Electrode materials

Desired characteristics of electrode materials

1) Large capability of Lithium adsorption
2) High efficiency of charge/discharge
3) Excellent cyclability
4) Low reactivity against electrolyte
5) Fast reaction rate
6) Low cost
7) Environmental -friendly, non-toxic

1) High discharge voltage
2) High energy capacity
3) Long cycle life
4) High power density
5) Light weight
6) Low self-discharge
7) Absence of environmentally hazardous elements

- Commercial anode materials:

Hard Carbon, Graphite

- Commercial cathode materials:

$LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, $LiFePO_4$

- Role of electrolyte

1) Ion conductor between cathode and anode
2) Generally, Lithium salt dissolved in organic solvent
3) Solid electrolyte is also possible if the ion conductivity is high at operating temperature.

- **Characteristics of Electrolyte**

1) Inert
2) High ionic conductivity, low viscosity
3) low melting point & high dielectric constant (ε)
4) Appropriate concentration of Lithium salt
5) Chemical/thermal stability, High flash point (Tf), nontoxic,
6) Low cost
7) Environmental -friendly, non-toxic

- Commercial electrolytes: $LiPF_6$ in Carbonate solvent, propylene carbonate, 1,2 dimethoxy ethane

Types of Electrolytes

1) Liquid electrolyte: $LiPF_6$ in 1,2, dimethoxy ethane

2) Molten lithium salt: LiCl, LiBr etc

3) Amorphous Polymer Electrolytes: Lithium salts in Propylene carbonate

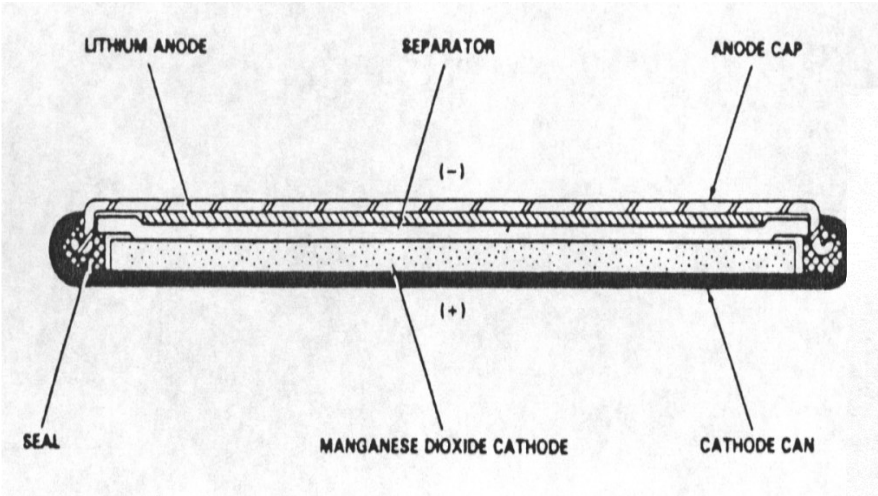
Electrolyte additives

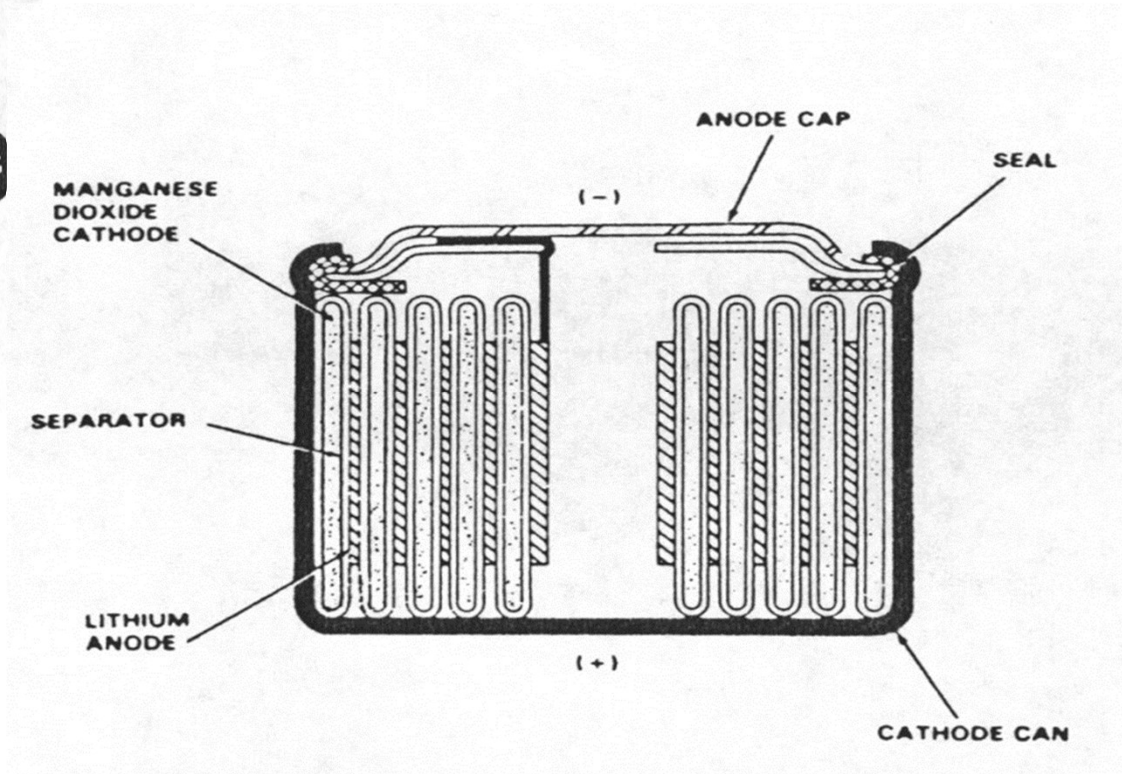
1) Those used for improving the ion conduction properties in the bulk electrolytes

