

ChE 331

Electrochemical Engineering



Dr. Michael Fowler

Chemical Engineering
University of Waterloo
Waterloo, Ontario, Canada

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Course Outline

♥ **Course Description:** This lecture course provides students with a strong background in electrochemical techniques with a broad range of applications in **eletroplating, electrorefining, fuel cell, battery, and corrosion** technologies.

The course objectives are to make sure each student:

- understands the fundamentals of electrochemical techniques;
- understands electroplating, corrosion, fuel cell, battery operation;
- acquires necessary knowledge for any industry were electrochemistry is involved.

1. Introduction

- basics of electrochemical reactions and processes
- overview of applications
- some basic concepts and conventions
- Faraday's law

2. Transport Phenomena in Electrolytes

- electrolytic conduction
- diffusion, migration and convection

3. Electrode Reactions (Equilibrium)

- reversible electrode potential, Nernst equation
- cell emf
- applications of equilibrium potentials (reference electrodes, specific ion electrodes)

4. Electrode Reactions (Non-Equilibrium)

- electrode kinetics, overpotentials
- transport-controlled electrode reactions
- electrolytic and galvanic cells
- potential distribution across cells
- applications

5. Electrochemical Engineering

- reactor design of electrochemical reactors (CSTR)
- current efficiency of cells

6. Applications

- materials
- corrosion
- batteries, fuel cells

Some Suggested Texts:

- ♥ *Electrochemical Engineering, Thomas Fuller, Wiley, 2018.*
- ♥ *Industrial Electrochemistry* 2nd ed., by D. Pletcher and F. Walsh, Chapman and Hall, 1990.
- ♥ *Electrochemical Methods: Fundamentals and Applications*, Bard and Faulkner, John Wiley & Sons, 2001
- ♥ *Electrochemical Engineering Principles*, Geoffrey Prentice. Prentice-Hall, 1991
- ♥ *Principles of Fuel Cells*, Xianguo Li, Taylor & Francis, 2005.
- ♥ *PEM Fuel Cell Electrocatalysts and Catalyst Layers:Fundamentals and Applications* Jiujun Zhang (ed.), Springer, 2008
- ♥ *Advanced Batteries: Materials Science Aspects*, Robert A. Huggins, Springer, 2008
- ♥ *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Application,* B. E. Conway, Springer, 1 edition (April 30, 1999)

Final Grade

▪ Assignments	24	%
▪ Quizzes	12	%
▪ Design 3 Minute Pitch	4%	
▪ Group Design/Fuel Cell Stack	5%	
▪ Midterm	15	%
▪ <u>Final exam:</u>	<u>40</u>	<u>%</u>
Total:	100	%

Must pass Midterm OR Final Exam

What is an Electrochemical Reaction?

One way to answer this question is to try to distinguish electrochemical reactions from other chemical reactions.

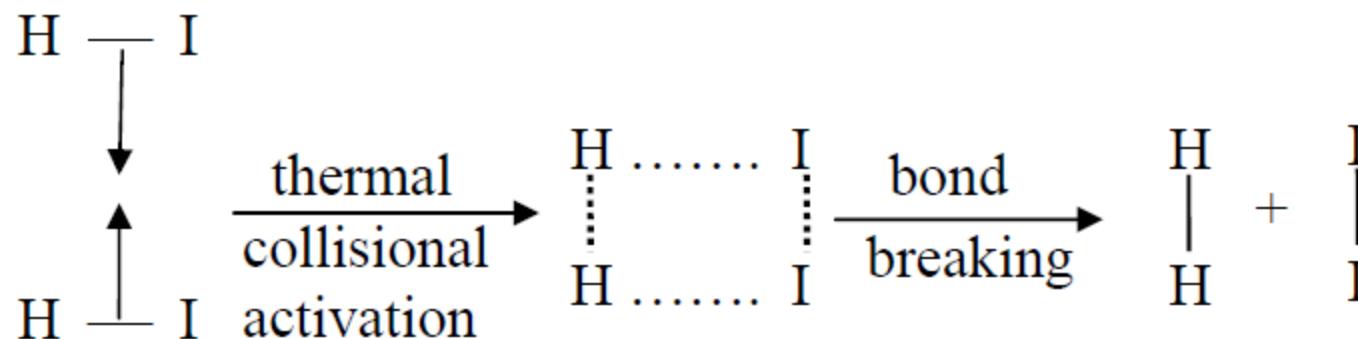
What characterizes electrochemical reactions is that the process of forming or breaking bonds results in either the complete release of an electron or the consumption of an electron that has come from somewhere else. Electrons actually move within the system. In ordinary chemical reactions, there is no separate movement of electrons.

In many cases, electrochemistry provides another means of carrying out a given overall reaction. Consider the case of

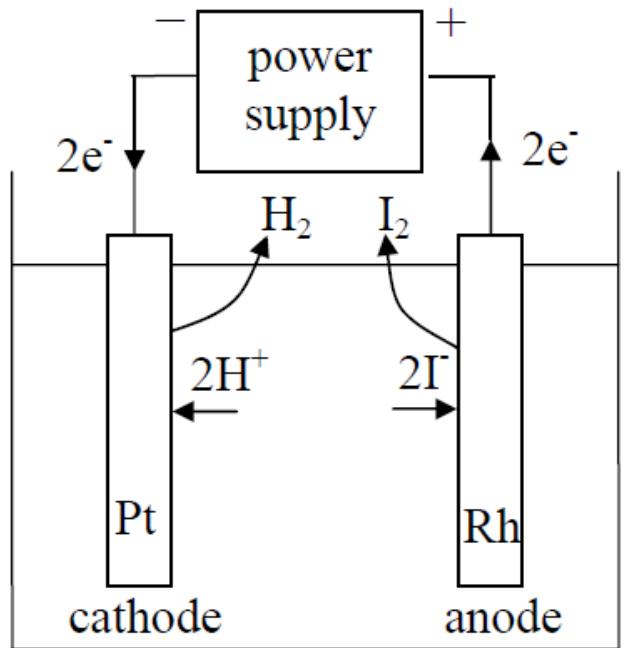


This reaction can be accomplished two ways as follows:

1. Chemical reaction - heat up pure HI gas until it decomposes

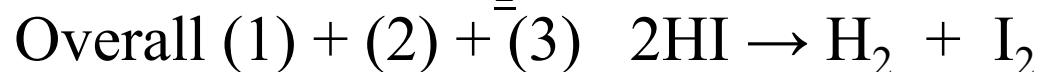
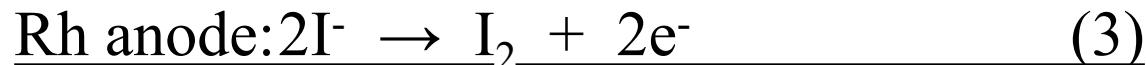
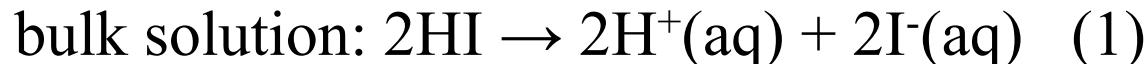


2. Electrochemical reaction

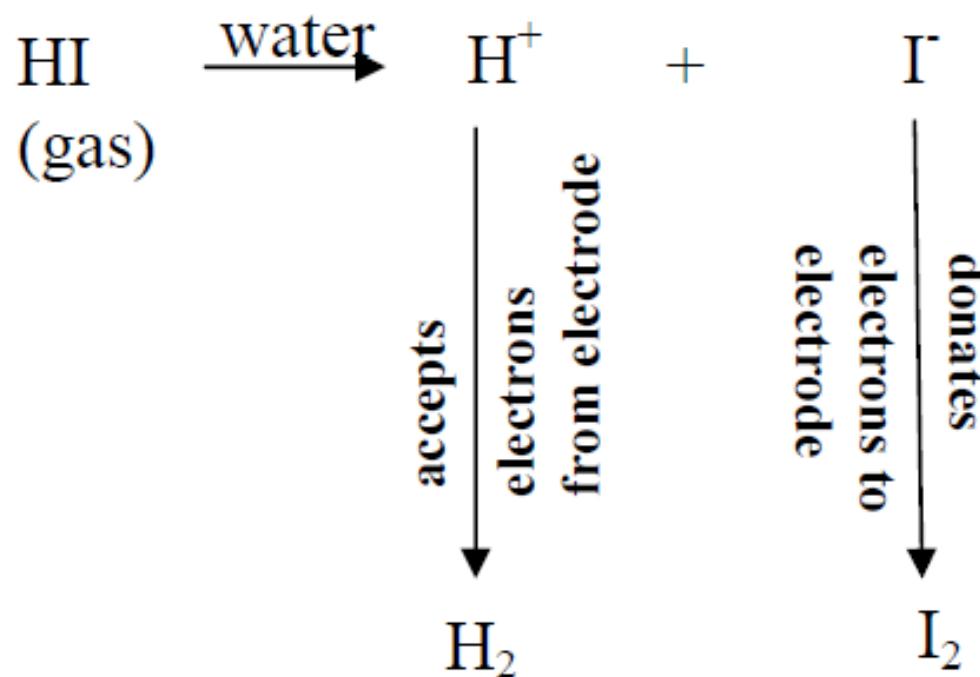


Immerse strips of Pt and Rh into an aqueous solution of HI. Hook the Rh to the positive terminal of a voltage source, Pt to the negative end. Increase voltage until you begin to see gas bubbles coming off each electrode.

The following processes have occurred:



In the electrochemical way, the reactant HI molecules do not collide with each other but with separated sources and sinks of electrons.



Chemical reaction	Electrochemical reaction
Electron transfer from one species to another takes place directly in the same medium.	Electron transfer from one species to another takes place indirectly through electrodes.
Energy is liberated in the form of heat, light and sound.	Energy is liberated in the form electrical energy.
The chemical reaction is instantaneous proceeding at a finite rate.	This reaction takes place only on the application of electricity.
Redox reactions take place in the same medium.	Redox reaction takes place separately at the Anode and cathode surface.

Advantage of an Electrochemical Route

- Separation of gas products is simple since they are formed on separate surfaces
- High purity Gases can be formed
- Can be carried out at low temperature

Disadvantages

- Production rate lower than with a thermal process since it depends on **electrode area** and on **solubility** of the reactant (HI)

How to solve the problem?

What is Electrochemical Engineering?

(Hint it involves engineering systems that combines chemistry and electricity)

- Batteries
- Fuel Cells / Hydrogen
- Supercapacitors
- Electrosynthesis/Electrorefining
- Electroplating
- Corrosion
- Sensors

10% of US electricity goes to electrosynthesis/refining

4% of US economy is eaten-up by corrosion each year

Why Electrochemical Energy

- Frontier Applications of Electrochemistry
 - Batteries
 - Fuel Cells
 - Supercapacitors
 - Photoelectrochemical cells
 - Electrochemical sensors

Grand Challenges for Next 50 Years

from Nobel Laureate Richard Smalley: 1943-2005

- 1. ENERGY**
- 2. WATER**
- 3. FOOD**
- 4. ENVIRONMENT**
- 5. POVERTY**
- 6. TERRORISM & WAR**
- 7. DISEASE**
- 8. EDUCATION**
- 9. DEMOCRACY**
- 10. POPULATION**



2004	6.5	Billion People
2050	~ 10	Billion People

Energy

Definition:

- The property of matter and radiation that is manifest as a capacity to perform work.
- The strength and vitality required for sustained physical or mental activity.
- The capacity of a physical system to perform work.
- Several different forms, such as kinetic, potential, thermal, electromagnetic, chemical, nuclear, and mass have been defined to explain all known natural phenomena.



Lightning is the electric breakdown of air by strong electric fields, which produce a force on charges. When these charges move through a distance, a flow of energy occurs. The electric potential energy in the atmosphere then is transformed into thermal energy, light, and sound, which are other forms of energy

Units and Conversions of Energy :

Unit of energy is **Joule (J)**

$$W = \int \mathbf{F} \cdot d\mathbf{x}$$

force distance

$$1 \text{ J} = 1 \text{ N m} = 1 \text{ kg} \frac{\text{m}^2}{\text{s}^2}$$

$$1 \text{ J} = 1 \text{ Coulomb Volt}$$

$$1 \text{ J} = 1 \frac{\text{Watt second}}{\text{Power time}}$$

To get an idea of the joule in everyday terms. **1 Joule is:**

- the energy required to lift a small apple (102 g) one meter against Earth's gravity.
- the amount of energy, as heat, that a quiet person produces every hundredth of a second.
- the energy required to heat one gram of dry, cool air by 1 degree Celsius.
- one hundredth of the energy a person can get by drinking a single 5 mm diameter droplet of beer.

Forms of Energy

Kinetic energy – the energy possessed by a moving mass

$$\text{Kinetic energy} = (\text{mass} \times \text{speed}^2)/2$$

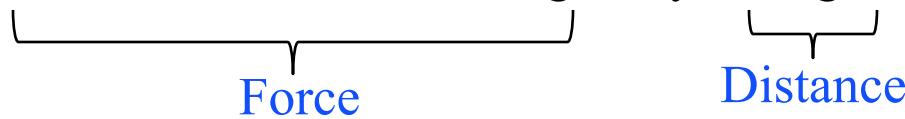
Kinetic energy within a body determines its temperature

- matter consists of atoms or molecules
- atoms or molecules in have kinetic energy manifested as vibration or motion
- the higher the temperature the faster the atoms or molecules are moving
- this atomic scale kinetic energy is known as *thermal energy*



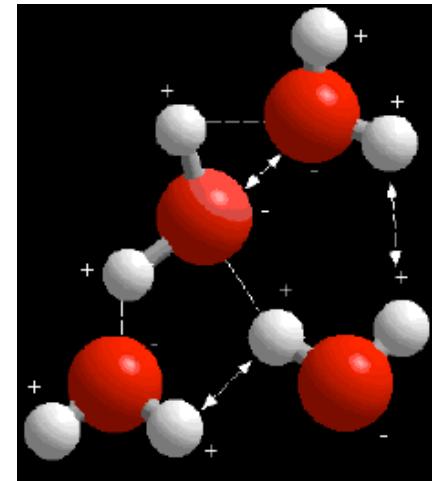
Potential or gravitational energy

$$\text{Potential energy} = \text{mass} \times \text{acceleration due to gravity} \times \text{height}$$



At the atomic scale gravitational force is insignificant and electrical force (forces between charges) dominates

- **Electrical energy** is the energy associated with electrical forces
- At the atomistic scale this electrical energy is **chemical energy** (the energy associated with chemical bonds)



Forms of Energy

Macroscopically (and technologically) electrical energy is manifested as **electrical currents** driving loads. For example a current of one amp through a load of one ohm resistance operating for one second is our old friend a Joule.

Electrical energy is also associated with fields (electrical and magnetic)

Light is a form of electromagnetic energy

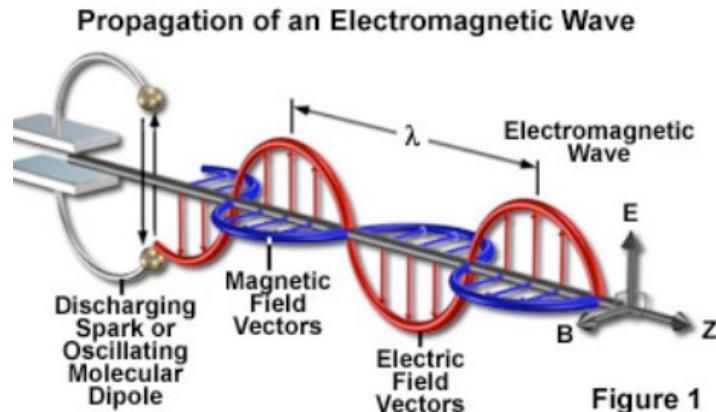
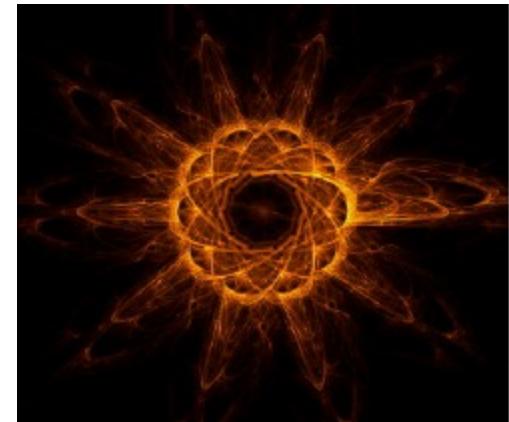


Figure 1

- **Nuclear energy** is the energy associated with the forces between the particles in the atoms nucleus
- At the sub-atomic length scales of the nucleus, these forces are much stronger than electrical forces
- Nuclear reactions convert mass to energy $E = mc^2$

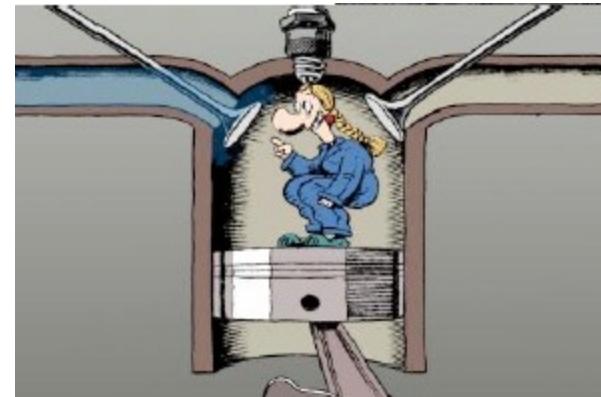


Energy Conversion

- The **first law of thermodynamics** says that in all processes, energy is conserved; neither created or destroyed (must include mass energy if considering nuclear processes).
- However, **the second law of thermodynamics** says that in converting from one form of energy to another, the useful output is always less than the input Energy Conversion
- The **efficiency** is the ratio of useful output to required input

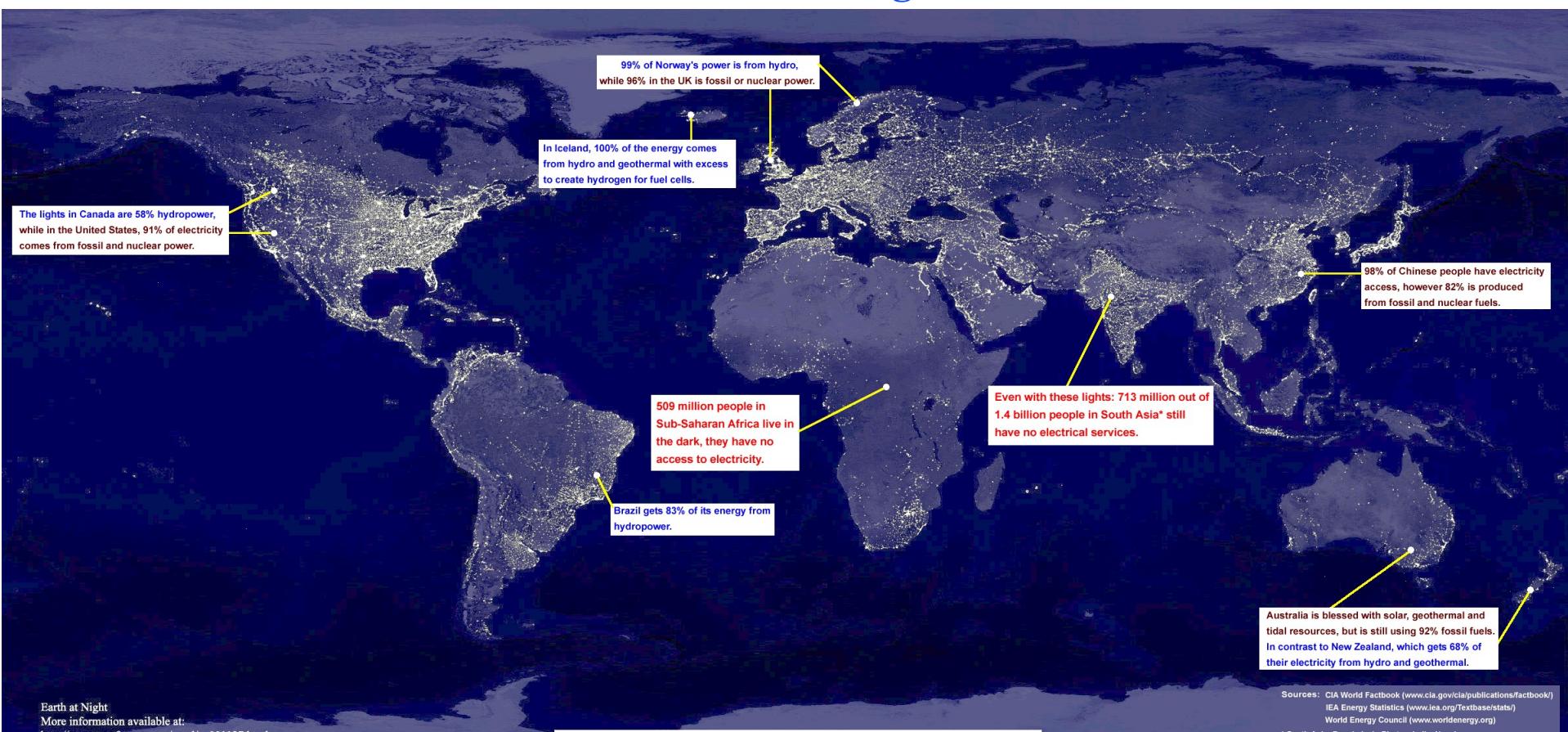
Typical efficiencies

1. Water turbine 90 %
2. Electrical Motor 90 %
3. Coal fired power station 35 – 40 %
4. Internal combustion engine 10 – 20 %
5. Solar cells 10 – 40 %



Distribution of Energy Consumption

The world at night



Earth At Night
More information available at:
<http://antwrp.gsfc.nasa.gov/apod/ap001127.html>

Online Version of this Map: www.geni.org/globalenergy/multimedia/earth-at-night.shtml

Electricity is Essential for Development

The Earth at Night map from NASA shows areas of prosperity -- those people with access to electricity. 1.6 billion, 25% of humanity, remain in the dark -- with no access to running water, refrigeration or lighting. Nearly all the lights in this picture are supplied via high-voltage transmission lines, and 100 nations already exchange power across borders. To meet the UN Millennium Development Goals, a combination of grid-connected and stand-alone renewable electricity development will

elevate a community out of basic poverty in an environmentally sustainable manner. While most nations use polluting fossil and nuclear fuels, abundant renewables -- hydro, geothermal, biomass, wind and solar -- exist on every continent. **Linking the renewable electricity resources in Africa and South Asia will provide the foundation for ending hunger and poverty.**

Sources: CIA World Factbook (www.cia.gov/cia/publications/factbook/)
IEA Energy Statistics (www.iea.org/Textbase/stats/)
World Energy Council (www.worldenergy.org)
* South Asia: Bangladesh, Bhutan, India, Nepal, Pakistan and Sri Lanka

Crowded

<http://www.census.gov/main/www/popclock.html>

00:24 UTC (EST+5) Jan 03, 2012

World =**6,985,321,489**

China	= 1.37B
India	= 1.20B
Americas	= 0.94B
Africa	= 0.92B
Europe	= 0.82B
The Rest	= 1.56B

US growth rate 18 births every 4 minutes

World growth rate **615** births every 4 minutes



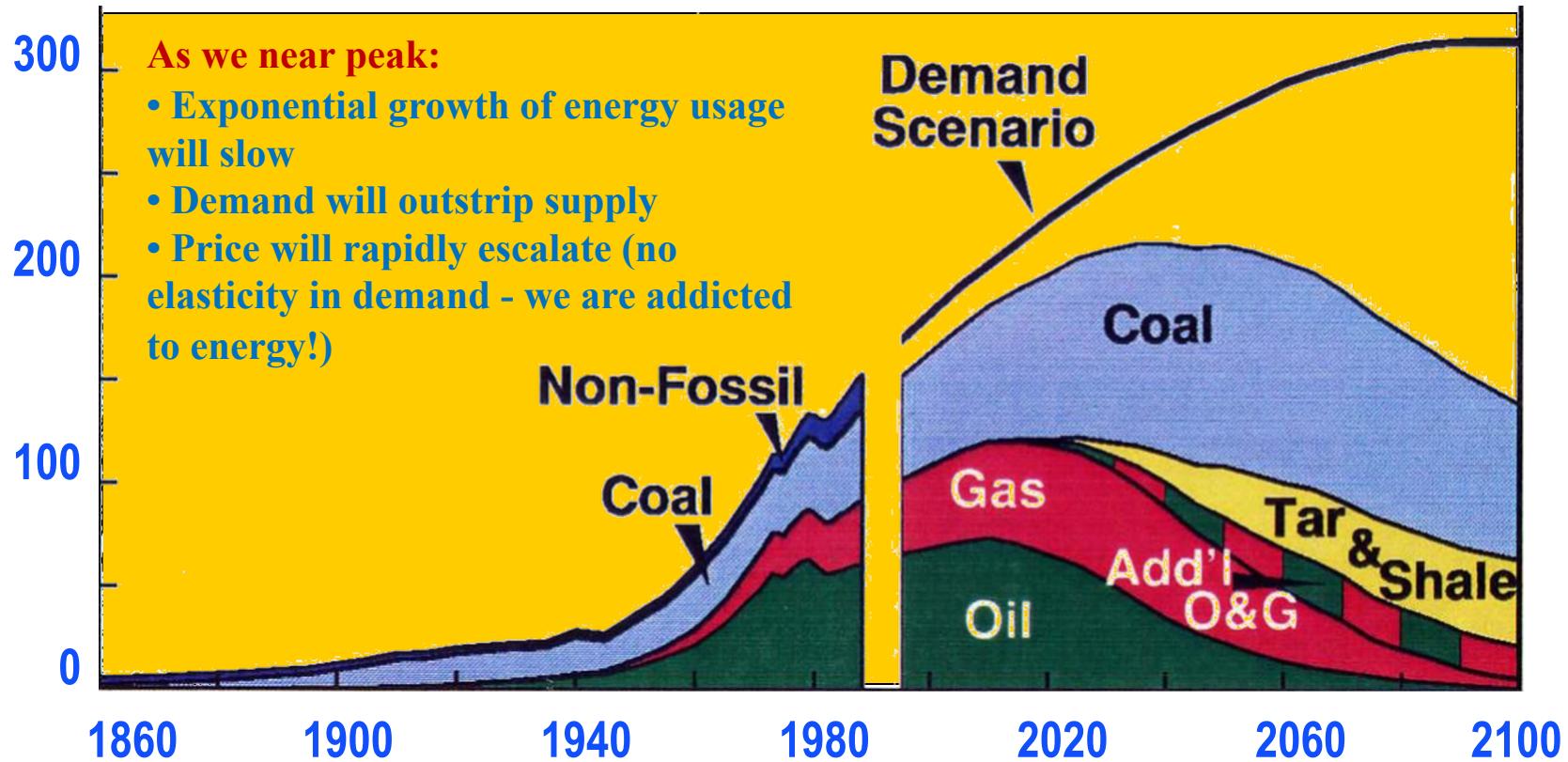
Mumbai, India - Rush Hour



A Crowded Beach In China

World Energy

Millions of Barrels per Day (Oil Equivalent)



Source: John F. Bookout (President of Shell USA), "Two Centuries of Fossil Fuel Energy" International Geological Congress, Washington DC; July 10, 1985. Episodes, vol 12, 257-262 (1989).

