

Carbothermal reduction synthesis of $\text{Li}_x\text{Mo}_y\text{O}_z/\text{C}$ composite material as a cathode material for Li-ion batteries

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Introduction

Li_2MnO_3 is extensively investigated as a cathode material for Li-ion batteries. However, oxygen loss (oxygen will oxidize prior to Mn^{4+} to Mn^{5+}) resulting in irreversible structural changes decreases the electrochemical performance.

The layered disordered NaFeO_2 type structured cathode material Li_2MoO_3 has several advantages over Li_2MnO_3 .

- Accessibility of the $\text{Mo}^{4+}/\text{Mo}^{6+}$ redox couple
- Improved kinetics due to the higher electronic conductivity
- Lower oxygen evolution from the cathode's active material oxygen sublattice.

Synthesis of Li_2MoO_3 in literature:

- Reducing Li_2MoO_4 under Ar/H_2 flow¹ or N_2/H_2 flow².
 - (-) The use of H_2 comprises severe safety issues.
- Solid state reaction between Li_2CO_3 and MoO_2 with acetylene black as an additive under inert Argon atmosphere³
 - (+) Excluding the use of H_2 .
 - (-) Extended anneal period of 24 hours at 900°C or 1000°C .

Here, we report the synthesis of $\text{Li}_x\text{Mo}_y\text{O}_z/\text{C}$ composite materials via a carbothermal reduction method with organic ligands serving as the carbon source, requiring an anneal period of 12 hours at 900°C under Ar.

