# Cation-disordered Cathode Materials (DRX+): Overview

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Project ID: 570

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# Overview

## Timeline

- Start date: October 2022
- End date: September 2025
- Percent complete: 60%

## Budget

- Total project funding
  - FY24 $3.2 M (LBNL, UCSB)
- BAT570, BAT589, BAT597 and BAT598 (LBNL, ORNL, PNNL, ANL, SLAC, UCSB)

## Barriers Addressed

- Energy density
- Cycle life
- Cost

## Partners

- Lawrence Berkeley National Laboratory (lead)
- Pacific Northwest National Laboratory
- Oak Ridge National laboratory
- Argonne National laboratory
- SLAC National Accelerator laboratory
- UC Santa Barbara

# Relevance/Objectives

- Current high density cathode materials rely on Ni and/or Co, which limit further cost reduction for Li-ion batteries and pose potential resource issues. $LiFePO_4$ has limited energy density
- Cation-disordered Li-excess rocksalt (DRX) compounds have been shown to be capable of delivering over 1000 Wh/Kg and 3000Wh/l in energy densities, providing an opportunity to develop high-energy and high-rate cathodes based on earth-abundant metals free of nickel and cobalt.
- Build onto the understanding gained from the previous deep-dive DRX program, the DRX+ consortium aims to:
  I. Optimize Gen1/2-DRX to achieve 650Wh/kg at 100mA/g for 100 cycles
  II. Develop more stable Gen3-DRX based on Gen1, achieving 750Wh/kg at 100mA/g for 300 cycles

# Milestones

| Date | Milestones | Status |
|---|---|---|
| December 2023 | Demonstrate > 10g scale synthesis of Gen1-DRX with capacity no more than 5% lower than that of lab-scale standard DRX cycled between 2 and 4.8 V | Completed |
| March 2024 | Perform composition refinement and synthesis tuning of Gen1-DRX to achieve 650Wh/kg at 100mA/g for at least 100 cycles | Completed |
| June 2024 | Complete the investigation of at least 3 upper cutoff voltages and 3 upper voltage holds, and 2 low voltage cutoffs. Demonstrate the best overall cycling protocol for a combination of high energy, high energy efficiency, and maximum energy throughput to end of life. | Mostly Complete |
| September 2024 | Integrate new electrolyte formulation and coating for Gen1 to develop Gen2-DRX with 700Wh/kg at 100mA/g for at least 300 cycles. | On schedule |

# DRX+ Team Organized Around Five Tasks

**TASK 1: Electrolytes**: Investigate additives and solvent and salt modifications to enable more stable cycling of Gen1 and Gen2 cathodes at high voltage.
**TASK 2:** Apply **inorganic and carbonaceous coatings** to DRX to protect DRX and create electronic pathways through the composite cathode with lower carbon content.
**TASK 3:** Optimize composition and morphology and scale-up **Gen1-DRX** (
**TASK 4: GEN3**: Investigate **partially disordered Mn-based materials** as high energy, high rate cathodes made with scalable synthesis methods by investigating in detail the structure and synthesis pathways of these metastable materials, leading to materials with > 1000Wh/kg.
**TASK 5:** Optimize and improve **electrode fabrication** with DRX materials by lowering the carbon content, optimizing particle size and morphology, and establishing optimal voltage limits and cycling protocols. Perform basic thermal stability testing.

