CRYSTAL CHEMISTRY OF LITHIUM ION BATTERY CATHODES

ARUMUGAM MANTHIRAM
Department of Mechanical Engineering
The University of Texas at Austin

Affiliations:
Materials Science and Engineering Program
Texas Materials Institute
Center for Nano and Molecular Science and Technology
CURRENT RESEARCH ACTIVITIES

- Lithium Ion Batteries
  - High capacity cathodes (portable electronic devices)
  - Low cost cathodes (electric and hybrid electric vehicles)

- Proton Exchange Membrane and Direct Methanol Fuel Cells
  - New non-platinum catalysts (oxygen reduction & fuel oxidation)
  - New high temperature, low methanol permeability membranes

- Solid Oxide Fuel Cells (Intermediate temperature: 500-800 °C)
  - New oxide catalysts (oxygen reduction & hydrocarbon fuel oxidation)

- Supercapacitors
  - New low cost electrode materials

- Solid State Chemistry of Inorganic Materials
  - Synthesis, characterization, structure-property-performance relationships
  - Nanostructured materials, alloys, oxides, and nitrides
• **Issues with Current Lithium Ion Battery Cathodes**

• **Layered Oxide Cathodes**
  - Factors limiting the reversible capacity
  - Factors influencing the power capability
  - New class of high energy density layered oxide cathodes for portables

• **Spinel Manganese Oxide Cathodes**
  - Factors influencing the capacity fade
  - New class of high power spinel oxyfluoride cathodes for EV and HEV

• **Conclusions**
LITHIUM ION BATTERIES

- Higher voltage, 4 V
- Higher energy density
- Compact, light weight
- Longer shelf life (> 10 years)
- Wider temp. range (-40 to 70 °C)

\[ C_6 + LiCoO_2 \leftrightarrow Li_xC_6 + Li_{1-x}CoO_2 \]

The University of Texas at Austin
ISSUES WITH THE CATHODES

Layered LiCoO$_2$
- Only 50% of its theoretical capacity could be utilized
- Co is expensive and toxic; safety concerns
- Currently used for portable devices, but could not be employed for HEV and EV

Spinel LiMn$_2$O$_4$
- Mn is inexpensive and environmentally benign
- With a 3-dimensional structure provides high rate (power capability) and safety
- Attractive for HEV and EV applications
- Exhibits severe capacity fade at elevated temperatures

Olivine LiFePO$_4$
- Fe is inexpensive and environmentally benign
- With covalently bonded PO$_4$ groups, offers excellent chemical stability and safety
- Electronic insulator and low Li$^+$ ion conductivity
- Needs to be made as nanocrystalline and decorated with conductive carbon

The University of Texas at Austin
LAYERED OXIDE CATHODES
LAYERED LiMO$_2$ (M = Co, Ni, Mn) CATHODES (O3 TYPE)
### Reversible Capacity Limits of Layered Cathodes

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Reversible capacity (mAh/g)</th>
<th>% of theoretical capacity</th>
<th>Intercalation range in Li_{1-x}MO_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_{1-x}[Co]O_2</td>
<td>140</td>
<td>50</td>
<td>0.5 ≤ (1-x) ≤ 1.0</td>
</tr>
<tr>
<td>Li_{1-x}[Ni_{0.85}Co_{0.15}]O_2</td>
<td>180</td>
<td>65</td>
<td>0.35 ≤ (1-x) ≤ 1.0</td>
</tr>
<tr>
<td>Li_{1-x}[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2</td>
<td>190</td>
<td>70</td>
<td>0.30 ≤ (1-x) ≤ 1.0</td>
</tr>
<tr>
<td>Li_{1-x}[Ni_{1-y-z}Mn_{y}Li_{z}]O_2</td>
<td>250</td>
<td>80</td>
<td>0.20 ≤ (1-x) ≤ 1.0</td>
</tr>
</tbody>
</table>

Theoretical capacity: ~ 280 mAh/g

Why do the materials show different capacities even though they all have the same crystal structure?
CHEMICAL LITHIUM EXTRACTION

• Chemical synthesis

\[ \text{LiMO}_2 + x \text{ NO}_2\text{BF}_4 \rightarrow \text{Li}_{1-x}\text{MO}_2 + x \text{LiBF}_4 + x \text{NO}_2 \]

(Acetonitrile medium under argon atmosphere at room temp.)

