

Batteries

ACME Faculty, EHVE course
B.Sc. Studies, III year, V semester

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Introduction to Lithium-ion cells. Anodes for Lithium-ion cells.

Lithium-ion cells

The first research leading to invention of Lithium-ion cells was discovery in 1920s that some materials can intercalate alkali metals ions (graphite). In 1970s lithium conducting polymers were discovered (PEO, Armand's research). In 1980s first works on so-called „Rocking chair” cell started, research on graphite continued and investigation started metal sulfides and oxides that, as just discovered, also could intercalate lithium (Goodenough research).

Among numerous institutes and companies that conducted such research in parallel, the first company that introduced Lithium-ion cells to the market was Sony Corp.

Lithium-ion cells

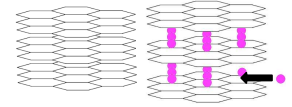
Principle of operation:

On charging: Lithium cation “leaves” graphite structure, that cause graphite to give away its charge to the external circuit. Lithium cation flows through the electrolyte due to the potential difference between anode and cathode. Cation builds into the cathode structure, where transition metal changes its oxidation state due to receiving electron from the external circuit. Lithium cation takes place near to the transition metal atom.

On discharge the cation path is reversed.

Intercalation materials

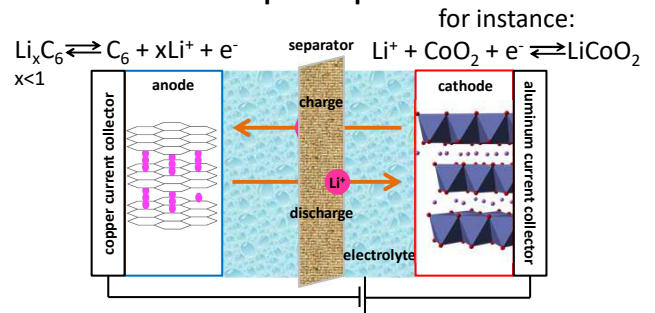
Intercalation materials can **reversibly** accept ions or molecules of other



substances between layers of their own crystal structure. Usually such layers keep together by Van der Waals forces. In order to get between them, ions or molecules have to be of a proper size. They also need to have a sufficient energy to overcome Van der Waals forces in their vicinity (push layers apart to get between them). This energy may come from charge transfer between ion and intercalation material, for instance.

Lithium-ion cells

Principle of operation

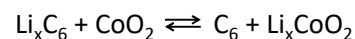


Li_xC_6 | electrolyte | transition metal compound

Lithium-ion cells

The “Rocking chair” name came from the operation principle: lithium cation does not change its oxidation state, it just moves between electrodes. The “Lithium-ion” name comes from the state of the lithium in the cell: it has a form of the cation during whole life of the cell.

Example of the overall reaction:



Li-ion cells: design

Most common designs are:

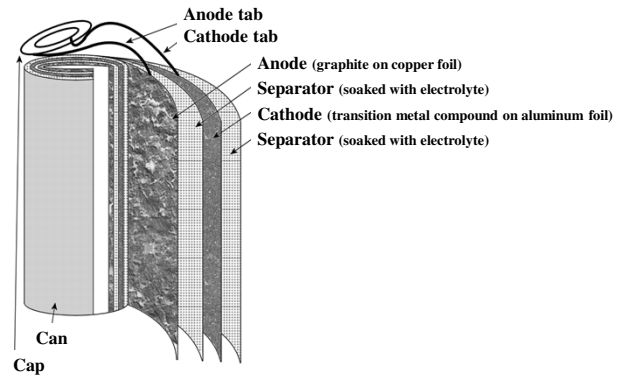
- prismatic;
- cylindrical;
- coin / button.

Recently few other designs have been developed:

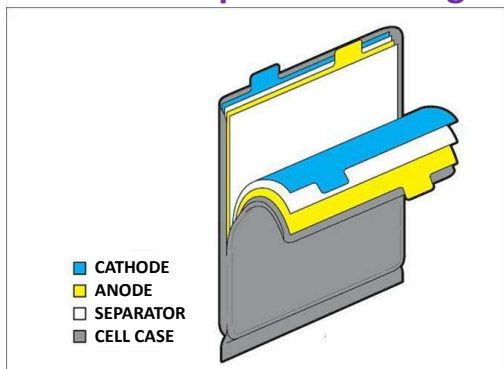
- flexible (Samsung);
- terraced (Apple, modification of prismatic design);
- hexagonal (LG, modification of prismatic design).

