

Supporting information

Oxygen activity in Li-rich disordered rock-salt oxide and influence of LiNbO₃ surface modification on the electrochemical performance

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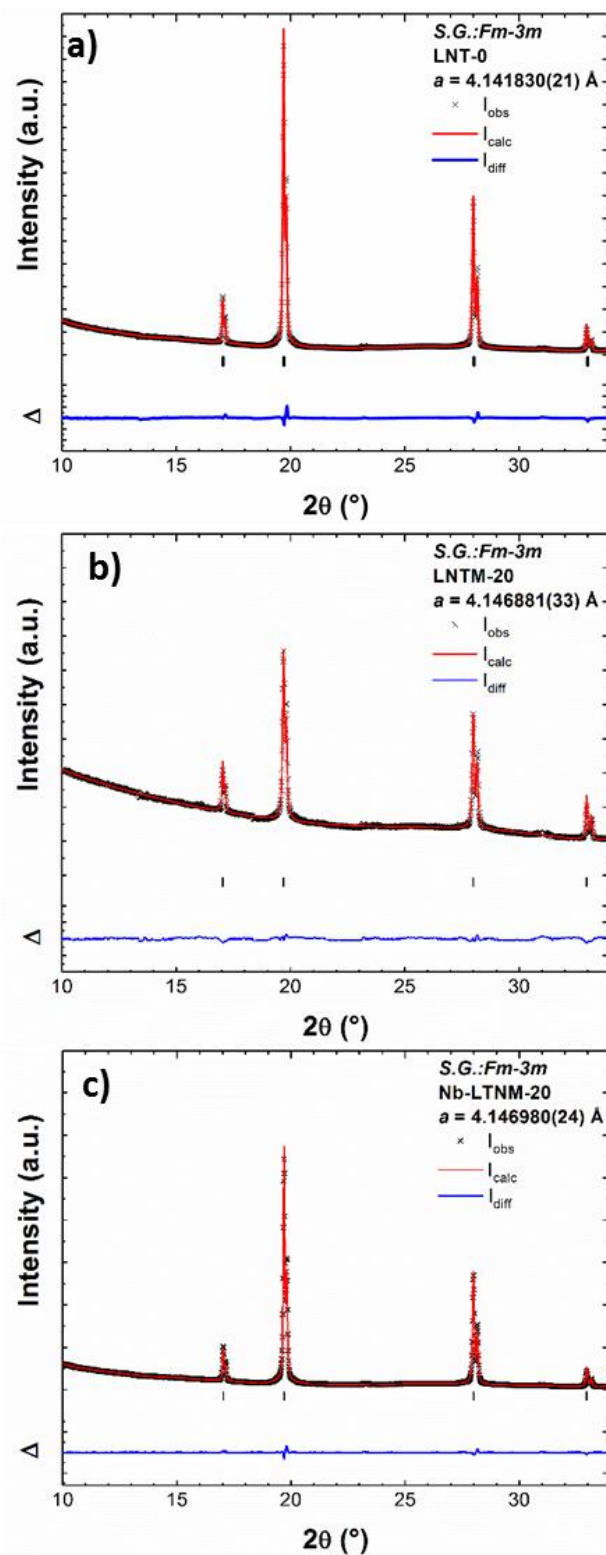


Figure S1: Rietveld refinements on the XRD pattern of a) $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ (LNT-0) b) $\text{Li}_{1.20}\text{Ni}_{0.333}\text{Ti}_{0.333}\text{Mo}_{0.133}\text{O}_2$ (LNTM-20) c) 5wt% coated $\text{Li}_{1.20}\text{Ni}_{0.333}\text{Ti}_{0.333}\text{Mo}_{0.133}\text{O}_2$ sintered at 400°C (Nb-LNTM-20)

