Lithium-Ion Batteries and Beyond

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III. Cathodes

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Cathode Materials for/in Li Cells: Classification According to Charging Voltage, Structure and Li-Storage Mechanism

"5-Volt"	$xLi_2MnO_3/(1-x)LiMO_2$ (M = Mn, Ni, Co,…)	2-D, layered composite
	$LiCoPO_4$	1-D olivine-type, insertion-type
	$LiNi_{0.5}Mn_{1.5}O_4$	3-D spinel, insertion-type
"4-Volt"	$LiCoO_2$	(2-D layered, insertion-type)
	$LiNiMnCoO_2$, $LiNiCoAlO_2$	(2-D layered, insertion-type)
	$LiMn_2O_4$	(3-D spinel, insertion-type)
	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	(2-D layered, insertion type)
	$LiFePO_4$, $LiMnPO_4$	(1-D olivine-type, insertion)
"3-Volt"	V_2O_5	(2-D layered, insertion-type)
	MnO_2	(3-D composites, insertion type)
"2-Volt"	TiS_2	(2-D layered, insertion-type)
	MoS_2	(2-D layered, insertion-type)

- After assembly: Cathode is Li^+ source in the lithium-ion cell (3-V and 4-V materials)
- Cathode is Li^+ sink in a lithium-metal cell configuration (2-V and 3-V materials)

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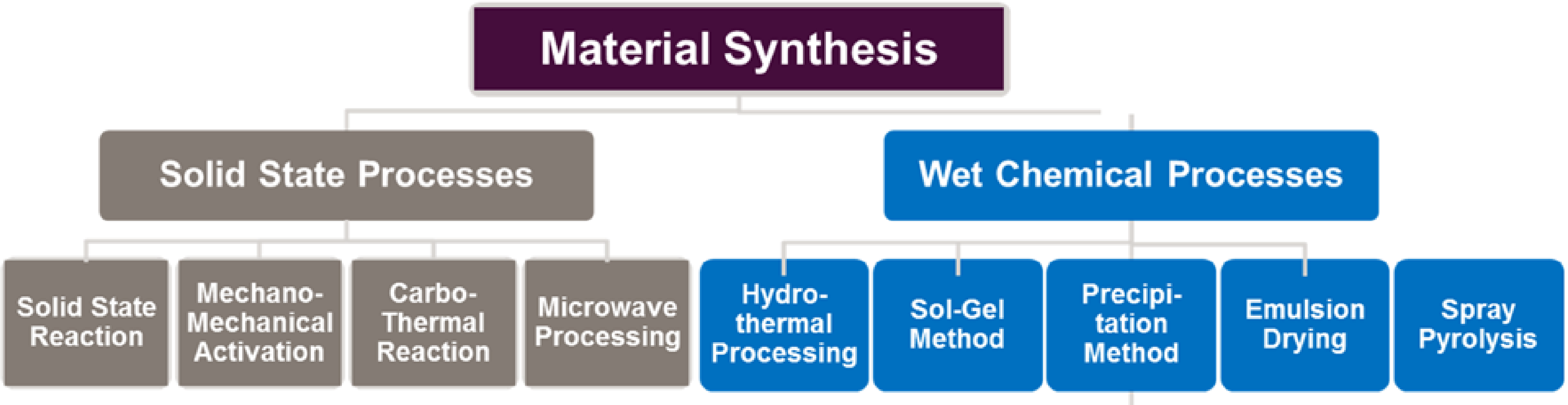
General Synthesis Methods
(There are Additional Derivative Methods)



