Mastering the electrochemical interface
From the electronic structure of solids to the double later structure

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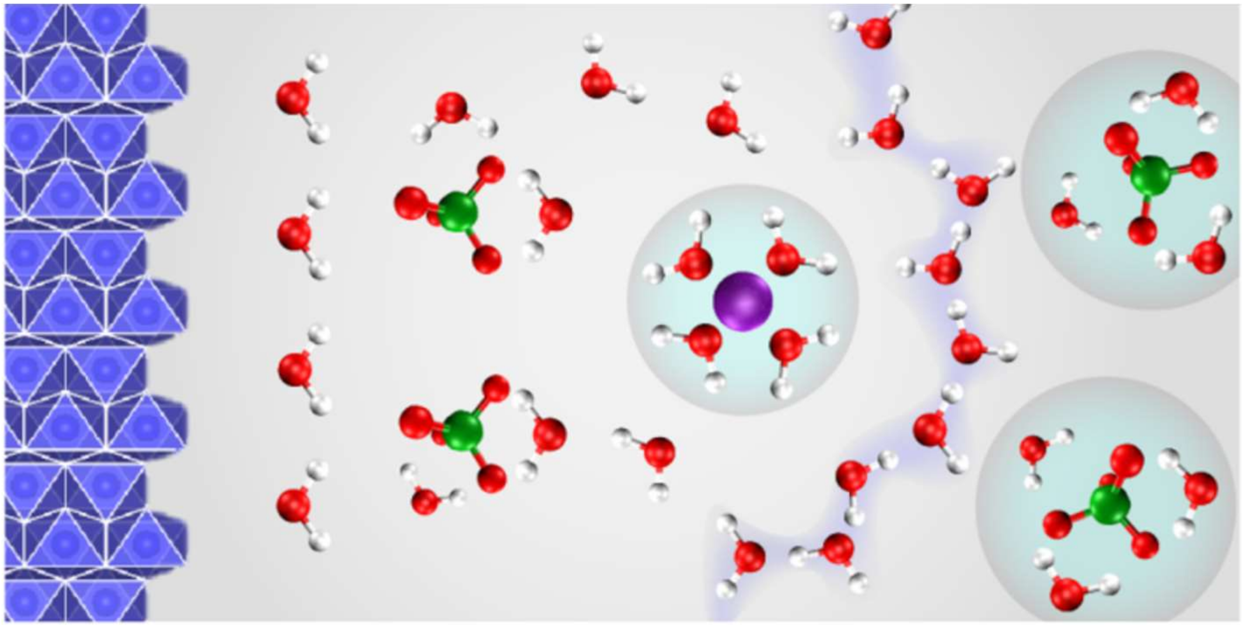
Summer School Moscow – 17th September 2019

The complexity of the solid/liquid interface

Solid
Bulk vs surface

Double layer
Reactivity

Liquid
Structure/chemistry of the electrolyte



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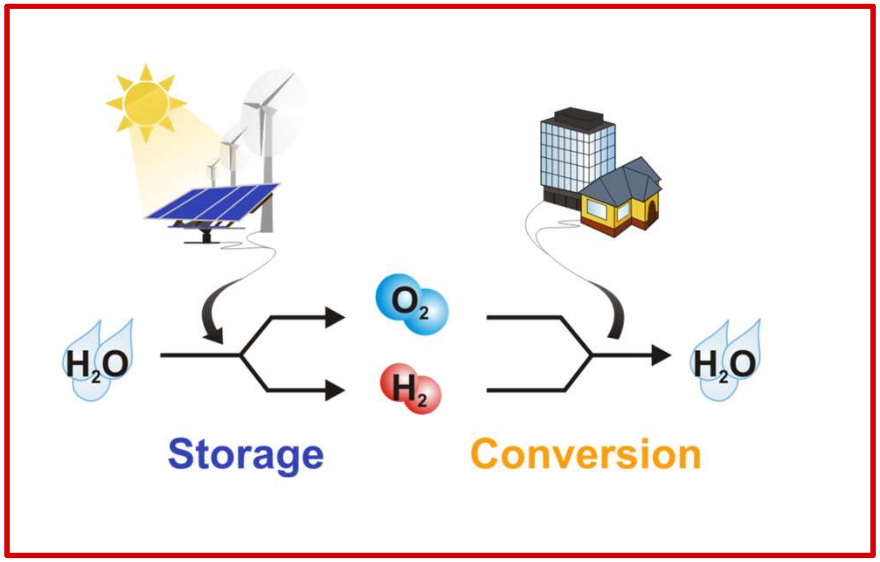
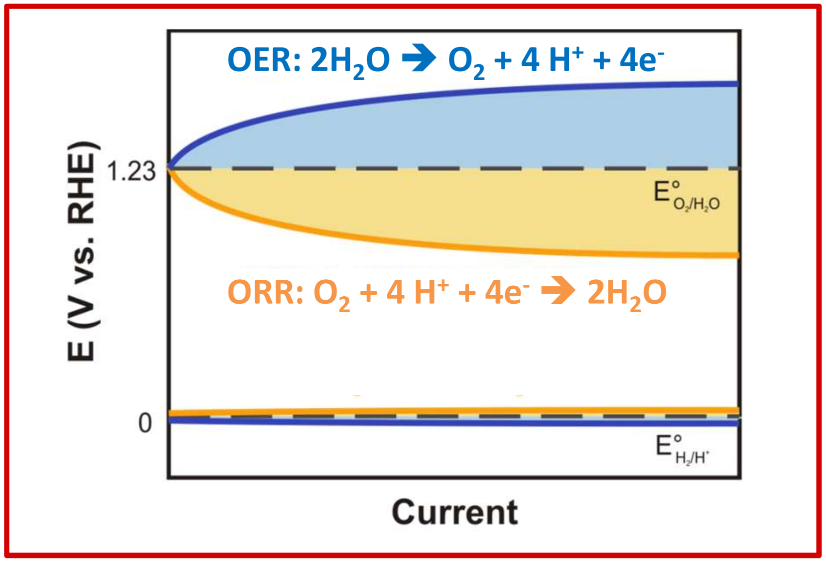
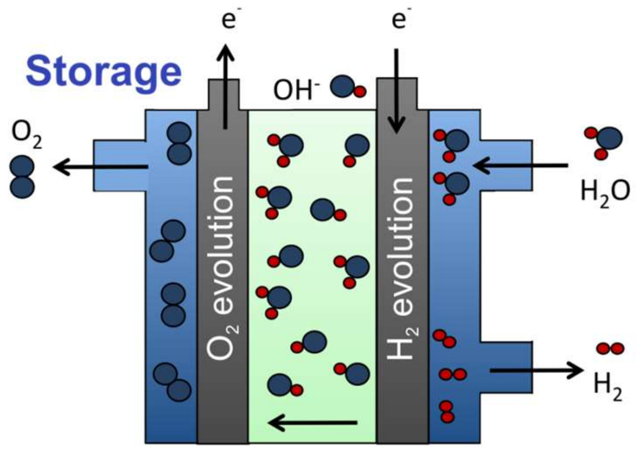
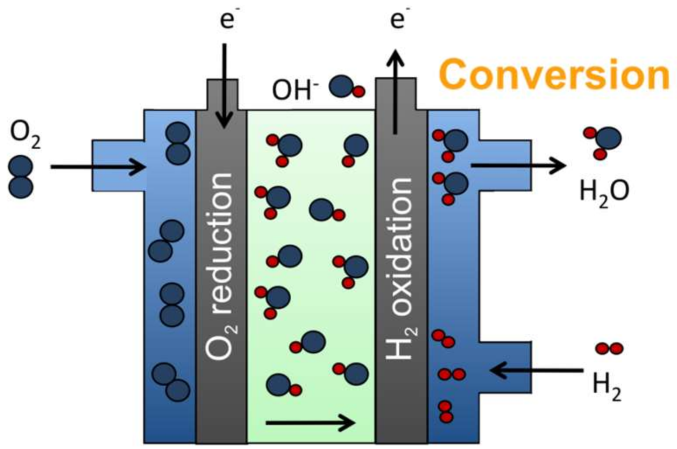
Water electrolyser / fuel cell for energy storage and conversion