## Organizational

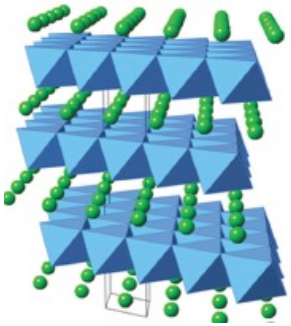
- Each task has a lead
- Bi-weekly meetings reporting on tasks + two annual all-hands meetings
- Task teams meet in off-weeks
- Single materials supply of GEN-1 DRX to make results from different groups comparable

Berkeley Lab
Pacific Northwest National Laboratory
Proudly Operated by Battelle Since 1965
Oak Ridge National Laboratory
Argonne National Laboratory
SLAC National Accelerator Laboratory
UC Santa Barbara

# Disordered rocksalt cathodes (DRX): Concept

**Ordered layered materials**

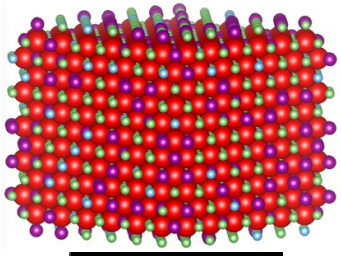
$LiCoO_2$/NMC

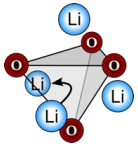


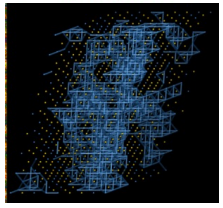
Restricted to Co and Ni as redox active materials

Resource constrained. Would require multiple million tons of Ni/Co by 2030

**Disordered Rocksalt**





Can use any transition metal (including Mn and Fe)

Unconstrained
Inexpensive

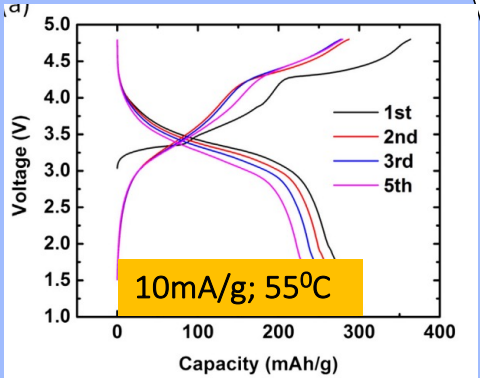
- **Layered materials will always require some amount of Nickel and/or Cobalt.**
- **DRX cathode materials do NOT require Nickel or Cobalt and can have 30% higher energy density than current NMC cathodes**
- **DRX can be synthesized from inexpensive Manganese and Titanium oxides.**
- **Cathode cost potentially < $10/kg**

J. Lee, G. Ceder et al., Science, 343 (6170), 519-522 (2014)
US Patent 9,780.363 B2

# DRX: from poor rate materials to high performing GEN1 and Gen3

## 2014-2015

$Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$




Wang, R., Ceder, G. et al, Electrochemistry Comm, 60 (2015) 70-73

- Low rate
- High T required
- Poor cycling
- Use of Nb

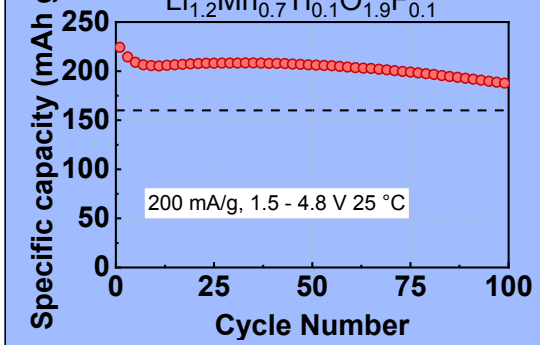
## Gen1 and Gen2-DRX

LMTF 2622

$Li_{1.2}Mn_{0.6}Ti_{0.2}O_{1.8}F_{0.2}$

$Li_{1.2}Mn_{0.7}Ti_{0.1}O_{1.9}F_{0.1}$

$Li_{1.2}Mn_{0.7}Ti_{0.1}O_{1.9}F_{0.1}$

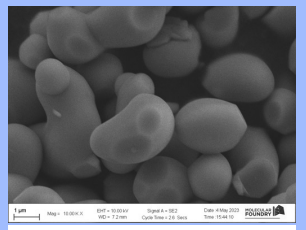


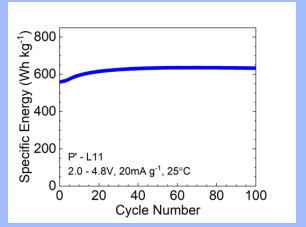

- Increased Mn content
- No use of Nb.
- Higher rate achieved
- Good cycling
- Scale-up achieved
- Used for electrode optimization

