In situ analysis of cathode materials for Li-ion batteries with X-ray absorption spectroscopy

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Li-ion batteries with high energy and power density are key components of differnt electronic products and most likely the source of energy for many autonomous electrical power consumers including the automotive industry. Sustainable development and the demand for the rechargeable batteries with a higher energy density foster new approaches towards higher energy materials. A new class of silicate and titanate based materials Li_2MSiO_4 and Li_2MTiO_4 (M=Mn, Fe, Co, V, Ni) [1-4] including non-aliovalent doping with phosphorus, aluminium or fluorine are the most promising candidates for cathode materials, which could deliver higher energy densities and longer lifetime than the currently available materials. In addition, these materials are cheaper, safer, environmental friendly, thermally more stable, and consist of elements abundant in nature.

In situ X-ray absorption spectroscopy analysis with synchrotron radiation can provide crucial information on the mechanism of charge transfer and the dynamics of the battery operation on the atomic level, and clarify the role of metal cations in the electrochemical activity of the material [1-4]. In this presentation we demonstrate the feasibility and reliability of in situ XANES analysis as a tool to monitor gradual changes of oxidation state of transition-metal cations during lithium exchange, i.e. during charging and discharging of the Li-ion battery. The strengths and weak points of such an in-situ XANES analysis are demonstrated with several examples of new Li_2MSiO_4 and Li_2MTiO_4 cathode materials. Different approaches including a linear-combination fitting of XANES spectra, and possible sources of systematic errors are discussed. The information is complemented by simultaneous in situ EXAFS analysis which provides information on deformations of the local structure around the transition metal cations, accompanying the change of their valence state. The degree of reversibility of the process in one or several cycles is exposed.

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