COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
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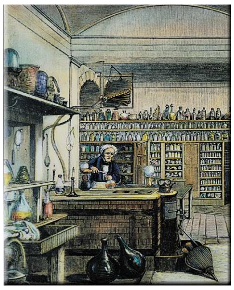
JF Chemistry CH 1101 2012

Introduction to Electrochemistry.



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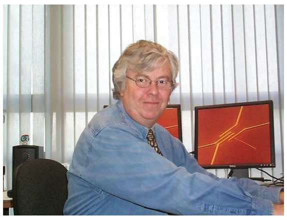

Recommended Reading

- Silberberg. Chemistry: the molecular nature of matter and change', Chapter 21. pp.892-949 (3^{rd} Edition) ; pp.902-959 (4^{th} edition).
- Atkins and Jones. Chemical Principles: the quest for insight. 3^{rd} edition. Chapter 12.pp.444-482.
- Atkins & de Paula. Elements of Physical Chemistry.4^{th} Edition. Chapter 9. pp.200-228.
- Kotz, Treichel & Weaver. Chemistry and Chemical Reactivity. 7^{th} edition. Chapter 20. pp.896-961.
- Burrows et al. Chemistry^3, Chapter 17, pp.774-808.

Lecture 12

Electrochemistry: Simple ideas.

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What is electrochemistry?

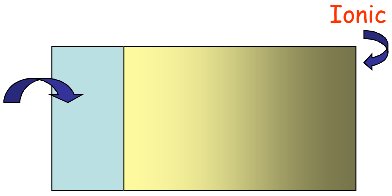
- Electrochemistry is the science which deals with the consequences of the transfer of electric charge from one phase to another.
- An electrochemical reaction is a heterogeneous process which involves electron transfer across a phase boundary or interface.
- Electrochemical reactions are labelled as redox (oxidation/reduction) processes.
- Electron transfer occurs at interfaces between a metallic conductor (an electrode) and an ionic conductor (an electrolyte).
- Oxidation is the loss of electrons.
- Reduction is the gain of electrons.

- Electrode : contains mobile electrons. Acts as source or sink of electrons.
  - Metals: Pt, Au, Ni, Cu, Hg
  - Non metals: glassy carbon, graphite.
  - Semiconductors.
  - Metal oxides.
  - Electroactive polymers : poly(pyrrole), poly(aniline).
- Electrolyte: contains mobile ions.
  - Solvents + salts.
  - Aqueous solutions.
  - Non aqueous solutions.
  - Solid elecrtrolytes.
  - Polymer electrolytes.

Electrolyte: Ionic conductor

Chemistry[3], section 17.1,17.2.
Kotz, 20.1. Balancing redox reactions
pp.898-905.

Electrode: Electronic conductor



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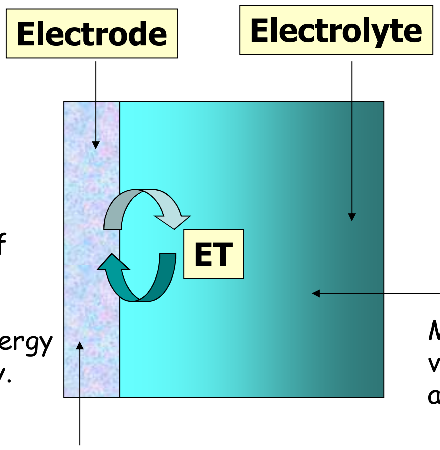
The electrode/electrolyte interface.



Ionically conducting medium : electrolyte solution, molten salt, solid electrolyte, polymeric electrolyte, etc.

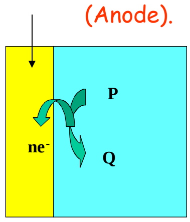
Conduction occurs via migration of electrons . Solid state Physics : energy band theory.

Material transport occurs via migration, diffusion and convection

Electronically conducting phase : metal, semiconductor, Conducting polymer material etc.

Anodes and cathodes.

Electron sink electrode (Anode).

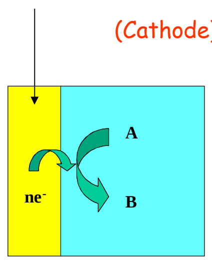


Oxidation or de-electronation

P = reductant (electron donor)

Q = Product

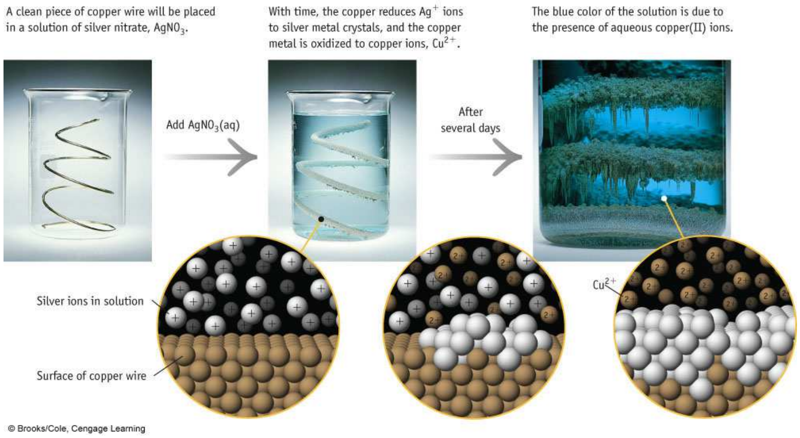
Electron source electrode (Cathode).

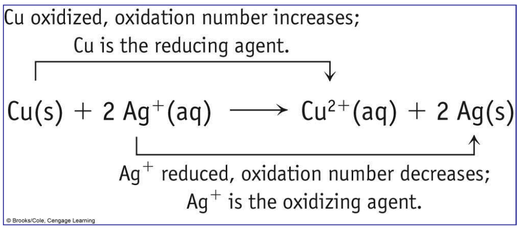


Reduction or electronation

A = oxidant (electron acceptor)

B = Product





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- Whether an electrochemical process releases or absorbs free energy it always involves the movement of electrons from one chemical species to another in an oxidation/reduction or redox reaction.
- In any redox process oxidation involves the loss of electrons and reduction involves the gain of electrons.
- An oxidising agent is the species that performs the oxidation, taking electrons from the species being oxidised.
- A reducing agent is the species that performs the reduction, giving electrons to the substance being reduced.
- After the reaction the oxidised substance has a higher (more positive, less negative) oxidation number, and the reduced substance has a lower (less positive, more negative) one.
- Oxidation (electron loss) always accompanies reduction (electron gain).
- The oxidizing agent is reduced and the reducing agent is oxidized.

