Modern Methods in Heterogeneous Catalysis Research

Charge transport across interfaces

Sebastien Cap
sebastiencap@fhi-berlin.mpg.de

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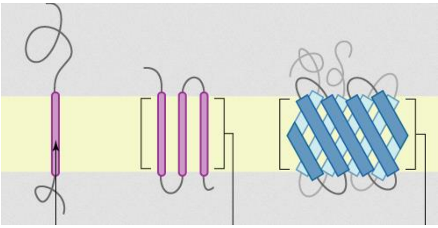
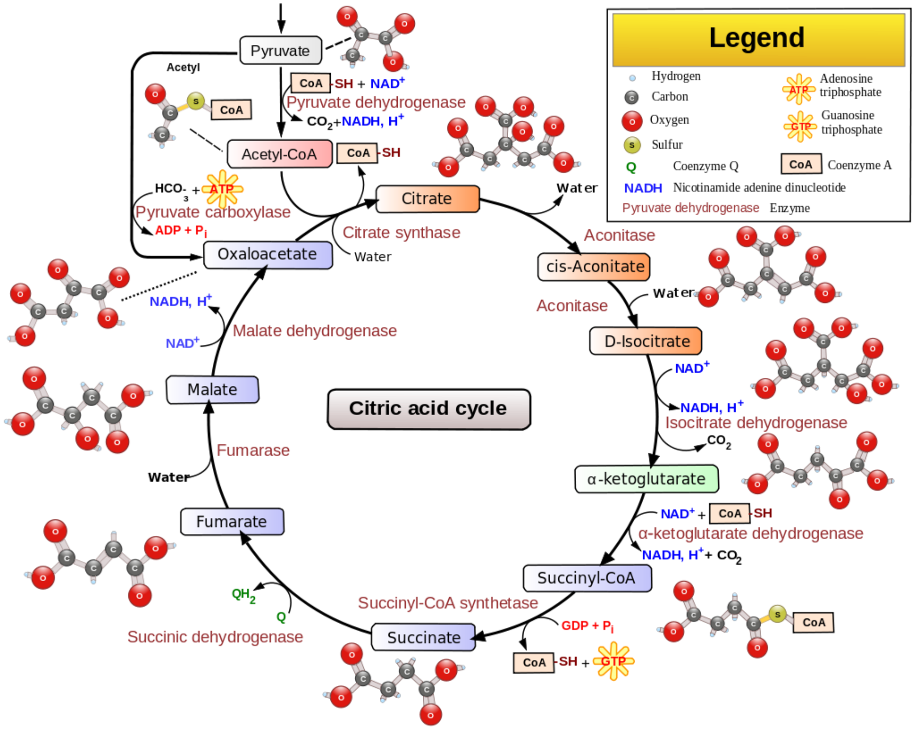
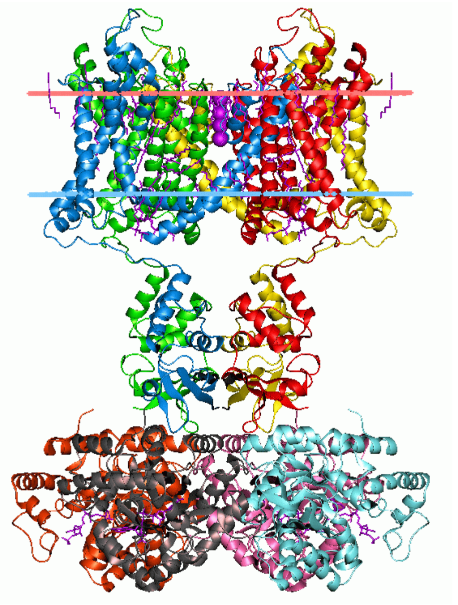
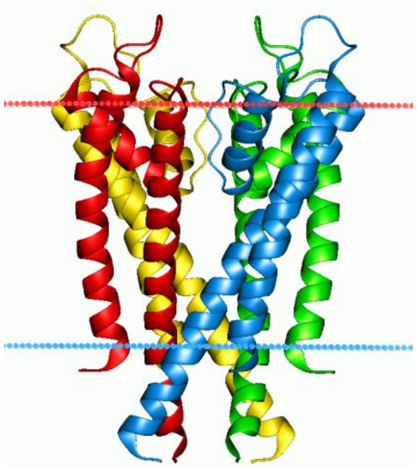
I) Charge transport in biology / transmembrane ion channel family





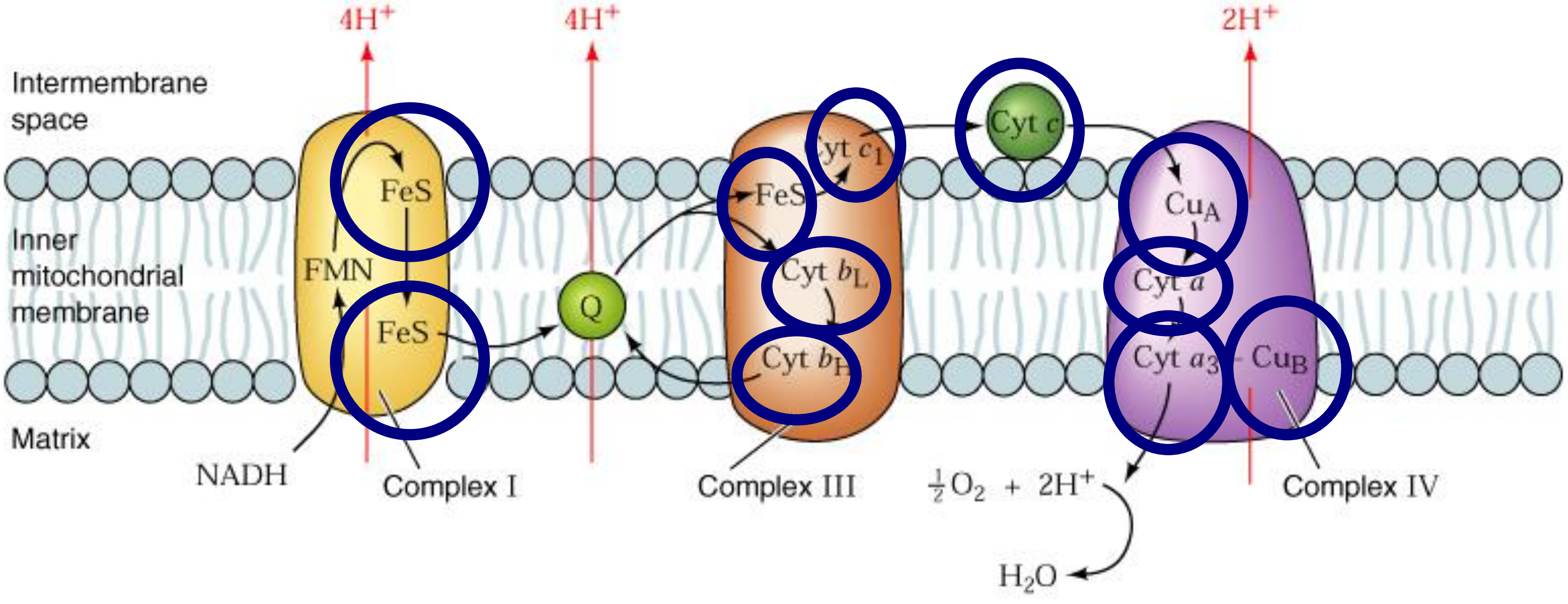




Left: Potassium channel structure in a membrane-like environment.

Right: Potassium channel. Calculated hydrocarbon boundaries of the lipid bilayer are indicated by red and blue dots.

Krebs Cycle
Results in oxidative phosphorylation



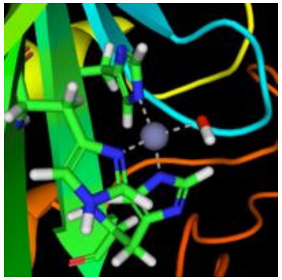
I) Metallo-enzymes

Carbonic anhydrase:

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

$CO_2 + OH^- \rightleftharpoons HCO_3^-$

Active site of carbonic anhydrase



Vitamine B12:

Catalyzes the transfer of methyl groups

Superoxide dismutase

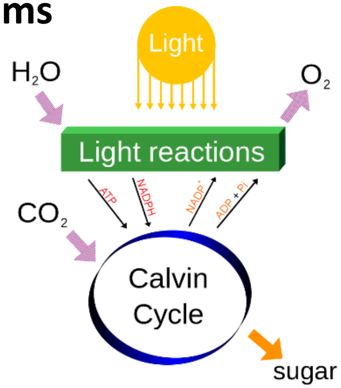
O^{2-} is produced by reduction of O_2

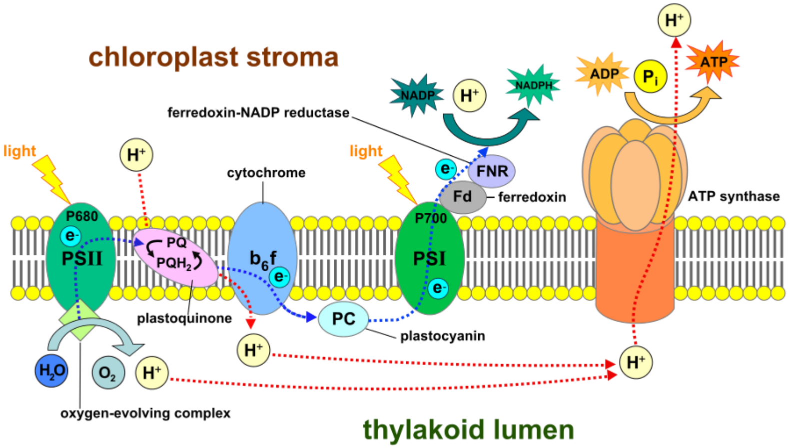
O^{2-} is very oxidizing

SOD catalyse its dispoportionation to O_2 and H_2O_2

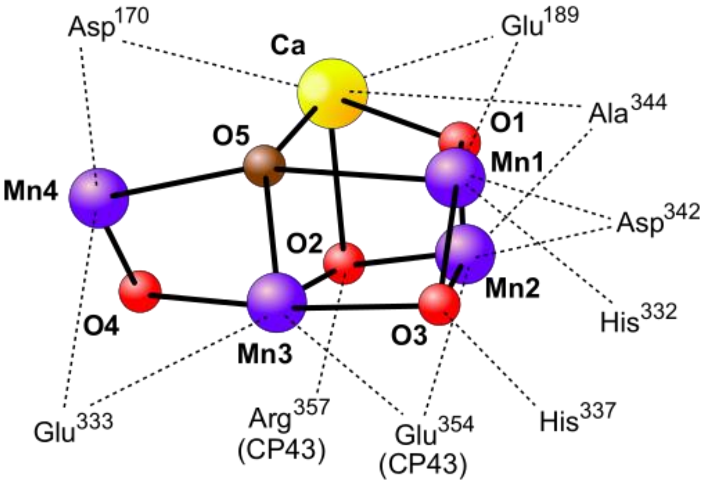
Active metal is Cu

Chlorophyll systems

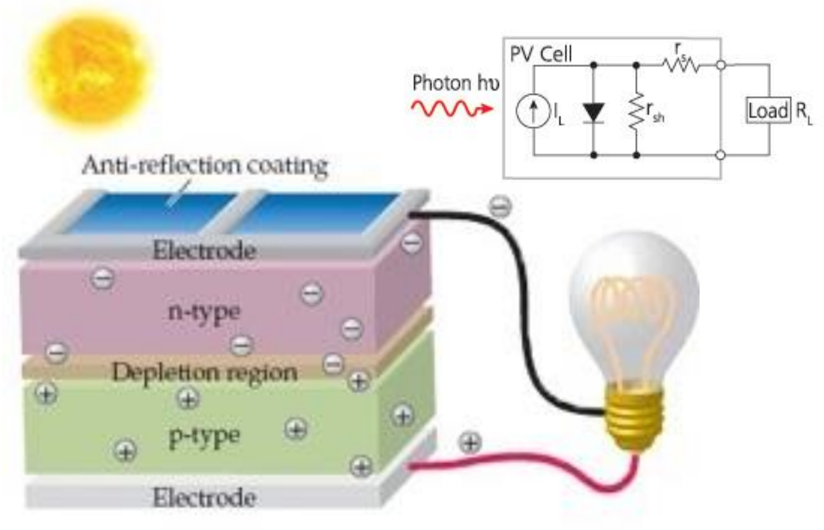




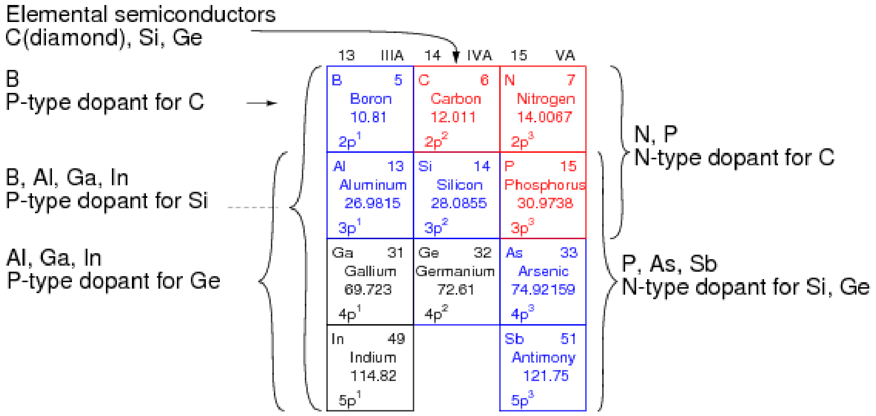
Oxygen-evolving complex (OEC)



I) Charge transport in photovoltaic cells "Current from light"



Semiconductors and dopants ("impurities")



Elemental semiconductors
C(diamond), Si, Ge

B
P-type dopant for C

B, Al, Ga, In
P-type dopant for Si

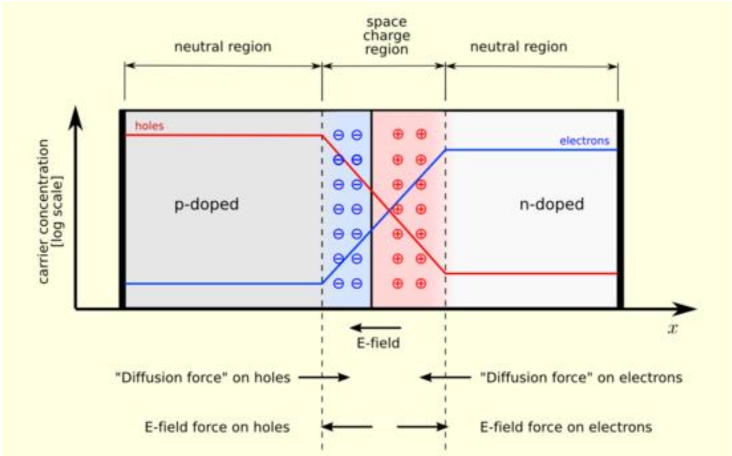
Al, Ga, In
P-type dopant for Ge

N, P
N-type dopant for C

P, As, Sb
N-type dopant for Si, Ge

13 IIIA	14 IVA	15 VA
B 5 Boron 10.81 $2p^1$	C 6 Carbon 12.011 $2p^2$	N 7 Nitrogen 14.0067 $2p^3$
Al 13 Aluminum 26.9815 $3p^1$	Si 14 Silicon 28.0855 $3p^2$	P 15 Phosphorus 30.9738 $3p^3$
Ga 31 Gallium 69.723 $4p^1$	Ge 32 Germanium 72.61 $4p^2$	As 33 Arsenic 74.92159 $4p^3$
In 49 Indium 114.82 $5p^1$		Sb 51 Antimony 121.75 $5p^3$

PN junction

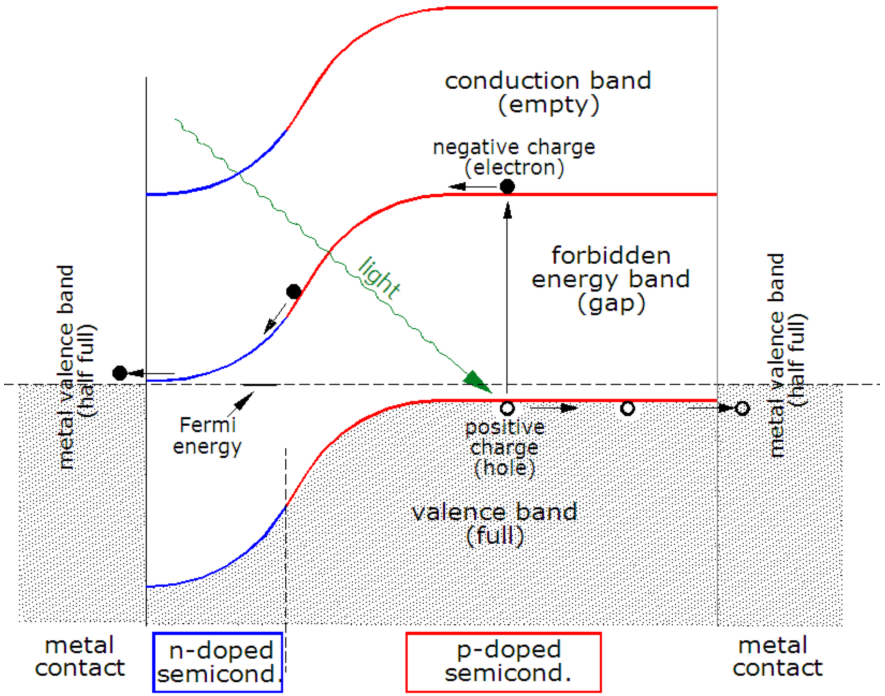


A photovoltaic cell comprises P-type and N-type semiconductors with different electrical properties, joined together.

Photovoltaic solar cell. Sunlight absorbed in the **depletion region** of the cell causes a separation of charges that generates an electrical potential, which enables current to flow through an external electrical circuit (lightbulb).

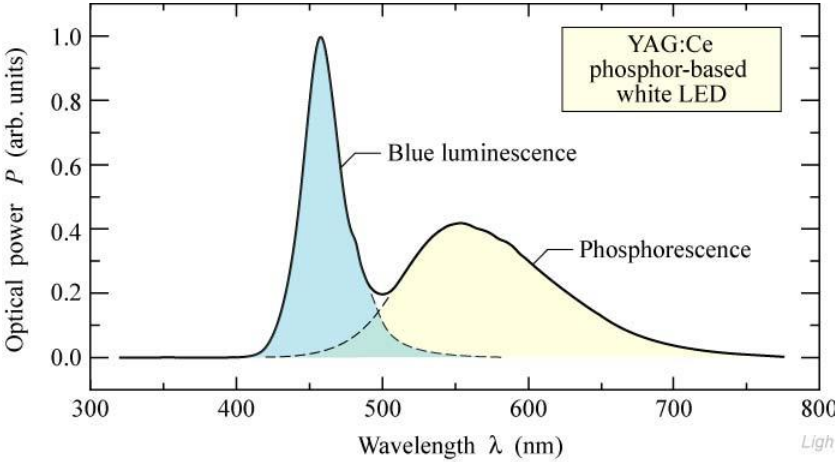
http://www.eoearth.org/view/article/161616/

PN junction (short circuit)

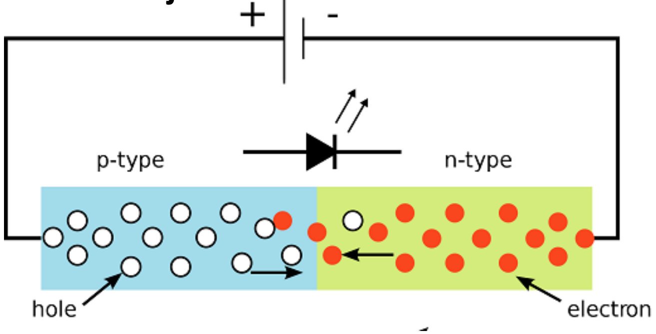


I) Then the opposite “light from current”

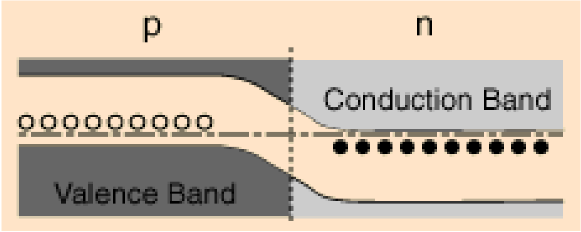
Emission spectrum of a phosphor-based LED



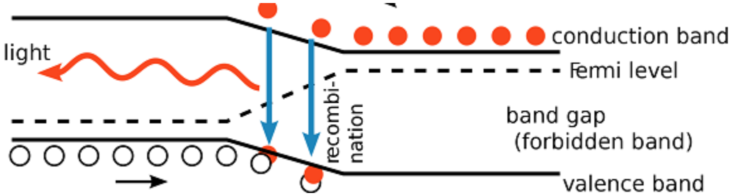
Diode PN junction



Energy bands at equilibrium

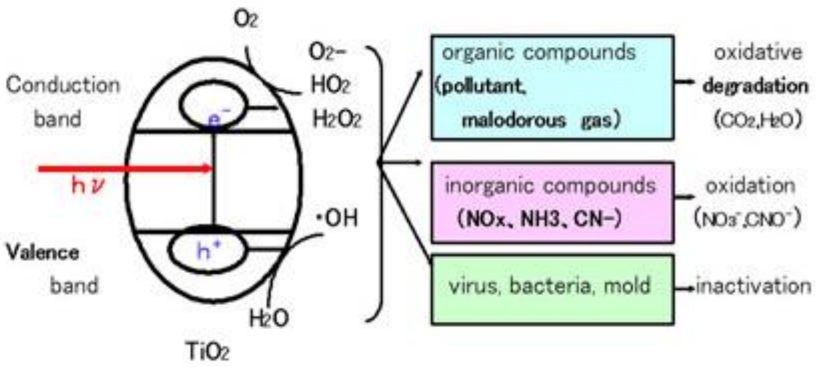


Energy bands at “work”



I) Photocatalysis with TiO_2

TiO_2 as photocatalysis (oxidation)



