COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
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Physical & Interfacial Electrochemistry 2014

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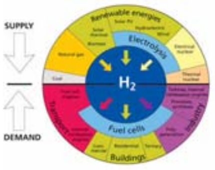
Module JS CH3304 Molecular Thermodynamics and Kinetics

Fundamental Physical & Interfacial Electrochemistry.

- Lecture 1.
  - Review of basic concepts & survey of some EC systems.
- Lecture 2.
  - Ion-Solvent Interactions : Born Model of ionic solvation.
- Lecture 3.
  - Ion-Ion interactions: Debye-Huckel (DH) Theory
- Lecture 4.
  - Equilibrium electrochemistry .
- Lecture 5.
  - The electrode/solution interface.
- Lecture 6/7.
  - Material transport in electrochemical systems.
    - Diffusion, migration, convection.
- Lecture 8/9.
  - Electron transfer kinetics at electrode/solution interfaces
    - Phenomenological approach
    - Microscopic QM approach (Marcus Theory).

Recommended Reading.

- Hibbert, **Introduction to electrochemistry** (Macmillan, 1993). Good simple treatment. OK for this course.
- Compton & Banks, **Understanding Voltammetry**, 2nd edition, Imperial College Press, 2011. Great book for theory of voltammetry.
- Brett & Brett, **Electrochemistry : Principles, methods and applications** (OUP,). More advanced account but good clear explanations.
- Rieger, **Electrochemistry**, 2nd edition. (Chapman &Hall, 1994). More advanced account.
- Bard and Faulkner, **Electrochemical techniques : fundamentals & applications**, 2nd edition, (Wiley, 2001). The electrochemical bible for graduate study.
- Girault, **Analytical and Physical Electrochemistry**, Marcel Dekker/EPFL Press, 2004. Excellent and thorough presentation of essentials written with characteristic French mathematical rigor.
- Bond, **Broadening electrochemical Horizons**, (OUP, 2002). ****Another excellent book explaining the principles of electrochemical methodology.



Physical & Interfacial Electrochemistry 2013

Lecture 1

Redox reactions at interfaces :
devices and applications
in energy conversion & synthesis.

Definitions of **Electrochemistry** on the Web:

- Chemical changes and energy produced by electric currents.
www.angelfire.com/pa/baconbacon/page4.html

- Chemical reactions driven by electrical energy.
highered.mcgraw-hill.com/sites/0072480823/student_view0/glossary.html

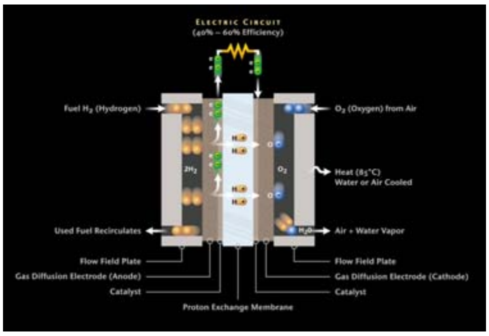
- The study of chemical changes resulting from electrical action and electrical activity resulting from chemical changes.
www.bioon.com/book/biology/genomicglossaries/labels_sig_and_detection_gloss.asp.htm

- The branch of chemistry concerned with the electrical aspects of chemical reactions, particularly electrolysis and cells (batteries).
www.malton.n-yorks.sch.uk/MSWeb/ScienceWeb/chemistry/glossary.html

- Branch of chemistry that deals with the chemical action of electricity and the production of electricity by chemical reactions
wordnet.princeton.edu/perl/webwn

- Electrochemistry is the science of the reactions that can take place at the interface of an electronic conductor (the electrode, which can be a metal or a semiconductor including graphite) and an ionic conductor (the electrolyte).
If a chemical reaction is caused by an external voltage, or if a voltage is caused by a chemical reaction, as in a Battery (electricity), it is an *electrochemical* reaction. In general, electrochemistry deals with situations where an oxidation and a reduction reaction is separated in space.
en.wikipedia.org/wiki/Electrochemistry

Electrochemistry underlies much important technology :
Metal plating,
Fuel Cells/Energy Conversion,
Corrosion, Biosensors.



Physical Analytical & Materials Electrochemistry Center (PAME-TCD)
School of Chemistry & CRANN, TCD.

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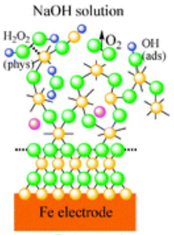
Electrochemical Technology & Innovation (ETI) Group

Trinity Electrochemical Energy Conversion & Electrocatalysis (TEECE) Group



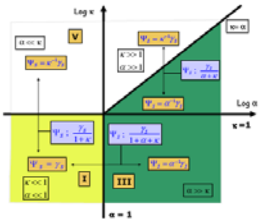
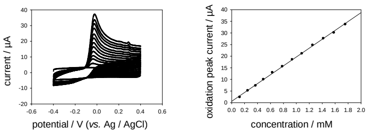


Figure 8. Kinetic case diagram illustrating the α,κ plane.

Electroactive Materials Electrochemistry
& Sensors (EMES) Group



SWCNT modified Carbon for AA detection

Modeling & Simulation of Electrochemical Systems (MSES) Group

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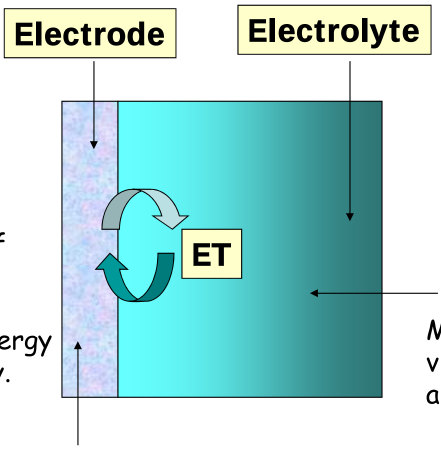
The electrode/electrolyte interface.



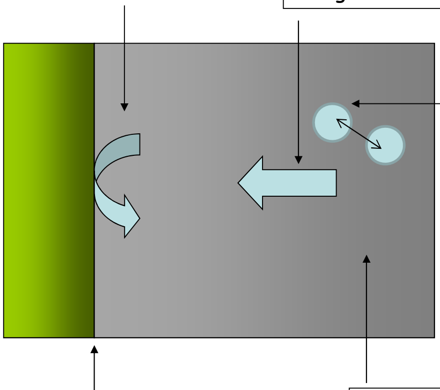
Ionically conducting medium : electrolyte solution, molten salt, solid electrolyte, polymeric electrolyte, etc.

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.

The elements of Physical Electrochemistry



Heterogeneous interfacial ET kinetics : Butler-Volmer, Marcus Theory.

Material transport through electrolyte via diffusion, convection & migration.

Ionics.
Ion-Ion interactions,
Ion-solvent interactions.

Experimental Methodology:
Electrochemical.
Spectroscopy.
Probe Microscopy.

Homogeneous chemical kinetics.

Structure of 'double layer'
Interface region.
Diffusion layer approximation.

Bard et al. The electrode/solution interface- a status report.
J. Phys. Chem. 97 (1993) 7147-7173.