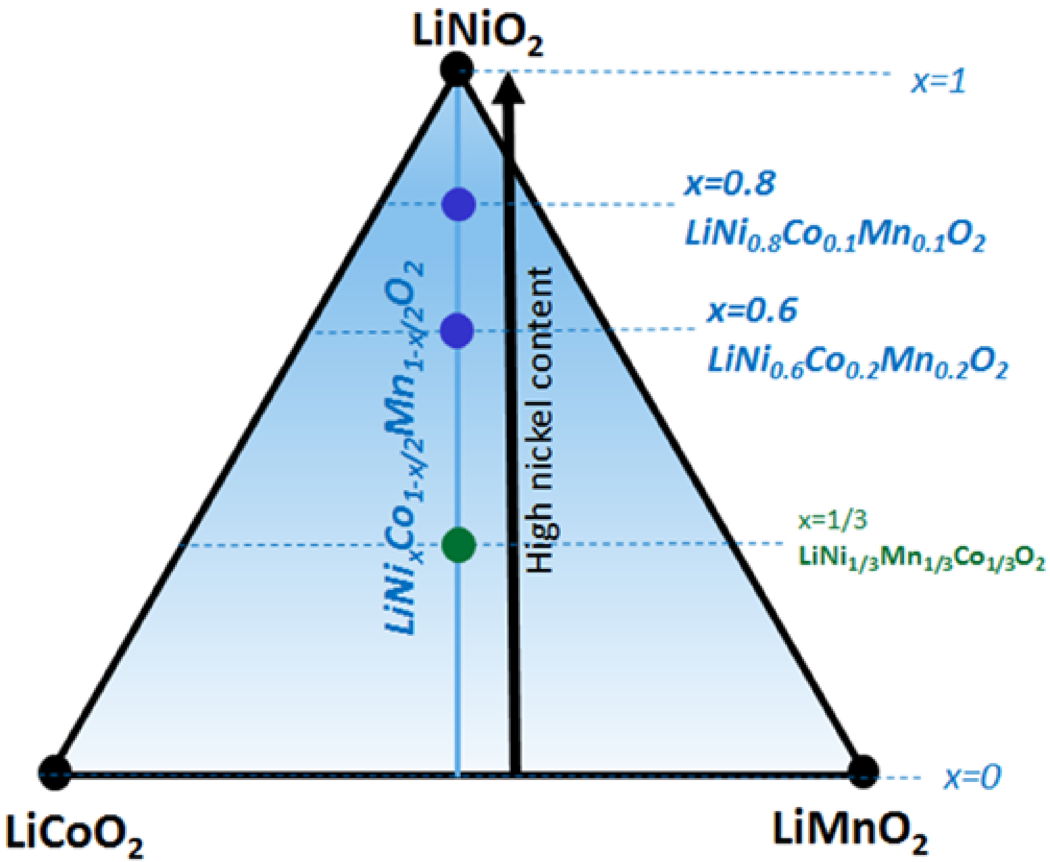
- Starts with solids, such as metal oxides, carbonates and hydroxides
- Usually high-temperature synthesis
- Particle size and morphology of the product depend on the precursor-particle properties
- Good access to desired precursors or pre-treatment of precursors is necessary

- Solvents: e.g., water, ethanol, with dissolved salts containing the product constituting M^{n+}-cations, e.g.: Hydrothermal, sol-gel, co-precipitation Others: Emulsion Drying, Pecchini, etc.
- Usually lower temperatures during synthesis, but a high temperature post-step (annealing)
- Particle-size and morphology can be tailored by synthesis conditions

The synthesis method has a strong effect on properties such as **particle size, chemical composition**, and **purity**, as well as on the required **energy** for synthesis and the **processing time.**

Layered Ni-rich NCM622 and NCM811
$LiNi_xMn_{1-x/2}Co_{1-x/2}O_2$ with $x \geq 0.6$

Phase Diagram of solid solutions of $LiNiO_2$, $LiCoO_2$ and $LiMnO_2$



- State-of-the-art: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NCM11) is more and more often replaced by $LiNi_{0.5}Mn_{0.2}Co_{0.3}O_2$ (NCM523)
- The near (?) future: Ni-rich materials, e.g., $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NCM811) and $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NCM622)