• Structural characterization
  - X-ray diffraction (Rietveld analysis)

• Chemical characterization
  - Atomic absorption spectroscopy – Lithium content
  - Redox titration (iodometry) – Oxidation state
  - Thermogravimetric Analysis – Oxygen loss vs proton insertion
  - Mass Spectrometry – Oxygen loss vs proton insertion
  - Prompt Gamma-ray Activation Analysis – Proton content
Oxidation state becomes constant due to proton insertion caused by chemical instability.

## COMPARISON OF PROTON CONTENTS IN CATHODES

<table>
<thead>
<tr>
<th>System</th>
<th>AAS Li content</th>
<th>PGAA H content</th>
<th>REDOX TITRATION</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
<td>0.03</td>
<td>0.44</td>
<td>3.64</td>
<td>H₀.₃₃Li₀.₀₃CoO₂</td>
</tr>
<tr>
<td>LiNiO₂</td>
<td>0.08</td>
<td>-</td>
<td>3.88</td>
<td>H₀.₀₅Li₀.₀₈NiO₂</td>
</tr>
<tr>
<td>LiNiO₂</td>
<td>0.22</td>
<td>0.06</td>
<td>3.76</td>
<td>H₀.₀₂Li₀.₂₂NiO₂</td>
</tr>
<tr>
<td>LiNi₀.₁/₃Mn₀.₁/₃Co₀.₁/₃O₂</td>
<td>0.02</td>
<td>0.48</td>
<td>3.58</td>
<td>H₀.₄₀Li₀.₀₂Ni₀.₁/₃Mn₀.₁/₃Co₀.₁/₃O₂</td>
</tr>
<tr>
<td>LiNi₀.₅Mn₀.₅O₂</td>
<td>0.07</td>
<td>0.59</td>
<td>3.58</td>
<td>H₀.₃₉Li₀.₀₇Ni₀.₅Mn₀.₅O₂</td>
</tr>
<tr>
<td>α-LiMnO₂</td>
<td>0.25</td>
<td>0.03</td>
<td>3.70</td>
<td>H₀.₀₅Li₀.₂₅MnO₂</td>
</tr>
<tr>
<td>LiMn₂O₄ (spinel)</td>
<td>0.03</td>
<td>0.03</td>
<td>3.97</td>
<td>H₀.₀₃Li₀.₀₃Mn₂O₄</td>
</tr>
<tr>
<td>LiMn₁.₅₈Ni₀.₄₂O₄</td>
<td>0.10</td>
<td>-</td>
<td>3.94</td>
<td>Li₀.₁₅Mnₑ.₅₈Ni₀.₄₂O₄</td>
</tr>
<tr>
<td>LiFePO₄</td>
<td>0.15</td>
<td>-</td>
<td>2.87</td>
<td>Li₀.₁₅FePO₄</td>
</tr>
</tbody>
</table>

- Layered LiCoO₂, LiNi₀.₅Mn₀.₅O₂, and LiNi₁/₃Mn₁/₃Co₁/₃O₂: Significant amount of proton insertion at deep lithium extraction
- LiNiO₂, α-LiMnO₂, LiMn₂O₄, and LiFePO₄: Little or no proton insertion
- Proton insertion may be related to chemical instability at deep lithium extraction
As the overlap of the M^{3+/4+}:3d band with the top of the O^{2-}:2p band increases, the lithium content at which chemical instability sets in during charge increases, which limits the reversible capacity.
PHASE RELATIONSHIPS OF DELITHIATED CATHODES


- Why does the crystal chemistry of delithiated phases vary?
STRUCTURAL NOMENCLATURE

O3 (ABCABC)

P3 (AABBCC)

O1 (ABABAB)