## Gen3 – δ–DRX

LMTF 1811

$Li_{1.1}Mn_{0.8}Ti_{0.1}O_{1.9}F_{0.1}$





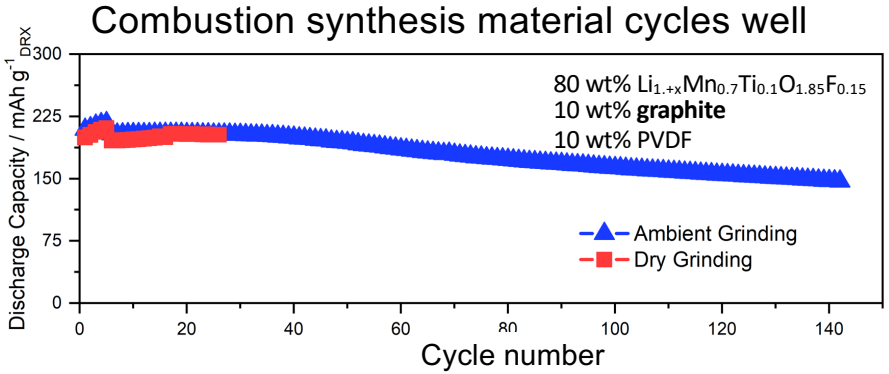

- Single crystal DRX
- Pre-processing to create δ-DRX
- Highly stable cycling
- Starting scale-up and electrode optimization

# Technical Accomplishment: Gen1/2-DRX successfully scaled up

### Solid-state synthesis

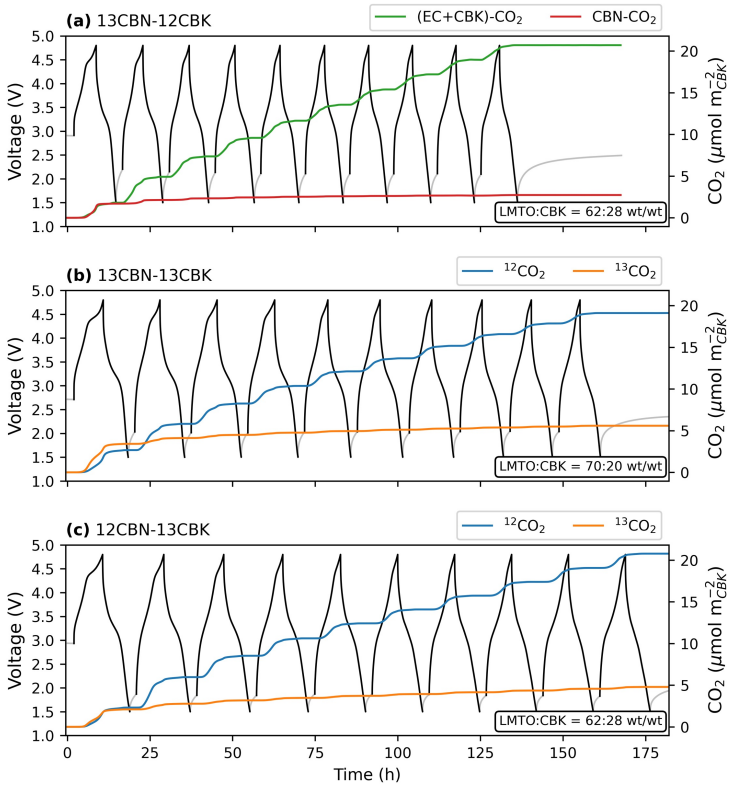
| Batch | RPM (equiv.) | CAM:$ZrO_2$ | Yield | Shipped |
|---|---|---|---|---|
| 1 | 400 (1200) | 1:4 | ~50g | Nov. 2022 |
| 2 | 400 (1200) | 1:4 | ~50g | May 2023 |
| 3 | 400 (1200) | 1:4 | ~60g | Sept. 2023 |
| 4 | 400 (1200) | 1:4 | ~110g | Jan. 2024 |