2) Those used for SEI chemistry modifications

3) Those used for preventing overcharging of the cells

$LiMnO_2$ Battery





Anode: Li

Cathode-MnO_2(heat treated)

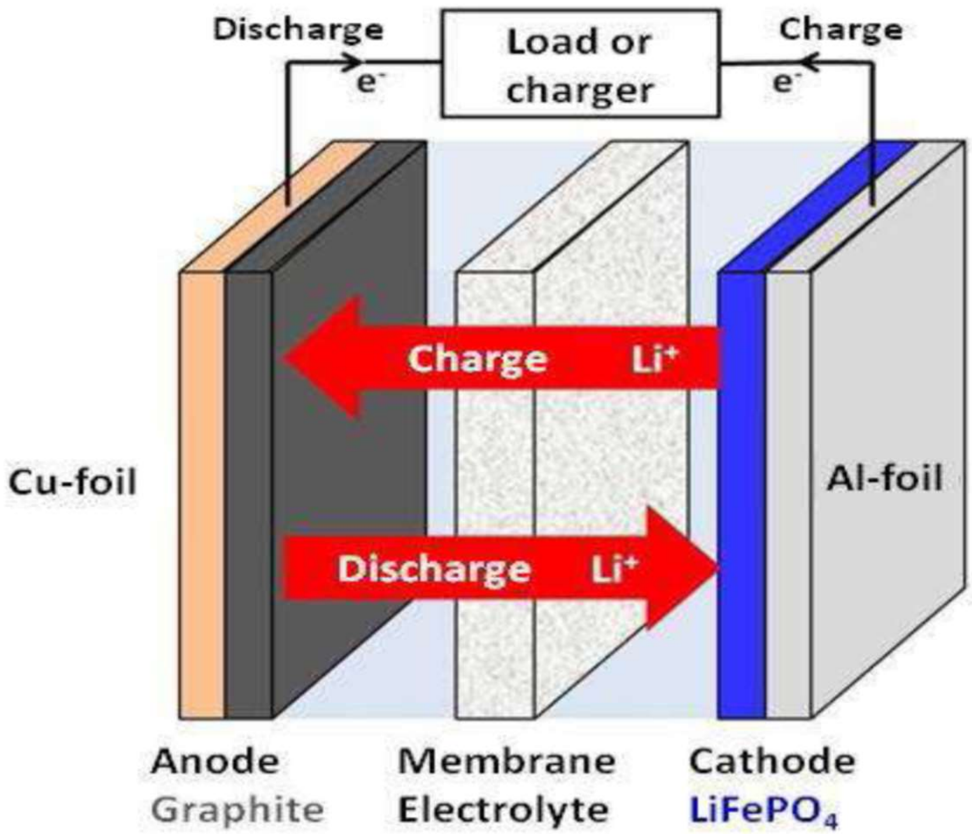
Electrolyte-Lithium salt like LiCl, LiBr, $LiAlCl_4$ in mixed organic solvent like 1, 2-dimethoxy ethane and Propylene carbonate Reactions:

