Effect of annealing temperature on crystal structure and lithium ion battery performance of TiO_2 surface modified $LiNi_{0.5}Mn_{1.5}O_4$

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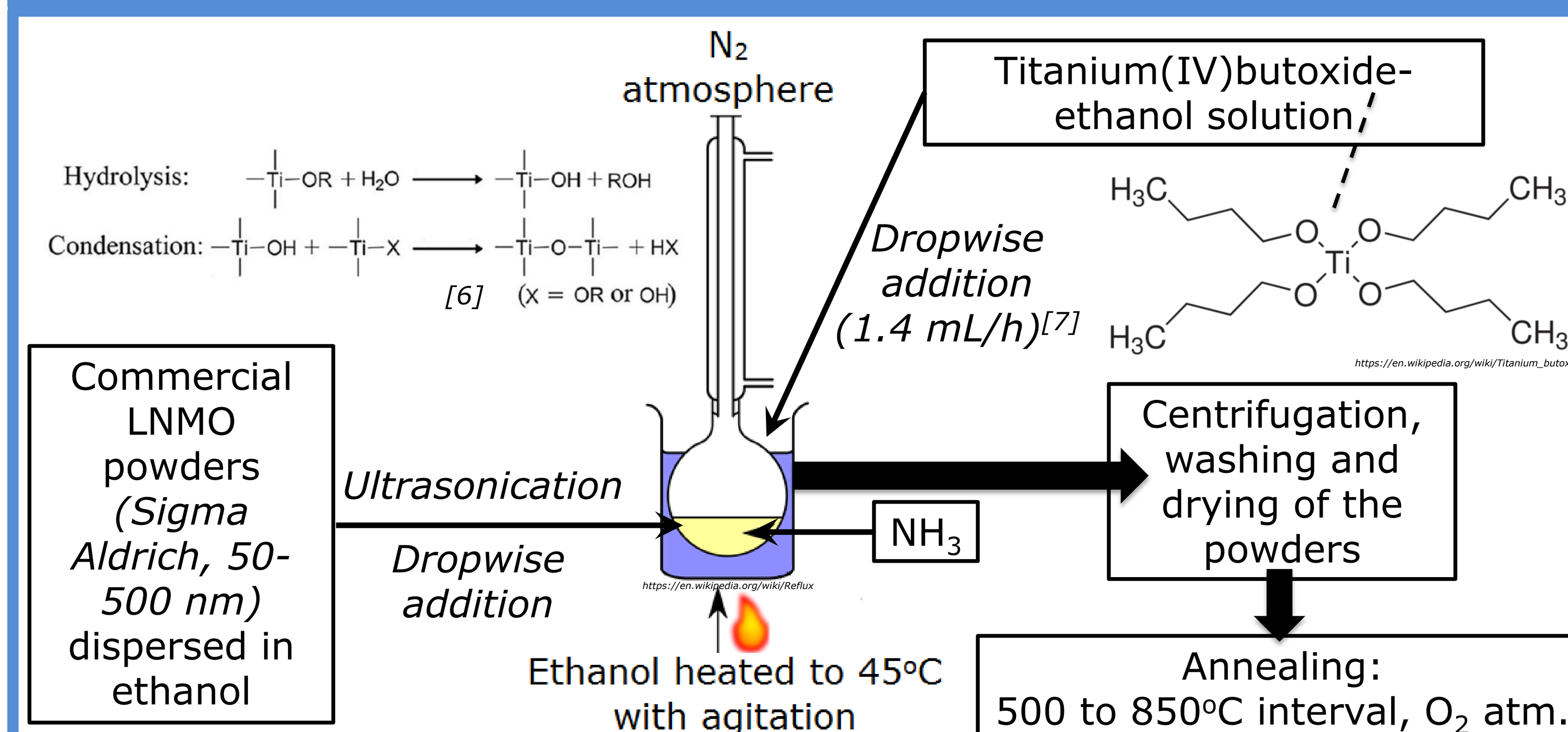
Introduction

