ZrO_2/Zr^{4+} surface coating/doping of $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ for lithium ion battery positive electrodes

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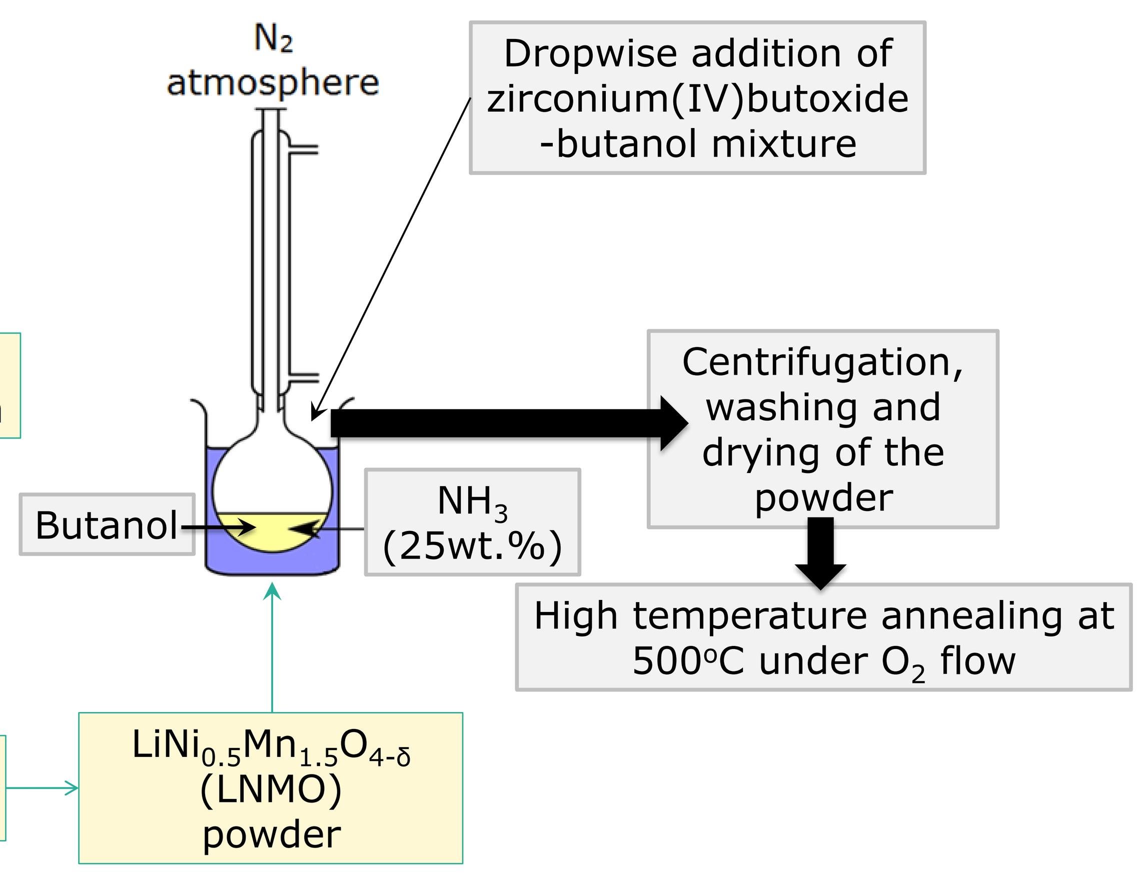
Introduction

High energy and power density lithium ion batteries 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]. $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ (LNMO) is a high voltage lithium ion battery cathode material with potential for high power applications requiring good rate capability, such as hybrid/full electric vehicles [2].

The cyclic stability of LNMO remains an issue since all cathode materials containing Mn are challenged with a capacity fade problem due to Mn leaching into commercial electrolytes, during cycling or storage [1, 3]. One of the mechanisms causing Mn leaching is by hydrofluoric acid corrosion. HF forms by hydrolysis of $LiPF_6$ salt in electrolyte in presence of traces of water [3]. One way to prevent the Mn loss is to modify the surface of the cathode particles by coating or doping the surface with a chemically stable material. Zr^{4+}/ZrO_2 is a good canditate to be used as a surface modification material since Zr-O has a high bond-dissociation energy (766.1±10.6 kJ/mol [4]). Zr-O presence at the surface can make the particle more stable against leaching compared to Mn-O (362±25 kJ/mol) or Ni-O (366±30 kJ/mol) presence at the surface. Purpose of this study is therefore to coat or dope the LNMO particle surfaces with ZrO_2 shell or Zr^{4+} cation, respectively, to obtain batteries having better cycle life and rate performance than the LNMO without any surface modification.

