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

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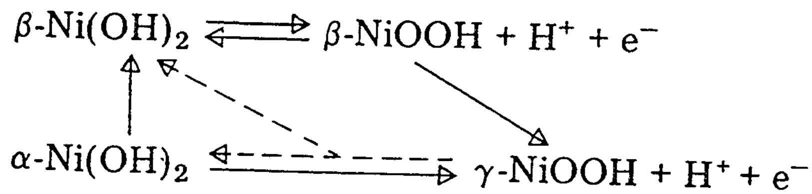
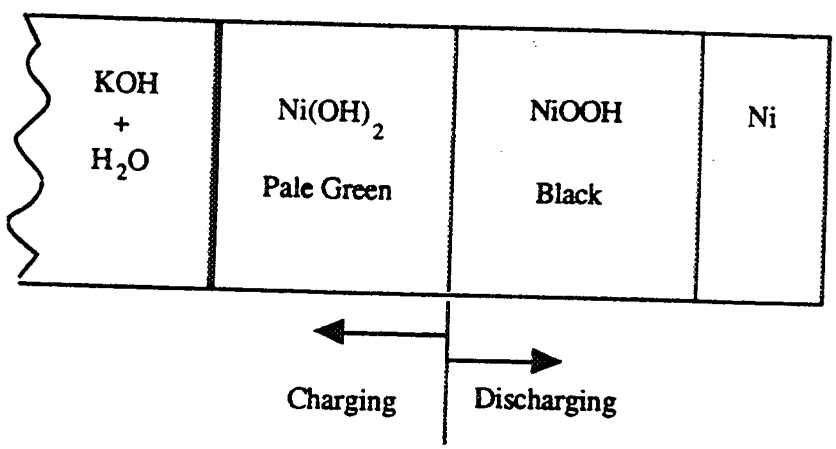
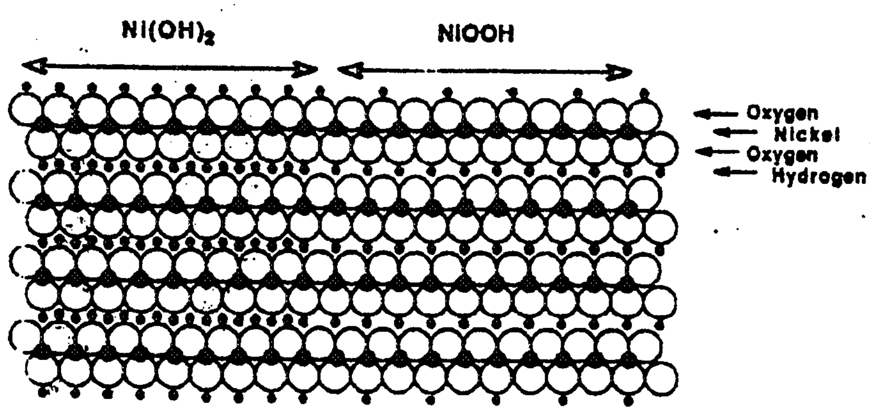
Objectives

- Identify atomic-level signatures of electrochemical activity of the active material on the Ni positive plate of Ni-H_2 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-H_2 batteries.

Charge/Discharge of (α,β)-Ni(OH)2 / (γ,β)-NiOOH Couples







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.

