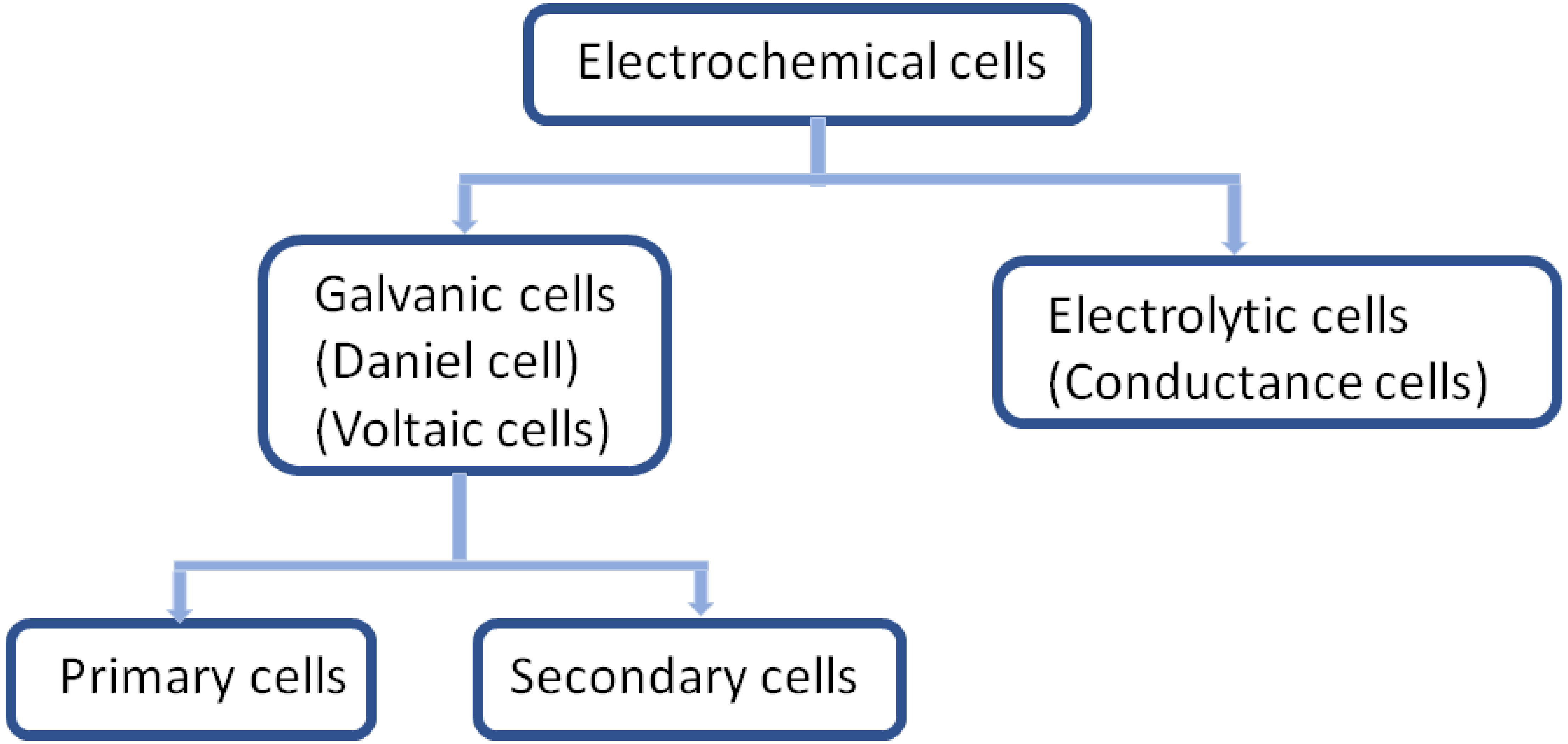
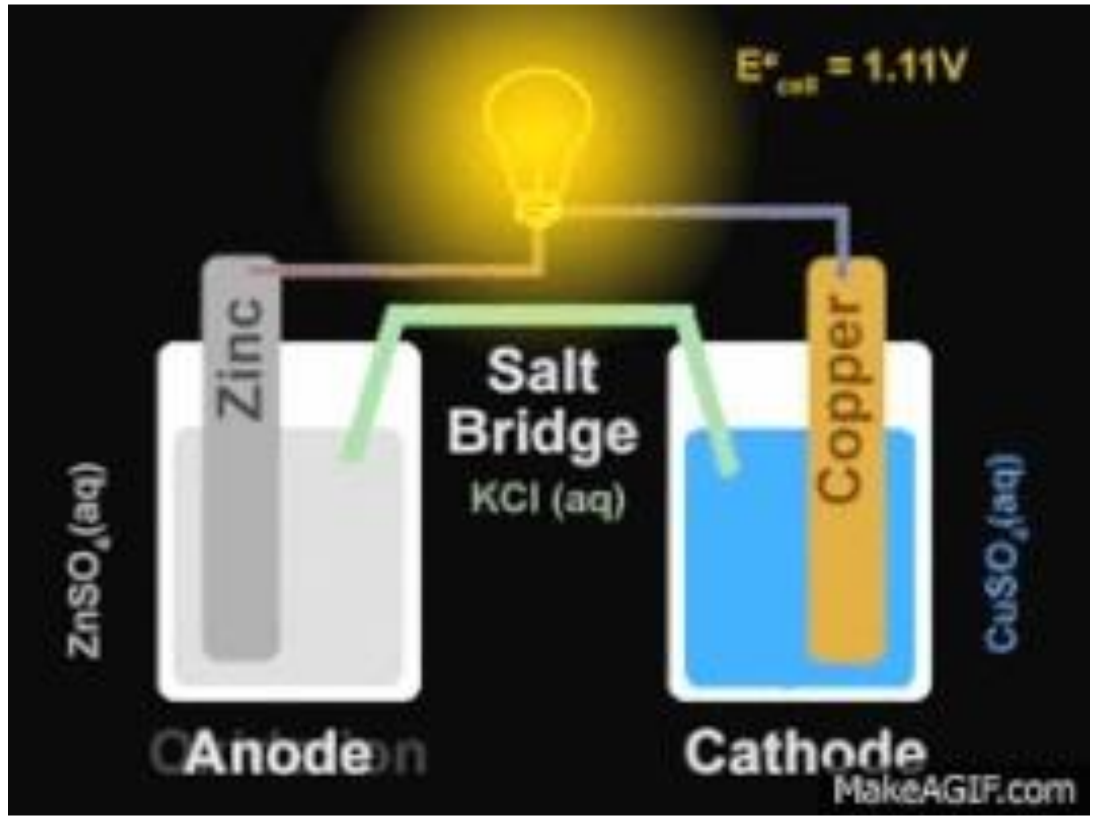
UNIT-V

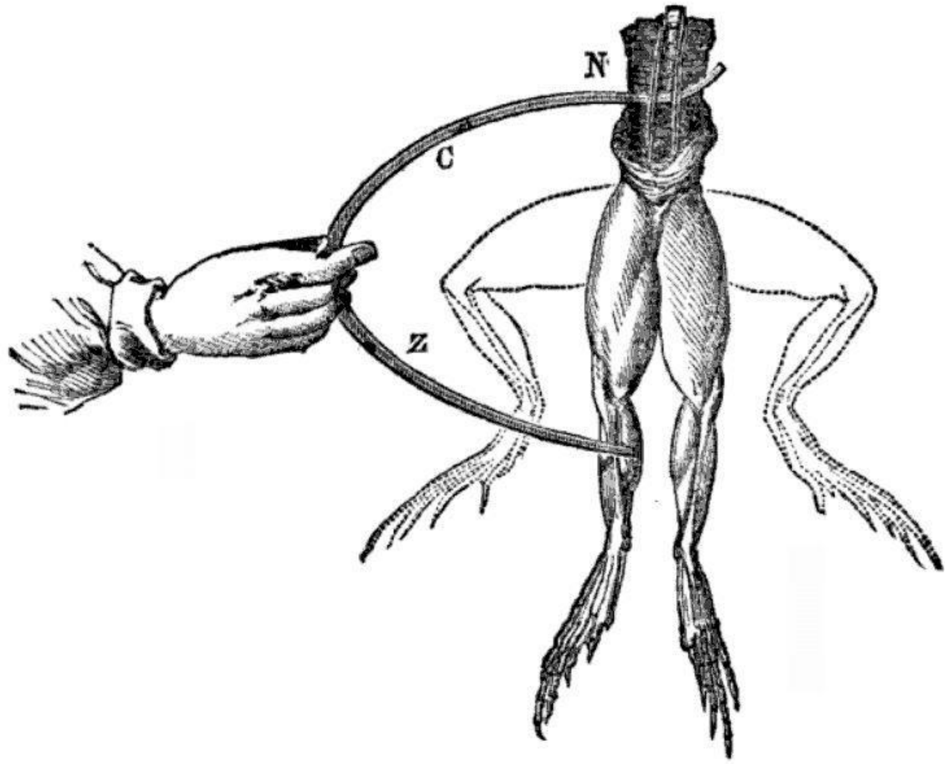
Advanced energy systems
Syllabus **Battery technology:** Introduction to Electrochemistry, characteristics of battery, Lithium-Ion battery, Lithium air battery. **Super capacitors:** Storage principle, types (EDLC, pseudo and asymmetric capacitor) with examples and applications. **Photovoltaics**: organic/inorganic solar cells, quantum dot sensitized (QDSSC's). Photo catalytic water splitting.

Electrochemical devices

Electrochemical cell is a device in which chemical energy is converted into electrical energy or electrical energy into chemical energy by oxidation-reduction reaction.



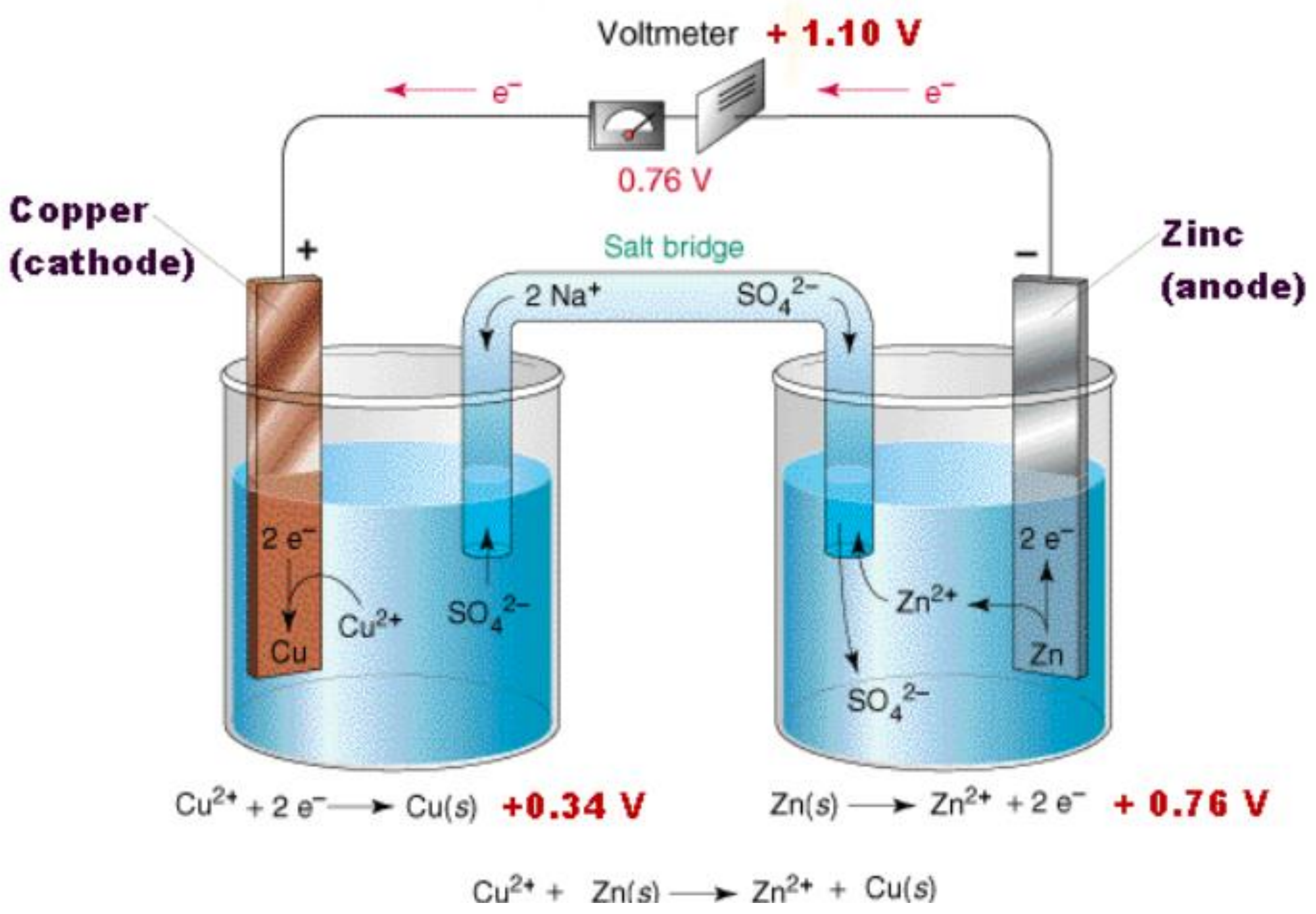


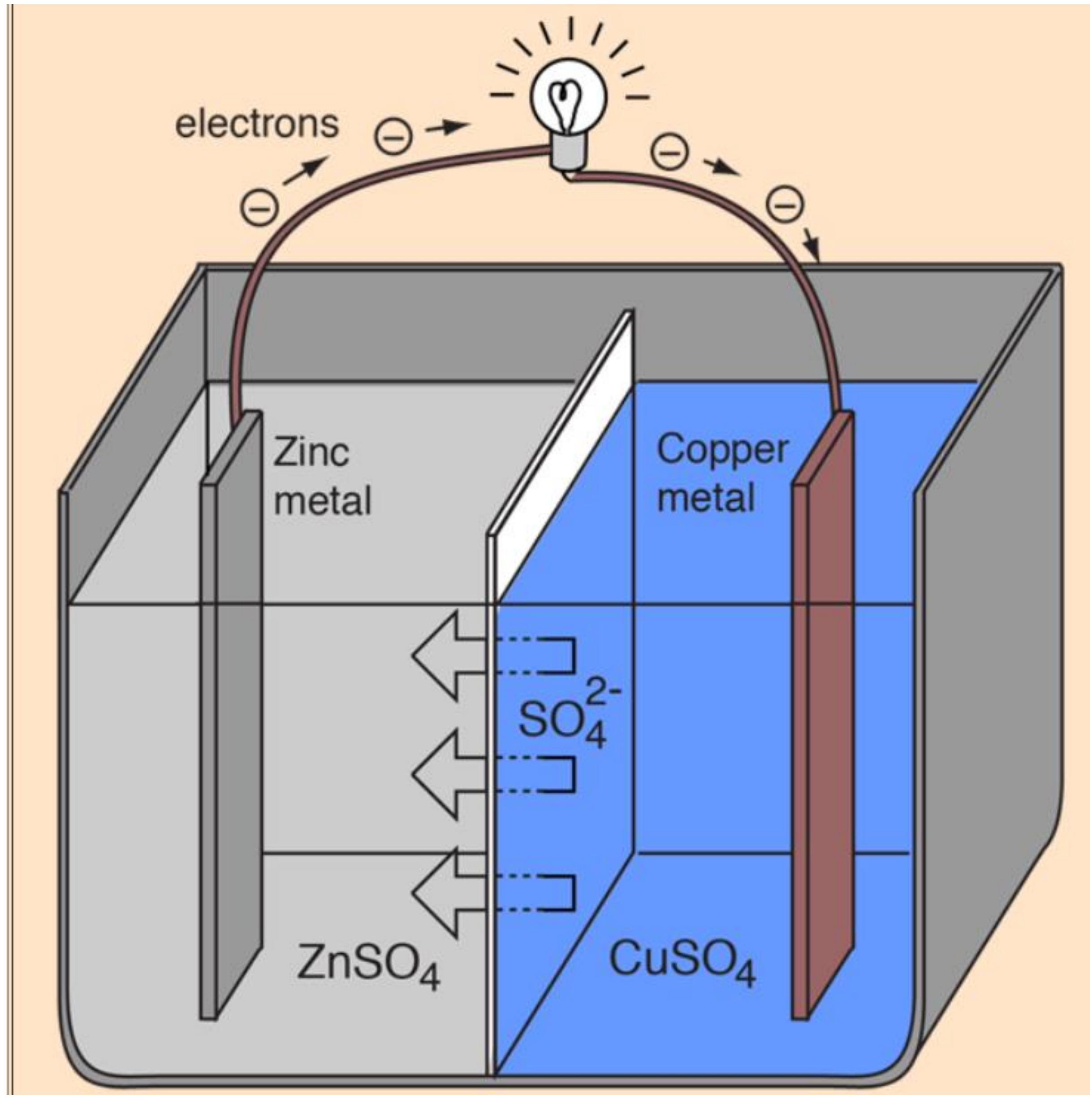


Luigi Galvani

Galvanic Cell

Animal Electricity!!!