### Combustion synthesis




- Multiple large DRX-GEN1 batches(50-100g) synthesized at ANL through **solid-state synthesis** and distributed to Consortium. Performance is very near small-scale synthesis
- **Co-precipitation approach** developed for creating mixed (Mn,Ti) precursor which is then calcined. Performance is approaching solid-state material
- **Combustion synthesis** developed at ORNL for rapid DRX (GEN-2) synthesis

# Technical Accomplishment: Electrolyte decomposition at carbon identified as degradation mechanism in Gen1/2-DRX




*See poster by Bryan McCloskey for more details*

- High voltage electrolyte breakdown at carbon leads to carbonate formation, which in subsequent cycles releases $CO_2$.
- 3 cells with different carbon:DRX ratios, different types of carbon black ($^{13}C$ vs C65 Super P), and total DRX content studied over first 10 cycles (C/10 rate)
- $^{13}C$ isotope labelling used to deconvolute $CO_2$ evolved from electrolyte degradation, adventitious $Li_2CO_3$ degradation, and carbon black degradation
- When $CO_2$ evolution is normalized to carbon black surface area ($m^2_{CBK}$, see figure), $CO_2$ evolution from electrolyte degradation (Elyte $CO_2$) is statistically equal across cells

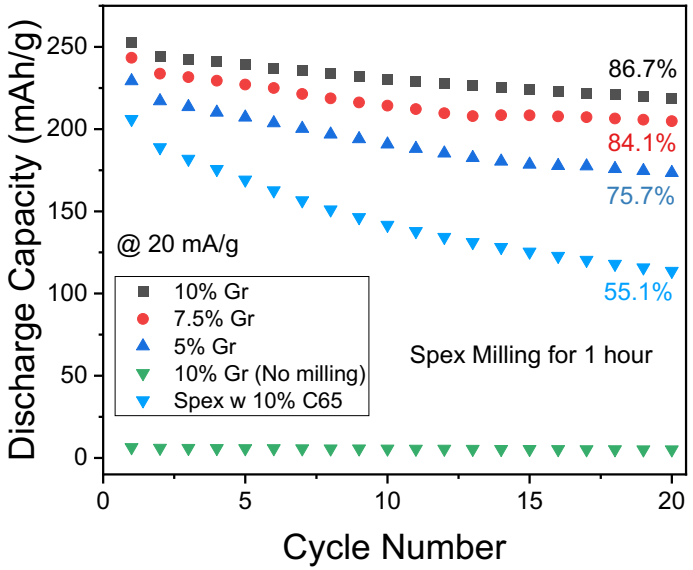
| Cell | μmol $CO_2$ $g_{DRX}^{-1}$ | μmol $CO_2$ $m_C^{-2}$ |
|---|---|---|
| a | 600 | 20.5 |
| b | 775 | 19 |
| c | 1350 | 20.5 |

