

ELECTROCHEMISTRY



1

Electrochemistry

- Study of chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte)
- An electrochemical reaction is one which:
 - A chemical reaction is driven by an external applied voltage (electrolysis) [electrolysis; the Greek word *lysis* means *to break up*]
 - A voltage is created by a chemical reaction as in a battery

2

There are 2 types of electrochemical cell:

- 1. Galvanic - a **spontaneous** chemical change generates a current of electrons - does work by releasing free energy from a spontaneous reaction to produce electricity such as a battery
- 2. Electrolytic - a current **causes** a **non-spontaneous** chemical change - does work by absorbing free energy from a source of electricity to drive a non-spontaneous reaction such as electroplating.

3

Electrodes

- The electrodes typically are two metals, which naturally have different reaction potentials relative to the electrolyte.
- This causes ions of one of the electrodes to preferentially enter the solution at one electrode, and another ion to leave the solution at the other electrode.
- This generates an electric current across the electrolyte, which will drive electric current through a wire that makes an exterior connection to each of the electrodes.

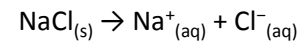
4

- The anode is defined as the electrode where oxidation occurs and the cathode is the electrode where the reduction takes place.
- Electrodes can be made from any sufficiently conductive materials, such as :
 - metals,
 - semiconductors,
 - graphite,
 - conductive polymers
- In between these electrodes is the electrolyte, which contains ions that can freely move.

5

Electrolyte

- An electrolyte is any substance containing free ions that behaves as an electrically conductive medium.
- Electrolytes commonly exist as solutions of acids, bases or salts.
- For example, when table salt, NaCl, is placed in water, the salt (a solid) dissolves into its component elements, according to the dissociation reaction



6

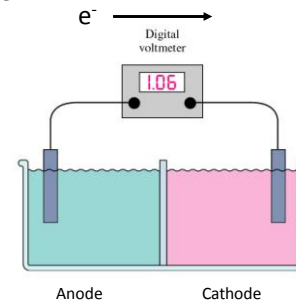
Volt & EMF

- The force on the electrons causing them to flow is referred to as the electromotive force (EMF). The unit used to quantify this force is the volt (V)
- 1 volt = 1 Joule/Coulomb of charge
- $V = J/C$

7

Cell Potentials (cont.)

- We can measure the magnitude of the EMF causing electron (i.e., current) flow by measuring the voltage.



8

Oxidation and Reduction

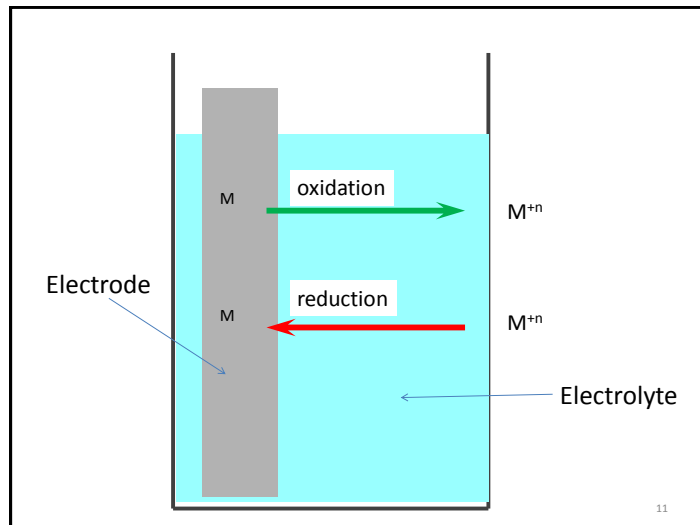
- An atom or ion that gives up an electron to another atom or ion has its oxidation state increase.
- An atom or ion that receives an electron from another atom or ion has its oxidation state decrease.
- Oxidation and reduction always occur in a paired fashion such that one species is oxidized when another is reduced.