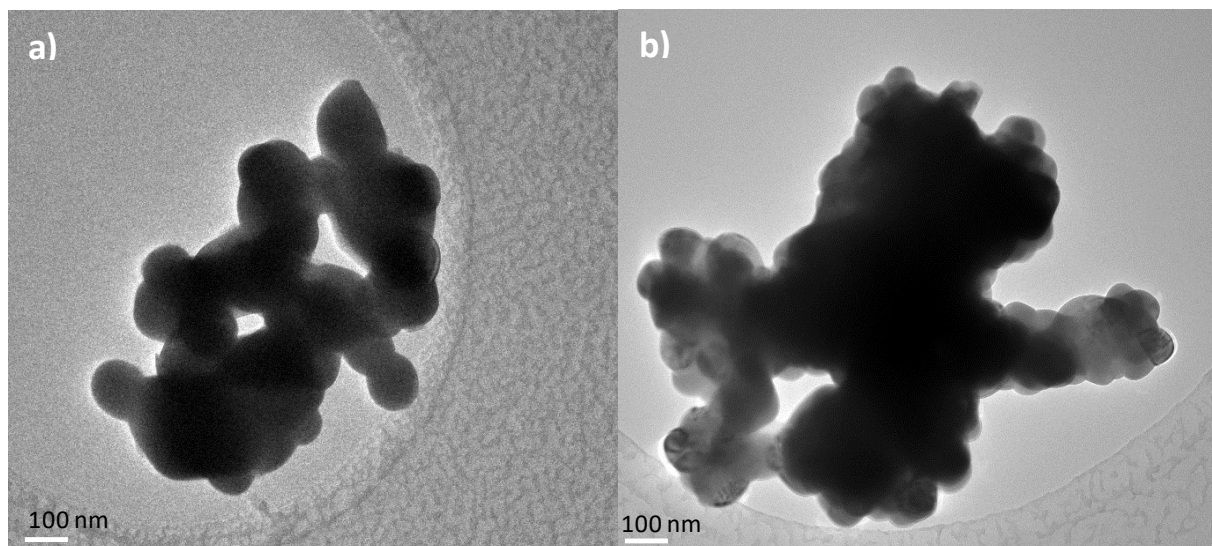


Figure S2: Bright-field TEM image of 2 h sintered compounds. a) LNT-0 and b) LNTM-20.

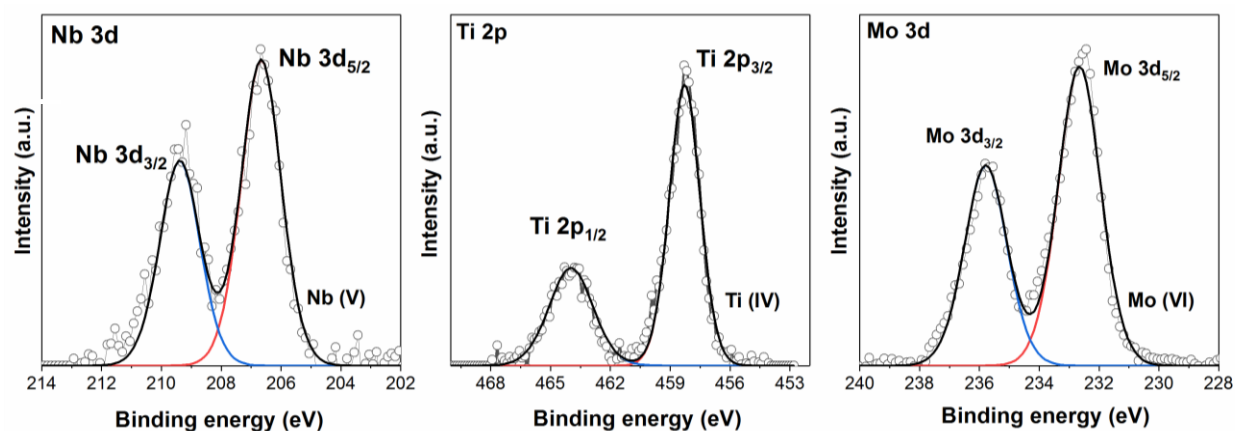


Figure S3: HR-XPS spectra of the Nb 3d, Ti 2p, Mo 3d core levels in Nb-coated $\text{Li}_{1.2}\text{Ni}_{1/3}\text{Ti}_{1/3}\text{Mo}_{2/15}\text{O}_2$.

The binding energies of the Nb 3d_{5/2} and Nb 3d_{3/2} peaks are 206.7 and 209.4 eV, respectively, confirming the Nb oxidation state +V.