The University of Texas at Austin
## CHEMICAL LITHIUM EXTRACTION RATE

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Time required to extract all the lithium (h)</th>
<th>Structure of the end-member, MO₂</th>
<th>% Cation disorder</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
<td>&lt; 1</td>
<td>P3 (O1)</td>
<td>-</td>
</tr>
<tr>
<td>LiCo₀.₉Ni₀.₁O₂</td>
<td>1</td>
<td>P3 (O1)</td>
<td>-</td>
</tr>
<tr>
<td>LiCo₀.₈Ni₀.₂O₂</td>
<td>1</td>
<td>P3 (O1)</td>
<td>-</td>
</tr>
<tr>
<td>LiCo₀.₇Ni₀.₃O₂</td>
<td>1</td>
<td>P3 (O1)</td>
<td>-</td>
</tr>
<tr>
<td>LiCo₀.₅Ni₀.₅O₂</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LiCo₀.₃Ni₀.₇O₂</td>
<td>6</td>
<td>O₃’</td>
<td>2.1</td>
</tr>
<tr>
<td>LiCo₀.₁₅Ni₀.₈₅O₂</td>
<td>12</td>
<td>O₃’</td>
<td>3.0</td>
</tr>
<tr>
<td>LiNiO₂</td>
<td>48</td>
<td>O₃’</td>
<td>5.0</td>
</tr>
<tr>
<td>LiNi₀.₇₅Mn₀.₂₅O₂</td>
<td>36</td>
<td>O₃’</td>
<td>8.2</td>
</tr>
<tr>
<td>LiNi₀.₅Mn₀.₅O₂</td>
<td>36</td>
<td>O₃</td>
<td>11.8</td>
</tr>
</tbody>
</table>
Samples with cation disorder take longer time to extract all the lithium.

How do we understand the differences in the structures?
As the Co content increases, O3 $\rightarrow$ O1 $\rightarrow$ P3 occurs

• **At high Co content (e.g. LiCoO$_2$)**
  - Fast chemical lithium extraction rate (high charging rate) due to good cation ordering stabilizes the metastable P3 phase over O1 phase
  - High proton content may stabilize the P3 phase

• **At medium Co content (e.g. LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$)**
  - Moderate chemical lithium extraction rate (slow charging) due to some cation disorder (< 3 %) gives the thermodynamically stable O1 phase

• **At low Co content (e.g. LiNi$_{0.5}$Mn$_{0.5}$O$_2$)**
  - High cation disorder (> 6 %) prevents the formation of O1 or P3 phases due to a strong electrostatic repulsion across the shared faces
STABILITY OF Li_{1-x}MO_2: ELECTROSTATIC EFFECTS

Edge sharing alone

Edge and face sharing

The University of Texas at Austin
RATE CAPABILITY OF $\text{LiNi}_{0.5-0.5y}\text{Mn}_{0.5-0.5y}\text{Co}_y\text{O}_2$

- Charge-discharge between 3.0 – 4.3 V at C/10 rate to 4C rate
- Rate capability decreases with decreasing Co content
- Why does the rate capability decrease with decreasing Co content?
CATION DISORDER AND LITHIUM EXTRACTION RATE IN LiNi_{0.5-0.5y}Mn_{0.5-0.5y}Co_{y}O_{2}

• Cation disorder increases with decreasing Co content due to an increasing Ni^{2+} content and a smaller size difference between Ni^{2+} (0.69 Å) and Li^{+} (0.76 Å) (Co^{3+}: 0.0545 nm, Ni^{3+}: 0.056 nm; Mn^{3+}: 0.0645 nm; Mn^{4+}: 0.053 nm).

• Chemical lithium extraction rate (with NO_{2}BF_{4} in acetonitrile medium) decreases with decreasing Co content (0.15 ≤ y ≤ 1) due to an increasing cation disorder.
CATION DISORDER AND LITHIUM EXTRACTION RATE IN LiNi_{0.5-0.5y}Mn_{0.5-0.5y}Co_{y}O_{2}

- Decreasing chemical lithium extraction rate due to an increasing cation disorder leads to a decrease in electrochemical rate capability with decreasing Co content.
HIGH CAPACITY LAYERED OXIDE CATHODES


- Solid solution between layered Li$_2$MnO$_3$, Li(Li$_{1/3}$Mn$_{2/3}$O$_2$) and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$
- Large IRC in first cycle
- Surface modification modifies SEI layer, suppresses IRC from ~80 to 40 mAh/g, and increases reversible capacity (285 mAh/g)

- Two times higher energy density compared to layered LiCoO$_2$
- Attractive for portable electronic devices

The University of Texas at Austin
Advantages:
• Mn is inexpensive and environmentally benign
• Good structural and chemical stability (high rate capability) due to
  - 3-dimensional edge-shared MnO$_6$ octahedral framework
  - Mn$^{3+/4+}$.e$_g$ band lying well above the O$^{2-}$.2p band

Problem:
• Severe capacity fade at elevated temperatures (55 °C)
  - Mn dissolution from the lattice (2Mn$^{3+}$ $\rightarrow$ Mn$^{2+}$ + Mn$^{4+}$)
# CATION SUBSTITUTED MANGANESE SPINEL OXIDES

