Batteries

How Li-based batteries work

Batteries in general:

- A reducing (negative) electrode
- An oxidizing (positive) electrode
- A membrane - the ionic conductor

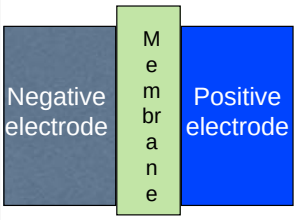
Rechargeable batteries

- Reactions must be reversible
- Not too many irreversible side reactions

Anode/cathode in rechargeable batteries

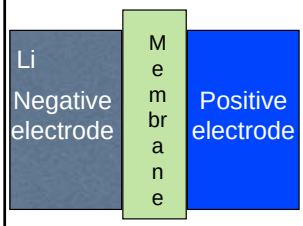
- The electrodes in rechargeable batteries will change between being anode and cathode depending on if the battery is charged or discharged
- The terms positive and negative electrode may be used instead

Electrodes



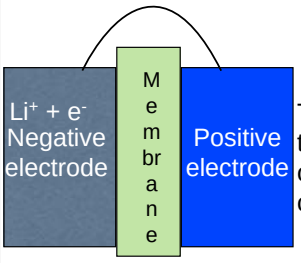
In a battery, the positive electrode withdraws electrons from the negative.

Electrodes



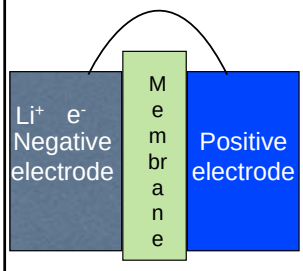
In a battery, the positive electrode withdraws electrons from the negative. In this case from Li

Electron transport



The electrons can not move through the membrane, only through the external circuit

Electron transport



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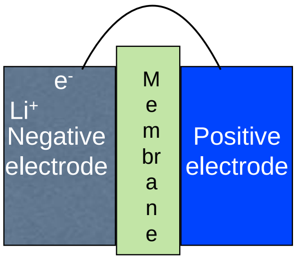

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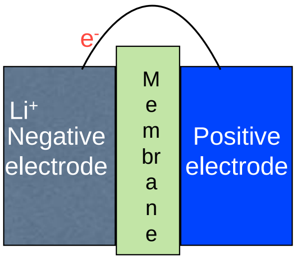

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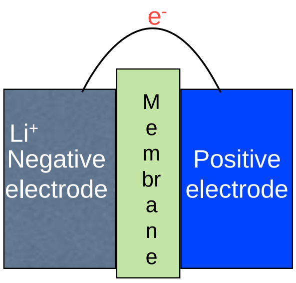

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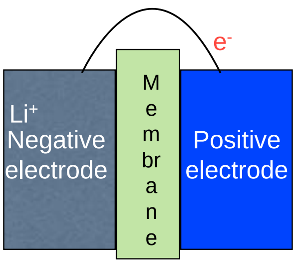

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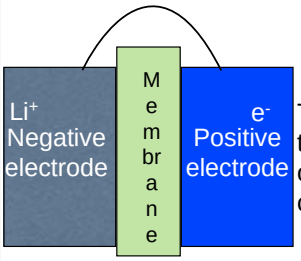

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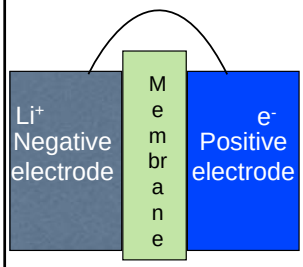
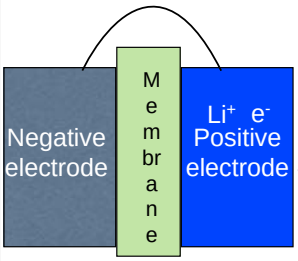
Ion transport



If ions do not follow from the negative to the positive electrode, the cell reaction will stop.

Ion transport



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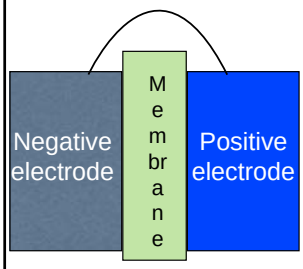
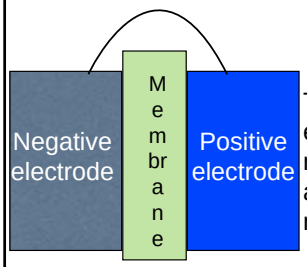
Two kinds of charge transport



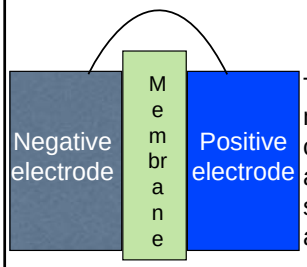
The terms positive and negative electrode may be misleading. (Faraday)