9

Oxidation and Reduction

- loss of electrons from an atom or molecule is called oxidation, and the gain of electrons is reduction
- Best remembered as "*OIL RIG*" (Oxidation Is Loss, Reduction Is Gain)
- The atom or molecule which loses electrons is known as the *reducing agent*, or *reductant*,
- The substance which accepts the electrons is called the *oxidizing agent*, or *oxidant*.

10



Oxidation and Reduction

- The oxidizing agent is always being reduced in a reaction
- The reducing agent is always being oxidized.
- Despite the name, an oxidation reaction does not necessarily need to involve oxygen.
- For reactions involving oxygen, the gain of oxygen implies the oxidation of the atom or molecule to which the oxygen is added (and the oxygen is reduced).

12

Oxidation and Reduction

- In many organic compounds, the loss of hydrogen implies oxidation of the molecule from which it is lost (and the hydrogen is reduced).
- Conversely, loss of oxygen or gain of hydrogen from a molecule implies reduction.

13

Broader definition of: Oxidation and Reduction

- **Oxidation** describes the *loss* of electrons / hydrogen or *gain* of oxygen / *increase* in oxidation state by a molecule, atom or ion.
- **Reduction** describes the *gain* of electrons / hydrogen or a *loss* of oxygen / *decrease* in oxidation state by a molecule, atom or ion

14

Reduction- Oxidation (Redox)

- An electron can be transferred to or from a molecule or ion changing its oxidation state.
- This reaction can occur through the application of an external voltage or through the release of chemical energy.
- Such a reaction is known as Reduction-Oxidation (Redox).

15

Redox

- **Redox** (shorthand for **reduction-oxidation** reaction) describes all chemical reactions in which atoms have their oxidation number (oxidation state) changed.
- Describing the overall electrochemical reaction for a redox process requires a *balancing* of the component half-reactions for oxidation and reduction.

16

Galvanic cell

- Electrochemical cell that converts chemical energy into electrical energy, by using spontaneous chemical reactions that take place at the electrodes.
- A Galvanic cell has its own characteristic voltage (defined as the energy release per electron transfer from one electrode to the other).

17

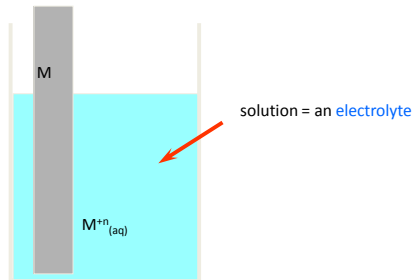
Galvanic cell

- A simple galvanic cell will consist only of an electrolyte and two different electrodes.
- A galvanic cell uses electrodes of different metals
- Galvanic cells can also be made by connecting two half-cells, each with its own electrode and electrolyte, by an ion-transporting "bridge", usually a salt bridge.

18

A Half Cell

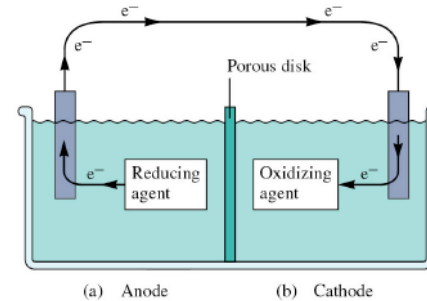
- metal = an **electrode**



19

Galvanic Cell

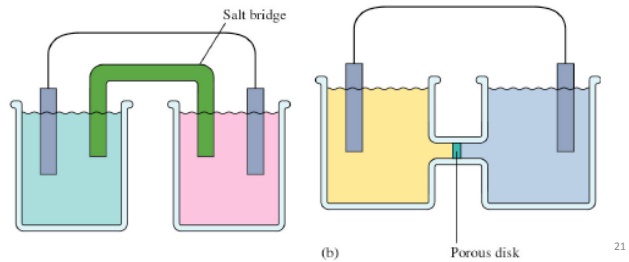
- Reduction occurs at the cathode
- Oxidation occurs at the anode
- **CAT**ions migrate towards the **CAT**hode
- **AN**ions migrate towards the **AN**ode



20

Galvanic Cells

- Salt bridge/porous disk: allows for ion migration such that the solutions will remain neutral.