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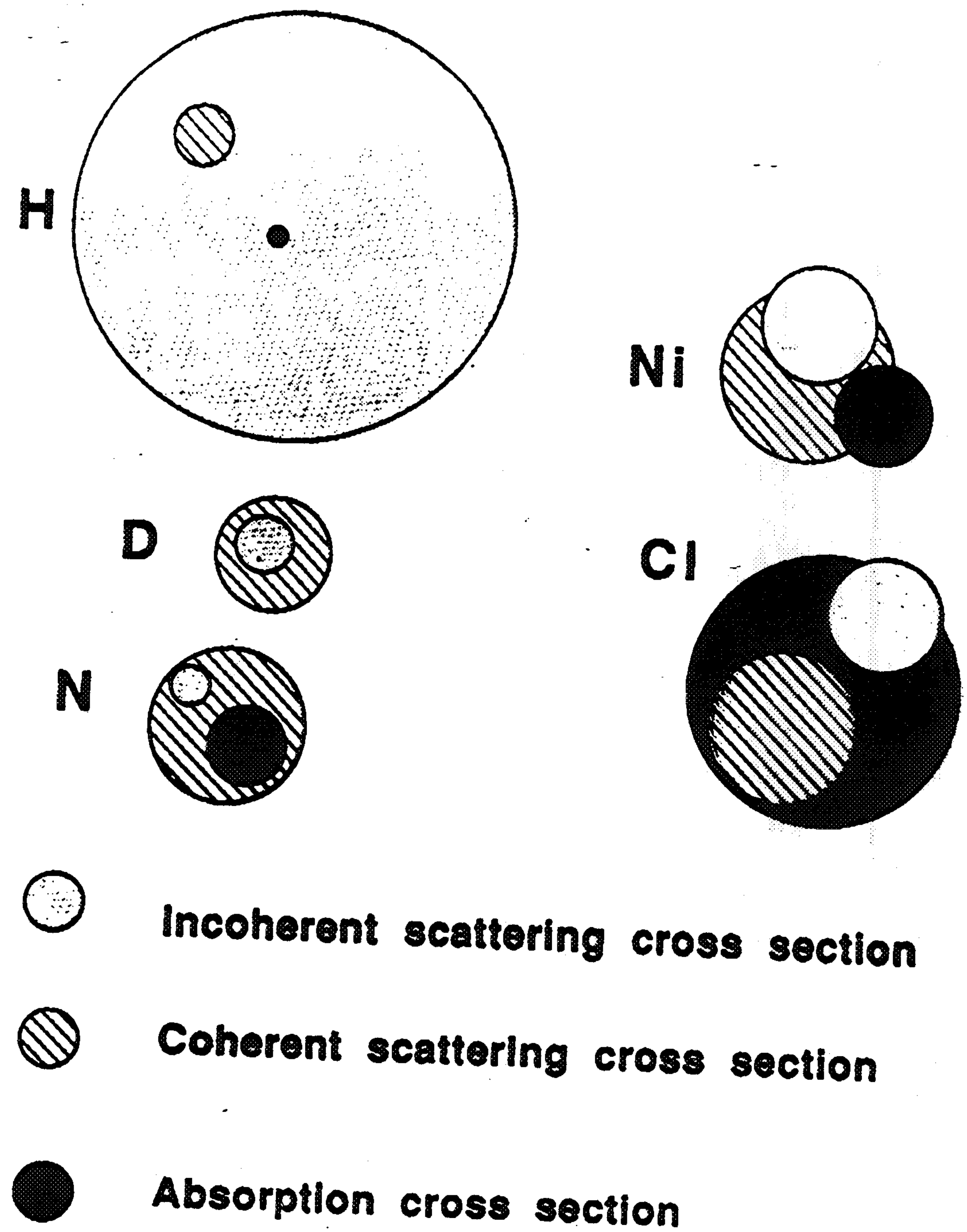
H
Ni
D
Cl
N
Incoherent scattering cross section
Coherent scattering cross section
Absorption cross section

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;.ΔE = 50 - 4000 cm^{-1}
  - 12-24 hrs. data collection time
  - T=15K