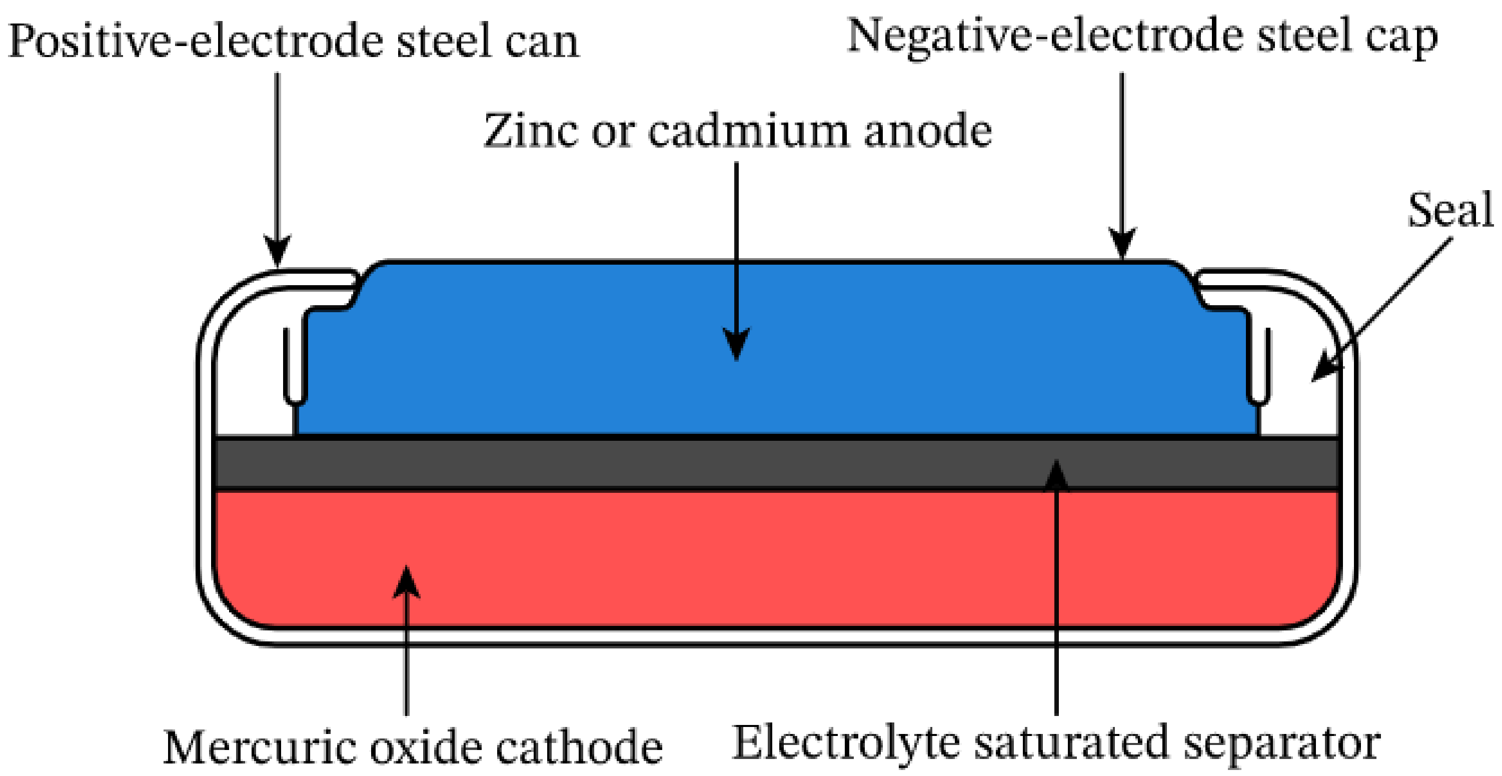
Galvanic Cell

- Spontaneous redox reactions convert chemical energy to electric energy.
- Application lies in batteries.

Electrochemical Cell

- Non-spontaneous redox reactions convert the electric energy to chemical energy
- Application lies in purifying copper and electroplating.

Primary Galvanic Cell



Mercury Cell

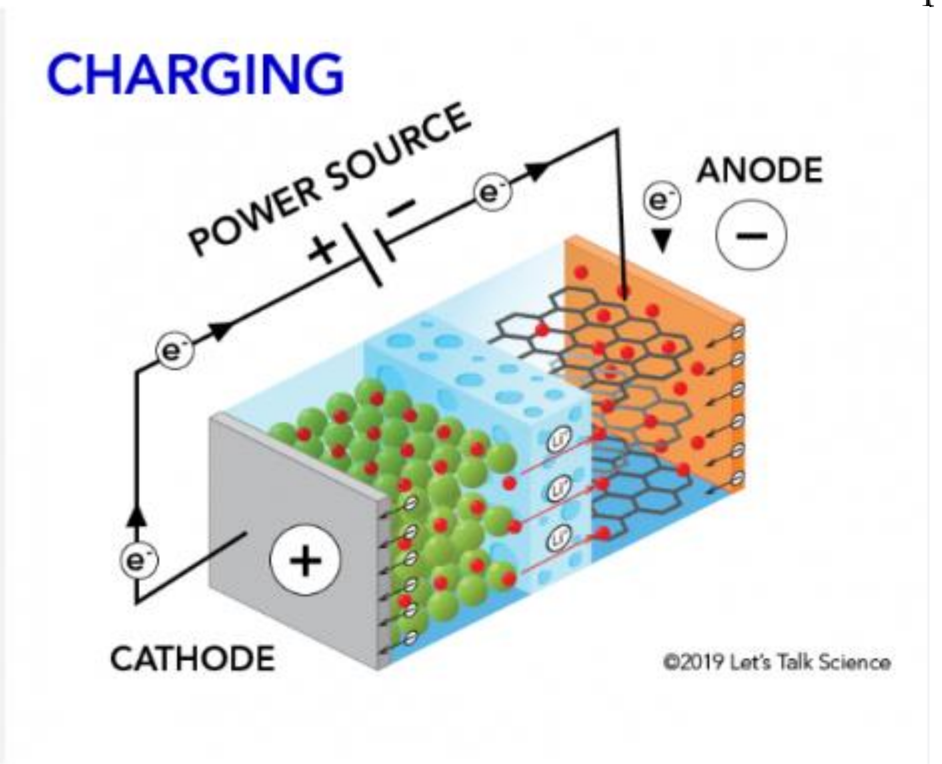
(It is no longer used due to toxicity)

$$Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^-$$

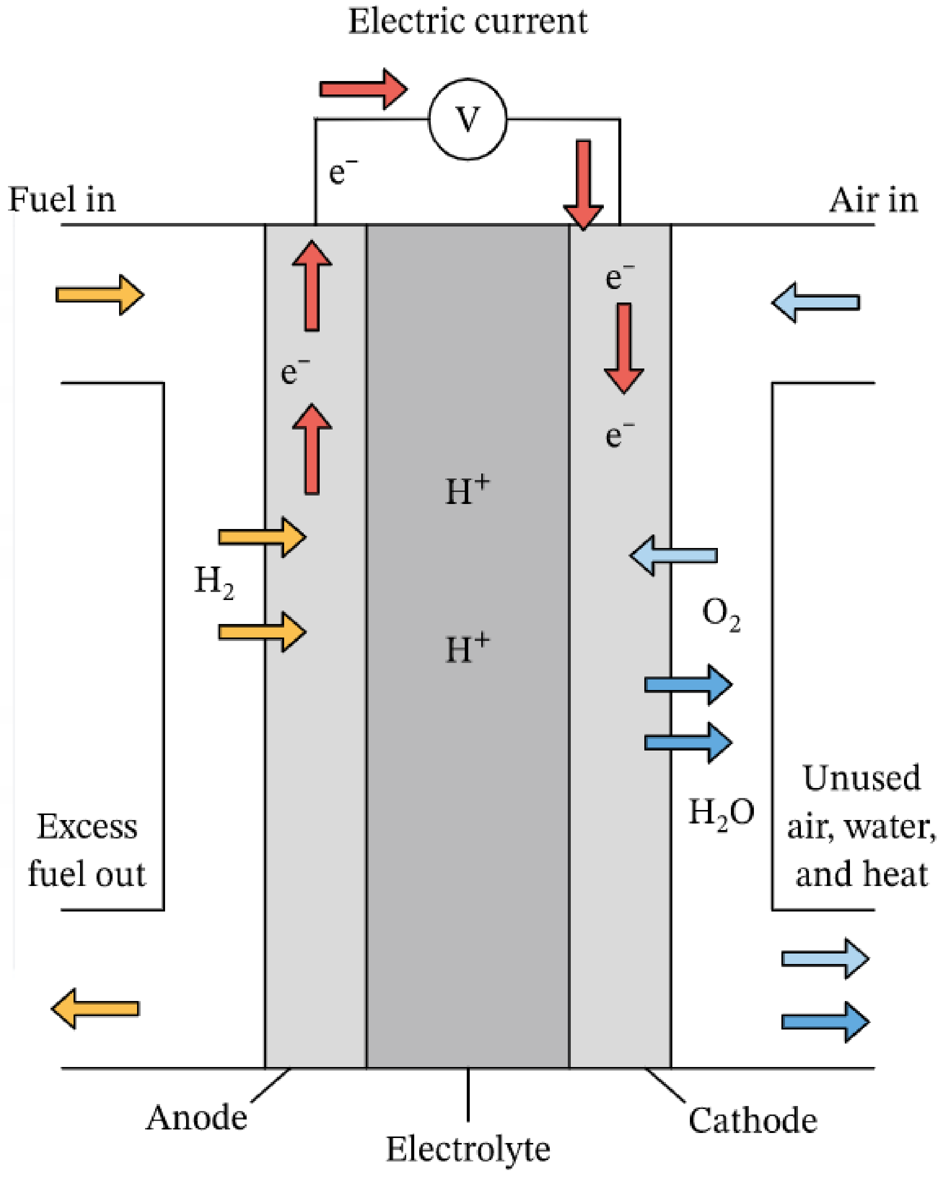
$$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-(aq)$$

$$Zn(s) + HgO(s) \longrightarrow ZnO(s) + Hg(l), \quad E^{\ominus}_{cell} = +1.35\ V$$

Secondary Galvanic Cell



Rechargeable Batteries



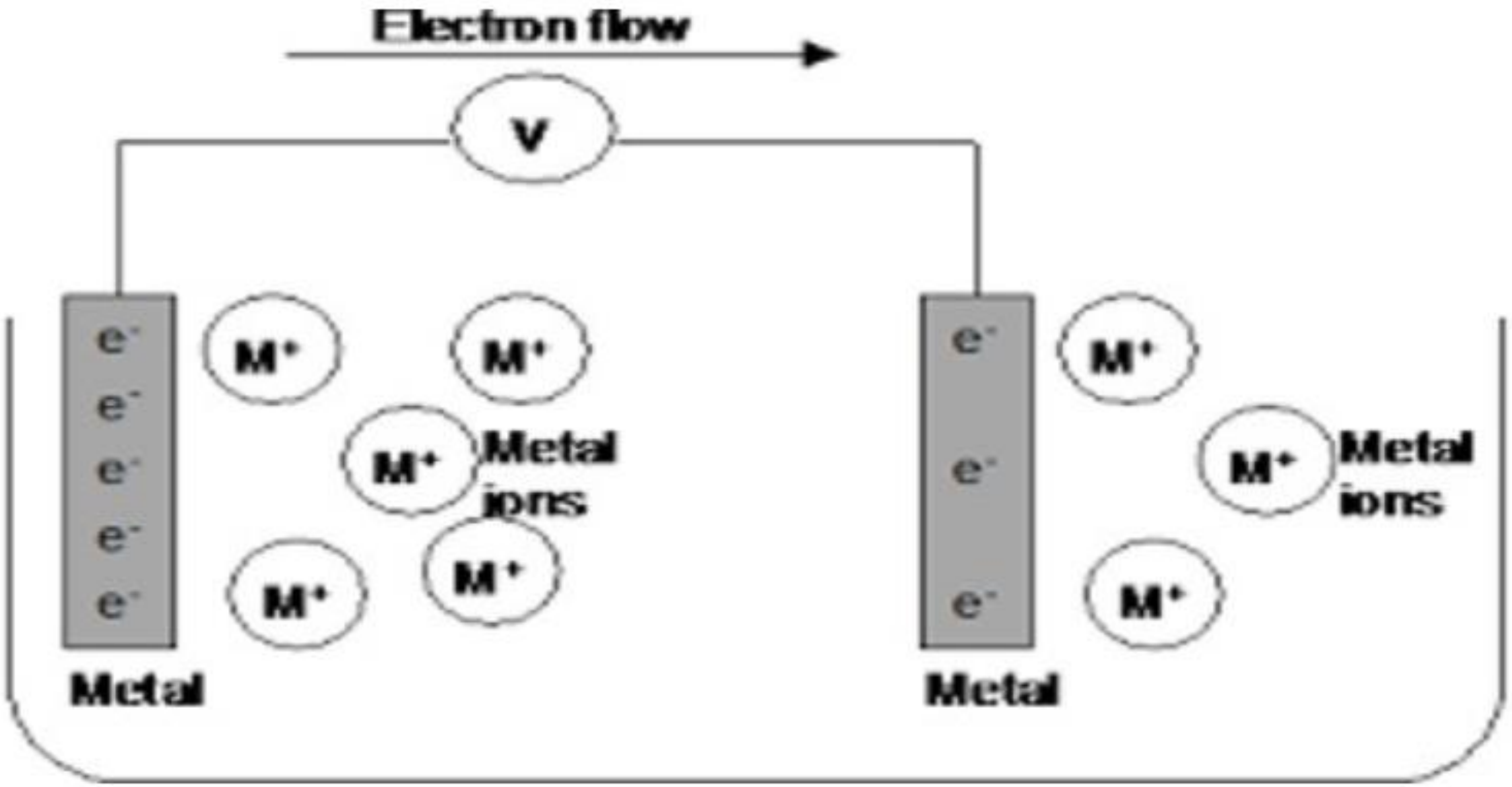
Fuel Cell

- A primary Galvanic cell is a non rechargeable battery that produces energy from the chemical reaction.
- A secondary Galvanic cell is a rechargeable battery that produces energy from the chemical reaction.