Anode reaction: .... Li → Li + + e-

Cathode reaction: ………..…$Li^+ + MnO_2$ + e- --> $LiMnO_2$

Overall reaction…………..……$Li + MnO_2$ --> $LiMnO_2$

Construction and working of Li-ion batteries

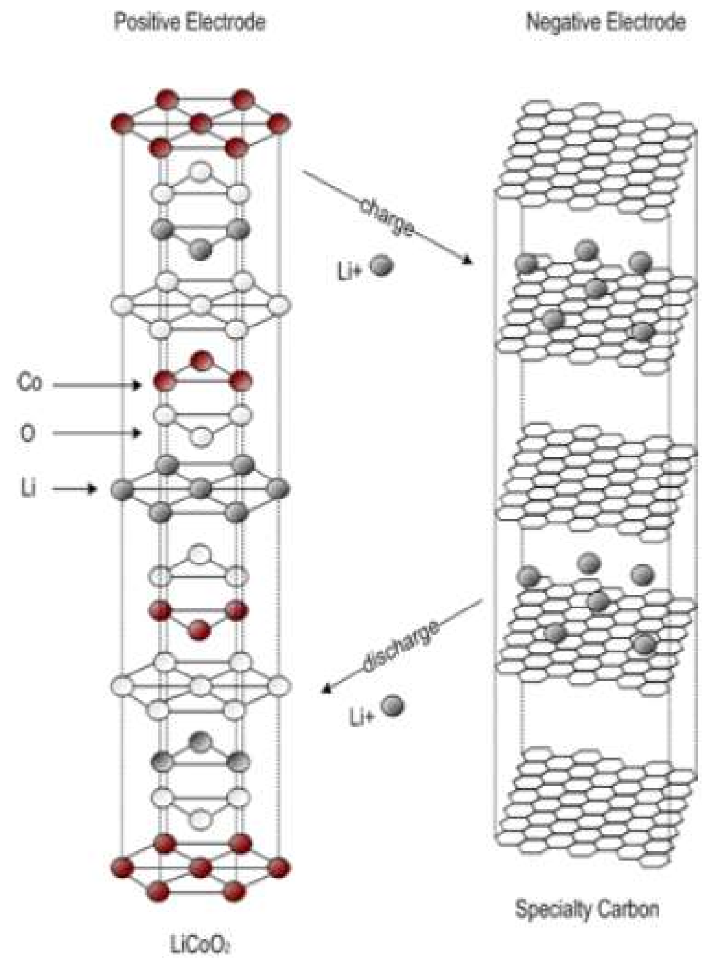


Construction and working of Li-ion batteries

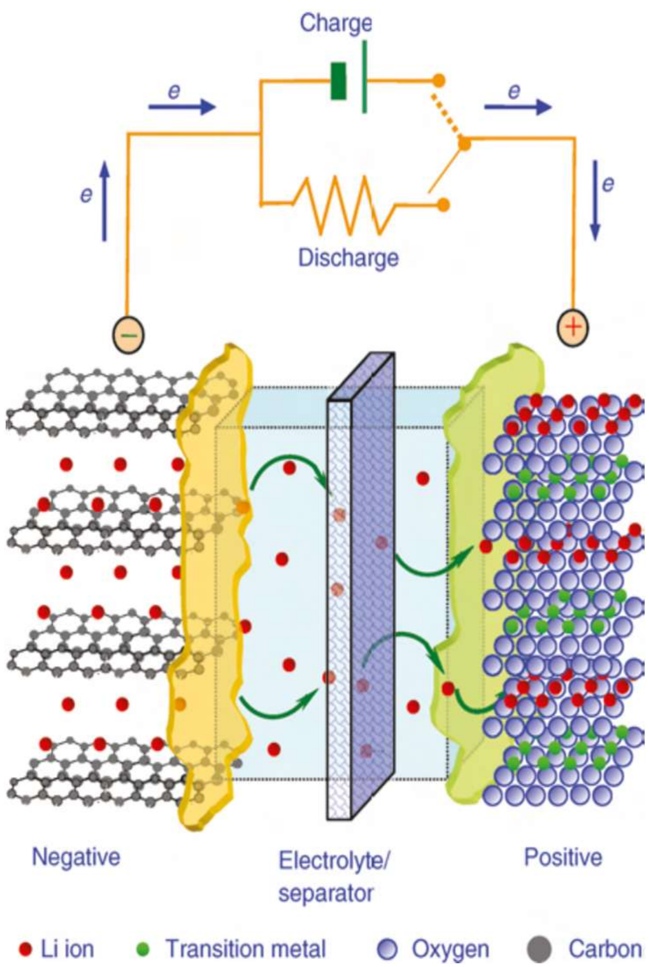
•Positive electrode: Lithiated form of a transition metal oxide (lithium cobalt oxide-$LiCoO_2$ or lithium manganese oxide $LiMn_2O_4$)

• Negative electrode: Carbon (C),
usually graphite (C_6)

