



Understanding the improved electrochemical performance of Ti substituted Li_2MnO_3

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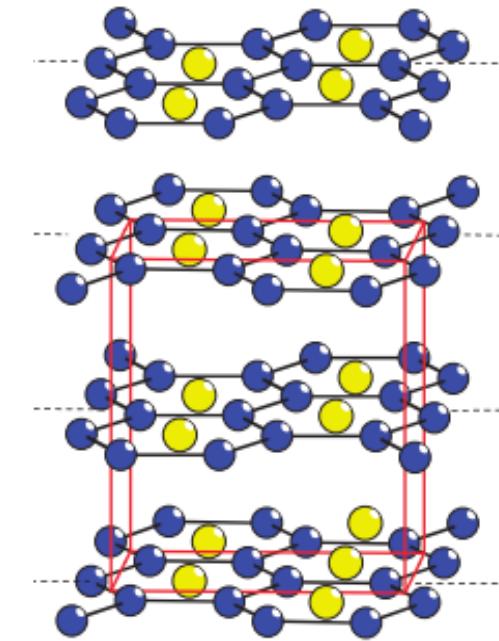
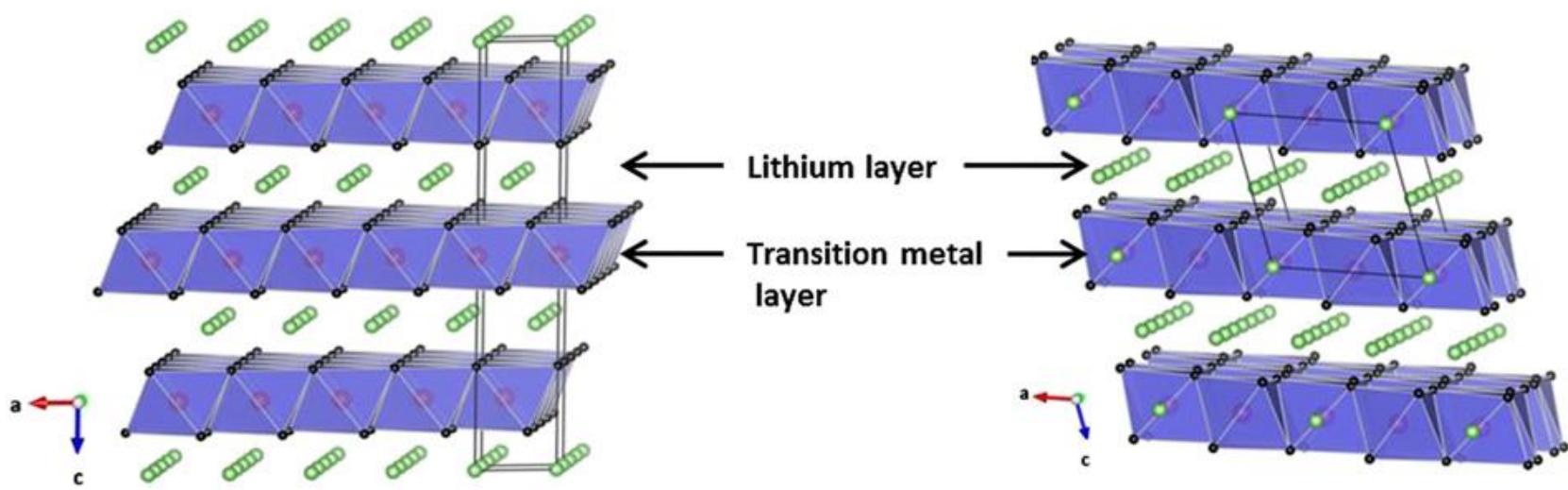
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Outline

- **Introduction**
 - Voltage fade & anionic redox chemistry in Li_2MnO_3
- **On the synthesis of Ti substituted Li_2MnO_3 via a facile solution-gel route**
- **On the structure of pristine Ti substituted Li_2MnO_3 at atomic scale level**
 - Mn(IV) and Ti(IV) cation distribution and ordering?
- **On the unique electrochemical properties of Ti substituted Li_2MnO_3**
- **On the structure of Ti substituted Li_2MnO_3 after extended galvanostatic cycling**
- **Conclusion**



Crystal structure of Li_2MnO_3



Structural degradation in Li_2MnO_3 as a cathode material for Li-ion batteries upon extended galvanostatic cycling

Fractional occupation of Li sites with TM cations / phase transition



Reduction size of tetrahedral void



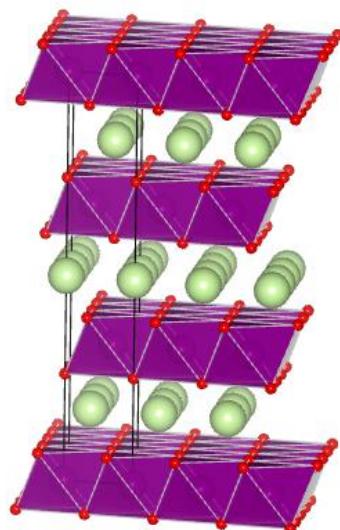
High migration barrier for Li ions

in tetrahedra having

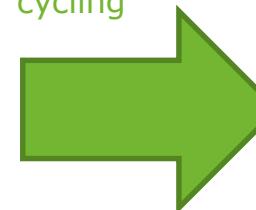
in tetrahedra having

3

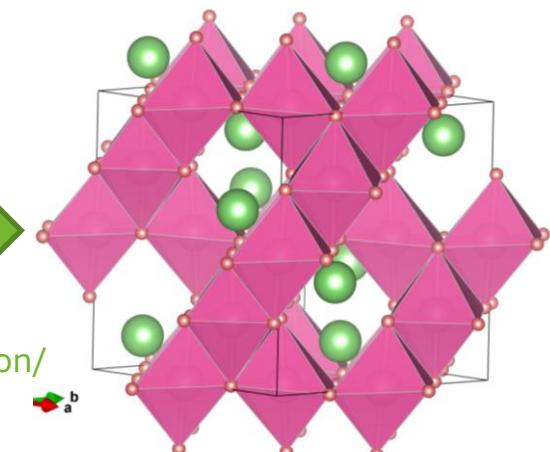
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Extented
galvanostatic
cycling



Cation migration/
Oxygen loss



(Expected) stabilization of the structure of Li_2MnO_3 by cationic substitutions

- Why Ti substitution?

