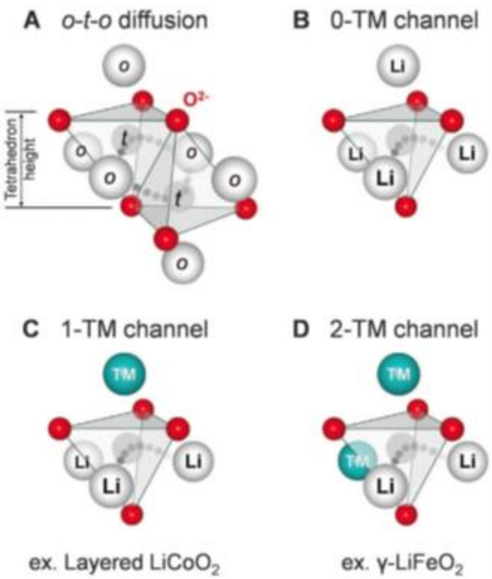
In a disordered rock salt:

- Both Li and TM occupy a cubic close-packed lattice of octahedral sites
- Li diffusion occurs by hopping from one octahedral site to another via an intermediate tetrahedral site (*o-t-o* diffusion)
- Very small changes in lattice parameters during cycling

Disordered structures appear to have performance advantages

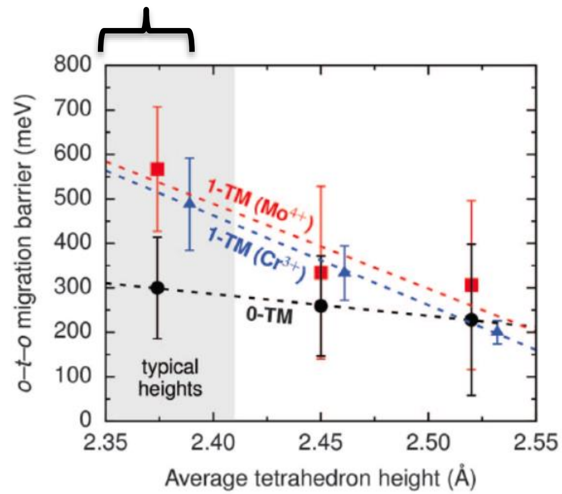
Are Fast Kinetics Possible?

Ceder, *Science*, **343** (2014)

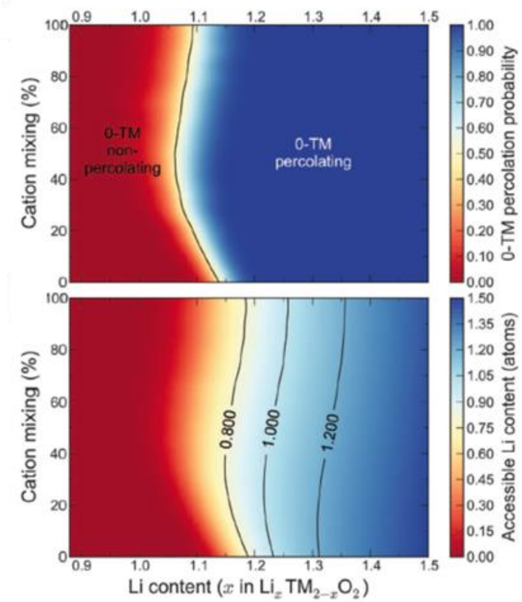


Multiple possible pathways for Li transport

Tetahedron heights of disordered materials



0-TM pathway is energetically favored



Li content needs to be high for 0-TM percolation

Percolation network provides means of fast lithium transport

Rich Compositional Space

Year	Author et al.	Material	Journal	capacity
2014	J. Lee	$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$	Science	280 mAh/g
2015	Chen	Li_2VO_2F	Adv. Energy Mater.	320 mAh/g
2015	Yabuuchi	$Li_{1.3}Nb_xM_{0.7-x}O_2$ (M = Mn, Ni, Co, Fe)	PNAS	300 mAh/g
2015	Wang	$Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$	Electrochem. Commun.	290 mAh/g
2015	J. Lee	$Li_{1.2}Ni_{0.333}Ti_{0.333}Mo_{0.133}O_2$	Energy Environ. Sci.	230 mAh/g
2015	Glazier	$Li_{1+x}Ti_{2x}Fe_{1-3x}O_2$	Chem. Mater.	250 mAh/g
2016	Freire	$Li_4Mn_2O_5$	Nat. Mater.	350 mAh/g
2016	Yabuuchi	$Li_{1.3}Nb_{0.3}V_{0.4}O_2$	Chem. Commun.	270 mAh/g
2017	Yabuuchi	$Li_{4/3}Mo^{6+}{}_{2/9}Mo^{3+}{}_{4/9}O_2$	ACS Energy Letters	330 mAh/g
2017	J. Lee	$Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$	Nat. Commun.	250 mAh/g
2017	Yabuuchi	$LiMoO_{2-x}$ -LiF ($0 \leq x \leq 2$)	Journal of Power Sources	320 mAh/g
2018	Bruce	Li_2MnO_2F	Energy Environ. Sci.	280 mAh/g
2018	J. Lee	$Li_2Mn_{2/3}Nb_{1/3}O_2F$ / $Li_2Mn_{1/2}Ti_{1/2}O_2F$	Nature	320 mAh/g
2018	Kitchaev	Li-Mn(II)-V(IV)-O-F	Energy Environ. Sci.	310 mAh/g