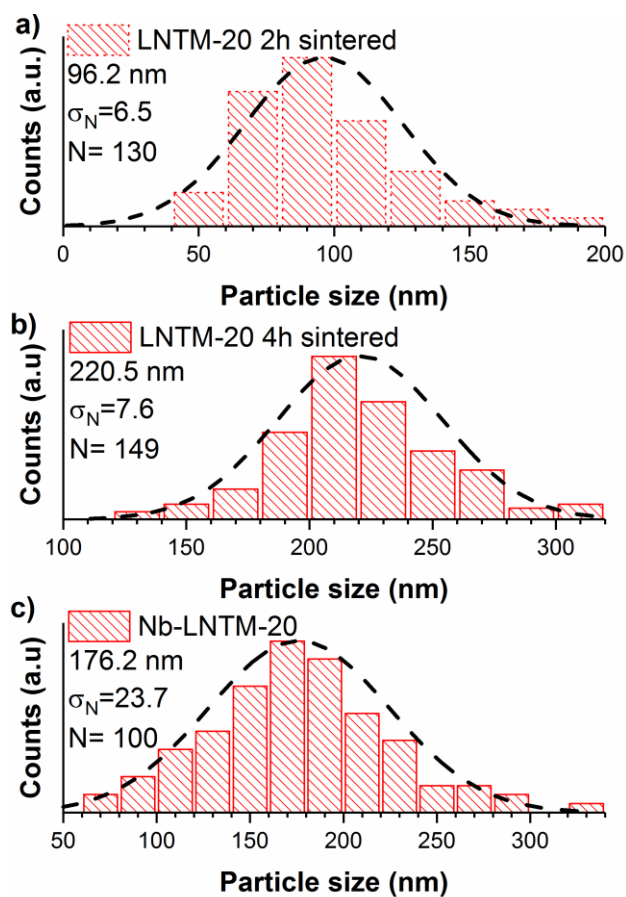


Figure S4: Particle size distribution for a) LNTM-20 2h sintered, b) LNTM-20 4h sintered and c) Nb-LNTM-20.

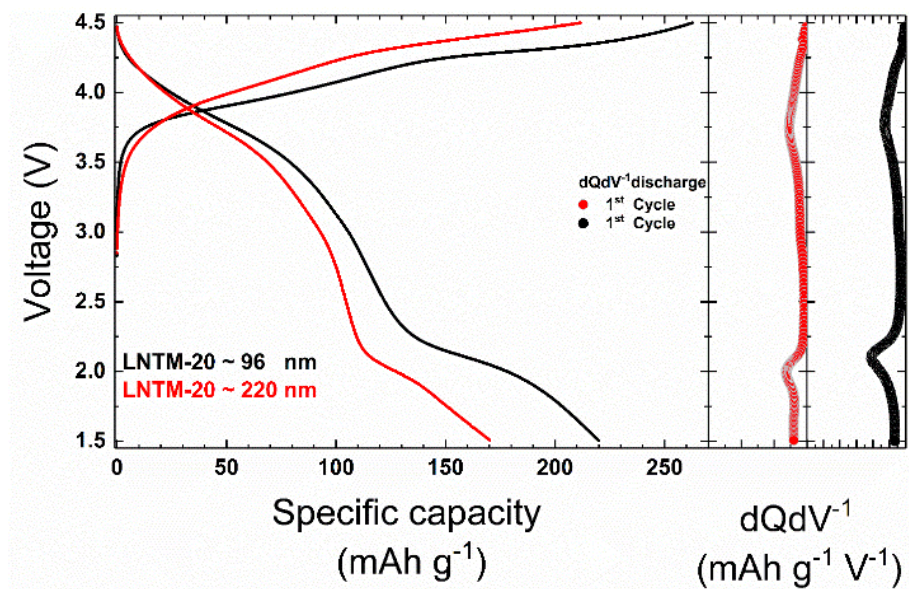


Figure S5: Charge-discharge profiles of LNTM-20 for different particle sizes with corresponding differential capacity plots during discharge at 20 mA g^{-1} .