- Substitution of Ti for Mn in NMC results in decrease of O_2 loss
- The ionic radii of Ti(IV) (0.605 \AA) and Mn(IV) (0.53 \AA) are quite comparable
- Ti-O bond is stronger than Mn-O bond



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Synthesis procedure of $\text{Li}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$

Solution-gel synthesis route

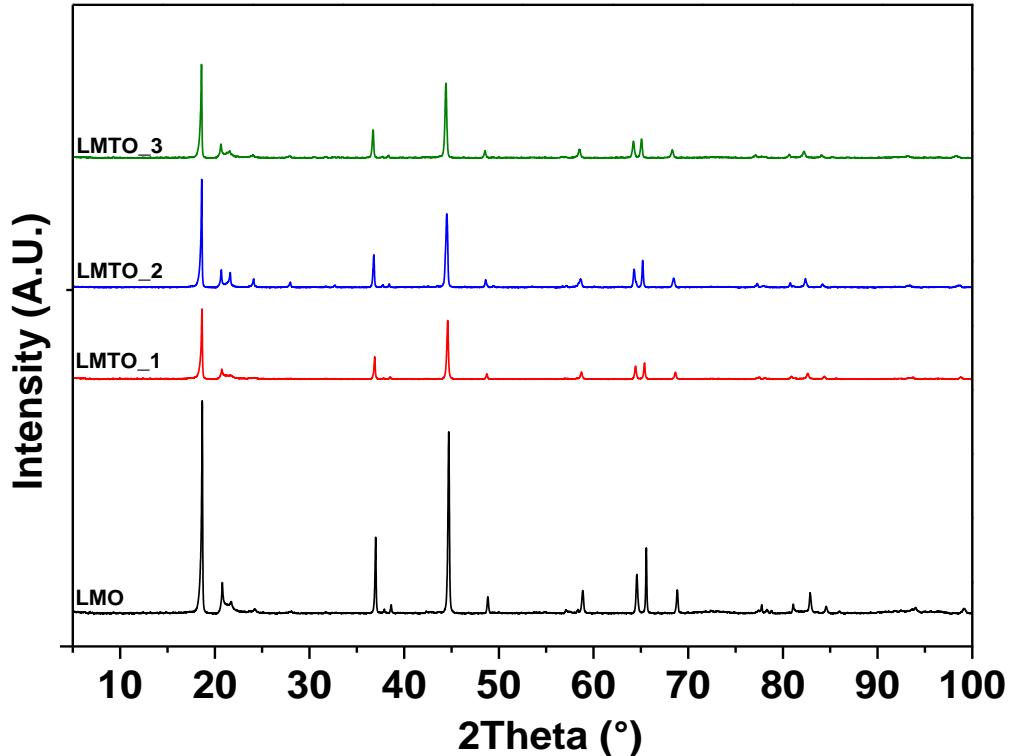
- Step 1:
 - Synthesis of aqueous multimetal (peroxo)citrate precursor starting from aq. Li citrate (+excess), $\text{Mn}(\text{NO}_3)_2$ and Ti(IV) (synthesized starting from Ti(IV) isopropoxide precursor) solutions
- Step 2:
 - Gelation (at 60° C) (**homogeneous gel**) and pre calcination (at 200° C) under atmospheric conditions
- Step 3:
 - Calcination and subsequent anneal in tube furnace
 - Step 1: 500° C (dynamic O_2 atmosphere)
 - Step 2: After cooling down to RT: Grinding by mortar and pestle
 - Step 3: 900° C (dynamic dry air atmosphere during heating step)



ICP-AES: no Li deficiency

PXRD characterization of $\text{Li}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$

- No secondary phases detected
- Increase in unit cell parameters and volume due to ionic radius Ti(IV) (0.60\AA) > Mn(IV) (0.53\AA) (monoclinic, O_h)



	LMO ($x=0$)	LMTO-1 ($x=0.1$)	LMTO-2 ($x=0.2$)	LMTO-3 ($x=0.3$)
a (\AA)	4.9342(6)	4.9466(6)	4.9554(8)	4.9496(6)
b (\AA)	8.5335(3)	8.5533(3)	8.5784(5)	8.5998(1)
c (\AA)	5.0226(0)	5.0344(4)	5.0556(0)	5.0542(2)
β ($^\circ$)	108.879(9)	108.987(8)	109.331(4)	109.113(1)
$V(\text{\AA}^3)$	200.100(0)	201.415(1)	202.794(3)	203.275(5)



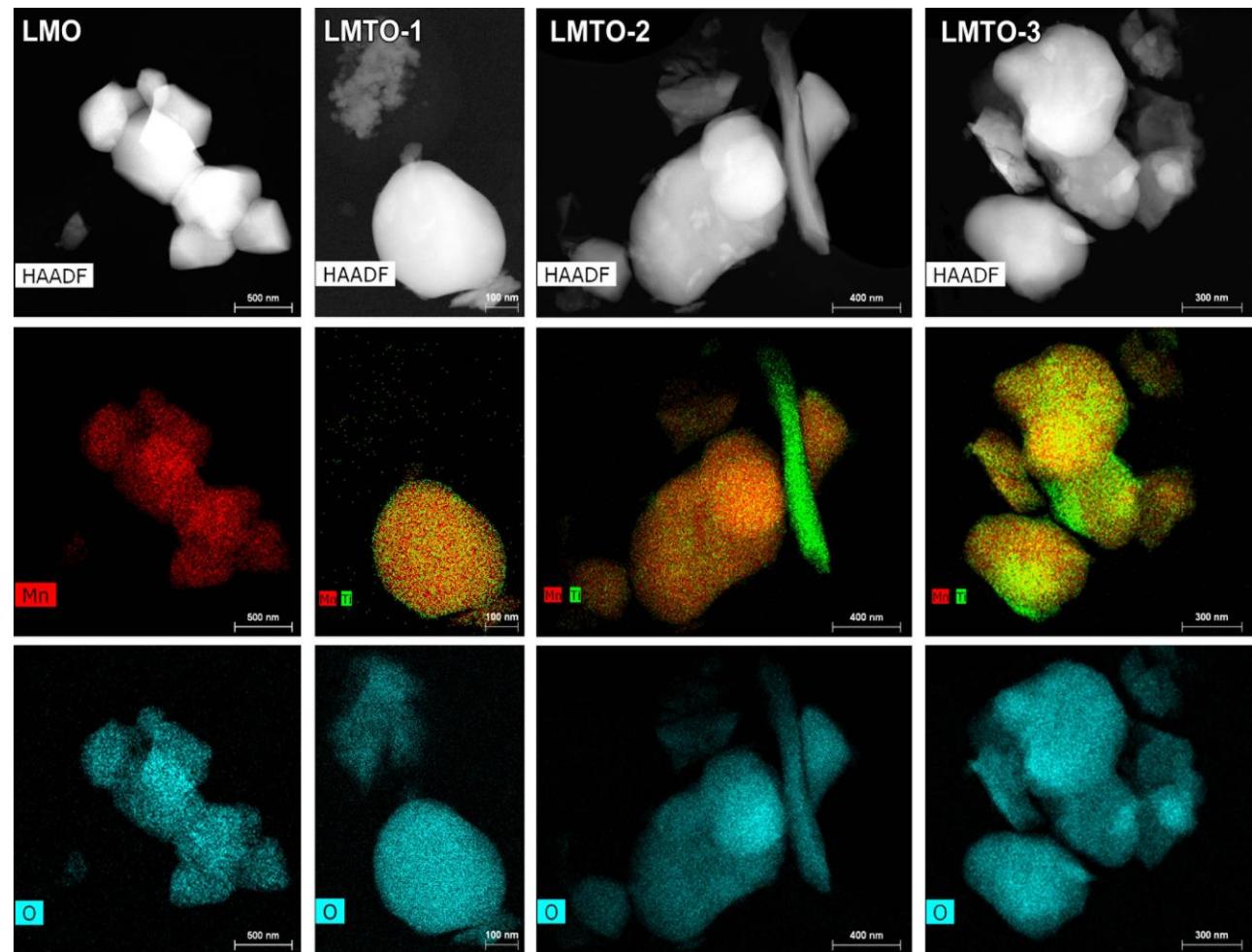
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HAADF-STEM & STEM-EDX characterization of $\text{Li}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$