Hong, Risch, Stoerzinger, Grimaud, Suntivich and Shao-Horn, EES 2015

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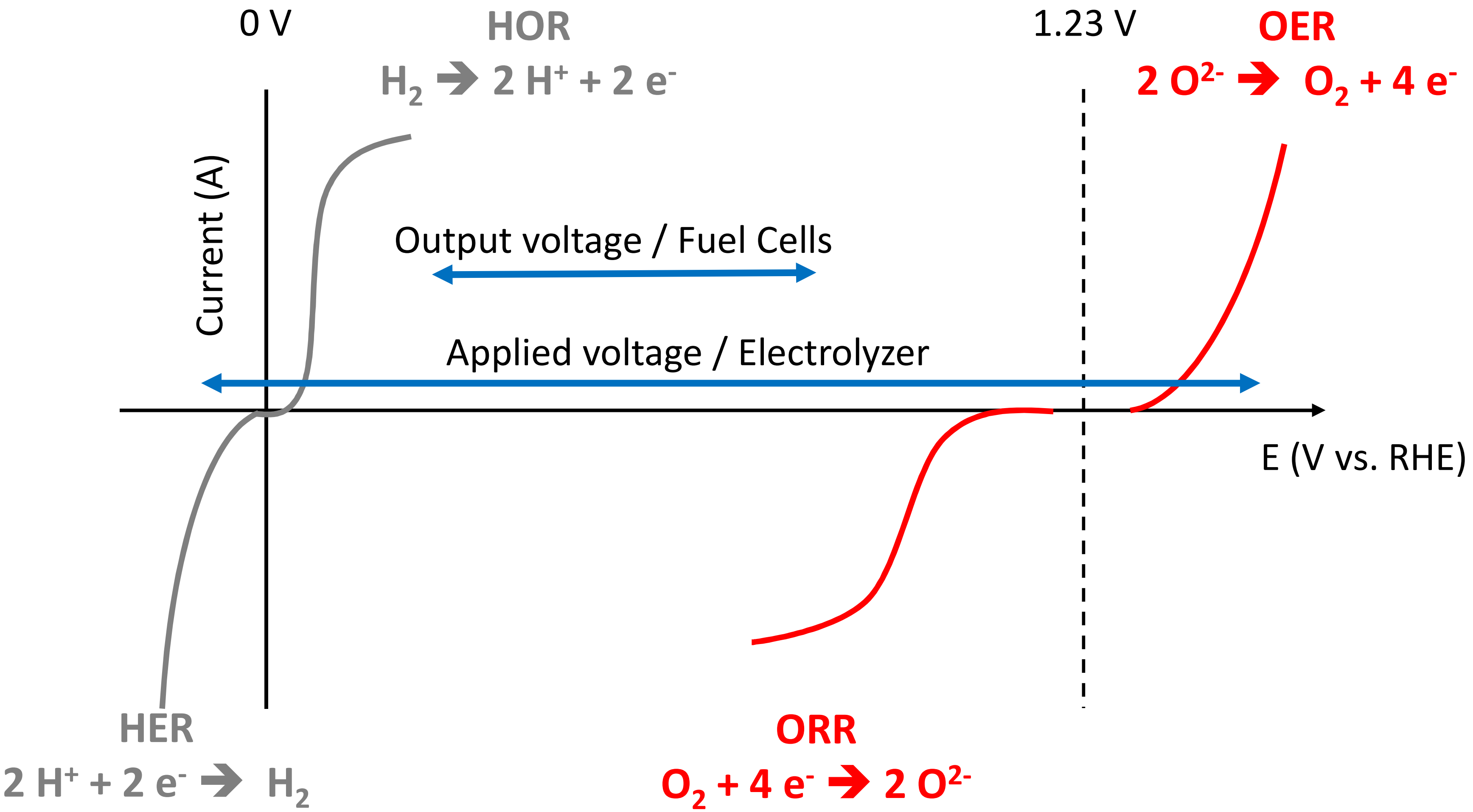
Oxygen and hydrogen reactions for Energy Storage



0 V

HOR

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

1.23 V

OER

$2\,O^{2-} \rightarrow O_2 + 4\,e^-$

Current (A)

Output voltage / Fuel Cells

Applied voltage / Electrolyzer

E (V vs. RHE)

HER

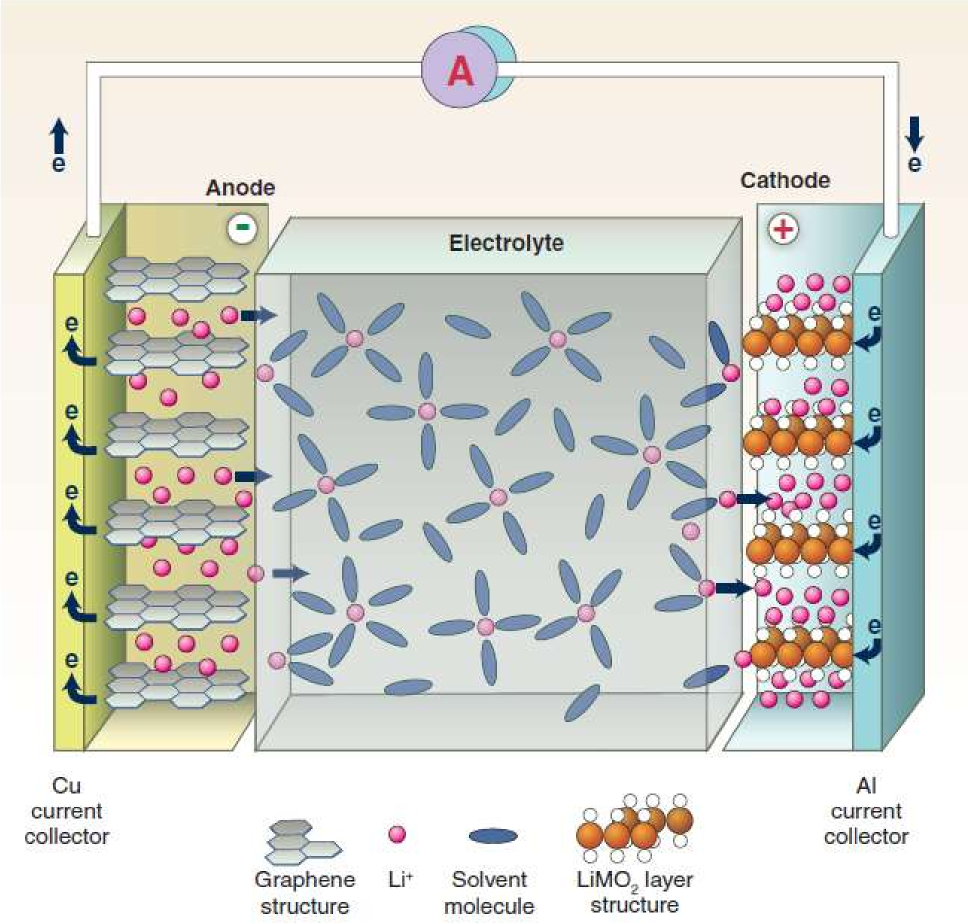
$2\,H^+ + 2\,e^- \rightarrow H_2$

ORR

$O_2 + 4\,e^- \rightarrow 2\,O^{2-}$

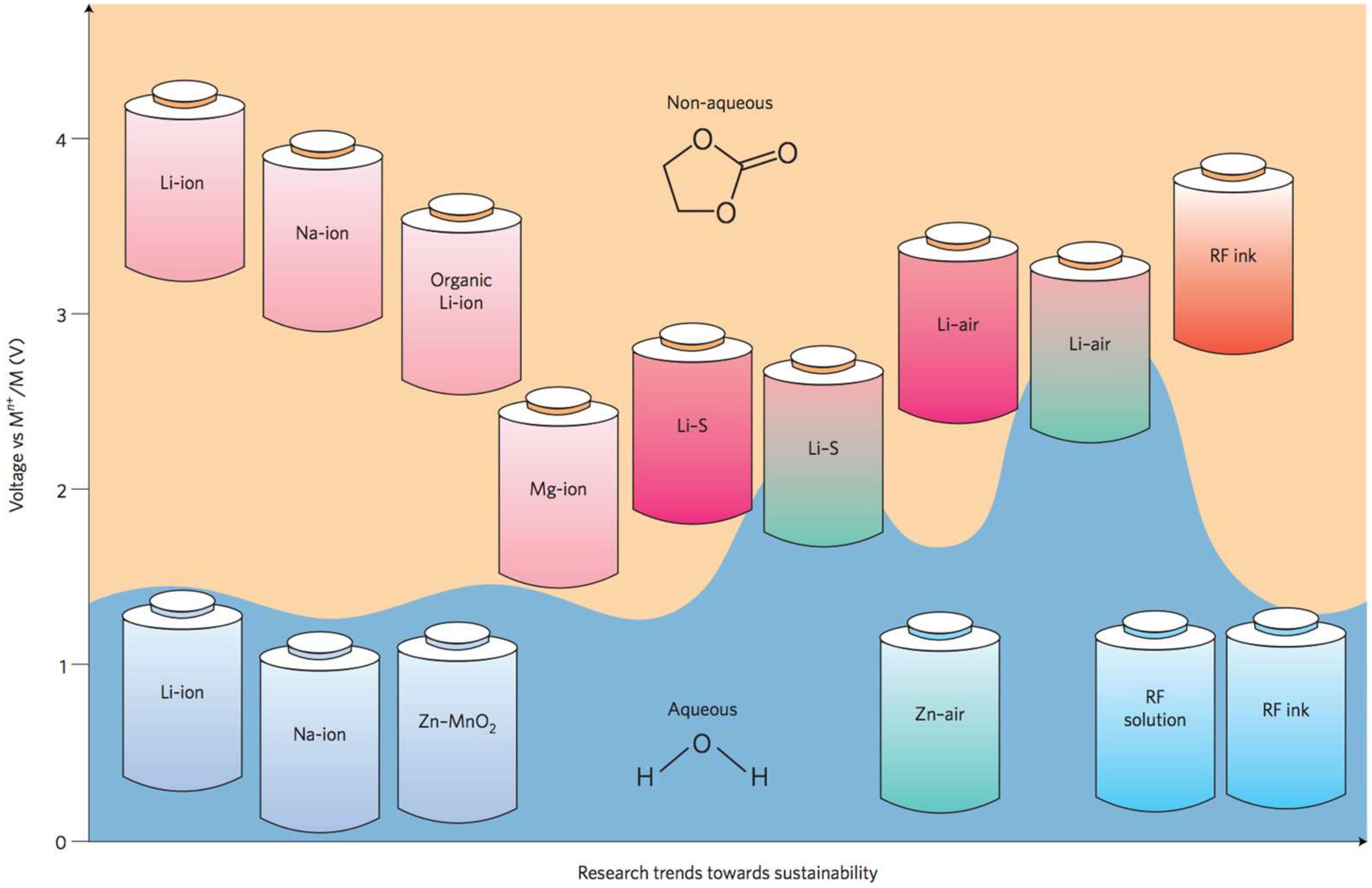
Interface at the heart of electrochemical energy storage

