Study of the effects of nanometer $\beta - \text{Ni(OH)}_2$ in nickel hydroxide electrodes

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Outline

• Background: A proposed mechanism
• Experimental parameters and conditions
• Results and discussions
  a) Transmission electron microscopy (TEM)
  b) X-ray powder diffraction (XRD)
  c) Cyclic voltammetry (CV)
  d) Charge/discharge test
  e) X-ray absorption spectroscopy (XAS)
Background: Ni(OH)$_2$ Charge/Discharge Mechanism

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\text{Ni(OH)$_2$ + OH}^- \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + \text{ne}^-
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Transmission electron microscopy (TEM)

TEM morphology of the nanometer Ni(OH)$_2$ prepared by supersonic coordination–precipitation method. The mean grain size was about 50 nm, with a range of 20–70 nm. The morphology of the nanometer Ni(OH)$_2$ prepared by this method exhibited an irregular structure, which is different from the spherical structure of commercial Ni(OH)$_2$. 
The crystallite sizes of the main feature lines were calculated from Scherrer formula from which a mean grain size of 13.1 nm of nanometer Ni(OH)$_2$ was attained. Average grain size of spherical Ni(OH)$_2$ is 455.4 nm, which is nearly 35 times of that of nanometer Ni(OH)$_2$. 
Cyclic voltammetry (CV)

Cyclic voltammetry was applied to measure the proton diffusion coefficient. Peak current, $I_p$, in cyclic voltammogram can be expressed as:

$$I_p = 0.446n^{3/2}F^{3/2}S(RT)^{-1/2}D^{1/2}c^0\nu^{1/2}$$

$n$: electron number of the reaction ($\approx 1$ for Ni(OH)$_2$);
F: Faraday’s constant;
S: Electrode surface area;
D: Diffusion coefficient;
$\nu$: Scanning rate;
c$^0$: Initial concentration of the reactant.
Approach: Cyclic voltammetry (CV)

It is easy to notice the linear relationship between $I_p$ and $\nu^{1/2}$ as shown in the left figure, which to certain extent confirms that electrode reaction of nickel hydroxide is controlled by proton diffusion coefficient $D$.

Smaller size of nanometer Ni(OH)$_2$ provides more chances for the particles to contact the electrode solution, therefore proton diffusion is enhanced, which in turn will accelerate the electrode reaction.
As a whole, cathode discharge specific capacity (CDSC) of charge/discharge with nanometer Ni(OH)$_2$ is higher than that of micrometer Ni(OH)$_2$, while not much difference was discovered after 350 cycles. Effect of nanometer Ni(OH)$_2$ in increasing CDSC is more apparent for the first 100 cycles. More conglobation may occur with more cycles, which could reduce the effect of nanometer Ni(OH)$_2$. 
X-ray absorption spectroscopy (XAS)

- **X-ray absorption spectroscopy** (XAS) refers to the details of how x-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom. Specifically, XAFS is the modulation of an atom’s x-ray absorption probability due to the chemical and physical state of the atom. XAFS spectra are especially sensitive to the formal oxidation state, coordination chemistry, and the distances, coordination number and species of the atoms immediately surrounding the selected element.

**a. X-ray absorption near-edge spectroscopy** (XANES) is strongly sensitive to formal oxidation state and coordination chemistry (e.g., octahedral, tetrahedral coordination) of the absorbing atom.

**b. Extended x-ray absorption fine-structure spectroscopy** (EXAFS) is used to determine the distances, coordination number, and species of the neighbors of the absorbing atom.
X-ray absorption spectroscopy (XAS)

- 4W1B beamline of Beijing Synchrotron Radiation Facility (BSRF);
- Transmission mode;
- The electron storage ring was operated at 2.2 GeV with a current of 30–50 mA;
- The incident and output beam intensities were monitored and recorded using a nitrogen gas flowing ionization chamber;
- Scanning range: 8.2–9.2 keV, which covers the K edge absorption of Ni atoms;
- Energy resolution was about 1.5 eV for XANES and about 3.0 eV for EXAFS;
- The EXAFS functions were normalized by using the absorption jump and were Fourier transformed to R-space with $\kappa^3$-weighting over the range from 2.3–12.7 Å$^{-1}$. 
X-ray absorption spectroscopy (XAS)

Normalized XANES spectra of fully charged (a) and discharged (b) Nano-E and Micro-E.

**Plot (a): Fully charged state.**
- Intensity of peak B is higher for Nano-E due to the structure distortion;
- Visible edge shift to higher energies in Nano-E, which means higher Ni oxidation state than

**Plot (b): Discharged state.**
- Higher intensity of peak B for Nano-E, indicating an increase in structure distortion in discharged Nano-E;
- An obvious edge shift to lower energy for Nano-E interprets a lower oxidation state of Ni at discharged state;
- A shape difference can be seen in region C. The peak for Nano-E means that the conversion of NiOOH to Ni(OH)$_2$ is more complete.
X-ray absorption spectroscopy (XAS)

Normalized XANES spectra of fully charged (a) and discharged (b) Nano-E and Micro-E.

Plot (a): Fully charged state.
- Ni-Ni bond length for Nano-E is longer than that for Micro-E, indicating a higher oxidation state of Ni in fully charged Nano-E.
- The magnitude for Ni-O and Ni-Ni peaks are larger in Nano-E, indicating a higher coordination number of Ni and O around the absorbing Ni.

Plot (b): Discharged state.
Ni-O bond length for Nano-E is longer than that for Micro-E, which means that Ni in discharged Nano-E has a lower oxidation number.
Conclusion

• Nanometer b-Ni(OH)$_2$ prepared by the proposed method has larger proton diffusion coefficient than commercial spherical Ni(OH)$_2$;

• Nearly 10% increased cathode discharge specific capacity (CDSC) was obtained with addition of 8 mass% nanometer Ni(OH)$_2$;

• Effect of nanometer Ni(OH)$_2$ in increasing CDSC is more obvious for the first 100 cycles;

• More disorder effects were found in nanometer Ni(OH)$_2$ from a broadening of the (1 0 1) line;

• XAS(XANES and EXAFS) has revealed a higher oxidation state of Ni in fully charged Nano-E and a lower one in discharged Nano-E;

• XANES showed increasing distortion in Nano-E during charge-discharge process;

• Promotion of the conversion between Ni$^{2+}$ and Ni$^{3+}$ due to enhanced proton diffusion in distorted Nano-E has been supposed to be one explanation of increasing discharge specific capacity with the addition of nanometer Ni(OH)$_2$. 
Questions?