

## Supplementary information

### The nickel battery positive electrode revisited: stability and structure of the $\beta$ -NiOOH phase.

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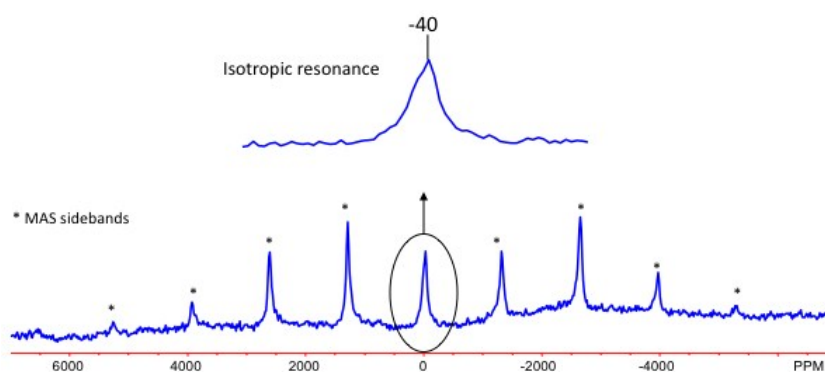
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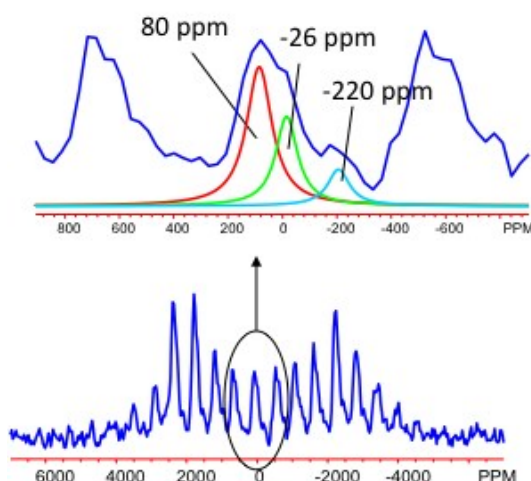
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#### Ageing of $\beta$ -NiOOH

(a)



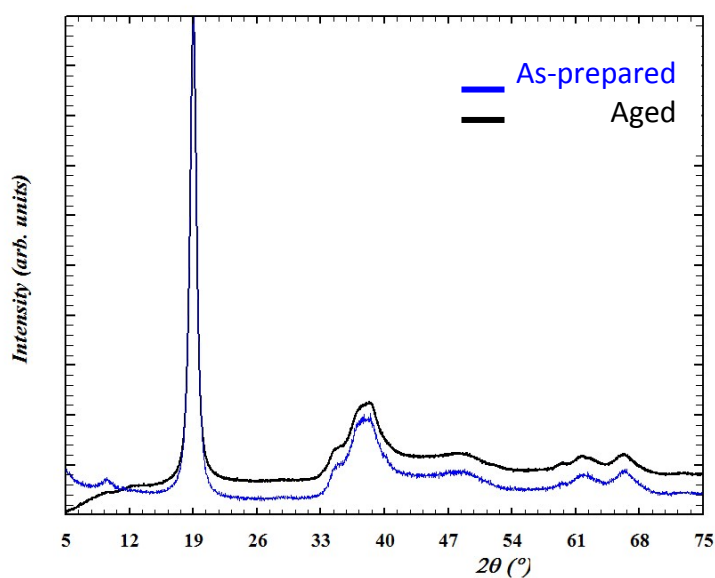
(b)



**Figure S1.** The  $^2\text{H}$  NMR rotor synchronized Hahn-echo spectra of (a)  $\beta$ -Ni(OD)<sub>2</sub> acquired with a MAS frequency of 48 kHz with an evolution time of two rotor periods, and (b)  $\beta$ -Ni(OOD) acquired with a MAS frequency of 17.5 kHz and an evolution period of one rotor period.

The spectrum of  $\beta$ -Ni(OOD) shown in Figure S1(b) is taken from a sample prepared by chemical oxidation of  $\beta$ -Ni(OH)<sub>2</sub> in aqueous solution using NaClO as oxidizing agent and further deuterated by agitating for 6h a suspension of the powder in D<sub>2</sub>O. This sample gives a spectrum that is qualitatively similar given the errors associated with the deconvolution of the overlapping resonances. <sup>1</sup>H NMR spectra were also acquired of the same batch of  $\beta$ -Ni(OOH) used for the neutron diffraction experiments with a time elapse of a few years but we did not observe the peak at approximately -44 ppm.