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Li-ion cells: cylindrical design



Li-ion cells: prismatic design



© C. Philpot, Car and Driver 04-2011

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Li-ion cells: pros and cons

Advantages:

- Maintenance-free; leak-proof;
- Light (highest energy density);
- Scalable (up to few dozen Ah);
- Tolerates partial charge and discharge (no memory effect);
- Slow voltage change over discharge;
- Negligible self-discharge;
- Highest voltage of all common cell types;
- Withstands high rates of charge/discharge (up to 5C), however at the expense of capacity drop during given cycle.

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Li-ion cells: pros and cons

Disadvantages:

- Does not tolerate deep discharge (overcharge is tolerated slightly better but still not helpful);
- Impulse discharge is tolerated by some chemistries;
- Intolerant towards low temperatures (below -20°C);
- Most expensive manufacturing (expensive components);
- The highest purity requirements for components, manufacturing atmosphere and the worst of all: moisture content.

There are modifications that enable use at low temperatures and with impulse discharges at the expense of decreasing some parameters.

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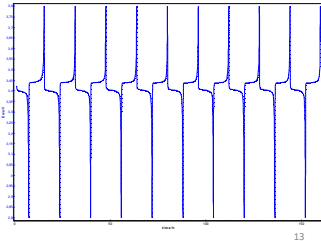
Li-ion cells: operating conditions

- OCV is dependent of electrodes composition – from ca. 3 to 4.2 V (and increase with advances in technology);
- Large voltage changes only at the beginning and at the end of charge/discharge; however, voltage changes during cycling are big enough for proper state of charge indication, approximate at least;
- Small change of cell potential during life;
- Cycle efficiency of 90%;
- No electrolyte concentration changes apart from the first cycle and initial SEI formation;

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Li-ion cells: operating conditions

- Lifespan depends on cell components, commonly in 800-4000 charge-discharge cycles range;
- Operation range, depending on cell components, from 2.5 V to 4.5 V (or higher). Most of the traditional chemistries (graphite/LiCoO₂) from ca. 3.2 to 4.2 V.



Li-ion cells: operating conditions

Storage:

- Keep away from sunlight and heat sources;
- Storage temperature not lower than -10°C and not higher than 60°C; In reality, in order not to decrease the lifespan substantially, it should be kept below 20°C;
- For long-term storage state of charge (SoC) should not exceed 80% and should not be lower than 20%.

Li-ion cells: applications

- All modern (manufactured after ca. 2005) mobile devices: notebooks, palmtops, smartphones, tablets, 2in1, music players;
- Electric vehicles: cars, scooters, bikes, buses, ferries, forklifts, UAVs;
- In the prototype phase: electric trucks and acceleration/recuperation for subway trains;
- Backup power supply for buildings (however lead-acid are still predominant);
- Grid energy storage and voltage leveling, frequency regulation, etc.

Anodes for Li-ion cells

Anodes 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;
- Low 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;

Anodes for Li-ion cells

Natural anode for lithium cell is metallic lithium. Energy density of such anode is enormous - over 3840 mAh g⁻¹. Lithium is also a good electronic conductor (does not require conductivity-enhancing additives). Unfortunately, metallic lithium has two main disadvantages:

- 1) It is so reactive, that most materials are not compatible with it and reacts with it.
- 2) During cycling dendrites form at the lithium surface. They can cause short circuit. Also, after they break, it is a permanent capacity loss.

Anodes for Li-ion cells

Due to still unsolved issues with metallic lithium anode, it is used only for primary cells nowadays, where there is no charging (that puts all risk on a cell with lithium anode).

Issues connected to lithium reactivity were partially solved on laboratory scale, but a lot of research is still needed to make it to the industrial scale...

Anodes for Li-ion cells: graphite

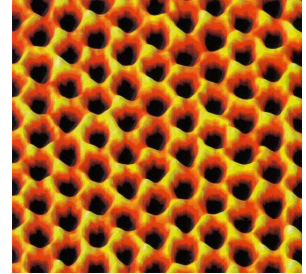
Basic component of anodes for Li-ion cells is graphite. It was a first material proposed for Li-ion cells that properly worked as an intercalating material. Advantages of graphite: it is relatively cheap and relatively weakly reactive with substances present in the cell. It is a good electronic conductor (it does not need additives to enhance conductivity). Its density during lithium intercalation (on charge) is changing relatively little – ca. 10%. Unfortunately, it has (relatively) low theoretical capacity – only 372 mAh g⁻¹ (for LiC₆ stoichiometry).

