Electrochemistry. — Derek Pletcher, Frank C. Walsh } Industrial Electrochemistry

An electrochemical cell (EC) is a device capable of either deriving electrical energy from chemical reaction or facilitate chemical reactions through the introduction of electrical energy.

There are two types of EC, Based on Rxn:-

1. Spontaneous reactions → Galvanic (voltic) cells.
   $\Delta G = -ve$

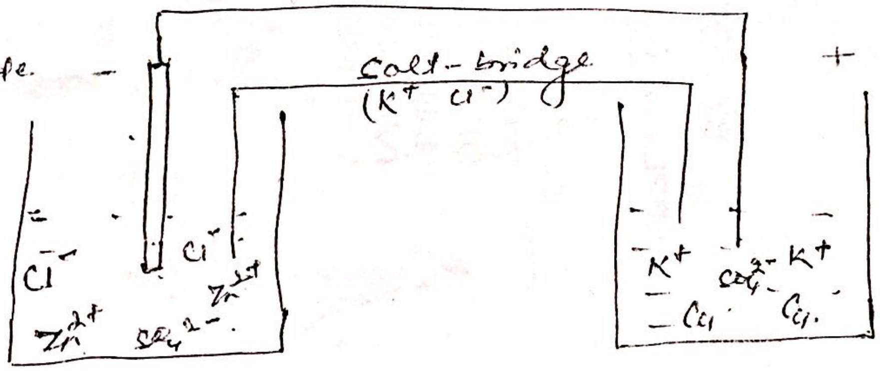
2. Nonspontaneous reactions → Electrolytic cells.
   eg chlor-alkali cells.

1. Galvanic (voltic cells)
→ by separating the oxidizing agent from the reducing agent, electrons are transferred via an external conducting medium (redox reaction involved)

eg. $Cu^{2+}(aq) + Zn(s) \rightleftharpoons Cu(aq) + Zn^{2+}(aq)$

Anode − where oxidation occurs

Cathode + where reduction occurs



$Zn(s) \downarrow Zn^{2+}(aq) + 2e^-$

$Cu^{2+}(aq) + 2e \downarrow Cu(s)$

Anode — Cathode

$Zn(s) / Zn^{2+}(aq) \,||\, Cu^{2+}(aq) \,|\, Cu(s)$

phase boundary — salt bridge — phase boundary

→ Zn–Cu Galvanic cell (Daniell cell)

Read in XII.
– oxidation – Red
– half cells
– EMF
– Nernst eq
– Laws of electrolysis.

→ 16th Century ↓ Beg of scientific understanding of electricity and magnetism

Sperm Motility

The motility of sperm in cauda epididymis was hampered to a greater extent after administration of sulphaguanidine which could be attributed to altered milieu of different parts of epididymis due to reduced androgen supply to the organ, which rendered it hostile to the motility of spermatozoa and finally the fertilizing ability.[24]

→ Mid 18th Century ↓ Like charge repel each other and unlike charges attracts.

It has been reported that androgen binding protein (ABP) binds with testosterone and makes the ABP – testosterone complex then reaches to the epididymis through the testicular fluid.[25] and maintains the epididymal testosterone levels, this study suggests that the action of the drug could target the internal milieu of the epididymis due to the low level of testosterone.[26]

→ 18th Century ↓ Birth of electrochem

Low fructose concentration in seminal vesicle following sulphaguanidine treatment to rats may be another cause of low sperm motility. Fructose is a main secretory product of seminal vesicle and an energy source for sperm.[27] ~~Carballada and Esponds in 1992~~[28] observed that when seminal vesicle is partially removed from fertile male rats the fertility was completely suppressed.

→ First reaction was in 1800 AD, separation of Hydrogen and oxygen from water by electrolysis by English chemist.

Sperm Density

Determination of sperm counts in the testis, epididymis and ejaculated semen is an important assessment of testicular function and male fertility. The marked reduction in cauda epididymal and testicular sperm counts were noticed after sulphaguanidine drug treatment. This finding may be a consequence of an

E_{cell} = Higher Red Pot – Lower Red Pot
= $E_{right} - E_{left}$
= $E_{red} - E_{oxi}$

→ Galvanic Cells produce direct current.

→ Another example, lead-acid battery contains a number of glavanic cells. The two electrodes are lead and lead oxide.

$$EMF = E^{\circ}_{right} - E^{\circ}_{left} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

Salt Bridge

As electron leave one half of a glanic cell and flow to other, difference in charge develop. If salt-bridge is not there, charge diff will prevent the flow of electrons.

