Week 2: Lithium ion cells

Copper Zinc Daniel cell and lead acid batteries, both of which are standard electrochemical cells. NiMH cells negative electrode works on a different principle. Recall, the metal hydride absorbs hydrogen much like a sponge absorbs water, without changing its structure or chemical composition, hence NiMH cells tend to have much longer lifetimes than lead-acid cells..

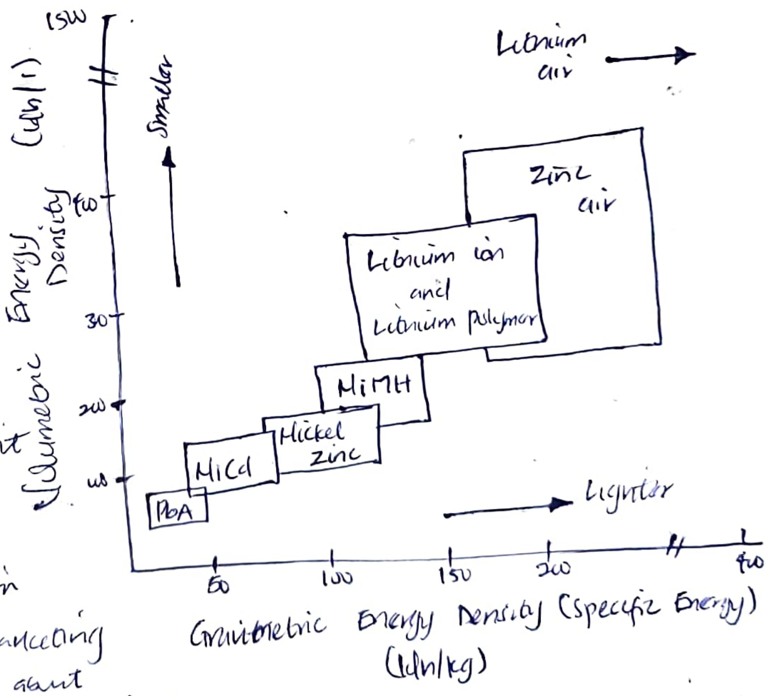
Lithium-ion cells both electrodes work on this principle unlike negative electrode in NiMH cell. If PbA cell in an automobile last for 5 years, most likely that Lithium-ion battery cell will last for atleast 10 yrs.

NiMH cell really work well for hybrid electric vehicle type of applications, where there is not a huge need for a lot of energy storage but where we do need to have higher power.

#1 Specific Energy and Energy Density

Specific energy and energy density measure the maximum stored energy per unit weight or volume respectively.

- For a given weight, higher specific energy store more energy
- For a given storage capacity, higher specific energy cells are lighter.
- For a given volume, higher energy density stores more energy
- For a given storage capacity, higher energy density cells are smaller



Lithium ion has higher energy density and specific energy than historic chemistries.

PbA - largest & heaviest

Li-ion is lighter & smaller that is why they are used in application such as powering different types of electrified drive train vehicles, where both size and weight must be minimized.

- Lithium polymer is a type of lithium ion, sometimes it's just used as a marketing term, and sometimes it's used to talk about a cell that has a solid polymer electrolyte instead of a gel electrolyte

Zinc air & Lithium air, the negative electrode is a solid metal, either zinc or lithium and the positive electrode is oxygen that is scavenged from air, and because air is around us everywhere, the weight of the air is not really included in the weight of the cell and that's one reason why they can be smaller and lighter.

- The ultimate battery technology is Li-air but at this present time ~~that~~ there are difficulties making it work robustly and repeatedly in real world applications.