Li-ion batteries ➔ using the electrolyte/additive decomposition to form an SEI



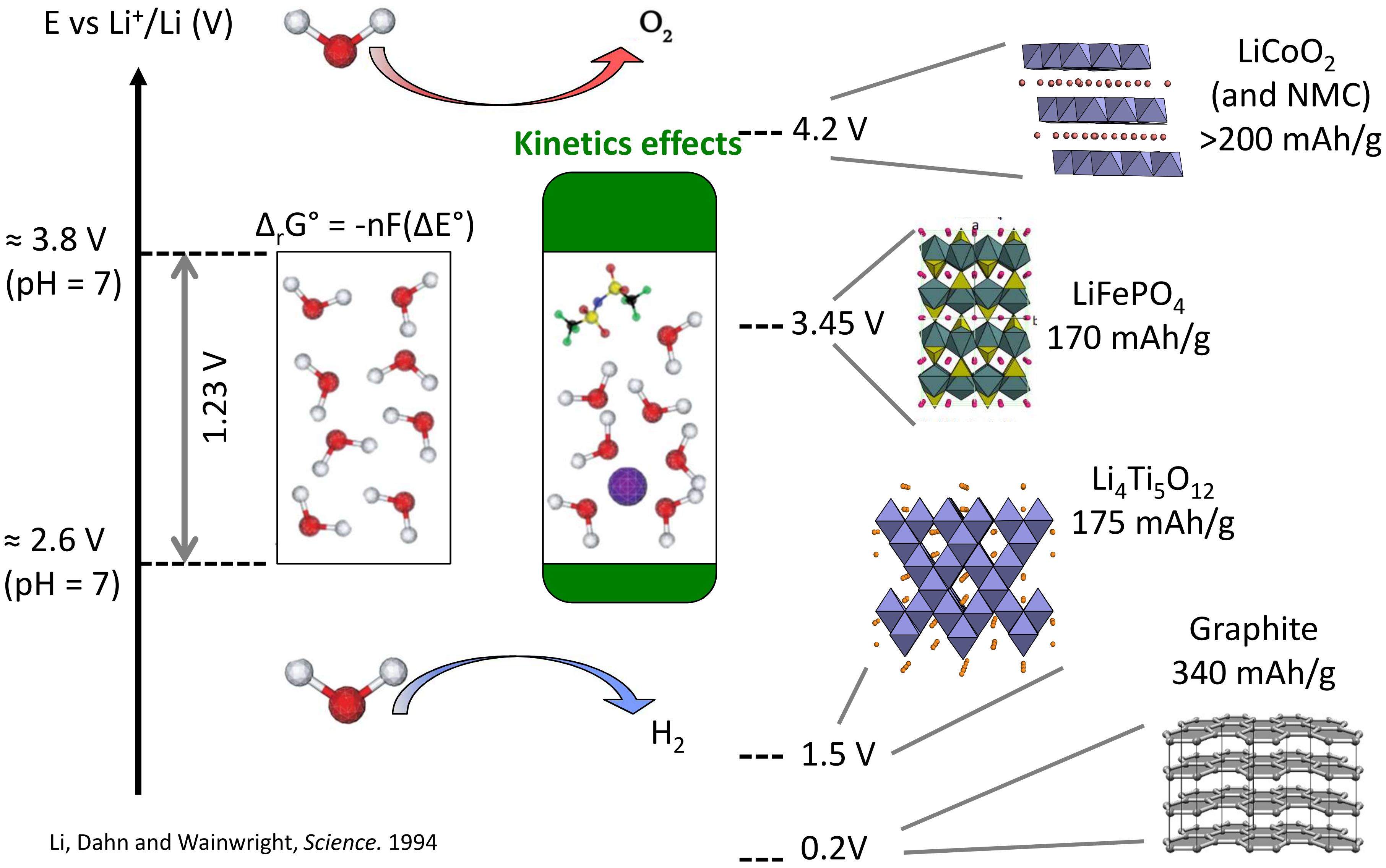
Towards the development of aqueous batteries

✓ **Replacing flammable and toxic organic solvents by aqueous-based systems**



Grey and Tarascon, *Nature Mater.* 2016

Increasing the voltage window of aqueous electrolytes



E vs Li^+/Li (V)

O_2

Kinetics effects

≈ 3.8 V
(pH = 7)

≈ 2.6 V
(pH = 7)

1.23 V

$\Delta_r G° = -nF(\Delta E°)$

H_2

--- 4.2 V

--- 3.45 V

--- 1.5 V

--- 0.2V

$LiCoO_2$
(and NMC)
>200 mAh/g

$LiFePO_4$
170 mAh/g

$Li_4Ti_5O_{12}$
175 mAh/g

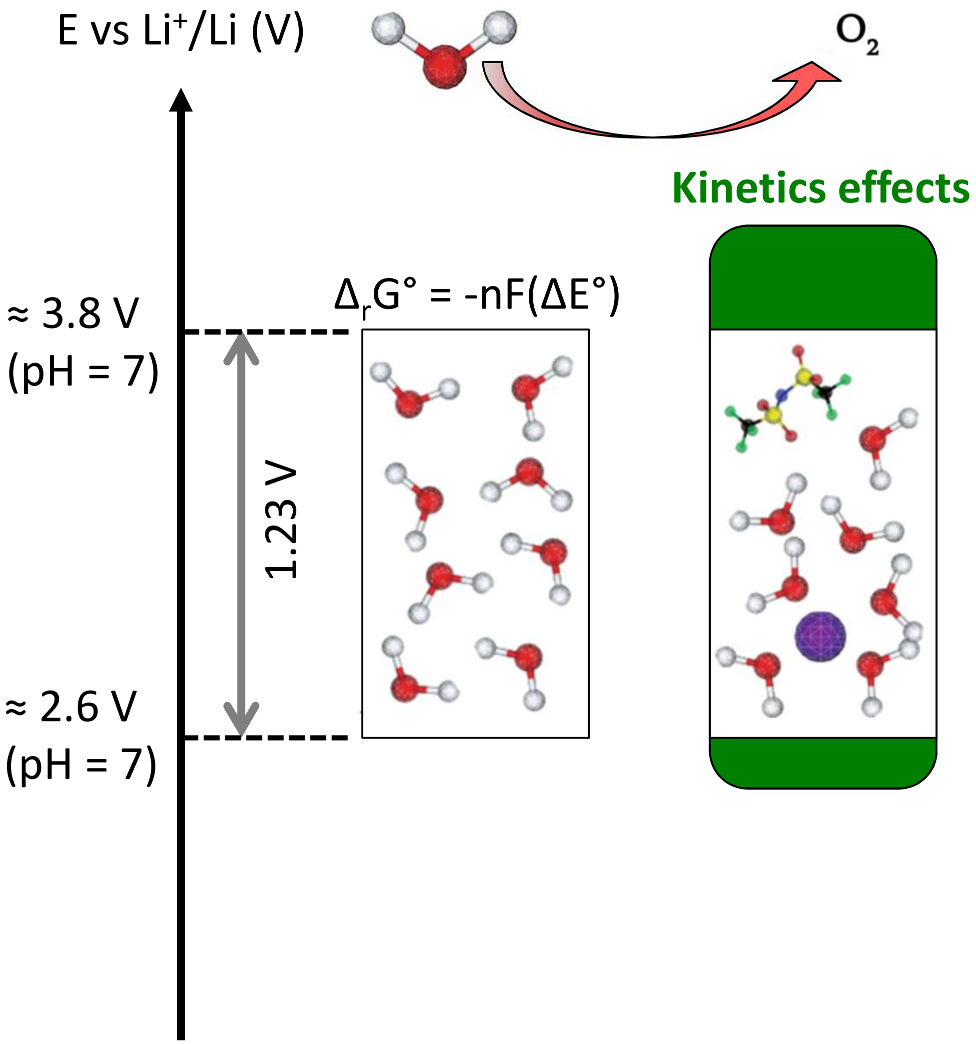
Graphite
340 mAh/g

Li, Dahn and Wainwright, *Science.* 1994

Understand the water oxidation/reduction reactions kinetics to either boost them or stop them

