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Effect of pristine nanostructure on first cycle EC-characteristics in Li-excess cathode ceramics

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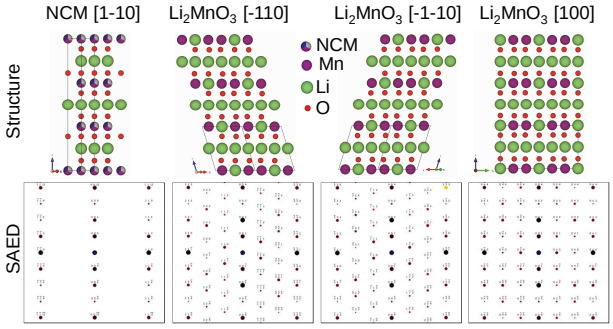
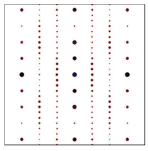
Motivation: Li-excess materials with the composition $0.5Li_2MnO_3{:}0.5Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ offer a high theoretical discharge capacity of 250 mAg^{-1} and are therefore a suitable canditate for battery powered electro-mobility. The material forms a nano composite with platelet shaped domains of Li_2MnO_3 and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (NCM) cation configurations embedded in a coherent, rhombohedrally distorted cubic closed packed oxygen (ccp-O) lattice. During the first cycle, Li_2MnO_3 is activated by the loss of oxygen and electrochemically (EC-) active $LiMnO_2$ is formed. The extent of this activation process strongly depends on the nanostructure configuration. This phenomen is investigated by correlating the nanostructure and EC-characteristics of two samples with the same composition $0.5Li_2MnO_3{:}0.5$NCM. Our results do not only show a strong dependence of the Li_2MnO_3 activation on nanostructure configuration but also suggest an EC-active Li_2MnO_3 component.

Theoretical Aspects of the Structure



Nano-domain structure: The Li_2MnO_3 components exist in three quasi-equal orientations that are coherently embedded via ccp-O lattice within the NCM matrix resulting in a combined SAED pattern:



EC-Reaction of the Formation Cycle

1. Delithiation of the NCM component:

$$0.5Li_2MnO_3 + 0.5LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 \xrightarrow[charge]{OCV-4.4V} 0.5Li_2MnO_3 + 0.5Ni_{1/3}Mn_{1/3}Co_{1/3}O_2 + 0.5Li^+ + 0.5e^-$$

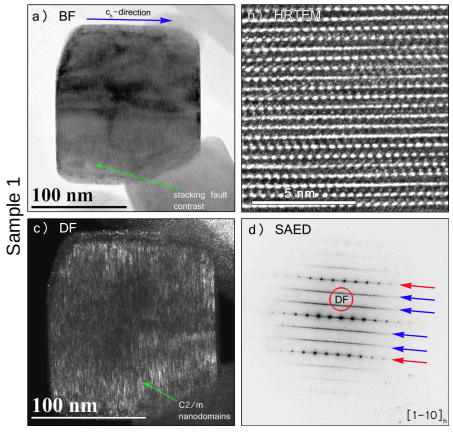
2. Activation of the Li_2MnO_3 component:

$$0.5Li_2MnO_3 + 0.5Ni_{1/3}Mn_{1/3}Co_{1/3}O_2 \xrightarrow[charge]{4.4V-4.8V} (0.5-\eta)Li_2MnO_3 + \eta MnO_2 + 0.5Ni_{1/3}Mn_{1/3}Co_{1/3}O_2 + 2\eta Li^+ + \eta(\tfrac{1}{2})O_2 + 2\eta e^-$$