Types of electrodes

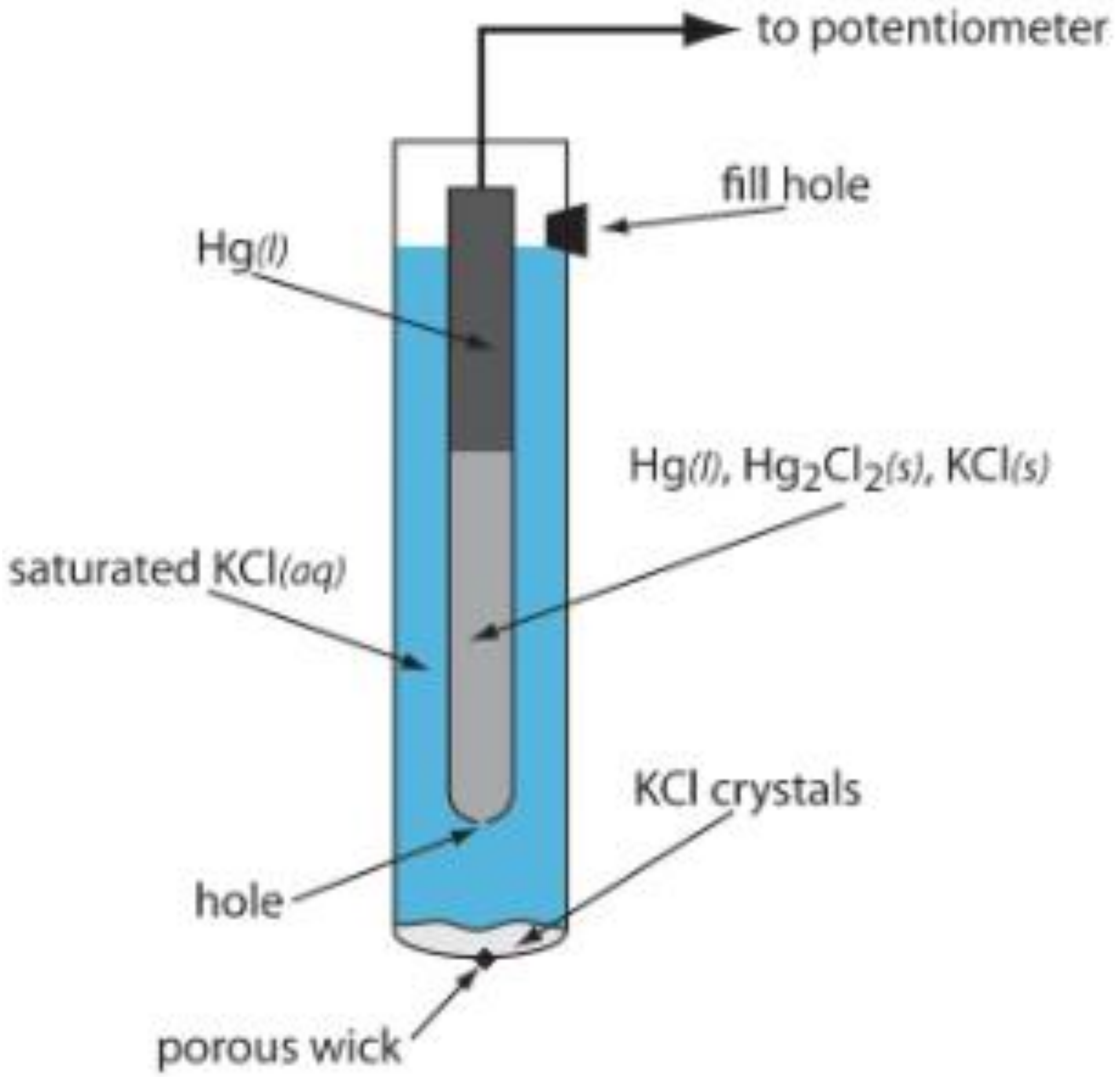
1. **Metal-metal ion electrode:** Electrode consists of a metal in contact with a solution of its own ions.

   Ex: Zinc in a solution of zinc sulphate, copper in a solution of copper sulphate.



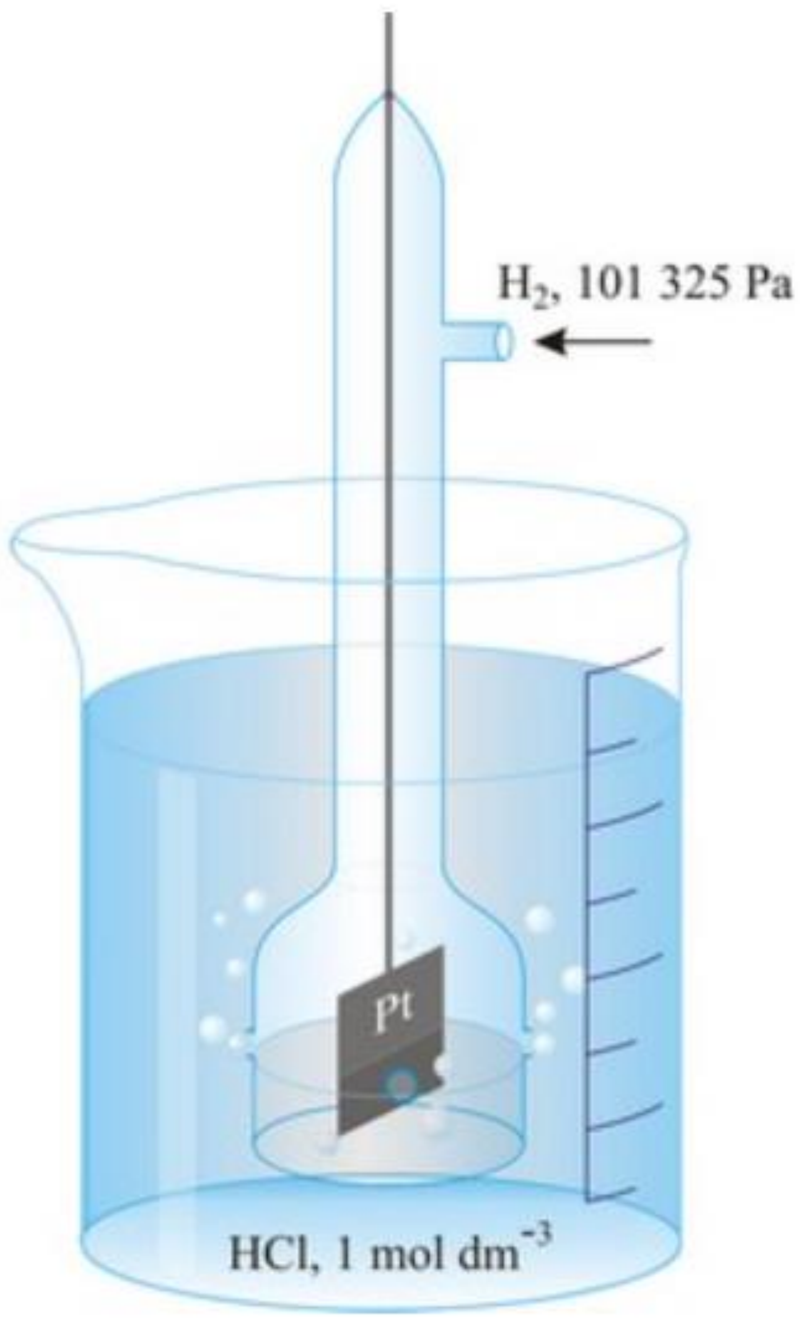
2. **Metal-metal ion salt electrode:** electrode consists of a metal in contact with one of its sparingly soluble salts and a solution of a soluble salt having a common anion with the sparingly soluble salt

Ex: Calomel electrode Hg(l)| Hg_2Cl_2(s) |KCl Or Pt, Hg(l), Hg_2Cl_2(s) |KCl



3. **Metal gas electrode:** A gas electrode consists of a particular gas flushed around an inert electrode (Pt), which is dipped in a solution containing ions to which the gas is reversible.

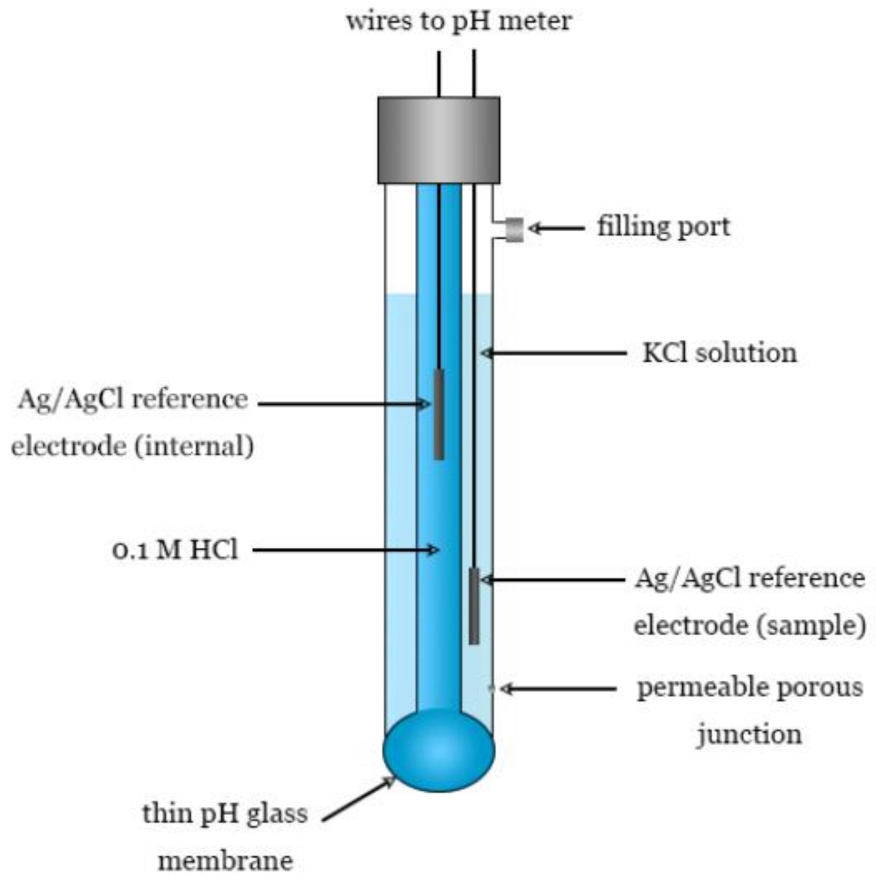
Ex: SHE: Pt | H_2 (1atm) | H^+ (1M), Chloride electrode [Pt/Cl_2/Cl].



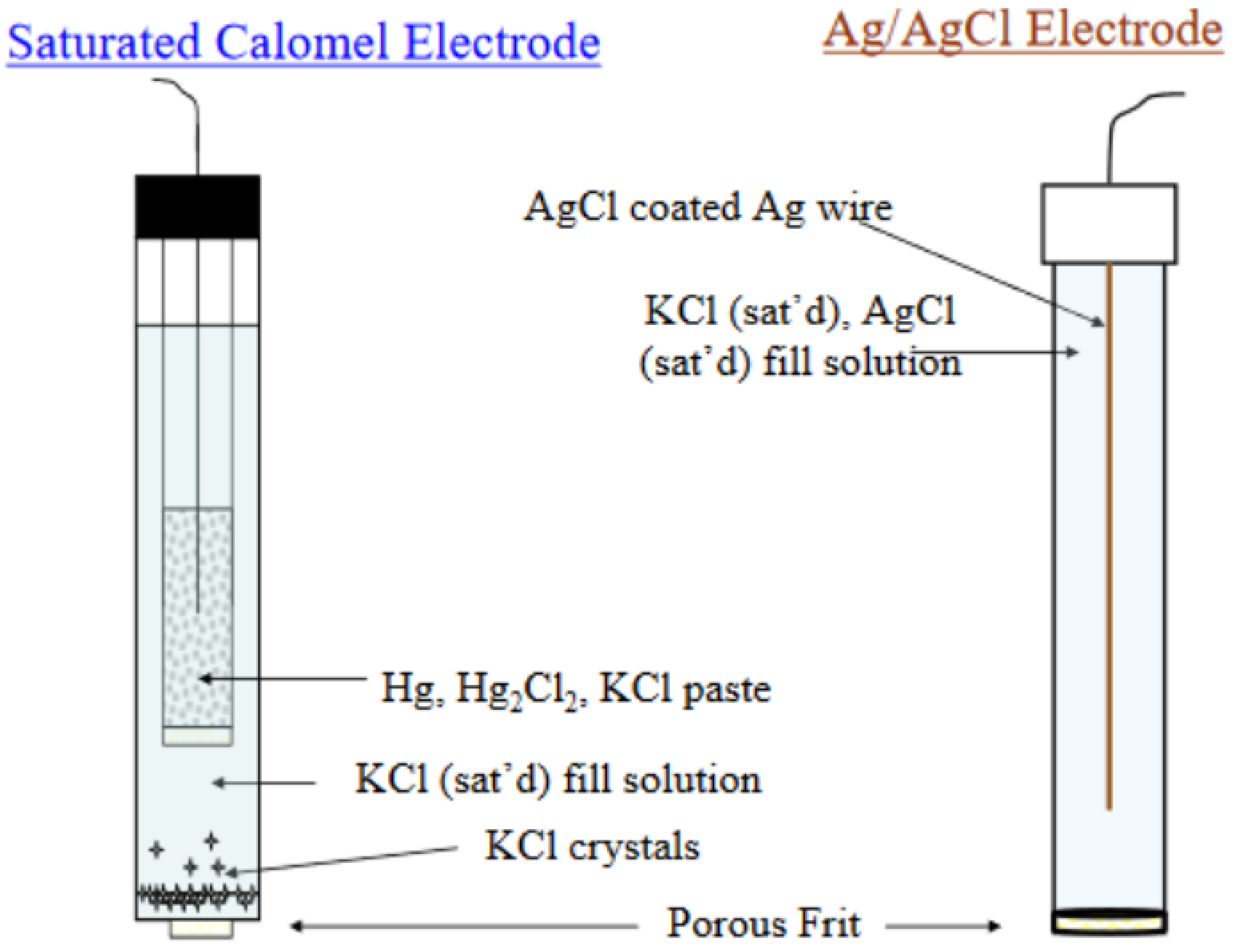
4. **Redox electrode:** electrode consists of an inert electrode (Pt or Au) immersed in a mixed solution containing both the oxidized and reduced forms of a molecule or ion.

$Ce^{+4} + Fe^{+2} \rightleftarrows Ce^{+3} + Fe^{+3}$	
Half cell reaction	**Electrode potential**
$Ce^{+4} + e \rightleftarrows Ce^{+3}$	1.44 volt
$Fe^{+2} \rightleftarrows Fe^{+3} + e$	–077 volt

5. **Ion selective electrode:** In ion selective electrode, a membrane is in contact with a solution, with which it can exchange ions. These are the electrodes which certainly respond to specific ions and determine the potential. Example: Glass electrode.



