

Batteries
ACME Faculty, EHVE course
B.Sc. Studies, III year, V semester
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Cathodes for Lithium-ion cells

Cathodes for Li-ion cells

Cathode required properties (wish list):

- **High capacity** (high energy density);
- **Compatibility with other cell components**;
- Long life (both in cycles and time);
- **Cheap** (cheap, simple manufacturing and cheap materials);
- High current density;
- High potential;
- As slow degradation over cycling as possible;
Small capacity loss (irreversible) during first cycle;
- Small density change during cell operation;
- Capacity retention with the cycle rate (rate capability);
- Safe and environment-friendly;

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Cathodes for Li-ion cells

Cathodic material required properties (wish list):

- Contains ion/atom that oxidizes/reduces easily (usually a transition metal);
- Reacts with lithium in a reversible way (intercalation, lithium ion acceptance into structure without its change);
- Reacts with lithium with a high free energy; high capacity: ≥ 1 lithium ion per one metal atom; high potential: > 4 V;
- Reacts with lithium quickly (good kinetics) on lithium ions intake or release;
- Good electronic conductor (reaction occurs in whole volume of material, not only at the cathode active material-additive enhancing conductivity and electrolyte contact; thus, no additives for conductivity enhancement are required, resulting in better overall energy density);

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Cathodic materials

Parameters affecting cathode properties:

- Crystallographic form;
- Manufacturing method (e.g. chemical, solvothermal, thermal, electrochemical, CVD, etc.);
- Grain size;
- Defect level (how much real structure differs from the ideal one for the given crystallographic form);
- Temperature of operation (range).

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Cathodic materials - history

Beginning of the cathodic materials research started with work on primary lithium cells (1970s), in which fluorinated graphite (CF_x) was used as a cathode. In CF_x lithium intercalated almost irreversibly, as upon intercalation, lithium reacted with fluorine to form inert LiF. Historically, the first cathode material fulfilling all basic requirements for Li-ion cell application was titanium sulfide (TiS_2), which had a layered structure (intercalation mechanism similar to that of graphite).

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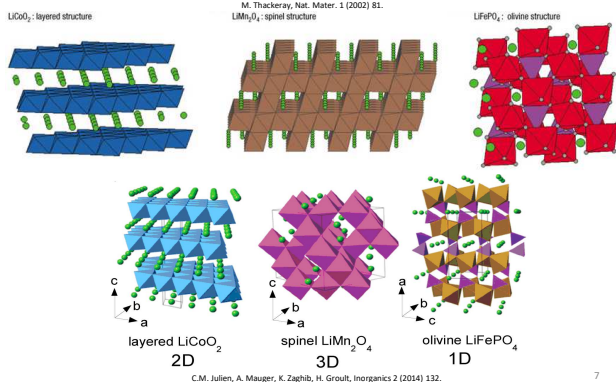
Cathodic materials - history

TiS_2 with layered structure was chosen from numerous dichalcogenides (i.e. MO_2 , MS_2 , MSe_2 , MTe_2), as it was the lightest among them. There are no phase transitions undergoing in it during operation. It conducts electrons well, so there is no need to add graphite, for instance. Unfortunately, TiS_2 has a low potential against lithium (2.5 V vs Li).

Oxides were not investigated initially, as it was assumed at the time, that they do not work (!). When finally research on them started, it was MoO_3 (too slow reaction with lithium) and V_2O_5 (that is unstable due to phase transitions and undergo big potential changes during cycling in the range 2-4 V vs Li).

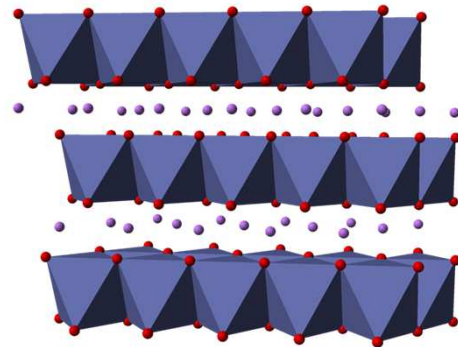
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Cathodic materials



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Cathodes for Li-ion cells – CoO₂



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Cathodes for Li-ion cells – CoO₂

- Layered structure of Li_xCoO_2 , intercalation mechanism similar to that of graphite, lithium is pushing apart layers of CoO_2 , cobalt is reducing from 4+ to 3+. Lithium atoms fill octahedral sites.
- In reality, utilizing whole theoretical capacity is not possible as when lithium content is above $x = 0.5$ phase transitions start to occur which cause density changes, cracking and permanent capacity drop. Thus during cycling it is possible to use only about half of the capacity (e.g. 140-150 out of 272 mAh/g)