High energy and power density lithium ion batteries (LIB) are extensively being studied for their potential applications in portable electronics and hybrid/full electric vehicles as well as for their ability to store solar, wind and other renewable energies with high efficiency[1]. $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) attracts attention as a high voltage cathode material (4.7 V vs. Li/Li+) with good capacity (147 mAh/g); having potential for high power applications[2]. However, cyclic stability of LNMO still remains an issue since all cathode materials containing Mn are challenged with capacity fade problem due to Mn leaching within commercial electrolytes[1]. Introducing a shell layer on LNMO that is stable at high voltages can prevent Mn dissolution and increase cycle life; while also enabling good conductivity, if ionically and electronically conductive[3]. Materials such as $Li_4Ti_5O_{12}$[4], Li_2TiO_3[5] and TiO_2[4] attract attention as shell material candidates in literature, owing to their structural stability within organic electrolytes at high voltages, as well as their 3D Li^+ diffusion paths allowing good ionic conductivity.

TiO_2 is used as the surface modification material in this work; synthesized using a sol-gel approach. Different from previous studies; effect of different annealing temperatures (500 to 850°C) on Ti^{4+} diffusion from surface towards the core of LNMO is investigated. Electrochemical performances are compared while also considering the ordering/disordering changes within the LNMO crystal structure.

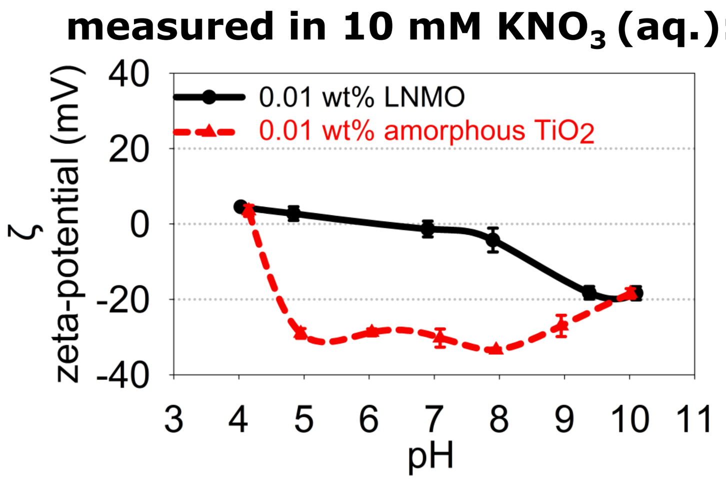
Experimental [6,7]



Results

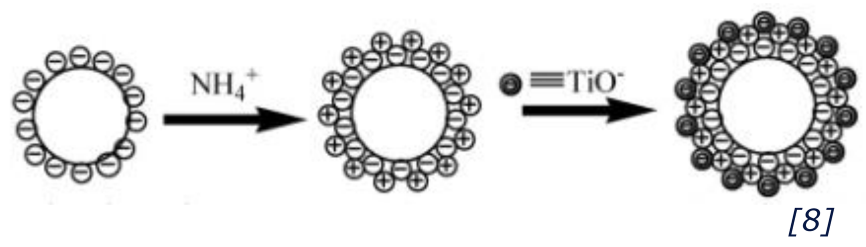
Zeta-potential measurements

measured in 10 mM KNO_3 (aq.):



