BASIC PHYSICS

Dr. Vahid Esfahanian
An Introduction to Battery Technologies
Lecture #4

FLUID FLOW AND CURRENT FLOW ANALOGY

Charge: Represented by the amount of water in a tank (Volume)

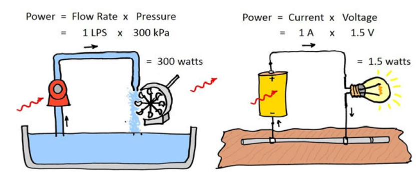
Voltage: Represented by the water pressure (P)

Current: Represented by the flow of water (Q)

Power: Represented by the total amount of water flowing in a given time

Resistance: Represented by a constriction in the pipe, which resists the flow of water (Pressure loss)

Power = Flow Rate x Potential



CHARGE, CURRENT, VOLTAGE, RESISTANCE

Electric current is measured in amperes (A).

Quantity of electric charge is measured in coulombs (C).

The coulomb is defined as the quantity of electricity carried in one second by a current of one ampere.

$$1\text{ A} = 1\frac{\text{C}}{\text{s}}$$

The current is forced through the circuit by an electrical potential difference, which is measured in volts (V). It takes one joule of work to move one coulomb from a lower to a higher potential when the potential difference is one volt.

$$1\text{ V} = 1\,\frac{\text{J}}{\text{C}}$$

$$\varepsilon = IR$$

Resistance is measured in ohms (Ω). The Siemens (S) is the SI unit for electrical conductance. It measures how easily electric current can flow through a material. 1 Siemens is equal to 1/ Ω.

WHAT IS CONDUCTION?

Metallic Conduction

An electric current is the flow of electric charge. In metals this charge is carried by electrons, and electrical conduction of this type is called metallic conduction.

Ionic Conduction

The charge is carried by ions and is exhibited principally by molten salts and by aqueous solutions of electrolytes.

GALVANIC CELL (VOLTAIC)

It is a cell in which chemical energy is converted to electrical energy. (spontaneous reactions)

This cell consists of two half cells:

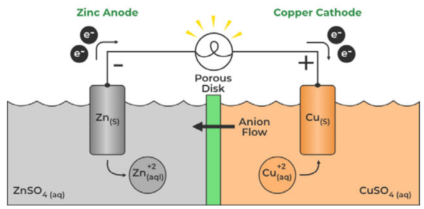
1)Anodic half cell

2)Cathodic half cell

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu^0_{(s)}$

$Zn^0_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$

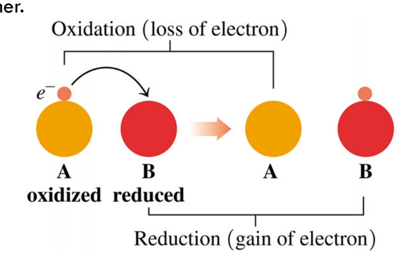
$Cu^{2+}_{(aq)} + Zn^0_{(s)} \rightleftharpoons Cu^0_{(s)} + Zn^{2+}_{(aq)}$



The movement of electrons from Zn to Cu produces a current in the circuit.

REDOX REACTION

In an **oxidation–reduction reaction**, electrons are transferred from one substance to another.



OIL RIG

Oxidation Is Loss of electrons. Reduction Is Gain of electrons.

REDOX REACTION

$2Cu(s) \rightarrow 2Cu^{2+}(s) + 4e^-$ oxidation

$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$ reduction

$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$

Core Chemistry Skill Identifying Oxidized and Reduced Substances

Identify each of the following as oxidation or reduction:

A. $Sn(s) \rightarrow Sn^{4+}(aq) + 4e^-$ Oxidation

B. $Fe^{3+}(aq) + 1e^- \rightarrow Fe^{2+}(aq)$ Reduction

C. $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ Reduction

REDOX REACTION

In light-sensitive sunglasses, UV light initiates an oxidation–reduction reaction.

$$2Ag^+ + 2Cl^- \rightarrow 2Ag + Cl_2$$

A. Which reactant is oxidized? chloride ion, Cl^-
$2Cl^- \rightarrow Cl_2 + 2e^-$

B. Which reactant is reduced? silver ion, Ag^+
$2Ag^+ + 2e^- \rightarrow 2Ag$

REDOX REACTION

In galvanic cell operation, an oxidation reaction occurs at anode, producing electrons. On the other hand, at cathode, a reduction reaction occurs, consuming electrons on the electrode surface

