The understanding of the fundamental processes during charging and discharging in a lithium ion battery (LIB) is of great interest for tailoring future electrode materials. To elucidate e.g. aging effects on a microscopic length scale, analysis is limited to a few methods. Post mortem-analysis, such as transmission electron microscopy (TEM) on battery sub-units, isolated from their electrochemical environment, is commonly applied, whereas the structural and compositional changes during cycling remain widely unexplored. Therefore, it would be high desirable to study these processes with spatial and temporal resolution in situ, i.e. under charging and discharging conditions. Here we report first analyses by means of in situ TEM in liquid environment to monitor structural changes with sub-10 nm resolution of lithium iron phosphate.

Therefore we have synthesized crystalline and carbon coated lithium iron phosphate nanoparticles (NPs) in a size range of 10–50 nm. This material is characterized by means of scanning electron microscopy, X-ray diffraction, infrared spectroscopy and elemental analysis. To evaluate its properties as a cathode material, a LIB cell with a lithium anode and an electrolyte (lithium hexafluorophosphate in a 1:1 mixture of ethylene and diethyl carbonate) was assembled. The material is not optimized regarding its specific capacity, but showed typical cycling behavior compared to literature.

By using an in situ TEM liquid flow sample holder, the degree of lithiation was analyzed by selected area electron diffraction (SAED) and electron energy loss spectroscopy (EELS). As a first set of experiments the particles were investigated inside these liquid cells under inert gas atmosphere. Despite of gaseous layers of several micrometers, high resolution TEM as well as SAED and EELS in the low loss region were feasible. In the second set of experiments the cell was filled with water. We found that particles with diameters down to 2 nm could be imaged with a 200 nm thick water layer. The opportunities and limitations, which arise from these in situ measuring conditions, will be discussed.


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Fig. 1: Lithium iron phosphate in H$_2$O.

Fig. 2: Magnification of the blue framed area in Fig. 1.

Fig. 3: Electron energy loss spectrum for thickness determination of the red circled area in Fig. 1.

$t/\lambda = 1.11$
$t = 183$ nm