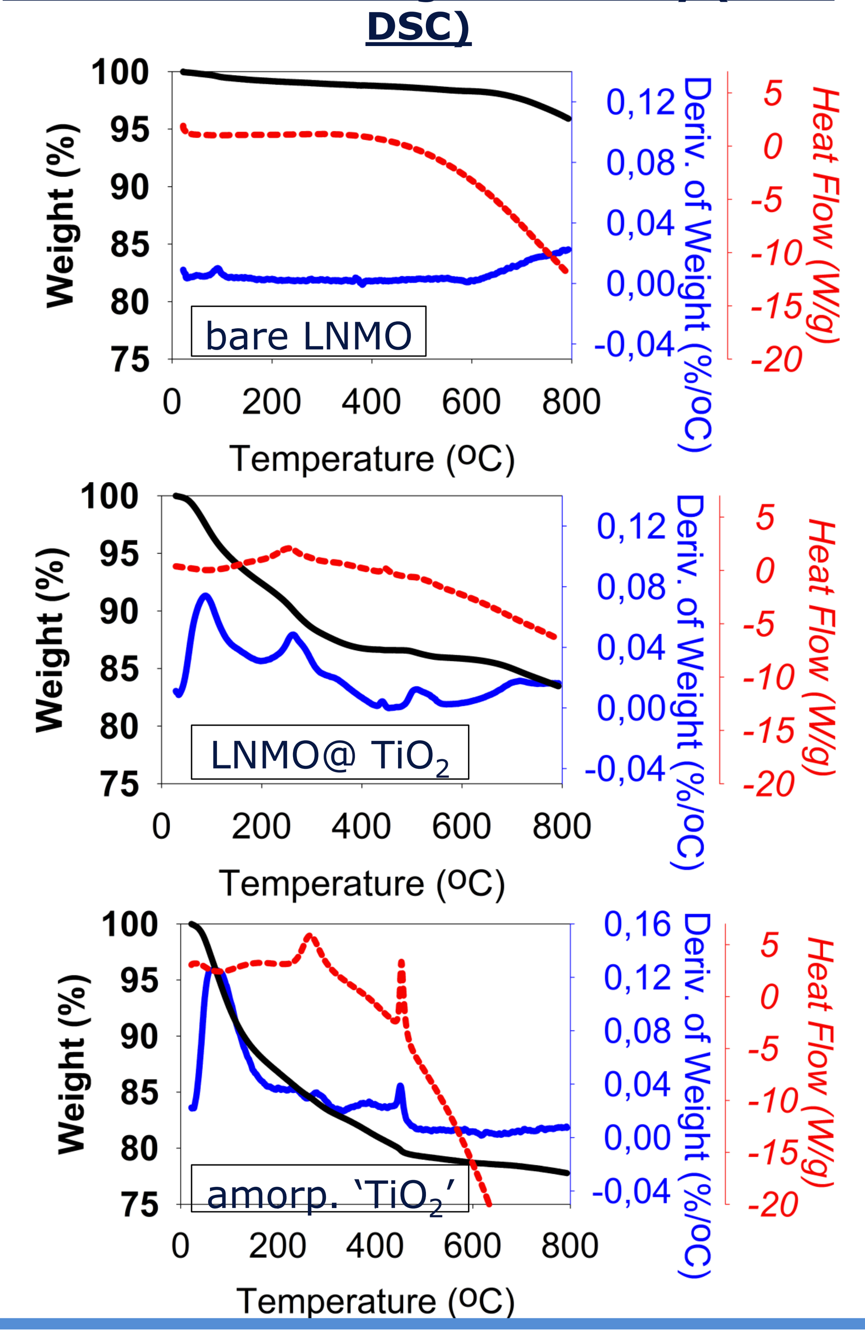
measured in ethanol:

Sample	pHe	ζ_{LNMO} (mV)	±error
Before NH_3	9.3	-10.82	0.6
After NH_3	10.9	+17.8	1.8



Electrostatic attraction between positively charged LNMO core and negatively charged titania species