Climate Change

- Weather changes threaten loss of polar ice, rising sea levels, unpredictable rain falls, crop failures, and loss of many species
- Energy solutions must account for global warming

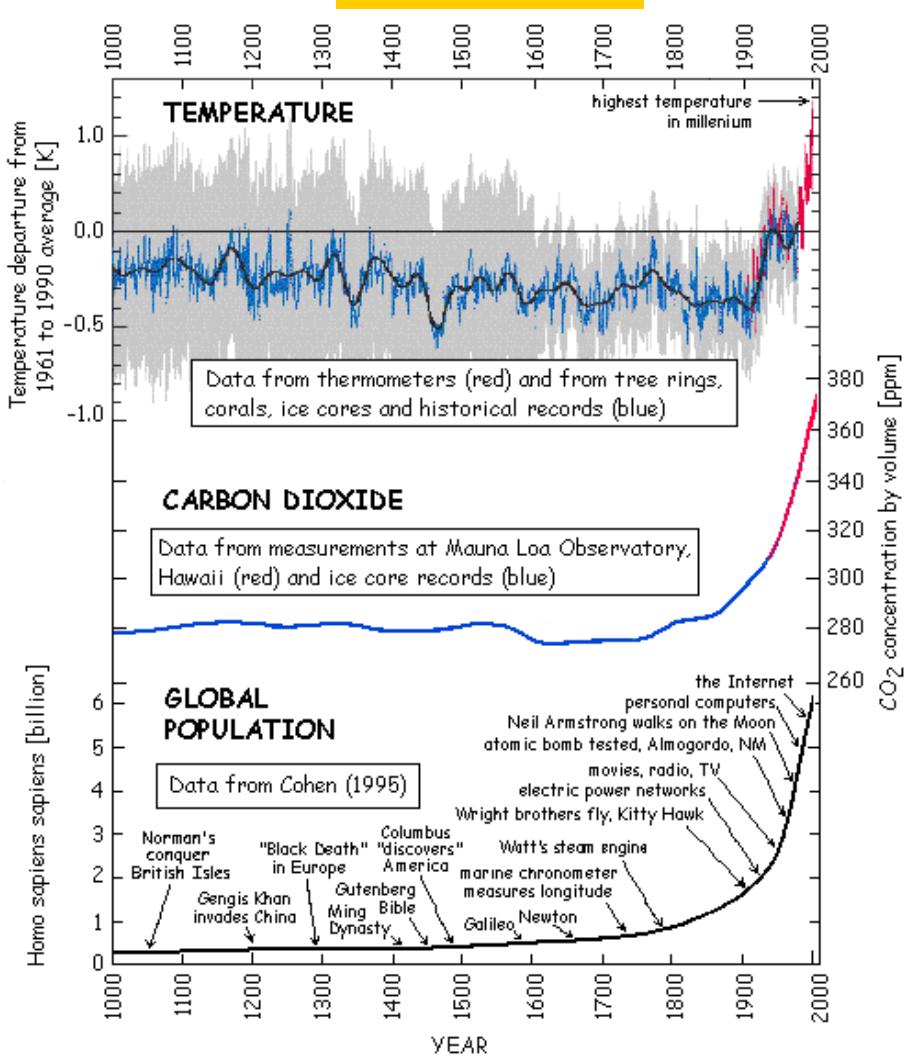
Shepard Glacier, Glacier National Park, Montana



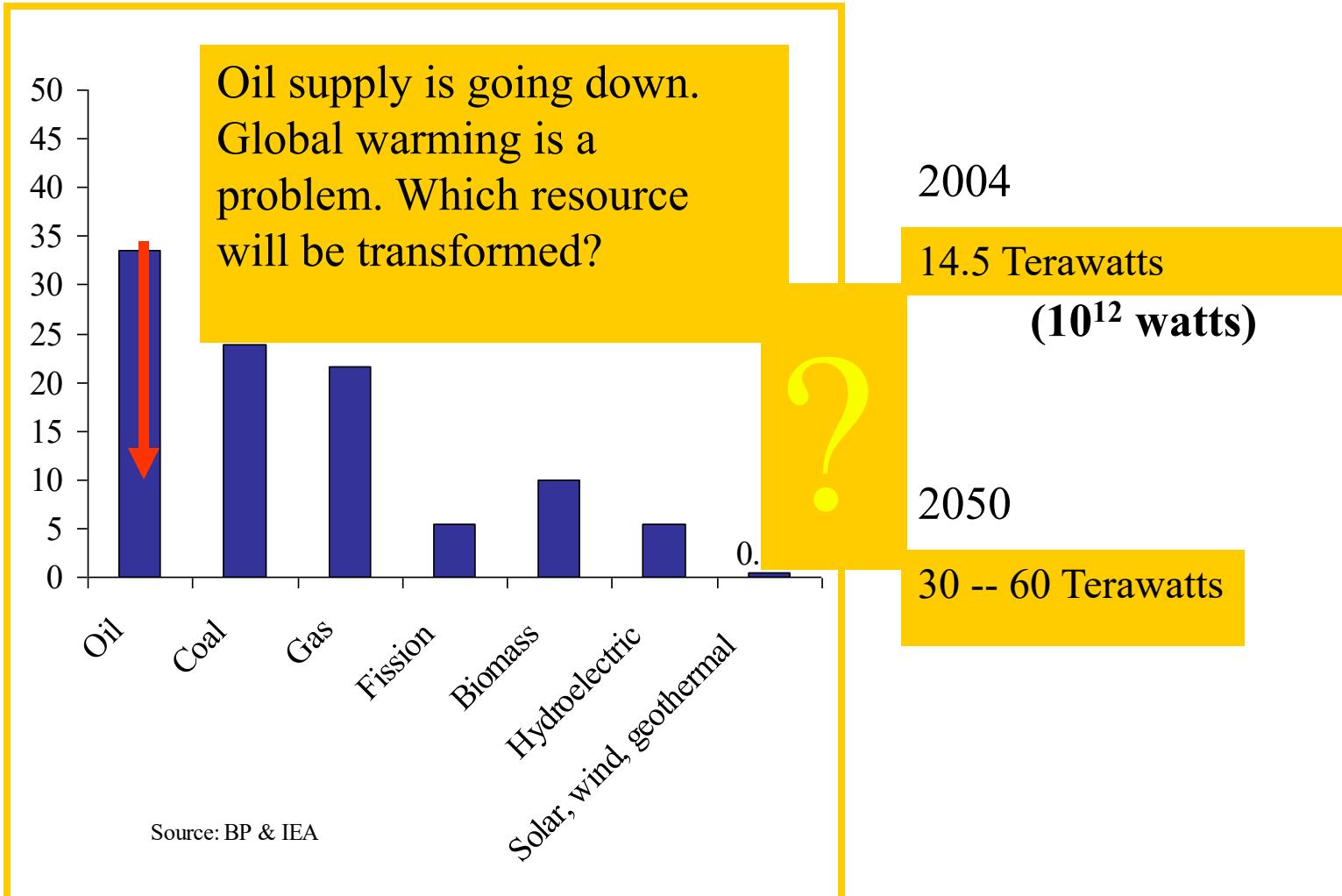
scientists predict that the park will be glacier free by 2030.

If all land ice in the world melt, sea level will rise approximately 230 feet (70 meters) worldwide.

From Hoffert



Transforming Global Energy Resources



Source: bp and IEA

Transition to Sustainable Energy

Current state (~15 TW)



Future state (~30 TW)



Technology Deployment
Policy



Goals: Inform & Accelerate Transition via new Science & Technology and System of Systems Models

Sustainable Energy Technologies

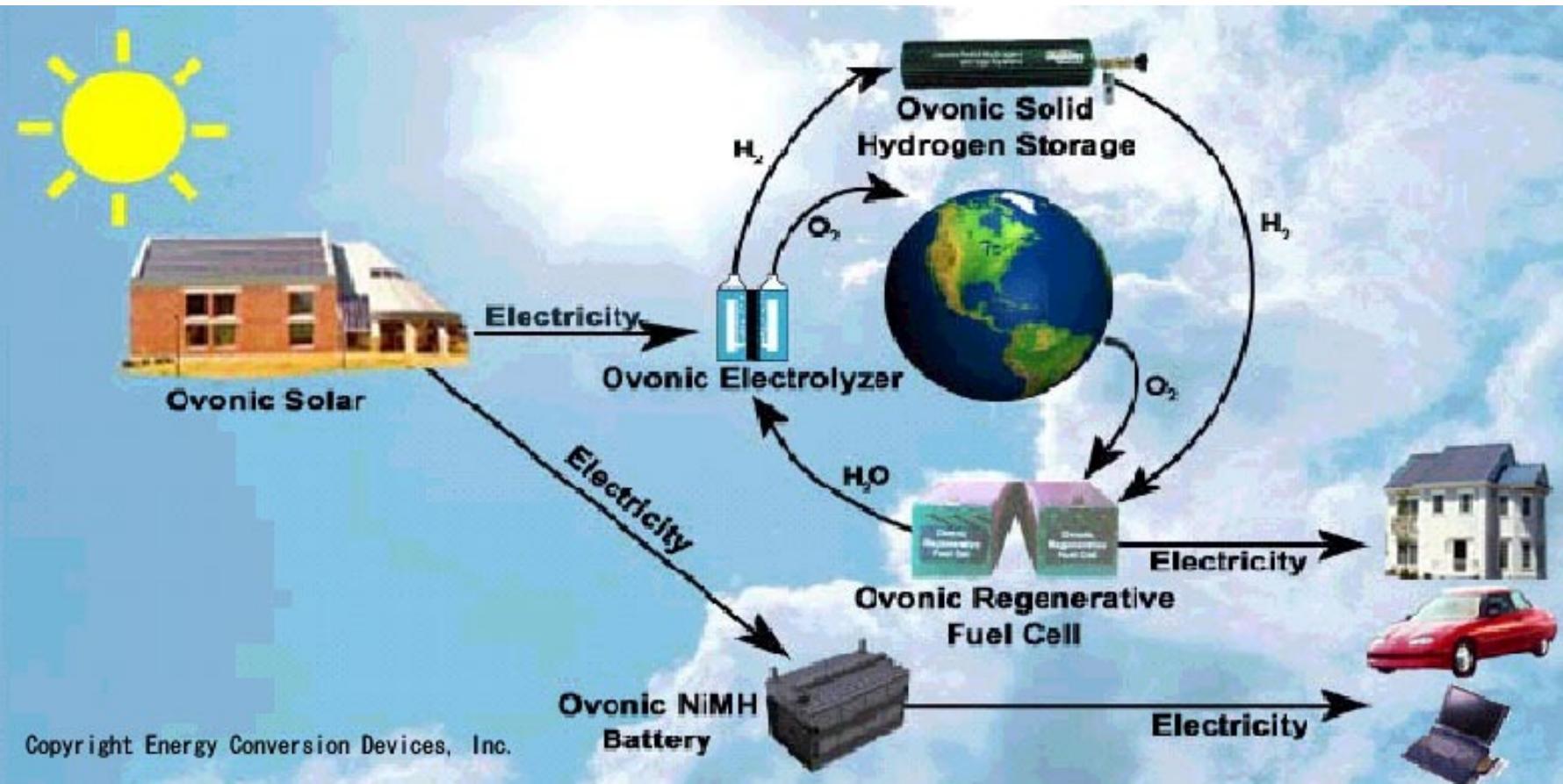
- ♥ Stop climate change by reducing consumption of fossil fuels and emission of GHG
- ♥ Sustainable energy technologies
 - Nuclear, Solar, Wind, Ocean, Geothermal Power
 - Biofuels from biomass
 - **Hydrogen and Fuel Cells**
 - **Electrochemical Energy Storage**
 - Energy Efficiency and Conservation
 - Clean Coal with CO₂ Capture and Sequestration

Magic Storage Device would have:

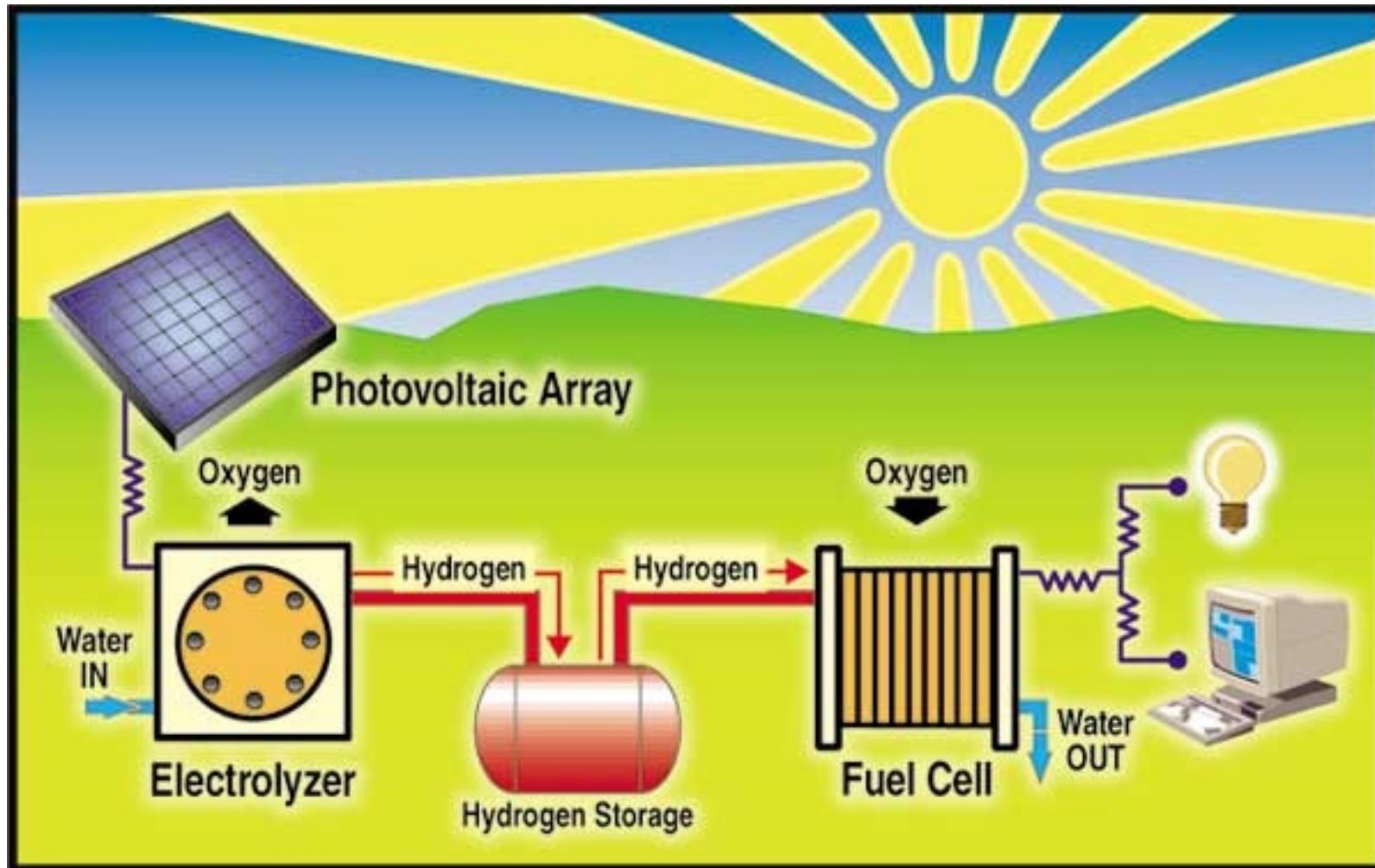
- Maximum power capabilities
- Maximum energy storage capabilities
- Insensitive to charging/discharging parameters
- Instant response
- Long life without degradation of properties
- Portable
- Lightweight
- Small Volume
- **Low cost**



Integrated renewable system



Hydrogen Economy - integrated renewable system



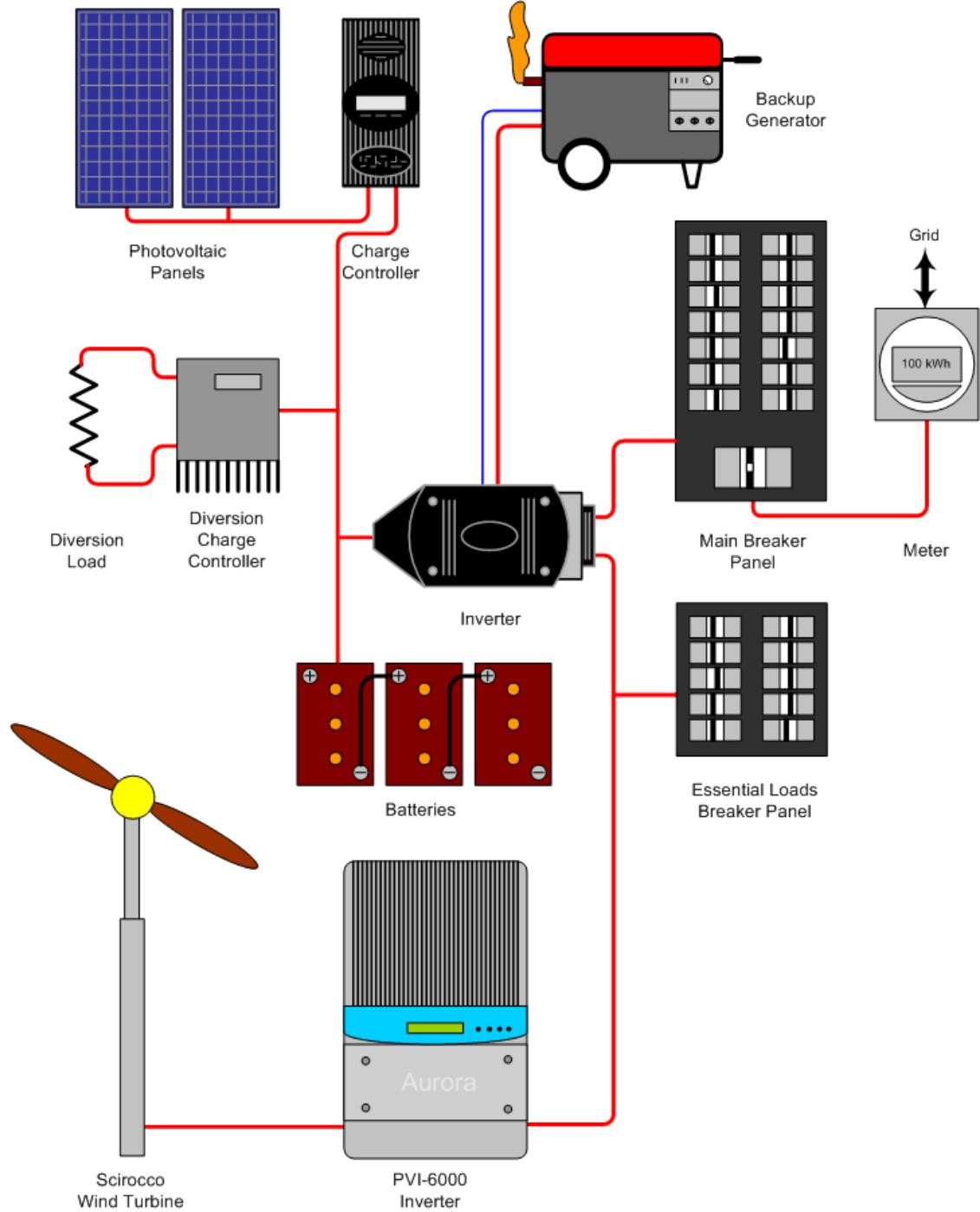
Hydrogen Production

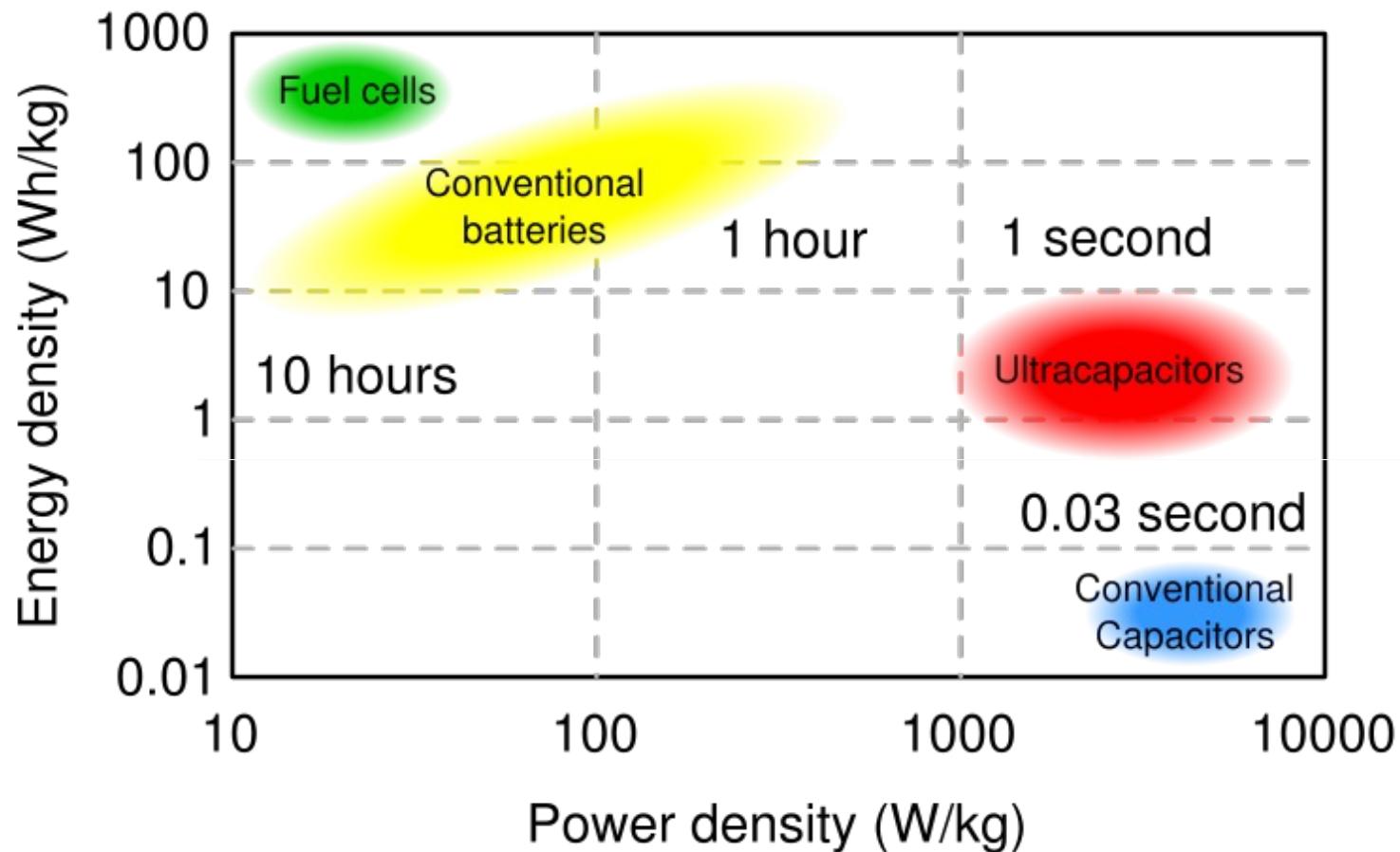
- ♥ Electrolysis (Hydro, Solar, Wind, Nuclear)
- ♥ Fossil Fuel Conversion (Natural Gas, Coal, Gasoline or Diesel)
 - Cracking
 - Reforming
 - Methanol at 260C
 - Water Gas Shift
- ♥ Bio-mass Conversion
- ♥ Bio-Diesel, Ethanol

Renewable Energy System



Renewable Energy System





Ragone plot showing energy density vs. power density for various devices along with discharge time.

Battery: More than just flashlight power!