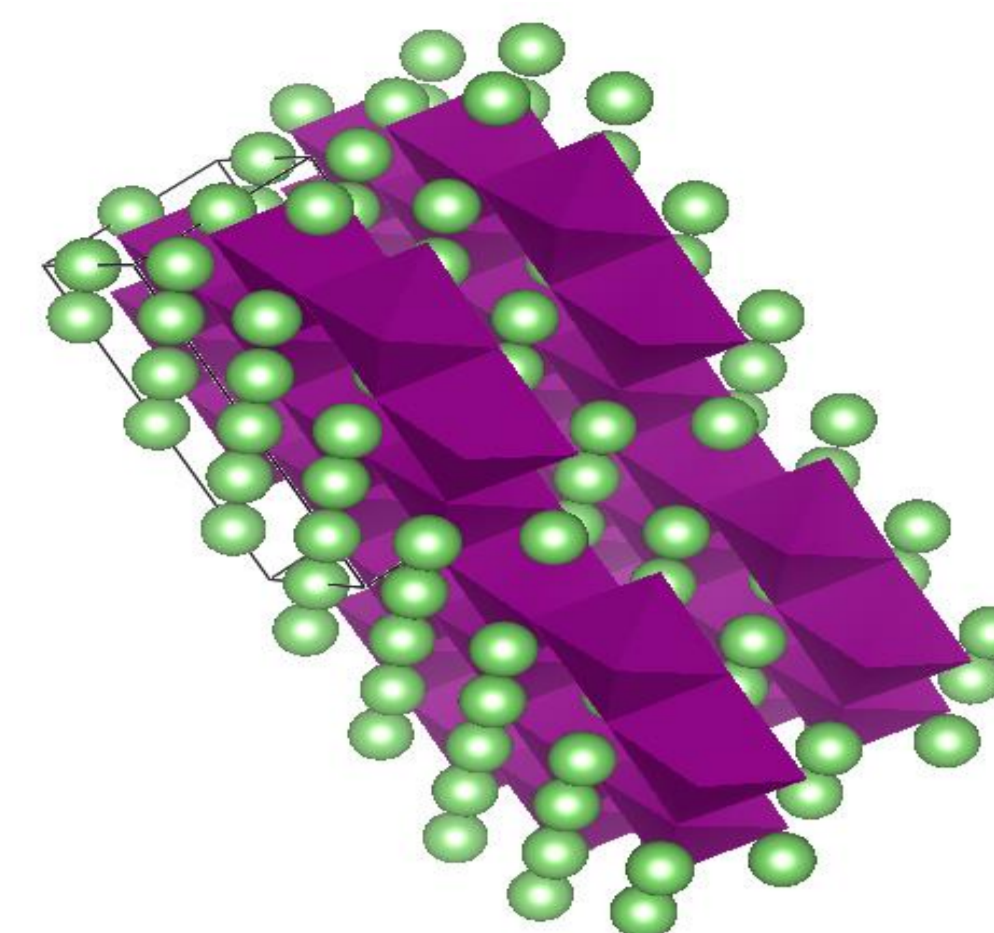
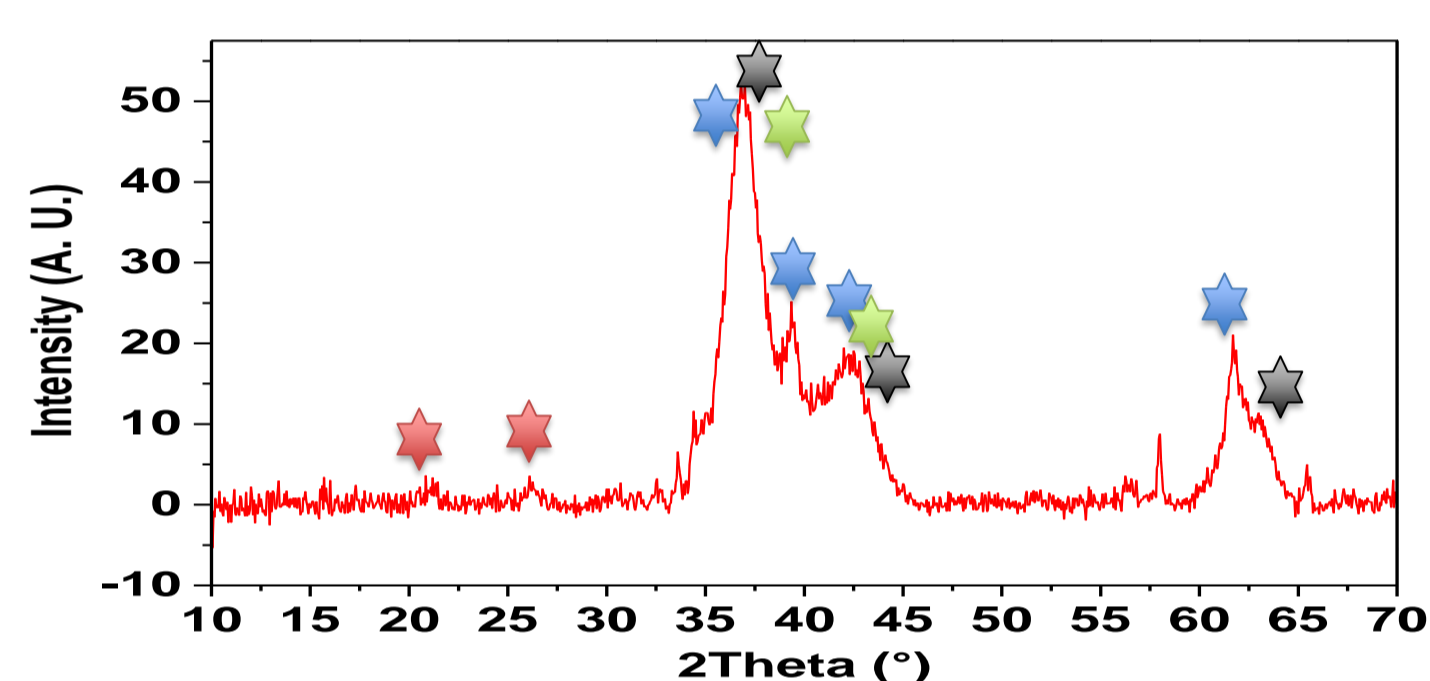