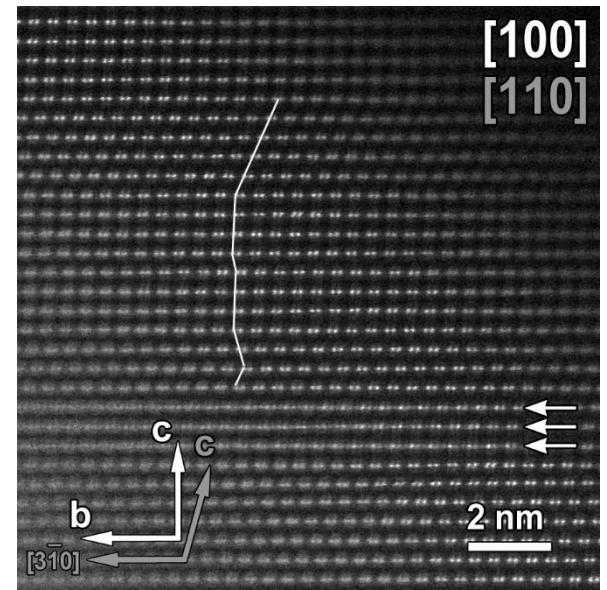
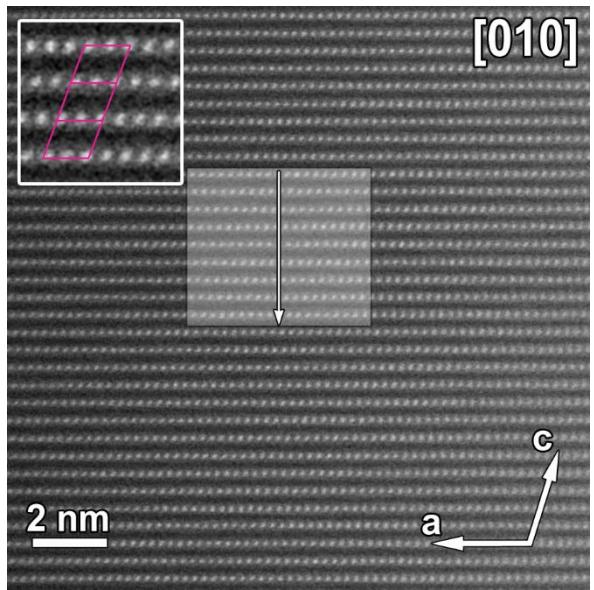
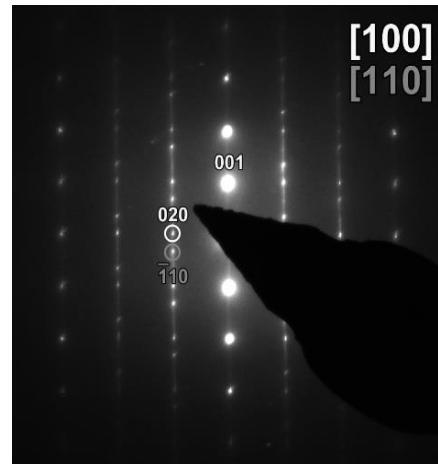
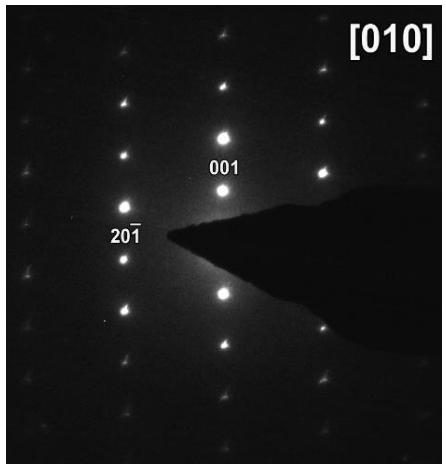
- Ti & Mn atomic percentages close to expected stoichiometry
- Overall homogeneous TM distribution
- Few enriched Ti (surface) areas
- Few TiO_2 particles for $x \geq 0.2$
- O, C containing particles
 - Post-synthesis contamination

	Expected Mn [%]	Expected Ti [%]	EDX Mn [%]	EDX Ti [%]
LMTO-1	90	10	90.9(8)	9.1(8)
LMTO-2	80	20	82.2(11)	17.8(11)
LMTO-3	70	30	74.3(32)	25.7(32)



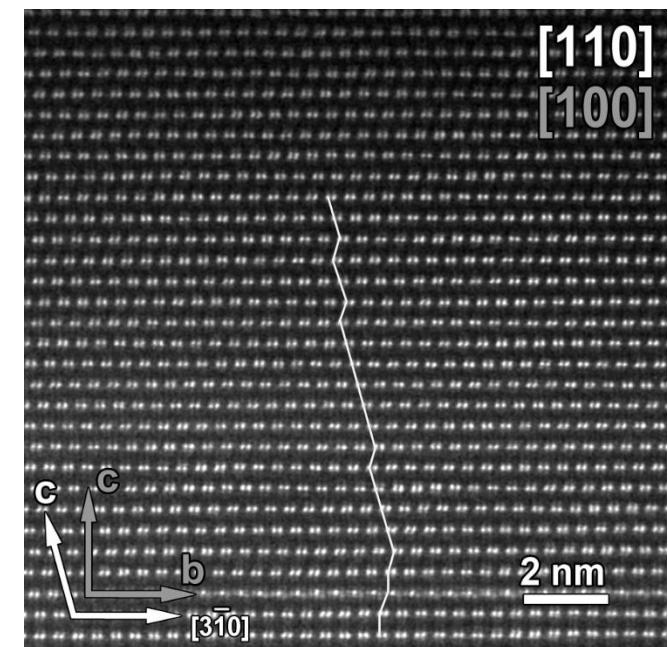
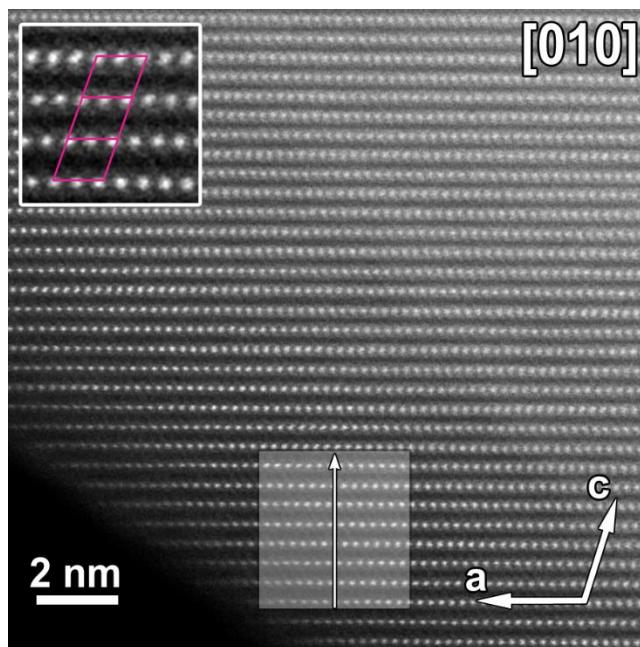
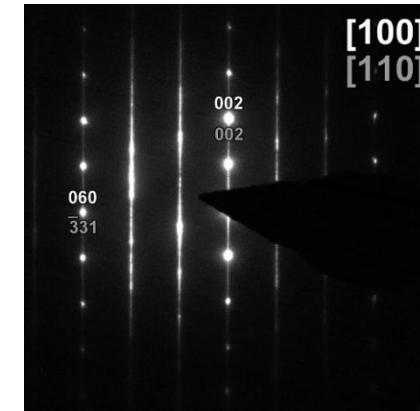
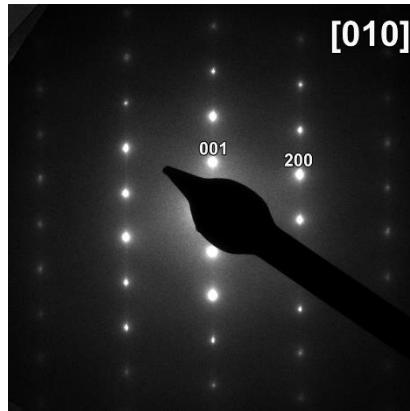
SAED & HAADF-STEM characterization of LMO