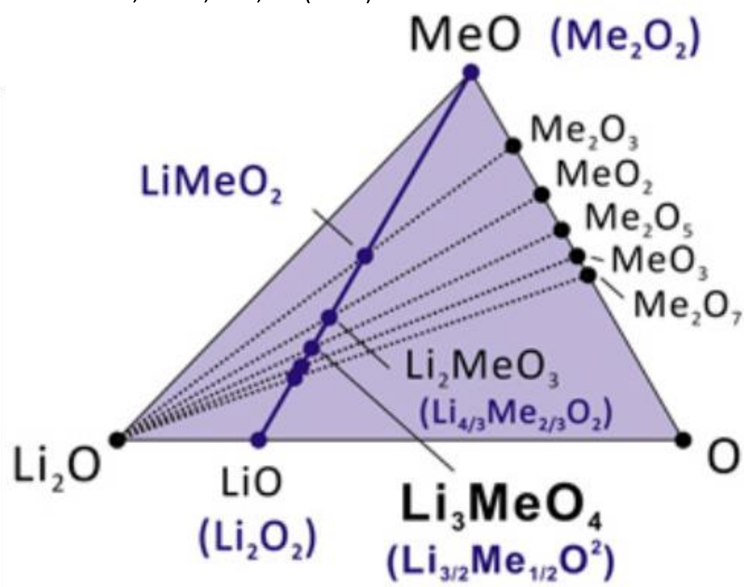
NCM622 = 185 mAh/g

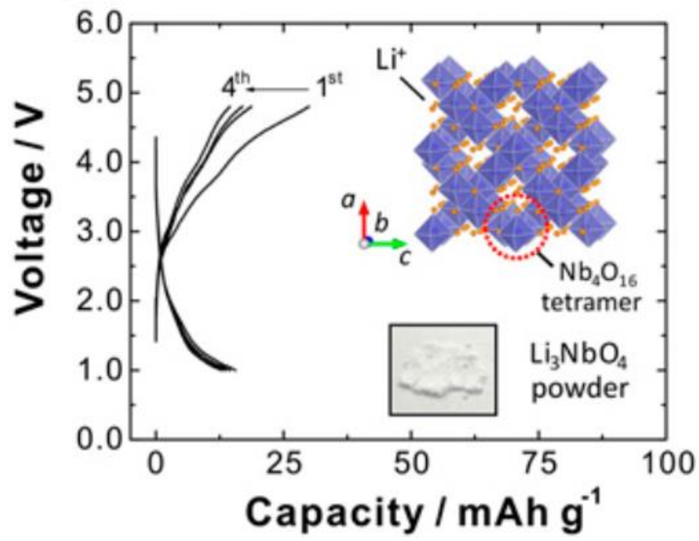
Ceder, *IMLB* (2018)

Disordered rocksalts offer a rich compositional space to explore

Nb-based Materials

Yabuuchi, *PNAS*, **112**, 25 (2015)



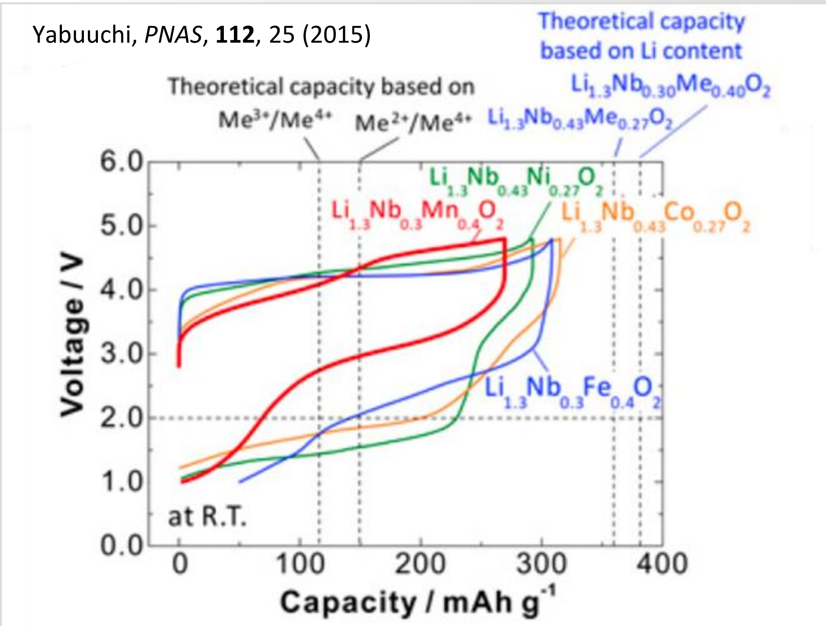


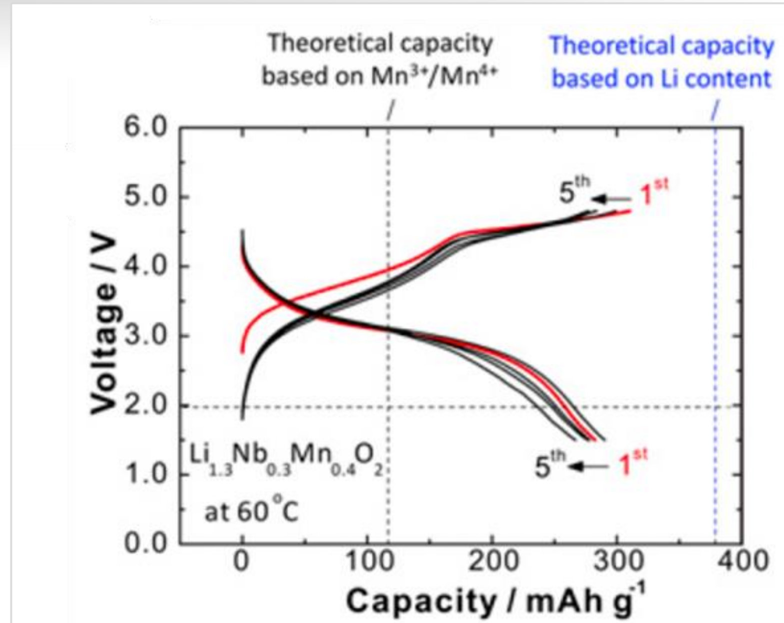
Many cation ordered/disordered rocksalt phases on tie-line between MeO and LiO, including $Li_3Nb^{5+}O_4$