• Electrolyte: solid lithium-salt electrolytes
($LiPF_6$, $LiBF_4$, or $LiClO_4$)
and organic solvents (ether)



Li-ion battery system



Electrochemical Reactions

- **Cathode**

$$LiCoO_2 \underset{d}{\overset{c}{\rightleftharpoons}} Li_{1\text{-}x}CoO_2 + xLi^+ + x\,e^-$$

- **Anode**

$$C_n + xLi^+ + x\,e^- \underset{d}{\overset{c}{\rightleftharpoons}} C_nLi_x$$

- **Overall**

$$LiCoO_2 + C_n \underset{d}{\overset{c}{\rightleftharpoons}} Li_{1\text{-}x}CoO_2 + C_nLi_x$$

Cell reaction/Working of Li-ion batteries

- Chemical reaction (charging)
  - Positive electrode $LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$

Through electrolyte

Through load

  - Negative electrode $xLi^+ + xe^- + 6C \longrightarrow Li_xC_6$

- Overall $LiCoO_2 + C_6 \longrightarrow Li_{1-x}CoO_2 + C_6L_x$

- In the above reaction *x* can be 1 or 0

- With discharge the Co is oxidized from Co^{3+} to Co^{4+}. The reverse process (reduction) occurs when the battery is being charged.