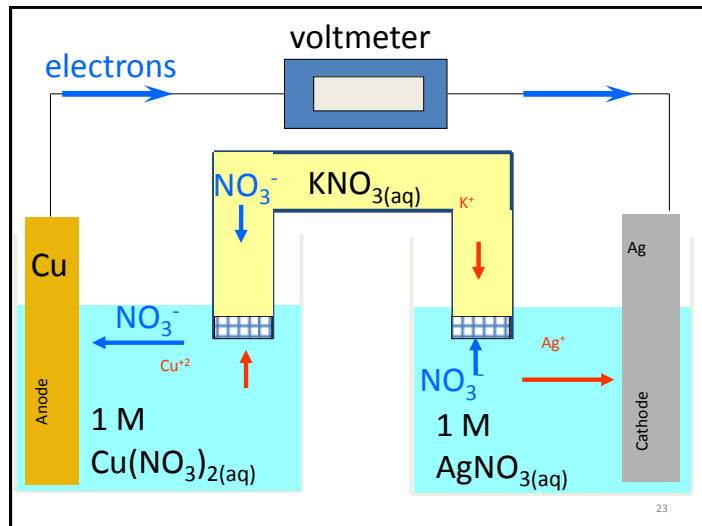


21

Salt Bridge

- Pack tube with a viscous, aqueous solution of KCl or KNO_3 .
- The viscosity prevents mixing with the electrolytes.
- The ions permit exchange of charge.
- The chosen ions have similar mobility to minimize junction potentials.

22



23

Standard electrode potential

- Tabulations of Standard Electrode Potential are referenced to the standard hydrogen electrode (SHE).
- The standard electrode potential for the SHE is zero, by definition.
- The polarity of the standard electrode potential provides information about the relative reduction potential of the electrode compared to the SHE.

24

Standard Potential Table

- If the electrode has a positive potential with respect to the SHE, then that means it is a strongly reducing electrode

$F_2 + 2e^-$	$2F^-$	+2.87
$Co^{3+} + e^-$	Co^{2+}	+1.81
$Au^+ + e^-$	Au	+1.69
$Ce^{4+} + e^-$	Ce^{3+}	+1.61
$Br_2 + 2e^-$	$2Br^-$	+1.09
$Ag^+ + e^-$	Ag	+0.80
$Cu^{2+} + 2e^-$	Cu	+0.34
$Sn^{4+} + 2e^-$	Sn^{2+}	+0.15
$2H^+ + 2e^-$	H_2	0.0000

25

Standard Potential Tables

- if the measured potential is negative, the electrode is more oxidizing than the SHE

$2H^+ + 2e^-$	H_2	0.0000
$Pb^{2+} + 2e^-$	Pb	-0.13
$Sn^{2+} + 2e^-$	Sn	-0.14
$In^{3+} + 3e^-$	In	-0.34
$Fe^{2+} + 2e^-$	Fe	-0.44
$Zn^{2+} + 2e^-$	Zn	-0.76
$V^{2+} + 2e^-$	V	-1.19
$Cs^+ + e^-$	Cs	-2.92
$Li^+ + e^-$	Li	-3.05

26

Selected Standard Electrode Potentials

Half-Reaction

E^0 (V)

$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	-0.23
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.05

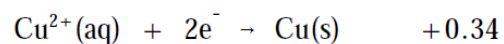
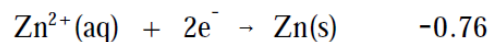
27

- $F_2(g)$ is the BEST oxidizing agent (and the most easily reduced i.e. it is electronegative)
- $Li^+(aq)$ is the WORST oxidizing agent (and the most difficult to reduce i.e. receive electrons)
- $Li(s)$ is the BEST reducing agent (and the most easily oxidized i.e. it is electropositive)
- $F^-(aq)$ is the WORST reducing agent (and the most difficult to oxidize i.e. donate electrons)

28

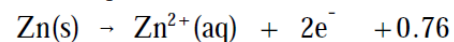
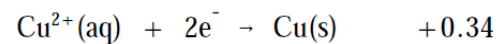
How do we obtain Standard Cell Potentials from Standard Reduction Potentials?