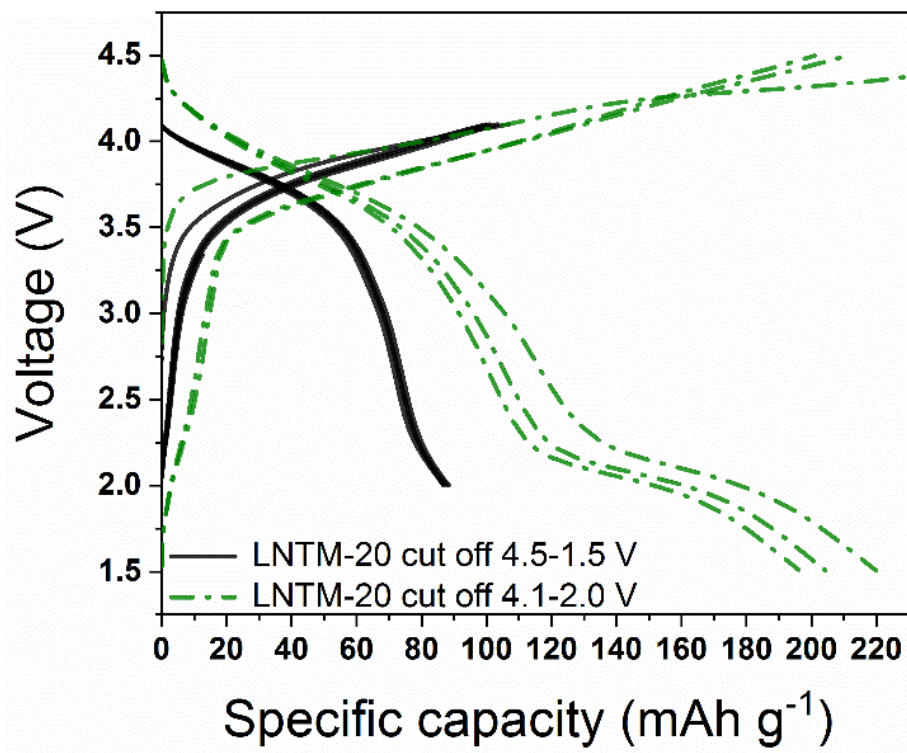


Figure S6 Charge-discharge profile of LNTM-20 for different cut-off voltages at 20 mA g^{-1}

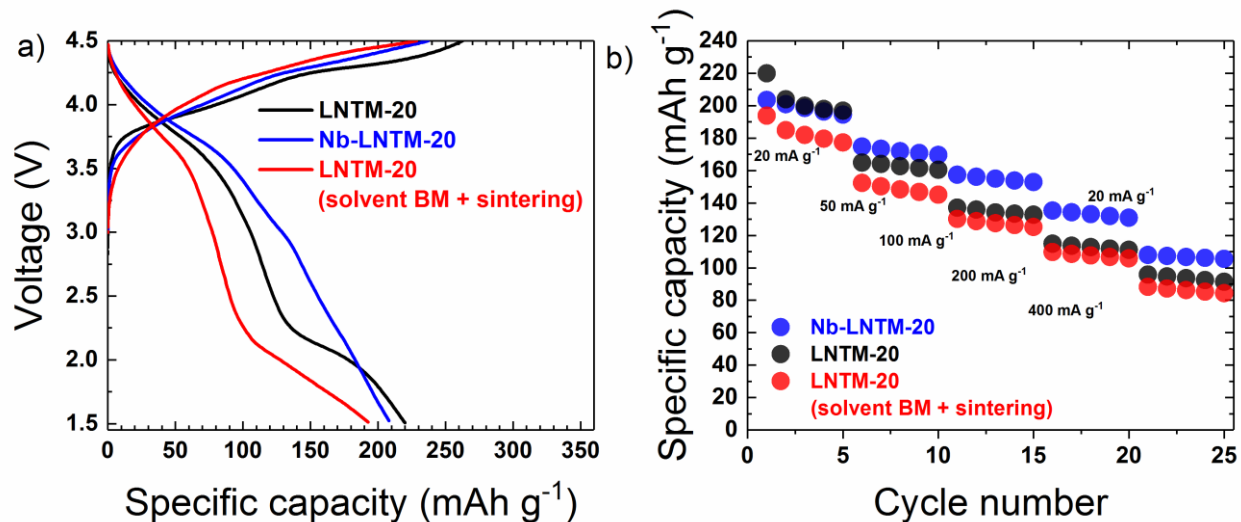


Figure S7: a) Charge-discharge profile of LNTM-20, Nb-LNTM-20 and LNTM-20 processed at the same conditions as Nb-LNTM-20 (additional solvent ball milling and sintering), cycled at 20 mA g^{-1} . b) Rate capability test for all compounds in the range of 4.5-1.5 V.

