

Abstract

The rechargeable battery technology has undergone a tremendous development since the invention of the Li-ion battery presented on the commercial market in 1991. The breakthrough of the Li-ion battery was primarily due to it surpassing the previous types of rechargeable batteries in both volumetric (watts per cm³) and gravimetric energy density (watts per kg). This resulted in a boom of portable electronics employing the Li-ion technology. The technology is now facing new challenges. In 2015, the production of Li-ion batteries for vehicles alone exceeded the total production of Li-ion batteries for electronics products measured on capacity, and in 2017 the production was again already doubled. The request for larger battery packs is therefore already dominant. At the same time, initiatives towards utilizing more renewable energy sources typically based on intermittent sources, such as solar and wind, requires effective energy storage on a large scale. Rechargeable batteries are one of the most promising readily available technologies for energy storage. But, expansion to large scale applications sets new demands on price, lifetime and safety. At this stage, understanding the active materials on the atomic scale is necessary to improve the technology further.

In this thesis, structural changes in a number of promising electrode materials for rechargeable batteries are investigated. Specifically, nanocrystalline titanium oxides, structurally disordered lithium vanadium oxides and vanadium oxide nanotubes. In particular, the structural response to Li⁺ intercalation and extraction during battery operation was investigated by so-called *operando* X-ray diffraction and total scattering.

While anatase TiO₂ accepts Li⁺ through a reversible two-phase reaction, insertion of 1 Li/Ti into the rutile polymorph results in an irreversible phase transformation to a layered α -NaFeO₂-like structure. The transformation results in loss of crystallinity and a disordered phase between the layered domains are described herein. In addition, it was found that the structure exchanges Li⁺ ions through a solid solution mechanism with remarkably small volume change.

Insertion of Li⁺ in V₂O₅ to the stoichiometric Li₃V₂O₅ composition also results in an irreversible conversion to a disordered halite structure, with a local dispersed cation ordering within the ccp oxygen lattice. Furthermore, it is shown that subsequent discharging and charging follows a two-phase mechanism and a structure for the charged disordered phase is proposed.

Another interesting vanadium oxide material, the multi-walled nanotubes, has been examined as electrode for both Li- and Mg-ion batteries. Systematically and in-depth analysis of the structural response to Li⁺ and Mg²⁺ ions insertion in this material has been described here for the first time. The investigations prove that the structural changes are drastically dependent on the nature of the templating molecules or ions residing in the inter-layer space of the pristine tubes, and that certain conditions will lead to destruction of the multi-layer-structure of the tubes, while leaving the individual VO_x layers intact.

Overall, this work contributes with insight into the mechanisms of structural disordering in materials for rechargeable batteries caused by electrochemical insertion and extraction of the working ions. The work also points in new directions for which these mechanisms can be further explored.