Enhancing Oxygen Stability In Low-Cobalt Layered Oxide Cathode Materials

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Project ID: bat414

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
- Project start date: 12/01/2018
- Project end date: 12/31/2021
- Percent complete: 40%

Budget
- Total project funding $3.125 million
  - DOE Share $2.5 million
  - Contractor share $625K
- Funding for FY 2019: $1.15 million
- Funding for FY 2020: $1.01 million

Barriers
- Barriers addressed
  - Cost
  - Performance
  - Life

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
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

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Status</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td><strong>Jan 2019</strong>&lt;br&gt;Dopant Selection and Material Synthesis</td>
<td>Completed</td>
<td>Computational down-selection to 2–4 elements for synthesis. Achieve NMC-D electrode materials with Co content &lt;= 3%, Ni &gt;= 90%, Dopant metal (Ti or Al) = 2%</td>
</tr>
<tr>
<td><strong>April 2019</strong>&lt;br&gt;Structural Fidelity</td>
<td>Completed</td>
<td>Structural study by synchrotron XRD, and aberration-corrected scanning TEM to confirm that the desired layered structure and 3D composition are achieved.</td>
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<tr>
<td><strong>July 2019</strong>&lt;br&gt;Electrode Performance and Fabrication of PPCs</td>
<td>Completed</td>
<td>Evaluate electrochemical performance of BP 1 materials and compare it with the commercial 811 baseline &gt;100 cycles in Li</td>
</tr>
<tr>
<td><strong>October 2019</strong>&lt;br&gt;Go/No Go</td>
<td>Completed</td>
<td>Delivery of a high-Ni and low-Co cathode material with an electrochemical performance comparable to the commercial NMC811 baseline (energy and capacity retention &gt; 90% of NMC811 @ 100 cycles).</td>
</tr>
<tr>
<td><strong>Jan 2020</strong>&lt;br&gt;Dopant Refinement</td>
<td>Completed</td>
<td>Refine prediction of surface/bulk dopants</td>
</tr>
<tr>
<td><strong>April 2020</strong>&lt;br&gt;Synthesis Scale-up</td>
<td>On track</td>
<td>Scale up synthesis of BP 1 materials to 100 g scale.</td>
</tr>
<tr>
<td><strong>July 2020</strong>&lt;br&gt;Performance Evaluation</td>
<td>On track</td>
<td>Best of BP1 and BP2 materials achieves a comparable performance to the 811 baseline &gt;300 cycles in Gr</td>
</tr>
<tr>
<td><strong>Oct 2020</strong>&lt;br&gt;Go/No Go</td>
<td>On track</td>
<td>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)</td>
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</table>
**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.
• 3D-doping of Ti is achieved in NMC-811 and cycle life is significantly improved.
• Can we use the 3D doping approach to improve LiNiO$_2$?

ACS applied materials & interfaces 11 (41), 37885-37891
Technical Accomplishments and Progress
Gen-2 Co-free Chemistry: 3D-doped LiNiO₂ [Ni 96%, Mg 2% , Ti 2%]

3D-doping of Ti and Mg is achieved in LiNiO₂. Cycle life and thermal stability are much improved compared with LiNiO₂.

Cathode loading: 1.5-1.6 mAh/cm²

Energy (eV)

Soft XAS Ni L-edge

Improved cycle life

Improved thermal stability

Chemistry of Materials 31 (23), 9769-9776
Technical Accomplishments and Progress
Rationalize Surface Dopant Segregation

Dopant Segregation Energy

\[ \Delta E = E_{il} - E_{5l} \]

LiM_{0.019}Ni_{0.981}O_2 (104)

\[ \Delta G = \Delta H - T \Delta S = \Delta H + T N k_B (x_A \ln x_A + x_B \ln x_B) = 0 \]

Total number of atoms: 217 (53 Ni + 1M)

\[ \Delta G = \Delta H - T \Delta S = \Delta H + T N k_B (x_A \ln x_A + x_B \ln x_B) = 0 \]

For Al, \[ \Delta G = \Delta H = 6 \text{ meV/f.u., } T = 755 \text{ K} \]

LiNiO_2 is synthesized around 900 K

- Dopant segregation behavior is thermodynamically driven

Bulk-enrich: Mg

Surface enrich: W, Sb, Ta, Ti, Y, B

Uniform: Al

Chemical Electron Tomography
• 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.

- 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 LiNiO₂.
Technical Accomplishments and Progress
Preferential Site on the Surface

\[ \Delta E^\text{Ni-Li}_f \]: Formation energy difference between doping at Ni and Li site

A negative \( \Delta E^\text{Ni-Li}_f \) implies Ni site is more favorable than Li site.