- Monoclinic C2/m symmetry
- [010]: O₃ stacking of close-packed oxygen layers
- [100]/[110]: stacking faults along c direction



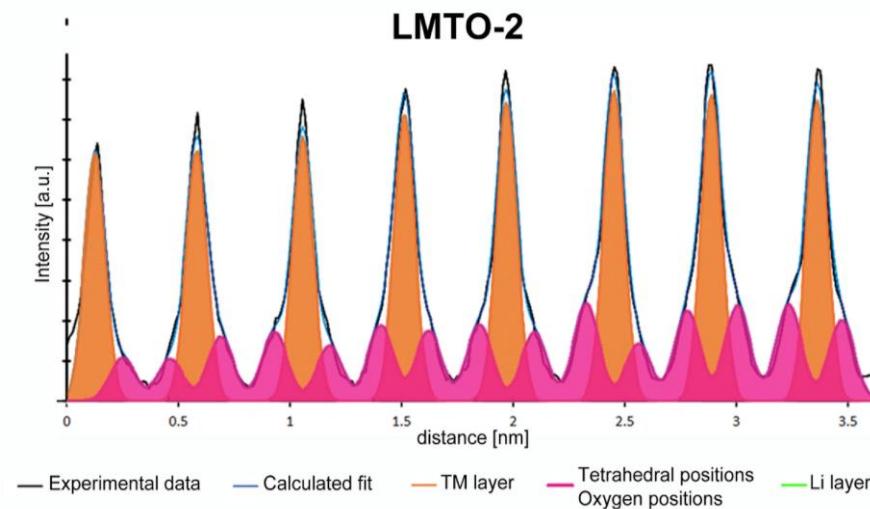
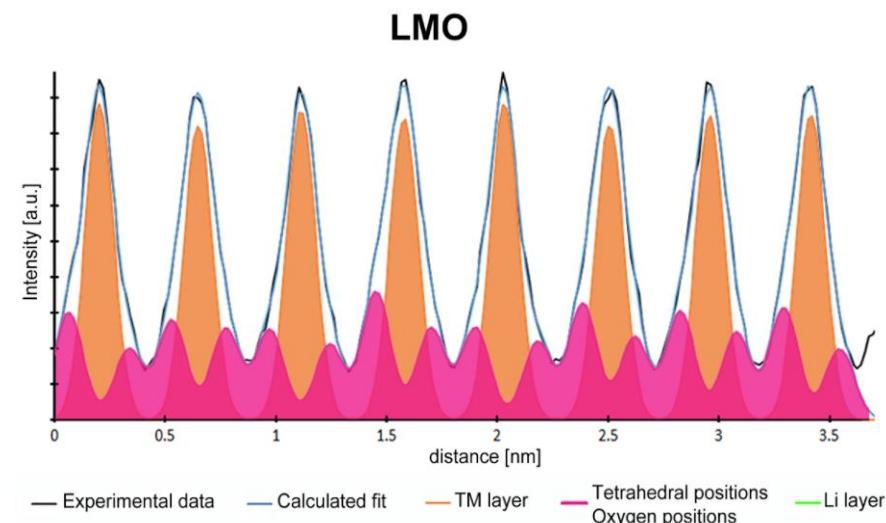
SAED & HAADF-STEM characterization of LMTO-2

- Monoclinic C2/m symmetry
- [010]: O₃ stacking of close-packed oxygen layers
- [100]/[110]: stacking faults along c direction



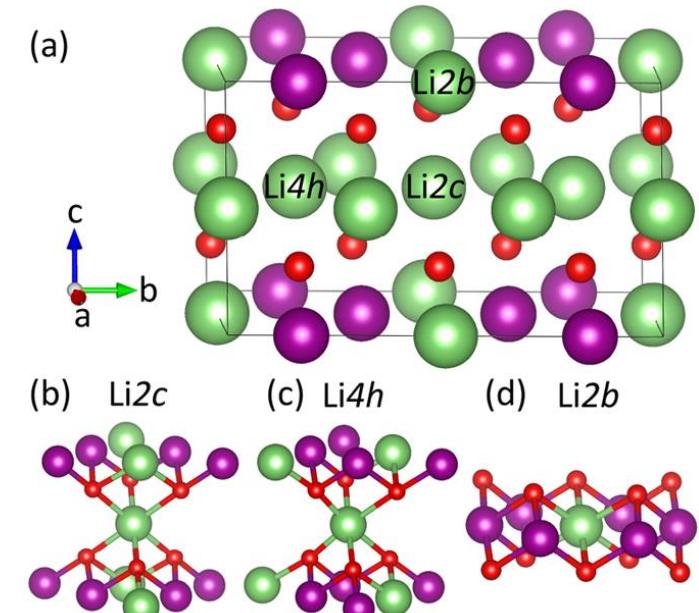
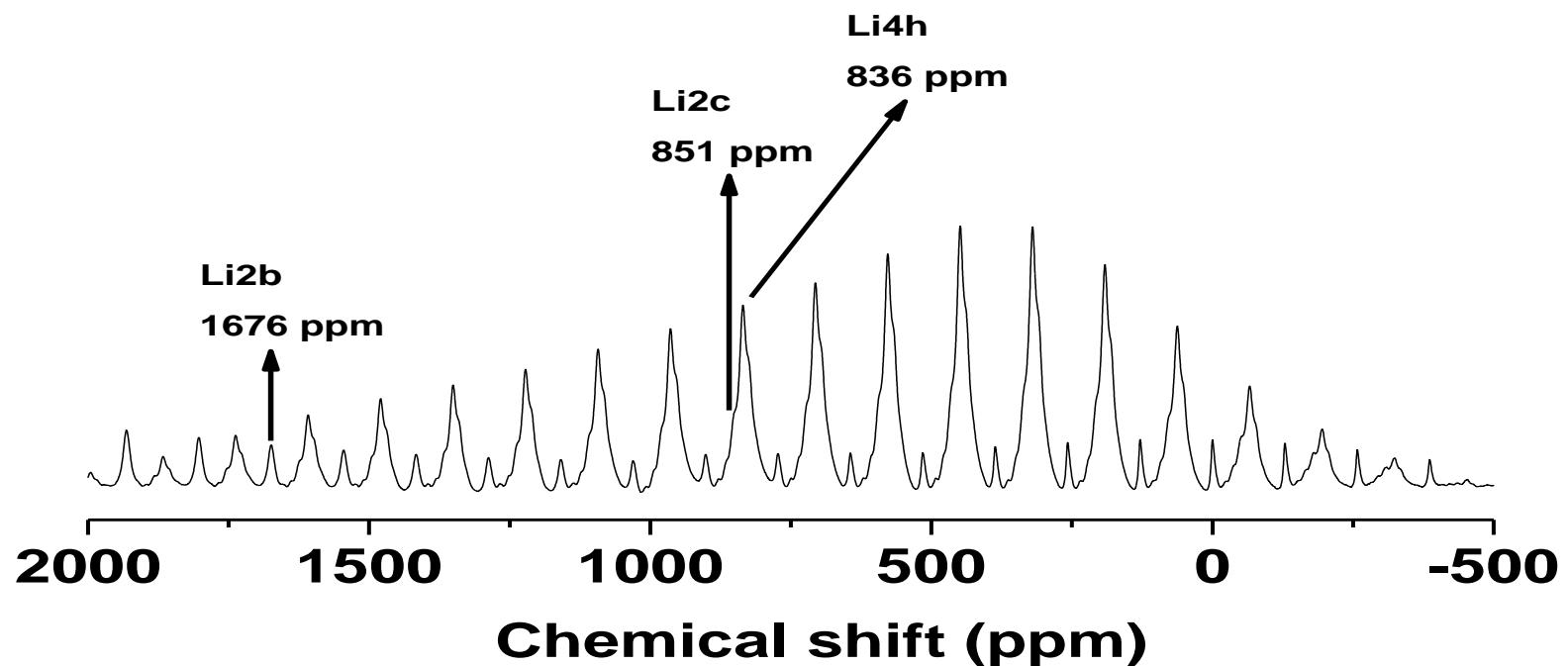
HAADF-STEM line profiles for LMO & LMTO-2