- What would the Standard Cell Potential be for a Cu|Cu²⁺ and Zn|Zn²⁺ cell?
- Step 1. Write out the two S.R.P. equations:



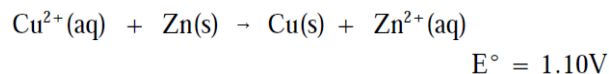
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- Step 2. The half-reaction with the **more positive half cell potential goes as written and the other half-cell is driven in the reverse direction**



30

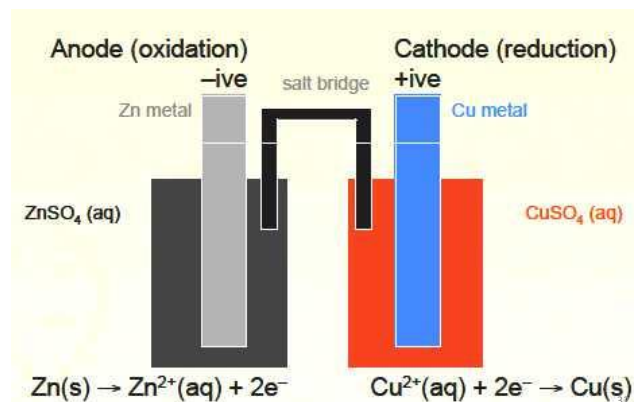
- Step 3. Are the electrons balanced?
- Step 4. Now add



- Note that the E° value is POSITIVE, i.e. the reaction is spontaneous

31

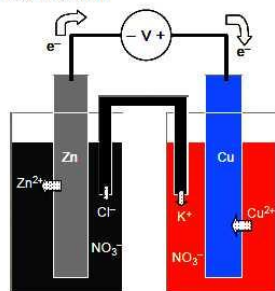
A Zn/Cu Galvanic cell



A Zn/Cu Galvanic cell

Flow of Charge

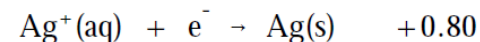
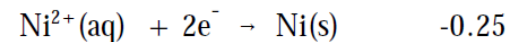
How does charge flow in a cell?



If concentrations are 1M, then the cell is at standard conditions and the measured potential is +1.10 V.

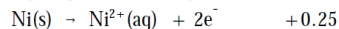
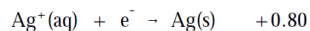
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- Now look at the Ni|Ni²⁺_(aq) and Ag|Ag⁺_(aq) cell.
- What is the spontaneous cell reaction, anode, cathode, E°?
- Step 1. Get SRPs from Tables

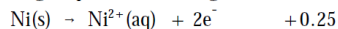
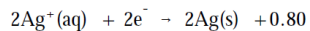


34

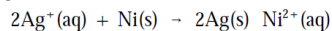
- Step 2: More +ve goes as written, other in reverse



- Step 3. Get electrons to balance:



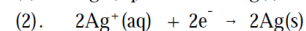
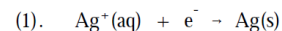
Step 4. Now add



$$E^{\circ} = +1.05 \text{ V}$$

35

- Does anything strike you as odd about this??
- Although we multiplied the coefficients in the Silver half-cell by 2, we did NOT double the half-cell voltage. Why NOT ??
- Compare



36

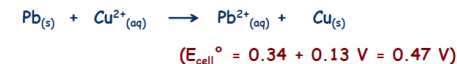
- The **ENERGY release by (2) is certainly twice that** of (1), but remember that

$$\text{Voltage} = \text{Joules/Coulombs}$$

- (energy per coulomb of charge transferred)
- Equation (2) involves twice the energy, but it also involves twice the coulombs - so the **VOLTAGE** does not change.

