Enhancing Oxygen Stability In Low-Cobalt Layered Oxide Cathode Materials

PI: Huolin Xin
University of California, Irvine
Co-PIs: Feng Lin (VT), Kristin Persson (UCB),
Wu Xu (PNNL), Jiang Fan (ALEC)
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Project ID: bat414

Overview

Timeline

- Project start date: 12/01/2018
- Project end date: 12/31/2021
- Percent complete: 80%

Barriers

- Barriers addressed
  - Cost
  - Performance
  - Life

Budget

- Total project funding $3.125 million
  - DOE Share $2.5 million
  - Contractor share $625K
- Funding for FY 2020: $1.01 million
- Funding for FY 2021: $0.97 million

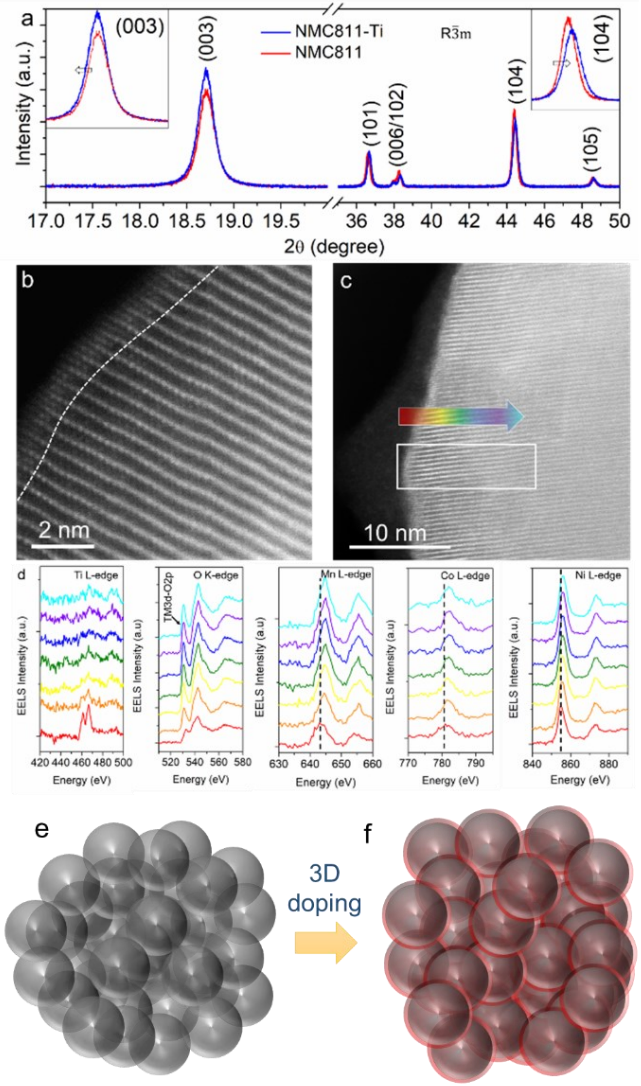
Partners

- UC Irvine: Project Lead Huolin Xin
- Virginia Tech: Feng Lin
- UC Berkeley: Kristin Persson
- PNNL: Wu Xu
- American Lithium Energy: Jiang Fan
- Collaborations: BNL, NSLSII, SSRL, ANL

Relevance: Objectives

Overall objectives

- Displace Co while maintaining high-Ni content and high energy density
  - Cobalt concentration < 50 mg/Wh or No-Co
  - Energy density > 750 Wh/kg (C/3, 2.5-4.4 V) at cathode level
  - Cost ≤ $100/kWh
- Improve cycle and calendar life by retaining oxygen through a 3D doping technology
  - Capacity retention > 80% at 1,000 cycles
  - Energy retention > 80% at 1,000 cycles
  - Calendar life: 15 years
- Deliver a theoretical model
  - High-throughput DFT calculations that rationalize the selection of oxygen-retraining surface and bulk dopants
- Formulate new electrolytes
  - New functional additives
  - Understanding of the CEI's influence on high-Ni low-Co cathodes.
- Offer a knowledge base by performing proactive studies
  - Thermal stability, oxygen loss, and the degradation of the cathode/electrolyte interfaces.



Milestones

Milestone	Status	Description
Jan 2019 Dopant Selection and Material Synthesis	Completed	Computational down-selection to 2–4 elements for synthesis. Achieve NMC-D electrode materials with Co content <= 3%, Ni >= 90%, Dopant metal (Ti or Al) = 2%
April 2019 Structural Fidelity	Completed	Structural study by synchrotron XRD, and aberration-corrected scanning TEM to confirm that the desired layered structure and 3D composition are achieved.
July 2019 Electrode Performance and Fabrication of PPCs	Completed	Evaluate electrochemical performance of BP 1 materials and compare it with the commercial 811 baseline >100 cycles in Li||NMC cells at 4.5 V cutoff and Gr||NMC cells at 4.4 V cutoff. Delivery of PPCs to DOE.
October 2019 Go/No Go	Completed	Delivery of a high-Ni and low-Co cathode material with an electrochemical performance comparable to the commercial NMC811 baseline (energy and capacity retention > 90% of NMC811 @ 100 cycles).

Milestone	Status	Description
Jan 2020 Dopant Refinement	Completed	Refine prediction of surface/bulk dopants
April 2020 Synthesis Scale-up	Completed	Scale up synthesis of BP 1 materials to 100 g scale.
July 2020 Performance Evaluation	Completed	Best of BP1 and BP2 materials achieves a comparable performance to the 811 baseline >300 cycles in Gr||NMC pouch cells at 4.4 V cutoff.
Oct 2020 Go/No Go	Completed	Delivery of a high-Ni and low-Co cathode that has a comparable performance to the NMC811 baseline. (Energy target = 650-750 Wh/kg C/3, 2.5-4.4 V at the cathode level; capacity retention: 70%-90% at 500 cycles; cobalt concentration: 50 mg - 70 mg/Wh)

Milestones

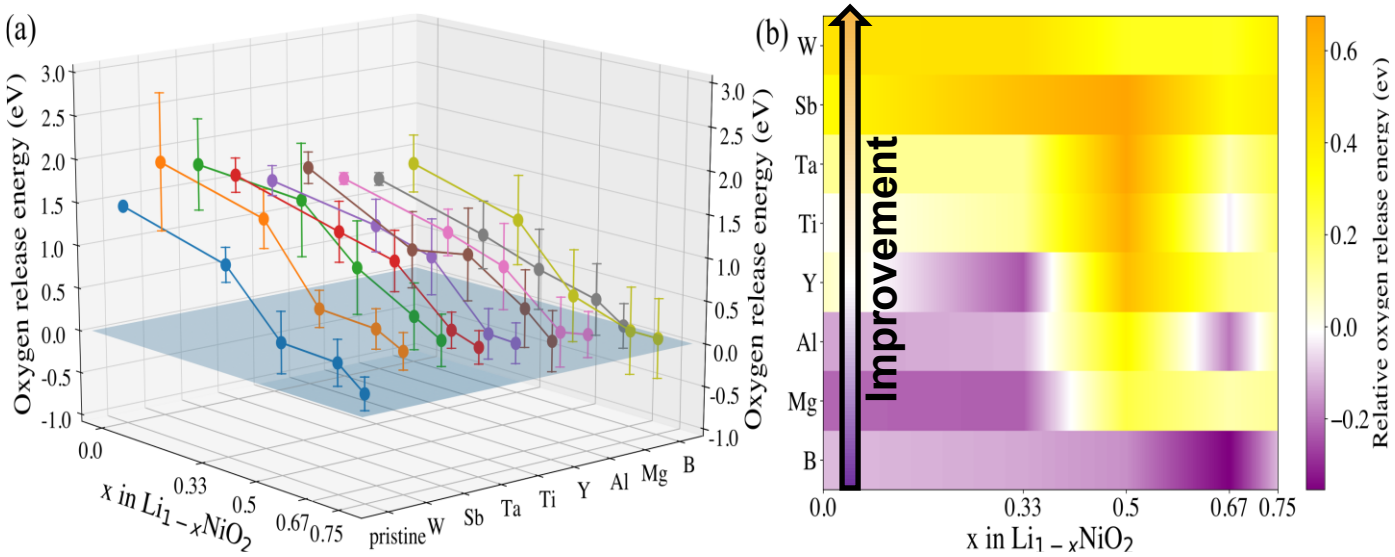
Milestone	Status	Description
Mar 2021 Model Delivery	Complete	Deliver a final model for predicting oxygen retention elements on the surface and in the bulk of high-Ni low-Co oxides.
June 2021 Final Scale-up	On track	Scale up synthesis of the best of BP 1, BP 2, and BP 3 materials to 100-200 g scale.
Sept 2021 Pouch Cell Study	On track	Full pouch cell-level study of the best-performing materials >1000 cycles in Gr||NMC pouch cells at 4.4 V cutoff.
Dec 2021 PCCs Delivery	On track	**Fabricate 21 Projection Completion Cells (PCCs)** and deliver them to DOE with the following specifications: Energy Target: > 750 Wh/kg (C/3, 2.5-4.4 V) at cathode level; Capacity retention: > 80% at 1,000 cycles; Energy retention: >80% at 1,000 cycles; Cobalt concentration: < 50 mg/Wh; Cost≤$100/kWh; Calendar life: 15 years.

Approach/Strategy

- **We utilize a three-dimensional (3D) doping technology that is a hierarchical combination of surface and bulk doping.**
  - Surface doping stabilizes the interface between the primary particles and the electrolyte
  - Introduction of dopants to the bulk enhances oxygen stability, conductivity and structural stability in low-Co oxides under high voltage and deep discharging operating conditions.
  - A composition controlled and thermodynamics driven synthesis will be used to accurately achieve the desired 3D doping structures.
- **Use high-throughput computational materials design to screen surface and bulk dopants for a low-Co environment.**
- **Formulate new electrolytes that stabilize the cathode/electrolyte interfaces at deep charging conditions.**
- **Advanced computational and characterization techniques are developed to study**
  - Dopant environment and chemistry
  - Thermal stability, oxygen loss, and the degradation of the cathode/electrolyte interfaces.

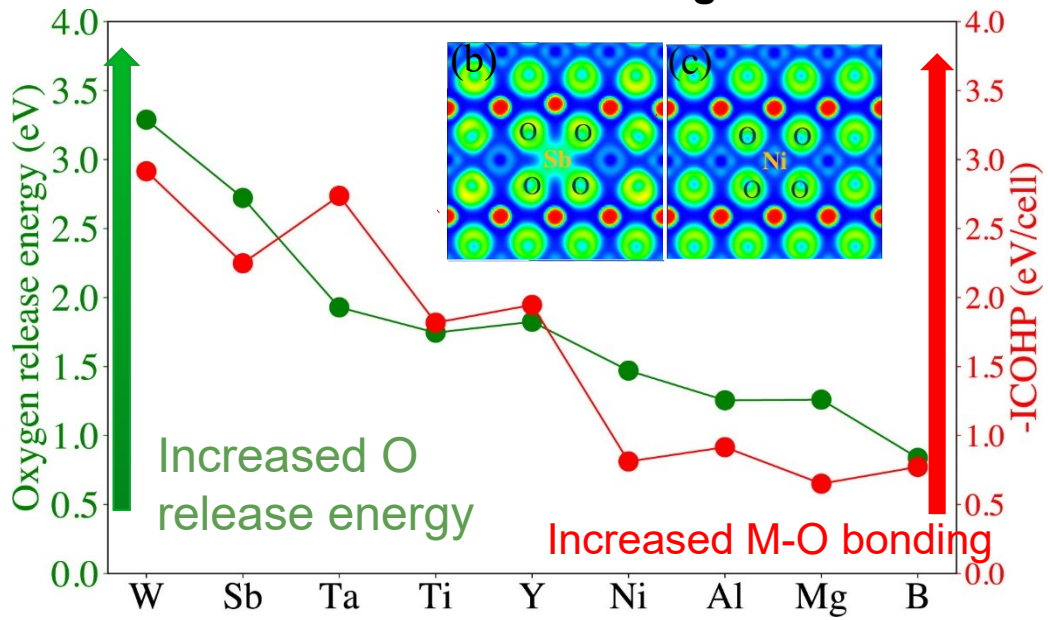
Previous Results
Computational Downselection of Oxygen Retaining Surface Dopants

Oxygen Release Energy



- Upon delithiation, the thermodynamic oxygen release energy decreases rapidly
- At high charge state, e.g. 75% of Li extraction, oxygen is close to spontaneously release from the surface for pristine LNO

M-O Bond Strength

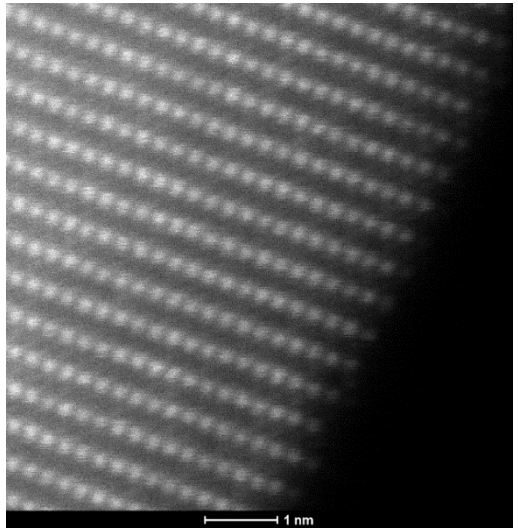


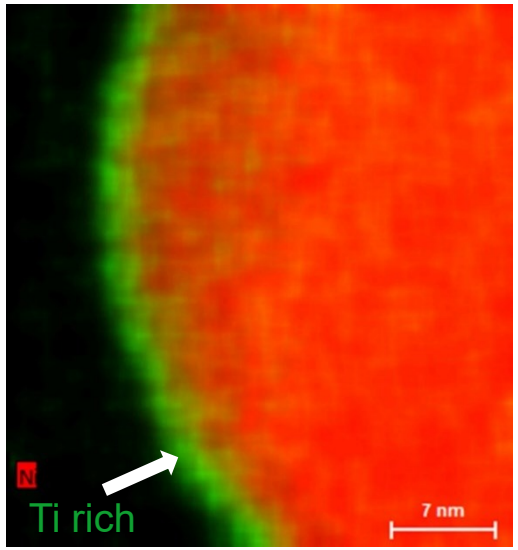
- W, Sb, Ta, and Ti bond more strongly to oxygen than Ni, Al, Mg, and B, and reduce the oxygen release.

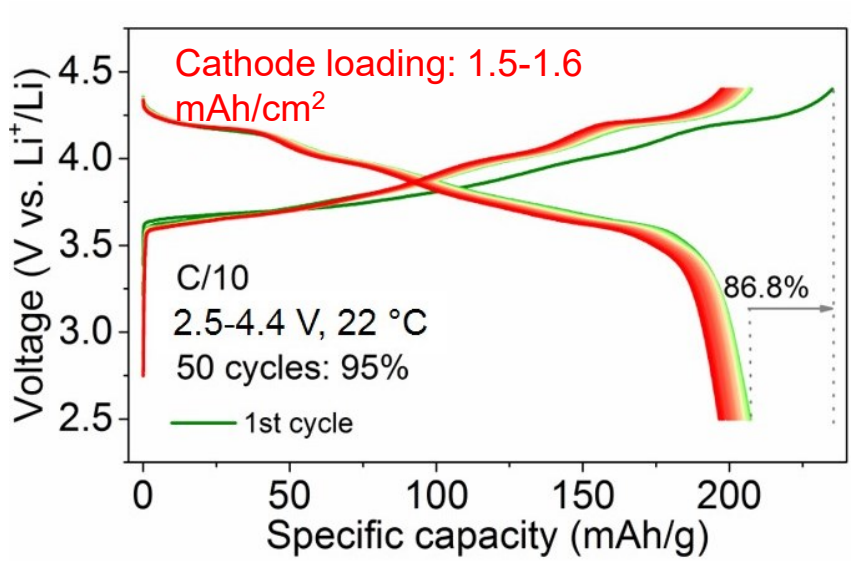
- **W, Sb, Ta and Ti** are found to enhance **surface** oxygen retention of $LiNiO_2$

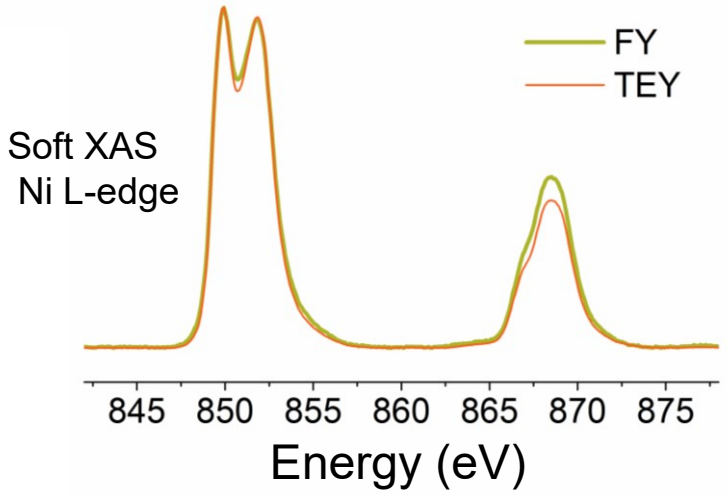
J. Mater. Chem. A, 2020,8, 23293-23303

Previous Results
Co-free Chemistry: 3D-doped $LiNiO_2$ [Ni 96%, Mg 2% , Ti 2%]

