Lithium Hexaoxometalates – Potential Cathode Materials for Li-Ion Batteries

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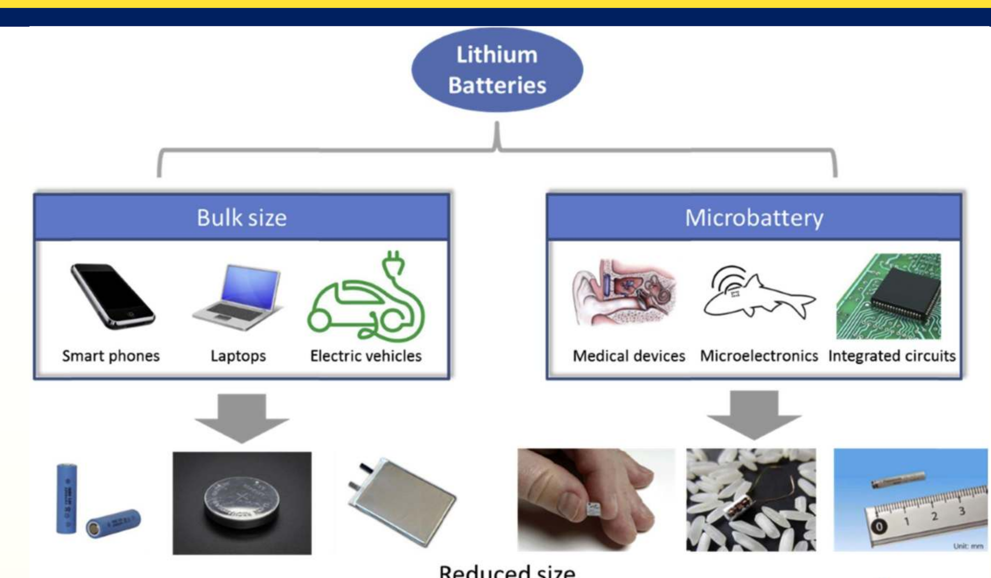
I. Abstract

The specific capacity of advanced anode materials for lithium-ion batteries exceeds 1000 mAh/g, but the specific capacity of cathode materials is limited to 150–200 mAh/g. Therefore, it is important to increase the specific capacity of the cathode to improve the overall performance of Li-ion batteries. Previous work in the Stein lab[1-3] suggested Li_8ZrO_6 as a high capacity cathode material due to its high lithium content, a pseudolayered crystal structure that promotes efficient delithiation, and an unusual charge storage mechanism involving oxidation and reduction of oxygen. However, Li_8ZrO_6 is limited to low-power applications due to its poor conductivity. To address this limitation, we studied two high-lithium compounds, Li_7NbO_6 and Li_7TaO_6, as potential cathode materials that possess similar properties as Li_8ZrO_6 but have higher conductivity. Metal oxides (Nb_2O_5, Ta_2O_5) and lithium precursors were pyrolyzed under different conditions to yield nanosized Li_7NbO_6, Li_7TaO_6, and Li_7NbO_6/C and Li_7TaO_6/C nanocomposites with enhanced conductivity and minimal impurity phases. Galvanostatic charge-discharge tests of half-cells assembled using our nanocomposite cathodes showed reversible cycling, suggesting hexaoxometalates as potential cathode materials.