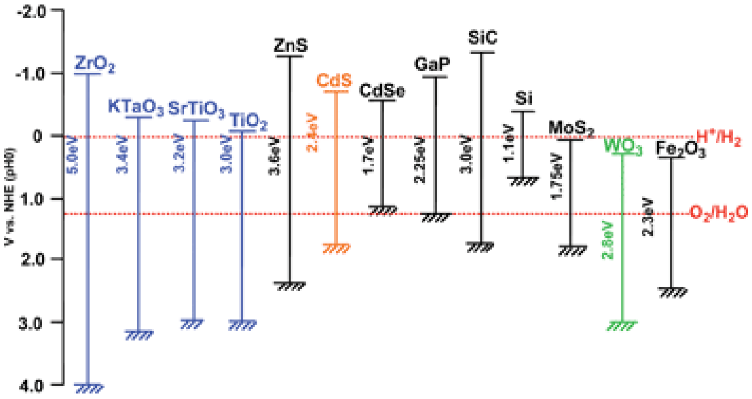
Free radicals generated from TiO_2 oxidize organic matter

$$\text{photocatalyst} \xrightarrow{\text{irradiation}} e^- + h^+$$

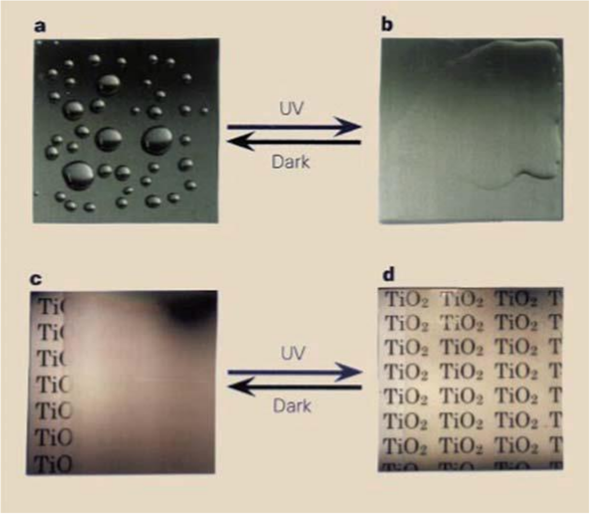
$$H_2O + h^+ \longrightarrow \bullet OH + H^+$$

$$O_2 + e^- \longrightarrow \bullet O_2^- \xrightarrow{H^+} HO_2\bullet$$

$$2HO_2\bullet \longrightarrow O_2 + H_2O_2 \xrightarrow{\bullet O_2^-} \bullet OH + OH^- + O_2$$



Superhydrophilicity of TiO_2 (anti-fooling agent)
Before and after UV irradiation (TiO2 thin film)



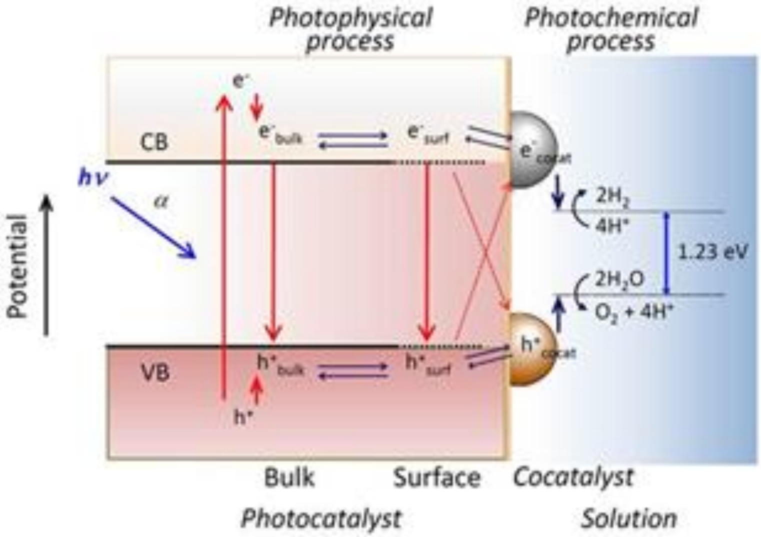
Drelich J., Soft Matter, 2011, 7, 9804

I) Photocatalytic water splitting

Water splitting by photocatalysis

Photo-generated electrons and holes

$$\mathrm{TiO_2} \xrightarrow{h\nu} e^-_{\mathrm{TiO_2}} + h^+_{\mathrm{TiO_2}}$$



For hydrogen production, the CB level should be more negative than hydrogen production level

For oxygen production the VB should be more positive than water oxidation level

Challenges:

Photocorrosion (CdS, SiC)

Recombination of photo-generated electron/hole pairs

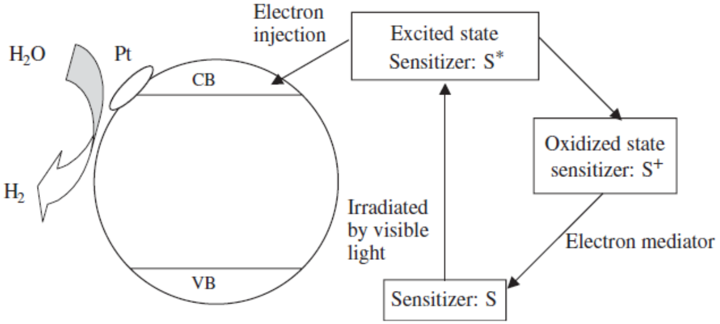
Fast backward reaction, recombination of hydrogen with water reforming water

Need UV light as TiO2 band gap is 3.2eV. Only 4% of sun light is UV

Mediation (H_2 production enhancer I^- / IO^{3-})

Adding carbonate to suppress backward reactions

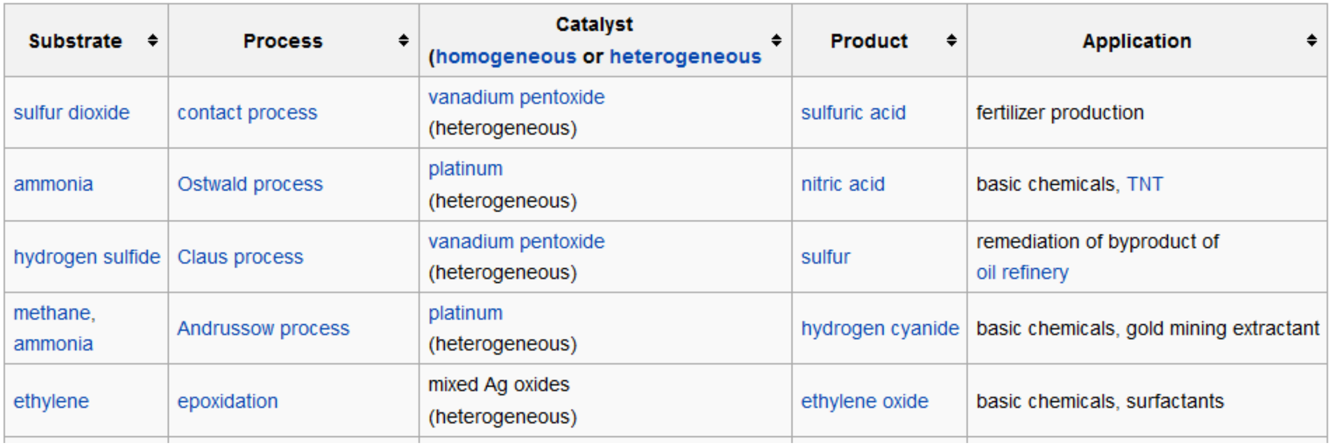
Loading with noble metals and dye sensitization



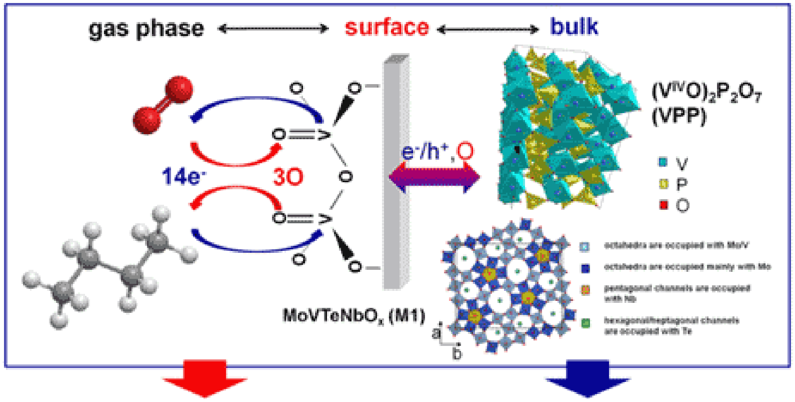
M. Ni et al. / Renewable and Sustainable Energy Reviews 11 (2007) 401–425

I) Red-Ox catalysts

Catalytic oxidation:



Substrate	Process	Catalyst (homogeneous or heterogeneous)	Product	Application
sulfur dioxide	contact process	vanadium pentoxide (heterogeneous)	sulfuric acid	fertilizer production
ammonia	Ostwald process	platinum (heterogeneous)	nitric acid	basic chemicals, TNT
hydrogen sulfide	Claus process	vanadium pentoxide (heterogeneous)	sulfur	remediation of byproduct of oil refinery
methane, ammonia	Andrussow process	platinum (heterogeneous)	hydrogen cyanide	basic chemicals, gold mining extractant
ethylene	epoxidation	mixed Ag oxides (heterogeneous)	ethylene oxide	basic chemicals, surfactants

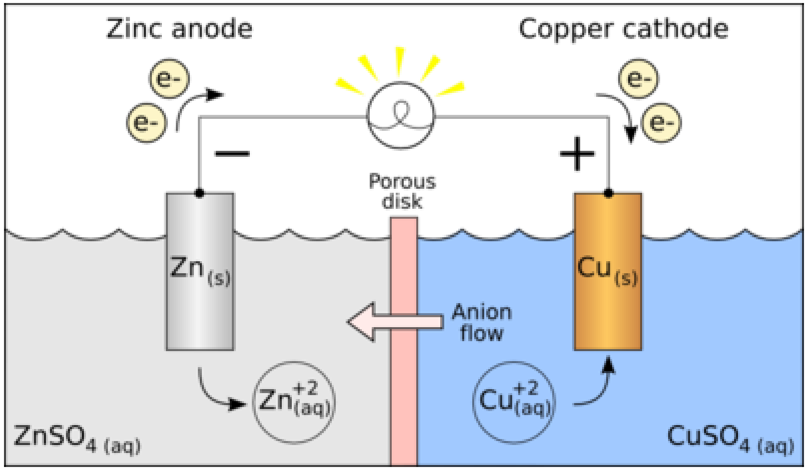


Is the catalytic reaction a localized surface event ("active site") and the bulk only an "innocent" support?

Or are bulk charge carriers participating in the reaction and is interfacial bulk-surface charge transport relevant?

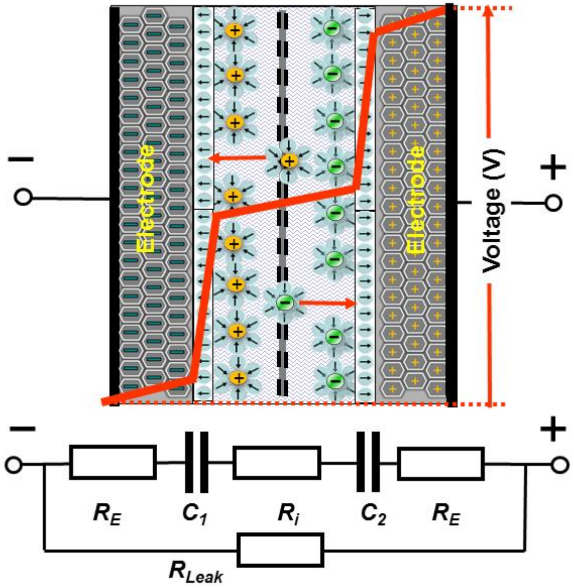
Electrochemical energy storage devices

Electrochemical cell:



Energy density: 100 Wh/Kg (bulk storage)
Low power density: 10 W/Kg (Diffusion)

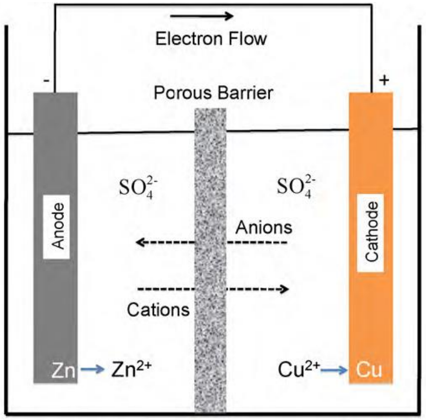
Supercapacitors:



Low energy density: 1 - 10 Wh/Kg (surface charge storage
Low power density: 1000 W/Kg

Transport and kinetics at electrode

Standard cell potential:



Half-reactions for each process

$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$ $\quad E^o_{\text{reduction of Cu2+}} = +\,0.339\ V$

$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$ $\quad E^o_{\text{reduction of Zn2+}} = -\,0.762\ V$

Overall standard potential

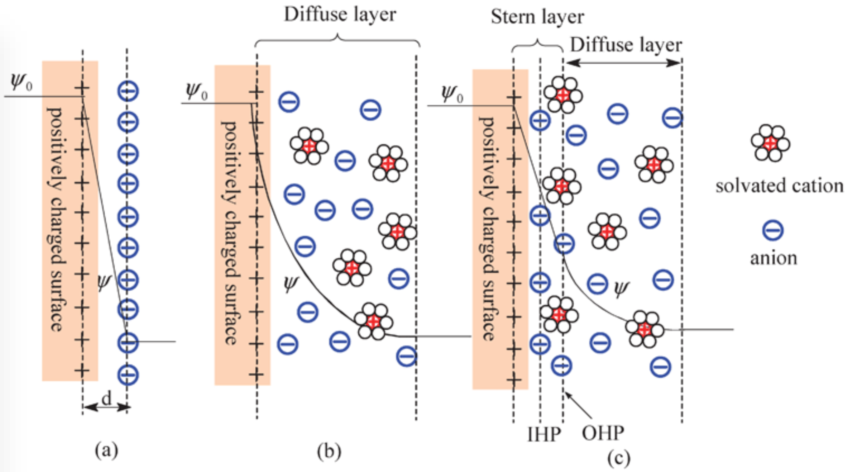
$$\mathbf{E^o_{cell} = E^o_{reduction} + E^o_{oxidation}}$$

$$E^o_{\text{oxidation of Zn}} = -\,(\,-\,0.762\ V) = +\,0.762\ V$$

Nernst relationship (Thermodynamic)

$$E = E^0 + \frac{RT}{nF}\ln\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

Electrical double layer: models



(a) the Helmholtz model
(b) the Gouy–Chapman model
(c) the Stern model

(IHP): Inner Helmholtz plane (IHP)
(OHP): Outer Helmholtz plane (OHP

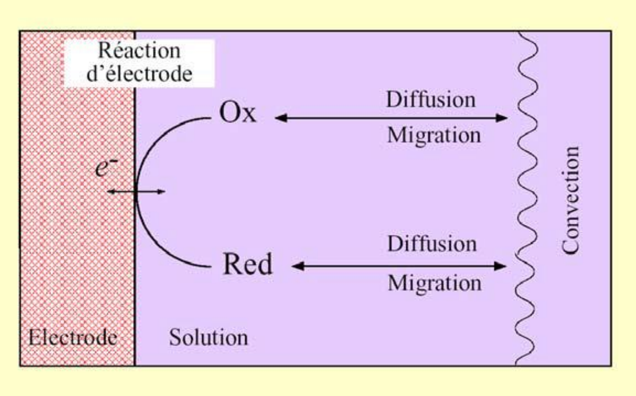
Chem. Soc. Rev. 2009, **38**, 2520-2531

Dynamics events at electrode: transport and kinetics at electrode

Steps:

1) Reactant product transport to the electrode surface
2) Electron transfer kinetics at electrode surface

From a classical macroscopic point of view, the transition state theory is use and results in the **Butler-Volmer Equation**



$$A(aq) \xrightarrow{-e^-} B(aq)$$

$$B(aq) \xrightarrow{+e^-} A(aq)$$

- Oxidation and Reduction processes are microscopically reversible.
- Net current i at interface reflects a balance between i_{ox} and i_{red}.
- Symmetry factor β determines how much of the input electrical energy fed into the system will affect the activation energy barrier for the redox process. Note 0< β < 1 and typically β = 0.5.

$$i = i_{ox} - i_{red}$$

Net rate

Symmetry factor

Normalised potential

$$i = i_0 \left\{ \exp[\beta\theta] - \exp[-(1-\beta)\theta] \right\}$$

BV equation

Exchange current

Oxidation component

Reduction component

- Exchange current provides a measure of kinetic facility of ET process.

overpotential

Thermodynamic Nernst potential

$$\theta = \frac{F\eta}{RT} = \frac{F(E - E_N)}{RT}$$

Applied potential

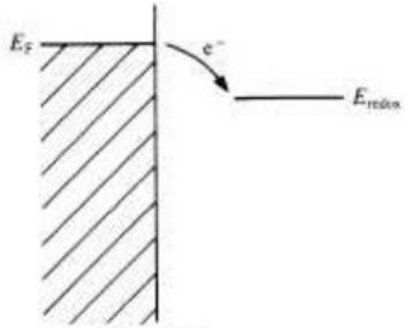
Exchange current →

$$i_0 = FAk^0 a^{\infty 1-\beta} b^{\infty \beta}$$

Standard rate constant

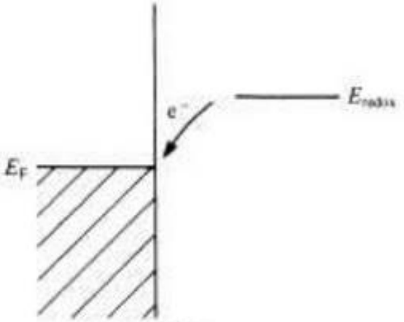
Fermi level shift due to applied potential to the electrode

By applying a potential to the electrode, we influence the highest occupied electronic level of the metal, (the fermi level, EF)



Reduction

('negative' electrode potential)

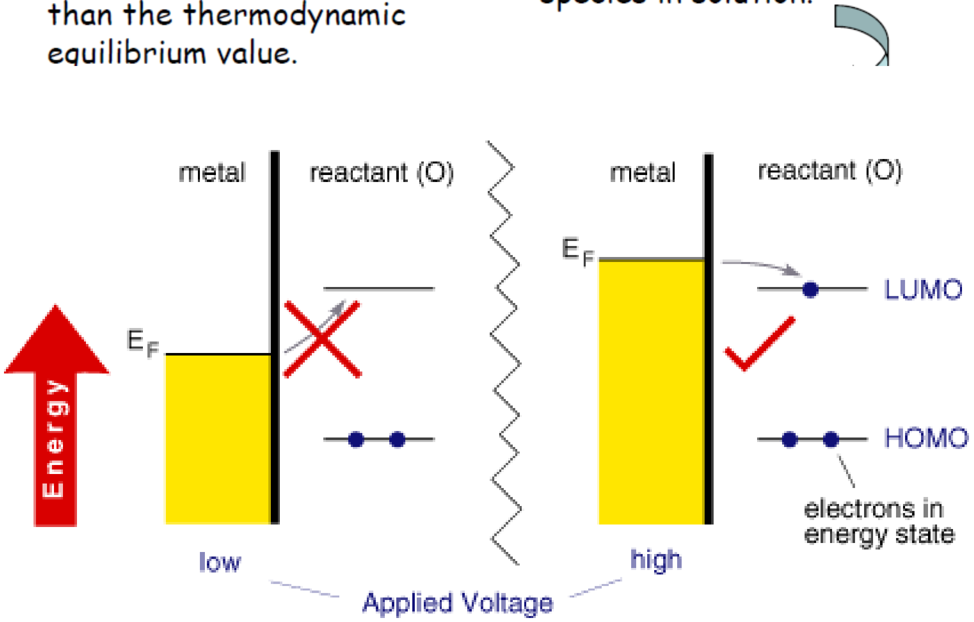


Oxidation

('positive' electrode potential)

Energy of electrons in metal ***increases*** upon application of a potential more negative than the thermodynamic equilibrium value.

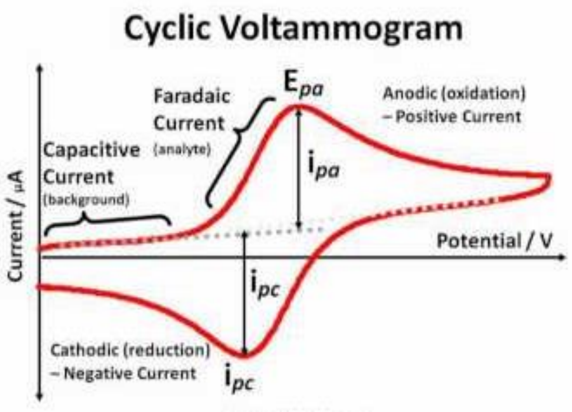
A net reduction (cathodic) current flows from metal to LUMO levels of redox active species in solution.

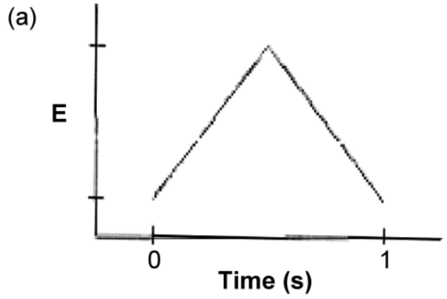


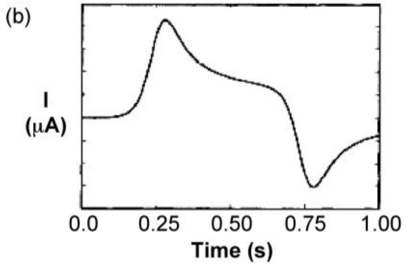
Application: Electrochemical band gap determination with cyclic voltammetry

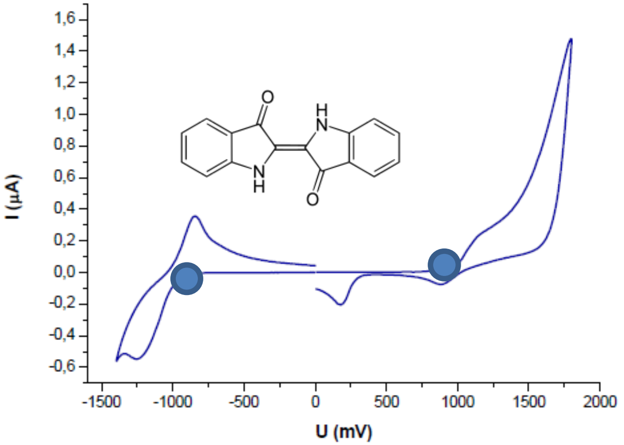
Cyclic voltammetry (CV) has been successfully employed for several decades in the quantitative estimation of the HOMO and LUMO levels of electro-active molecular species soluble in suitable solvents.