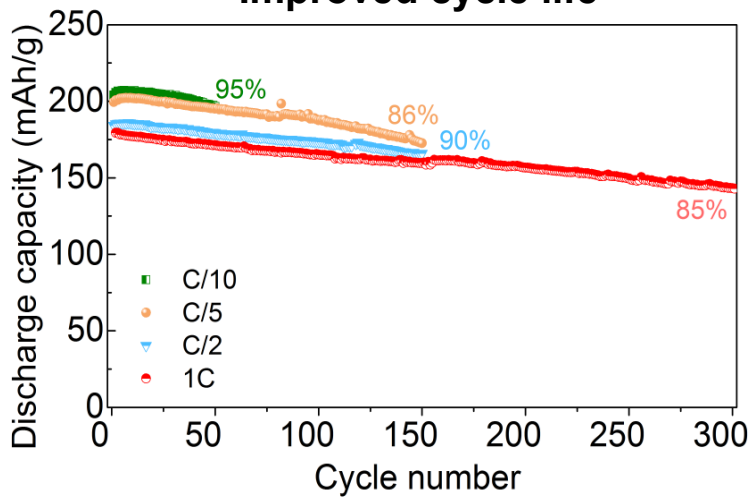




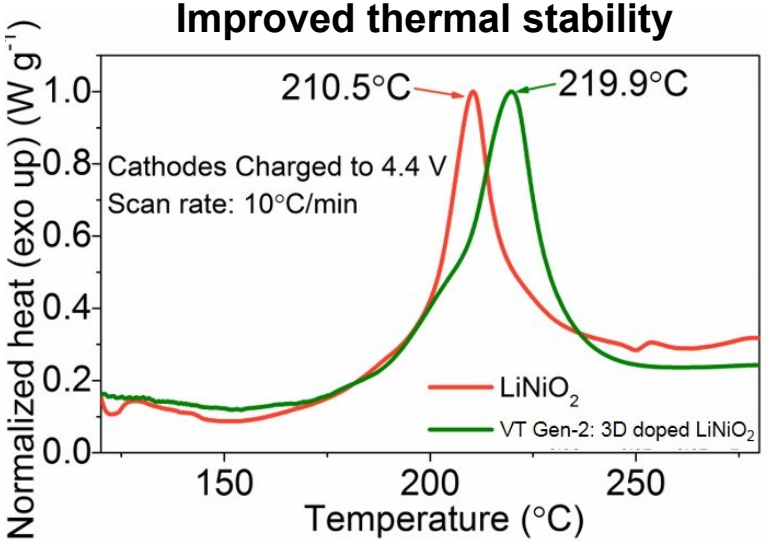




Improved cycle life



Improved thermal stability

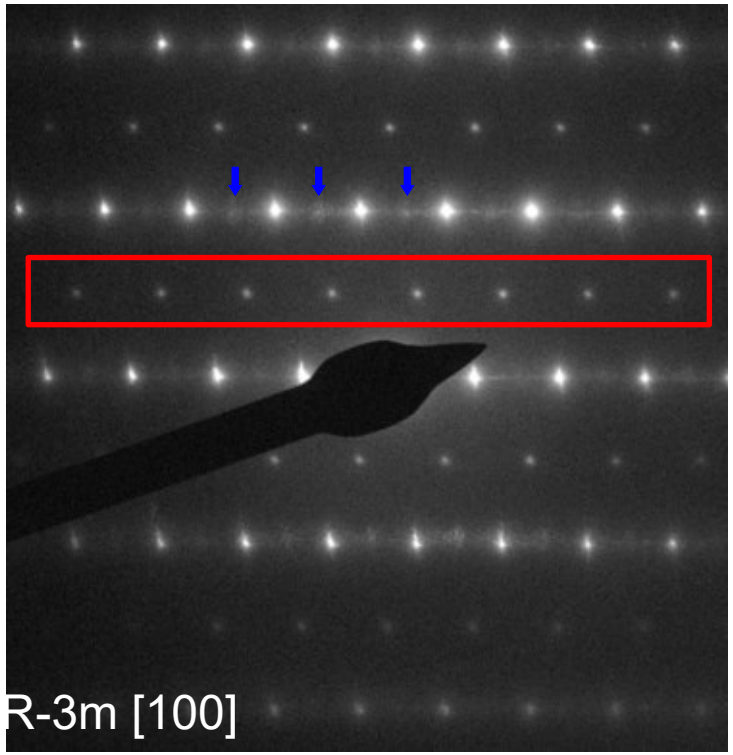


- **3D-doping of Ti and Mg is achieved in $LiNiO_2$. Cycle life and thermal stability are much improved compared with $LiNiO_2$.**

Chemistry of Materials 31 (23), 9769-9776

Technical Accomplishments and Progress
Resolving the O1/O3 misfit structures in $LiNiO_2$

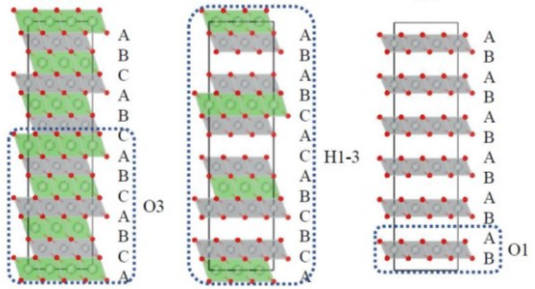
Delithiated LNO (at 4.4 V)

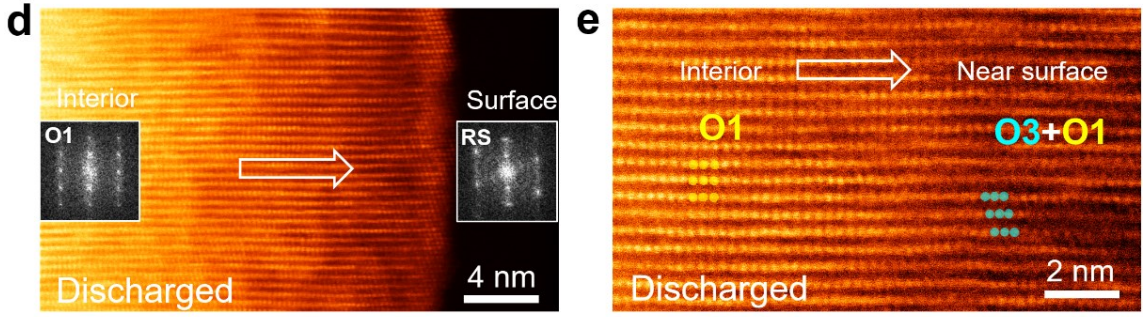


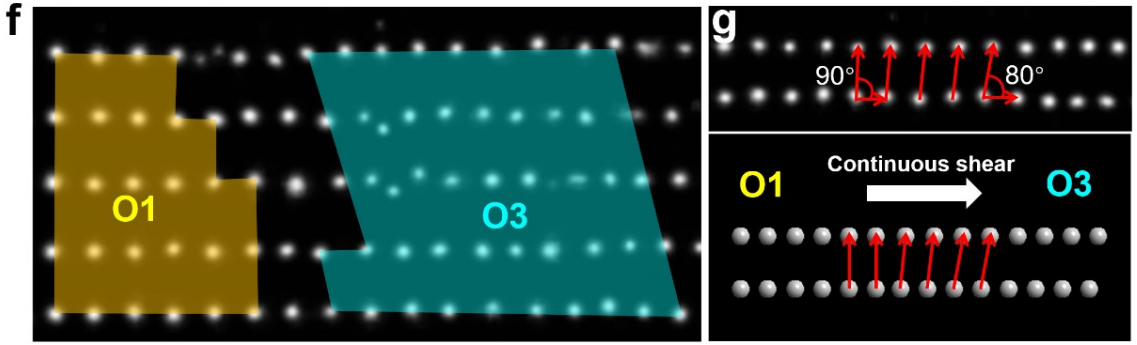
Extra spots: H1-3 phase

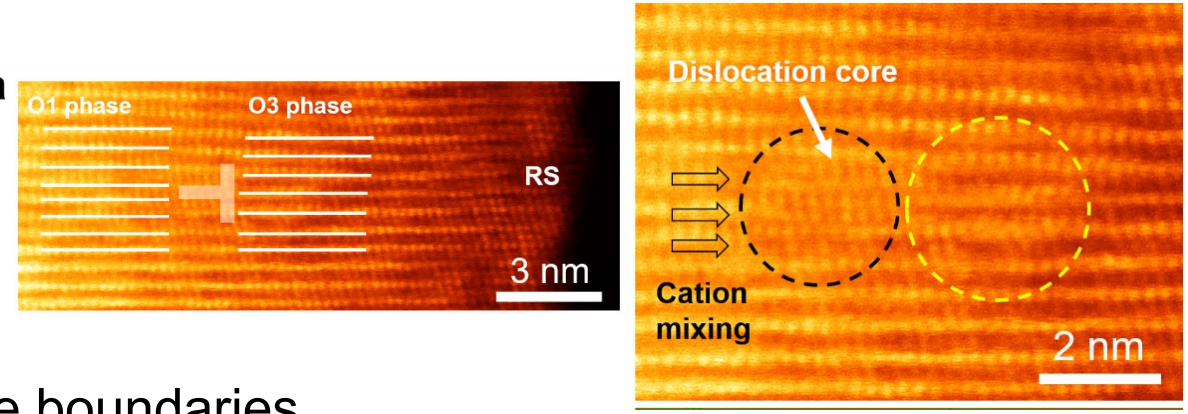
Cation mixing

Streaking: SFs





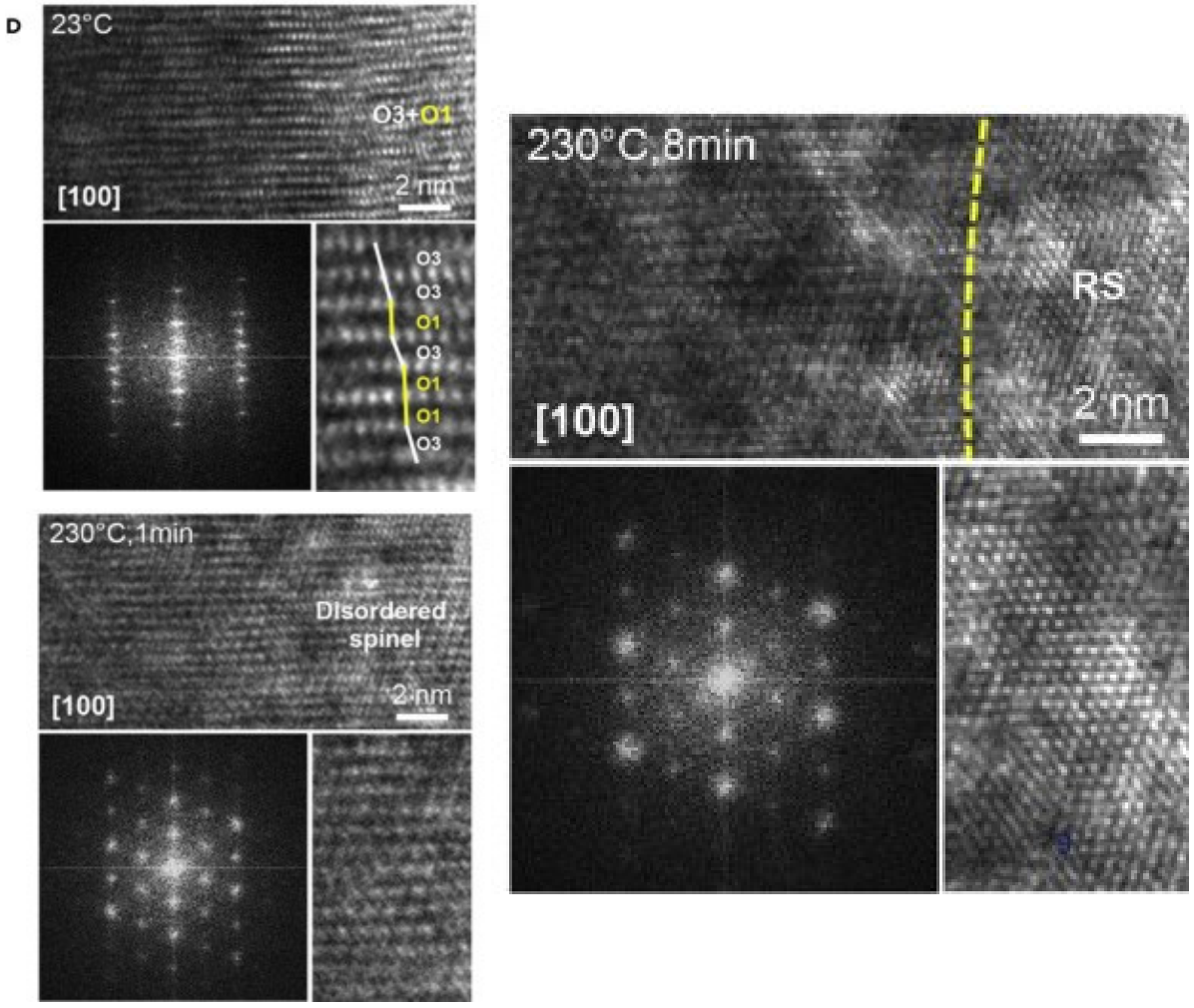


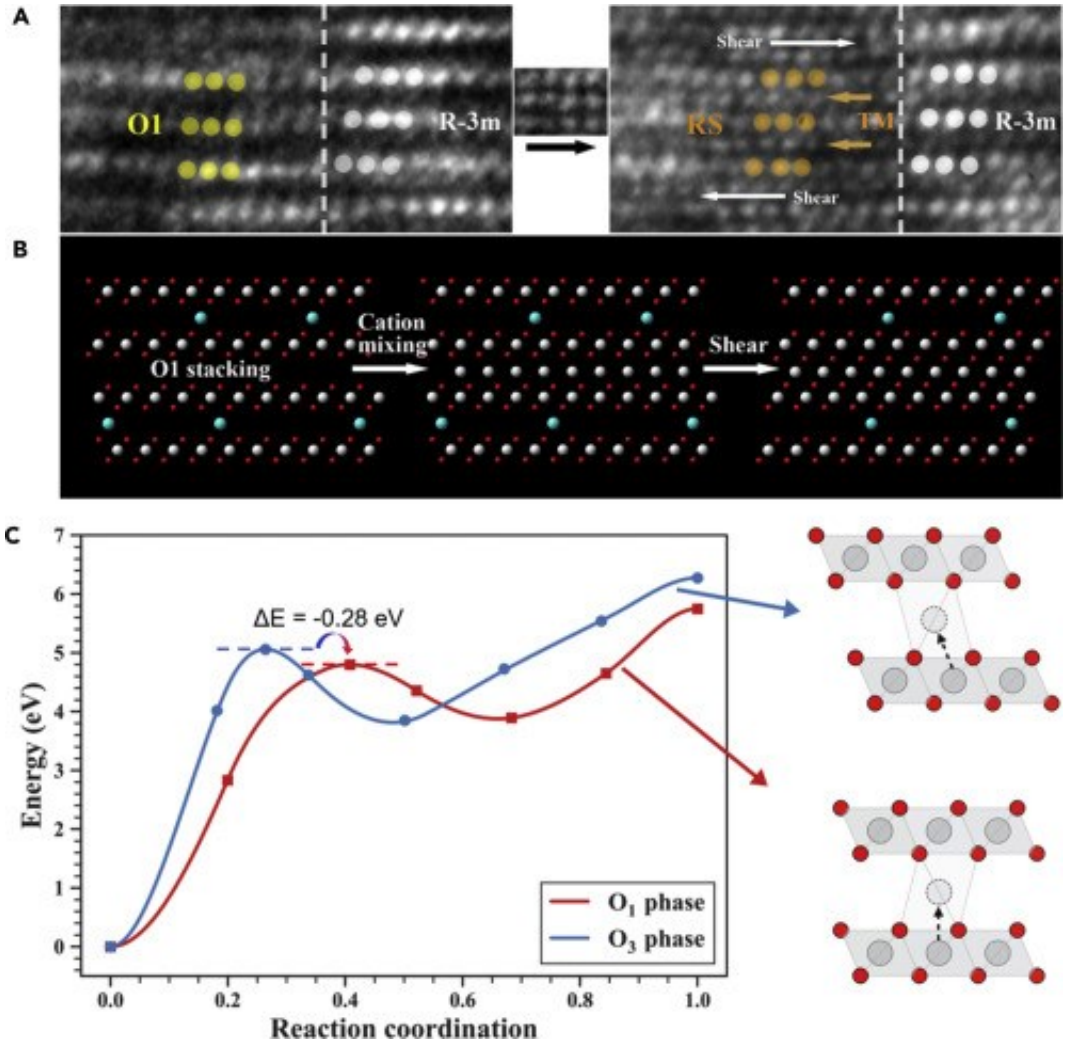


- Coexistence of O3/O1 structures at high voltages.
- Observation of misfit dislocation at the O1/O3 phase boundaries
- Severe cation mixing at the dislocation core.

