Effect of Lithium-Molybdenum-Phosphate Surface Coatings on Ni/Mn-Based Co-Free Layered Cathode for Li-ion Batteries

Taewoo Kim[1] (Mentor: Yoojin Ahn[2] and Dr. Meilin Liu[2])

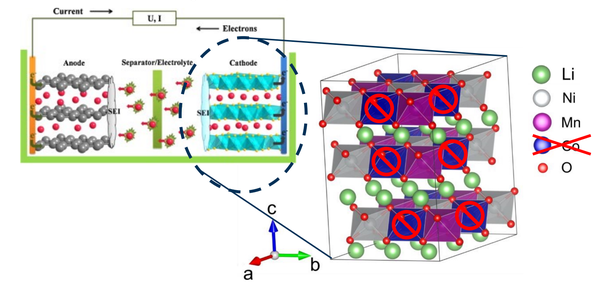
[1] School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332

[2] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332

Introduction

Eliminating Cobalt from Layered Oxide Cathode Materials

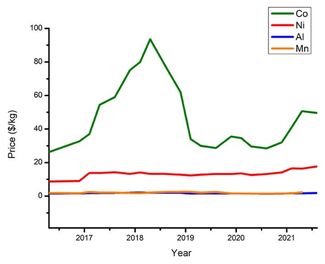
B. Xu et al., *Mater. Sci. Eng. R* 2012, 73, 51



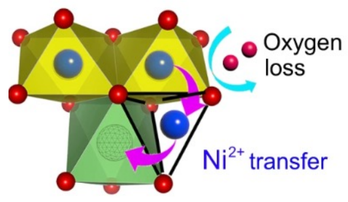
J. C. Garcia et al., *J. Phys. Chem. C* 2017, 121 (15), 8290

Pros
+ Material cost reduction
+ Mitigated supply chain risks
+ Improved sustainability

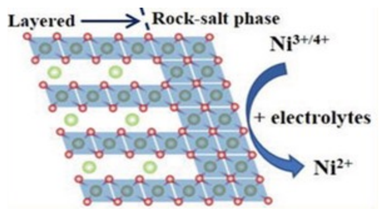
Cons
- Severe structural degradation & interfacial instability
- Lower electronic conductivity



D. Kuruahmet et al., *ACS Omega* 2023, 8, 17, 15124



H. Yu et al., *Nat. Commun.* 2021, 12, 4564



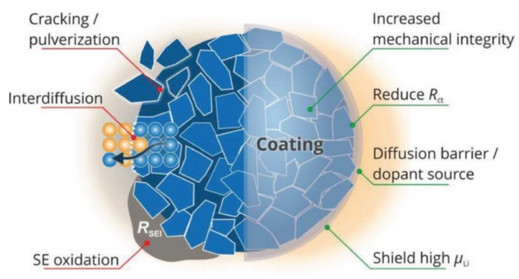
H. Li et al., *Small* 2023, 19:2302208

Objectives

- To enhance the structural and surface stability of Co-free cathode active material (NMX) by introducing a Li-Mo-PO_4 (LMP) coating
- To demonstrate the improved electrochemical performance and durability with a coating layer
- To elucidate the coating chemistry through microscopic characterizations and rationalize the effects of LMP treatment

Technical Approaches

Surface Coatings



U. Nisar et al., *Energy Storage Mater.*, 2021, 38, 309

- Act as physical barriers against the electrolyte
- Prevent electrolyte decomposition, HF/chemical attack
- Good Li^+ & e^- conductor
- Redox-inactive

