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First Steps Towards In-Situ Heating Experiments of Monolithic $LiNiO_2$ Particles in O_2 Atmosphere

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Layered transition metal oxides of the form $Li(Ni_{1-x-y}Co_xMn_y)O_2$ (NCM) and $Li(Ni_{1-x-y}Co_xAl_y)O_2$ (NCA) are the current choice for cathode materials in lithium-ion batteries (LIBs) that deliver specific capacities of more than 170 mAh g^{-1} [1]. To further increase the capacity of the batteries, as well as to reduce their cost, researchers are trying to increase the Ni content to 80% and more. However, the drawback is a reduced cycling stability of the battery, amongst others due to particle cracking because of anisotropic volume change of the polycrystalline particles during (de-)lithiation [2]. These issues can be mitigated by using single (or monolithic) crystals instead of polycrystalline ones [3]. The electrochemical performance of the samples can be further enhanced by optimizing the surface morphology and structure with an annealing step at elevated temperatures [4]. To prevent oxygen loss from the surface these annealing steps are often conducted in an oxygen atmosphere [5].

To further improve the preparation conditions, a thorough understanding of the annealing mechanisms on a structural level is of utmost importance. Thus, we investigate $LiNiO_2$ (LNO) as a model system for Ni-rich layered transition metal oxides in an in-situ transmission electron microscopy setup to observe structural changes of monolithic LNO particles during annealing in an oxygen atmosphere in this work.

To mimic the real-world annealing process of LNO particles in our in-situ experiment as closely as possible, an agglomerate of monolithic particles with a size of approximately 3-4 μm^3 was chosen for examination compared to a single primary particle having a size of only a few hundred nanometers. While a sample consisting of individual primary particles could be readily prepared by dispersing the particles on the heating chip of the atmosphere holder, the sample preparation of large LNO secondary particles, which was established in this work, is rather challenging and goes significantly beyond a regular FIB lift-out.

Initially, a 25 µm x 10 µm x 2 µm large silicon lamella was cut from a Si-wafer and attached to a regular copper FIB grid, which is placed on a rotatable FIB holder. After attachment the lamella is rotated by 90° and a hole of the size of a LNO secondary particle is cut out using the focused ion beam. After rotating the lamella back to its original upright orientation, a single LNO secondary particle consisting of a few monolithic grains is picked up from a FIB-stub, on which LNO powder was sprinkled, with a micromanipulator needle and placed inside the hole (see figure 1 a). The secondary particle is then thinned down using the H-bar method [6] which leaves the lower part of the Si-lamella intact (see figure

a b). In the final step, the grid is rotated by 90° and the thinned down lamella is detached from the grid with the micromanipulator needle and finally placed flatly on the silicon nitride window of the heating chip (see figure 1 c) of the protochips atmosphere holder [7].
For the experiment the atmosphere holder is connected to an oxygen bottle. A flow valve controls the flow of oxygen between the bottle and the holder. A pressure valve controls the oxygen pressure downstream of the holder to reach atmospheric pressure of 1 bar in the holder tip.

This setup enables us to examine the surface as well as the bulk structural changes of monolithic LNO primary grains within a secondary particle structure, which is found in real-world annealing processes, using Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS).

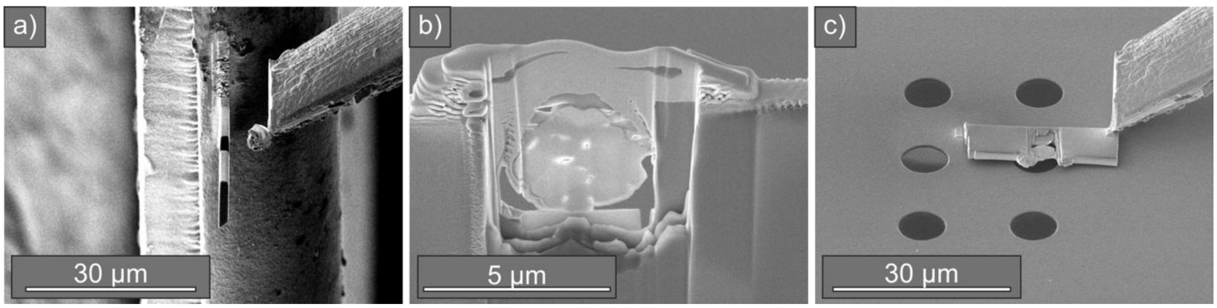

Figure 1: a) The LNO secondary particle is about to be placed inside the pre-cut hole within the Si lamella. b) Thinning process of the LNO secondary particle using the H-Bar method. c) Placing the finished sample on the silicon nitride window of the protochips heating chip.

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