

# IN SITU NEUTRON DIFFRACTION STUDY OF THE NICKEL OXYHYDROXIDE ELECTRODE

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Nickel based alkaline batteries are, in spite of the emergence of the lithium technology, still widely used, their domain of application being extremely large and ranging from portable electronics to electric vehicles or space applications. Even if these batteries have been in use for more than a century, our understanding of the mechanisms and phases involved in the charge-discharge processes of the positive Nickel Oxyhydroxide Electrode (NOE) is still not complete. Indeed, a phenomenon such as the so-called “second plateau” is detrimental for the electrochemical performance of the NOE, but its origin is still controversial. The aim of our study was to follow by in situ neutron diffraction the charge/discharge process for the NOE. Experiments were conducted both on the D1B and D20 diffractometers at ILL. Cells specifically designed for in situ neutron powder diffraction in alkaline media [1] (Fig. 1) were prepared with electrode materials with different phases/oxidation state and particle size. The evolution of the phases involved in the redox process was followed along charge/discharge cycles, with special attention in the transition to the “second plateau”. Given the fact that the crystal structure for some of the phases involved in the NOE is not known, batches of reduced and oxidized “model phases” were chemically prepared to serve as references during the experiment. The syntheses were done by usual chemical means to yield nickel hydroxides and oxyhydroxides and also in deuterated media to yield deuteriooxides and oxydeuteriooxides, as neutron diffraction experiments are made in deuterated media to avoid the diffusion resulting from the interaction of protons with neutrons. The presence of deuterium is found to greatly affect the intensity of the lower angle peaks for the  $\beta$ -Ni(OH)<sub>2</sub> phase but not for the other studied phases. The experiment was also complicated by the fact that very crystalline phases that are easier to observe by neutron diffraction have very poor electrochemical performances. On the contrary, samples with small particle size present higher performances (kinetics) but result in broader diffraction peaks more difficult to observe. Nevertheless, we were able to follow the phase transformations taking place upon cycling of some NOEs, focussing on the discharge process. Interesting differences were observed depending on the nature of the oxidized samples. We were able to confirm our previous results indicating direct reduction of  $\gamma$ -NiOOH into  $\beta$ -Ni(OH)<sub>2</sub> (Fig. 2) during the second discharge plateau. [2,3] Nevertheless, this second plateau was also observed during in situ cycling of a  $\beta$ -Ni(OH)<sub>2</sub> without being associated to such a phase transformation, as also observed by Léger et al. [4] In summary, our observations seem to support a diverse origin for this plateau, depending on the intrinsic nature of the active material and processing of the electrode.

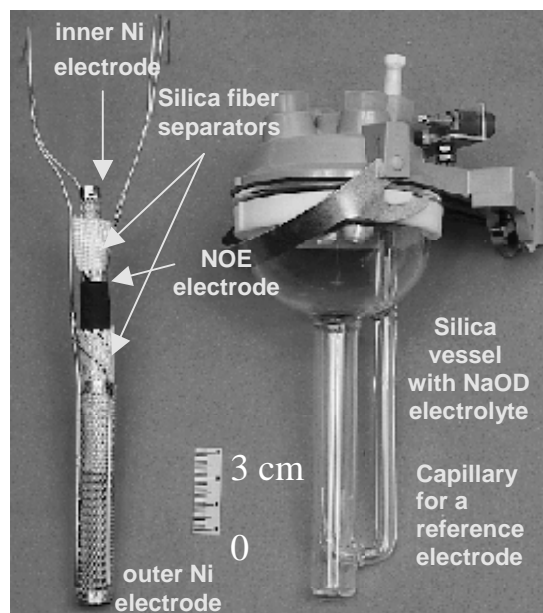


Figure 1. Electrochemical cell used for the in situ neutron diffraction experiments conducted on the NOE electrode.

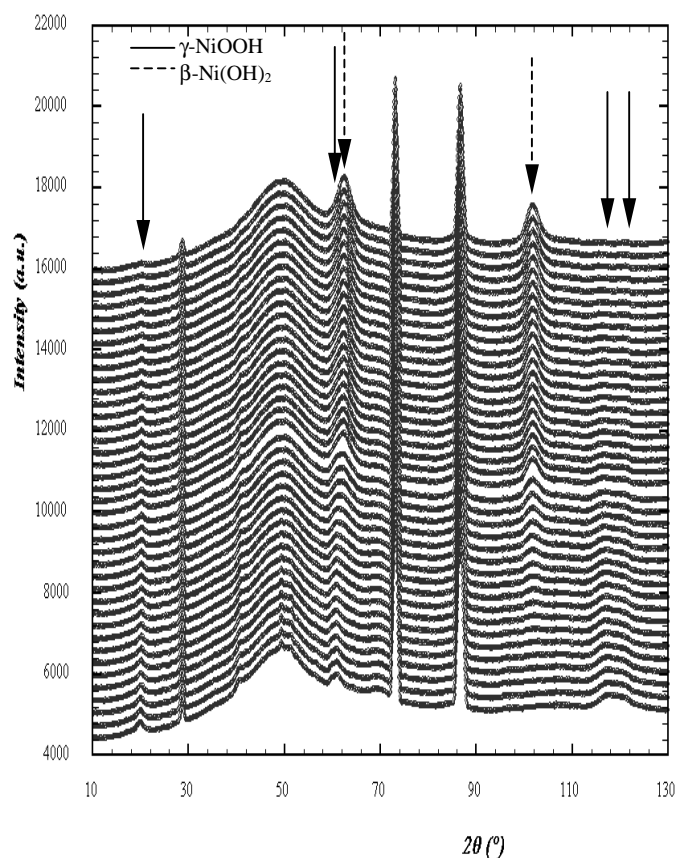


Figure 2. Neutron diffractograms corresponding to the in situ reduction of  $\gamma$ -NiOOH into  $\beta$ -Ni(OH)<sub>2</sub> where the phase transformation can be observed. The peaks corresponding to both phases are indicated, the other being due to diverse components of the electrochemical cell.

## References

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