Redox example in a Li-ion battery:

Anode (Ox): $LiC_6 \rightarrow Li^+ + e^- + C_6$

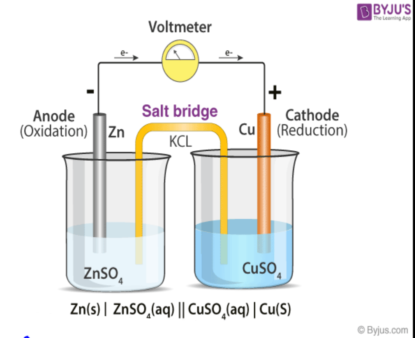
Cathode(Red): $Li^+ + e^- + CoO_2 \rightarrow LiCoO_2$

Overall: $LiC_6 + CoO_2 \rightarrow LiCoO_2 + C_6$

GALVANIC CELL NOTATION

anode(s) | || | cathode

phase-change ↙ ↘ Salt bridge



Ox. $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$

Re. $Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$

$\rightarrow Fe_{(s)} | Fe^{2+}_{(aq)} || Ni^{2+}_{(aq)} | Ni_{(s)}$

GALVANIC CELL NOTATION

$Zn + Co^{3+} \rightarrow Zn^{2+} + Co^{2+}$

Ox. $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Red. $Co^{3+}_{(aq)} + e^- \rightarrow Co^{2+}_{(aq)}$

$\rightarrow Zn_{(s)} | Zn^{2+}_{(aq)} || Co^{3+}_{(aq)}, Co^{2+}_{(aq)} | Pt_{(s)}$

Inert Reference electrode

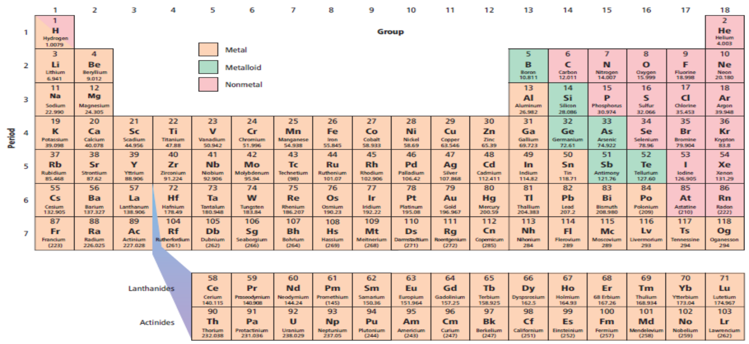
$Cu_{(s)} + Cl_{2(g)} \rightarrow Cu^{2+}_{(aq)} + 2Cl^-_{(aq)}$

Ox. $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$

Re. $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$

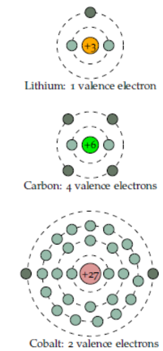
$Cu_{(s)} | Cu^{2+}_{(aq)} || Cl_{2(g)} | Cl^-_{(aq)} | Pt_{(s)}$

PERIODIC TABLE : A SIMPLE SUMMARY



PERIODIC TABLE : A SIMPLE SUMMARY

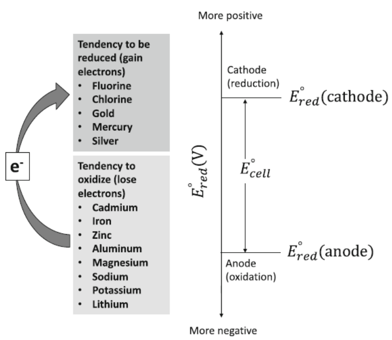
Strong reducing elements are grouped to the left, while the **strong oxidizing elements** are grouped to the right. Elements within each individual group (generally) have the same number of valence electrons, or number of electrons in their outer valence shell (but, transition metals are a little strange).



ELECTRODE MATERIAL

The electrode pair is selected by looking for the largest potential difference, which would give the highest cell voltage.