Redox reactions.

- The number of electrons gained by the oxidizing agent always equals the number of electrons lost by the reducing agent.

Terminology	Example: $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$
OXIDATION • Electrons are lost • Reducing agent is oxidized • Oxidation number increases	Zinc **loses** electrons. Zinc is the reducing agent and becomes **oxidized.** The oxidation number of Zn **increases** from 0 to +2.
REDUCTION • Electrons are gained • Oxidizing agent is reduced • Oxidation number decreases	Hydrogen ion **gains** electrons. Hydrogen ion is the oxidizing agent and becomes **reduced.** The oxidation number of H^+ **decreases** from +1 to 0.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

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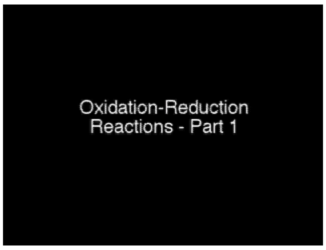
Oxidation and Reduction Movie I.



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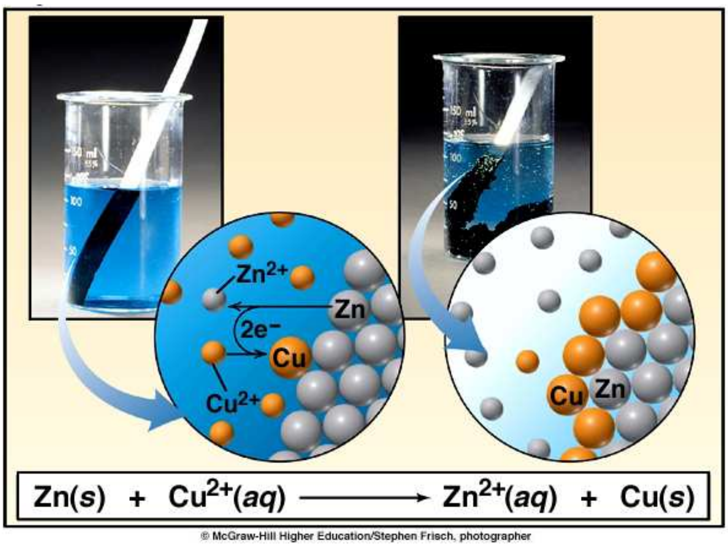
Spontaneous redox chemistry involving copper and zinc.



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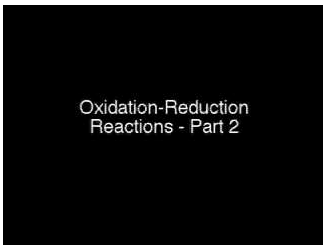
Oxidation and Reduction Movie II.



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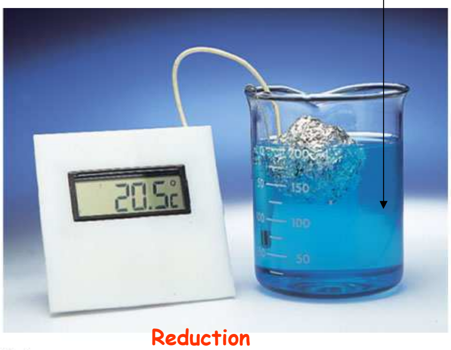
Spontaneous coupled redox reactions:
Copper + Aluminium

Kotz, Example 20.1, pp.900-901.

$Cu(NO_2)_2$ + NaCl



(a)

(b)

Reduction

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

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^{-}$$

Oxidation

$$3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq) + heat$$

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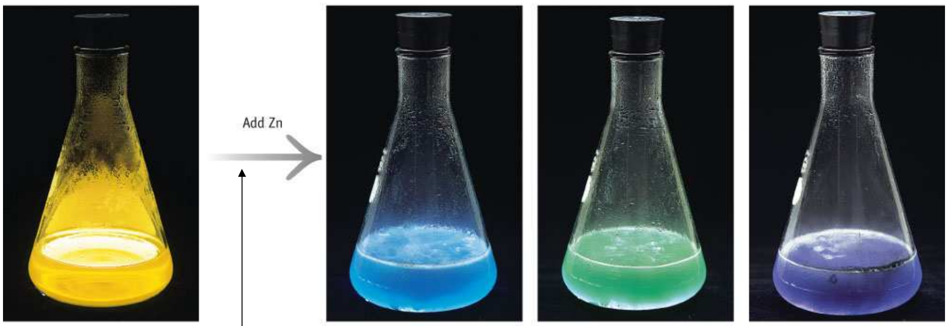
Reduction of Vanadium(V) ion with zinc.

Kotz example 20.2. pp.901-903.

Mass balance, Charge balance required.

The VO_2^+ ion is yellow in acid solution. | Zn added. With time, the yellow VO_2^+ ion is reduced to blue VO^{2+} ion. | With time, the blue VO^{2+} ion is further reduced to green V^{3+} ion. | Finally, green V^{3+} ion is reduced to violet V^{2+} ion.



VO_2^+ | VO^{2+} | V^{3+} | V^{2+}

$$Zn(s)+4H^+(aq)+2VO_2^+(aq)\rightarrow Zn^{2+}(aq)+2VO^{2+}(aq)+2H_2O(\ell)$$

Read problem solving tips 20.1 & 20.2

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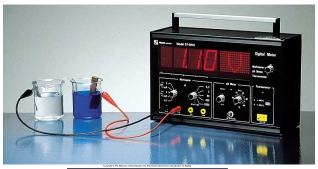
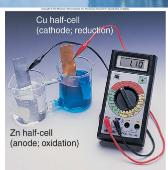
Electrochemical cells.





- Electrochemistry is the study of the relationship between chemical change and electrical work.
- It is examined via the use of electrochemical cells which are systems that incorporate a redox reaction to produce or utilize electrical energy.
- Isolated oxidation and reduction processes are not much good. These reactions must be coupled together in some way to perform a technologically useful function.
- An electrochemical cell is formed by coupling together individual oxidation and reduction processes in a specific configuration.
- There are two types of electrochemical cells based upon the general thermodynamic nature of the reaction (expressed as whether the change in Gibbs energy is positive or negative.
- Oxidation and reduction reactions occurring at individual electrode/electrolyte interfaces can be coupled together either to produce an electrical voltage or to produce chemicals.