Can we develop predictive « descriptors » to capture these kinetics ?

Oxygen evolution reaction



E vs Li$^+$/Li (V)

O_2

Kinetics effects

$\Delta_r G° = -nF(\Delta E°)$

≈ 3.8 V
(pH = 7)

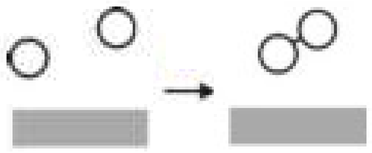
1.23 V

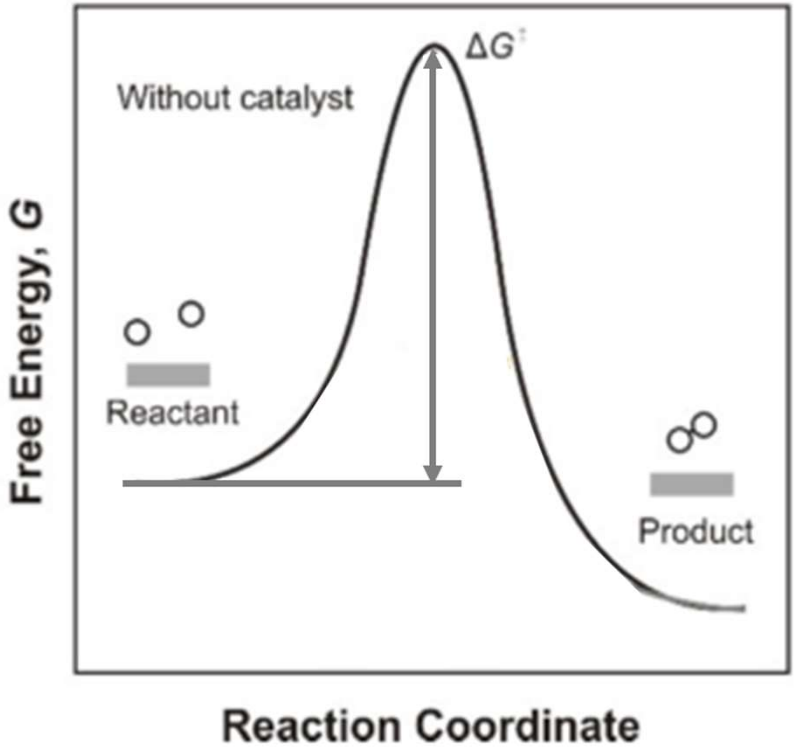
≈ 2.6 V
(pH = 7)

$$2\ H_2O = O_{2(g)} + 4\ H^+ + 4\ e^-$$

The use of electrocatalysts

Reaction rate α $\exp(-\frac{\Delta G^{\ddagger}}{RT})$





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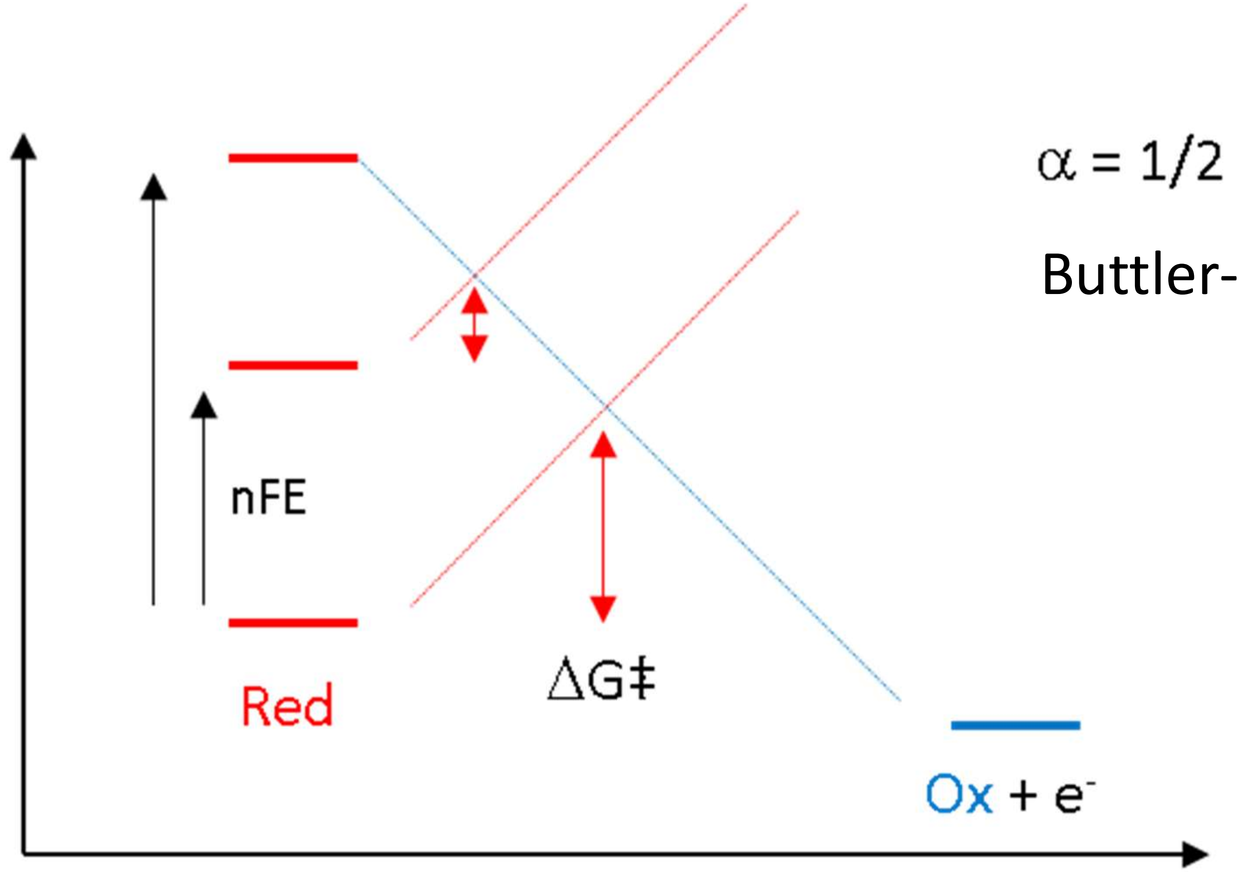
How do we achieve this reaction?

Simple case of an inert electrode

e^-

Red

Ox + e^-



$\alpha = 1/2$

Buttler-Volmer

? How do we achieve this reaction?

