TiO_2 surface modified $LiNi_{0.5}Mn_{1.5}O_4$ cathode powder synthesis using different temperatures for lithium ion batteries

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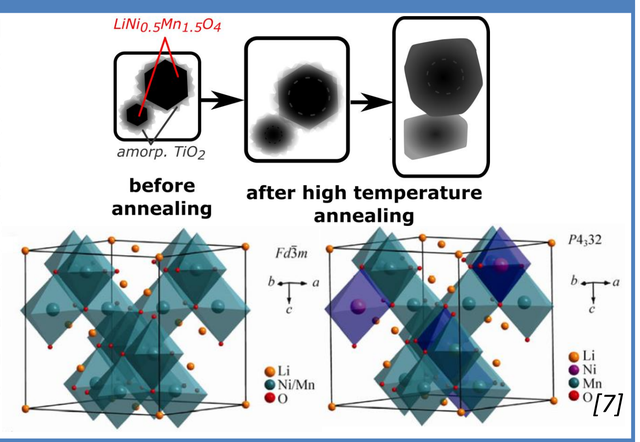
Introduction

$LiNi_{0.5}Mn_{1.5}O_4$ is surface modified with TiO_2 (LNMO@TiO_2). The effects of annealing under oxygen atmosphere between temperatures of 500 to 850°C on Ti^{4+} positions, morphology, crystal structure and electrochemical performance are investigated. A sol-gel approach is used to homogeneously modify the surface of ~30-500 nm diameter LNMO core particles with TiO_2. Metal oxide shell synthesis on LNMO through wet-chemical routes usually results in amorphous deposits [1-3]. The shell is then crystallized by high temperature anneals; ranging from 500 to 800°C [1-4]. The annealing temperature and atmosphere deserve, however, special attention, since these can cause Ti diffusion from the shell towards the surface or bulk of the LNMO particles, as well as causing changes in cation ordering inside the LNMO. Ti surface doping is useful in increasing the LNMO's structural stability, while excess Ti doping may cause capacity drops [5]. In this study, we aimed to increase the cycle life of LNMO, by modifying the LNMO surface with titanium oxide, while at the same time, avoiding bulk doping.

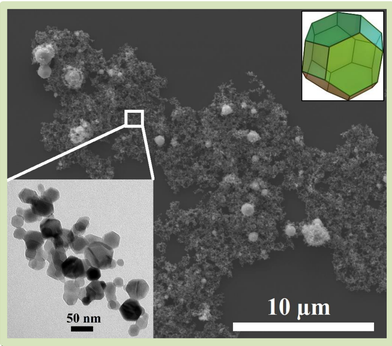
XRD patterns and refined lattice parameters show lattice expansion and secondary phase formation at high annealing temperatures. STEM-EDX mappings and HR-STEM show increased Ti and decreased Mn, Ni concentrations at the surface of LNMO with TiO_2 modification and 500°C anneal; while the LNMO spinel surface structure remains intact. In samples annealed at 800°C, increased levels of Ti at the core of LNMO particles is observed, indicating a high temperature diffusion effect. Galvanostatic charge-discharge measurements of cells with LNMO@TiO_2 annealed at 500°C vs. Li/Li^+ half cells, cycled 200 times between 3.4 and 4.9V at 0.5C, show superior cyclic stability and Coulombic efficiency compared to bare LNMO samples annealed at 500°C. These improvements are probably due to a decrease in dissolution of the transition metal ion at the LNMO surface into the electrolyte, by Ti surface doping [4,6].