Laptop battery

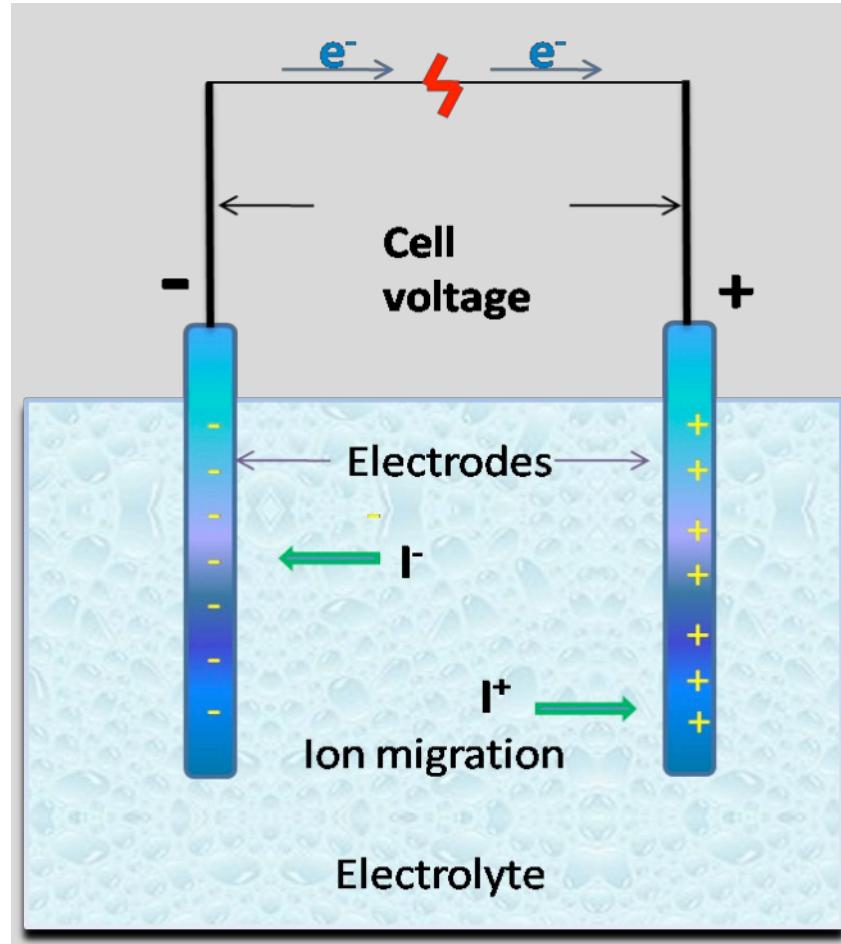


Medical battery



Implanted pacemakers, defibrillators, and neurostimulators rely on 10 year Li batteries

What a Battery Contains



4. Current collector

4. Current collector

2. Negative electrode (anode):

1. Positive electrode (cathode):

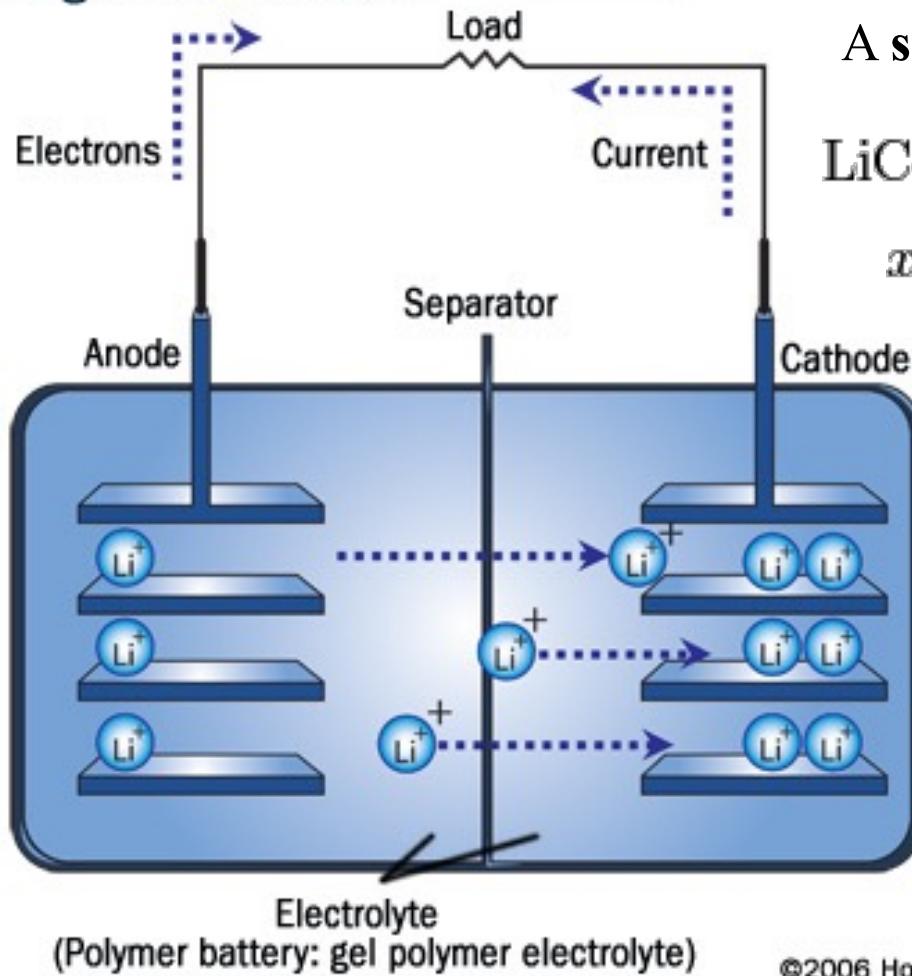
Not inert
Being oxidized when discharge

Not inert
Being reduced when discharge

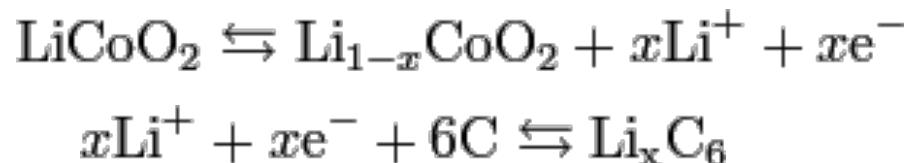
3. Electrolyte as or in Separator : ionic conductor, electronic insulator
Conducting Ions can be any: H^+ , OH^- , Li^+ , Na^+

Electrically conductive, electronically conductive

Lithium-ion rechargeable battery Discharge mechanism



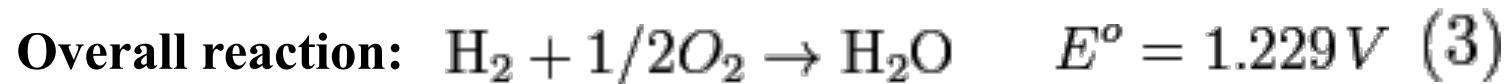
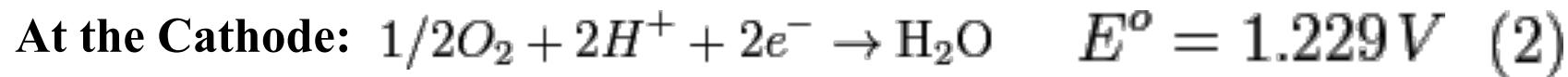
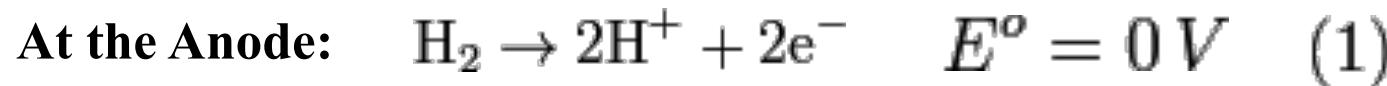
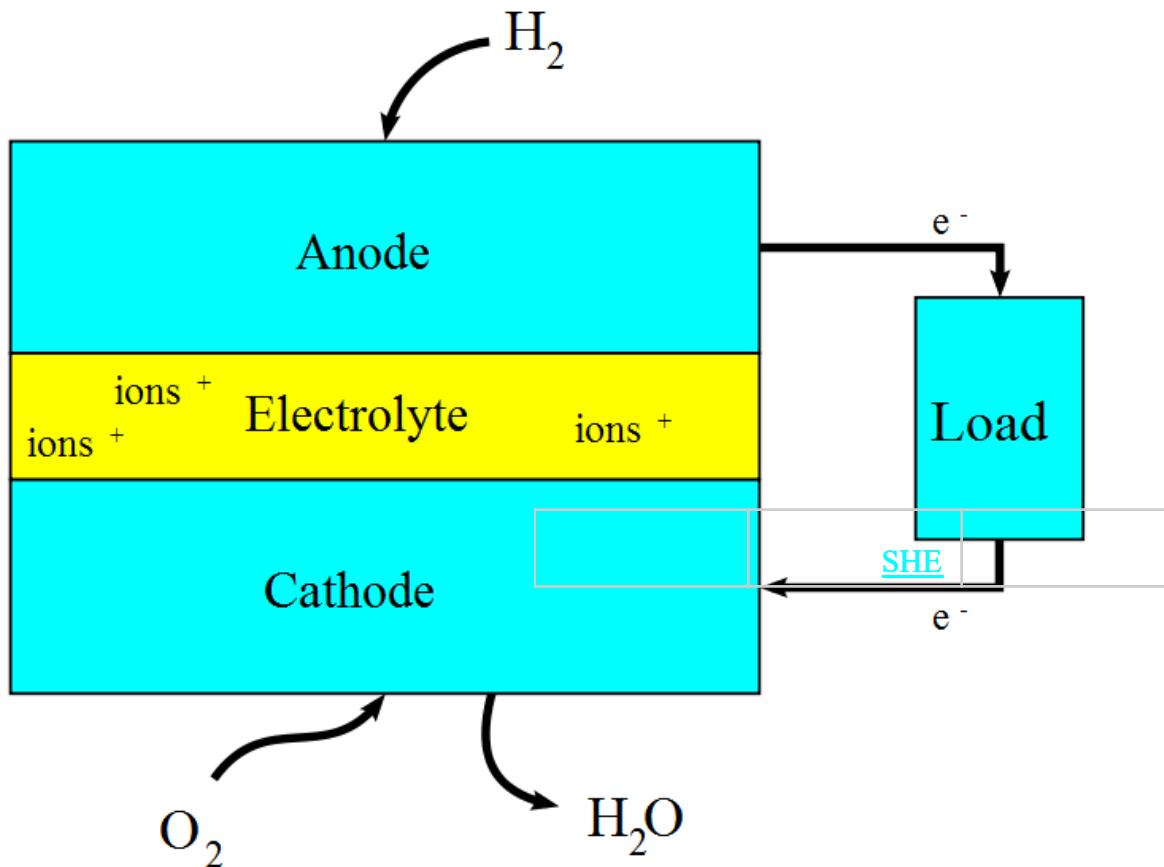
A Positive electrode
A Negative electrode
A separator

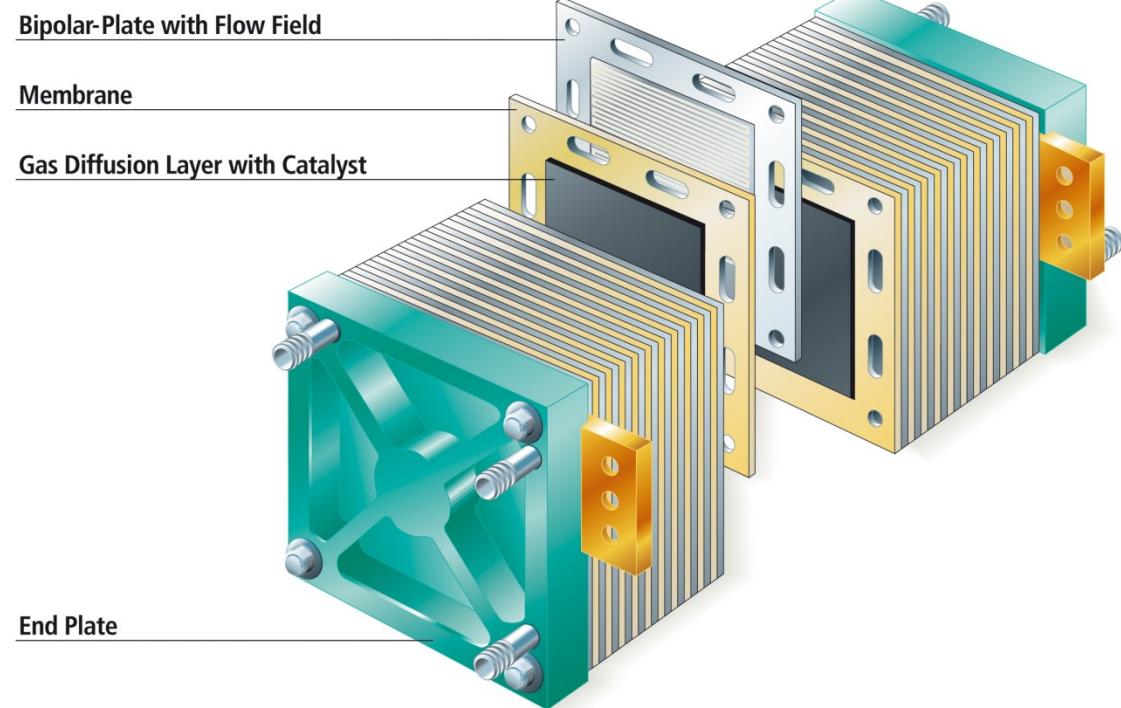
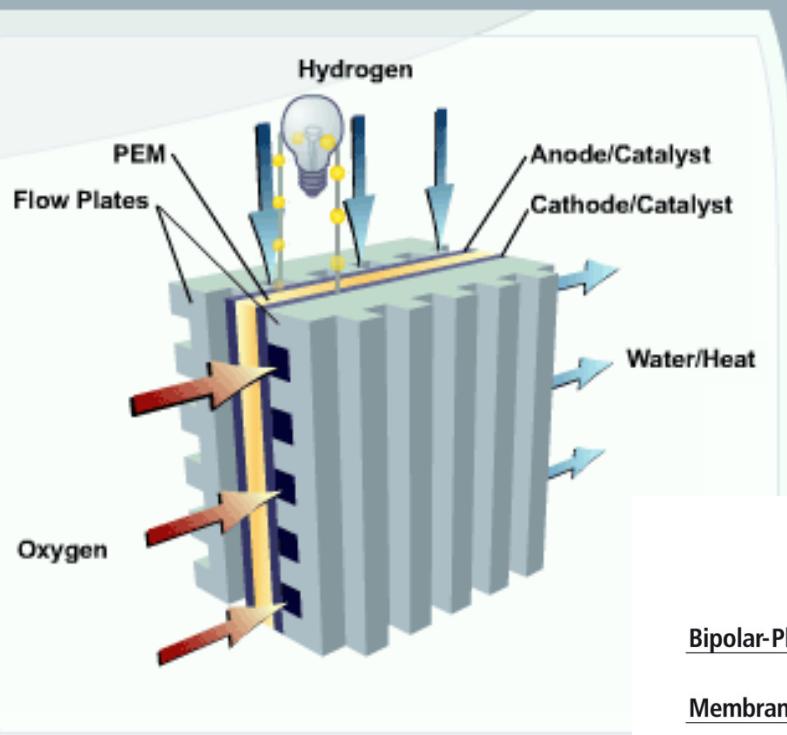


The positive electrode is made of Lithium cobalt oxide, or LiCoO_2 . The negative electrode is made of carbon. When the battery charges, ions of lithium move through the electrolyte from the positive electrode to the negative electrode and attach to the carbon. During discharge, the lithium ions move back to the LiCoO_2 from the carbon.

©2006 HowStuffWorks

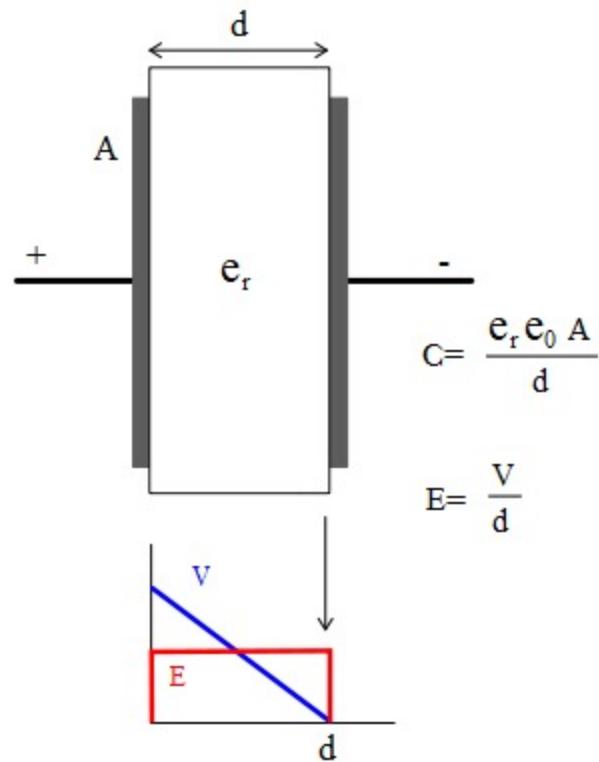
Fuel Cells: More than just a battery!



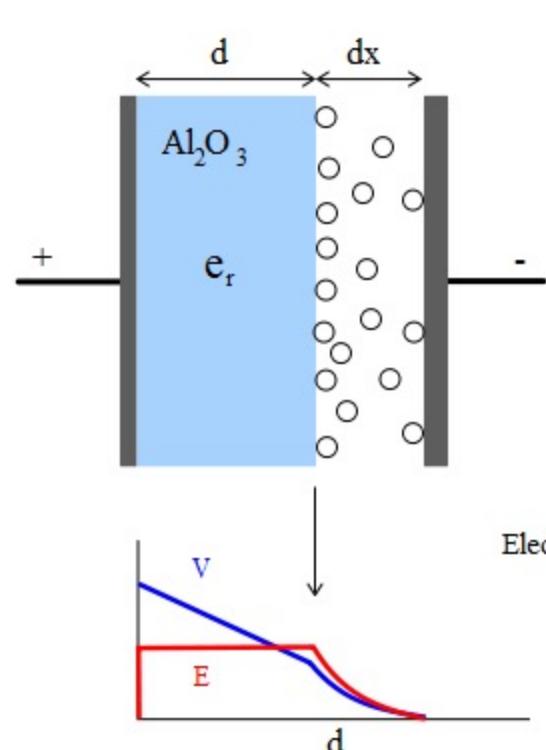


An **electric double-layer capacitor**, also known as **supercapacitor**, supercondenser, pseudocapacitor, electrochemical double layer capacitor (EDLC), or ultracapacitor, is an electrochemical capacitor with relatively high energy density, typically on the order of thousands of times greater than an electrolytic capacitor.

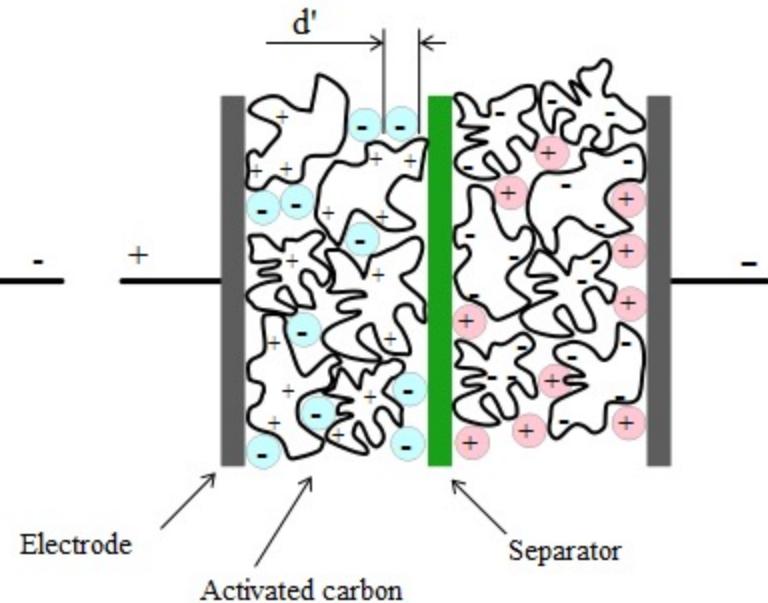
Electrostatic



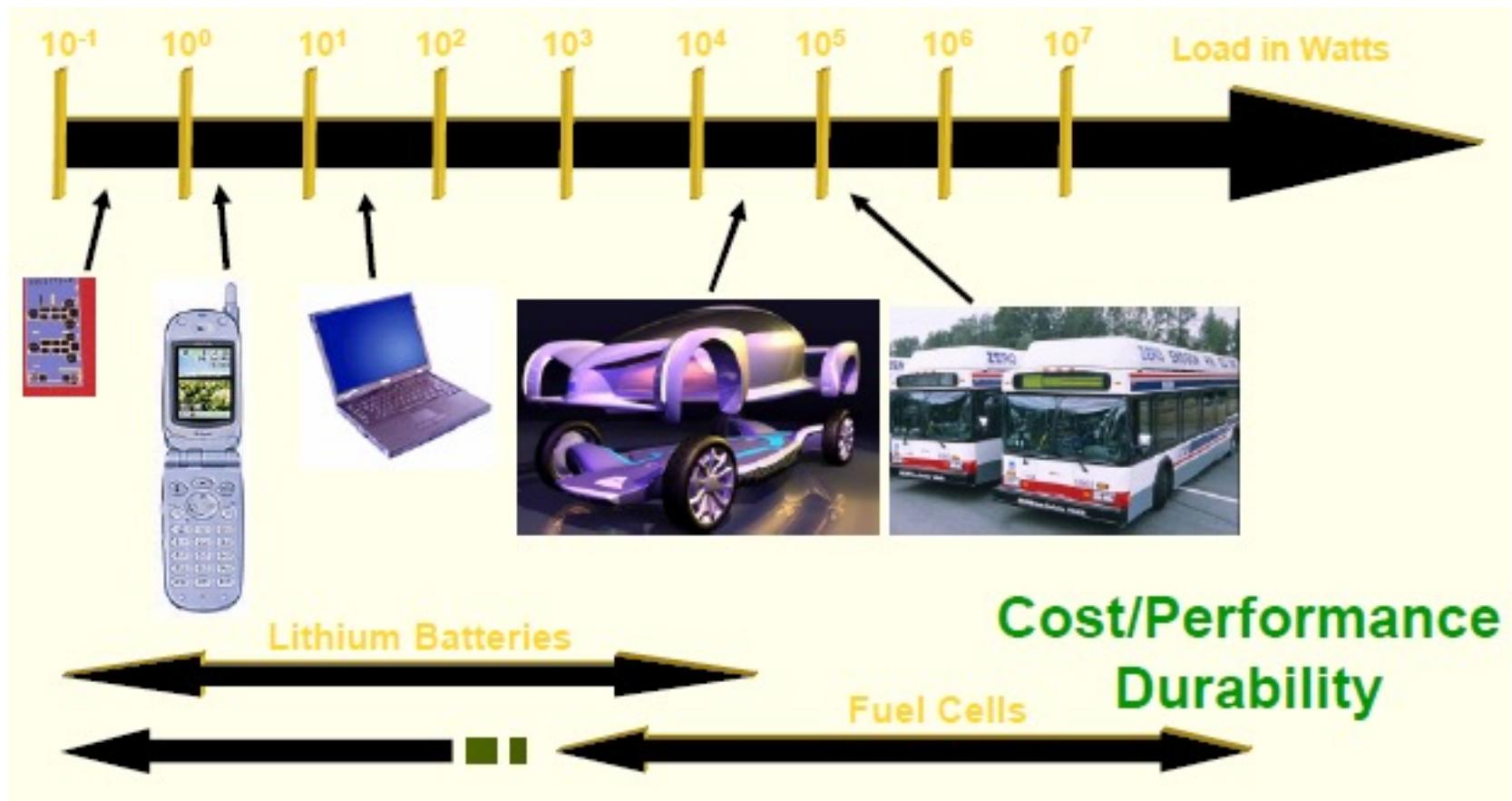
Electrolytic



Electrochemical double-layer

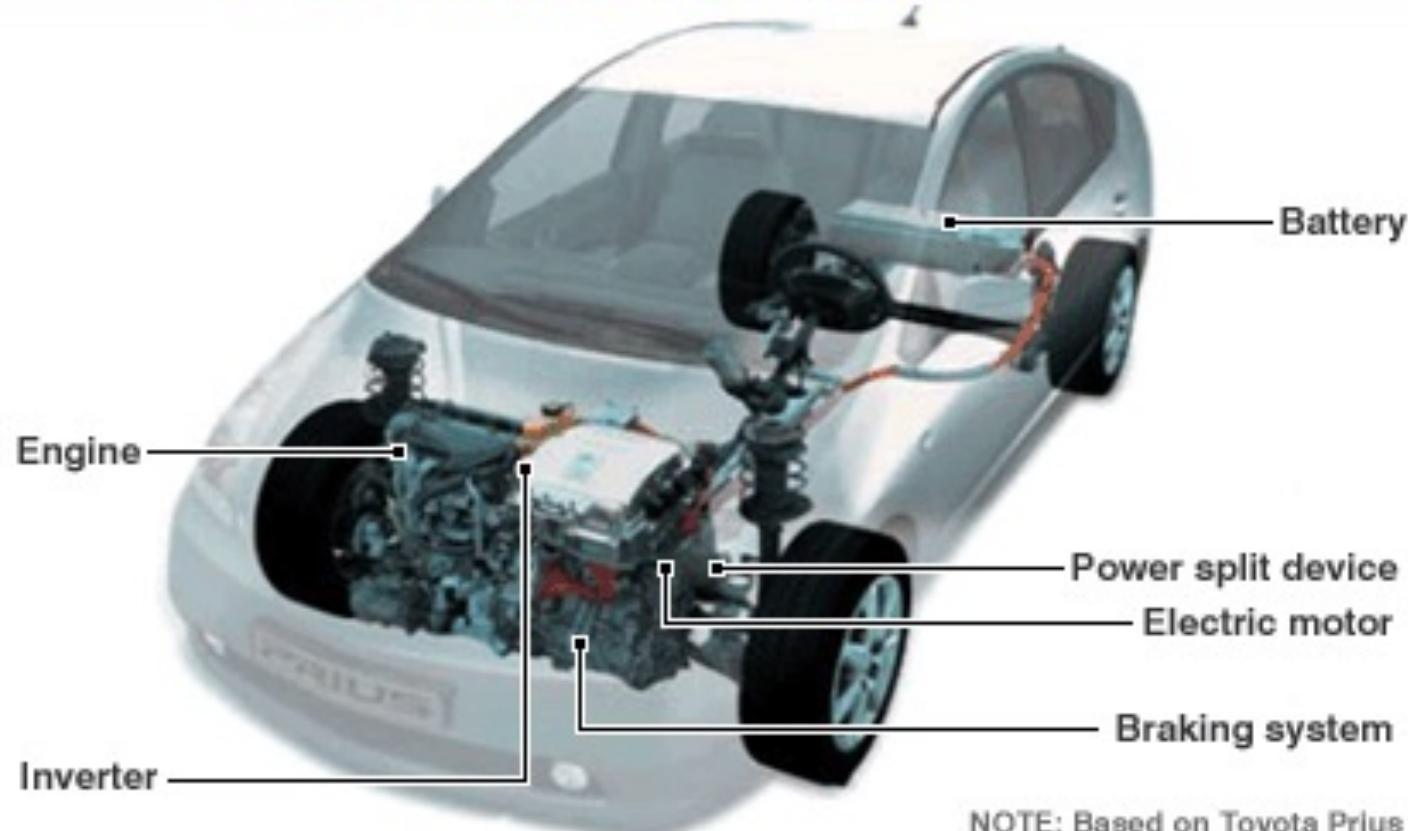
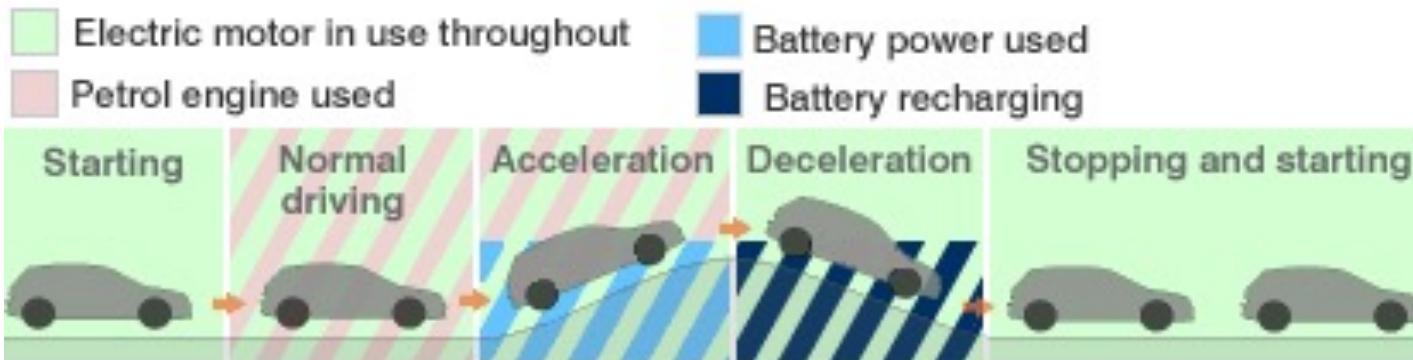