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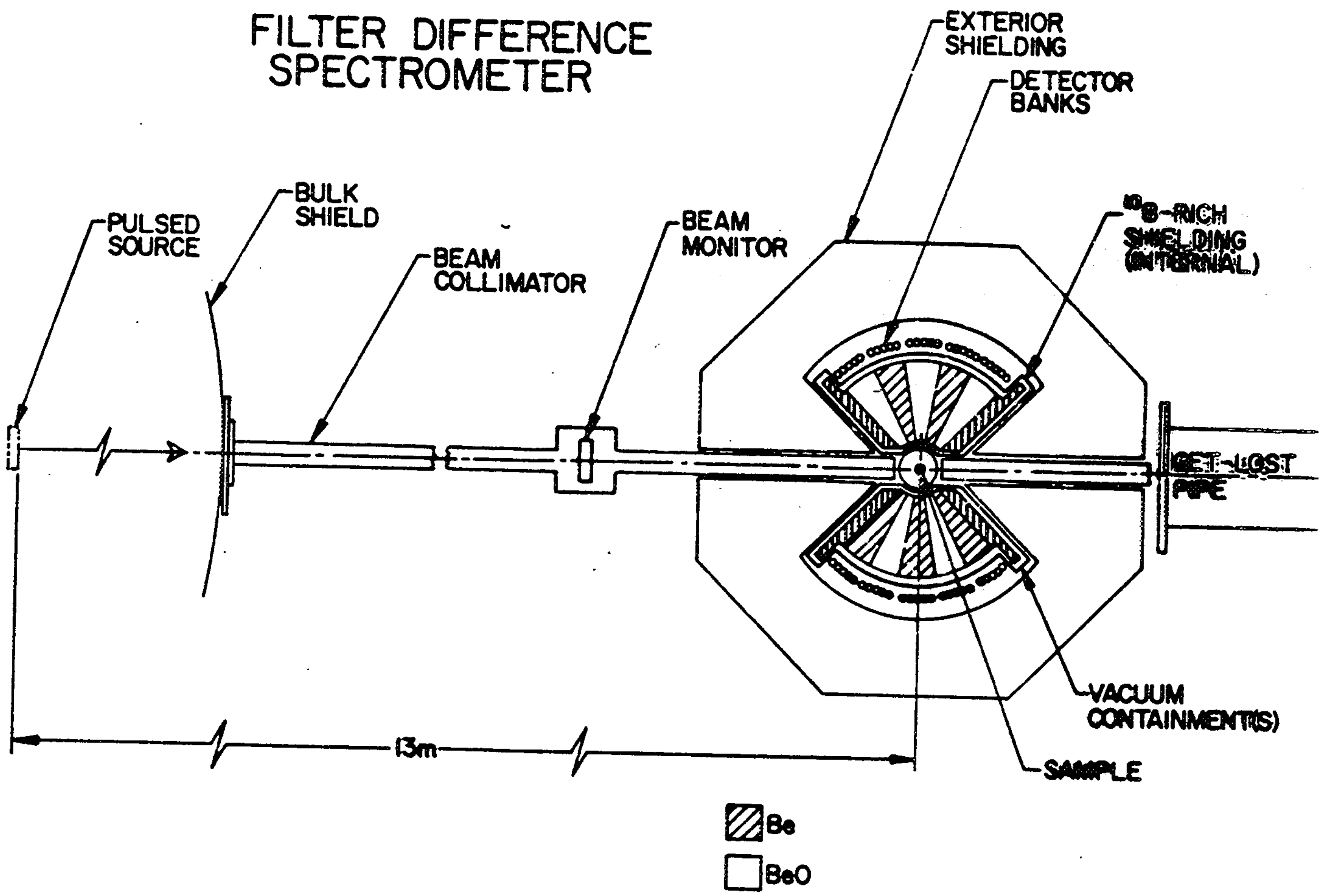
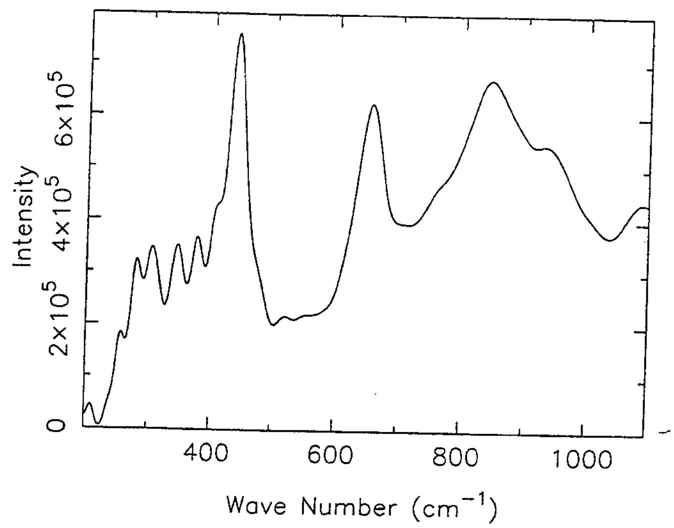
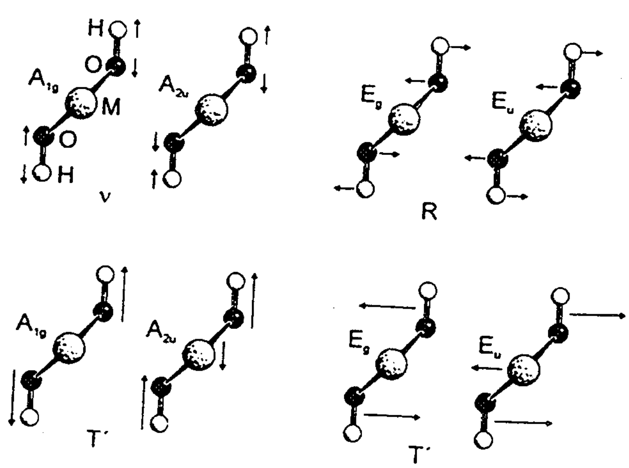