Nano Letters, 2021, 21, 8, 3657–3663

Technical Accomplishments and Progress
In-situ Study of a Two-Step Phase Transformation of $LiNiO_2$ under Thermal Abuse Conditions





- O1 transform to rock salt faster than O3 under thermal abuse conditions.
- In situ atomic imaging show a two-step pathway involving (1) cation mixing and (2) shear along (003) planes.

Matter, 2021, 4, 1-14, 2021 https://doi.org/10.1016/j.matt.2021.03.012

Technical Accomplishments and Progress

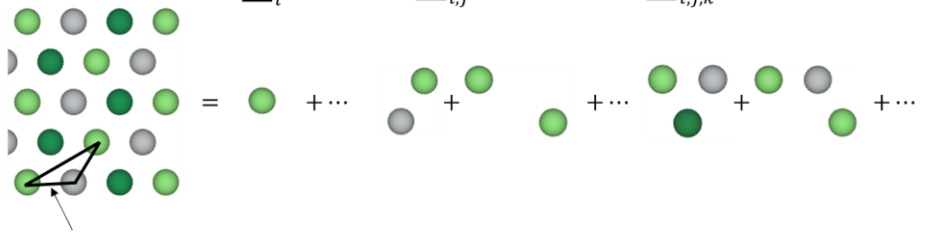
Cluster Expansion for Calculating the Thermal Dynamics of Li_xNiO_2 and Doped-Li_xNiO_2

$E(\text{Lattice configuration}) = \Sigma J(\text{Cluster}) \times \sigma(\text{Cluster})$

J: effective cluster interaction (ECI), i.e., energy associated with this cluster

σ: occupation variable, i.e., how often does this cluster show up per lattice site

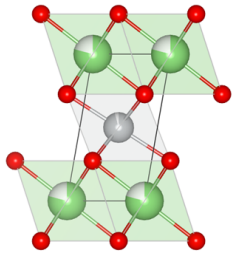
$$E = \sum_i J_i\sigma_i + \sum_{i,j} J_{ij}\sigma_{ij} + \sum_{i,j,k} J_{ijk}\sigma_{ijk} + \cdots$$



3-body cluster (triplet)

Li+, Vacancy

Ni^{3+}, Ni^{4+}

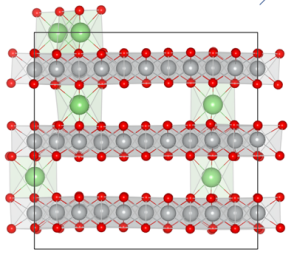


Pair: 9 Å, 33 clusters

Triplet: 6 Å, 56 clusters

Quadruplet: 4 Å, 2 clusters

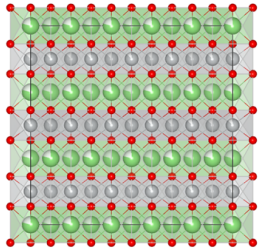
Input structure



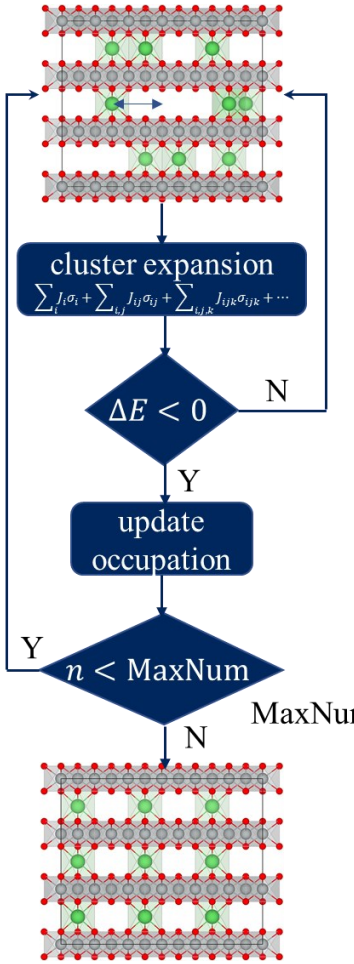
200 structures

Scaling matrix

Cluster supercell



1. Occupancy list
2. Correlation vector
   $[\sigma_1, \sigma_2, \sigma_3 \ldots]$,
   $[\sigma_1, \sigma_2, \sigma_3 \ldots]$,
   ...
   $[\sigma_1, \sigma_2, \sigma_3 \ldots]$
3. Fit ECIs to DFT energies of sampled structures using a L1-regularized least-squares regression

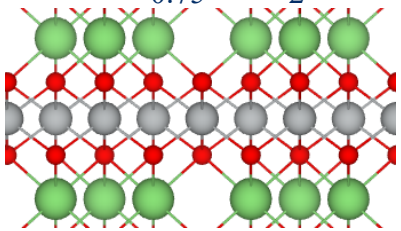


Obtain representative Li_xNiO_2

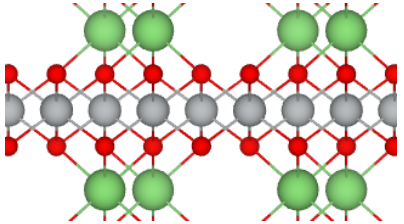
Flip Li^+/vacancy, Ni^{3+}/Ni^{4+}

MaxNum = 400,00

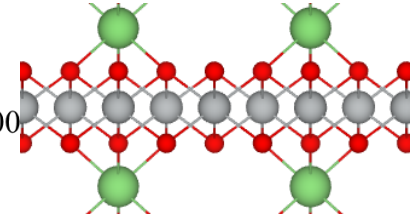
$Li_{0.75}NiO_2$



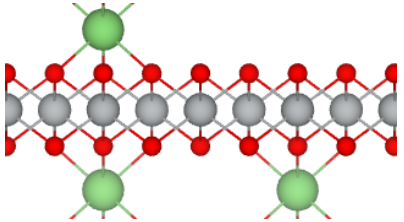
$Li_{0.5}NiO_2$



$Li_{0.25}NiO_2$



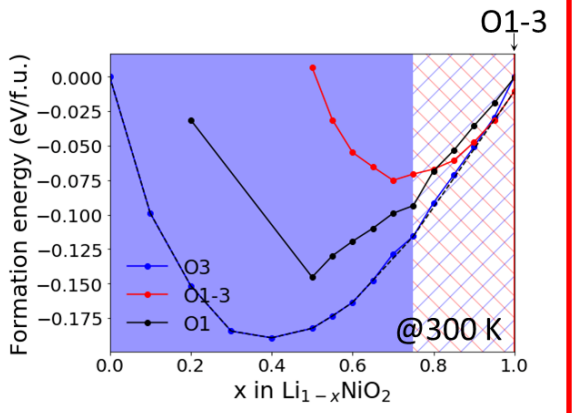
$Li_{0.05}NiO_2$

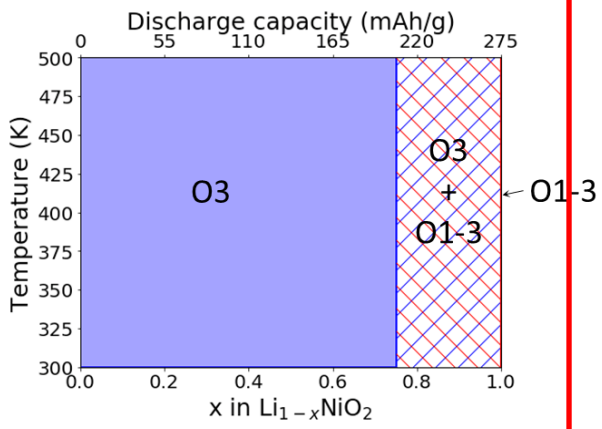


- We have employed a cluster expansion technique in conjunction with MC simulations to calculate the phase diagrams of Li_xNiO_2 and Doped- Li_xNiO_2.

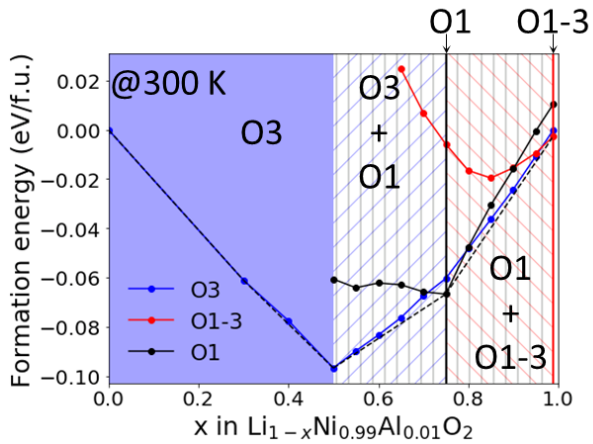
Technical Accomplishments and Progress
Full Convex Hull Calculation for $Li_{1-x}NiO_2$, $Li_{1-x}Ni_{1-y}Al_yO_2$, $Li_{1-x}Ni_{1-y}Ti_yO_2$

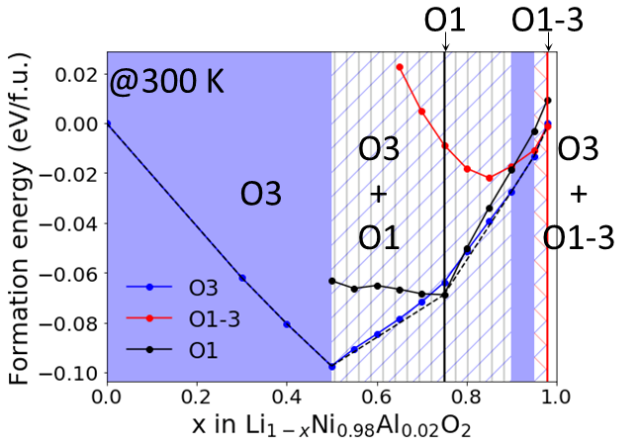
$Li_{1-x}NiO_2$

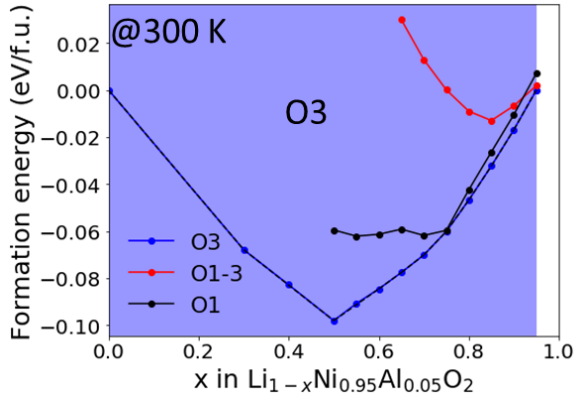




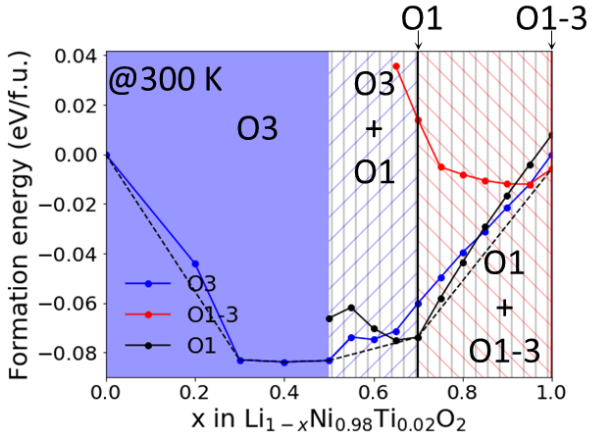
$Li_{1-x}Ni_{1-y}Al_yO_2$

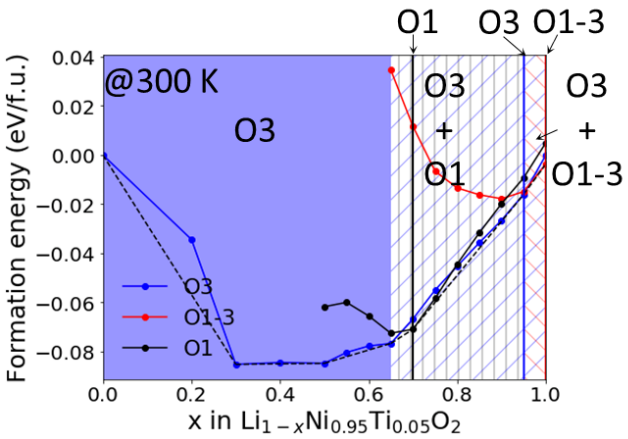


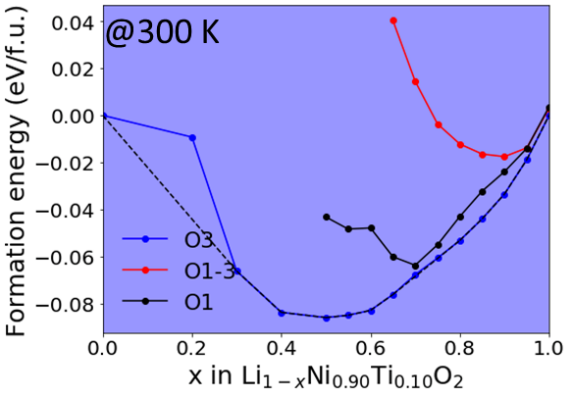




$Li_{1-x}Ni_{1-y}Ti_yO_2$



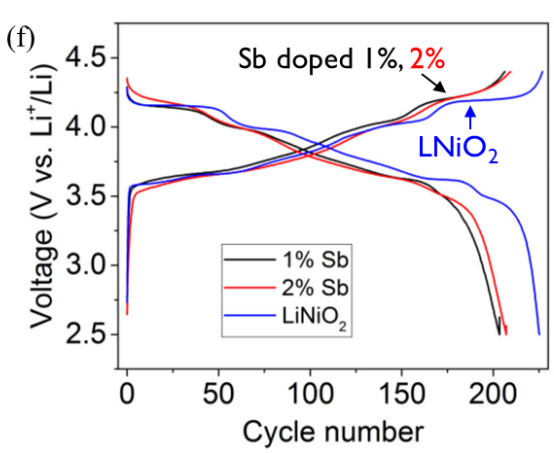


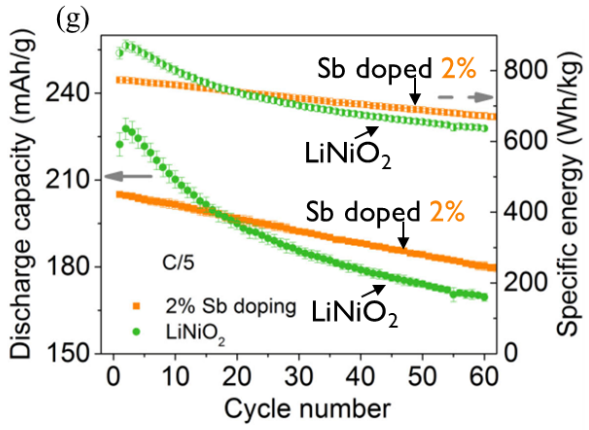


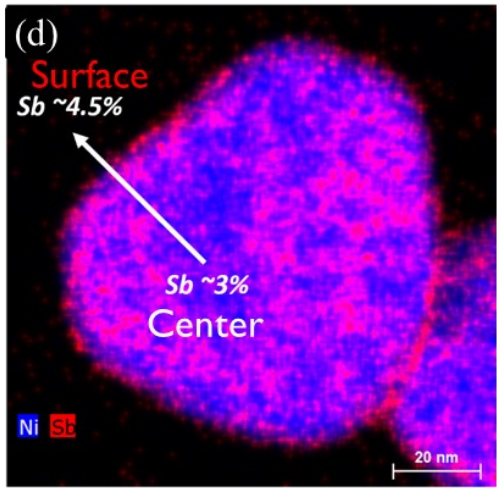
- The correct amount of doping can delay or inhibit the formation of O1 related phases.
- O3 phase can be stabilized during the entire charging process in $LiNi_{0.95}Al_{0.05}O_2$ and $LiNi_{0.9}Ti_{0.1}O_2$.