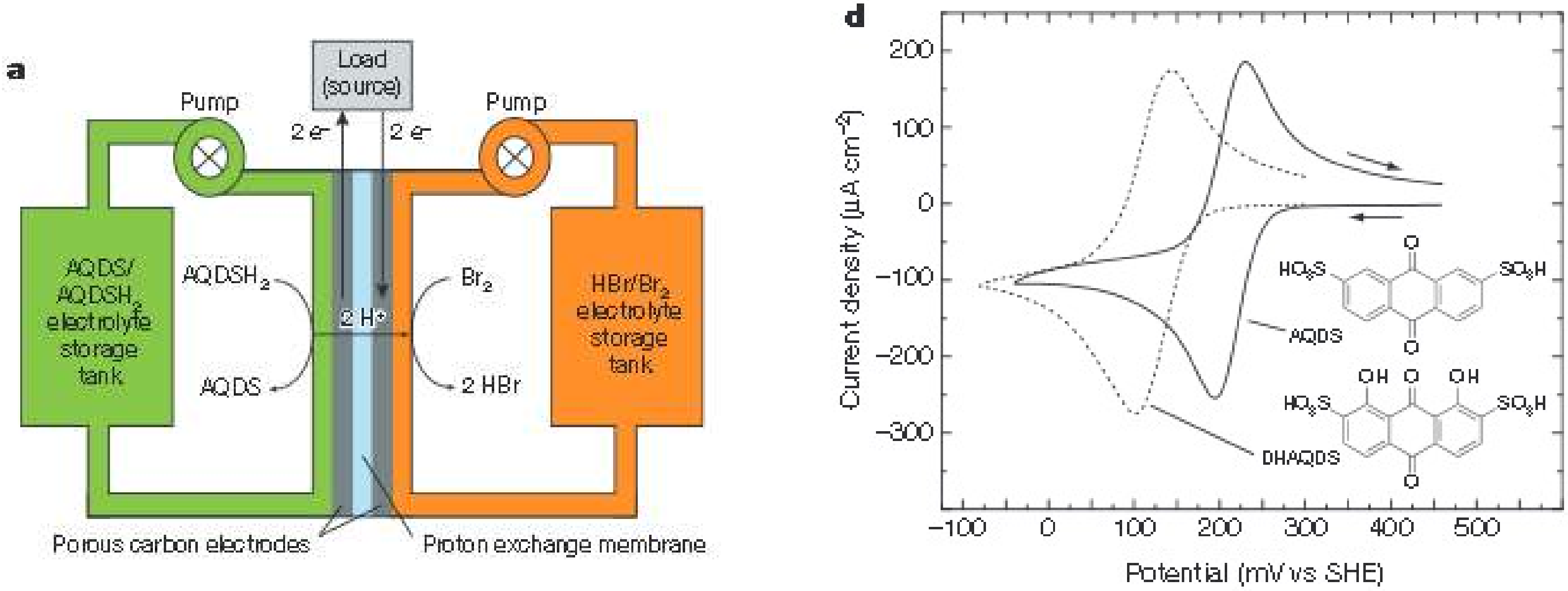
Simple case of an inert electrode

e^-

Red

Ox + e^-

<u>Exemple</u>: Fast redox couple such as redox mediator
Androquinone aqueous flow battery



Huskinson, … Aziz et al, Nature 2014

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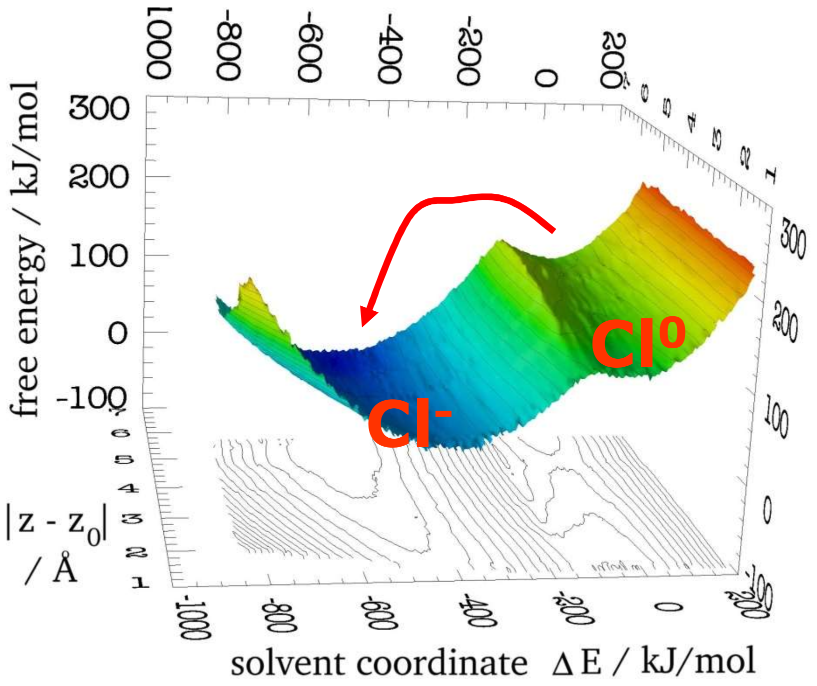
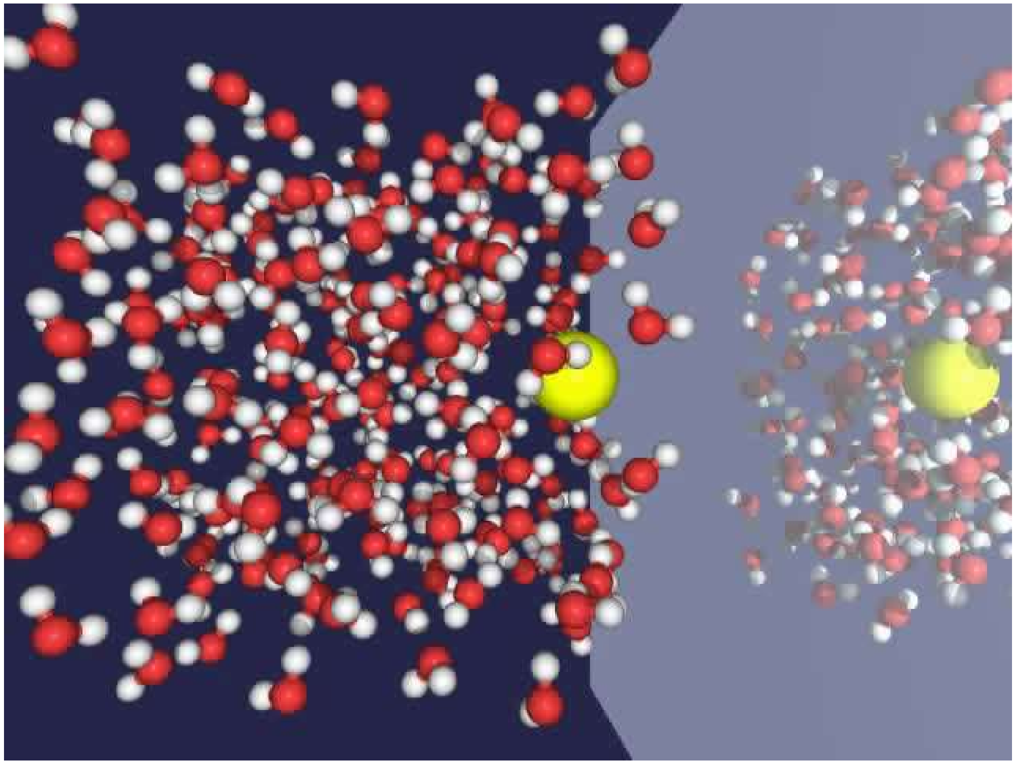
Case of multiple electron transfer reactions

Single electron transfer ➔ no intermediate





$Cl^0 + e^- \Leftrightarrow Cl^-$

C.Hartnig, M.T.M.Koper, J.Am.Chem.Soc. 125 (2003) 9840

?

Case of multiple electron transfer reactions

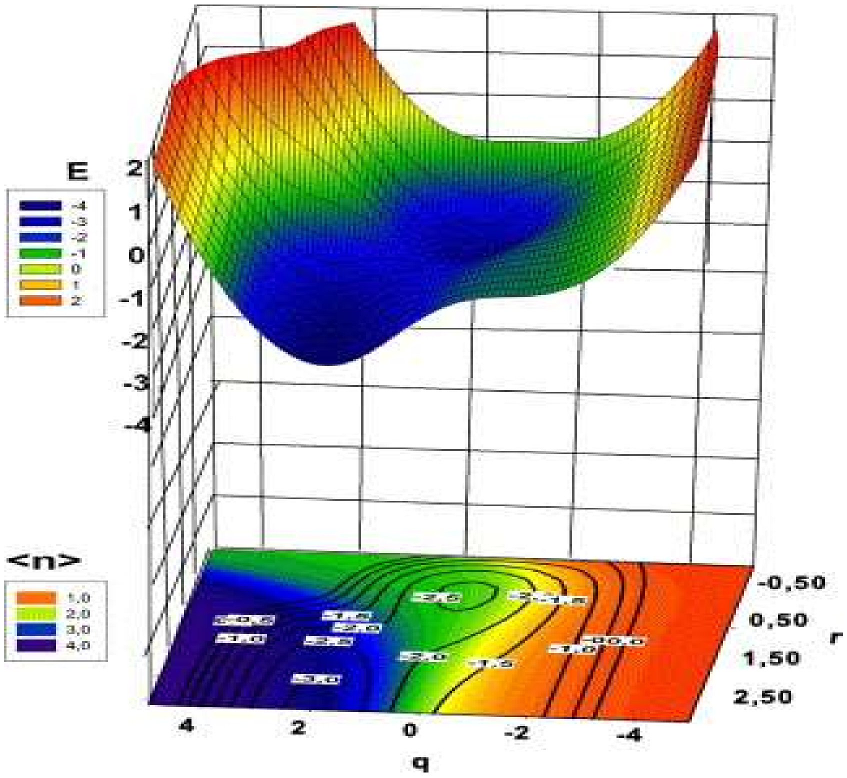
Hydrogen evolution reaction $2H^+ + e^- \rightarrow H_2$

