Identical Location TEM Studies on Conductivity vs. Structure in Metal Oxide Anodes

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Metal Oxide Anodes

- Capacity key for future high power applications (energy grid, hybrid electric vehicles)
- Metal oxides – promising category for Li-ion anodes
- Poor cyclability
  - Fundamental understanding of reaction mechanisms
Carbon Storage Mechanism

Anode (Graphite)

Electrolyte (LiPF$_6$ in organic electrolyte)

Cathode (LiCoO$_2$, LiMnO$_2$)

Reaction Mechanisms for Transition Metal (Oxide) Anodes

- **Intercalation**
  - Conversion
  - Intercalation
  - Alloying

- **Conversion**
  - Ni/Co/Fe/Cu oxides

- **Intercalation**
  - Li$_4$Ti$_5$O$_{12}$ + 3 Li $\leftrightarrow$ Li$_7$Ti$_5$O$_{12}$ (~1.6 V)

- **Alloying**
  - Sn, Si
  - Volume expansion
  - Pulverization

Charge/Discharge Mechanism for NiO

Charge (Lithiation)

NiO + 2Li⁺ + 2e⁻ → Ni + Li₂O

Discharge (Delithiation)

NiO + 2Li⁺ + 2e⁻ → Ni + Li₂O

One Charge/Discharge Cycle

Nickel Oxide (NiO) as Anode

Even More NiO Structures

**Reflux-ppt (R-NiO)**

0.5M Ni(NO$_3$)$_2$ in 10M NH$_4$OH boiled 24h

**NaOH-ppt (N-NiO)**

0.5M Ni(NO$_3$)$_2$ in H$_2$O, 10M NaOH added

**Direct calc. (P-NiO)**

Ni(NO$_3$)$_2$•6H$_2$O calcined in air

**Ord. Meso. (O-NiO)**

SBA-15 wet impreg. w/0.5M Ni(NO$_3$)$_2$
Critical to understand what happens not only before/after on the macroscale, but as the process unfolds on the nanoscale.

Structural Changes During Cycling using Identical Location TEM

- 100 mesh, 3 mm Cu TEM grid (Ted Pella, Inc.)
- Sprayed ~100 µg/cm² NiO:PVDF ink (90:10 wt% in NMP)
- Applied grid to custom Cu disk electrode with Teflon cap
- Pressure Critical

Before/after electrochemical testing

Using Ordered Mesoporous NiO as a Probing NiO structure

Formation of template

Surfactant + Silicate, HCl

Filling with precursor (Ni(NO₃)₂)

Etching of template

Calcination

(A)

Quantity Absorbed (cm³/g STP)

Relative Pressure (P/P₀)

(B)

dV/dlog(D) (cm³/g per nm)

Pore diameter (nm)

(111) (200) (220) (311) (222)

θ
Results for IL-TEM on O-NiO

Results for IL-TEM on O-NiO

Impact of Structural Change on Capacity Retention of O-NiO

- **C/5 Charge/Discharge in 20mm coin cell**
- Even after only 7 cycles < 50% capacity retained
  - Links to structural degradation by IL-TEM (and XRD)
- Consistent with most NiO studies in literature
NiO Studies Showing Good Capacity Retention

- Very low loading, < 0.1 g/cm²
  - Thickness < 250nm

- Agarose templated NiO/C on Stainless Steel,


NiO Studies Showing Good Capacity Retention

- Very high carbon content
  - 50:50 NiO:C

When NiO anodes show good capacity retention, conductivity is nearly always artificially enhanced
- We also see this for O-NiO


Improvements in Capacity Retention with Increased Conductivity (1C)

- Have we improved structural reversibility?
Surprisingly, the structure is totally lost!

Does this mean that the structure doesn’t matter?