37

- Always combine half cells to obtain an overall cell potential that is positive.
- A cell will always run spontaneously in the direction that produces a positive cell potential



38

- The oxidation half cell potential will be the reverse of a tabulated reduction potential.
- The overall cell potential is then given by:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} - E^{\circ}_{\text{oxidation}}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

- This equation applies for Galvanic cells

39

Electrolysis

- The splitting of a substance or decomposing by **forcing** a current through a cell to produce a chemical change for which the cell potential is **negative**.

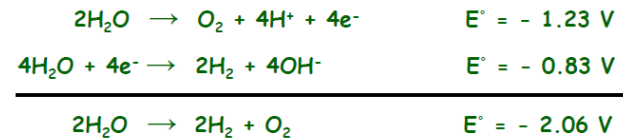
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- An electrolytic cell has three component parts: an electrolyte and two electrodes (a cathode and an anode).
- The electrolyte is usually a solution of water or other solvents in which ions are dissolved.

41

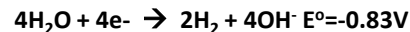
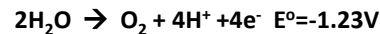
Electrolysis of water

- Electrolysis involves the use of electrical energy to produce a chemical change
- Forcing current through a cell to produce a chemical change for which the cell potential is negative i.e. using electrical energy to make a non-spontaneous process occur

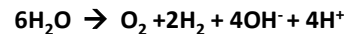


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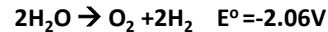
Electrolysis of water



- Overall reaction is:



- Note that $4\text{OH}^- + 4\text{H}^+ = 4\text{H}_2\text{O}$, therefore the Net reaction is

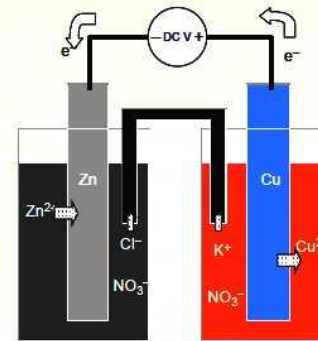


- Since it is the same reagent being used on both sides, the two sides of the equation are added up.

43

An Electrolytic cell

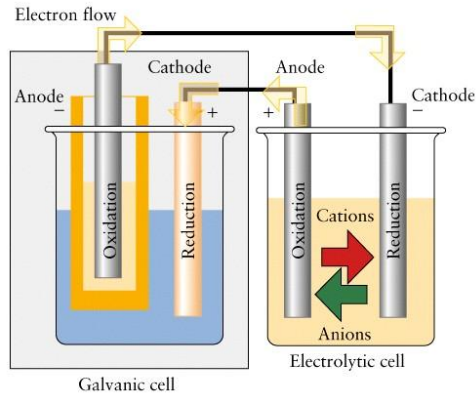
What about running the cell in reverse?



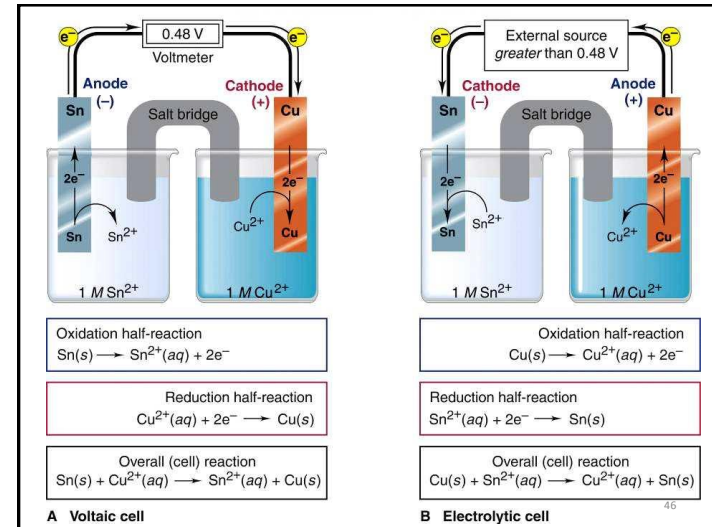
- apply an external voltage of opposite polarity.
- magnitude must exceed the +1.10 V that the cell produces on its own.
- Cu electrode now dissolves and Zn now plates out on its electrode.