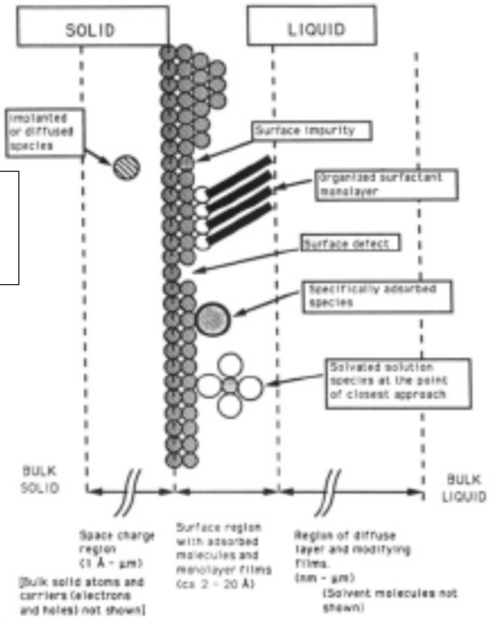


Figure 1. Schematic representation of the liquid–solid interfacial region showing possible species and features.[346]

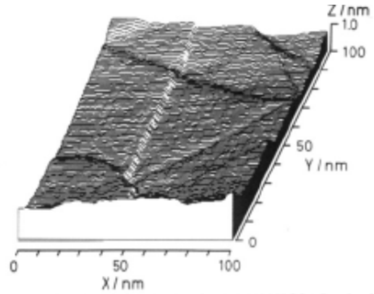


Figure 2. STM image of a Pt(111) surface in 0.05 M H_2SO_4. Reprinted with permission from ref 19. Copyright 1990 American Institute of Physics.

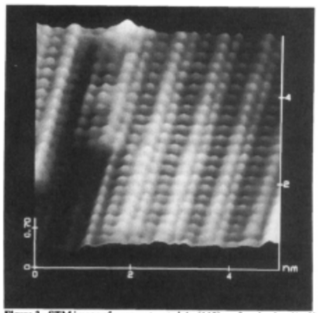


Figure 3. STM image of a reconstructed Au(110) surface having (1×2) symmetry in 0.1 M $HClO_4$.[21]

Electrode/solution interface
Imaged by STM & AFM.

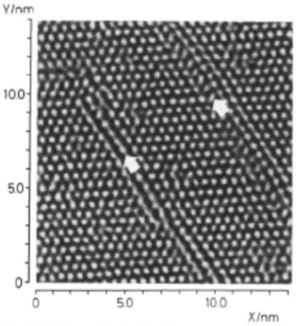
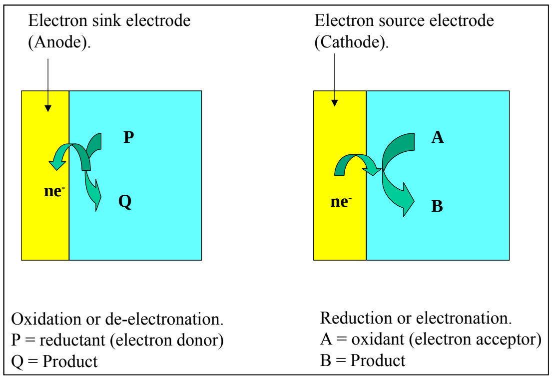


Figure 5. STM image of the first Cu adlayer. Arrows indicate phase boundaries.[29]

Interfacial electron transfer at electrode/solution interfaces:
oxidation and reduction processes.

- Oxidation (electron loss) and reduction (electron gain) are termed (redox) processes and lie at the heart of electrochemistry.

- The rates of such processes are influenced by the structure of the interface region located between an electrode and an electrolyte solution.



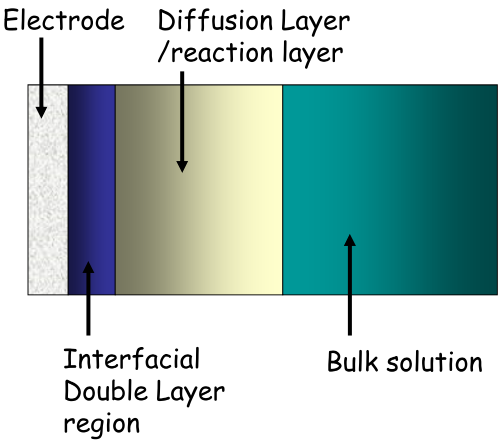
Electron sink electrode
(Anode).

Electron source electrode
(Cathode).

Oxidation or de-electronation.
P = reductant (electron donor)
Q = Product

Reduction or electronation.
A = oxidant (electron acceptor)
B = Product

Local geography of electrode/solution interface region.

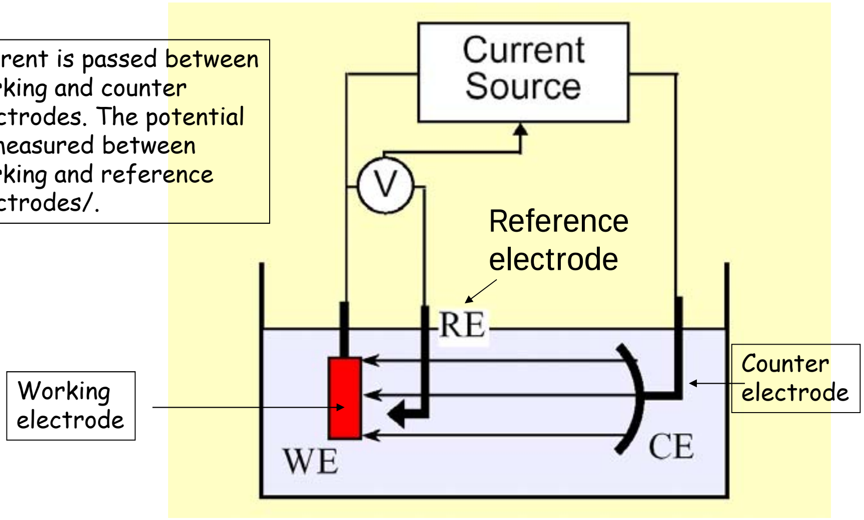


- Occurrence of ET reactions tend to make the composition of the solution near the electrode surface different from that further away.

A **Diffusion layer** is generated. This is considerably thicker than the **electrical double layer**.

- Homogeneous chemical reactions can also occur. These generate **reaction layers** which are quite thin. Reaction layer thickness depends on magnitude of chemical rate constant.
- If electrodes are rotated the solution near the electrode surface moves. This generates a **hydrodynamic layer**. A similar layer is generated if the solution flows past or impinges on a stationary electrode.

Fundamentals of the electrochemical measurement.



Current is passed between working and counter electrodes. The potential is measured between working and reference electrodes/.

Negative electrode
Cathode
Reduction

$Cu^{2+} + 2e^- \longrightarrow Cu^0$

Positive electrode
Anode
Oxidation

$2Cl^- \longrightarrow Cl_2 + 2e^-$

Electrode:
Electronic
Conductor

Electrolyte:
Ionic conductor

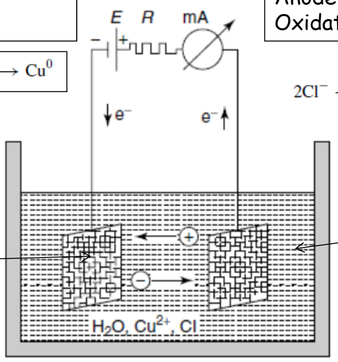
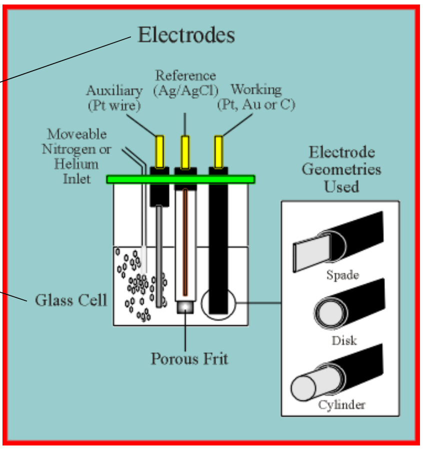


Figure 1. Electrochemical cell for the electrolysis of aqueous $CuCl_2$ solution. E: d.c. voltage; *R*: resistance; mA: galvanometer for current measurement.