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Cathodes for Li-ion cells – CoO₂

- It is stable over ca. 800 cycles;
- Potential range 3-4.2 V vs Li;
- Real capacity up to 150 mAh g⁻¹ (taking into account that max $x = 0.5$);
- Slow lithium diffusion in grains, poor electronic conductivity, thus the graphite is added in small amounts (few %) as well as active material is used as very fine particles, which helps with poor diffusion in grain bulk.
- Change of the LiPF_6 electrolyte to other that do not form HF (HF reacts with Co^{4+}) will allow to charge CoO_2 deeper – up to 4.5 V and up to 180 mAh g⁻¹.

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Cathodes for Li-ion cells – CoO₂

CoO_2 is mediocly safe material and it was the first one that was used in commercially available Li-ion cells. Due to that, it dominated the market for long years and it is still the most popular cathode material on the market. Unfortunately, big scale of production (still rising) caused a great cobalt demand. However, cobalt is scarce in the earth crust, so when faced with large demand caused price increase of the already expensive metal. Problem is lack of unsustainability as well as social unsustainability (uneven distribution on Earth and in the unstable region). This caused massive search for not only better, but cheaper materials.

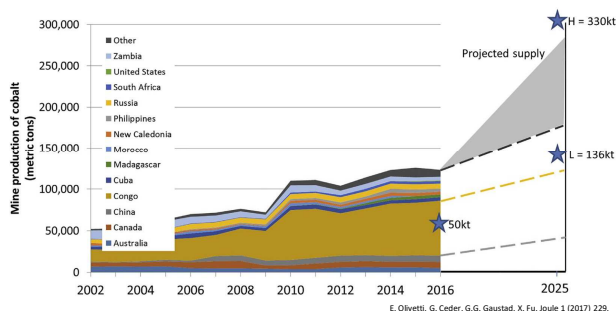
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Cathodes for Li-ion cells

Cobalt prices after abrupt Li-ion cells production increase soared. Thus materials based on nickel and especially manganese gained interest of the industry. In 2010-2015 cobalt prices slowly decreased from 40 to 30 \$/kg. It still occasionally however reaches 100\$ and now it fluctuates in 50-60\$ range. Meanwhile manganese prices dropped from 3 to 1.6 \$/kg. The main problem with cobalt remains – world reserves and production are located mainly in unstable (civil wars) DR Congo which still bases its industry on child labor.

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Cathodes for Li-ion cells



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Cathodes for Li-ion cells

Other layered oxides unfortunately did not rise to expectations. Investigations focused on NiO_2 due to the very high potential vs lithium and on MnO_2 due to the low price of manganese.

NiO_2 turned out to be unstable and very hard to synthesize.

MnO_2 in pure form is also electrochemically unstable, as the stable form of MnO_2 is spinel form LiMn_2O_4 (other than layered form).

Thus, research turned towards mixed metal oxides, in which manganese presence would lower the price, nickel would increase the potential vs Li and cobalt would stabilize the whole oxide.

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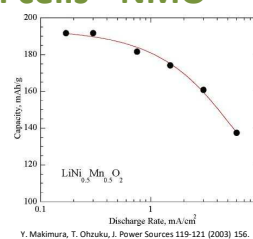
Cathodes for Li-ion cells - NMO

One of the first concepts for mixed oxides was to make nickel-manganese oxide with $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (NMO) stoichiometry. Oxides of the general formula $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ with different stoichiometries were synthesized, but $x = 0.5$ stoichiometry eventually turned out to be the optimal one. Cycling in real cells gives good results (no capacity fade) until around 4.7 V vs Li. Unfortunately, nickel presence between oxide layers causes lithium diffusion rate between layers to drop and also decrease electrode capacity as well as its cycle life in cycles.

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Cathodes for Li-ion cells - NMO

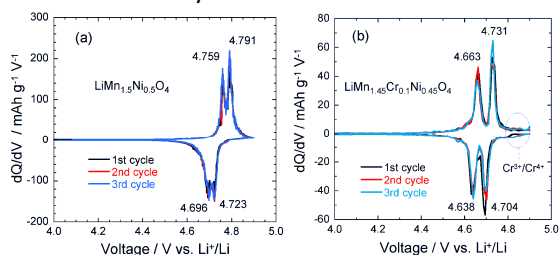
- Capacity, depending on potential range of cycling take values in the range 140-160 mAh g^{-1} ;
- Tolerates fast cycling;
- The wider potential range during cycling, the faster capacity fades;
- Grain surface modifications mitigate cycling issues at high potentials (although make material more expensive).
- Theoretically good, but overall stability and cycle life are mediocre.