- Advantages of Lithium-ion
  - They have higher energy density & specific energy than most other types of secondary cells.
  - They operate at higher voltages than other rechargeable cells, typically about 3.7V for Lithium-ion vs 1.2V for NiMH or NiCd
  - Lower self-discharge rate than other types of rechargeable cells, NiMH & NiCd cells can loose anywhere from 1-5% of their charge per day, even if they are not installed in a device
    - Lithium-ion cells will retain most of their charge even after months of storage
  - Long life due to gentler intercalation mechanism in each electrode instead of more standard and harsh redox reaction

- Disadvantages of Lithium ion
  - They are presently more expensive than similar capacity NiMH or NiCd batteries
  - More complex to manufacture, and presently manufactured in much smaller numbers than NiMH or NiCd batteries
    ↳ for laptop & ~~computer~~ consumer electronics they are manufactured in very high volumes
  - Lithium ion cells tend to be less stable electrochemically, which means if overcharged, it is possible to catch fire. Hence, they require special safety precautions
  - ~~Caution~~: The quality of cell materials and cell construction matters!
    The quality of cell materials and cell construction matters!
    - Impurities limit cell performance that can be achieved
    - Cells from different manufacturers with similar cell chemistries and similar construction may yield different performance.

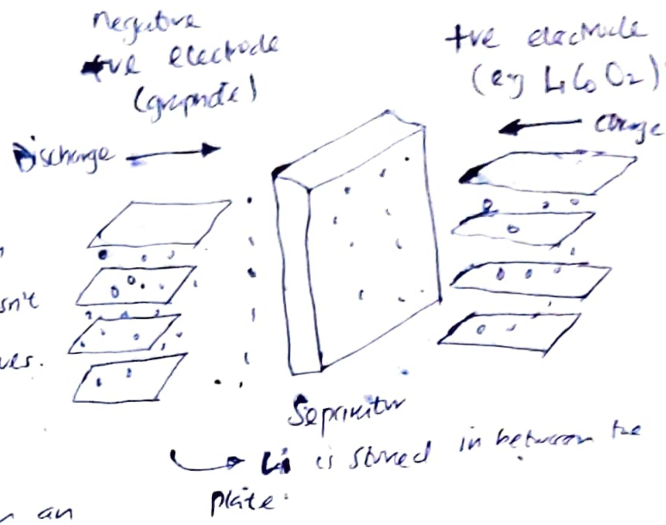
Summary

- Benefit of Li-ion: High energy density & specific energy, long life, higher voltage and lower self-discharge rates
- Disadvantage: need for proper management to guarantee safety, cost. However, lithium ion cells and electronics are becoming less expensive and over time we should see their price decrease significantly.

#2 Lithium ion battery process of intercalation

Lithium-ion cells work differently from the electrochemical cells. In lithium-ion both electrodes depend on an intercalation mechanism rather than violent Redox reactions.

- While nickel metal hydride cell stores hydrogen in its negative electrode, lithium ion cells are able to store lithium in either one and both of the electrodes.



- Lithium is stored in the electrodes much like water is stored in a sponge; it doesn't change the structure of the electrodes themselves.
- Li is stored in the electrode, and Li^+ moves through the electrolyte
- Li^+ enters an electrode, becoming Li when an electron is available; Li exits an electrode and become Li^+ when it can give up an electron.

- **Requirements of the electrode structure**

Intercalation process involves inserting lithium ions into a structure of the host electrode without changing the structure (Crystal Structure). However, to do so, the electrode for Li-ion should have two (2) key properties:

i. Open crystal structure, allowing insertion or extraction of lithium ions in the vacant spaces

ii. Ability for the material to accept compensating electrons from the external circuit or to give up electrons to that external circuit.

When a lithium atom is stored inside of the electrode, it is essentially unchanged, neutral charged. Researcher confirmed that there is a slight positive charge on the lithium, and slightly negative charge in the surrounding region in the crystal structure. Lithium is not tightly bonded in one place; it is actually quite free to move around.

- **Discharge Process**

- During discharge, Li exits the surface of the negative-electrode particles, gives up an electron, becoming Li^+ in the electrolyte
- When Li leaves the particle, it leaves behind a vacancy at the surface of this -ve electrode particle; this vacancy could be filled with another lithium atom. Lithium moves through a diffusion process from higher concentration in the center of the particle toward the outside of the particle to have equal concentration of lithium throughout the particle.

