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

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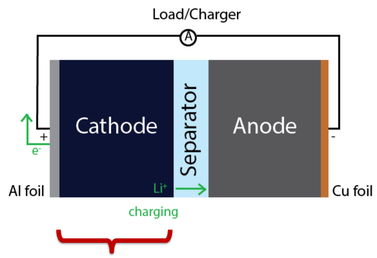
Commercial cathodes for Li-ion batteries typically use $LiMO_2$ materials

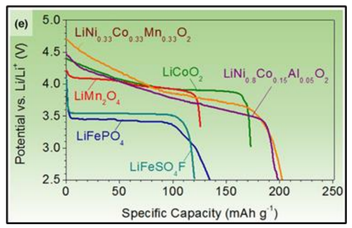


Discharging

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

Charging

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



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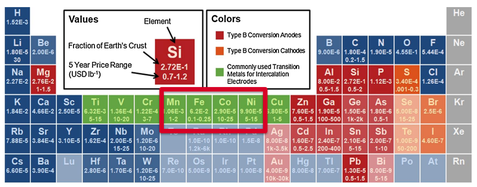
The chemical formulas of most common cathode materials follow a $LiMO_2$ format where M stands for one or more transition metals such as nickel (Ni), cobalt (Co) or manganese (Mn)

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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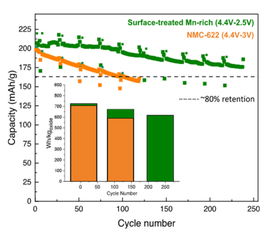
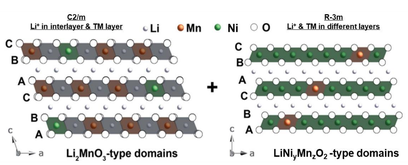


Chen, et al. *J. Electrochem. Soc.*, **168**, 080506 (2021)

LMR electrodes demonstrate acceptable capacity retention even under aggressive cycling protocols

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



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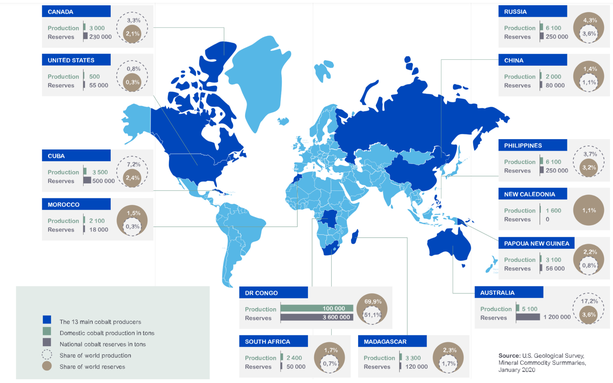
The excess Li^+ in these materials enables high energy densities

What is the effect of including cobalt in LMR materials?

- **Cobalt is commonly used in lithium-ion batteries, but is expensive and difficult to access – creates supply chain issues and drives up the cost of lithium-ion batteries that use it**



https://www.cobaltinstitute.org/about-cobalt/cobalt-life-cycle/

- **Co stabilizes the structures of other cathode chemistries, but its effect in LMR materials is not well-studied. In general:**
  - **Cobalt-containing oxides have good electrochemical reversibility**
  - **Co^{3+} improves electronic conductivity within oxide & reduces impedance → facilitates fast energy storage**

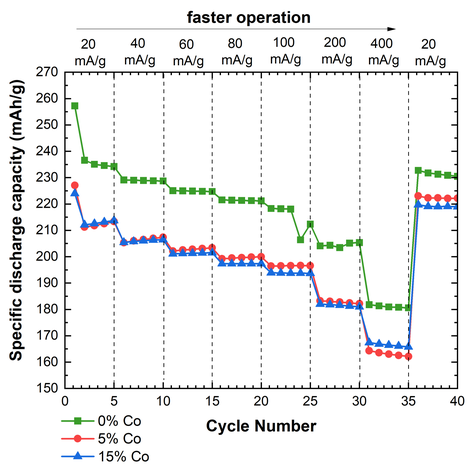
Cobalt-containing electrodes deliver less energy during discharge compared to cobalt-free electrodes

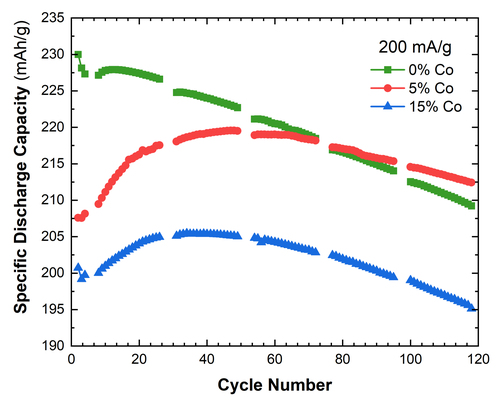
We electrochemically tested LMR materials with varying amounts of cobalt:

0% Co: $0.3Li_2MnO_3 * 0.7LiMn_{0.50}Ni_{0.50}O_2$

5% Co: $0.3Li_2MnO_3 * 0.7LiMn_{0.47}Ni_{0.47}Co_{0.05}O_2$

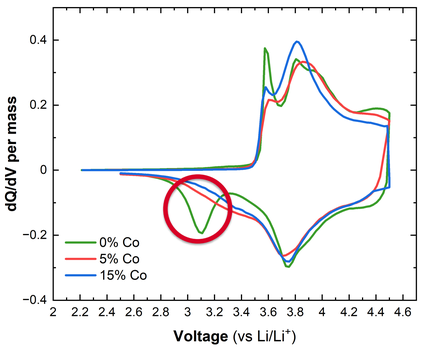
15% Co: $0.3Li_2MnO_3 * 0.7LiMn_{0.42}Ni_{0.42}Co_{0.15}O_2$





Why does including cobalt deteriorate the performance of LMR materials?

- **Adding a small amount of cobalt limits the energy storage capacity→ the voltage under 3.2V isn't accessed in the cobalt-containing materials**



Conclusions & Open Questions

- **LMR materials with cobalt cannot access low-voltage capacity during initial use**
  - **cobalt-containing materials having less energy storage capacity than cobalt-free materials**
  - **For small amounts of cobalt (5%), access to this low-voltage capacity can be regained upon cycling**
- **There don't seem to be any significant differences in the structures of cobalt-containing and cobalt-free LMR materials. Why is the low-voltage capacity initially inaccessible in Co-containing materials?**

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