Two kinds of charge transport



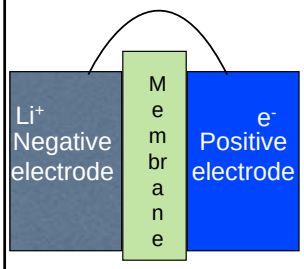
To begin with, both electrodes are electrically neutral. (They have equal amounts of positive and negative particles)

Two kinds of charge transport



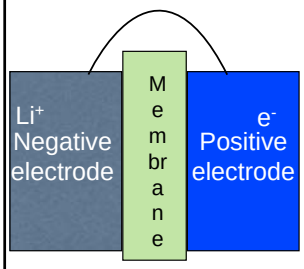
The term positive electrode means that this electrode contains something that attracts electrons. Two such examples are Cu^{2+} are Co^{4+}

Two kinds of charge transport



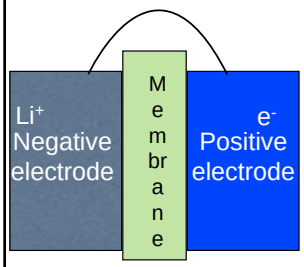
When electrons are pulled over, the electrodes will be charged in a way that stops any further reaction

Two kinds of charge transport



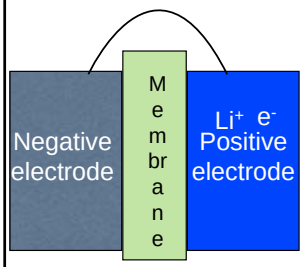
(One may say that the positive electrode gets a negative charge, and the negative electrode gets a positive charge)

Two kinds of charge transport



The ion transport equalizes the charge and allows the reaction to go on.

Two kinds of charge transport



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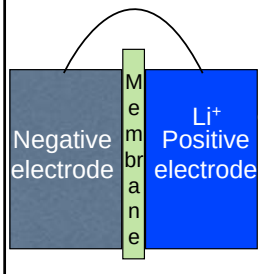


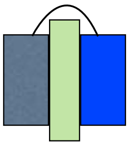
Membranes in general have low conductivity, and should be thin, with a large surface (not long and narrow)

Li-based batteries

- Oxidation (negative electrode): $Li \rightleftharpoons Li^+ + e^-$
- Reduction (positive electrode): Consists of compounds containing transition metals with more than one oxidation state. E.g. cobalt: $Co^{4+} + e^- \rightleftharpoons Co^{3+}$

Uncharged battery

Negative electrode made of graphite

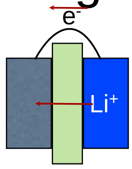


Positive electrode made of $LiCoO_2$

$LiCoO_2$ contains Li^+ and Co^{3+} ions

Charging

$Li^+ + e^- \rightarrow Li$



$Co^{3+} \rightarrow Co^{4+}$

When the battery is charged, electrons and Li-ions are «pumped» over to the graphite electrode and makes Li-metal

Simultaneously, Co^{3+} is oxidized to Co^{4+}

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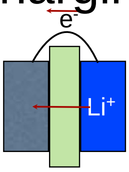

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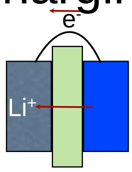

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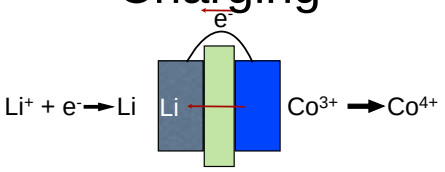

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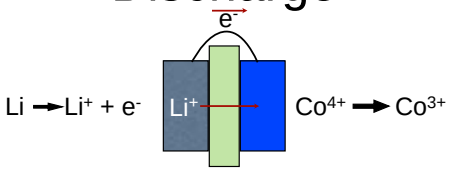
Discharge



Co^{4+} is a strong oxidation agent (attracts electrons powerfully), and Li is easily oxidized. This gives Li-cobalt batteries a high voltage (Normally about 3,7 V)

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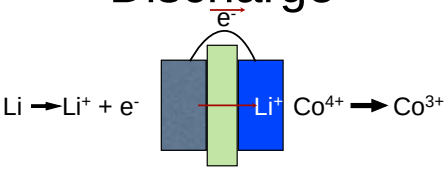

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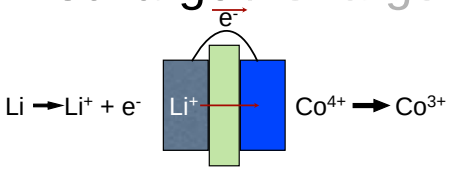
Discharge / Charge