44

A voltaic (Galvanic) cell can power an electrolytic cell



45



46

Primary cell

- A **primary cell** is any kind of electrochemical cell in which the electrochemical reaction of interest is not reversible, so is used in disposable batteries. The most common primary cells today are found in alkaline batteries; earlier, carbon-zinc cells, with a carbon post as cathode (+) and a zinc shell as anode (-) were prevalent.

47

Examples of Electrochemical Cells: Dry cell

- Dry cells do not have a fluid electrolyte, instead, they use a moist electrolyte paste.
- The anode is a zinc container surrounded by a thin layer of manganese dioxide
- A moist electrolyte paste of ammonium chloride and zinc chloride is mixed with starch.
- The cell's cathode is represented by a carbon bar inserted on the cell's electrolyte, usually placed in the middle.

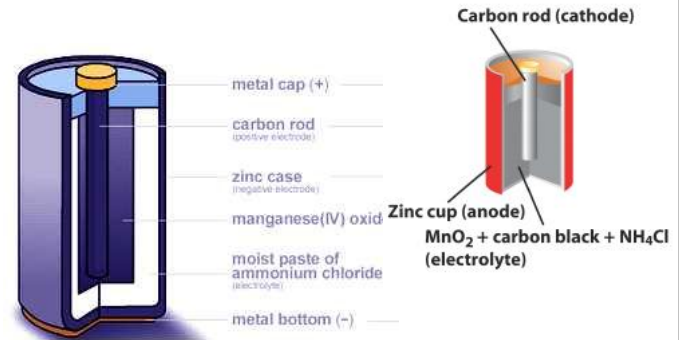
48

Zinc-carbon battery

- A **zinc-carbon dry cell or battery** is packaged in a zinc can that serves as both a container and anode. The cathode is a mixture of manganese dioxide and carbon powder. The electrolyte is a paste of zinc chloride and ammonium chloride dissolved in water. Zinc chloride cells are an improved version from the original ammonium chloride variety. Zinc-carbon batteries are the least expensive primary batteries and thus a popular choice by manufacturers when devices are sold with batteries included. They can be used in remote controls, flashlights, toys, or transistor radios, where the power drain is not too heavy.
- The battery has an e.m.f. of about 1.5 V.

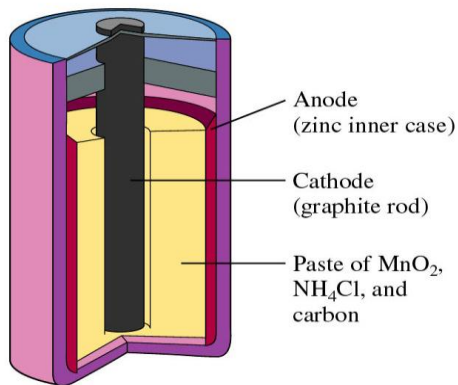
49

Zinc-carbon battery



50

Zinc-carbon battery



51

Zinc-carbon battery

- Zinc anode (the can itself)
- Graphite cathode surrounded by MnO₂(s) and NH₄Cl(aq), which is acidic
- The approximate equation is:
- $\text{Zn(s)} + 2\text{MnO}_2\text{(s)} + 4\text{NH}_4^+\text{(aq)} \rightarrow \text{Zn(NH}_3)_4^{2+}\text{(aq)} + 2\text{MnO(OH)(s)} + 2\text{H}^+\text{(aq)}$
- Approximately 1.5 V.
- 6 V battery = 4 cells in series
- 9 V battery = 6 cells in series

52

Alkaline battery

- The alkaline battery gets its name because it has an alkaline electrolyte of potassium hydroxide, as opposed to the acidic electrolyte of the zinc-carbon batteries which are offered in the same nominal voltages and physical size.
- The half-reactions are:
- $\text{Zn (s)} + 2\text{OH}^- \text{(aq)} \rightarrow \text{ZnO (s)} + \text{H}_2\text{O (l)} + 2\text{e}^-$
 $2\text{MnO}_2 \text{(s)} + \text{H}_2\text{O (l)} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 \text{(s)} + 2\text{OH}^- \text{(aq)}$

