

Nanoscale Electrochemical Mapping for Enhanced Battery Electrodes

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Rechargeable batteries exhibit energy density and lifetime far below their theoretical capabilities. Limitations in ionic and electronic conductivity occur at the interfaces between electrodes and electrolyte. Mastering interface control is the main challenge in battery research, in which electrochemical properties are directly related to the structural properties of the electrolyte and electrode films, i.e. crystal structure (orientation and symmetry) as well as defect structure. SPM techniques give the ability to measure the electrochemistry that takes place on the nanoscale, which can be used to elucidate structure/function relationships in battery materials with exceptional resolution (at the level of features such as individual grains, crystal facets and interfaces within the electrode layers). The development of First Order Reversal Curve current-voltage (FORC-IV) analysis [1,2] enabled the probing of nanoscale electrochemistry due to the capability to measure local ionic currents. In FORC-IV measurements, current through the sample is measured with an AFM probe in contact mode as a function of the bias waveform, a triangular wave with increasing amplitude, which allows the measurement of a variety of electrochemical processes. Depending on the rate and reversibility of these processes, this will result in hysteretic I-V curves, proportional to the electrochemical activity at given spot. Here, we show that by structural engineering of stable, epitaxial LiMn_2O_4 cathode thin films the electrochemical properties can be controlled as compared to polycrystalline samples. By changing the crystal orientation of the underlying single crystalline substrate ((100), (110) and (111)) we can control the specific orientation of the LiMn_2O_4 thin film and, therefore, the cathode surface towards the electrolyte. The loop opening map results unveil the direct relation with topography (Figure 1), showing variation in electrochemical activity for different crystal facets, defined by the Li-ion diffusion. These results provide enhanced understanding of the importance of the specific crystal facet in contact with the electrolyte as shown for truncated structures [3] and thin films [4].

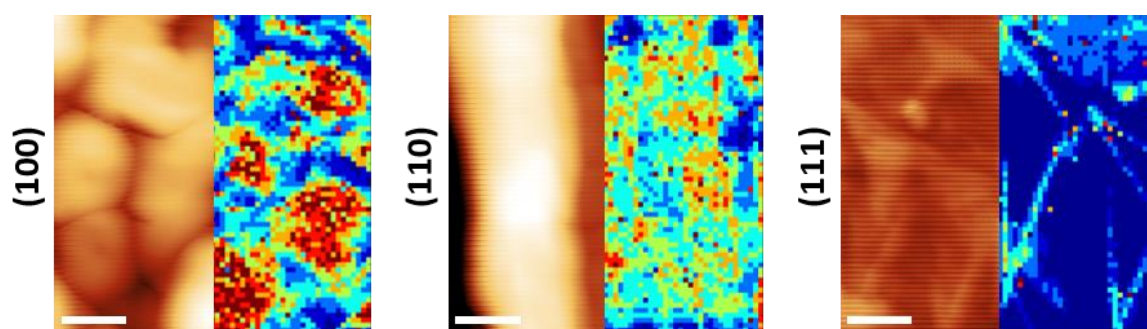


Figure 1 – Panels show topography (left) and loop opening map (right) of LiMn_2O_4 grown with the (100), (110) and (111) (left to right) orientation. Contrast indicates electrochemical activity for the different crystal facets. Scale bar is 200 nm.

References:

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