

Thermodynamics and kinetics for stabilization of conversion-type electrodes for lithium-ion batteries based on nanoscaled 3d transition metal oxides

(subproject #3)

Subproject #3: Microstructure features behind the degradation of nanocrystalline 3d transition metal oxide composites in conversion type electrodes for lithium-ion batteries^a

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The aim of the project is to improve the bad cycling stability of the electrode materials that are based on the conversion mechanism. The aim of this particular subproject is to understand the microstructure features behind the degradation of the nanocrystalline 3d transition metal oxide composites in conversion type electrodes, which is the first step to the improvement of the cycling stability of these electrode materials.

The experimental work within this subproject is focussed on the microstructure analysis using X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray and electron spectroscopy (EDX and EELS in TEM). XRD is employed for the phase analysis and for the analysis of the crystallite size and microstrain. TEM with EDX and EELS are intended for the visualisation of the morphology of crystallites, for the imaging of the cation distribution as well as for the local chemical and phase analysis. In the first founding period, we showed that the conversion and displacement reactions take place during the electrochemical cycling of the 3d transition metal oxide phases in the system Cu-Fe-O (CFO). Copper oxide is reduced to metallic copper in a conversion reaction; $\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4$ transforms to $\alpha\text{-LiFeO}_2$ during a displacement reaction (cf. Fig. 1). Although both mechanisms (conversion and displacement) led to a serious fragmentation of the crystallites, the displacement reaction could be recognized on a strong orientation relationship between the neighbouring crystallites (cf. Fig. 2).

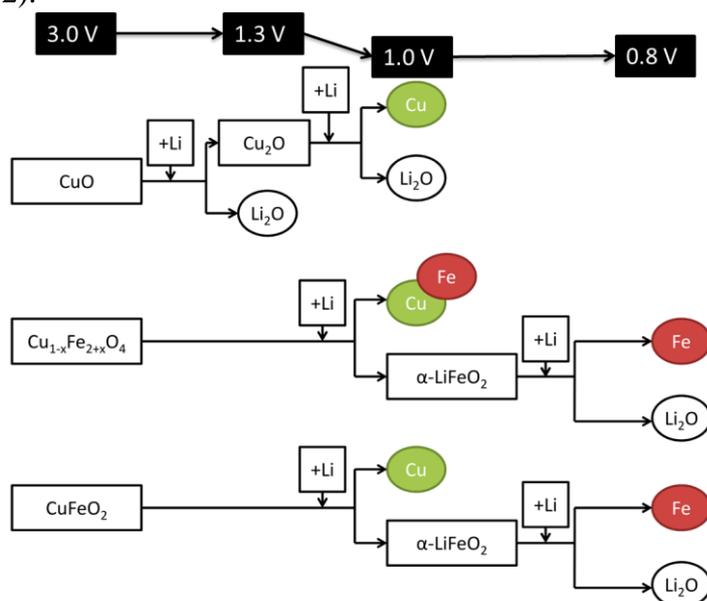


Figure 1: Schematic drawing of phases occurring during the reduction and lithiation of CFOs containing CuO (space group $C2/c$), $\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4$ (space group $Fd\bar{3}m$) and CuFeO_2 (space group $R\bar{3}m$) in the initial state.

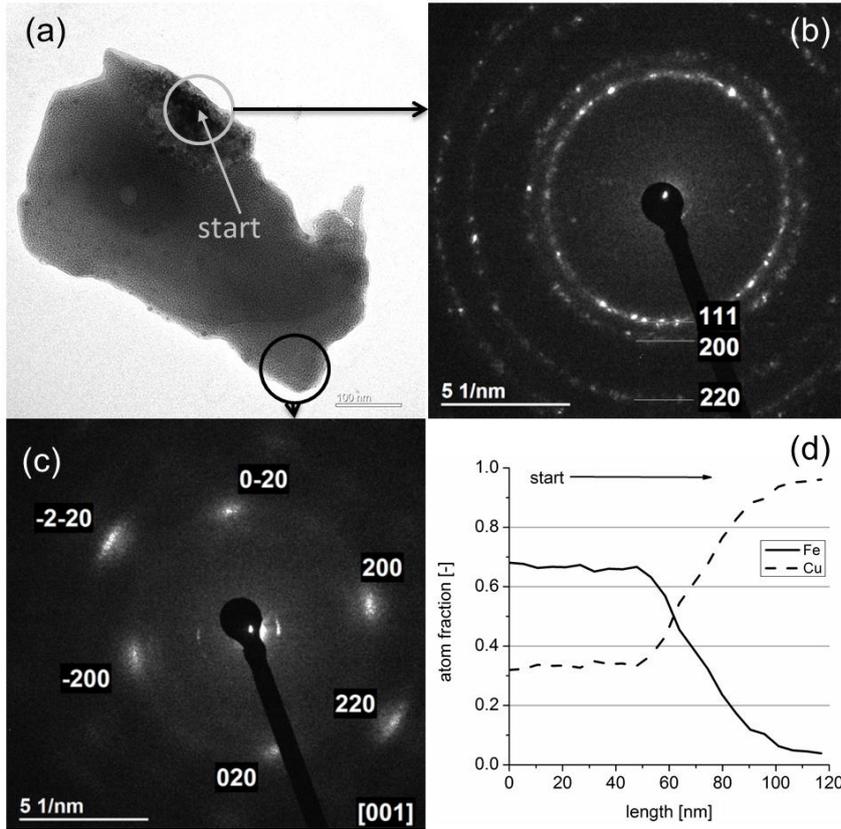


Figure 2: (a) Bright-field STEM micrograph taken on one particle of the active material in the discharge state at 0.95 V (Sample Cu:Fe = 2:1). The SAED pattern identified randomly oriented Cu nanocrystallites in the upper part of the particle (b) and strongly preferentially oriented crystallites of α -LiFeO₂ in the lower part of the particle (c). The α -LiFeO₂ crystallites were oriented along [001] with respect to the direction of the primary electron beam. The EDX line scan (d) shows the homogeneous presence of Cu in the region of α -LiFeO₂.

In the second founding period we will focus the microstructure analysis on the systems Ni-Co-O and Cu-Co-O, which shows opposite electrochemical cycling stability. For the achievement of objectives a coin cell for *in situ* XRD experiments was developed. The results from these investigations will accompany the synchrotron experiments of subproject #1.