However, $Li_3Nb^{5+}O_4$ has poor capacity due to poor electronic conductivity, with no electrons in a conduction band ($4d^0$ configuration for Nb^{5+})

Nb phases provide a particularly promising area for exploration

Disordered Material Capacity





TM substitution for some of the Nb^{5+} and Li^{+} induces electronic conductivity in Li_3NbO_4 – yielding capacities beyond limit of redox for TM's

Electrochemical performance of $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$ (1.5 – 4.8V, 10 mA/g, 60°C) [$0.43Li_3NbO_4$-$0.57LiMnO_2$]

Observed capacity is higher than theoretical based on TM redox

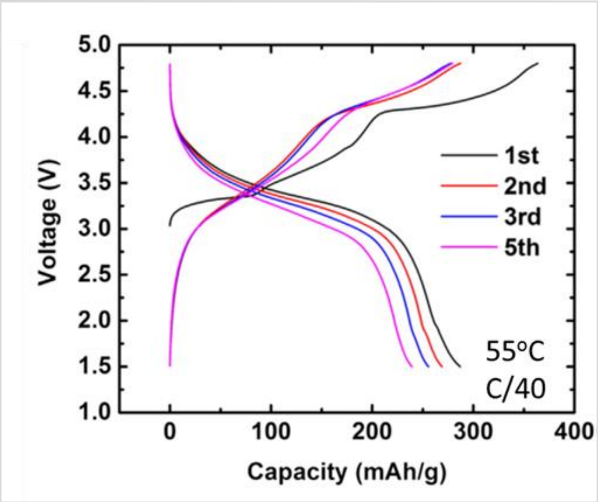
Disordered Rocksalt Challenges

Phase 1

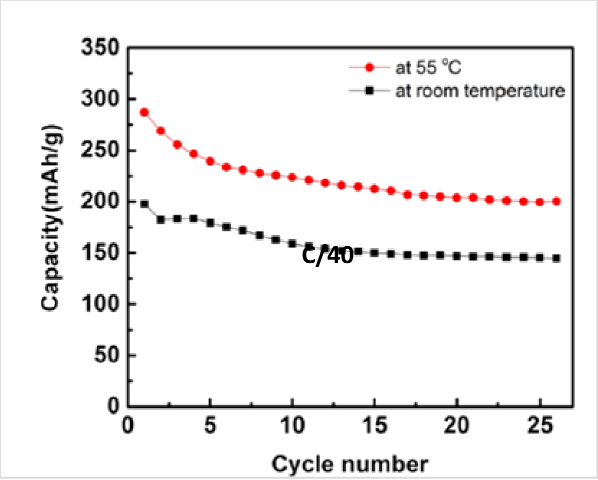
1. Poor rate performance/conductivity
   - Most literature results are at C/40 and at elevated temperature

Phase 2

2. Low discharge voltage
   - Capacity above 3.0V is less than 250 mAh/g
3. Poor cycle life
   - Mainly reported in half cells

