Operando Raman measurements on $LiNi_{0.5}Mn_{1.5}O_4$ cathodes for Li-ion batteries

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Lithium ion batteries play a key role in many consumer applications such as cellular phones, laptops, digital cameras and tablets. In addition, there is a high demand for electric mobility. Zero-emission mobility and the storage of renewable energy, whose generation is temporarily fluctuating, are upcoming challenges in the next decades. $LiNi_{0.5}Mn_{1.5}O_4$ is a promising candidate for high-energy-density cathodes in lithium-ion batteries. The material has not yet achieved any commercial success, as there remain problems with capacity fade after extended charge and discharge cycling. In order to enable improvements, it is necessary to understand the underlying fundamental processes in the material. In this study, we present detailed *operando* Raman measurements, recorded during the charge and discharge process of LNMO in the range of 3.5 to 5.0 V *vs.* Li/Li^+. The primary goal of this is to clarify the oxidation states of nickel and manganese and the accompanying structural changes during electrochemical cycling via Raman spectroscopy. Furthermore we analysed the cathode surface with Raman spectroscopy, if there are any side products or surface layer on the cathode after 300 cycles. We present *operando* Raman measurements from a study of the potential-resolved structural evolution of $LiNi_{0.5}Mn_{1.5}O_4$ as a cathode material during the charging and discharging process. Using Raman only two phases can be distinguished in this system, namely $LiNi_{0.5}Mn_{1.5}O_4$ and $Ni_{0.5}Mn_{1.5}O_4$. Furthermore, the dynamics of the structural changes between the $LiNi_{0.5}Mn_{1.5}O_4$ and the $Ni_{0.5}Mn_{1.5}O_4$ phase differs significantly for lithiation and delithiation. Long-term measurements show a change on the cathode surface and the consumption of PF_6^- anions. The results demonstrate that Raman spectroscopy is a strong tool for performing *operando* measurements and analysing structural changes on the surface of the material.

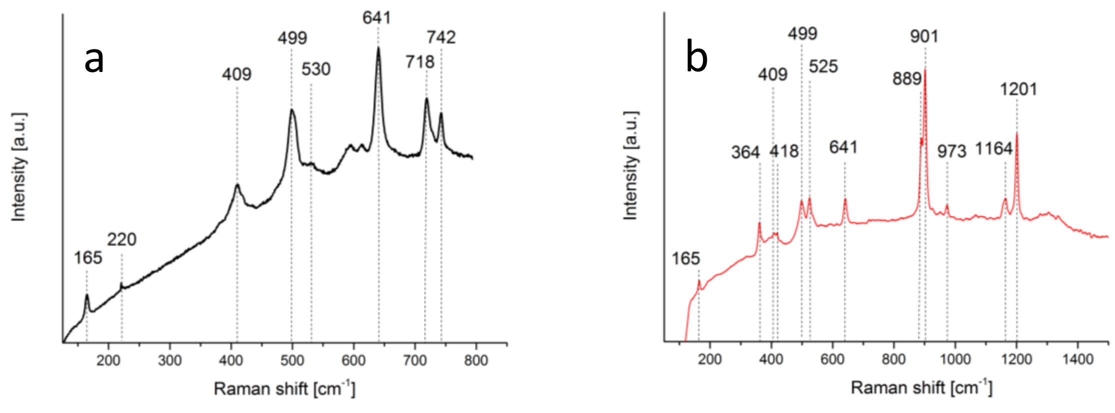

Fig.1: a) Raman measurement of o-LNMO after 2 cycles b) after 300 cycles in LP30 vs. Li/Li^+.