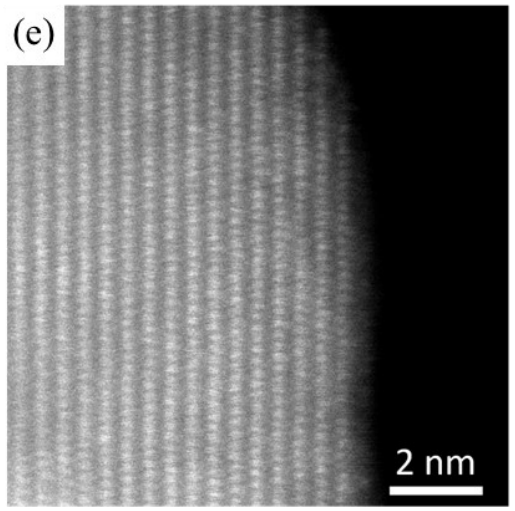
Previous Results
New Co-free Chemistries Under Investigation

$LiNiO_2$ with 2% Sb doping

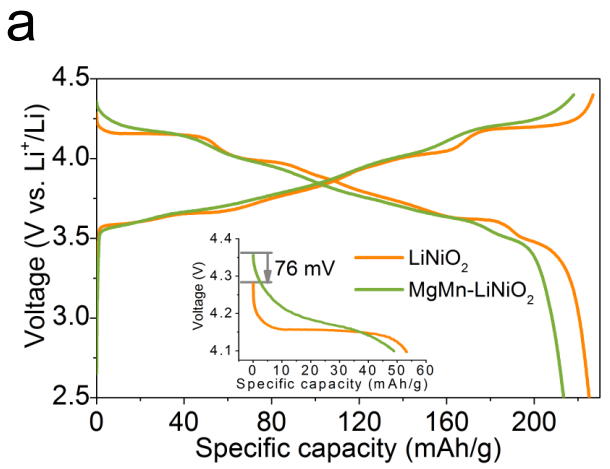


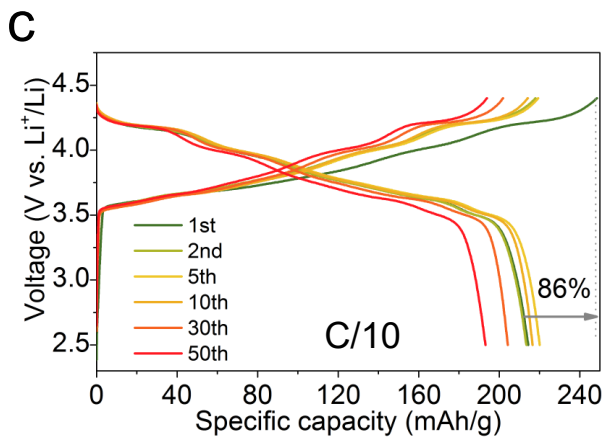


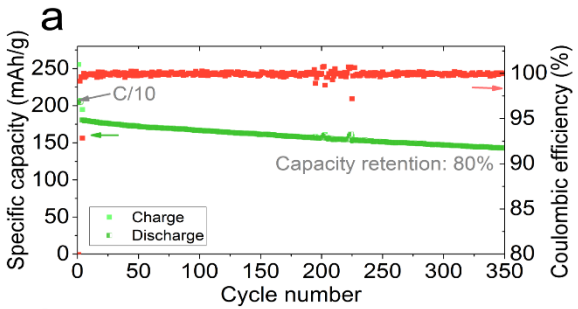


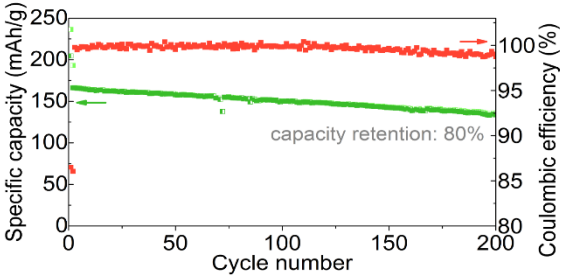


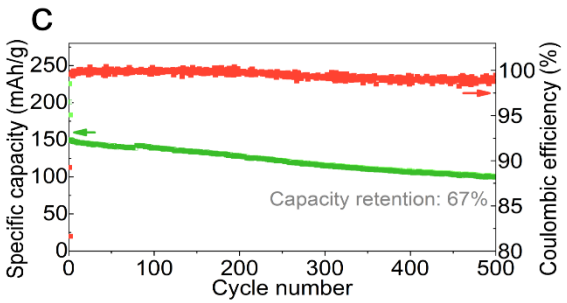
$LiNiO_2$ with 2% Mg, 2% Mn co-doping











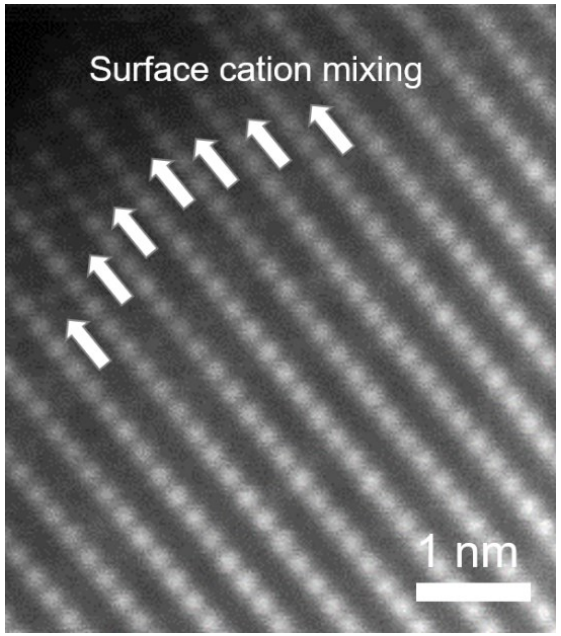
- **Two new Co-free chemistries have shown promising electrochemical performance.**

J. Mater. Chem. A, 2020,8, 23293-23303, ACS Applied Materials & Interfaces 12 (11), 12874-12882

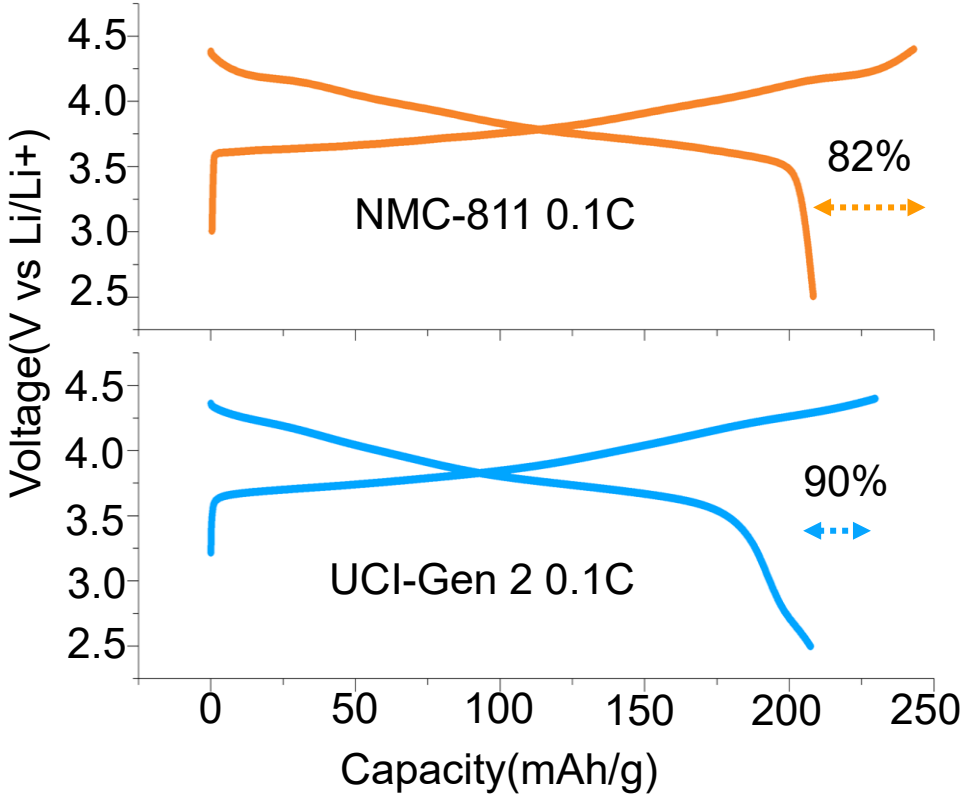
Technical Accomplishments and Progress
New UCI-Gen 2 Chemistry [High Ni, Co Free]

Structure, capacity, energy density and phase transformation

HAADF-STEM

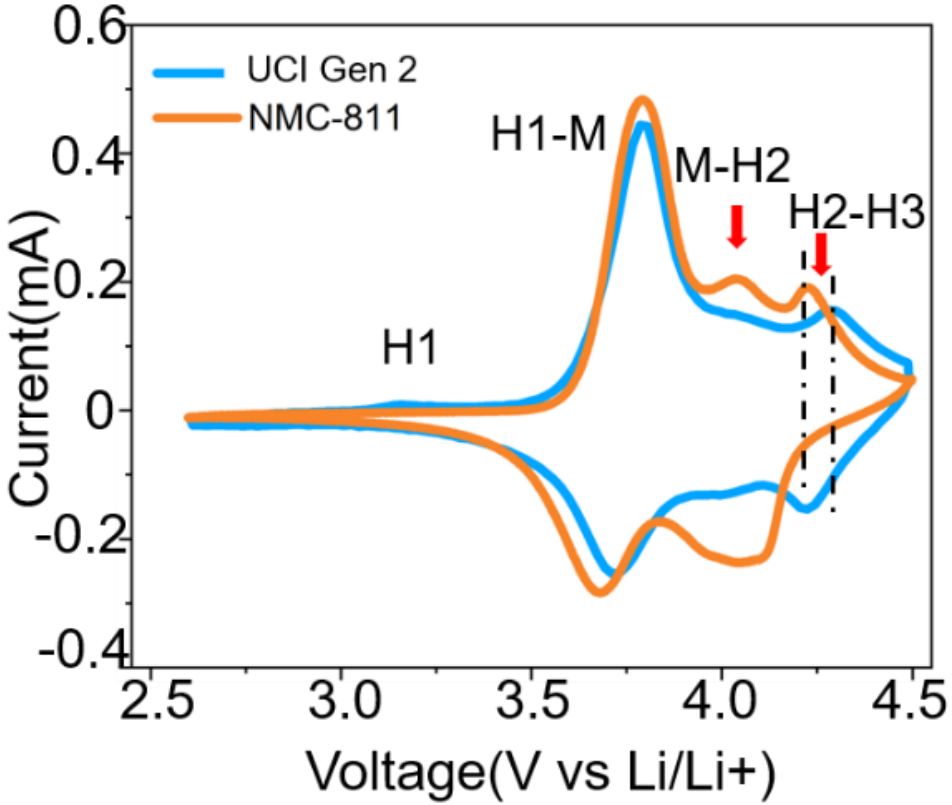


Layered structure



Higher 1st cycle Coulombic Efficiency
Discharge capacity = 210 mAh/kg
Energy density >789 Wh/kg

CV

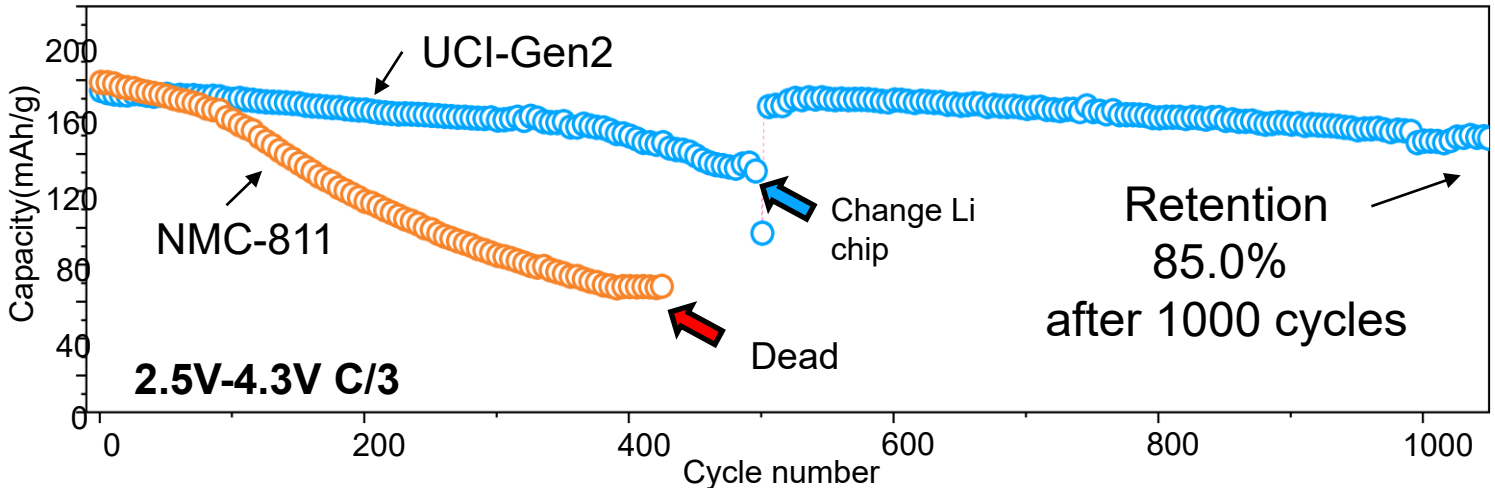


Delayed and reduced H2-H3 transition

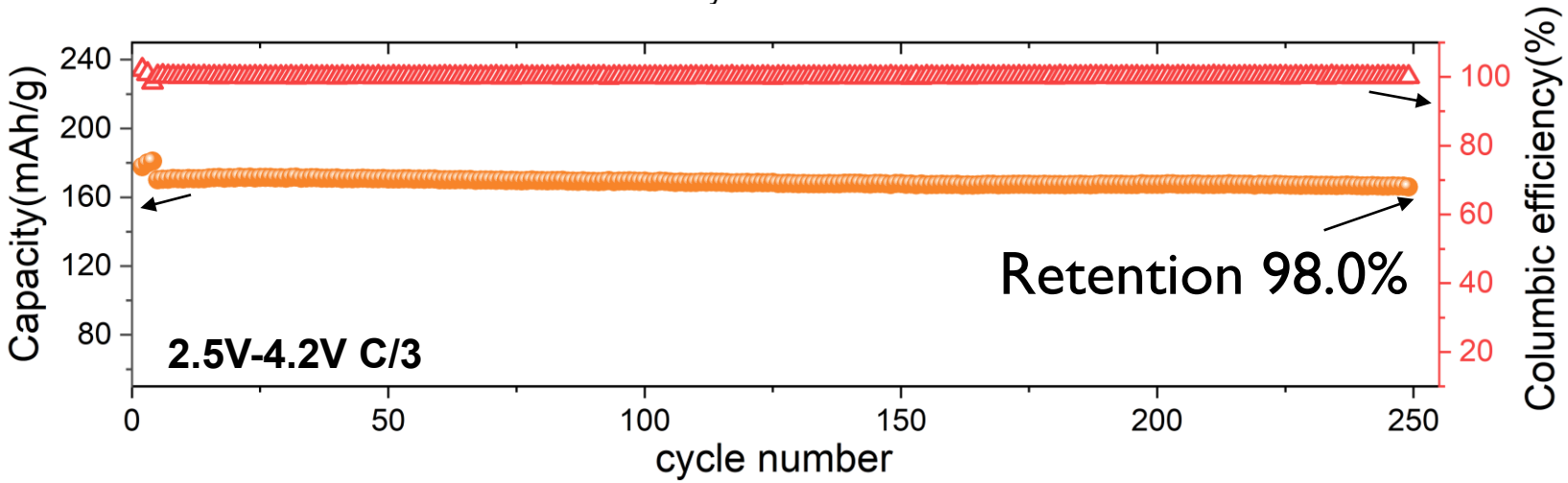
Technical Accomplishments and Progress
New UCI-Gen 2 Chemistry [High Ni, Co Free]