These batteries can be charged and discharged many times, and is sometimes called Rocking chair batteries

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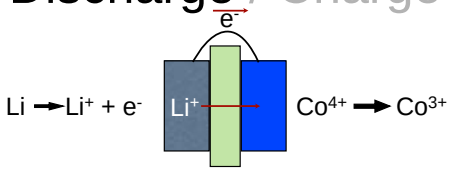

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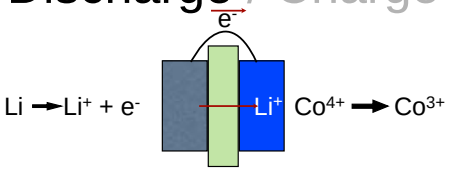

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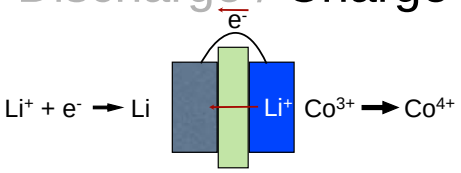

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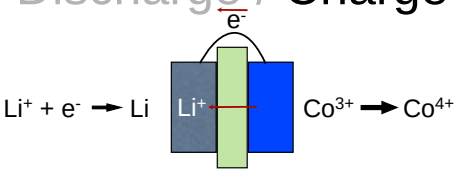

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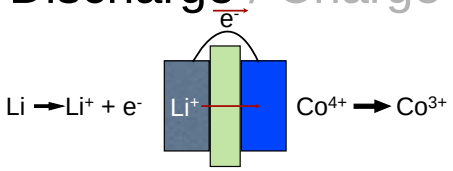

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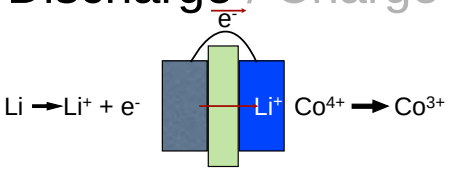

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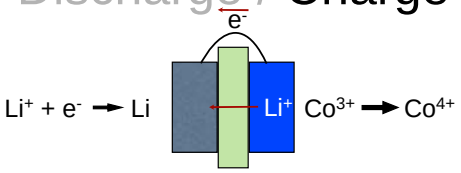

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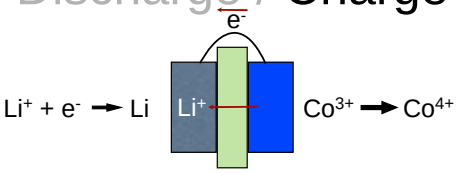

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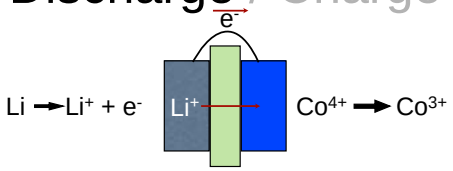

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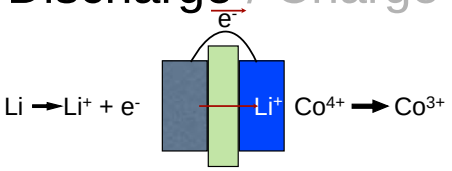

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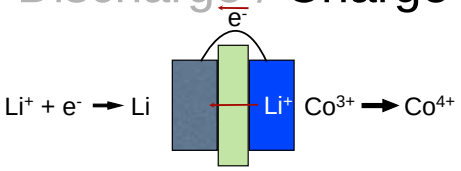

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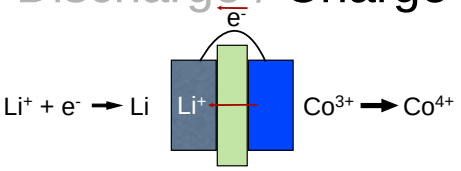

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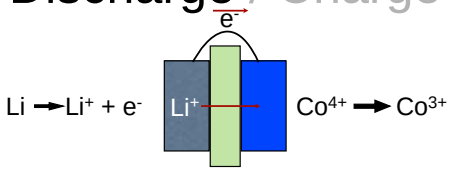

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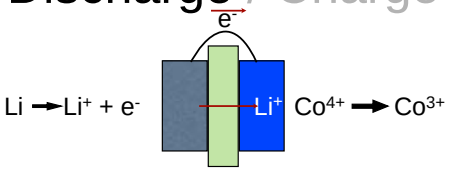

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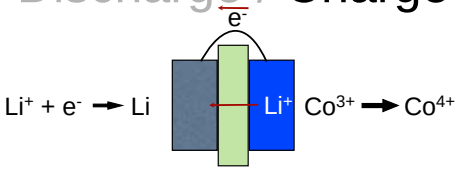

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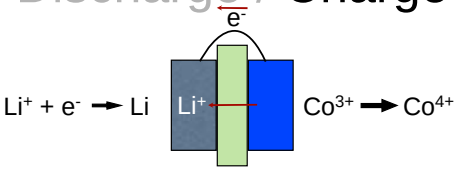

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Li-based batteries

Their components:

Negative electrode

Litium is very reactive (reducing agent), but when solved (*intercalated*) i graphite, it can be used safely in batteries.