FILTER DIFFERENCE SPECTROMETER
EXTERIOR SHIELDING
DETECTOR BANKS
10B-RICH SHIELDING (INTERNAL)
BULK SHIELD
PULSED SOURCE
BEAM MONITOR
BEAM COLLIMATOR
GET-LOST PIPE
VACUUM CONTAINMENT(S)
SAMPLE
13m
Be
BeO

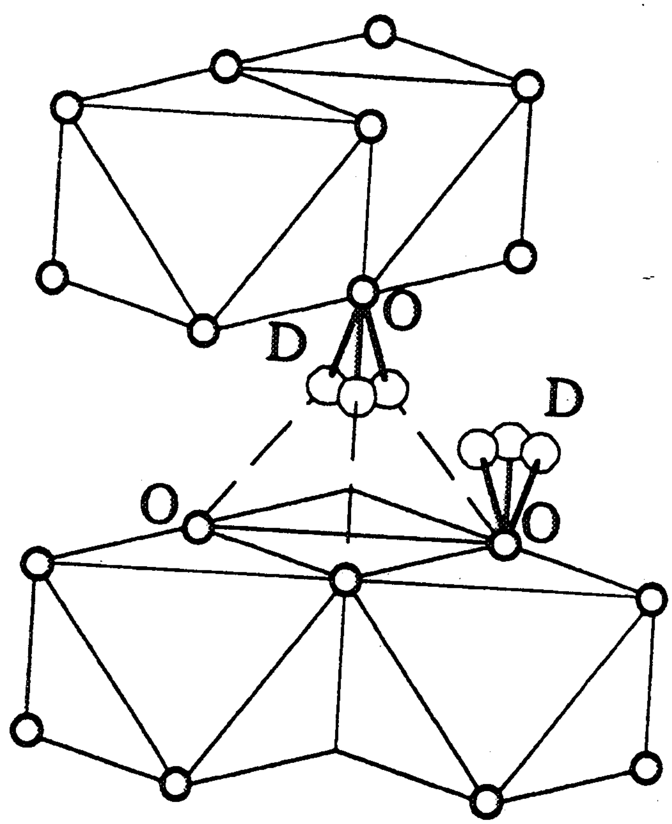
Assignment of β-$Ni(OH)_2$ vibrational bands





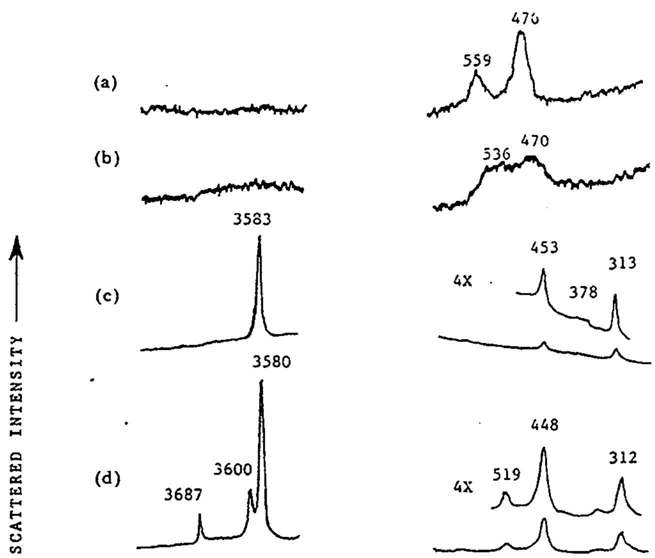
INS (cm^{-1})	IR, Raman (cm^{-1})	Assignment
315,290	318	ν(NiO); A_{1g}
358	350	δ(ONiO); E_u
390		ν(NiO); A_{2u}
451,412	449	δ(ONiO); E_g
	452	accoust. + E_u
	530	
673		γ(OH) E_u
867		γ(OH) E_g
929		