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Electrochemical Cells.

- Galvanic cell.
  - This is an electrochemical power source.
  - The cell does work by releasing free energy from a spontanouus reaction to produce electricity.
    - Battery
    - Fuel cell
- Electrolytic cell.
  - This is an electrochemical substance producer.
  - The cell does work by absorbing free energy from a source of electricity to drive a non-spontaneous reaction.
    - Electrosynthesis.
    - Electroplating.

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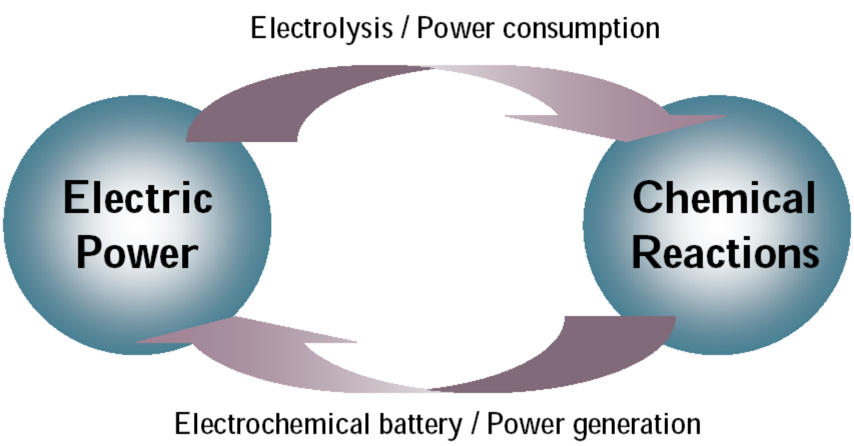
Electric power conversion in electrochemistry



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Galvanic and electrolysis cells.

- A voltaic cell (or a Galvanic cell) uses a spontaneous reaction (ΔG negative) to generate electrical energy. The reacting system does work on the surroundings. All batteries are made from voltaic cells.
- An electrolytic cell uses electrical energy to drive a non-spontaneous reaction (ΔG positive). Here the surroundings do work on the reacting system. Chemicals are prepared from electrical energy. This procedure is termed electrolysis or electrochemical synthesis.
- All electrochemical cells have several common features.
  - They have two electrodes.
  - Anode: the oxidation half reaction takes place at the anode.
  - Cathode: the reduction half reaction takes place at the cathode.
  - The two electrodes are dipped into an electrolyte, a medium that contains a mixture of ions which will conduct electricity.

Kotz section 20.2, pp.905-915.

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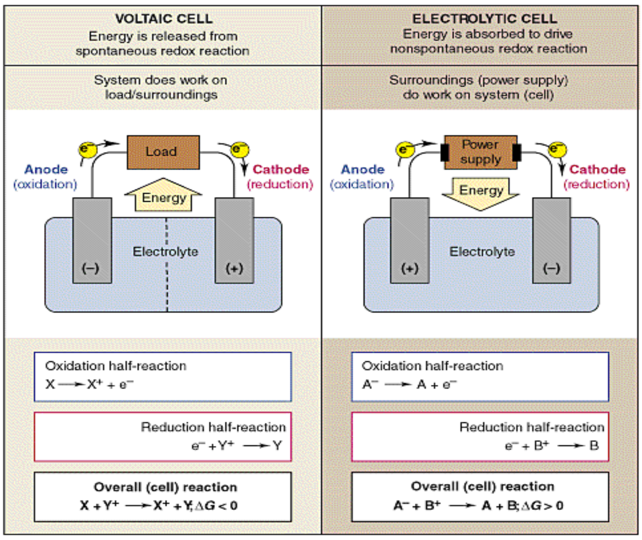
Electrochemical cells : Galvanic (self driving & energy producing) and electrolytic (driven & energy consuming).



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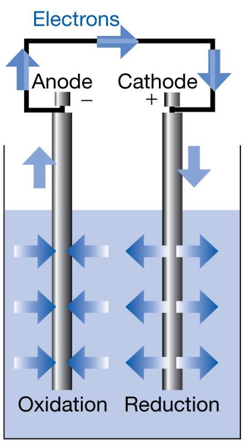
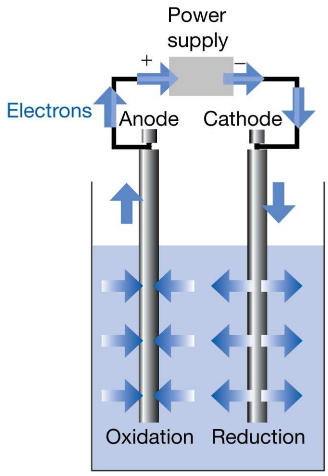
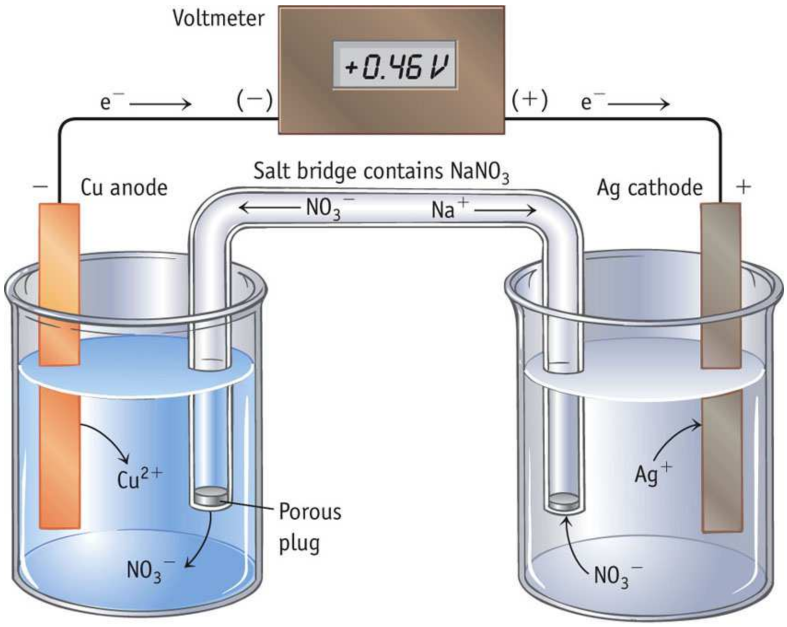
Self driving Galvanic cell :
Spontaneous redox reactions generate electrical energy.