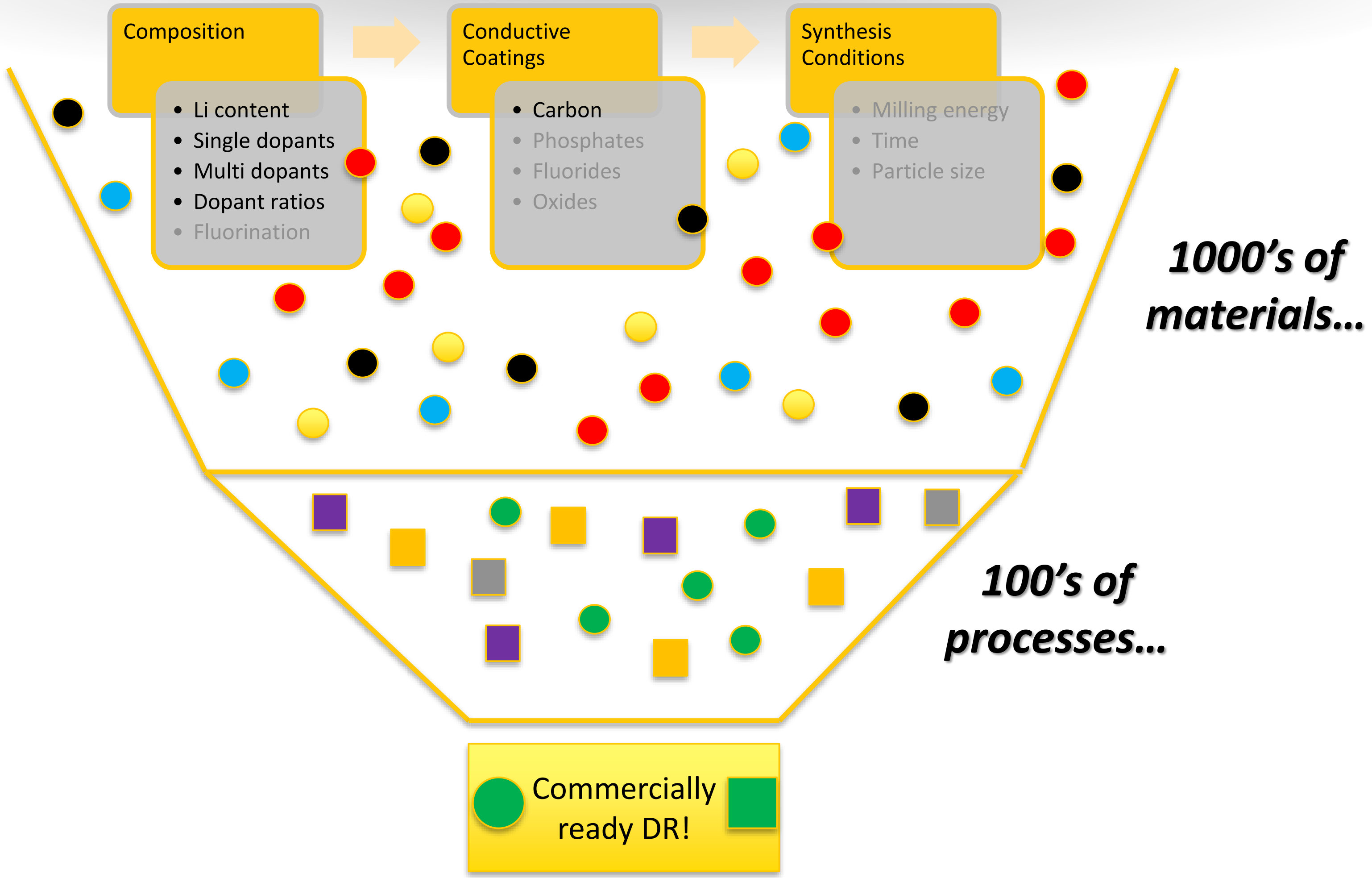


Ceder, *Electrochem. Comm.*, **60** (2015)



Disordered materials have high energy, but other metrics need improvement

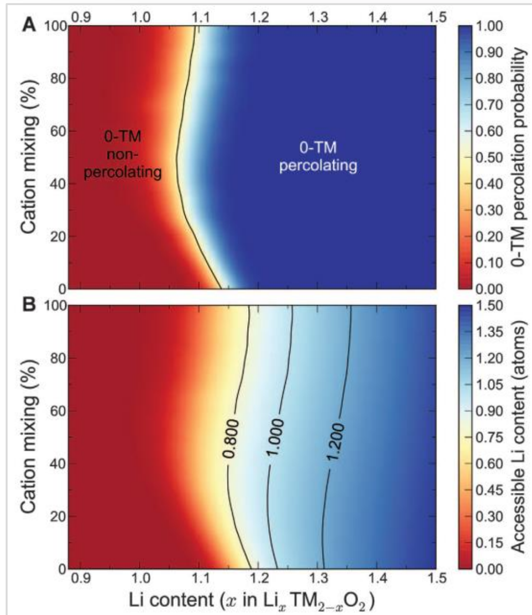
High Throughput Material Development



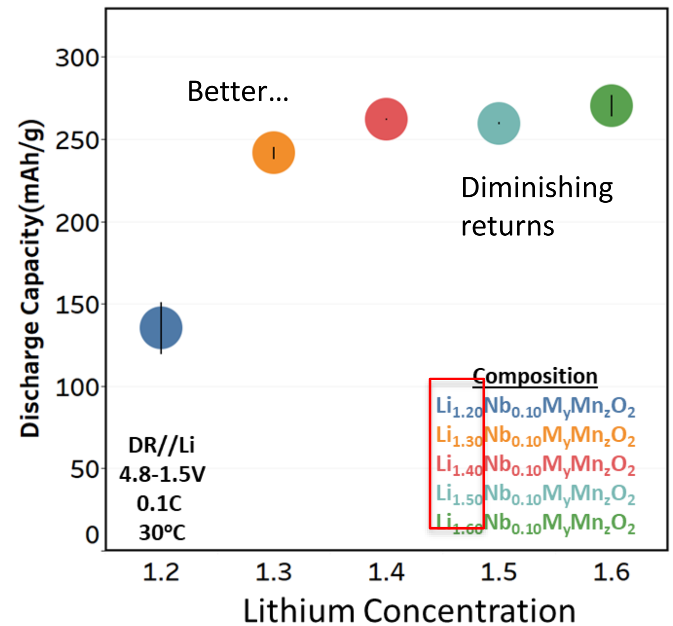
Success depends upon finding the right _combination_ of materials and processes

Conductivity Improvement via Composition

- Conductivity sensitive to both Li content and cation mixing
- For given TM's, Li content can be studied to optimize conductivity



