

# HOMO- AND HETEROVALENT DOPING OF NANOSTRUCTURED LiCoPO<sub>4</sub>

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Among the olivine cathodes LiMPO<sub>4</sub> (M = Fe, Mn, Co, Ni), LiCoPO<sub>4</sub> is characterized by high working potential (~4.8 V vs. Li/Li<sup>+</sup>) and relatively high theoretical specific capacity (167 mAh/g). Many efforts have been done to improve its low intrinsic electronic conductivity and Li-ion diffusion, including carbon coating, cation doping and particle size reduction. The atomistic simulations showed favorable energies only for divalent ion substitution for M<sup>2+</sup> at M site in the olivines but are against the possible substitution of polyvalent ions on either M or Li sites [1]. Homogeneous doping does not require any charge compensation and hence does not increase the number of charge carriers. On the contrary, polyvalent doping is energetically unfavorable, suggesting that these ions are unstable within the LiMPO<sub>4</sub> crystal structure. This leads to formation of secondary phases.

In the present study, the effect of homo- (Fe<sup>2+</sup>) and heterovalent (V<sup>3+,4+</sup>) doping on the structure and electrochemistry of LiCoPO<sub>4</sub> has been studied. Fe and V doped LiCoPO<sub>4</sub> were prepared by mechanochemically assisted carbothermal reduction of Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> using a high-energy AGO-2 planetary mill. The activated reagent mixtures were subsequently annealed at 750 °C under Ar flow. The samples were characterized in detail by XRD using Rietveld refinement, FTIR and Mössbauer spectroscopy, SEM, TEM, EDX, NEXAFS (BESSY II), galvanostatic cycling and GITT. Phase transformations upon cycling were studied by *in situ* synchrotron diffraction (PETRA III, DESY).

All as-prepared LiCo<sub>1-y</sub>Fe<sub>y</sub>PO<sub>4</sub> (0 ≤ y ≤ 1) samples are single-phase solid solutions, crystallized in the orthorhombic structure (S.G. *Pnma*). All Fe ions are in 2+ oxidation state. Fe-doped LiCoPO<sub>4</sub> samples show improved electrochemical performance due to enlarged 1D Li diffusion channels and the reduced cell volume changes upon Li extraction/insertion. A systematic decrease in the Co<sup>2+</sup>/Co<sup>3+</sup> average potential vs. y is observed. *In situ* synchrotron diffraction shows that upon charging of LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub>, a two-phase mechanism changes for a single-phase one.

When doped with vanadium, the (1-y)LiCoPO<sub>4</sub>/yLi<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> composites were formed. The EDX elemental maps showed that LiCoPO<sub>4</sub> and Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> are finely mixed with the Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> phase predominantly segregated at the surface. According to NEXAFS, V ions in the composites are in 3+,4+ oxidation state. On charge-discharge curves, all plateaus, characteristic of phase transformations for LiCoPO<sub>4</sub> and Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, are maintained. In contrast to LiCo<sub>1-y</sub>Fe<sub>y</sub>PO<sub>4</sub> solid solutions, no noticeable shift of the Co<sup>2+</sup>/Co<sup>3+</sup> redox potential was observed for the composites.

[1] C.A.J. Fisher, V.M.H. Prieto, M.S. Islam, J. Chem. Mater. 20 (2008) 5907–5915.

[2] N.V. Kosova, O.A. Podgornova, E.T. Devyatkina, V.R. Podugolnikov, S.A. Petrov, J. Mater. Chem. A 2 (2014) 20697-20705.