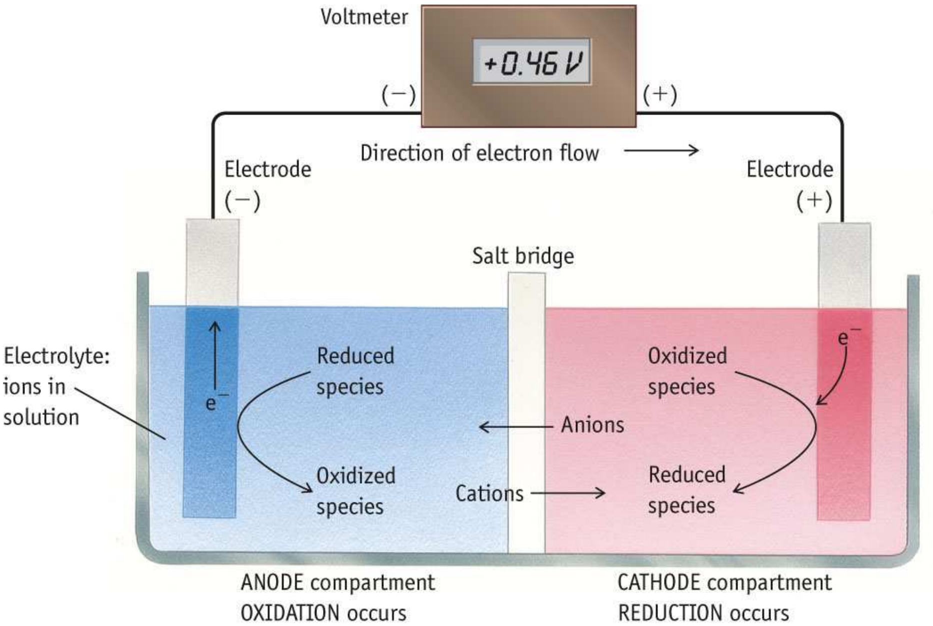


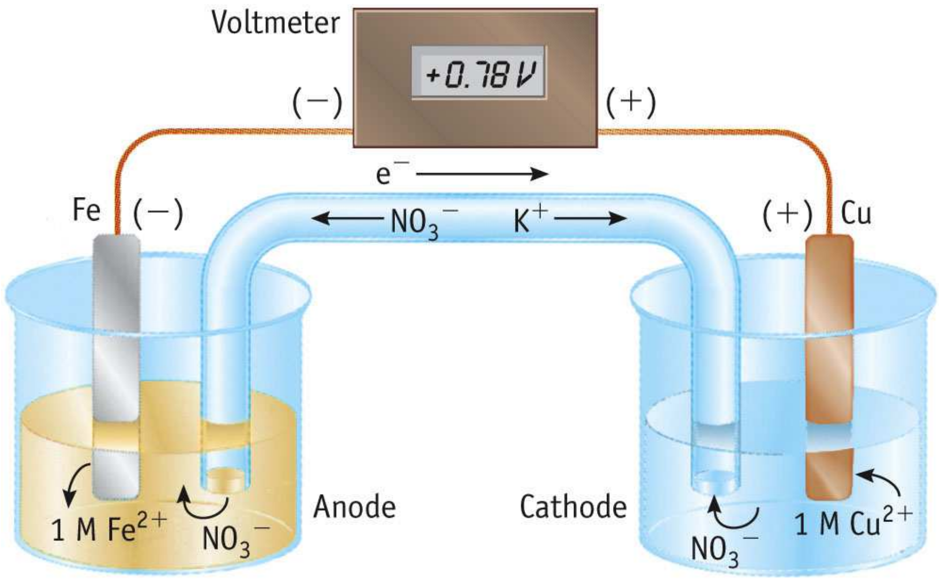
Driven Electrolysis cell :
Electrical energy drives Non spontaneous chemical Reactions : electrosynthesis.





Net reaction: $Cu(s) + 2\,Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$


Voltmeter
+0.46 V
(−)
(+)
Direction of electron flow
Electrode
(−)
Electrode
(+)
Salt bridge
Electrolyte:
ions in
solution
e⁻
Reduced
species
Oxidized
species
Anions
Cations
Oxidized
species
Reduced
species
ANODE compartment
OXIDATION occurs
CATHODE compartment
REDUCTION occurs


Voltmeter
+0.78 V
(−)
(+)
e⁻
Fe
(−)
NO₃⁻
K⁺
(+)
Cu
1 M Fe²⁺
NO₃⁻
Anode
Cathode
NO₃⁻
1 M Cu²⁺

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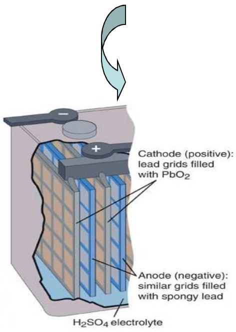
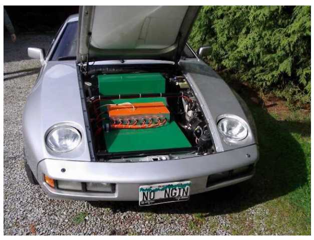
Electrochemical Power Sources.



Fuel Cell Technology: Electric Cars.

Figure 9. Honda's newest fuel cell powered vehicle, the FCX-V4.



Fuel Cells: What are they?

- Fuel cells are devices which convert chemical energy directly to electrical energy. This is very different from conventional combustion based power plant which convert chemical energy to thermal energy, then thermal energy to kinetic energy, and only then kinetic energy to electrical energy.
- The thermal to kinetic and kinetic to electrical conversion stages have efficiency losses associated with them which engineers have spent the last 150 years or so trying to reduce. The key loss however is in the combustion process (chemical to thermal stage). Due to the inherent thermodynamics of combustion there is an ultimate efficiency which cannot be exceeded by any combustion engine - The Carnot Limit - a limit which does not apply to fuel cells.
- Using hydrogen as a fuel (which can be extacted from hydrocarbon fuels or renewable sources) a fuel cell electro-chemically oxidises the hydrogen using oxygen from the air generating electricity and some heat.
- The fuel cell makes more efficient use of the fuel and produces fewer pollutants e.g. reduced nitrgen oxides and carbon dioxide emissions, and no particulates.