Results

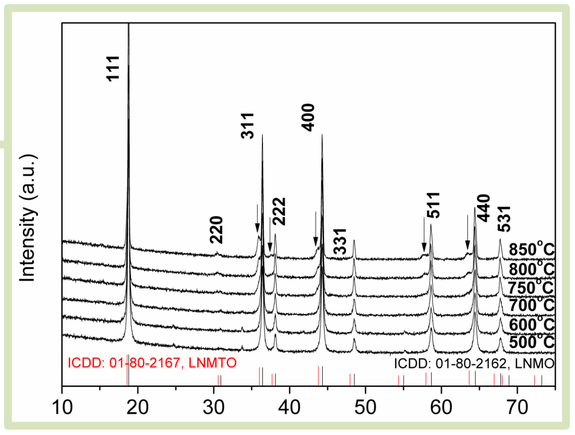
Materials characterization

Particle size & distribution: TEM / SEM:



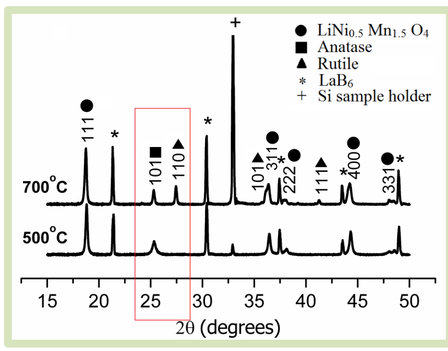
A second phase formation is observed for surface modified LNMO from 750°C onwards; indicated by arrows (spinel $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$).

	Average LNMO diameter ± std. error (nm)	
	SEM	TEM
Smaller LNMO particles	N/A	34 ± 2
Larger LNMO particles	575 ± 73	N/A

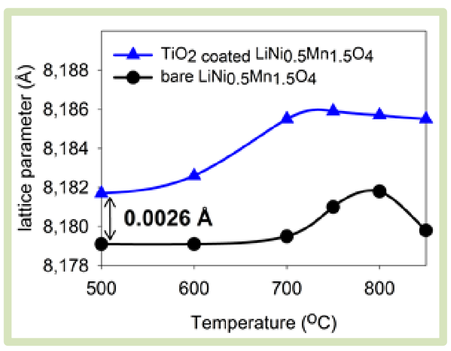


TiO_2 peaks cannot be observed probably due to low titania loading.

X-Ray Diffraction (XRD):



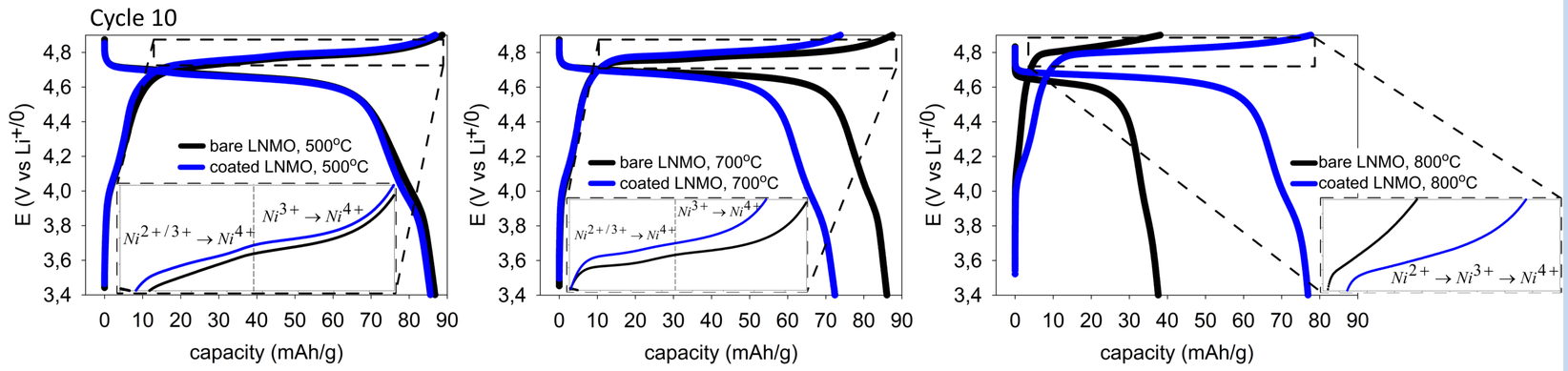
Increased titania loading within LNMO: anatase and/or rutile formation upon 500 or 700°C anneals