• Meanwhile, electron travels through external circuit to positive electrode. Li^+ join with the electron, and Li enters positive-electrode particles at their surface. Li diffuses into positive electrode particle to equalize concentration (over time).

- The charge process

The process is completely reversible; thus lithium pass back and forth between electrodes during charging and discharging.

• During charge, lithium exits the surface of the positive-electrode particle. Now, it becomes positively charged in the electrolyte, it gives up an electron and this electron is forced by the charger through the external circuit across to the negative electrode.

• At the negative electrode, a positively charged Li cation from the electrolyte joins with this electron, forms and neutrally charged lithium atom which then enters the negative electrode particle at the surface. There will be higher concentration of lithium at the surface of the negative electrode particle than there is at the interior of the particle.

• Lithium diffuse inward and over time we will get an equilibrium concentration.

- Particle nature of electrode

Electrodes consist of particles of material. They are not homogeneous, just block of materials.

It is critical to understand that the electrodes are not homogeneous blocks, but rather millions of small particles.

- Mesophase Carbonaceous spheres (graphite) used in the negative electrodes of many lithium-ion battery cells.

- Lithium manganese oxide used in the positive electrode of some lithium-ion battery cells.

Nature of electrode is not homogeneous in order to increase the overall surface area of the electrode as much as reasonably possible. Therefore, if we want high power lithium-ion battery cells, we want to increase the surface area as much as possible. Trade-off: cell particles to be small to get high power, also want them to be large so that the cells degrade more slowly.

- Polished electrode cross section

To see the spaces between the particles, the voids, and these voids are filled with electrolyte inside an actual electrode. Other material in the electrodes that we can't see in are:

- Binders (to glue things together) so that the particle remain in contact with each other and don't easily separate. Important so that there is a pathway for the electrons to flow to the external circuit.

- Conductive additives (to enhance electron conduction, which is otherwise poor in positive-electrode materials).

+ These binders & conductive additives are not "active" portions of the cell, so are not often mentioned, but are always present.

- Electrolyte often also has additives to inhibit some of the side reactions which otherwise cause the cell to age and degrade. These additives in the electrolytes are not often talked about either, but they are always present in a practical cell.

* Summary

i. Lithium-ion cell electrodes are made of small particles to increase surface area and therefore to increase their power capability.

ii. Particles are made from compounds that internally have an open crystal structure that can accept lithium into them without changing that structure.

iii. Lithium can intercalate into these particles and can deintercalate out of the particles, something that happens at the surface.

iv. Inside the particles, lithium diffuses over time to equalize the concentration of lithium.

v. During discharge, lithium moves from the negative electrode particles to the positive electrode particles through intermediary electrolyte, where Li^+ are charge carriers.

v. During the charging process, the same thing happens but in the opposite direction.

vi. Electrons move through the external circuit. When discharging, they move from the negative electrode to the positive electrode

#3 Lithium ion Cell Formats

There are 3 basic form of lithium-ion battery calls
i) Cylinderical (ii) Prismatic (iii) Pouch, cells are flat but compressed stacked plates

- Electrode Coating
Electrodes in lithium-ion cells of any form factor are of similar structure and are made by similar processes. The particles that comprise the electrode are coated on both sides of metallic foils which act as the current collectors conducting the current into and out of the cell.
  - Two basic electrode structure are used, depending on cell form factor:
    - i A Stacked structure for use in pouch cells
    - ii A Spiral wound structure for use in cylinderical / prismatic cells.

- Stacked Electrode Structure
  - Pouch / prismatic cells often used for high capacity battery applications to optimize the use of space
  - Pouch designs use a stacked electrode structure in which the negative - and positive electrode foils are cut into individual electrode plates which are stacked alternately and kept apart by the separator.
  - Separator may be cut to the same size as electrodes but more often is a long strip wound zig-zag between alternate electrodes on the stack. The electrodes themselves are stamped or cut into mere individual plate shapes out of a longer roll of electrode material, and they are stamped to all have exactly the same size to fit on top of each other neatly.
  - All negative-electrode tabs are welded in parallel and to the cell's negative terminal; all positive-electrodes tabs are welded in parallel and to the cell's positive terminal

- Cylinderical and Prismatic Electrode Structure
For cylinderical cells the negative and positive electrode foils are cut into two long strips which are wound on a cylinderical mandrel, together with the separator to hold the electrodes apart, to form a jelly roll.