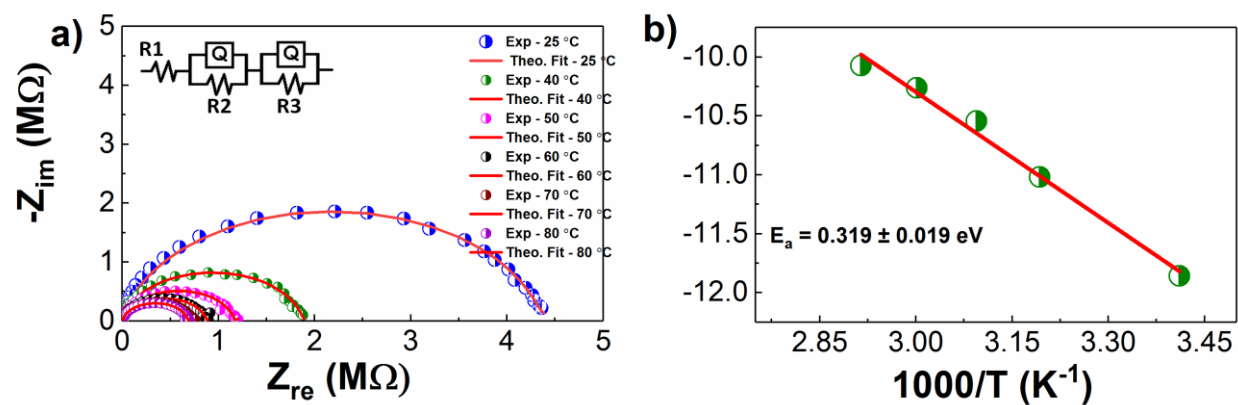


Figure S8: a) Nyquist plots of the impedance at different temperatures (25-80 $^{\circ}\text{C}$) for LNT-0. b) Arrhenius plots of the activation energy for LNT-0.

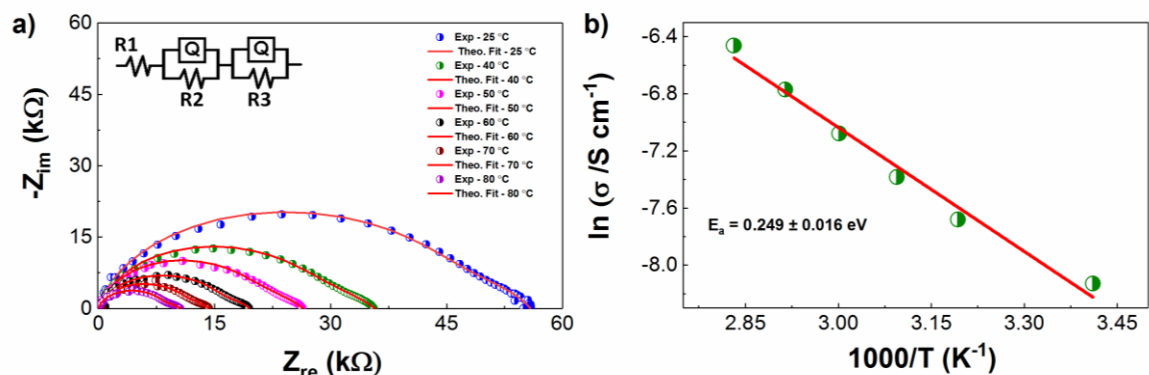


Figure S9: a) Nyquist plots of the impedance at different temperatures (25-80 °C) for LNTM-20. b) Arrhenius plots of the activation energy for LNTM-20