$* + H^+ + e^- \rightarrow *H$

then

$*H + H^+ + e^- \rightarrow H_2$

Or $2\ *H \rightarrow H_2$

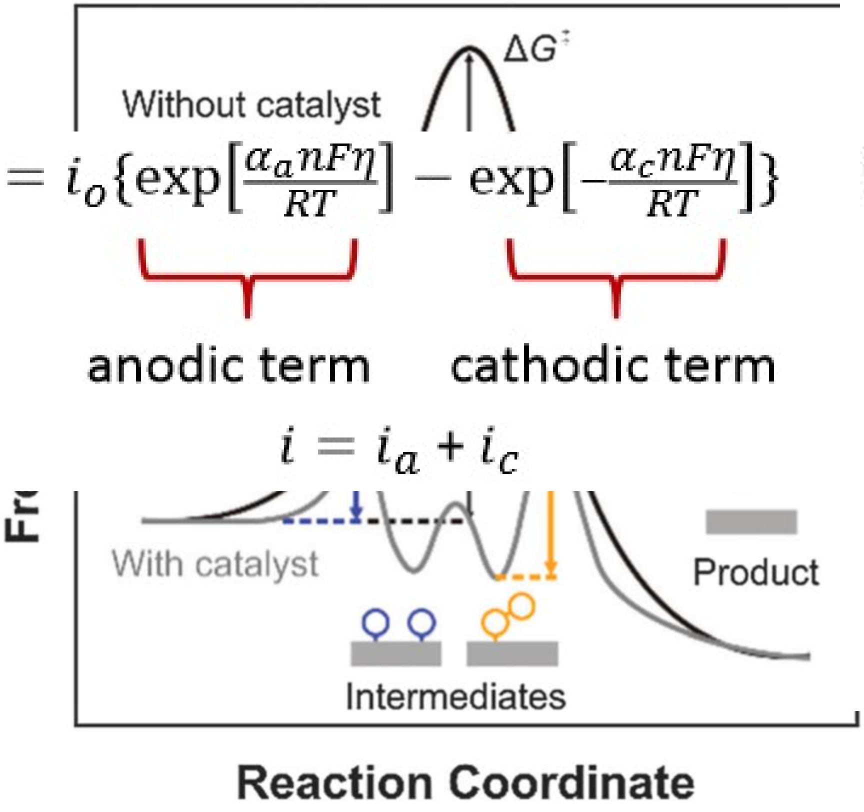


E.Santos, M.T.M.Koper, W.Schmickler, Chem.Phys. 344 (2008) 195

The use of electrocatalysts

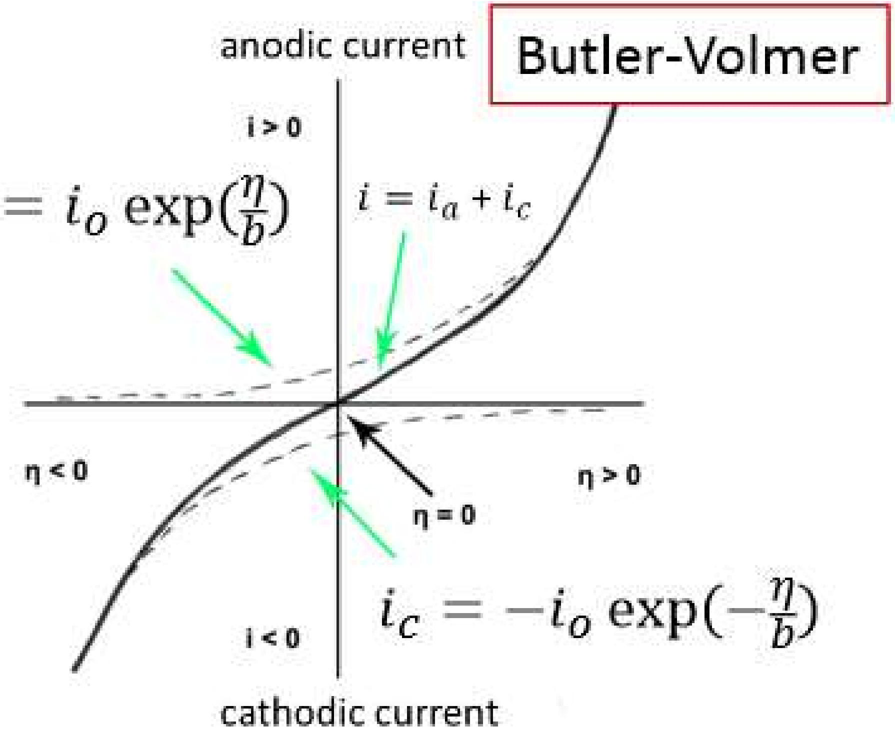
Reaction rate $\alpha \exp(-\frac{\Delta G^{\ddagger}}{RT})$

Linear Free Energy Relationship
The kinetics scale with a thermodynamic factor



$$i = i_o\{\underbrace{\exp[\frac{\alpha_a nF\eta}{RT}]}_{\text{anodic term}} - \underbrace{\exp[-\frac{\alpha_c nF\eta}{RT}]}_{\text{cathodic term}}\}$$

$$i = i_a + i_c$$



$$i_a = i_o \exp(\frac{\eta}{b})$$

$$i_c = -i_o \exp(-\frac{\eta}{b})$$

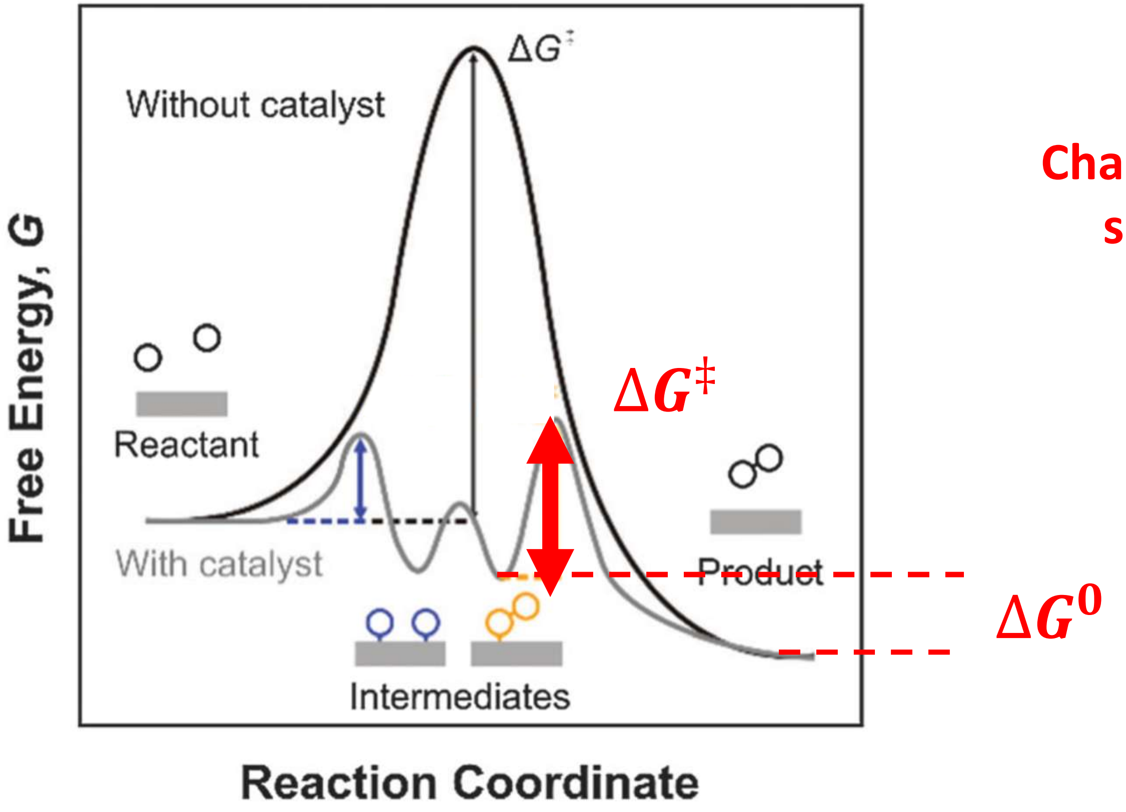
Hong, Risch, Stoerzinger, Grimaud, Suntivich and Shao-Horn, EES 2015