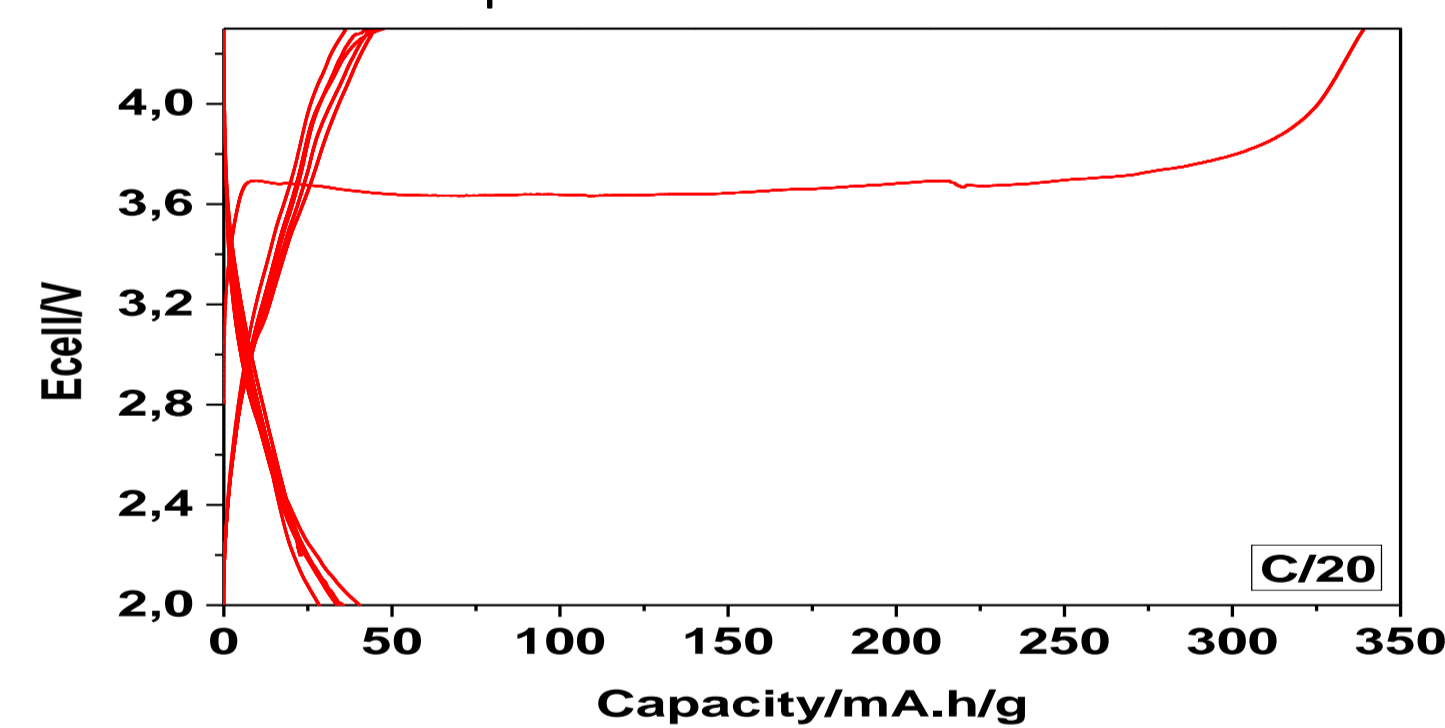
Fig. Schematic structure of layered Li-TM oxide drawn with VESTA

