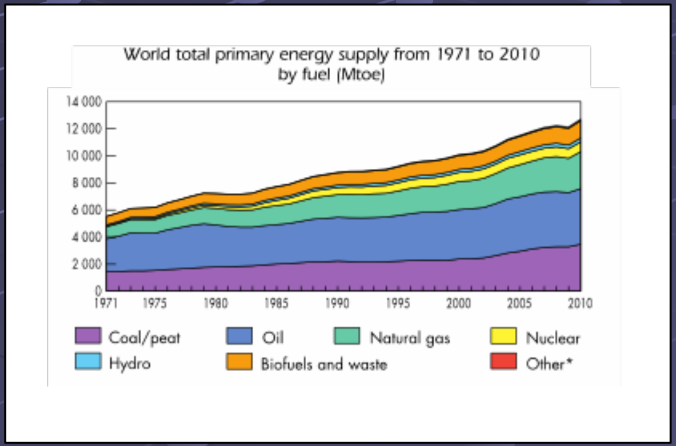
Materials Physics: quantum dynamics of electrons in liquids and solids

Nicola Seriani

The Abdus Salam International Centre for Theoretical Physics,
Strada Costiera 11, 34151 Trieste, Italy

The energy challenge

- Sustainably providing clean energy for the needs of tomorrow is one of the key challenges humankind has to face



World Energy Statistics,
International Energy Agency

- Shift towards renewable energy sources. Here: solar energy
- Source is irregular → importance of energy storage (batteries, solar-to-fuel, hydrogen storage,...)

Solar energy

- Solar energy is abundant
- Source is irregular → importance of energy storage (batteries, solar-to-fuel, hydrogen storage,...)
- So far, mainly photovoltaics: but electricity is difficult and expensive to store
- Moreover, some applications need storage at high energy density: liquid fuels for airplanes
- Solar fuels: the goal is to use solar energy to produce fuels (hydrogen, hydrocarbons, methanol,...)

The energy challenge

The energy challenge for chemistry

unicat Unifying Concepts in Catalysis

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- The use of renewable energies without large admixtures of fossil sources for electricity is impossible without chemical energy storage, even when a “smart grid” exists.
- In addition, chemical energy carriers are needed.
- Chemical storage is essential: “Solar hydrogen” may be used to generate chemical energy carriers through catalysis.
- Saving strategies are useful and helpful for short times but cannot replace missing base supply.

R. Schlögl, Max Planck Institute

The energy challenge

The energy challenge for chemistry

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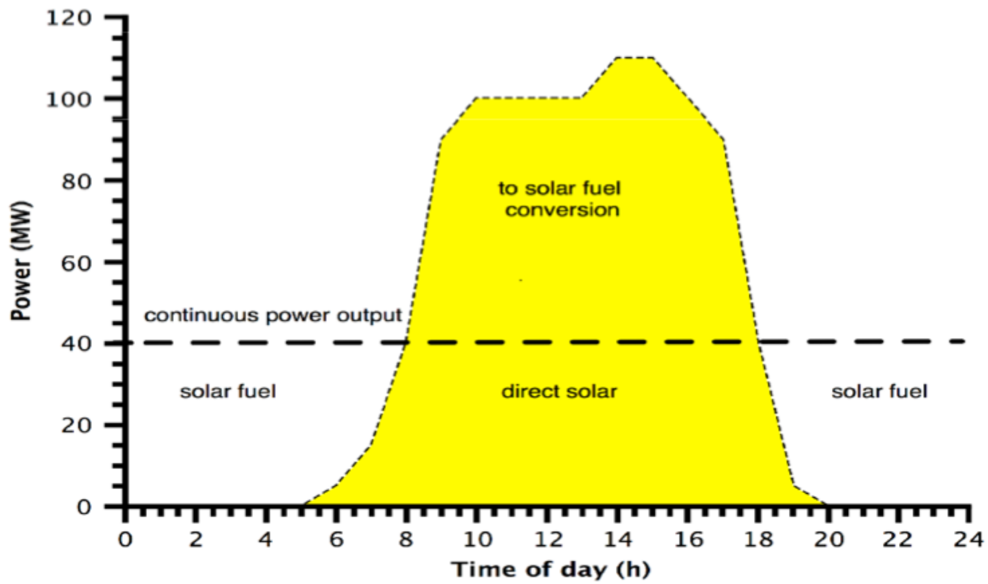


An effective regenerative power station
With 24/7 production.

R. Schlögl, Max Planck Institute

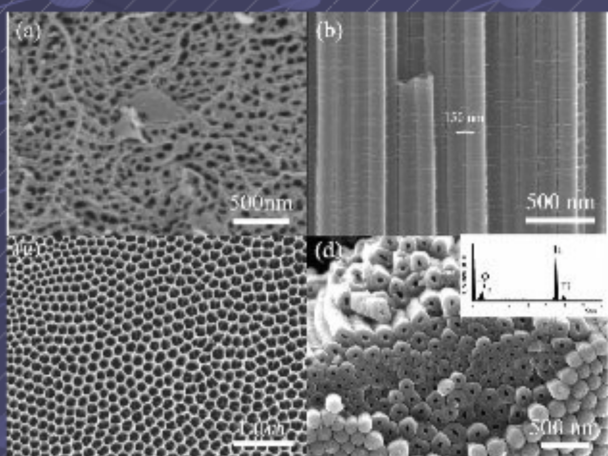
Solar fuels

- Solar fuels: the goal is to use solar energy to produce fuels (hydrogen, hydrocarbons, methanol,...)

- I am interested in understanding systems that can do this through photo(electro)catalysis

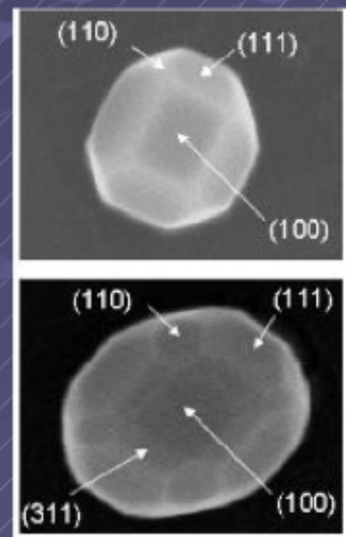
Nanostructures for energy applications

- Ability to control, manipulate and understand materials at the nanoscale could lead to major advancement in the field of energy conversion and storage
- Properties at the nanoscale different from bulk