4. Reference electrode: Reference electrodes are those whose potentials are known.



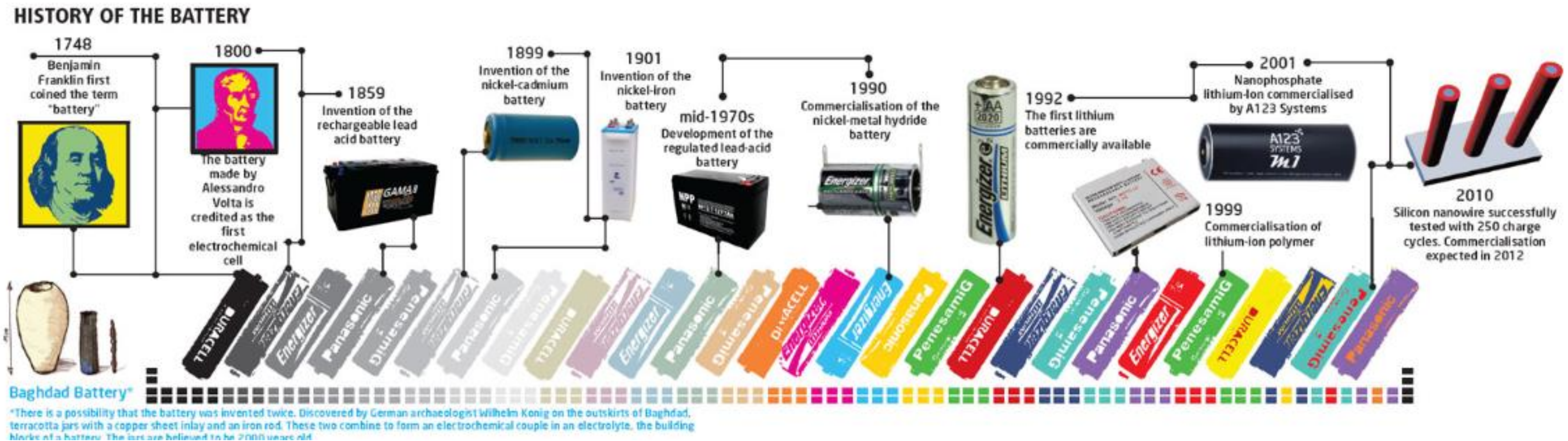
Ex: SHE (Standard Hydrogen Electrode)
SCE (Saturated Calomel Electrode)
Silver/Silver chloride electrode

Battery technology

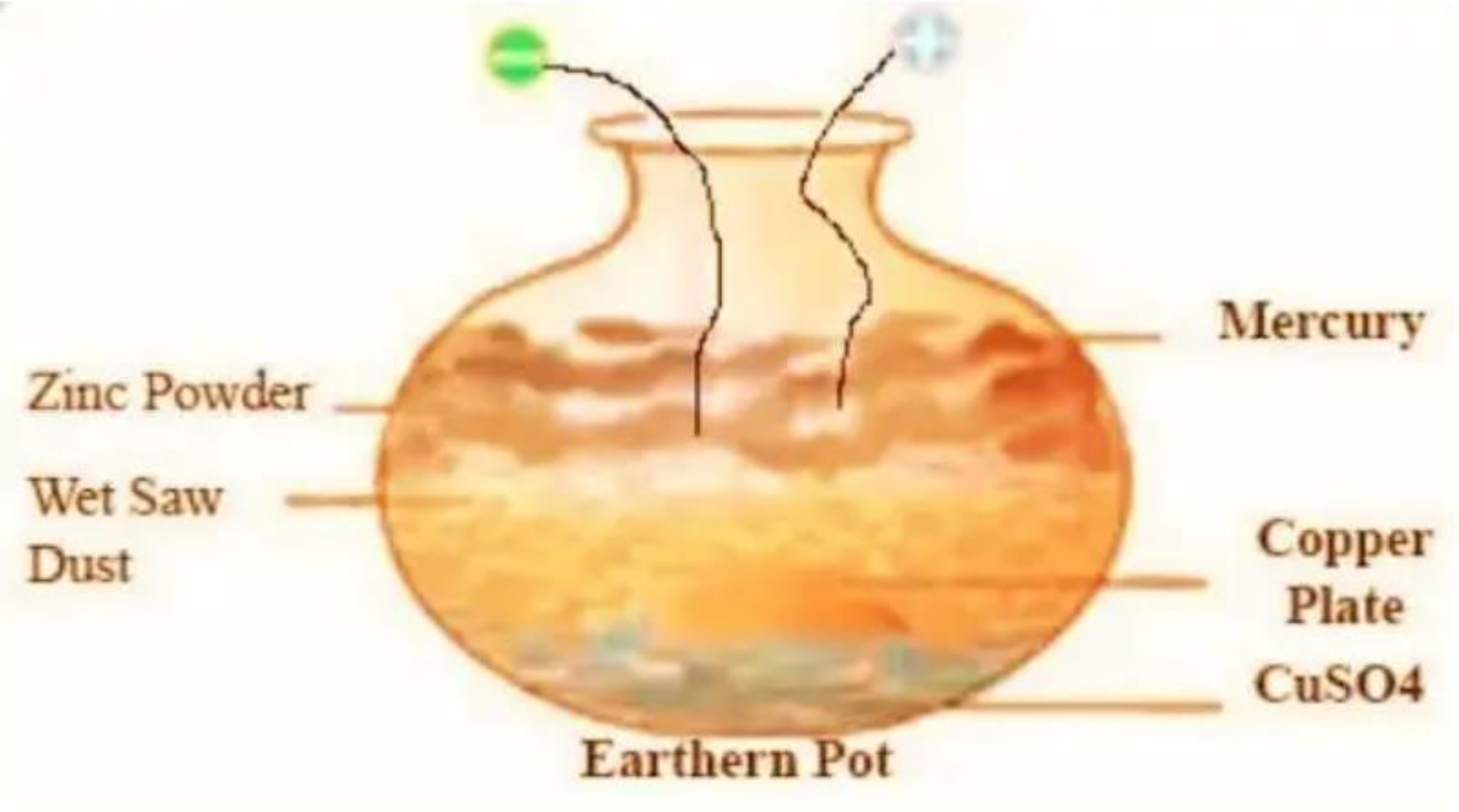
CELL: A cell designates a single unit. The conversion of chemical energy into electrical energy is a function of cells or batteries.

BATTERY: A Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage.

Uses: Calculator, watch, mobile phones**,** emergency lightning in hospitals, electroplating industrial tractions and military and space applications.

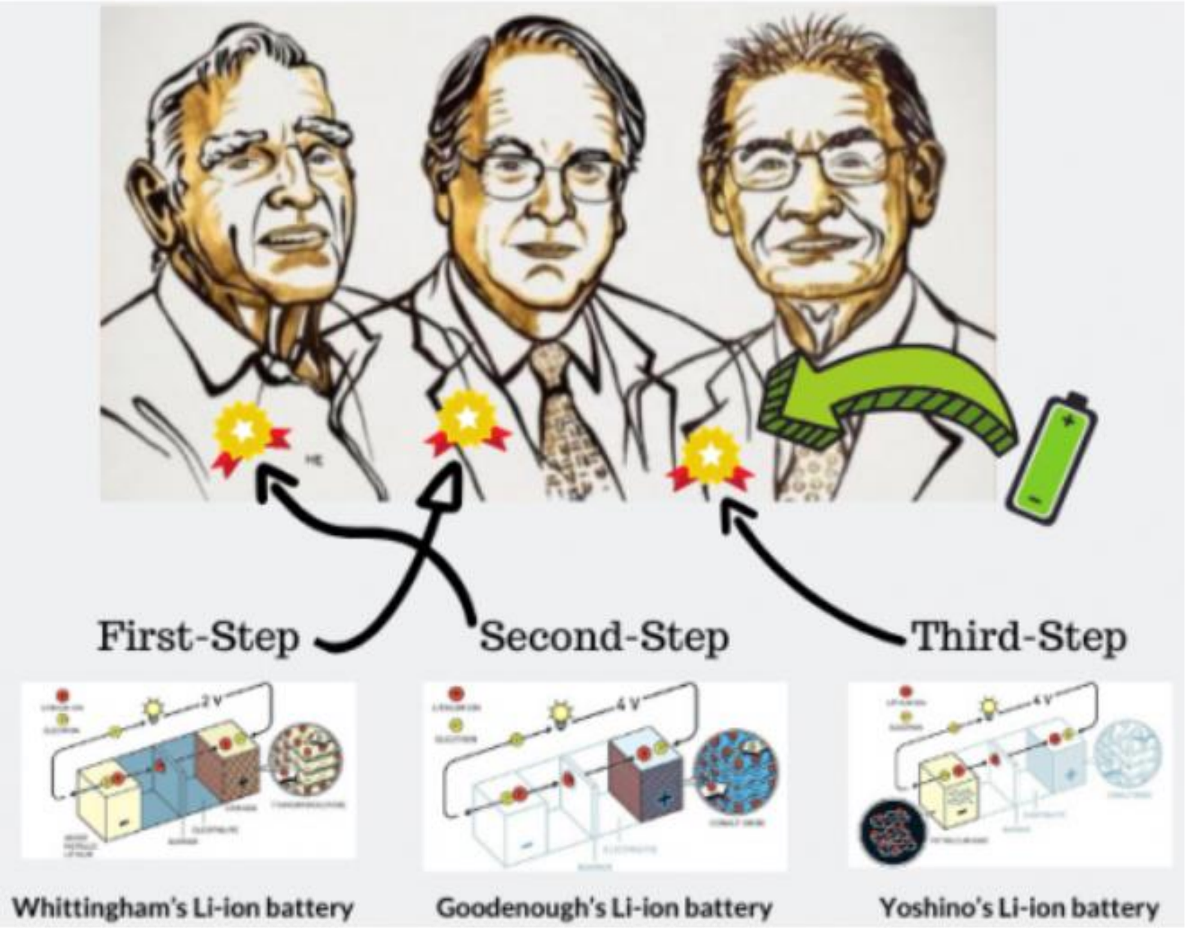


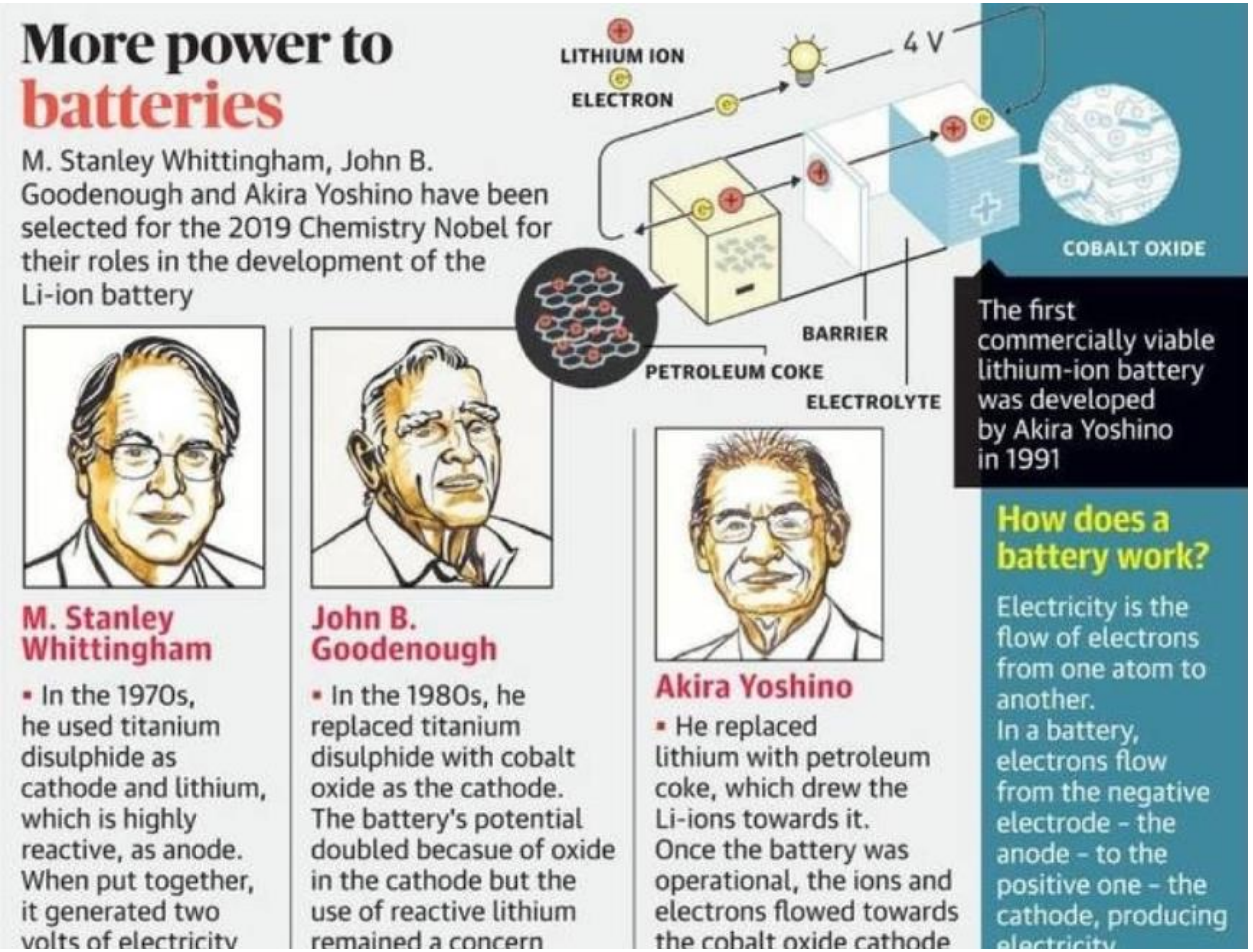
Voltaic Pile



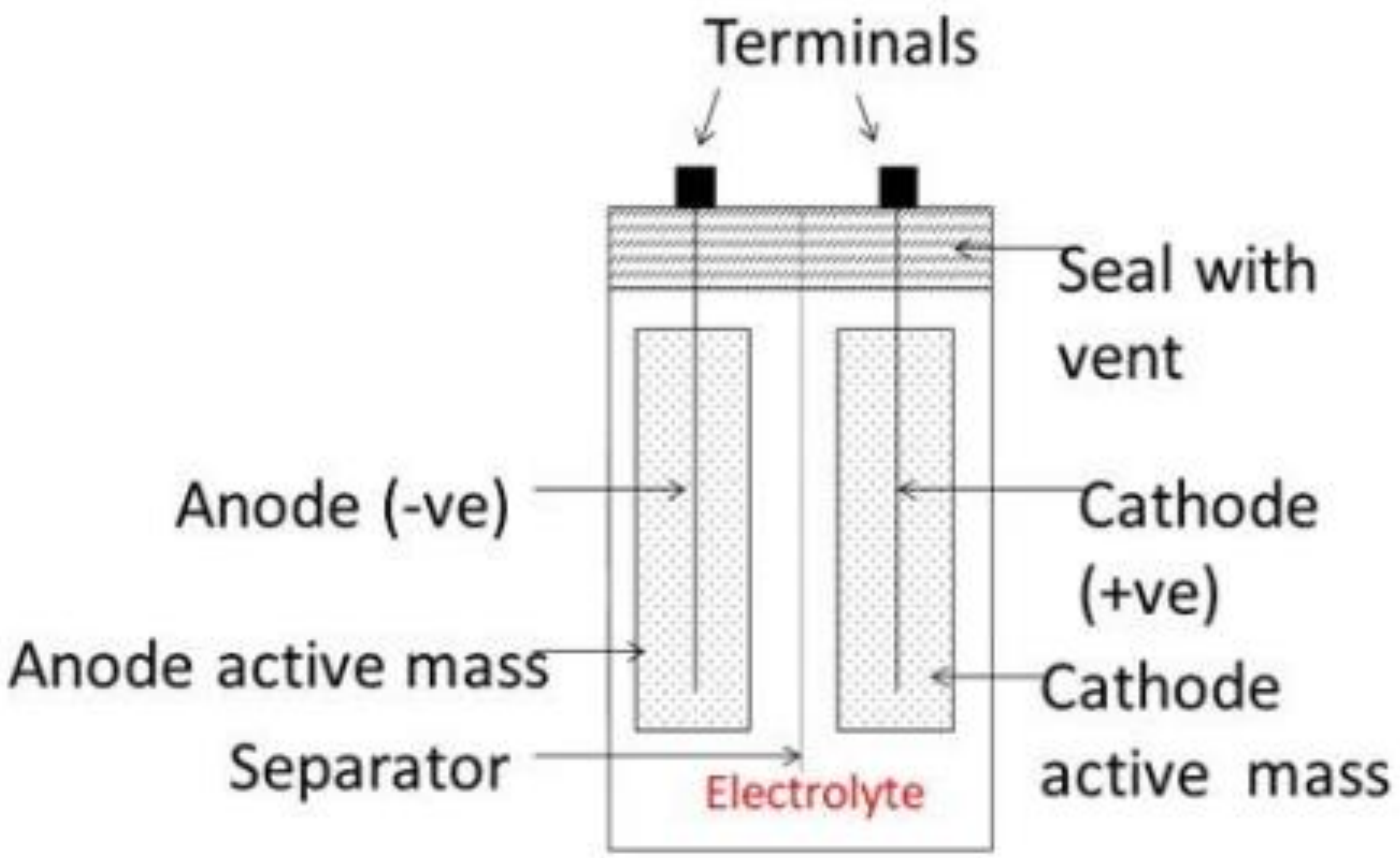
Agastya Battery

Nobel prize for 2019 in chemistry





Components of Battery:



Anode : It is a reducing electrode that releases electrons to the external circuit and oxidizes during the electrochemical reaction.

