Structure analysis on the nm scale: The amorphous LiNbO3 coatings for solid state batteries

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Background

To enhance the chemical stability of a cathode active material (CAM) in a Li ion solid state battery (SSB) a protective coating is applied. Such a coating should have - in addition to the chemical stability - a high Li ion conductivity. LiNbO3 is one material having these properties, which is already successfully applied in SSBs [1,2]. Its ionic conductivity depends strongly on the structure, amorphous LiNbO3 has higher ionic conductivity than crystalline one. This leads to the need of detailed knowledge of the structure and the morphology of the material when applied as thin coating in a battery cell and the correlation of these properties with the electrochemical performance [1].

Methods

In this work we use three different LiNbO3 coatings calcinated at 80°C, 350°C and 550°C on LiNi0.6Co0.2Mn0.2O2 (NCM622) as CAM. To get insights on the structure of the coatings various scanning transmission electron microscopy techniques (STEM) like high angle and virtual annular dark-field imaging (HAADF & VADF), energy dispersive X-Ray spectroscopy (EDS), electron energy loss spectroscopy (EELS) and scanning precession electron diffraction (SPED) were used. To further elucidate the amorphous structure of the coating the reduced pair distribution function (rPDF) [3,4], which contains information about nearest neighbor distances in the material, is calculated from the SPED diffraction patterns. These structural results are then correlated to the electrochemical performance of a battery cell with the respective coated CAM.

Results

HAADF and EDS images show that for the samples calcinated at 350°C and 550°C the coating forms a homogeneous layer covering the entire NCM622 particles. In contrast to that the coating covers only a few parts of the NCM622 particle for the sample calcinated at 80°. SPED measurements show that in the case of 550°C calcination temperature the coating is crystalline whereas for lower calcination temperatures such as 350°C and 80°C the coating is amorphous. Further quantification of the structure of these two amorphous samples through the rPDFs reveals distinct differences in the inter atomic distances. These structural differences of the three samples also influence their electrochemical performance. The battery cell with the coated CAM calcinated at 350°C shows a higher capacity after around 300 cycles compared to the cell with the uncoated CAM. For the cells with the coated CAM calcinated at 550°C and 80°C the capacity during cycling is inferior to the cell with the uncoated CAM.

Conclusion

Correlations between structural results of LiNbO3 coating on NCM622 calcinated at different temperatures to the electrochemical performance of the material in a battery cell show that the best performance is achieved by an amorphous coating covering the whole NCM622 particles. This is achieved at a calcination temperature at 350°C. Higher temperatures lead to a crystalline structure of the coating. Lower temperatures lead to a different amorphous structures as well as an only partial coverage of the coating. 550°C and 80°C calcination temperature of the coated CAM lead then to a poorer electrochemical performance of the battery cell.

Graphic:

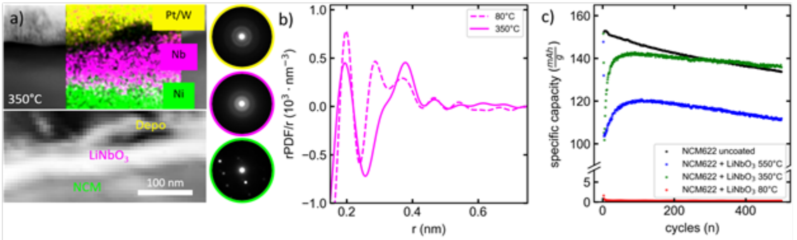

Figure 1 a) top STEM HAADF image of NCM622 coated with $LiNbO_3$ calcinated at 350°C and EDS maps as inset. bottom VADF image of a SPED 4d dataset of the same sample. PED patterns of the NCM, $LiNbO_3$ and the Pt/W depo right show the amorphous nature of the coating. b) rPDF of the diffraction patterns of the $LiNbO_3$ coating with 80°C and 350°C calcination temperature underlining the different amorphous structures of the two samples. c) Electrochemical performance of a battery cell with NCM622 uncoated as well as coated with $LiNbO_3$ calcinated at different temperatures. The cell with the coated CAM calcinated at 350°C shows after around 300 cycles the best performance.

Keywords:

SPED EPDF AMORPHOUS BATTERY COATING

Reference:

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