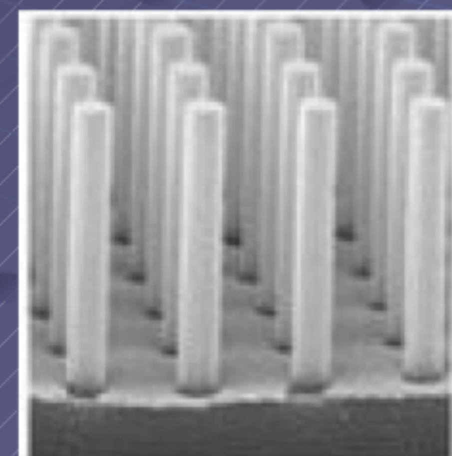
TiO_2 nanotubes as anode material for dye-sensitized solar cells

Li et al., Chem. Mater. 22, 5707 (2010)



Platinum nanoparticles for fuel cells

Komanicky et al., Electrochim. Acta 55, 7934 (2010)



Silicon nanowires as anode for Li batteries

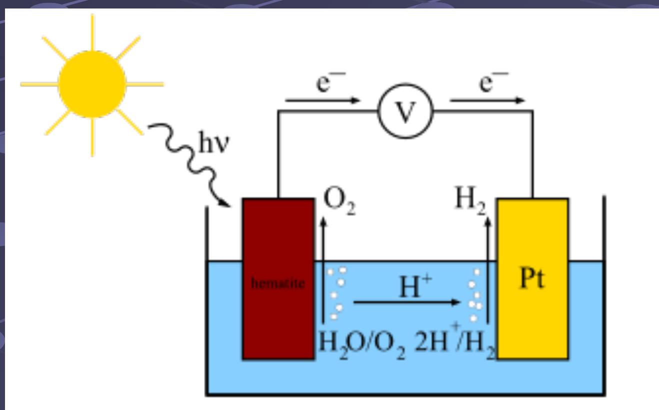
Chang et al., Adv. Funct. Mater. 20, 4364 (2010)

Understanding functional materials at the atomic level

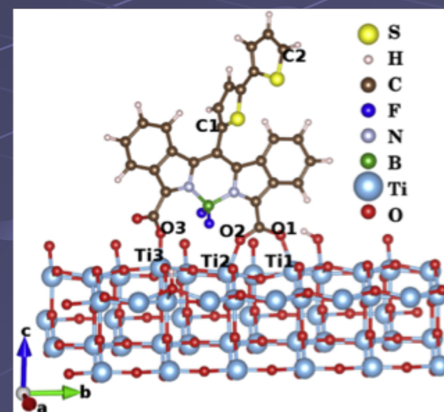
Photocatalysis for solar fuels

Photovoltaics

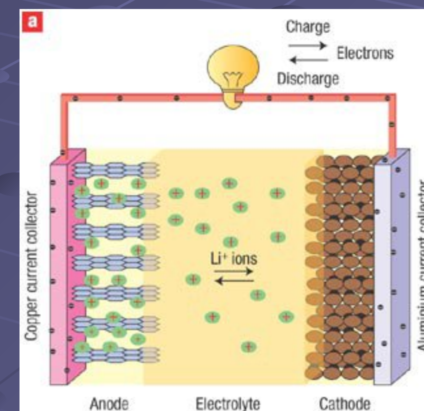
Batteries



N. Seriani, J. Phys.: Condens. Mat. 29, 463002 (2017)



Songkhao et al., Dyes and Pigments 142, 558 (2017)



B. Scrosati, Nature Nanotechnology 2, 598 (2007)

Complex composition: defects, dopants,...

Complex environment affecting composition and interfaces

Complex processes: photoabsorption, charge dynamics, interface reactions

Computational materials science for sustainable energy

Environment
(pressure, temperature, applied voltage, pH,...)

↓

Properties
(atomic structure, stability, electronic properties,...)

↓

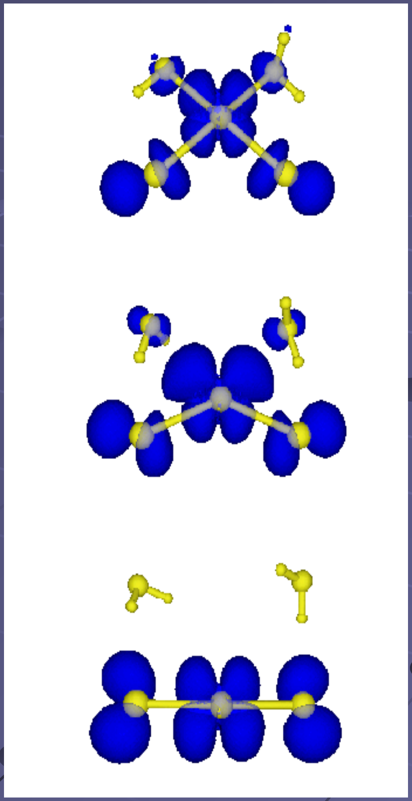
Function
(photocatalytic activity, lithium storage capacity,...)

↑ Materials design

Density functional theory and high-performance computing

Ab-initio molecular dynamics

- Model consists of atomic nuclei and electrons
- Atomic nuclei follow classical mechanics
- Electrons are quantum particles
- Adiabatic approximation → during motion, electrons are always in the instantaneous ground state



Density functional theory

- Method to reduce the many-electron Schrödinger equation to equations for one-electron wavefunctions (Kohn-Sham equations)

Schrödinger equation

$$[-\sum_{i}^{N}\frac{\hbar^2}{2m}\nabla_i^2+\sum_{i}^{N}V(\vec{r}_i)+\sum_{i<j}U(\vec{r}_i,\vec{r}_j)]\Psi(\vec{r}_1,...,\vec{r}_N)=E\Psi(\vec{r}_1,...,\vec{r}_N)$$

↓

$$[-\frac{\hbar^2}{2m}\nabla_i^2+V(\vec{r}_i)+\int\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+V_{xc}[n(\vec{r})]]\phi_i(\vec{r})=\varepsilon_i\phi_i(\vec{r})$$