Cycling performance

Half cell Li||UCI-Gen2



Full cell Gr||UCI-Gen2



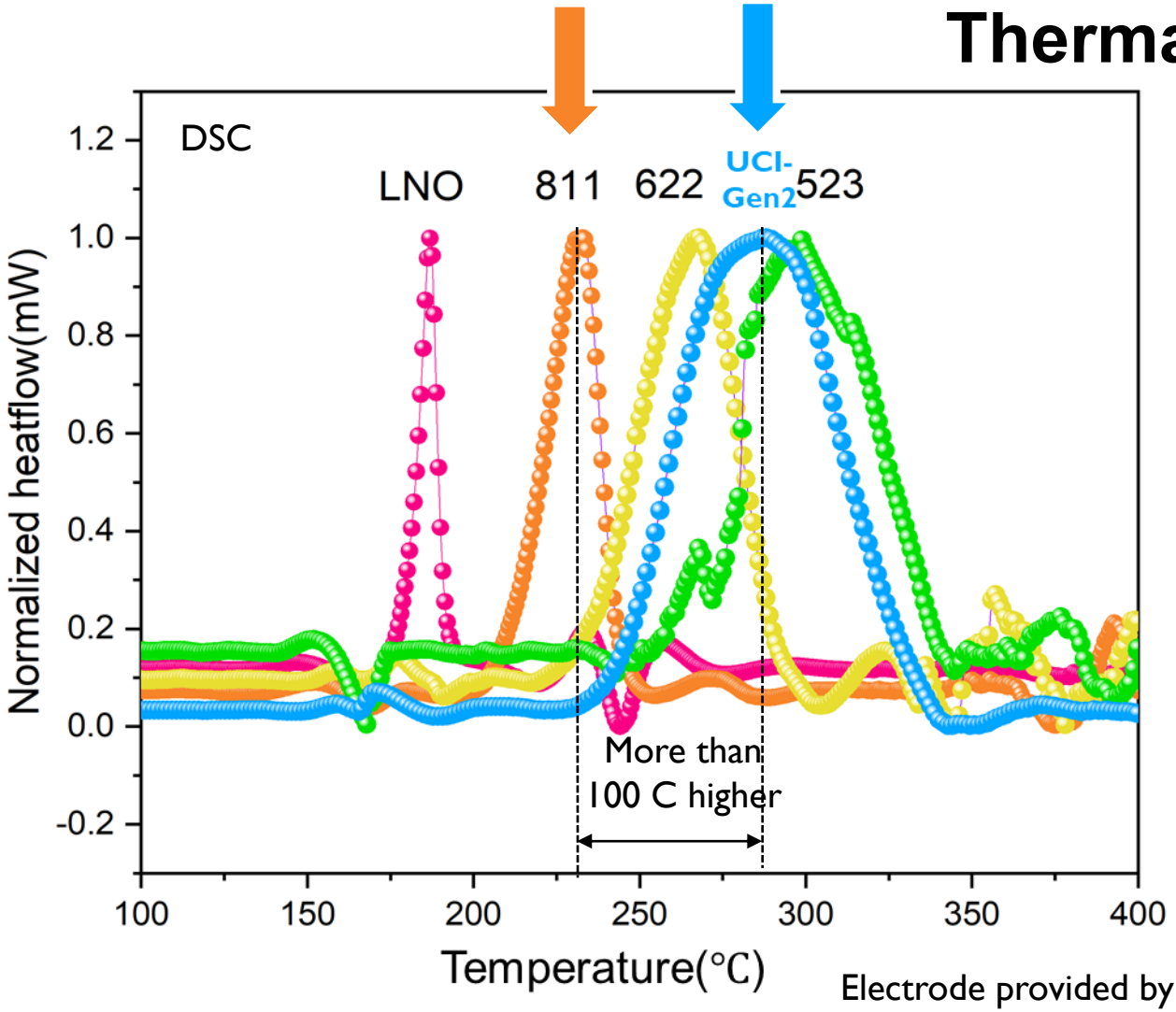
UCI Gen 2 has excellent cycle lif

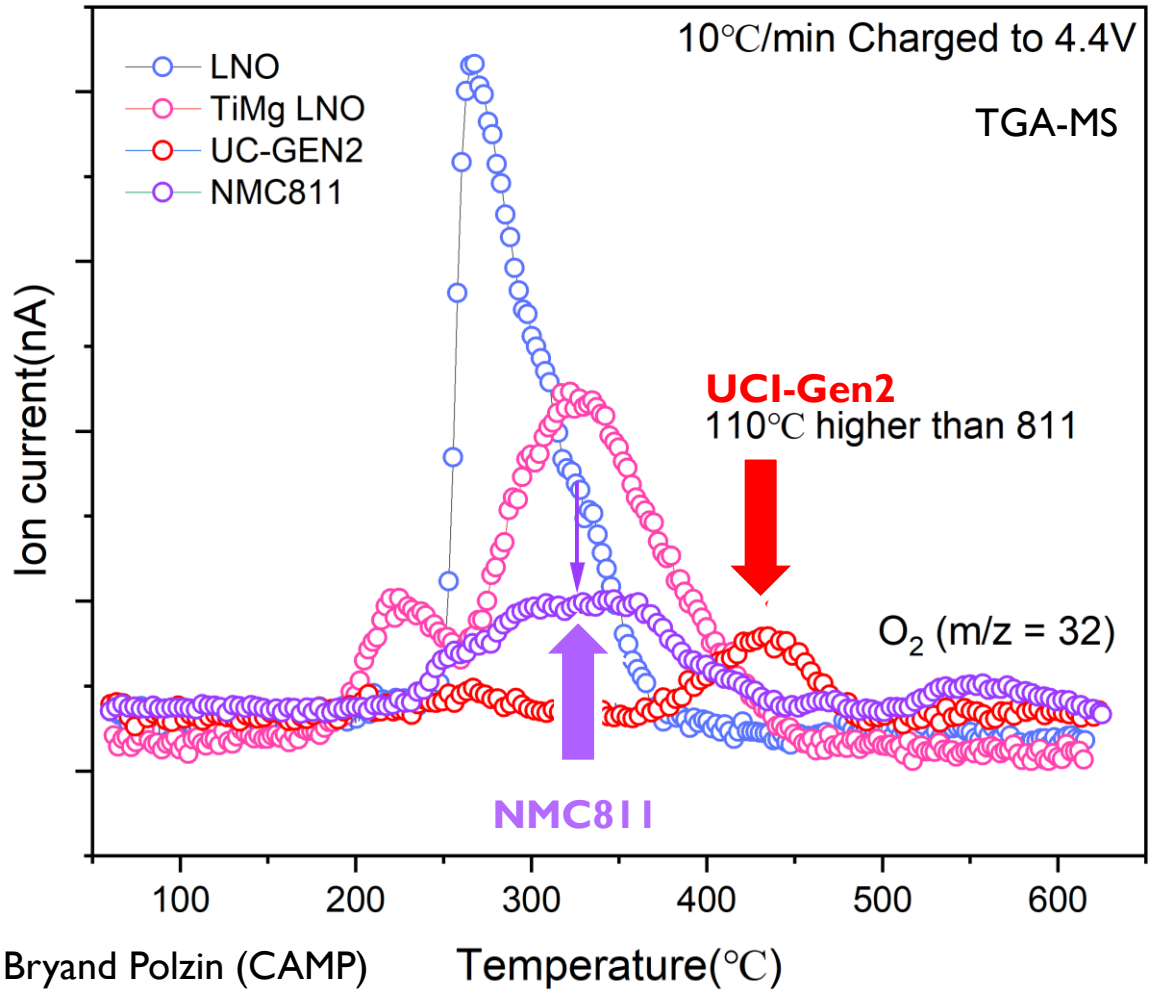
-85% capacity retention after 1000 cycles (Li||UCI-Gen2)

-98% capacity retention after 100 cycles (Gr||UCI-Gen2, 4.2V)

Technical Accomplishments and Progress
New UCI-Gen 2 Chemistry [High Ni, Co Free]

Thermal Stability



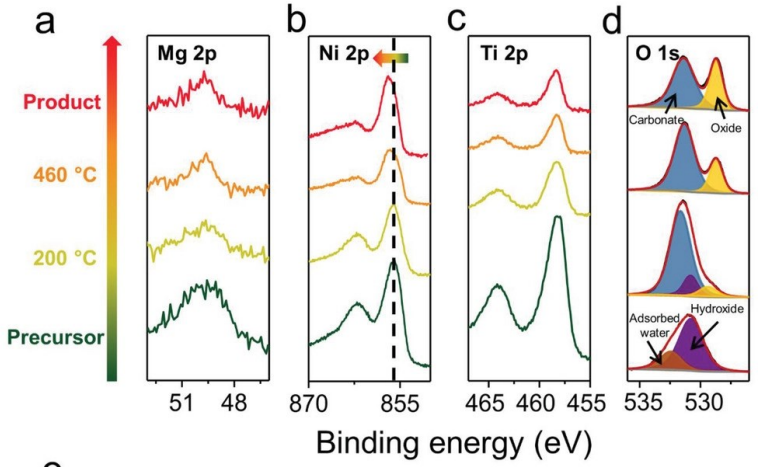


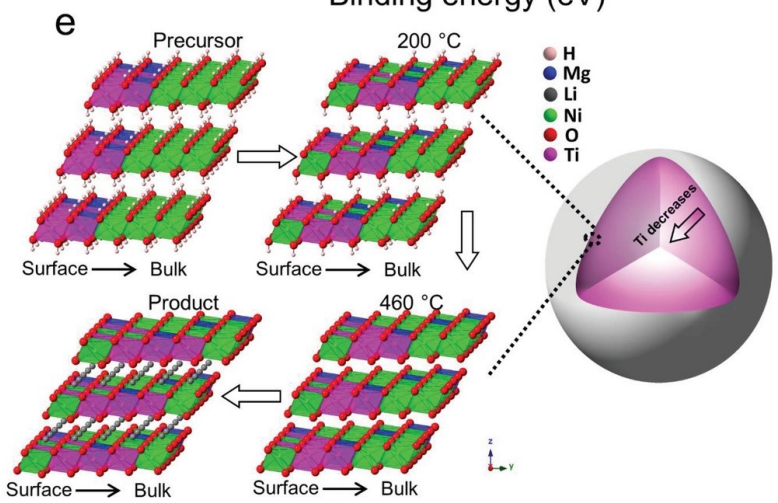
Electrode provided by Bryand Polzin (CAMP)

- Although UCI-Gen2 has much higher Ni content, it has better thermal stability than 622. The thermal stability of UCI-Gen2 is comparable to NMC532.

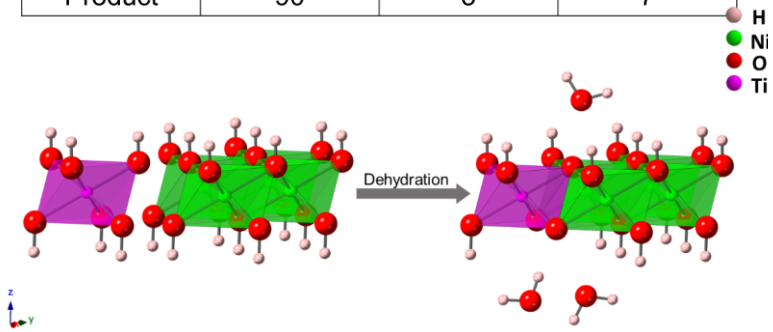
Technical Accomplishments and Progress

Diagnostic Study of Oxidation State and Dopant Distribution during Synthesis

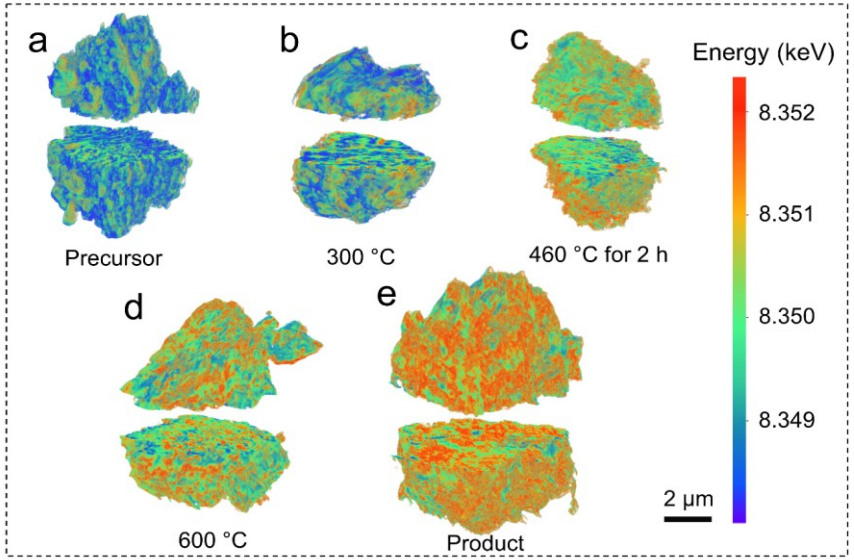


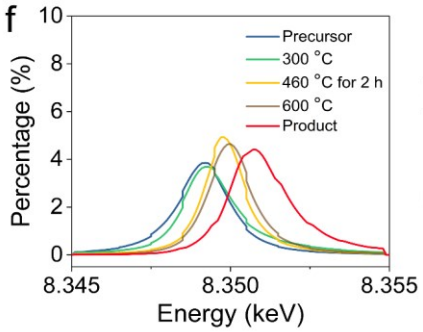


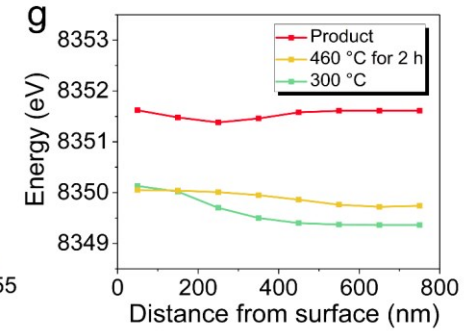
	Ni (%)	Mg (%)	Ti (%)
Precursor	80	5	15
200 °C	89	3	8
460 °C	89	3	8
Product	90	3	7



Dopants undergo dynamic redistribution in the $Ni(OH)_2$ host lattice at the early stage of calcination (**below 300 °C**). Such a redistribution behavior exhibits a strong dopant-dependent characteristic, enabling the targeted surface and bulk doping.





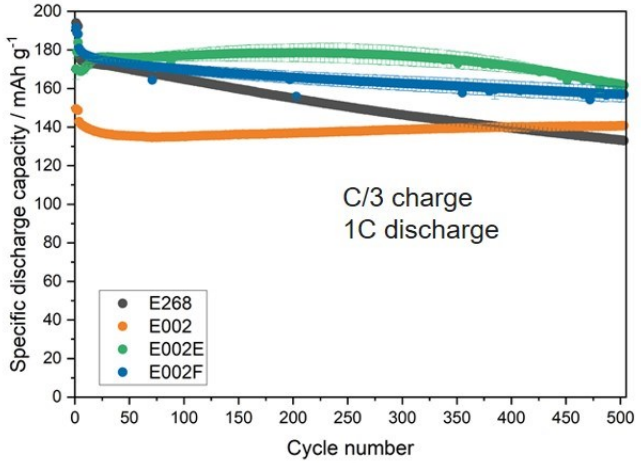


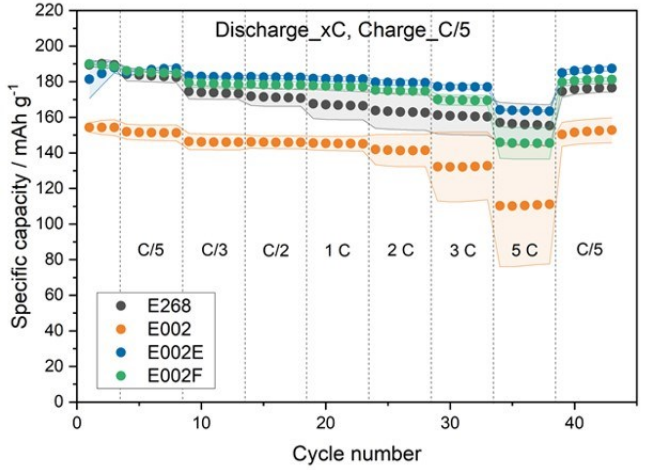
The Ni oxidation heterogeneity along the radial direction decreases upon calcination and becomes insignificant when calcination completes, while the mosaic-like heterogeneity remains throughout the whole calcination process.

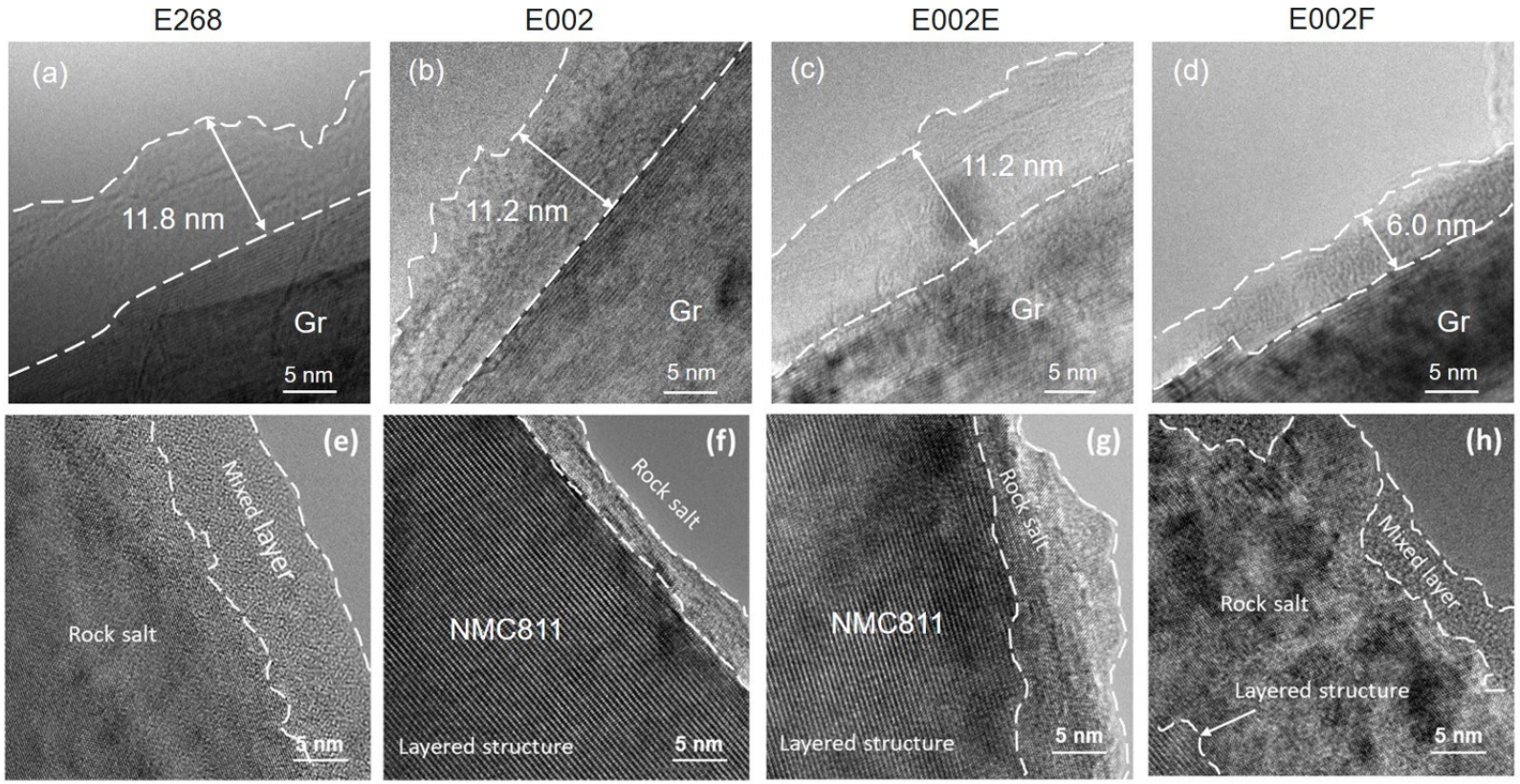
Yang Z., Lin, F. et al. Advanced Energy Materials, 11, 2002719 (2021)

Technical Accomplishments and Progress
Optimization of DME-based LHCEs for Gr||NMC811

- 3 new DME-based LHCEs (LiFSI-1.1DME(-0.2EC/FEC)-3TTE) were developed for Gr||NMC811 cells.
- NMC811: 1.5 mAh cm^{-2}; Gr: 1.8 mAh cm^{-2} (Both from ANL CAMP).
- Voltage range: 2.5 – 4.4 V. 1C= 1.5 mA cm^{-2}. 3 formation cycles: 1×C/20 + 2×C/10.