Most prismatic cells are constructed similarly, by winding electrode on flat mandrel. Historically, cylinderical cells have been very popular because they're the easiest to manufacture and they are still the cell of choice in Tesla automobiles but the cylinderical arrangement of batteries creates unnecessary space which can be used for ventilation or cooling.

– Negative Electrode : Microscale Structure of graphite

All commercial lithium battery cells use some form of graphite for their negative electrodes. Graphite is very common. is the material that is used inside pencils. Graphite is the form of carbon and it's formed by layers of graphene stacked together.

Graphene is extremely strong and these honeycomb structure are difficult to break apart.

It is the weak bonding between the layers that makes graphite useful for an electrode material. These layers are loosely stacked and there is room for lithium to intercalate between them.

– Mesoscale Structure of Graphite

The region where graphene aligns is called the grain of the particle and the boundaries between different alignments is called grain boundaries. The grain's bonding may be fairly well aligned or they may be completely random.

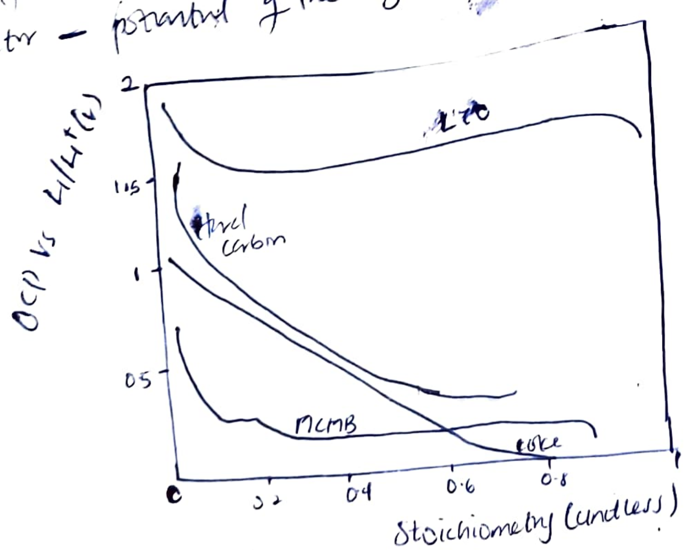
Carbon used in negative electrodes can come from natural or synthetic source which have somewhat different layering properties), or from natural "hard" or disordered carbons, which have many small pockets of graphene layers, arranged in random configuration. These carbons have somewhat different voltage and lifetime properties.

– Alternate negative-electrode material LTO

Lithium titanate oxide ($Li_4Ti_5O_{12}$, LTO) is an alternative negative-electrode material. Graphite is used in probably every commercial lithium-ion cell on the market; not every, almost every lithium-ion battery cell that's used in the market. The dischchange very different crystal structure from graphite.

LTO has a very different crystal structure from graphite. The disadvantage of LTO is that it has **high open-circuit** potential (making cell voltage low).

The voltage of a battery cell overall is equal to the potential of the positive electrode current collector − potential of the negative electrode current collector.



MCMB – Meso carbon microbead

LTO has the highest potential of all material for a negative electrode

LTO battery are nearly **indestructible** – they can be charged and discharged tens of thousand of times with very little noticeable **capacity** loss.

- Future negative electrode material – silicon

Silicon is a very promising negative-electrode material. They can store more lithium than carbon can. If we use graphite as electrode material, we can store up to one Li atom per six carbon atoms. If silicon is used, we store up to 4 lithium atoms for every single silicon atom.

24 : 1 advantage using silicon over carbon

Therefore, the energy density using silicon electrodes can be much higher. Unfortunately, while volume change for a charge/discharge cycle for graphite is around 10%, but it is around 400% for silicon. Hence, silicon electrodes tend to fracture very quickly and so they are short lives.