Comparable cation disorder



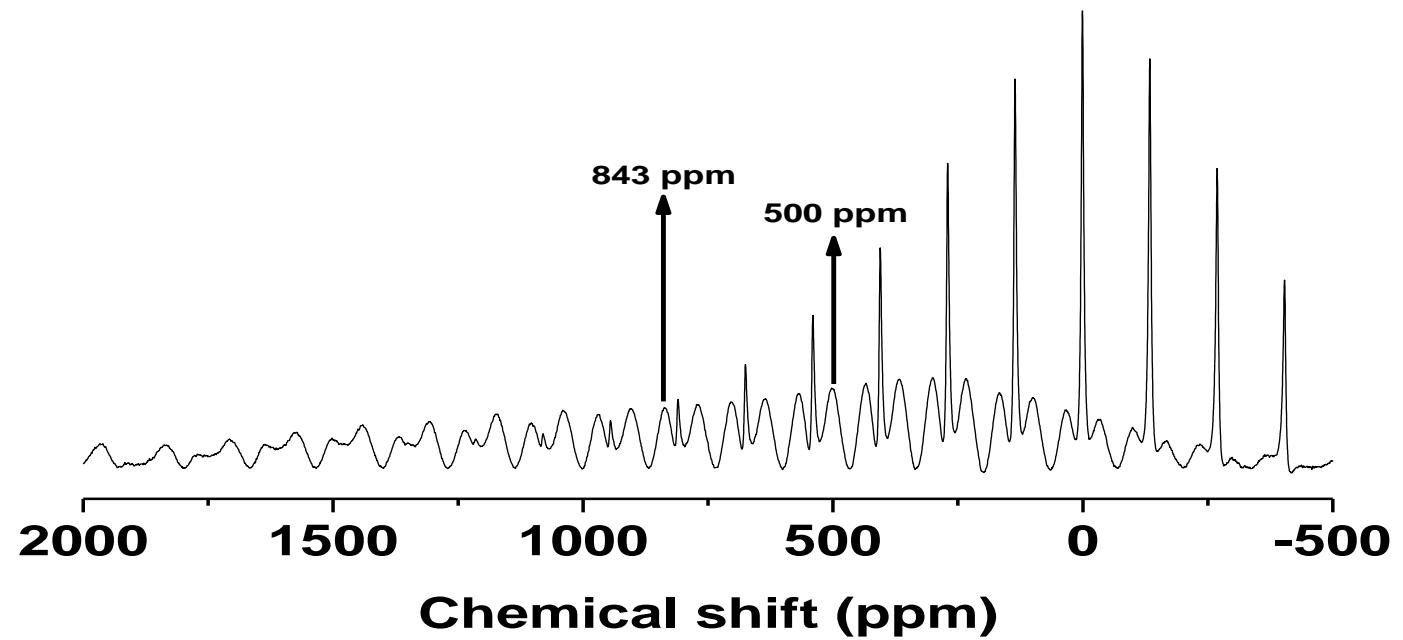
⁷Li NMR characterization of LMO

Chemical shifts in agreement with literature



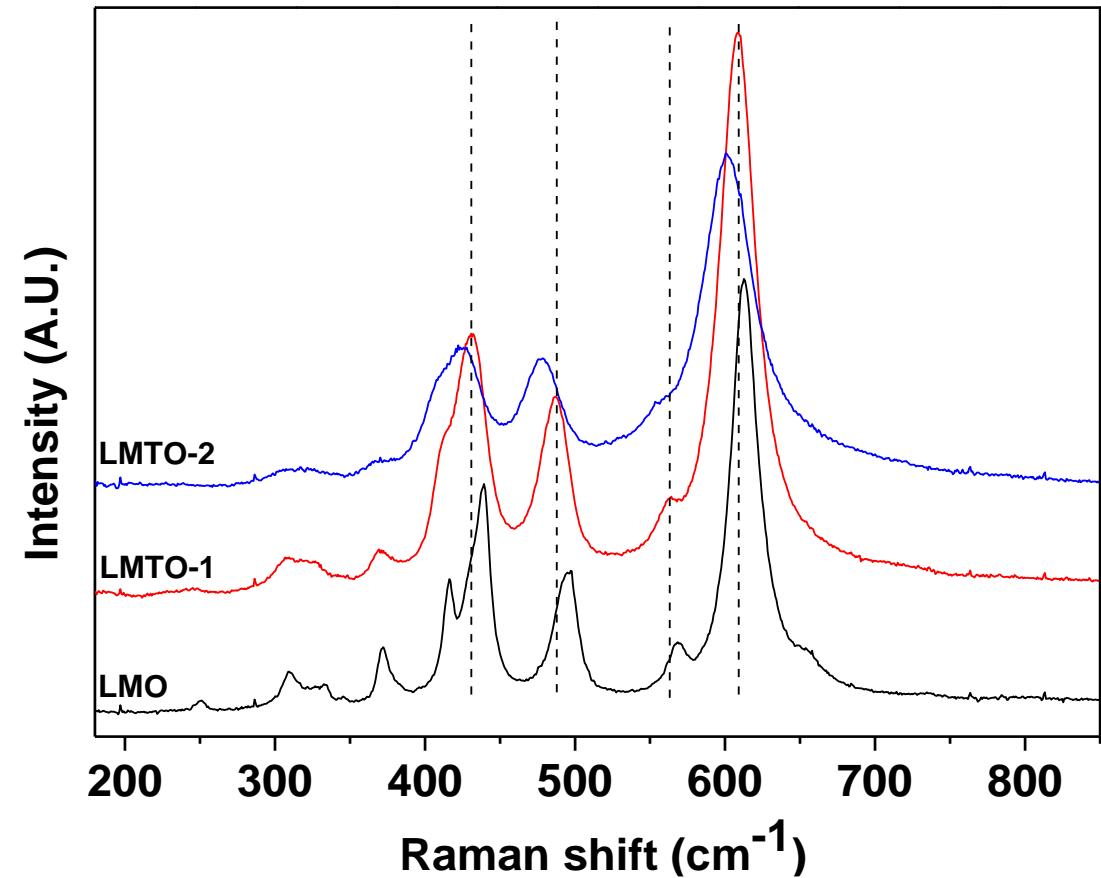
⁷Li NMR characterization of LMTO-2