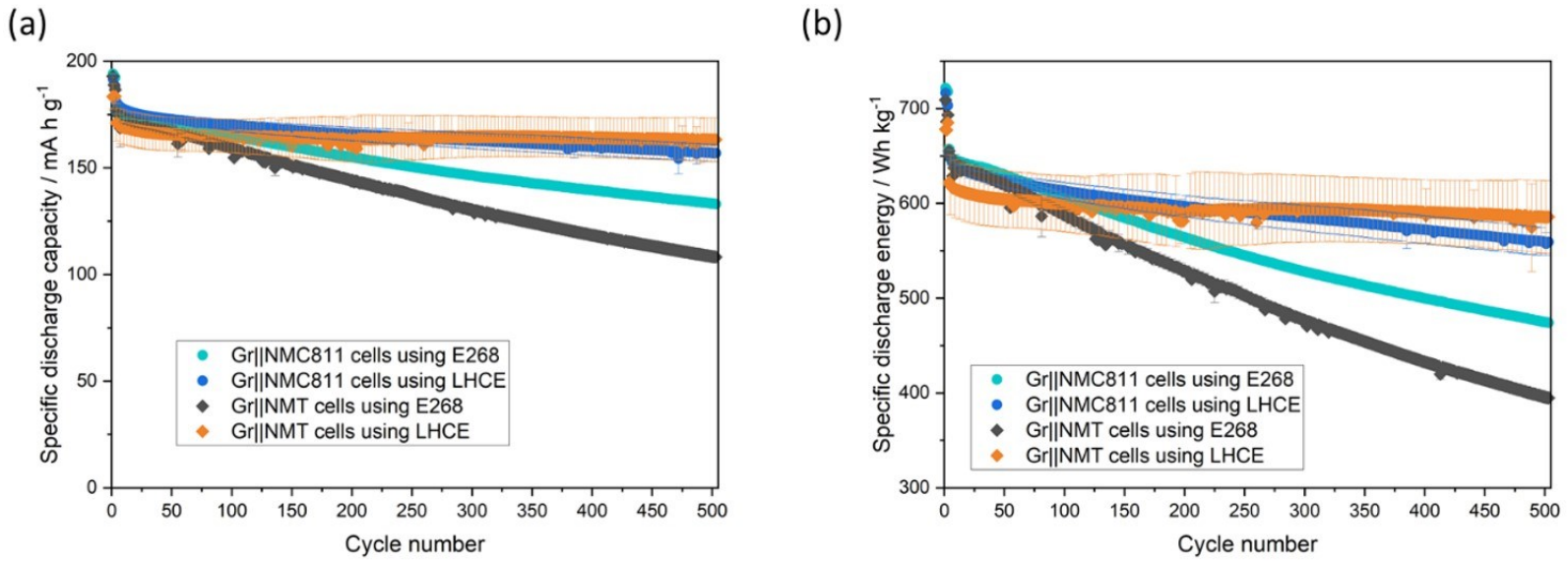
- Adding additives EC and FEC into DME-LHCE increases reversible capacity, cycling stability and rate capability.
- After 500 cycles, EC-based DME-LHCE forms thicker SEI than FEC, but thinner CEI.
- FEC shows good SEI formation but causes a lot of rock-salt layer on NMC811 surface.

H. Jia, W. Xu, et al., *ACS Appl. Mater. Interfaces*, 2020, **12**, 54893-54903.

Technical Accomplishments and Progress

Development of advanced electrolytes for Gr||NMT cells (Go/No-go goal) — Ether-based LHCE in coin cells

- NMT (1.5 mAh cm^{-2}) coated at PNNL
- NMC811 (1.5 mAh cm^{-2}) from ANL CAMP
- Gr (1.84 mAh cm^{-2}) from ANL CAMP
- Electrolyte amount 50 µL
  - DME-LHCE
  - E268 (Baseline)
- 2.5 – 4.4 V
- Formation: 1 × C/20 + 2 × C/10
- Cycling: C/3
- 25 °C

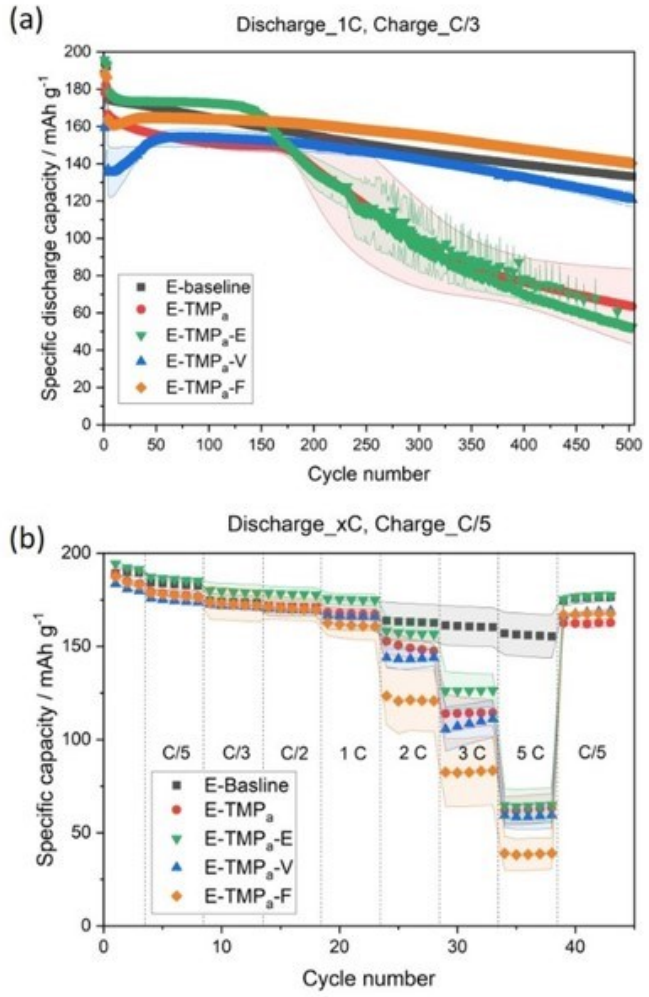


Cell information	Discharge capacity at C/3 at 500th cycle	Capacity retention	Cathode specific energy at C/3 at 500th cycle	Specific energy retention
Gr||NMC811 + E268	132.8 mAh g^{-1}	75.0%	~474 Wh kg^{-1}	~72%
Gr||NMC811 + LHCE	156.9 mAh g^{-1}	86.8%	~559 Wh kg^{-1}	~86%
Gr||NMT + E268	108.1 mAh g^{-1}	61.1%	~395 Wh kg^{-1}	~60%
Gr||NMT + LHCE	163.2 mAh g^{-1}	95.3%	~586 Wh kg^{-1}	~94%

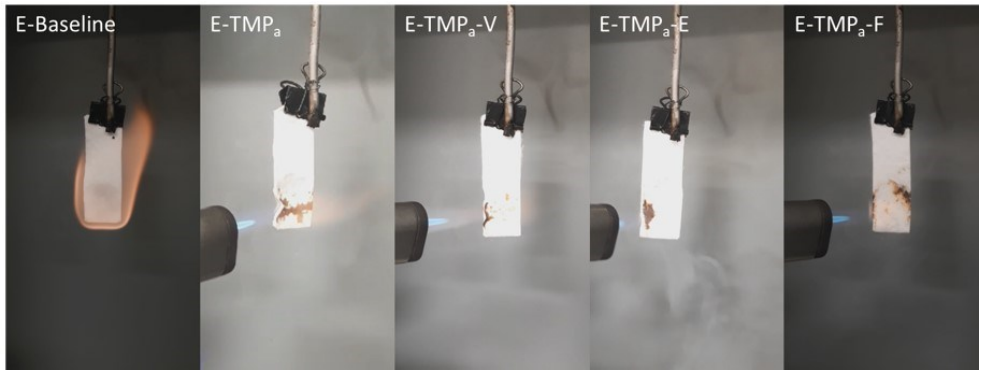
✓ DME-LHCE enables Gr||NMT and Gr||NMC811 cells to have higher and more stable capacity and specific energy than Baseline electrolyte.

➢ Gr||NMT cells with DME-LHCE show lower capacity and specific energy, probably due to NMT issue.

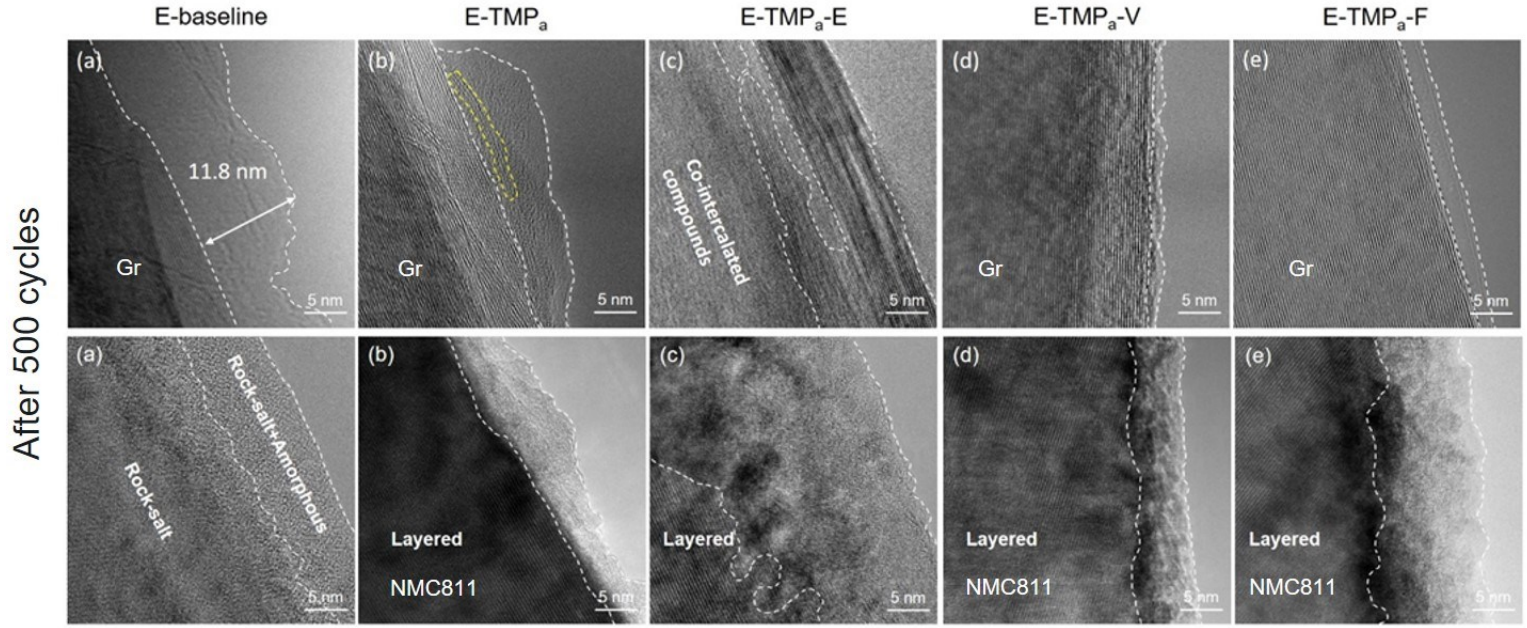
Low-flammability LHCEs based on trimethyl phosphate (TMP_a) for Gr||NMC811 batteries at 4.4 V



H. Jia, W. Xu, et al., *Angew. Chem. Int. Ed.*, 2021, DOI:10.1002/anie.202102403

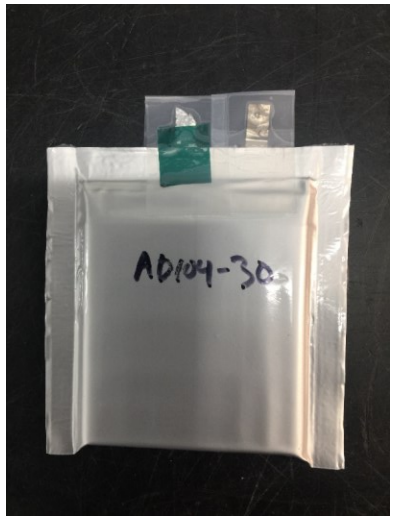


- E-baseline is highly flammable.
- ✓ All TMP_a-LHCEs cannot be ignited.



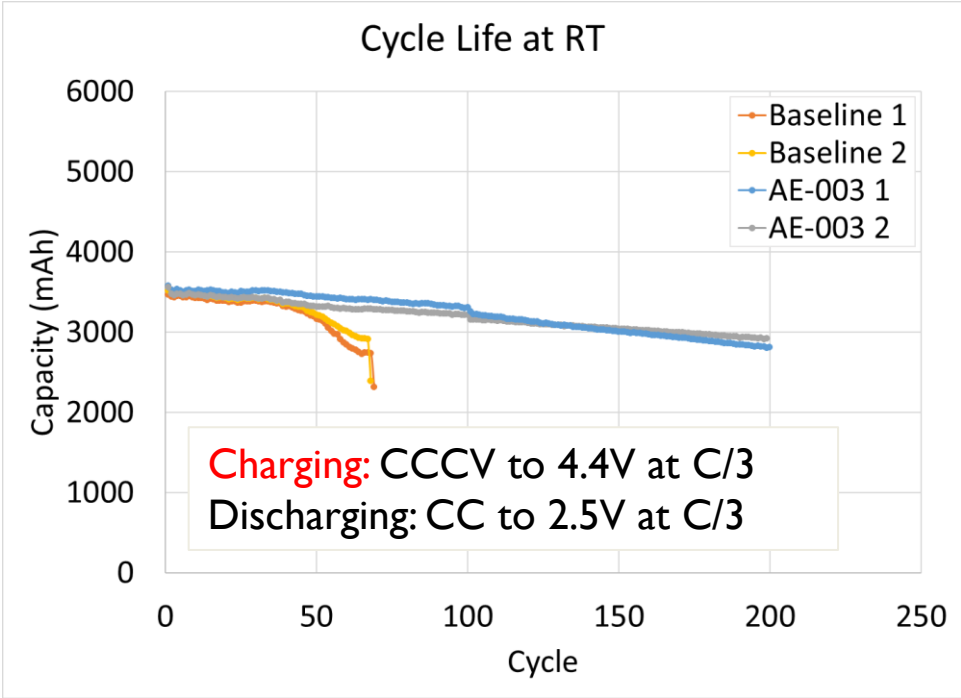
- ✓ LiFSI/TMP_a-TTE-FEC shows slightly higher capacity and better capacity retention than the control electrolyte, and relatively thin SEI and CEI.