The lighter the material, the better characteristics a battery has in kWh/kg, which is called specific energy



BATTERY MATERIAL :STANDARD POTENTIAL TABLE

Cathode (reduction) half-reaction	Standard potential E^0 (volts)
$Li^+ + e^- \Rightarrow Li_{(s)}$	−3.01
$K^+ + e^- \Rightarrow K_{(s)}$	−2.92
$Ca^{2+} + 2e^- \Rightarrow Ca_{(s)}$	−2.84
$Na^+ + e^- \Rightarrow Na_{(s)}$	−2.71
$Zn^{2+} + 2e^- \Rightarrow Zn_{(s)}$	−0.76
$2H^+ + 2e^- \Rightarrow H_{2(g)}$	0.00
$Cu^{2+} + 2e^- \Rightarrow Cu_{(s)}$	0.34
$O_{3(g)} + 2H^+ + 2e^- \Rightarrow O_{2(g)} + H_2O_{(l)}$	2.07
$F_{2(g)} + 2e^- \Rightarrow 2F^-$	2.87

indicating that it would rather undergo oxidation (and hence is the strongest reducing agent of those listed).

it reduces most easily, and therefore is the best oxidizing agent of those listed

BATTERY CELL VOLTAGE

$$E^\circ_{cell} = E^\circ_{red}(\text{cathode}) - E^\circ_{red}(\text{anode})$$

$$Zn_{(s)} + Cl_{2\,(g)} \rightarrow ZnCl_{2\,aq}$$

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-, E^\circ_{red} = -0.76\text{ V}$$

$$Cl_{2\,(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}, E^\circ_{red} = +1.36\text{ V}$$

$$E^\circ_{cell} = E^\circ_{red}(\text{cathode}) - E^\circ_{ox}(\text{anode}) = 1.36 - (-0.76) = 2.21\text{ V}$$

THEORETICAL BATTERY CAPACITY

The total energy a battery has the ability to store.

Mass of a substance consumed in a battery is directly proportional to the quantity of electricity involved in the reaction.

What is g-equivalent?
is the atomic or molecular weight of the active material in grams divided by the number of electrons involved in a reaction.

Faraday's law?
1 g-equivalent of any active battery electrode material produces 96,487 C or 26.8 Ah.

THEORETICAL BATTERY CAPACITY: EXAMPLE

Example : Calculate the theoretical capacity of an electrochemical cell comprising Zn and Cl2.

$$Zn + Cl_2 \rightarrow ZnCl_2$$

$$mw_{Zn} = 65.4\text{ g} \quad ; \quad n = 2 \quad ; \quad \text{g} - \text{equiv} = 32.7\text{ g}$$

$$26.8 \div 32.7 = 0.82\text{ Ah/g}$$

If we repeat same for Cl : 0.76 Ah/g

$$1.22\text{ g/Ah} + 1.32\text{ g/Ah} = 2.54\text{ g/ Ah or } 0.394\text{ Ah/g}$$

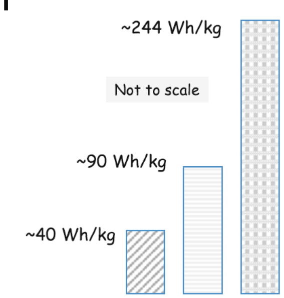
$$\text{Specific Energy (Wh/g)} = 2.12\text{ V} \times 0.394\text{ Ah/g} = 0.835\text{ Wh/g or } 835\text{ Wh/kg}$$

PRACTICAL ENERGY OF A BATTERY

Theoretical or maximum capacity is considered with all materials considered as active material. However, in real life batteries, all the weight is not active material and other components are included for assuring safe reliable operation of battery for example , current collectors or electrode substrates, electrolyte, separator, terminals, seals, and a container also, cooling and battery electrical management systems.

Electrochemical losses:

- Slow reaction activation on the electrodes
- Incomplete utilization of active material
- Ionic and electronic resistance (called ohmic losses)
- Mass transport losses that come from the active mass concentration reduction at the electrode.
- These losses typically cause a 50–75% reduction in actual energy.

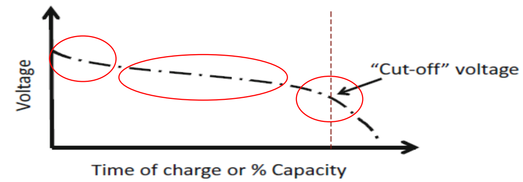


Theoretical, practical, and actual specific energy for Ni-Cd battery

PRACTICAL ENERGY OF A BATTERY

System	Theoretical specific energy (Wh kg^{-1})	Practical specific energy (Wh kg^{-1})	Percentages from theoretical (%)
Lead acid, LAB	167	33	20
Nickel–cadmium, NiCd	240	45	19
Nickel–metal hydride, NiMH	300	79	26
Nickel zinc, NiZn	320	80	25
Zinc bromium, ZnBr	435	90	21
Lihium ion, Li-ion	450	120	27
Sodium sulfur, NaS	795	90	11

VOLTAGE CHANGE



Constant current discharge

it is possible to calculate the practical battery capacity by integrating current over time, starting from fully charged state and ending at fully discharged state, i.e., when the cutoff discharge voltage is reached.

