Li-ion basics

ATHENS WUT21 course

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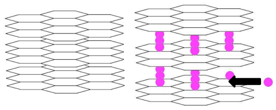
Intercalation materials



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

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

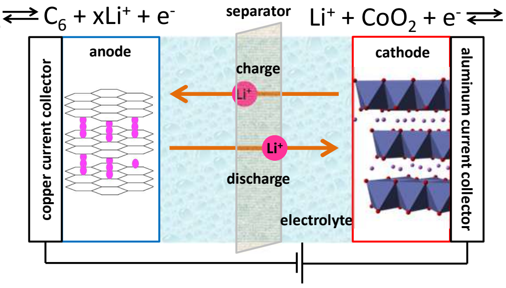
Principle of operation

for instance:

$Li_xC_6 \rightleftarrows C_6 + xLi^+ + e^-$

x<1

$Li^+ + CoO_2 + e^- \rightleftarrows LiCoO_2$



Li_xC_6 | electrolyte | transition metal compound

Lithium-ion cells

Principle of operation:

On discharging: 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 charge the cation path is reversed.

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:

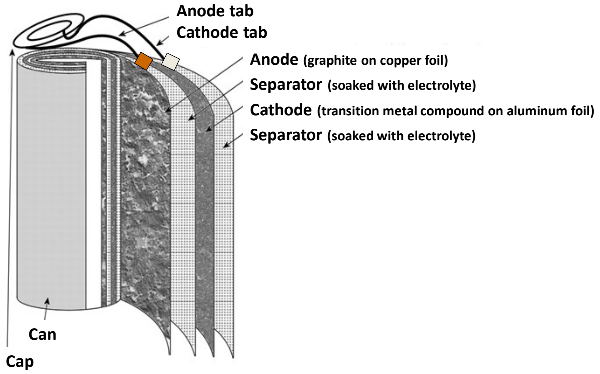
$$Li_xC_6 + CoO_2 \rightleftarrows C_6 + Li_xCoO_2$$

Li-ion cells: design

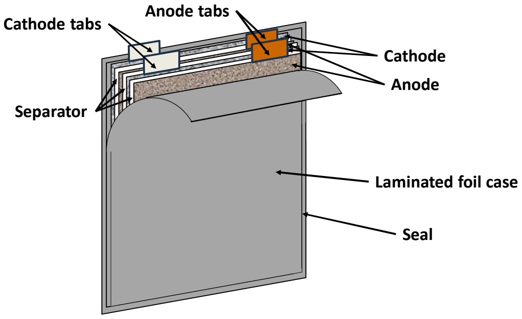
Most common designs are:
- prismatic (metal case or hard plastic case) or pouch (laminated flexible foil case, or pre-formed flexible foil case);
- cylindrical;
- coin.

Modifications of designs are also possible:
- flexible (pouch design modification);
- terraced (modification of prismatic design);
- hexagonal (modification of prismatic design).

Li-ion cells: cylindrical design



Li-ion cells: pouch design



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.

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.

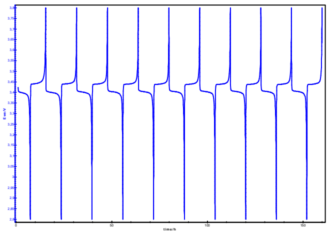
There are modifications that enable use at low temperatures and with impulse discharges at the expense of decreasing some parameters.

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;

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/$LiCoO_2$) 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%.

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

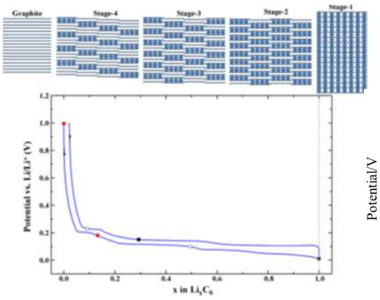
Natural anode for lithium cell is metallic lithium. Energy density of such anode is enormous - over 3840 mAh g^{-1}. Lithium is also a good electronic conductor (does not require conductivity-enhancing additives). Unfortunately, metallic lithium has two main disadvantages:

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.

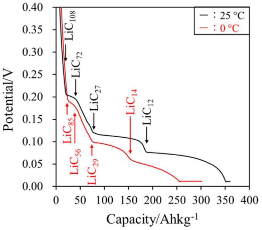
Anodes for Li-ion cells: graphite

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 LiC_6 stoichiometry).