II. Introduction



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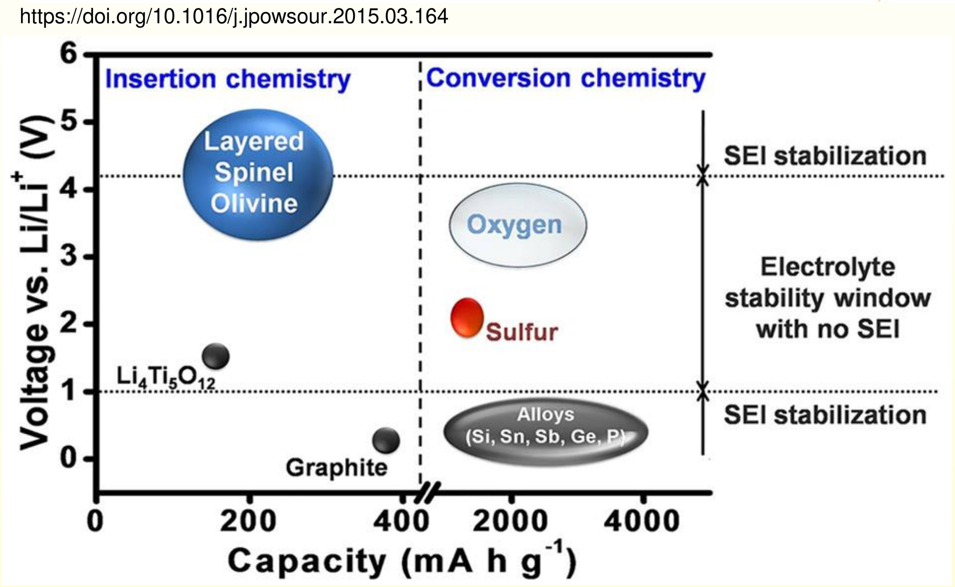
- Lithium-ion batteries (LIBs) can be found in various electronic devices.
- LIBs: High energy density and power density



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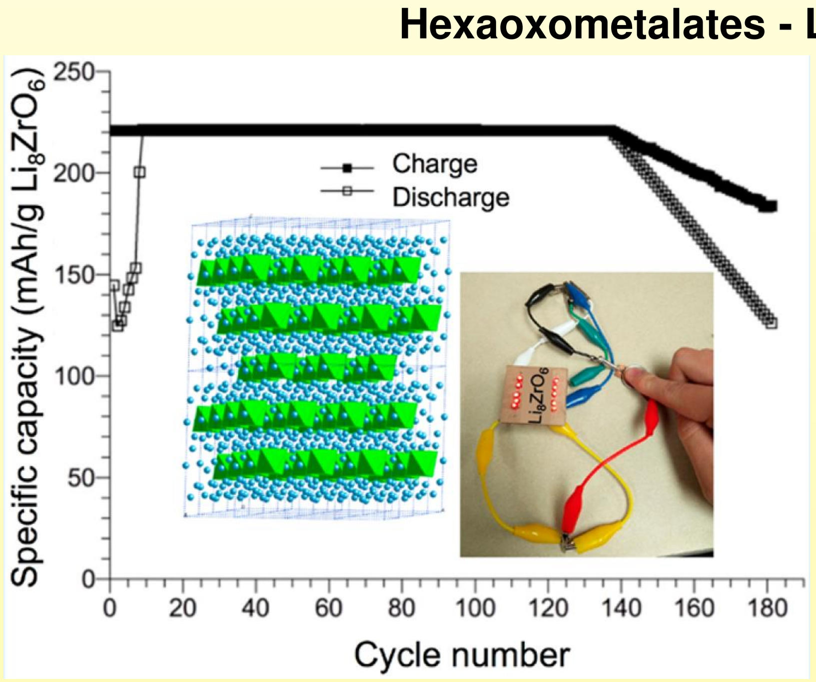
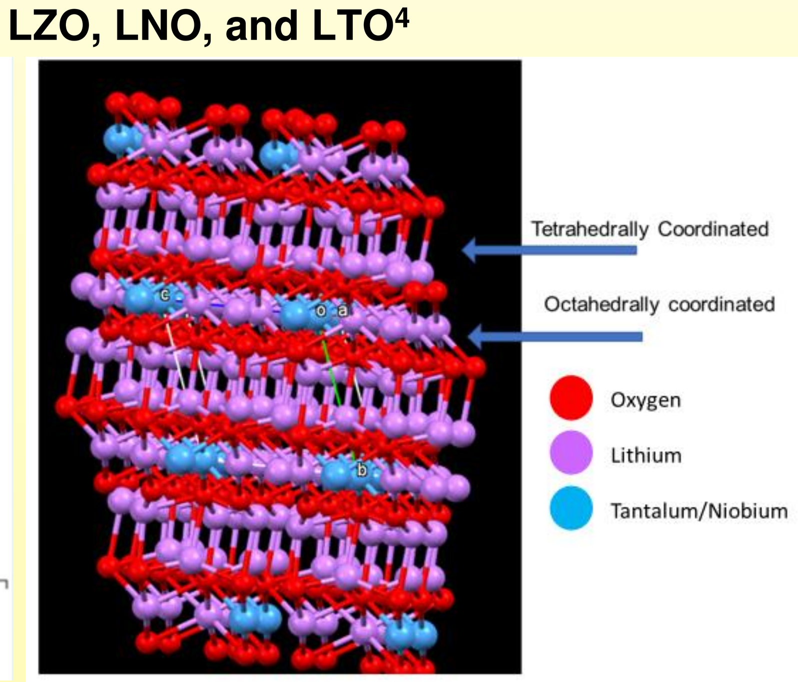
- Capacity discrepancy - anode (> 400 mAh/g) vs. cathode (< 200 mAh/h)
- Commercialized cathode materials are Li-ion insertion materials:
  - ✓ High working voltage
  - ✗ Limited capacity