Results and discussion

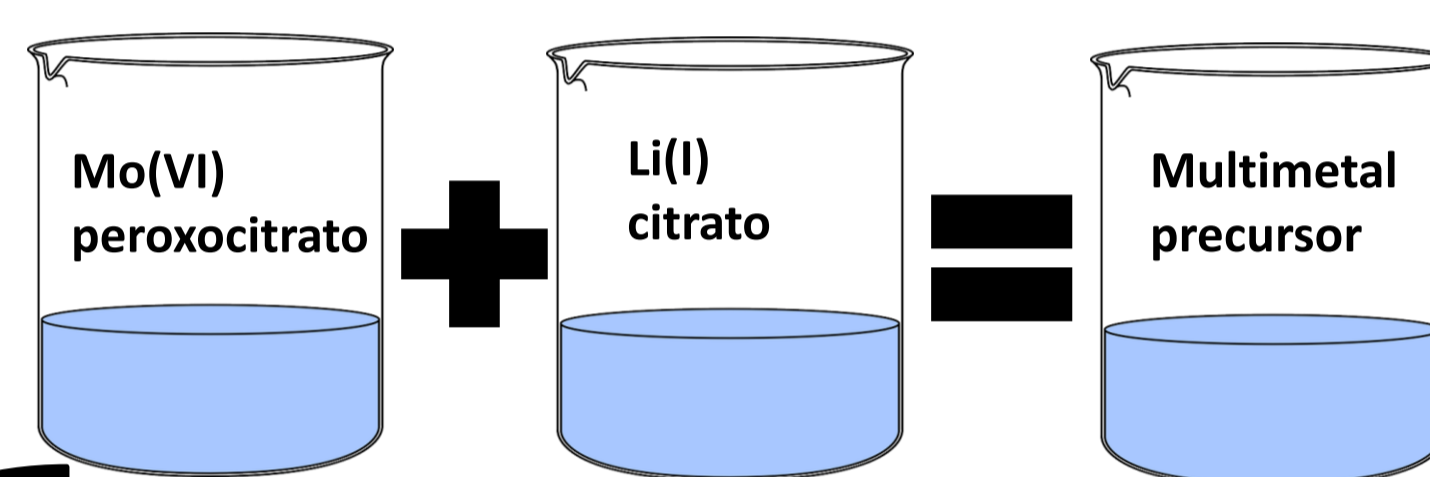
After 1st anneal period



- The PXR D pattern indicates Li_2MoO_3 (indicated with black stars) $\text{Li}_4\text{Mo}_5\text{O}_{12}$ (indicated with green stars) as major Li-Mo-O phases, hinting the ability to effectively reduce Mo^{6+} to Mo^{4+} by our synthesis method.
- Li_2MoO_4 present as minor admixture phase (indicated with red stars)
- $\text{MoC}/\text{Mo}_2\text{C}$ (indicated with blue stars) present as admixture phases



- Galvanostatic cycling has been performed within the 2.0V-4.3V window at C/20.
- The initial galvanostatic charging curve has a similar shape as compared to literature for Li_2MoO_3 , including the prominent potential plateau around 3.7V.
- Irreversible capacity during initial charge/discharge cycle probably ascribed to decomposition of $\text{MoC}/\text{Mo}_2\text{C}$.