Experimental [5,6]

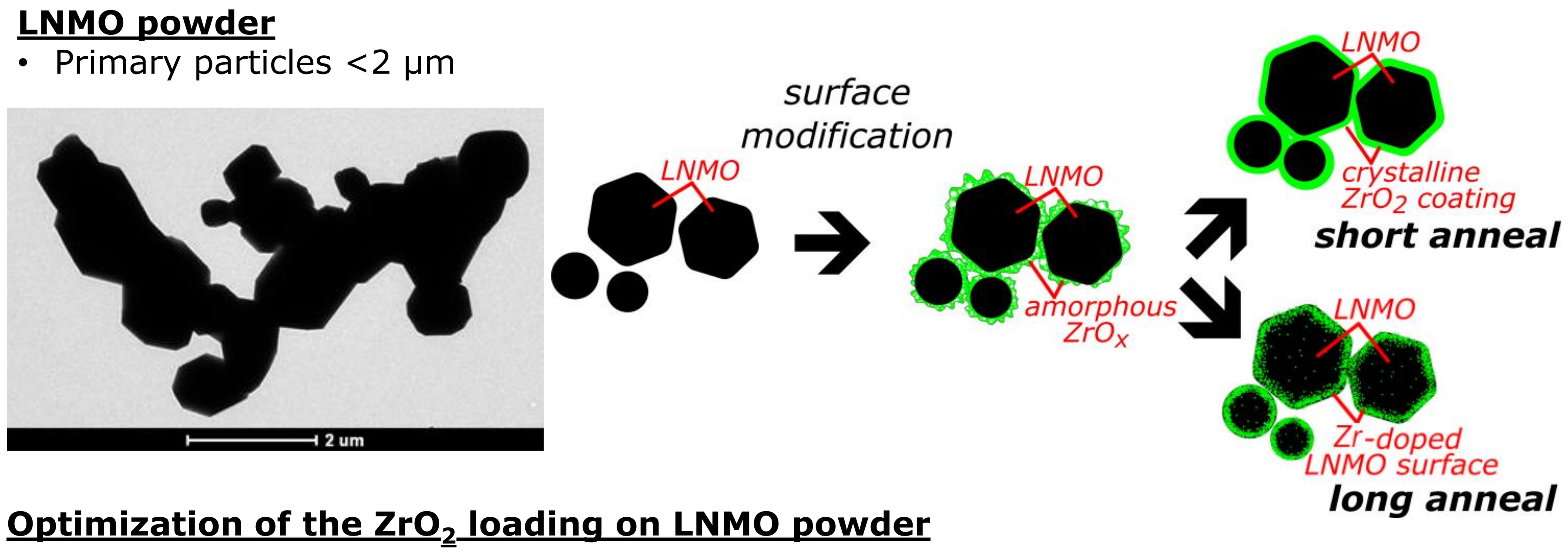
- 0.1 M aqueous solution of Li, Ni and Mn acetate
- 1:1 molar ratio of citric acid to metal ions
- pH fixed to 7 by ammonia
- 4 h stirring under reflux conditions at 85°C for gelation
- Drying and decomposition at 80 and 200°C
- Ball milling of the dry powder
- Calcination at 900°C, 10h, DA, 5°C/min heating rate
- $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ (LNMO) powder