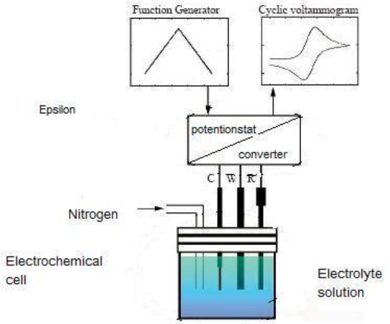
The main advantage of CV is the mild experimental conditions at which the measurements are performed, compared to techniques such as photoelectron and tunneling spectroscopy.

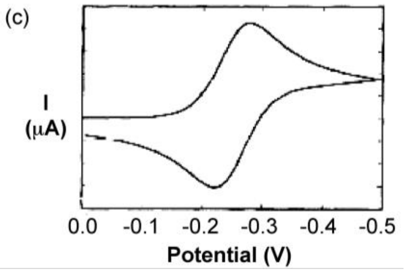












$$E\,(\mathrm{HOMO}) = -e\,[E_{ox}^{\,onset} + 4.4]$$

$$E\,(\mathrm{LUMO}) = -e\,[E_{red}^{\,onset} + 4.4]$$

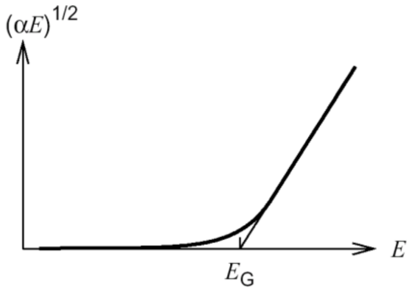
Estimated band gap ca. 1.7eV

Leonat L., U.P.B. Sci. Bull., Series B, Vol. 75, Iss. 3, 2013

Application: and comparison with optical band gap "Tauc plot"

The absorption coefficient, α, due to interband transition near the band-gap is well described: $\alpha\hbar\omega = B\,(\hbar\,\omega - E_g)^2$

$\hbar\omega$ is photon energy, E_g is optical gap. This Tauc plot defines the optical gap in amorphous semiconductors.



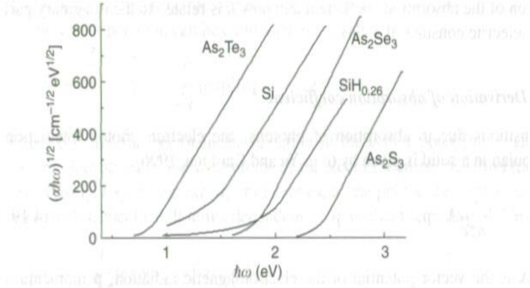
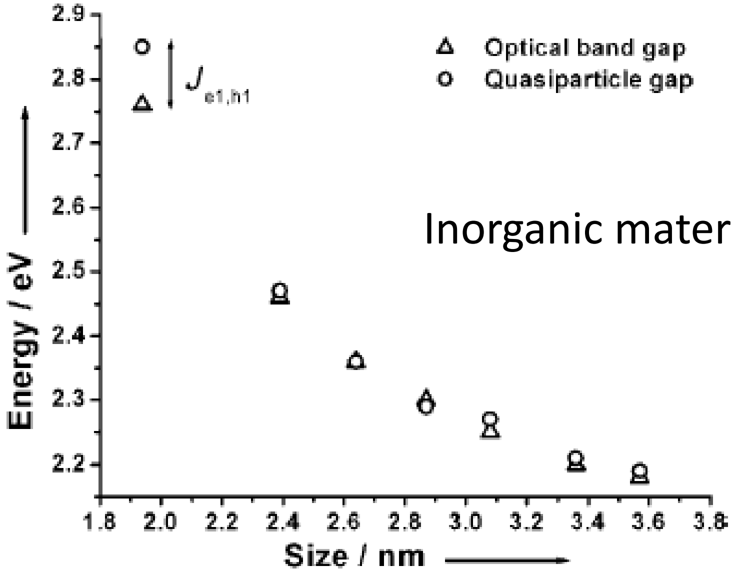


Figure 4.5 Tauc plots for different a-semiconductors (Morigaki, 1999).

Comparison of optical and electrochemical band gap for qdots



Inorganic materials

Organic materials

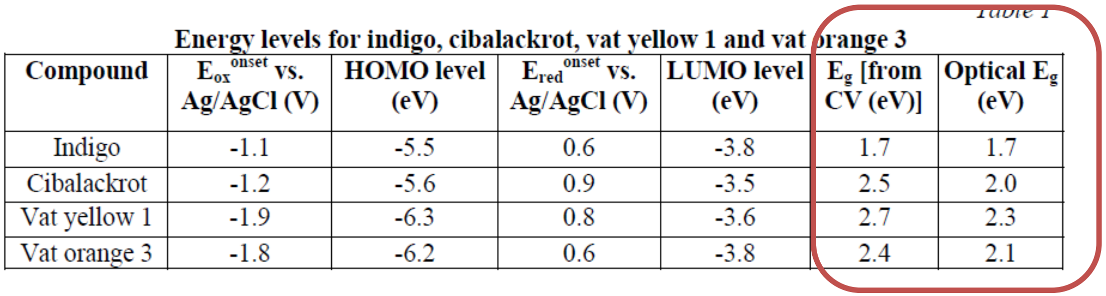


Table 1

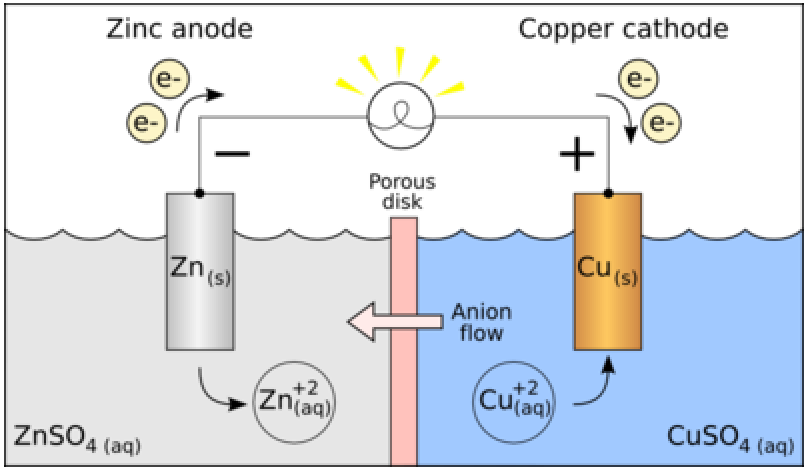
Energy levels for indigo, cibalackrot, vat yellow 1 and vat orange 3

Compound	E_{ox}^{onset} vs. Ag/AgCl (V)	HOMO level (eV)	E_{red}^{onset} vs. Ag/AgCl (V)	LUMO level (eV)	E_g [from CV (eV)]	Optical E_g (eV)
Indigo	-1.1	-5.5	0.6	-3.8	1.7	1.7
Cibalackrot	-1.2	-5.6	0.9	-3.5	2.5	2.0
Vat yellow 1	-1.9	-6.3	0.8	-3.6	2.7	2.3
Vat orange 3	-1.8	-6.2	0.6	-3.8	2.4	2.1

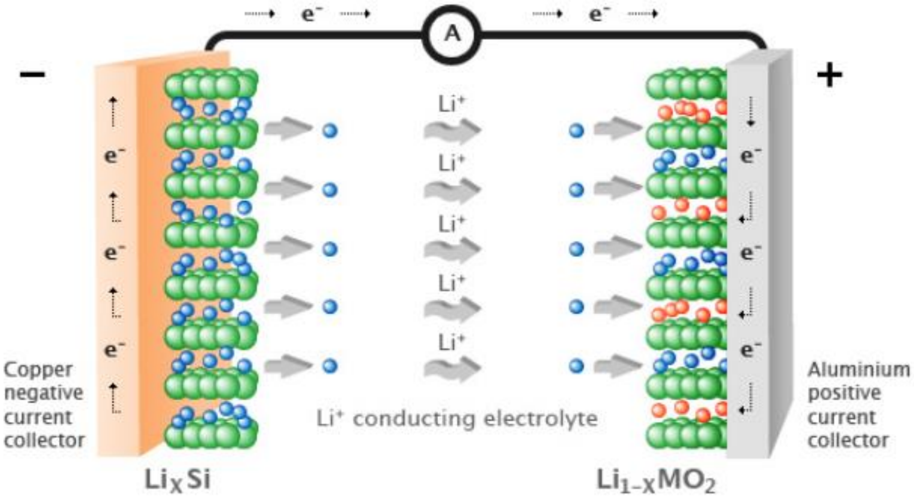
ChemPhysChem 2008, 9, 2574 – 2579 J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi, 15 627 (1966).

Charge transport in modern electrochemical devices

Galvanic cell



Si based lithium ion battery (LIB)

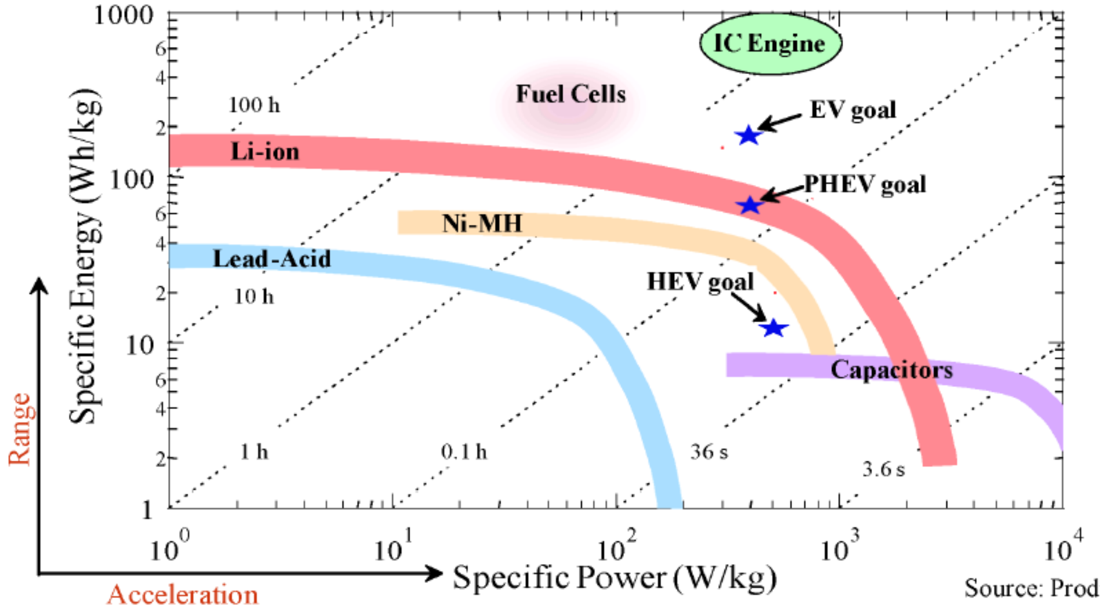


The Ragone plot

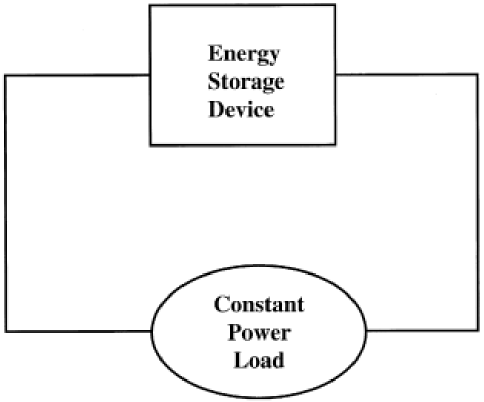
“specific energy”:
[in watthours per kilogram (Wh/kg)] and “energy density” [in watt-hours per liter (Wh/L)] are used to compare the energy contents of a system

“specific power” (in W/kg) and“power density” (in W/L) are expressing a rate capability.

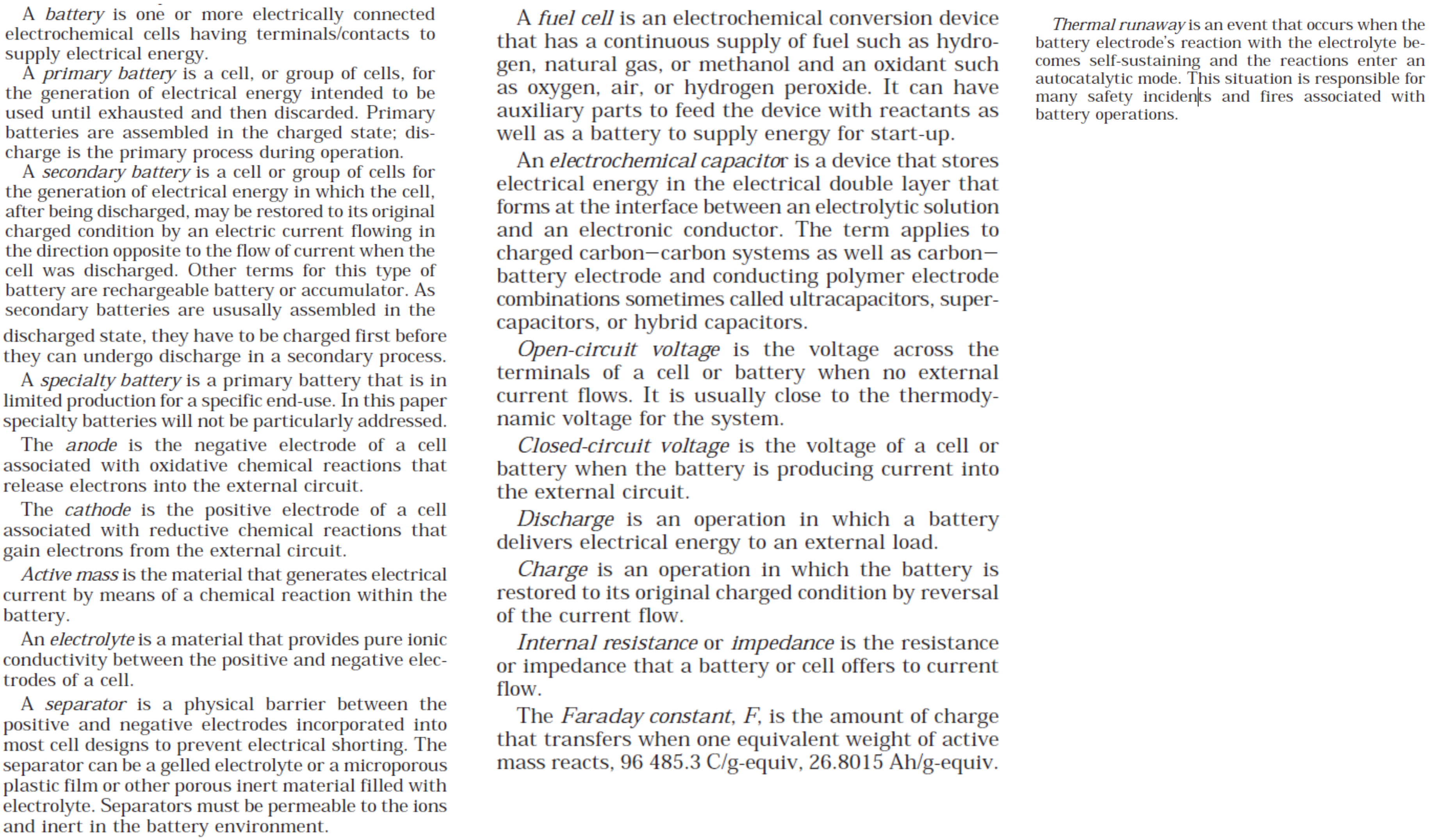
The attributes “gravimetric” (per kilogram) and “volumetric” (per liter):
are used To compare the power and energy capabilities, a representation known as the Ragone plot or diagram has been developed.



Source: Product data sheets



And a bit more of some “useful” definitions



A *battery* is one or more electrically connected electrochemical cells having terminals/contacts to supply electrical energy.

A *primary battery* is a cell, or group of cells, for the generation of electrical energy intended to be used until exhausted and then discarded. Primary batteries are assembled in the charged state; discharge is the primary process during operation.

A *secondary battery* is a cell or group of cells for the generation of electrical energy in which the cell, after being discharged, may be restored to its original charged condition by an electric current flowing in the direction opposite to the flow of current when the cell was discharged. Other terms for this type of battery are rechargeable battery or accumulator. As secondary batteries are ususally assembled in the discharged state, they have to be charged first before they can undergo discharge in a secondary process.

A *specialty battery* is a primary battery that is in limited production for a specific end-use. In this paper specialty batteries will not be particularly addressed.

The *anode* is the negative electrode of a cell associated with oxidative chemical reactions that release electrons into the external circuit.

The *cathode* is the positive electrode of a cell associated with reductive chemical reactions that gain electrons from the external circuit.

Active mass is the material that generates electrical current by means of a chemical reaction within the battery.

An *electrolyte* is a material that provides pure ionic conductivity between the positive and negative electrodes of a cell.

A *separator* is a physical barrier between the positive and negative electrodes incorporated into most cell designs to prevent electrical shorting. The separator can be a gelled electrolyte or a microporous plastic film or other porous inert material filled with electrolyte. Separators must be permeable to the ions and inert in the battery environment.

A *fuel cell* is an electrochemical conversion device that has a continuous supply of fuel such as hydrogen, natural gas, or methanol and an oxidant such as oxygen, air, or hydrogen peroxide. It can have auxiliary parts to feed the device with reactants as well as a battery to supply energy for start-up.

An *electrochemical capacitor* is a device that stores electrical energy in the electrical double layer that forms at the interface between an electrolytic solution and an electronic conductor. The term applies to charged carbon−carbon systems as well as carbon−battery electrode and conducting polymer electrode combinations sometimes called ultracapacitors, supercapacitors, or hybrid capacitors.

Open-circuit voltage is the voltage across the terminals of a cell or battery when no external current flows. It is usually close to the thermodynamic voltage for the system.

Closed-circuit voltage is the voltage of a cell or battery when the battery is producing current into the external circuit.

Discharge is an operation in which a battery delivers electrical energy to an external load.

Charge is an operation in which the battery is restored to its original charged condition by reversal of the current flow.

Internal resistance or *impedance* is the resistance or impedance that a battery or cell offers to current flow.

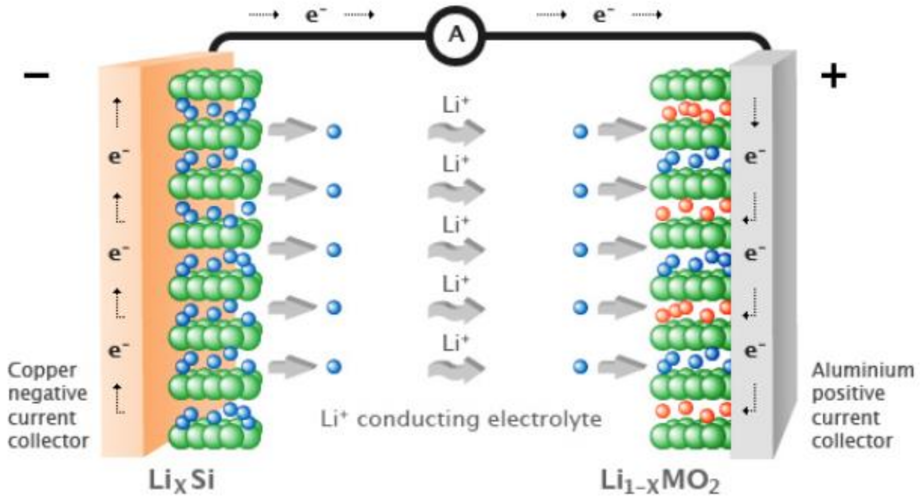
The *Faraday constant, F*, is the amount of charge that transfers when one equivalent weight of active mass reacts, 96 485.3 C/g-equiv, 26.8015 Ah/g-equiv.

Thermal runaway is an event that occurs when the battery electrode’s reaction with the electrolyte becomes self-sustaining and the reactions enter an autocatalytic mode. This situation is responsible for many safety incidents and fires associated with battery operations.

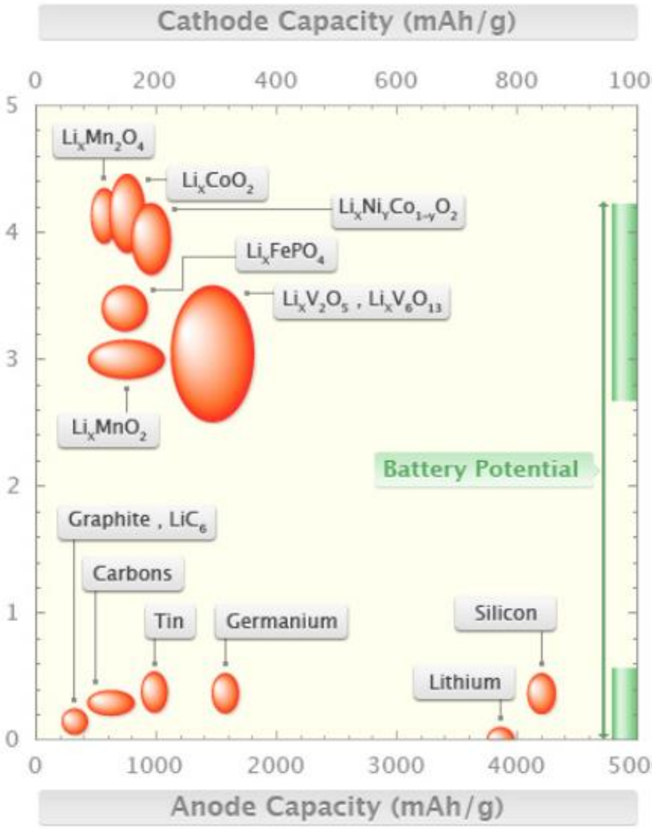
Winter M., Chem. Rev. 2004, 104, 4245 - 4269

Charge transport in modern systems systems

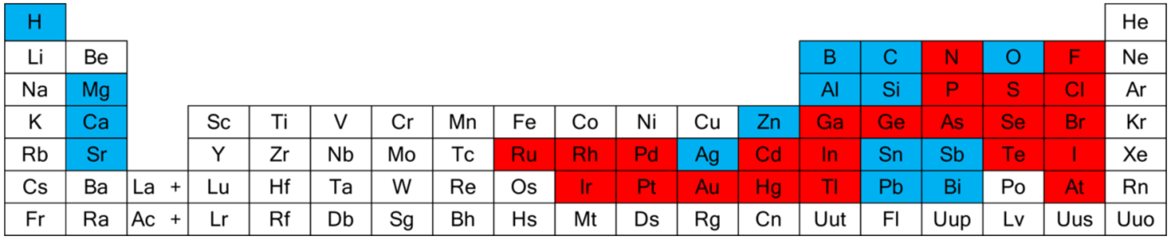
Si based lithium ion battery (LIB)



Capacity of Anode and Cathode materials



Known active elements for Li storage



H																		He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La +	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac +	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Li$^+$-solvation and Ion transport in electrolyte

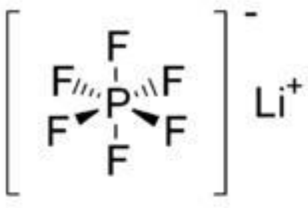
Ideal solvent:

High electrical permittivity -> to dissolve the salt
Low viscosity –> to facilitate ion transport
Stable at the anode and cathode interface

-> So far this compound is unknown

Salt:

$LiPF_6$



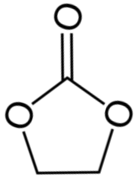
As compromise a mixture of components are used:

Salt: $LiPF_6$

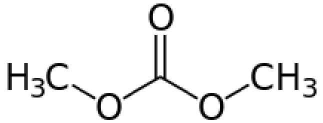
As solvent:
- High dielectric permittivity: Etylene carbonate (EC)
- Low viscosity: Various acyclic carbonate and carboxylic esters.
- such as : Dimethyl carbonate (DMC), Diethyl carbonate (DEC)

Solvent:

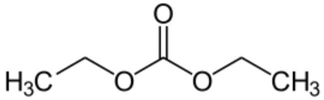
EC



DMC



DEC



Today state of the art electrolytes typically have:
- An ionique conductivity: 5 – 10 mS/cm
- Routine cell operation: -30 to 60°C

-> Solvents are not thermodynamically stable within the battery working voltage (0 to 5V vs. Li$^+$).