Cathode: It is the positive or oxidizing electrode that acquires electrons from the external circuit and is reduced during the electrochemical reaction.

Electrolyte: It is the medium that provides the ion transport mechanism between the cathode and anode of a cell. Electrolytes are often thought of as liquids, such as water or other solvents, with dissolved salts, acids,or alkalis that are required for ionic conduction.
It should however be noted that many batteries including the conventional (AA/AAA) batteries contain solid electrolytes that act as ionic conductors at room temperature.

Characteristics of battery

Voltage (V): The voltage of any battery depends on the emf of the cells which constitute the battery system.

$$E_{cell} = E_{cathode} - E_{anode}$$

The emf of the cell depends on the free energy in the overall cell reactions as given by Nernst equation.

$$E = E^0 - \frac{2.303RT}{nF}\log Q$$

$$where\ E^0{}_{cell} = E^0{}_{cathode} - E^0{}_{anode} \text{ and } Q \text{ is the reaction quotient } Q = \frac{[\text{product}]}{[\text{reactant}]}$$

Q is the ratio of the molar concentrations of product and reactants.

- **Current (A):** Current is a measure of the rate at which the battery is discharging.
  Higher the rate of spontaneous reaction, higher is the current.
  Higher the surface area of the electrodes, higher is the rate of reaction. Current is measured in Ampere (A).

$$I=V/R$$

Where I is the current, V is voltage and R is resistance of the battery.

- **Capacity (Ah):** Capacity is a measure of the amount of electricity that may be obtained from the battery.

  It is expressed in Ah (ampere hours). It is proportional to the amount of charge in Coulombs that may be transported from anode to cathode through the external circuit. The charge (C) in Coulombs is given by the Faraday's relation:

$$C = \frac{w \times n \times F}{M}$$

Where, C is Capacity of battery (in Ah), W is Weight of the active material (Kg), n is number of electrons involved in discharge reaction, F is Faraday's constant, 96500 C/mol, M is Molar mass of electro active materials.

Energy density (A/Kg): It is the amount of electricity stored in the battery per unit weight of the battery. i.e., it is the capacity per unit weight.

It can be expressed in Coulombs/kg or in A/kg. The weight includes the weight of all components of the battery (i.e. total weight of active material, electrolyte, terminals etc.).

$$Energy\ density = \frac{I(current)\ x\ t\ (time)\ x\ V\ (Voltage\ of\ a\ battery)}{Capacity\ of\ a\ battery}$$

Power density (Wh/ Kg): The ratio of the power available from a battery to its weight or its volume (W / V) is called power density.

$$Power\ density = \frac{I\ (current) x\ V(EMF\ of\ battery)}{Mass\ of\ electroactive\ material}$$

- **Energy efficiency:** it is the ratio of energy released during discharge to energy consumed during charging. The energy efficiency of a rechargeable battery is given by

$$\boxed{\%\ \text{Energy efficiency} = \frac{\text{Energy released during discharging} \times 100}{\text{Energy consumed during charging}}}$$

- **Cycle life:** The number of recharges per discharge cycle that are possible before the failure of a secondary battery is called cycle life.

- **Shelf life**: The duration of storage under specific conditions at the end of which battery still retains the ability to give specific performance is called shelf life.

Problems on Battery Characteristics

$$E = E^0 - \frac{2.303RT}{nF}\log Q$$

$$where\ E^0{}_{cell} = E^0{}_{cathode} - E^0{}_{anode}\ \text{and}\ Q\ \text{is the reaction quotient}\ Q = \frac{[\text{product}]}{[\text{reactant}]}$$

$$Energy\ (Wh) = Capacity(Ah) \cdot Voltage(V)$$

$$C = \frac{w \times n \times F}{M}$$

$$\%\ \text{Energy efficiency} = \frac{\text{Energy released during discharging} \times 100}{\text{Energy consumed during charging}}$$

Criteria for commercial batteries

An efficient commercial cell should have following basic characteristics

- Portability: cells should be easily transportable without any environmental issues
- Compact: Battery should be more compact and lightweight
- Economy: batteries should have less price with continuous electric supply.
- Power and energy density: batteries should have high power and energy density
- Recharging; It should be able to charge as well as discharge battery in faster rate with recyclability
- Cycle and shelf life: Batteries should be having high cycle life and shelf life without self-discharge.

Classification of batteries:

Primary battery: non-rechargeable (cell reactions are irreversible) - Self-discharges whether used or not

Applications: Torch light, portable radios, toys, novelties, etc. Mg/MnO_2 cell

Military communication equipment, voting machines, etc.

Secondary battery: Rechargeable (cell reactions are reversible) batteries.

Lead-Acid Battery (Pb/H+), Nickel-Cadmium Battery (Ni-Cd), Nickel-Iron Battery (Ni-Fe), Nickel-Metal hydride Battery (Ni-MH), Lithium battery (Li-LiMxOy), lithium-Ion battery (C-LiMxOy), Lithium-Ion Polymer Battery (C-LiMxOy)

Reserve battery: one of the key cell components, usually the electrolyte, is kept isolated from the rest and is added at the time of need

Examples: Mg/Cu_2Cl_2, Mg/AgCl (sea water activated battery), Applications: Torpedoes, Defence fields

Anode materials

Desired characteristics of anode materials

1) High efficiency of charge/discharge

2) Excellent cyclability

3) Low reactivity against electrolyte

4) Low cost

5) Environmental friendly, non-toxic

- **Commercial anode materials:**

Porous carbon, graphene

Desired characteristics of Cathode materials

- High discharge voltage
- High energy capacity
- Long cycle life
- High power density
- Light weight
- Low self-discharge
- Absence of environmentally hazardous elements

- Commercial cathode materials:

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

Electrolytes

Ion conductor between cathode and anode

- **Characteristics of Electrolyte**

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

- **Commercial electrolytes:** $LiPF_6$ in Carbonate solvent (propylene carbonate)

Types of Electrolytes

1) **Aqueous electrolyte**: $LiNO_3$, Li_2SO_4 dissolved in water
2) **Non-aqueous electrolyte:** $LiPF_6$ in 1,2, dimethoxy ethane
3) **Ionic liquid (IL) electrolyte**: Imidazolium based ILs
4) **Polymer Electrolytes:** Poly(ethylene oxide)

Electrolyte additives

1) Those used for improving the ion conduction

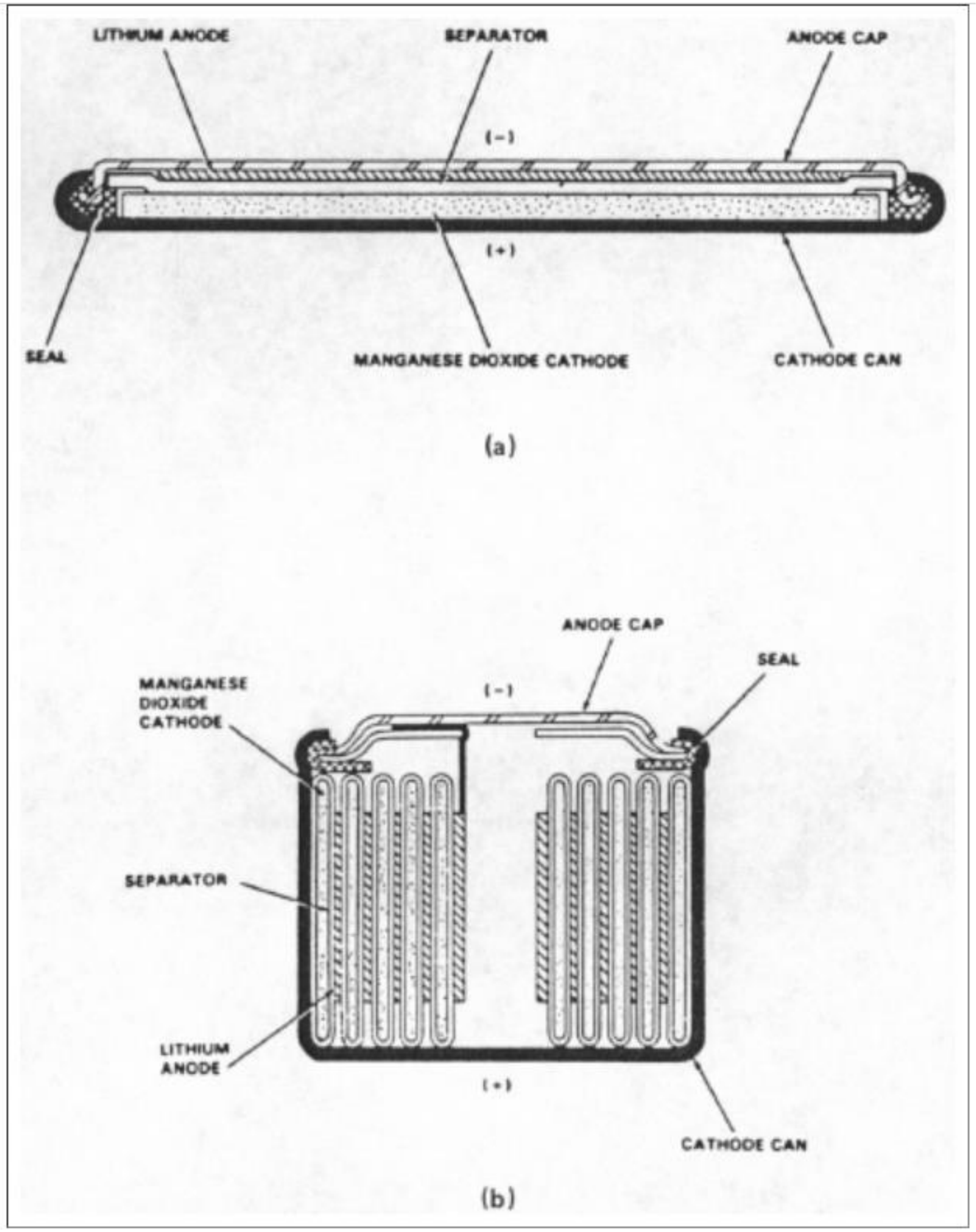
properties in the bulk electrolytes

2) Those used for SEI chemistry modifications

3) Those used for preventing overcharging of the cells

Primary lithium ion batteries

- These are batteries in which redox reactions proceed only in one direction.



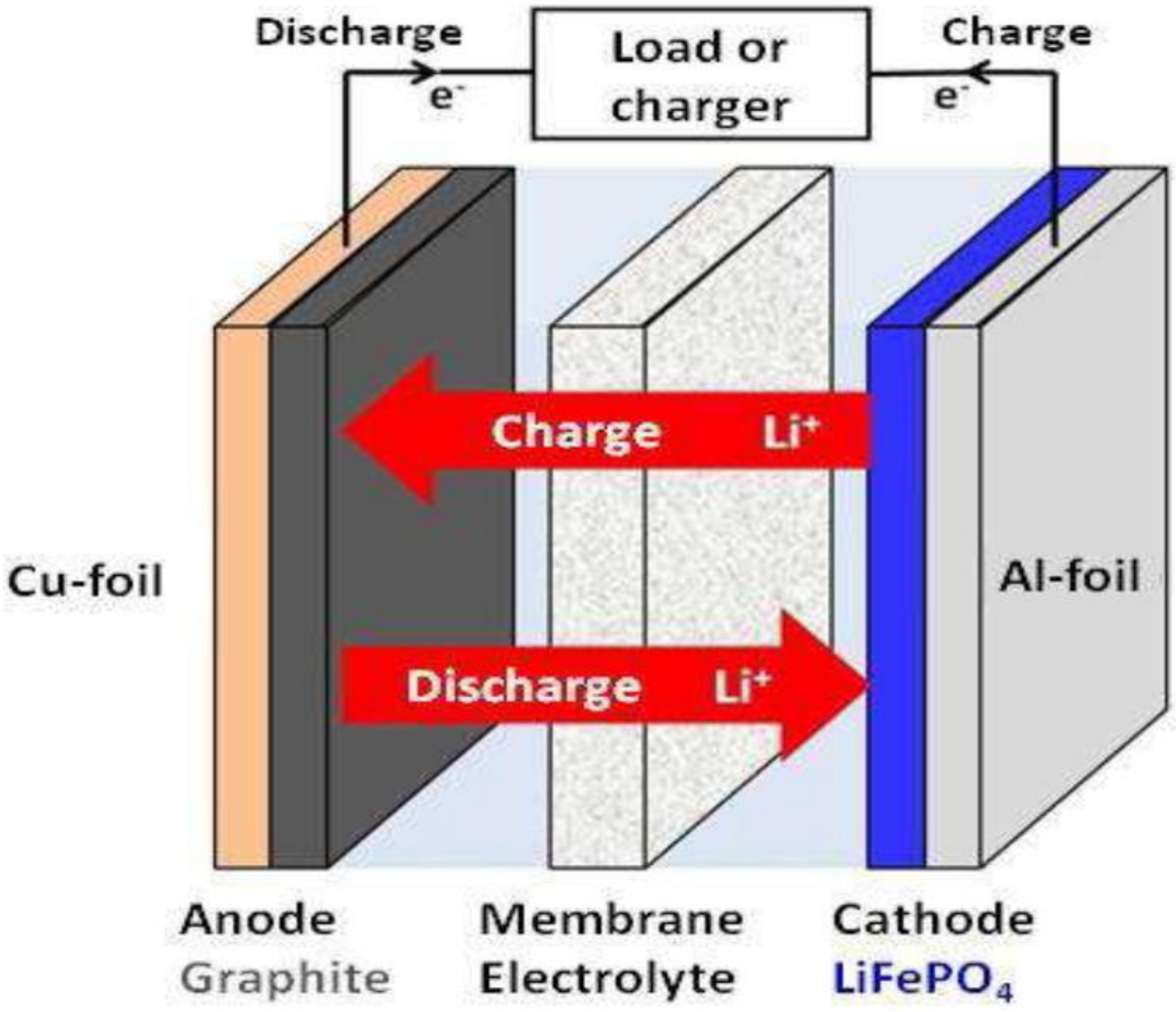
(a)