System Power Requirements and Challenges



KEY COMPONENTS OF A HYBRID CAR

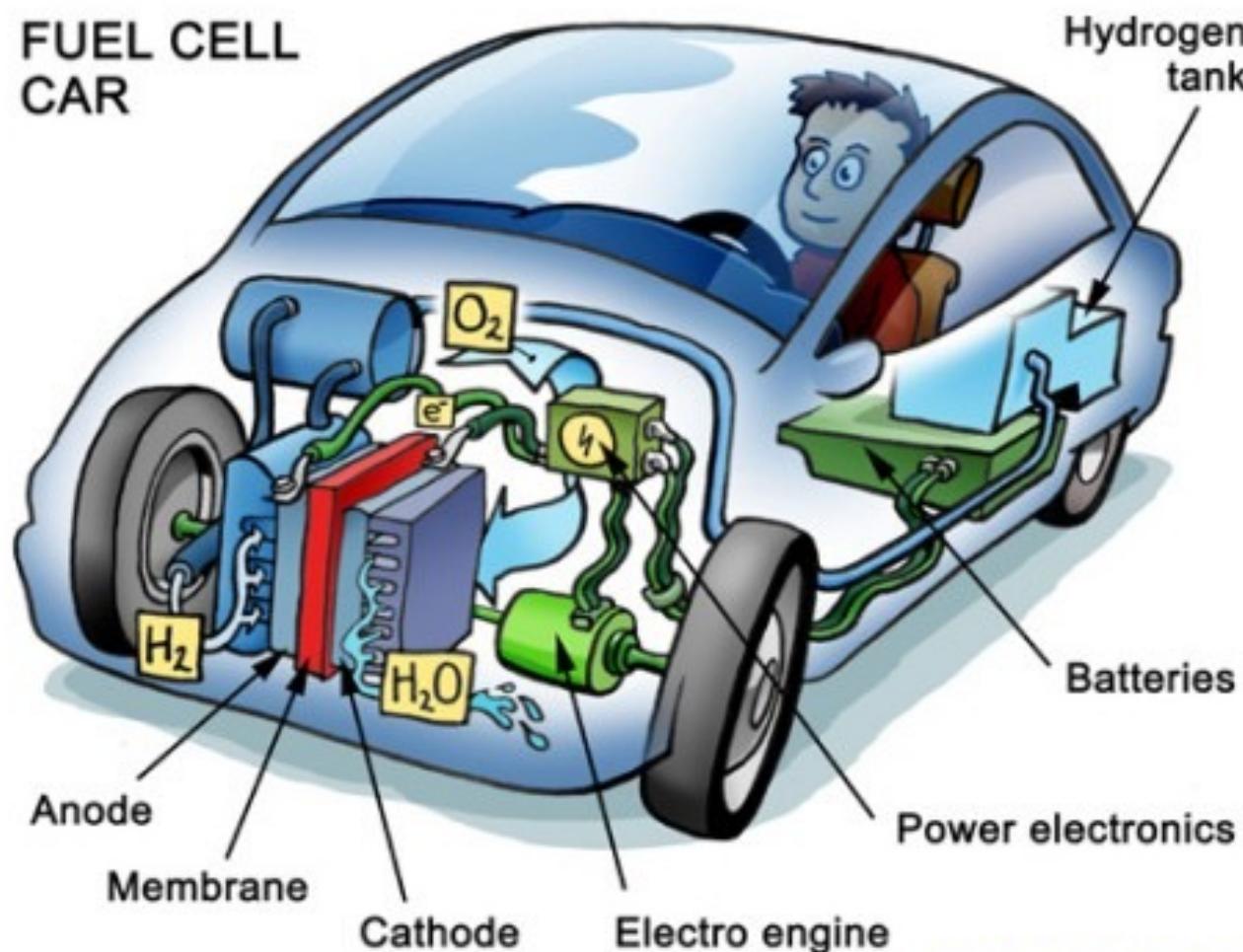
Many hybrid cars cut fuel consumption by combining a petrol engine with additional power sources - such as battery power



NOTE: Based on Toyota Prius



FUEL CELL CAR



www.imageproduction.nl



Overview of Electrochemical Processes

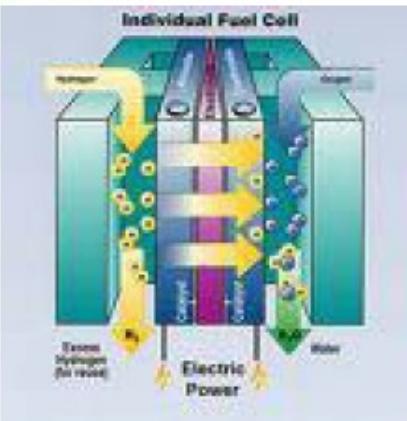
Electrochemical engineering: interrelation between electrical and chemical effects

- ❑ Corrosion and electroplating (\$400 billion)
- ❑ Electrochromic display
- ❑ Electrochemical sensor
- ♥ **Batteries, fuel cells, solar cells**

86.2 B \$1 B \$2.5 B \$11B

2010
↓
2016

\$9.1 B \$15.1B \$60.8B



Enabling Tech Revolutions

1. Photovoltaics -- drop cost by 10 fold.
2. Photocatalytic reduction of CO₂ to methanol.
3. Direct photoconversion of light + water to produce H₂.
4. **Batteries, supercapacitors, flywheels -- improve by 10-100x for the distributed Store/Gen Grid, and automotive applications (especially plug-in hybrid vehicles).**
5. Power cables (superconductors, or quantum conductors) with which to rewire the electrical transmission grid, and enable continental, and even worldwide electrical energy transport; and also to replace aluminum and copper wires -- particularly in the windings of electric motors and generators.
6. H₂ storage -- light weight materials for pressure tanks and LH₂ vessels, and/or a new light weight, easily reversible hydrogen chemisorption system (material X).
7. **Fuel cells -- drop the cost + durability + price**

Section II

REVIEW OF REDOX TERMS

Oxidation and reduction in terms of electron transfer

Remember that in terms of electrons:

LEO – Loss of Electrons Oxidation

GER – Gain of Electrons Reduction

REDOX equilibria:



When solid magnesium forms its ions, it loses electrons. The magnesium is being oxidized.



When the copper(II) ions gain electrons to form copper, they are being reduced.

Reducing agents and oxidizing agents

A *reducing agent* reduces something else. That must mean that it gives electrons to it.

Magnesium is good at giving away electrons to form its ions. Magnesium must be a good reducing agent.

An *oxidizing agent* oxidizes something else. That must mean that it takes electrons from it.

Copper doesn't form its ions very readily, and its ions easily pick up electrons from somewhere to revert to metallic copper. Copper(II) ions must be good oxidizing agents.

The electrochemical series

equilibrium	E° (volts)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li(s)}$	-3.03
$\text{K}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{K(s)}$	-2.92
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ca(s)}$	-2.87
$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na(s)}$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg(s)}$	-2.37
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al(s)}$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn(s)}$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe(s)}$	-0.44
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb(s)}$	-0.13
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$	+0.34
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag(s)}$	+0.80
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Au(s)}$	+1.50

Judging the oxidising or reducing ability from E° values

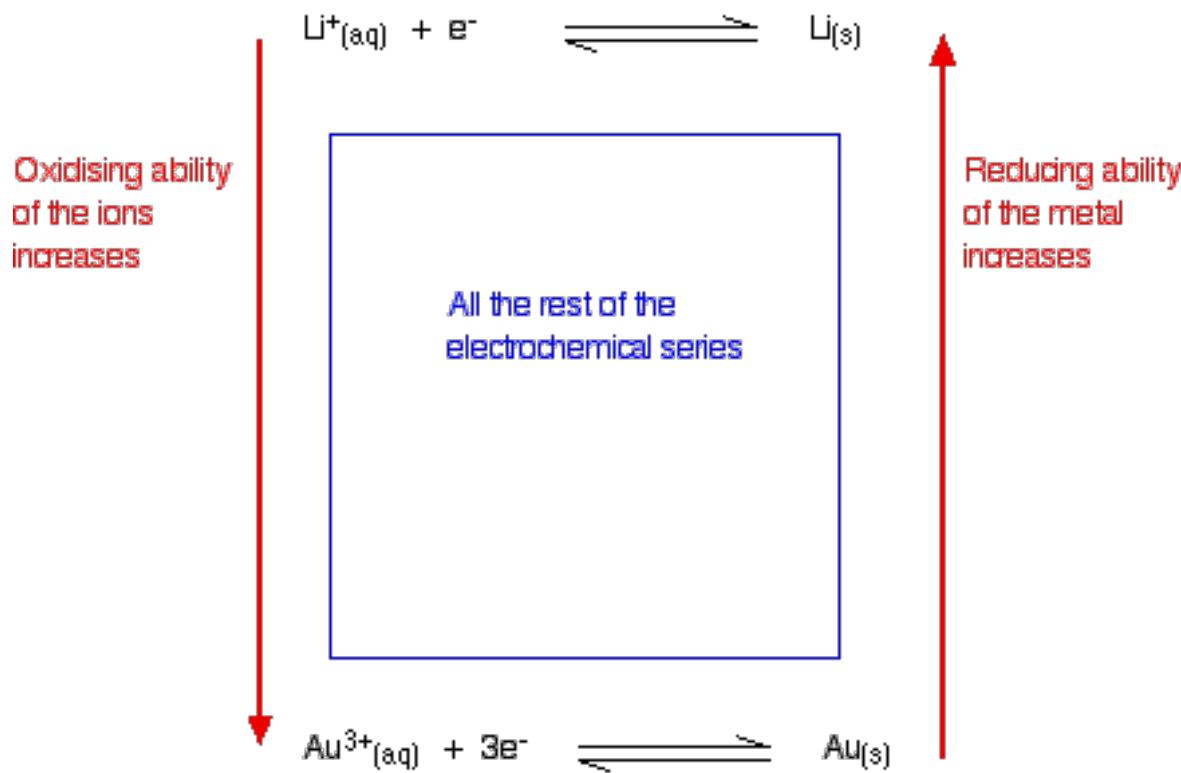
The more negative the E° value, the more the position of equilibrium lies to the left - the more readily the metal loses electrons. **The more negative the value, the stronger reducing agent the metal is.**

The more positive the E° value, the more the position of equilibrium lies to the right - the less readily the metal loses electrons, and the more readily its ions pick them up again. **The more positive the value, the stronger oxidising agent the metal ion is.**

Summarizing this on the electrochemical series

Metals at the top of the series are good at giving away electrons. They are good reducing agents. The reducing ability of the metal increases as you go up the series.

Metal ions at the bottom of the series are good at picking up electrons. They are good oxidising agents. The oxidising ability of the metal ions increases as you go down the series.

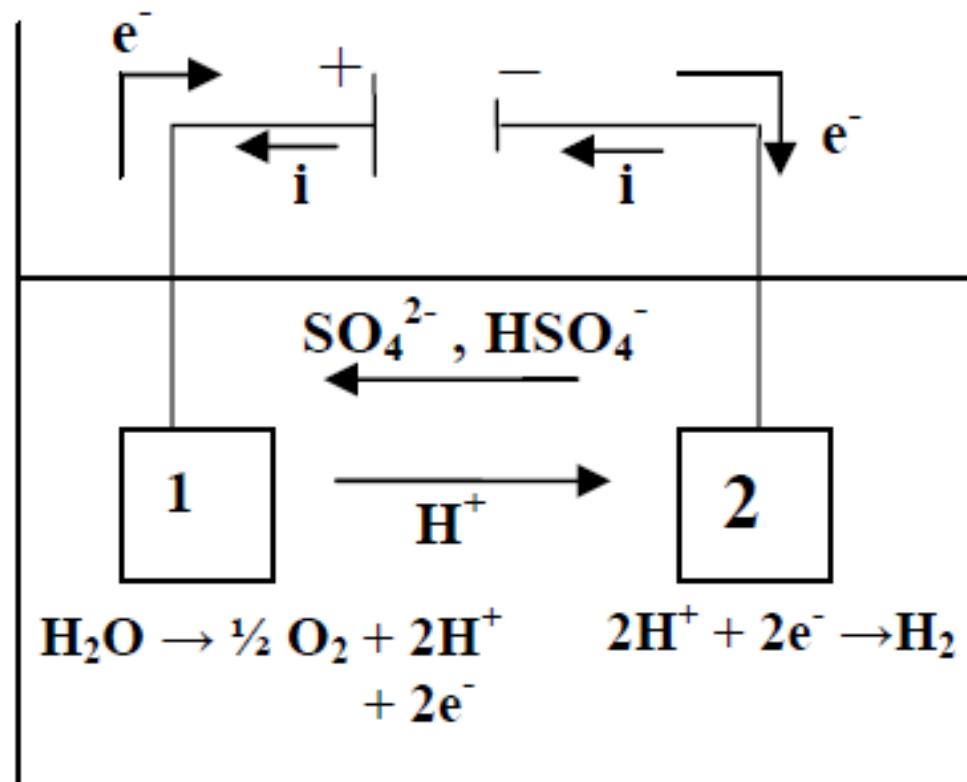


Some Basic Electrochemical Cells

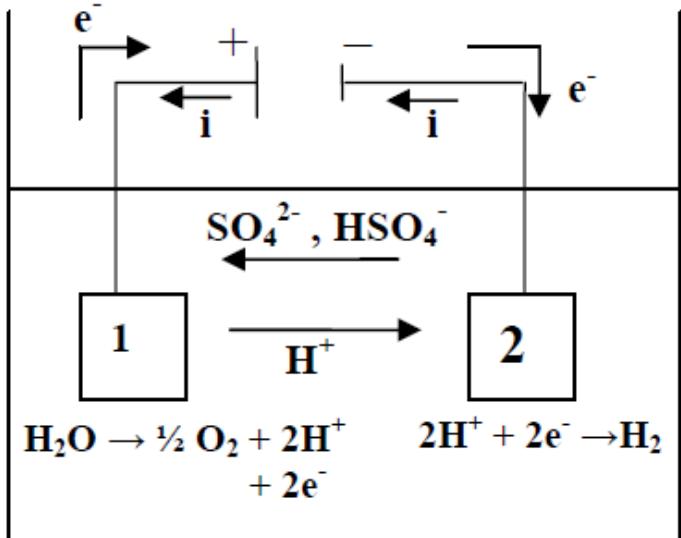
We can think of electrons as being as much of a reactant or product as, let's say, an ion diffusing to a surface and reacting. One important aspect of electrochemical reactions is that **electrons** can only move within an **electronic conductor**, eg. metal or semiconductor, whereas **ions** can only move within an **ionic conductor**, eg. electrolyte.

Some Basic Electrochemical Cells

You are probably familiar with the following type of electrochemical cell for the electrolysis of H_2O in H_2SO_4 .



Some Basic Electrochemical Cells



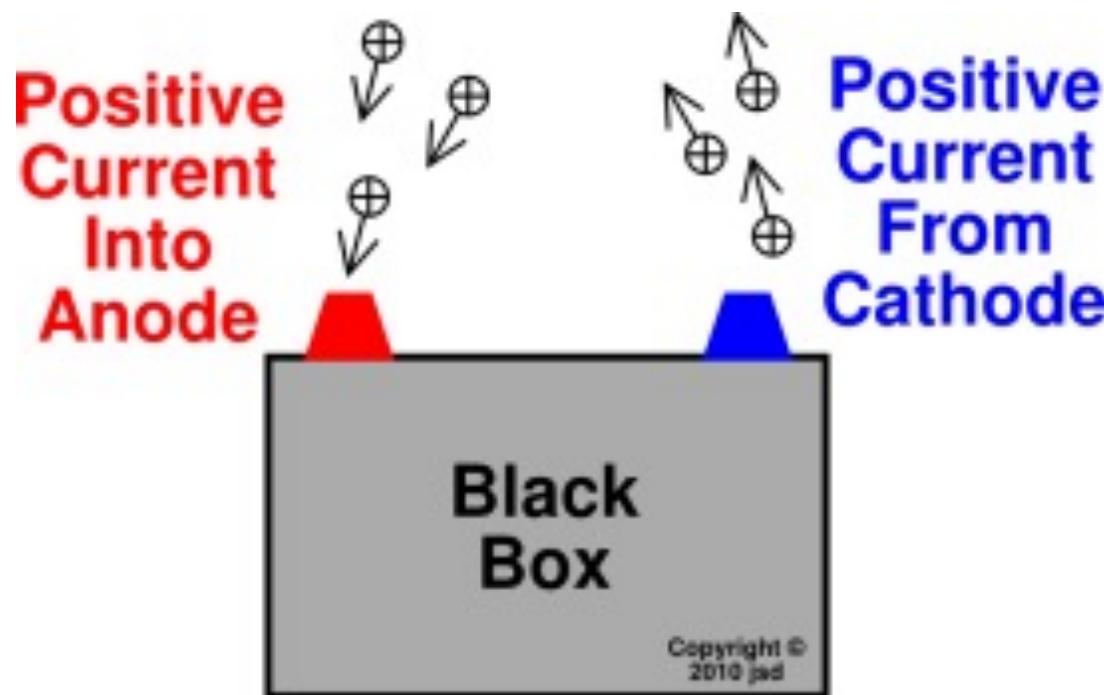
Electrolytic Cell

Voltage is applied between two metal strips immersed in an aqueous solution so that a current begins to flow. Current is simply a measure of the flow rate of electrons through the circuit. Electrons begin to flow because the two electrode reactions begin to occur.

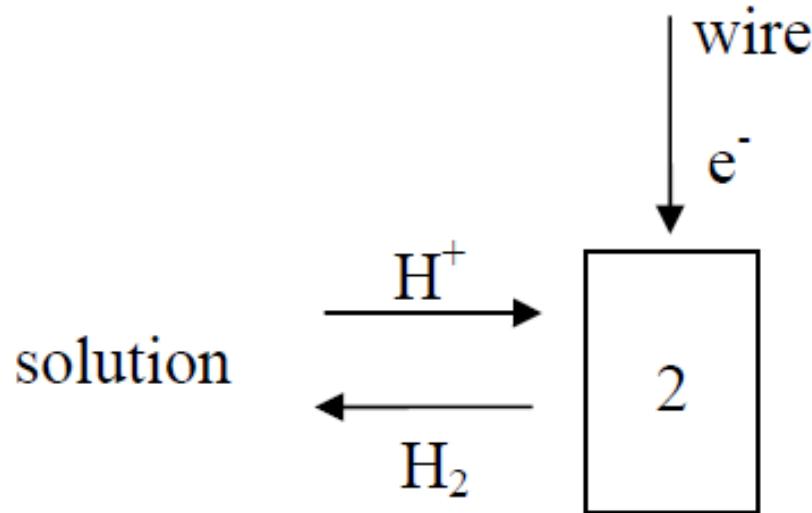
In the case shown, the power supply pumps electrons or negative charge carriers from the negative terminal in a clockwise direction around the circuit to the positive terminal (by convention, current moves in the opposite direction). Electrons flow from the negative terminal through the wire until they reach electrode 2.

Anode and Cathode

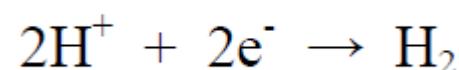
The *anode* of a device is the terminal where current flows in from outside. The *cathode* of a device is the terminal where current flows out.



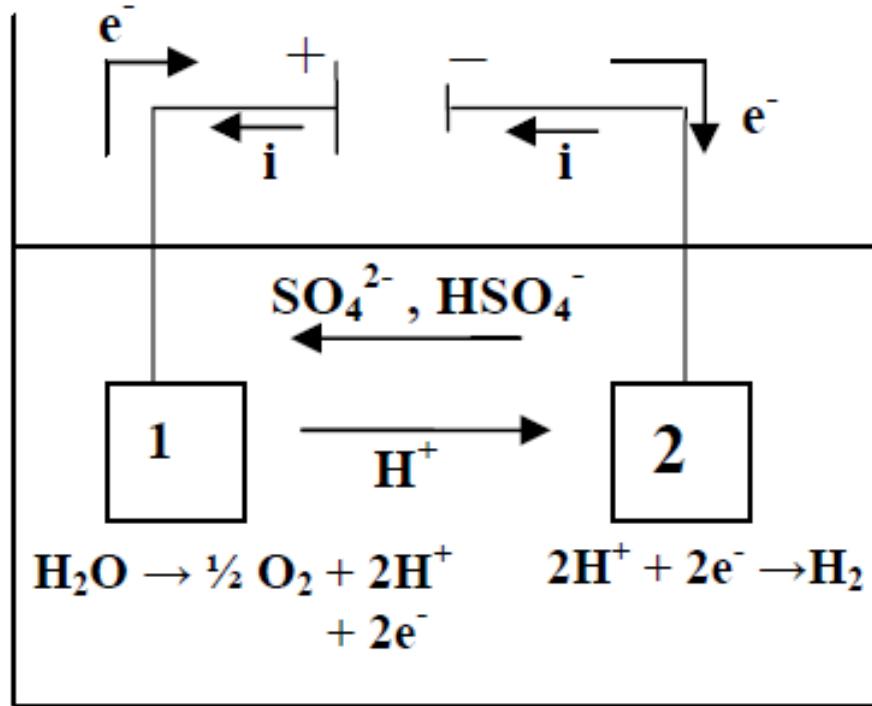
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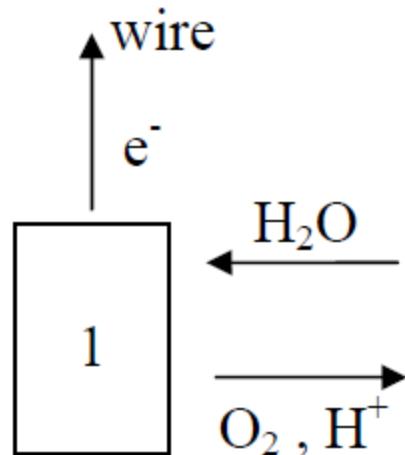
the electrons combine with H^+ from the solution via the reaction to produce H_2



Cathode: cathodic reaction, reduction reaction

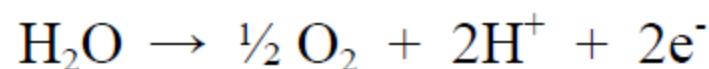


An important characteristic of the electrolyte is that it tries to maintain electroneutrality everywhere. With the consumption of H^+ ions at the cathode, local electroneutrality can be maintained if other H^+ ions can move into take their place or if negative charge carriers move away from the electrode. In this case, the negative charge carriers in the solution are SO_4^{2-} and HSO_4^- , but not electrons since the electrolyte is not an electronic conductor.



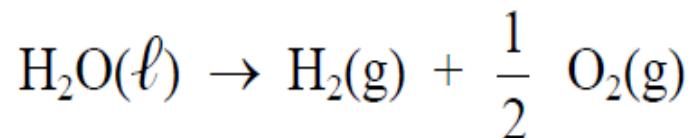
Electrons always appear as products in these reactions and are transferred from a species in the solution (H_2O in this case) to the electrode and the wire.

electrons are returned to the external circuit by the reaction



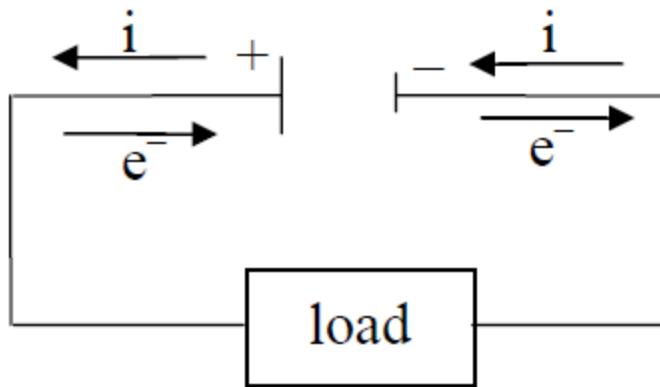
Anode: anodic reaction, oxidation reaction

N.B. This is an example of an electrolytic process. In such a process, electrical energy is used to drive the overall reaction

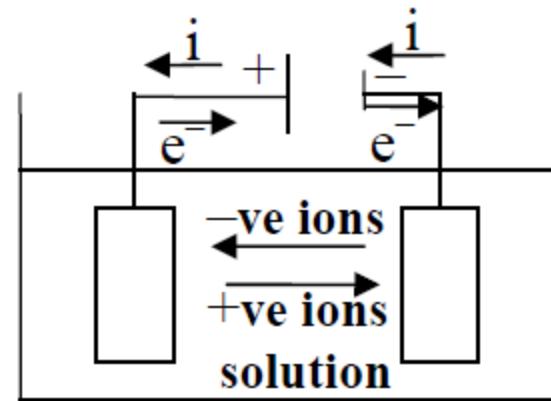


that would not otherwise occur.

Analogy Between Electric Circuits and Electrochemical Circuits



electric circuit



electrochemical circuit

There is obviously a close analogy between the two types of circuits. In fact, one way of analysing electrochemical circuits is by converting them to their electrical circuit analogues.

Analogy between electrochemical system and fluid flow?