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Modifications of cathodes - example

Additives/dopants can reduce overpotentials, which decreases differences between charge and discharge peaks for the same process steps. This increases efficiency of the cell.



C.M. Julien, A. Mauger, K. Zaghib, H. Groult, Inorganics 2 (2014) 132.

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Cathodes for Li-ion cells - NMC

During research on NMO it turned out, that cobalt dopant significantly improves material parameters. Optimal layered structure material was mixed nickel-manganese-cobalt oxide with $\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC) stoichiometry. It satisfies all assumptions made during concept phase of mixed oxides. It is now commonly used in Li-ion cells. Density changes during operation are of the 2% level (CoO_2 changes ca. 10%). Material is slightly cheaper and one can cycle it up to ca. 4.5 V vs Li.

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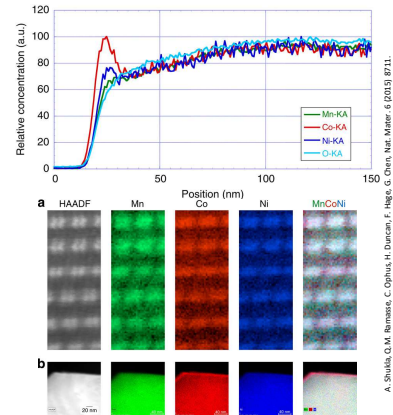
Cathodes for Li-ion cells - NMC

Nickel in the NMC structure is present between the oxide layers to a lesser extent (2-3%) than it is in NMO (ca. 10%). It results in better lithium ions conductivity in material grains and thus, the better capacity. In reality, nickel is not active until about 4.5 V vs Li, but it increases the potential of the whole material vs Li.

Cobalt is the main active component, which turns out during measurements (despite higher manganese content). Especially at the surface of NMC cobalt is responsible for 'letting in' the lithium to the grain bulk.

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Cathodes for Li-ion cells - NMC



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Cathodes for Li-ion cells - NMC

- Due to the small density changes NMC is more durable than other mixed oxides;
- Capacity is reaching 190 mAh g⁻¹ when cycled up to ca. 4.5 V vs Li; 160-170 mAh g⁻¹ to 4.2 V vs Li;
- Regardless of the stoichiometry average voltage is 3.7 V vs Li;
- Small/slow capacity fade during cycling;
- Tolerates fast rate cycling.
- Much higher substrates cost and more expensive manufacturing (cobalt presence, thermal method ca. 900°C, high energy costs).

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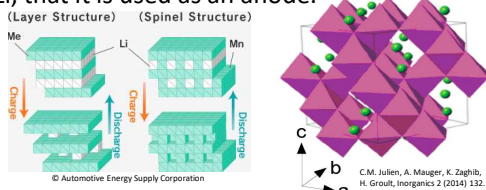
Cathodes for Li-ion cells - NMC

- Thanks to the technology development, advances in manufacturing processes and in crystalline structure research the capacity of cathode is increasing while cobalt (and manganese) content is decreasing.
- For the last few years the wider range of better and better NMC-family materials is produced (notation describes ratio of metals in the cathode active material): 532 (means LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂), 622, 811 and work continues on 9:0.5:0.5.

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Cathodes for Li-ion cells – MnO₂ (spinel)

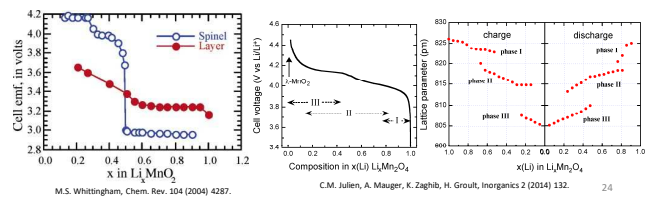
Materials with spinel structure keep lithium ions in their structure evenly – in all three dimensions there are voids that allow lithium ions movement and storage. It increase the lithium conductivity in grains. Lithium titanate Li₄Ti₅O₁₂ (anode material) has also spinel structure, but it has so low potential vs Li, that it is used as an anode.



