









CATHODE MATERIALS FOR NEXT GENERATION LITHIUM-ION BATTERIES: DESIGN, SYNTHESIS, AND CHARACTERIZATION OF LOW-COBALT CATHODES

Project ID: BAT251

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Overview

Timeline

- Start: October 1, 2018
- End: September 30, 2021
- Percent complete: 85%

Budget

- Total project funding:
 FY20 \$4.0M
- ANL, NREL, ORNL, LBNL, PNNL

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
 - Cost
 - Performance
 - Safety
 - Cobalt content

Partners

ANL, NREL, ORNL, LBNL, PNNL

Students supported from:

- University of Illinois at Chicago
- University of Rochester
- Oregon State University

Relevance



"The battery industry uses 42 percent of global cobalt production, while the rest is used in industrial and military applications, and all are competing for supply." – supplychainbrain.com



Cost, sustainability, and lack of mature alternatives are the major drivers for continued work in layered transition metal oxides

BatPaC Projected Cost for a 100kWh_{Total}, 80kW Battery Pack

- Layered transition-metal (TM) oxides represent the best option for near-term advancements for EV batteries
- Li-ion continues to grow and is likely to dominate the market for several decades to come no guarantees with other technologies (Li-S, "Li-air", multivalent, solid state...)
- Major drivers (safety, energy, power, lifetime, cost) still have room to improve
- However, sustainability is a critical factor to the success of the predicted, massive future Li-ion market

Milestones

- This project seeks to make significant progress towards the realization of cobalt-free, TM-oxide cathodes for next-generation, Li-ion batteries
- The goals of cathode design are represented by two prototypical materials



- LNO serves as a physiochemical baseline for understanding the design and properties of high nickel oxides
- LiMn_{0.5}Ni_{0.5}O₂ serves as a baseline for understanding the design and properties of 'high Mn', MnNi-based oxides
- NMC-622 serves as a baseline for minimum performance metrics

See also BAT252, 253, 167, 476



- The team has developed a multi-thrust approach driven by cathode design and synthesis
- Each thrust has two coordinators and works in parallel, on the same materials, as the other thrusts
- All materials tested and characterized according to program protocols to identify promising strategies

* Matched to Superior Graphite A-A015(A)



Comprehensive study of the synthesis-property relationships between LNO-based oxides having ≥90% Ni

see also BAT167/BAT252

Development of optimized, high-performing LiNiO₂ by controlling the calcination process: Temperature

- Optimized the calcination temperature (under pure oxygen)
- The best performer (LNO-665) is characterized with:
 - Lower Li/Ni mixing (Synchrotron-XRD)
 - Higher Li-slab distance (Synchrotron-XRD)
 - Minimal layer stacking faults (HAADF-STEM)
- With increasing calcination temperature:
 - Li-local ordering develops (⁶Li-MAS-NMR)
 - Primary particle size increases (SEM)









Development of optimized, high-performing LiNiO₂ by controlling the calcination process: O₂ gas atm.

- Effect of calcination under a lower oxygen pressure is studied (pO₂ = 1.0; 0.8; 0.6; 0.4; 0.2 atm)
- As pO_2 decreases from 1 atm:
 - Primary particle size increases
 - c/a lattice parameter ratio decreases indicating the tendency of less Li/Ni layering
 - Capacity retention marginally decreases
- The advantage of high pO₂ for LNO and Ni-rich NMC calcination is confirmed, however the data also suggest that the true effect of high pO₂ is only limited when other synthesis parameters are optimized



see also BAT167



- Gas evolution
 - Oxygen evolution is observed when LiNiO₂ is charged above 4.5 V
 - Isotope oxygen labeling experiment is under progress to elucidate the origin of released oxygen and its implication in the cathode stability
- Effect of cut-off voltage on the low-SOC kinetics
 - The H2-H3 transition process improves the low-SOC lithiation kinetic at 3.5 V
 - DFT calculation suggests that the anti-site defect Ni in Li layer migrates back to the Ni layer sites during the high voltage charging
- Accelerating mechanical degradation
 - The direction of c-axis strain changes at the H2-H3
 transition region
 - c-axis expansion during the LV charging (< 4.2 V) and caxis contraction during the HV charging (above 4.2 V) resulting in:

/oltage (V)

(1) two expansion-contraction cycles per 1 chargedischarge cycles

(2) particle-to-particle SOC deviation may result in opposite strains within the secondary particle structure

LiNiO₂: Synthesis-structure-properties



Initial charge-discharge profiles (left), initial coulombic efficiency/initial capacity loss (inset) and Li transportation kinetics (right) of LiNiO₂ after different charge cut-off potential

Residual Li species: LNO Storage

- Guideline for LNO dry room storage
 - LNO powder: Ar-box (several weeks) > dry room (several days) > ambient-air.
 - LNO electrode: No noticeable Li₂CO₃ XPS signal development up to 6 weeks of ambient-air exposure

Builds-up of residual Li species on LNO powder samples stored in different conditions (Surface Li_2CO_3 estimated from the $(CO_3)^{2^-}$ and C1s XPS signals)