(b)

Anode: Li

Cathode: MnO_2

Construction and working of Li-ion batteries

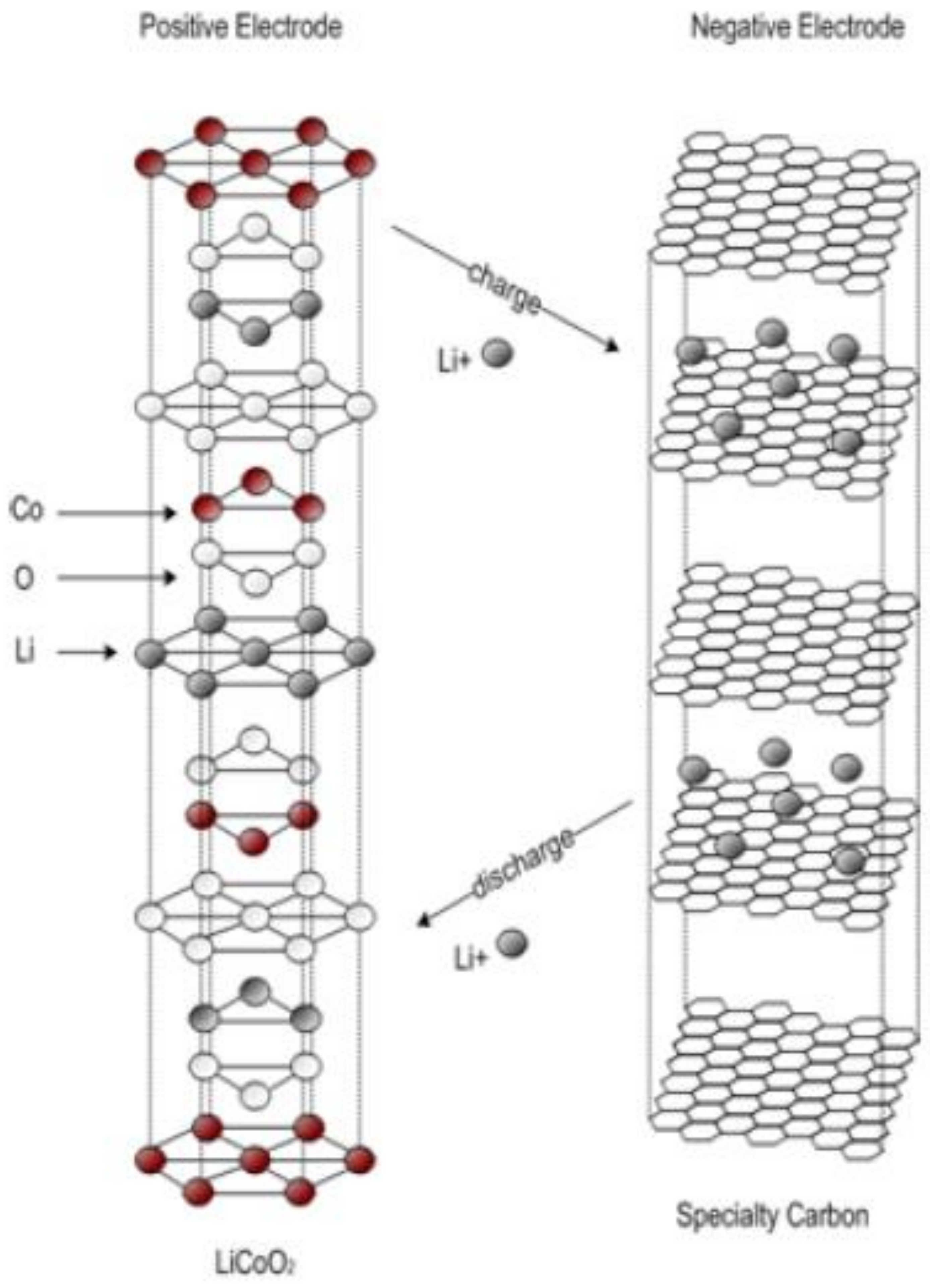


Lithium ion batteries

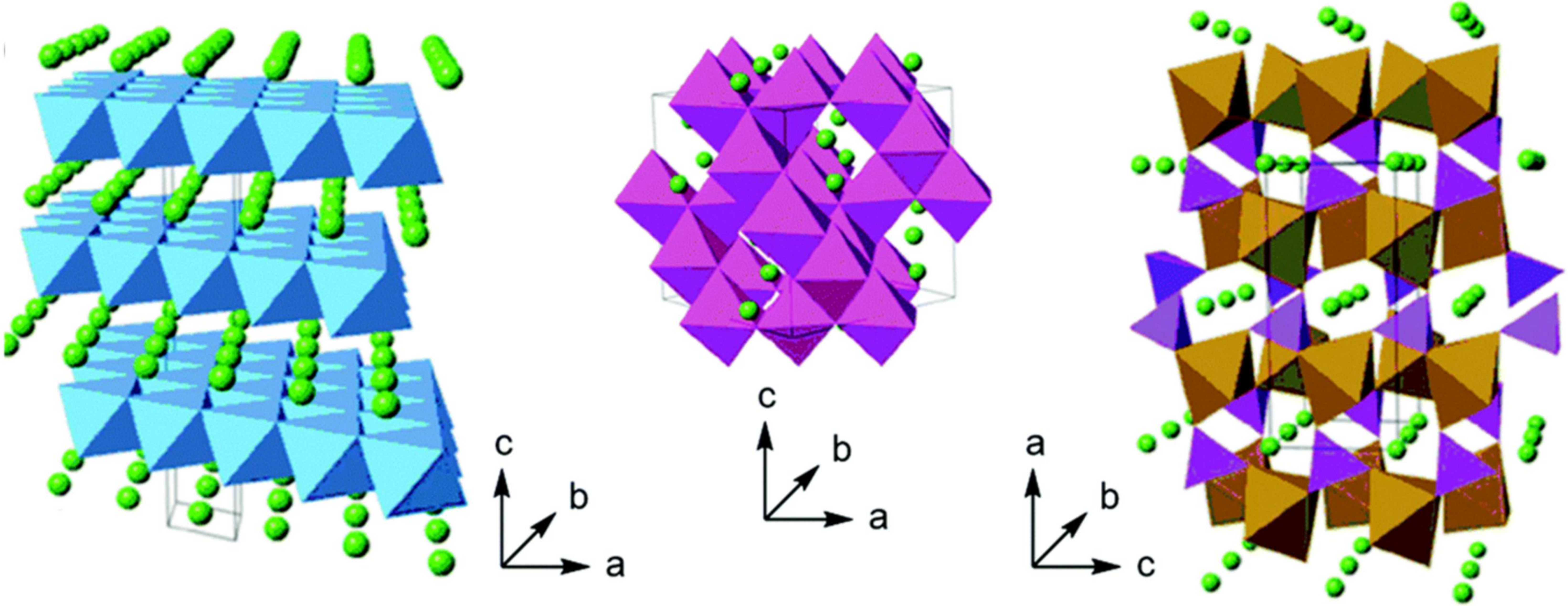
- Positive electrode: Lithiated form of a transition metal oxide (lithium cobalt oxide-$LiCoO_2$ or lithium manganese oxide $LiMn_2O_4$)

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

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

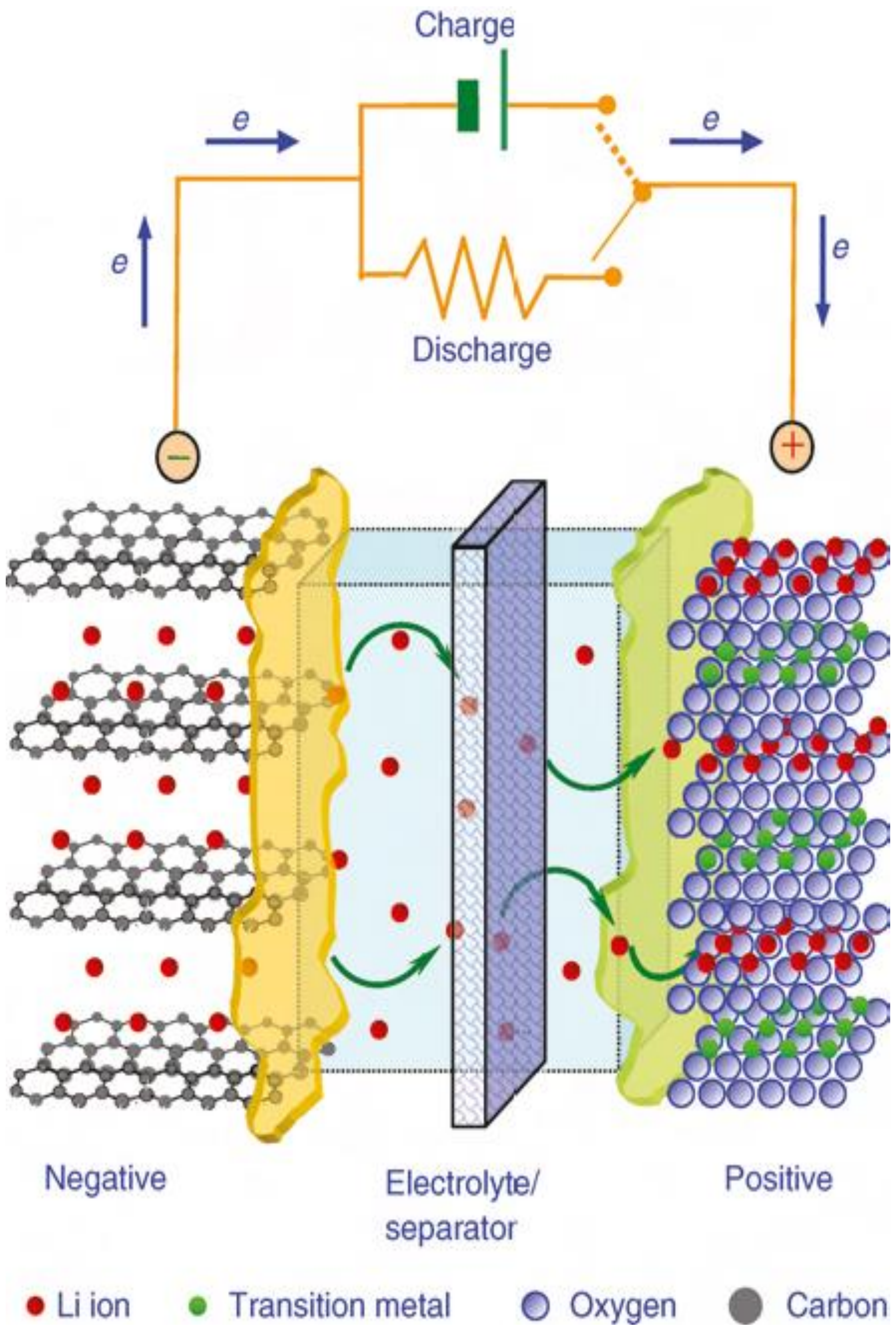


Crystal Structure



Layered $LiCoO_2$ Spinel $LiMn_2O_4$ Olivine $LiFePO_4$

Li-ion battery system



Electrochemical Reactions

- Cathode

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

- Anode

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

- Overall

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

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

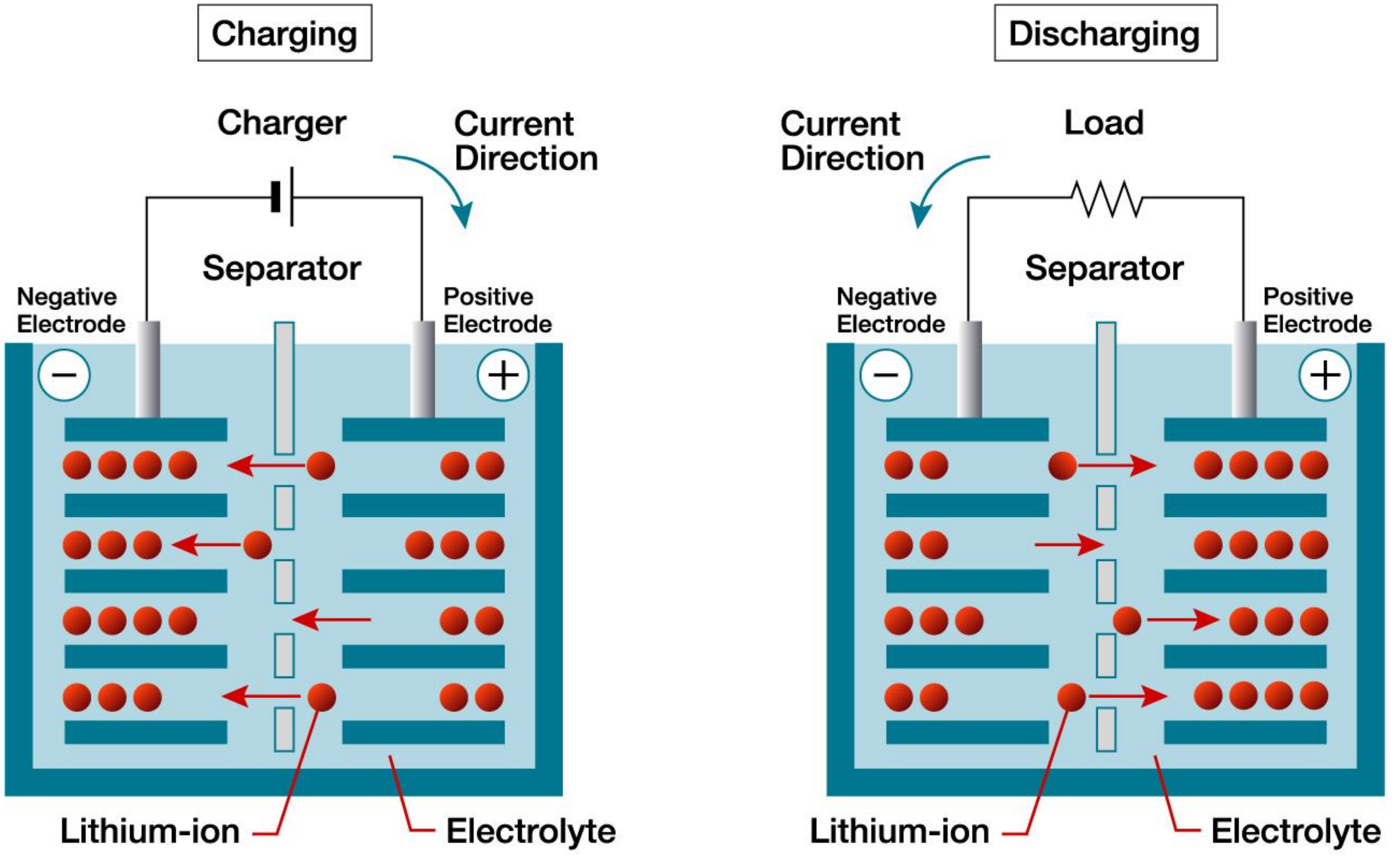
  - Negative electrode $xLi^+ + xe^- + 6C \longrightarrow Li_xC_6$