Fluid flow rate



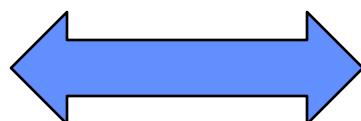
Current

Pressure drop



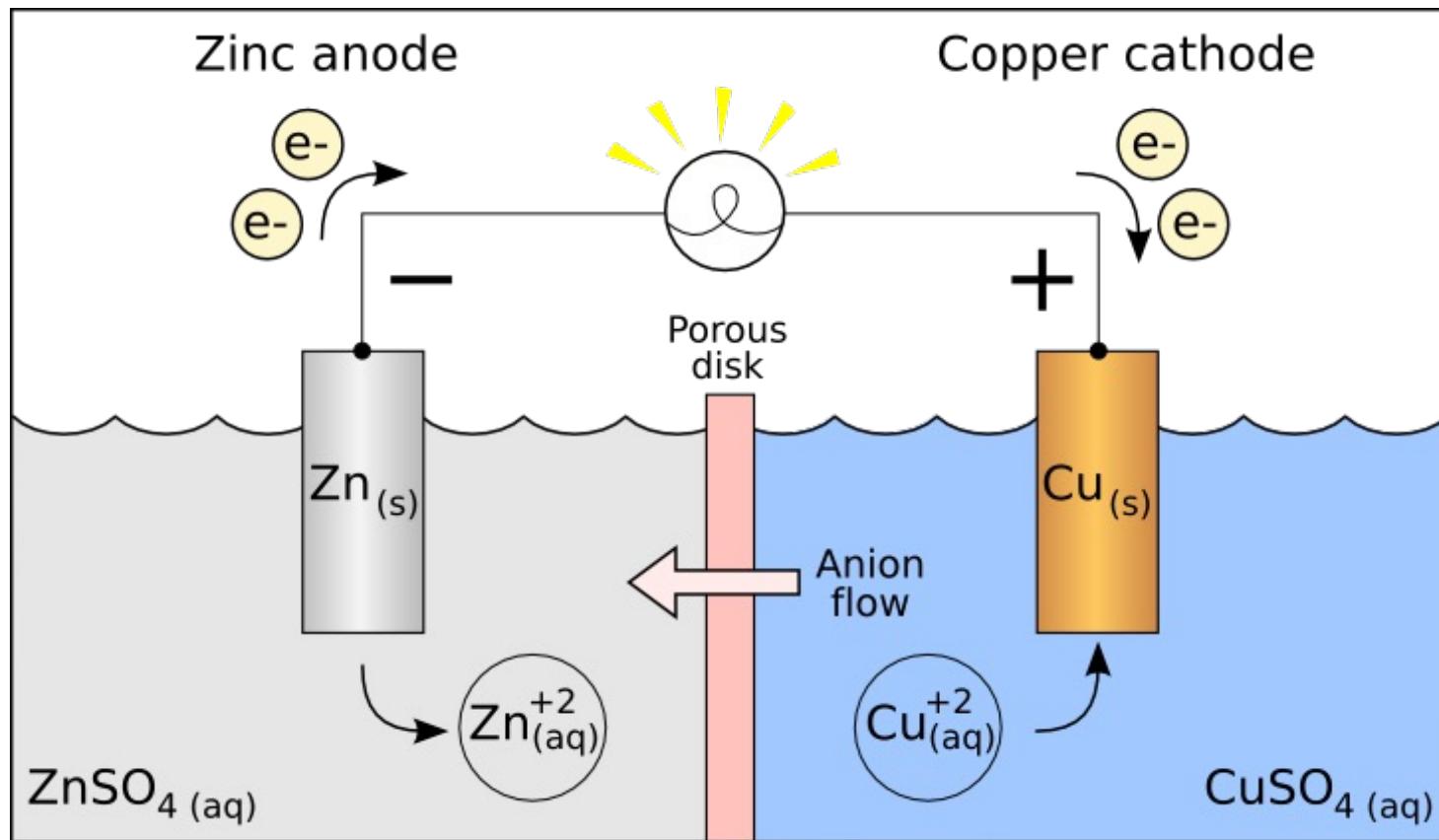
Voltage

pump



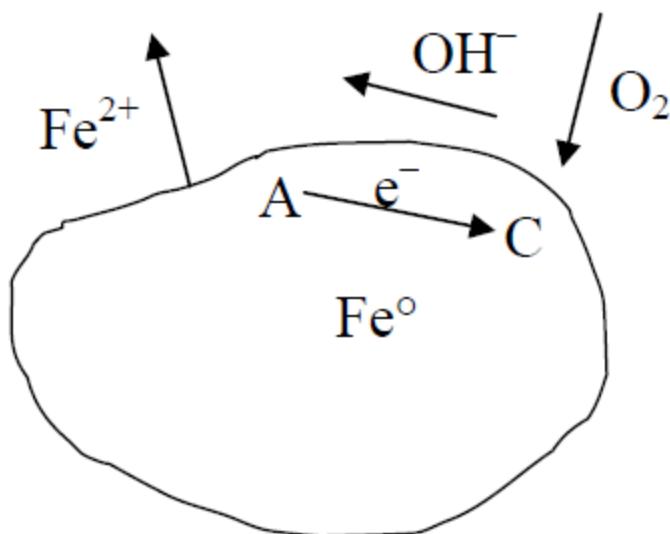
Electric power supply

Galvanic cell

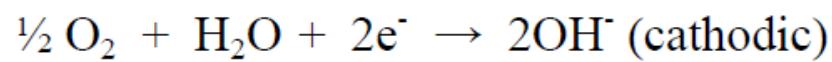


Galvanic cell

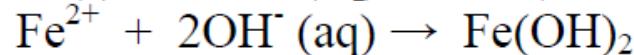
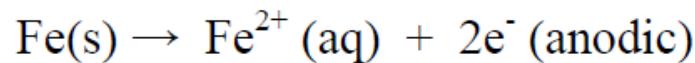
A piece of iron is exposed to moist air. What do you think will happen? The iron will corrode. What does that mean?



A thin invisible layer of water forms on the iron surface. O_2 in this layer reacts at sites denoted C on the surface as follows:



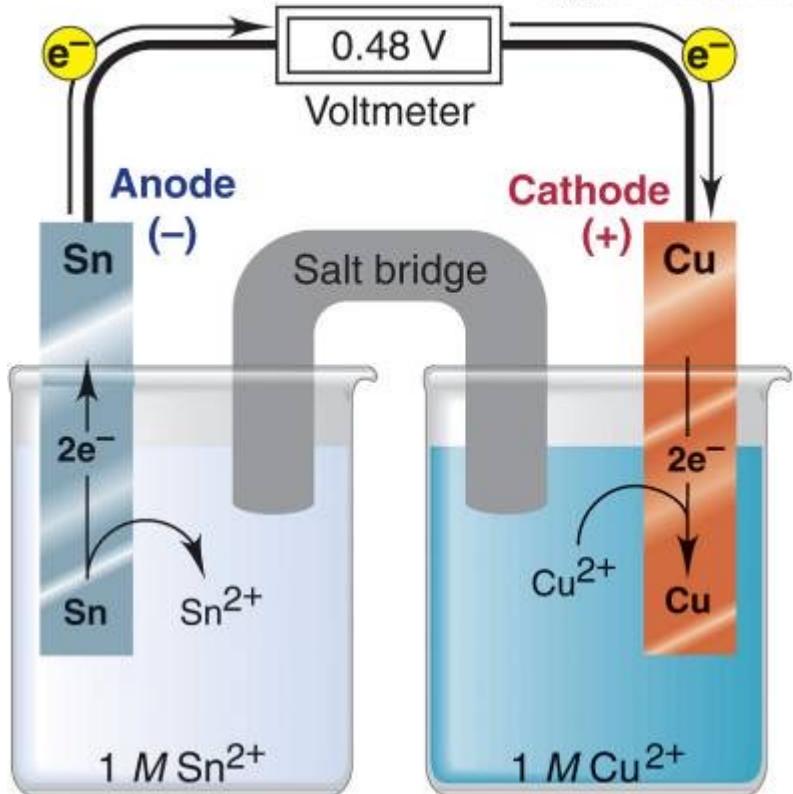
On sites denoted A, the following reactions occur



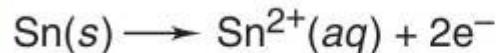
The electrons produced by this reaction at site A are conducted through the iron piece to site C where they are consumed.

In a galvanic cell, the spontaneous electrode processes generate a flow of electrons. Whereas this has a detrimental effect in the case of corrosion, it can also be used to great advantage as the basis, for example, of energy conversion and storage devices such as batteries, fuel cells, solar cells. Electrolytic cells operate in exactly the opposite manner – external source of electrical energy is used to drive reactions that would otherwise not occur.

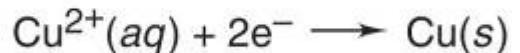
Galvanic Cell Spontaneous Reaction Cathode– Reduction + Anode – Oxidation -	E_{cell} is Positive ΔG is Negative	In a galvanic cell. Current flows from the positive electrode (cathode in this case) through the external load and then into the negative electrode (anode in this case).
Electrolytic Cell Need an External Power Source Cathode - Reduction - Anode – Oxidation +	E_{cell} is Negative ΔG is Positive	In the case of an electrolytic cell, current leaves the positive terminal of the power source, flows through the anode (positive electrode), then across the electrolyte to the cathode, then through the cathode and back to the negative terminal of the power supply.
Current (opposite to the flow of electrons)	positive current into the Anode	
Anodic Reaction	Current is +	Electrode reaction equivalent to a transfer of positive charge from the electronic to the ionic conductor. An anodic reaction is an oxidation process. An example is: $Me \rightarrow Me(+n) + n(e^-)$. LEO – loss of electron oxidation
Cathodic Reaction	Current -	Electrode reaction equivalent to a transfer of negative charge from the electronic to the ionic conductor. A cathodic reaction is a reduction process. An example is: $Ox + n(e^-) \rightarrow Red$. GER – gain of electron Reduction



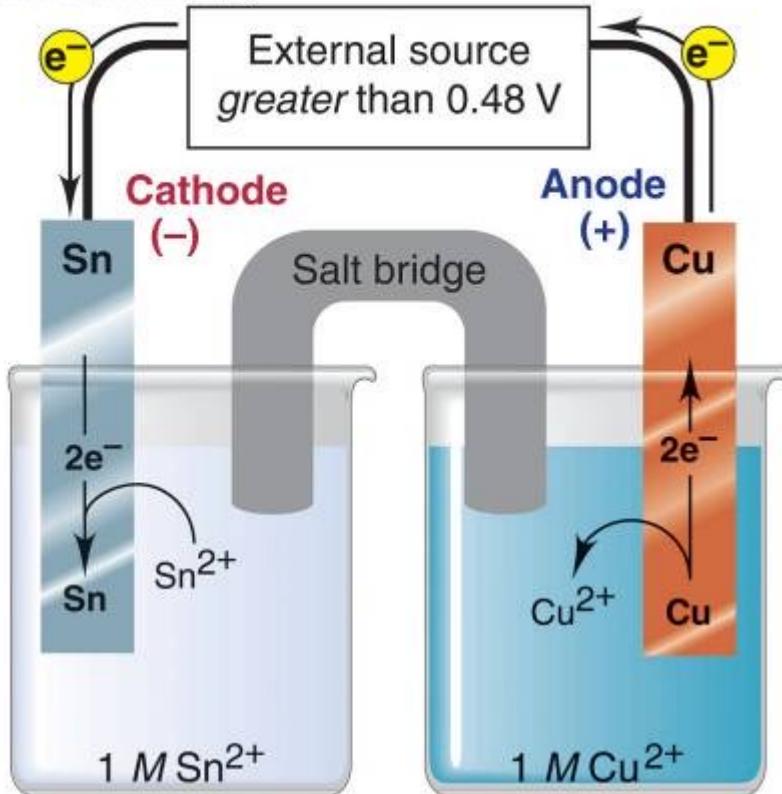
Oxidation half-reaction



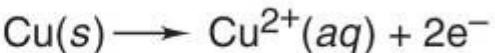
Reduction half-reaction



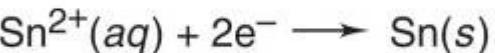
Overall (cell) reaction



Oxidation half-reaction



Reduction half-reaction

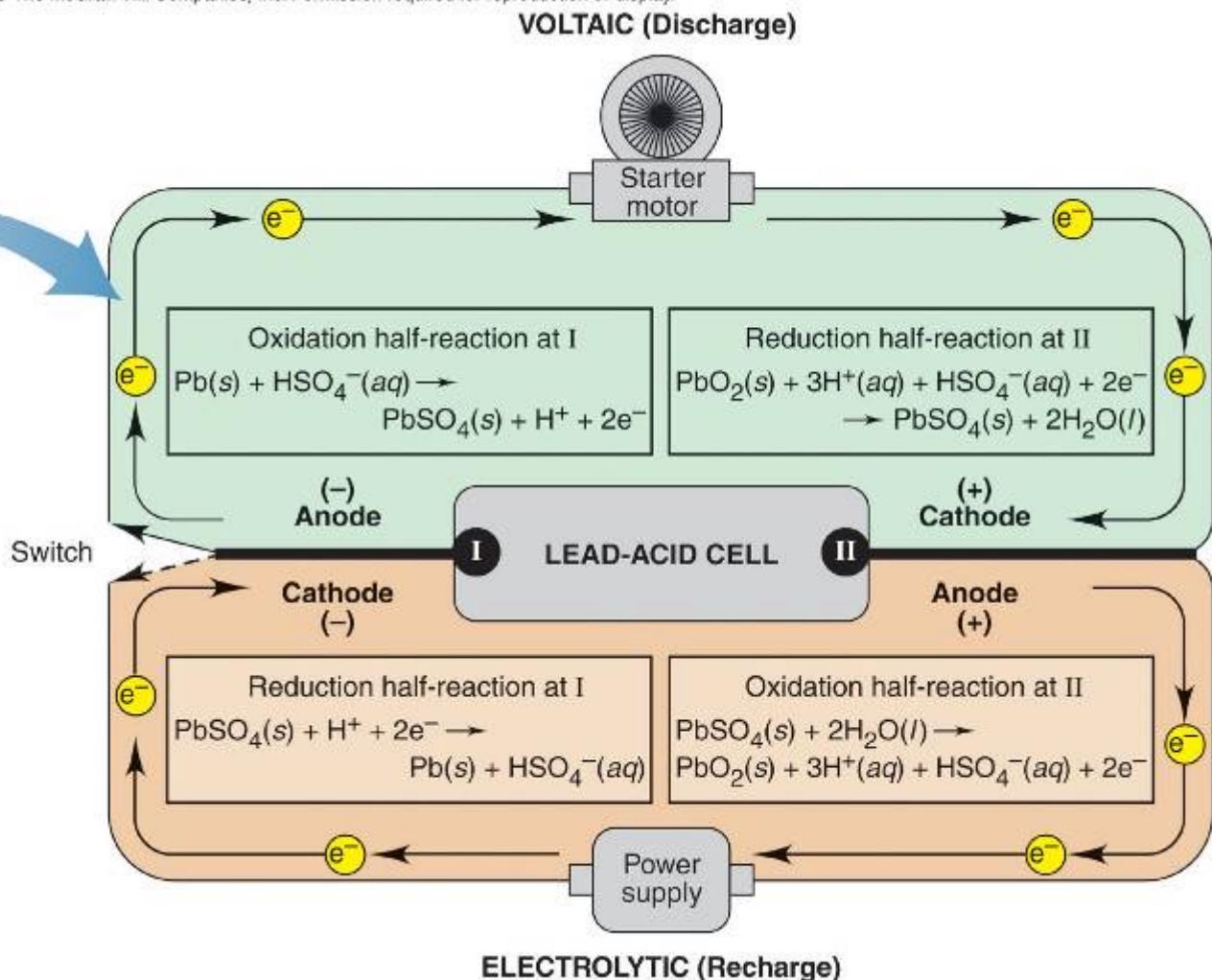


Overall (cell) reaction



Car battery, both voltaic and electrochemical cell.

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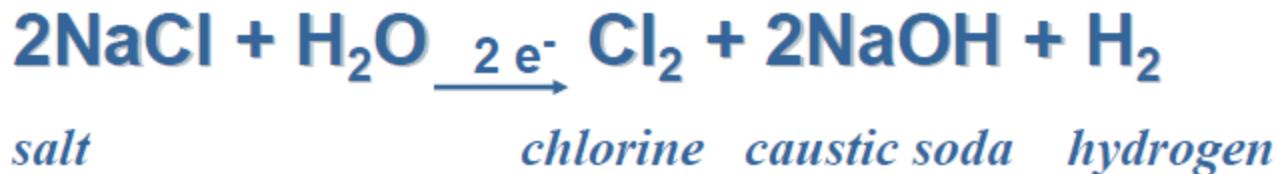


Application of electrochemical engineering

Electrosynthesis (1.9)

- Inorganic chemicals
 - Chloro-alkali industry
 - Metals
 - Other inorganic chemicals
- Organic chemicals

Chloro-alkali industry



- The chlor-alkali industry is a major contributor to the economic activity.
- Chlorine is produced via electrolysis of salt solutions, and this process requires large inputs of electricity. Largest electrolytic industry on the basis of volume production
- Consumes **2% of all electric power** generated in the US.
- Although chlorine is a key building block for the chemical industry, its co-product caustic soda is also important due to its wide applications.
- Chlorine and caustic soda are used in more **than half of all commercial chemistry applications** to create hundreds of secondary compounds that in turn contribute to plastics, pharmaceuticals and thousands of other products.

Chloro-alkali industry

Commodity Chemicals

- 1. Sulfuric Acid
- 2. Nitrogen
- 3. Oxygen
- 4. Ethylene
- 5. Lime (CaO)
- 6. Ammonia
- 7. Propylene
- 8. Phosphoric Acid
- 9. Caustic Soda
- 10. Chlorine
- 11. Sodium Carbonate
- 12. Ethylene Dichloride
- 16. Vinyl Chloride

Chlorine and caustic soda are building blocks that cascade through the chemical manufacturing chain

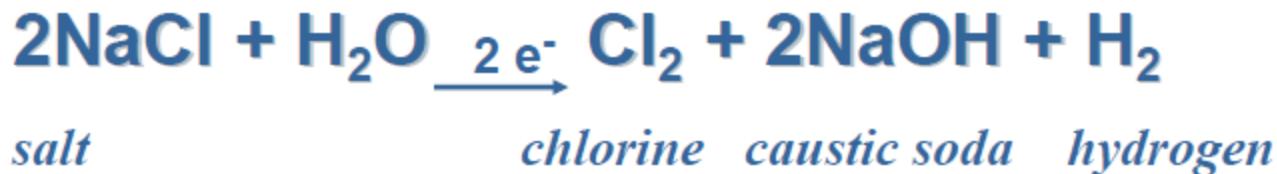
Chloro-alkali industry

The products of the chlor-alkali industry rarely go directly to consumers. However, an enormous range of products and 2,000,000 jobs in Europe depend directly or indirectly on chlorine:

Chlorine and caustic soda – key chemical building blocks			
Adhesives	Ceramics	Fibre-glass	Lubricants
Advanced composites	Computers	Flame-proofing	Paints
Air bags	Cosmetics	Footballs	Paper
Antibiotics	Credit cards	Fungicides	Perfumes
Antifreeze	Detergents	Gaskets	Pharmaceuticals
Bleach	Disinfectants	Golf bags	Plastics
Blood bags	Drilling fluids	Greenhouses	Refrigerants
Brake fluids	Drinking water	Hairdryers	Roller blades
Bullet-resistant glass	Dry cleaning	Herbicides	Roofing
Bumpers	Dyestuffs	Inks	Safety belts
Car seats	Electronics	Insulation	Vitamins
Carpets	Explosives	Intravenous drips	Window frames ...
CDs and DVDs	Fertilisers	Lighting	... and much more.

Sources: Euro Chlor, Annual Report 2006-2007

Chloro-alkali industry

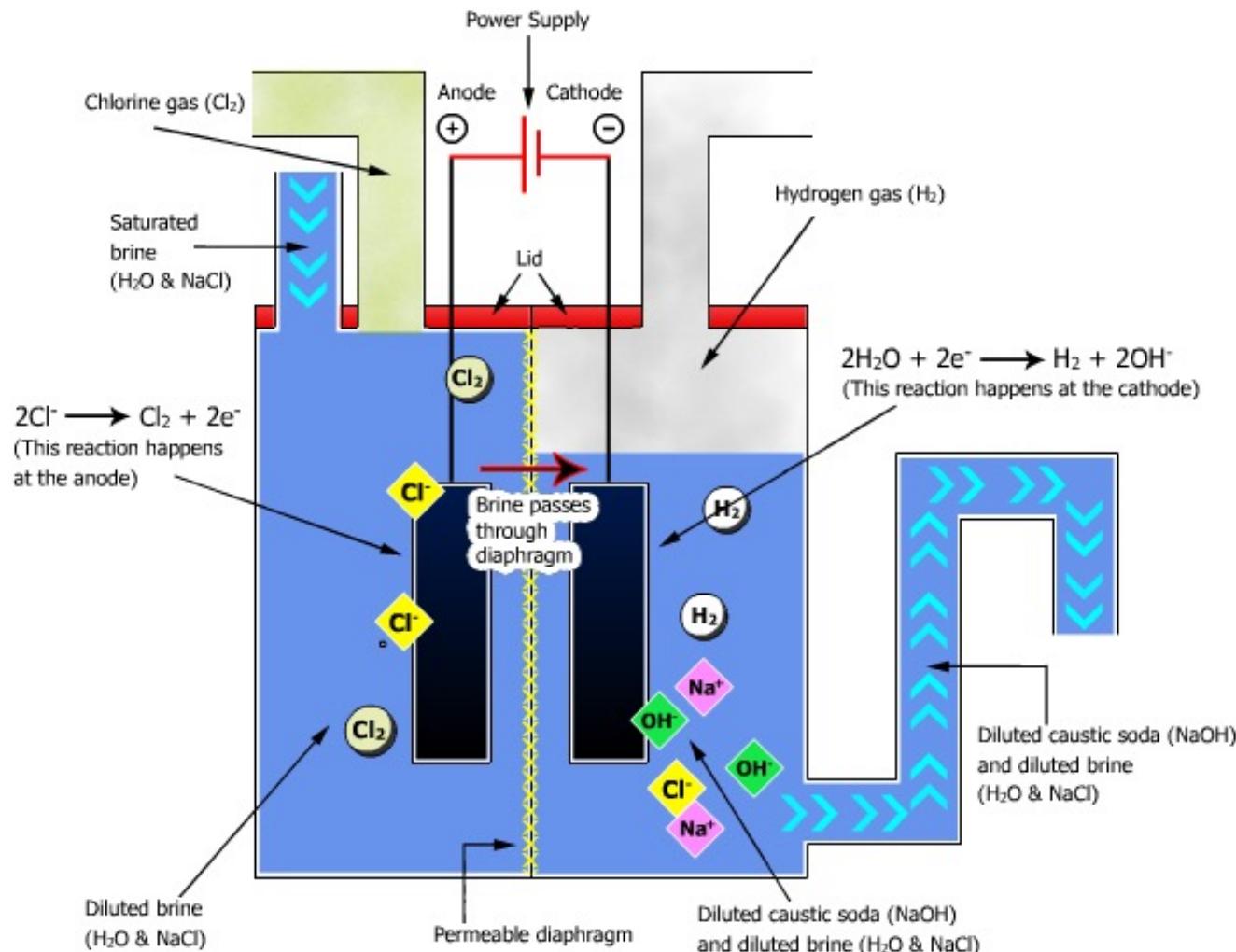


Three different processes:

- mercury, diaphragm, membrane cell process
- process type varies by country/region
- New plants is generally considered membrane

<http://www.eurochlor.org/makingchlorine>

The diaphragm cell process



- oldest method (1880's)



The diaphragm cell process

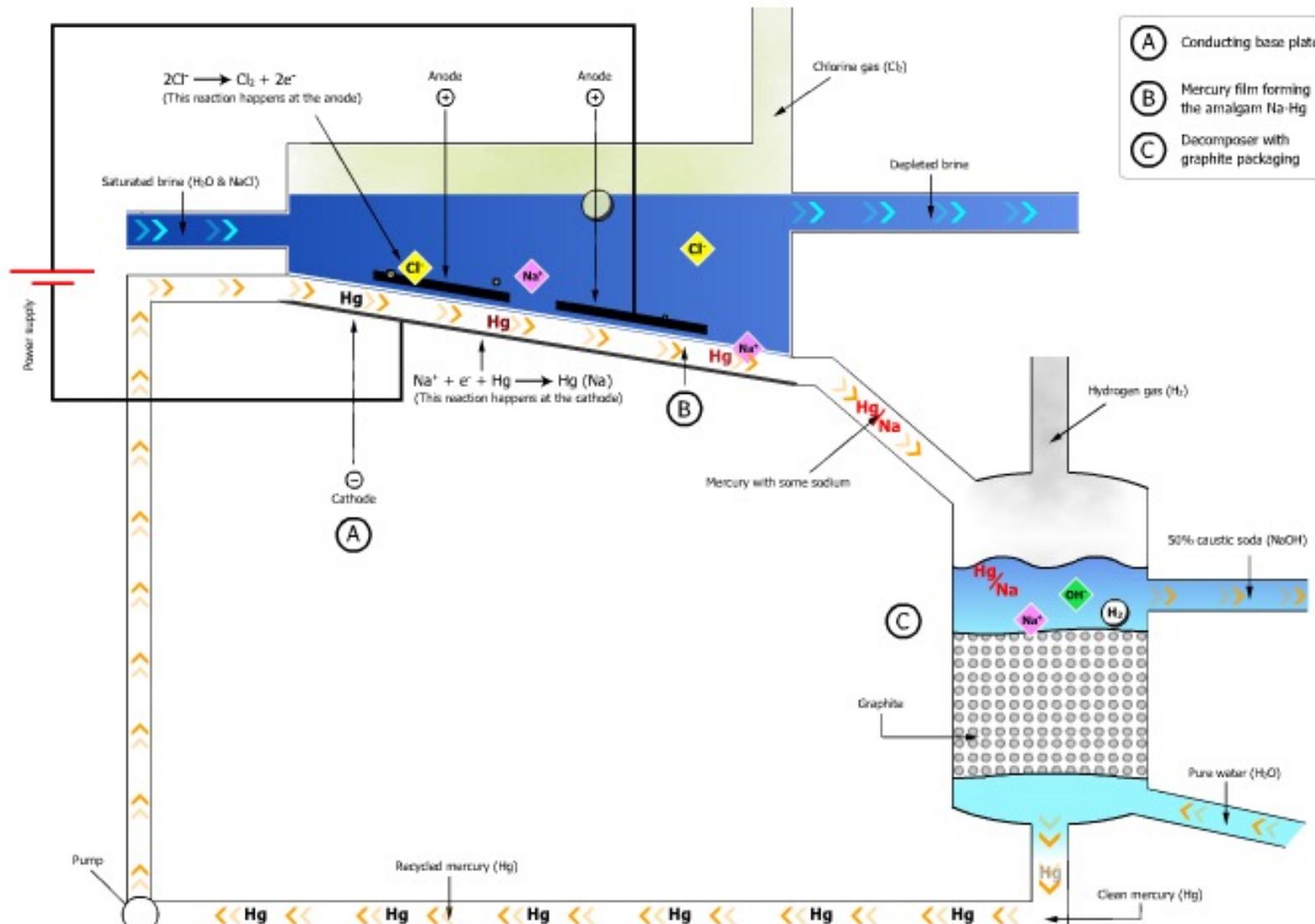
In the diaphragm cell process the anode area is separated from the cathode area by a permeable diaphragm. Uses a steel cathode, and **the reaction of NaOH with Cl₂ is prevented** using a porous diaphragm, often made of asbestos fibers. The brine is introduced into the anode compartment and flows through the diaphragm into the cathode compartment.

A diluted caustic brine leaves the cell. The caustic soda must usually be concentrated to 50% and the salt removed. This is done using an **evaporative process** with about three tonnes of steam per tonne of caustic soda. The salt separated from the caustic brine can be used to saturate diluted brine. The chlorine contains oxygen and must often be purified by liquefaction and evaporation.

In 2009, the diaphragm process accounted for **14%** of total installed European chlorine production capacity.