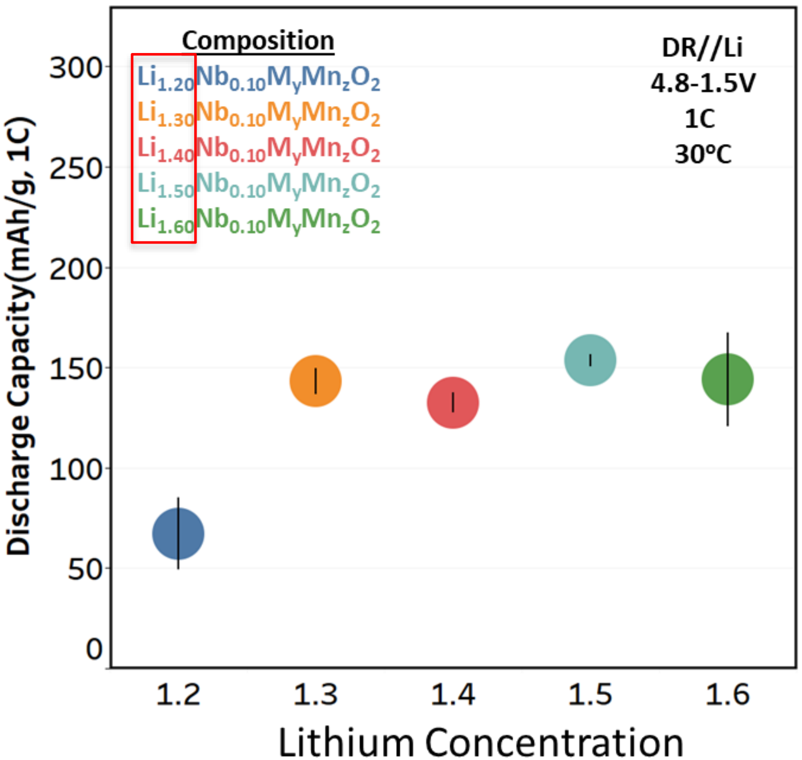
Cedar, ***Science***, 343, 2014



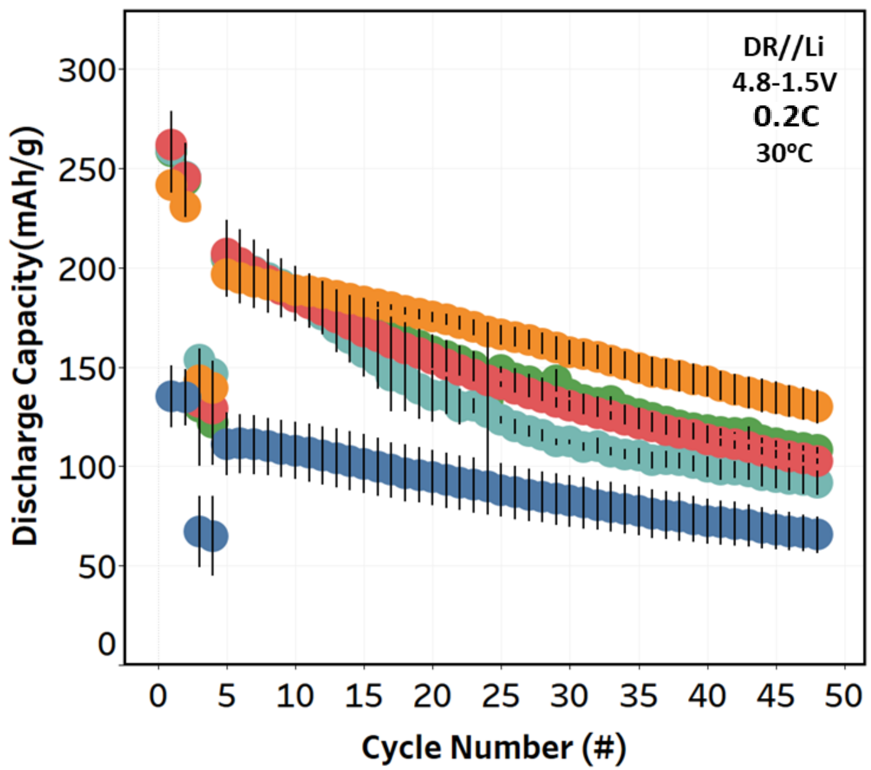
Li^+ percolation can be optimized by changing composition

Conductivity Improvement via Composition

1C Capacity



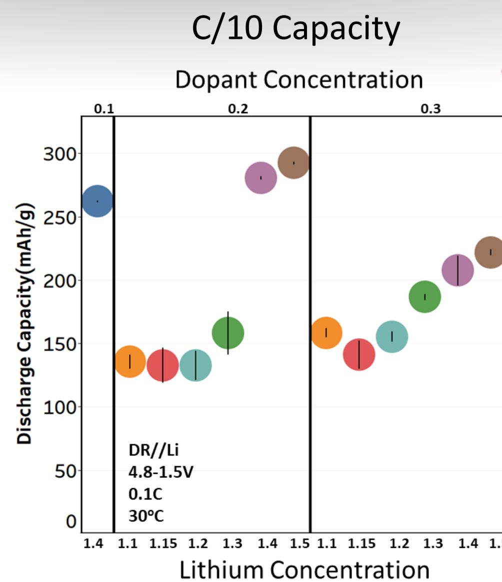
Cycling



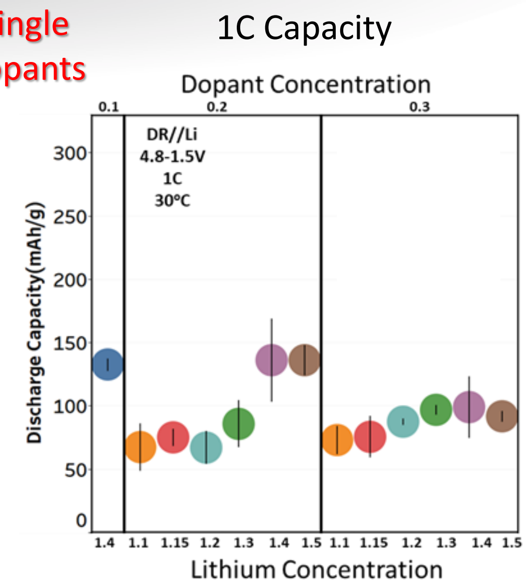
Li content can be optimized, but other improvements are needed

Effect of Dopants on Performance

- Some TM's can stabilize the oxygen dimer
  - d-band of TM overlapping p-band of oxygen
  - Prevents O_2 release from material