Hexaoxometalates - LZO, LNO, and LTO[4]

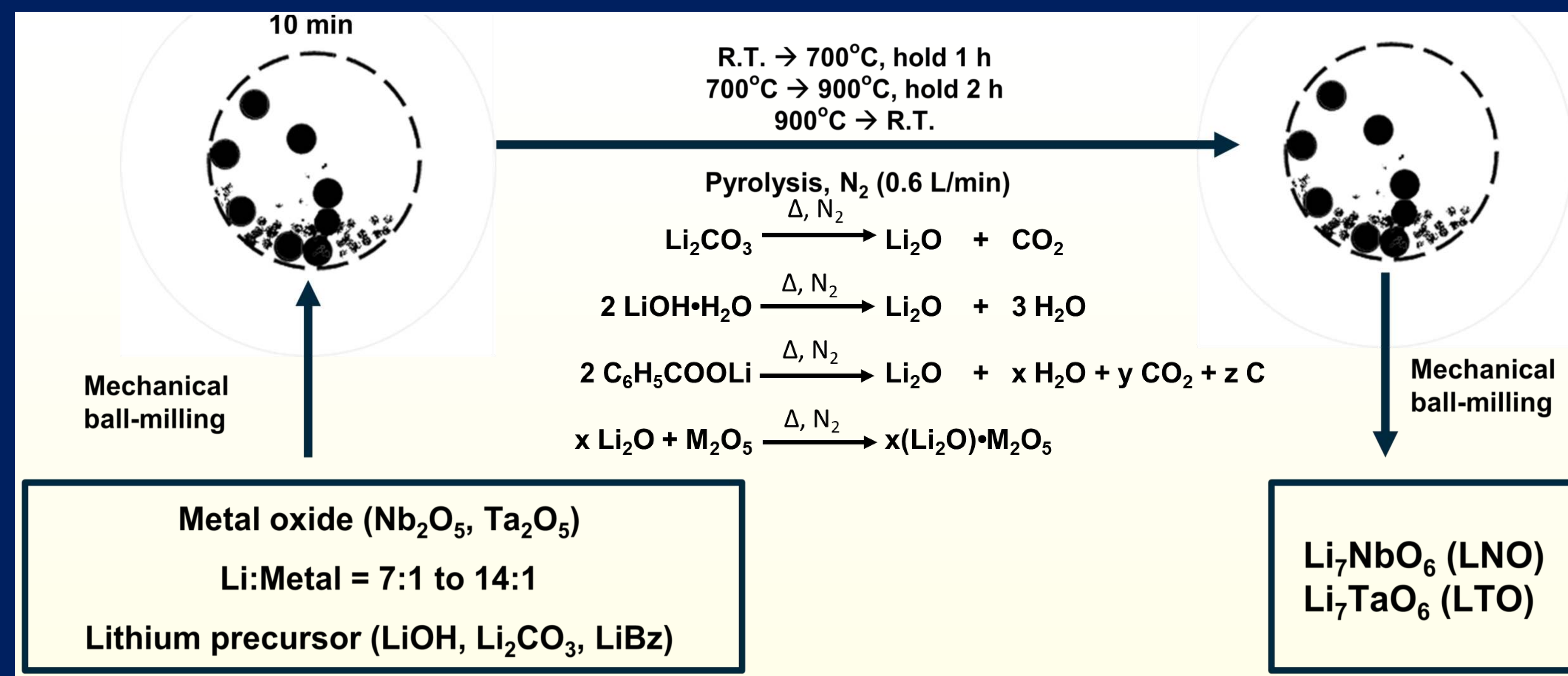




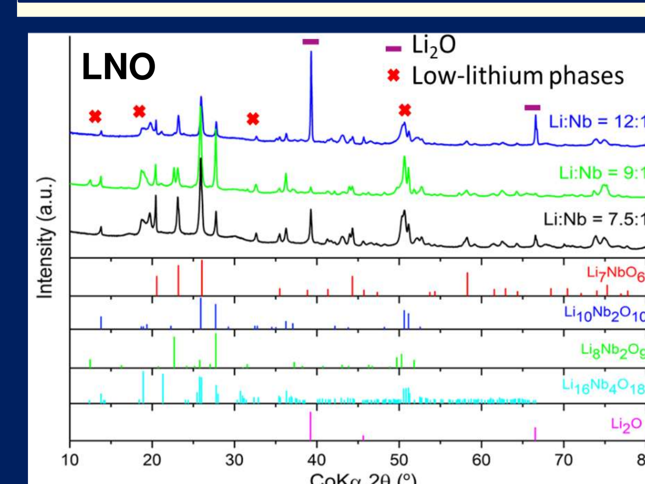
Li_8ZrO_6 (LZO)
- ✓ Pseudolayered cathode material[1]
- ✓ High-specific-capacity (220-330 mAh/g)