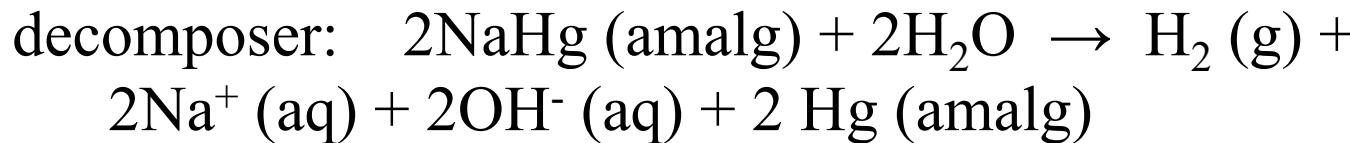
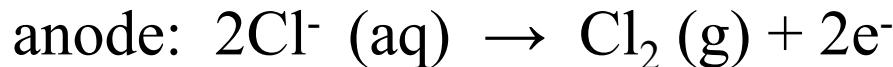
The mercury cell process

Mercury Cell



The mercury cell process

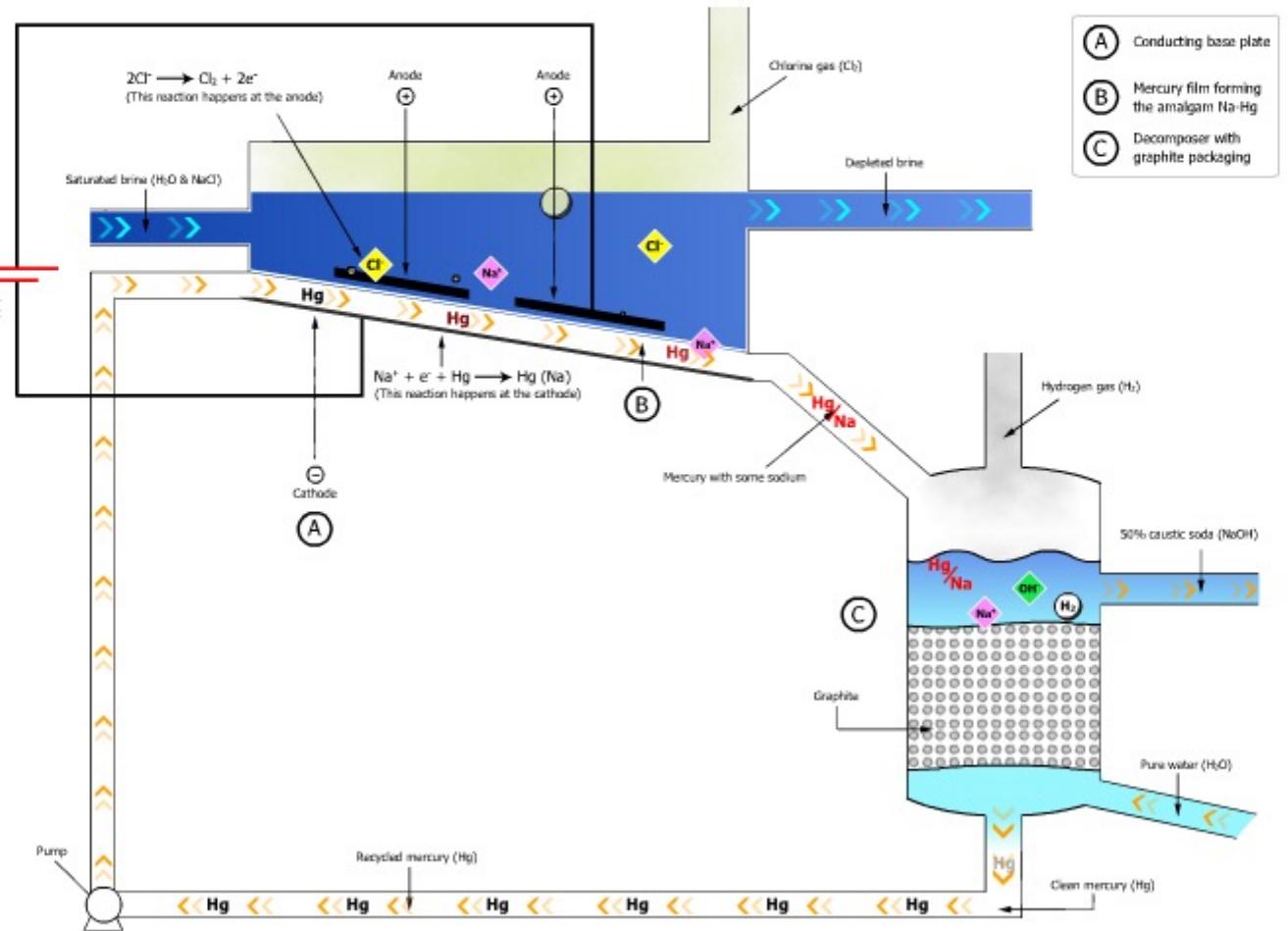
- also developed in late 19th century



- produces NaOH + H_2 in decomposer

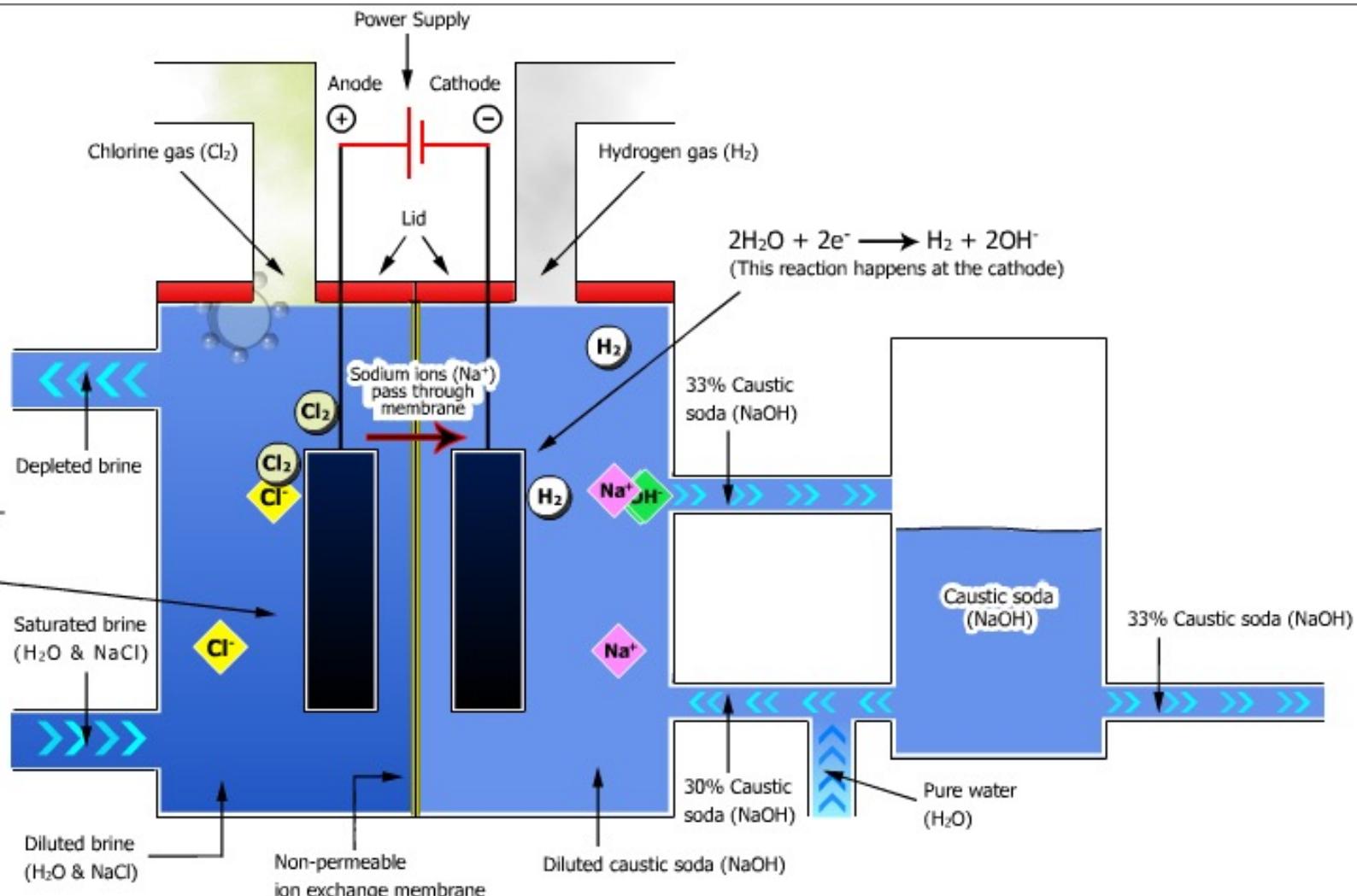
- In the mercury cell process, sodium forms an amalgam with the mercury at the cathode. The amalgam reacts with the water in a separate reactor called a decomposer where hydrogen gas and caustic soda solution at 50% are produced.
- The products are extremely pure. The chlorine, along with a little oxygen, generally can be used without further purification.
- Of the three processes, the mercury process uses the most electricity, but no steam is required to concentrate the caustic solution. The use of mercury demands measures to prevent environmental contamination. Also, mercury must be removed from the hydrogen gas and caustic soda solution.

Mercury Cell



Forty-two mercury-based chlorine plants remain to be voluntarily phased out or converted to non-mercury technology by 2020 at a cost of more than EUR 3,000 million. These plants account for an ever decreasing part (37.7% in 2007) of European chlorine capacity.

The membrane cell process



- developed in 1970's



The membrane cell process

- The anode and the cathode are separated by an **ion-exchange membrane**. Only sodium ions and a little water pass through the membrane.
- The brine is de-chlorinated and re-circulated. Solid salt is usually needed to re-saturate the brine. After purification by precipitation-filtration, the brine is further purified with an ion exchanger.
- The caustic solution leaves the cell with about 30% concentration and, at a later stage in the process, is usually concentrated to 50%. The chlorine gas contains some oxygen and must often be purified by liquefaction and evaporation.
- The consumption of electric energy is **the lowest** of the three processes and the amount of steam needed for concentration of the caustic is relatively small (less than one tonne per tonne of caustic soda).
- Chlorine producers across Europe are progressively moving towards this method of making their product as the membrane cell process is the most environmentally sound way of manufacturing chlorine. In 2009, membrane cell capacity accounted for **52%** of total installed chlorine production capacity in Europe.

Advantage of the Mercury Cell over the Diaphragm cell ?

NaOH is produced in a separate decomposer so it does not have to be separated from the unreacted NaCl

Advantages of a Membrane Cell?

- ♥ Eliminate the use of asbestos and mercury
- ♥ Membrane is Selective for Na^+ Cl^- and OH^-

This allows for the four products to be discharged separately from each other (i.e. Cl_2 , H_2 , NaOH Solution and depleted NaCl solution)

Electricity Consumption by Production Process

kWh (AC)/t Cl ₂	Mercury	Diaphragm	Membrane
Electricity process	3360	2720	2650
Electricity utilities	200	250	140
Calorific (steam)		610	180
Total	3560	3580	2970
Ratio to mercury		similar	~ 17% lower

Source: EU BREF, Euro Chlor

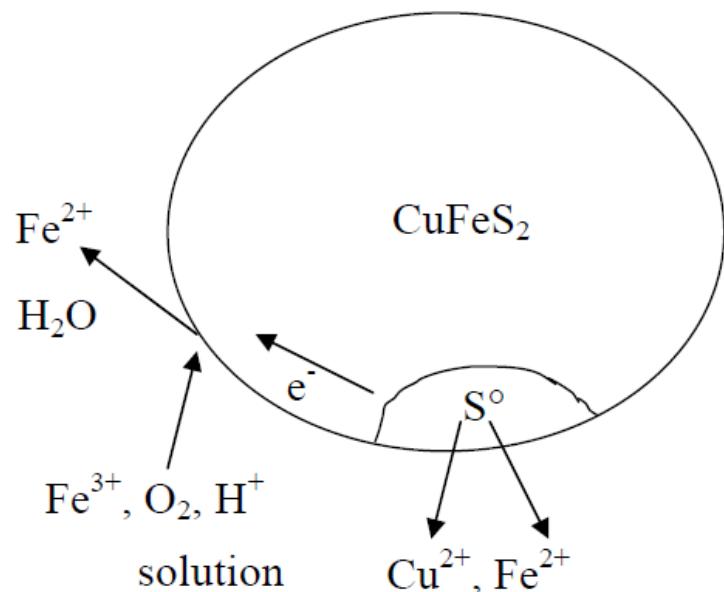
Electrosynthesis: (ii) Metals

several steps in the hydrometallurgical processing of metals from ores are electrochemical in nature

1. Leaching (1.10)
2. Cementation (1.10)
3. Electrowinning (1.11)
4. Electrofining (1.13)

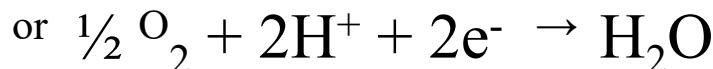
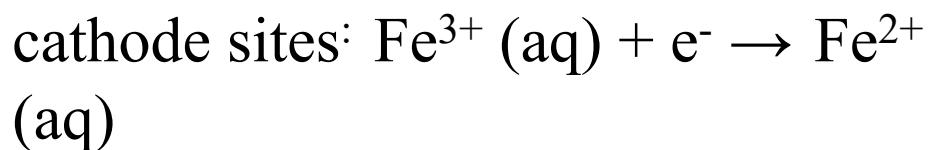
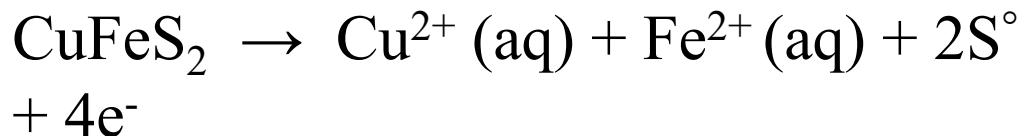
Leaching (1.10)

oxidizing agent used to **dissolve out metal ions** from an aqueous suspension of finely ground sulphide minerals very similar to **corrosion** from electrochemical point of view



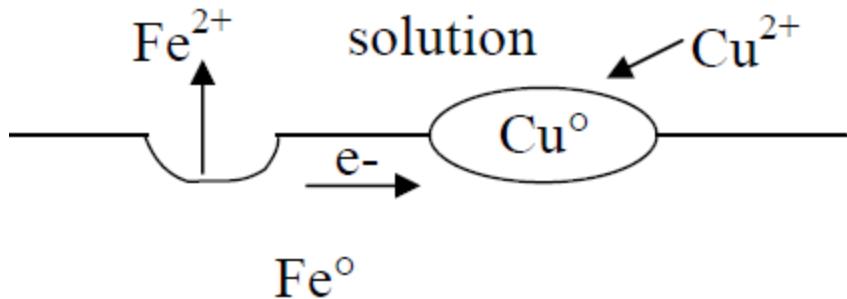
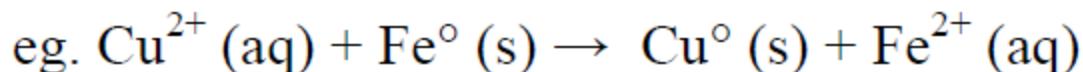
- galvanic cell set up within each CuFeS_2 particle
- metal sulphides are semiconductors and can support electrode reactions

anode sites:

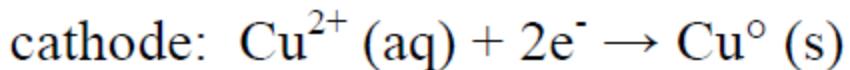
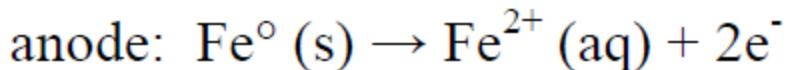


Cementation (1.10)

method for recovery of a desired metal from solution by the addition of another metal in elemental form



- galvanic cell set up with very strong driving force ($\Delta G \ll 0$)



Electrowinning (1.11)

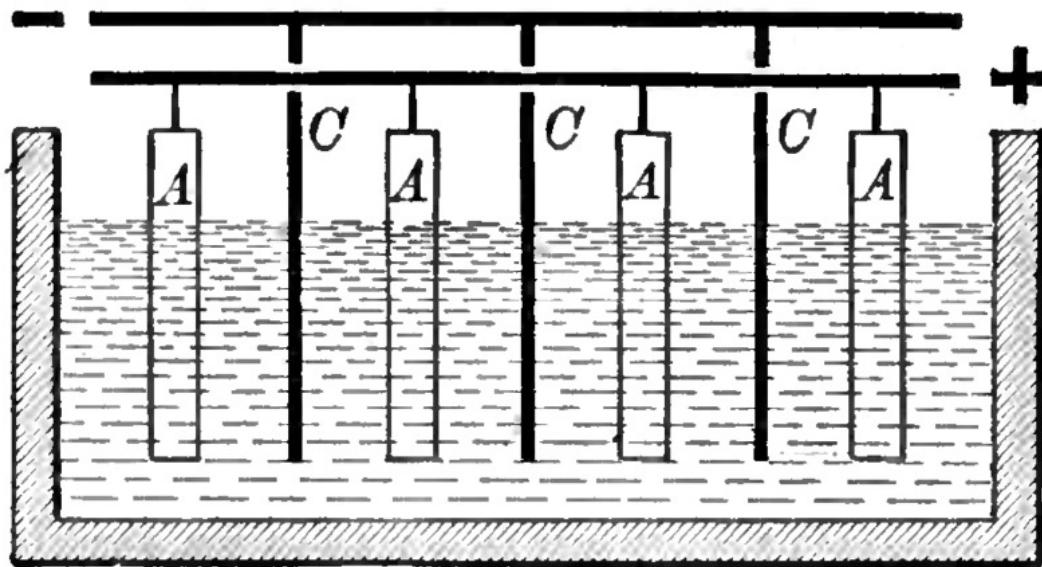
(electroextraction)

is the electrodeposition of metals from their ores that have been put in solution or liquefied. In electrowinning, a current is passed from an **inert anode** through **a liquid leach solution containing the metal** so that the metal is extracted as it is **deposited** in an electroplating process onto the cathode. Electrowinning is the oldest industrial electrolytic process

Electrolytic process for production of **high purity metals**:

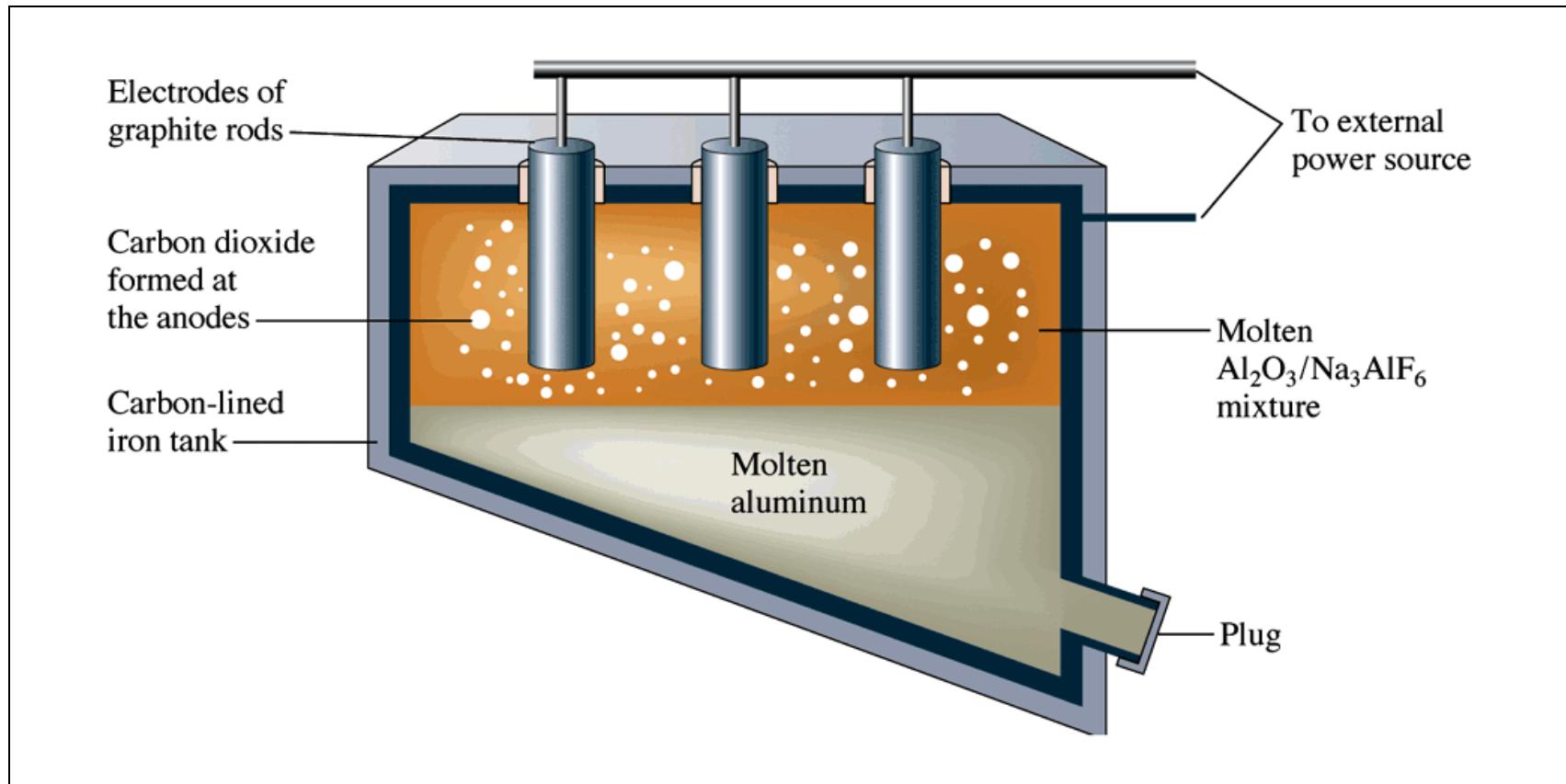
- **source** of metal being plated is the solution
- used in the production of Cu, Al, Zn, Ni, Au, Ag, Cd, Co, Na, Li, Mg, etc.
- can be carried out in aqueous solutions (eg. Cu, Zn, Ni, Au, Ag, Cd, Co) or in molten salt baths (eg. Al, Na, Li, Mg)

Cu Electrowinning (1.11)



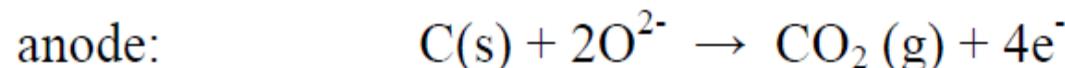
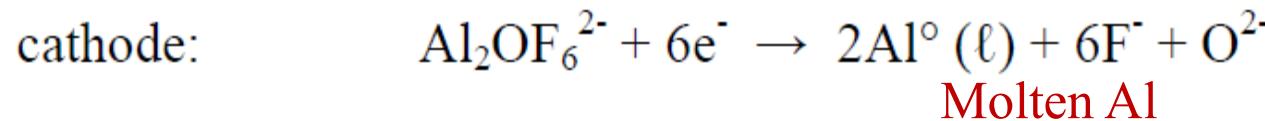
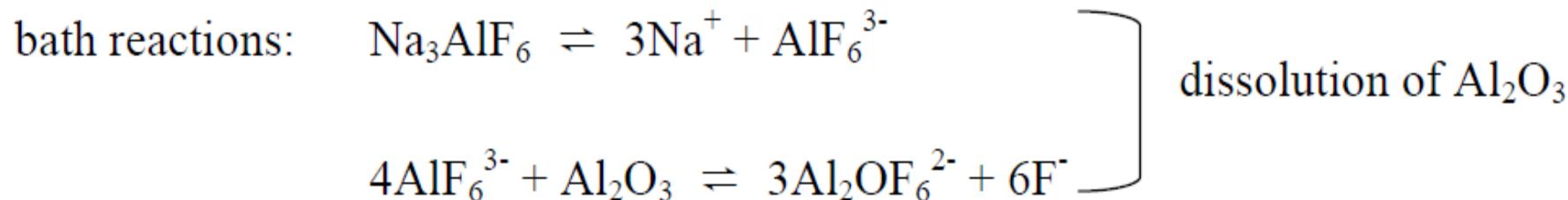
- metal plating onto flat cathode sheets
 - carried out in concentrated H_2SO_4 solutions ($\sim 50\text{-}150 \text{ gpl}$) containing 20-50 gpl Cu^{2+}
- cathode: $\text{Cu}^{2+} \text{ (aq)} + 2\text{e}^- \rightarrow \text{Cu}^\circ \text{ (s)}$
- anode: $2\text{H}_2\text{O} \rightarrow \text{O}_2 \text{ (g)} + 4\text{H}^+ \text{ (aq)} + 4\text{e}^-$

Al electrowinning - source of aluminium fed to the cell is Al_2O_3 (bauxite)



Hall-Heroult Process

- continuous process carried out in a bath of a molten cryolite salt (Na_3AlF_6) bath at temperatures of 940-980°C.
- Al_2O_3 is continually fed by a hopper
- C(s) is fed to the top of each anode and bakes into a solid form
- bottom of carbon anode is continuously consumed; so anode is continuously lowered to keep anode-cathode spacing constant.



Why is Al electrowinning not carried out in aqueous solution?

graphite anodes

$e^- \rightarrow +$

CO_2
bubbles

from
power
source

$Al_2O_3 (l)$

carbon-lined steel vessel
acts as cathode

Draw
off
 $Al (l)$

$Al (l)$



The Hall Process for Aluminum

- ♥ Electrolysis of molten Al_2O_3 mixed with cryolite – lowers melting point
- ♥ Cell operates at high temperature – 1000°C
- ♥ Aluminum was a precious metal in 1886.
- ♥ Bars of aluminium were exhibited alongside the French crown jewels at the Exposition Universelle of 1855
- ♥ A block of aluminum is at the tip of the Washington Monument!

Electrofining (1.13)

- electrolytic process to refine “impure” metals produced during metallurgical processing (pyrometallurgical), eg. Cu, Ni, Co, Pb, Sn
- **source** of metal being plated is the anode

Two purposes:

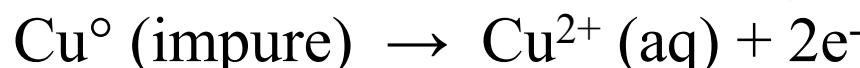
- 1) produce highest purity metal possible for electronic applications (eg., > 99.9% Cu)
- 2) separate valuable impurities (eg. Au, Ag, Pt, etc.) from “impure” metal

eg. copper electrorefining (1.13)

- cells are very similar to electrowinning cells, although they usually contain many more electrodes

Anode: “blister” copper produced by smelting

- contains 2-3% impurities (Ni, Fe, Au, Ag, Pt, As)



- some impurity metals are also oxidized and dissolve (eg., Ni, Fe, Co, As)

- some impurity metals remain unoxidized, but fall off anode as fine “slime” particles (eg., Au, Ag, Pd, Pt) which are recovered for further processing

Cathode: $\text{Cu}^{2+} \text{ (aq)} + 2\text{e}^- \rightarrow \text{Cu}^\circ \text{ (pure)}$

How does Electrofining differ from Electrowinning?