So, a salt bridge only allow the flow of ions and hence maintains the electrical neutrality between the oxidation and reduction half keeping the content separate.

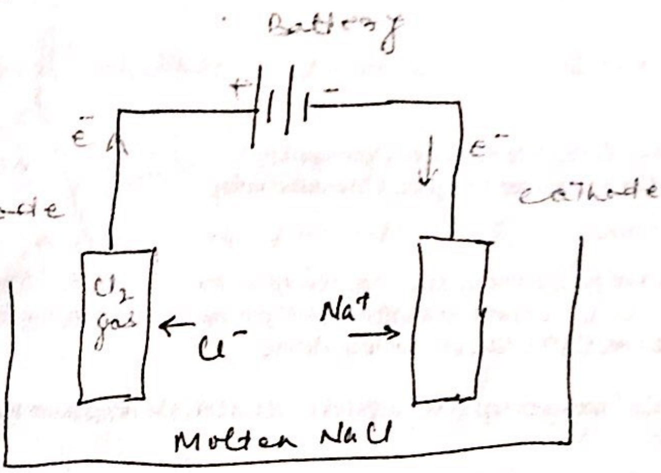
It is made up of usually KCl or NaCl or KNO_3 gelefied over agar-agar (a gelatinous substance from red algae).

Agarose polymer (linear polymer of disaccharide agarobiose, D-galactose + 3,6-anhydro-L-glactopyranose.

Electrodes

	Electrolytic cell	Galvanic cell
	Anode → +ve (Attracts anions from the solution)	−ve (spontaneous oxidation is source of electrons)
	Cathode → −ve	+ve
Anode →	oxidation	oxidation
Electron flow →	Anode to Cathode	Anode to Cathode

Electrolytic Cell



Electrical energy is required to induce the electrolysis reaction. The Na^+ migrate towards cathode $2Na^+ + 2e^- \rightarrow 2Na$

Cl^- migrate towards anode $2Cl^- \rightarrow 2e^- + Cl_2(g)$

This type of cell is used to produce sodium and chlorine. Sodium being less dense than molten salt and is removed as it floats to the top of the reaction container.

Cells are classified into two broad categories:-

i) Primary Cells:- when initial supply of reactants is exhausted, energy cannot be readily ~~restor~~ restored by electrical means. eg. Zn-carbon cells
Alkaline cells
Manganese oxide bat

(ii) Secondary Cell:- can be recharged. original composition can be restored.

eg. lead-acid cell.
Ni-Cd cell
Ni metal hydride cells

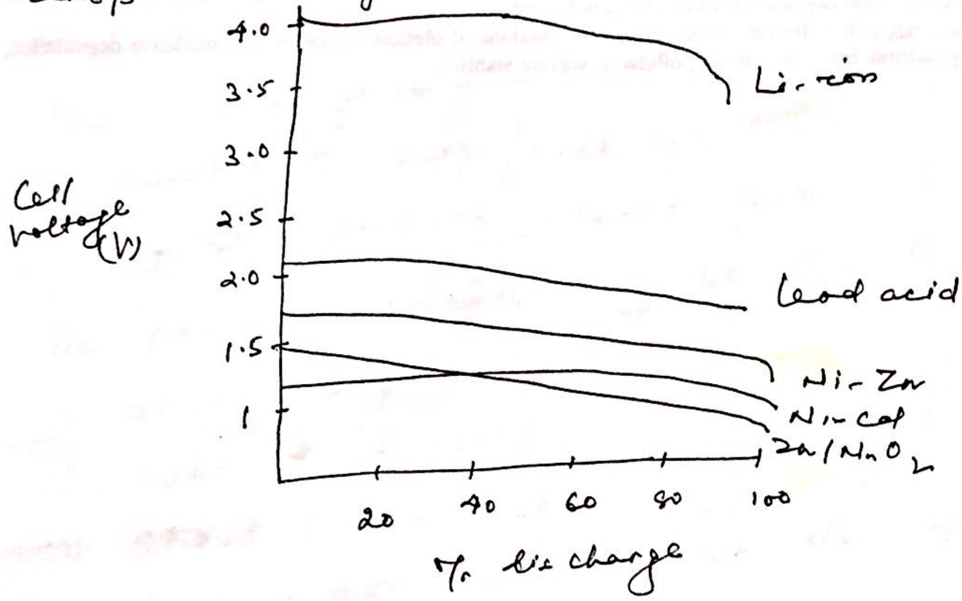
Italian Physicist Alessandro Volta in 1792
1800 he invented the first battery

Battery characteristics :-

1. Type → whether primary or secondary

2. Voltage → 1.2 V for a Ni-Cd battery to 3.7 V for Li-ion
There is always difference between the theoretical calculations and actual outputs.