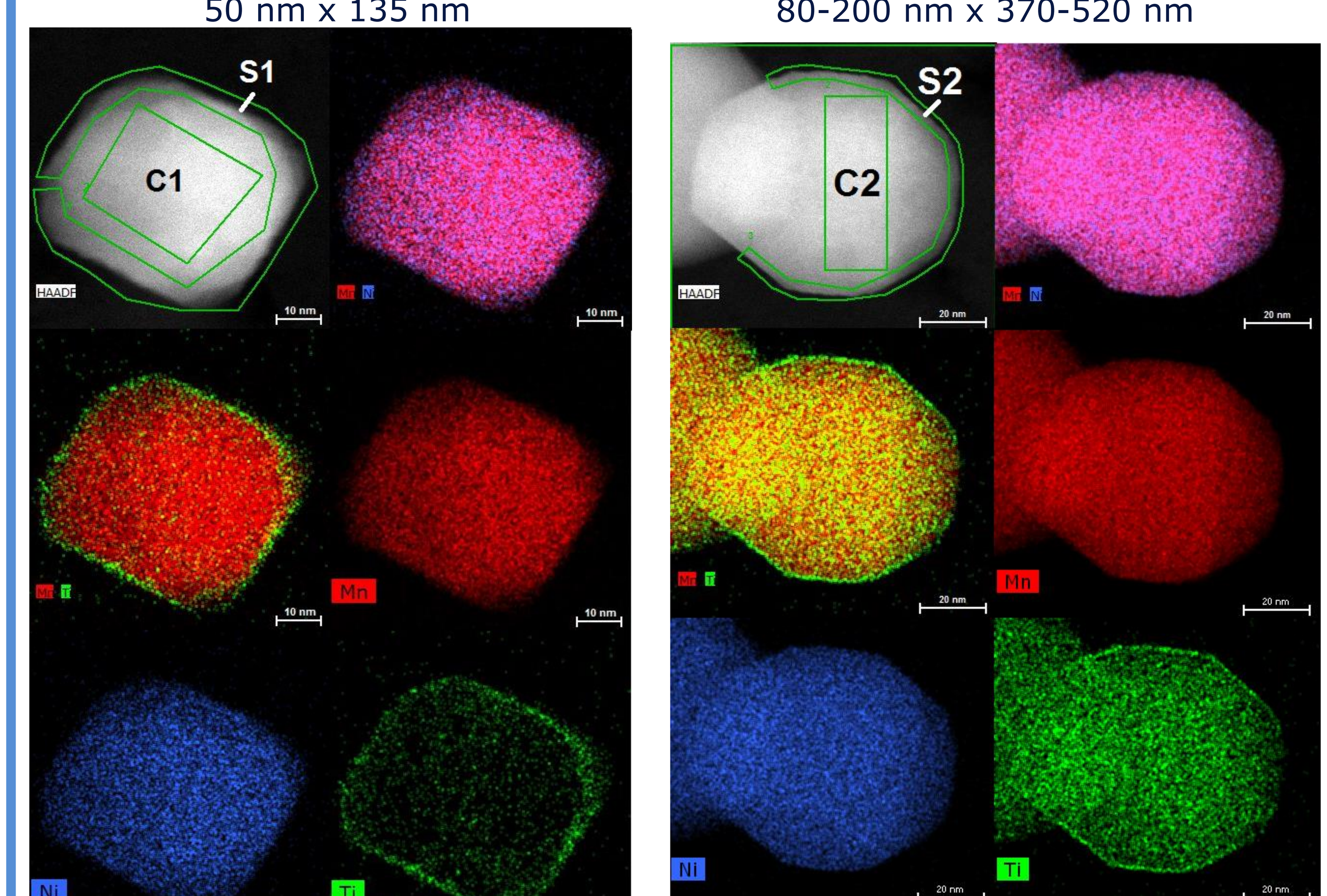
Thermogravimetric analysis coupled by differential scanning calorimetry (TGA-DSC)



