The effect of cobalt on the electrochemical performance of lithium and manganese-rich oxide materials for Li-ion batteries

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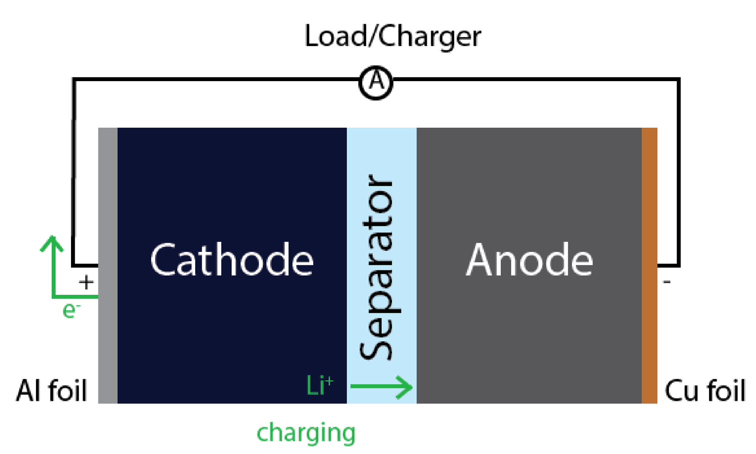
Commercial cathodes for Li-ion batteries typically use $LiMO_2$ materials

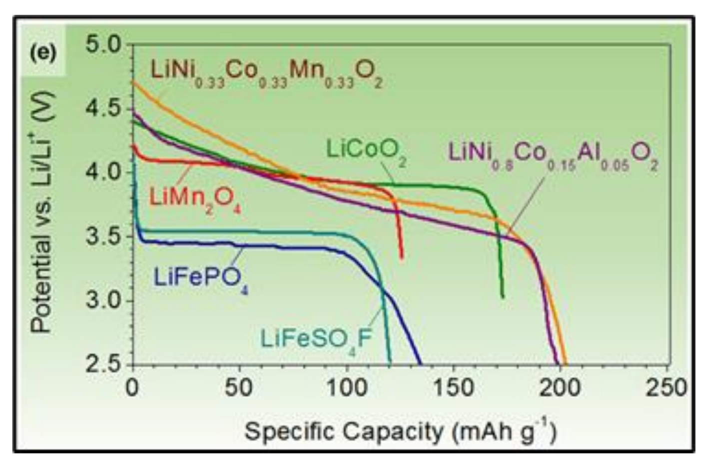


Discharging

$$\text{Cathode: } Li_{(1-x)}MO_2 + xLi^+ + xe^- \rightarrow LiMO_2$$
$$\text{Anode: } Li_xC_6 \rightarrow 6C + xLi^+ + xe^-$$

Charging

$$\text{Cathode: } LiMO_2 \rightarrow Li_{(1-x)}MO_2 + xLi^+ + xe^-$$
$$\text{Anode: } 6C + xLi^+ + xe^- \rightarrow Li_xC_6$$



Nitta, Yushin, *et al. Mat. Tod.* **18** (5), 252-264 (2015)

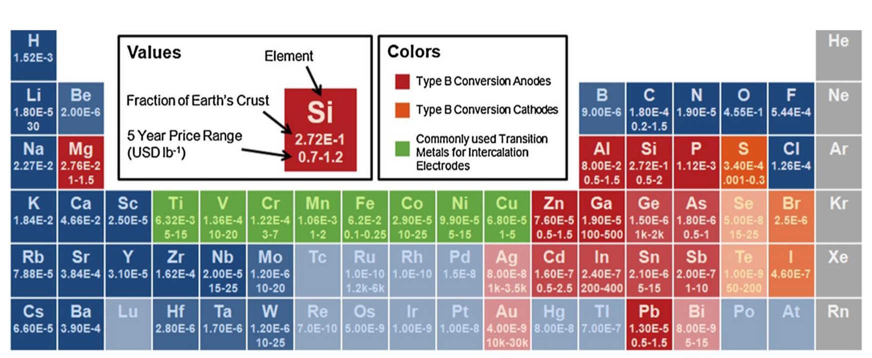
The chemical formulas of most common cathode materials follow a $LiMO_2$ format where M stands for one or more transition metals such as nickel (Ni), cobalt (Co) or manganese (Mn)

The ratio of lithium to transition metals in the $LiMO_2$ chemistry is 1:1 → for every one transition metal atom, one lithium atom contributes to charge storage

Why lithium and manganese rich oxides?