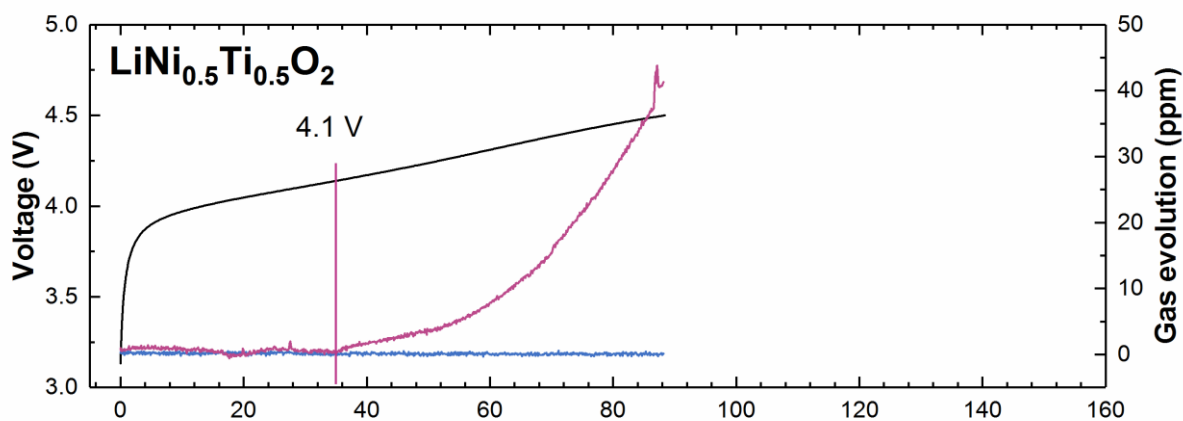


Figure S10: DEMS measurement of the first charge cycle at C/10 to 4.5 V for LNT-0 (half-cells). The cell voltage (black) is shown together with the O_2 (blue) and CO_2 (red) evolution.

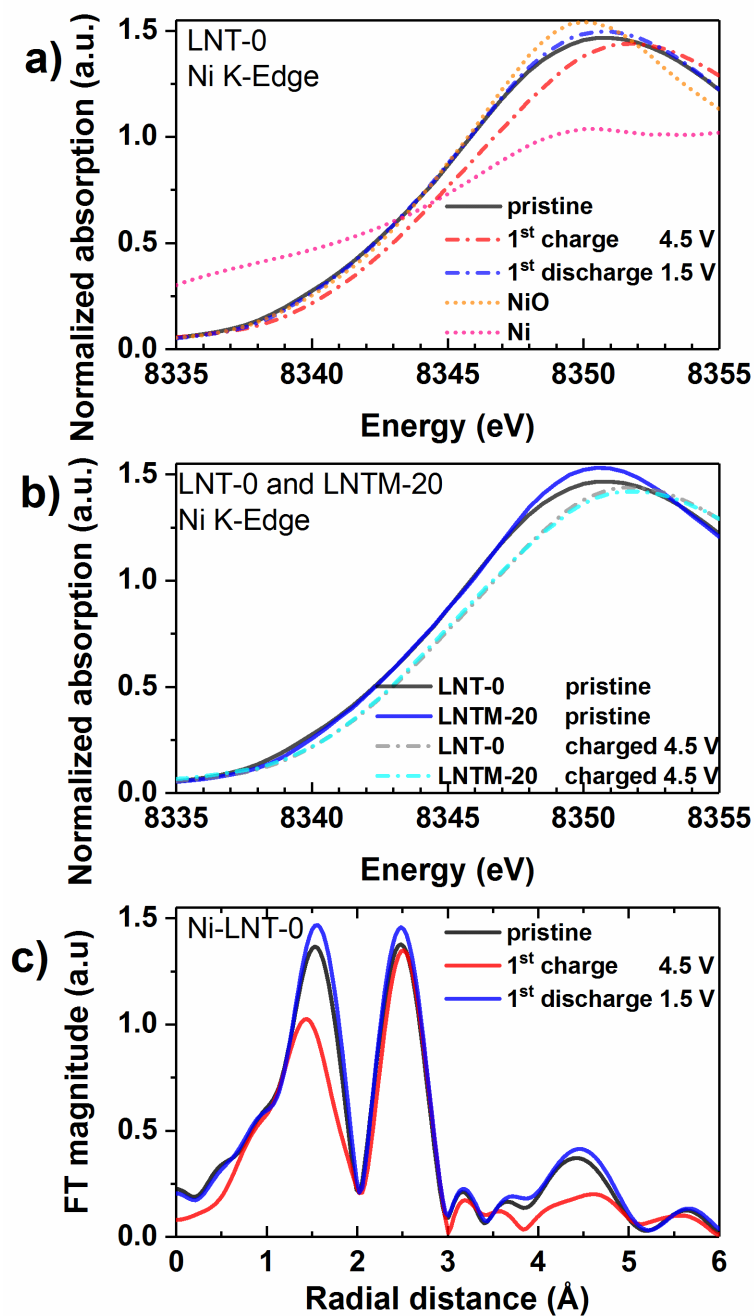


Figure S11: XANES Ni K-edge spectrum for different states of charge for. **a)** LNT-0 and **b)** Comparison of Ni K-edge data obtained on pristine and charged LNT-0 and LNTM-20. **c)** FT-EXAFS of Ni in LNT-0.