Anodes for Lithium-ion: graphite



R. Kostecki *et al.*, J. Power Sources 195 (2010) 3655.



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

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 occurs).

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).

Anodes for Li-ion cells: hard carbon

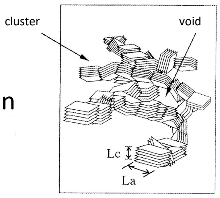
Hard carbon is a strongly disordered material, graphene layers (carbon layers with a flat structure, where carbon atoms form hexagons) are randomly scattered, there is no long-distance order, so material is isotropic (it has identical properties irrespective of the direction). Hard carbon is non-crystalline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

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%).

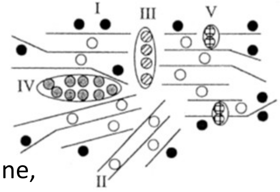


I. Mochida, Carbon 39 (2001) 399.

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. Mochida, Carbon 39 (2001) 399.

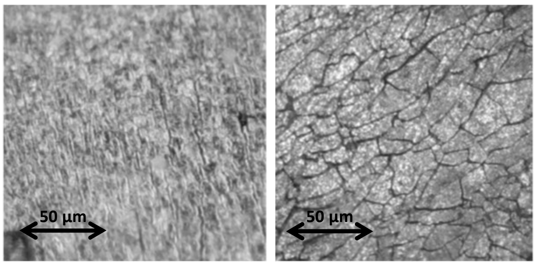
I-V occur in hard carbon, I-III in soft carbon

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 $Li_{22}Si_5$ ($Li_{4.4}Si$) stoichiometry. It causes mechanical properties change and large volume change (density drop) – by ca. 300%.

Anodes for Li-ion cells: silicon



J.B. Ratchford *et al.*, ARL-TR-5818, 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.

Anodes for Li-ion cells: silicon

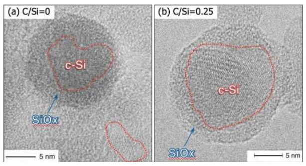
Low silicon price and large capacity are strong magnet for all anode researchers. That is the source of all modifications and composites involving silicon.

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.

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.



K. Homma, Sci. Technol. Adv. Mater. 15 (2014) 025006.

Anodes for Li-ion cells: titanate

The only exception to materials based on carbon, silicon or their composites is lithium titanate – $Li_4Ti_5O_{12}$. 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.

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.

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.

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).

Anodes – summary and comparison

Anode	Mechanism	E / V vs Li	d / g cm^{-3}	Charge density Q / mAh/g	Max C	Life / cycles	Safety
graphite (natural / artificial)	intercalation (layered)	~0.1	1.9-2.3	372	3	800	average
hard carbon	intercalation (layered-defects)	~0.1	0.9-1.5	400-500	10	500-1000	average
Si/C composite	alloying / intercalation	0.1-0.4	1.5	560-2200 (5-50%)	3-10	500-1000+	average
Silicon	alloying	0.3-0.4	2.3	4211	1-5	200?	average
LTO ($Li_4Ti_5O_{12}$)	intercalation (layered)	1.55	3.48	175	20	10000	high
Lithium	-	0	0.534	3860	?	<100	low

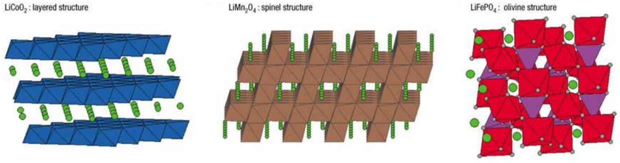
Cathodes for Li-ion cells

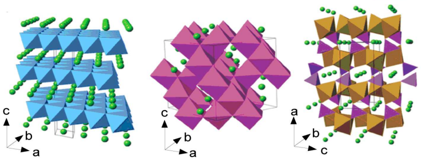
Cathode required properties (wish list):

- **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;

Cathodic materials

M. Thackeray, Nat. Mater. 1 (2002) 81.





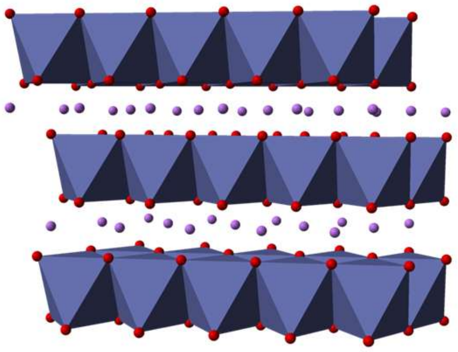
layered $LiCoO_2$ 2D

spinel $LiMn_2O_4$ 3D

olivine $LiFePO_4$ 1D

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

Cathodes for Li-ion cells – CoO_2



Cathodes for Li-ion cells – CoO_2

- 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)

Cathodes for Li-ion cells – CoO_2

- 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}.