-> Solvent typically “polymerize” on the electrode surface forming a passivation layer (SEI).

Portfolio of solvents and lithium salts

Desired properties:

Electrolyte solvent must be polar to dissociate the salt

Good ionic conductivity

Electrically insulating

Electrochemically inert (0 to 5V)

-> these constrains limits to a “small” family of aprotic organic compounds

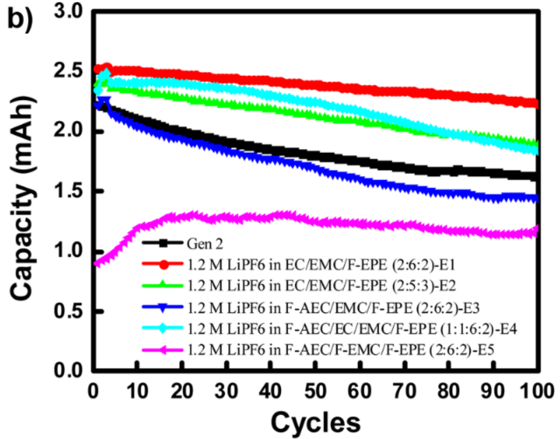
Fine tuning of solvent properties is often performed by fluorination:

Adding Fluor will results in a drop of the energy level of the HOMO and LUMO.

-> better resistance to oxidation

-> “poorer” resistance to reduction

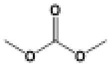
The SEI is formed at higher voltage (1.5V vs Li$^+$) forming a “better” passivation layer thus improving the overall cycling behavior.

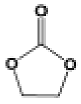


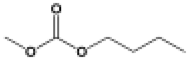
Effect of fluorinated carbonates and ethers

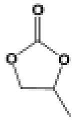
Note the significant influence of the solvent nature on the cycling behavior.

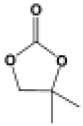
-> Highlights of the strong relevance of interfacial processes in LIB

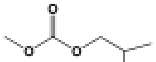

DMC (reference)

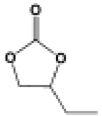

EC

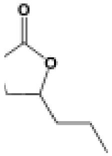

n-BMC

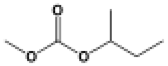

PC

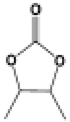

i-BC

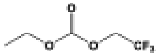

i-BMC

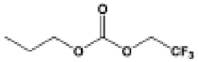

BC

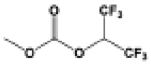

PIC

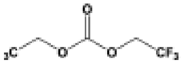

s-BMC

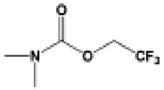

2,3-BC

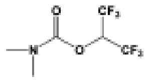

ethyl-2,2,2-trifluoroethyl carbonate (ETFEC)


propyl-2,2,2-trifluoroethyl carbonate (PTFEC)


methyl-2,2,2,2',2',2'-hexafluoro-*i*-propyl carbonate (MHFPC)


li-2,2,2-trifluoroethyl carbonate (DTFEC)


2,2,2-trifluoroethyl-*N,N*-dimethyl carbamate (TFECm)


hexafluoro-*i*-propyl-*N,N*-dimethyl carbamate (HFPCm)

Solvents and lithium salts

Fluorinated Esters:

Reversible capacity in presence of fluorinated esters is not affected.
Coulombic efficiency of the first cycle is generally improved

-> this improvement is related to the interfacial chemistry suggesting their participation in the SEI formation.

Esters of carboxylic acid:

Do not form an SEI
Offer a wider temperature range
Improves the solubility of certain Li salts
Faster interfacial kinetics (Interfacial impedance reduced)

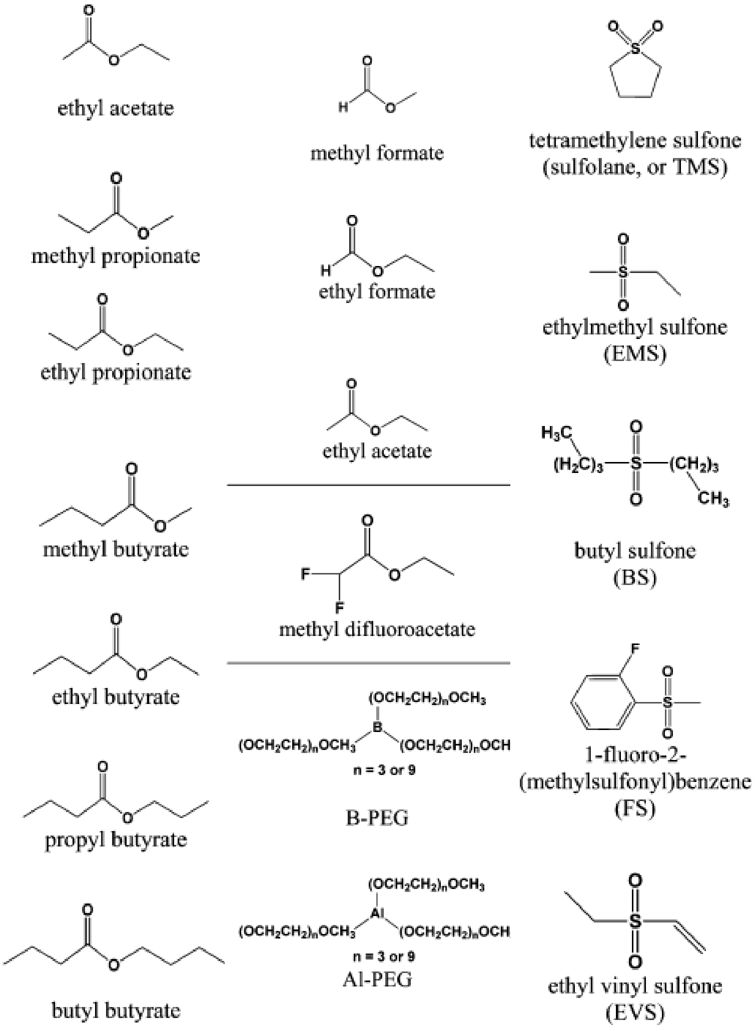
Sulfones and sulfoxides:

Improves the electrochemical stability at high voltage but viscous

Nitirile: acetonitrile

Phosporus-based solvent

Ethers



Example of solvents

Solvents and lithium salts

Standard Li-salt: $LiPF_6$

It’s dominance will not change soon.

$LiPF_6$ was the “best” compromise when evaluated against LIB applications.

$LiPF_6$ is far from “perfect”.

-> $LiPF_6$ is chemically and thermally instable

Alternative salts attempt to replace the labile P-F bound with more stable linkage, such as alkyls, aryls or oxo-chelate.

Oxalate-chelate (TFOP)

Oxalate based anion reduced at 1.7V vs Li^+, pre-forming an SEI, as a consequence better capacity retention were reported.

Ex-situ XPS reported a large amount of oxalate in the SEI and much smaller amount of LiF.

Borate or Boron-based cluster

The most famous is $LiBF_4$.

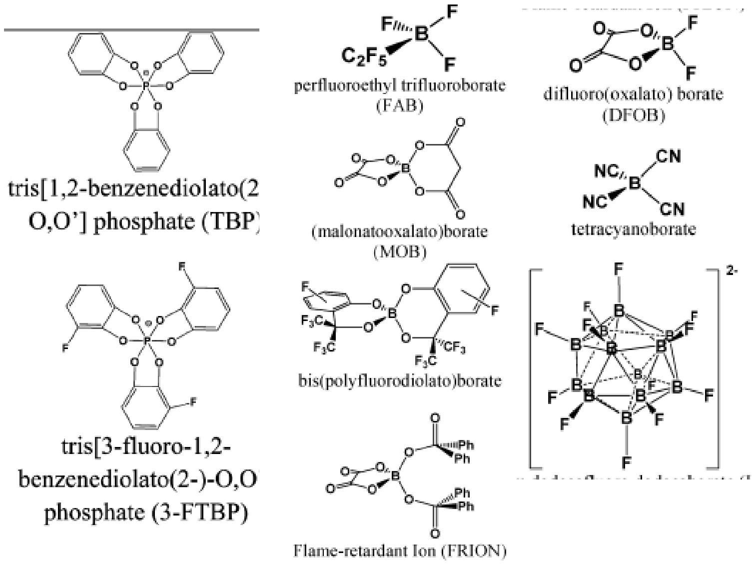
Poor ionic conductivity and solubility

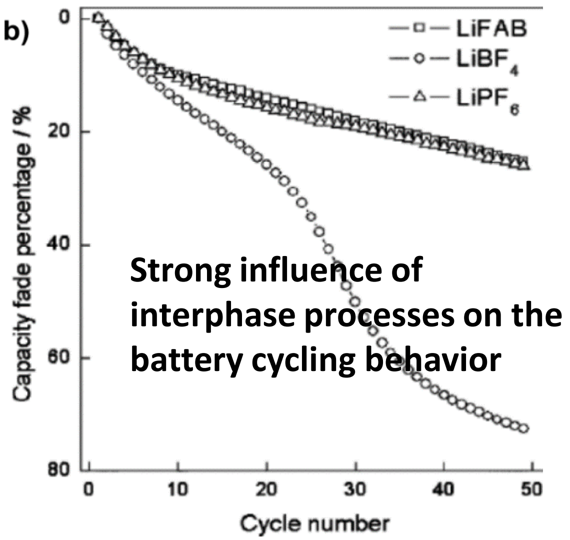
Hybrid between boron-based and oxalate-chelate salt

Currently these are maybe the most promising salt,

Such as the LiDFOB (difluoro(oxalato)borate)

Other salts: Heterocyclic anions, Aluminates, and more





Strong influence of interphase processes on the battery cycling behavior

Capacity fading using various Li-salts

Ionic conduction

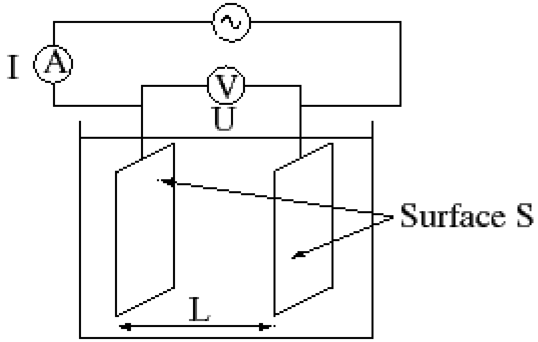
Basics:

Electrolyte: A substance that conducts electricity through the movement of ions

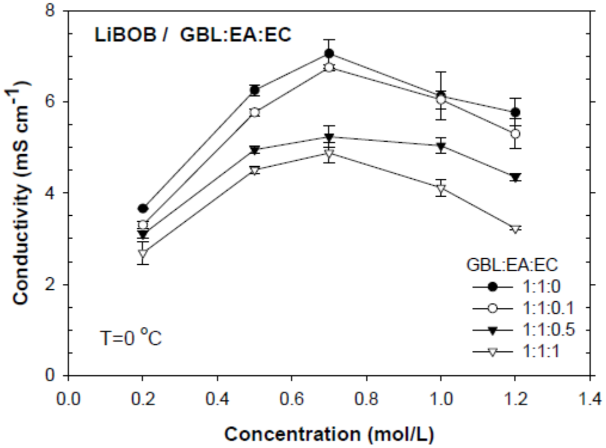
Metals:
Conductivity range: 10 to 10^5 S/cm
Charge carrier: electron
Conduction increase with temperature

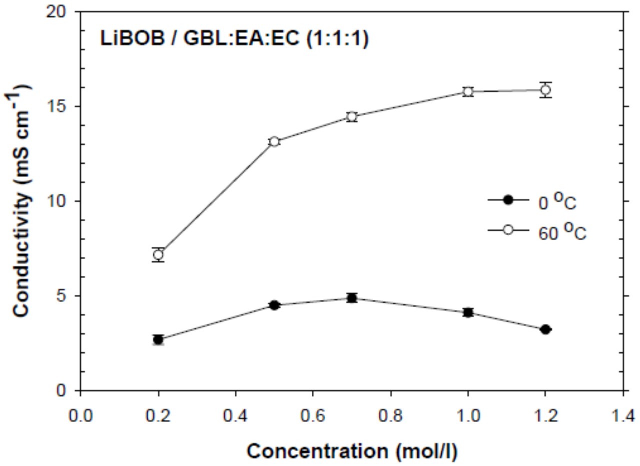
Solid electrolyte
- Conductivity range 10^{-3} to 10 S/cm
- Ions carry the current
- Conductivity decreases with temperature (activated transport)

Measurement principle of electrolyte conductance



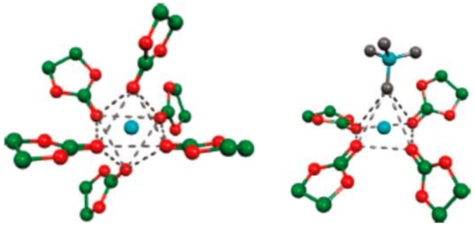
Liquid electrolyte conductivity

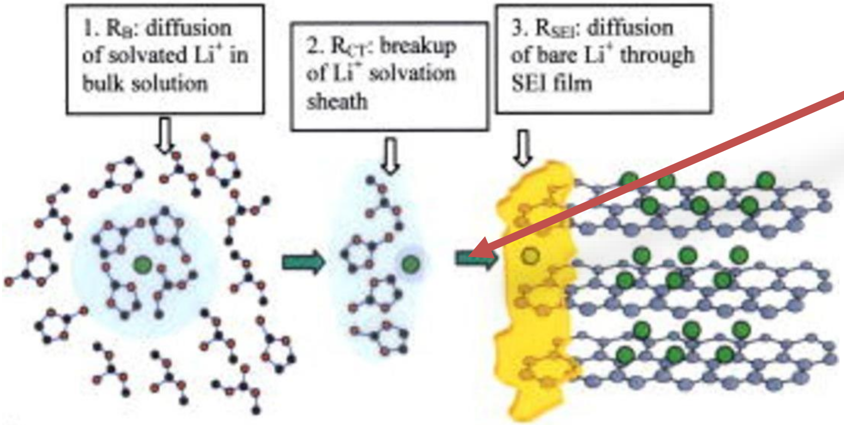




“Charge-Transfer” Process at Graphite/Electrolyte Interface

Li-salt dissolves through ion-solvent interaction



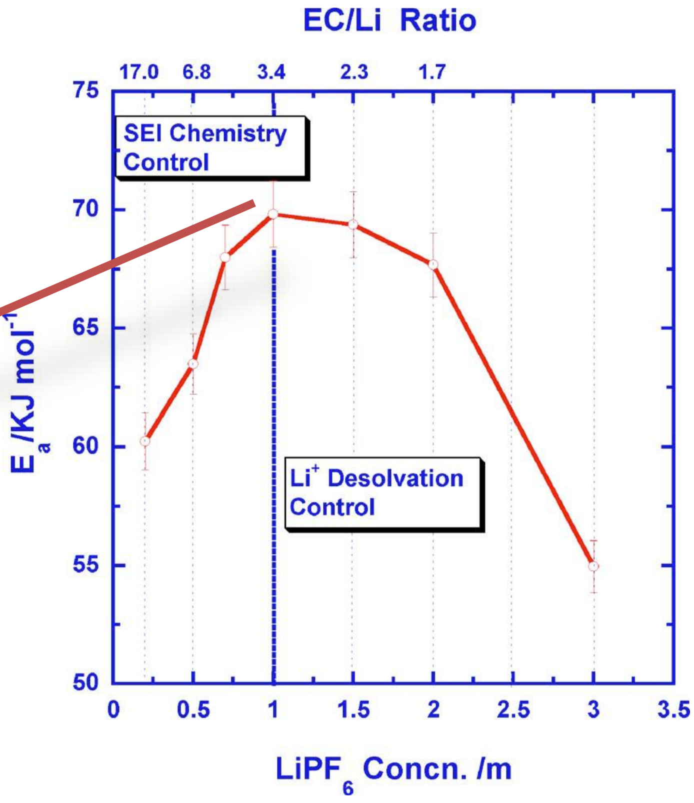


1. R_B: diffusion of solvated Li^+ in bulk solution

2. R_{CT}: breakup of Li^+ solvation sheath

3. R_{SEI}: diffusion of bare Li^+ through SEI film

Charge-transfer activation energies on the [Li-ion]

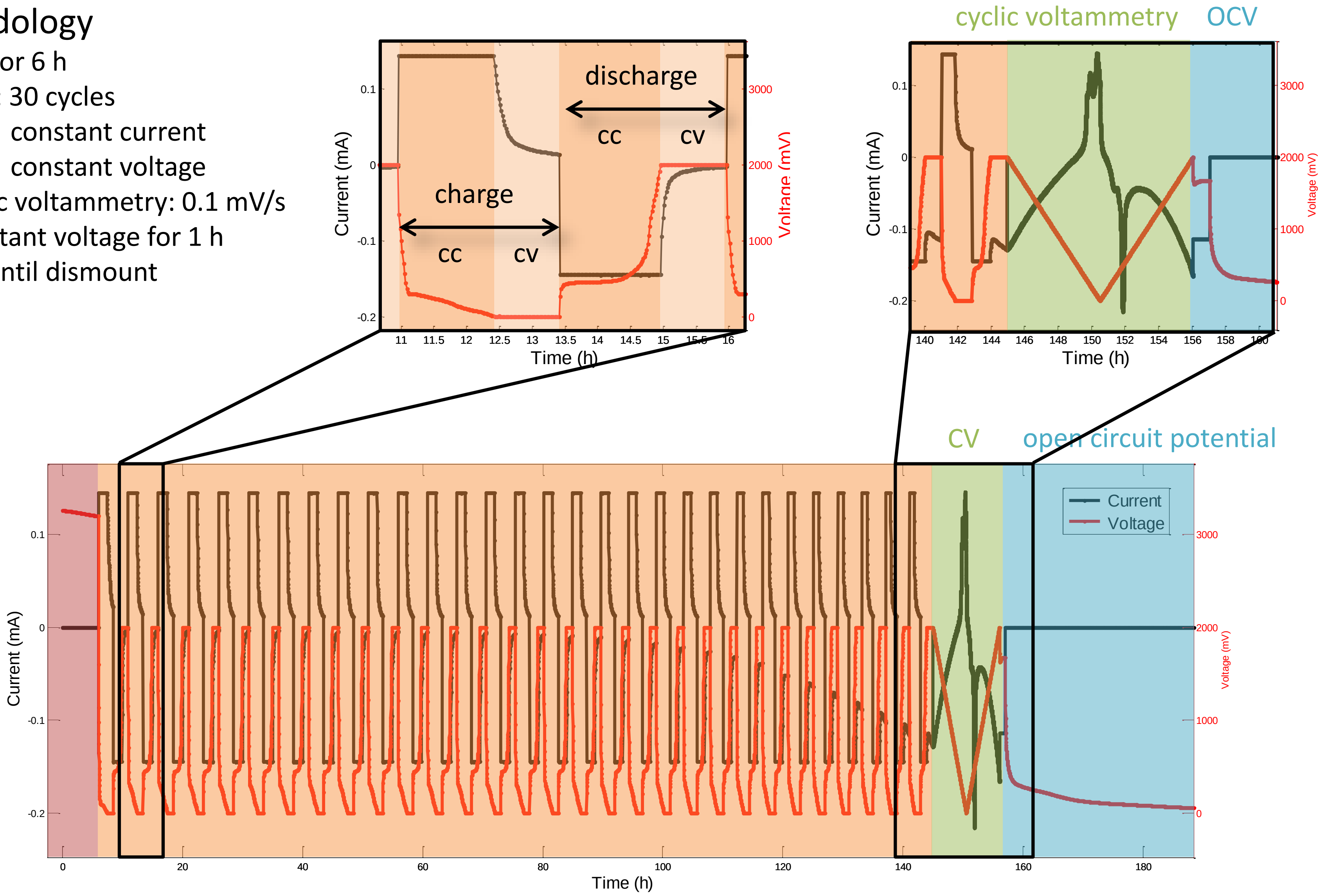


Journal of The Electrochemical Society, **154** 3 A162-A167 2007

A typical battery “cycling” evaluation

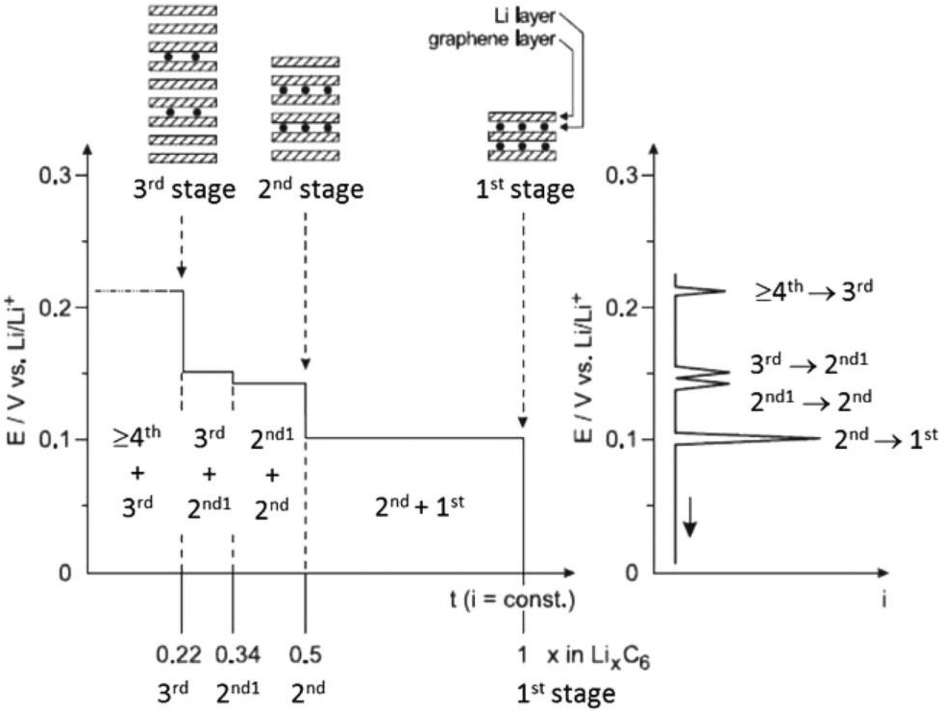
Methodology

1. V_{OC} for 6 h
2. cccv: 30 cycles
   - constant current
   - constant voltage
3. cyclic voltammetry: 0.1 mV/s
4. constant voltage for 1 h
5. V_{oc} until dismount