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Anodes for Li-ion cells: graphite

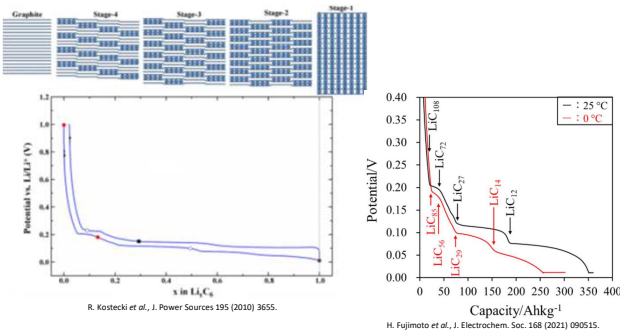
Graphite charges gradually – it accepts lithium cations in steps, allowing its original structure to gradually deform.

Graphite layer as visible in the TEM



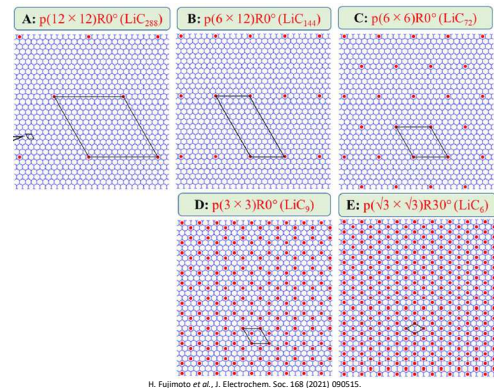
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Anodes for Lithium-ion: graphite



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Anodes for Lithium-ion: graphite



H. Fujimoto et al., J. Electrochem. Soc. 168 (2021) 090515.

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Anodes for Li-ion cells: graphite

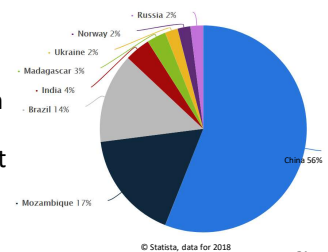
Graphite properties are a consequence of its structure. It is crystalline and perfectly ordered (apart from the edges of layers). Carbon layers are arranged tightly (0.335 nm gap between them), so lithium cation intercalation results in density change. Graphite has different properties depending on which plane it works (it is anisotropic).

Graphite has also disadvantages – it exfoliates (layers are torn from it) upon contact with some solvents, e.g. propylene carbonate. It also works poorly under high rate cycling (above 2C). It is hard to modify as well.

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Anodes for Li-ion cells: graphite

- Graphite is mined in underground mines (e.g. China, Mozambique, Brasil, etc.) and its production is reaching ca. 1.1 million tons annually;
- Synthetic graphite can be manufactured, but it rarely has similar parameters and purity like the natural one (mined). Its production costs are higher than that of natural one, but they are stable, unlike those of graphite.



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Anodes for Li-ion cells: graphite

- Rise of market demand for graphite caused sudden price growth. In 2005-2015 (drops in capacity in western countries, increase of the Li-ion battery field needs) period graphite price has tripled, then it dropped. Then it again increased rapidly (ca. 6-fold) in years 2017-2018 and dropped again.
- Batteries account for 25% of the graphite consumption in the world. Other consumers are electric engines components (brushes), steel additives, fire-resistant materials, automotive components (including carbon fibers) and lubricants.
- In Li-ion cell there is 10 times more graphite than lithium.

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Anodes for Li-ion cells: carbon

Other carbon forms also can form anode materials. Among them hard carbons and soft carbons play an important role as well as various nanostructures – graphene in a number of variety, nanowires, nanotubes, etc. Those materials do not exist in nature; they are all manufactured (synthesized, engineered).

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Anodes for Li-ion cells: hard carbon

Hard carbon is a material produced as a result of precursor carbonization through pyrolysis (self-ordering to graphite does not occur).

Material precursor is a starting material that transforms to the final one under influence of the external factors. In case of carbon materials it is usually an organic compound that transforms during pyrolysis to the carbon form with a designed spatial configuration and/or designed density and/or designed chemical composition (carbon atoms ratio to other elements).

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Anodes for Li-ion cells: hard carbon

Hard carbon is a strongly disordered material, graphene layers (carbon layers with a flat structure, where carbon atoms form hexagons) are randomly scattered, there is no long-distance order, so material is isotropic (it has identical properties irrespective of the direction). Hard carbon is non-crystalline – amorphous. Large average gaps between layers (0.380 nm) result in negligible density changes during cell cycling.