Figure S2 shows the evolution of the diffraction pattern of the same sample used in the neutron diffraction experiment but also measured with a time elapse of a few years. While the main reflections exhibit little variation, the peak at  $2\theta \approx 9.3^\circ$  has almost vanished. The disappearance of this peak, indexed as (001) reflection in C2/m space group, is indicative of a structural change in which the doubling of the unit cell is almost completely lost. This change could be at the origin of the different P:T ratio obtained in the NMR experiment of this sample.



**Figure S2.** XRD diffraction patterns of a sample of  $\beta$ -NiOOH measured as-prepared (blue) and a few years later.

According to the metastability of the TP2 polymorph as calculated by DFT, a possible explanation to these changes could be the progressive transformation towards the more stable P3 polymorph. This transformation would involve shearing of the layers so as to lead to an AABCC oxygen stacking sequence. Our hypothesis is that this is the origin of the variations in the intensity ratios of the approx. 75 ppm to -44 ppm resonance. A partial transformation has occurred in the sample measured by NMR, so that it consists of a mixture of both polytypes, as the transformation is incomplete. This transformation may be exacerbated by the second deuteration procedure. Whether both polytypes are separated in different regions or appear as local stacking faults cannot be ascertained.

Implicit in this hypothesis is the assignment of the 75 ppm resonance to the P environment. To explore this further we now consider the local environments in these different polymorphs. The environments in these materials proposed based on the DFT calculations and experimental structural investigations comprise D-O-Ni<sub>3</sub> local environments (i.e., a deuteron connected to an oxygen coordinated to three Ni<sup>2+</sup> ions) but differ in the specific H-O-Ni bond angles. Shifts of Ni<sup>2+</sup> and Ni<sup>3+</sup> containing materials are challenging to analyze by using simple arguments based on bond angles as, by analogy with Li-containing materials, Li/D-O-Ni<sup>2/3+</sup> interactions with 180° bond angles (involving a direct delocalization of unpaired electron spin density in the e<sub>g</sub> orbitals) give rise to large positive shifts, while Li/D-O-Ni<sup>2/3+</sup> interactions with 90° angles give rise to smaller negative shifts, with intermediate bond angles giving intermediate shifts that will be smaller in magnitude but that could be either positive or negative in value.<sup>1</sup> Smaller shifts are usually seen for Ni<sup>3+</sup> vs. Ni<sup>2+</sup> materials. The Jahn-Teller distortion for Ni<sup>3+</sup> further complicates the analysis, the shift strongly depending on the occupancy of the e<sub>g</sub> orbitals that are involved in the hyperfine interaction. Deuterons in a stoichiometric crystalline sample of  $\beta$ -Ni(OD)<sub>2</sub>, a material that adopts the brucite structure, resonate at -40 ppm (Figure S1 (a)), the three D-O-Ni bond angles in this material all being 119.5°. Similar bond angles are expected for the P3 phase. The deuteron in a T site, since it is likely to be H-bonded to an oxygen in the layer above will have different bond angles. Angles of 102, 135, and 136° are predicted from the neutron diffraction structure, the first angle resulting in a more negative shift while the latter two resulting in more positive shifts (ignoring the effect of a static Jahn Teller distortion). Clearly more DFT calculations of the NMR shifts are required to make definitive assignments, since quite subtle changes in structure are involved. These will also need to take the effect of the dynamics of the Jahn Teller distortion into account.<sup>2</sup> An assignment of the P site to the 75 ppm resonance is only justified if the delocalization mechanism dominates over the 90° (polarization) mechanism at an angle of close to 119.5°. Although these assignments must remain tentative, they do not detract from the main message that emerges from the NMR spectra, namely that more than one deuteron environment exists in these materials.

[1] D. Carlier, M. Menetrier, C.P. Grey, C. Delmas and G. Ceder, *Phys. Rev. B*, **67**, 174103, (2003).

[2] D. S. Middlemiss, A. J. Illott, R. J. Clément, F. C. Strobridge and C. P. Grey, in preparation.