Kohn-Sham equation

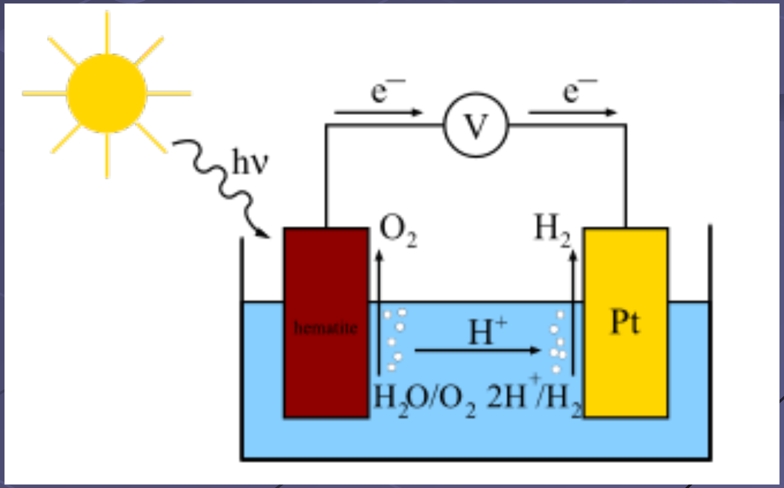
Approximations necessary for V_{xc}

Photoelectrocatalysis

Overall: $2H_2O \rightarrow O_{2,g} + 2H_{2,g}$

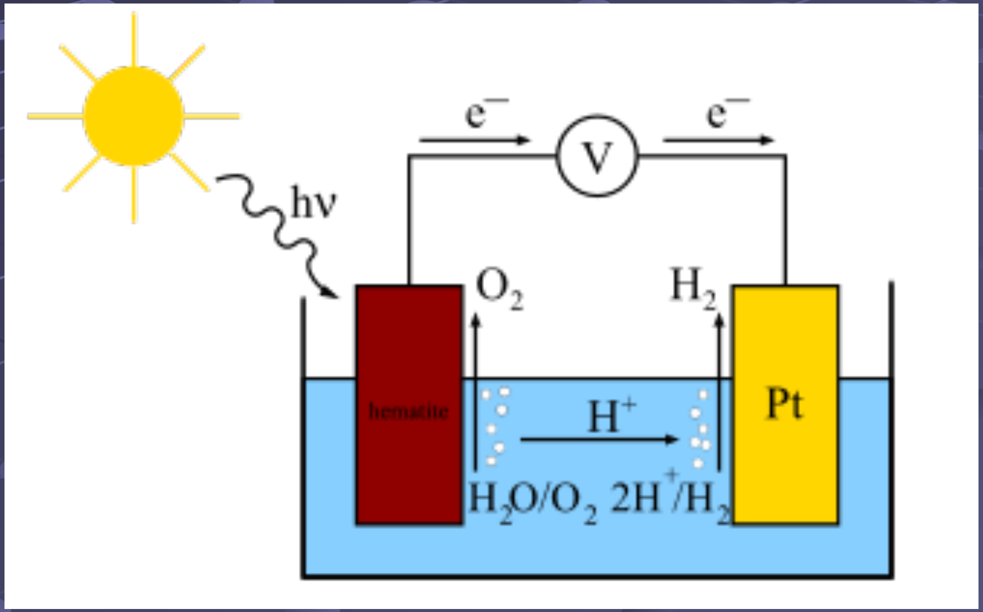
At the anode: $2H_2O \rightarrow O_{2,g} + 4H^+_{aq} + 4e^-$