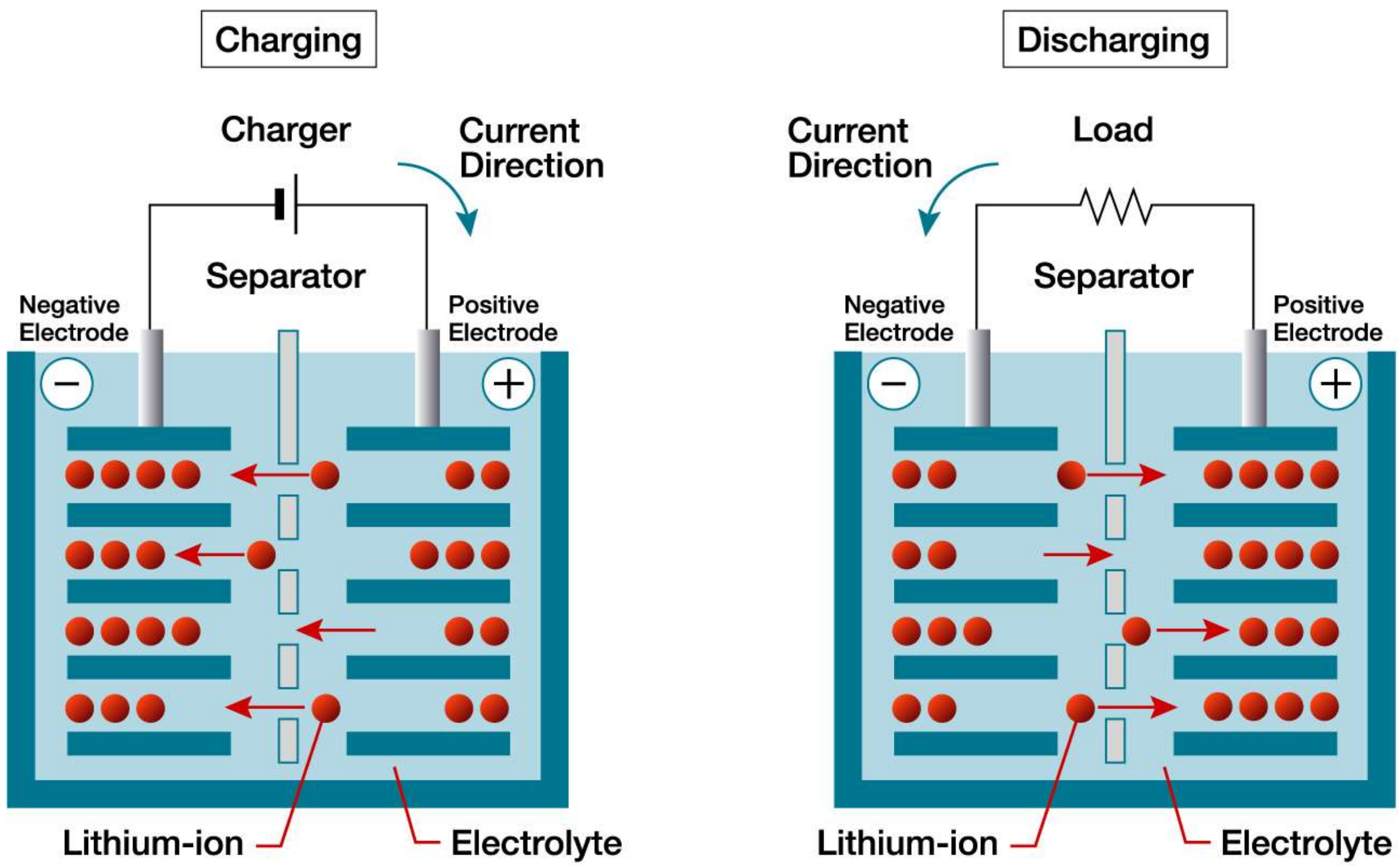
Charging and discharging reactions

Cathode (+): $$LiCoO_2 \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li_{1-x}CoO_2 + xLi^+ + xe^-$$

Anode (-): $$C_n + xLi^+ + xe^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} C_nLi_x$$

Overall: $$LiCoO_2 + C_n \underset{discharge}{\overset{charge}{\rightleftharpoons}} C_nLi_x + Li_{1-x}CoO_2$$

Charging and discharging reactions



Li-ion battery system

Advantages of lithium-ion batteries:

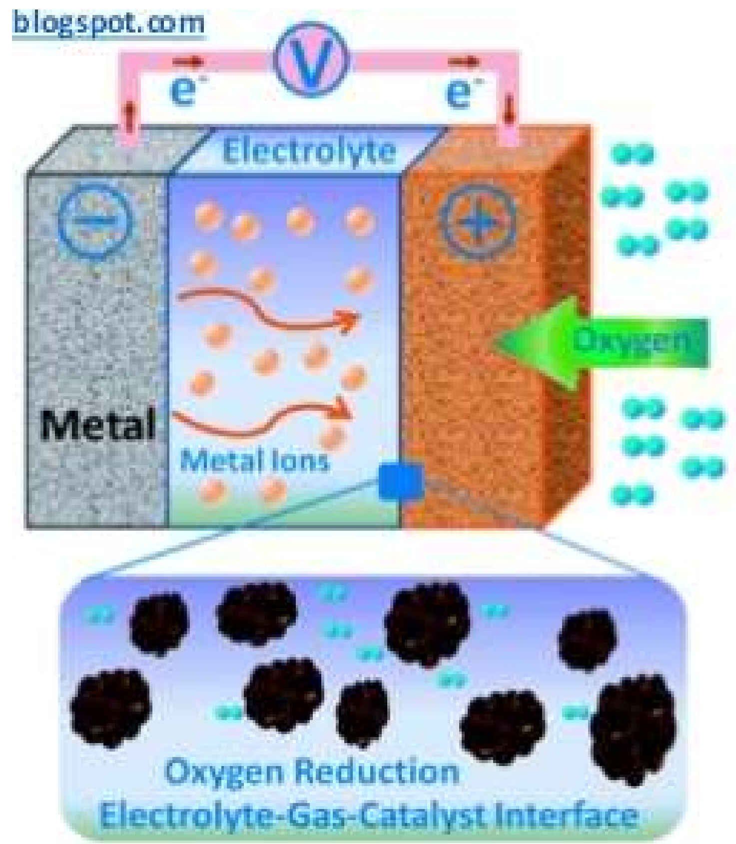
- Lightweight compared to other batteries
- Higher theoretical energy density than other types of batteries
- Rate of loss of charge is very less
- Operates at higher voltages than other batteries
- High adaptability to several applications
- As there is no memory effect, no need to completely drain the battery
- Low self-discharge compared to lead acid battery
- Easy maintenance

Limitations of lithium-ion batteries:

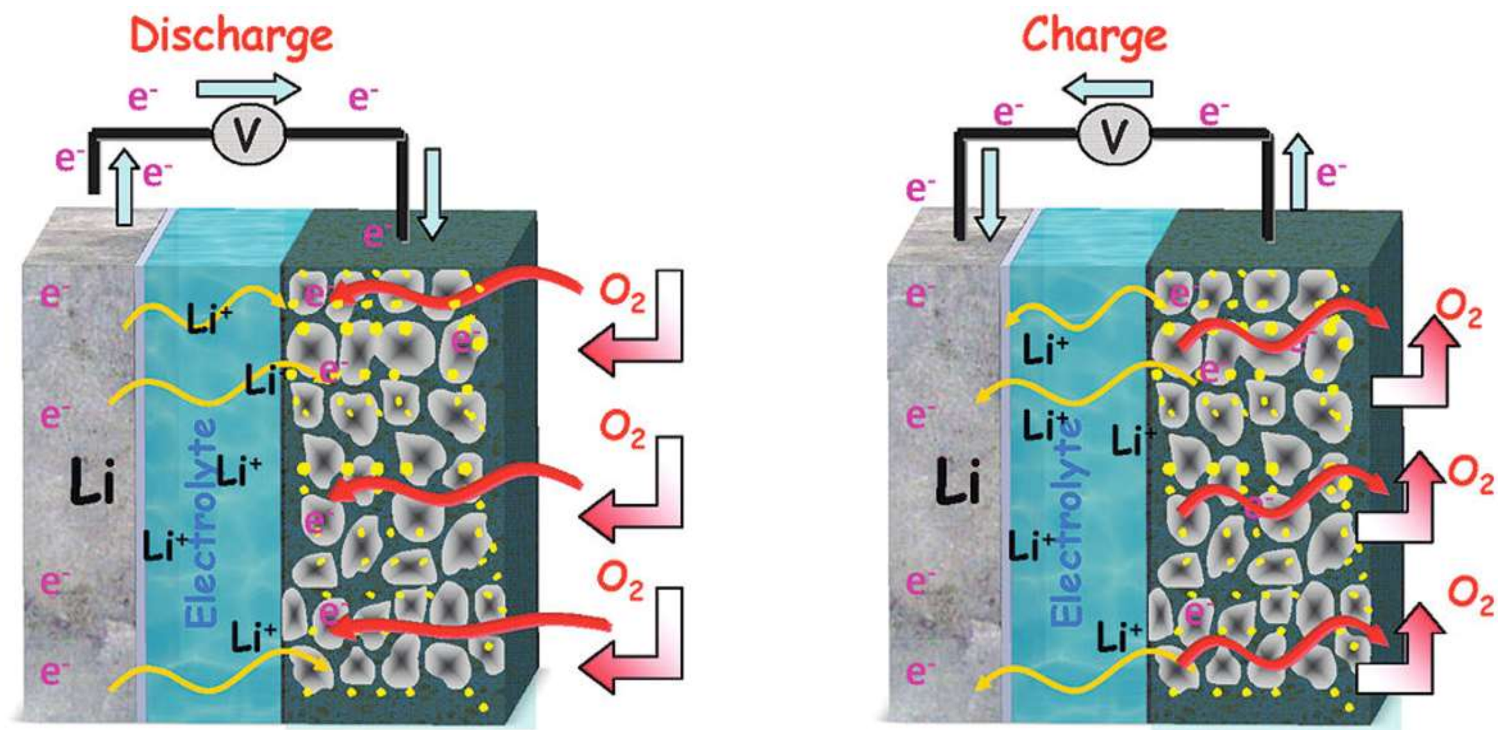
- Sourcing of lithium is difficult
- As lithium is not abundant, extraction of it doesn't meet global need
- Expensive than the other commercially available battery
- This battery is temperature sensitive; at higher temperature it may degrade with explosion
- Extra protection is required if want to employ them in large scale application
- Disposal may a problem because of heavy metal cathodes

Li-air batteries: introduction

- The lithium-air battery (Li-air) is a metal–air electrochemical cell.
- It works by oxidation of lithium at the anode and reduction of oxygen at the cathode to induce a current flow.
- A metal–air electrochemical cell is an electrochemical cell that uses an anode made from pure metal and an external cathode of ambient air, typically with an aqueous or aprotic electrolyte.