Net Reaction

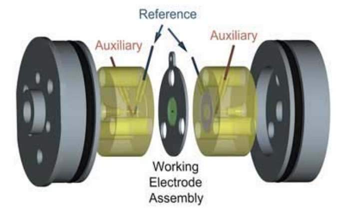
$$\begin{array}{r} Cu^{2+} + 2e^- \longrightarrow Cu^0 \\ 2Cl^- \longrightarrow Cl_2 + 2e^- \\ \hline Cu^{2+} + 2Cl^- \longrightarrow Cu^0 + Cl_2 \end{array}$$

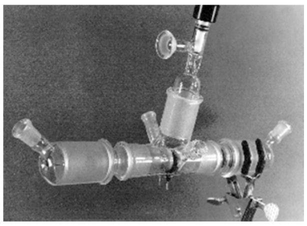


Potentiostat

Practical setup for dynamic Electrochemical measurements: Potentiostat and electrochemical cell. Refer to JS P.Chem Expt. on Cyclic Voltammetry.

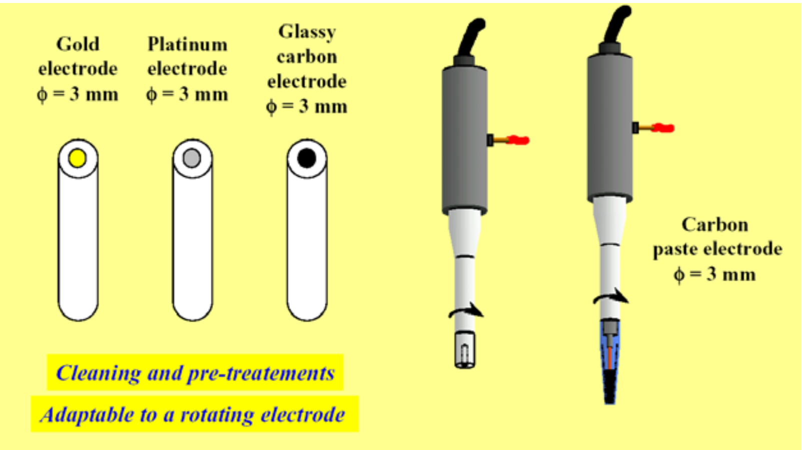
Electrochemical cells





EC Cells are a tribute to the art of glassblowing.

Typical electrode configurations.

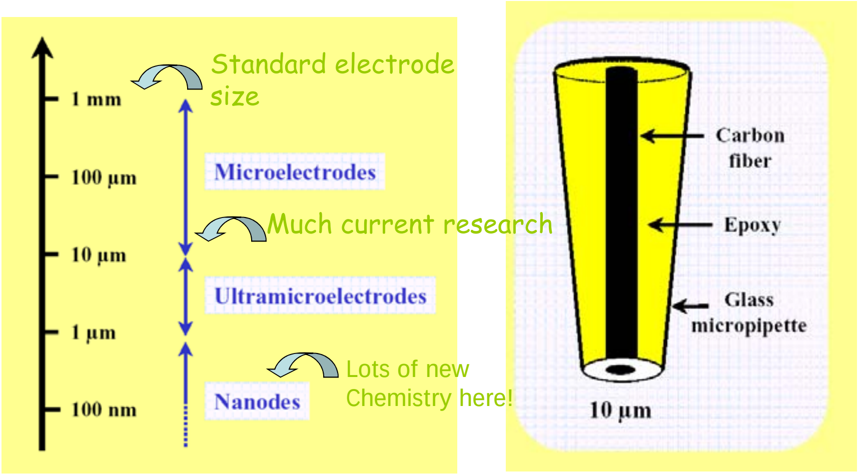


Cleaning and pre-treatements

Adaptable to a rotating electrode

Typical range of electrode size.

Small size = new chemistry and physics !
Better space, time and energy resolution.



Nano-sized carbon fibre electrodes.

Chen & Kucernak, Electrochem. Commun. 4 (2002) 80-85
Chen & Kucernak, J. Phys. Chem.B. 106 (2002) 9396-9404

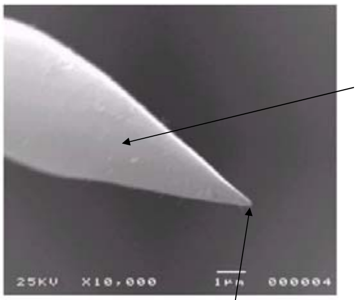


Fig. 1. SEM image of an etched carbon fiber.

Electrophoretic paint

Nanoelectrode

This is the JS voltammetry expt.
Using nanosize electrodes.

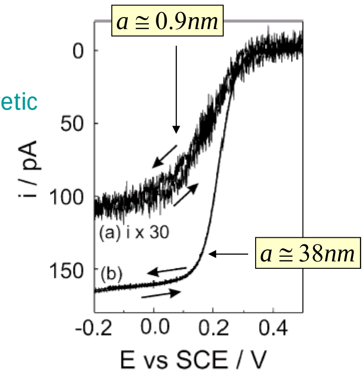
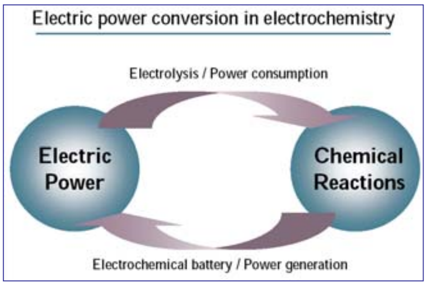


Fig. 3. The steady-state voltammograms (both forward and reverse scans) of reduction of 0.01 mol dm^{-3} $K_3Fe(CN)_6$ in 0.5 mol dm^{-3} KCl. Both electrodes were fabricated using three repeated EDP coating/heating cycles. The effective radii are calculated from the diffusion limited currents as 0.9 nm, (a); and 38 nm, (b). Scan rate of 10 mV s^{-1}.

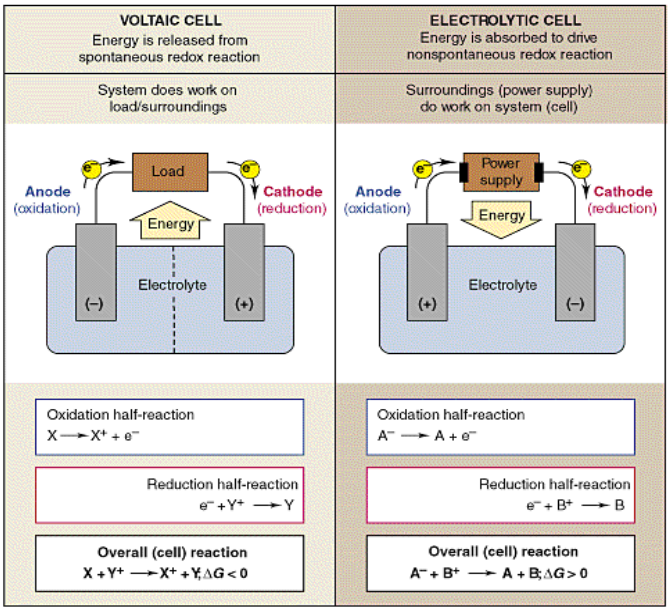
The Ying / Yang of Electrochemistry

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 to form a useful device.
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.