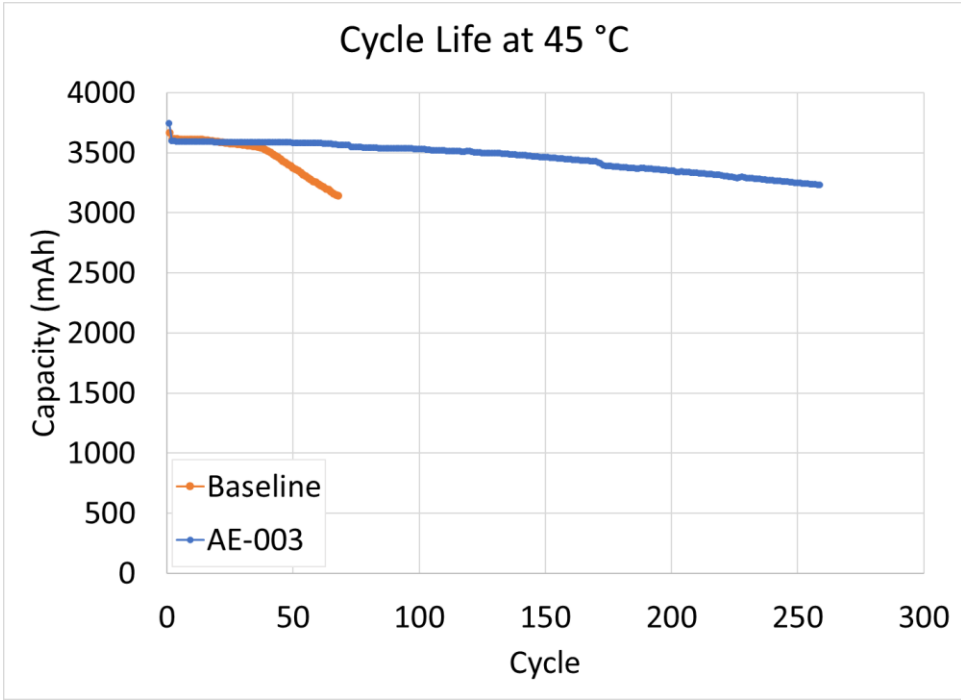
Technical Accomplishments and Progress
3.5Ahr Pouch Cell Tests



3.5 Ahr/cell

AE-003: LiFSI-1.1DME(-0.2EC/FEC)-3TTE
Baseline: 1.0 M LiPF6 in EC-EMC (3:7 by wt.) with 2 wt% VC





Cell ID	# of Cycles (80% capacity)	Avg. C.E. (%)
Baseline 1	63	95.2
Baseline 2	70	98.3
AE-003 1	200 (80.17%)	98.99
AE-003 2	200 (83.26%)	99.85

- AE-003 cycle life at 45 °C is excellent, with >99.9% C.E.

Responses to Previous Year Reviewers' Comments

- The approach is systematic, and the strategy covers the path to test several hypotheses to meet the project objectives.
- The work is intending to apply a scientific approach to doping high-Ni metal-oxide cathode materials in order to replace the function of the Co. The reviewer reported that the project has a good blend of experimental and theoretical approaches that should help better understand the concept and potential efficacy.
- The reviewer asserted that there was impressive computational work for dopants selection and an excellent demonstration of the electrolyte formulations on SEI-CEI stability.
- The team has used its collaborations to its advantage. The work done is great and seems that all parts are working together.
- Even though the project is only 40% completed, the reviewer commented that great progress was made in demonstrating the feasibility of Co-free nickelates. Due to the high 4.4 V cut-off, in addition to cycle life, the team needs to demonstrate progress toward achieving the stated 15-year calendar-life goal in fully charged cells. The team should also demonstrate performance using cathode loadings of 3-4 mAh/cm2 in order to meet the energy-density targets.

Response: Our commercial partner ALE has a proprietary electrode formation techniques to form with 3-4 mAh/cm2 high-Ni electrodes with good rate capabilities. We will supply 0.5 kg of our scaled-up materials to ALE for thick electrode formation and 2Ahr pouch cell fabrication. Due to COVID-19, we are slightly behind for calendar-life testing but we expect to fully complete this test by Q3 of 2021.

Responses to Previous Year Reviewers' Comments

- The project is very relevant for a program on low-Co cathodes. The PI should elaborate on the uniqueness of the doped nickelates by taking into consideration the Co-free nickelates effort published by Dahn's group—*JES* 166(4), A429 (2019). While the PI demonstrated feasibility of LiNiO2 doped with Mg and Mn, the absence of Mn in Dahn's LiNi0.95Mg0.05O2 might reduce the TM- dissolution issue.
- Response: one of the key metrics that our program is trying to address is impoving the thermal stability of high-Ni Co-free cathodes. We have developed a UCI-Gen 2 chemistry that has delivered a high-Ni Co-free cathode material that has a thermal that is 110 degree Celsius higher than that of NMC-811—reaching the stability of NMC-532.

Collaboration and Coordination with Other Institutions

Sub-recipients	Institution	Tasks
Feng Lin	Virginia Tech	Synthesis and X-ray Diagnostics
Kristin Persson	UC Berkeley	High-throughput DFT calculation
Wu Xu	PNNL	Synthesis scale-up and electrolyte formulation
Fan Jiang	American Lithium Energy	Electrode and Cell Fabrication

Collaborators	Institution	Nature of Collaboration
Xiao-Qing Yang	Brookhaven National Lab	X-ray Diagnostics
YoungHo Shin	Argonne National Lab	Sample Supplies
Bryant Polzin	Argonne National Lab	Electrodes and electrode formation
Ozge Kahvecioglu	Argonne National Lab	Synthesis
Kim Kisslinger	Brookhaven National Lab	FIB Sample Prep
Dennis Nordlund	SSRL/SLAC	Soft X-ray Absorption
Jack Kan	Australian Nuclear Science and Technology Organisation. Now at China Spallation Neutron Source.	Neutron Scattering Refinement

Remaining Challenges and Barriers

- Scale-up of calcination to kilograms per batch level for pre-commercialization validations.

Proposed Future Research

- Deploy the developed new chemistries to 2Ahr-scale pouch cells.
- Investigation of cathode-anode cross-talk and study the cathode electrolyte interface and interphases.
- Calendar life study of at both the coin cell and pouch cell levels.
- Develop calcination conditions for kilogram scaled up synthesis.

Any proposed future work is subject to change based on funding levels

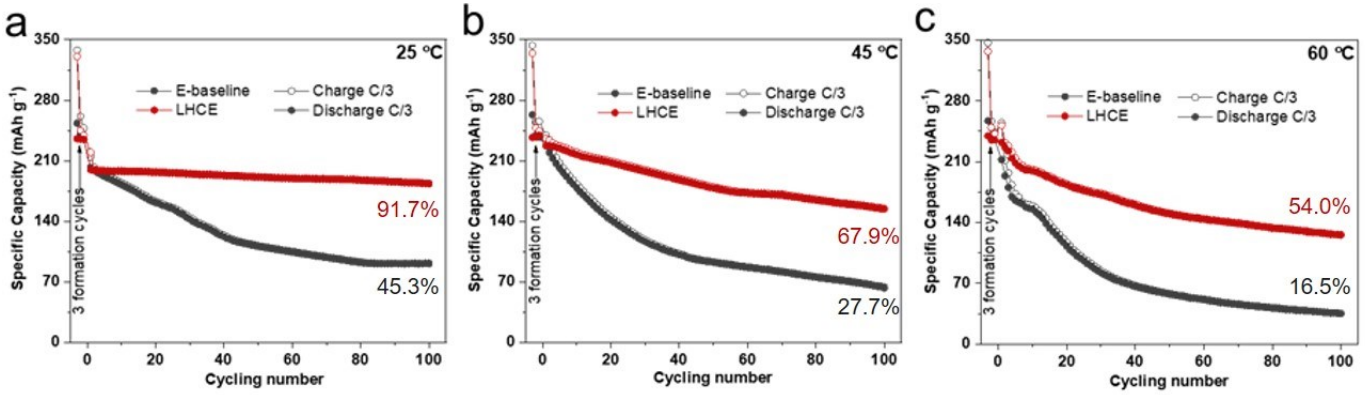
Summary

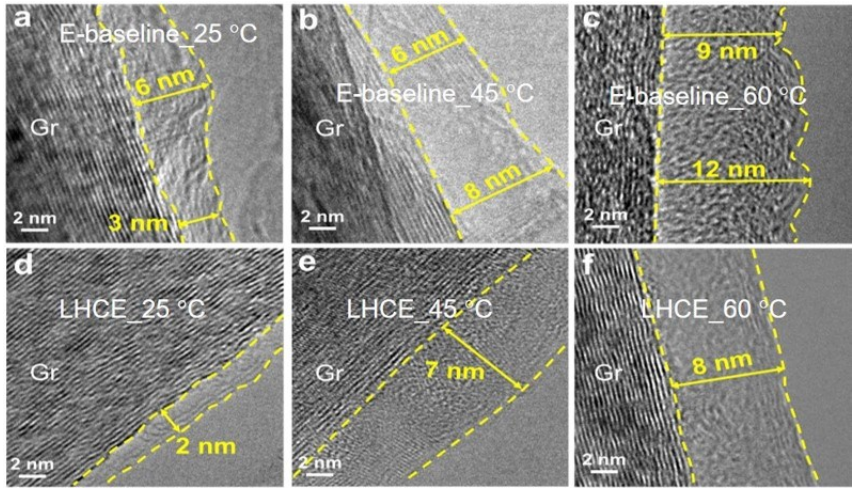
- First-principles calculations in conjunction with diagnostic studies offer insights into how dopants stabilize the $LiNiO_2$ bulk lattices at highly charged states.
- Based on the theory-diagnostic-study driven understanding, We have successfully developed a new chemistry that meets the energy density and thermal stability target of the project.
- We have scaled up the coprecipitation/calcination synthesis with improved hierarchical morphology and tap density control of secondary cathode particles.
- Different LHCEs based on carbonate, ether and phosphate solvents and various additives were developed and evaluated in Gr-based LIBs with LMR, NMC811 and NMT cathodes. Both solvents and additives significantly affect the battery performance of LIBs.
- Achieved 500 cycles of Gr||NMT pouch cells with DME-LHCE at capacity retention at 79.4%, greatly improved performance compared to the baseline electrolyte.

Technical Back-Up Divider Slide

Development of DMC-based LHCE for Gr||LMR cells

- LiFSI in DMC-EC-TTE (LHCE) was developed for Gr||$Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$ (LMR) cells.
- LMR: 1.34 mAh cm^{-2}; Gr: 1.8 mAh cm^{-2} (Both from ANL CAMP).
- Voltage range: 2.7 – 4.7 V. 1C= 1.34 mA cm^{-2}. 3 formation cycles: 1 × C/20 + 2 × C/10.
- 25, 45 and 60 °C were selected as the operating temperatures.

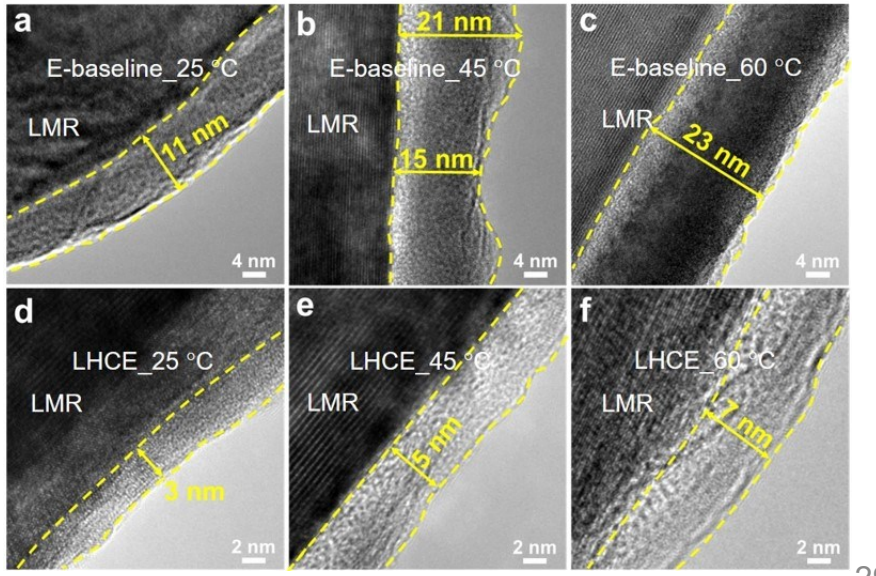




- LHCE cells show much <u>better cycling stability</u> than E-baseline ones under the same testing temperatures.

TEM images of Gr and LMR surfaces after 100 cycles:

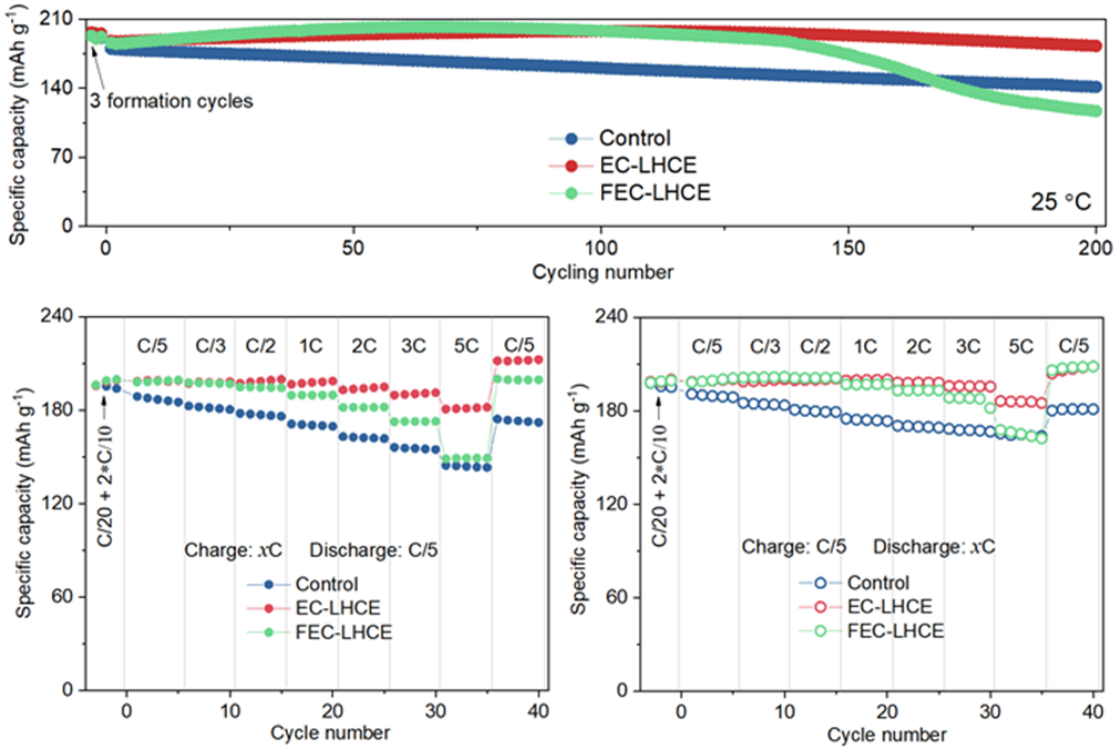
- The thicknesses of SEI and CEI layers in both electrolytes show <u>a monotonous growth</u> as temperature increases.
- ✓ SEIs and CEIs formed in LHCE <u>are less susceptible towards elevated temperatures</u> than those in E-baseline.
- ✓ LHCE results in <u>thinner and more uniform SEIs and CEIs</u>, which are more protective and can effectively suppress electrolyte decomposition.

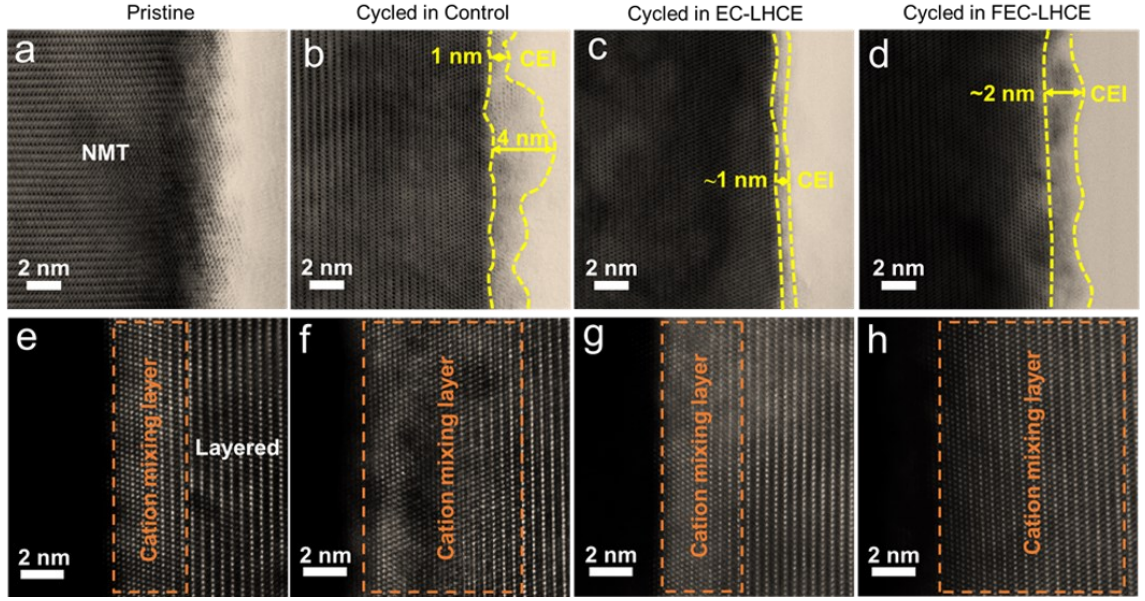


X. Zhang, W. Xu, et al., *J. Power Sources Adv.*, 2020, 5, 100024.

Development of DMC-based LHCEs for Gr||NMT cells

- 2 DMC-based LHCEs (LiFSI-2DMC-0.2EC/FEC-3TTE) were developed for Gr||$LiNi_{0.96}Mg_{0.02}Ti_{0.02}O_2$ (NMT) cells.
- NMT: 1.5 mAh cm^{-2} (home-made); Gr: 1.8 mAh cm^{-2} (from ANL CAMP).
- Voltage range: 2.5 – 4.4 V. 1C= 1.5 mA cm^{-2}. 3 formation cycles: 1×C/20 + 2×C/10.



