German Conference for Research with Synchrotron Radiation, Neutrons and Ion Beams at Large Facilities



Contribution ID: 417

Type: Talk

Phase diagram and redox behavior of (Nd/Pr)2NiO4+δ electrodes explored by in situ neutron powder and synchrotron single crystal diffraction during electrochemical oxygen intercalation

Monday, 17 September 2018 12:00 (15 minutes)

Oxygen intercalation/deintercalation in Pr2NiO4+ δ and Nd2NiO4+ δ was followed by in situ neutron powder and single crystal synchrotron diffraction during electrochemical oxidation/reduction, in dedicated reaction cells [1]. For both systems three phases, all showing the same line-width, were identified.

The starting phases, Pr2NiO4.23 and Nd2NiO4.24, 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 $\leq \emptyset \leq 0.10$ and P42/ncm space group, which on further reduction transform, again in a 2-phase reaction step, towards the respective stoichiometric (Pr/Nd)2NiO4.0 phases, with Bmab space group. Electrochemical oxidation does, however, not proceed fully reversibly for both cases: while the re-oxidation of Nd2NiO4+ δ is limited to the tetragonal intermediate phase with $\delta = 0.10$, the homologous Pr2NiO4+ δ can be re-oxidized up to $\delta = 0.17$, showing orthorhombic symmetry. For the intermediate tetragonal phase, we were able to establish for Pr2NiO4.09 complex anharmonic displacement behavior for the Pr2O2 rock salt layer, as analyzed by single crystal neutron diffraction and Maximum Entropy Analysis, in agreement with a low-T diffusion pathway for oxygen ions, activated by low energy phonon modes [2-4]. References:

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[3] A. Piovano, A. Perrichon, M. Boehm, M. R. Johnson, W. Paulus, Phys. Chem. Chem. Phys., 18 (2016) 17398-17403

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Session Classification: Micro symposium 1

Track Classification: MS1 In-situ and in-operando studies with special focus on energy materials and catalysis