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition</th>
<th>Mn Valence</th>
<th>Lattice Parameter (Å)</th>
<th>Sample No.</th>
<th>Composition</th>
<th>Mn Valence</th>
<th>Lattice Parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiMn$_2$O$_4$</td>
<td>3.5</td>
<td>8.2489</td>
<td>15</td>
<td>LiMn$<em>{1.9}$Fe$</em>{0.05}$Li$_{0.05}$O$_4$</td>
<td>3.58</td>
<td>8.225</td>
</tr>
<tr>
<td>2</td>
<td>LiMn$<em>{1.95}$Li$</em>{0.05}$O$_4$</td>
<td>3.56</td>
<td>8.2319</td>
<td>16</td>
<td>LiMn$<em>{1.9}$Co$</em>{0.05}$Li$_{0.05}$O$_4$</td>
<td>3.58</td>
<td>8.2212</td>
</tr>
<tr>
<td>3</td>
<td>LiMn$<em>{1.9}$Li$</em>{0.1}$O$_4$</td>
<td>3.63</td>
<td>8.2179</td>
<td>17</td>
<td>LiMn$<em>{1.8}$Co$</em>{0.1}$Li$_{0.1}$O$_4$</td>
<td>3.67</td>
<td>8.2013</td>
</tr>
<tr>
<td>4</td>
<td>LiMn$<em>{1.9}$Al$</em>{0.1}$O$_4$</td>
<td>3.53</td>
<td>8.2411</td>
<td>18</td>
<td>LiMn$<em>{1.9}$Ni$</em>{0.05}$Li$_{0.05}$O$_4$</td>
<td>3.61</td>
<td>8.2181</td>
</tr>
<tr>
<td>5</td>
<td>LiMn$<em>{1.9}$Ti$</em>{0.1}$O$_4$</td>
<td>3.47</td>
<td>8.2493</td>
<td>19</td>
<td>LiMn$<em>{1.85}$Ni$</em>{0.05}$Li$_{0.1}$O$_4$</td>
<td>3.68</td>
<td>8.2041</td>
</tr>
<tr>
<td>6</td>
<td>LiMn$<em>{1.9}$Al$</em>{0.05}$Ti$_{0.05}$O$_4$</td>
<td>3.55</td>
<td>8.2401</td>
<td>20</td>
<td>LiMn$<em>{1.88}$Ni$</em>{0.06}$Li$_{0.06}$O$_4$</td>
<td>3.63</td>
<td>8.2138</td>
</tr>
<tr>
<td>7</td>
<td>LiMn$<em>{1.9}$Co$</em>{0.1}$O$_4$</td>
<td>3.53</td>
<td>8.2319</td>
<td>21</td>
<td>LiMn$<em>{1.9}$Ni$</em>{0.075}$Li$_{0.025}$O$_4$</td>
<td>3.59</td>
<td>8.2222</td>
</tr>
<tr>
<td>8</td>
<td>LiMn$<em>{1.8}$Co$</em>{0.2}$O$_4$</td>
<td>3.56</td>
<td>8.2103</td>
<td>22</td>
<td>LiMn$<em>{1.875}$Ni$</em>{0.075}$Li$_{0.05}$O$_4$</td>
<td>3.63</td>
<td>8.2133</td>
</tr>
<tr>
<td>9</td>
<td>LiMn$<em>{1.9}$Ni$</em>{0.1}$O$_4$</td>
<td>3.58</td>
<td>8.2319</td>
<td>23</td>
<td>LiMn$<em>{1.85}$Ni$</em>{0.075}$Li$_{0.075}$O$_4$</td>
<td>3.66</td>
<td>8.208</td>
</tr>
<tr>
<td>10</td>
<td>LiMn$<em>{1.85}$Ni$</em>{0.15}$O$_4$</td>
<td>3.62</td>
<td>8.2086</td>
<td>24</td>
<td>LiMn$<em>{1.85}$Ni$</em>{0.1}$Li$_{0.05}$O$_4$</td>
<td>3.65</td>
<td>8.2126</td>
</tr>
<tr>
<td>11</td>
<td>LiMn$<em>{1.8}$Ni$</em>{0.2}$O$_4$</td>
<td>3.67</td>
<td>8.2139</td>
<td>25</td>
<td>LiMn$<em>{1.8}$Ni$</em>{0.1}$Li$_{0.1}$O$_4$</td>
<td>3.72</td>
<td>8.2023</td>
</tr>
<tr>
<td>12</td>
<td>LiMn$<em>{1.9}$Cu$</em>{0.1}$O$_4$</td>
<td>3.58</td>
<td>8.2289</td>
<td>26</td>
<td>LiMn$<em>{1.9}$Cu$</em>{0.05}$Li$_{0.05}$O$_4$</td>
<td>3.61</td>
<td>8.2228</td>
</tr>
<tr>
<td>13</td>
<td>LiMn$<em>{1.9}$Al$</em>{0.05}$Li$_{0.05}$O$_4$</td>
<td>3.58</td>
<td>8.2293</td>
<td>27</td>
<td>LiMn$<em>{1.8}$Cu$</em>{0.1}$Li$_{0.1}$O$_4$</td>
<td>3.72</td>
<td>8.2069</td>
</tr>
<tr>
<td>14</td>
<td>LiMn$<em>{1.85}$Ti$</em>{0.075}$Li$_{0.075}$O$_4$</td>
<td>3.58</td>
<td>8.2305</td>
<td>28</td>
<td>LiMn$<em>{1.9}$Ga$</em>{0.05}$Li$_{0.05}$O$_4$</td>
<td>3.58</td>
<td>8.2324</td>
</tr>
</tbody>
</table>