- ✗ Poor conductivity
- ✗ High polarization

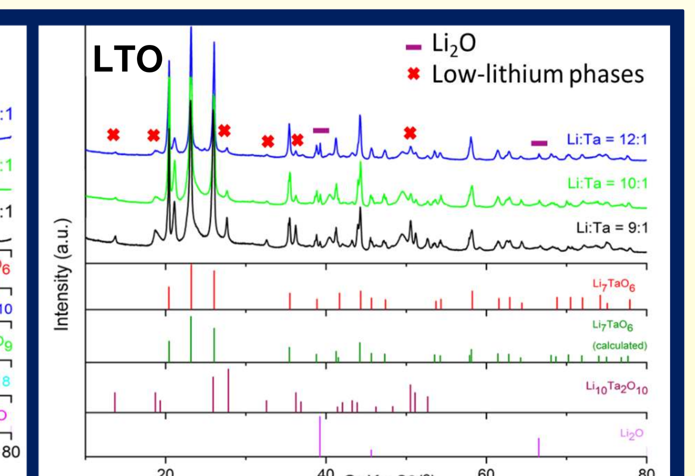
Li_7NbO_6 (LNO) and Li_7TaO_6 (LTO)
- ✓ Isostructural
- ✓ Octahedral vacancies - enhanced Li diffusion efficiency and conductivity