53

Alkaline battery

- In an alkaline battery, the anode (negative terminal) is made of zinc powder (which allows more surface area for increased rate of reaction therefore increased electron flow) and the cathode (positive terminal) is composed of manganese dioxide. Alkaline batteries are comparable to zinc-carbon batteries, but the difference is that alkaline batteries use potassium hydroxide (KOH) as an electrolyte

54

Lithium Ion Batteries

- Lithium Ion Batteries based on lithium insertion into different solids
- Process of lithium insertion is known as intercalation
- Lithium has different electrochemical potentials in different solids
- Anode: Typically graphite; Li^+ has lower potential
- Cathode: Typically LiCoO_2 or LiMnO_2 ; Li^+ has larger potential

55

Lithium Ion Battery

- Very expensive.
Not usually available in "common" battery sizes
Very common in laptop computers, moderate to high-end digital cameras and camcorders, and cellphones.
Very low rate of self discharge.
Volatile: Chance of explosion if short circuited, allowed to overheat, or not manufactured with rigorous quality standards.

56

Lead-acid battery

- The lead-acid battery used in motor vehicles, consists of a series of six identical cells assembled in series.
- Each cell has a lead anode and a cathode made from lead dioxide packed in a metal plaque.
- Cathode and anode are submerged in a solution of sulfuric acid acting as the electrolyte.

57

Lead-acid battery

- $\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \quad \mathcal{E}^{\circ} = 1.69 \text{ V}$
- $\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \quad \mathcal{E}^{\circ} = -0.35 \text{ V}$
- $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
Or
- $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \quad \mathcal{E}^{\circ} = 2.04 \text{ V}$

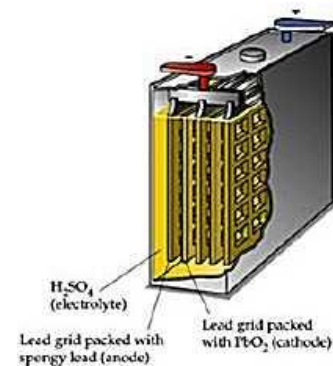
58

Lead-acid battery

- At standard conditions, each cell may produce a potential of 2 V, hence overall voltage produced is 12 V.
- lead-acid batteries are rechargeable.
- If an external voltage is supplied to the battery it will produce an electrolysis of the products in the overall reaction (discharge), thus recovering initial components which made the battery work.

59

Lead Acid Battery



60

Lead Acid Battery

- Moderately expensive.
Moderate energy density.
Moderate rate of self discharge.
Higher discharge rates result in considerable loss of capacity.
Environmental hazard due to Lead.
Common use - Automobile batteries

61

Lithium rechargeable battery

- A graphite bar acts as the anode, a bar of lithium cobaltate acts as the cathode, and a polymer, swollen with a lithium salt, allows the passage of ions and serves as the electrolyte.
- In this cell, the carbon in the anode can reversibly form a lithium-carbon alloy.

62

Lithium rechargeable battery

- The advantage of this kind of battery is that Lithium possess the highest negative value of standard reduction potential.
- It is also a light metal and therefore less mass is required to generate 1 mole of electrons.
- Lithium ion battery technologies are widely used in portable electronic devices because they have high energy storage density and are rechargeable.

63

Nickel-Cadmium (NiCad) Battery

- Rechargeable, but not indefinitely
- $\text{Cd(s)} + \text{NiO}_2\text{(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Cd(OH)}_2\text{(s)} + \text{Ni(OH)}_2\text{(s)}$
- Approximately 1.35 V
- Cadmium is highly toxic – these batteries should be recycled and not dumped.