- Galvanic cell.
  - This is an electrochemical power source.
  - The cell does work by releasing free energy from a spontaneous 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.

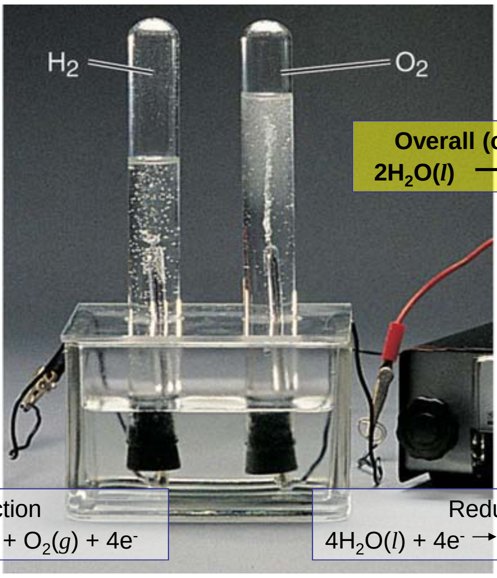


Electrolysis.

- 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.

Weinberg, J. Chem. Ed.,60 (1983) 268-271.

The electrolysis of water



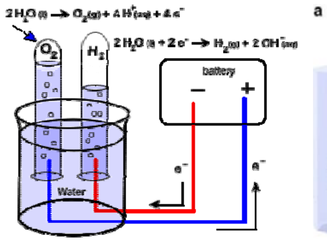
Overall (cell) reaction
$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

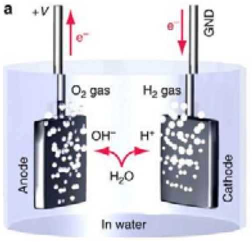
Oxidation half-reaction
$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

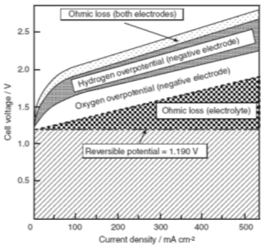
Reduction half-reaction
$4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$

Electrolysis cell: electrochemical substance producer

Electrical energy produces chemicals.







Performance (voltage *vs.* current density) of a basic (unactivated), unipolar electrolyzer running at 90 °C.

Overpotential losses increase
net electrical energy needed as
input to drive reactions at electrodes.

Thermodynamics
(Nernst Potential)

Kinetics: Cathode reaction
Overpotential

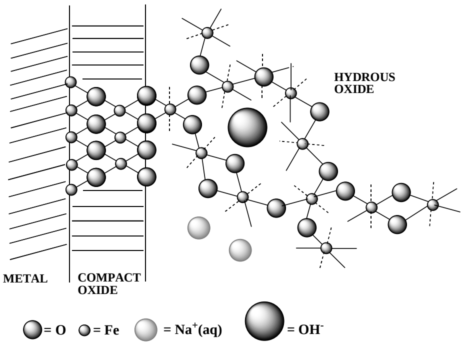
Ohmic potential:
Cell design

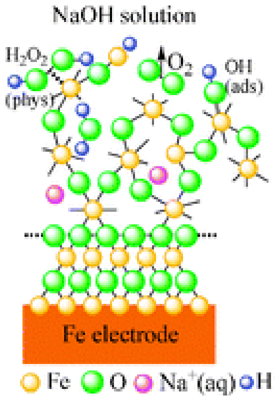
$$E(i) = E_{e,cell} + \left|\eta_C\right| + \eta_A + IR$$

Kinetics: Anodic reaction overpotential

Need to minimize
all overpotential
losses to make
applied potential
as close to Nernst
potential as possible.

Burke-Lyons Duplex Layer Model
Oxide/solution interface





Lyons Brandon OER
Mechanism (2010)
Oxidized Ni.

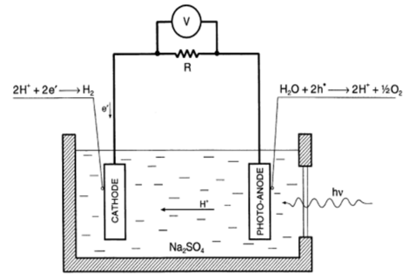
$$[\mathrm{Ni(III)O}_m(\mathrm{OH})_n]^{p-} + \mathrm{OH}^- \rightarrow [\mathrm{Ni(III)O}_{m+1}(\mathrm{OH})_{n-1}]^{p-} + \mathrm{H_2O} + e^-$$
$$[\mathrm{Ni(III)O}_{m+1}(\mathrm{OH})_{n-1}]^{p-} \rightarrow [\mathrm{Ni(III)O}_m\ \underline{\mathrm{OOH}}(\mathrm{OH})_{n-2}]^{(p-1)-} + e^- \text{ ...RDS}$$
$$[\mathrm{Ni(III)O}_m\ \underline{\mathrm{OOH}}(\mathrm{OH})_{n-2}]^{(p-1)-} + 2\mathrm{OH}^- \rightarrow [\mathrm{Ni(III)O}_m\ \mathrm{O}_2\ (\mathrm{OH})_{n-1}]^{p-} + \mathrm{H_2O} + e^-$$
$$[\mathrm{Ni(III)O}_m\ \underline{\mathrm{OO}}(\mathrm{OH})_{n-1}]^{p-} + \mathrm{OH}^- \rightarrow [\mathrm{Ni(III)O}_m(\mathrm{OH})_n]^{p-} + \mathrm{O}_2 + e^-$$

(a) M.E.G. Lyons, M.P. Brandon Phys.Chem. Chem. Phys., 11(2008) 2203.
(b) M.E.G. Lyons, M.P. Brandon, J. Electroanal. Chem., 631 (2009) 62.
(c) M.E.G. Lyons, M.P. Brandon, J. Electroanal. Chem., 641 (2010) 119.

Metal oxide plays intrinsic role in OER.

Photoelectrochemical cells or 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.

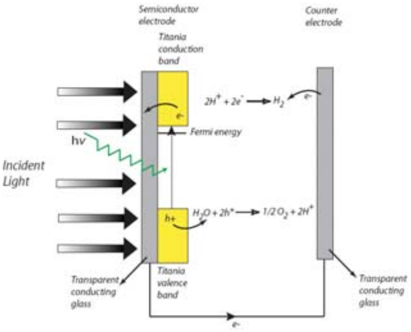
3. Electrode processes: oxidation of water to H^+ and H_2O by the holes at the photo anode and reduction of H^+ ions to H_2 by electrons at the cathode.

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.

$2h\nu = 2e^- + 2h^+$

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.

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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Industrial scale electrolysis: Chlor-alkali process.

We consider the electrolysis of brine (a concentrated NaCl solution). This electrolysis process converts an inexpensive salt to valuable chemicals such as H_2 , Cl_2 and NaOH.

In a modern electrolysis unit, a steel cathode and a titanium anode coated with a conductive mixed metal oxide such as RuO_2/TiO_2 is generally used. The latter are termed dimensionally stable anodes (DSA).