EFFECT OF INITIAL MANGANESE VALENCE

• Two regions with a boundary around a Mn valence of 3.58+

CAPACITY RETENTION OF SPINEL CATHODES

![Graph showing capacity retention of spinel cathodes at 25°C and 60°C.](image)

- **LiMn$_2$O$_4$**
- **LiMn$_2$O$_{3.92}$F$_{0.08}$**
- **LiMn$_{1.8}$Li$_{0.2}$O$_4$**
- **LiMn$_{1.8}$Li$_{0.2}$O$_{3.88}$F$_{0.12}$**
- **LiMn$_{1.8}$Li$_{0.2}$O$_{3.79}$F$_{0.21}$**
- **LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_4$**
- **LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_{3.9}$F$_{0.1}$**
- **LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_{3.8}$F$_{0.2}$**

- 3.5 – 4.3 V
- C/5 rate

*The University of Texas at Austin*
XRD PATTERNS OF SPINEL OXYFLUORIDES


- **Composition**
  - LiMn$_2$O$_4$
  - LiMn$_{2.02}$O$_{3.79}F_{0.21}$
  - LiMn$_{1.80}$Li$_{0.20}$O$_{3.88}F_{0.12}$
  - LiMn$_{1.80}$Li$_{0.20}$O$_{3.79}F_{0.21}$
  - LiMn$_{1.80}$Li$_{0.10}$Ni$_{0.10}$O$_{3.90}F_{0.10}$
  - LiMn$_{1.80}$Li$_{0.10}$Ni$_{0.10}$O$_{3.80}F_{0.20}$

- **Mn valence**
  - 3.50
  - 3.46
  - 3.78
  - 3.71
  - 3.72
  - 3.67
  - 3.61

- **Lattice parameter (Å)**
  - 8.2451
  - 8.2497
  - 8.2002
  - 8.2034
  - 8.2113
  - 8.2091
  - 8.2138
  - 8.2252

The University of Texas at Austin
RATE CAPABILITY AND STORAGE CHARACTERISTICS

The University of Texas at Austin
RELATIONSHIP BETWEEN IRC AND CAPACITY FADE

1: LiMn$_2$O$_4$
2: LiMn$_2$O$_{3.92}$F$_{0.08}$
3: LiMn$_{1.8}$Li$_{0.2}$O$_4$
4: LiMn$_{1.8}$Li$_{0.2}$O$_{3.88}$F$_{0.12}$
5: LiMn$_{1.8}$Li$_{0.2}$O$_{3.79}$F$_{0.21}$
6: LiMn$_{1.8}$Li$_{0.1}$Ti$_{0.1}$O$_4$
7: LiMn$_{1.8}$Li$_{0.1}$Ti$_{0.1}$O$_{3.9}$F$_{0.1}$
8: LiMn$_{1.8}$Li$_{0.1}$Cu$_{0.1}$O$_4$
9: LiMn$_{1.8}$Li$_{0.1}$Cu$_{0.1}$O$_{3.9}$F$_{0.1}$
10: LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_4$
11: LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_{3.9}$F$_{0.1}$
12: LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_{3.8}$F$_{0.2}$