Stage intercalation of lithium

Stage intercalation of Li



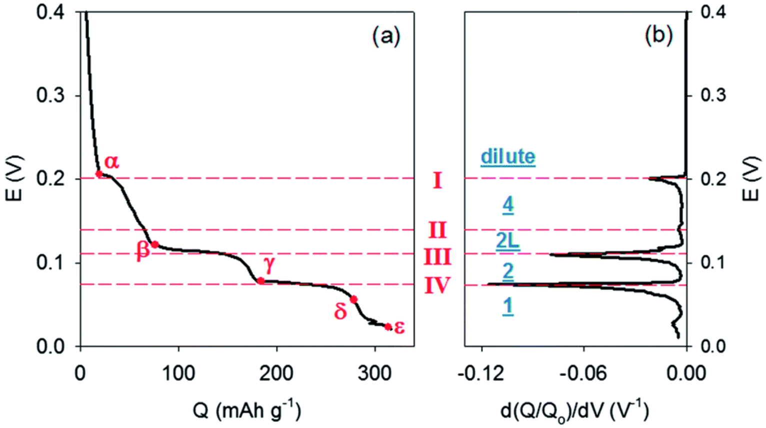
LiC_{72} (dilute stage) $\leftrightarrows$ LiC_{36} (stage 4) (I)

LiC_{36} (stage 4) $\leftrightarrows$ LiC_{27} (stage 3) $\leftrightarrows$ LiC_{18} (stage 2L) (II)

LiC_{18} (stage 2L) $\leftrightarrows$ LiC_{12} (stage 2) (III)

LiC_{12} (stage 2) $\leftrightarrows$ LiC_6 (stage 1) (IV)

Chronopotentiostatic measuremnt



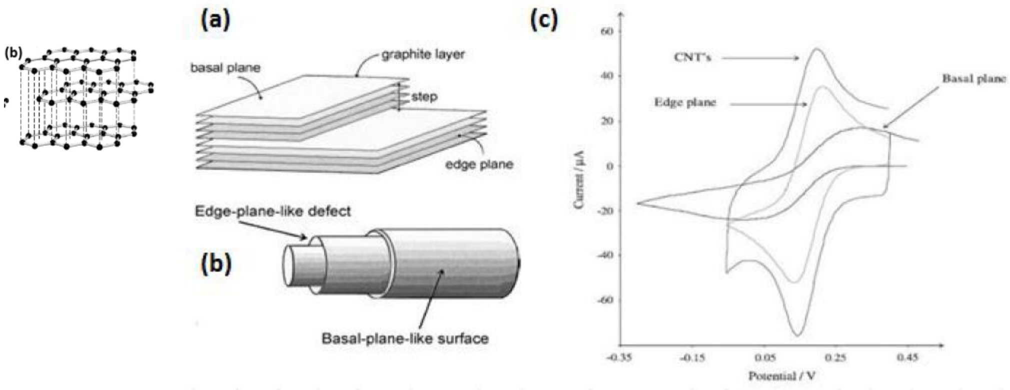
a) Chronopotentiometric profile of lithiation of natural graphite

b) Differential capacity with respect to potential

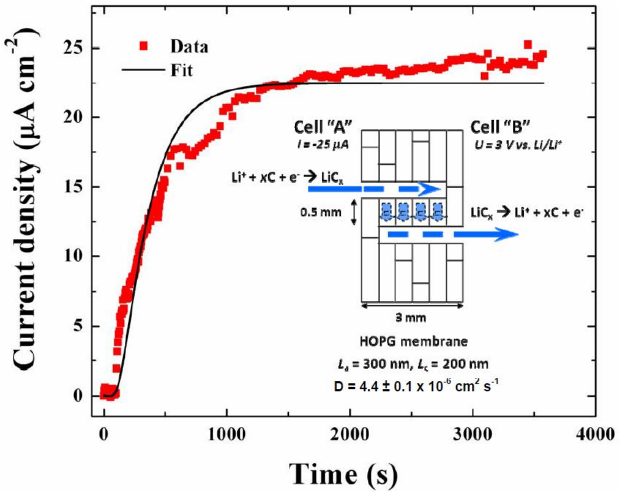
RSC Adv., 2014, 4, 16545

Lithium diffusion in graphite anisotropy (edge/basal plan)

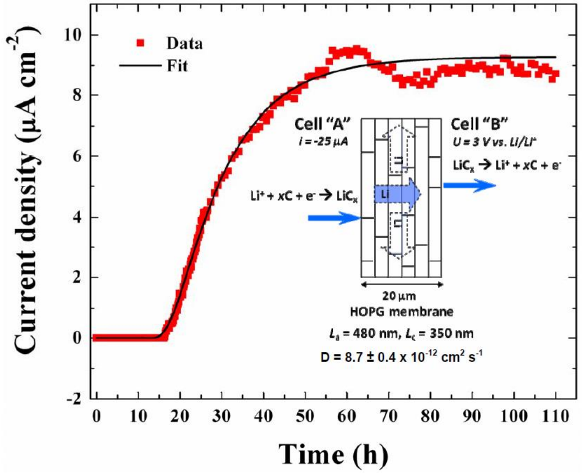
The current corresponds to the de-intercalative flux of lithium-ions from the HOPG membrane into the electrolyte



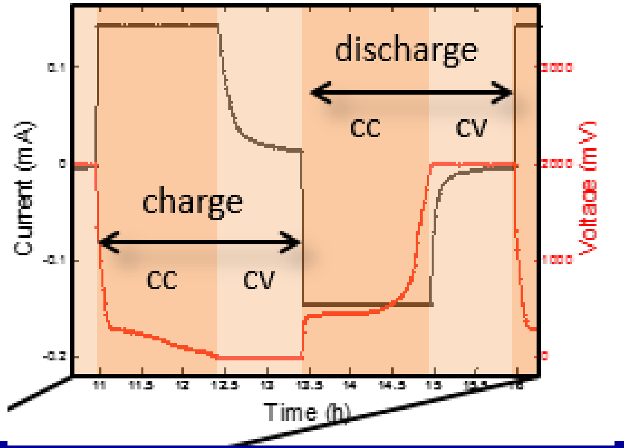
Edge-plane configuration



Basal-plan configuration



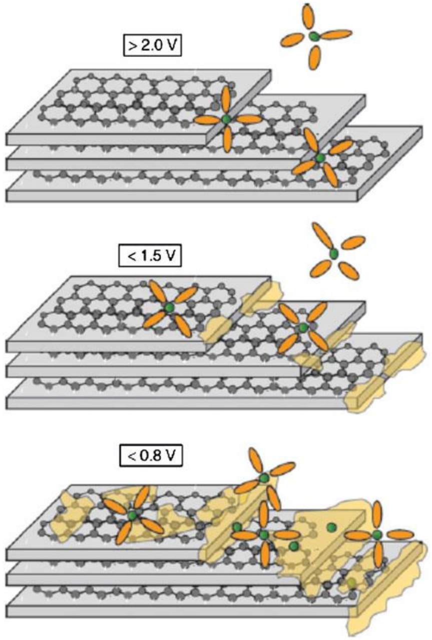
CCCV or GCPL cycling methods over CC only

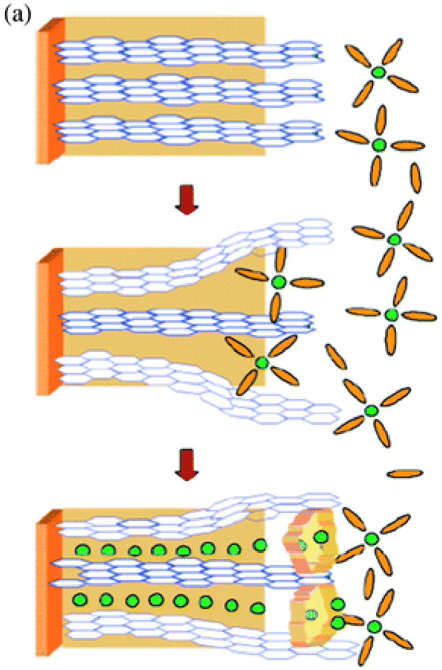


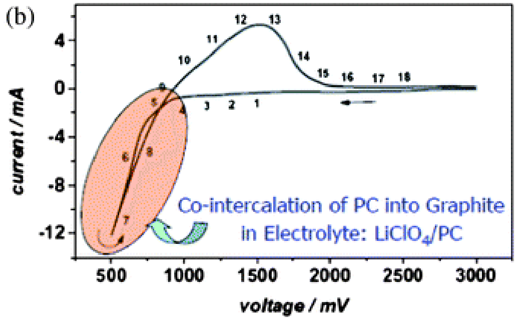
Nanotechnology and Nanomaterials » "Advances in Graphene Science“, DOI: 10.5772/55728

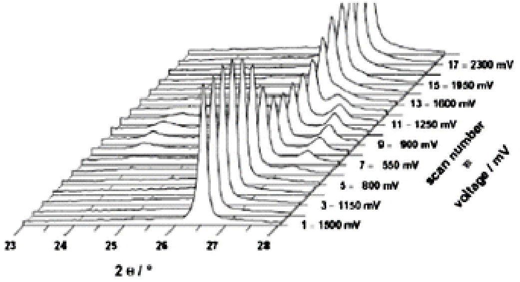
Solvent CO-intercalation in graphite to form “stable” SEIs

EC / PC cycling difference







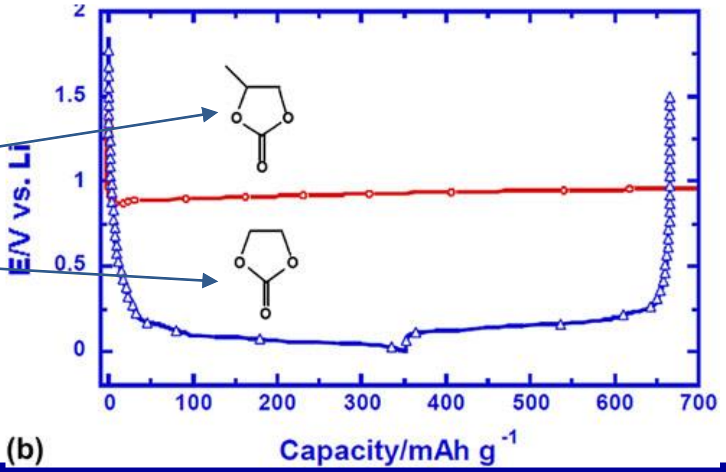


SEI formation from the co-intercalated species

Direct consequence

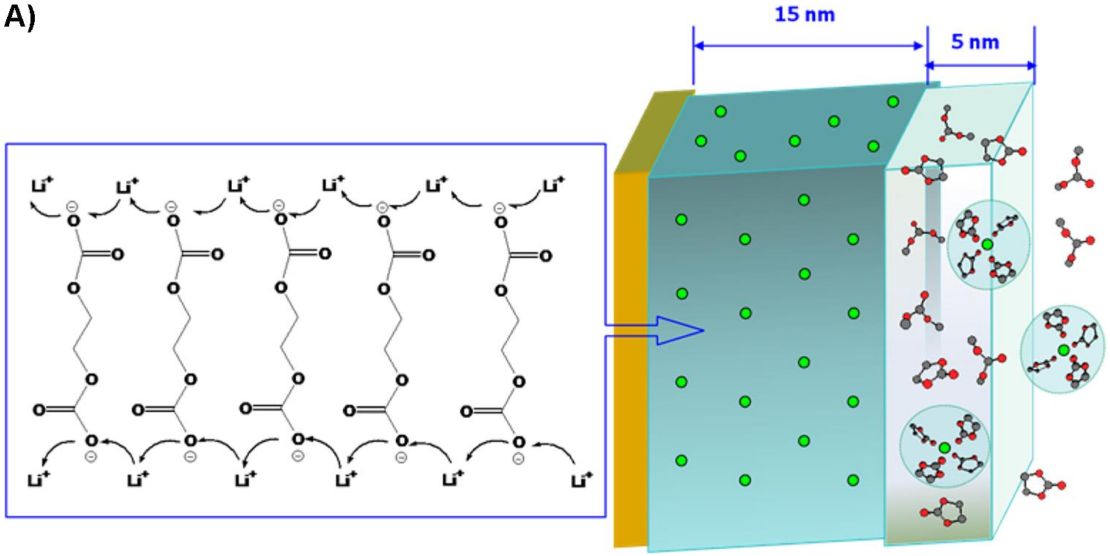
PC: Do not co-intercalate

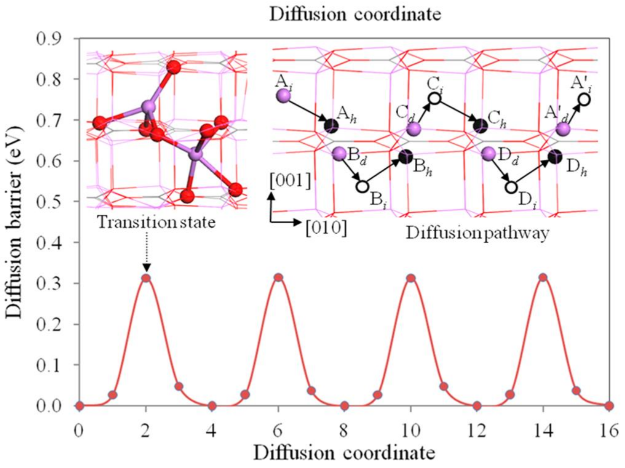
EC: Co-intercalate



Phys. Chem. Chem. Phys., 2014, 16, 13229-13238 / *J. Electrochem. Soc. 2003 volume 150, issue 12, A1628-A1636* / J. Mater. Res., Vol. 27, No. 18, Sep 28, 2012

Li-ion migration through the SEI





The SEI allows Li-ion migration.

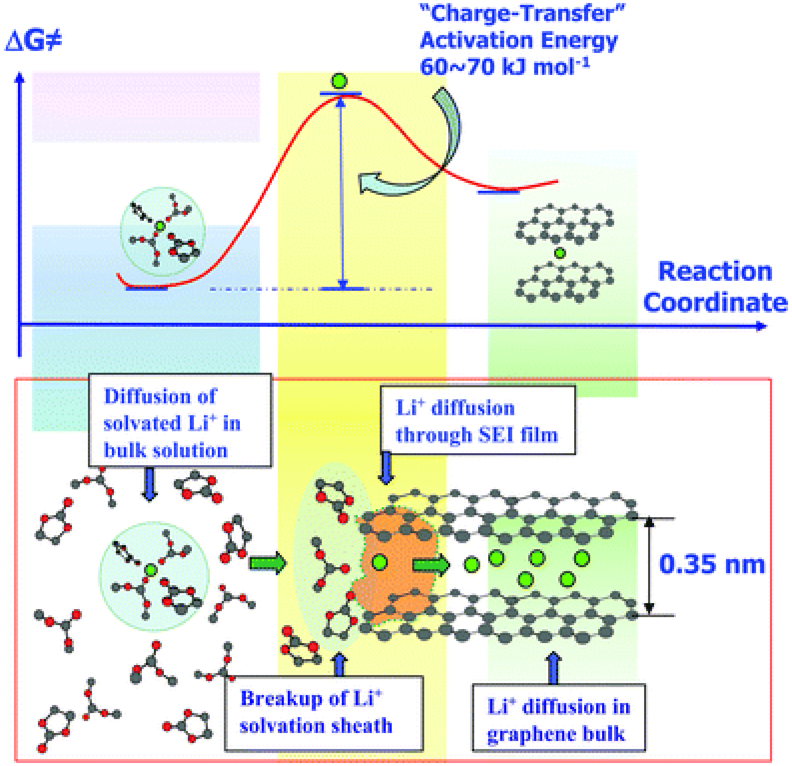
Electronic insulating / Ionic conductor

Studies using Li isotope substitution suggested that the SEI function like a “cation-echanger” via a “Grotthus-like” conducting mechanism.

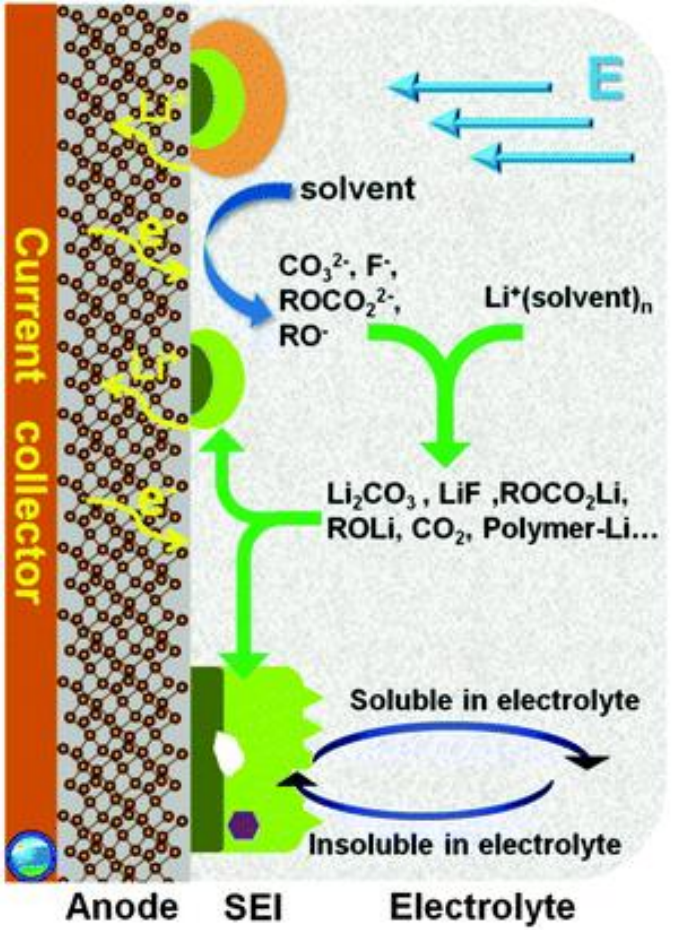
Shi, S. J. Am. Chem. Soc. 2012, 134, 15476

Dynamic formation scheme of the SEI on the anode.