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Fuel Cells: some history

- The fuel cell concept arises directly from the operating principle of the galvanic cell; it is in effect a galvanic cell in which the electrodes are supplied with reactants, allowing continuous operation without depleting the electrodes.
- As early as 1880 Wilhelm Ostwald wrote: "I do not know whether all of us realise fully what an imperfect thing is the most essential source of power which we are using in our highly developed engineering – the steam engine" - indicating a growing awareness that chemical processes, such as those in galvanic cells, could approach 100% efficiency whereas the efficiencies of heat engines were limited by the Second Law to the Carnot efficiency of around 60%.
- The fuel cell was first demonstrated in 1839 by William Grove . Unfortunately development of viable technology for exploitation of the principle has been slow, primarily due to the incompatibility of the required material properties . Inevitably the first uses were space and military applications, in which cost is of secondary importance to performance.
- With increasing understanding of fuel cell and relevant materials science, driven by these specialist applications, there have been a number of false dawns when fuel cells have been proclaimed the solution to all of our energy needs, only to realise that there are inherent limitations on a particular technologies applications. This roller coaster road to development has however generated a wide range of fuel cell systems with one or more suitable for virtually every power application imaginable.

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Fuel Cells power space vehicles.

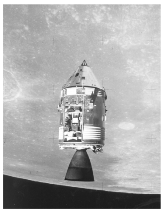
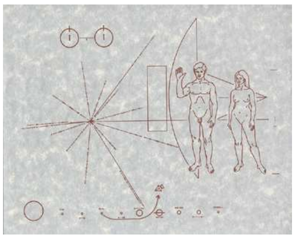


Figure 2. Apollo command and service modules.



Fuel cells: terrestial applications

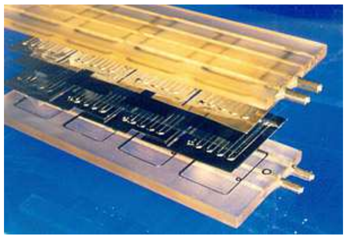
Avista Laboratory's 7.5KW PEM fuel cell power plant,
with 60-watt hot-swap submodules,
for residential applications

Plug Power's 7KW residential PEM fuel cell power plant

Fuel Cells can be small!

Warsitz Enterprises' portable fuel cell power unit

A Ballard fuel cell powers
a laptop computer.



Micro-fuel cell developed by Fraunise ISE
for use in applications such as cellular phones

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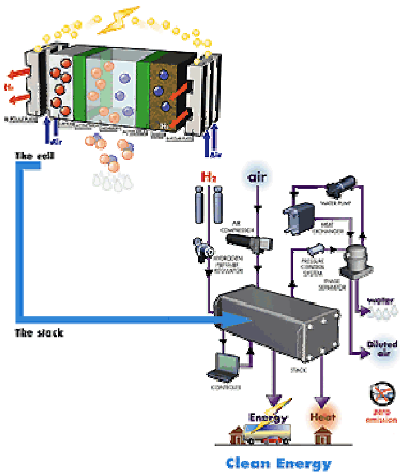
Fuel cells can be big!



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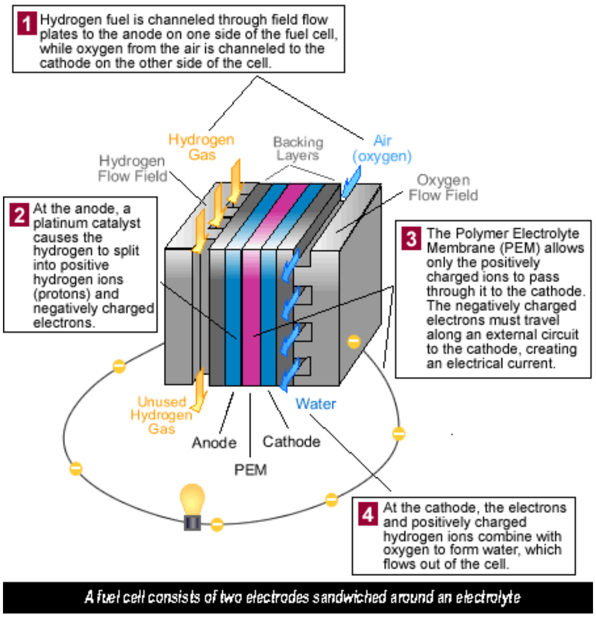
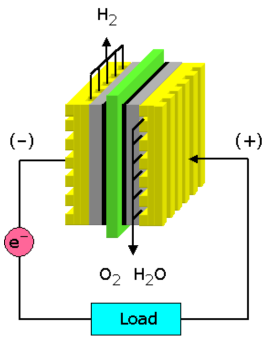
Polymer electrolyte membrane (PEM) fuel cell.





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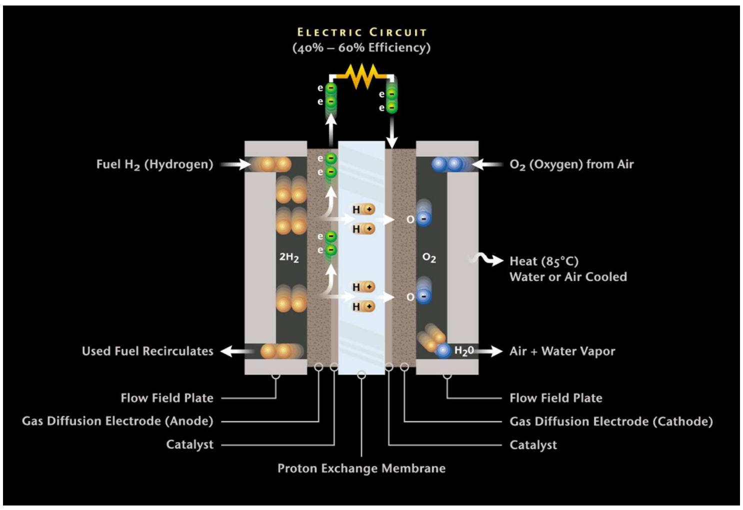
Ballard PEM Fuel Cell.