3. Discharge curve → This is a plot of voltage against percentage of capacity discharged. A flat discharge curve is desirable as this means that the voltage is constant as battery is being used up. Usually internal resistance cause the drop in voltage.



4. Capacity → The theoretical capacity $Q = xnF$
where x = no of moles of reactions
n = no of electron transfer per mole of reaction
F = Faraday constant
This is basically quantity of electricity involved in the electro-chemical reactions.

5. Energy density :→ Energy that can be derived per unit volume of cell. watt-hrs/litre. which is meas Same unit as pressure

6. Specific Energy density :-

Energy derived per unit weight of active electrode material / cell weight watt hr/Kg

7. Power density :- Power per unit weight of cell.

8. Temperature Dependance :-

Low Temp → higher internal resistance

→ electrolyte may freeze giving lower voltage

High Temp → Unwanted reactions / reverse reaction may start

9. Service Life :-

For a rechargeable battery, it can be defined as the number of charge/recharge cycles a secondary battery can perform before falling 80% of its capac

The premature death may be due to :-

(i) over-charging
(ii) over-discharging
(iii) short circuiting
(iv) Drawing more current than its capacity
(v) subjecting to extreme Temp.
(vi) " to physical shock.
(vii) Depletion of active materials used.

10. Physical requirements :-

- geometry of cell
- its size
- weight
- shape
- location of terminals

11. Charge/discharge cycle — no. rate at which charge is drawn from the cell C/n

12. Cycle life — no. of charge/discharge cycles that are possible before failure. C = capacity, n = hours etc

13. Cost — Initial + maintaining

14. Ability to deep discharge :-

There is a logarithmic relationship between depth of discharge and life of a battery. Usually mobile battery lasts 5-6 time longer if it is only 80%. discharged before recharging.

15. Application requirements :-

Zinc/Carbon Batteries :-
- Leclanche Cell by Georges Leclanche in 1866.
- voltage 1.5 – 1.75 V
- Service life : 110 min (continuous use)
- Shelf life : ~ 1-2 years at room temp.

Chemistry

Anode – Zinc

Cathode – Manganese dioxide

* carbon is added to the cathode to increase the conductivity and retains moisture.

Anode $\rightarrow Zn \rightarrow Zn^{2+} + 2e^-$

Cathode $\rightarrow 2NH_4^+ + 2MnO_2 + 2e^- \longrightarrow Mn_2O_3 + H_2O + 2NH_3$

However this is complicated by the fact that NH_4^+ produces two gaseous products,

$$2NH_4^+ + 2e^- \longrightarrow 2NH_3 + H_2$$

These are removed as

$$ZnCl_2 + 2NH_3 \longrightarrow Zn(NH_3)_2Cl_2$$

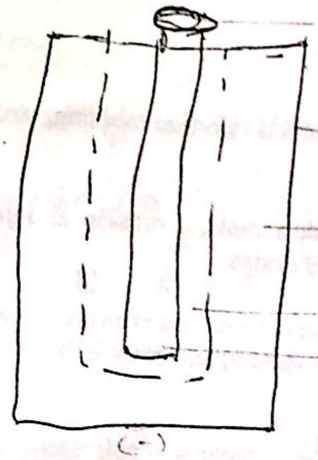
$$2MnO_2 + H_2 \longrightarrow Mn_2O_3 + H_2O$$

$Zn(NH_3)_2^{2+} + H_2O$

Over all Rxn :-

$Zn(s) + 2MnO_2(s) + 2NH_4^+ \ldots \rightarrow Zn(NH_3)_2^{2+} + H_2O$

Construction



Electrolyte

NH_4Cl — 26 %.

$ZnCl_2$ — 8.8 %.

H_2O → 65.27 %.

Corrosion inhibitor — 0.25–1 %.

Application

torches, radios, toys

Lead Storage

1859 by French physicist Gaston Plante

- voltage : 2V (for SLI used in motor vehicle)
- service life : several years

SLI - starting vehicle lighting ignition

Chemistry

Lead as anode

$$Pb(s) + HSO_4^- \longrightarrow PbSO_4 + H^+ + 2e^-$$

Lead oxide as cathode

$$PbO_2 + 3H^+ + HSO_4^- + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

Overall $$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

During charging process, the reactions at each electrode are reversed, the anode becomes the cathode and cathode becomes anode.