Charge Discharge Cycles – RT, 1C, 40% Carbon

- Coin cell, RT, 1C, 40% C

![Graphs showing the charge discharge cycles of R-NiO, N-NiO, D-NiO, and O-NiO at RT, 1C, and 40% Carbon.](image-url)
50\textsuperscript{th} Charge/Discharge Cycle – Coin Cells, RT, 1C
Rate Capability and Retention

Graphs showing the capacity (mAh/g) over cycle number for different rates and compositions of NiO materials (R-NiO, D-NiO, N-NiO, O-NiO).
Battery at particular state of charge (SOC)
- Short current pulsed to electrode, draws Li$^+$ in, voltage changes
- Current off, voltage relaxes back to equilibrium value

\[ \Delta E = \left( \frac{dOCV}{dx} \right)_V m i \tau \]

\[ D_{eff} \text{ can be extracted from the linear fit of } \Delta E \text{ vs. } t^{-1/2} \text{ plot} \]

Two Phase Parallel Diffusivity Model

- To get to diffusion coefficients, we use parallel resistance model:

\[
\frac{1}{\Phi_{\text{tot}}} = \frac{1}{\Phi_{\text{NiO,SOC}}} + \frac{1}{\Phi_{\text{Li}_2\text{O}+\text{Ni}}} \quad (1)
\]

\[
\Phi_i = \frac{RT\ell}{n^2 F^2 AD_{\text{LiC}}} \quad (2)
\]

- Plugging in each resistance gives the following expression:

\[
r_{\text{tot}} D_{\text{eff}} = r_{\text{NiO,SOC}} D_{\text{NiO}} + r_{\text{Li}_2\text{O}+\text{Ni}} D_{\text{Li}_2\text{O}+\text{Ni}} \quad (3)
\]

- Dividing by \( r_{\text{NiO,SOC}} \) gives:

\[
\left(\frac{r_{\text{tot}}}{r_{\text{NiO,SOC}}}\right) D_{\text{eff}} = D_{\text{NiO}} + \left(\frac{r_{\text{Li}_2\text{O}+\text{Ni}}}{r_{\text{NiO,SOC}}}\right) D_{\text{Li}_2\text{O}+\text{Ni}} \quad (4)
\]

Diffusion Coefficients

- $D_{\text{eff}}$ deconvoluted into two diffusion coefficients
- $D_{\text{NiO}}$ similar – both elementally identical
- $D_{\text{Li}_2\text{O}+\text{Ni}}$ for N-NiO $\gg$ R-NiO, matches improved performance

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Electronic conductivity plays a key role in the capacity retention of NiO anodes

Good capacity retention is not necessarily and indicator of structural reversibility

Need to probe the interface between the carbon and NiO

- Electron mobility
- Structure of SEI

Good capacity retention is possible with NiO
Acknowledgements

- **Staff Scientist**
  - Lichun Zhang

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  - Neil Spinner
  - Alessandro Palmieri

- **Undergraduates**
  - Nicole Beauregard
  - James Campanella

- **Facilities**
  - Center for Clean Energy Engineering – C2E2
  - Institute of Materials Science – IMS
Questions?

http://mustain.engr.uconn.edu
Charge-discharge curves for plain carbon black anode with 10% binder at C/5 rate
We prepare our ink using PVDF 5% Wt in NMP as binder and NMP itself as the solvent for both the active material and the binder.

Afterwards, we spray the ink using a spray gun and nitrogen as inert gas on a thin copper foil, 2.5 cm width and variable length, alternating a drying step after each layer of AM.

Eventually, we put the electrode into an oven and let it drying overnight under vacuum. The day after it got pressed at 2000 lbs and lastly, the active loading is calculated.
**Coin Cell Preparation**

- **Metal cap**
- **Compression spring**
- **Spacer plate**
- **Gasket**
- **Anode (NiO on Cu)**
- **Celgard 2320**
- **PP/PE/PP separator**
- **Cathode (pure Li)**
- **Metal case**