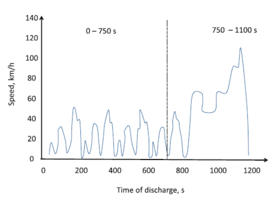
$$Q = \int_0^T I(t)dt = I \times t_d$$

MODES OF DISCHARGE

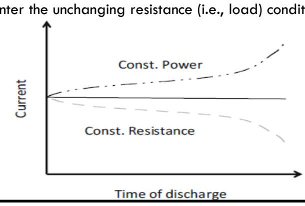
Modes of discharge :

1-Constatnt current
2-Constant load or resistance
3-Constant power

It is totally realistic to expect variable currents or loads such as automotive load regime:



The current itself will be constant for the constant current discharge;
For the constant power mode, current increases with progression of discharge because voltage decreases.
For constant load current decreases with voltage decrease to counter the unchanging resistance (i.e., load) conditions.



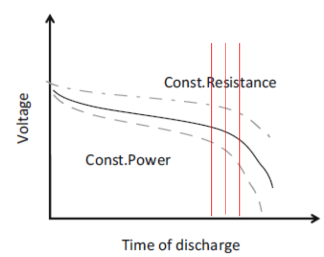
MODES OF DISCHARGE

In each case, the shape of curve is similar, but useful capacity is exhausted and **sharp voltage drop** takes place at different times.

This point is reached the soonest in the case of constant power.

It is followed by a longer discharge time for constant current (solid line)

constant resistance takes the longest time to reach the full discharge because the current adjusts with the voltage drop to, keep the load constant hence both voltage and current decrease means that the discharge slows down near the end of the process.

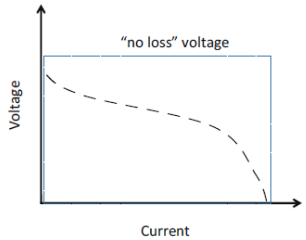


DISCHARGE CURRENT EFFECT ON VOLTAGE

It is obvious that the higher the discharge current, the lower is the voltage.

The theoretical assumption is that only after active mass is completely used in a reaction will the voltage drop to zero.

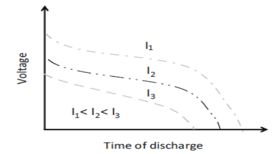
Practical voltage is, however, very different. In the first region, even at small current densities, the voltage is lower than the open circuit or thermodynamic, i.e., theoretical voltage. The reason for this is a voltage drop described as activation overpotential.

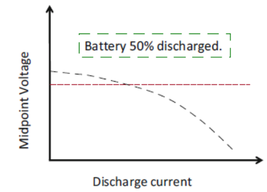


DISCHARGE CURRENT EFFECT ON VOLTAGE

As current increases, the resistive losses become significant and dominate the voltage loss for the majority of the curve. At the highest current densities for a specific battery, the voltage sharply drops because of the inability of a system to provide reactants fast enough. At that point, there are really no reactants left, which means that everything is converted to products. So, the concentration or availability of anode approaches zero and causes a voltage drop, which leads to the end of discharge reaction.

Below this nominal current, the midpoint voltage is higher and above the nominal current the midpoint voltage is lower. For current higher than the nominal, the midpoint voltage value is lower.





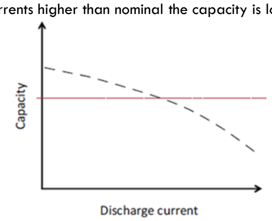
A midpoint voltage is the **nominal voltage** of a battery and is measured when a battery is discharged to 50% of the capacity.

DISCHARGE CURRENT EFFECT ON CAPACITY

As we know:

Battery capacity is the total number of ampere-hours(Coulombs) that a battery can deliver under specified or nominal discharge current and temperature. (declared by manufacturer)

Since nominal capacity is given for a certain discharge current, it must be that the capacity changes with the value of the discharge current. The nominal capacity is obtained for certain, nominal discharge current and is indicated by the horizontal line. For currents lower than the nominal discharge current, capacity higher than nominal or 100% is obtained, while for currents higher than nominal the capacity is lower.