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Engineering a PEM Fuel Cell

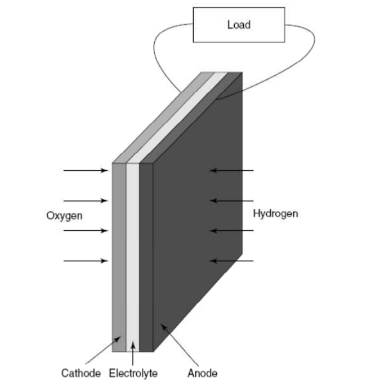

Figure 1.2 Basic cathode–electrolyte–anode construction of a fuel cell.

Figure 1.20 The 75-kW (approx.) fuel cell system for a prototype Mercedes Benz A-class car. (Photograph reproduced by kind permission of Ballard Power Systems.)

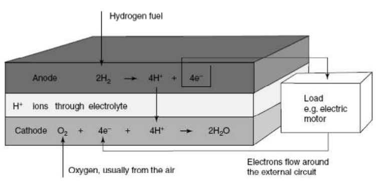

Figure 1.3 Electrode reactions and charge flow for an acid electrolyte fuel cell. Note that although the negative electrons flow from anode to cathode, the 'conventional current' flows from cathode to anode.

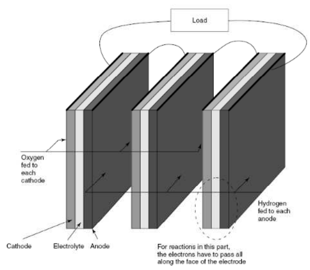

Figure 1.7 Simple edge connection of three cells in series.

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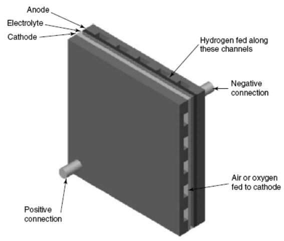

Figure 1.8 Single cell, with end plates for taking current from all over the face of the electrodes, and also supplying gas to the whole electrode.

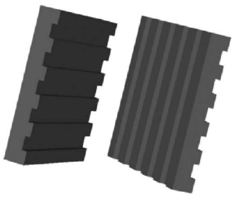

Figure 1.9 Two bipolar plates of very simple design. There are horizontal grooves on one side and vertical grooves on the other.

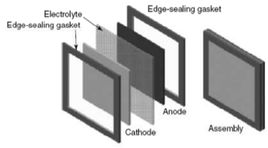

Figure 1.11 The construction of anode/electrolyte/cathode assemblies with edge seals. These prevent the gases leaking in or out through the edges of the porous electrodes.

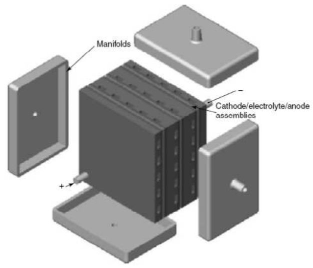

Figure 1.12 Three-cell stack, with external manifolds. Unlike Figure 1.10, the electrodes now have edge seals.

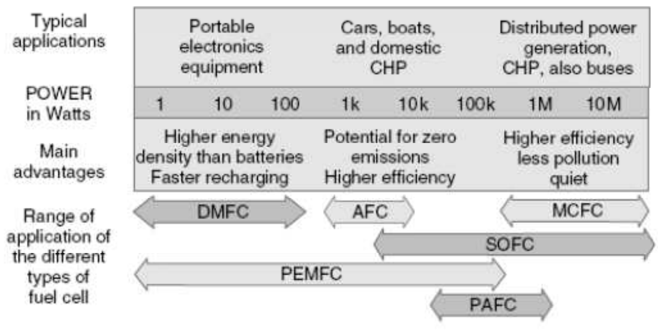

Figure 1.21 Chart to summarize the applications and main advantages of fuel cells of different types, and in different applications.

Electrolysis.

- Redox reactions in which the change in Gibbs energy ΔG is positive do not occur spontaneously.
- However they can be driven via application of either a known voltage or a known current.
- Electrolysis is the process of driving a reaction in a non spontaneous direction by using an electric current.
- Hence an electrolytic or driven cell is an electrochemical device in which an electric current from an external source is used to drive a non spontaneous chemical reaction.
- Electrolysis provides the basis of electrosynthesis and industrial electrochemistry.

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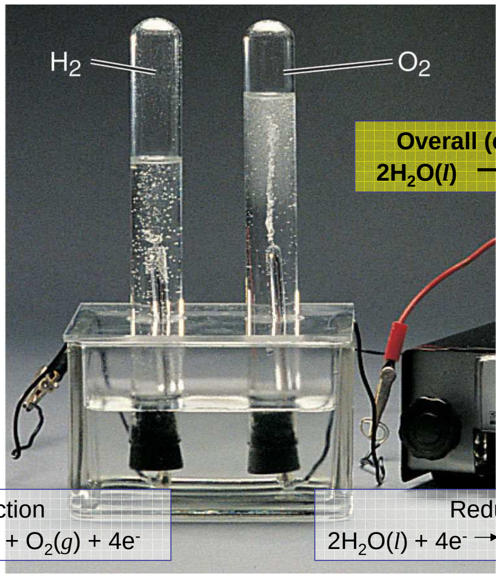
The electrolysis of water



Oxidation half-reaction
$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

Reduction half-reaction
$2H_2O(l) + 4e^- \rightarrow 2H_2(g) + 2OH^-(aq)$

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Electrolysis: Hydrogen energy

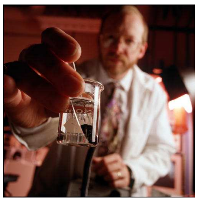
Today, almost all hydrogen is produced via steam reforming of natural gas at oil refineries.

Today, hydrogen is transported to where it will be used by cryogenic liquid tankers.

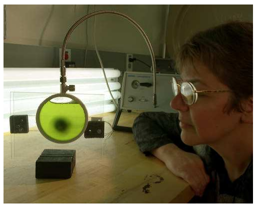
Hydrogen Technologies for Our *Future*

In the future, hydrogen will be produced from water, using high-tech photoelectrochemical devices and specially designed microorganisms, and in electrolyzers that run on electricity generated by the sun and wind.