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Cathodes for Li-ion cells – MnO₂ (spinel)

Spinel structures materials are characteristic in that they have usually at least one phase transition (structure change) during lithium intercalation, at around 1 Li:2 Me ratio.



M.S. Whittingham, Chem. Rev. 104 (2004) 4287.

C.M. Julien, A. Mauger, K. Zaghib, H. Groult, Inorganics 2 (2014) 132.

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Cathodes for Li-ion cells – MnO₂ (spinel)

Advantages of spinel-MnO₂:

- High safety – resistance to overcharging and thermal runaway (unlike NMC and CoO₂);
- Good resistance to high rate cycling, but above 5C at the cost of capacity drop (in that cycle) with rate;
- Low price – raw materials ca. 5 times cheaper than those for NMC (low materials cost, but manufacturing cost is still higher);
- Environmentally friendly (no cobalt or nickel).

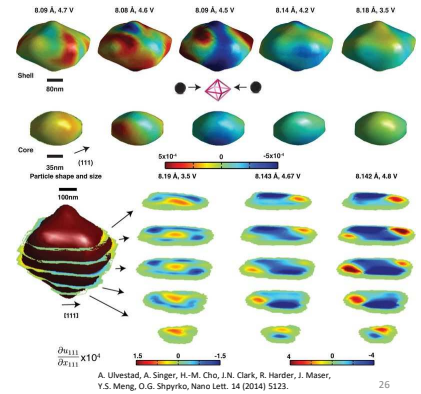
Disadvantages:

- It utilizes only one structural form, resulting in low energy density, capacity is ca. 110 mAh g⁻¹.

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Stress in grains of active material

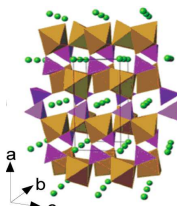
One of the main reasons of cathode capacity drop are mechanical stresses in grains: in a bulk and at the surface during cycling, due to which cracks form.



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Cathodes for Li-ion cells – LiFePO₄

Materials based on transition metal salts and anions of inorganic acids usually have olivine structure and lithium intercalates into its lengthwise voids (tunnels) in the cathode structure. Due to its nature material is highly anisotropic and in practice has low ionic conductivity (ions have to get inside “one by one”). Due to that it is hard to charge the material with currents higher than 1C.

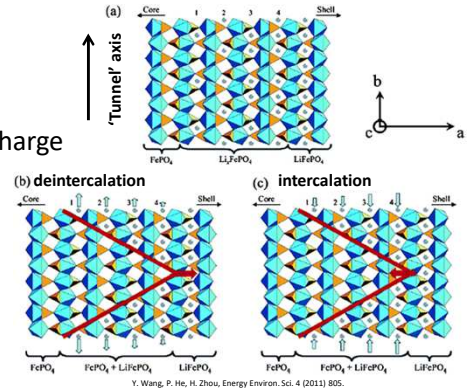


C.M. Julien, A. Mauger, K. Zaghib, H. Groult, Inorganics 2 (2014) 132.

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Cathodes for Li-ion cells – LiFePO₄

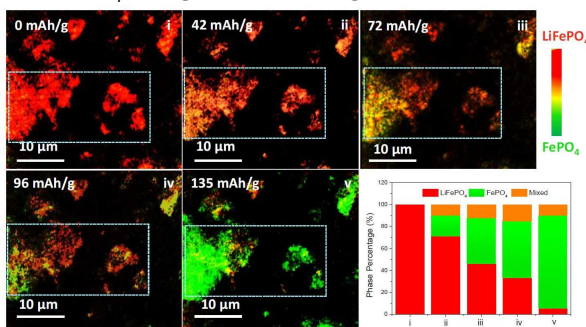
LiFePO₄ charge and discharge



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Cathodes for Li-ion cells – LiFePO₄

LiFePO₄ charge and discharge



J. Wang, Y.-C.K. Chen-Wiegart, J. Wang, Nat. Commun. 5 (2014) 4570.

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Cathodes for Li-ion cells – LiFePO₄

LiFePO₄ advantages:

- Low price;
- Environmentally friendly/non-toxic, manufacturing process uses water, ascorbic acid and similarly safe and non-toxic compounds;
- Practically no degradation/capacity fade during cycling;
- Safe;
- High theoretical capacity – max 170 mAh g⁻¹, most of which can be utilized – ca. 150 mAh g⁻¹.