- Possible workarounds; mix graphite with silicon or build small forest of silicon nanowires with space in-between to allow the expansion.

* Summary

i) Lithium-ion cells are manufactured in pouch, prismatic and cylindrical form factors.

ii) In any of these cases, current-collector metal foils are generally coated on both sides with electrode active materials.

iii) In the negative electrode, the most common active material or some form of carbon: natural or synthetic graphite, or hard carbon.

iv) Lithium titanate oxide (LTO) is an alternative material, which greatly increase cell longevity, but it is costly and significantly lowers energy density.

v) Future lithium-ion cells will probably include silicon in the negative electrode to improve energy density (presently, cycle life of silicon is low)

#4 Positive Electrodes for Lithium-ion Cells

The first intercalation material that was discovered for positive electrodes and Lithium-ion battery cells was **Lithium Cobalt Oxide (LCO)**. The material was discovered in 1980 by Prof. Goodenough and his research team.

They discovered that $Li_x CoO_2$ (LCO) was a viable material for lithium intercalation. The overall structure has layers of this cobalt oxide material, a lot like graphite has layers of graphene. Because cobalt oxide has layered structure, it's given called a layered cathode material.

The x in the formula $Li_x CoO_2$ show that there is a variable amount of lithium in this structure. If there is no lithium at all in this structure, then x is zero(0). If the structure has some amount of lithium but not full lithiation, then x is going to be a number between 0 & 1. If it can hold as much lithium then $x = 1$. x is actually an average over the whole electrode or at least over a local region of how much lithium is present which is why it can be a fractional number.

As we charge or discharge the battery, the value of x changes. The value indicates an electrode state of charge, called **stoichiometry**.

- LCO is commonly used in portable electronics cells (→ phone, laptops), but suffers some problems when trying to scale up for large battery application (vehicle or utility grid use):
  - cobalt is rare, toxic, and expensive
  - only about half of cobalt capacity (theoretic) can be used. x value can only go between 0.5 and 1. If it goes below 0.5, we have some capacity degradation issues that happen.
- To make it more practicable for large scale application, **Ni** can substitute CO, giving higher energy density (higher voltage, same capacity), but not very thermally stable (if battery is overcharged, it is more likely to combust). → **LNiO**
  - For Cobalt, we can also substitute Aluminium, Chromium, or Manganese.
- The most popular substitution presently is to replace some of the cobalt with nickel and some with **manganese**. Hence, we end up with a nickel cobalt manganese, or **NCM** material. This material has exactly the same atomic crystalline structure.
- The nickel in the structure tends to increase the voltage, and the manganese tends to make the material more thermally stable which is a desirable property.
  → many automotive battery packs are made with **NCM** or **NMC** type of battery

- Another alternative is to replace some of the cobalt with nickel and some with aluminium NCA battery cell. The type of battery cell that is used in Tesla

* Spinel cathodes

- In 1983, Goodenough and Thackeray proposed $Li_xMn_2O_4$ (LMO) - Lithium Manganese Oxide as an alternate intercalation material: Mn sits in the octahedral sites, Li in the tetrahedral. The name of the crystal structure is called **Cubic Spinel**. It allows 3D diffusion (vs. 2D for layered and 1D for olivine).
- In the chemical equation of lithium manganese oxide, $Li_xMn_2O_4$, x can go from 0 - 2. However, if x is larger than 1, the material tends to dissolve in the electrolytes commonly used in lithium-ion battery cells. For this reason, we use x from 0 to 1 almost always in practice.
- LMO is cheaper and safer than LCO, but can have short lifetime due to the manganese dissolving into the electrolyte under some conditions, manganese in the structure is very susceptible to acidic electrolyte conditions
- LMO battery cell is quite inexpensive to obtain the material for a research lab. The life of the battery can be prolonged by adding different chemicals to the electrolytes that preferentially scavenges the acid, so that the acid attacks the added materials instead of attacking the electrode itself
- Sometimes, the electrode is being coated to protect the particles from the acid. NB: any battery cell that uses lithium manganese oxide is going to have something as part of its design in order to extend its life. But it's usually not disclosed because it is a trade secret.