$CO_2$ produced scales with carbon surface area, NOT with DRX

# Reduced electrode carbon content and increased cycling stability through use of more graphitic cabons

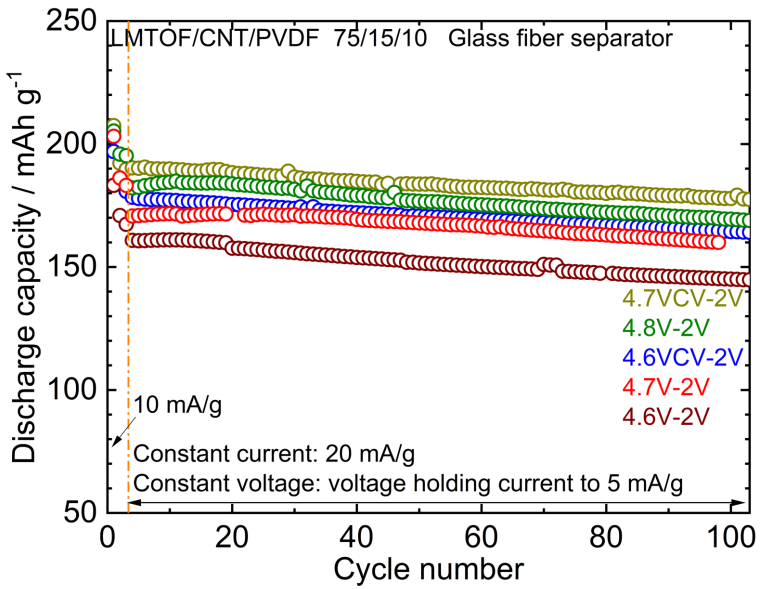
1. Soft milling DRX + carbon powders
2. Pyrolysis, PVD, and CVD of carbon precursors on DRX materials
3. Solution methods fpr Graphite/graphene coatings

**Key Findings**
- More carbon → better cycling
- C65 accelerates capacity fade (correlated with high voltage processes)
- Graphitic carbons give less capacity fade
- Carbon content reduced to 5 wt% graphite