The use of electrocatalysts

Reaction rate $\alpha \exp(-\frac{\Delta G^{\ddagger}}{RT})$

Linear Free Energy Relationship
One case: Bronsted-Evans-Polanyi

$$\exp(-\frac{\Delta G^{0}}{RT}) \ \alpha \ \exp(-\frac{\Delta G^{\ddagger}}{RT})$$



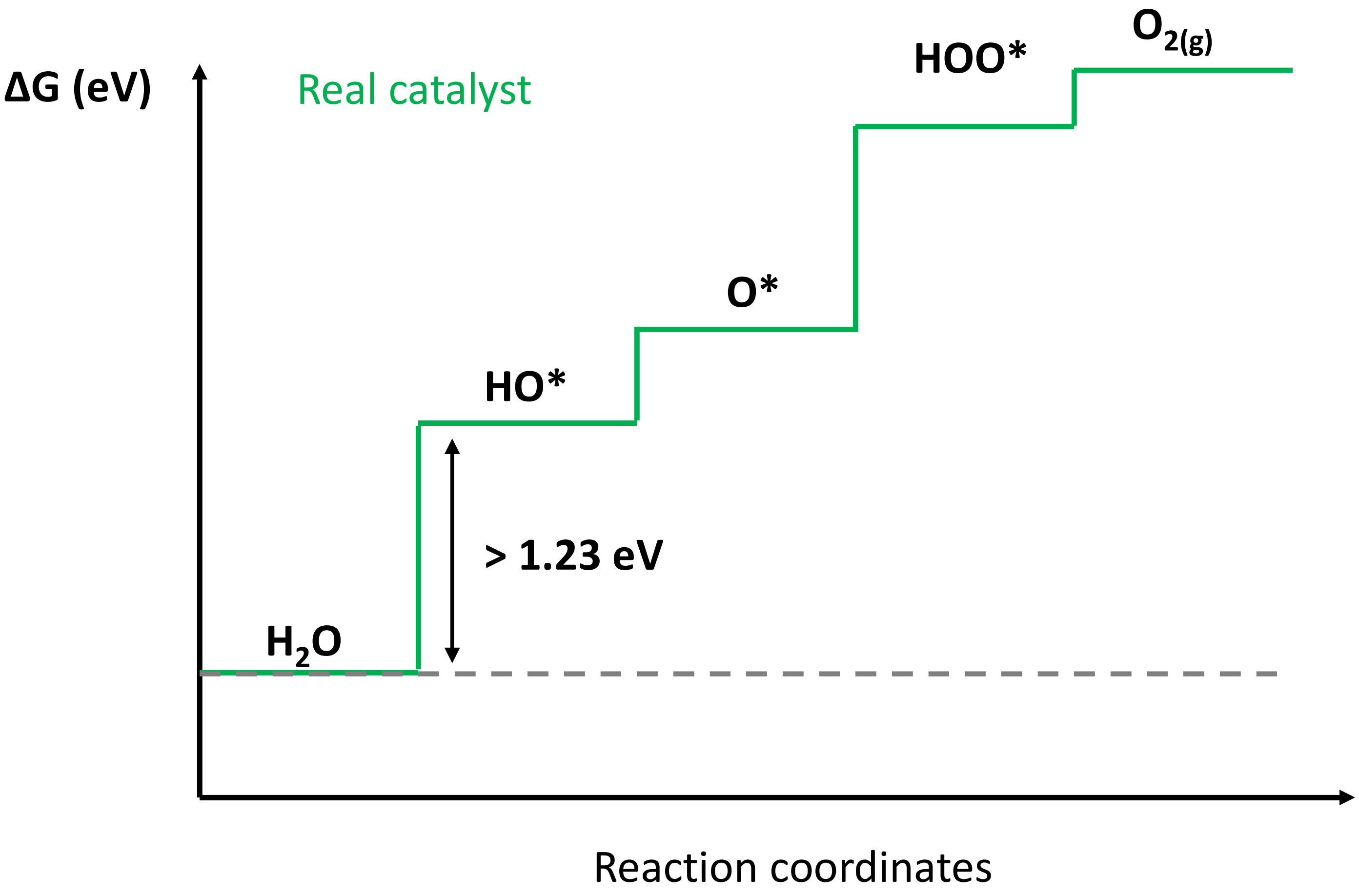
Change in intermediate energy scales with the change of activation energy

Hong, Risch, Stoerzinger, Grimaud, Suntivich and Shao-Horn, EES 2015

The case of the oxygen evolution reaction (OER)

Oxygen Evolution Reaction (OER):
2 H_2O ➔ $O_{2(g)}$ + 4 H^+ + 4 e^-

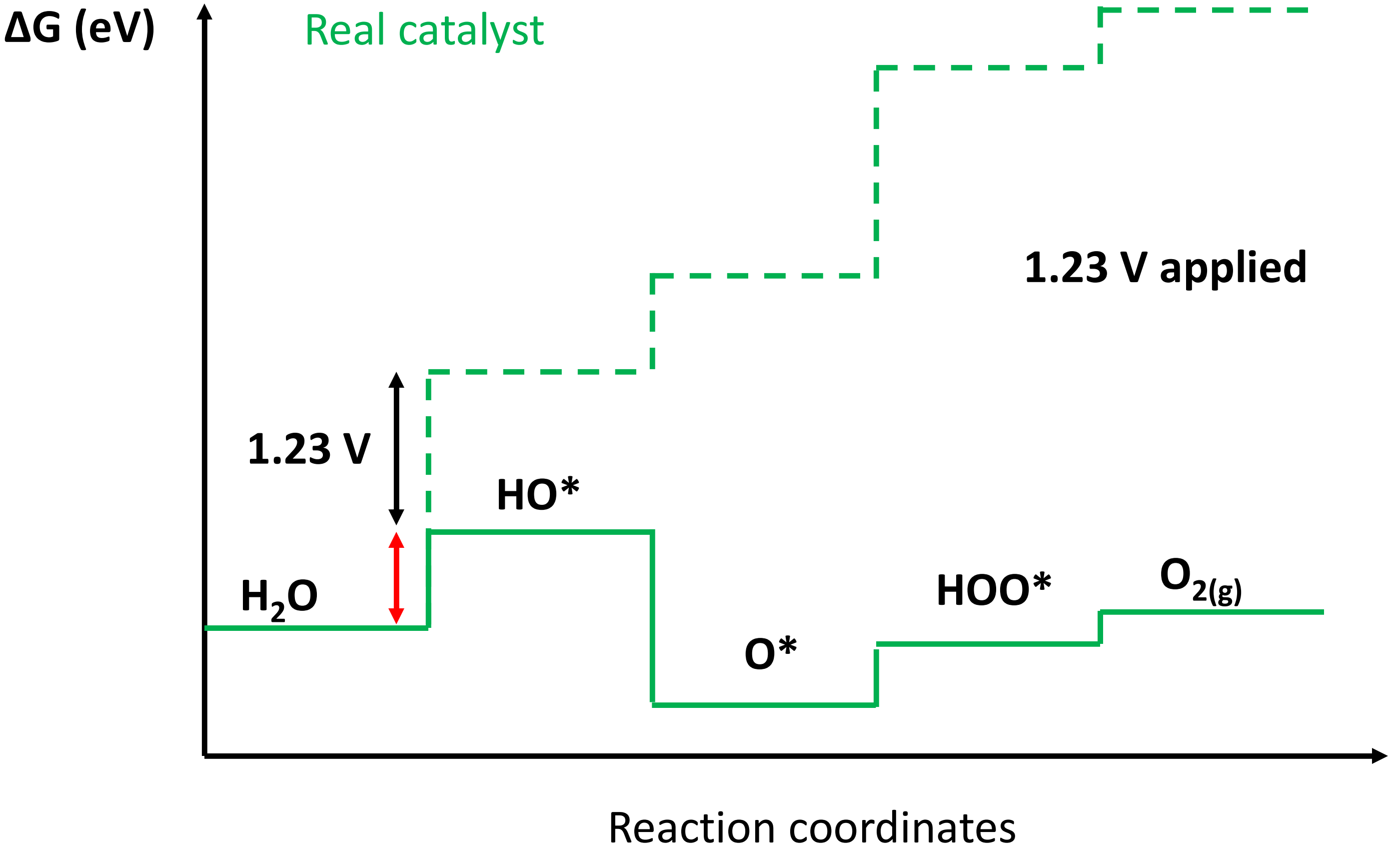
4 e^-/H^+ reaction ➔ believed to be 4 steps