Li-air batteries

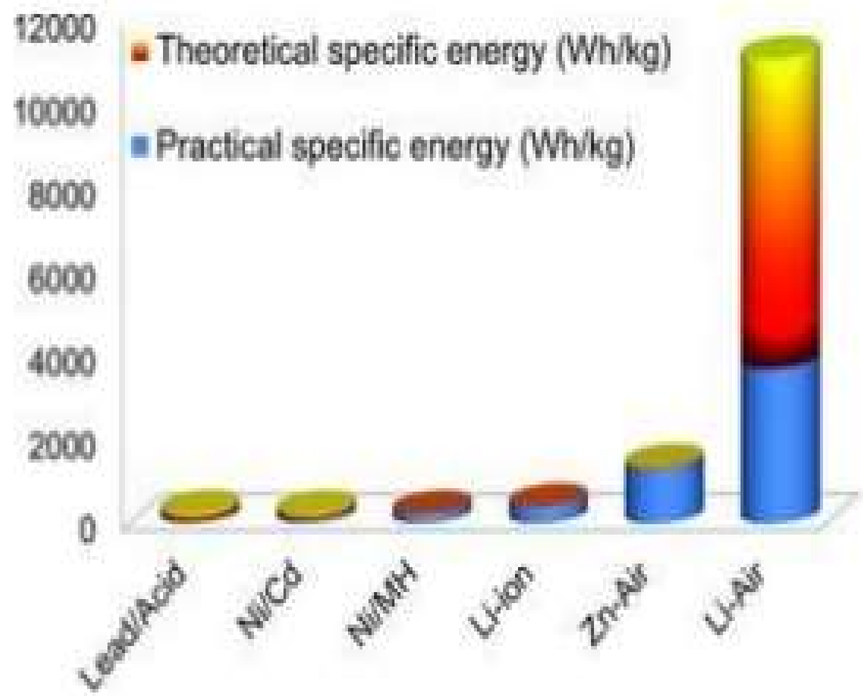


https://www.youtube.com/watch?v=8pMFLpiqPAc

Li-air batteries

High specific energy density batteries are attracting growing attention as possible power sources for electric vehicles (EVs).

Lithium–air batteries are the most promising system, because of their far higher theoretical specific energy density than conventional batteries.



Anode material

- Lithium metal is the typical anode choice.
- At the anode, electrochemical potential forces the lithium metal to release electrons via oxidation (without involving the cathodic oxygen).
- The half-reaction is

$$\boxed{Li \leftrightarrow Li^{+} + e^{-}}$$

- Upon charging/discharging in aprotic cells, layers of lithium salts precipitate onto the anode, eventually covering it and creating a barrier between the lithium and electrolyte.
- This barrier initially prevents corrosion, but eventually inhibits the reaction kinetics between the anode and the electrolyte.

Cathode material/reactions

- At the cathode during charge, oxygen donates electrons to the lithium via reduction.
- Mesoporous carbon has been used as a cathode substrate with metal catalysts that enhance reduction kinetics and increase the cathode's specific capacity.
- Manganese, cobalt, ruthenium, platinum, silver, or a mixture of cobalt and manganese are potential metal catalysts.
- In a cell with an aprotic electrolyte lithium oxides are produced through reduction at the cathode:

$$Li^+ + e^- + O_2 + * \rightarrow LiO_2^*$$

$$Li^+ + e^- + LiO_2^* \rightarrow Li_2O_2^*$$

- where "*" denotes a surface site on Li_2O_2 where growth proceeds, which is essentially a neutral Li vacancy in the Li_2O_2 surface.

Electrolyte

In a cell with an aqueous electrolyte the reduction at the cathode can also produce lithium hydroxide:

- **Acidic electrolyte**

$$2Li + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Li^+ + H_2O$$

  - A conjugate base is involved in the reaction.
  - The theoretical maximal Li-air cell specific energy and energy density are 1400 W·h/kg and 1680 W·h/l, respectively.

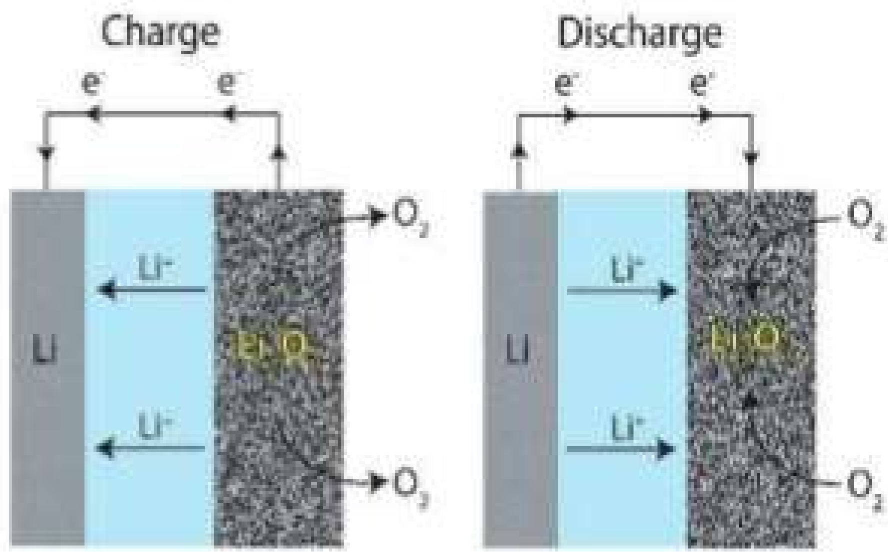
- **Alkaline aqueous electrolyte**

$$2Li + \frac{1}{2}O_2 + H_2O \rightarrow 2LiOH$$

  - Water molecules are involved in the redox reactions at the air cathode.
  - The theoretical maximal Li-air cell specific energy and energy density are 1300 W·h/kg and 1520 W·h/l, respectively

Working

- In general lithium ions move between the anode and the cathode across the electrolyte.
- Under discharge, electrons follow the external circuit to do electric work and the lithium ions migrate to the cathode.
- During charge the lithium metal plates onto the anode, freeing O_2 at the cathode.
- Both non-aqueous (with Li_2O_2 or LiO_2 as the discharge products) and aqueous (LiOH as the discharge product) Li-O_2 batteries have been considered.
- The aqueous battery requires a protective layer on the negative electrode to keep the Li metal from reacting with water.