Lithium & manganese rich (LMR) oxide materials have lithium : transition metal ratios greater than one, and manganese makes up over 50% of the transitional metal content. This chemistry has several benefits—

Manganese is earth-abundant, economically viable, and known to enhance cathode safety (especially compared to cobalt and nickel)



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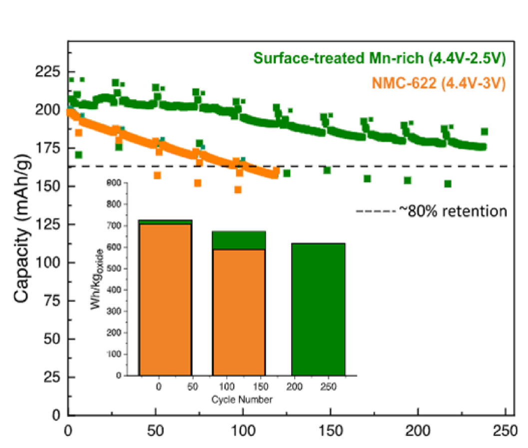
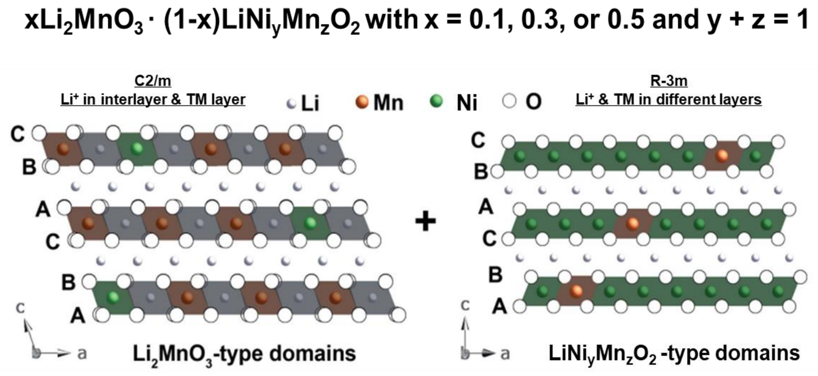


Chen, et al. *J. Electrochem. Soc.*, **168**, 080506 (2021)

The excess Li in these materials enables high energy densities

LMR electrodes demonstrate acceptable capacity retention even under aggressive cycling protocols

$xLi_2MnO_3 \cdot (1\text{-}x)LiNi_yMn_zO_2$ with x = 0.1, 0.3, or 0.5 and y + z = 1



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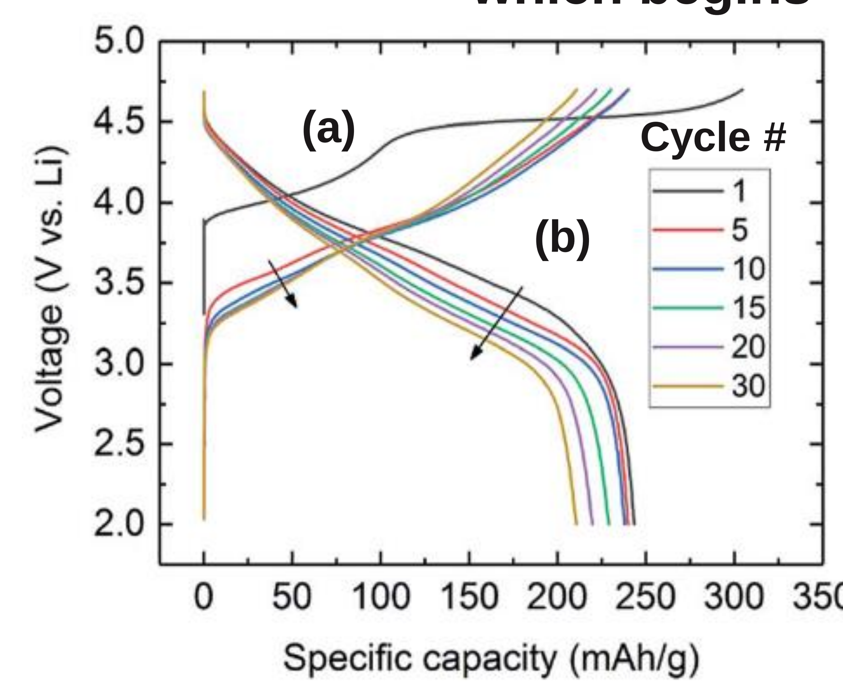
Challenges facing LMR materials: structural degradation upon prolonged or fast cycling

