

## MS42-P01 | PHASE DIAGRAM AND REDOX BEHAVIOR OF (Nd/Pr)<sub>2</sub>NiO<sub>4+δ</sub> ELECTRODES EXPLORED BY IN SITU NEUTRON POWDER DIFFRACTION DURING ELECTROCHEMICAL OXYGEN INTERCALATION

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Oxygen intercalation/deintercalation in Pr<sub>2</sub>NiO<sub>4+δ</sub> and Nd<sub>2</sub>NiO<sub>4+δ</sub> was followed by *in situ* neutron powder diffraction during electrochemical oxidation/reduction, in a dedicated reaction cell at room temperature [1]. For both systems three phases, all showing the same line-width, were identified. The starting phases, Pr<sub>2</sub>NiO<sub>4.23</sub> and Nd<sub>2</sub>NiO<sub>4.24</sub>, considered with an average orthorhombic *Fmmm* symmetry, although both show a slight monoclinic distortion, get reduced in a 2-phase reaction step to tetragonal intermediate phases with  $0.07 \leq \delta \leq 0.10$  and *P4<sub>2</sub>/ncm* space group, which on further reduction transform, again in a 2-phase reaction step, towards the respective stoichiometric (Pr/Nd)<sub>2</sub>NiO<sub>4.0</sub> phases, with *Bmab* space group. Electrochemical oxidation does, however, not proceed fully reversibly for both cases: while the re-oxidation of Nd<sub>2</sub>NiO<sub>4+δ</sub> is limited to the tetragonal intermediate phase with  $\delta = 0.10$ , the homologous Pr<sub>2</sub>NiO<sub>4+δ</sub> can be re-oxidized up to  $\delta = 0.17$ , showing orthorhombic symmetry. For the intermediate tetragonal phase, we were able to establish for Pr<sub>2</sub>NiO<sub>4.09</sub> complex anharmonic displacement behaviour of the apical oxygen atoms, as analysed by single crystal neutron diffraction and Maximum Entropy Analysis, in agreement with a low-T diffusion pathway for oxygen ions, activated by lattice [2-3].

[1] M. Ceretti *et al.*, *Inorg. Chem.*, (2018), 57, 8, 4657-4666

[2] M. Ceretti *et al.*, *J. Mat. Chem. A*, (2015), 21140-21148.

[3] A. Piovano *et al.*, *Phys. Chem. Chem. Phys.*, (2016), 17398-17403