Results

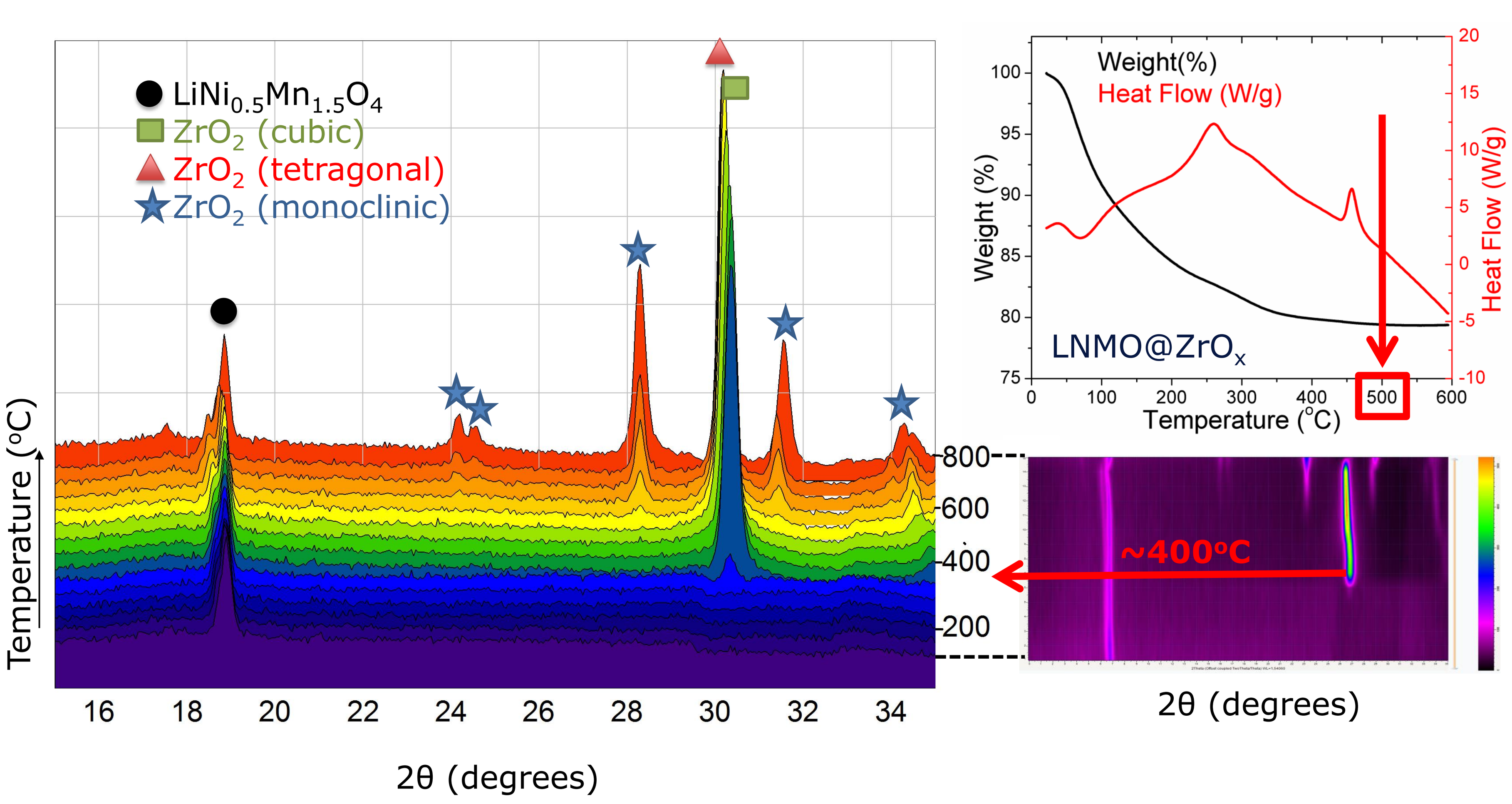
LNMO powder

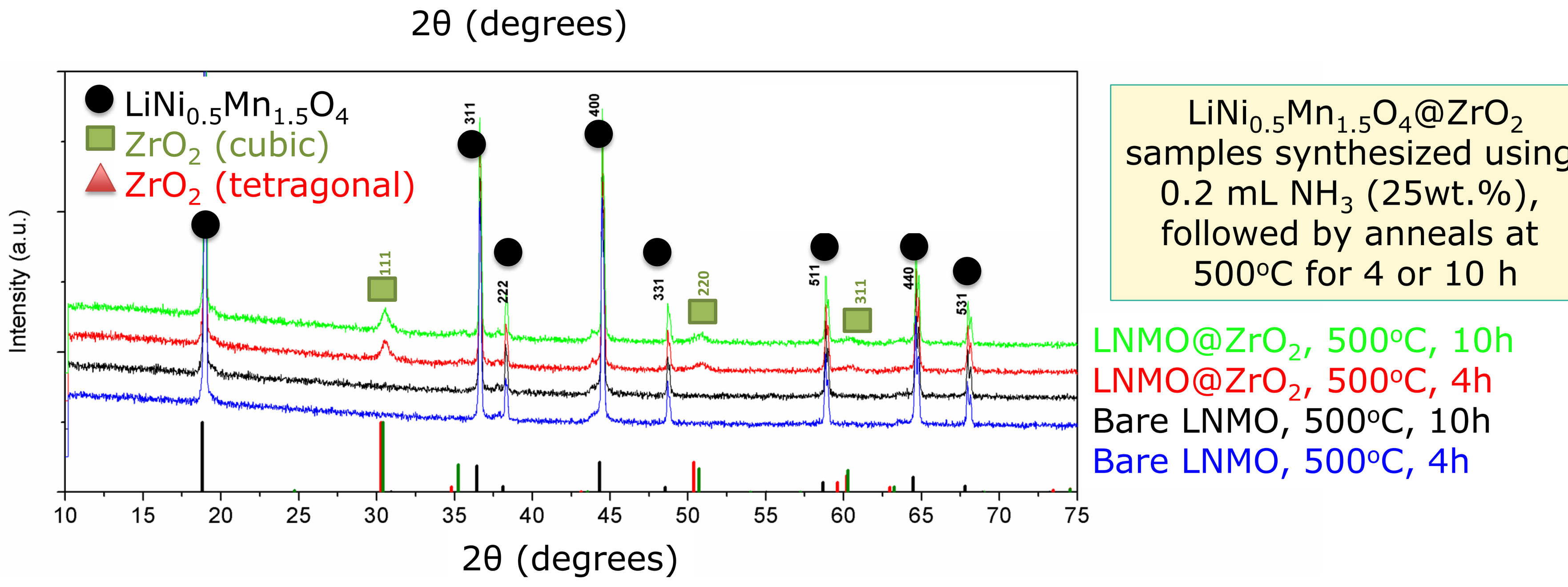
- Primary particles <2 µm



Optimization of the ZrO_2 loading on LNMO powder

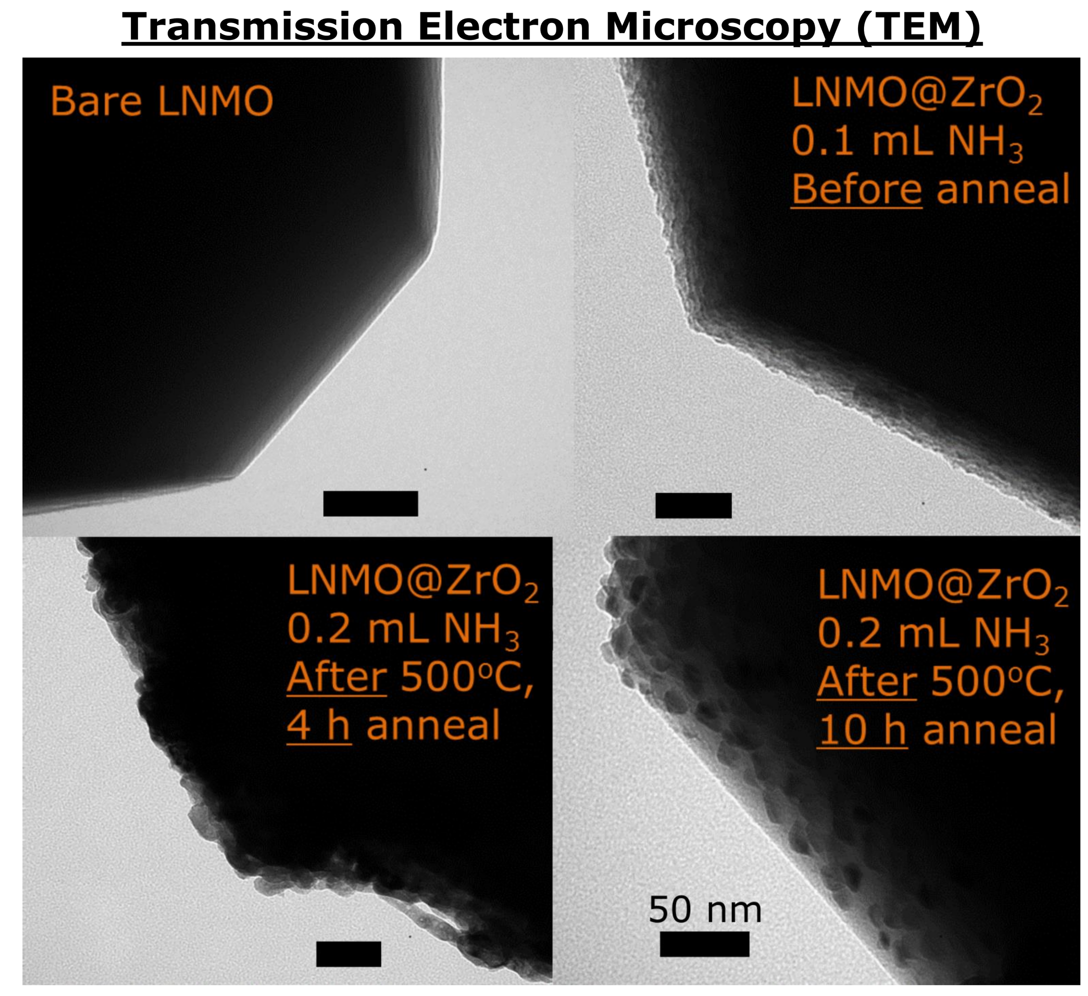
Sample	LNMO (g)	Zirconium butoxide (mL)	NH_3 (25wt.%) (mL)	Annealing
1	0.2	20	0.5	*HT-XRD*
2	0.4	5	0.2	500°C, 4h
3	0.4	5	0.2	500°C, 10h
4	0.4	5	0.1	500°C, 4h
5	0.4	5	0.1	500°C, 10h