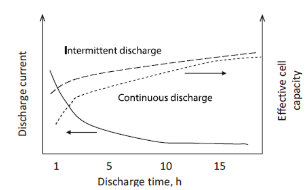


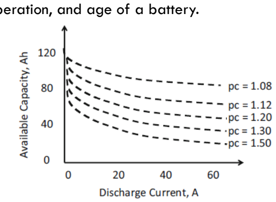
DISCHARGE CURRENT EFFECT ON CAPACITY

The Peukert equation gives the means to calculate capacity for a specific current if capacity is known for another current.

$$Q_2 = Q_1 \left(\frac{I_1}{I_2}\right)^{pc-1}$$

The calculated capacity Q2 is mainly dependent on the Peukert coefficient (pc), which is related to internal resistance of the cell and varies not only by battery systems but also by design of the same battery chemistry, temperature of operation, and age of a battery.





Battery system/type	pc
Lead–acid, flooded	1.2–1.4
Lead–acid, VRLAB	1.15–1.25
Ni–Cd	1.10–1.20
Ni–MH	1.05–1.15
Li–ion	1.05–1.1
Ideal battery	1.0

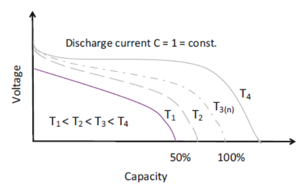
THE EFFECT OF TEMPERATURE ON BATTERY PERFORMANCE

For all reactions : Temperature ↑ ⟹ Rate of reaction ↑

For batteries: Temperature ↑ ⟹ cell voltage and capacity ↑

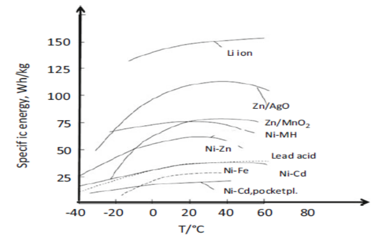
One hundred percent capacity should be obtained at the nominal temperature of 25 C (curve 3). At higher temperatures, higher capacity is obtained and at lower temperature, lower capacity.

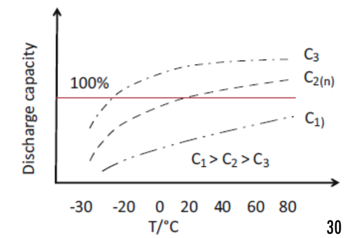
Lower temperatures and higher C rates result in lower cell voltages; and higher temperatures and lower C-rates lead to higher cell voltages.



THE EFFECT OF TEMPERATURE ON BATTERY PERFORMANCE

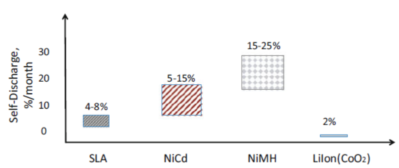
When capacity versus temperature is plotted for different C-rates a trend revealed is an increase in capacity from lower to higher temperature and for lower C rates. The dashed line represents nominal capacity at a certain C rate, typically C/12 and nominal temperature, typically 20°C. For higher C-rates and lower temperatures, the capacity is lower and for lower C rates and higher temperature the capacity is higher than nominal.

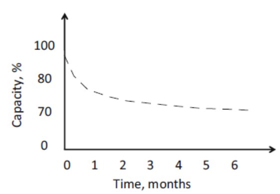




SELF-DISCHARGE

refers to a loss of capacity through involuntary reaction during the battery storage and when battery is not connected to a load. The reactions are mainly caused by thermodynamic instabilities between active masses and cell components, resulting in consumption of active masses.



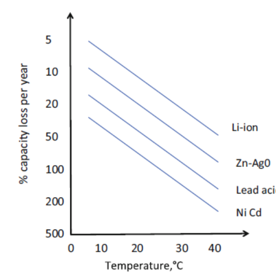


The rate of self-discharge is dependent on the battery type. Each battery system has different rate of self-discharge.

SELF-DISCHARGE

Storing batteries at high temperatures is detrimental to their capacity retention since self-discharge reaction rates increase. Note that the capacity loss per year can be larger than 100%, which means that a battery capacity will be completely lost in less than a year.