**Hardware:** 20mm diameter coin cells (Hohsen Corp./Pred Materials)

**Electrolyte:** 1M LiPF$_6$ in (1:1:1) DMC:DEC:EC

**Anode:** NiO (with 10% Kynar PVDF binder) on Cu foil

**Cathode:** Lithium metal

**Equipment:** Arbin MSTAT battery test system
Open-Circuit Voltage vs. x

\[
\Delta E = \frac{dOCV}{dx}V_m \tau \left( \frac{AF}{\sqrt{\pi D_{eff}}} \right)
\]

Cycled once to remove irreversible effects (SEI)

\[xLi^+ + xe^- + 6C \leftrightarrow Li_xC_6 \quad (0 < x < 1)\]
(State of charge equal to x)

\[NiO + 2Li^+ + 2e^- \leftrightarrow Ni + Li_2O \quad (0 \leq x \leq 2)\]
(State of charge equal to 0.5x)

Charged to certain SOC

Taken where \(dOCV/dx\) most linear
CPR Results

<table>
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<tr>
<th>x</th>
<th>SOC</th>
<th>$D_{\text{eff}}$ (cm$^2$/s x $10^{11}$)</th>
<th>R-NiO</th>
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<tr>
<td>0.5</td>
<td>0.25</td>
<td>3.580</td>
<td>7.522</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.30</td>
<td>3.859</td>
<td>8.048</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>0.35</td>
<td>4.242</td>
<td>8.502</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.40</td>
<td>4.356</td>
<td>8.737</td>
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<tr>
<td>0.9</td>
<td>0.45</td>
<td>3.985</td>
<td>11.515</td>
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<tr>
<td>1.0</td>
<td>0.50</td>
<td>4.135</td>
<td>11.957</td>
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- $D_{\text{eff}}$ for N-NiO > $D_{\text{eff}}$ for R-NiO
- All values as x ↑
- Change in phase composition

Two-Phase Diffusivity Model

- Spherical particles
- Volumetric expansion (Li$_2$O+Ni phase growth) proportional to SOC
- Parallel resistance model through Li$_2$O+Ni and NiO phases
Model Derivation

• To get to diffusion coefficients, we use parallel resistance model:

\[
\frac{1}{\phi_{\text{tot}}} = \frac{1}{\phi_{\text{NiO,SOC}}} + \frac{1}{\phi_{\text{Li}_2\text{O}+\text{Ni}}} \quad (1)
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\]
Model Derivation

• Growing $\text{Li}_2\text{O}+\text{Ni}$ phase is a function of disappearing NiO phase:

$$r_{\text{Li}_2\text{O}+\text{Ni}} = K (r_{\text{NiO}} - r_{\text{NiO,SOC}})$$  \hspace{1cm} (5)

$$K = \left[ \frac{0.5 (LP_{\text{Ni}})^3 + (LP_{\text{Li}_2\text{O}})^3}{LP_{\text{NiO}}} \right]^{1/3} = 1.18$$  \hspace{1cm} (6)

• NiO radius expands 18% during charge, or 65% volume expansion.

• The total particle length at any SOC can also be written as a sum of the two individual phase lengths:

$$r_{\text{tot}} = r_{\text{NiO,SOC}} + r_{\text{Li}_2\text{O}+\text{Ni}}$$  \hspace{1cm} (7)
Model Derivation

- Assuming expansion is proportional to SOC, we can get $r_{NiO,SOC}$:

\[
 r_{NiO,SOC} = r_{NiO}(1 - SOC)^{1/3} \quad (8)
\]

\[
 r_{Li_2O+Ni} = K(r_{NiO} - r_{NiO,SOC}) \quad (5)
\]

\[
 r_{tot} = r_{NiO} \left[ K + (1 - K)(1 - SOC)^{1/3} \right] \quad (9)
\]

- Substituting red boxed expressions for lengths, simplifying:

\[
 \left[ K(1 - \left( \frac{r_{tq,t}}{r_{NiO,SOC}} \right)^{1/3} )D_{ef,K} \right]D_{ef,NiO}D_{NiO,NiO,SOC}^{-1/3} - 1 \right]D_{Li_2O+Ni} \quad (4)
\]

\[
 y = b + x \cdot m
\]
Diffusion Coefficients

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