At the cathode: $4H^+_{aq} + 4e^- \rightarrow 2H_{2,g}$

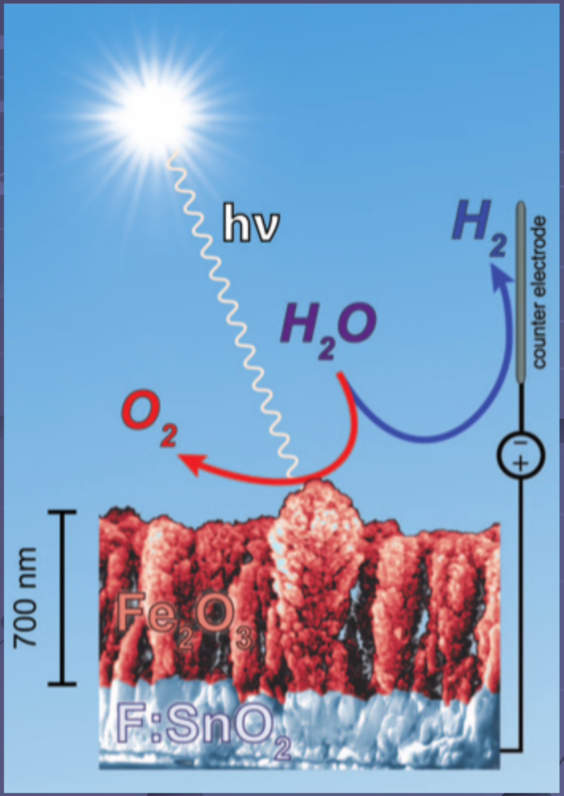


N. Seriani, J. Phys.: Condens. Mat. 29, 463002 (2017)

Photoelectrochemical cells for solar-fuel production

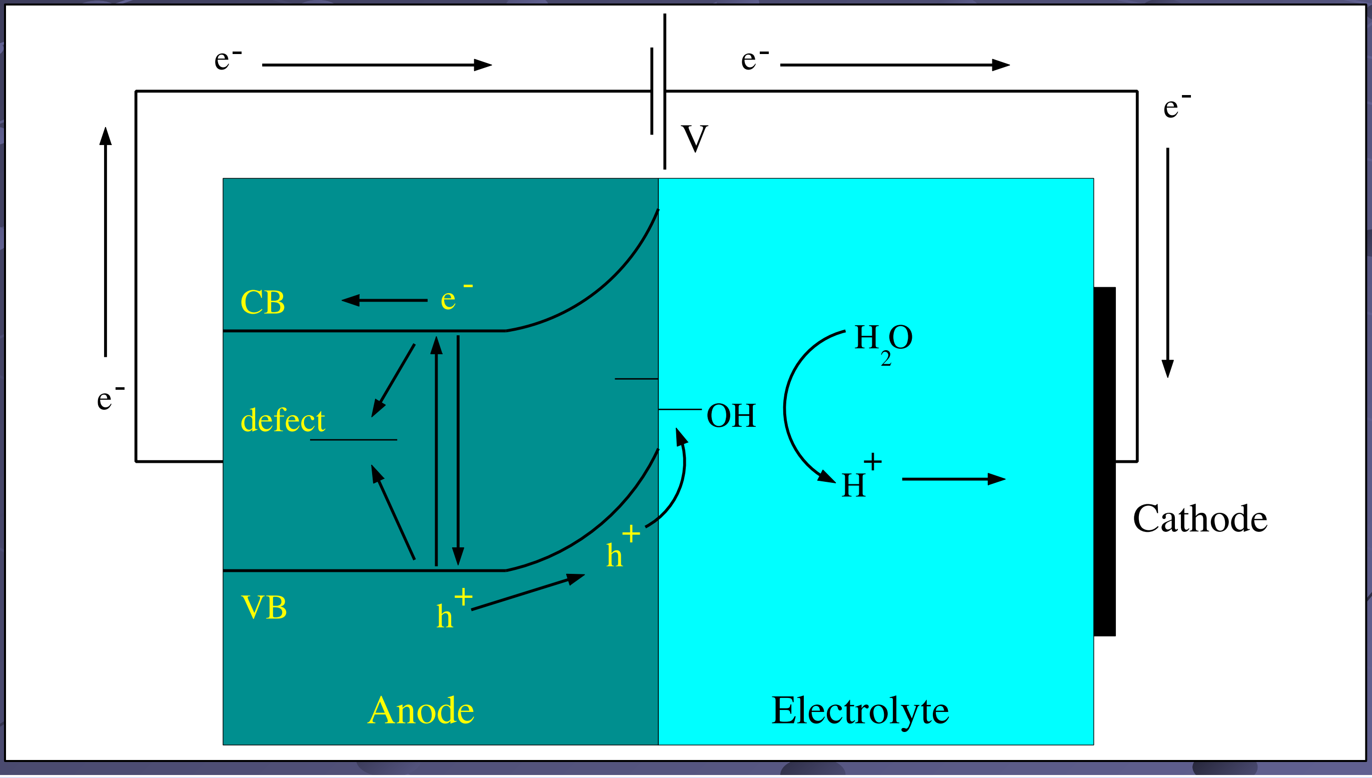


N. Seriani, J. Phys.: Condens. Mat. 29, 463002 (2017)



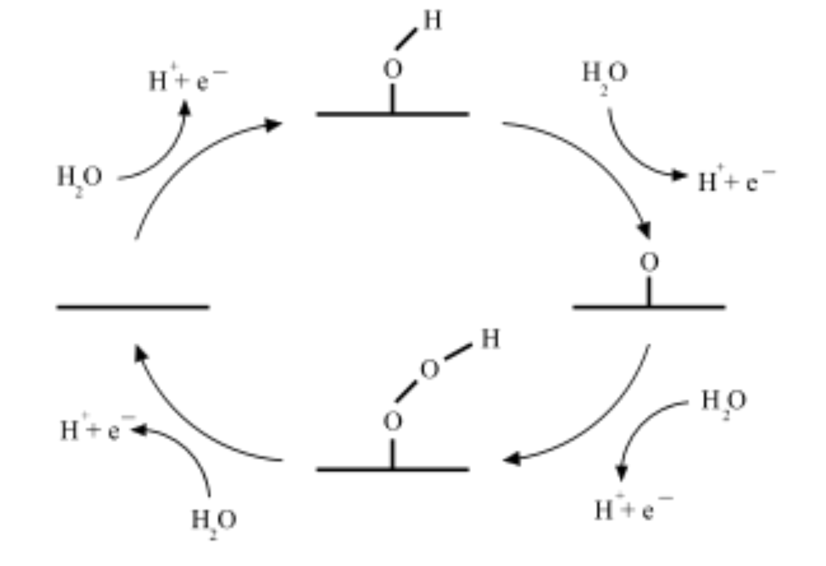
K. Sivula et al., ChemSusChem 4, 432 (2011)

Complex (photo-)physics and (photo-)chemistry

- Photoabsorption, recombination, charge separation, charge transfer, adsorption, proton-coupled electron transfer, ...
- 

Water oxidation at the photoanode

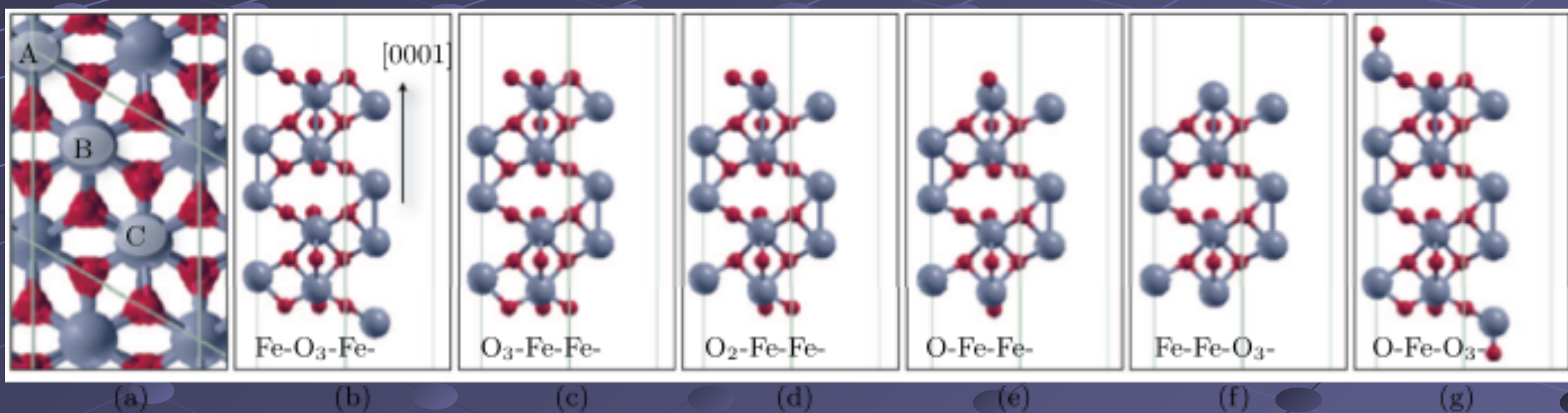
At the anode: $2H_2O \rightarrow O_{2,g} + 4H^+_{aq} + 4e^-$



At the surface of the photoanode, the reaction proceeds through 4 elementary steps (proton coupled electron transfers)