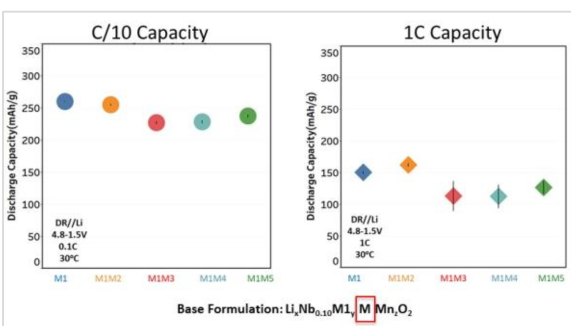


Single dopants

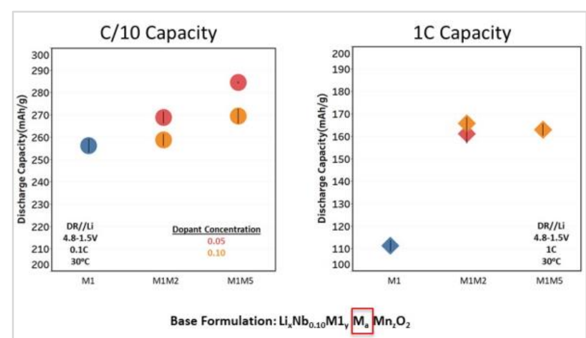


Base Formulation: $Li_xNb_{0.10}M_yMn_zO_2$

Multiple dopants



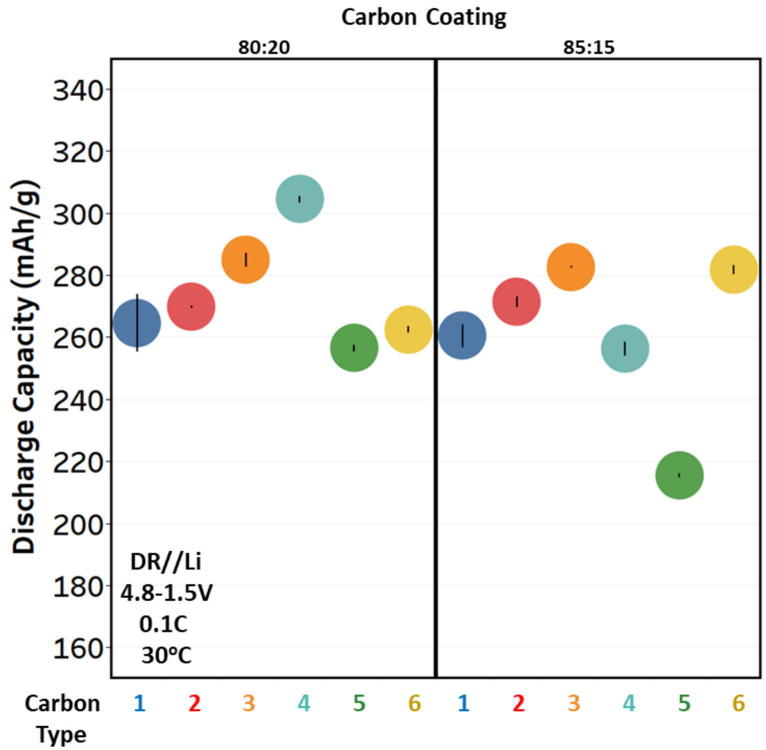
Dopant ratios



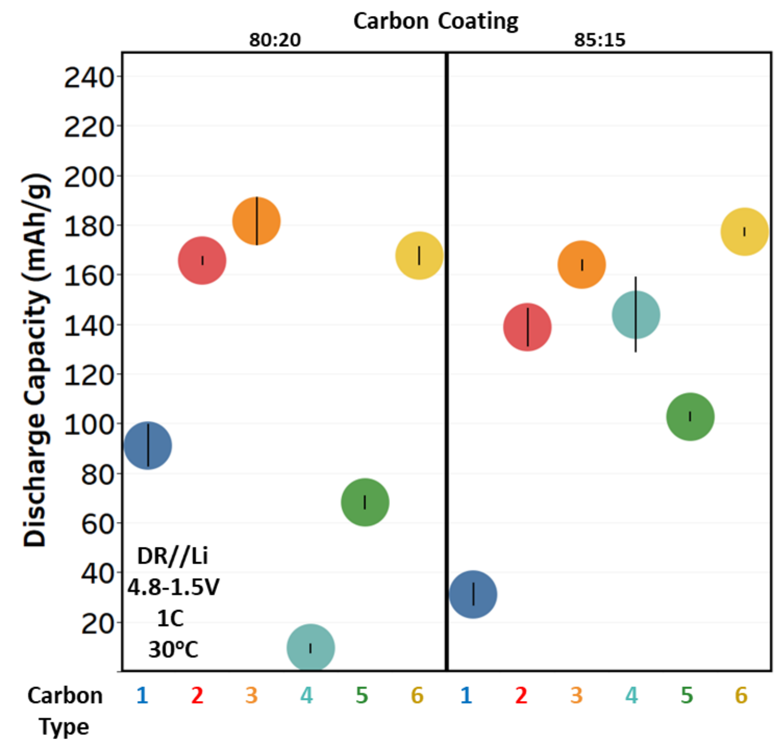
Complex DOE's required to optimize both lithium and dopant compositions