- 👍 Discharge capacity: >200 mAh g^{-1} at low rate (0.1C)
- 👍 Average discharge potential is $\approx$ 3.8 V vs. Li/Li^+
- 👍 Potential range: $\approx$ 3.0 – 4.3/4.4V vs. Li/Li^+
- 👍 Higher Ni content → higher capacity
- 👎
- 👎

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Optimized synthesis
→ Small Li^{+}/Ni^{2+} Cation Mixing → Better Rate Capability

- Ideal Li*M*O_2 layered materials show alternating Li and *M*O_2 layers
- Because Li^{+} and Ni^{2+} ions in LNCM materials have a very similar radius, Ni^{2+} can be present in the Li^{+} layer and vice versa = 'Li^{+}/Ni^{2+} cation mixing'
- A little Ni^{2+} in the Li^{+} layers is desired as it enhances structural stability

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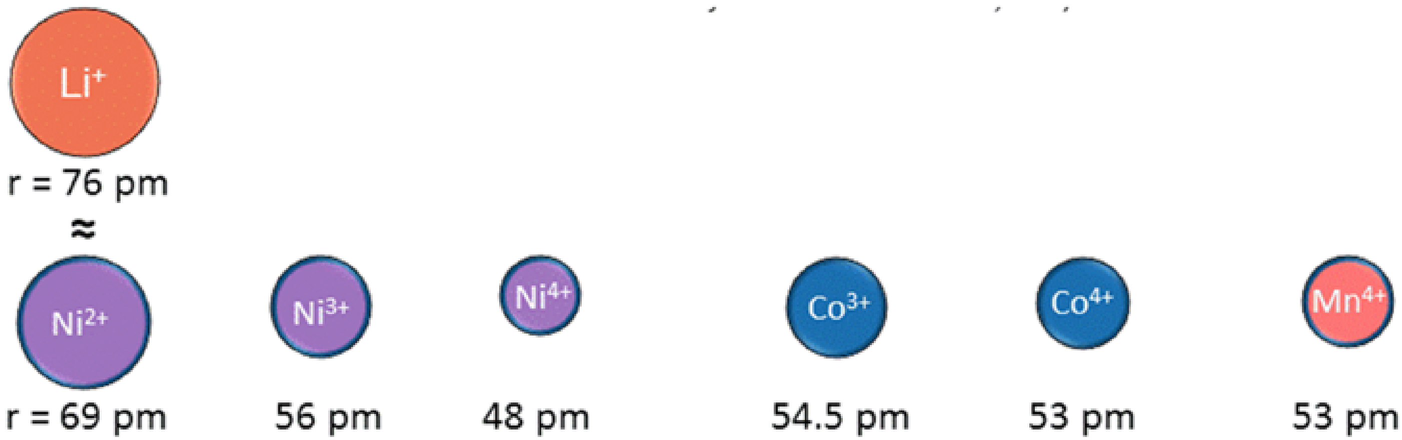

Commercialized for a Long Time, Still High Impact: $LiNiCoAlO_2$ (LNCA or NCA)

- Started as $LiNi_{0.8}Co_{0.15}Al_{0.5}O_2$, now even higher Ni contents (at the expense of Co content)
- High discharge capacity: 180 – 200 Ah/kg
- LNCA is not as thermally and electrochemically stable as LNCM with lower Ni content
- Unlike LNCM, LNCA is Mn-free → Less metal dissolution → More compatible with graphite anode
- Safety is related to high energy density; → Can be addressed by material modification

Modifications have been focused on:

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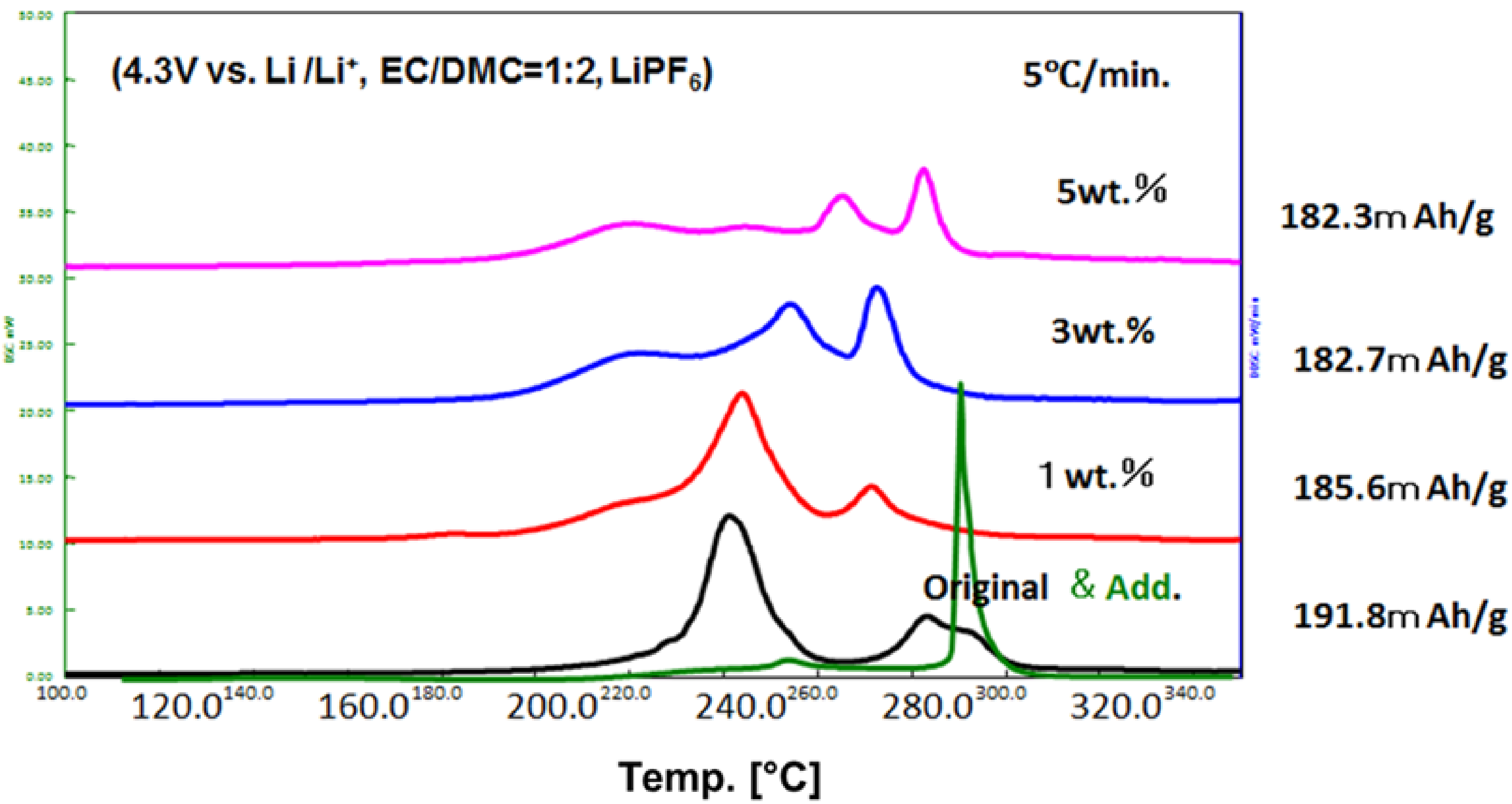
Coating of LNCA with LNCM → Better Safety*

- Coating with LNCM improves overall thermal stability, as the exothermal (= heat-releasing) reactions appear at higher temperatures during the ramping up of the temperature by 5 ° C/min steps
- Increased coating amounts do shift the main exothermal reaction to higher temperatures



*Courtesy: M. Kruft, Toda

Challenges and Opportunities of 'Lithium-Rich' Cathodes

- Average discharge potential: ≈ 3.5 V vs. Li/Li^+
- Potential range: ≈2.5 – 4.6/4.8 V vs. Li/Li^+