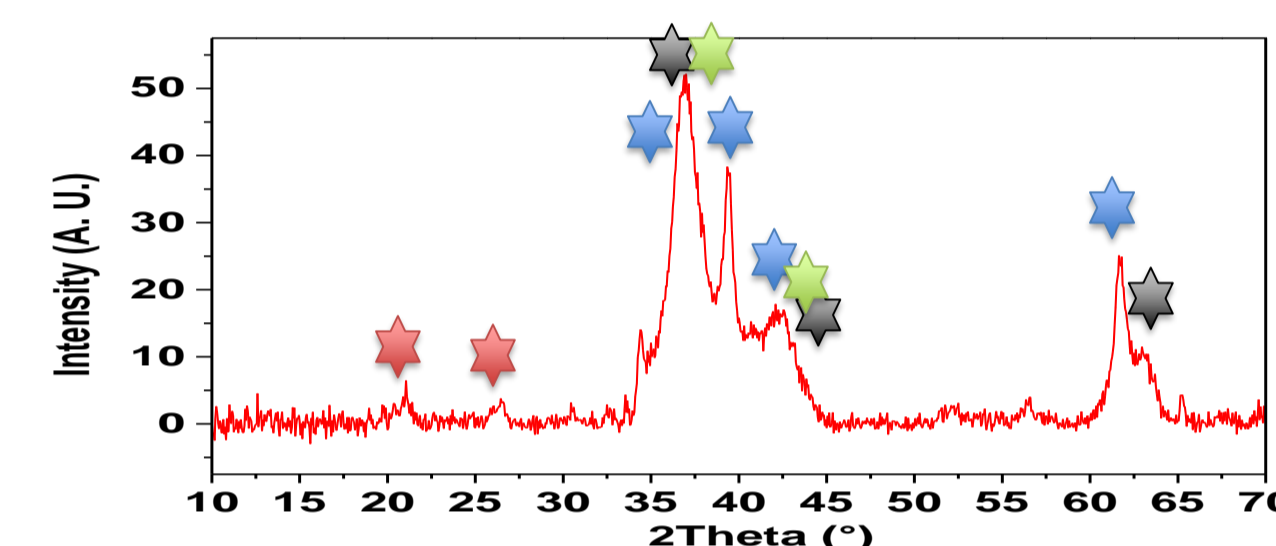


Gelation
60°C overnight

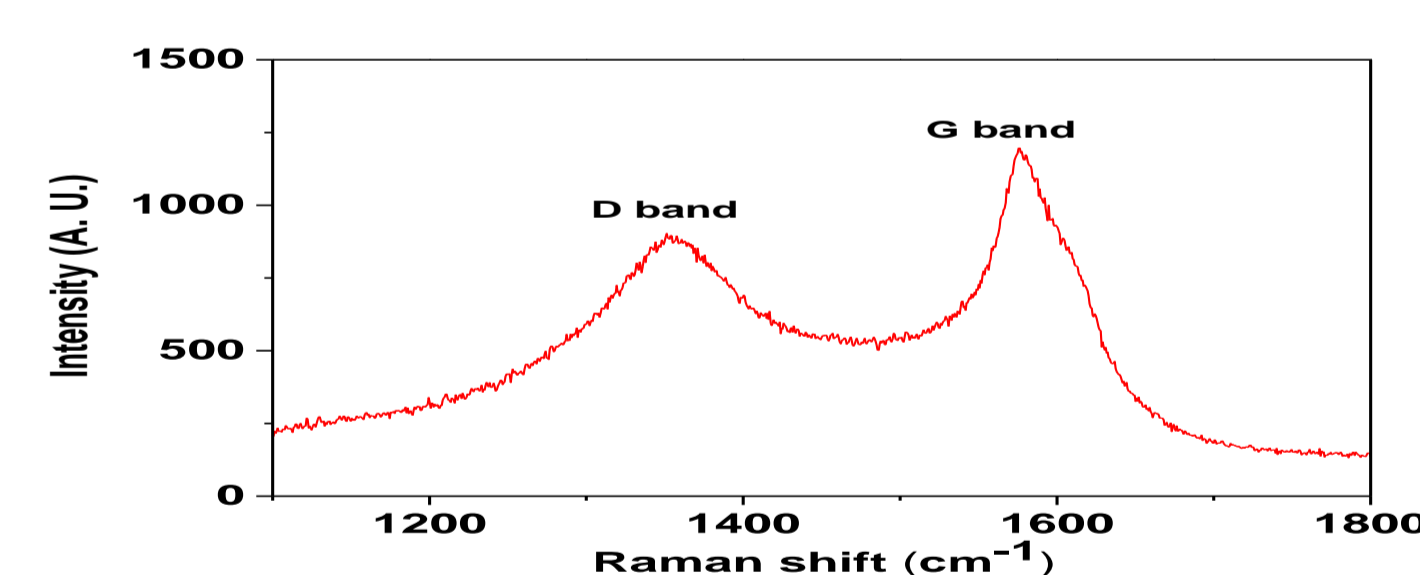
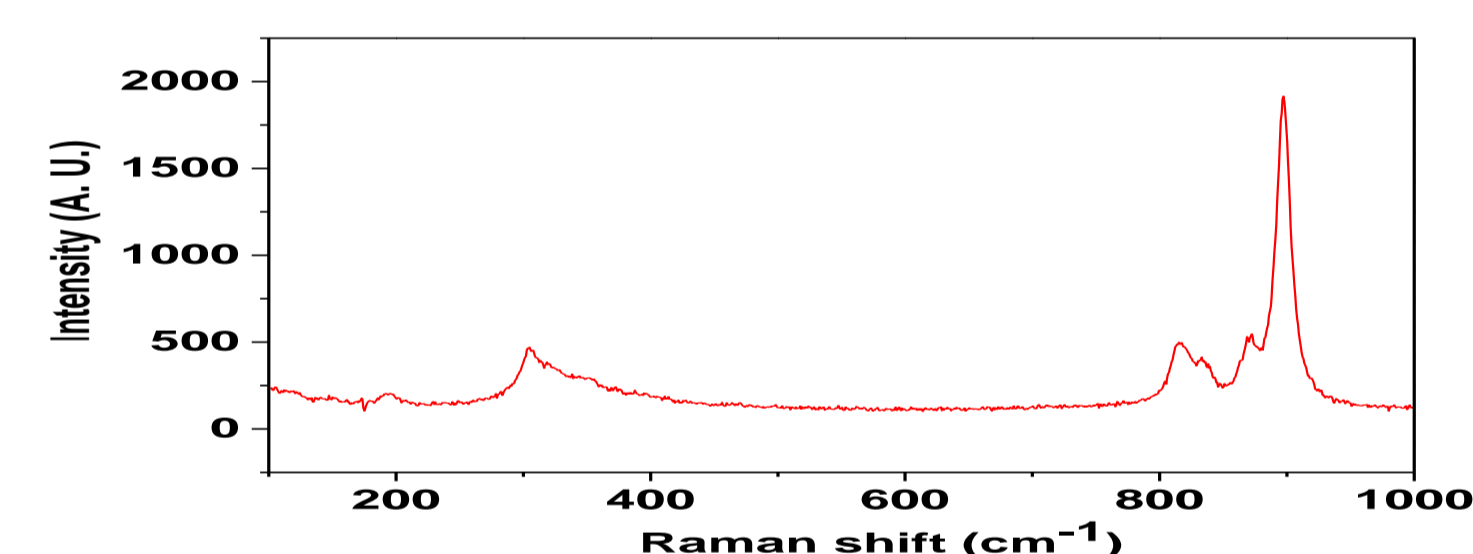
1st anneal
12h@900°C, Ar