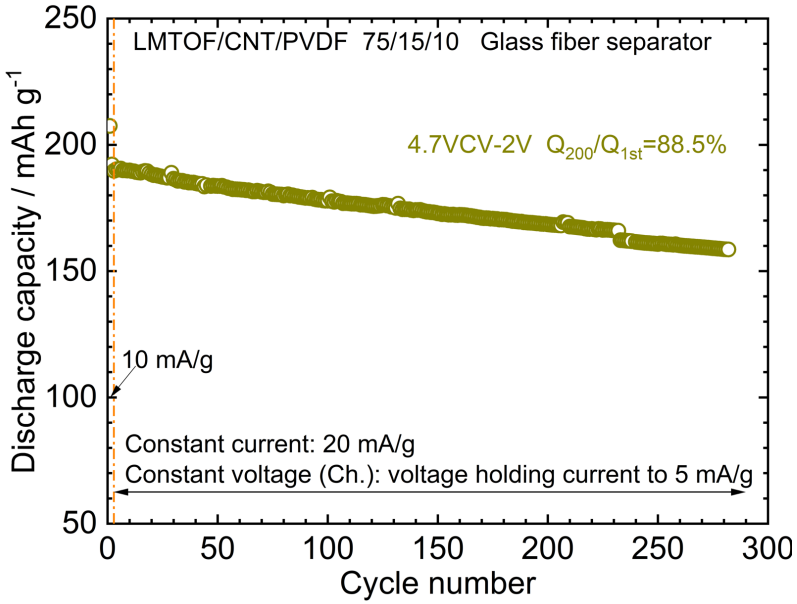



*See poster by Robert Kostecki for more details*

# Cycling of GEN-1: 300 Cycles Through optimization of Voltage Protocol and Carbon Additive



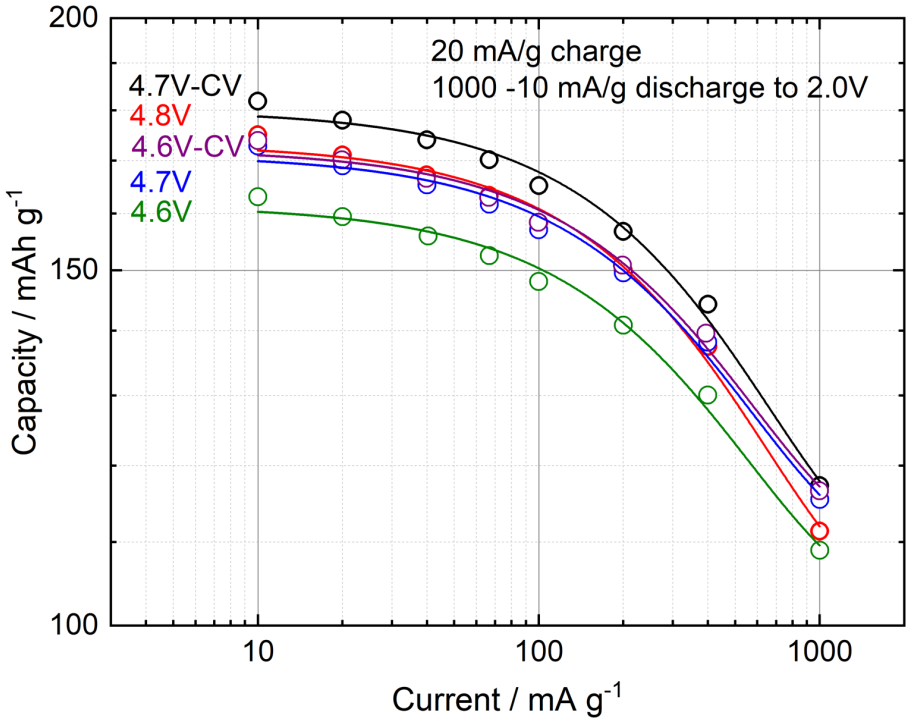

4.7V charge cutoff with CV hold results in optimal performance



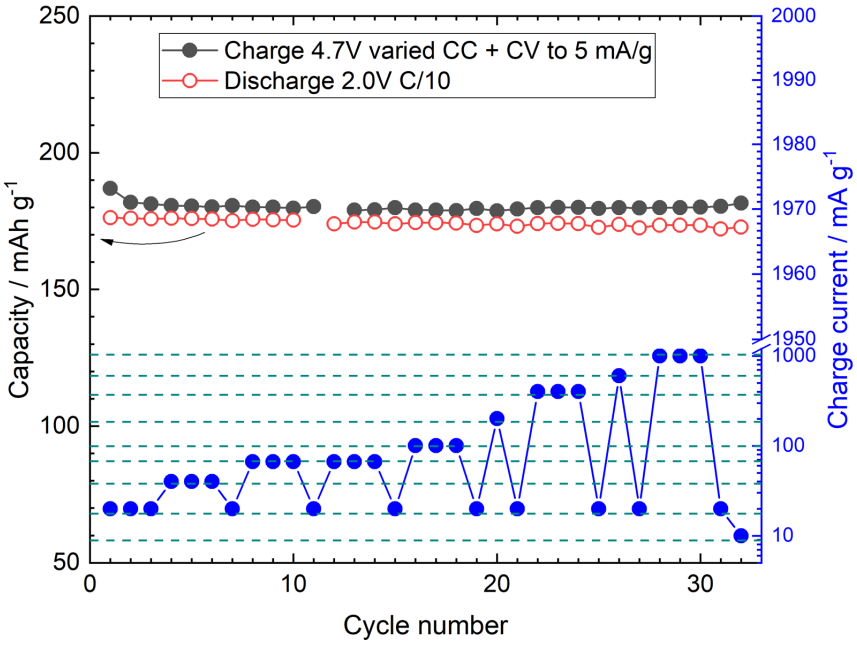

83.5% capacity retained after 300 cycles

# GEN-1 Power Characteristics

**Slow charge/rapid discharge Ragone plot**



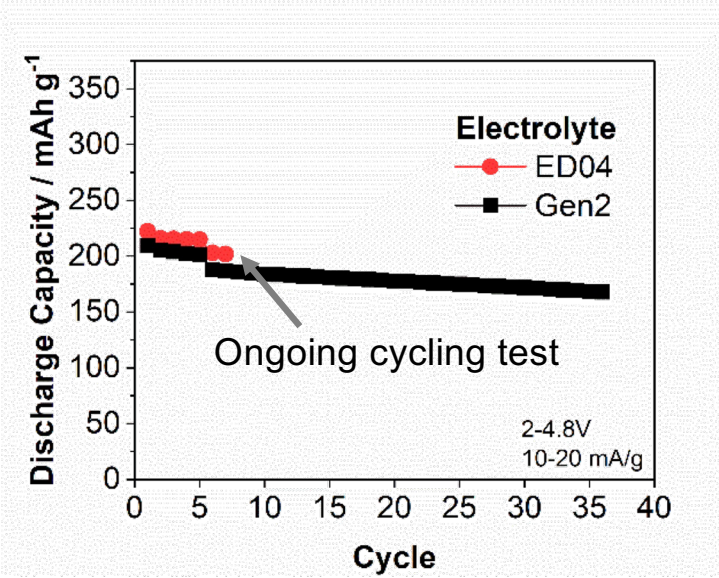

**Charge at 1000mA/g + voltage hold leads to full discharge capacity**




- Limited capacity loss up to 200mA/g
- 500mA/g achievable

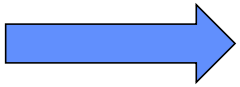
# Further Improvements of Gen1/2 DRX

- Further optimization of graphitic-like carbon coatings on DRX
- Integration of electrode innovations with new PNNL electrolyte