👍 High practical discharge capacity: >250 mAh/g at low rate (0.1C) → Excellent partner of Si anode

👍 Potentially low cost (High Mn: cheap)

👎 Due to conversion in initial cycle and continued phase transformation into LMO during cycling, Li-rich cathode has severe challenges:

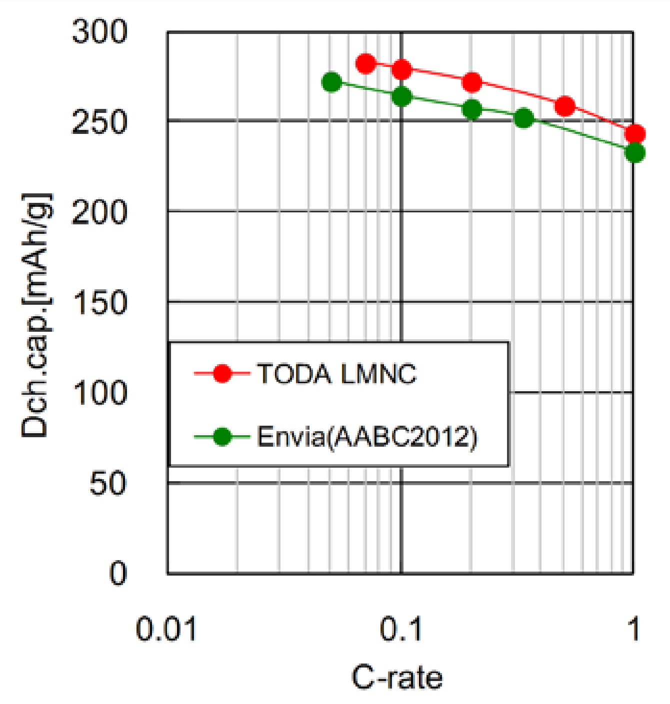
- Low first cycle Coulombic efficiency → Phase change accompanied by oxygen release
- Fast capacity fading
- Voltage decay → low voltage stability
- Poor energy efficiency

👍 Cathode coating reduces voltage decay

👎 Further challenges:

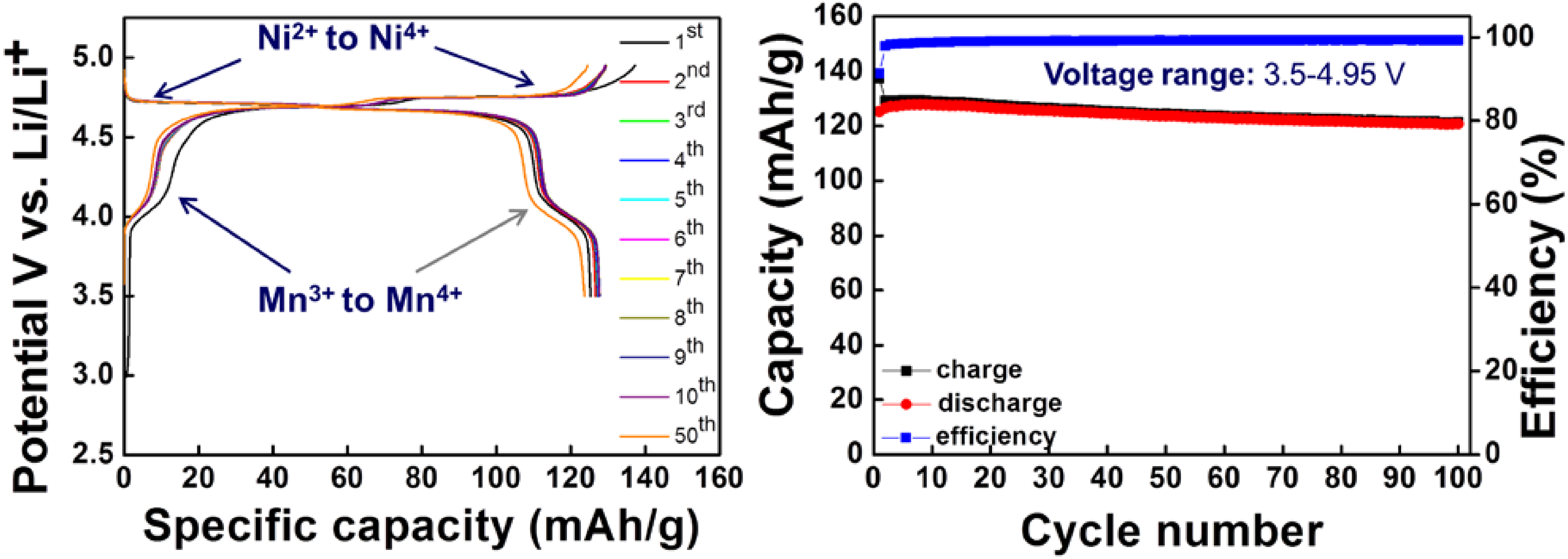
- Low energy density (Wh/L)
- Low rate capability

