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Inelastic Neutron Scattering Spectroscopy
from Discharged Ni Positive Plates Studied by
Effects of Cycling Conditions on Active Material
Objectives

• Identify atomic-level signatures of electrochemical activity of the active material on the Ni positive plate of Ni-H₂ batteries.
• Relate findings to cycling conditions and histories
• Develop INS spectroscopy as a non-destructive testing technique for the evaluation of Ni-positive plates of Ni-H₂ batteries.
Charge/Discharge of $(\alpha, \beta)$-Ni(OH)$_2$ / $(\gamma, \beta)$-NiOOH Couples

\[
\begin{align*}
\beta \text{-Ni(OH)}_2 & \rightleftharpoons \beta \text{-NiOOH} + H^+ + e^- \\
\alpha \text{-Ni(OH)}_2 & \rightleftharpoons \gamma \text{-NiOOH} + H^+ + e^- 
\end{align*}
\]

KOH + H$_2$O
Ni(OH)$_2$ | NiOOH | Ni
Pale Green | Black

Charging  Discharging

1997 NASA Aerospace Battery Workshop
-569- Nickel Electrode Design Focused Session
Fundamentals of Vibrational Spectroscopy by Inelastic Neutron Scattering

- neutrons are scattered by the atomic nuclei and not the electrons (as are photons)
  - scattering cross-sections a nuclear property
  - H scatters neutrons >10 times more strongly than other atoms
- absorption cross-sections for neutrons are very low:
  - probe the bulk of the sample
  - in-situ methods are easy (no windows required)
- all vibrational modes are observable
  - intensities are weighed by nuclear cross-sections: INS spectra are dominated by modes involving large displacements of H atoms.
  - intensities are readily quantifiable and are proportional to the number of scatterers.
Incoherent scattering cross section

Coherent scattering cross section

Absorption cross section
INS Vibrational Spectroscopy

- technique is well suited for application to battery material
  - bulk probe
  - sensitivity to protons (H)

- experiments are carried out at the Lujan Center of LANL
  - 5 - 10g samples from battery plates
  - FDS instrument; $\Delta E = 50 - 4000 \text{ cm}^{-1}$
  - 12-24 hrs. data collection time
  - $T=15K$
Assignment of $\beta$-Ni(OH)$_2$ vibrational bands

![Graph showing vibrational bands of $\beta$-Ni(OH)$_2$](image)

<table>
<thead>
<tr>
<th>INS (cm$^{-1}$)</th>
<th>IR, Raman (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
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<tbody>
<tr>
<td>315,290</td>
<td>318</td>
<td>$\nu$(NiO); $A_{1g}$</td>
</tr>
<tr>
<td>358</td>
<td>350</td>
<td>$\delta$(ONiO); $E_u$</td>
</tr>
<tr>
<td>390</td>
<td></td>
<td>$\nu$(NiO); $A_{2u}$</td>
</tr>
<tr>
<td>451,412</td>
<td>449</td>
<td>$\delta$(ONiO); $E_g$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>account. + $E_u$</td>
</tr>
<tr>
<td>673</td>
<td>530</td>
<td>$\gamma$(OH) $E_u$</td>
</tr>
<tr>
<td>867</td>
<td></td>
<td>$\gamma$(OH) $E_g$</td>
</tr>
<tr>
<td>929</td>
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</table>
Hydrogen disorder in brucite structures
Raman Scattering Spectra of Ni electrode materials

B. C. Cornilsen and collaborators

Fig. 1. Raman spectra of nickel electrode active mass and model compounds. (a) Charged γ active mass; (b) discharged α active mass; (c) recrystallized β-Ni(OH)₂; (d) first precipitate β-phase.

Raman spectra of: (a) discharged active mass (ID no. 16-09); (b) 'phase-X
Vibrational Modes of Hydration Water

**Internal modes**

- $V_1 (V_{sym})$
- $V_2 (\delta)$
- $V_3 (V_{asym})$

**Librations**

- $R_t (twist)$
- $R_t (rock)$
- $R_t (wag)$

**frequency ranges (cm$^{-1}$)**

- stretching modes ($\nu$) \hspace{1cm} 3600 - 3000
- bending modes ($\delta$) \hspace{1cm} 1660 - 1590
- librations ($R$) \hspace{1cm} 1050 - 350
- translatory modes ($T$) \hspace{1cm} 350 - 100
INS Spectra of Reference Compounds

$\text{Ni(OH)}_2 \{\text{BP1} - \beta\}$

Intensity

Wave Number (cm$^{-1}$)
INS results

- discharged materials are mainly $\beta$-Ni(OH)$_2$
- changes in the Ni-O stretching and bending regions:
  - $d$ decreases from 3.13 Å ($\beta$-Ni(OH)$_2$) to 2.89 Å ($\beta$-NiOOH)
  - distortion of NiO$_6$ octahedron
  - frequency shifts and band splittings result
- water librations above ~ 500 cm$^{-1}$
  - vacancies may allow formation of Ni(H$_2$O)
- protons in O-H···O hydrogen bonds: $\beta$-NiOOH
Structural Models for Hydrogen in NiOOH and bound H₂O
C. Greaves et al. / Structure of the mixed conductor Ni$_2$O$_3$H

FIGURE 2
Schematic representation of the structure of Ni$_2$O$_3$H

FIGURE 3
Fourier section, $y = 0$, based on observed intensities and calculated phases
Conclusions

- (1) Irreversible formation of NiOOH; scales with number of cycles
- (2) additional protons are bound in the lattice to form Ni-(H$_2$O) complexes; increases with KOH concentration in the cell.
- (3) These processes occur only in the outermost layers of the plate material but lead to the failure of the battery cells.
Acknowledgments

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