This takes place however in a complex environment

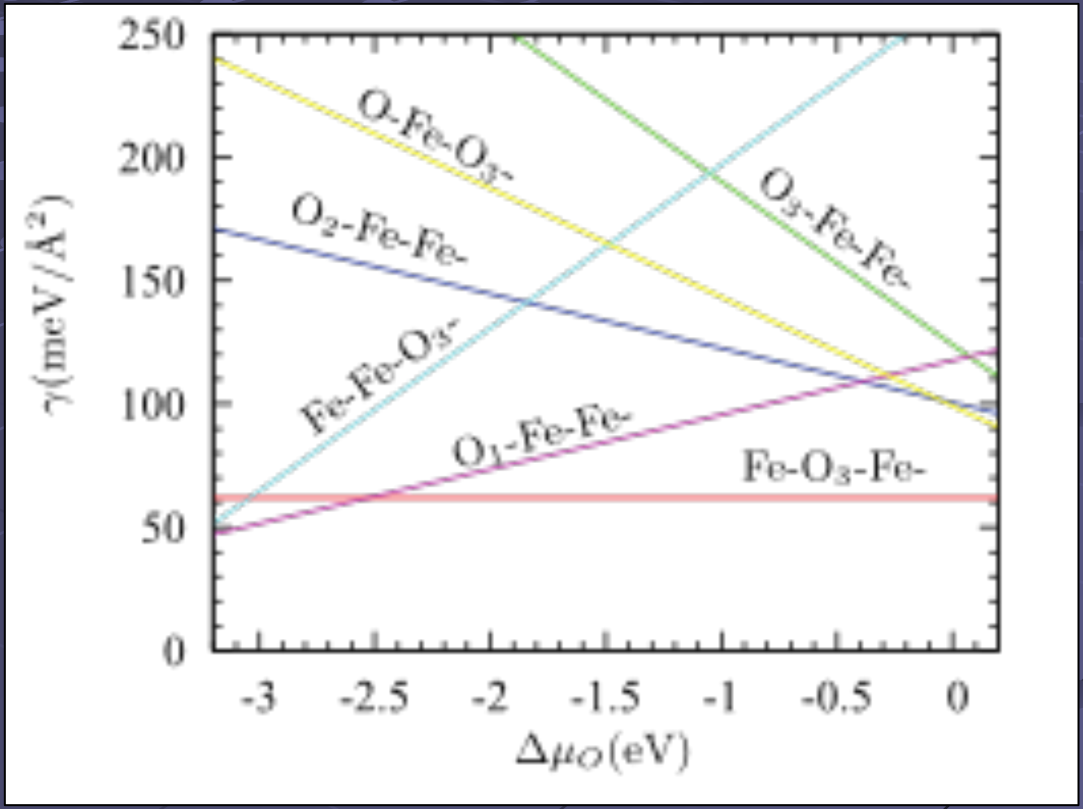
Thermodynamics of the surface process: 1. Surface termination of hematite α-Fe_2O_3 (0001)



Many surface terminations are possible

Nguyen, Seriani, Gebauer, J. Chem. Phys. 138, 194709 (2013)

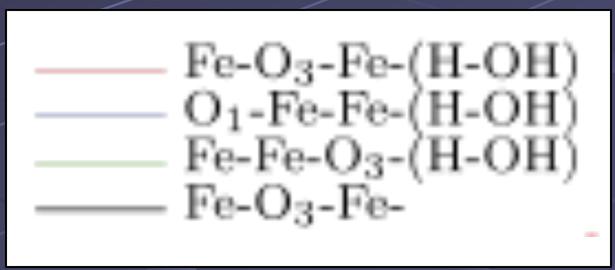
Terminations of hematite α-Fe_2O_3 (0001)

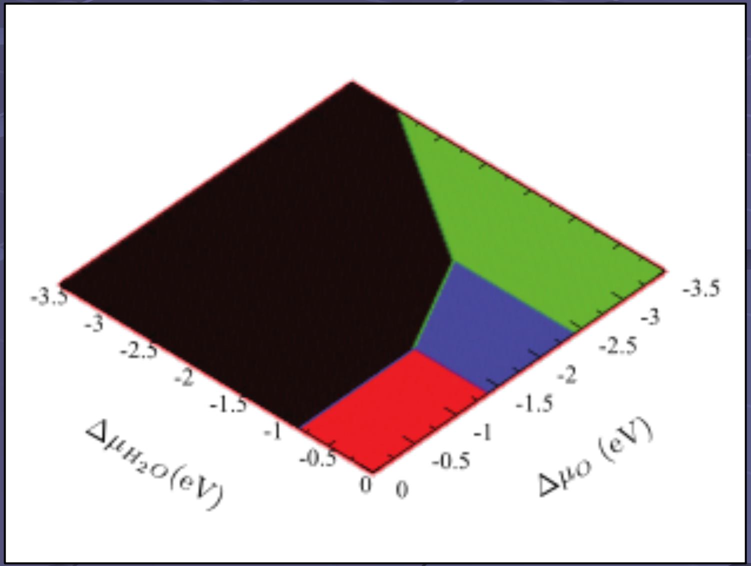


Surface free energies as function of the chemical potential of oxygen

Nguyen, Seriani, Gebauer, J. Chem. Phys. 138, 194709 (2013)

Hematite α-Fe_2O_3 (0001) in contact with water and oxygen

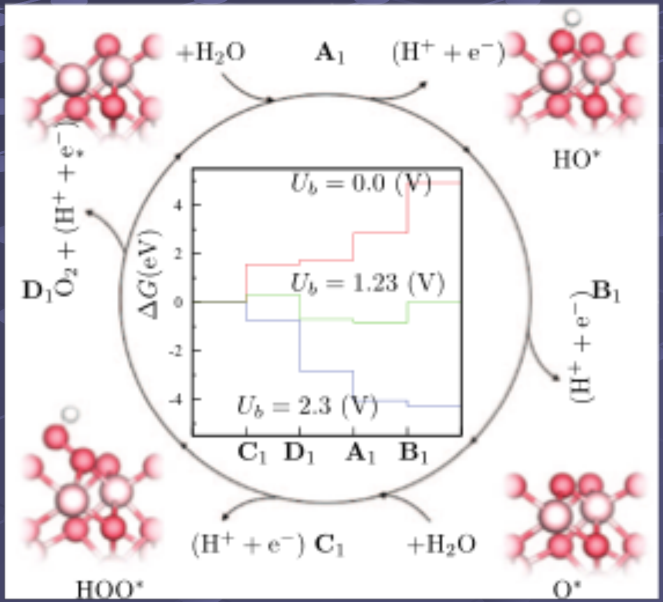




Surface free energies as function of the chemical potential of oxygen and of water

Nguyen, Seriani, Piccinin, Gebauer, J. Chem. Phys. 138, 194709 (2013)

Reactions at the interface: water splitting



Nguyen et al., J. Chem. Phys. 140, 064703 (2014)

Seriani, J. Phys.: Condens. Mat. 29, 463002 (2017)