Refined lattice parameters of LNMO@TiO_2 are slightly higher than that of bare LNMO

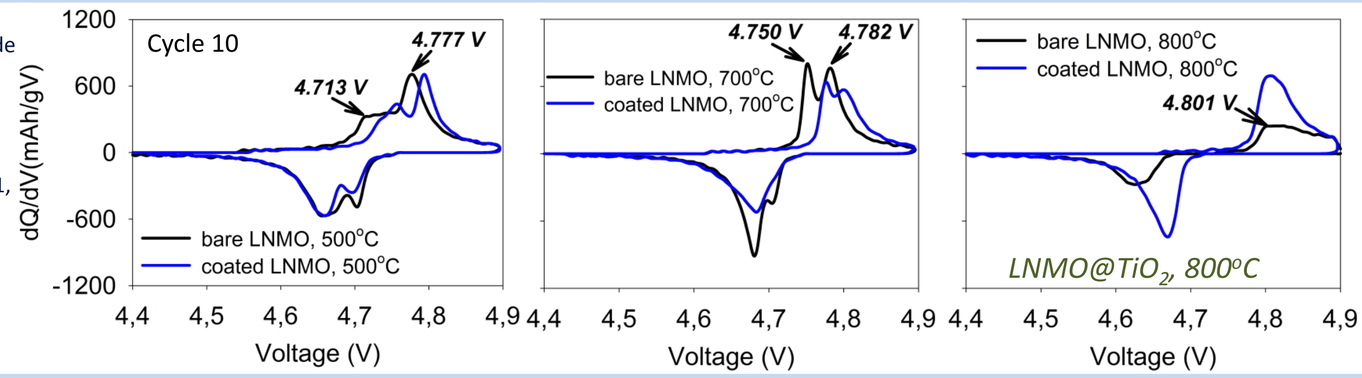
Electrochemical characterization

Capacity curves: 500°C 700°C 800°C



dQ/dV plots: 500°C 700°C 800°C

- → Half cells with Li as anode
- → 80 wt% active material, 10 wt% PVDF in NMP, 10 wt% carbon black; 3 to 4 mg/cm² loading
- → 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

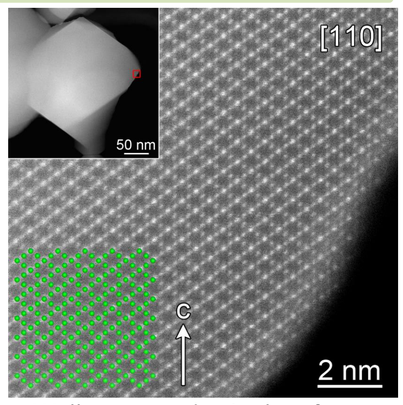


STEM-EDX elemental mapping & HR-STEM:

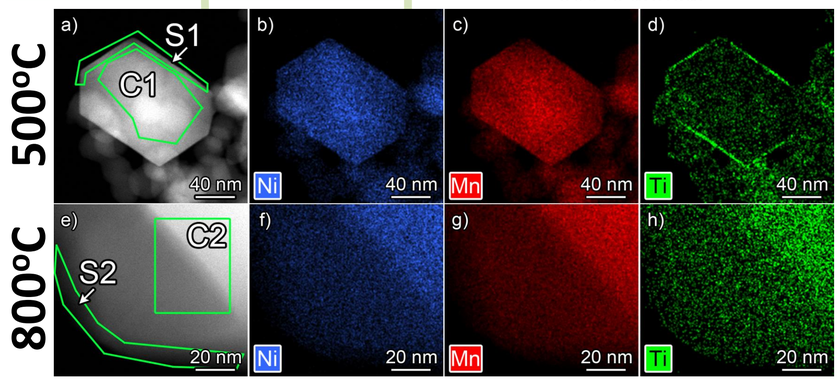
Ni, Mn and Ti atomic percentages for LNMO@TiO_2 samples with 500 or 800°C anneals. Regions show in figure below.