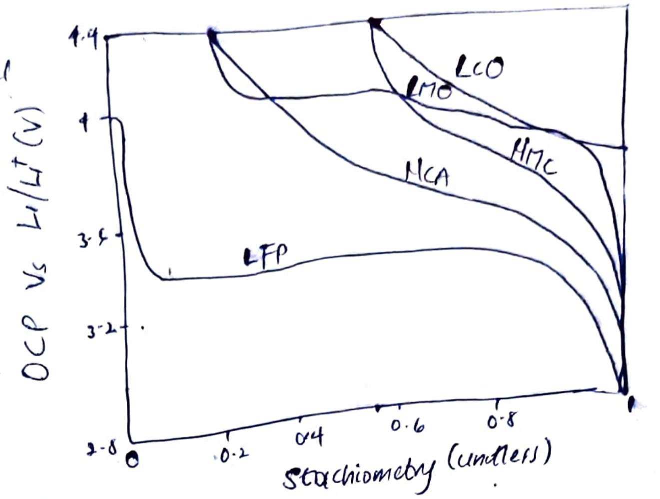
* Olivine cathodes

- The third variety of positive-electrode active material was once again discovered by Prof. Goodenough's research team. These are the **olivine-style phosphates**
- The most commonly found member of this family is called **Lithium Iron phosphate** Li_xFePO_4 (LFP)
- The material is very inexpensive and non-toxic but it has a low energy density due to a low open-circuit potential and low specific energy due to heaviness of Fe.
- 1D structure tends to have high resistance, which can be overcome in part by using very small particles and including conductive additives. (low electron conductivities)

Summary

- Since essentially all lithium-ion cells presently in use have graphitic (-ve) negative electrode, lithium-ion cells are often referred to simply by their positive-electrode chemistry (e.g an "LFP cell", e.t.c). So, it is quite common to refer to a lithium cell by the chemistry of its positive electrode only.

- The open circuit potential curves for different positive electrode chemistries are drawn:



- Lithium iron phosphate has the lowest potential of all the electrodes; it tends to have low energy ~~tendency~~ density

- It difficult to estimate/determine the state of charge of batteries made from LFP

- LMO also have some flat curve in the diagram but unlike LFP. However, it's a little easier to estimate state of charge for an LMO cell.

- NCA & NMC cells would be easier to estimate ~~calculate~~ state of charge because there is fairly consistent slope or a fairly consistent change in voltage across the state of charge range.

- They are the easiest cells to write good state of charge estimate algorithm for. So when choosing a cell chemistry in the design of the battery pack, there is going to be implications beyond simply energy density or power density but also implications on the ability of the battery management system to regulate the activity of the battery pack.

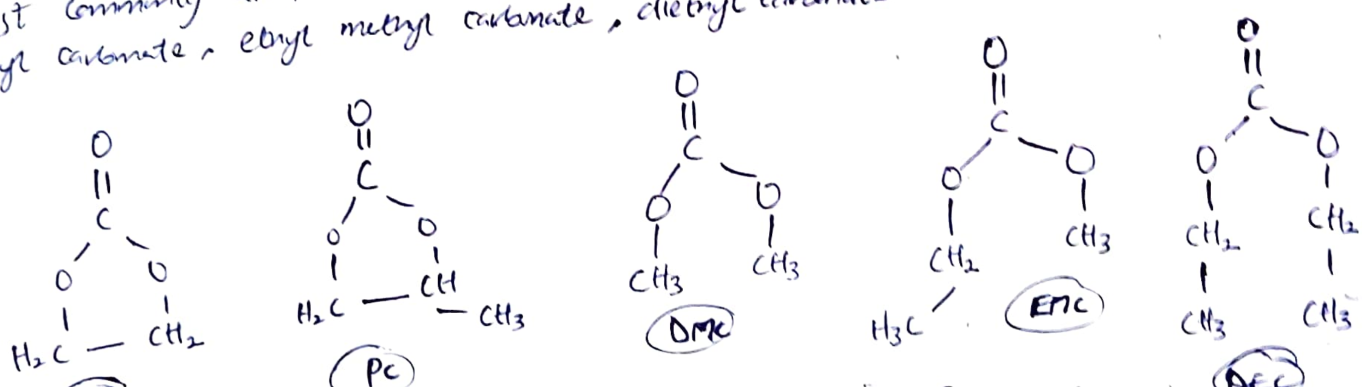
- Layered cathodes (LCO, NMC, NCA) can use only around half of their theoretical capacity because if the lithium between the separate layer is used up, it will be difficult to insert lithium between the layers anymore.