Hydrogen disorder in brucite structures



Raman Scattering Spectra of Ni electrode materials

B. C. Cornilsen and collaborators



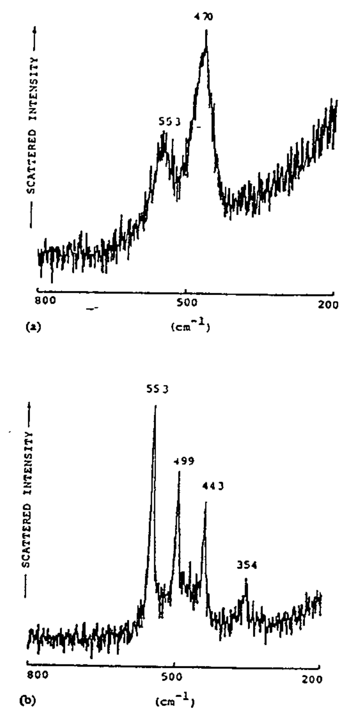
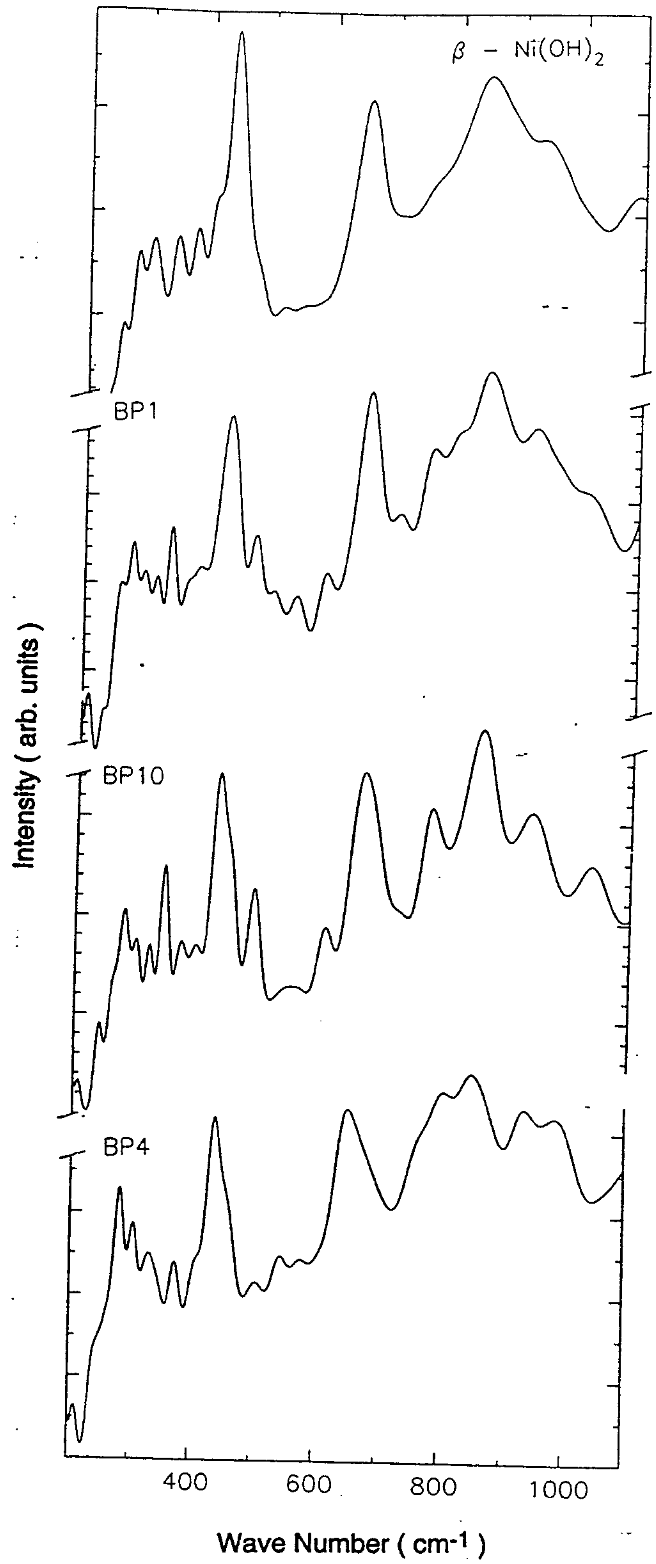