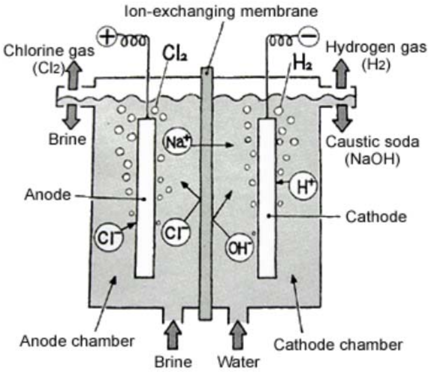
Molecular hydrogen is evolved at the Cathode.

$$\boxed{2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-}$$

Recent developments in electrochemical research have led to the development of high surface area nickel or nickel alloy cathodes which function more effectively.

The anode reaction is chlorine evolution.

$$\boxed{2Cl^- \rightarrow Cl_2(g) + 2e^-}$$



The solution in the anode compartment is usually acidified to pH 3-4 in order to suppress the evolution of molecular oxygen . Hence the net cell reaction is :

$$\boxed{2H_2O + 2Cl^- \rightarrow H_2(g) + Cl_2(g) + 2OH^-}$$

Now NaOH is produced directly in the cathode compartment. This must be prevented from mixing with the anolyte solution because hypocholorite and chlorate would be generated as side products if NaOH reacted with the electrogenerated Cl_2 .

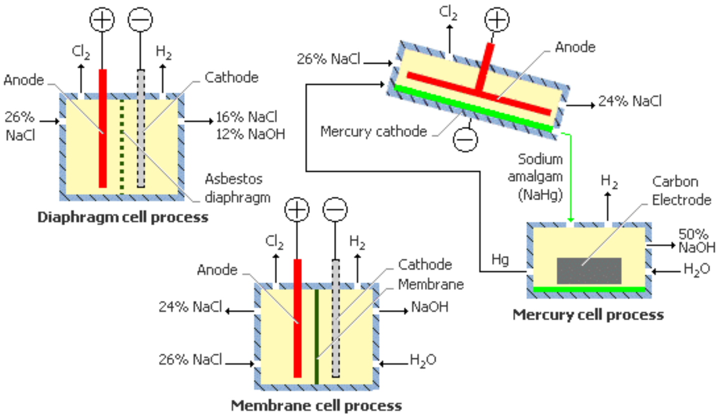
In the diaphragm cell an asbestos diaphragm separates the anolyte and catholyte compartments . However only dilute NaOH is produced using such a cell.

In the yet more technologically advanced membrane cell, a cation selective ion exchange membrane is used instead.

The latter allows Na^+ ions to pass through from the anode compartment to the cathode compartment, but there is no flow of solution between the compartments. Concentrated NaOH may be produced using this type of membrane system. There is currently much research effort conducted into the design of membrane materials which exhibit optimal performance under cell operating conditions.

<u>Chlor-alkali electrolysis</u> is a technique for the industrial production of chlorine and the alkali known as caustic soda (sodium hydroxide) from brine, a solution of common table salt (sodium chloride) in water.

Three processes are in use: the diaphragm-cell process, the membrane-cell process, and the mercury-cell process.



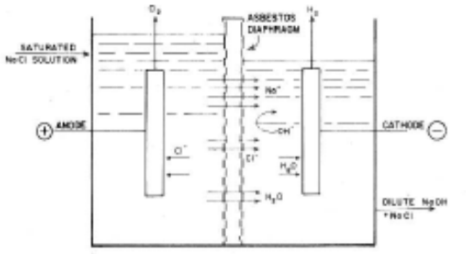


Figure 1. Schematic of a diaphragm type chlor-alkali cell.

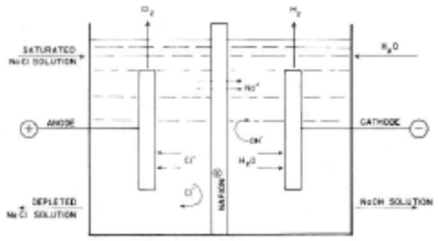


Figure 2. Schematic of an ion-exchange membrane cell.

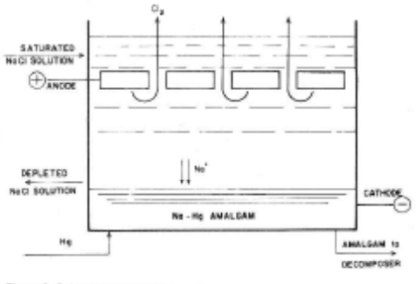


Figure 3. Schematic of a mercury cell.

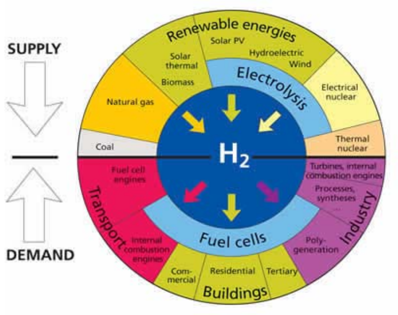
Venkatesh & Tilak, J. Chem. Ed., 60 (1983) 276-278.

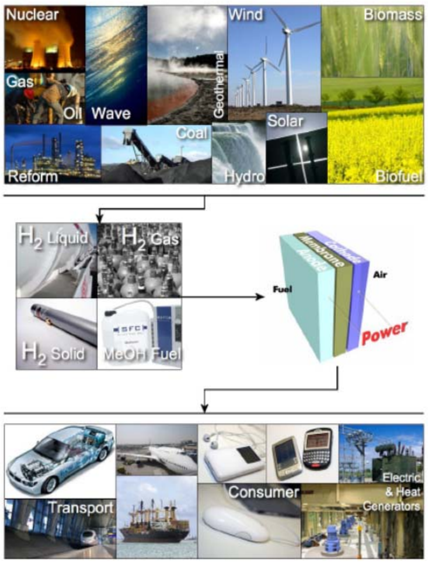
In the diaphragm-cell process, a porous diaphragm divides the electrolytic cell, which contains brine, into an anode compartment and a cathode compartment. When an electric current passes through the brine, the salt's chlorine ions and sodium ions move to the electrodes. Chlorine gas is produced at the anode, and sodium ions at the cathode react with the water, forming caustic soda. Some salt remains in the solution with the caustic soda and can be removed at a later stage.

In the membrane-cell process, the compartments are separated by a membrane rather than a diaphragm. Brine is pumped into the anode compartment, and only sodium ions pass into the cathode compartment, which contains pure water. Thus, the caustic soda produced has very little salt contamination.

In the mercury-cell process, mercury, which flows along the bottom of the electrolytic cell, serves as the cathode. When an electric current passes through the brine, chlorine is produced at the anode and sodium dissolves in the mercury, forming an amalgam of sodium and mercury. The amalgam is then poured into a separate vessel, where it decomposes into sodium and mercury. The sodium reacts with water in the vessel, producing the purest caustic soda, while the mercury returns to the electrolytic cell.

The Hydrogen Economy: Hydrogen as an energy carrier.





G.W. Crabtree, M.S. Dresselhaus, M.V. Buchanan, 'The hydrogen Economy' Physics Today, Dec.2004, pp.39-45.
U. Bossel, 'Does a hydrogen economy make sense?' Proc. IEEE, 94 (10)(2006), pp.1826-1836.

P.P. Edwards, V.L. Kuznetsov, W.I.F. David, N. Brandon. Energy Policy 36(2008) 4356-4362.

http://www.foresight.gov.uk/Energy/hydrogen_and_fuel_cells_towards_a_sustainable_future.pdf

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Fuel Cells : Introduction

- 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.

