



Contribution ID: 417

Type: Talk

Phase diagram and redox behavior of (Nd/Pr)₂NiO_{4+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 Pr₂NiO_{4+δ} and Nd₂NiO_{4+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, Pr₂NiO_{4.23} and Nd₂NiO_{4.24}, 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 $0.07 \leq \delta \leq 0.10$ and P42/ncm space group, which on further reduction transform, again in a 2-phase reaction step, towards the respective stoichiometric (Pr/Nd)₂NiO_{4.0} phases, with Bmab space group. Electrochemical oxidation does, however, not proceed fully reversibly for both cases: while the re-oxidation of Nd₂NiO_{4+δ} is limited to the tetragonal intermediate phase with $\delta = 0.10$, the homologous Pr₂NiO_{4+δ} can be re-oxidized up to $\delta = 0.17$, showing orthorhombic symmetry. For the intermediate tetragonal phase, we were able to establish for Pr₂NiO_{4.09} complex anharmonic displacement behavior for the PrO₂ 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:

- [1] M. Ceretti, O. Wahyudi, G. André, M. Meven, A. Villesuzanne, W. Paulus, *Inorg. Chem.* 57,8, 4656-66 (2018)
- [2] M. Ceretti, O. Wahyudi, A. Cousson, A. Villesuzanne, M. Meven, B. Pedersen, J. M. Bassat, W. Paulus, *J. Mat. Chem. A*, 3,42 (2015), 21140-21148
- [3] A. Piovano, A. Perrichon, M. Boehm, M. R. Johnson, W. Paulus, *Phys. Chem. Chem. Phys.*, 18 (2016) 17398-17403
- [4] Paulus, H. Schober, S. Eibl, M. Johnson, T. Berthier, O. Hernandez, M. Ceretti, M. Plazanet, K. Conder, C. Lamberti, *J. Am. Chem. Soc.* 130 (47) (2008) 16080-85,

Primary author: Prof. PAULUS, Werner (Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM)

Co-authors: Dr WAHYUDI, Olivia (Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM, Université de Montpellier, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France); Dr CERETTI, Monica (Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM,); Dr MAITY, Avishek (Institute for Physical Chemistry, Georg August University Göttingen, Outstation at Heinz Meier Leibniz Zentrum (FRM(II))); Dr DUTTA, Rajesh (Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM); Dr MEVEN, Martin (Institute of Crystallography, RWTH Aachen University and Jülich Centre for Neutron Science (JCNS) at Heinz Maier-Leibnitz Zentrum (MLZ)); Dr CHERNYSHOV, Dmitry (Swiss Norwegian Beamlines SNBL@ESRF)

Presenter: Prof. PAULUS, Werner (Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM)

Session Classification: Micro symposium 1

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