Performance degradation of air and dry-room stored LNO powder samples

Ex-situ XPS (C1s) of LNO electrodes showing no noticeable Li_2CO_3 signal up to 6 weeks of ambient air exposure

LiNiO₂: Residual Li

Residual Li species: formation mechanism

- In situ UV Raman experiment elucidated the nature and formation mechanism of residual Li on LNO surface
 - Two-step formation of Li₂CO₃ via LiOH as an intermediate
 - Li₂CO₃ is the major residual Li species in ambient condition
 - Li₂CO₃ can be partially converted to LiOH when exposed to excessively wet conditions

300

200

400

500

600

Raman shift (cm⁻¹) from 390 nm

LiNiO₂: Residual Li

(a) Pristine

1000 1100 3400 3500 3600 3700

(Top) UV Raman system equipped with wavelength-tunable laser sources and a high-temperature in situ Raman cell, (Right) In situ UV Raman spectra of LiNiO₂ showing the formation mechanism of LiOH and Li_2CO_3 impurity species on LNO surface depending on the exposed atmosphere

Characterization LiNiO₂ by Solid State NMR

Motivation : Understanding the effect of annealing temperature and cycling on lithium local ordering in LiNiO₂ **Approach** : ⁶Li MAS NMR is used to study the changes in bulk and surface lithium environments

An optimum annealing T of 665°C shows a symmetric and sharp peak~ 700 ppm in NMR as a signature of high crystallinity and order

⁶Li NMR of LiNiO₂ (annealed at 665°C) after 1st cycling

LiNiO₂: Synthesis-structure-properties

- Synthesis methods of AI incorporation have shown differing local environments
- DSC of charged (4.3 V) electrodes reflects the influence of AI site distribution on thermal response
- Corresponding synchrotron X-ray data being analyzed to correlate with structure

ALD coatings-performance

Voltage (V) g⁻¹) 0, min_ (nmo (120 Line 10 L 15 CO_2 10 20 30 60 70 100 80 40 Time (h)

NM- 90-05-05//AIF₃

- Fluoride-based coating developed within the project show an ability to greatly mitigate impedance rise in some NMC//graphite cells under protocols (left)
- Similar coatings have shown that gassing is also mitigated in higher nickel-content electrodes such as NMC-90-05-05 (right)
- However, capacity fade, impedance rise, and thermal response (DSC) were more effected by oxide composition than by using similar coatings on all compositions

NMCs properties vary across compositions and surface modifications should be tailored to match

see also BAT252

Technical Accomplishments: Mn-rich cathodes

Synthesis of Al-doped NMC directly from CSTR

Old method $M^{2+} + 6 \text{ NH}_3 \longleftrightarrow M(\text{NH}_3)_6^{2+}$ Single solution $Al^{3+} + 6 \text{ NH}_3 \longrightarrow \text{weak}$ Single solution $M(\text{NH}_3)_6^{2+} + \text{OH}_- \longleftrightarrow M(\text{OH})_{2(s)} + 6 \text{ NH}_3$ $Al^{3+} + 3 \text{ OH}^- \longleftrightarrow Al(\text{OH})_3(s) \text{ Ksp} = 2 \times 10^{-31}$

New method $M^{2+} + 6 \text{ NH}_3 \longleftrightarrow M(\text{NH}_3)_6^{2+}$ Separated solutions $Al^{3+} + 4 \text{ OH}^- \longleftrightarrow Al(\text{OH})_4^-$ Separated solutions $M(\text{NH}_3)_6^{2+} + \text{OH}^- \longleftrightarrow M(\text{OH})_{2(s)} + 6 \text{ NH}_3$ $Al(\text{OH})_4^- \longleftrightarrow Al(\text{OH})_3(s) + \text{OH}^- \text{ Ksp} = 5 \times 10^{-3}$ Synthesis-structure-properties

 $\rm Ni_{0.6}Mn_{0.35}Co_{0.04}Al_{0.01}$

- Al-doped NMC can improve the structural stabilization and suppress the oxygen release at high voltage
 - Reduce Co content by substituting with AI
- Co-precipitation of Al³⁺ with Ni²⁺, Mn²⁺, and Co²⁺ is challenging
 - Quick precipitation of AI(OH)₃
 - Weak AI(NH₃)₆ complex formation
- New, improved co-precipitation process produced welldefined precursor particles with homogeneous Aldistribution
 - Pre-convert AI precursor to AI(OH)⁴⁻ and
 - Feed AI(OH)⁴⁻ separately with NMC solution into the reactor

Technical Accomplishments: Mn-rich cathodes

Electrochemical Performance of high Mn, AL-doped oxides

- Incorporation of excess Li/Mn along with 1.4% Al:
 - Reduces Co content
 - Improves rate performance
 - Gives similar capacity/energy as 622

2.5

50

– NMC622

Sample

100

Capacity, mAh/g

150

- Ni60 best

200

- Al-d

see also BAT167

Synthesis of this promising composition is now being studied via TVR reactors for further scale up and validation