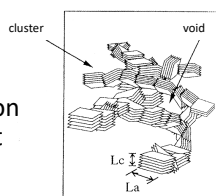
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Anodes for Li-ion cells: hard carbon

Hard carbon advantages are potentially higher energy density than that of a graphite, no risk of exfoliation, better behavior during fast rate cycling, easiness of modification (to use it as a composite component or for doping it with additives).

Hard carbon capacity reaches 500 mAh g⁻¹ (depending on a precursor and pyrolysis conditions).

Main disadvantage of hard carbon is a large capacity loss in the first cycle (10-20%).



I. Mochida, Carbon 39 (2001) 399. 29

Anodes for Li-ion cells: soft carbon

Soft carbon is a material formed through carbonization of organic precursor, that during heating melts first and then pyrolyzes. Resulting structure resembles that of a graphite.

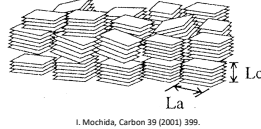
Thus, structure is organized and occasionally similar to graphite, although distances between graphene layers are various and on average a little higher than that of a graphite (0.375 nm). Soft carbon is partially crystalline and anisotropic.

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Anodes for Li-ion cells: soft carbon

Soft carbon advantages are low price, much better cycling behavior at high rates than that of a graphite (good capacity retention).

Disadvantages are low capacity compared to the graphite (below 300 mAh g^{-1}), risk of exfoliation (like graphite), worse mechanical properties and relatively high capacity loss in first cycle.



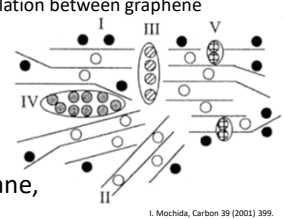
I. Mochida, Carbon 39 (2001) 399.

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Anodes for Li-ion cells: carbon

Capacities of soft and hard carbon result from additional sites to which lithium cations can attach/adsorb (apart from intercalation between graphene layers). These are:

- I: surface sites,
 - II: intercalated sites,
 - III: inserted in cluster gap,
 - IV: inserted in microvoids surrounded by hexagonal plane,
 - V: inserted in atomic defects in hexagonal plane/heteroatom void
- I-V occur in hard carbon, I-III in soft carbon



I. Mochida, Carbon 39 (2001) 399.

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Anodes for Li-ion cells: carbon

Common property of hard carbon, soft carbon and graphite is formation of repeatable and lithium cation conductive SEI (solid-electrolyte interphase).

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Anodes for Li-ion cells: graphene and nanostructures

Other carbon forms like graphene (single carbon layers with graphite structure), nanotubes, nanoribbons and other nanostructures (2D, 3D).

Advantages: high capacities (graphene 960 mAh g^{-1} , nanotubes 1100 mAh g^{-1} , other with similar parameters), good cycling behavior (fast too), relatively low capacity loss in first cycle, good cycling life.

Main disadvantage is enormously high manufacturing price, lack of big scale manufacturing technology (above big laboratory scale), inadequate production repeatability; still too low knowledge on these materials.

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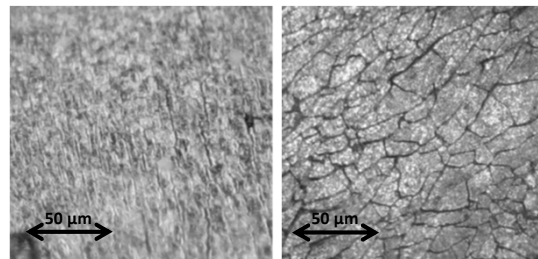
Anodes for Li-ion cells: silicon

Theoretical capacity ca. 4200 mAh g^{-1} .

Silicon during lithium absorption changes its structure from crystalline to amorphous (disordered). The resulting alloy has $\text{Li}_{22}\text{Si}_5$ ($\text{Li}_{4.4}\text{Si}$) stoichiometry. It causes mechanical properties change and large volume change (density drop) – by ca. 300%.

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Anodes for Li-ion cells: silicon



J.B. Hutchings et al., ANL TR-5888, 2011.

Such big volume changes cause stress and material cracking which results in quick capacity drop due to the irreversibility of these processes and loss of electrical contact with part of the material.

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Anodes for Li-ion cells: silicon

Apart from big disadvantage which causes anode cracking and fast capacity loss (few % per cycle), silicon is also forming poor and unstable SEI upon contact with typical electrolytes that employ fluorine compounds.

Large capacity is a result of the alloy composition (atoms ratio) in which lithium atoms surround individual silicon atoms contrary to carbon materials in which lithium atoms are collected between layers (intercalation, for instance).