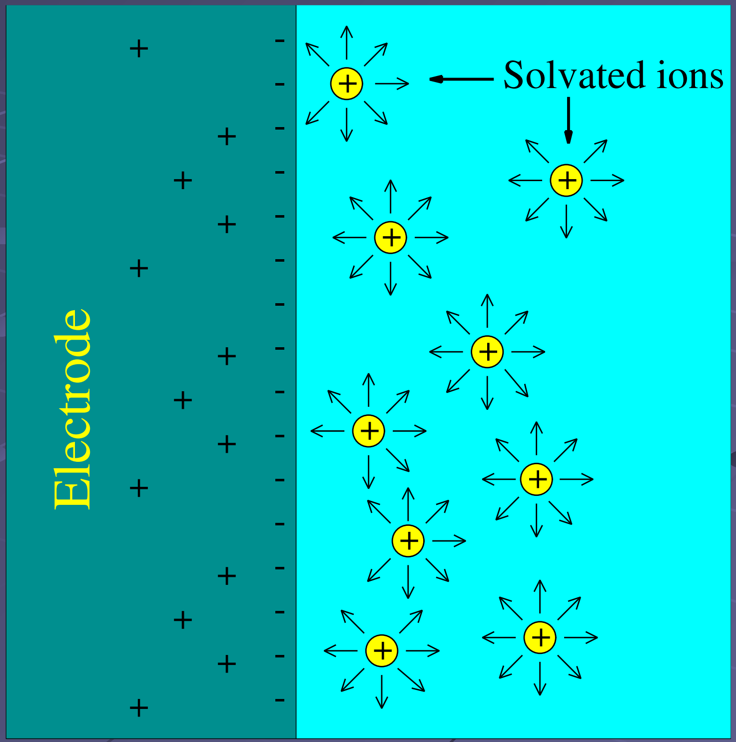
Crucial to take into account the photoelectrochemical conditions (in water, under illumination)

We find an overpotential of 0.8 V for photo-driven water oxidation, in fair agreement with experiments

The electrochemical interface

A crucial role is played by the electrochemical interface, specially for charge dynamics:

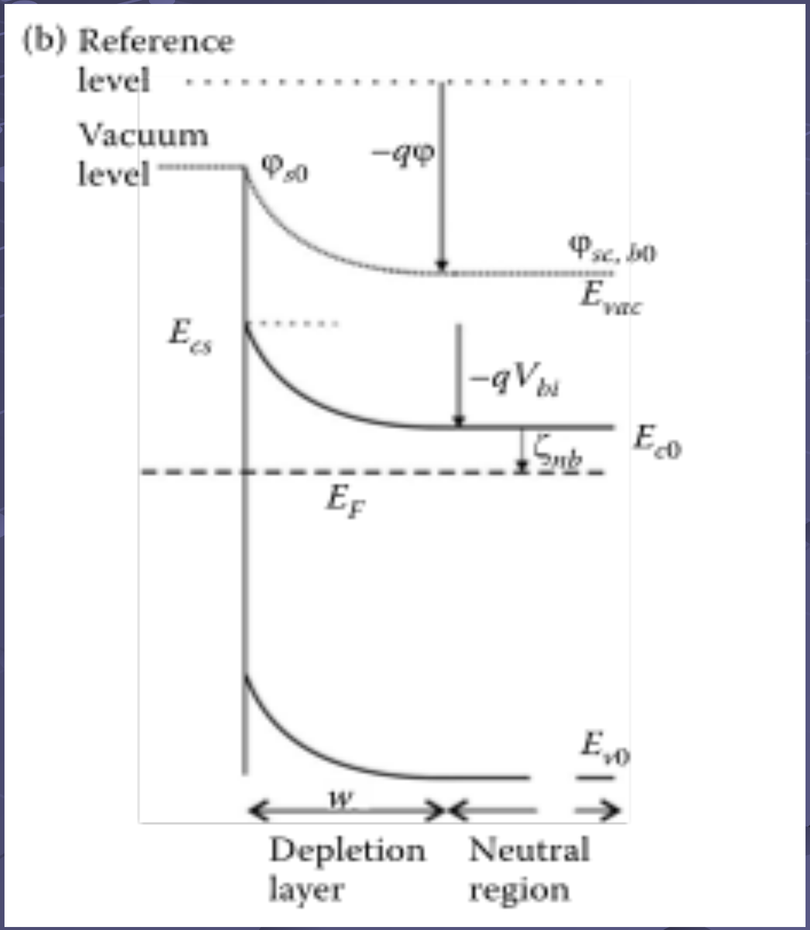
space charge layer,
double layer,
ions,
electric field,
illumination,
hole transfer



Goal is to take a second look (with new tools) at old models** of the interface and of the double layer

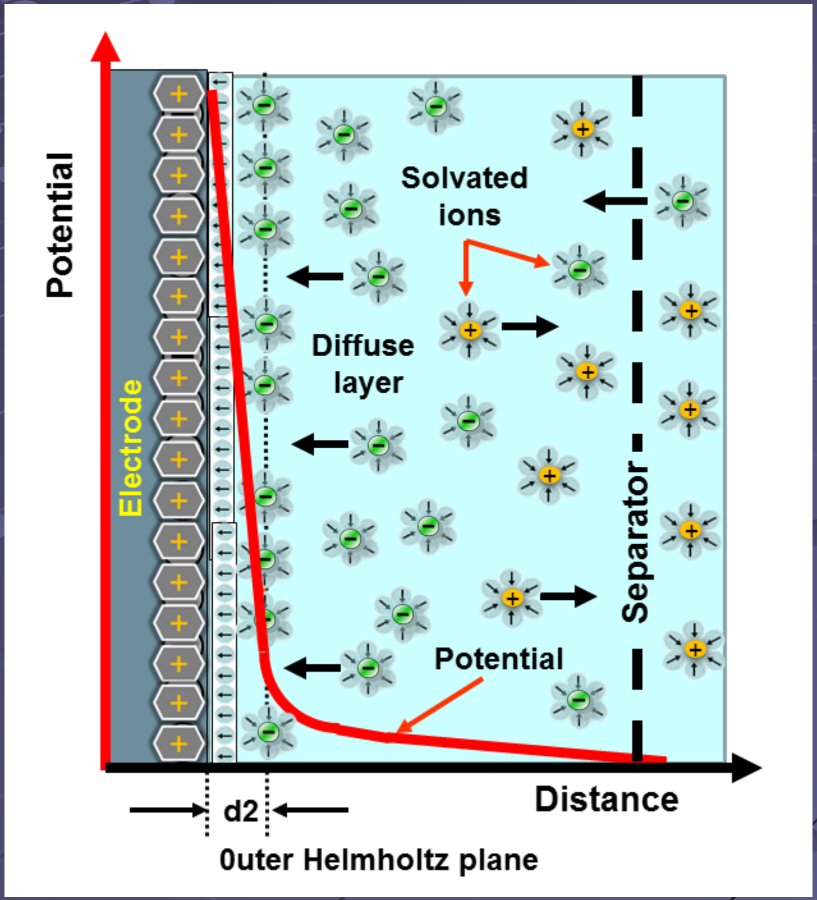
** Stern, Z. Electrochem., 30, 508 (1924)
** Gouy, J. Phys. 9, 457 (1910)