The anodic reaction is different:

Cu Electrowinning: anode: $2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$

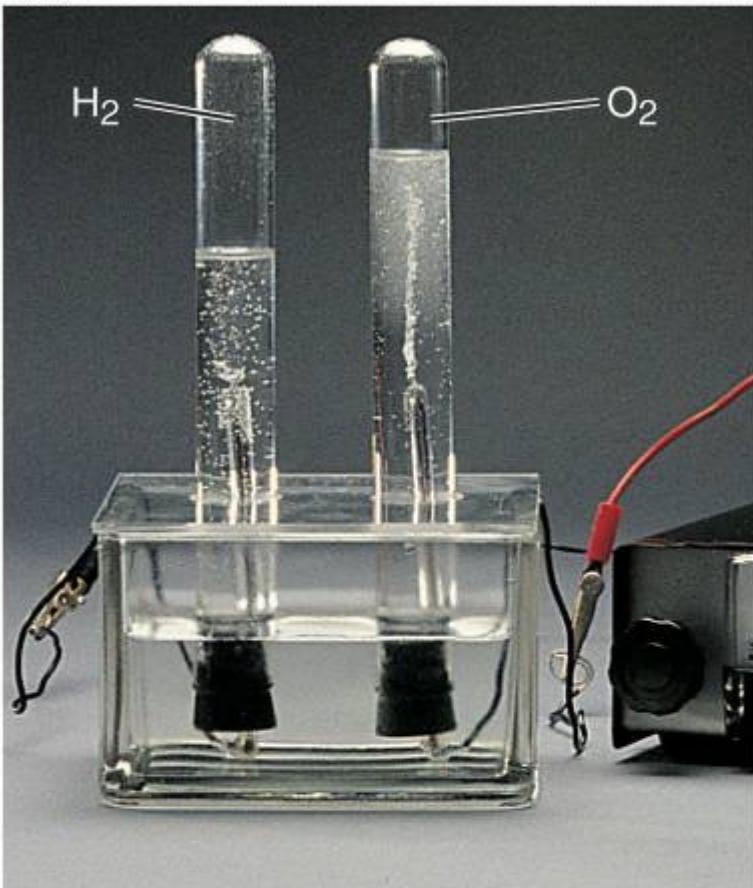
Metal salt in solution is the source of metal to be deposited

Cu Electrofining: anode: $\text{Cu}^\circ(\text{impure}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$

Anode metal is the source of metal to be deposited

iii) other inorganic chemicals

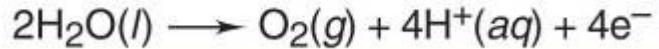
- electrolysis used to produce the following
 - strong oxidizing agents, eg. KMnO_4 , NaClO_3 , F_2 , H_2O_2 , O_3
 - metal oxides (eg. MnO_2 , Cu_2O)
 - H_2 and O_2 by water electrolysis
 - metal salts



water electrolysis

The electrolysis of water produces hydrogen gas at the cathode (on the left) and oxygen gas at the anode (on the right).

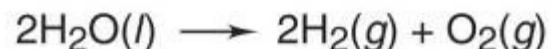
Oxidation half-reaction



Reduction half-reaction

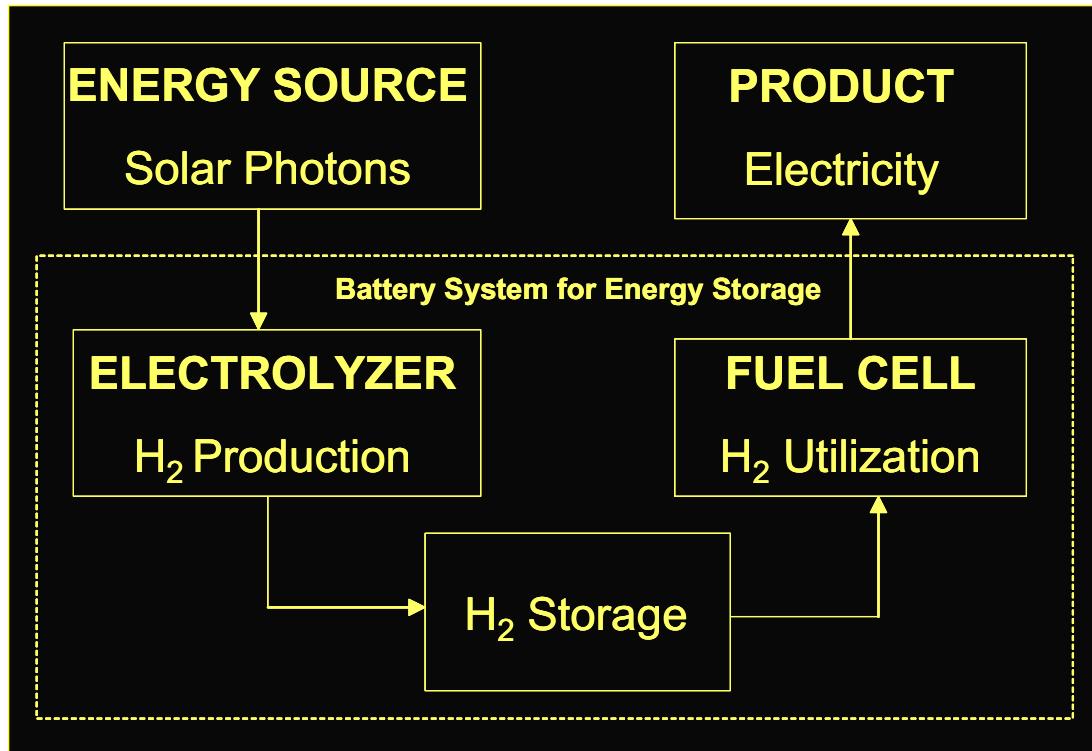


Overall (cell) reaction



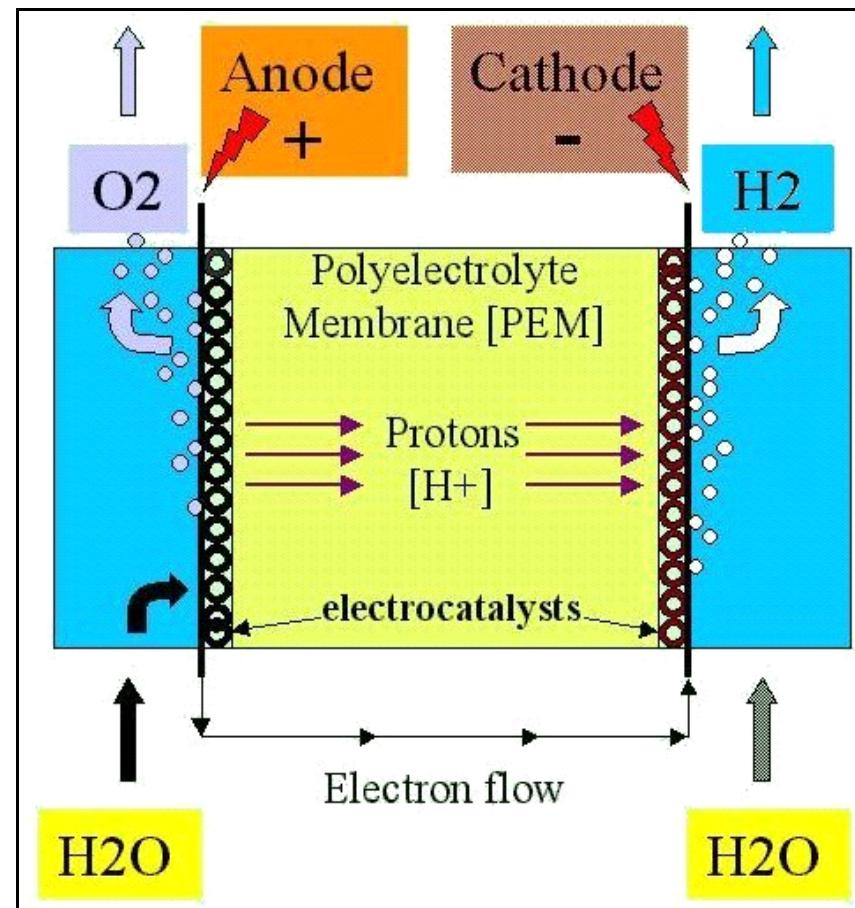
What is the Solution?

- ♥ Water electrolysis to generate H₂ as an energy carrier
- ♥ PEM Electrolyzer integrated with photovoltaic array (PV-H₂)

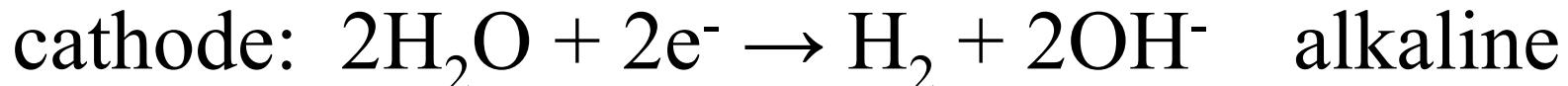
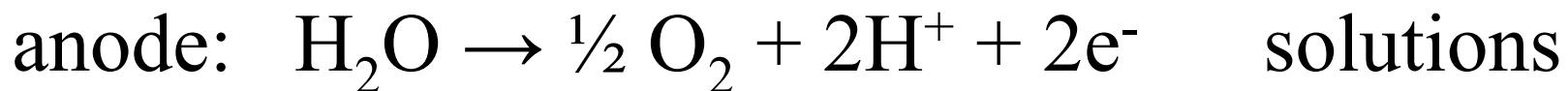
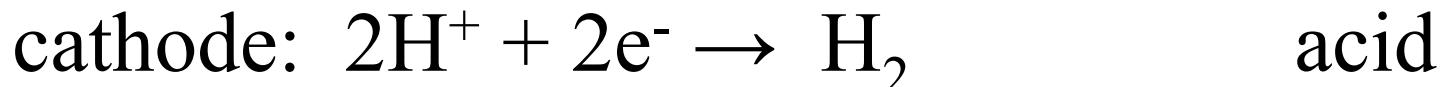


PEM Electrolysis Basics

- ♥ H₂ and O₂ are produced by water electrolysis
- ♥ Polymer-electrolyte membrane (PEM) separators in use today can achieve over 85% efficiency in conversion [PEGO, 2003]



-alternating rows of anodes and cathodes



Electrolyzer Advantages

- ♥ Clean (no CO₂ production)
- ♥ Renewable
- ♥ Sustainable
- ♥ Feasible
- ♥ Modular and easy to integrate into the home
- ♥ Simple and well-researched



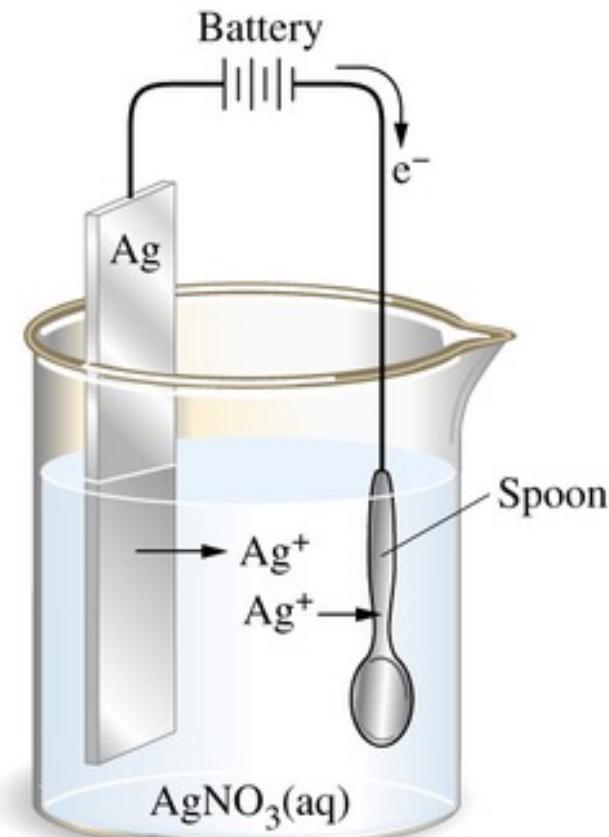
2. Metal Finishing

- usually involves formation of **thin metal coatings**

wide range of processes carried out to modify the surface properties of a metal for a number of reasons:

1. corrosion resistance
2. enhancement of physical or mechanical properties
3. decoration
4. enables use of expensive metals in thin layers

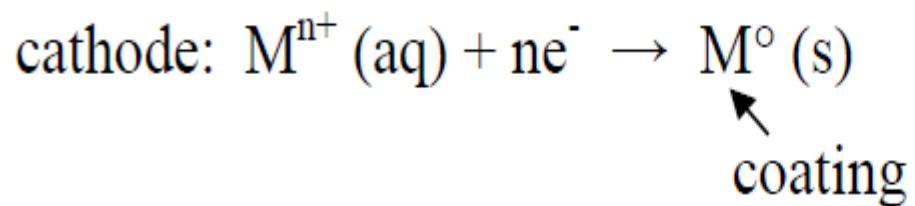
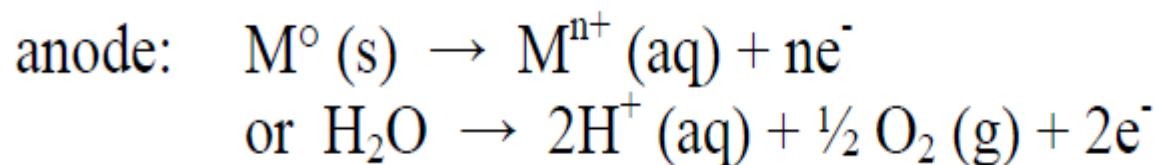
Electroplating



**Global Electroplating Market to Reach \$13.64 Billion by 2015,
According to New Report by Global Industry Analysts, Inc.**

Electroplating

electroplating – eg. chrome plating, gold plating for electronics, printed circuit boards, electrical contacts, alloy plating



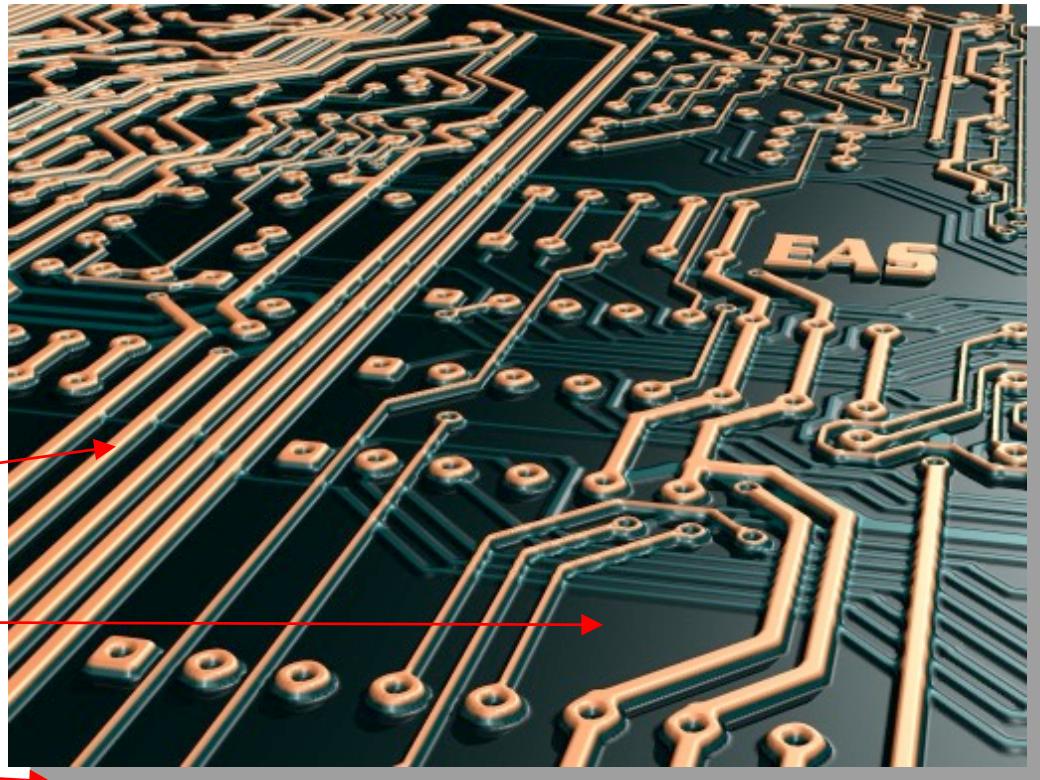
Manufacturing of printed circuit boards (1.16)

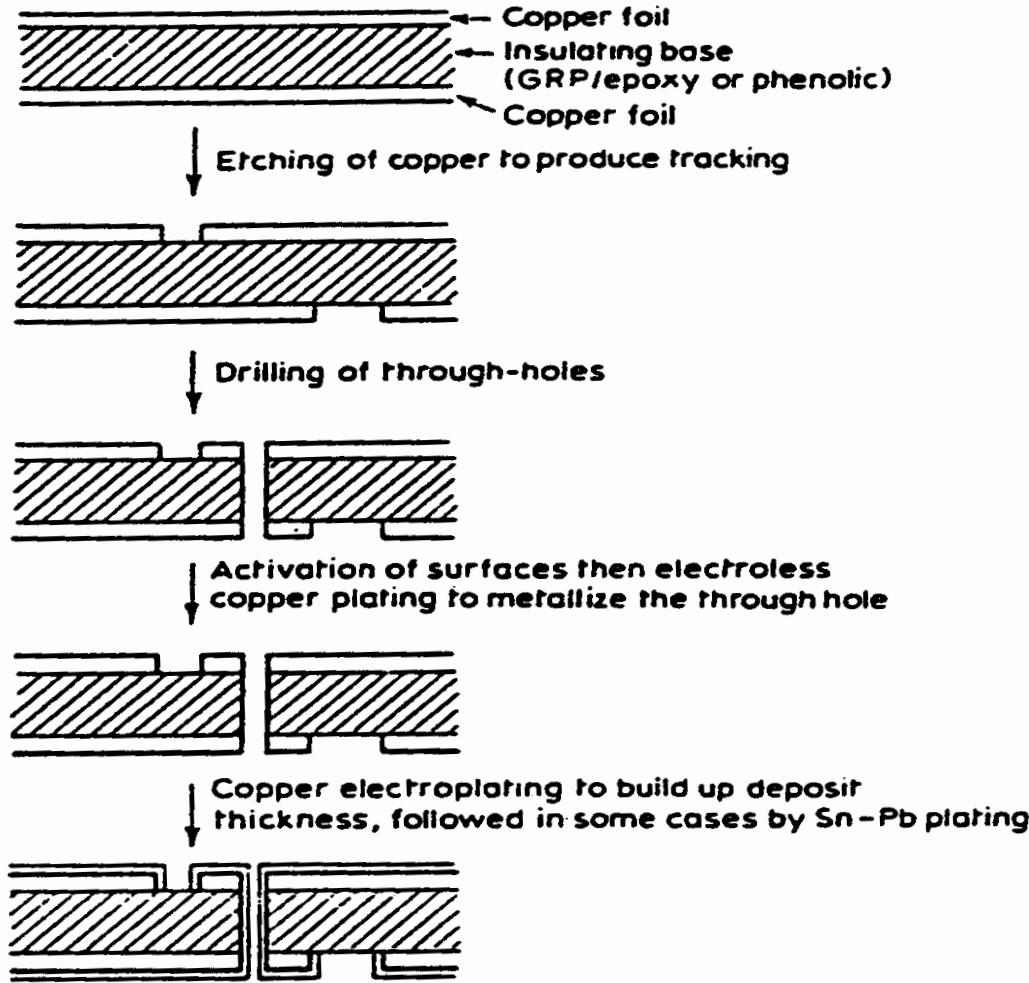
Typical PCB

copper connections

protective covering

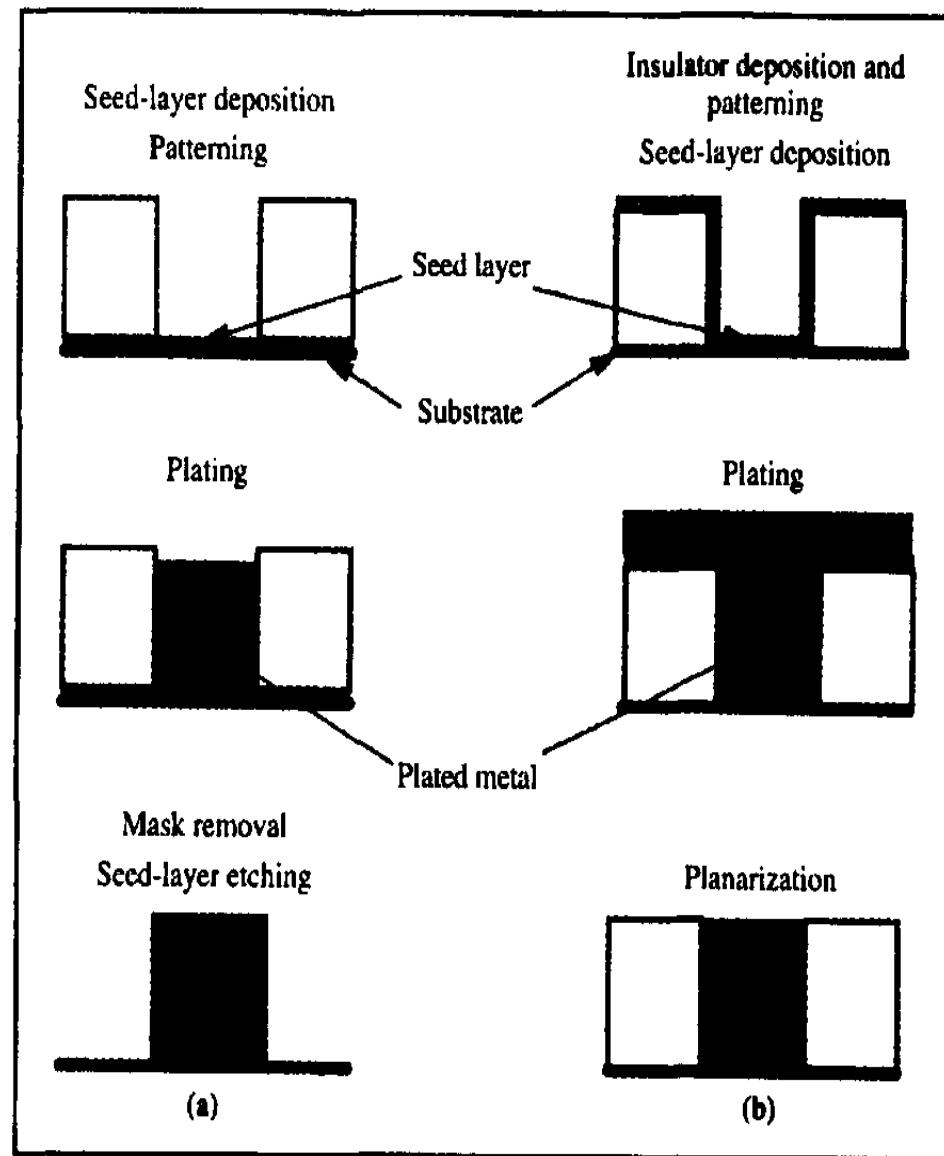
insulated substrate





The steps involved in the subtractive technique for the manufacture of printed circuit boards. A very simplified schedule is shown to obtain a double-sided board, i.e. one which has copper tracks on each side interconnected by 'plated-through' holes.

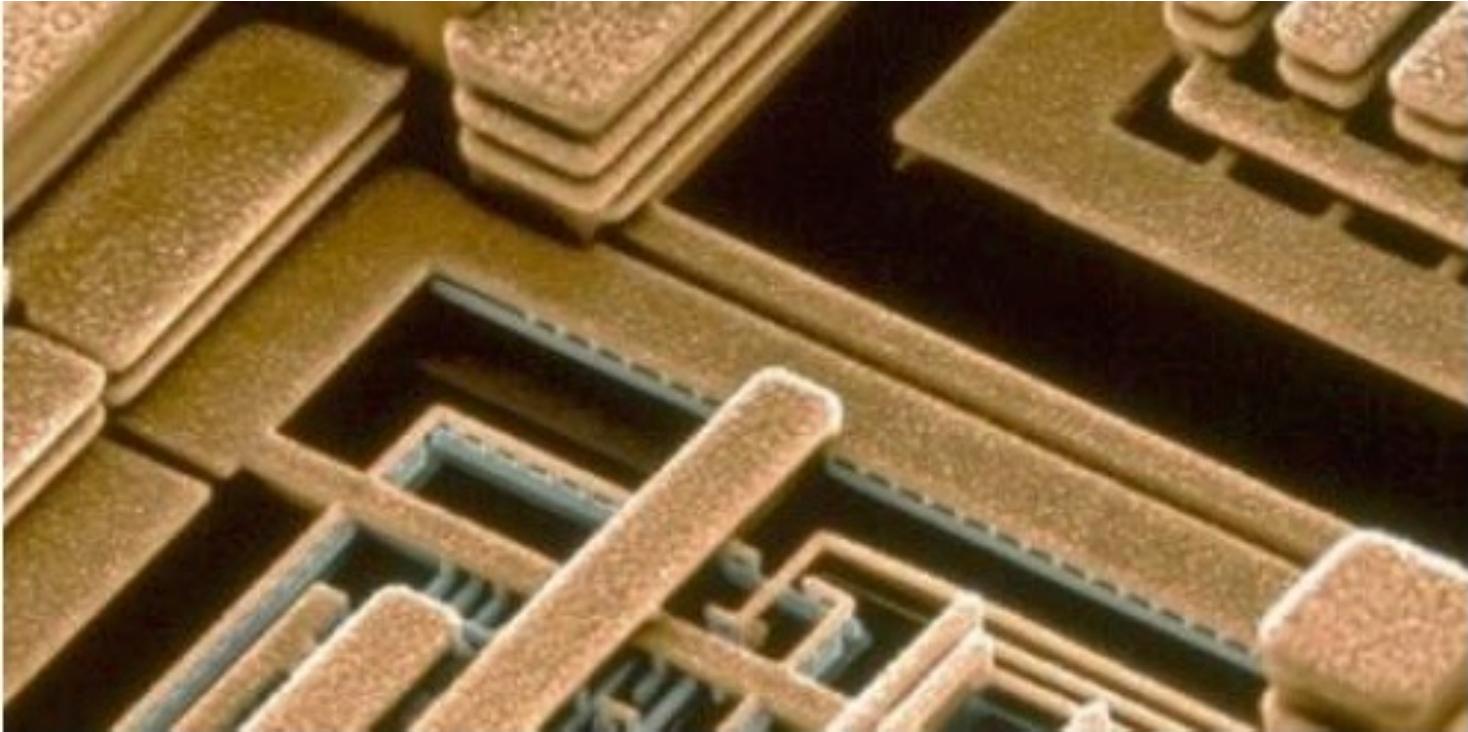
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Process steps for the integration of an electroplating process in device fabrication: (a) Through-mask plating; (b) damascene plating.