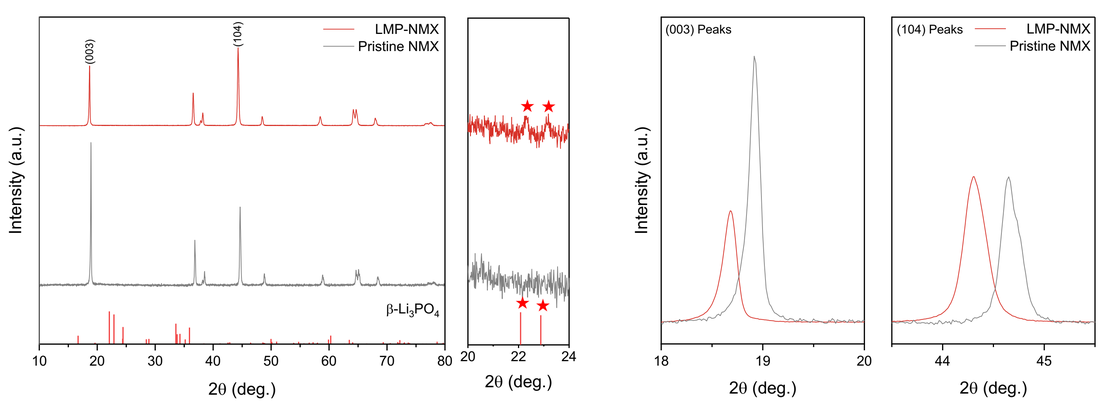
Material Synthesis Workflow

Coating Precursor Li + Mo + PO_4 → (Ball-milling) → Nanoparticle LMP Mixture + Co-free Cathode Active Material (NMX) → (Planetary Mixing) → Homogeneous LMP-NMX Mixture → (Calcination) → LMP-coated NMX

Key variables: composition of the precursor, weight percent of the coating material, calcination conditions , …

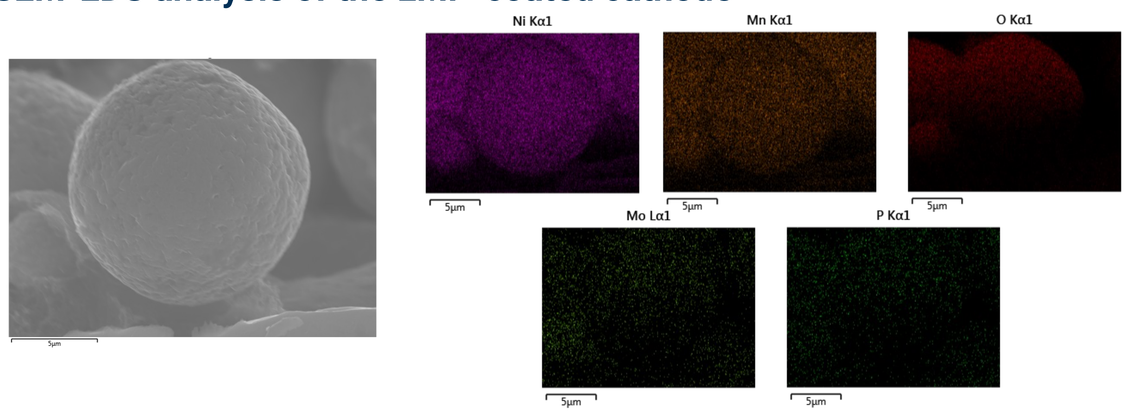
Results & Discussions

- **XRD analysis of the LMP-coated cathode**

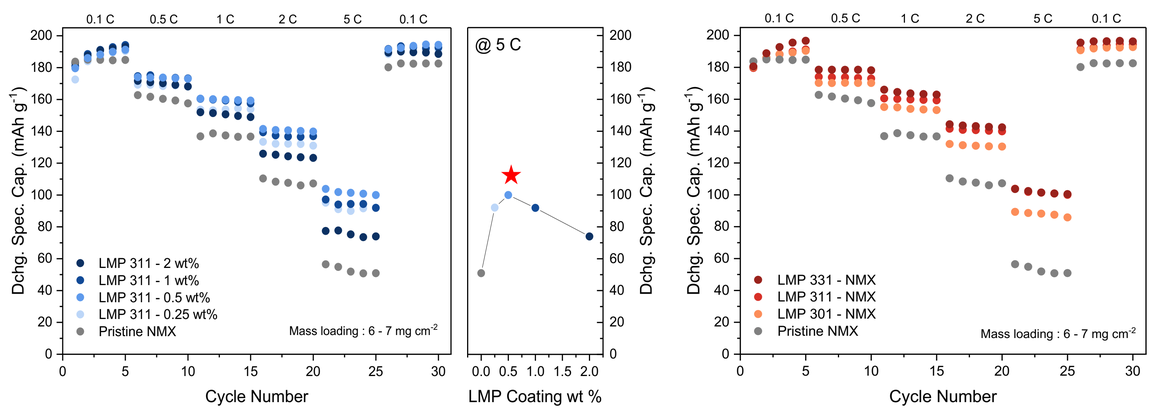


- β-Li_3PO_4 peaks are detected as an additional phase, suggesting that a Li_3PO_4 layer has formed on the surface
- The diminished (003) peak and shifted peaks after the treatment imply that Mo has been doped into the bulk