The formed SEI can deposit on the surface of the electrode, dissolve and drift in the electrolyte.
The overall charge transport process:



Combined with



Phys. Chem. Chem. Phys., 2014, 16, 13229-13238 / *J. Electrochem. Soc. 2003 volume 150, issue 12, A1628-A1636* / J. Mater. Res., Vol. 27, No. 18, Sep 28, 2012

Current understanding of the EEI interface

Electrode–Electrolyte Interface in Li-Ion Batteries: Current Understanding and New Insights

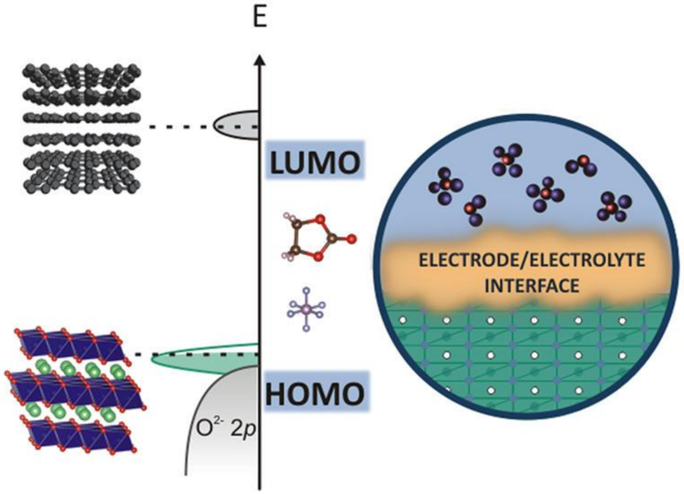
Magali Gauthier,[†,‡] Thomas J. Carney,[‡,§] Alexis Grimaud,[†,‡] Livia Giordano,[†,‡,⊥] Nir Pour,[†,‡] Hao-Hsun Chang,[†,‡] David P. Fenning,[‡,∥] Simon F. Lux,[∇] Odysseas Paschos,[¶] Christoph Bauer,[¶] Filippo Maglia,[¶] Saskia Lupart,[¶] Peter Lamp,[¶] and Yang Shao-Horn*[,†,‡,§,∥]

[†]Research Laboratory of Electronics, [‡]Electrochemical Energy Laboratory, [§]Department of Materials Science & Engineering, and [∥]Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States

[⊥]Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via Roberto Cozzi 55, 20125 Milan, Italy

[∇]BMW Group Technology Office USA, 2606 Bayshore Parkway, Mountain View, California 94043, United States

[¶]BMW Group, Petuelring 130, 80788 München, Germany

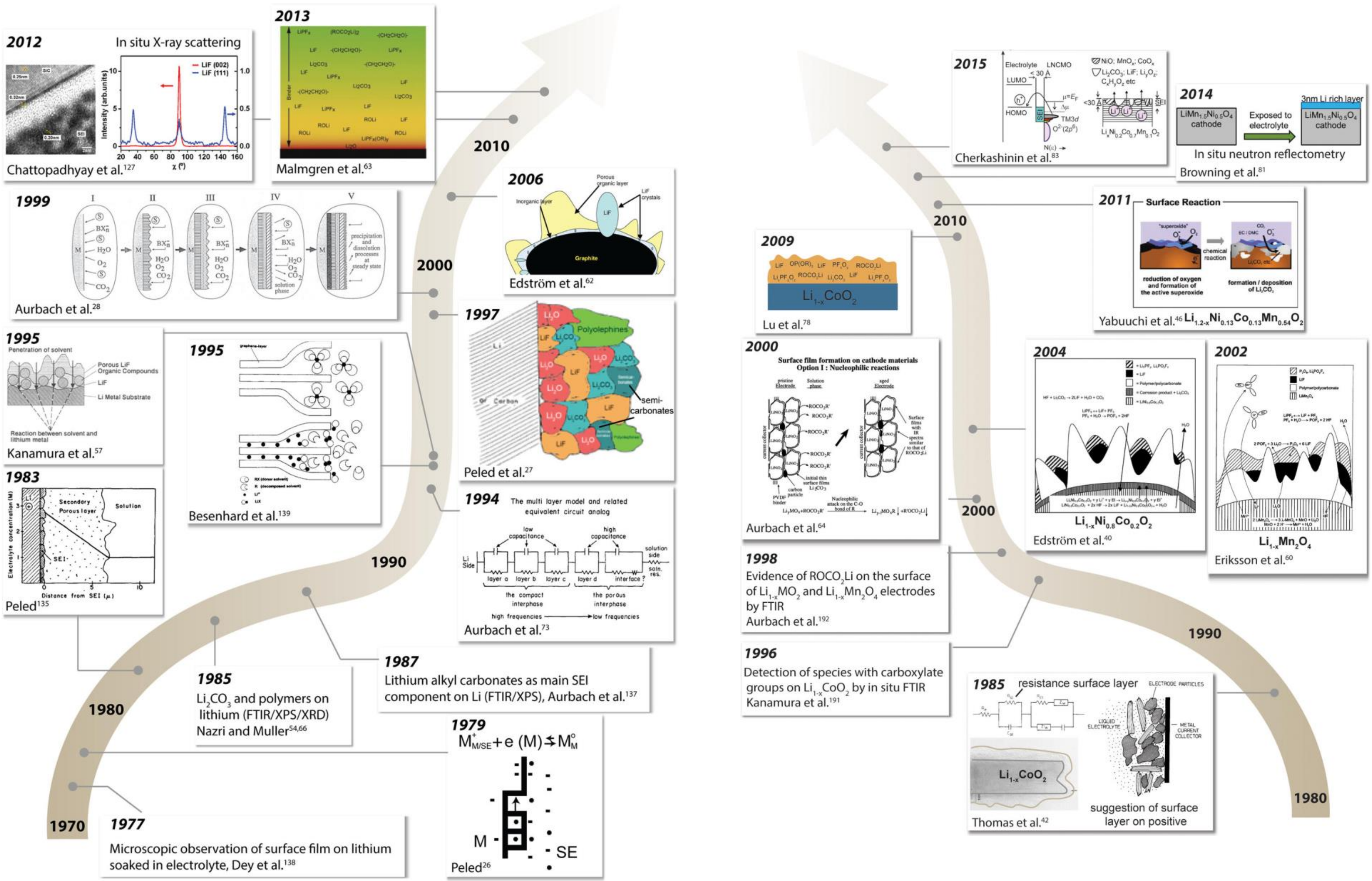


There is still limited understanding on what EEI layers consist of, by what mechanisms they are formed, and how they influence EEI properties and battery performance.

Although the well-known mosaic model of the SEI on lithium and graphite described is well accepted in the community, it has not been fully experimentally established and enough challenged.

J. Phys. Chem. Lett. 2015, 6, 4653−4672

Knowledge evolution on the EEI on the Anode and the Cathode side



1977
Microscopic observation of surface film on lithium soaked in electrolyte, Dey et al.[138]

1979
$M^{+}_{M/SE} + e(M) \rightleftarrows M^{\circ}_{M}$
Peled[26]

1983
Peled[135]

1985
Li_2CO_3 and polymers on lithium (FTIR/XPS/XRD)
Nazri and Muller[54,66]

1987
Lithium alkyl carbonates as main SEI component on Li (FTIR/XPS), Aurbach et al.[137]

1994 The multi layer model and related equivalent circuit analog
Aurbach et al.[73]

1995
Kanamura et al.[57]

1995
Besenhard et al.[139]

1997
Peled et al.[27]

1999
Aurbach et al.[28]

2006
Edström et al.[62]

2012 In situ X-ray scattering
Chattopadhyay et al.[127]

2013
Malmgren et al.[63]

1985
Thomas et al.[42]
suggestion of surface layer on positive

1996
Detection of species with carboxylate groups on $Li_{1-x}CoO_2$ by in situ FTIR
Kanamura et al.[191]

1998
Evidence of $ROCO_2Li$ on the surface of $Li_{1-x}MO_2$ and $Li_{1-x}Mn_2O_4$ electrodes by FTIR
Aurbach et al.[192]

2000
Surface film formation on cathode materials
Option I : Nucleophilic reactions
Aurbach et al.[64]

2002
$Li_{1-x}Mn_2O_4$
Eriksson et al.[60]

2004
$Li_{1-x}Ni_{0.8}Co_{0.2}O_2$
Edström et al.[40]

2009
Lu et al.[78]

2011 Surface Reaction
Yabuuchi et al.[46] $Li_{1.2-x}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$

2014
In situ neutron reflectometry
Browning et al.[81]

2015
Cherkashinin et al.[83]

J. Phys. Chem. Lett. 2015, 6, 4653−4672

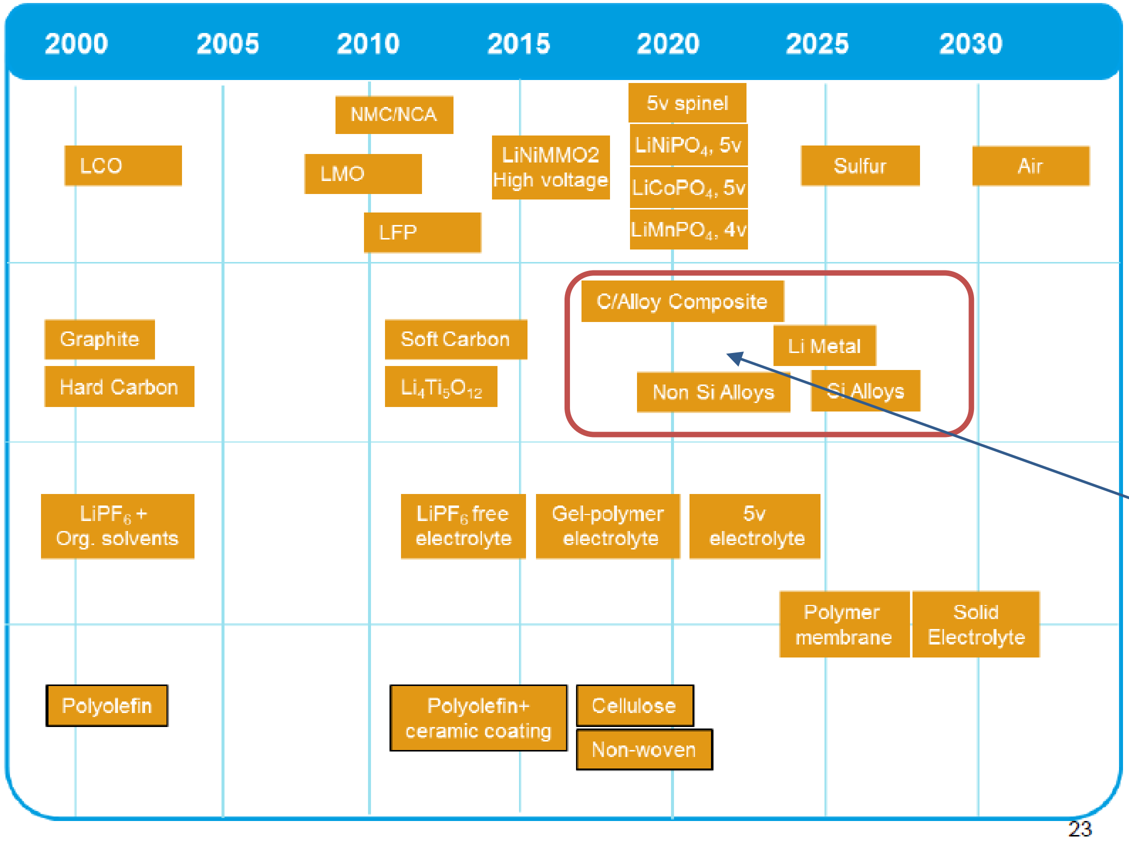
Some concluding words

There is a need to study model electrode surfaces such as thin films, which allows for investigating the reactivity of the electrolyte with the active material surface alone.

Guided by these questions, researchers will be able to elucidate reaction mechanisms at the EEI and develop design principles to predict and control the interfaces of Li-ion batteries.

Adapted from J. Phys. Chem. Lett. 2015, 6, 4653−4672

Time to market for new materials in LIB industry



	2000	2005	2010	2015	2020	2025	2030
CATHODE	LCO		NMC/NCA LMO LFP	LiNiMMO2 High voltage	5v spinel $LiNiPO_4$, 5v $LiCoPO_4$, 5v $LiMnPO_4$, 4v	Sulfur	Air
ANODE	Graphite Hard Carbon		Soft Carbon $Li_4Ti_5O_{12}$		C/Alloy Composite Non Si Alloys	Li Metal Si Alloys	
ELECTROLYTE	$LiPF_6$ + Org. solvents		$LiPF_6$ free electrolyte	Gel-polymer electrolyte	5v electrolyte	Polymer membrane	Solid Electrolyte
SEPARATORS	Polyolefin		Polyolefin+ ceramic coating	Cellulose Non-woven			

Si, Sn, etc…
semiconductors

Charge transport in semiconductors….?

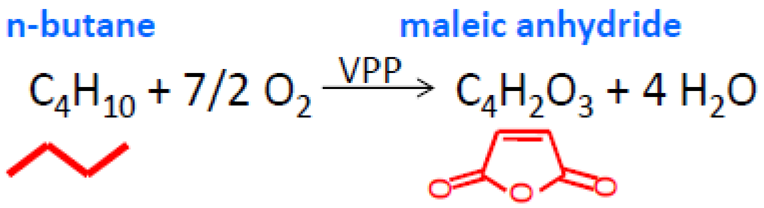
….,battery, gas sensors, PV, , catalysis, research,…

Avicenne market review, report 2014

Charge transport in metal oxides

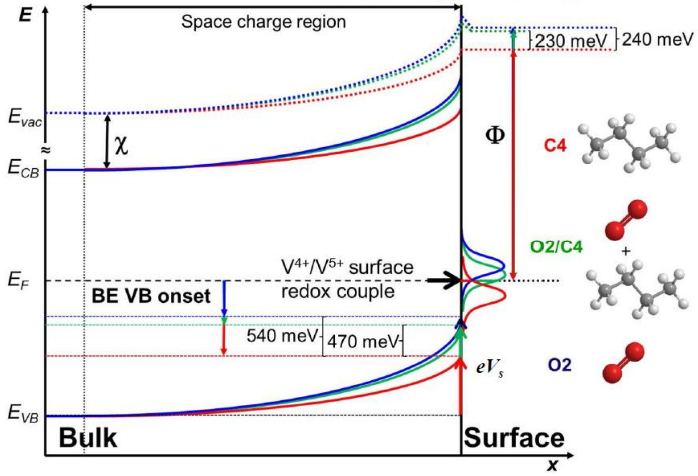
Most metal oxides are semiconductors and Oxidation catalysts are most often metal oxides.

A key application of charge transport in metal oxides are gas sensors



n-butane **maleic anhydride**

$C_4H_{10} + 7/2\ O_2 \xrightarrow{VPP} C_4H_2O_3 + 4\ H_2O$



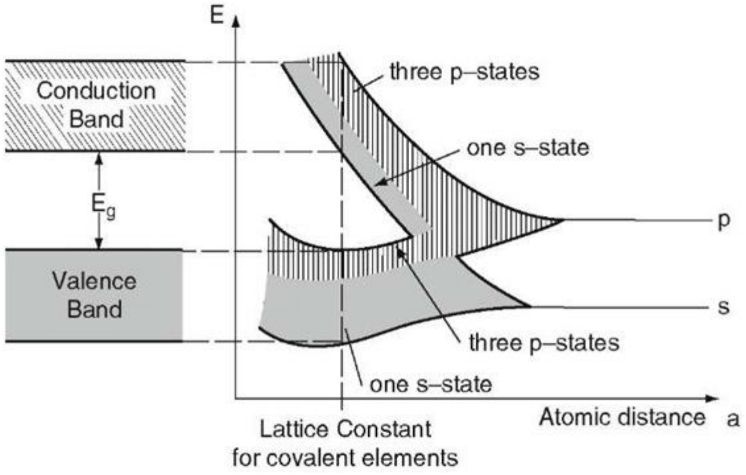
Semiconductors physics: From isolated molecules to energy band diagram

Band diagram

Kronig-Penney model

Free electrons are affected by periodic lattice potential splitting of energy following Pauli exclusion principle

Energy bands for diamond versus lattice constant (*Covalent element!*)



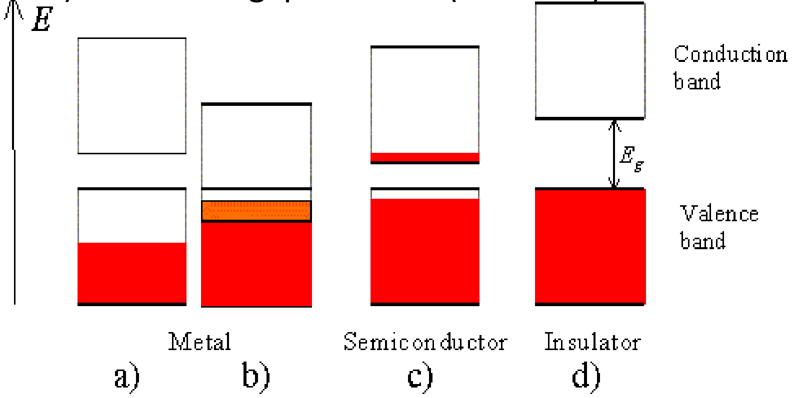
A further reduction of the lattice constant (<a0) causes the 2s and 2p energy bands to merge and split again into two bands

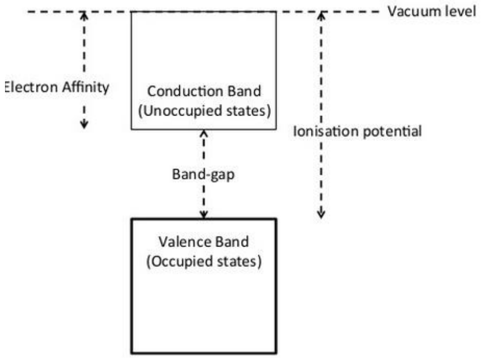
Possible energy band diagrams of a crystal.

a-b) Metal: a half filled band, two overlapping bands

c) semiconductor: an almost full band separated by a small bandgap from an almost empty band

d) Wide bandgap material (insulator)





Fermi-Dirac statistics

Occupancy of electrons in a band is determined by **Fermi-Dirac statistics**

Fermi-Dirac distribution (for an electron gas):

$$f(E) = \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right)+1}$$

E...Energy

k_B...Boltzmann constant

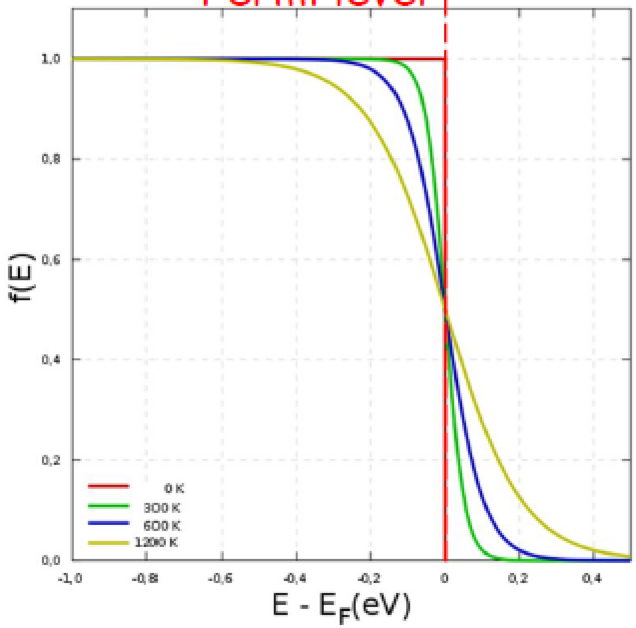
T...Temperature

μ...(Electro-)Chemical potential

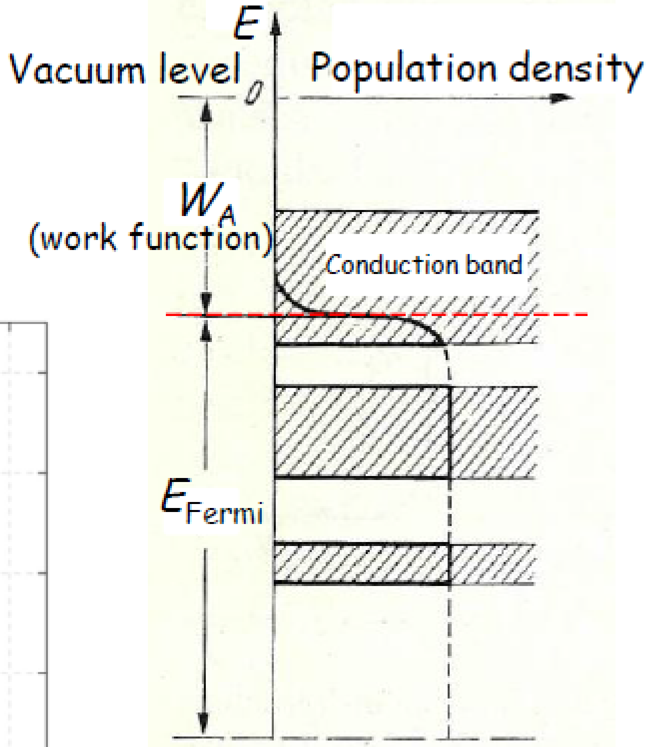
$$\mu(T=0) = E_{\mathrm{Fermi}}$$

$$f(E=\mu) = 1/2$$

= Fermi level



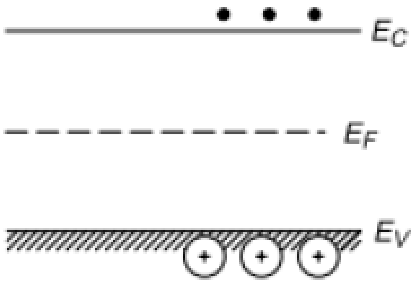
P. A. Tipler, *Physik*, Spektrum Verlag



The Fermi curve determines the population of occupied states, independent of the existence of states in the regarded *E* region

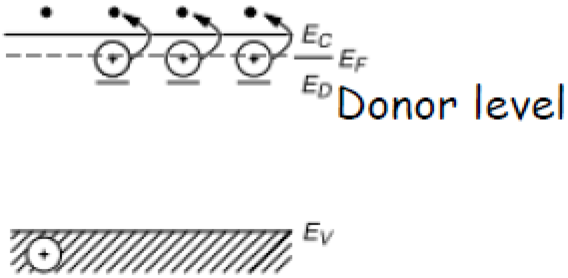
Extrinsic n- and p- type semiconductors, e.g. Si

Intrinsic semiconductor



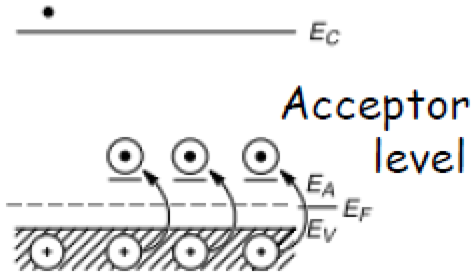
e.g. Si (band gap at 300 K = 1.12 eV)

(Extrinsic) n-type semiconductor

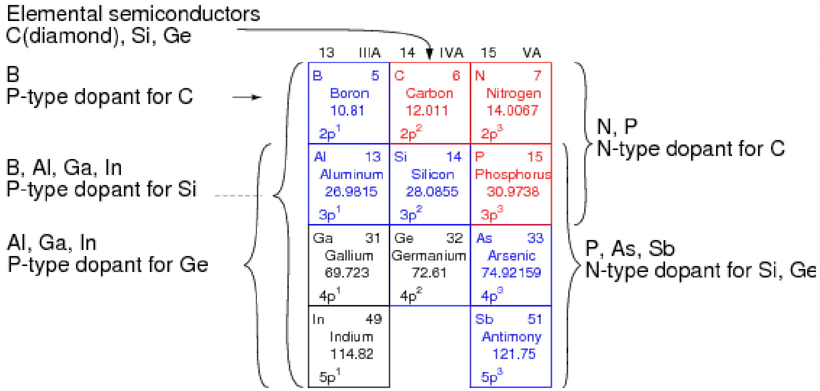


e.g. As-doped Si

(Extrinsic) p-type semiconductor



e.g. Ga-doped Si



Elemental semiconductors C(diamond), Si, Ge

B
P-type dopant for C

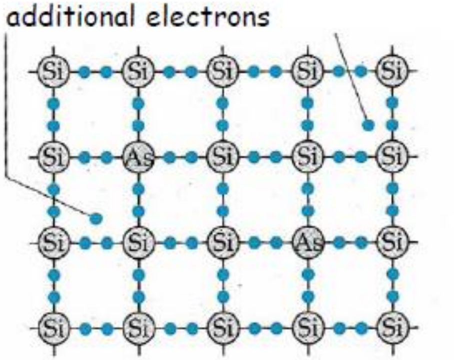
B, Al, Ga, In
P-type dopant for Si

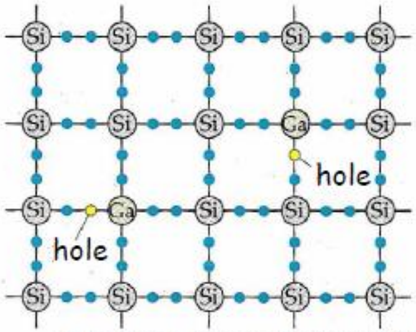
Al, Ga, In
P-type dopant for Ge

N, P
N-type dopant for C

P, As, Sb
N-type dopant for Si, Ge

13 IIIA	14 IVA	15 VA
B 5 Boron 10.81 $2p^1$	C 6 Carbon 12.011 $2p^2$	N 7 Nitrogen 14.0067 $2p^3$
Al 13 Aluminum 26.9815 $3p^1$	Si 14 Silicon 28.0855 $3p^2$	P 15 Phosphorus 30.9738 $3p^3$
Ga 31 Gallium 69.723 $4p^1$	Ge 32 Germanium 72.61 $4p^2$	As 33 Arsenic 74.92159 $4p^3$
In 49 Indium 114.82 $5p^1$		Sb 51 Antimony 121.75 $5p^3$





