Mechanical Degradation of $LiMn_{1.95}Al_{0.05}O_4$ Electrodes

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Lithium ion batteries are promising candidates for future electrical energy storage. For many applications the long term reliability of these systems is of very high importance. We have chosen $LiMn_{1.95}Al_{0.05}O_4$ (LAMO) as a model system for an insertion material and performed electrochemical tests and electron microscopic investigations to investigate degradation effects. Conventional composite electrodes were made from a commercial LAMO powder and tested against lithium to up to 1000 cycles. Using a dedicated SEM technique and sample preparation procedure it was possible to exclude reactions with atmosphere [1] and to be able to repeatedly monitor a selected section of the electrode over the course of many cycles.

In the experiments, a capacity loss was found and a significant amount of mechanical damage was detected which mainly consists of cracks running through the electrode particles (figure 1). Such cracks create additional surfaces but also can lead to the loss of electrical contact. This damage is associated with mechanical loading due to volume changes that occur during the insertion and extraction of lithium. In the experiments it was shown that cracks can form and grow during lithiation as well as during delithiation of LAMO.

A quantitative analysis of larger sections of the electrode was used to determine fracture probabilities for different particle sizes. It was found that the probability of fracture increases strongly with increasing particle size. Small particles with sizes below 200 nm almost never exhibit cracks and particles with diameters beyond 4 µm almost always show damage after several hundred cycles.

Experiments at different rates and state of charge have been performed to further investigate the underlying mechanisms of this mechanical phenomenon. In the presentation possible mechanisms that can account for the observations are introduced and the recorded data is used to assess models [1-3] such as ‘electrochemical shock’, weakest link concepts and phase transformations as a source of stress.

Besides fracture, an additional mechanism was identified at higher number of cycles. Here shear deformation of particles occurred. This type of damage appears to be based on dislocation mediated plasticity and increases with increasing number of cycles. The evolution and the form of this damage show similarities to fatigue damage as known from metals.

In this presentation, details on the damage mechanism will be given, its effect on the electrochemical performance will be addressed and suggestions will be made in order to improve the long term reliability of LAMO based electrodes.

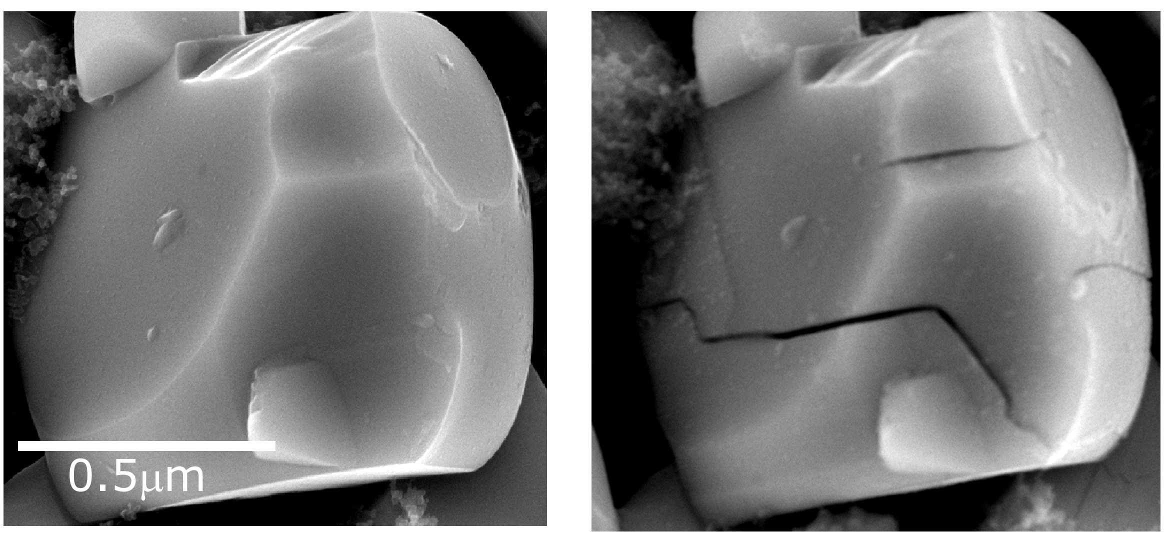

Figure 1: LAMO electrode particle before and after 1000 cycles at 1C.

References

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