Summary

- A series of LNO-based oxides with >90% Ni has been synthesized via TVR reactors in collaboration with ANL's MERF facility, these oxides have been fabricated into high-quality electrodes by the ANL's CAMP facility and distributed program wide for systematic studies
 - Non-trivial effort that requires optimization and process control over precursors, lithiated products, and electrode fabrication
 - Allows for large-scale systematic studies of high-quality, LNO-based compositions
- Detailed studies of LNO synthesis and processing conditions have led to continued performance improvements and insights into controlling LNO-based oxide properties including mechanisms related to surface impurities
- Characterization of LNO-based oxides shows the importance of dopant control as well as mechanisms related to the possible migration of Ni during high SOC cycling
- New cathodes have been developed that contain substantial amounts of Mn (>30%) with less than 5% Co These cathodes have the potential to outperform NMC-622 ongoing studies are looking into advanced processing and scale-up

Future Work

- Continued exploration of the complex relationships between synthesis and performance of LNO-based oxides including local and long-range structure, primary and secondary morphologies and surface impurities
- Collaboration with theory (see BAT253) to synthesize LNO-based compositions with targeted surface and bulk substitutions identified by calculation
- Systematic studies to increase manganese content and decrease Ni, while further reducing or eliminating cobalt
- Mechanistic studies on processing of Mn rich precursor materials using advanced TVR reactors
- Continued efforts in support of overall program goals to synthesize and study (see BAT 252, 253) low/no cobalt oxides

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Major Research Facilities

- Materials Engineering Research Facility
- Post-Test Facility
- Cell Analysis, Modeling, and Prototyping
- Spallation Neutron Source
- Environmental Molecular Sciences Laboratory
- Advanced Light Source
- Battery Manufacturing Facility
- Advanced Photon Source (APS)
- Laboratory Computing Resource Center (ANL)
- NMR Spectroscopy Lab (ANL)

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Collaboration and Coordination

Response to Previous Year's Reviewer Comments

Comment: reviewer found the electrochemical results obtained with the LNO system to be impressive. The project team introduced aluminum (AI) as a dopant by ALD and wet-chemistry coating before high-temperature calcination. It could be of interest to see if the AI can be incorporated into the precursor structure during calcination, too

Response: We thank the reviewer for the positive feedback and question. Yes, the Al is incorporated into the lattice during calcination. The study shows that by using ALD, at the precursor level, subsequent calcination leads to a more uniform distribution of Al into the lattice of the oxides over conventional wet methods. This results in better electrochemical performance and reveals the importance of having a high level of process control.

Comment: The reviewer observed that the LNO electrochemical results were great. The LNO-based oxides with truncated polyhedron and octahedron morphologies are very interesting; they can help to better understand the electrolyte reactivity on the particle surfaces. Doping with Al using ALD resulted in uniform distribution of the additive improving the cycling performance. The study with single-crystals powders in collaboration with the Theory Group may yield important practical and theoretical insight.

Response: Yes, we agree and ongoing studies with single crystals are in fact validating some of the facet-dependent properties that have been predicted in this program's theory component (see BAT253)

Response to Previous Year's Reviewer Comments

Comment: In the last year, the team has made significant progress in both directions of the studies. Specifically, the temperature-evolution behavior of pure LNO is quite meaningful and the electrochemistry results are beautiful. Also, the smaller introduction of Co into lithium manganese nickel oxide (LMNO) (only 5%) could drastically improve the electrochemical performance, which is also a striking achievement....

In a recent paper published in the Journal of the Electrochemical Society (JES), the author claims the unnecessary usage of Co in layered cathodes, it would be worth understanding the perspective from the team to consider having some minor Co content in both LNO-based and Mn-rich-based compositions.

Response: Cobalt has never been needed to synthesize well-layered, high-capacity LNO-based oxides as shown in the current work. The stability of such cathodes during cycling, as well as safety, have been the main concerns. In addition, many reports do not make adequate one-to-one comparisons of high-performing baseline materials. The systematic synthesis studies we have undertaken in this program concerning pure LNO have resulted in better performance than most reports of doped (e.g., Mg, Mn, Al...) LNO in the literature. This point reiterates the importance of having a high level of process control and meaningful, high-quality baseline results. Such results will then allow a more complete understanding of what various substitutions actually contribute to material performance. The conclusions of these studies are forthcoming.

Response to Previous Year's Reviewer Comments

Comment: Data on Mn-rich cathodes seem to confirm the importance of Co. It was hard to understand if the results suggest that removing Co is hard or impossible or provide some glimmer of hope.

Response: We agree that this is a complicated issue. The data on the Mn rich NMC-type compositions, however, reveal some hope in terms of eliminating cobalt. This study sought to take advantage of what the Deep Dive program has uncovered with respect to local ordering vs composition in layered oxides. By maintaining optimized Li:Ni:Mn ratios, the amount of cobalt needed to help establish a layered structure can minimized. The sample reported contained substantial amounts of Mn and only ~5% cobalt and performed equally to that of NMC-622. We are currently following up these studies by developing lower cobalt compositions that achieve still better performance.