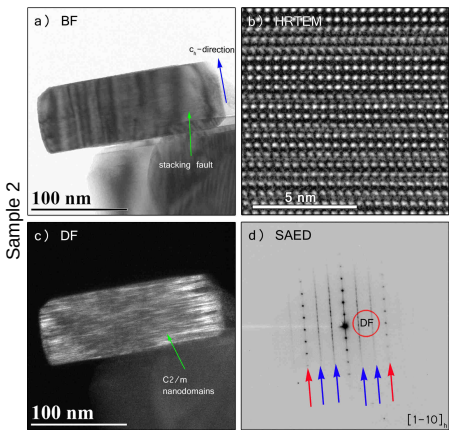
3. Lithiation and formation of $LiMnO_2$:

$$(0.5-\eta)Li_2MnO_3 + \eta MnO_2 \cdot 0.5Ni_{1/3}Mn_{1/3}Co_{1/3}O_2 + (0.5+\eta)Li^+ + (0.5+\eta)e^- \xrightarrow[discharge]{4.8V-2.0V} (0.5-\eta)Li_2MnO_3 + \eta LiMnO_2 + 0.5LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$$

TEM Analysis



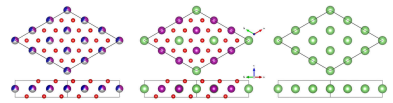
Sample 1: very thin platelet shaped Li_2MnO_3 nano domains are evenly dispersed in the particle.



Sample 2: thicker platelet shaped Li_2MnO_3 nano domains with larger diameter evenly dispersed in the particle.

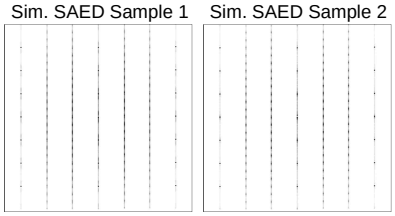
DIFFaX Simulations and Synchrotron-XRD Data

Modelling



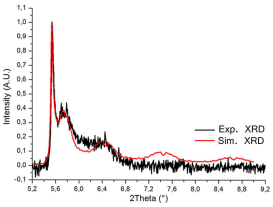
Defined layers for DIFFaX modelling. Stacking sequences were chosen according to TEM results.

Sim. SAED Sample 1 | Sim. SAED Sample 2



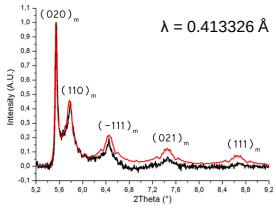
DIFFaX is used to estimate Li_2MnO_3 domain thickness and diameter by implementing defect free Li_2MnO_3 stacking sequences in randomly stacked Li_2MnO_3 and NCM layers.

Sample 1



Defect free stacking sequences of 1-5 Li_2MnO_3 layers and a layer diameter of 100 nm has been used.

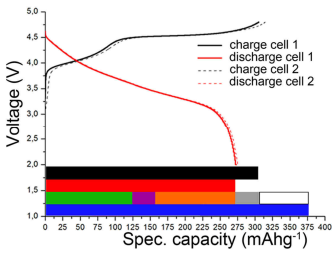
Sample 2



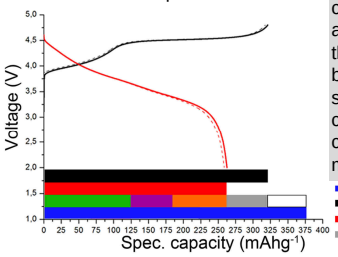
Defect free stacking sequences of 5-35 Li_2MnO_3 layers and a layer diameter of 180 nm has been used.

EC-Characterisation

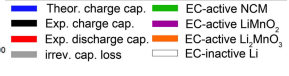
Sample 1



Sample 2



The value for theoretical charge capacity is related to overall amount of Li ions. The theoretical capacity for NCM is based on accessible oxidation states of Ni and Co. The capacity contributions were calculated using the presented mechanism.



Conclusion: The TEM analysis shows considerable differences in domain thickness and diameter for the two stoichiometrically identical samples. The differences have been veryfied by DIFFaX simulations to synchrotron powder XRD patterns. The EC-analysis shows that the given reaction mechanism is not complete and cannot explain the anomalous capacity of an EC-acitve Li_2MnO_3 component. Correlating nano structure with EC-characteristics shows that $0.5Li_2MnO_3{:}0.5$NCM with platelet shaped Li_2MnO_3 domains of low thickness and diameter are superior to composite structures with larger Li_2MnO_3 domains in the first cycle.

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