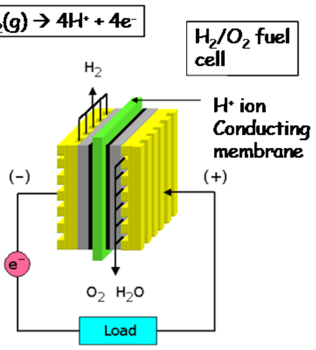
- Using hydrogen as a fuel (which can be extacted from hydrocarbon fuels or renewable sources) a fuel cell electro-chemically oxidises the hydrogen using oxygen from the air generating electricity and some heat.

- The fuel cell makes more efficient use of the fuel and produces fewer pollutants e.g. reduced nitrogen oxides and carbon dioxide emissions, and no particulates.

Hydrogen/oxygen fuel cell

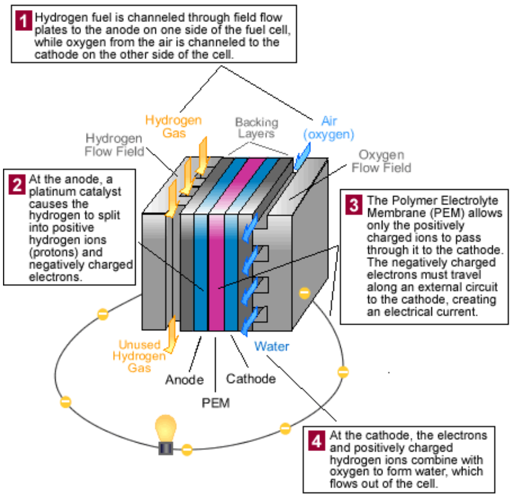
Anode reaction

$2H_2(g) \rightarrow 4H^+ + 4e^-$



Cathode reaction

$O_2(g) + 4e^- + 4H^+ \rightarrow 2H_2O$



1 Hydrogen fuel is channeled through field flow plates to the anode on one side of the fuel cell, while oxygen from the air is channeled to the cathode on the other side of the cell.

2 At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons.

3 The Polymer Electrolyte Membrane (PEM) allows only the positively charged ions to pass through it to the cathode. The negatively charged electrons must travel along an external circuit to the cathode, creating an electrical current.

4 At the cathode, the electrons and positively charged hydrogen ions combine with oxygen to form water, which flows out of the cell.

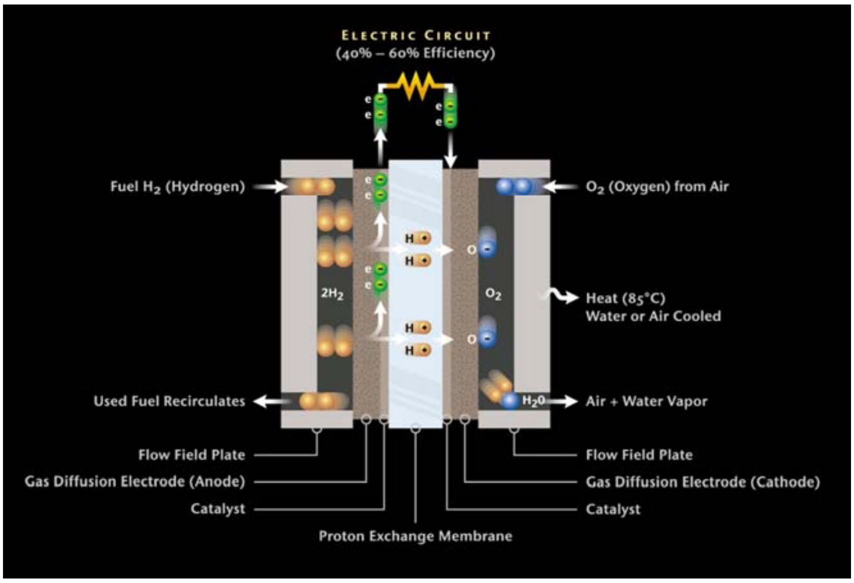
A fuel cell consists of two electrodes sandwiched around an electrolyte

Remember CH1101 Electrochemistry:

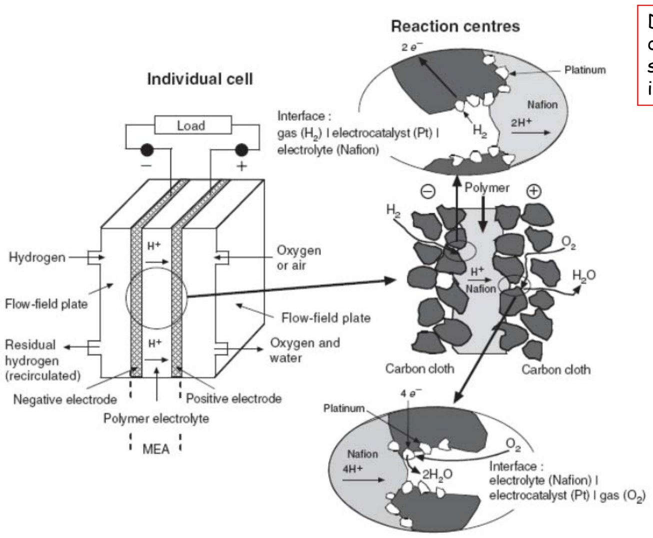
$$\Delta G = -nFE_{eq,cell}$$

$$E_{eq,cell} = E_{eq,C} - E_{eq,A}$$

Ballard PEM Fuel Cell.

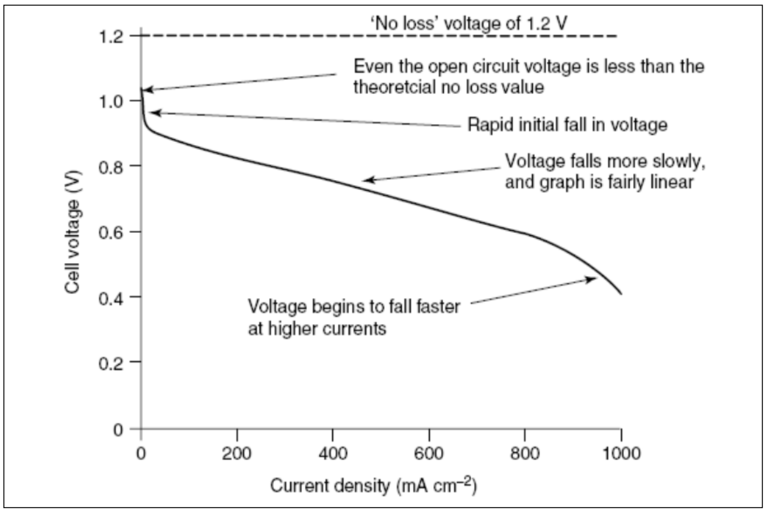


PEM Fuel Cell



Difficult to model due to complex structured interphase region.