Electroplating

<http://www.rschrome.co.uk/whatis.html>



State-of-the-art Intel, IBM, and AMD chips have 70 nm copper plated wires connecting a billion transistors!

Electroless Plating

1. metal plating without the use of electricity to drive the process
2. reducing agent added to create galvanic cell that deposits metal, eg., plating of nickel onto steel, copper plating onto printed circuit boards and plastics

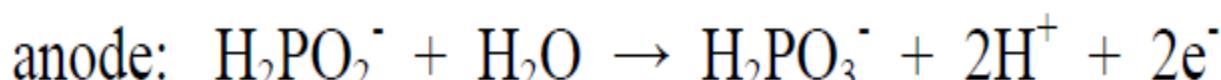
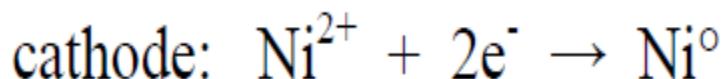
advantages:

- substrate doesn't have to be an electronic conductor
- can produce uniform deposits on irregular shapes
- deposits usually harder than electrodeposits
- deposits usually denser and more corrosion-resistant than electro-deposits

disadvantages:

- plating solutions relatively expensive
- slower deposition than in electrolytic process
- requires careful control of bath composition

e.g. electroless nickel plating using hypophosphite

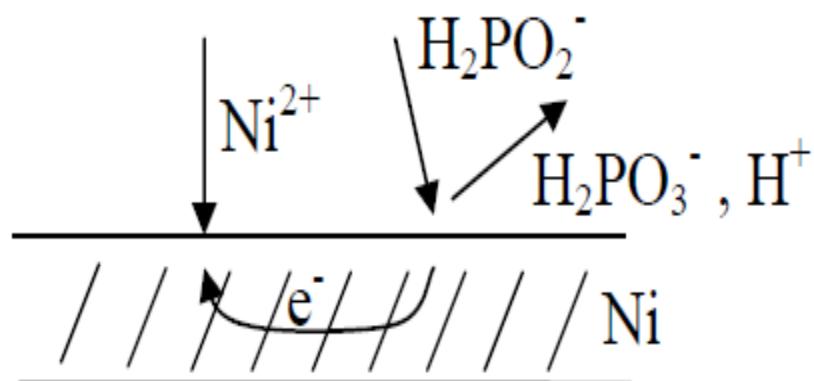


reducing agent

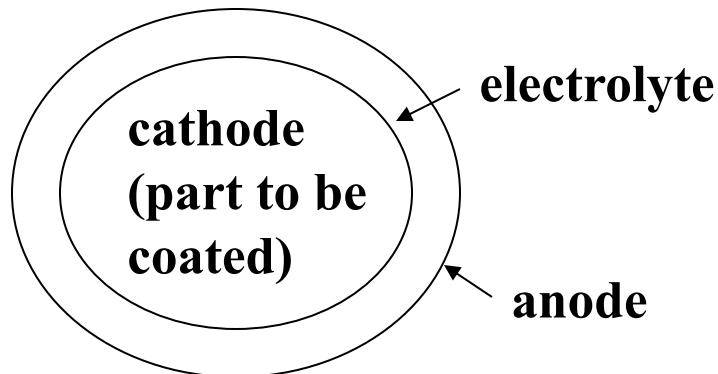
solution

occur

spontaneously



Let's say we want to coat the entire surface of this shape. If we use electrolytic approach, the spacing between cathode and anode must be kept fixed.

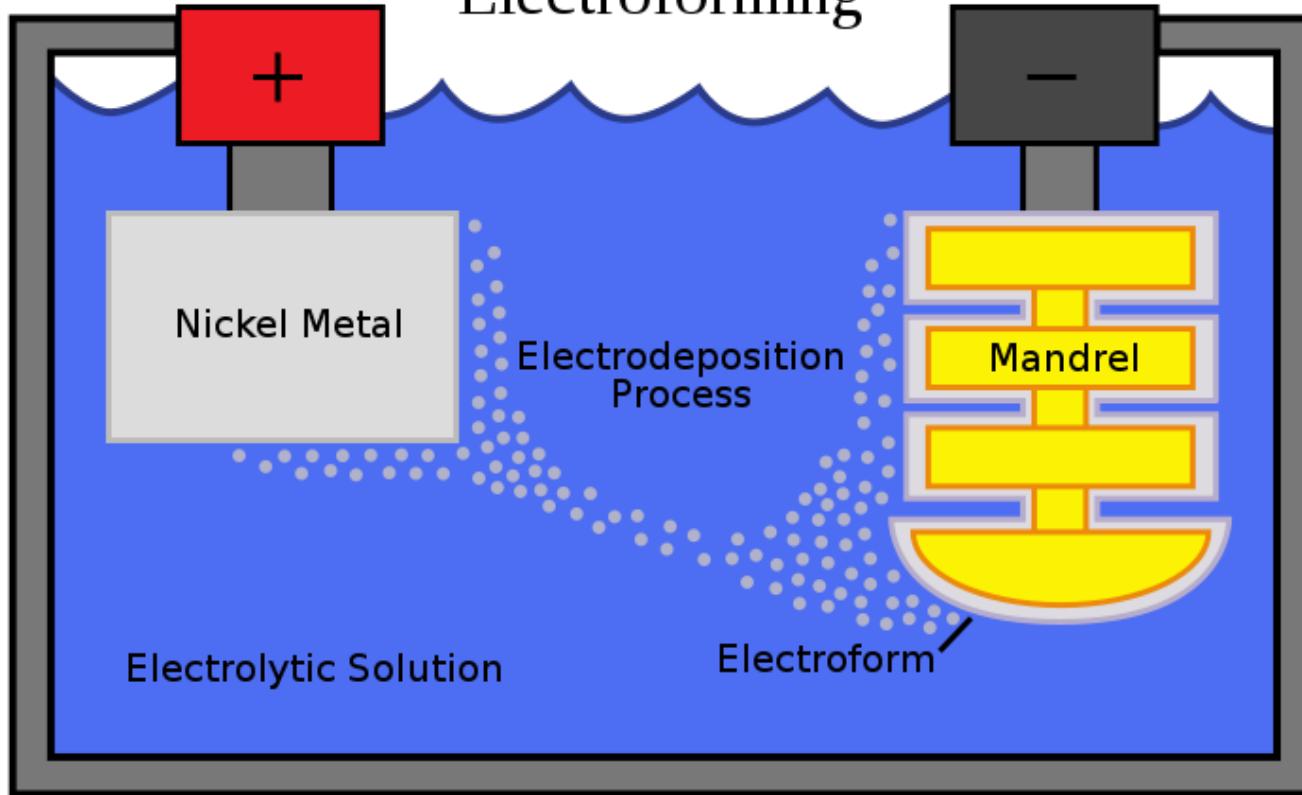


So we must design anode with same shape. This can sometimes be difficult. However, if we want to coat this object electrolessly, all we have to do is ensure object is immersed in solutions containing reducing agent. We will end up with uniform coating since all of surface is **equally exposed to solutions**.

3. Metals and Materials Processing

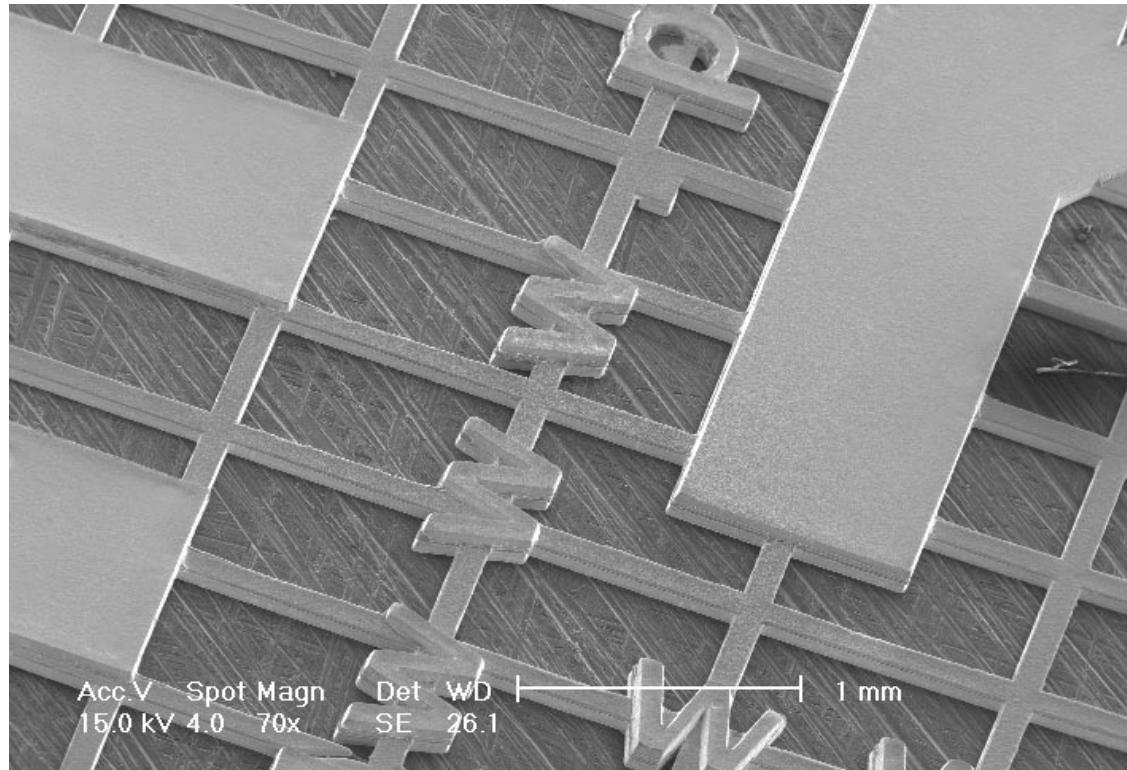
Electrochemical processes have been developed to manufacture or surface-finish metal articles, components, etc. which are too difficult to make by traditional mechanical workshop means

Electroforming



- Complete manufacturing of a part by electrolytic deposition, eg., thin foil, metal gauzes, moulds, dyes, pens, etc.
- Carried out as in electroplating, except use mandrel with shape to be formed as cathode and a conforming anode
- This process differs from electroplating in that the plating is much thicker and can exist as a self-supporting structure when the mandrel is removed

Laser Evolved ElectroForming



<http://www.precisionmicro.com/49/processes/laser-evolved-electro-forming---leef>

Electrochemical Machining

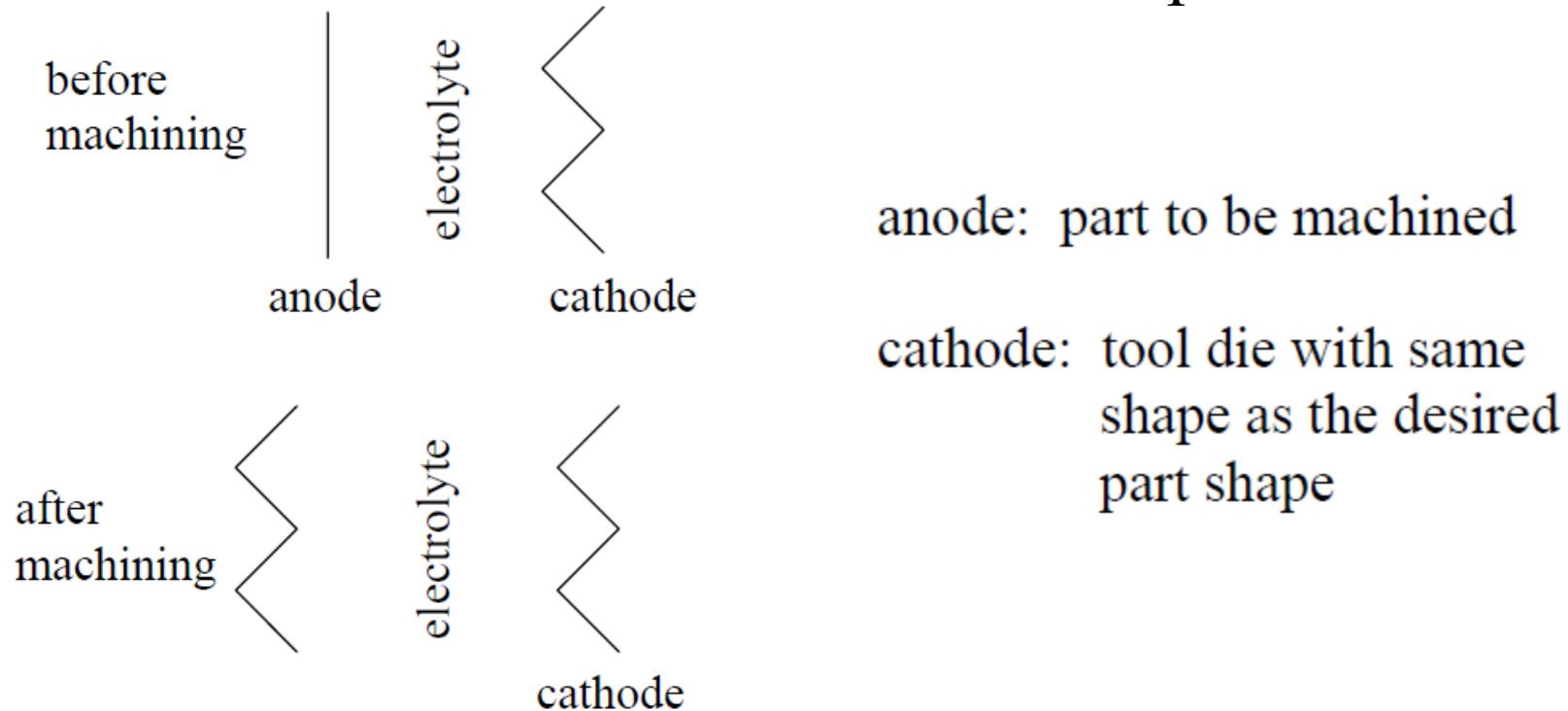
Electrochemical machining (ECM) is a method of removing metal by an electrochemical process. It is normally used for mass production and is used for working extremely hard materials or materials that are difficult to machine using conventional methods. Its use is **limited to electrically conductive materials**

1. electrolytic process in which part to be “machined” is made the anode so that a hole or a contour in the surface can be produced by dissolution
2. used to manufacture engine casings, turbine discs and blades, etc.

Electrochemical Machining

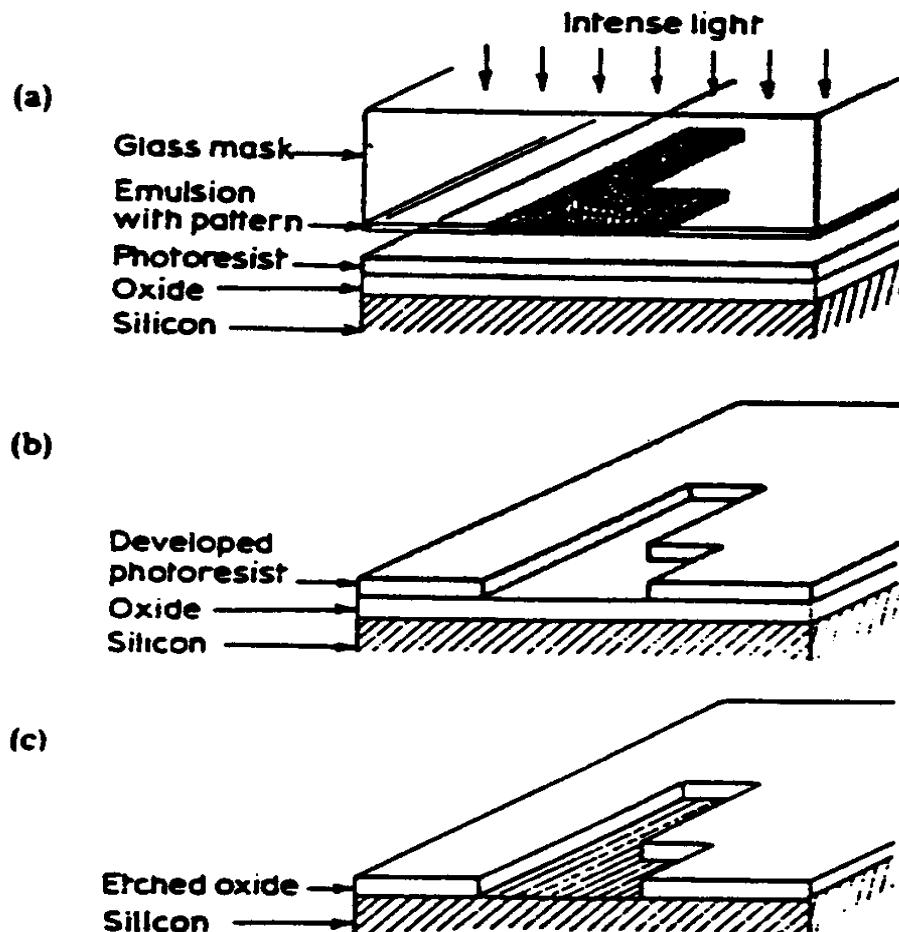
Advantages:

- can machine alloys that are too hard to be easily machined mechanically
- no scratches or burrs are produced
- very little stress introduced into the part



Electrochemical Etching

- deliberate removal of conducting or semiconducting material by electrochemical means (galvanic)
- examples:
 - 1) metallographic analysis of crystal & grain structure
 - 2) surface roughening to enhance adhesion
 - 3) selective, patterned removal of metal in fabrication of printed circuit boards
 - 4) selective etching of semiconductors in the manufacture of microelectronic devices



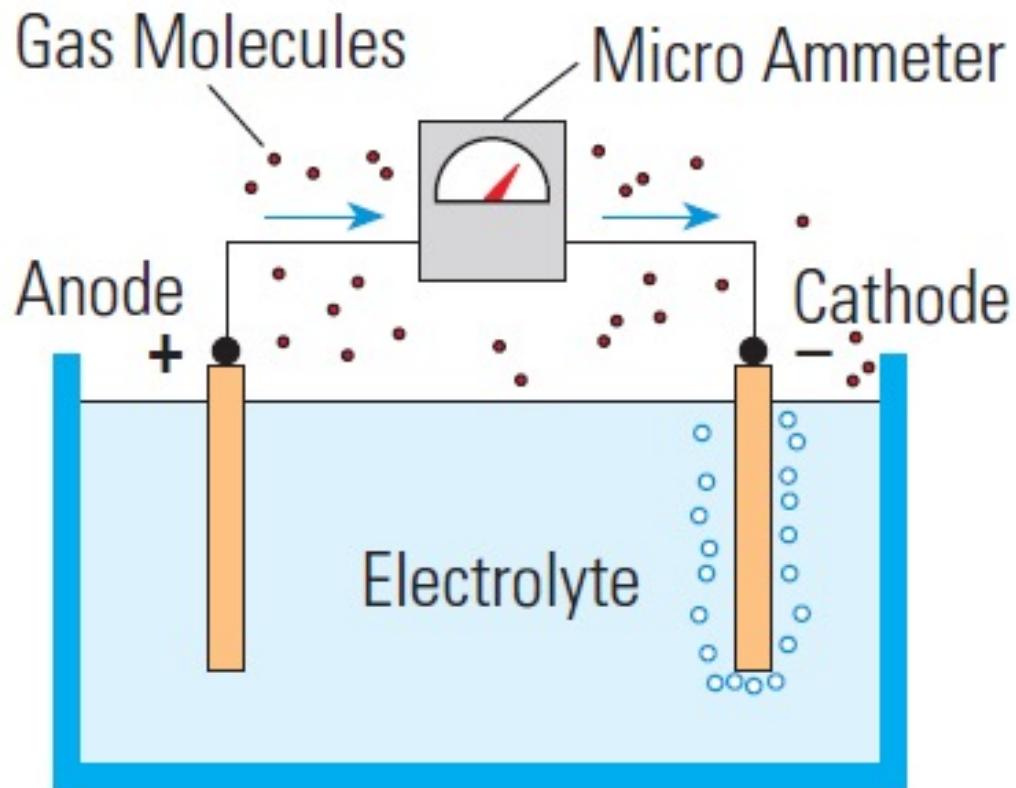
10. A simplified drawing of the selective removal of silica dioxide from silicon wafers during the fabrication of metal-oxide-silica semiconductor devices. (a) Photore sist exposure. (b) Patterned photoresist. (c) Etched pattern.

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- a) impart a pattern using photolithographic technique
 - i.e., i) glass mask is coated with emulsion in desired pattern (shaded region)
 - ii) place glass mask onto photoresist material to impart pattern emulsion onto photoresist
 - iii) shining of UV light induces photochemical reaction in emulsion only
 - iv) remove mask
- b) when substrate is immersed in developer solution, only patterned emulsion region dissolves
- c) etching step dissolves all of the exposed surface
 - all of the exposed photoresist and oxide surface dissolves; since region which was dissolved in step b) is thinner, it reaches silicon layer first

- once silicon in patterned region is reached, etching is stopped
- consider operation of a battery in a radio, calculator, etc.
- when radio is switched off, the two terminals of battery are not in electrical contact; electrode reacting in battery cannot proceed
- when radio switched on, the two terminals of battery are now in electrical contact; electrode reactions in battery now proceed at a rate to match power required to operate radio.

Electrochemical Sensors



Electrochemical sensors are the largest group of chemical sensors, representing approximately 58% of the total.

Fig. 2 Basic Sensor

What is Corrosion ?

Corrosion is the “destructive interaction between a *material* and its *operation environment*”. It leads to material degradation and contamination of the environment.

It is a more general term than “rusting”, a concepts that only relates to a homogeneous type of attack (often of iron or steel, in natural environments).

Also non-metals can “corrode”.

Advantages of Adequate Corrosion Control

- ♥ Extended Coating and Structure Life yielding Cost Savings
- ♥ Protection of Environment
- ♥ Improved Public and Employee Safety
- ♥ Avoidance of costly Litigation resulting from non-adherence to Laws and Regulations

Carlsbad, NM Explosion



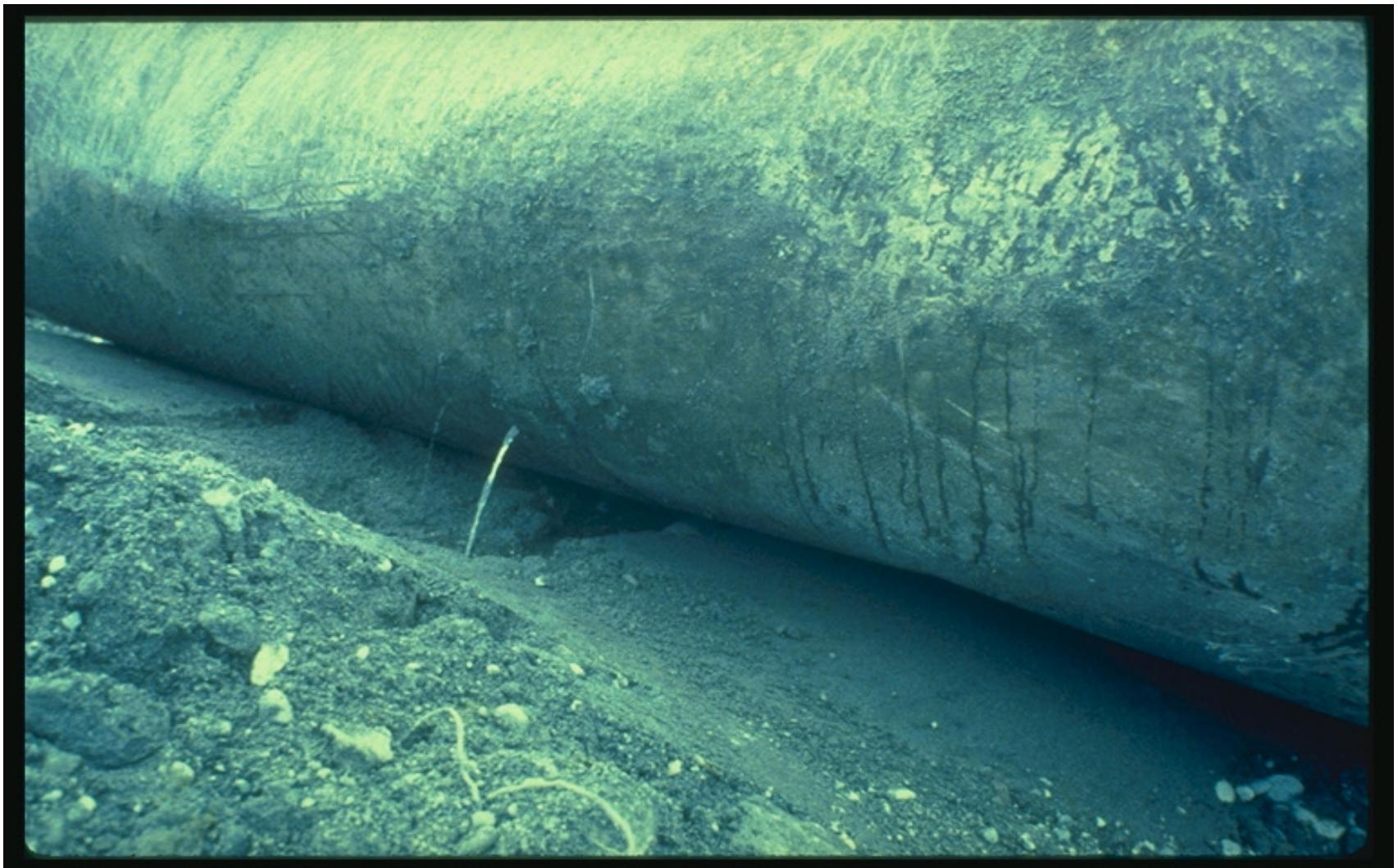
Upstream View of Rupture Crater

Lively, TX Explosion

- ♥ Gas Explosion - killed 2 teenagers
- ♥ Oil Company did not maintain Cathode Protection system and falsified records
- ♥ Jury awarded over 300 million dollars to Plaintiff



Removed & Leaking Underground Storage Tank



Tank Wall Completely Penetrated Due to Pitting Corrosion

Eight Forms of Corrosion

1. General or Uniform Attack
(anode and cathode randomly distributed)

TYPES OF LOCALIZED or NON-UNIFORM CORROSION

2. Galvanic Corrosion

- Factors
 - **galvanic series differential**
 - **environment**
 - **distance**
 - **area**

3. Crevice Corrosion

- environment
- oxygen depletion
- excess +ve charge produces high H^+ and Cl^-

4. Pitting

- autocatalytic

Eight Forms of Corrosion

5. Intergranular

Corrosion

- grain boundaries are more reactive
- (sensitisation)
- (weld decay in stainless steels)

6. Selective Leaching

- Dezincification of brass

7. Erosion Corrosion

- surface films
- velocity
- turbulence
- (cavitation)
- (fretting)

End