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Anodes for Li-ion cells: silicon

Low silicon price and large capacity are strong magnet for all anode researchers. That is the source of all modifications and composites involving silicon.

Popular methods to omit density/volume changes during cycling are:

- using silicon nanoparticles in which volume changes are relatively small (due to small amount of silicon atoms);
- using composites containing silicon domains, but enclosed in other materials matrices, e.g. carbon.

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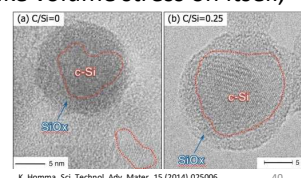
Anodes for Li-ion cells: silicon

So-called nanosilicon (silicon nanoparticles) have a capacity up to 2000 mAh g⁻¹ and although the capacity is stable during cycling, in first cycle it losses irreversibly up to 30% of whole capacity. It is a result of an anode large surface (as the material is very fine). SEI formation process uses anode material and electrolyte and in such a big surface uses relatively big share of anode material (same surface depth in big particle is a smaller share of volume than in small particle). Nanosilicons are also very expensive to manufacture. Big advantage of nanosilicons is their great tolerance of fast cycling (above 5C).

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Anodes for Li-ion cells: silicon

Composites with silicon have rarely capacity higher than 1500 mAh g⁻¹, however, they usually are stable during cycling, resistant to fast cycling and have good mechanical properties. Unfortunately, they usually also loose a lot of capacity in the first cycle (irreversible capacity). Composites concepts usually base on surrounding silicon nanoparticles with more flexible buffer phase that take volume stress on itself, allowing for silicon nanoparticles to expand and shrink at their will without any mechanical properties consequences.



Anodes for Li-ion cells: tin

Tin, similarly to silicon can form lithium intercalation compounds/alloys with Li₂₂Sn₅ stoichiometry. However, theoretical capacity of tin is 'only' 994 mAh g⁻¹, which is much less than for silicon (but still much more than for graphite). Unfortunately, it has the same disadvantages as silicon, i.e. large volume changes during cycling resulting in quick capacity fade. Tin is also more expensive than silicon and according to some investigators, it forms whiskers on the surface when in Li-ion cell interior-like conditions (so, the same as lithium metal).

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Anodes for Li-ion cells: titanate

The only exception to materials based on carbon, silicon or their composites is lithium titanate – Li₄Ti₅O₁₂. Its main advantage is extremely long life (up to 20 000 cycles with stable and negligible capacity fade), good tolerance to mildly fast (5C) discharge (still with long life) and quite good tolerance to operation at 10C rate (with only slight capacity fade). Titanate is also safe: good mechanical parameters (no density changes during cycling and flexibility – does not break under externally induced stress), resistant to overheating, nonflammable, tolerance to very low temperatures (down to ca. -40°C, slight capacity drop below -20°C) and does not self-ignite from overheating.

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Anodes for Li-ion cells: titanate

Main disadvantage of titanate is its very high potential (materials based on silicon and carbon have electrochemical potential near 0 V vs Li, so without any effect on cell voltage) – 1.5 V vs Li, which means, that titanate-based cells have voltage around 2.5 V (resulting in 2/3 energy density of typical Li-ion cell just because of that).

The next disadvantage is low capacity of the material itself – only ca. 175 mAh g⁻¹, which is half of the graphite capacity.

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Anodes for Li-ion cells: titanate

Despite two big disadvantages, advantages cannot be overestimated. Long life and high safety attracted attention of electric cars manufacturers, where titanate found its main application – traction cells.

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Anodes for Li-ion cells

- In reality, commercially available cells contain graphite (ca. 80% - half of natural/mined and half of artificial one) and titanate – ca. 5% (for chosen applications) and hard carbon – ca. 6% of the market.
- Number of manufacturers that add silicon (in small amounts – up to 15%) to the graphite anodes increases (actually this is a silicon-carbon composite), and not always make that information public, so it is hard to estimate exact share of the market for such industrial solution (in 2015 it was ca. 2% of the market, but it is known, that this share is quickly increasing). In the last 3 years mean mass produced cells capacity is increasing (it is considered mostly effect of silicon addition).

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Anodes for Li-ion cells: other

Multiple other materials are proposed for Li-ion cells anodes – germanium, aluminum and other alloying materials. Silicon monoxide (SiO, not SiO₂) is also investigated, as well as metal oxides, sulfides, phosphides, nitrides and others both in pure form and in composites (usually carbon is the other component). Common property of all those materials is very initial phase of research on them and usually very high manufacturing cost (even potentially, due to the high components cost). Work on better anodes is still in progress.

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