- Further reduction of carbon content in electrode
- Use appropriate F-content.  Batch1 ANL had low F content.  Higher F content in newer batches will improve cycling stability



# GEN 3: δ-DRX $Li_{1.1}Mn_{0.8}Ti_{0.1}O_{1.9}F_{0.1}$

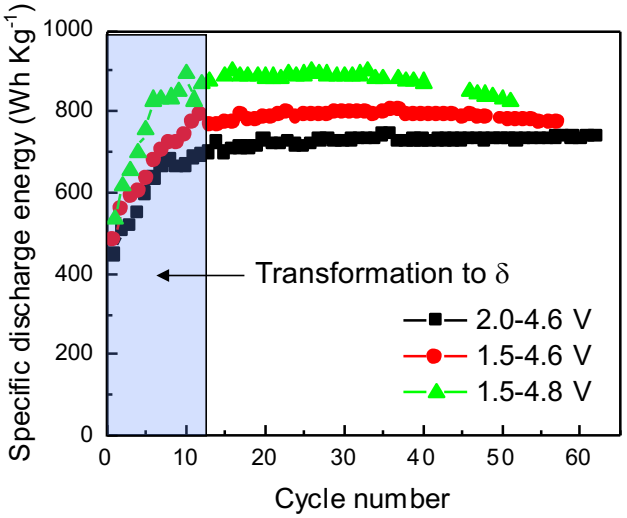
- GEN 3 δ-DRX is a novel approach. By post-processing high Mn content DRX limited re-ordering is achieved. This flattens voltage profile and increases rate capability
- Multiple methods for post-processing have been developed
- High Mn content limits O-redox and improves cycling stability
- Increased particle size leads to lower surface area and lower degradation



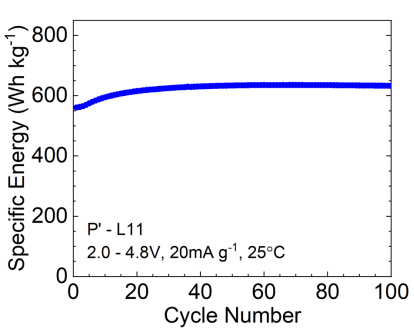
Take the lessons learned from GEN1 DRX and apply to GEN3

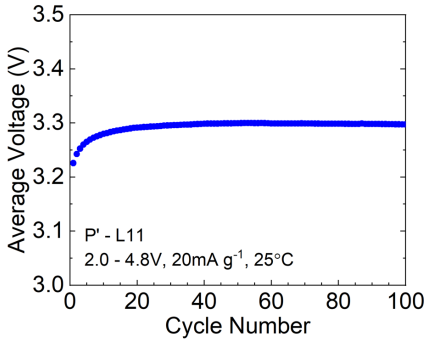
# δ-DRX : Small versus Large Particle Size