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.

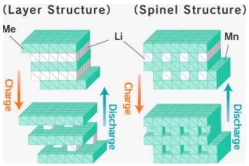
- Much higher substrates cost and more expensive manufacturing (cobalt presence, thermal method ca. 900°C, high energy costs).

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 $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$), 622, 811 and work continues on 9:0.5:0.5.

Cathodes for Li-ion cells – MnO_2 (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 $Li_4Ti_5O_{12}$ (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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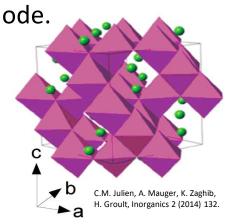


C.M. Julien, A. Mauger, K. Zaghib, H. Groult, Inorganics 2 (2014) 132.

Cathodes for Li-ion cells – MnO_2 (spinel)

Advantages of spinel-MnO_2:

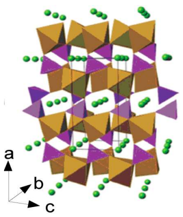
- High safety – resistance to overcharging and thermal runaway (unlike NMC and CoO_2);
- Good resistance to high rate cycling, but above 5C at the cost of capacity drop (in that cycle) with rate;
- Low price – raw materials ca. 5 times cheaper than those for NMC (low materials cost, but manufacturing 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}.

Cathodes for Li-ion cells – $LiFePO_4$

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.

Cathodes for Li-ion cells – $LiFePO_4$

$LiFePO_4$ advantages:

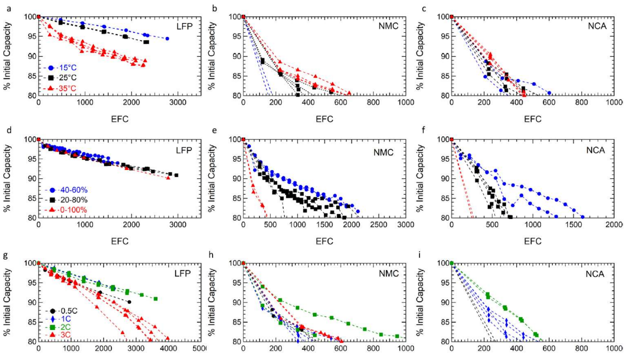
- Low price;
- Environmentally friendly/non-toxic, manufacturing process uses water, ascorbic acid and similarly safe and non-toxic compounds;
- Practically no degradation/capacity fade during cycling;
- Safe;
- High theoretical capacity – max 170 mAh g^{-1}, most of which can be utilized – ca. 150 mAh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

Cathodes for Li-ion cells – $LiFePO_4$

$LiFePO_4$ 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.

Cathodes – comparison



Y. Preger, H. M. Barkholtz, A. Fresquez, D.L. Campbell, B.W. Juba, J. Romàn-Kustas, S.R. Ferreira, B. Chalamala, J. Electrochem. Soc. 167 (2020) 120532.

Cathodes – comparison

cathode	structure	E / V	d / g cm^{-3}	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
$LiMn_2O_4$	spinel (3D)	3.8	4.3	110	420	10	600	medium
$LiFePO_4$	olivine (1D)	3.45	3.6	160	550	1	3000	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	600	medium

Electrolytes for Li-ion cells

Cell parameters depending on electrolyte parameters (exclusively, among other or indirectly) :

- Current density (conductivity);
- Storage and operation temperature (thermal stability);
- Charge-discharge cycle efficiency (cation transference number, conductivity);
- Energy density (electrochemical stability and compatibility enabling using better anodes and/or cathodes);
- Safety and environmental friendliness (safety, toxicity);
- Cost (cost).