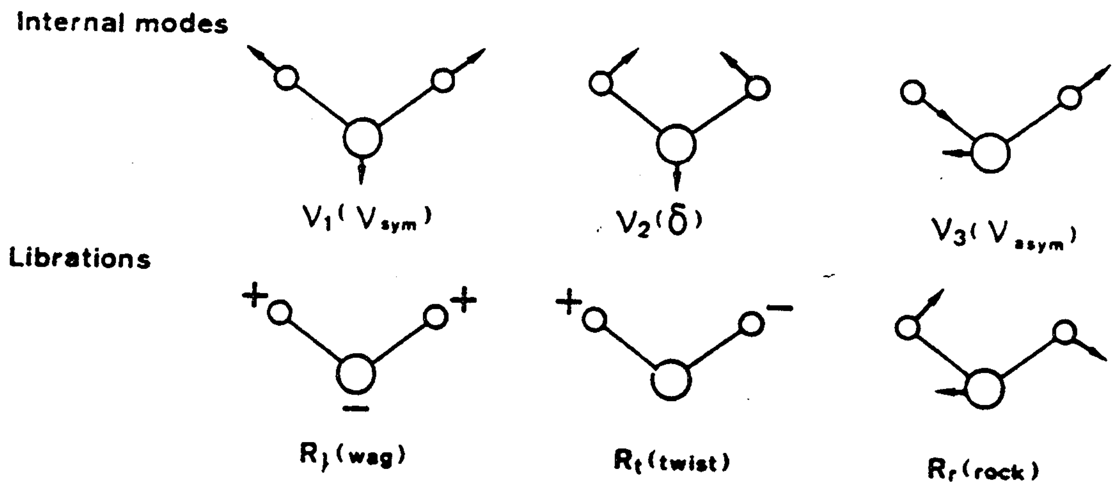
Fig. 1. Raman spectra of nickel electrode active mass and model compounds. (a) Charged γ active mass; (b) discharged α active mass; (c) recrystallized β-$Ni(OH)_2$; (d) first precipitate β-phase·

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

KOH Concentration		Number of Cycles
BP1	21 %	38,191
BP4	31 %	3,286
BP10	23.5%	28,495



