

Phase transitions occurring upon lithium insertion-extraction of LiCoPO_4

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Olivine-like metallophosphates LiMPO_4 ($M = \text{Mn, Fe, Co, Ni}$) are perspective cathode materials for lithium-ion batteries. Previously, in-situ synchrotron diffraction was applied to study the mechanism of the electrochemical lithium extraction from LiCoPO_4 and $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ [1]. The delithiation of LiCoPO_4 was reported to result in the formation of the lithium-poor phase, which is isostructural to the pristine compound. Nevertheless, due to the high polarisation of the electrochemical cell the charging was not completed. Additionally, only very small amount of lithium was reinserted in the cathode during discharge.

Here we performed complete charge-discharge cycle of LiCoPO_4 -based electrochemical cell. The in-situ electrochemical cell based on SwagelokTM-connection [2] was charged to the composition CoPO_4 as follows from the electrochemical data. The evolution of the diffraction pattern demonstrates a stepwise appearance of two new phases upon electrochemical lithium extraction (Fig.1). In the initial stage of charge the formation of a second olivine-like phase is indicated by the appearance of a second set of reflections, e.g. 200, 020 and 301 in figure 1, slightly shifted with respect to those from pristine LiCoPO_4 . This is consistent with previous reports on LiCoPO_4 delithiation [1]. The lattice parameters of this phase 2 ($a = 10.070(3) \text{ \AA}$, $b = 5.851(2) \text{ \AA}$, $c = 4.717(2) \text{ \AA}$) determined for the diffraction pattern corresponding to the extraction of 0.3 Li per formula unit LiCoPO_4 are very close to those of pristine LiCoPO_4 ($a = 10.1955(8)$, $b = 5.9198(5)$, $c = 4.6971(4) \text{ \AA}$) obtained from Rietveld refinement. After approximately 0.3 Li per formula unit LiCoPO_4 are extracted the reflections of a third phase appear. The increasing intensity of these reflections (phase 3) is accompanied by the decreasing intensity of the reflections from phase 2. During discharge, the transformation of the reflections proceeds in opposite direction in a reversible manner.

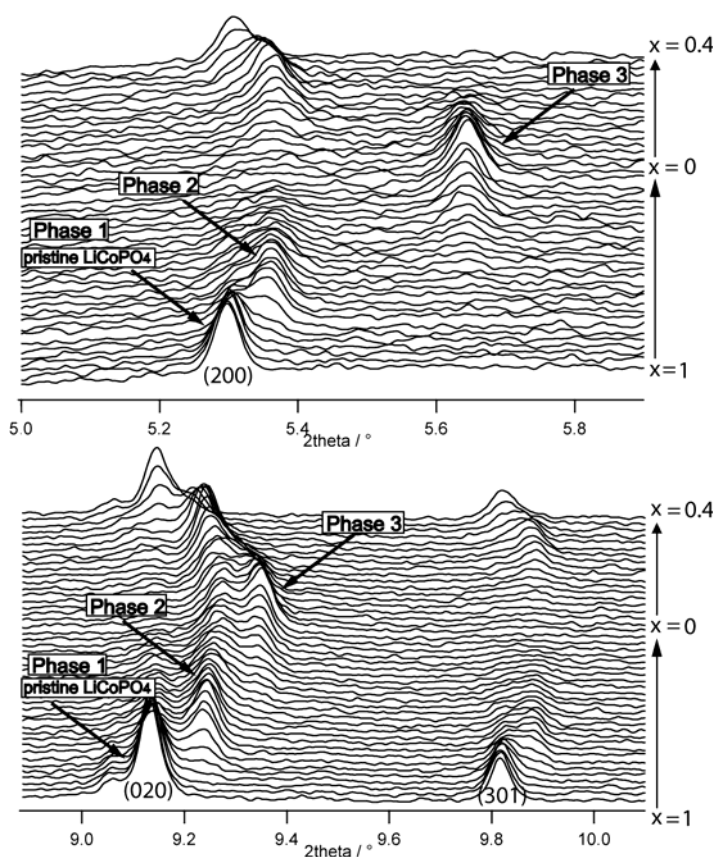


Figure 1: Selected regions in the diffraction patterns taken during the first charge-discharge of Li_xCoPO_4 . 200, 020 and 301 reflections are shown ($\lambda = 0.47189 \text{ \AA}$).

The formation of phase 3 upon lithium extraction from LiCoPO_4 has not been reported before. The only product of deintercalation was pointed out to be phase 2 with an ill-defined lithium content. The reflections of phase 3 could be indexed on the base of an orthorhombic unit cell ($a = 9.567(2) \text{ \AA}$, $b = 5.7806(9) \text{ \AA}$, $c = 4.7636(9) \text{ \AA}$). Rietveld refinement confirmed that phase 3 has the same olivine-like structure as the pristine compound.

The evolution of the cell voltage during charge-discharge of LiCoPO_4 agrees very well with two phase transitions observed by the synchrotron diffraction. During delithiation two plateaus at $0.7 \leq x \leq 1$ and $0 \leq x \leq 0.7$ in Li_xCoPO_4 were observed (Fig.2). This can be taken as a indication of lithium stoichiometry in lithium-poor phases. We believe that phase 3 is CoPO_4 with an olivine-like structure, which is unstable in air, but can be recovered under in-situ conditions. This is consistent with a amorphous character of the sample, obtained by the chemical delithiation of LiCoPO_4 [3]. Based on the extension of the first plateau in the voltage-composition the lithium content in phase 2 should be close to $x = 0.7$. Due to possible parasitic reactions at operation voltage close to 5 V vs Li/Li^+ the determination of lithium stoichiometry from electrochemical data is not reliable. Unfortunately, due to the low scattering factor of lithium for X-rays the amount of lithium could not be deduced from a refinement of the occupation factor on the Li-site. The stoichiometries of the delithiated phases have to be proved by additional techniques, especially by neutron diffraction.

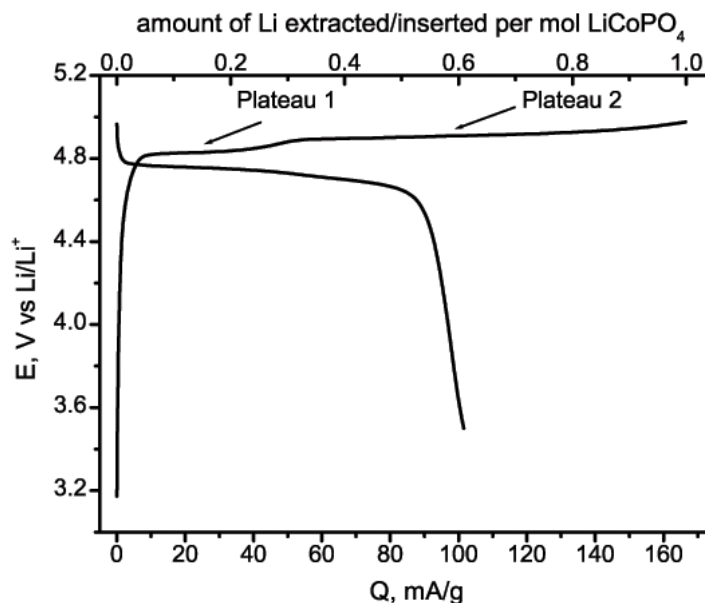


Figure 2: Voltage-composition curves taken for LiCoPO_4 -cell during galvanostatic charge-discharge at $C/6$.

References

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