On the semiconductor side: the space charge layer



J. Bisquert, Nanostructured energy devices (CRC Press)

On the electrolyte side: the double layer



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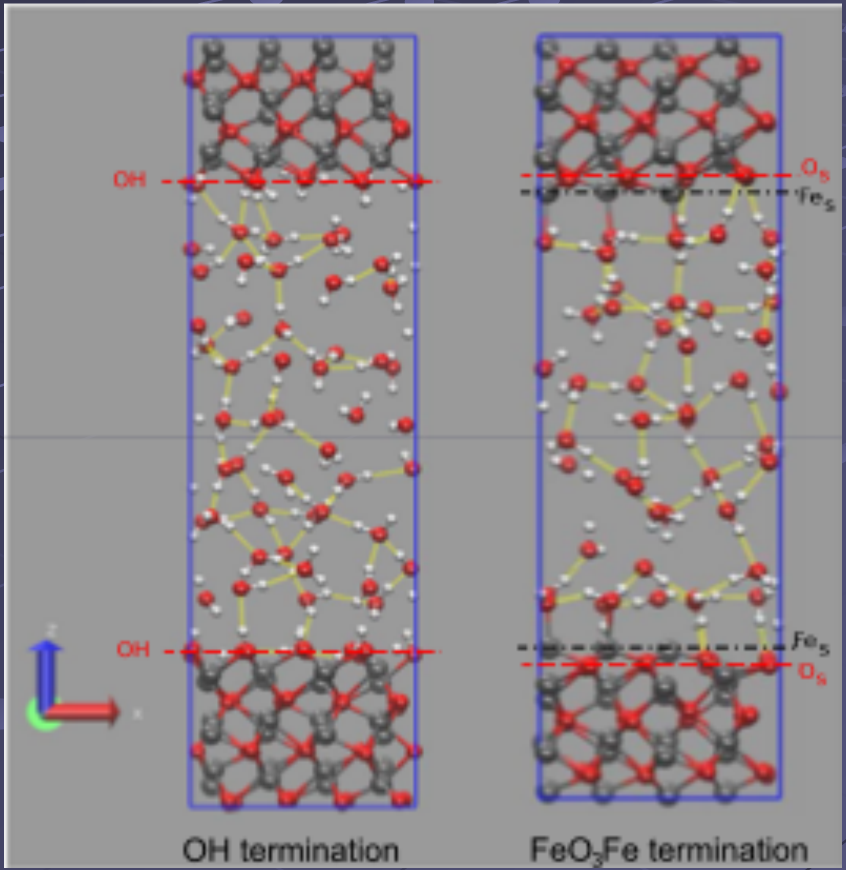
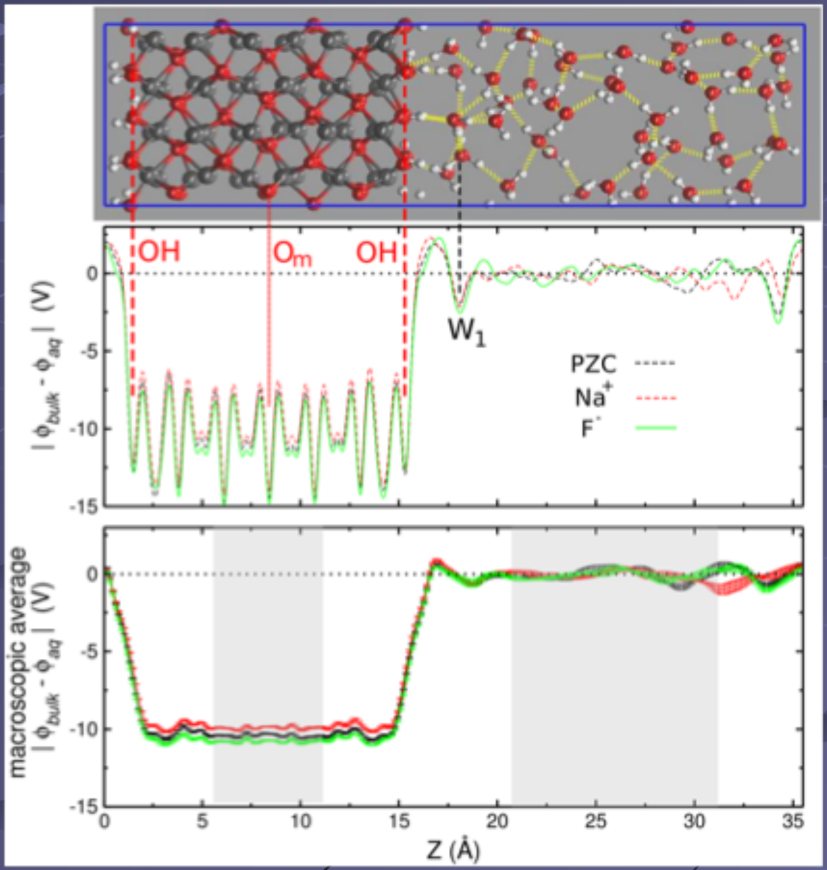
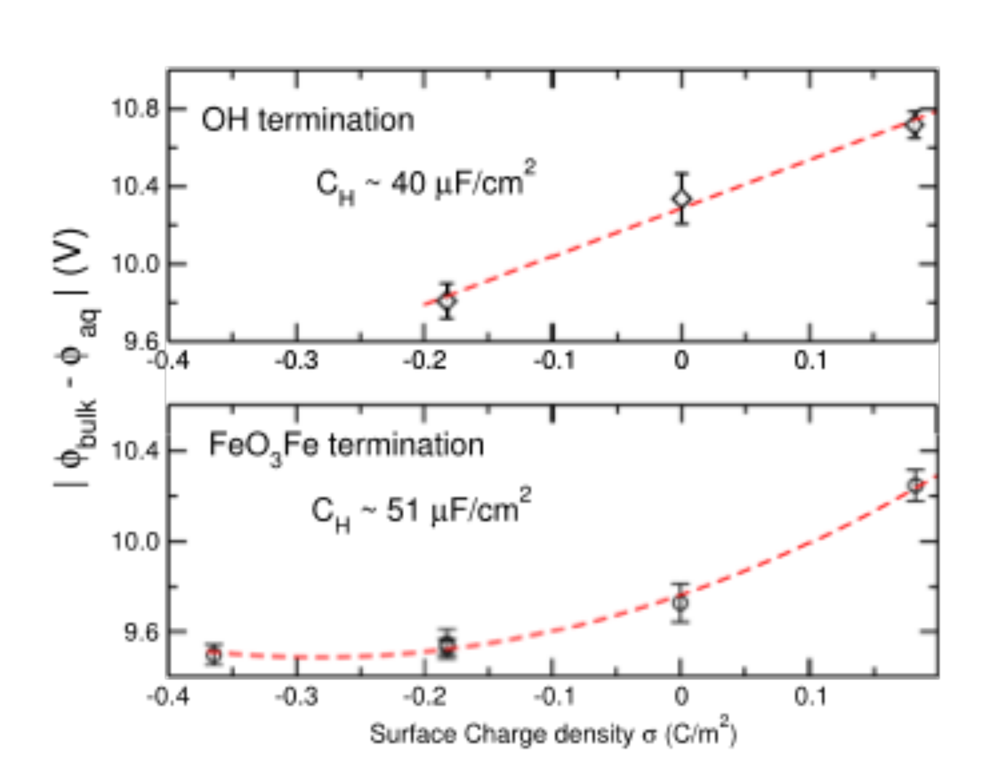
The double layer at the (0001) hematite surface