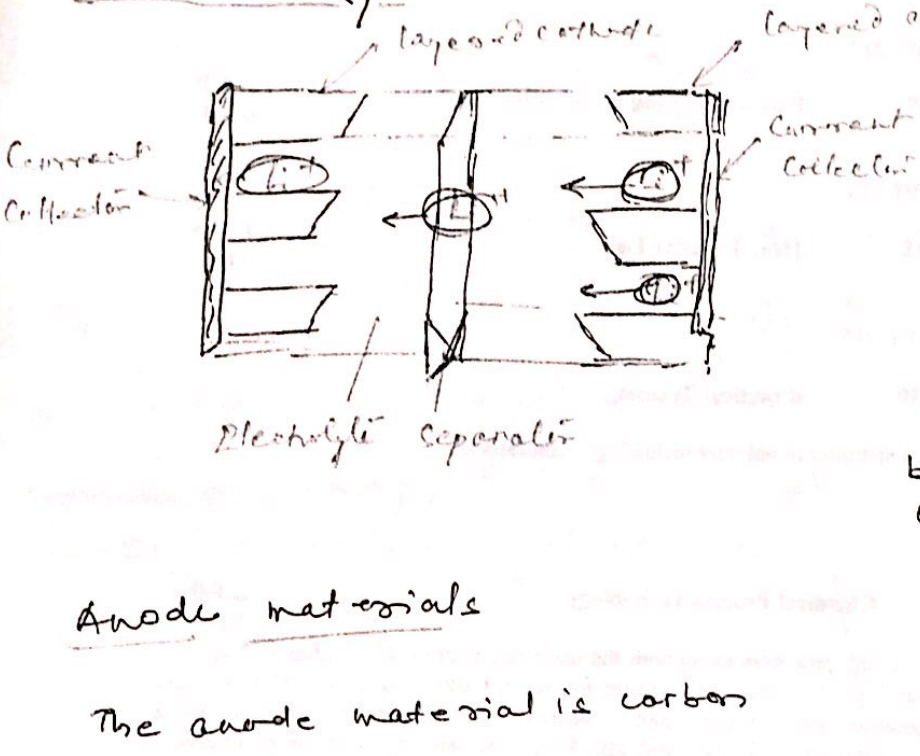
Lithium Batteries:-

Work started in 1912 under G N Lewis but only in 1970s first non-rechargeable Li-batteries became commercially available.

Due to safety problems, the Li-rechargeable batteries was difficult and hence non-metallic Li-ion batteries was typical. (Li-metal as such is very unstable and also with water gives vigorous reaction with flammable hydrogen as the product.

Hence in 1991, the Sony corporation commercialized the first Li-ion batteries and then other manufacturer

CHEMISTRY



The most common compds used for cathode materials are $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$

best performance but has other limitations: like - cost - toxic - active or limited Li content.

Cheap and better for environment.

Anode materials

The anode material is carbon based $Li_{0.5}C_6$.

Electrolyte

Since Li reacts fast and vigorous with water and the cell voltage is high enough for water decomposition hence, non-aqueous electrolyte must be used. One example is $LiPF_6$ dissolved in ethylene carbonate and dimethyl carbonate mixture.

At anode : $xLi^+ + Mn_2O_4 \longrightarrow Li_xMn_2O_4$

Cathode : $Li_xC_6 \longrightarrow xLi^+ + 6C + xe^-$

overall : $Li_xMn_2O_4 + 6C \longrightarrow Li_xC_6 + Mn_2O_4$

Advantages

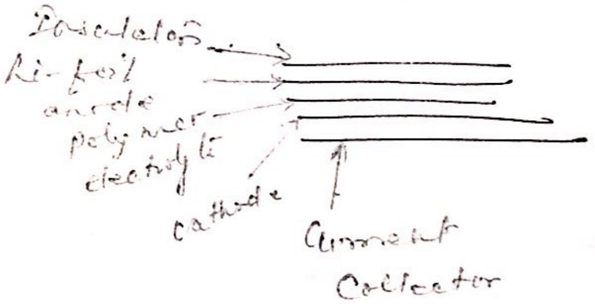
- high energy density and potential for higher capac
- one regular charge is enough
- Relatively low self discharge
- low Maintenance
- some cells can provide higher current also

Limitations

- Require protection circuit to maintain V and I within safe limits
- Subject to aging even if do not use
- Transportation restrictions
- Expensive to manufacture
- still in developing phase

Lithium Polymer batteries

Another way of overcoming the reactivity is to use solid polymer electrolyte.



Try to maintain the thin film of electrolyt to decrease total resistance.

Polycarbonmonofluoride, (CF)

The life cycle Li-ion = 500 to 1000 cycles.