STEM-EDX elemental mapping

LNMO@TiO_2 annealed to 500°C, 50 nm x 135 nm

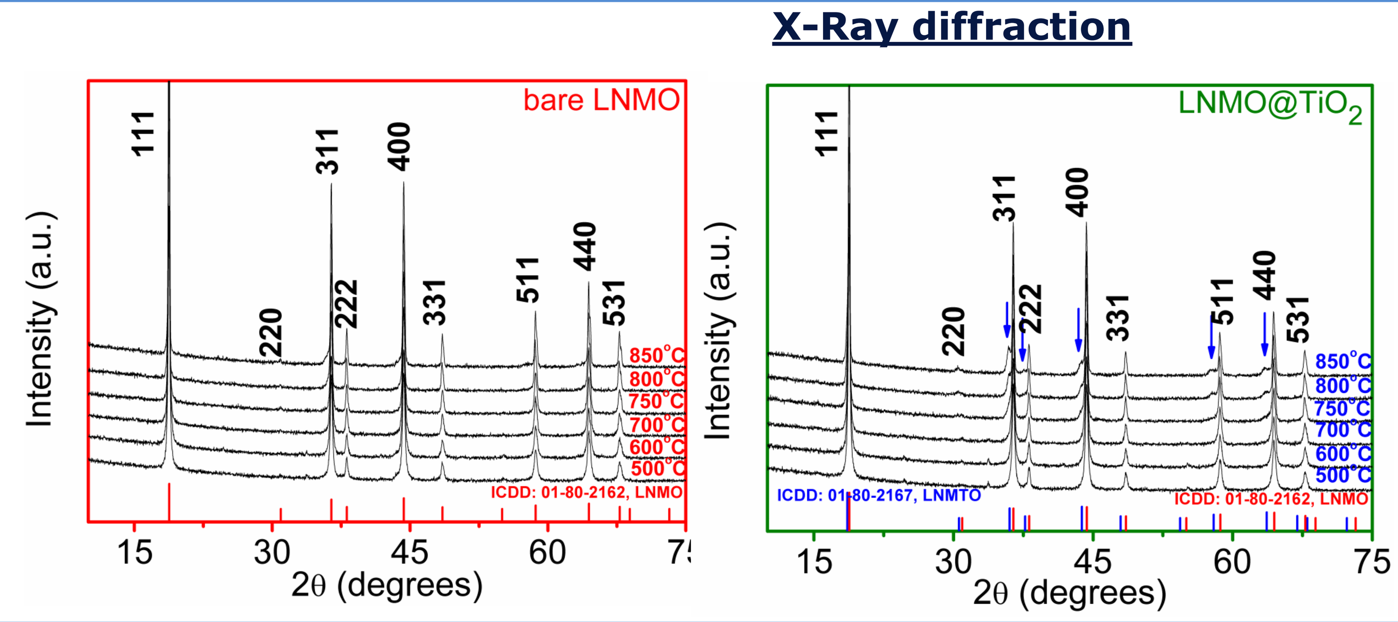
LNMO@TiO_2 annealed to 800°C, 80-200 nm x 370-520 nm



Region	Ni (at%)	Mn (at%)	Ti (at%)	Mn/Ni
Core1 (C1)	31.1	67.7	1.2	2.2
Surface1 (S1)	30.0	61.4	8.6	2.0

Region	Ni (at%)	Mn (at%)	Ti (at%)	Mn/Ni
Core2 (C2)	29.2	63.5	7.2	2.2
Surface2 (S2)	28.5	59.1	12.4	2.1