2nd anneal
12h@900°C, Ar

After 2nd anneal period



- The PXR D pattern indicates the presence of the same major Li-Mo-O phases as after first anneal (Li_2MoO_3 and $\text{Li}_4\text{Mo}_5\text{O}_{12}$)
- Indication of higher content of the admixture phases $\text{MoC}/\text{Mo}_2\text{C}$.



- The top Raman spectrum is characteristic for layered Li-Mo-O.
- The bottom Raman spectrum indicates the presence of amorphous carbon.
 - Formation of Li-Mo-O/C composite

Conclusion

- Via carbothermal reduction synthesis a Li-Mo-O/C composite material has been obtained with Li_2MoO_3 , $\text{Li}_4\text{Mo}_5\text{O}_{12}$, MoC , Mo_2C and amorphous carbon as main phases.
 - Ability to effectively reduce Mo^{6+} present in the multimetal precursor to Mo^{4+} under Ar, avoiding the use of H_2 .
- PXR D hints less $\text{MoC}/\text{Mo}_2\text{C}$ as an unwanted admixture phase after the first anneal step as compared to after the second anneal step.
- Further research is required to gain understanding of the origin(s) for the high irreversible capacity in the initial charge/discharge step and to further reduce the content of molybdenum carbide.

References

1. Self, E.C. et al., Chem. Mater. **30**, 5061-5068 (2018)
2. Yu, Z. et al., Int. J. Electrochem. Sci. **13**, 4504-4511 (2018)
3. Kumakura S. et al., Phys. Chem. Chem. Phys. **18**, 28556-28563 (2016)

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