Electrons and Li^+ can easily move into and out from the graphite electrode

Net reaction: $Li^+ + e^- \rightleftharpoons Li$

Membrane

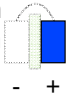
All batteries must have a membrane with good ionic conductivity, but no electronic conductivity

In old-fashioned batteries, this could be a paper moistened with a salt solution

Since Li reacts strongly with water, the membranes in Li-based batteries are either solid, or a solution of a Li-compound in an organic solvent.

Positive electrode

The positive electrode contains a transition metal able to switch between two oxidation states (Co, Mn,Fe, Ni, V...)



It must be a conductor, and have the ability to solve (intercalate) Li^+.

$LiCoO_2$ is a common electrode material with net reaction: $Co^{3+} \rightleftharpoons Co^{4+} + e^-$

Modern batteries are made in many shapes and sizes

Improving Li-based batteries

What are the problems?

Life time

- Li-based batteries only last for a few years because of:
- Irreversible reactions during charging
- and during heavy discharging
- - and at high temperatures

Performance

- High power can give irreversible damage
- limits the use in e.g. electric vehicles
- Membranes should have high conductance and resist high temperatures

Recharge time

- High power and temperatures give irreversible damage
- Resulting in long recharge time

Li supply

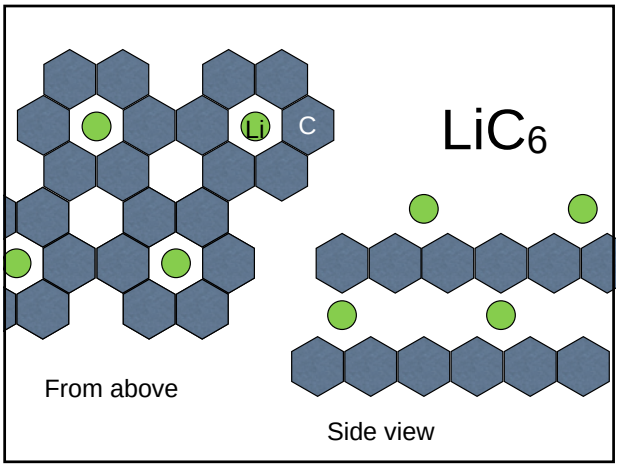
- The worlds supply of Li is limited
- Alternatives are tested (e.g. K, Mg, Al og Na)

Design

- To achieve better properties, electrodes, membranes and battery design must be optimized
- nano materials may be used to solve some of these problems

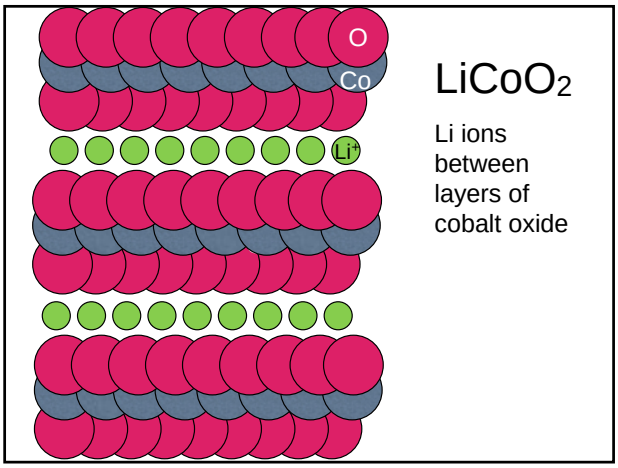
Intercalation in graphite

- Graphite is carbon with a layered structure
- In between these layers, there is enough space for e.g. Li- or K-ions to move in and out
- This is called intercalation, and is an important feature in battery electrodes
- One Li atom can be intercalated for every 6th carbon atom: $C_6 + Li^+ \rightleftharpoons e^-$ LiC_6



Intercalation in lithium cobalt oxide

- Lithium cobalt oxide's formula is $LiCoO_2$
- Li ions are intercalated between layers of cobalt oxide



Intercalation in lithium cobalt oxide

- High voltage may force electrons and Li ions out from this structure
- Similarly, cobalt ions are oxidized from Co^{3+} to Co^{4+}

Lithium-based batteries

- Rapidly developing technology
- One of several promising battery technologies