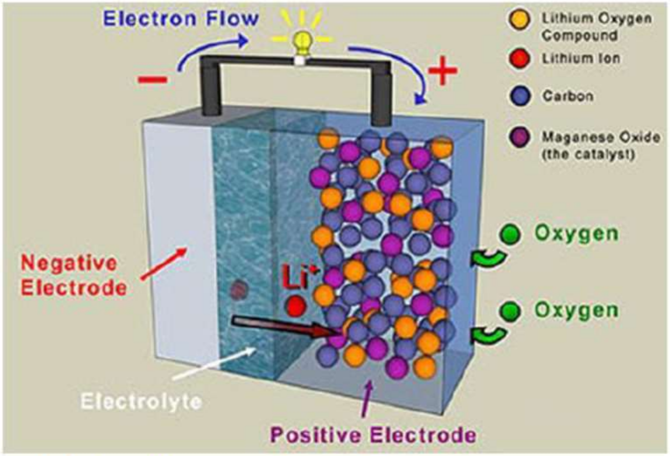


Thank you

Li-air batteries

Starting with the knowledge acquired from Li-ion batteries, to obtain batteries with higher energy density, up to 10 fold increase in gravimetric energy density.

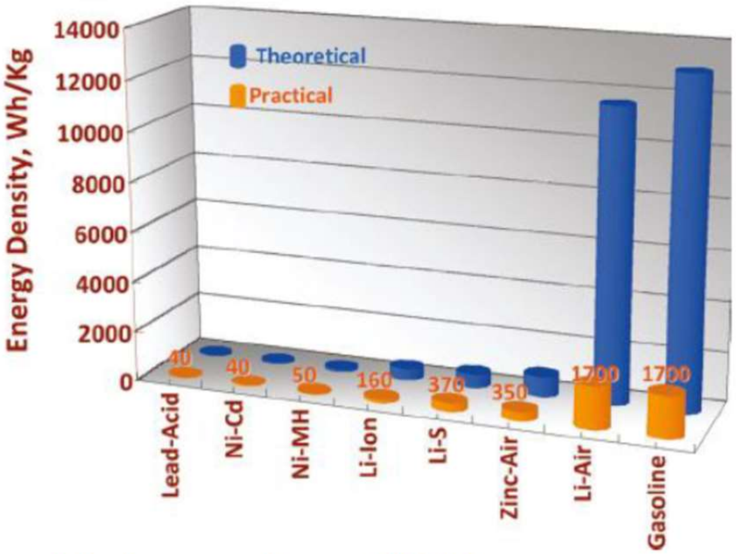
Li-Air BATTERIES



$Li_{(s)} \leftrightarrow Li^+ + e^-$ (anode)

$Li^+ + 1/2O_2 + e^- \leftrightarrow 1/2Li_2O_2$ (cathode)

$Li^+ + 1/4O_2 + e^- \leftrightarrow 1/2Li_2O$ (cathode)



- Discharge voltage of 2.7 V
- Theoretically energy density: >11500 Wh/kg based on Li only

Question: practically, can it really compete with Li-ion and what are main issues?

Aprotic(non aqueous)Li-air batteries

- Several chemical products may result from the reaction of Li with O_2, depending on the chemical environment and mode of operation.
- Most effort involved aprotic materials, which consist of a lithium metal anode, a liquid organic electrolyte and a porous carbon cathode.
- The electrolyte can be made of any organic liquid able to solvate lithium salts such as $LiPF_6$, $LiAsF_6$, $LiN(SO_2CF_3)_2$, and $LiSO_3CF_3$), but typically consisted of carbonates, ethers and esters.
- Most studies agree that Li_2O_2 is the final discharge product of non-aqueous Li-O_2 batteries.
- In nonaqueous Li/air batteries there are two principal electrode reactions of interest:

$$\boxed{2Li + \frac{1}{2}O_2 \leftrightarrow Li_2O} \quad \& \quad \boxed{2Li + O_2 \leftrightarrow Li_2O_2}$$

- In the absence of practical considerations the full reduction of O_2 to Li_2O is desired because of its higher specific energy and energy density, but it appears that Li_2O_2 is a product that forms more readily than Li_2O.
- In addition, when Li_2O_2 is formed full cleavage of the O-O bond may not be necessary, which is important from a kinetic point of view.