Electrolytes for Li-ion cells

Properties that electrolyte for Li-ion cells should have:

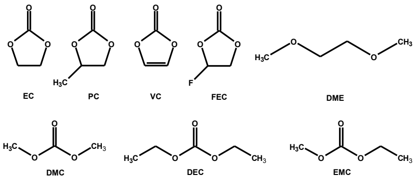
- Good ionic conductivity (>1 mS cm^{-1});
- No electronic conductivity;
- High lithium cation transference number (>0.3);
- Thermal stability (-20 - +150°C range);
- Electrochemical stability (2-4.5 V vs Li);
- Compatibility with other cell components (in temperature and potential ranges that can occur in cell);
- Non-toxicity;
- Low cost.

Electrolyte types

- Liquid ← used in all standard commercial cells
- Gel ← used in some cells for special applications
- Liquid polymer (oligomer)
- Solid polymer (SPE) ← used in narrow range of high-temperature cells but considered the future of Li-ion cells
- Ceramic
- Composite (*e.g.* gel with ceramic additive)
- Polyanions
- Ionic liquids
- other…

Why mixtures?

Solvent	Advantages (η / mPa s, T / ˚C)	Disadvantages
EC	high ε, high b.p. (+248), cheap	high m.p. (+36), high η (1.9)
~~PC~~	~~high ε, high b.p. (+242), cheap~~	~~graphite exfoliation, high η (2.5)~~
~~DME~~	~~very low η (0.45), low m.p. (-58)~~	~~unstable SEI~~
DMC	low η (0.58), cheap	low ε (3.1), low b.p. (+91), high m.p. (+4.6)
DEC	low η (0.75), low m.p. (-74)	low ε (2.8), expensive
EMC	low η (0.64), low m.p. (-53)	low ε (2.9), expensive

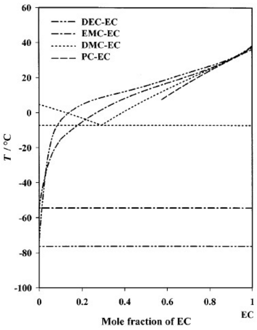


Why mixtures?

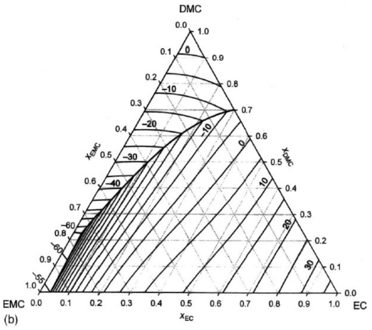
Commonly (commercially) used solvent mixtures from the more to the less common (typical ratios in brackets):

- **EC:DMC** (1:1, 3:7, 1:2)
- **EC:DEC** (3:7, 1:2)
- **EC:DEC:DMC** (1:1:1)
- **EC:EMC** (more expensive devices, 1:2)
- **EC:DMC:EMC** (low temperature applications, 1:1:1)
- **EC:DEC:DMC:EMC** (low temperature applications, 1:1:1:2)
- **EC:PC** (PC can be used in the presence of large amount of more polar EC, which then forms the lithium cation solvation layer)
- **EC:PC:DMC** (1:1:2, 1:1:1)
- **EC:DMC:DME** (1:2:0.125)**, etc.**

Why mixtures?



M.S. Ding, K. Xu, S. Zhang, T.R. Jow,
J. Electrochem. Soc. 148 (2001) A299.



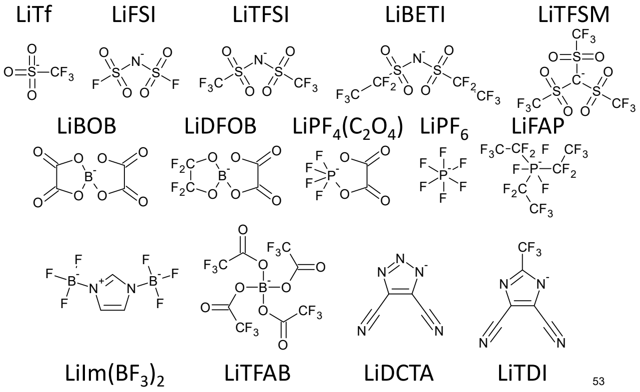
M.S. Ding, *J. Electrochem. Soc.* 151 (2004) A731.