Battery chemistry	Rechargeable	Typical self-discharge or shelf life
Lithium metal	No	10 years shelf life
Alkaline	No	5 years shelf life
Zinc–carbon	No	2–3 years shelf life
Lithium–ion	Yes	2–3% per month
Low self-discharge NiMH	Yes	As low as 0.25% per month
Lead–acid	Yes	4–6% per month
Nickel–cadmium	Yes	15–20% per month
Nickel–metal hydride (NiMH)	Yes	30% per month



CYCLIC LIFE

cyclic life:

It determines how many times a battery will be able to deliver charge–discharge cycles without its capacity dropping below a certain level, typically 80% of the original capacity.

The problem with battery cycle life is that it can only be estimated based on general empirical information and not absolutely determined.

Battery	Calendar	Cycle life
Lead–acid, SLI	3–6 months	200–700
Sealed NiCd (FNC)	5–20 months	500–10,000
Nickel metal hydride	2–5 months	300–600
Nickel iron	8–25 months	2000–4000
Zinc–silver oxide	2 months	50–100
Lithium cobalt oxide	/	300–1000

CYCLIC LIFE

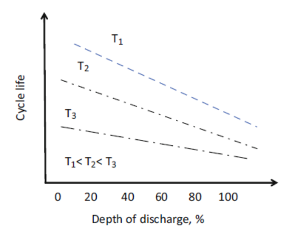
Why is it hard to determine battery end of life?

1-Experimental determination of the battery cycle life require a very long test time and a large number of batteries would need to be tested to failure.
2-higher C-rates and different load are experienced by the electronic device
3-The interconnectedness of numerous battery design parameters and operational factors such as voltage, current, self-discharge, internal resistance, and temperature
4-batteries employed in actual applications could be operating in very different conditions of temperature and actual depth of discharge

CYCLIC LIFE

How DoD effects battery life?

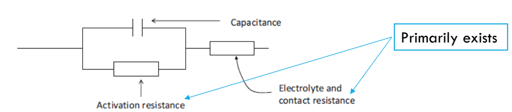
The greater the depth of discharge, the shorter or lower the cycle life. Battery cycle life depends on the battery chemistry, construction, and **materials used**; and a nominal cycle life will be determined assuming that all active electrode masses are going to be engaged in charge and discharge reactions in every cycle. But, if a battery is not fully discharged on every cycle some of the active masses are not involved in the reaction and this has a positive effect on the battery life.



INTERNAL RESISTANCE

The internal battery resistance determines how much current can pass through a cell. The internal resistance is one of the best indicators of battery health. It deteriorates gradually during the life of a battery and it sometimes shows early signs of reactions that contribute to its increase.

Equivalent circuit model:

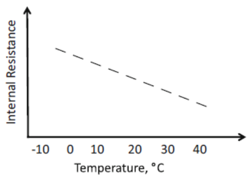


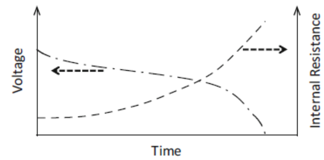
Over the lifetime of a battery, additional resistive and capacitive components may develop as a result of processes that produce passive layers or deposits. The appearance of those additional battery interfaces usually increases the internal resistance, reduces the rate of electrochemical reaction, increases resistance and ohmic losses, and slows down diffusion of species to electrode active sites.

INTERNAL RESISTANCE

During discharge of a battery, the internal resistance increases. This is mainly because of the changes in the electrolyte as in lead–acid batteries or as a result of formation of passivating layers through which the reactants have to diffuse.

As temperature increases, the internal resistance decreases. It is also obvious that ionic electrolyte conductivity increases with temperature increase due to higher ionic mobility.





SIDE REACTIONS

Side Reaction:

Side reactions are unwanted chemical processes that occur within a battery, competing with the primary charge-discharge reactions. These reactions can significantly impact a battery's performance, lifespan, and safety.

Common side reaction:

Electrolyte Decomposition: Electrolyte molecules can break down, forming gases (like hydrogen or oxygen) or solid-electrolyte interface (SEI) layers on the electrode surface.

Electrode Material Degradation: The active materials in the electrodes can undergo chemical changes, leading to capacity loss and power fade.

Dendrite Formation: In certain battery chemistries, metallic dendrites can grow on the electrode surface, causing short circuits and safety hazards.

Gas Evolution: The production of gases within the battery can cause swelling, pressure build-up, and potential explosions.