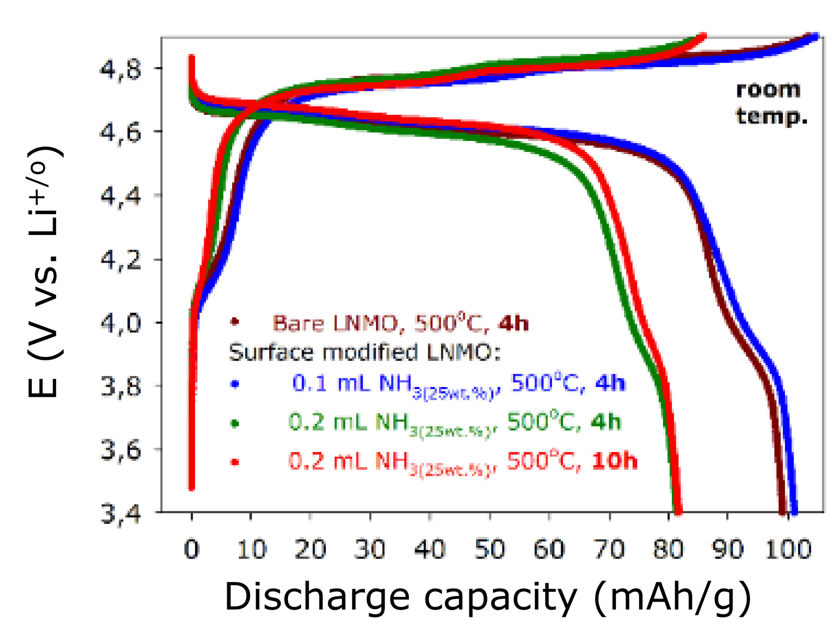


$LiNi_{0.5}Mn_{1.5}O_4@ZrO_2$ samples synthesized using 0.2 mL NH_3 (25wt.%), followed by anneals at 500°C for 4 or 10 h

