Order/Disorder Effects on LiNiO$_2$ as a Battery Material

Alex Bologna
Basic Structure and Applications of LiNiO$_2$

- Battery grade LiNiO$_2$ belongs to the R-3m space group (#166)
- LiNiO$_2$ can also take on the less ordered rocksalt space group Fm-3m (#225)
- LiNiO$_2$ is a major component of commercial battery cathodes
  - Increasing Ni content as Co decreases
- 5% of the world’s annual 2.5 million ton of Ni production goes to batteries
Battery Fundamentals

- Lithium ion batteries work by shuttling \( \text{Li}^+ \) ions and electrons between the anode and the cathode.
- Good battery materials can accept \( \text{Li}^+ \) ions into their structure:
  - Quickly
  - Predictably
  - Repeatably

https://letstalkscience.ca/educational-resources/stem-in-context/how-does-a-lithium-ion-battery-work
LiNiO$_2$ in Lithium Ion Batteries

- Alternating layers of Oxygen and Nickel or Lithium
- Layered structure is critical for battery applications
- Only ~50% of Lithium ions can be removed from structure
  - Otherwise crystal structure collapses

Lim, JM., Hwang, T., Kim, D. et al. Intrinsic Origins of Crack Generation in Ni-rich LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ Layered Oxide Cathode Material. Sci Rep 7, 39669 (2017). https://doi.org/10.1038/srep39669
Off Stoichiometry in Li$_{1-x}$Ni$_{1+x}$O$_2$

- Challenging to synthesize stoichiometric LiNiO$_2$
  - “Intrinsic off stoichiometry”
- Excess Ni will reside in the Li layer
  - Ni residing in the Li layer decreases Li mobility and hinders diffusion

Lim, J.M., Hwang, T., Kim, D. et al. Intrinsic Origins of Crack Generation in Ni-rich LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ Layered Oxide Cathode Material. Sci Rep 7, 39669 (2017). https://doi.org/10.1038/srep39669
Effect of Off Stoichiometry on Performance

- In Li_{1-x}Ni_{1+x}O_2, as x increases, the cell capacity decreases.

Effect of Off Stoichiometry on Performance

- As Ni content increases, there are larger volume changes associated with charging and discharging the cell
  - Stoichiometric samples see 3 phases
  - Off stoichiometric mixtures see 4 phases
- Changes in the physical structure of the cell lead to cell degradation

Effect of Off Stoichiometry on Performance

- Stoichiometric LiNiO$_2$ has greater electric conductivity than Ni rich alloys
- Increased conductivity contributes to faster charge/discharge rates

How to Determine Order vs Disorder

- Powder XRD gives similar diffraction patterns for space groups R-3m and Fm-3m
  - 37.7° and 43.8° peaks overlap
- Small impurities are very difficult to detect
- Magnetism can highlight structural differences

Magnetism of LiNiO$_2$

- LiNiO$_2$ displays complex magnetic behavior with 3 distinct regions
  - Low moment for Li$_{0.5}$Ni$_{1.5}$O$_2$
  - Uncompensated magnetism for intermediate Li$_{0.8}$Ni$_{1.2}$O$_2$
  - Low moment in pure LiNiO$_2$

- Magnetism caused by structural changes as Li content increases

Source of Ferrimagnetism in $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$

- **Rocksalt structure dominated by antiferromagnetic interactions among Ni$^{2+}$ atoms**
  - Magnetic moment is compensated
- **Ferrimagnetism arises from bridging interactions between Ni$^{3+}$ layers**
  - Ni$^{2+}$ atoms bridge Ni$^{3+}$ layers, creating ferromagnetic clusters
  - Uncompensated magnetism

# Summary of Magnetism in NiLiO₂

<table>
<thead>
<tr>
<th>Li₁₋ₓNi₁₊ₓO₂ Composition</th>
<th>Li₀.₄Ni₁.₆O₂</th>
<th>Li₀.₇Ni₁.₃O₂</th>
<th>LiNiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetism</td>
<td>G-type Antiferromagnet</td>
<td>Ferrimagnet</td>
<td>A-type Antiferromagnet</td>
</tr>
<tr>
<td>Structure</td>
<td>Rock Salt</td>
<td>Connected Layers</td>
<td>Repulsive Layers</td>
</tr>
<tr>
<td>Ni²⁺/Ni³⁺ Interactions</td>
<td>Ni²⁺ dominates Ni³⁺</td>
<td>Ni²⁺ connects Ni³⁺ layers</td>
<td>Only Ni³⁺ present</td>
</tr>
<tr>
<td>T_N</td>
<td>327K</td>
<td>240K</td>
<td>9K</td>
</tr>
</tbody>
</table>
Types of Antiferromagnetism

- LiNiO$_2$ displays A-type and Li$_{0.4}$Ni$_{1.6}$O$_2$ displays G-type
"A larger negative free energy change for a reaction \( xA + MX_n = A_xMX_n \) is expected when \( A \) is small and electropositive, \( MX_n \) contains a metal atom \( M \) in a high oxidation state, and \( X \) is small and electronegative."

Determining LiNiO$_2$ Order With Magnetism

- Lower magnetic ordering temperatures correspond to more stoichiometric samples.
- “The complex magnetism of Li$_{1-x}$Ni$_{1+x}$O$_2$ evolves as Ni enters the Li plane, the Ni$^{3+}$/Ni$^{2+}$ ratio changes, and the chemical coherence length shrinks.”

References

- https://letstalkscience.ca/educational-resources/stem-in-context/how-does-a-lithium-ion-battery-work