Vibrational Modes of Hydration Water

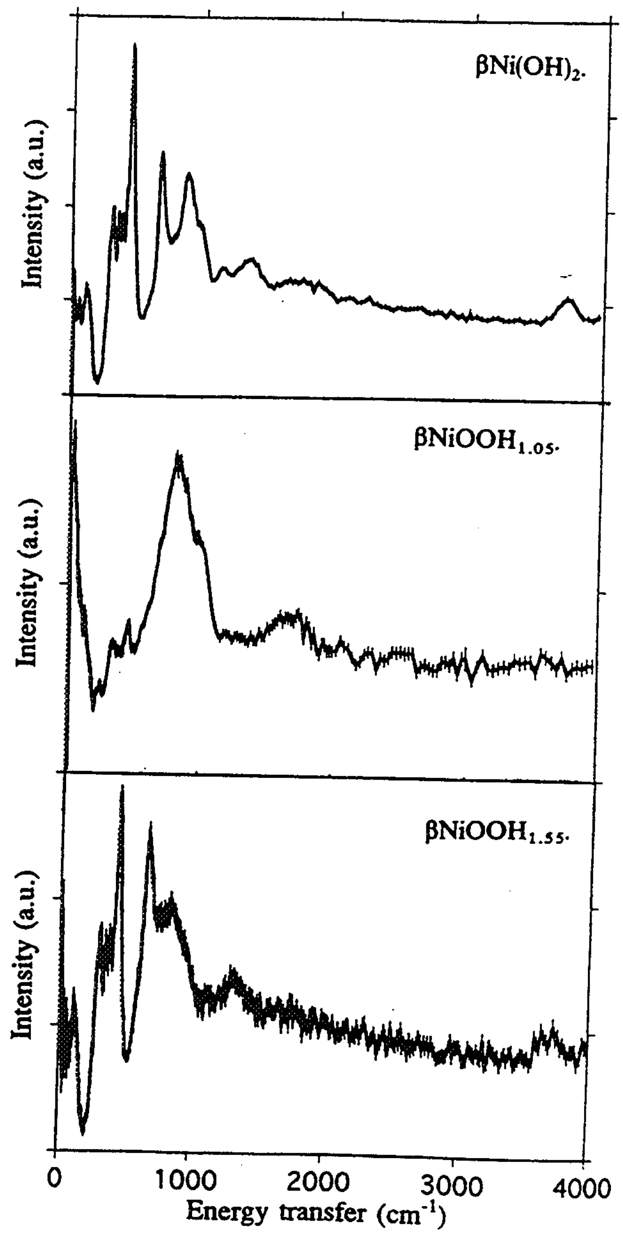


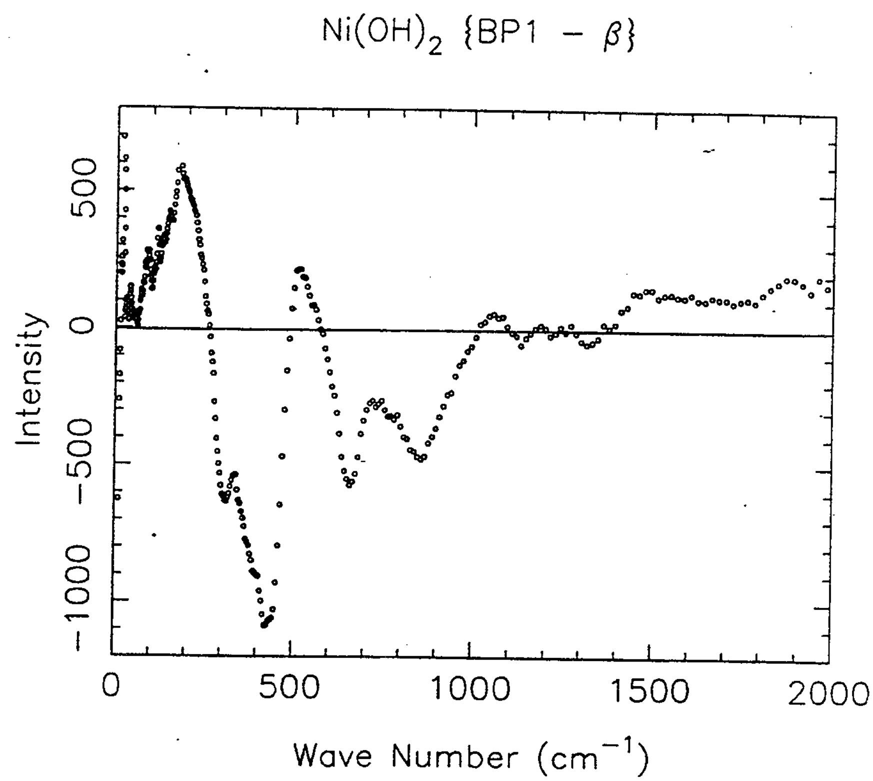
frequency ranges (cm^{-1})

stretching modes (v)	3600 - 3000
bending modes (δ)	1660 - 1590
librations (R)	1050 - 350
translatory modes (T)	350 - 100