LMR materials are "activated" by removing lithium ions from $LiMn_6$ sites, which begins ~ 4.5 V, as shown in (a)



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Activation maximizes cyclable energy storage capacity, but introduces two distinct degradation mechanisms:

- **Voltage fade (b): Lowers overall energy deliverable by the battery over time**
- **Charge/discharge hysteresis from transition metal migration: Can decrease efficiency of the charge-discharge process with cycling**

Co stabilizes the structures of other cathode chemistries, but its effect in LMR materials is not well-studied

- **Cobalt-containing oxides have good electrochemical reversibility**
- **Co^{3+} improves electronic conductivity within oxide & reduces impedance → facilitates fast energy storage**

Research Question & Objectives

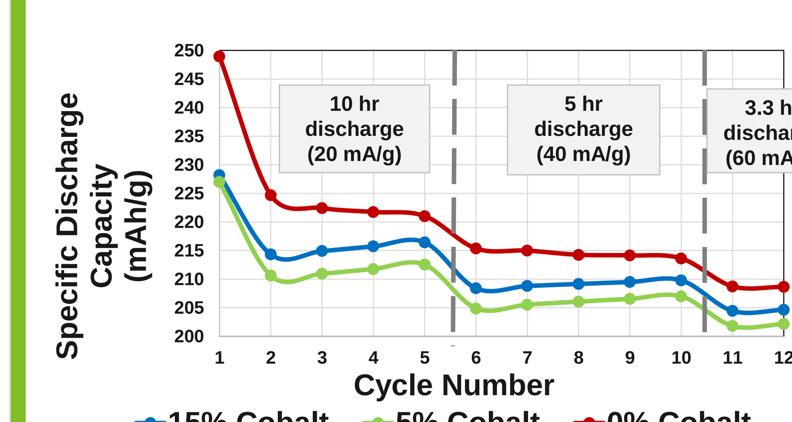
Can cobalt enhance the rate-dependent cycling stability of LMR oxides?

1) **Prepare cathodes with 0%, 5%, and 15% Co**

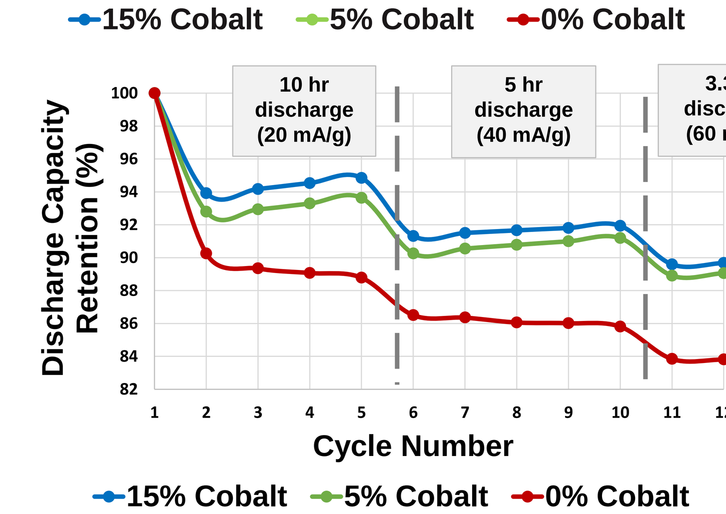
0% Co: $0.3Li_2MnO_3 * 0.7LiMn_{0.50}Ni_{0.50}O_2$
5% Co: $0.3Li_2MnO_3 * 0.7LiMn_{0.47}Ni_{0.47}Co_{0.05}O_2$
15% Co: $0.3Li_2MnO_3 * 0.7LiMn_{0.42}Ni_{0.42}Co_{0.15}O_2$