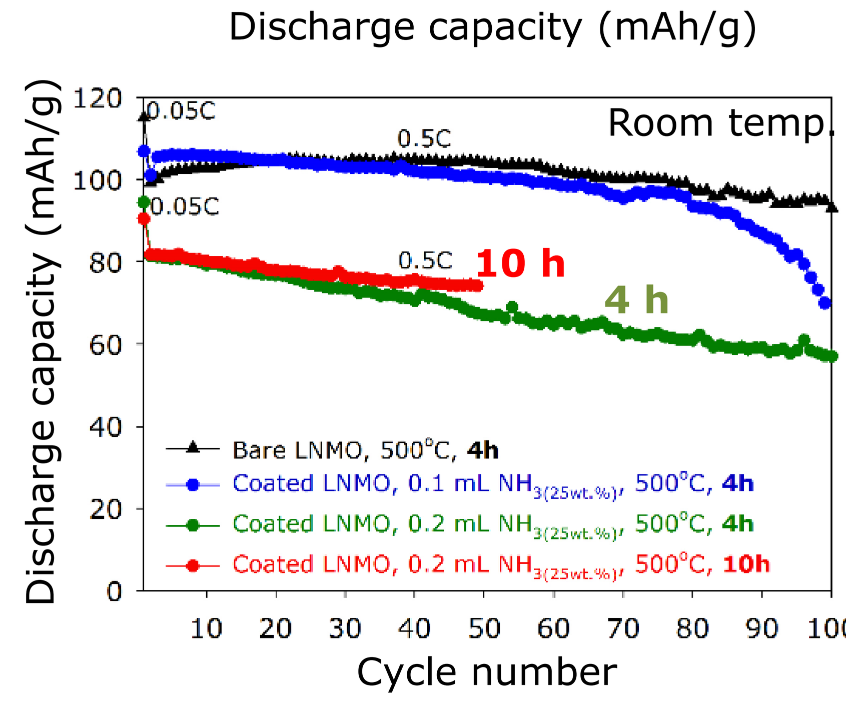
Transmission Electron Microscopy (TEM)