Salts

Most important salts proposed over the years:

- $LiClO_4$ – explosive at increased temperature;
- $LiBF_4$ (LiF formation, unstable and growing SEI);
- $LiPF_6$, $LiAsF_6$, $LiSbF_6$ – toxic, unstable;
- LiTf, LiFSI, LiTFSI, LiBETI – aluminum corrosion, expensive;
- LiBOB, LiDFOB, $LiPF_4(C_2O_4)$ – form unstable SEI;
- LiTFSM, LiTFAB – expensive manufacturing;
- Imidazole-BF_3 family – low conductivity;
- Aluminum salts family – low conductivity and unstable at required potential range;
- Azole salts family (e.g. LiTDI).

Salts

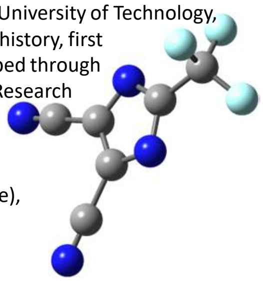


But not this salts…

$LiPF_6$ is so far the dominant salt in the battery market despite its known disadvantages (that is why so many substitutes were proposed over the past 30 years):

- Decomposition to toxic, caustic and carcinogenic compounds (e.g. HF, POF_3) upon contact with even traces of water (as low as 1 ppm, so with every solvent used, which usually contain up to 30 ppm) – that is why Li-ion cells should not be opened;
- Thermal decomposition starting from 70°C on (that is why there are warning labels on batteries against putting them into the direct sunlight, close to heat sources and heating above 60°C);
- Incompatibility with new electrode generations (both anodes – e.g. silicon, and cathodes – e.g. silicates);
- Low cycle efficiency (one of the reasons is low $T_{Li+} \approx 0.3$);

LiTDI salt – Polish product



Salt designed and developed at Warsaw University of Technology, second salt in the 30 years of Li-ion cells history, first European salt. Patented in 2008, developed through cooperation within ALISTORE European Research Institute. Wide cooperation just like any other large modern invention:
Warsaw University of Technology
Universite de Picardie Jules Verne (France),
Sapienza Universita di Roma (Italy),
Uppsala University (Sweden).

Commercialization in 2010-2018 by French company Arkema.

- **Siemens Award**
- **Prime Minister of Poland Award**
- **WUT President Award**
- **Ignacy Mościcki Science Award**

LiTDI salt

LiTDI:
- is stable up to 256°C; up to 4.7 V vs lithium and does not corrode aluminum; is stable against/in water;
- does not require stabilizing additives or acid/water sorbents (like $LiPF_6$);
- has higher Li^+ cation transference number (over 0.5) and the same effective conductivity (of Li^+ cations);
- is compatible with new electrode materials;
- is not as toxic as $LiPF_6$ and is not decomposing to the toxic compounds (but keep protecting your eyes);

It is the first salt that fulfills all industrial requirements toward lithium salts since the beginning of Li-ion cell industry (30 years).

LiTDI salt

Additionally, LiTDI salt thanks to its property of stable water complexing (without a loss of salt functional parameters) is effective water scavenger – drying up the rest of the cell and extending its life that way, e.g. by hindering the cathode material corrosion.

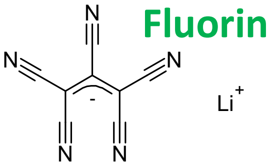
Thanks to that LiTDI is used also as an additive for standard electrolytes, which extends cell life by the factor of 2-3.

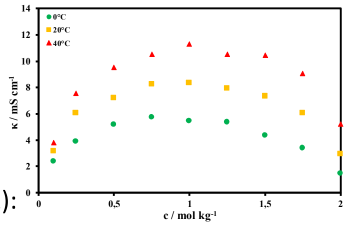
It particularly well extends cell life at higher temperatures, at which standard electrolytes based on $LiPF_6$ very quickly cease to work. For instance, at 45°C (temperature of smartphone during quick charge or when playing 3D game) cell with $LiPF_6$ works up to 200 cycles, but with LiTDI it easily work over 1000 cycles, or if LiTDI is an additive for $LiPF_6$, then up to 700 cycles.