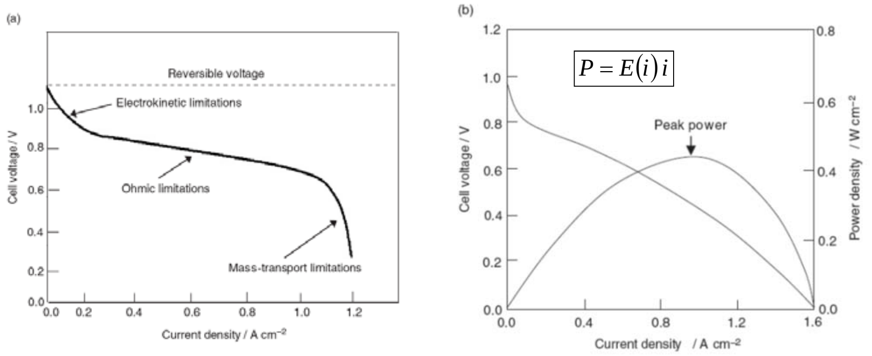
$$E(i) = E_{e,cell} - \Sigma\eta_{Anode} - \Sigma\eta_{cathode} - IR$$



Fall in output potential as current is drawn from cell caused
By kinetic, transport and cell design factors.

Self-driving Fuel Cell

Overpotential losses reduce net voltage output.



$P = E(i)\,i$

$$E(i) = E_{e,cell} - |\eta_C| - \eta_A - IR$$

Electrocatalytic Reactions

- Oxidation (several possible fuels)

  $H_2 \longrightarrow 2\,H^+ + 2\,e^-$

  $CH_3OH + H_2O \longrightarrow CO_2 + 6\,H^+ + 6\,e^-$

  $CH_4 + 2\,H_2O \longrightarrow CO_2 + 8\,H^+ + 8\,e^-$

  $C_xH_yO_z + (2x - z)\,H_2O \longrightarrow$

  $x\,CO_2 + (4x + y - 2z)\,(H^+ + e^-)$

- Reduction

  $O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$

SWCNT as catalytic platforms

Langmuir **2006**, *22*, 2392–2396

Single-Wall Carbon Nanotubes Supported Platinum Nanoparticles with Improved Electrocatalytic Activity for Oxygen Reduction Reaction

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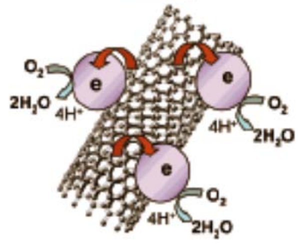
Radiation Laboratory, Departments of Chemistry & Biochemistry and Chemical & Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556-0579, and Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Scheme 1. Reduction of O_2 at the Pt/SWCNT Electrocatalyst



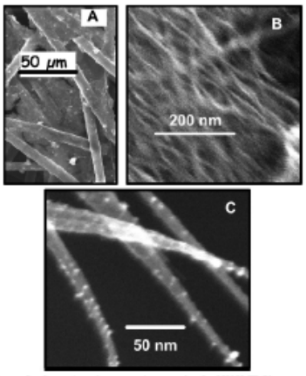


Figure 1. Scanning electron micrograph of a SWCNT film cast on carbon fiber (Toray) paper after deposition of Pt particles under different magnifications. Pt particles anchored on SWCNT can be seen in the magnified image (C).

Kinetic and Mechanistic analysis SWCNT/Pt nanoparticle composites

Table 1. Electrocatalytic Properties of Pt/SWCNT and Pt/C Electrodes

	ESCA (m^2/g_{Pt})	onset potential for O_2 reduction (mV)	Tafel slope (mV/dec) high *i*	Tafel slope (mV/dec) low *i*	k_{app} at 625mV, 24°C ($cm^4/mol\ s$)	ΔE (kJ/mol)
Pt/SWCNT	17.8	639	−59	−131	6.42	24.8 ± 0.3
Pt/C	33.5	632	−59	−111	3.28	24.8 ± 0.3

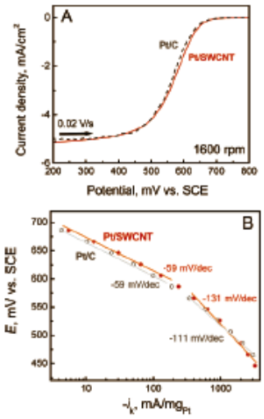


Figure 5. (A) Rotating disk voltammograms comparing the oxygen reduction on Pt/SWCNT (a) and Pt/C (b) in O_2 saturated 0.1 M $HClO_4$ solution at 24 °C. Rotating rate = 1600 rpm. Potential scan rate = 0.02 V/s. (B) The corresponding Tafel plots.

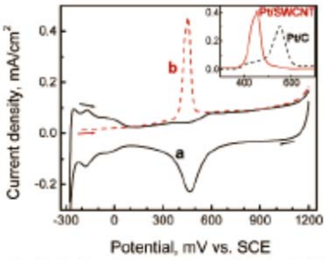
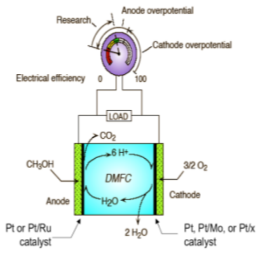


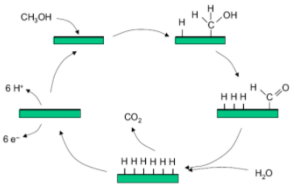
Figure 2. (a) Cyclic voltammogram recorded using Pt/SWCNT (14 μg/cm²) in deaerated 0.1 M perchloric acid at a scan rate of 0.02 V/s. (b) Linear sweep voltammogram recorded after adsorption of CO at the Pt/SWCNT electrode in the same solution. The peak area in panel b corresponds to stripping of adsorbed CO. The inset is the stripping voltammograms of CO at Pt/SWCNT and Pt/C.

Example: DMFC



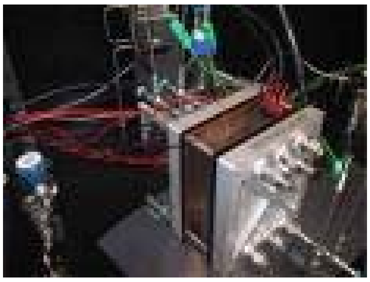
"Chemoelectricity"

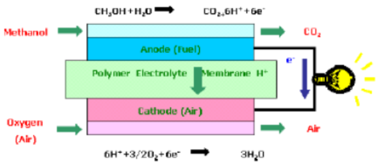
- First the chemistry, then the electricity…



Simple version of MeOH oxidation.

This is where much of current Fuel Cell research is at .

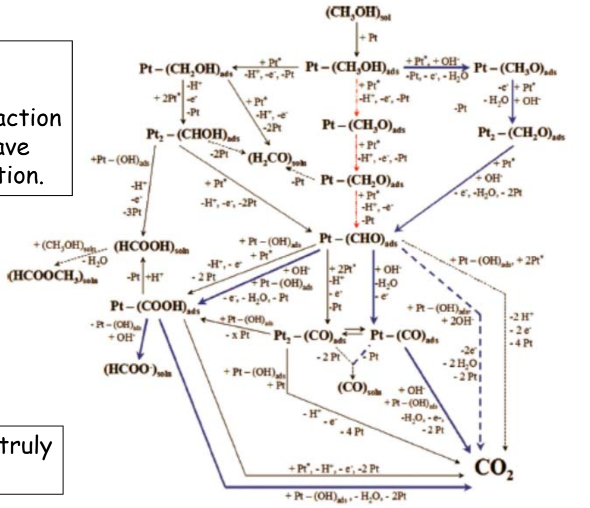




Schematic of a direct methanol fuel cell (Courtesy of Toshiba)

Large number of ET steps implies large number of adsorbed reaction intermediates, hence have complex multistep reaction.

Methanol oxidation is truly complex !