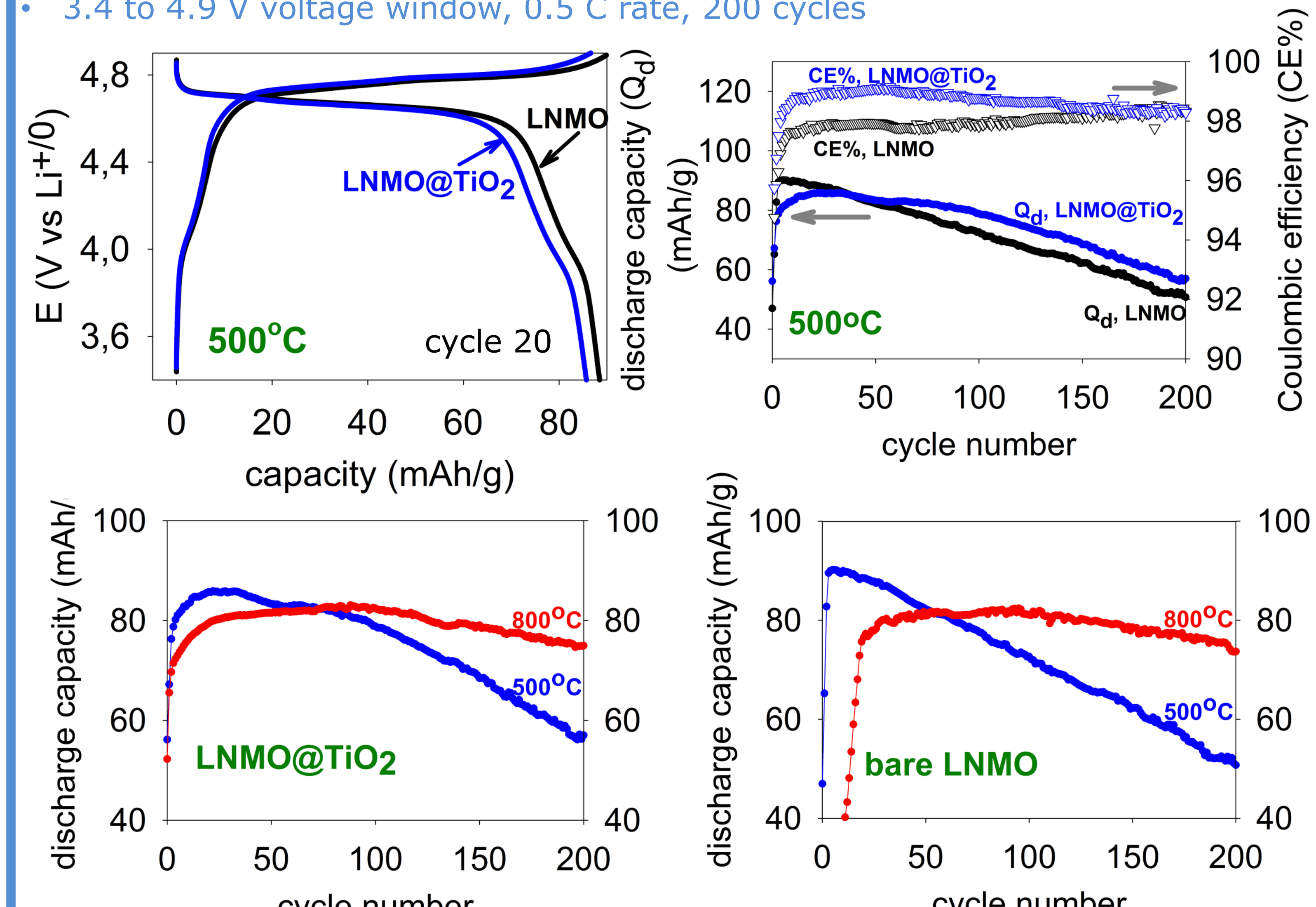
X-Ray diffraction



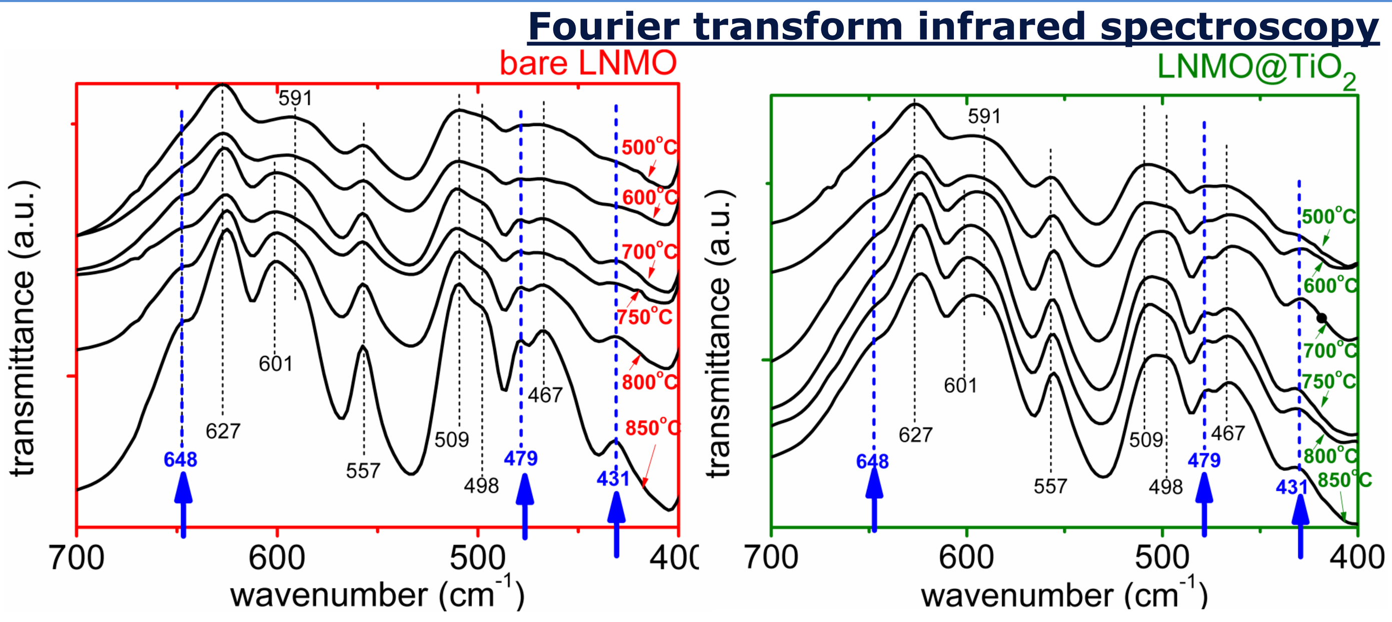
A second, spinel $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ phase forms from 750°C onwards by Ti diffusion towards the core; especially for the smaller LNMO core particles (50 nm).