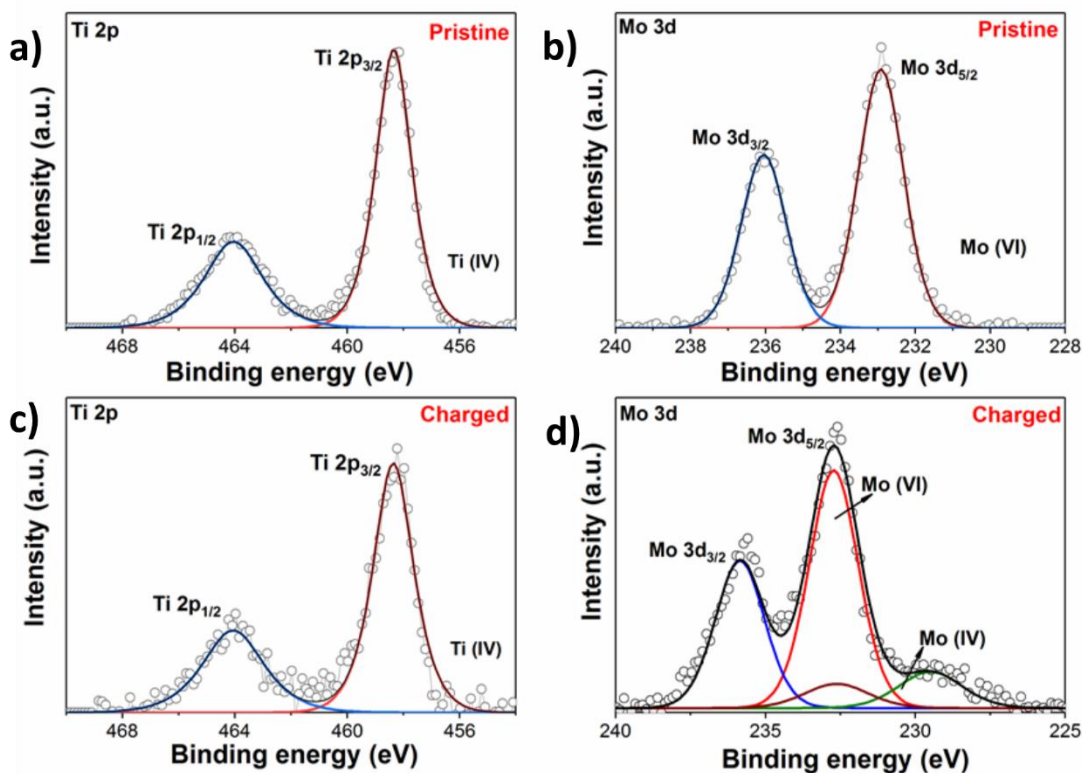


Figure S12 LNTM-20 XPS spectra of the Ti 2p core level in a) pristine state and c) charged state and of the Mo 3d core level in b) pristine state and d) charged state.

For LNTM-20, Ti is in +4 oxidation state at the surface in both pristine (Ti 2p_{3/2} = 458.3 eV, Ti 2p_{1/2} = 464.1 eV) and charged state (Ti 2p_{3/2} = 458.3 eV, Ti 2p_{1/2} = 464.1 eV). Mo is in +6 oxidation state at the surface in the pristine material (Mo 3d_{5/2} = 232.9 eV, Mo 3d_{3/2} = 236.0 eV). In the charged state, part of Mo is reduced to the oxidation state +4 (Mo 3d_{5/2} = 229.5 eV, Mo 3d_{3/2} = 232.6 eV); the majority of Mo remains, however, in the +6 oxidation state (Mo 3d_{5/2} = 232.7 eV, Mo 3d_{3/2} = 235.9 eV).

Table S1: Target ratio vs measured Li: Ni: Ti: Mo: Nb atomic ratio of all compounds from ICP-OES.

Material	Li-excess %	Target Li:Ni:Ti:Mo:Nb	Measured Li:Ni:Ti:Mo:Nb
LNT-0	0	1.0:0.5:0.5:0	0.99:0.51:0.5:0:0
LNTM-20	20	1.20:0.333:0.333:0.133:0	1.220:0.33:0.34:0.135:0
Nb-LNTM-20	25	1.232:0.333:0.333:0.133:0.032	1.253:0.33:0.34:0.135:0.031

Table S2: Fitting results for the impedance spectra in figure 3a,b

Sample	R₁ (Ω)	R₂(Ω)
2nd Cycle		
LNTM-20	9	21
Nb-LNTM-20	10	8
40th Cycle		
LNTM-20	9	67
Nb-LNTM-20	9	23