III. Synthesis/Characterization



Li:M Ratio and Product Phases

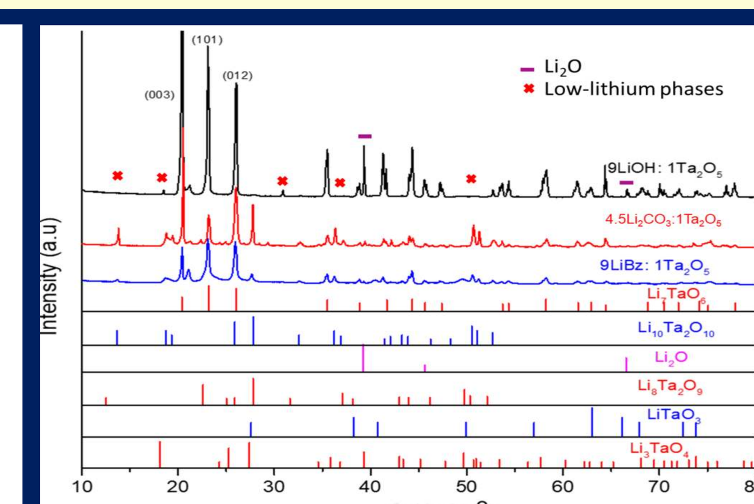




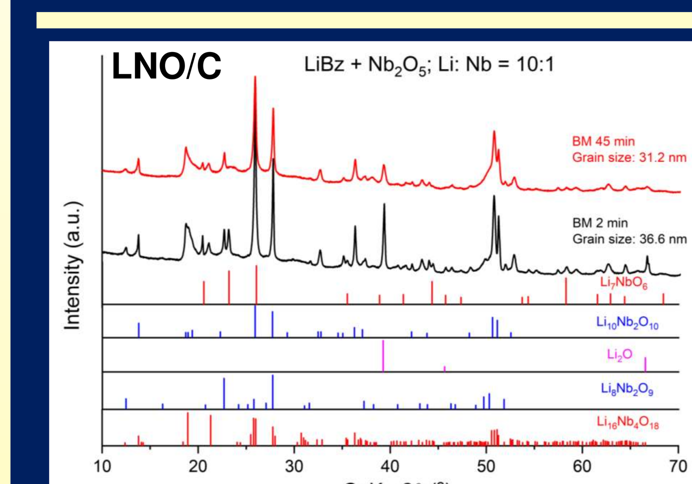
- Partial loss of Li_2O at high temperature
- LNO and LTO are unstable at high temperature - decompose into low-lithium phases ($Li_8M_2O_9$ and $Li_{10}M_2O_{10}$)
- Optimal starting Li:M ratio: 9:1 to 10:1

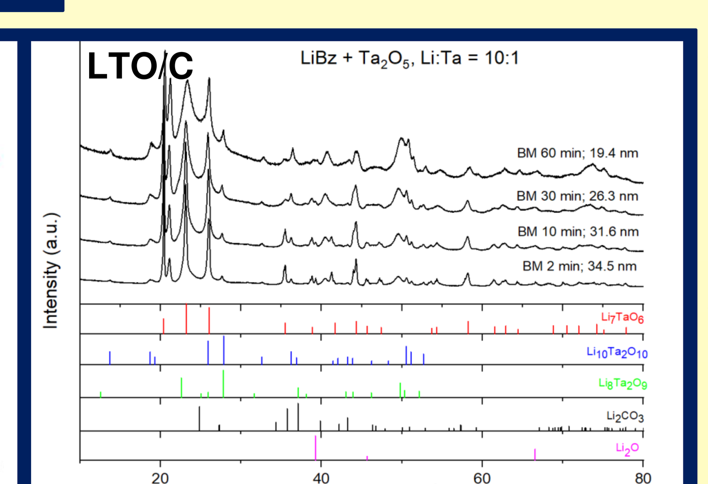
Lithium Precursor and Product Phases

- Optimal precursor: Bulk LNO and LTO – LiOH; LNO/C and LTO/C nanocomposites - Lithium benzoate (LiBz)
- Excess C from LiBz pyrolysis enhances the conductivity of LNO and LTO