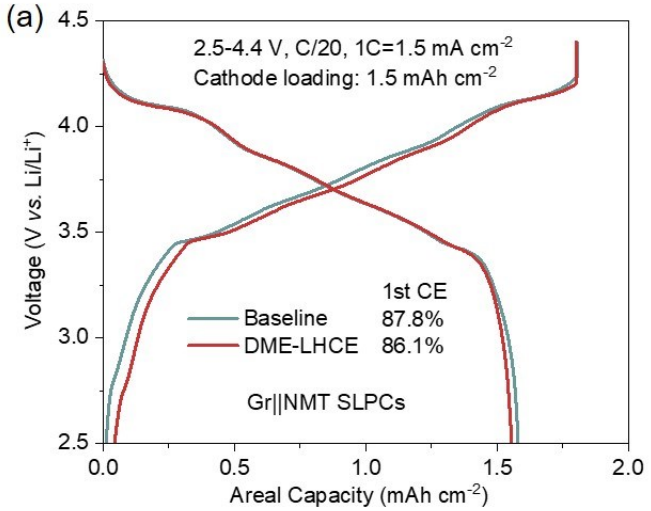


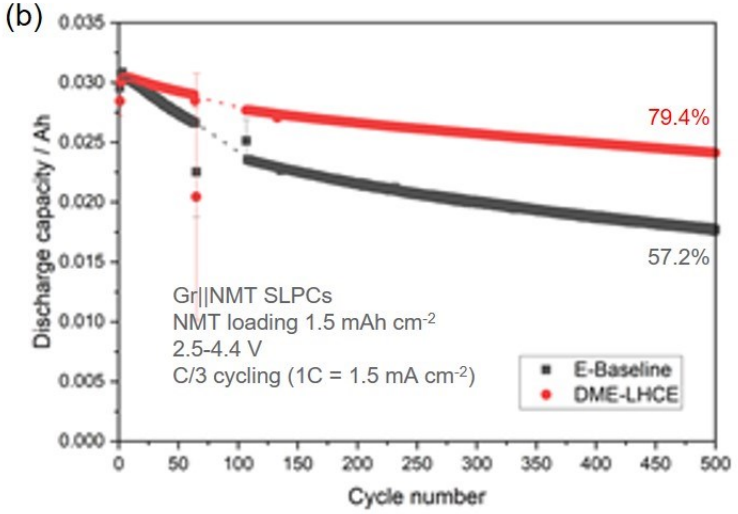
✓ EC-LHCE enables Gr||NMT cells to have higher capacity, longer cycling stability (97.2% retention after 200 cycles), and excellent rate capability (up to 5C) in both charge and discharge processes.

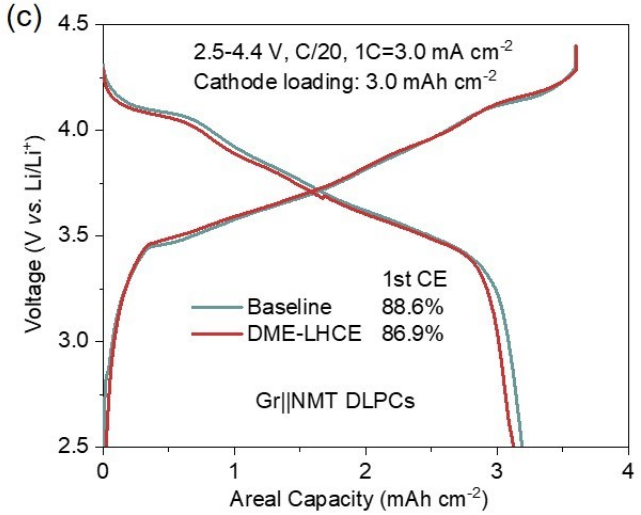
- Fresh NMT surface has cation mixing layer → Air sensitivity of NMT material.
- ➢ Control electrolyte leads to thick and non-uniform CEI as well as increased cation mixing layer.
- ➢ FEC-LHCE leads to relatively thick and non-uniform CEI and largely increased cation mixing layer, which is possibly responsible for the fast decay of capacity after certain cycles.
- ✓ **EC-LHCE yields ultrathin and uniform CEI and negligible cation mixing increase.**

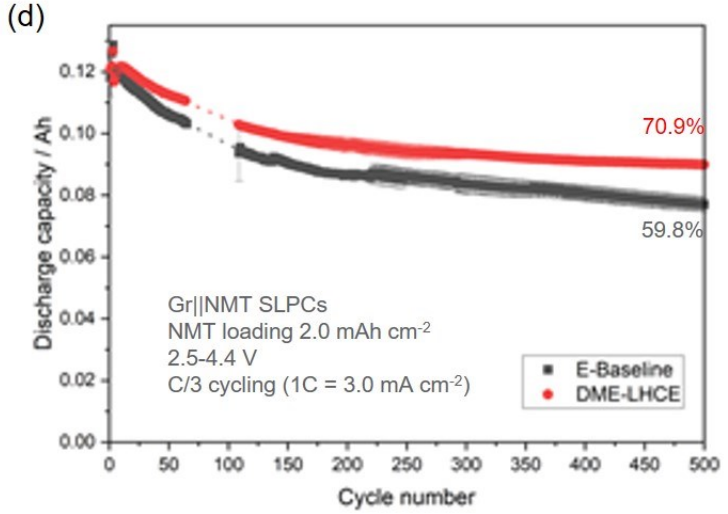
X. Zhang,# H. Jia,# W. Xu, et al., *ACS Energy Lett.*, 2021, **6**, 1324–1332.

Evaluation of NMT performance in pouch cells









- DME-LHCE leads to slightly lower first cycle CE but still comparable to Baseline electrolyte.
- Cells using DME-LHCE achieved significantly improved capacity retentions compared with those using E-baseline.
- After 500 cycles, the capacity retentions of SLPCs and DLPCs using DME-LHCE amounted to 79.4% and 70.9%, respectively, while those of SLPCs and DLPCs using E-baseline were merely 57.2% and 59.8%, respectively.

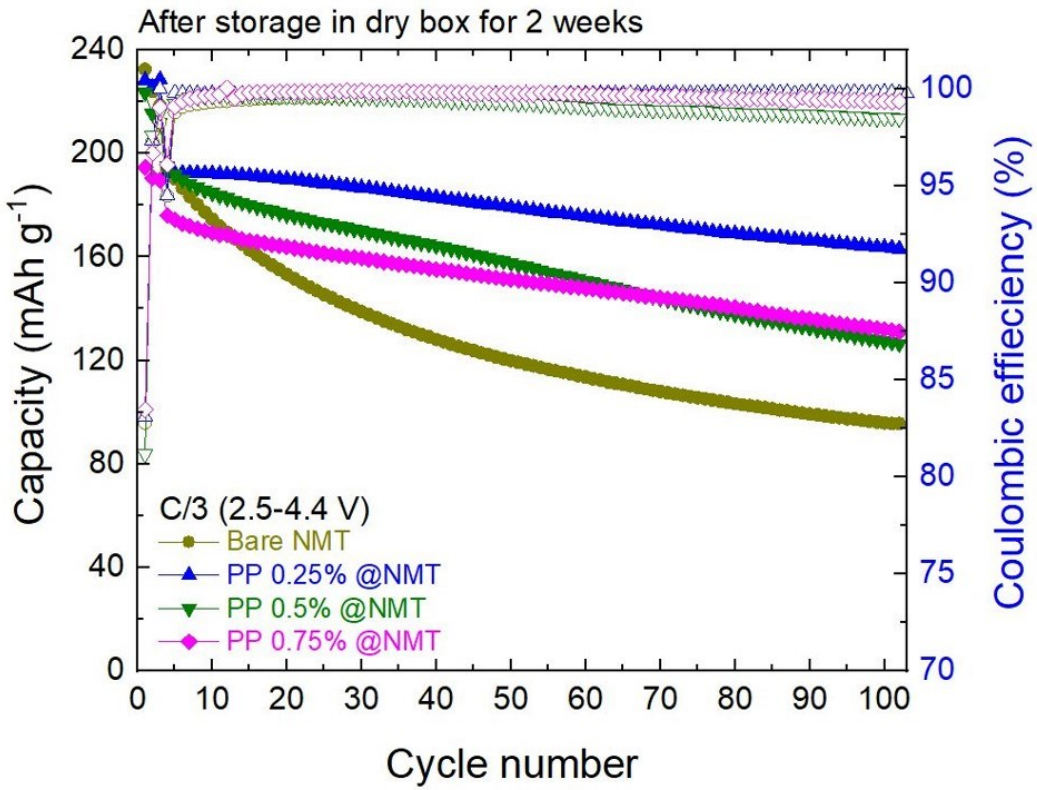
✓ DME-LHCE is a highly favorable electrolyte for the Gr||NMT cell chemistry.

- The gap (marked as broken lines) in the cycling performance is due to the battery tester malfunctioning where the cells were still being charged and discharged but the data were not recorded.

Development of polymer protective coating layers for NMT cathode

- NMT: 1.5 mAh cm^{-2} (synthesized and coated at PNNL)
- Gr: 1.84 mAh cm^{-2} (from ANL CAMP)
- Electrolyte: 1 M $LiPF_6$/EC-EMC (3:7 by wt.) + 2 wt.% VC, 75 µL
- 2.5 – 4.4 V

- Formation: 1 × C/20 + 2 × C/10
- Cycling: C/3
- 1C = 200 mA g^{-1} or 1.5 mA cm^{-2}
- 25 °C



- Bare and PP-coated NMT powders were stored in dry box for two weeks before testing cell performance.
- Among various coating amounts, PP 0.25wt.% coated NMT (referred to as PP 0.25%@NMT) shows the best cell performance.
- Gr||NMT cells with PP 0.25%@NMT show improved capacity retention of 84.7% after 100 cycles compared with Bare NMT (capacity retention of 49.5%).

Reviewer-Only Divider

Publications/Presentation

Publications

1. Chunyang Wang, Lili Han, Rui Zhang, Hao Cheng, Linqin Mu, Kim Kisslinger, Peichao Zou, Yang Ren, Penghui Cao, Feng Lin, Huolin L Xin.* Resolving atomic-scale phase transformation and oxygen loss mechanism in ultrahigh-nickel layered cathodes for cobalt-free lithium-ion batteries. *Matter*, 2021, 4: 1-14. doi.org/10.1016/j.matt.2021.03.012
2. Chunyang Wang, Rui Zhang, Kim Kisslinger, Huolin L Xin.* Atomic-Scale Observation of O1 Faulted Phase-Induced Deactivation of $LiNiO_2$ at High Voltage. *Nano Letters*, 2021, doi.org/10.1021/acs.nanolett.1c00862
3. Ruoqian Lin, Seong-Min Bak, Youngho Shin, Rui Zhang, Chunyang Wang, Kim Kisslinger, Mingyuan Ge, Xiaojing Huang, Zulipiya Shadike, Ajith Pattammattel, Hanfei Yan, Yong Chu, Jinpeng Wu, Wanli Yang, M Stanley Whittingham, Huolin L Xin*, Xiao-Qing Yang. Hierarchical nickel valence gradient stabilizes high-nickel content layered cathode materials. *Nature Communications*, 2021, 12(1): 1-10.
4. Hao Jia, Yaobin Xu, Xianhui Zhang, Sarah D Burton, Peiyuan Gao, Bethany E Matthews, Mark H Engelhard, Kee Sung Han, Lirong Zhong, Chongmin Wang, Wu Xu*, “Advanced Low-Flammable Electrolytes for Stable Operation of High-Voltage Lithium-Ion Batteries”, *Angewandte Chemie International Edition*, 2021, DOI:10.1002/anie.202102403
5. Jianli Cheng, Linqin Mu, Chunyang Wang, Zhijie Yang, Huolin L. Xin, Feng Lin and Kristin A. Persson, Enhancing surface oxygen retention through theory-guided doping selection in Li 1− x NiO 2 for next-generation lithium-ion batteries, J. Mater. Chem. A, 2020, 8, 23293-23303
6. Xianhui Zhang#, Hao Jia#, Lianfeng Zou, Yaobin Xu, Linqin Mu, Zhijie Yang, Mark H. Engelhard, Bethany E. Matthews, Chaojiang Niu, Chongmin Wang, Huolin Xin, Feng Lin, Wu Xu*, “Electrolyte Regulating towards Stabilization of Cobalt-Free Ultrahigh-Nickel Layered Oxide Cathode in Lithium-Ion Batteries”, *ACS Energy Letters*, 2021, 6, 1324-1332.
7. H. Jia Y. Xu, S.D. Burton, P. Gao, X. Zhang, B.E. Matthews, M.H. Engelhard, L. Zhong, M.E. Bowden, B. Xiao, K.S. Han, C. Wang, and W. Xu*. "Enabling ether-based electrolytes for long cycle-life of lithium-ion batteries at high charge-voltage“, *ACS Applied Materials & Interfaces*. 2020, 12, 54893-54903.
8. X. Zhang, H. Jia, Y. Xu, L. Zou, M.H. Engelhard, B.E. Matthews, C. Wang, J.G. Zhang, and W. Xu*. "Unravelling high-temperature stability of lithium-ion battery with lithium-rich oxide cathode in localized high-concentration electrolyte“, *Journal of Power Sources Advances*, 2020, 5, 100024.
9. Zhijie Yang, Linqin Mu, Dong Hou, Muhammad Mominur Rahman, Zhengrui Xu, Jue Liu, Dennis Nordlund, Cheng-Jun Sun, Xianghui Xiao, and Feng Li, Probing Dopant Redistribution, Phase Propagation, and Local Chemical Changes in the Synthesis of Layered Oxide Battery Cathodes, Advanced Energy Materials, 2021 https://doi.org/10.1002/aenm.202002719
10. Yang, Z.; Lin, F.* (2021) Heterogeneous, Defect-rich Battery Particles and Electrodes: Why They Matter and How One Can Leverage Them?" *The Journal of Physical Chemistry C*. Invited Perspective.
11. Mu, L.; Yang, Z.; Tao, L.; Waters, C. K.; Xu, Z.; Li, L.; Sainio, S.; Du, Y. ; Xin, H. L.; Nordlund, D.; Lin, F., The Sensitive Surface Chemistry of Co-Free, Ni-Rich Layered Oxides: Identifying Experimental Conditions that Influence Characterization Results *Journal of Materials Chemistry A 8, 17487-17497.*
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13. Tao, L.; Hu, A.; Yang, Z.; Xu, Z.; Wall, C. E.; Esker, A. R.; Zheng, Z.; Lin, F.* (2020) A Surface Chemistry Approach to Tailoring the Hydrophilicity and Lithiophilicity of Carbon Films for Hosting High-Performance Lithium Metal Anodes. *Advanced Functional Materials 30, 2000585. [Note: The Li cathode used in this paper is developed through the DE-EE000844]*

Publications/Presentation

Presentations

- H. Jia, Y. Xu, S.D. Burton, L. Zhong, C. Wang, and W. Xu. "Designing Stable Electrode/Electrolyte Interphases for Lithium-Ion Batteries with Low-Flammability Electrolytes“, 2021 Virtual MRS Spring Meeting & Exhibit, 04/22/2021. Virtual, United States.
- W. Xu. "Development of Non-Conventional Electrolytes for Lithium-Ion Batteries“, 38th International Battery Seminar & Exhibit, 03/10/2021. Virtual, United States. (**Invited**)
- X. Zhang, H. Jia, Y. Xu, L. Zou, M.H. Engelhard, B.E. Matthews, C. Wang, J. Zhang, and W. Xu. "Enhanced high-temperature stability of Li-ion battery with Li-rich oxide cathode by localized high-concentration electrolyte“, PRiME 2020, 10/08/2020. Virtual, United States.
- H. Jia, Y. Xu, S.D. Burton, P. Gao, X. Zhang, B.E. Matthews, M.H. Engelhard, C. Wang, and W. Xu. "Ether-Based Electrolytes Enabling Long Lifespan High-Voltage Lithium-Ion Batteries“, PRiME 2020, 10/07/2020. Virtual, United States.
- 2020 Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University (Sep 9, 2020), Jackson, MS, USA, “Ion Reactions to Modulate Solid-State Electrochemistry for Batteries” –Invited Seminar Speaker
- 2021 Department of Materials Science and Engineering, University of Maryland (Feb 5, 2021), College Park, MD, USA, “Investigating Structural Defects and Solid−Liquid Interfaces in Electrochemical Energy Materials” –*Invited Seminar Speaker*