**High surface area DRX:**
**700 – 900 Wh/kg achieved**

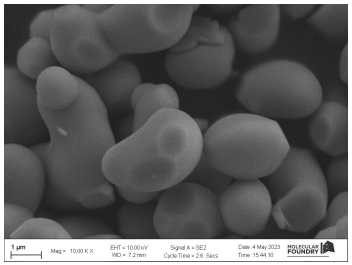



**Low surface area single-crystal DRX:**
**600 Wh/kg achieved with stable cycling**



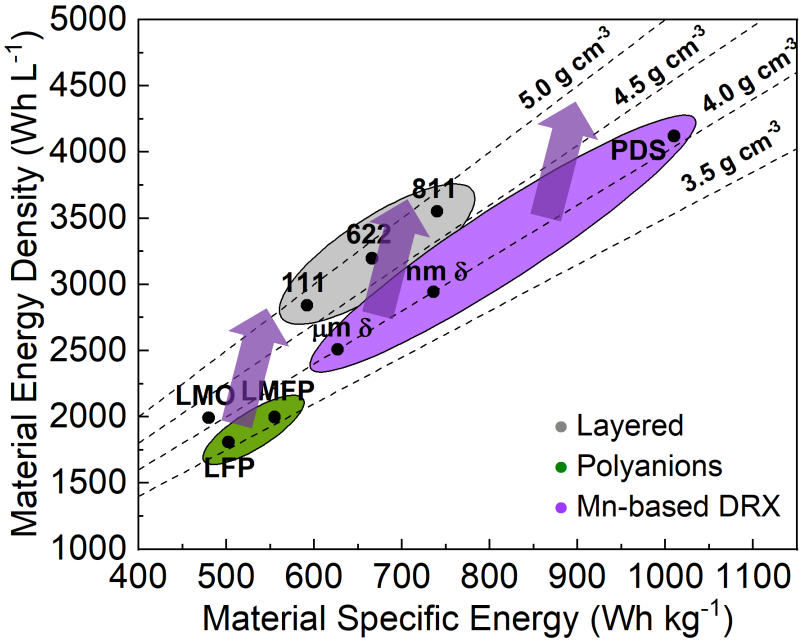




Externally preprocessed to form δ



Particle size 1.5 – 3μm

# Potential pack-level benefits from DRX




- Mn-based DRXs have a similar usable specific energy to NMCs, depending on composition and particle size
- DRX crystal density is larger than LFP and lower than NMC
- DRX cathodes are likely to be very thermally stable due to the charged state only consisting of $Mn^{4+}$ and $Ti^{4+}$ which are very stable valence states in air. This is likely to enable pack-level energy density gains similar to LFP.

# Summary

- Identified carbon as major source of electrolyte breakdown/capacity degradation at high voltage. Mechanism understood through modeling
- Lowered carbon content to 5-7.5% and improved cycle life with use of graphitic carbon
- Achieved scale-up of Gen1-DRX through solid-state synthesis
- Identified co-precipitation route towards Gen1-DRX
- Identified new LHCE electrolyte for potential use with DRX
- Achieved 300 cycles with 88% capacity retention in GEN1
- Started development of Gen3-$\delta$-DRX with higher Mn content and lower surface area. Initial results show very stable cycling. Further optimization of particle size is required

# Remaining Challenges/Future Work

- Need to identify more scalable approaches to apply graphitic carbon to DRX materials
- Understand mechanism of how electrolyte breakdown leads to capacity fade
- Further reduce carbon content in electrode
- Optimize trade-off between rate capability (small particle size) and good cyclability
- Scale-up GEN3-$\delta$-DRX and optimize preprocessing method to achieve $\delta$.
- Full-cell level testing to begin soon and ahead of schedule

# Contributors and Acknowledgement

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