In-situ structural features of Li intercalated molybdenum trioxide with layer- and fiber-like frameworks

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Molybdenum trioxides can be grown with either layer- or fiber-like structure (see Fig. 1 showing the Raman spectra of these phases). In this work, we present the *in-situ* XRD and Raman features were carried out during the intercalation-deintercalation process to investigate the structural modifications upon discharge-charge reaction. MoO_3 was found to react readily with lithium forming two well-defined discharge products, according to the x-ray data, which are different, but similar to the known high temperature Li_2MoO_3 phase. However, MoO_3 only reacts with about 1.5 Li/Mo. The electrochemical lithium insertion into MoO_3 frameworks with layer- and fiber-like structure was investigated. The discharge-charge profiles of anhydrous MoO_3 exhibit a gravimetric capacity of 280 mAh/g. Upon lithiation of Li_xMoO_3, the electronic conductivity increases from 10^{-4} S/cm for x=0 to ca. 10^{-1} S/cm for $0.3 \leq x \leq 0.9$. However, when the cell was recharged, reoxidation of Mo produces a resistive compound which induces a large polarization of the cell at the end of the charge. MoO_3 can be considered such as a good self-limiting over-charge material.

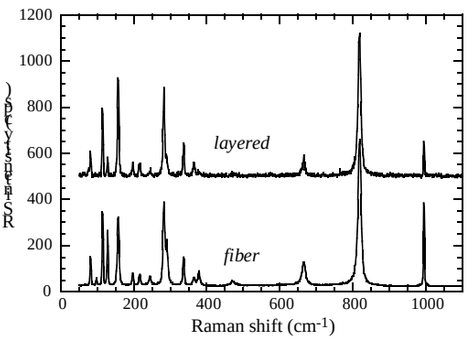

Fig. 1. Raman spectra of layered and fiber-like MoO_3.

To confirm the above suggestion, the structural changes occurring in the Li_xMoO_3 cathode materials during Li intercalation were followed by in situ x-ray diffraction measurements using a specially designed electrochemical cell. Results shown in Fig. 2, i.e. shape and positions of the Bragg lines, indicate that the framework structure of MoO_3 is almost unchanged during discharge reaction up to 1.5Li/Mo. However, one can observe the formation of a ternary phase, i.e. appearance of Bragg peaks at ca. $2\theta=47°$ for x>0.5Li/Mo. The new Bragg peaks disappears upon delithiation, this indicating continuous structure reorganization, which indicate complete reversibility of the insertion-deinsertion process for anhydrous material in the potential range 3.5-1.2 V.

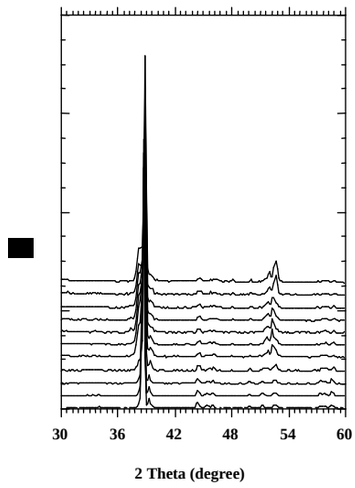

Fig. 2. In-situ x-ray patterns of anhydrous Li_xMoO_3 as a function of the degree of lithium insertion during the first discharge.