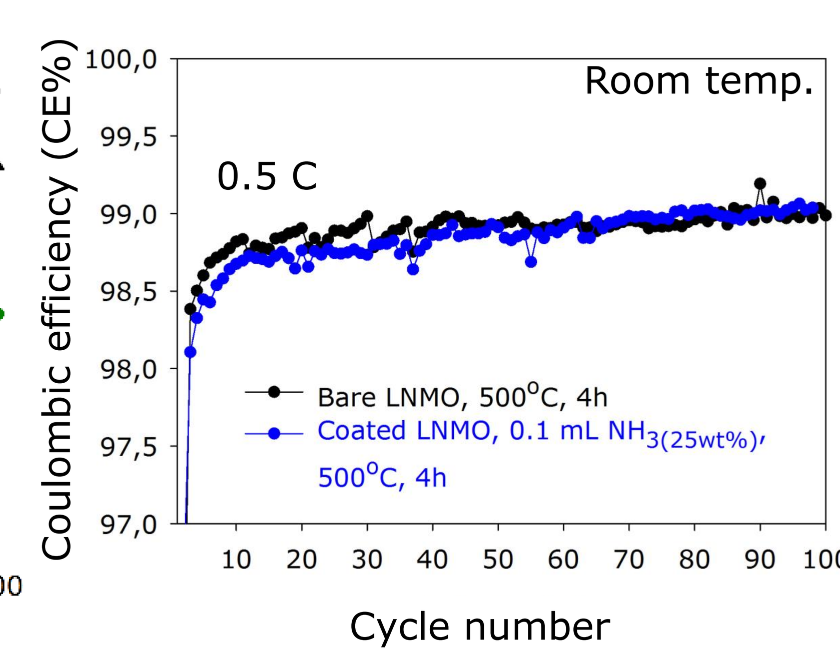


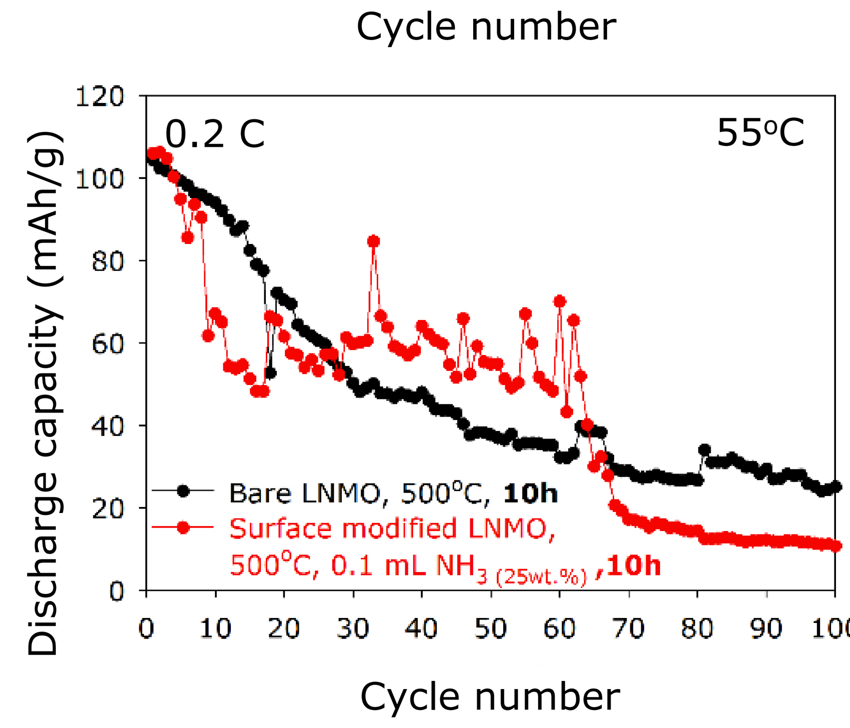
Electrochemical measurements

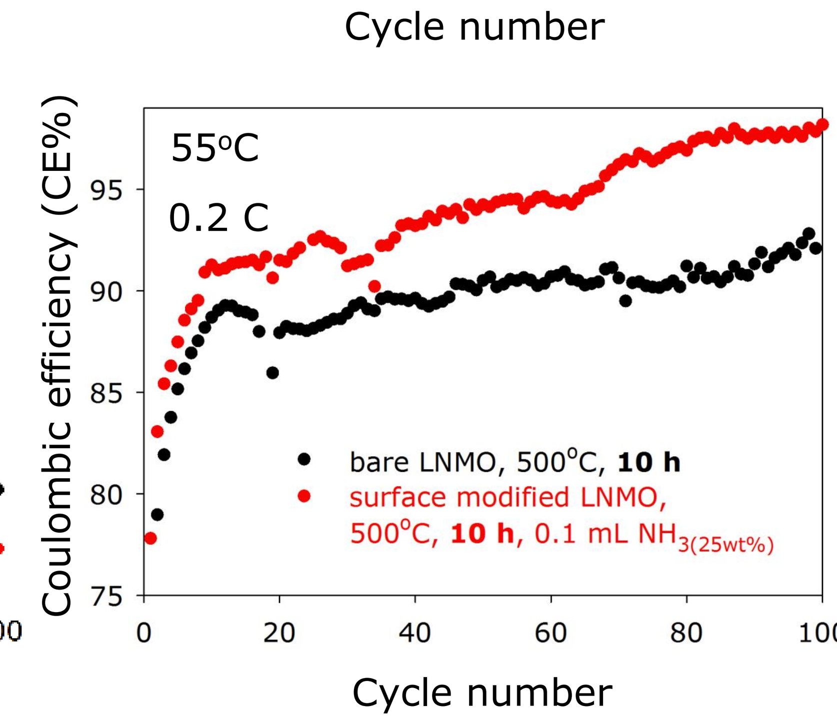


- Li-half cells of 80 wt% active material, 10 wt% PVDF in NMP, 10 wt% carbon black
- 1.0 M $LiPF_6$ EC/DEC (1:1, v/v) electrolyte, Al current collector, PP separator
- 3.4 to 4.9 V voltage window
- 0.05 C initial formation cycle followed by 100 cycles at 0.2 or 0.5 C rates









Conclusions

- Thick ZrO_2 coatings on LNMO cause initial capacity loss of ~20 mAh/g while thinner coatings do not cause an initial capacity loss.
- 10 hours anneal at 500°C in O_2 flow slightly improves cyclic stability compared to 4 hours anneal at the same conditions
- LNMO with a thin ZrO_2 coating annealed for 10 h at 500°C in O_2 flow does not show an improvement in cyclic stability or Coulombic efficiency compared to bare LNMO with room temperature cycling but shows improved Coulombic efficiency compared to bare LNMO with 55°C cycling

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Acknowledgements

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