INS Spectra of Reference Compounds

F. Fillaux et al., Physica B 213&214, 637 (1995)

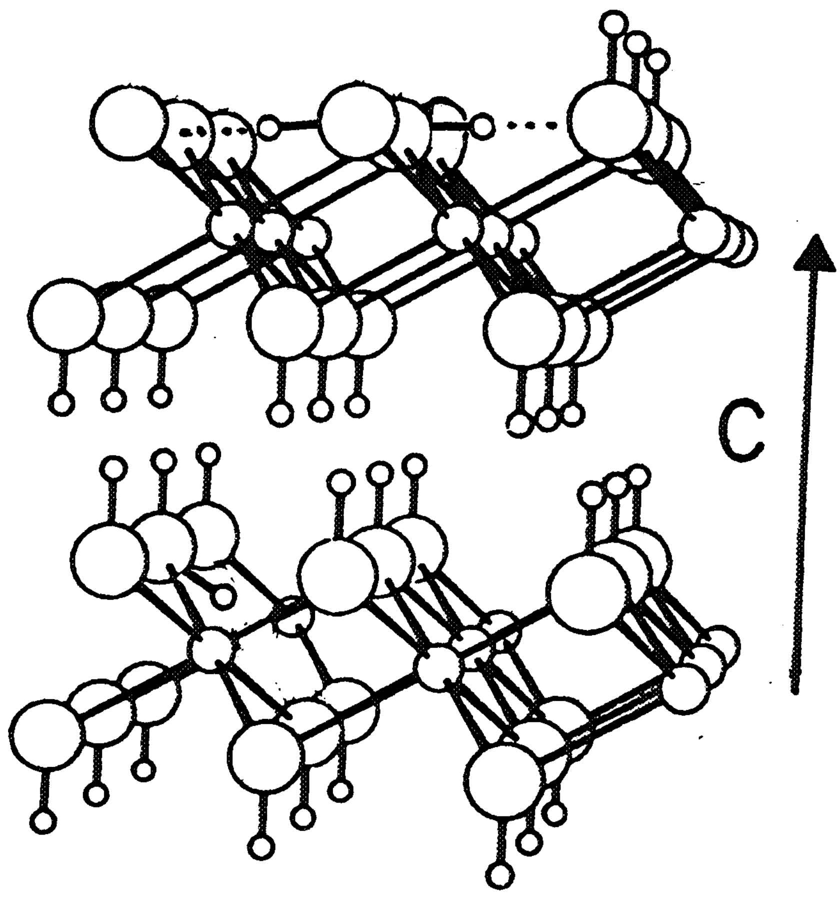



Ni(OH)2 {BP1 – β}
Intensity
500
0
–500
–1000
0
500
1000
1500
2000
Wave Number (cm⁻¹)

INS results

- discharged materials are mainly β-Ni(OH)$_2$
- changes in the Ni-O stretching and bending regions:
  - a decreases from 3.13 Å (β-Ni(OH)$_2$) to 2.89Å (β-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_2O)
- protons in O-H···O hydrogen bonds: β-NiOOH

Structural Models for Hydrogen in NiOOH and bound H_2O



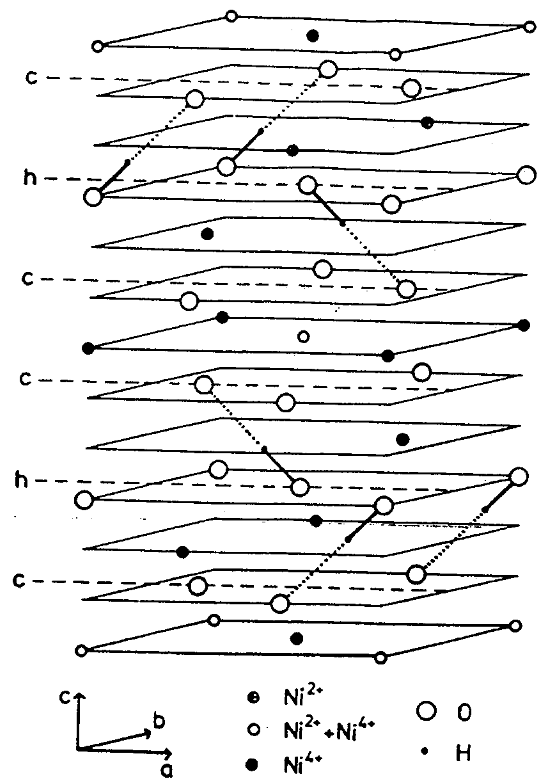


FIGURE 2
Schematic representation of the structure of Ni_2O_3H

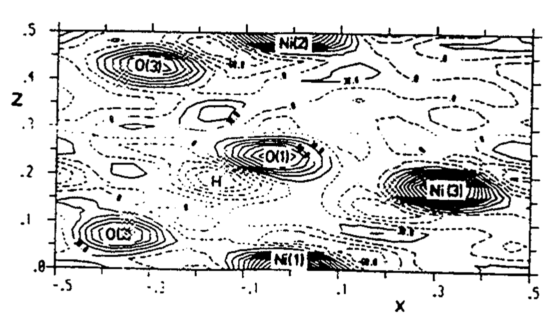


FIGURE 3
Fourier section, y = 0, based on observed intensities and calculated phases

Conclusions

- (1)Irreversible formation of NiOOH; scales with number of cycles
- (2) additional protons are bound in the lattice to form Ni-(H_2O) 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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