Solar-powered electrolysis system at SunLine Transit Agency



Photoelectrochemical hydrogen production



Algal hydrogen production

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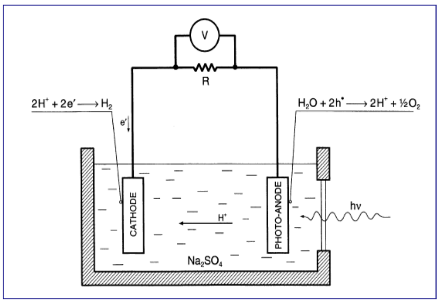
Photoelectrochemical cells

PECs are solar cells which generate electrical energy from light, including visible light. Each cell consists of a semiconducting photoanode and a metal cathode immersed in an electrolyte.

Some photoelectrochemical cells simply produce electrical energy, while others produce hydrogen in a process similar to the electrolysis of water.



PEC Cell :
Fujishima & Honda 1973

The PEC cell consists of a semiconductor photo anode which is irradiated with electromagnetic radiation. The counter electrode is a metal. The following processes take place in the cell when light is incident on the semiconductor electrode:

1. Photo generation of charge carriers (electron and hole pairs)

2. Charge separation and migration of the holes to the interface between the semiconductor and the electrolyte and of electrons to the counter electrode through the external circuit. Now, holes are simply vacancies created in the valence band due to promotion of electrons from the valence band to the conduction band. However, in the study of electronic behavior of materials, "holes" are considered to be independent entities, with their own mass.

3. Electrode processes: oxidation of water to H^+ and H_2O by the holes at the photo anode and reduction of H^+ ions to H_2 by electrons at the cathode.

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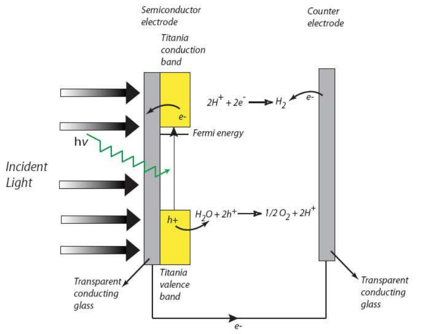
The lower yellow band is the valence band of the n-type semiconductor, while the upper yellow band is the conduction band. The energy difference between the top of valence band and the bottom of conduction band is termed as the band gap of semiconductor, E_g. Photons having energy greater than E_g are absorbed by the semiconductor and free electrons are generated in the conduction band and free holes in the valence band.

$2hv = 2e^- + 2h^+$

The electrons and holes are separated due to the potential generated at the interface of the semiconductor-electrolyte due to band bending. The holes move to the interface and react with water producing oxygen:

$2h^+ + H_2O = 1/2\ O_{2(gas)} + 2H^+_{(aq)}$



The electrons travel in the external circuit and arrive at the interface between the counter electrode and electrolyte. There, they reduce the H^+ ions to H_2:

$2e^- + 2H^+_{(aq)} = H_{2(gas)}$

The complete reaction is absorption of photon and splitting of water into hydrogen and oxygen.

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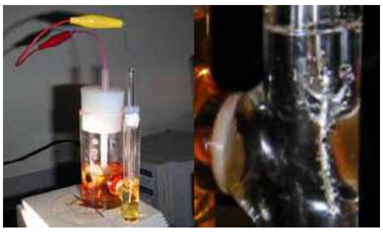
Some other configurations of the PEC cell are also possible:

1. The semiconducting material may be a p-type material. In this case, it will act as photo cathode, and reduction of H^+ ions to H_2 will take place at this electrode. The counter electrode may me a metal in this case.



2. Both electrodes, the cathode and anode, are photo active semiconducting materials. In this case, the n-type electrode will act as anode and oxidation of water to oxygen and H^+ will take place at this electrode. The p-type electrode will act as cathode, where H^+ ions will be reduced to H_2.

http://www.nature.com/nature/journal/v414/n6861/pdf/414338a0.pdf

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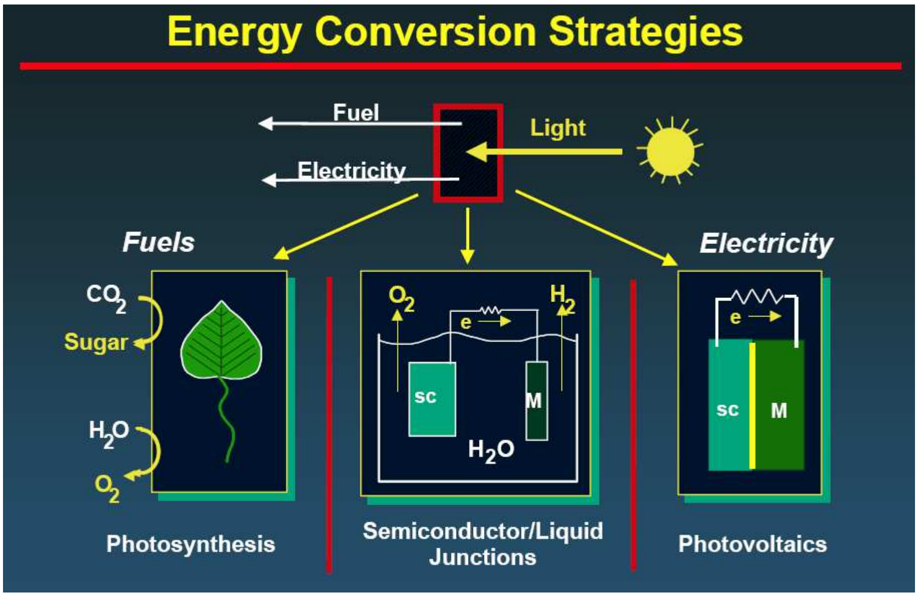

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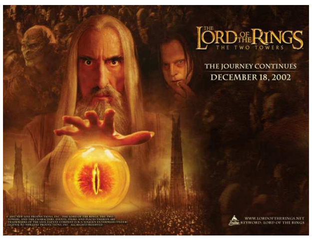
Electrolysis:
Metal Plating



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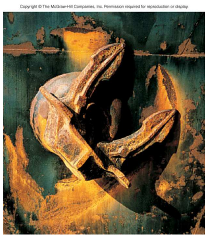
Electrochemical Corrosion

The Hendrix Group, Inc.
15823 N. Barkers Landing
Houston, Texas 77079

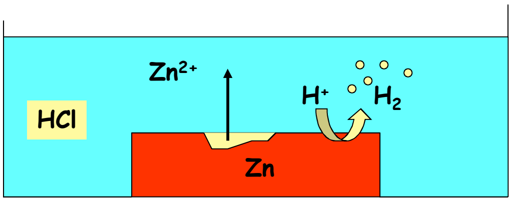


17-4 pH Stainless Steel H_2S SSC Cracks

Chloride Stress Corrosion Cracking Photograph

Hydrogen Embrittlement of Valve Capscrew Fasteners

Uniform corrosion of metals.