- Olivine cathode (LFP) have low voltage (and very little state information in their voltage).
- Spinel cathodes (LMO) are inexpensive and non-toxic, but can degrade rapidly.

#5 Electrolytes for lithium-ion cells

The electrolyte is the media that conducts ions between the electrodes internal to the cell. In a general electrochemical cell, the electrolyte consists of a solvent into which we dissolve either a salt, an acid, or a base.

- Some battery cells use an electrolyte whose solvent is water and it is called aqueous cells. But in electrochemical series, water dissociates into hydrogen gas and oxygen gas at a potential of around 2 volts.
- So any battery cell having voltage higher than 2V cannot use water as its solvent. The slight exception is the lead acid battery cell, with voltage a little bit over 2V per cell.
- Reason: when sulfuric acid is dissolved in the water, that slightly changes the voltage with which water breaks down into hydrogen and oxygen. It elevates the voltage and makes a 2V battery cell possible.
- Li-ion battery cells are made using electrolytes that are non-aqueous and they are built using organic solvents plus a lithium-based salt that dissolves into that solvent.
- Electrolyte in a lithium-ion battery cell acts purely as an ion conductor, it does not take part of the normal chemical reactions for charging & discharging the battery cell.
- Most commonly used solvents include ethylene carbonate, propylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate



EC PC DMC EMC DEC

- Each of these solvents has slightly different properties. Some of them become essentially solid at temperature below 0°c. So these solvent are not appropriate for battery cells that must operate at low temperatures.
- Even though the solvent doesn't participate in the charging & discharging of the battery cell it can participate in undesired side reactions that slowly cause the cell to deteriorate over time. The solvent can also be mixed together at a different ratio.
- A common feature to these solvents is the double-bonded oxygen, which develops a slight negative charge, polarizing the molecule so that it dissolves salts.

- Electrolyte salts used in Li-ion

The most commonly used salt in lithium-ion cell is Lithium hexafluorophosphate $LiPF_6$. Some other candidates include $LiBF_4$ (Lithium tetrafluoroborate) and $LiClO_4$ (Lithium perchlorate).

- the solvent does not participate in the (normal) chemical processes of a lithium ion cell but different solvents have different properties with respect to aging, and lower temperature performance. e.t.c
- Solvent doesn't participate in the chemical reaction, but the salt does because the salt is a charge carrier through the solvent.

- Separators for Lithium-ion cells

The separator is a permeable membrane that has tiny holes in it and the holes are large enough that ions can pass through them, but also small enough that the positive and negative electrode can't touch each other. If they were to touch each other, you would have a short circuit which would lead to heat buildup and thermal runaway, possibly a fire or an explosion.

The separator must be electronic insulator which can't allow electrons to flow across the separator but ions to flow ~~very~~ easily through the porous in the separator.

- Current Collectors

They are made from metal foils onto which the electrode materials are deposited. The purpose of the current collector is to conduct electrons from the electrode materials to the ~~tabs~~ of the terminals of the cell to the outside circuit.

These foils are subjected to very harsh environments inside the cells. The Li-ion in the electrolyte and also the fluorine based ions in the electrolyte tend to be very reactive chemically and they want to undergo chemical reactions.

Current collectors that will withstand the environment, such that they will not react with the electrolyte are needed.