$Pt + H_2O \longrightarrow Pt-(OH)_{ads} + H^+ + e^-$ $Pt + OH^- \longrightarrow Pt-(OH)_{ads} + e^-$

+ Pt* = Minimum reactive Pt sites needed. Nature of the Pt site is potential, and electrolyte, dependent (oxide-covered, hydroxide covered, or pristine).

- Pt = Pt sites regained after reaction takes place.

Fig. 1 Detailed pathway for the oxidation of MeOH in acid (—) and alkaline (blue solid line) electrolyte. Dashed lines represent pathways that have been suggested in the literature for acidic and alkaline electrolytes respectively, but are unlikely to occur under typical experimental conditions. The pathway (red line) corresponds to the initial dehydrogenation pathway as determined by UHV experiments.

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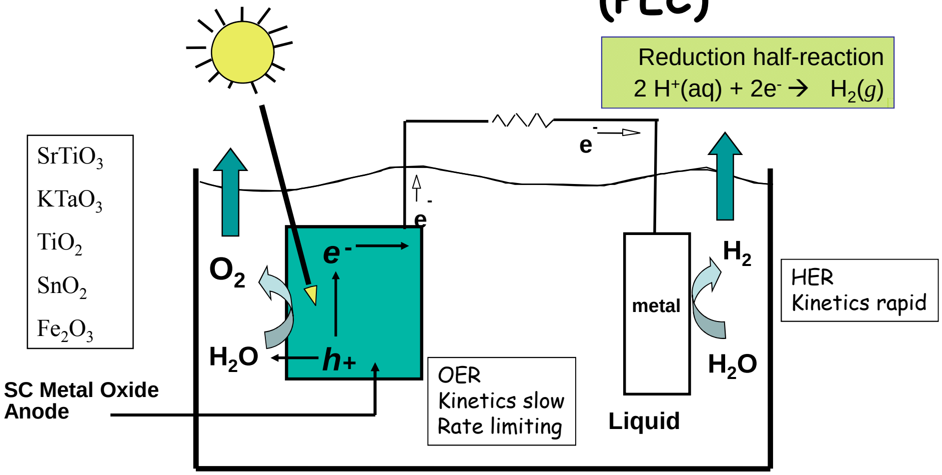
Photoelectrochemical Cell (PEC)

Overall (cell) reaction
$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

Reduction half-reaction
$$2\,H^+(aq) + 2e^- \rightarrow H_2(g)$$

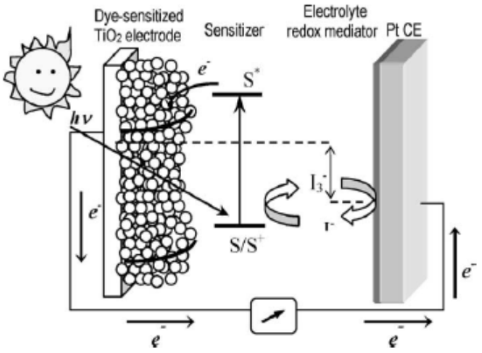


Oxidation half-reaction
$$4OH^-(aq) \rightarrow O_2(g) + 2H_2O + 4e^-$$

Light is Converted to Electrical + Chemical Energy

DSSC Systems

In recent years dye sensitized solar cells (DSSC) or 'Grätzel' cells have attracted considerable interest worldwide due to their low production cost, excellent stability (ca.10 years useful lifetime in outside applications) and high efficiency to convert solar energy into electricity (typically 10%).
Energy conversion in a DSSC device is based on the injection of an electron from a photoexcited state of the sensitizer dye (typically a bipyridine metal complex) into the conduction band of a nanocrystalline semiconductor (typically TiO2).
These cells employ a liquid electrolyte (usually an iodide/triiodide I^-/I_3^- redox couple dissolved in an organic solvent) to reduce the dye cation thereby regenerating the ground state of the dye. Regeneration of iodide ions which are oxidized in this reaction to tri-iodide is achieved at a platinized counter electrode.



$$TiO_2|S + h\nu \rightarrow TiO_2|S^*$$
$$TiO_2|S^* \rightarrow TiO_2|S^+ + e^-_{CB}$$
$$TiO_2|S^+ + e^-_{CB} \rightarrow TiO_2|S$$
$$TiO_2|S^+ + (3/2)I^- \rightarrow TiO_2|S + (1/2)I_3^-$$
$$(1/2)I_3^- + e^-_{Pt} \rightarrow (3/2)I^-$$
$$I_3^- + 2e^-_{CB} \rightarrow 3I^-$$

Light absorption is accomplished by a monolayer of photoactive dye (S) adsorbed chemically at the semiconductor surface and excited by interaction with an incident photon of light .
After excitation (S*) the excited dye transfers an electron to the semiconductor by an injection process.
The efficiency will depend on the relative energy levels between the semiconductor and the dye and on the kinetics of the electron transfer process at the interface.
For efficient cell operation the rate of electron injection must be faster than the rate of decay of S*. Furthermore the rate of re-reduction of the oxidized sensitizer, the dye cation S^+ by the electron donor (I^-) in the electrolyte must be higher than the rate of back reaction of the injected electrons with the dye cations, as well as the rate of reaction of injected electrons with the electron acceptor (I_3^-) in the electrolyte.
Finally the kinetics of the reaction at the counter electrode must also guarantee the fast regeneration of the charge mediator (I^-) or this reaction could also become rate limiting in the overall cell performance.

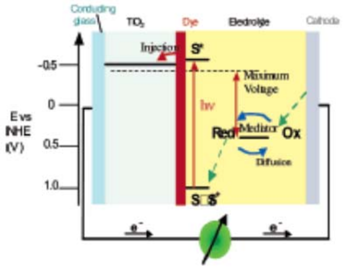


Figure 1. Principle of operation of the dye-sensitized nanocrystalline solar cell. Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of a semiconductor oxide film. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter electrode by electrons passed through the load. Potentials are referred to the normal hydrogen electrode (NHE). The energy levels drawn match the redox potentials of the N3 sensitizer ground state and the iodide/triiodide couple shown in Figure 5.

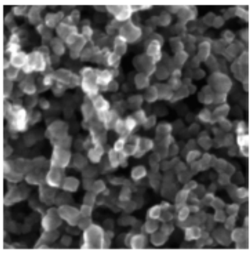


Figure 2. Scanning electron micrograph of a sintered mesoscopic TiO_2 film supported on an FTO glass. The exposed facets of the anatase nanocrystals are mainly oriented in the (101) direction. The average particle size is 20 nm.

M Gratzel, Inorg. Chem., 44 (2005) 6841-6851.
P.V. Kamar, J.Phys. Chem.B., 106 (2002) 7729-7744.

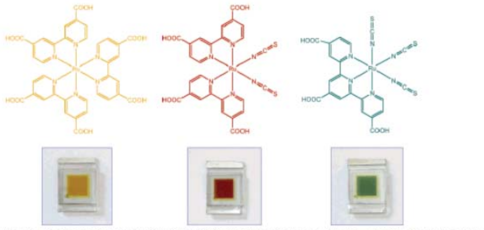


Figure 5. Structure of the ruthenium sensitizers RuL_3 (yellow) *cis*-$RuL_2(NCS)_2$ (red) and $RuL'(NCS)_3$ (green) where L = 2,2′-bipyridyl-4,4′-dicarboxylic acid and L′ = 2,2′,2″-terpyridyl-4,4,′4″-tricarboxylic acid. The lower part of the picture shows nanocrystalline TiO_2 films loaded with a monolayer of the respective sensitizer. The film thickness is 5 μm.