ESRF	**Experiment title:** Co and Ni doped MoO_2 nanoparticles as electrode materials for Li ion batteries - mechanistic aspects of dopants inclusion in the MoO_2 lattice	**Experiment number**: CH-3771
Beamline: BM01	**Date of experiment**: from: 19.06.2013 to: 25.06.2013	**Date of report**: 31.08.2013
Shifts: 18	**Local contact(s)**: Wouter van Beek	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Ofer Hirsch*, Malwina Staniuk*, Niklaus Kraenzlin*, Dorota Koziej*, Markus Niederberger

ETH Zurich, Department of Materials, Laboratory for Multifunctional Materials, Wolfgang-Pauli-Str. 10, 8093 Zurich, Switzerland

Report

The results obtained during the beamtime were published:

Aliovalent Ni in MoO_2 Lattice- Probing the Structure and Valence of Ni and Its Implication on the Electrochemical Performance

Ofer Hirsch, Guobo Zeng, Li Luo, Malwina Staniuk, Paula M Abdala, Wouter van Beek, Felix Rechberger, Martin J Süess, Markus Niederberger, Dorota Koziej

Chemistry of Materials 2014, 26, 4505, **DOI:** 10.1021/cm501698a

Abstract:

"Here, we present a synthesis of MoO2 nanoparticles doped with 2 at% of Ni in a mixture of acetophenone and benzyl alcohol at 200 °C. Based on in situ X-ray absorption near-edge structure (XANES) and ex situ extended X-ray absorption fine structure (EXAFS) measurements at Ni K-edge and Mo K-edge, we discuss scenarios on how the "doping" reaction, that is, the incorporation of Ni in the MoO2, proceeds. We can clearly exclude the formation of NiO or Ni nanoparticles. Moreover, within the resolution of our in situ XANES experiments, we observe that the ternary compound Ni:MoO2 nucleates directly in the final composition. Although the local structure around the Ni ion adopts the MoO2 crystal structure pointing at the substitution of tetravalent Mo by Ni, we find that Ni remains divalent. This aliovalent substitution results in the relaxation of the local structure, which is additionally reflected in the slight shrinking of the total volume of the unit cell of Ni:MoO2. Interestingly, such a small amount of divalent Ni has a tremendous effect on the performance of the material as anode in Li-ion batteries. The initial discharge capacity of Ni:MoO2 based anodes almost doubles from 370 mAh/g for MoO2 to 754 mAh/g for Ni:MoO2 at 0.1 C (1 C = 300 mA/g). Additionally, we observed an atypical increase of capacity for both MoO2 and Ni:MoO2 anodes upon cycling with increasing cycling rate."