Electrochemical characterizations

- Li-half cells of 80 wt% active material, 10 wt% PVDF in NMP, 10 wt% carbon b.
- 1.0 M $LiPF_6$ EC/DMC (1:1, v/v) electrolyte, Al current collector, PP separator
- 3.4 to 4.9 V voltage window, 0.5 C rate, 200 cycles

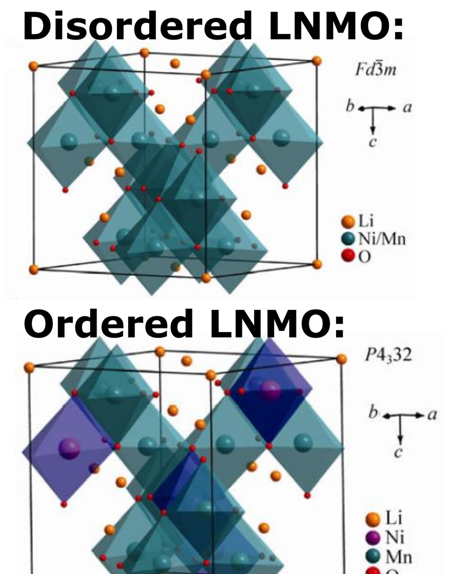


Fourier transform infrared spectroscopy



Disordered LNMO:

Ordered LNMO:



Conclusions

- 2-4 nm thick, homogeneously distributed titania shell layer is deposited on 50-500 nm diameter LNMO core powders via NH_3 catalyzed heterogeneous nucleation of titanium butoxide in an ethanol environment; enhanced by electrostatic attraction between core and shell particles.
- Increasing annealing temperatures cause Ti diffusion from the surface towards the core, as well as an increase in ordering of bare and surface modified LNMO crystal structures.
- Coating and annealing at 500°C shows detectable improvements in cycle life and coulombic efficiency compared to bare LNMO annealed at the same temperature.
- Increasing the annealing temperature to 800°C for titania surface modified LNMO leads to lower initial capacity but better cyclic stability than 500°C annealed sample. However, bare LNMO shows similar performance with 800°C annealing. Therefore, the better cyclic stability at 800°C is more dominantly attributed to increase in ordering of LNMO rather than the surface modification and increased Ti diffusion towards the core.

References

[1] Nitta, N., et al. Materials Today, 2015. **18**(5): p. 252-264
[2] Santhanam, R., et al. J. Power Sources, 2010. **195**(17): p. 5442-5451.
[3] Yang, L., et al. Electrochem. Solid-State Lett., 2010. **13**(8): p. A95.
[4] Hao, X., et al. J. Electrochem. Soc., 2013. **160**(5): p. A3162-A3170.
[5] Deng, H., at al. J. Mater. Chem. A, 2014. **2**(43): p. 18256-18262.
[6] Li, W., et al. J. Am. Chem. Soc, 2012. **134**(29): p. 11864-7.
[7] Liu, D., et al. Langmuir, 2007. **23**: p. 10333-10341.
[8] Wang, P., et al. Langmuir, 2006. **22**: p. 4832.
[9] Yang, J., et. Al. Nano Research, 2013. **6**(9): p. 679.

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