2) **Investigate the effect of Co on the electrochemistry (capacity retention, rate performance) of LMR oxides**

Electrodes with cobalt have less cyclable capacity; but can potentially access that capacity faster and more consistently



Despite starting with much higher capacity, the capacity for the 0% cobalt sample diminishes quickly to approach the capacities of the 5% & 15% cobalt samples

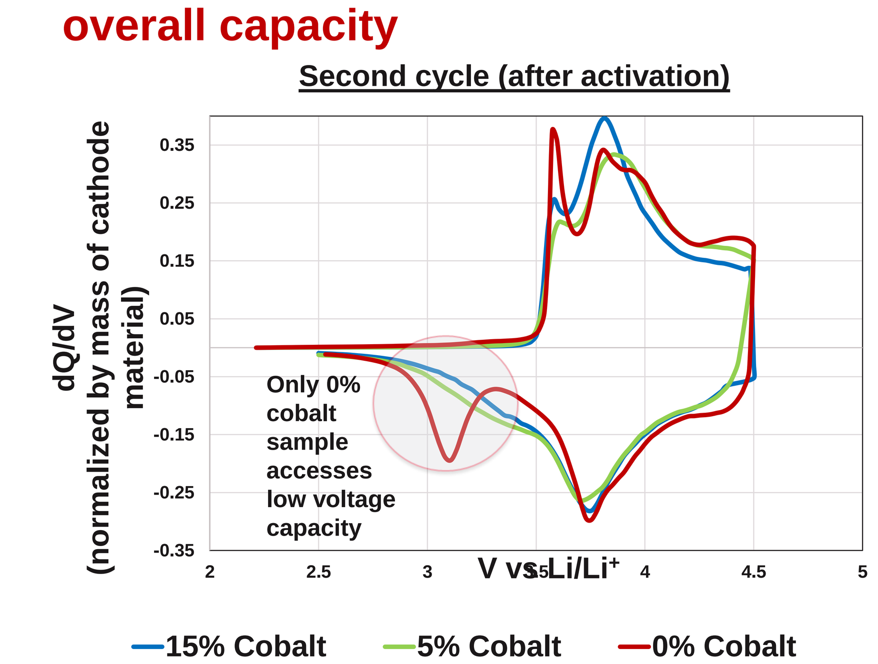


The 5% & 15% cobalt samples retain significantly more of their original discharge capacity compared to the 0% cobalt sample

In progress: continuing these tests of the rate performance under progressively faster discharge rates

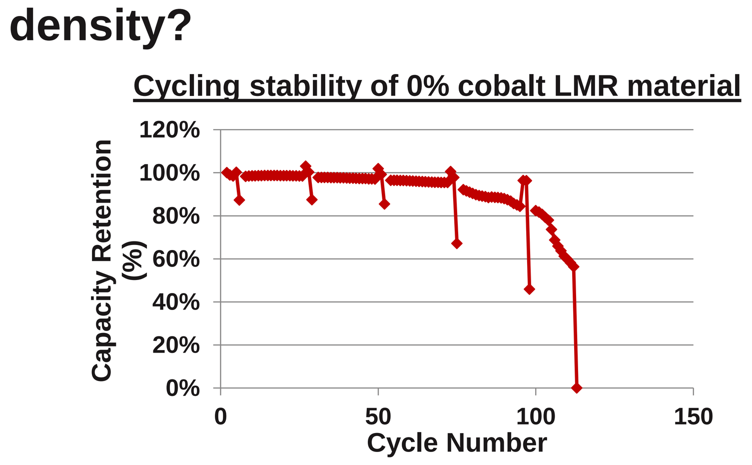
Cobalt affects the reversibility of the activation process

- **Adding a small amount of cobalt results in inaccessible low voltage sites → reducing overall capacity**



Ongoing work

- **Comparing the long term (100+ cycles) cycling stability at a variety of current rates**
- **If Co-containing materials show superior long-term cycling performance → can they be made into thick electrodes for high power density?**



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