• Ti, Al, Sb, Ta and W at low concentration tend to stay in the Ni site on the surface of LiNiO₂
Technical Accomplishments and Progress
Structure of charged MgTi-doped LiNiO$_2$ vs LiNiO$_2$

- MgTi co-doping reduces the transition to H1-3 phase and reduced SFs. It also reduces cation mixing.
Technical Accomplishments and Progress
Reducing the Destructive Phase Transition

- Mg is an effective dopant because it can inhibit the H2-H3 two-phase transition.

**Technical Accomplishments and Progress**

- **Reducing the Destructive Phase Transition**
  - Mg is an effective dopant because it can inhibit the H2-H3 two-phase transition.

**Free-energy calculation with doping concentration: 2.1%/2.8%**

- **Pristine**
  - $\Delta G = 0$ at $x \approx 0.8$: H2+H3 two-phase region appears when $x > 0.8$

- **Doped-LiNiO$_2$**
  - Effective dopants: Mg (2.1%~2.8%)

**Graphical Representation**

- Voltage (V vs. Li$^+/Li$) vs. Discharge capacity (mAh/g)
- H3 phase (O3 stacking rich)
- Excess Ni leads to O3

**Diagram**

- H2/H1-3 (O3-O1)
- O3 + H3 (O1-O3)
- Free energy calculation with doping concentration: 2.1%/2.8%

**Diagrams**

- Voltage vs. discharge capacity
- H3 phase (O3 stacking rich)
- Excess Ni leads to O3
**Technical Accomplishments and Progress**

**New Co-free Chemistries Under Investigation**

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

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**LiNiO₂ with 2% Sb doping**

- **Graph (f):**
  - Voltage (V vs. Li⁺/Li⁻) vs. Cycle number for Sb doped 1%, 2% LiNiO₂.
  - Specific energy (Wh/kg) vs. Cycle number for LiNiO₂.

- **Graph (g):**
  - Discharge capacity (mAh/g) vs. Cycle number for Sb doped 2% LiNiO₂.

**LiNiO₂ with 2% Mg, 2% Mn co-doping**

- **Graph (a):**
  - Voltage (V vs. Li⁺/Li⁻) vs. Specific capacity (mAh/g) for MgMn-LiNiO₂.
  - Specific capacity (mAh/g) vs. Capacity retention (%).

- **Graph (b):**
  - Specific capacity (mAh/g) vs. Cycle number for MgMn-LiNiO₂.

- **Graph (c):**
  - Voltage (V vs. Li⁺/Li⁻) vs. Specific capacity (mAh/g) for 1st, 2nd, 5th, 10th, 30th, 50th C/10 cycles.
  - Capacity retention (%).

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**Surface**

- Sb ~4.5%
- Sb ~3% Center
Technical Accomplishments and Progress
Development of DMC-based LHCEs for Gr||NMC811

- 5 new LHCEs (LiFSI in DMC-EC/VC-TTE) were developed for Gr||NMC811 cells.
- NMC811: 2.8 mAh cm\(^{-2}\); Gr: 3.5 mAh cm\(^{-2}\) (Both from ALEC).
- Voltage range: 2.5 – 4.4 V, 1C= 2.8 mA cm\(^{-2}\). 3 formation cycles: 1×C/20 + 2×C/10.

E-baseline
1.0 M LiPF6 in EC-EMC (3:7 by wt.) with 2 wt% VC

- AE003: Best cycling stability
  - 25°C: \(\eta(100^{th})=85.8\%\)
  - 60°C: \(\eta(100^{th})=94.9\%\)
- AE003 & AE004: Better low-T discharge performance. For AE003:
  - -10°C: 98.5% of “25°C”
  - -30°C: 85.6% of “25°C”
- AE003 and AE004: Best rate capability during charging and discharging up to 3C.
- AE003: Effectively suppressed particle cracking.
- AE003: Resulted in ultrathin, uniform SEI/CEI compared to E-baseline.

- All LHCEs enable thinner, more uniform and robust SEI/CEI, showing much better cycling stability, rate capability and low-temperature discharge performance than E-baseline.
- AE003 shows the best electrochemical performances among the 5 LHCEs.

Technical Accomplishments and Progress

New NMT from scaled-up precursor: Gr||NMT

- NMT was prepared from the scaled-up precursor (100g/batch).
- NMT: 1.5 mAh cm\(^{-2}\) (Coated at PNNL); Gr: 1.8 mAh cm\(^{-2}\) (From ANL CAMP)
- Voltage range 2.5 – 4.4 V, 1C = 1.5 mA cm\(^{-2}\) (200 mA g\(^{-1}\))
- 3 formation cycles: 1×C/20 + 2×C/10.