LiTDI in battery solvent mixtures

mixture	σ / mS cm^{-1}	T_{Li+}	σ_{Li+} / mS cm^{-1}
0.3 mol/kg LiTDI in EC:DEC:DMC (1:1:1)	5.52	0.333	1.84
0.7 mol/kg LiTDI in EC:DEC:DMC (1:1:1)	4.96	0.497	2.47
0.4 mol/kg LiTDI in EC:DEC (1:2)	3.24	0.601	1.95
0.7 mol/kg LiTDI in EC:DEC (1:2)	3.51	0.563	1.98
0.31 mol/kg LiTDI in EC:DMC (1:2)	5.09	0.622	3.17
0.63 mol/kg LiTDI in EC:DMC (1:2)	5.70	0.553	3.15
0.3 mol/kg LiTDI in EC:DEC:DME (8:16:1)	4.07	0.614	2.50
0.5 mol/kg LiTDI in EC:DEC:DME (8:16:1)	4.35	0.850	3.69
1.2 mol/kg LiTDI in EC:DEC:DME (8:16:1)	3.74	0.666	2.49
0.4 mol/kg LiTDI in EC:DMC:DME (8:16:1)	6.17	0.648	4.00
1 mol/kg LiTDI in EC:DMC:DME (8:16:1)	6.13	0.731	4.48
1 mol/kg $LiPF_6$ in EC:DEC:DMC (1:1:1)	10.08	0.244	2.46
1 mol/kg $LiPF_6$ in EC:DMC (1:2)	10.15	0.350	3.55

Fluorine-free salt - LiPCP

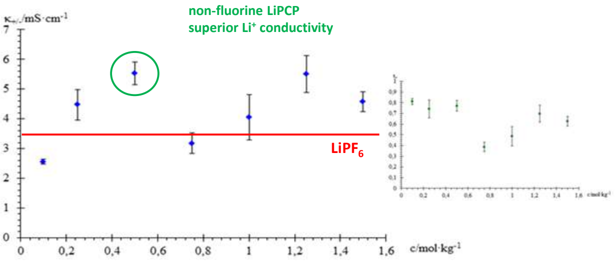




- Fluorine-free
  (first in history)
- LiPCP in EC:DMC (1:2):
  - high conductivity - **σ <u>> 8 mS cm^{-1}</u>**
  - high t_{Li+} > 0.5
  - electrochemical stability up to **4.4 V vs Li**
    (does not corrode aluminum)
  - thermal stability up to **<u>280˚C</u>**

L. Niedzicki *et al.*, patent PL 232856

Fluorine-free salt - LiPCP



Li^+ conductivity of LiPCP in EC:2DMC

LiPCP electrolyte in EC:2DMC has conductivity of ~8 mS/cm @ 20°C and T_{Li+} in 0.5-0.75 range, thus effective conductivity (lithium cation conductivity)a is **~5.5 mS/cm**, compared to ~3.5 mS/cm for $LiPF_6$ (conductivity of 10 mS/cm and T_{Li+} ~0.35).

Separators

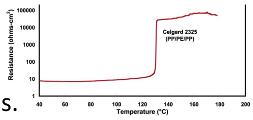
Main purposes of the separator is:

- Physical separation of electrodes (prevention against short circuit);
- Electric insulation (no electronic conductivity);
- Enabling electrolyte flow;
- Enhancing contact with electrode surfaces (wetting them with electrolyte) even at increased temperature or after the bending (rolling sheets to cylindrical shape);
- Other functions (*e.g.* protection against overheating).

Separators

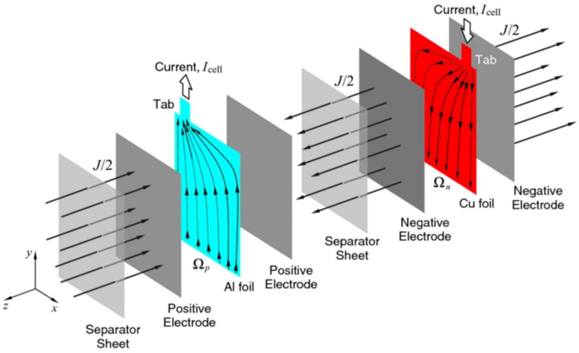
Required separators properties:

- Good wettability and absorbability (quick and full);
- Good electronic insulator;
- High porosity (40-60%, pores <1 μm diameter);
- Compatibility with other cell components;
- Resistance to high or low potentials;
- Thermal stability and no measurable shrinkage or crimping at elevated temperature (up to 90°C);
- Closing pores in case of really high temperature (>130°C);
- Resistant to compression;
- No impurities, holes and crimps.



Protection against overheating

(and thermal runaway)



P. Taheri, A. Mansouri, B. Schweitzer, M. Yazdanpour, M. Bahrami, J. Electrochem. Soc. 160 (2013) A1731.