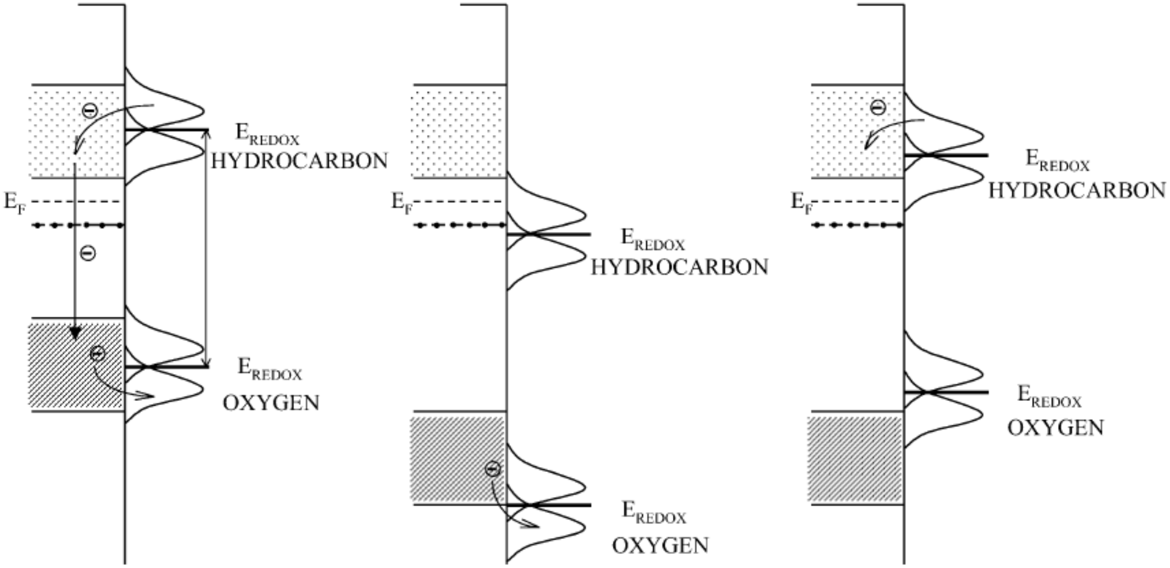
P. A. Tipler, *Physik*, Spektrum Verlag

Band and frontier orbitals of adsorbed hydrocarbons

Example: Oxidation of hydrocarbons

$$RH + O^{2-} \rightarrow R\text{–}O^{-} + H^{+} + 2e^{-},$$
$$\tfrac{1}{2}O_2 + 2e^{-} \rightarrow O^{2-},$$

Note: Rigid band assumptions



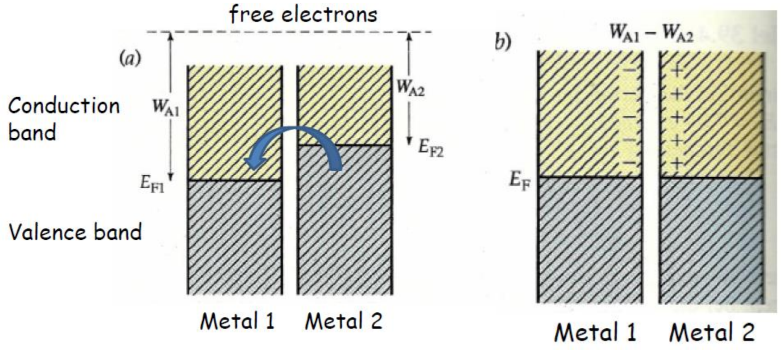
CATALYTIC OXIDATION OF HYDROCARBON MOLECULE CAN PROCEED

CATALYTIC OXIDATION OF HYDROCARBON MOLECULE CANNOT PROCEED, BECAUSE THE MOLECULE IS NOT ACTIVATED

CATALYTIC OXIDATION OF HYDROCARBON MOLECULE CANNOT PROCEED, BECAUSE THE CATALYST IS NOT REOXIDIZED

Space charge region

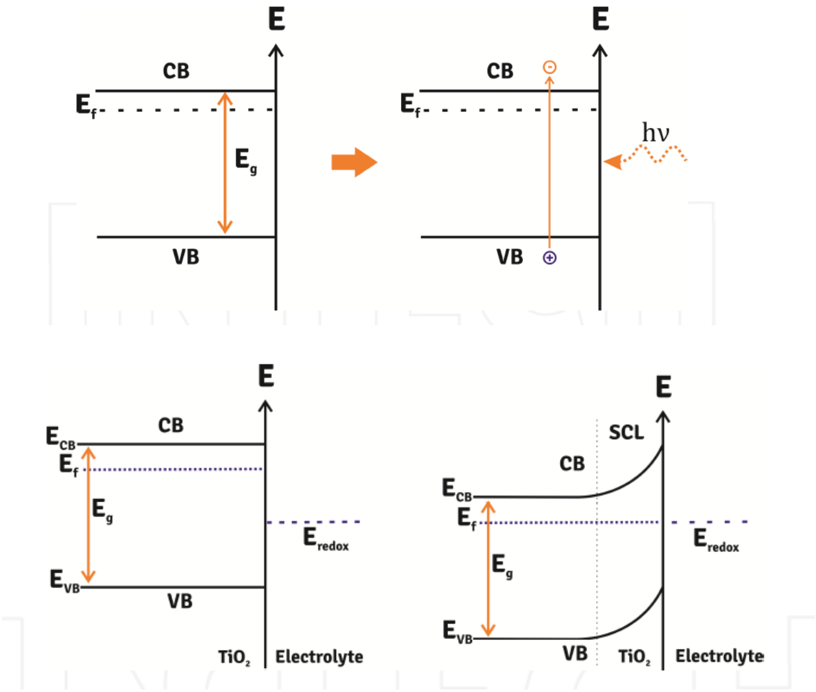
For metals



a) Energy states of two different metals with different Fermi energies and work functions.

b) With contact, electrons will flow from the metal with higher Fermi energy (lower work function) to the one with lower Fermi energy (larger work function) until the Fermi levels of both metals are equalized

For semiconductors

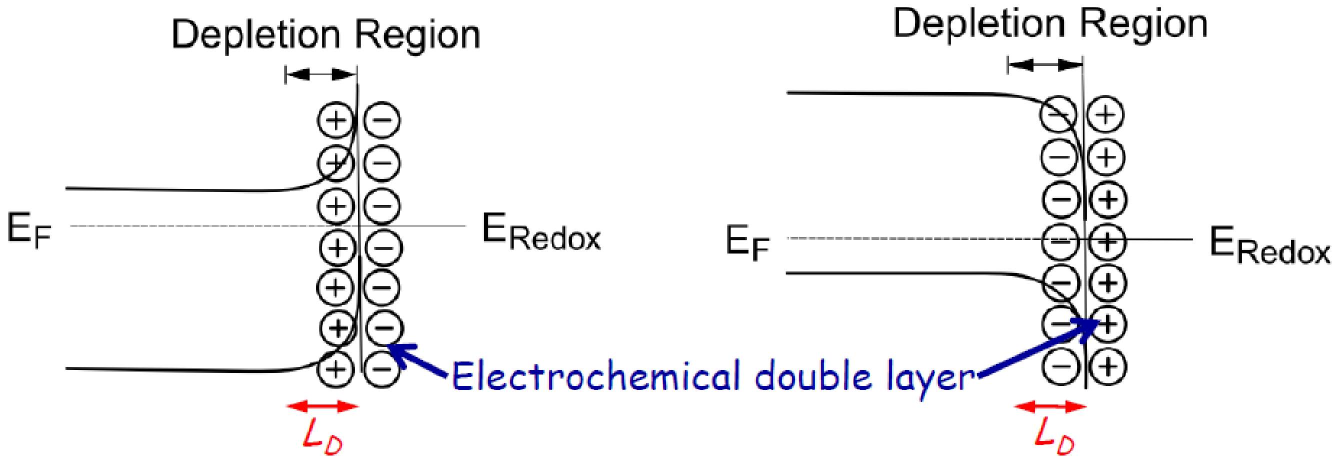


Energy band diagram for an **n-type semiconductor** before and after the equilibration of Fermi levels at the interface semiconductor/electrolyte, and the appearance of band-bending and the space charge layer (SCL)

Space charge region

n-type SC in contact with electrolyte

p-type SC in contact with electrolyte



Space Charge Region **Space Charge Region**

In metals: penetration depth (space charge region to compensate surface charge) of only a few lattice constants (high concentration of free charge carriers)

In SCs: Debye shielding, L_D, can amount from 10 nm to 1 μm

$$L_D = \sqrt{\frac{\varepsilon k_B T}{2\pi q^2 n_i}}$$

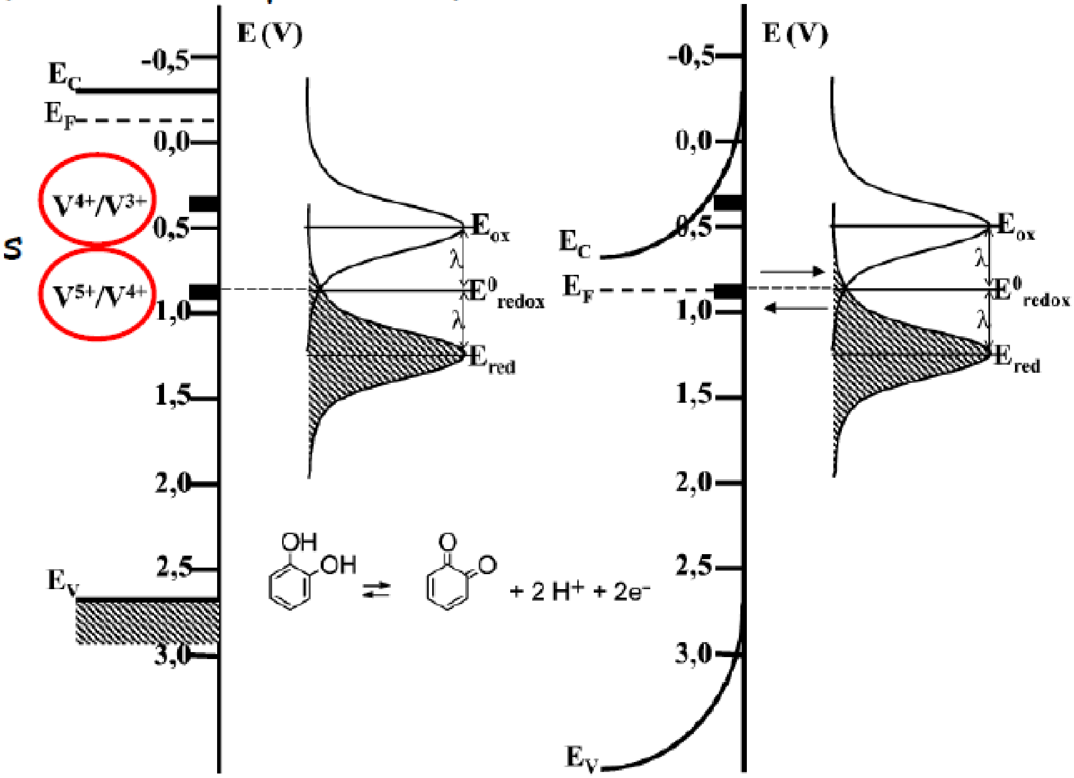
ε...Dielectric permittivity of crystal; q...Electron charge; n_i...Concentration of charge carriers in intrinsic semiconductor

A. W. Bott, *Current Separations* **1998**, *17*, 87

Electrocatalytic oxidation of catechol on vanadium-doped TiO_2 electrodes

Flat band potential
(no external potential)

With external potential



When an external potential is applied, the energy levels of the solid become bent upwards, the Fermi level shifts below the V^{4+} /V^{3+} and V^{5+} /V^{4+} levels, and the electrons from these levels are moved into the conductivity band, leaving them in the vanadium 5+ state.

Now these levels can mediate the transfer of electrons from the reacting molecules into the conductivity band of the solid and the oxidation reaction of catechol to o-chinon may take place.

J. Haber, M.Witko / Journal of Catalysis 216 (2003) 416–424

Band bending and local conductivity

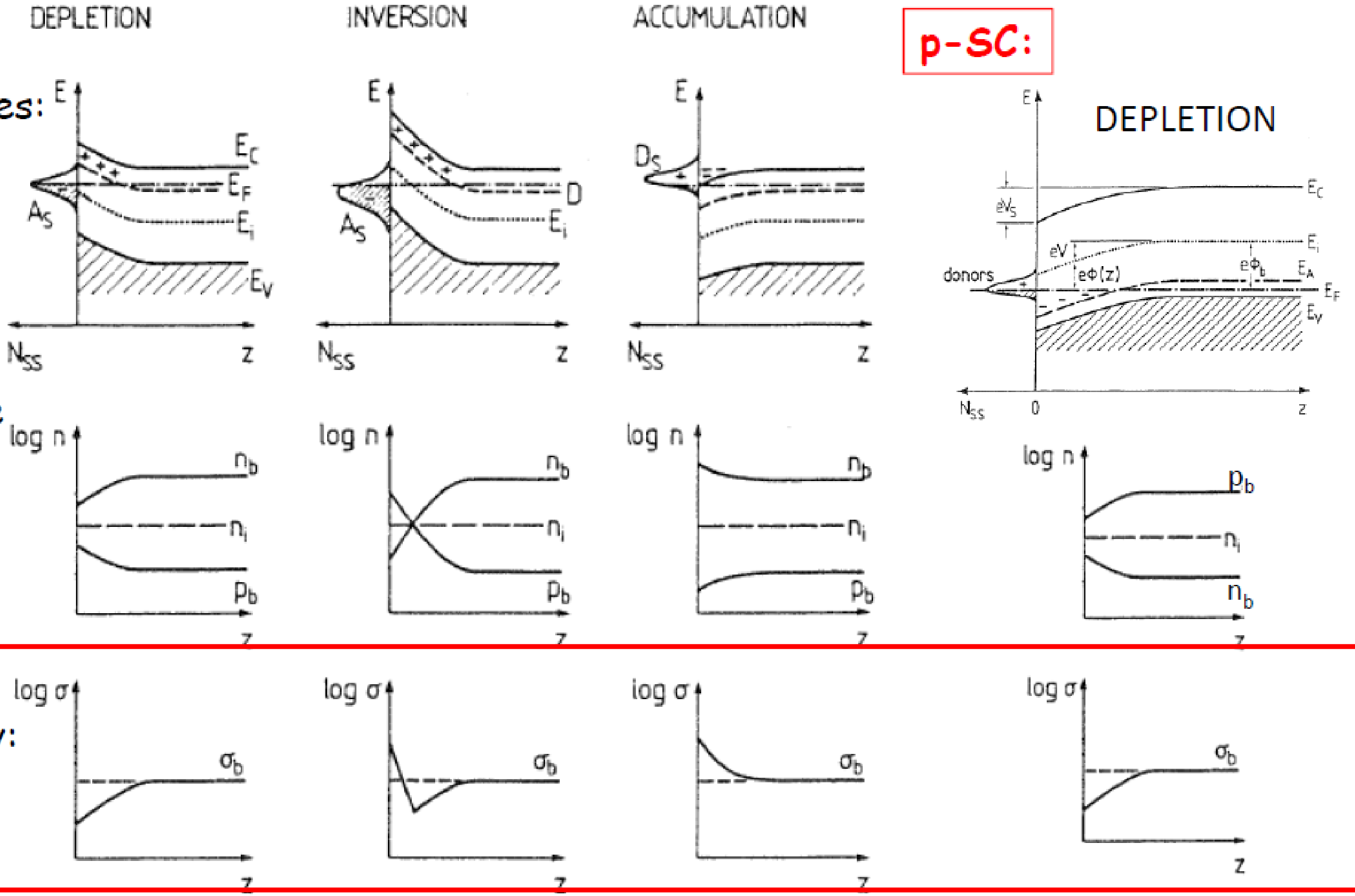
n-SC:

Band schemes:

Free charge carrier densities:

Local conductivity:

p-SC:

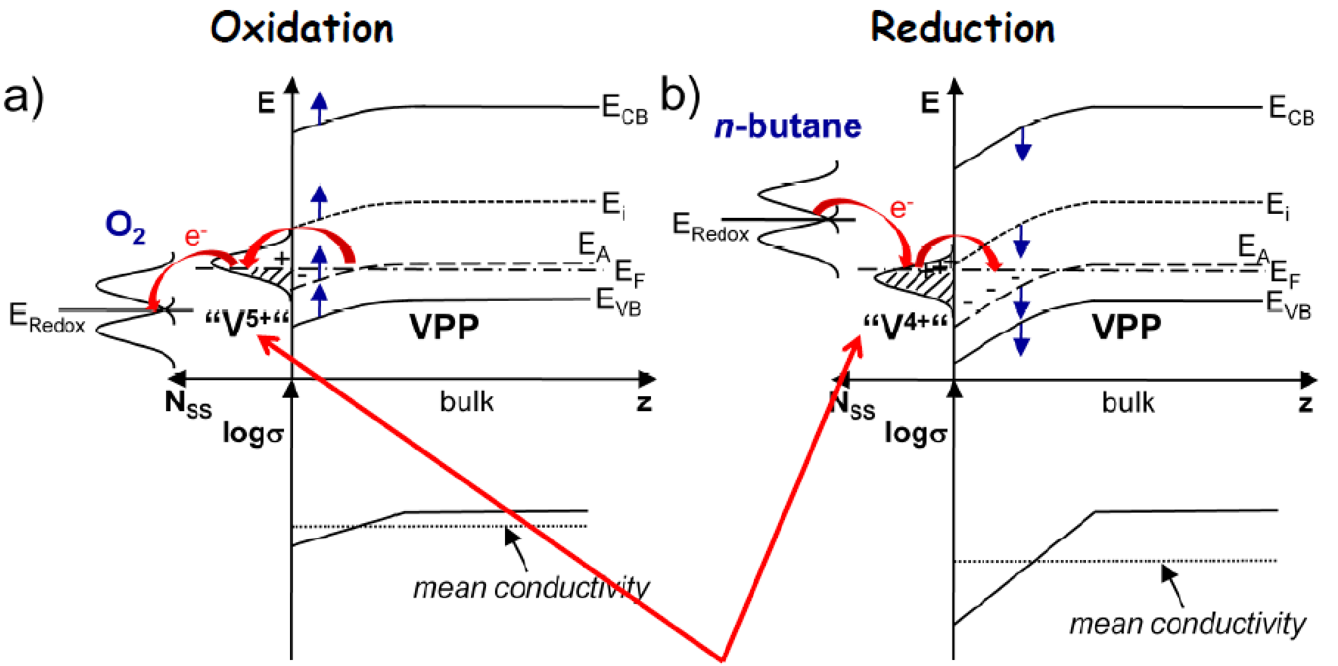


H. Lüth, *Solid Surfaces, Interfaces and Thin Films*, Springer **2001**

Adsorption and catalysis at active states (induced band bending)

Adsorption (catalysis) at surface states:

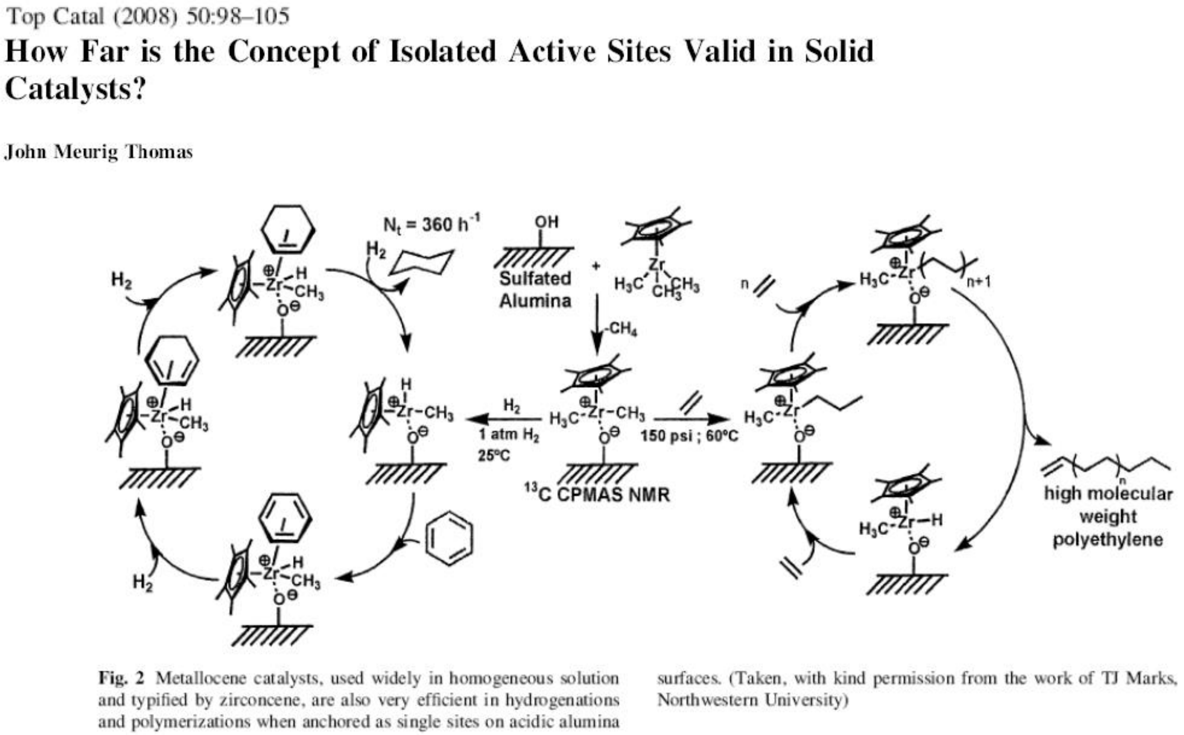
p-type semiconductor (e.g. $(VO)_2P_2O_7$ for butane oxidation to maleic anhydride)



Local surface state = active (isolated single) site → selective oxidation

Band bending match the chemical potential of the adsorbate
(reverse situation than with electrocatalysis of catechol)

After all this theory the motivation of the charge transport group is easier to define



Top Catal (2008) 50:98–105

How Far is the Concept of Isolated Active Sites Valid in Solid Catalysts?