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Cathodes for Li-ion cells – LiFePO₄

LiFePO₄ disadvantages:

- Low potential vs Li (3.45 V vs Li);
- Low maximum cycling rate (ca. 1C) both for continuous and impulse current.
- Electronic insulator (a lot of conductivity enhancing additive required);
- High capacity attainable only for low rate discharge – for higher rates it can reach only up to about 150 mAh g⁻¹ – it is a result of high conductive carbon content (decreases energy density) and poor tolerance to fast rate cycling.

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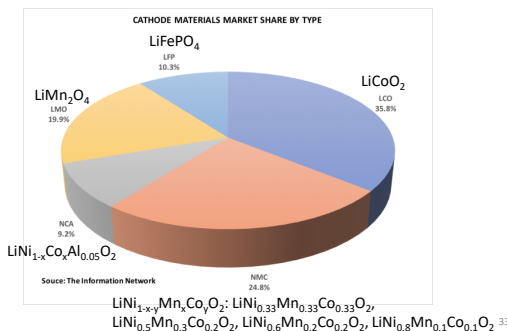
Cathodes for Li-ion cells

Materials that can intercalate more than one lithium cation per one transition metal atom (e.g. Li₂FeSiO₄, Li₂MnSiO₄) are considered the future of lithium-ion cells. It is not only due to potentially higher capacity, but also due to higher potentials vs Li and lower prices (at least per capacity unit). Most of the novel cathode materials are made of manganese, iron, silicon or phosphorous, which are the most abundant elements on earth and are cheap. Iron and silicon are the most abundant transition metal and non-metal, respectively (aside from oxygen, which is present in all cathode materials anyway).

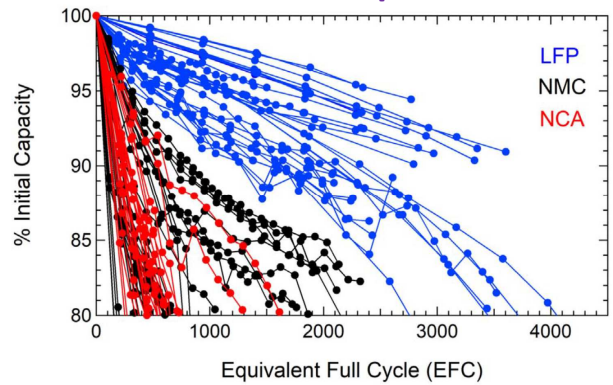
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Cathodic materials

Cathodic materials market share in 2017-2018:

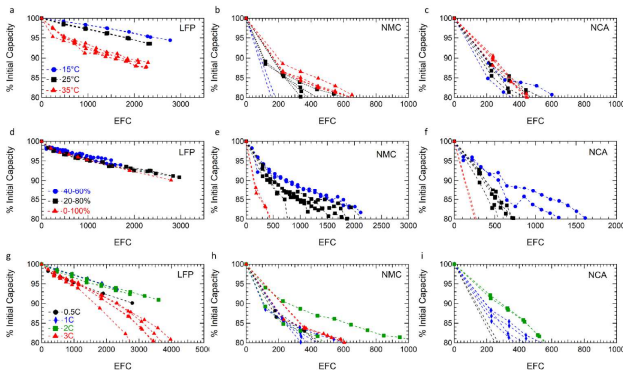


Cathodes – comparison



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Cathodes – comparison



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Cathodes – comparison

cathode	structure	E / V	d / g cm ⁻²	Q density / mAh/g	E density / Wh/kg	max C	life / cycles	safety
LiCoO ₂	layered (2D)	3.9	5.1	150	585	1	700	medium
LiMn ₂ O ₄	spinel (3D)	3.8	4.3	110	420	10	600	medium
LiFePO ₄	olivine (1D)	3.45	3.6	160	550	1	2000	high
Li(Ni _{0.33} Mn _{0.33} Co _{0.33})O ₂	layered (2D)	3.7	4.7	160	590	2	1000	medium
Li(Ni _{0.5} Mn _{0.3} Co _{0.2})O ₂	layered (2D)	3.7	4.6	165	610	5	1000	medium
Li(Ni _{0.6} Mn _{0.2} Co _{0.2})O ₂	layered (2D)	3.7	4.5	170	630	5	800	medium
Li(Ni _{0.8} Mn _{0.1} Co _{0.1})O ₂	layered (2D)	3.7	4.4	190	700	2	800	medium
Li(Ni _{0.8} Co _{0.15} Al _{0.05})O ₂	layered (2D)	3.7	4.7	180	665	1	700	medium

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