Absence of peak in 1500-1700 ppm region: intimate Mn(IV) and Ti(IV) distribution



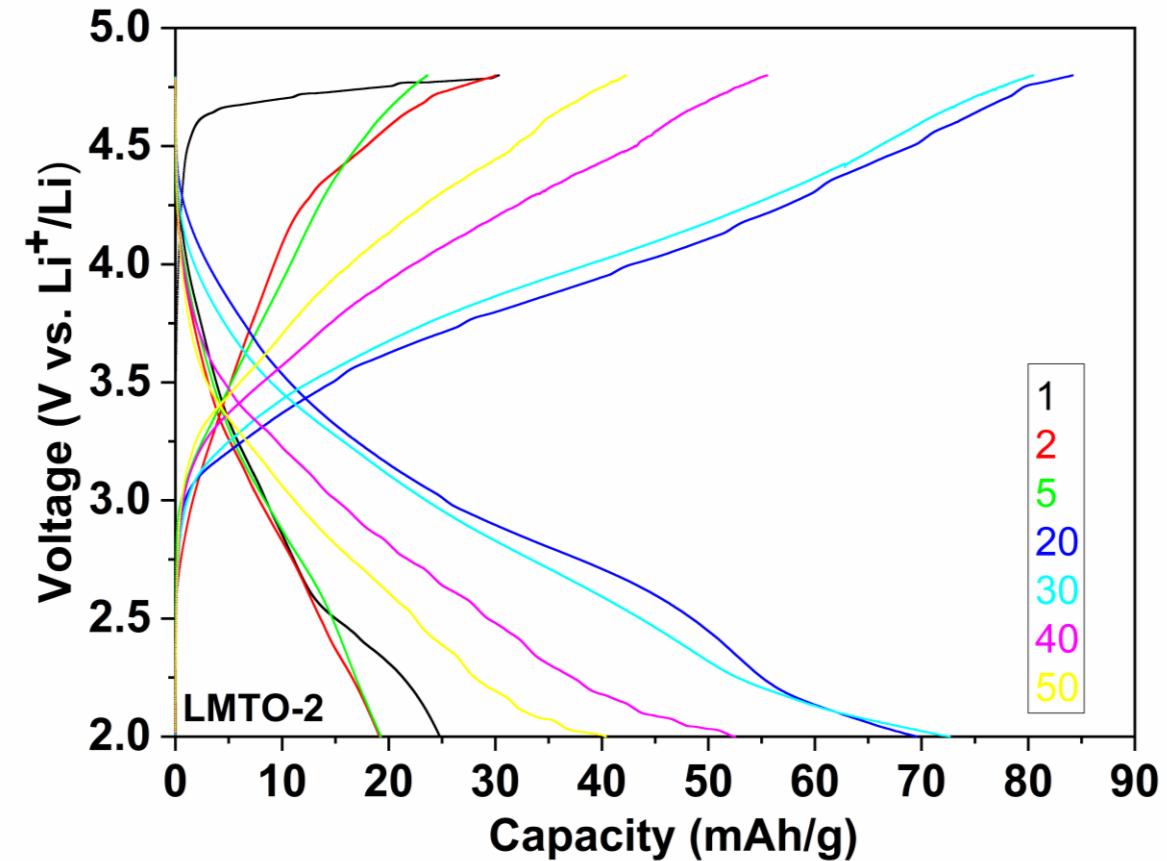
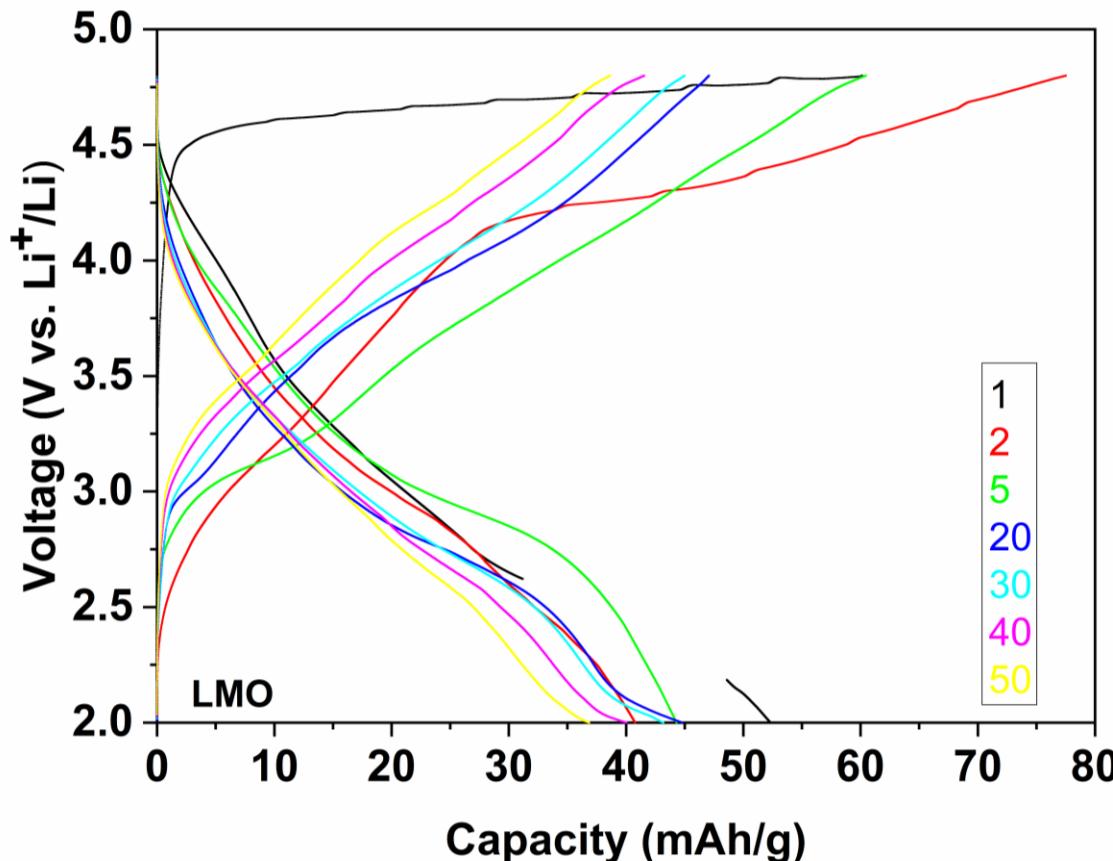
Raman spectroscopy characterization of LMO & LMTO-1 & LMTO-2