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

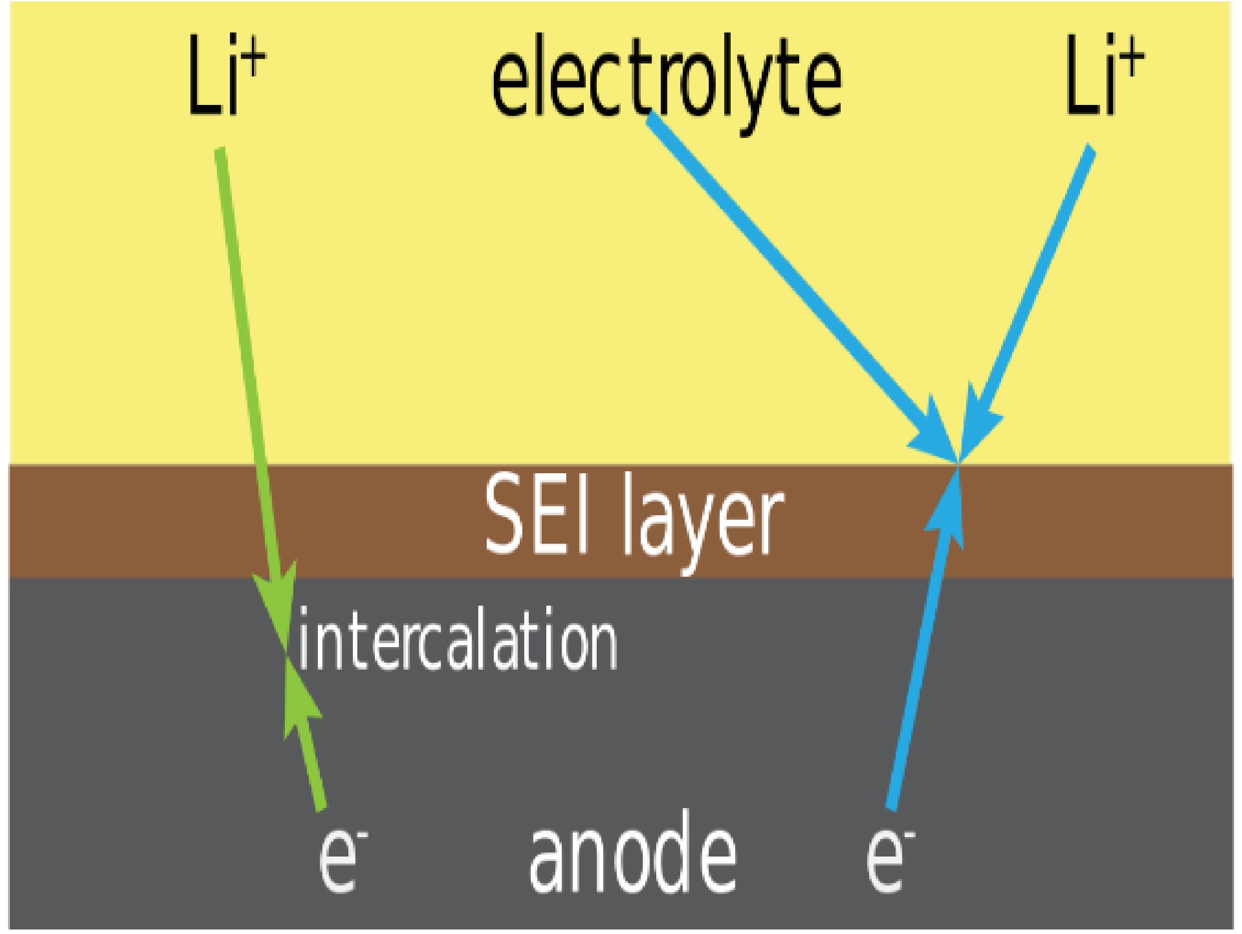
- In the above reaction *x* can be 1 or 0

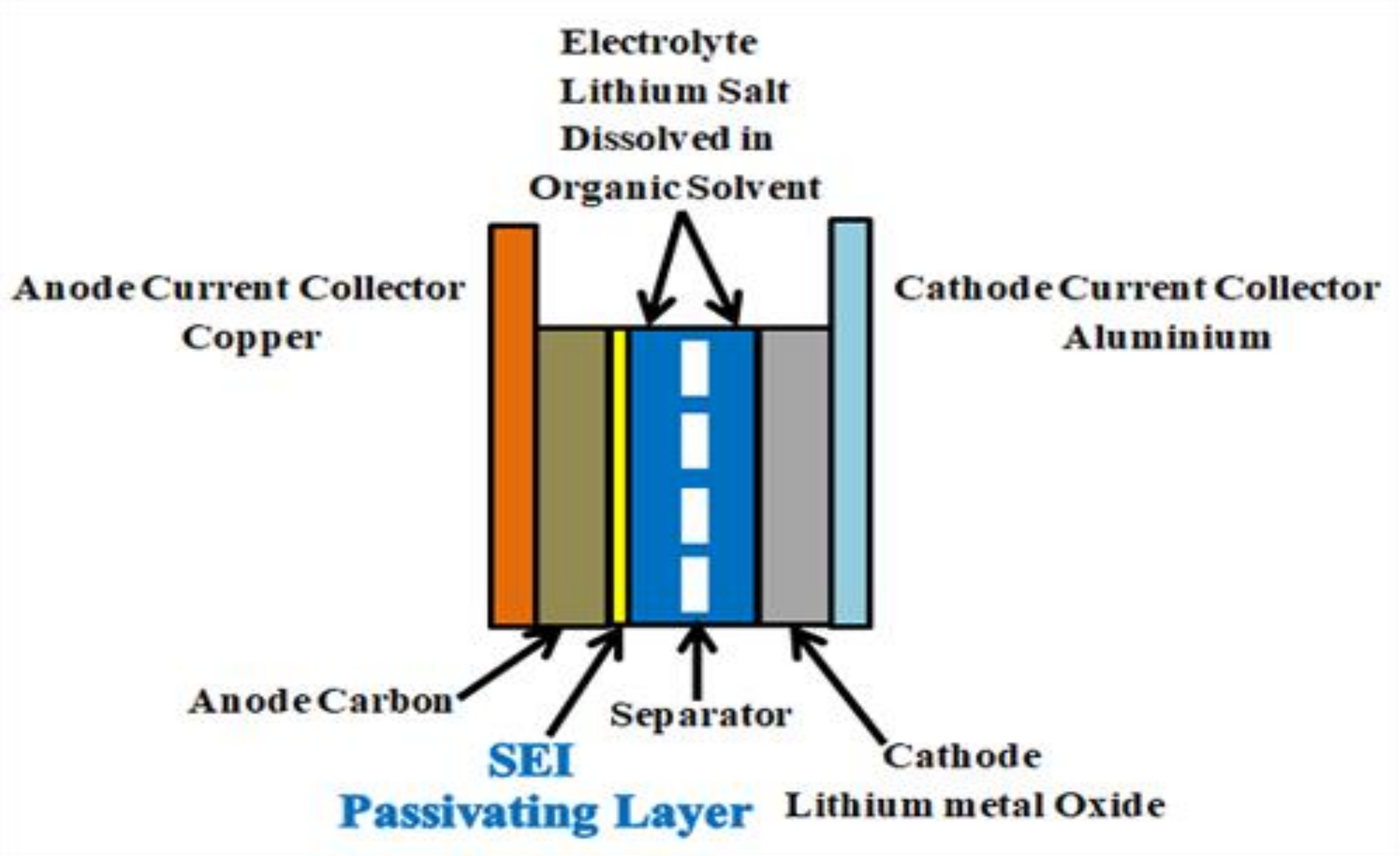
- With discharge the Co is oxidized from Co^{3+} to Co^{4+}. The reverse process (reduction) occurs when the battery is being charged.

Charging and discharging reactions



Solid Electrolyte Interface (SEI)





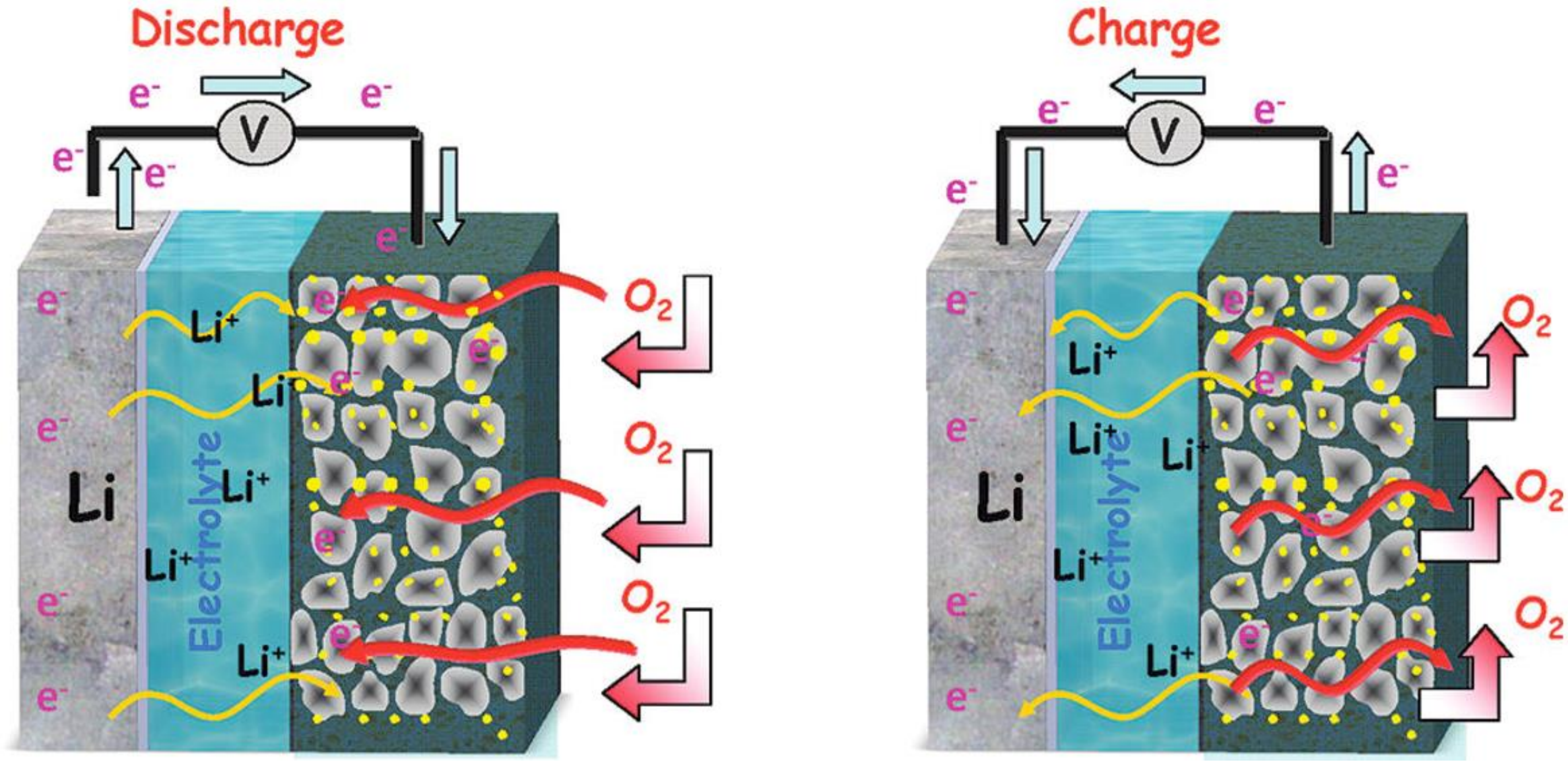
Advantages of lithium-ion batteries

- Light weight 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
- 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