- In Lithium-ion, the positive electrode current collector is aluminium foil. It is chosen because aluminium tends not to react to anything as long as its potential is about 3V or higher.
- Negative electrode (low potential region) uses Copper foil. Because any potential lower than about 2 volts, the copper is stable electrochemically and will not react.

Summary

1. Lithium-ion electrolyte solvents is usually a combination of EC, PC, DMC EMC, and/or DEC
2. Electrolyte salt is usually $LiPF_6$, but is sometimes $LiBF_4$ or $LiClO_4$
3. The most common salt $LiPF_6$ dissassociates to a lithium cation and PF_6 anion. The PF_6^- anion is inert toward strong reducing agents, such as lithium metal
4. Separator is a nonconductive porous membrane that prevents short circuits. The have holes that allows the electrolyte to permeate through the separator & allows the cation & anions in the electrolyte to move back & forth.
5. Current collectors are copper & alluminium foils.

* Will Lithium Run out?

Are we replacing a potential oil crisis with a lithium crisis? Will lithium be consumed at a high rate that it will eventually run out very soon?

- Lithium is between 20 & 100 times more abundant than Pb & Ni on the chart showing relative abundance of elements in earth's crust.
- It is difficult to find lithium deposits in nature since lithium is one of the most reactive elements. Lithium is not usually found isolated in its elemental form all by itself, it usually found in some lithium-based compounds.
- Relative abundance of Cadmium (Cd) & mecury (Hg) whose usage is deprecated because of their toxicity are about 1000 times less common than Li but still used commercially in battery cell.

- How much Lithium needed in Lithium-ion cell or EVs?

Consider a LCO cell (positive electrode = $LiCoO_2$)

- Lithium Cobalt oxide is approximately 7% lithium by weight
- The positive electrode particles comprise only a portion of the overall cell construct as it is made
- $LiCoO_2$ comprises $\lessapprox 33\%$ of cell weight, so Li content of electrode $\approx 2\%$ of cell weight
- Wondering of Lithium in negative electrode? When the cell is manufactured, there is no Lithium in the negative electrode. The first time you charge this cell is when lithium enters the negative electrode.
- There is some lithium in the salt used in the electrolyte such as $LiPF_6$. The electrolyte in total comprises about 10% of the cell weight. If $LiPF_6$ is used as the salt, the amount of lithium is about 10% of the 10%. Overally lithium in the electrolyte constitutes about one percent of cell weight.
- Combining the amount of lithium and lithium cobalt oxide and the electrolyte, the high energy lithium ion battery cell has about 3% of its weight that is made up from the lithium itself.

- What does this mean?

Lithium content in high-energy cell $\lessapprox 3\%$ by weight

- Battery cells used in xEV cells weigh about $7 kg\,kWh^{-1}$: Li content $\approx 0.2 kg\,kWh^{-1}$
- 200 mile EV needs $\approx$ 60 kWh battery: Li content $\approx$ 12 kg/EV
  - PHEV batteries $\lessapprox 10\%$ of EV-battery capacity
  - HEV batteries require even less capacity.

- 1 million EVs would consume ≤ 12,000 tons of Li (without recycling); 1 million P/HEVs would consume ≤ 1200 tons
- known available supply of Li is now 2200 billion tons, including from seawater by simple math: each human being presently alive could own more than 2000 EVs, without recycling!

Hence, "we really do not have a Lithium Crisis" — Dr. Gregory L. Plett

Nevertheless, some elements being used perhaps as electrode or electrolyte in Li-ion battery cell are scarce

- Carbon used in the negative electrode is nothing to be worried about because it is abundance
- Positive electrode materials are a little bit less certain e.g. Cobalt is quite rare and most of cobalt supply comes from Congo which also has some political instability.
  ↳ Democratic Republic of Congo (DRC)

- It may be reasonable to have worry about battery technologies for EVs but not because lithium might run out but because some of the other elements required for its production are rare

Summary

1. Lithium is one of the most abundant elements on the planet
2. Lithium known available supply is more than sufficient to meet demand for consumer electronics
3. Other elements such as Cobalt, are used in Lithium-ion cells are more scarce than lithium