The University of Texas at Austin
CUBIC TO CUBIC TRANSITION IN SPINEL CATHODES

Ex-situ (chemically delithiated)

In-situ (electrochemical - BNL)

The University of Texas at Austin
ORIGIN OF CAPACITY FADE IN SPINEL CATHODES


1: LiMn$_2$O$_4$
2: LiMn$_{2}$O$_{3.92}$F$_{0.08}$
3: LiMn$_{1.8}$Li$_{0.2}$O$_4$
4: LiMn$_{1.8}$Li$_{0.2}$O$_{3.88}$F$_{0.12}$
5: LiMn$_{1.8}$Li$_{0.2}$O$_{3.79}$F$_{0.21}$
6: LiMn$_{1.8}$Li$_{0.1}$Ti$_{0.1}$O$_4$
7: LiMn$_{1.8}$Li$_{0.1}$Ti$_{0.1}$O$_{3.9}$F$_{0.1}$
8: LiMn$_{1.8}$Li$_{0.1}$Cu$_{0.1}$O$_4$
9: LiMn$_{1.8}$Li$_{0.1}$Cu$_{0.1}$O$_{3.9}$F$_{0.1}$
10: LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_4$
11: LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_{3.9}$F$_{0.1}$
12: LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_{3.8}$F$_{0.2}$
## COMPARISON OF TRANSITION METAL ION DISSOLUTION

<table>
<thead>
<tr>
<th>Structure</th>
<th>Composition</th>
<th>Mn</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>total</th>
<th>$\text{Mn}^{n+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered</td>
<td>LiCoO$_2$</td>
<td></td>
<td>0.8</td>
<td></td>
<td></td>
<td>0.8</td>
<td>$\text{Mn}^{4+}$</td>
</tr>
<tr>
<td></td>
<td>LiNi$<em>{0.5}$Mn$</em>{0.5}$O$_2$</td>
<td>0.4</td>
<td>0.7</td>
<td></td>
<td></td>
<td>1.1</td>
<td>$\text{Mn}^{4+}$</td>
</tr>
<tr>
<td></td>
<td>LiNi$<em>{0.33}$Mn$</em>{0.33}$Co$_{0.33}$O$_2$</td>
<td>0.2</td>
<td>0.4</td>
<td>0.3</td>
<td></td>
<td>0.9</td>
<td>$\text{Mn}^{4+}$</td>
</tr>
<tr>
<td></td>
<td>LiNi$<em>{0.25}$Mn$</em>{0.25}$Co$_{0.5}$O$_2$</td>
<td>0.4</td>
<td>0.9</td>
<td>0.5</td>
<td></td>
<td>1.8</td>
<td>$\text{Mn}^{4+}$</td>
</tr>
<tr>
<td></td>
<td>LiMn$<em>{0.8}$Cr$</em>{0.2}$O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.6</td>
<td>$\text{Mn}^{3+}$</td>
</tr>
<tr>
<td></td>
<td>LiMnO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.2</td>
<td>$\text{Mn}^{3+}$</td>
</tr>
<tr>
<td></td>
<td>LiMn$_2$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.2</td>
<td>$\text{Mn}^{3.50+}$</td>
</tr>
<tr>
<td></td>
<td>LiMn$<em>{1.8}$Li$</em>{0.1}$Ti$_{0.1}$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>$\text{Mn}^{3.61+}$</td>
</tr>
<tr>
<td>4 V spinel</td>
<td>LiMn$<em>{1.8}$Li$</em>{0.1}$Ti$<em>{0.1}$O$</em>{3.9}$F$_{0.1}$</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
<td>1.7</td>
<td>$\text{Mn}^{3.56+}$</td>
</tr>
<tr>
<td></td>
<td>LiMn$<em>{1.8}$Li$</em>{0.1}$Ni$_{0.1}$O$_4$</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td>1.1</td>
<td>$\text{Mn}^{3.72+}$</td>
</tr>
<tr>
<td></td>
<td>LiMn$<em>{1.8}$Li$</em>{0.1}$Ni$<em>{0.1}$O$</em>{3.8}$F$_{0.2}$</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
<td>$\text{Mn}^{3.61+}$</td>
</tr>
<tr>
<td></td>
<td>LiMn$<em>{1.5}$Ni$</em>{0.5}$O$_4$</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
<td></td>
<td>0.6</td>
<td>$\text{Mn}^{4+}$</td>
</tr>
<tr>
<td>5 V spinel</td>
<td>Li$<em>{1.05}$Mn$</em>{1.53}$Ni$_{0.42}$O$_4$</td>
<td>0.2</td>
<td>0.1</td>
<td></td>
<td></td>
<td>0.3</td>
<td>$\text{Mn}^{4+}$</td>
</tr>
<tr>
<td></td>
<td>LiMn$<em>{1.42}$Ni$</em>{0.42}$Co$_{0.16}$O$_4$</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
<td></td>
<td>0.6</td>
<td>$\text{Mn}^{4+}$</td>
</tr>
<tr>
<td>Olivine</td>
<td>LiFePO$_4$</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The % capacity fade decreases with decreasing lattice parameter difference between the cubic phases.
HPPC Pulse Profile