Carbon Coating Can Improve Rate Performance

C/10 Capacity

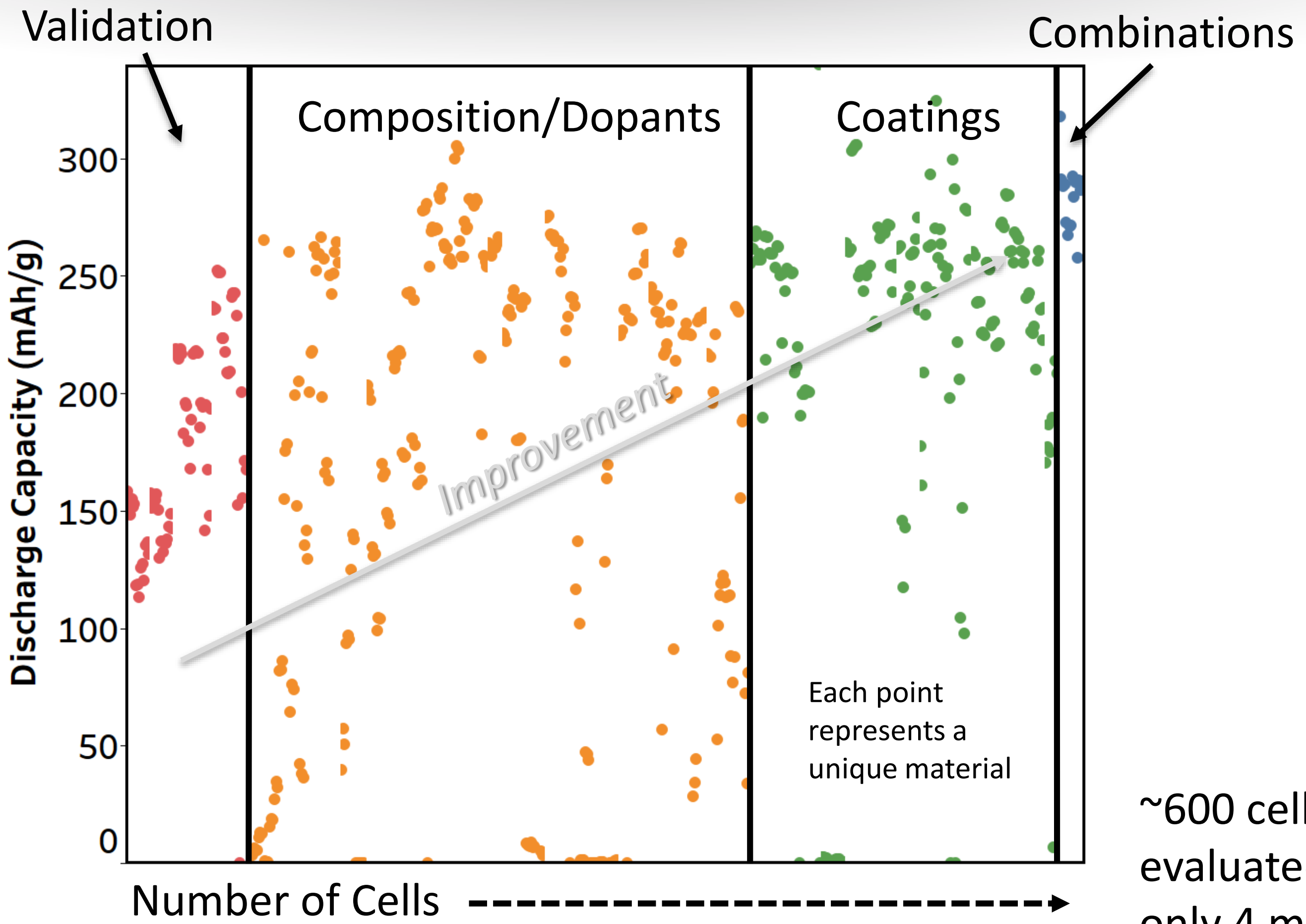


1C Capacity



Performance is very sensitive to both base composition and carbon coating

Development Progress

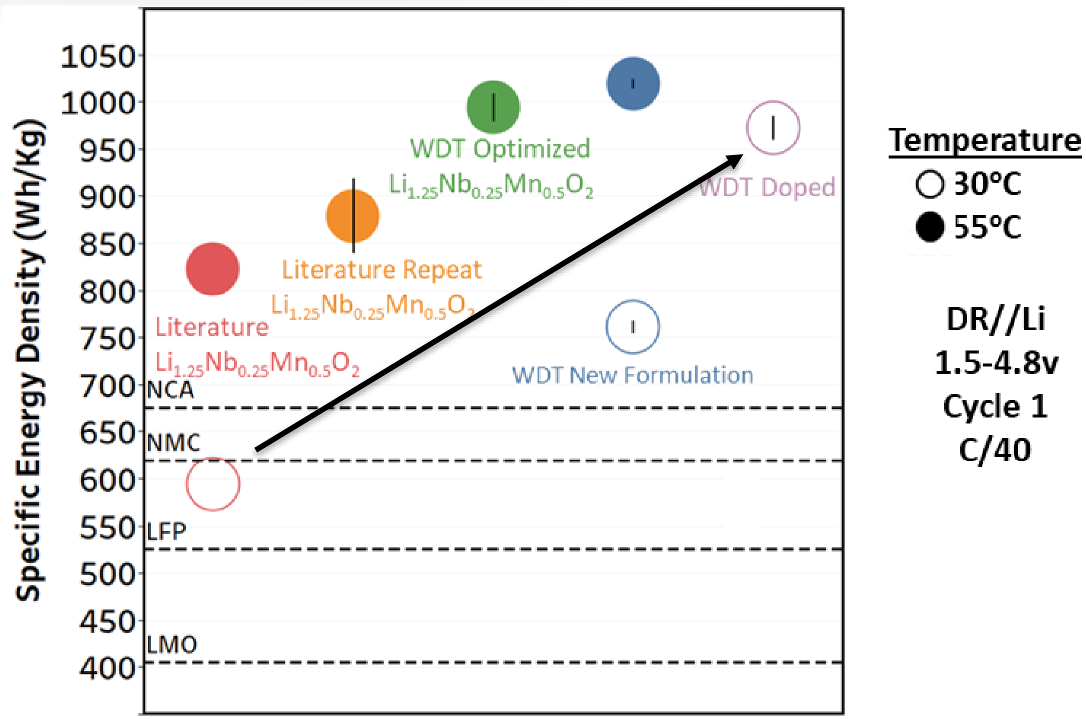


~600 cells evaluated in only 4 months

Complex DOE's enable systematic improvements

Development Progress

- Wildcat improved performance via:
  - Elemental ratios
  - Doping
  - Carbon coating
- Specific energy of best materials at 30°C outperform literature-reported materials at 55°C
- Phase 2 development will focus on improved cycle life and voltage plateau