64

Nickel-Cadmium (NiCad) Battery

- Nickel-Cadmium Battery is Dry-Cell that is rechargeable.
- Anode/Oxidation: Cadmium metal.
- $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$
- Cathode/Reduction: Nickel (III) compound on nickel metal.
- $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$
- Nickel oxyhydroxide, NiO(OH)
- Cell Potential: 1.30V

65

Nickel-Cadmium (NiCad) Battery

- During discharge, Cd metal is oxidized at the anode and nickel oxyhydroxide is reduced at the cathode.
- During discharge, the solid reaction products (cadmium and nickel hydroxides) adhere to the electrodes.
- Recharging reverses this reaction.
- Typical Ni-cadmium battery packs contain 3 or more cells in series to produce the higher required emf.

66

Nickel-Cadmium (NiCad) Battery

- Inexpensive.
High/low drain, moderate energy density.
Can withstand very high discharge rates with virtually no loss of capacity.
Moderate rate of self discharge.
Environmental hazard due to Cadmium - use now virtually prohibited in Europe

67

Nickel Metal Hydride Battery

- Nickel Metal Hydride battery is similar to NiCd battery Dry-Cell that is rechargeable.
- Anode/Oxidation: Metal Hydride.
- $MH + OH^-(aq) \rightarrow M + H_2O + e^-$
- Cathode/Reduction: Nickel (III) compound on nickel metal.
- $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$
- Nickel oxyhydroxide, NiO(OH)
- Cell Potential: 1.35V

68

Nickel Metal Hydride Battery

- Hydrogen Stored at Anode as Hydride in Metal Alloy
- Hydrogen Storage Metals: LaNi₅, FeTi
- H₂ Storage Capacity: LaNi₅ 0.11 g/cc (Higher than density of liquid hydrogen. Liquid H₂ is 0.07 g/cc)
- Higher energy density than NiCd by ~40%
- More expensive than NiCd by ~20%

69

Nickel Metal Hydride Battery

- Cheap.
Not useable in higher drain devices.
Traditional chemistry has high energy density, but also a high rate of self-discharge.
Newer chemistry has low self-discharge rate, but also a ~25% lower energy density.
Very heavy. Used in some cars.

70

Fuel cells

- The most popular is the oxygen-hydrogen fuel cell, where two inert electrodes (porous electrodes of nickel and nickel oxide) are placed in an electrolytic solution such as hot caustic potash, in both compartments (anode and cathode) gaseous hydrogen and oxygen are bubbled into solution.
- Oxidation and reduction take place in the anode and cathode separately.

71

Fuel cells

- Hydrogen-oxygen fuel cell
- Anode: $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \longrightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$
- Cathode: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$
- Used in space-shuttle program

72

Fuel Cells

- Reactants are continually supplied, so battery does not “run down” (reach equilibrium).
- Far more efficient than burning hydrogen, boiling water, generating steam, running a turbine to generate electricity
- Astronauts use the water produced in the cell for drinking.

73

Summary

- **Zinc-carbon battery** - Also known as a standard carbon battery, zinc-carbon chemistry is used in all inexpensive AA, C and D dry-cell batteries. The electrodes are zinc and carbon, with an acidic paste between them that serves as the electrolyte.
- **Alkaline battery** - Used in common Duracell and Energizer batteries, the electrodes are zinc and manganese-oxide, with an alkaline electrolyte.

74

- **Lithium photo battery** - Lithium, lithium-iodide and lead-iodide are used in cameras because of their ability to supply power surges.
- **Lead-acid battery** - Automobiles (rechargeable).
- **Nickel-cadmium battery** - The electrodes are nickel-hydroxide and cadmium, with potassium hydroxide as the electrolyte (rechargeable).
- **Nickel-metal hydride battery** - This battery is rapidly replacing nickel-cadmium (rechargeable).

75

Summary

- **Lithium-ion battery** - With a very good power-to-weight ratio, this is often found in high-end laptop computers and cell phones (rechargeable).
- **Zinc-mercury oxide battery** - This is often used in hearing aids.
- **Silver-zinc battery** - This is used in aeronautical applications because the power-to-weight ratio is good.

76