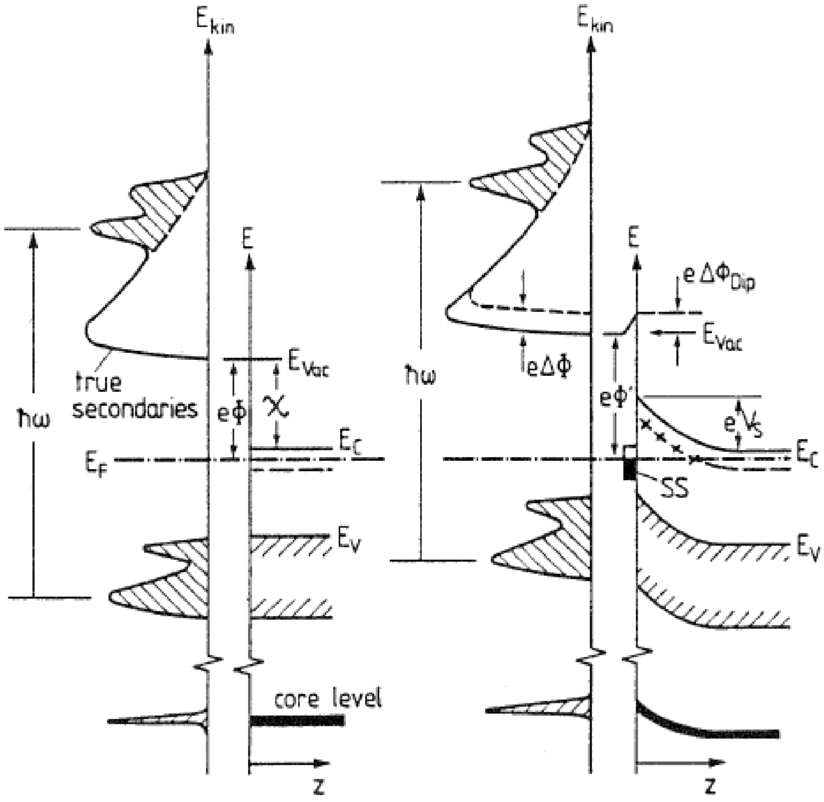
John Meurig Thomas

Fig. 2 Metallocene catalysts, used widely in homogeneous solution and typified by zirconcene, are also very efficient in hydrogenations and polymerizations when anchored as single sites on acidic alumina surfaces. (Taken, with kind permission from the work of TJ Marks, Northwestern University)

Solid State Aspects: Going underneath the surface and beyond the molecule

Experimental evidence

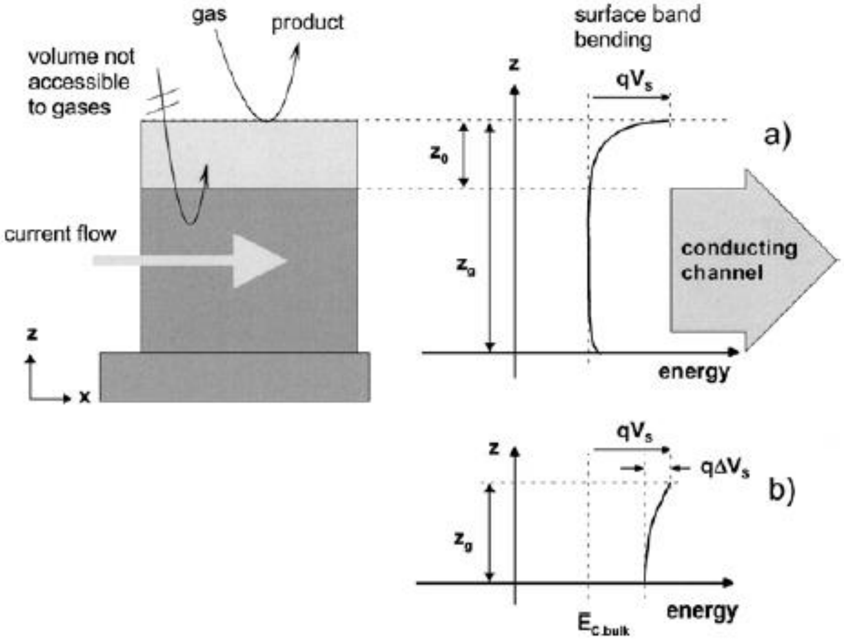
Photoemission spectroscopy



a) clean

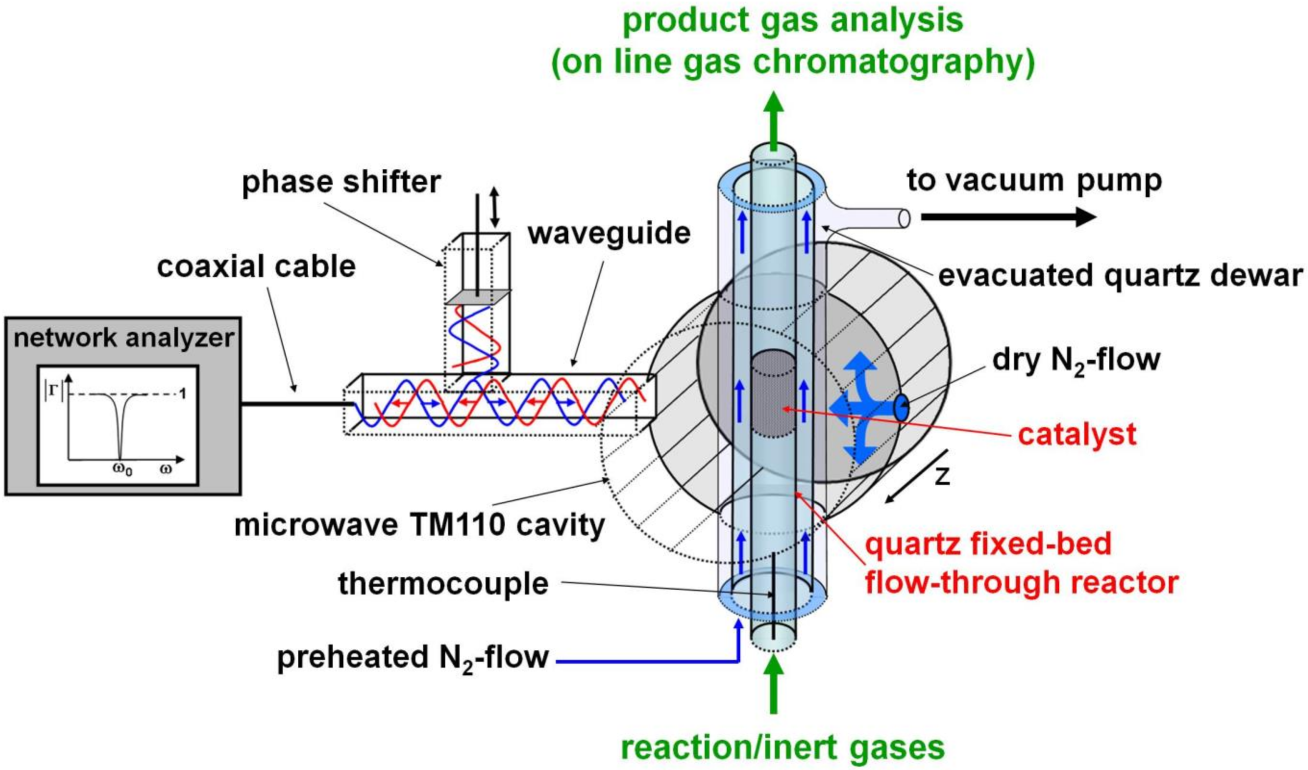
b) with adsorbate

Conductivity

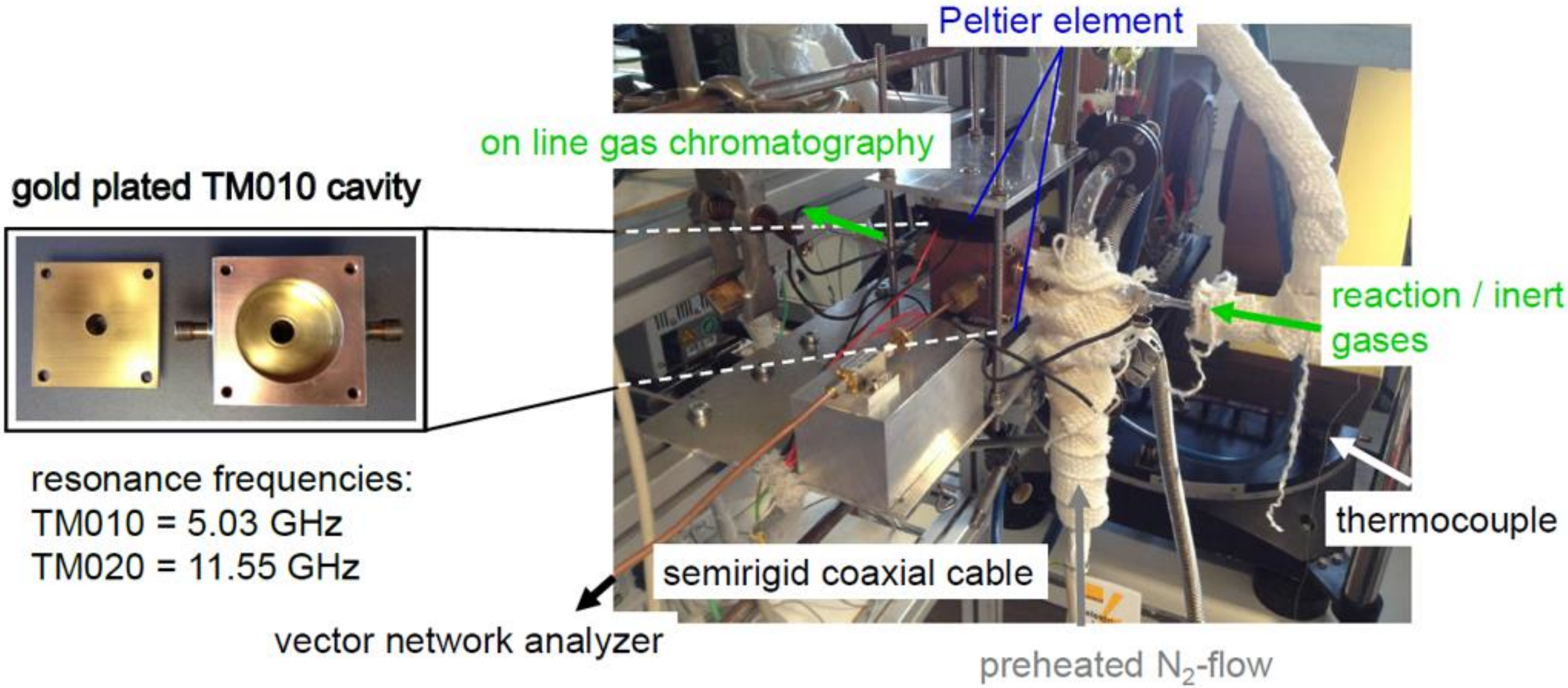


H. Lüth, Solid Surfaces, Interfaces and Thin Films, Springer **2001,** Journal of Electroceramics, 7, 143–167, 2001

Contactless conductivity measurements using the *microwave cavity perturbation technique*

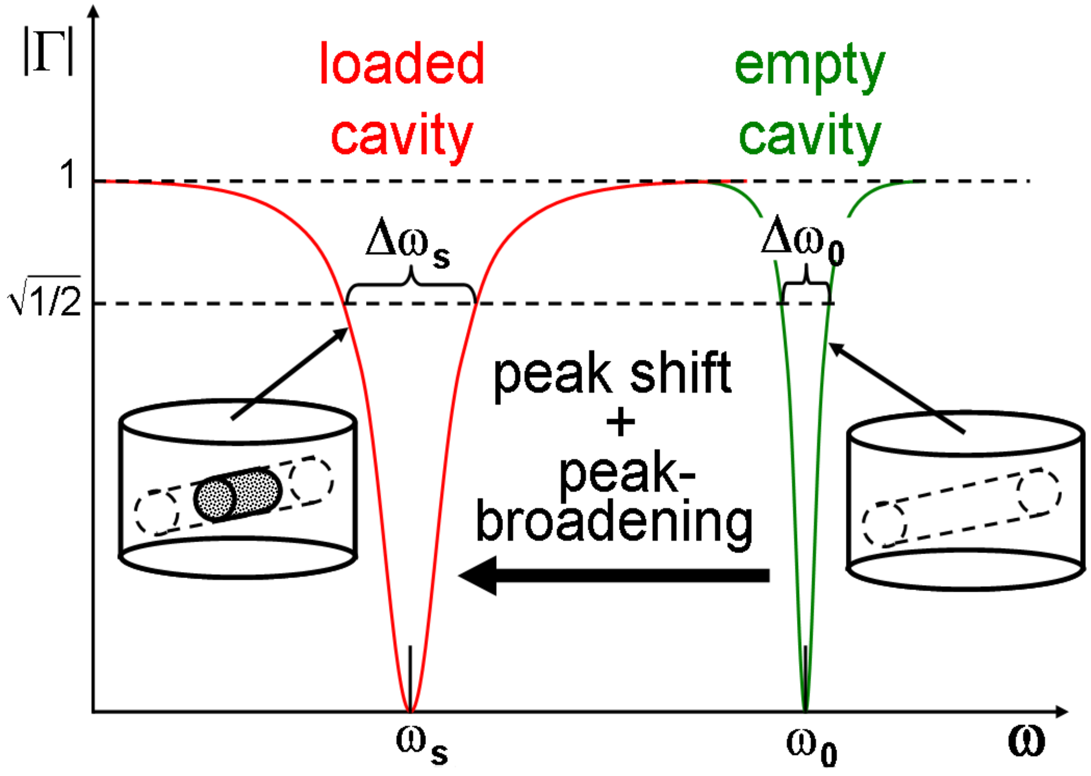


MCPT Setup



resonance frequencies:
TM010 = 5.03 GHz
TM020 = 11.55 GHz

Microwave Cavity Perturbation Technique



Absolute value of the reflexion factor in case of critical coupling.

Measured quantities: resonance frequency **ω** and resonance width **Δω**

Calculated sample properties: complex permittivity ***ε*** and electrical conductivity ***σ***

$$\varepsilon = \varepsilon_1 + i\varepsilon_2$$

$$\frac{\omega_s - \omega_0}{\omega_0} = A(\varepsilon_1 - 1)\frac{V_s}{V_c}$$

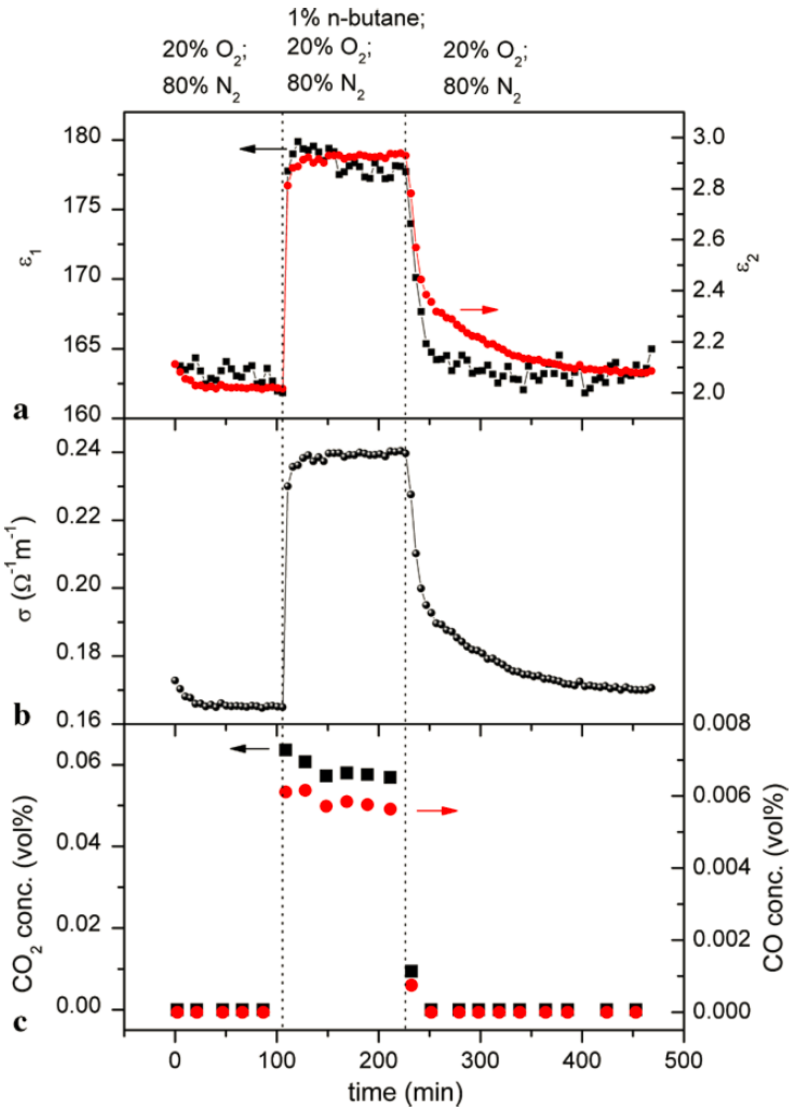
$$\frac{\Delta\omega_s - \Delta\omega_0}{\omega_0} = A\varepsilon_2 \frac{V_s}{V_c}$$

contactless measurement of the conductivity: $\sigma = \varepsilon_0 \varepsilon_2 \omega_s$

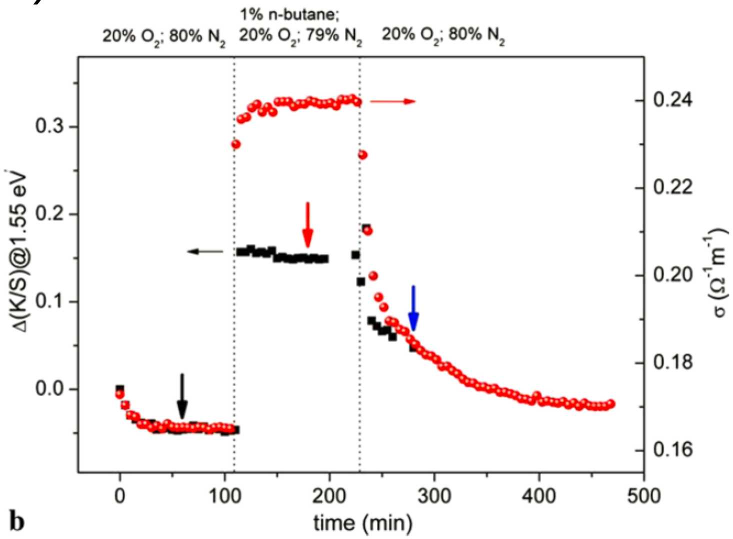
A: cavity constant; V_s: sample volume; V_c: cavity volume; ε_0: vacuum permittivity

J.C. Slater, *Rev. Mod. Phys.* **1946**, *18*, 441

Charge Carrier Analysis of V_2O_5



UV-Vis-NIR: absorption at 1.55 eV ($3d^1$-conduction band transition of V^{4+}):



Correlation between conductivity and V oxidation state – NAP-XPS.

→ **Band bending and selectivity,**

→ **See** C. Heine et al., *Appl. Phys. A* **2013,** 112, 289-296

C. Heine et al., *Appl. Phys. A* **2013,** 112, 289-296

Literature

(Examples)

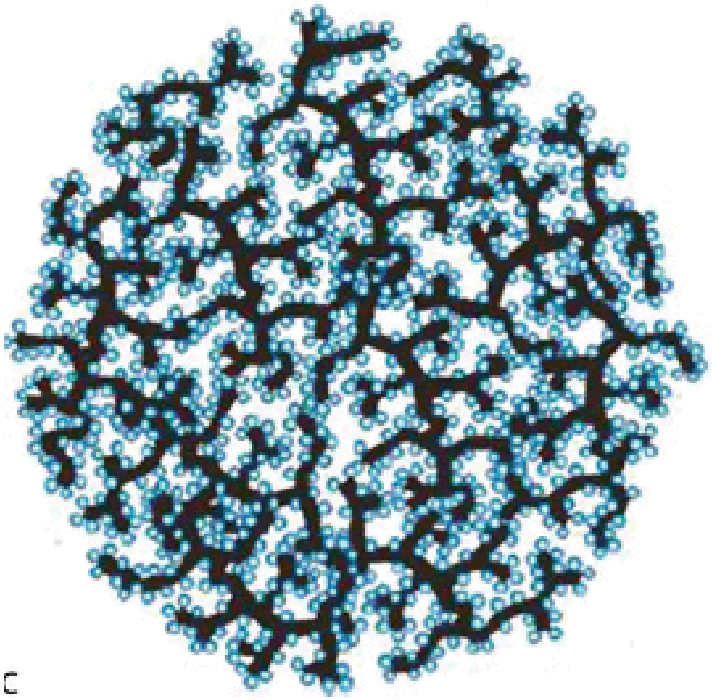
Adsorption/catalysis on semiconductors, e.g.:

- S. R. Morrison, "*The chemical physics of surfaces*", Plenum Press New York and London **1977** (semiconductor physics concepts of surfaces, includes chapter on heterogeneous catalysis)
- F. F. Volkenshtein, "*The electronic theory of catalysis on semiconductors*"; Pergamon Press **1963**.
- H. Lueth, "*Solid surfaces, interfaces and thin films*", Springer **2010**
- H. Lueth, "*Space Charge Layer*", Springer Verlag **2001**
- P. A. Cox, "*The electronic structure and chemistry of solids*", Oxford University Press **1989**
- R. Hoffmann, "*Solids and surfaces : a chemist's view of bonding in extended structures*" VCH **1988**

Fundamental textbooks, e.g.:

- N. W. Ashcroft, N. D. Mermin, "*Solid state physics*", Brooks/Cole Cengage Learning **2009**
- H. Ibach, H. Lueth, "*Solid-state physics : an introduction to principles of materials science*", Springer **2009**

What about charge transport in Si / C anode



Thank you !