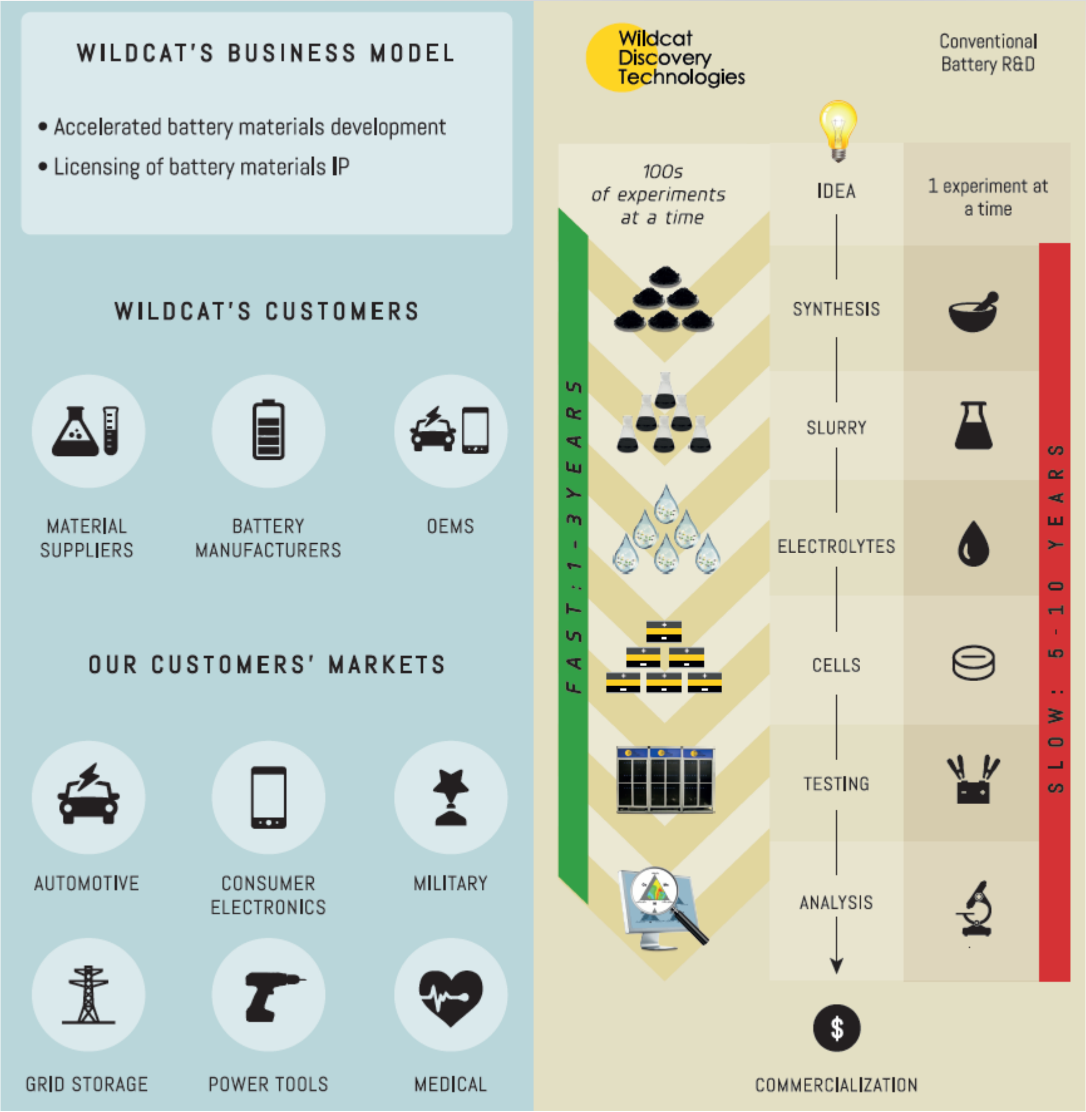


Wildcat's disordered rocksalt has energy density of ~975 Wh/kg at room temperature

Summary

- Auto LIB market is driving tremendous growth in NMC demand
- Cobalt's pricing and labor concerns - and the desire for more energy - are driving a strong move to higher nickel NMC's
- Disordered rocksalt offers a compelling alternative to NMC, with higher energy, lower $/kWh and no reliance on cobalt
- Disordered materials inherently offer more energy than layered materials, yet performance challenges exist: rate, cycle life, voltage plateau
- A vast DR compositional region remains unexplored with many opportunities to further improve performance
- High throughput is an excellent means of rapidly evaluating hundreds of new compositions
- DR is young, there are large improvements ahead!

Wildcat's Business Model



Wildcat Website:
www.wildcatdiscovery.com

High Throughput Video:
https://youtu.be/Eu1nvrCzJWQ

Acknowledgements

- Rogerio Ribas
- Robson Monteiro
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- Alex Freigang

Thank you for your attention!

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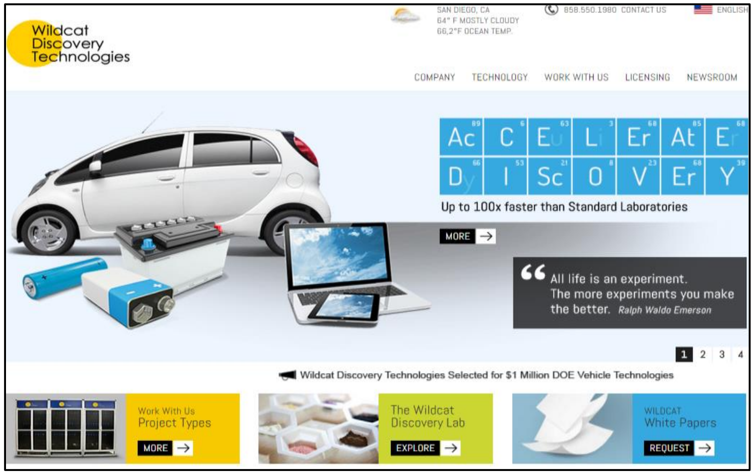

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