Distortion of MO_6 octahedra



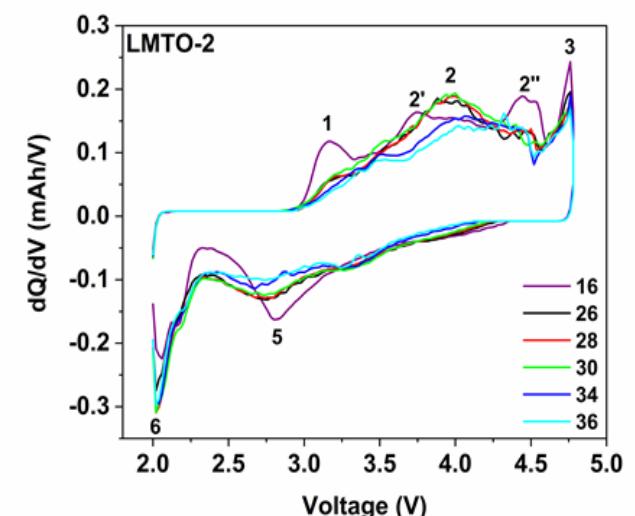
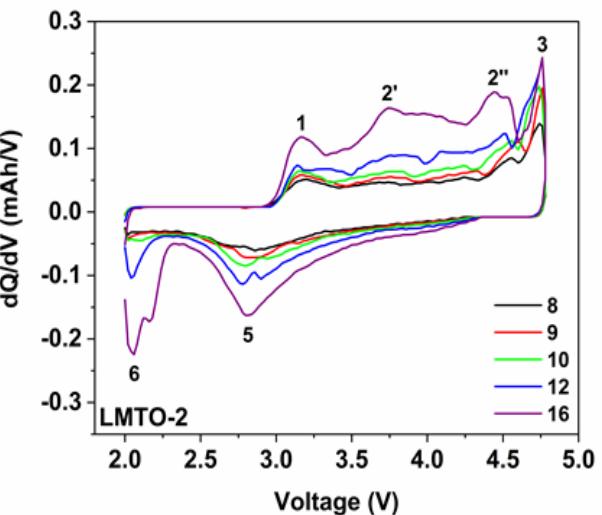
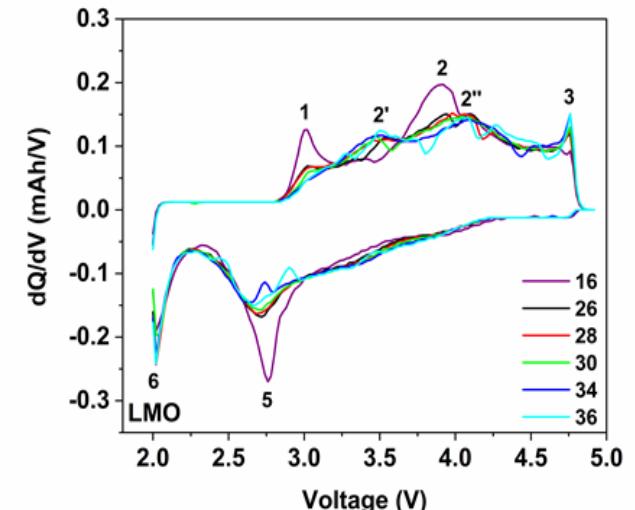
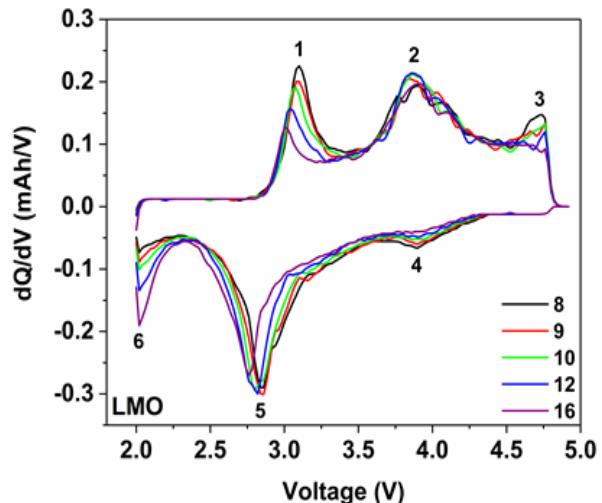
Galvanostatic cycling on LMO & LMTO-2

Higher discharge capacities for LMTO-2 at elevated cycle numbers



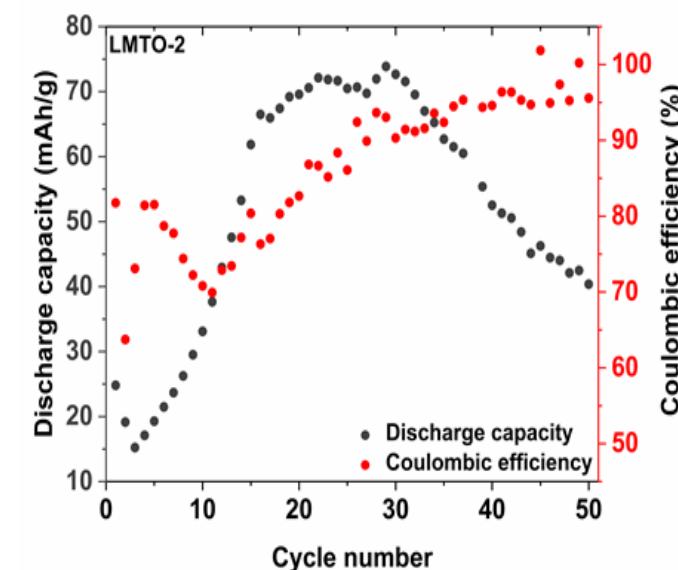
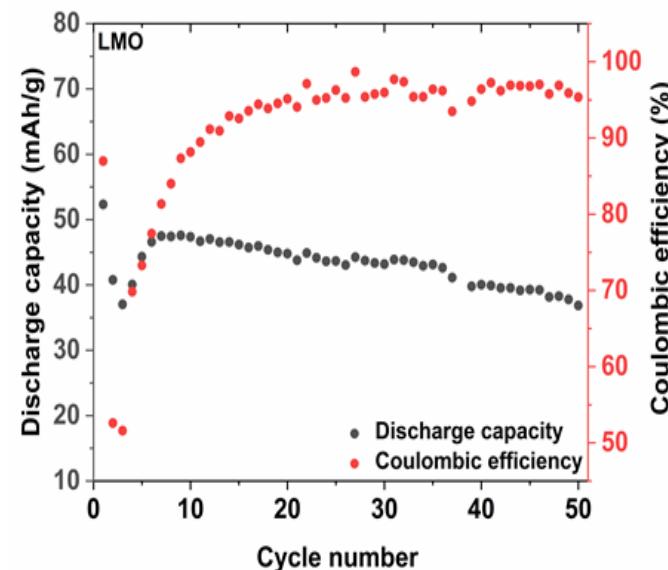
dQ/dV vs V for LMO & LMTO-2

- Oxidation peak 3 for LMTO-2 more pronounced
 - Higher contribution of irreversible oxygen release?