- **SEM-EDS analysis of the LMP-coated cathode**

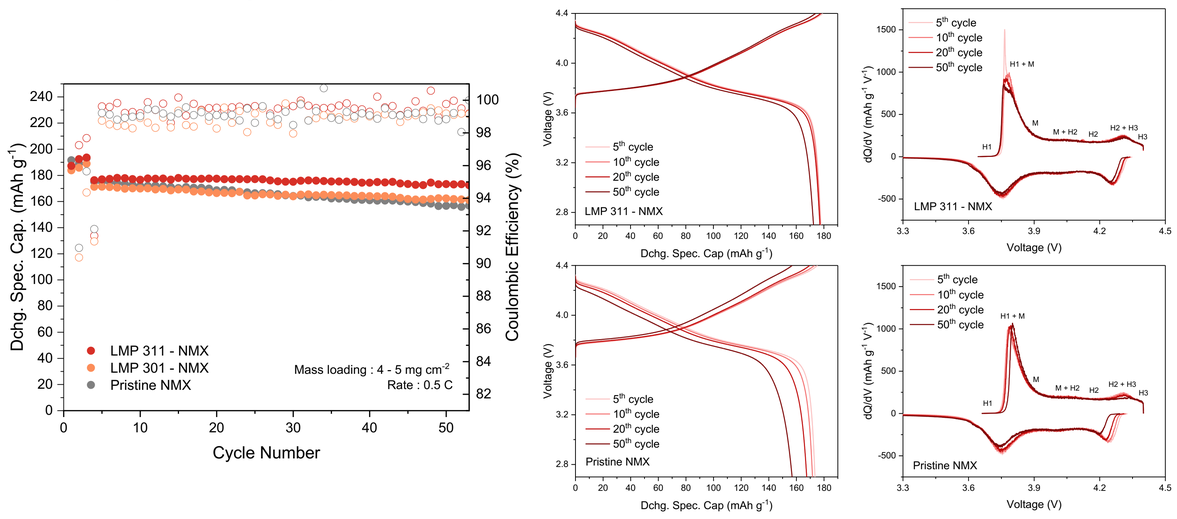


- **Rate capability test**



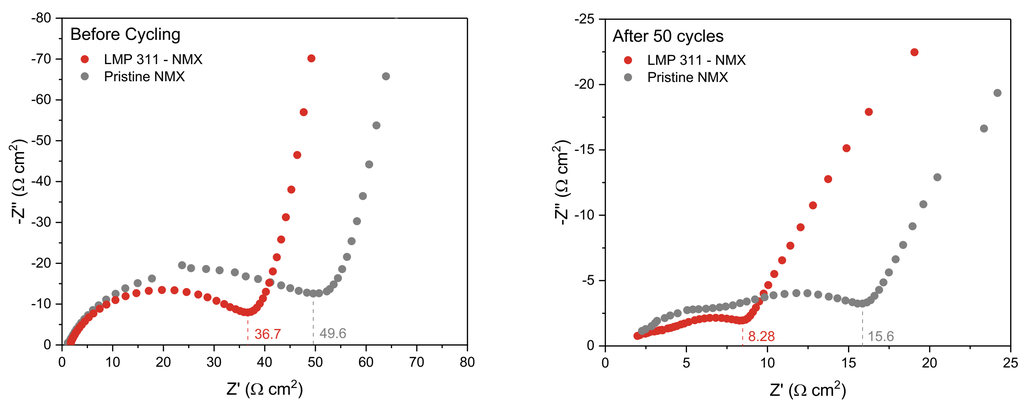
- The optimal recipe is obtained
  - Coating amount : 0.5 wt% of the active material
  - Precursor composition : Li : Mo : PO_4 = 3 : 1 : 1 (LMP 311)
- LMP 311 exhibits twice the capacity (~100 mAh g^{-1}) of the pristine sample at 5C

- **Long-term cycling test**



- LMP 311 retains 97.8% of its initial capacity after 50 cycles
- The sample with Mo exhibits a higher capacity than the sample without Mo
- The voltage profile and dQ/dV of LMP 311 demonstrate a more consistent H2-H3 phase transformation and lower polarization over cycles

- **Electrochemical Impedance Spectroscopy**



- LMP 311 has lower charge transfer resistance before and after cycling

Conclusions

- NMX coated with 0.5 wt% LMP 311 shows the best rate performance and capacity retention
- LMP-NMX exhibits better structural stability and enhanced redox kinetics compared to pristine NMX
- X-ray diffraction suggests the formation of a lithium phosphate coating layer and molybdenum-doped structure
- Further investigation is required to unravel the roles of molybdenum and phosphate in the coating chemistry