Practical capacities:



*Courtesy: M. Kruft, Toda

$LiNi_{0.5}Mn_{1.5}O_4$ – LNMO, THE High Voltage Cathode



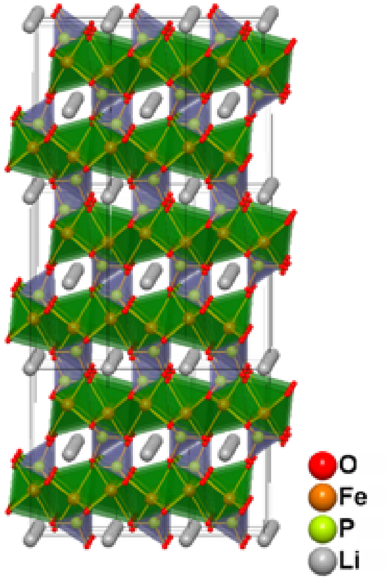
- High rate performance due to 3-dimensional Li diffusion → Good partner for high power LTO → ≈3.2V discharge voltage
- High, ≈4.75V vs. Li/Li^+ discharge potential, hence rel. high specific energy
- In comparison with parent $LiMn_2O_4$: less transition metal dissolution
- Challenges: capacity fade, limited cycling and electrolyte stability

Lithium Iron Phosphate – LFP

$$LiFePO_4 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} FePO_4 + Li^+ + e^-$$

- e^- → **Charge compensation**
- Li^+ → **Li-Ion de-intercalation**

Olivine Crystal Lattice



Measures vs. poor electronic conductivity:

- Add conductive additives (e.g., carbon)
- Thin film carbon-coating

- 👍 No O_2 release → excellent **safety** (electrochemical and thermal)
- 👍 High **rate capability** (discharge and charge, esp. nano-materials)
- 👍 Good **cycle life**
- 👍 Other $LMPO_4$ (M = Mn, Co, Ni) with higher potential: mixing possible

- 👎 Low operating **voltage** (compared to LCO, LNCM, LMO

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LIB Cathodes: Summary

- Future cathode material demand will be driven by automotive applications
- Whereas on the anode side, graphite and carbon dominate, a one-fits-all cathode solution is not available so far: selection is based on application requirements, cell design, anode, etc.
- The key challenge for the commercialization of next-generation cathodes will be the optimization / redesign of the LIB system (electrolyte, separator, binder, …) → Inactive materials chapter

Key drivers / requirements BEV / PHEV batteries:

- Improved specific energy and energy density
- Reduced system costs
- Ni-rich LNCM and LNCA are considered as materials of choice for next gen. cells

Key drivers / requirements for Start-Stop (12V) / Mild Hybrid:

- Cell chemistry needs to match 12V technology: → LFP / C or LMO / LTO
- Cost and life will be key selling points
- Power capability more important than energy density
- LMO can be a good fit