Li-air batteries

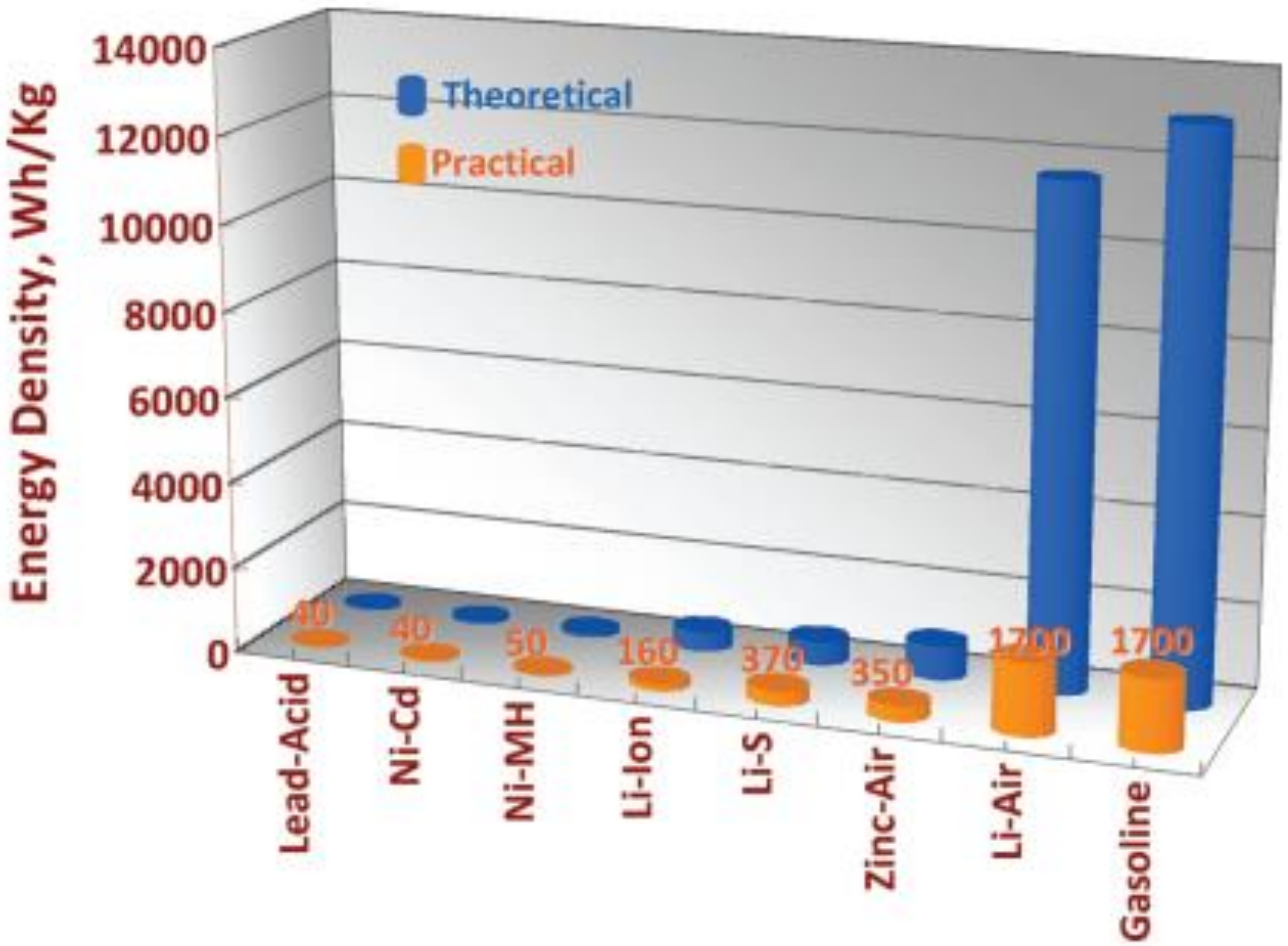


https://www.youtube.com/watch?v=8pMFLpiqPAc

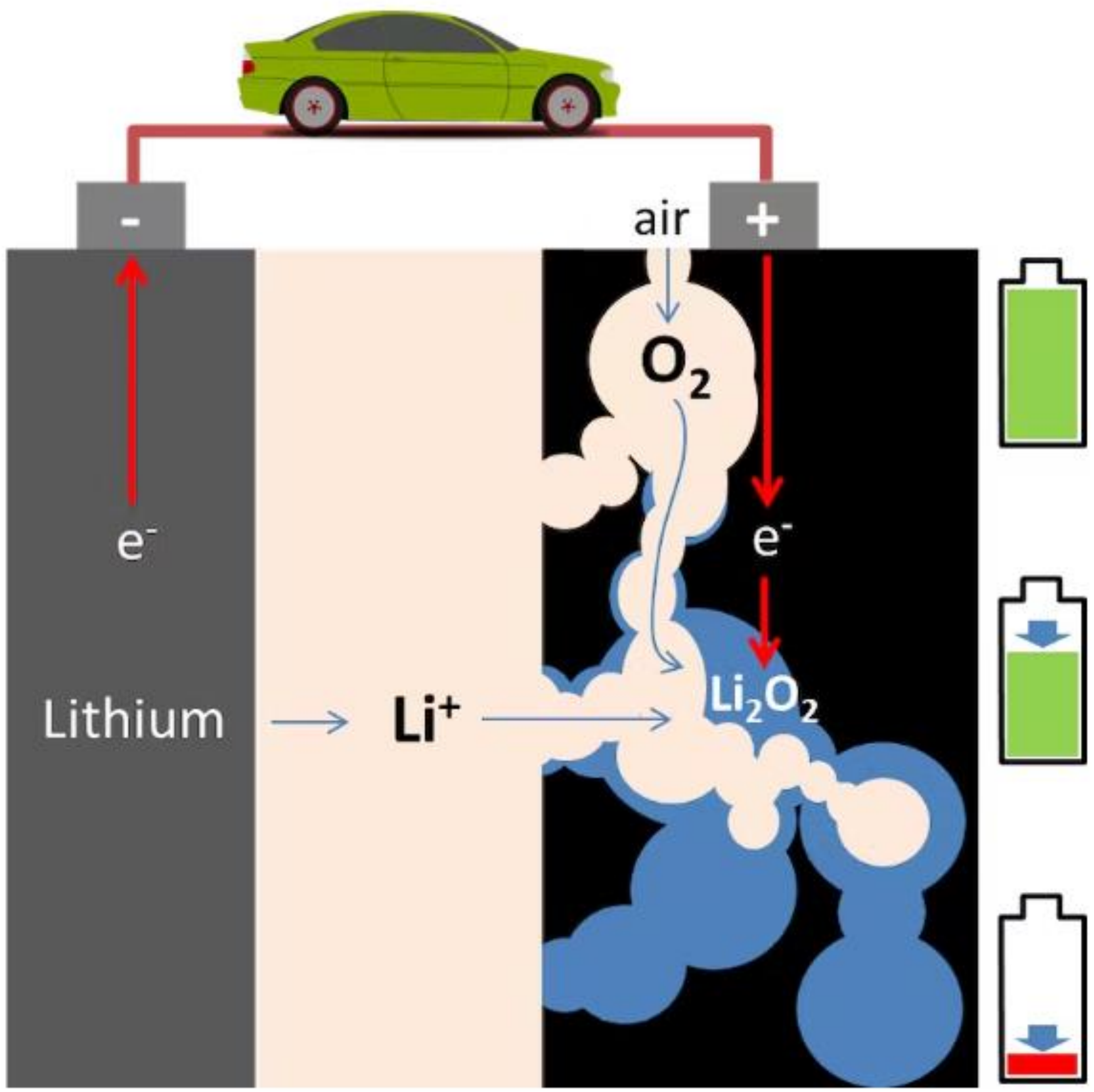
Why Li-air batteries?

- 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



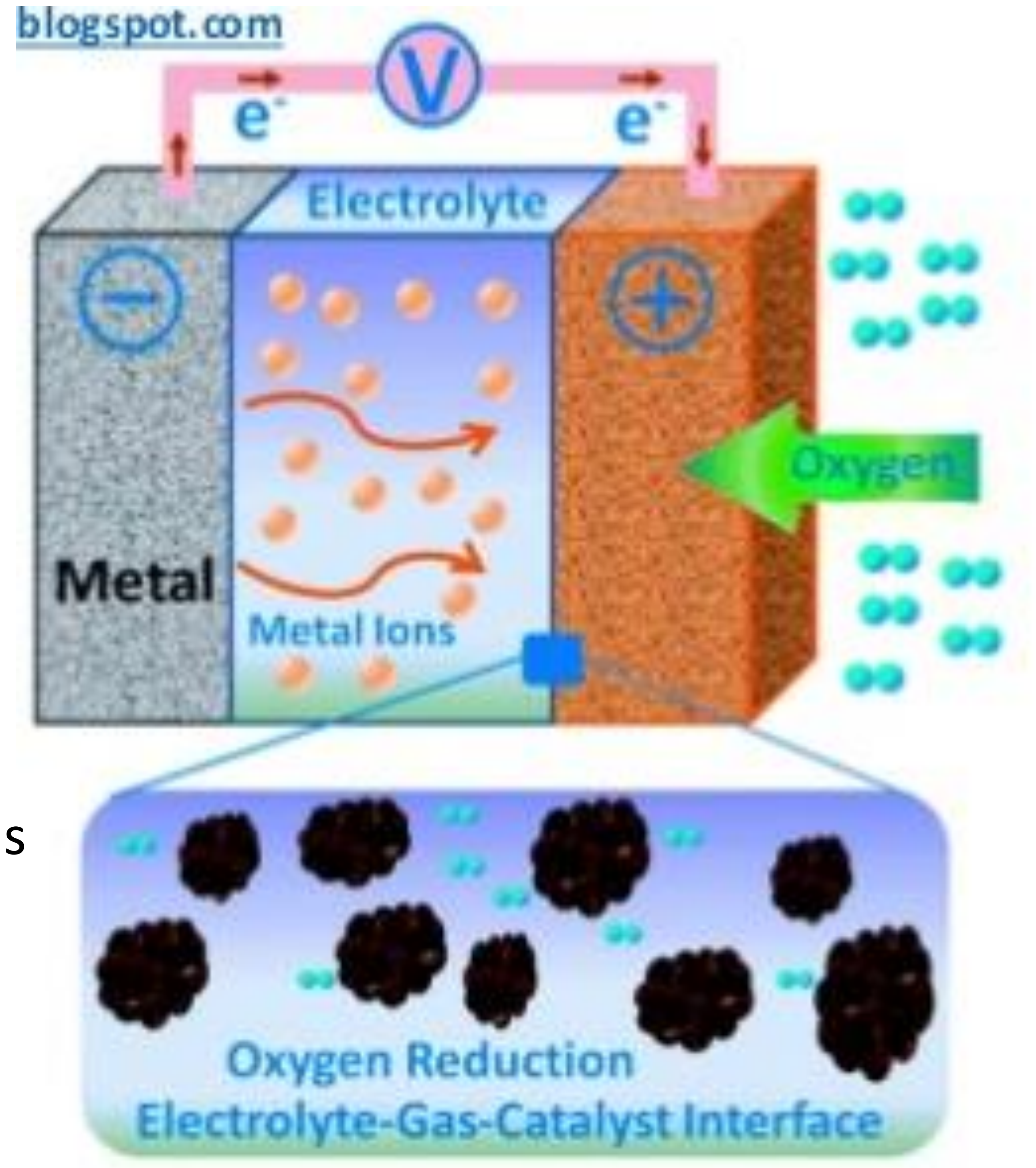
Li air battery mechanism



- Oxidation of lithium at the anode
- Reduction of oxygen at the cathode to induce a current flow

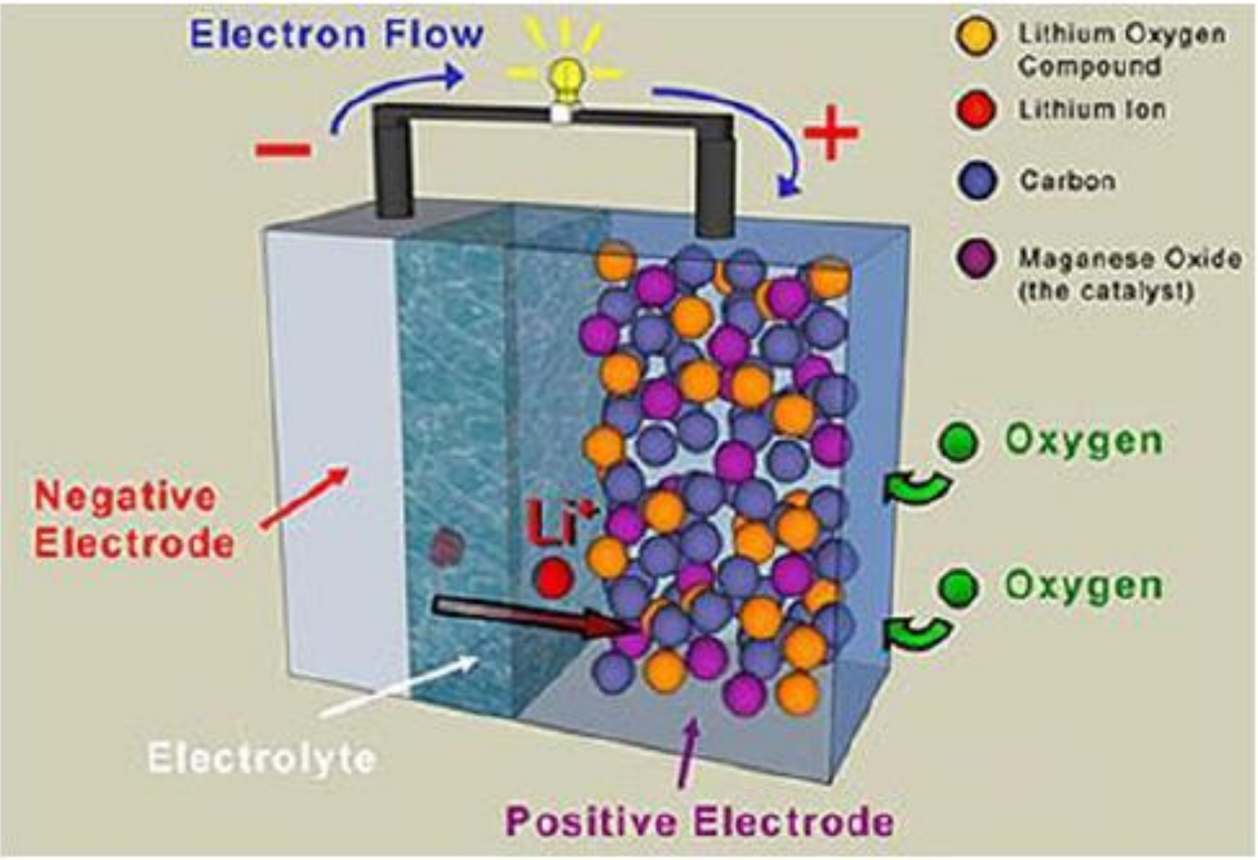
Li-air batteries: introduction

- 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

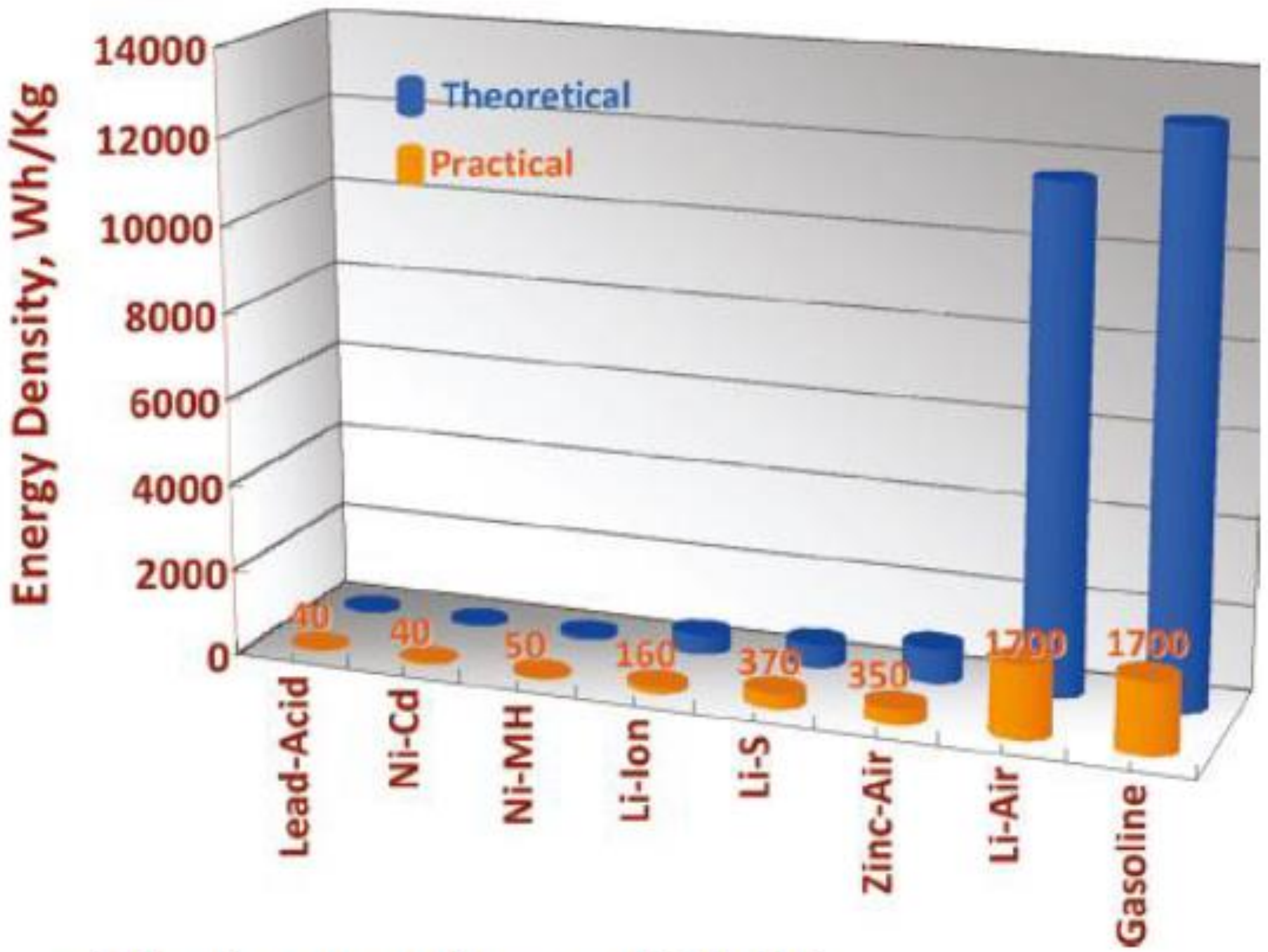
Li-Air BATTERIES



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

Electrolyte

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

Acidic electrolyte

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

Alkaline electrolyte

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

- Water molecules are involved in the redox reactions at the air cathode.

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

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

- 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.

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.