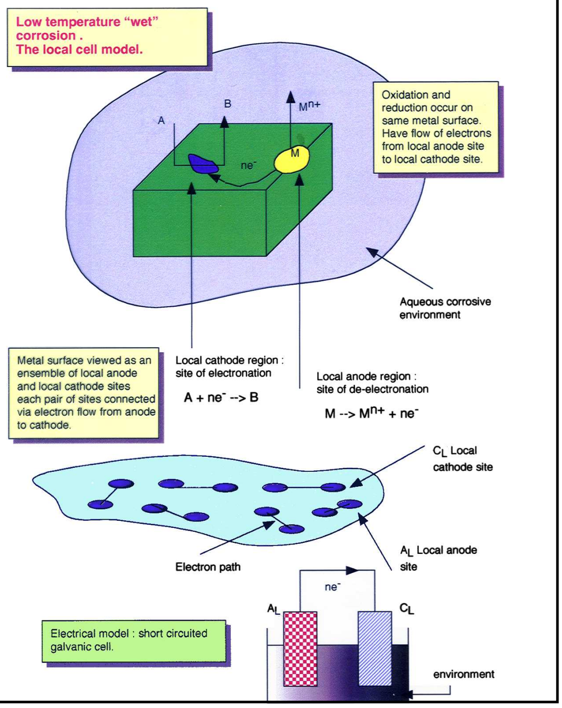


$$Zn + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

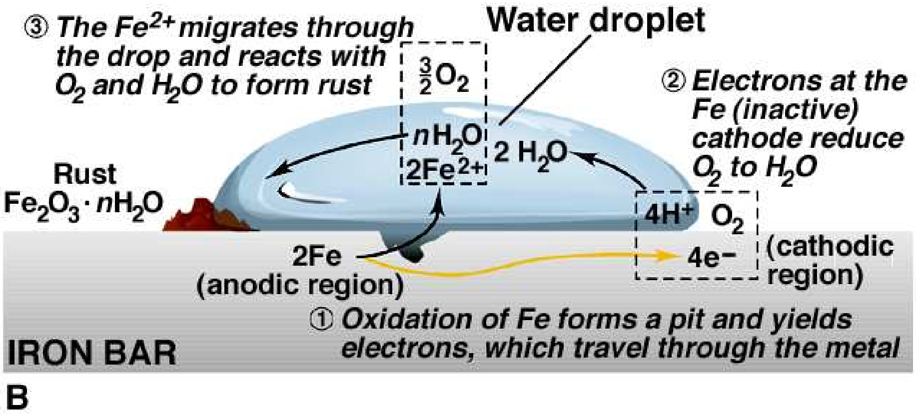
- 2 e⁻ — Oxidation, electron loss

+ 2 e⁻ — Reduction, electron gain

Uniform corrosion consists of two coupled redox reactions:
Oxidation : metal dissolution
Reduction : either hydrogen evolution or oxygen reduction.
Electrons flow through the metal from a local anode site where metal dissolution occurs, to a local cathode site where reduction of a species present in the environment occurs.
Both oxidation and reduction occur with equal rates.
The mechanism can be quite complex involving other chemical reactions resulting in oxide layer formation on the metal surface (rust).



The Corrosion of Iron



The Corrosion of Iron

About 25% of the steel produced in the United States is made just to replace steel already in use that has corroded. Rust arises through a complex electrochemical process.

1) Iron does not rust in dry air: moisture must be present.
2) Iron does not rust in air-free water: oxygen must be present.
3) The loss of iron and the deposition of rust often occur at *different* places on the *same* object.
4) Iron rusts more quickly at low pH (high $[H^+]$).
5) Iron rusts more quickly in contact with ionic solutions.
6) Iron rusts more quickly in contact with a less active metal (such as Cu) and more slowly in contact with a more active metal (such as Zn).

$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2\,e^-$ [anodic region; oxidation]

$O_{2\,(g)} + 4\,H^+_{(aq)} + 4\,e^- \longrightarrow 2\,H_2O_{(l)}$ [cathodic region; reduction]

$2\,Fe_{(s)} + O_{2\,(g)} + 4\,H^+_{(aq)} \longrightarrow 2\,Fe^{2+}_{(aq)} + 2\,H_2O_{(l)}$

$$4Fe^{2+}(aq) + O_2(g) + (4+2x)H_2O \rightarrow 2Fe_2O_3.xH_2O + 8H^+(aq)$$

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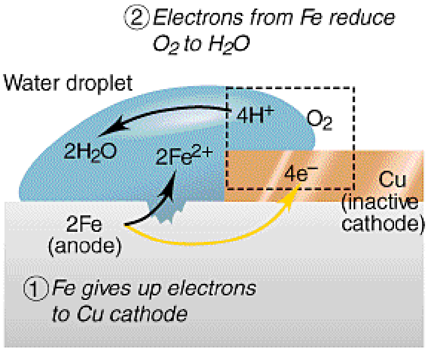
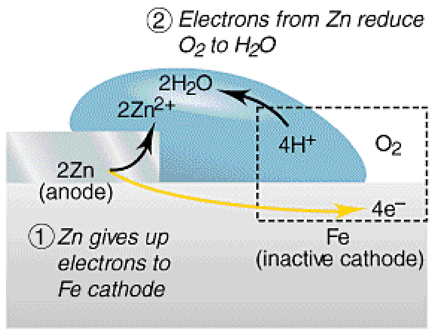
The Effect of Metal-Metal Contact on the Corrosion of Iron

$E^0(Cu^{2+},Cu) = 0.34V$
$E^0(Fe^{2+},Fe) = -0.44V$

$E^0(Zn^{2+},Zn) = -0.76V$
$E^0(Fe^{2+},Fe) = -0.44V$



A Enhanced corrosion



B Cathodic protection

Corrosion protection schemes :
- coat metal surface with paint.
- passivate metal surface with thin protective oxide layer.

- Galvanize iron surface with electroplated Zinc film.
- Cathodic protection : metal to be protected made cathode in electrochemical cell by combining it with a more active metal.
- Alloy formation (stainless steel: Fe/Cr alloy).