Ball-milling and Grain Size

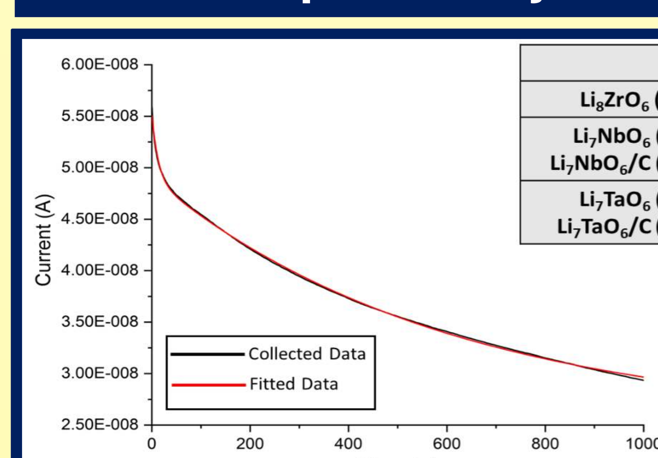




- Smaller grains → shorter Li diffusion path lengths that allow for better particle utilization
- Ball-milling 1 h: 20-30 nm grain
- No new phase or by-product

Chronoamperometry: Conductivity Measurement

✓ LNO and LTO have **higher conductivity** values than LZO

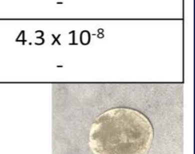


	σ_i (this work) (S/cm)	σ_i (literature[5]) (S/cm)
Li_8ZrO_6 (LZO)	-	1.1×10^{-11}
Li_7NbO_6 (LNO) Li_7NbO_6/C (LNO/C)	$(1.9 \pm 1.0) \times 10^{-8}$ (n=6) ~10^{-4} - 10^{-3}	2.1×10^{-8} -
Li_7TaO_6 (LTO) Li_7TaO_6/C (LTO/C)	$(7.4 \pm 2.0) \times 10^{-10}$ (n=4) ~10^{-4} - 10^{-3}	4.3×10^{-8} -

$$i = i_0 + A_1 e^{(-t/t_1)} + A_2 e^{(-t/t_2)}$$

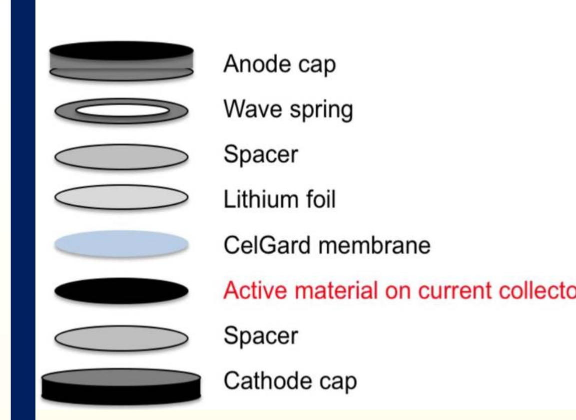
$$R_e = \frac{U}{i_0} \text{ (Electronic Resistance)} \quad R_i = \frac{U}{A_1 + A_2} \text{ (Ionic Resistance)}$$