ELY268 (E-baseline)
1.0 M LiPF6 in EC-EMC (3:7 by wt.) with 2 wt% VC

- New NMT material shows higher discharge capacity in AE003 than in ELY268 (i.e. E-baseline) during cycling and rate capability tests.
- AE003 enables superior cycling stability of Gr||NMT, with a capacity retention of 81.6% after 300 cycles.
- Gr||NMT cells with AE003 show superior discharge rate capability, with negligible capacity decay up to 3C, 187.7 mAh g\(^{-1}\) at 5C and 100% recovery after back to C/5.
- Gr||NMT cells with AE003 show better fast charging ability than with ELY268, with negligible capacity decay up to 3C, 189.7 mAh g\(^{-1}\) at 5C and 100% recovery after back to C/5.
• There are no reviewers’ comments on this project.
Collaboration and Coordination with Other Institutions

<table>
<thead>
<tr>
<th>Sub-recipients</th>
<th>Institution</th>
<th>Tasks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feng Lin</td>
<td>Virginia Tech</td>
<td>Synthesis and X-ray Diagnostics</td>
</tr>
<tr>
<td>Kristin Persson</td>
<td>UC Berkeley</td>
<td>High-throughput DFT calculation</td>
</tr>
<tr>
<td>Wu Xu</td>
<td>PNNL</td>
<td>Synthesis scale-up and electrolyte formulation</td>
</tr>
<tr>
<td>Fan Jiang</td>
<td>American Lithium Energy</td>
<td>Electrode and Cell Fabrication</td>
</tr>
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<tr>
<th>Collaborators</th>
<th>Institution</th>
<th>Nature of Collaboration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xiao-Qing Yang</td>
<td>Brookhaven National Lab</td>
<td>X-ray Diagnostics</td>
</tr>
<tr>
<td>Kim Kissinger</td>
<td>Brookhaven National Lab</td>
<td>FIB Sample Prep</td>
</tr>
<tr>
<td>Dennis Nordlund</td>
<td>SSRL/SLAC</td>
<td>Soft X-ray Absorption</td>
</tr>
</tbody>
</table>
Remaining Challenges and Barriers

• Improving the thermal stability of these extremely high nickel content chemistries.
• Scale-up of calcination to the hundreds of grams per batch level for project completion cell delivery.
Proposed Future Research

• Deploy the developed electrolytes to single-layer and 2Ahr-scale pouch cells.
• Investigation of cathode-anode cross-talk and study the cathode electrolyte interface and interphases.
• Develop calcination conditions for scaled up synthesis.
• Develop new Co-free chemistries with thermal stability comparable to NMC-622.
• Use experimentally observed surface and bulk transformation and degradation pathways to refine the selection of surface/bulk stabilizing elements for Co-free materials.

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

• First-principle calculations in conjunction with diagnostic studies offer predictions of new dopants that stabilizes the LiNiO$_2$ surfaces and bulk lattices.

• We have successfully realized 3D doping and developed MgTi-, MgMn- and Sn-doped Co-free LNiO$_2$ chemistries that meets the energy density target of the project.

• We have developed localized high-concentration electrolytes that introduce a uniform CEI film on the cathode and enhances the stability and cycle life of the MgTi-doped LNiO$_2$ cathode.

• We have scaled up the coprecipitation synthesis with improved hierarchical morphology and tap density control of secondary cathode particles.
Technical Back-Up Divider Slide
Technical Accomplishments and Progress
Optimization of DME-based LHCEs for Gr||NMC811

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

• Suppressed irreversible capacity in formation cycles by the introduction of EC and FEC into DME-based LHCE.
• Superior cycling performance of Gr||NMC811 cells achieved with DME-LHCEs containing EC and FEC.
Hydroxide precursor synthesis has been scaled up to 100 g per batch.

Optimization of calcination conditions for scaled-up precursor is being conducted.
## Technical Accomplishments and Progress
### Baseline Project Progress Cell Testing Results

#### Parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode-level Specific Capacity</td>
<td>219.01 mAh/g</td>
</tr>
<tr>
<td>Cathode-level Specific Energy</td>
<td>812.73 Wh/kg</td>
</tr>
<tr>
<td>Cell-level Specific Energy</td>
<td>275.60 Wh/kg</td>
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</tbody>
</table>

#### Cycling Protocol
- **Discharge**: CCD to 2.5 V at 0.833 A
- **Charge**: CCCV to 4.4 V at 0.833 A for 5 hrs

#### Graphs

- **Graph 1**: Voltage vs. Capacity (Ah)
  - 2.694 Ah @ 0.5 A
  - 2.699 Ah @ 0.5 A
  - 2.585 Ah @ 1.25 A
  - 2.485 Ah @ 2.5 A

- **Graph 2**: Capacity (Ah) vs. Cycle
  - Charge - 4.4V
  - Discharge - 4.4V
  - Charge - 4.2V
  - Discharge - 4.2V

#### Notes
- Channel issue...
- 2.5 V – 4.4 V
- Impedance <40 mΩ @ 1kHz
- CHG: CC 0.5A to 4.4V + CV 4.4V for 2hrs