• HPPC tests were performed after every 10 cycles at 100 % SOC
• Cycling was performed at C/2 rate
AFTER CYCLING WITH HPPC TEST (100 CYCLES)

**LiMn$_2$O$_4$**

before Cycling

![Graph](before_cycling_graph_li_mn2o4)

after Cycling

![Graph](after_cycling_graph_li_mn2o4)

**LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_{3.8}$F$_{0.2}$**

before Cycling

![Graph](before_cycling_graph_li_mn18li01ni01o38f02)

after Cycling

![Graph](after_cycling_graph_li_mn18li01ni01o38f02)
PERFORMANCE IN LITHIUM ION CELLS AT 60 °C

**Graph:**
- **Capacity (mAh/g)** vs **Cycle number**
- Points represent different compositions:
  - **LiMn$_2$O$_4$**
  - **LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_{3.8}$F$_{0.2}$**
  - **70 wt % LiMn$_{1.8}$Li$_{0.1}$Ni$_{0.1}$O$_{3.8}$F$_{0.2}$ + 30 wt% LiCoO$_2$**

**Text:**
- **Compositions and Dissolved Mn:**
<table>
<thead>
<tr>
<th>Composition</th>
<th>Dissolved Mn$^a$ (%)</th>
<th>Dissolved Mn$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>0.83</td>
<td>0.67</td>
</tr>
<tr>
<td>LiMn$<em>{1.8}$Li$</em>{0.1}$Ni$<em>{0.1}$O$</em>{3.8}$F$_{0.2}$</td>
<td>0.27</td>
<td>0.19</td>
</tr>
<tr>
<td>LiMn$<em>{1.8}$Li$</em>{0.1}$Ni$<em>{0.1}$O$</em>{3.8}$F$_{0.2}$ (70 %) + LiCoO$_2$ (30 %)</td>
<td>0.11</td>
<td>0.08</td>
</tr>
</tbody>
</table>

- **After storing at 4.7 V for 7 days at the end of first charge**
- **After storing at 3.5 V for 7 days at the end of first discharge**

- **Note:**
  - Charging the spinel + layered oxide mixture to 4.7 in the first cycle traps the proton in the layered oxide lattice and suppresses Mn dissolution.

The University of Texas at Austin
CONCLUSIONS

- Crystal chemistry plays a critical role in controlling the electrochemical performances of lithium ion battery cathodes

Layered cathodes

- Reversible capacity is limited by chemical and structural instabilities
- Rate (power) capability is controlled by lithium extraction rate, which decreases with increasing cation disorder
- Surface modified complex solid solutions between Li$_2$MnO$_3$ and Li[Ni,Mn,Co]O$_2$ offer high capacities of 285 mAh/g with low IRC

Spinel Cathodes

- Cation-substituted oxyfluorides exhibit excellent capacity retention at 60 °C with high power capability – Attractive for EV and HEV applications
- The better performance is due to a smaller lattice parameter difference between the two cubic phases formed and reduced Mn dissolution
ACKNOWLEDGMENTS

Postdoctoral Researchers and Students:
Current members: 14 Ph.D. students and 3 postdoctoral fellows
Ph.D. students graduated: 18

Emilio Alvarez  T. A. Arunkumar  Ramanan Chebiam
Jehwon Choi  Wonchang Choi  Fernando Prado
Youngjoon Shin  S. Venkatraman  Yan Wu

Financial Support:
Welch Foundation
Department of Energy (DOE)
National Aeronautics and Space Administration (NASA)
State of Texas