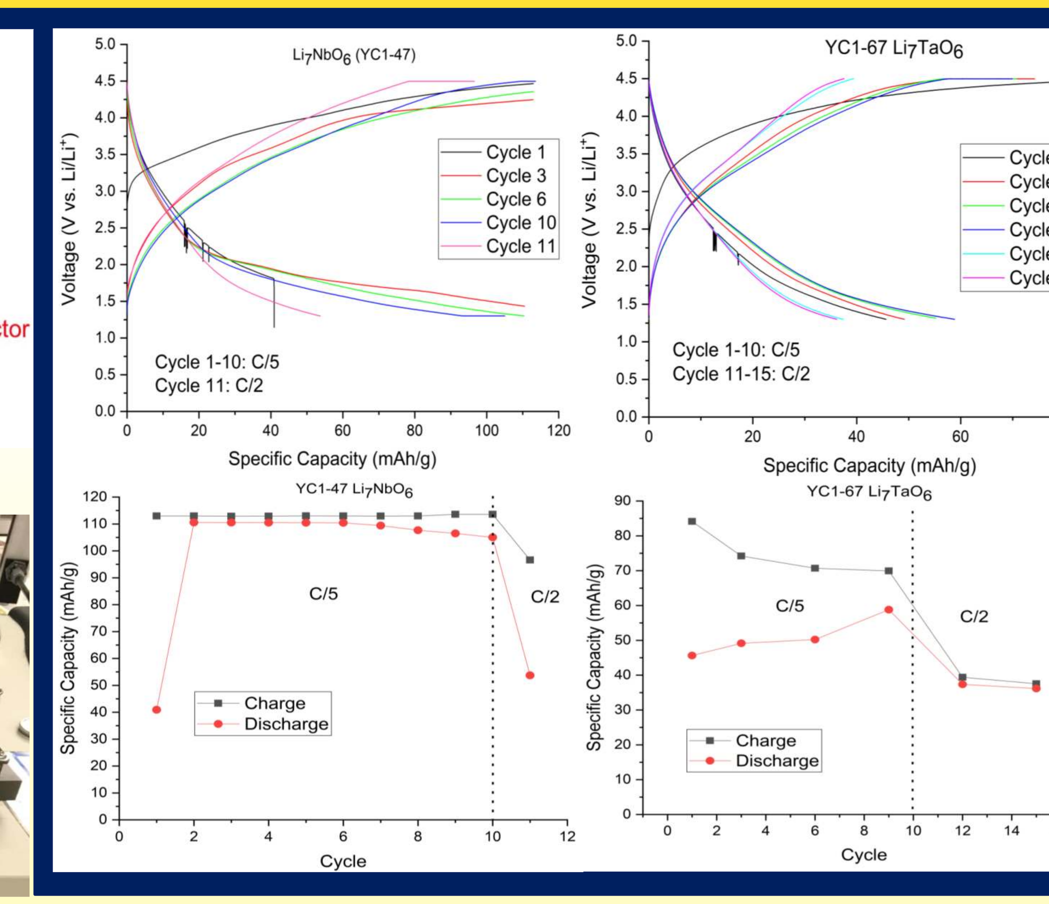
$$\sigma_e = \frac{d}{AR_e} \text{ (Electronic Conductivity)} \quad \sigma_i = \frac{d}{AR_i} \text{ (Ionic Conductivity)}$$



LTO pellet with Ag coating

IV. Battery Testing

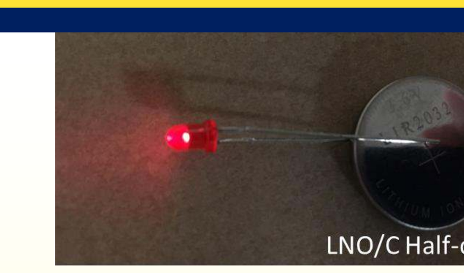




- Li-LNO/C and Li-LTO/C half-cells are tested by galvanostatic charging and discharging
- Testing limits: Potential (1.3-4.5 V); capacity (LNO/C: 113 mAh/g, LTO/C: 82 mAh/g)
- LNO/C shows promise as a cathode material
  - ✓ Good capacity retention
  - ✓ Higher specific capacity
- Performance is better at slow charge/discharge rate

V. Conclusion/Future Work

Conclusion



- Li_7NbO_6 and Li_7TaO_6 with small grain size were synthesized
- LNO and LTO have higher conductivity values than LZO
- LNO shows promise as a cathode material: reversible charge-discharge; high capacity

Future work

- Optimize pyrolysis conditions to minimize excess reagent (Li_2O) and phase impurities (Li_5MO_5, $Li_8M_2O_9$)
- Identify phase impurities to quantify the amount active material
- Conduct deep charge-discharge experiments to measure maximum specific capacities of the materials

VI. Acknowledgments

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VII. References

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