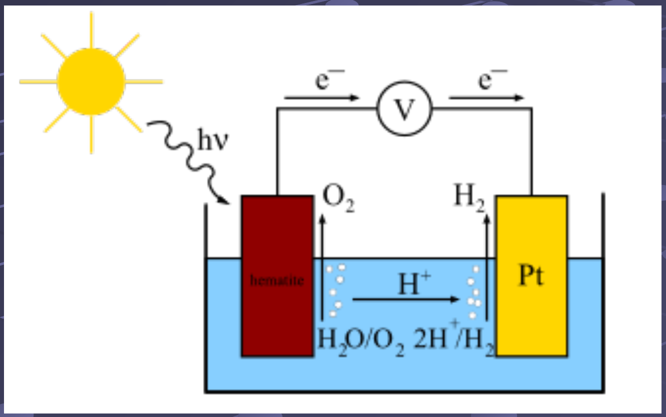
Ulman, Poli, Seriani, Piccinin, Gebauer,
J. Chem. Phys. 150, 041707 (2019)

The capacitance of the double layer

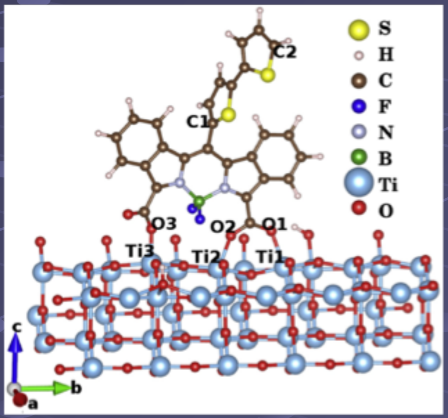


Ulman, Poli, Seriani, Piccinin, Gebauer,
J. Chem. Phys. 150, 041707 (2019)

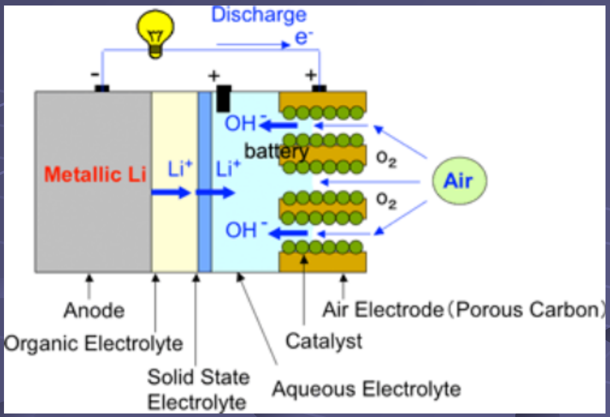
The road travelled...



Photocatalysis
for solar fuels



Photovoltaics



Batteries

In some cases we are able to understand some effects of the environment on properties and functionality:

-) simplified models of environment

-) only some properties: photoabsorption, thermodynamics of reactions

Open scientific issues

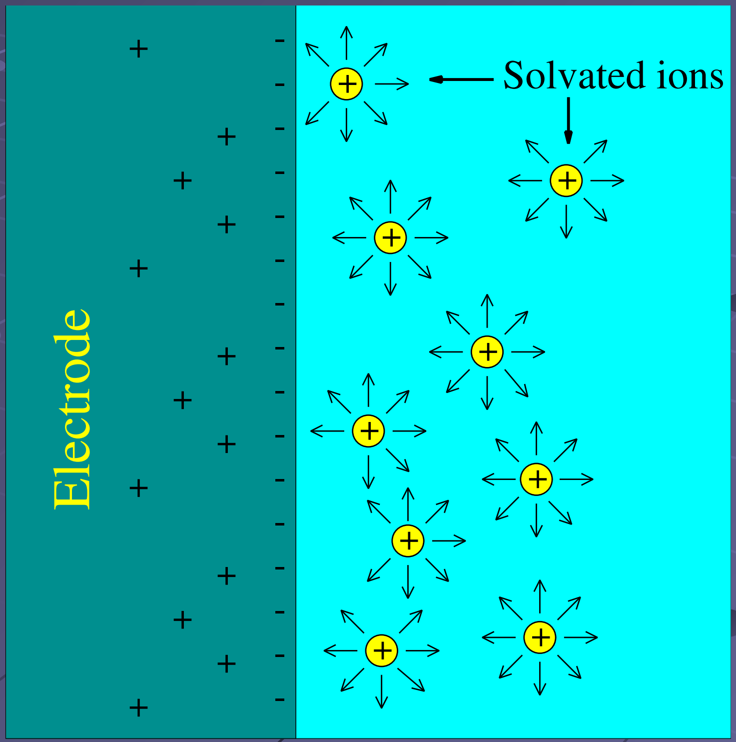
Which species are involved in the rate-limiting charge transfer?

How does their atomic configuration and dynamics depend on the structure of the interface?

Is it possible to engineer the interface to circumvent or change the nature of the rate-limiting step?

Interaction with experimentalists will be crucial

Use of advanced computational methods will be essential



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