Coulombic efficiency & discharge capacity vs cycle number for LMO & LMTO-2

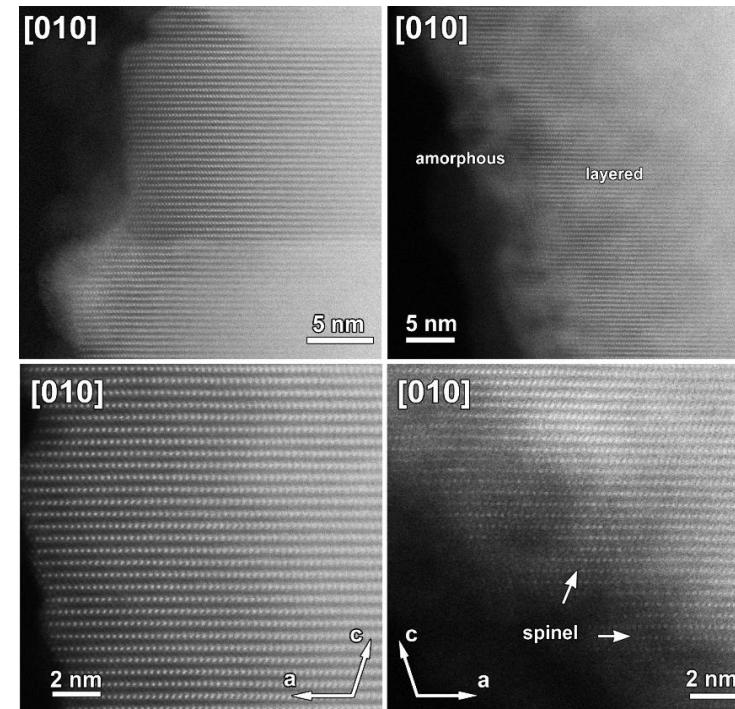
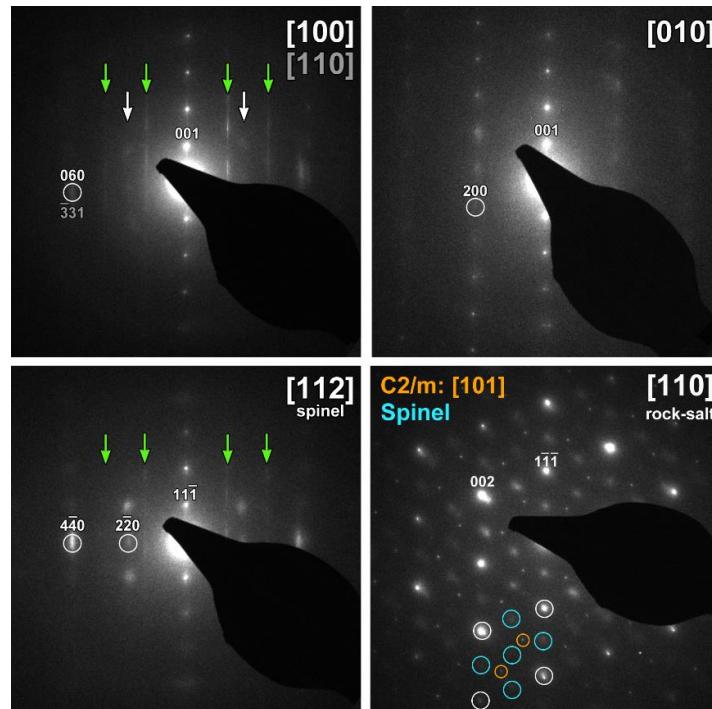
- Lower Coulombic efficiencies for LMTO-2
 - Confirms higher irreversible oxygen release (to be confirmed by DEMS)



SAED & HAADF-STEM of LMO

After 50 charge/discharge cycles at 0.1C

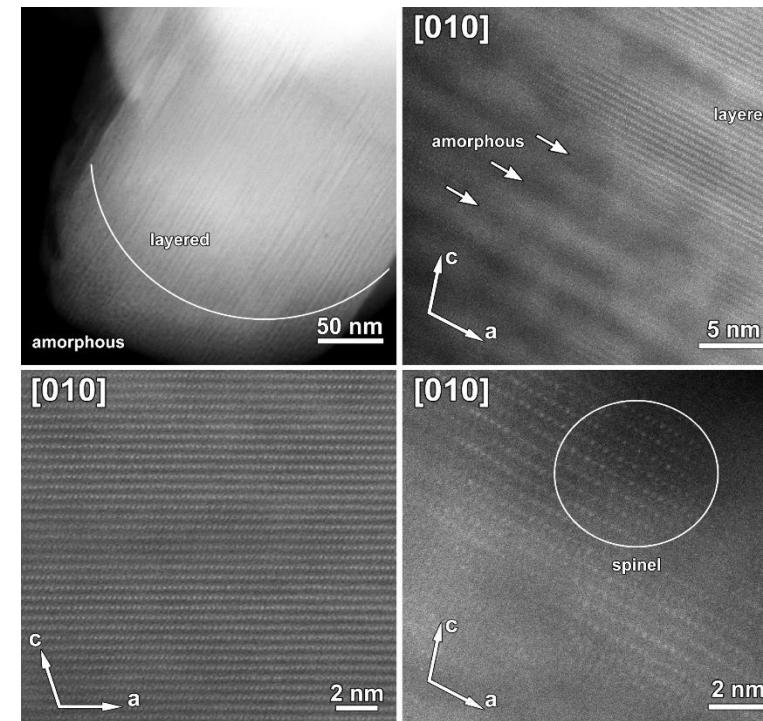
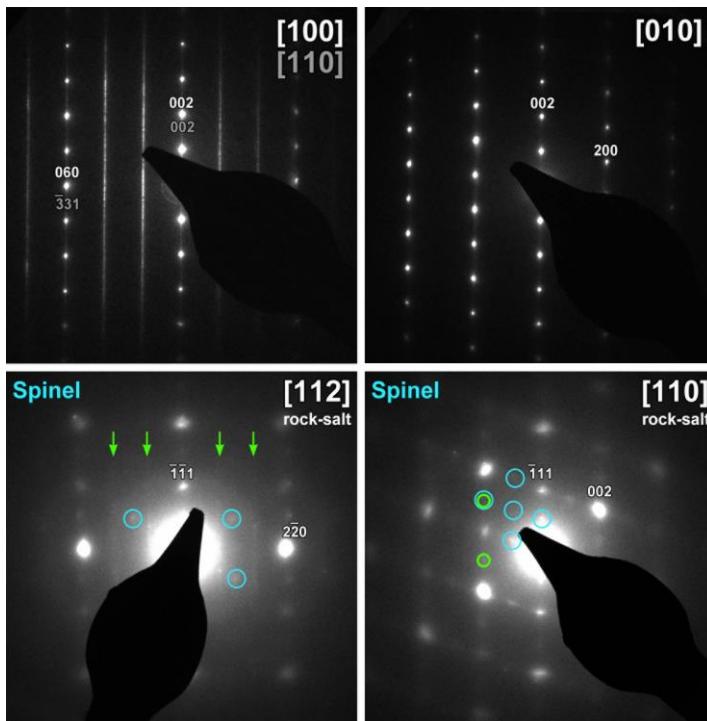
- SAED
 - Inhomogeneous structural degradation
- HAADF-STEM
 - Amorphous surface layer: 0-10 nm



SAED & HAADF-STEM of LMTO-2

After 50 charge/discharge cycles at 0.1C

- SAED
 - Inhomogeneous structural degradation
- HAADF-STEM
 - Amorphous surface layer: few nm – entire amorphous particles



Conclusion

- **Structure pristine materials**
 - C2/m symmetry and honeycomb order maintained upon Ti substitution
 - Homogeneous Mn, Ti atomic scale distribution
- **Electrochemical characterization**
 - Higher discharge capacities for LMTO-2 due to increased oxygen release
- **Structure after galvanostatic cycling**
 - Higher amorphization for LMTO-2
 - Mechanism behind unusual electrochemical behaviour of Ti substituted Li_2MnO_3 described in manuscript in preparation



Acknowledgements



M. von Holst (Hasselt University; preliminary Le Bail refinement)

Dr. O. M. Karakulina (University of Antwerp; PXRD measurements)

Funding:



**Research Foundation
Flanders**
Opening new horizons

Project number G040116N



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