Region	Ni (at%)	Mn (at%)	Ti (at%)	Mn/Ni
S1	28.9	63.1	**7.9**	2.2
C1	29.0	70.0	**1.0**	2.4
S2	26.2	68.5	**5.2**	2.6
C2	27.0	69.3	**3.7**	2.6

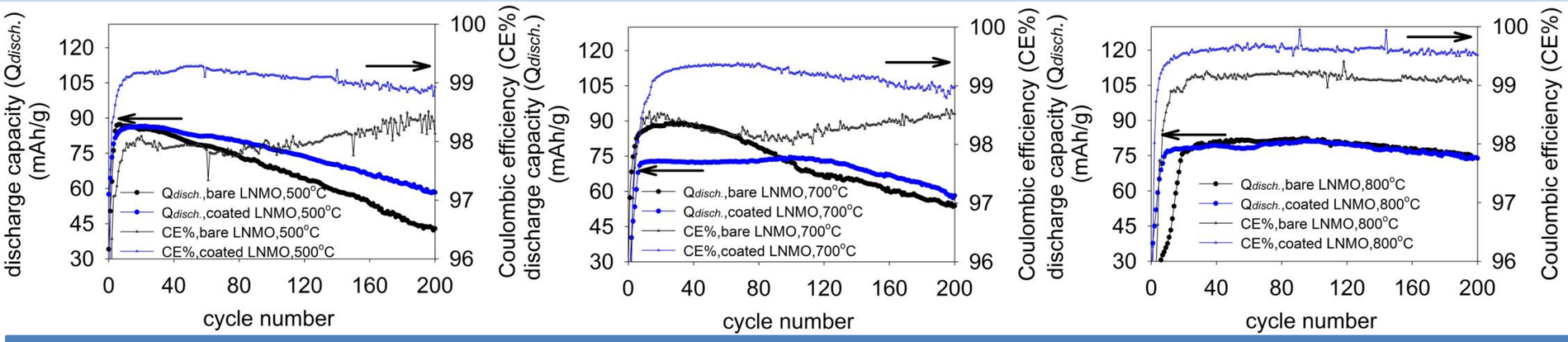
Dominant Ti presence at the LNMO surface with 500°C anneal



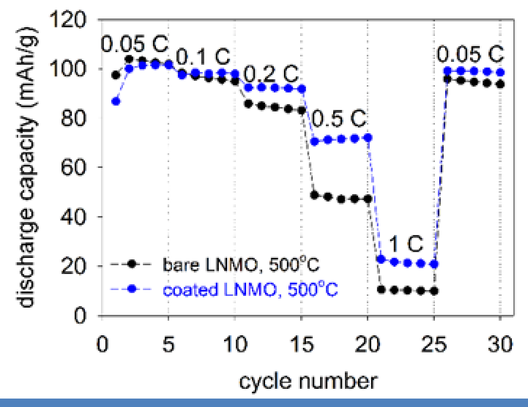
Well preserved spinel surface structure of LNMO@TiO_2 upon 800°C anneal



Cycle life and Coulombic efficiency: 500°C 700°C 800°C



Rate Performance



Conclusions

- Using an anneal at 500°C; Ti atoms were found to dope at the LNMO surface. Increasing the annealing temperature to 800°C caused these Ti atoms to diffuse towards the core. Above 750°C, a slight amounts of secondary $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ spinel phase were formed.
- A surface modification followed by an anneal at 500°C improves cycle life, CE% and rate performance. This is probably due to incorporation of stronger Ti-O bonds within the spinel LNMO surface structure, which reduces the Mn dissolution into the electrolyte upon cycling.
- Annealing at 800°C does not yield significant improvements in electrochemical performance upon cycling compared to an uncoated LNMO sample annealed at 800°C. This might be due to higher cation ordering and lower Mn^{3+} concentration within the bare LNMO sample.
- Disordered and Ti surface doped LNMO, annealed at 500°C, is an interesting candidate for applications requiring both good cycle life and rate performance. A further optimization of the Ti dopant concentration at the surface is expected to yield an increased cyclic stability.

References

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