The OER surface intermediates

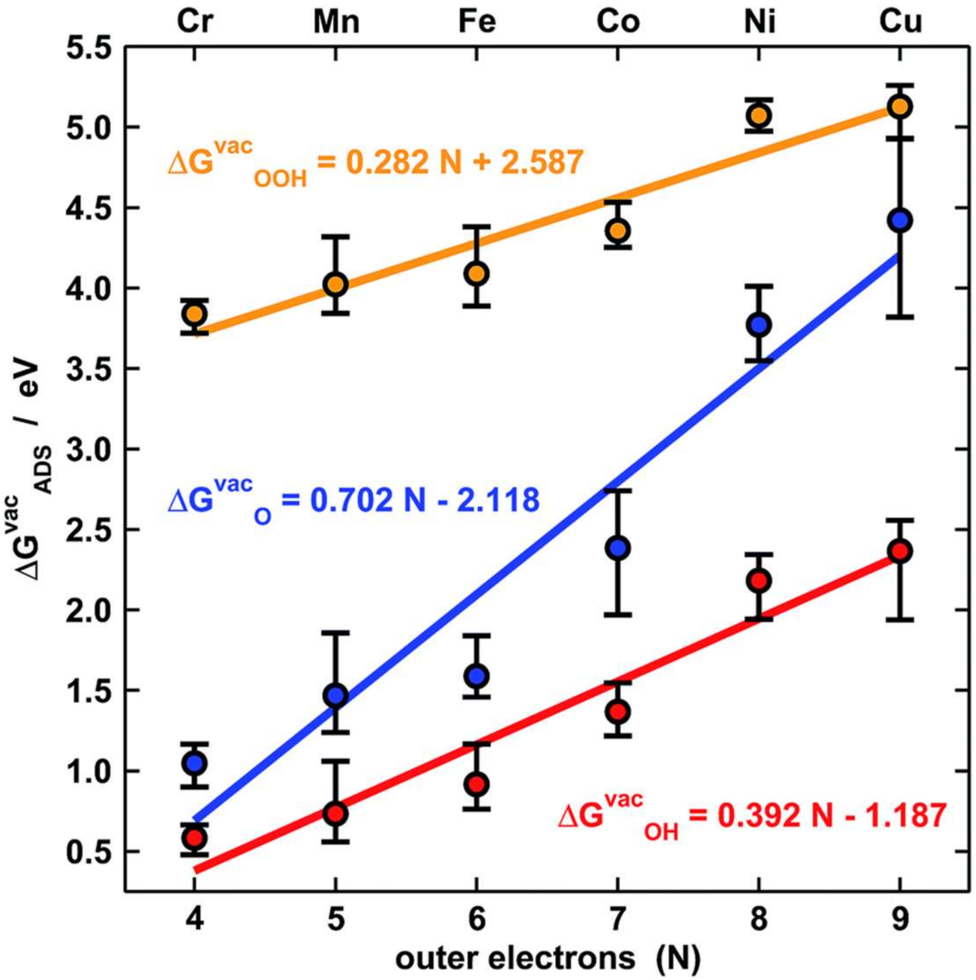
Oxygen Evolution Reaction (OER):
$2\ H_2O \rightarrow O_{2(g)} + 4\ H^+ + 4\ e^-$

4 e^-/H^+ reaction ➔ believed to be 4 steps



Intermediates energy scale with each others

The scaling relationship:

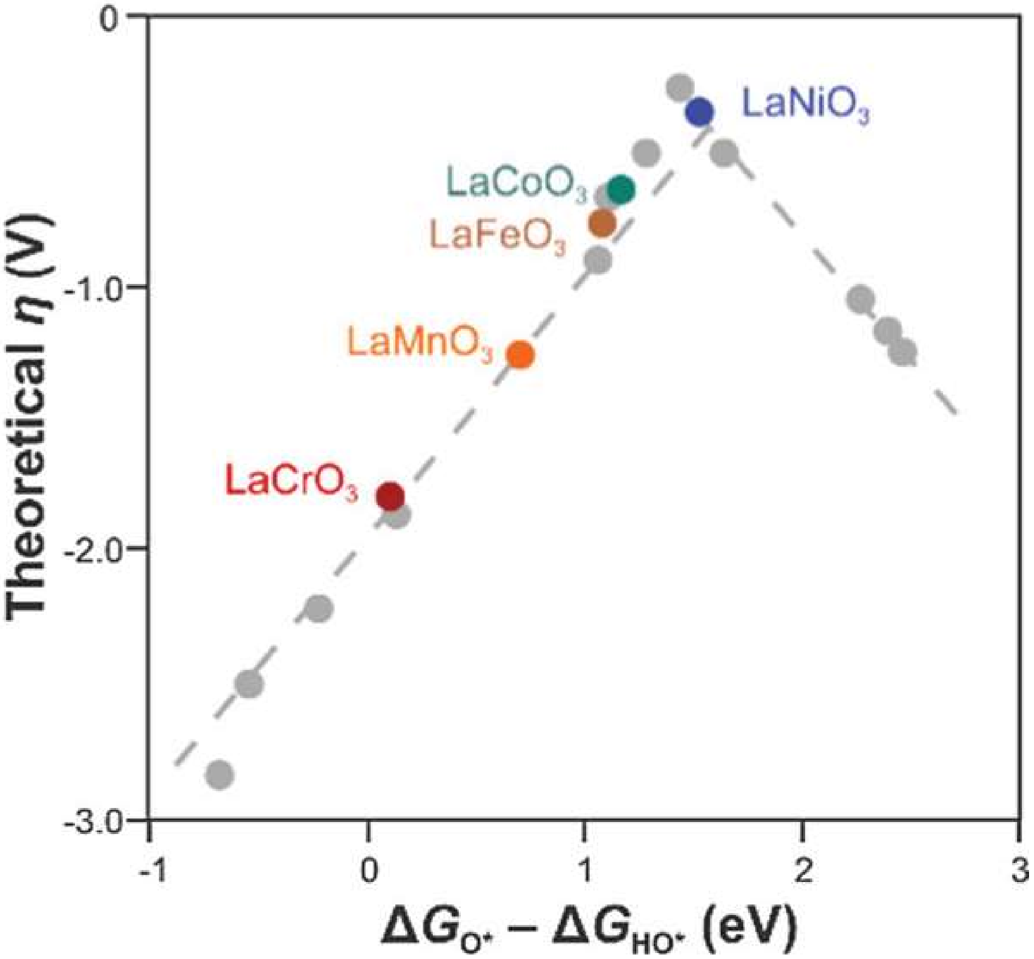


Calle-Vallejo et al, Chem. Sci. 2017, 8

The volcano plot

Strong binding strength

Weak binding strength



Hong, Risch, Stoerzinger, Grimaud, Suntivich and Shao-Horn, EES 2015

❑ First warning:

➔ This holds true for a SINGLE MECHANISM

➔ When the mechanism is changed (in other words when the intermediates are changed), scaling relationship can be broken and Volcano plot might not hold

How do we control these surface intermediates?

Or just estimate that a catalyst is better?

?

Electrochemical setup

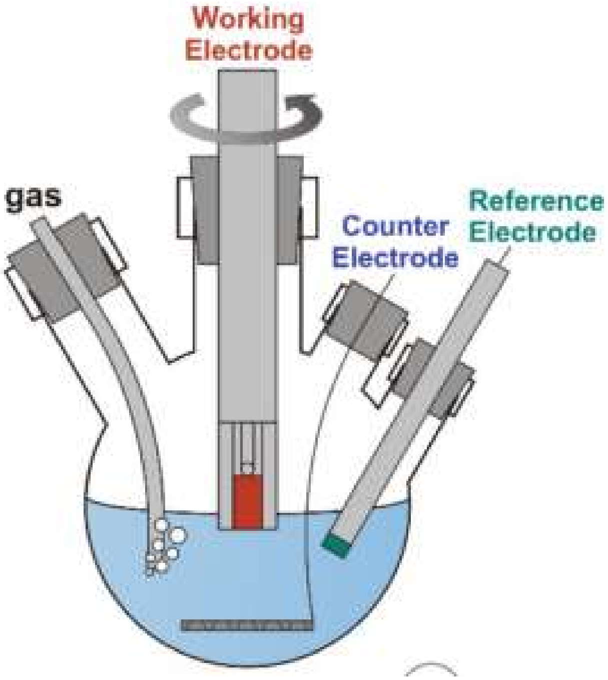
Measuring the OER

Avoid limitations due to mass transport and only probe the electrocatalytic activity of the catalyst

- ➢ Three electrodes setup and rotating disk measurement (RDE)

➔ Convection mouvement that limits the mass transport limitation

- ➢ Catalyst deposited on the surface of the WE in a small quantity



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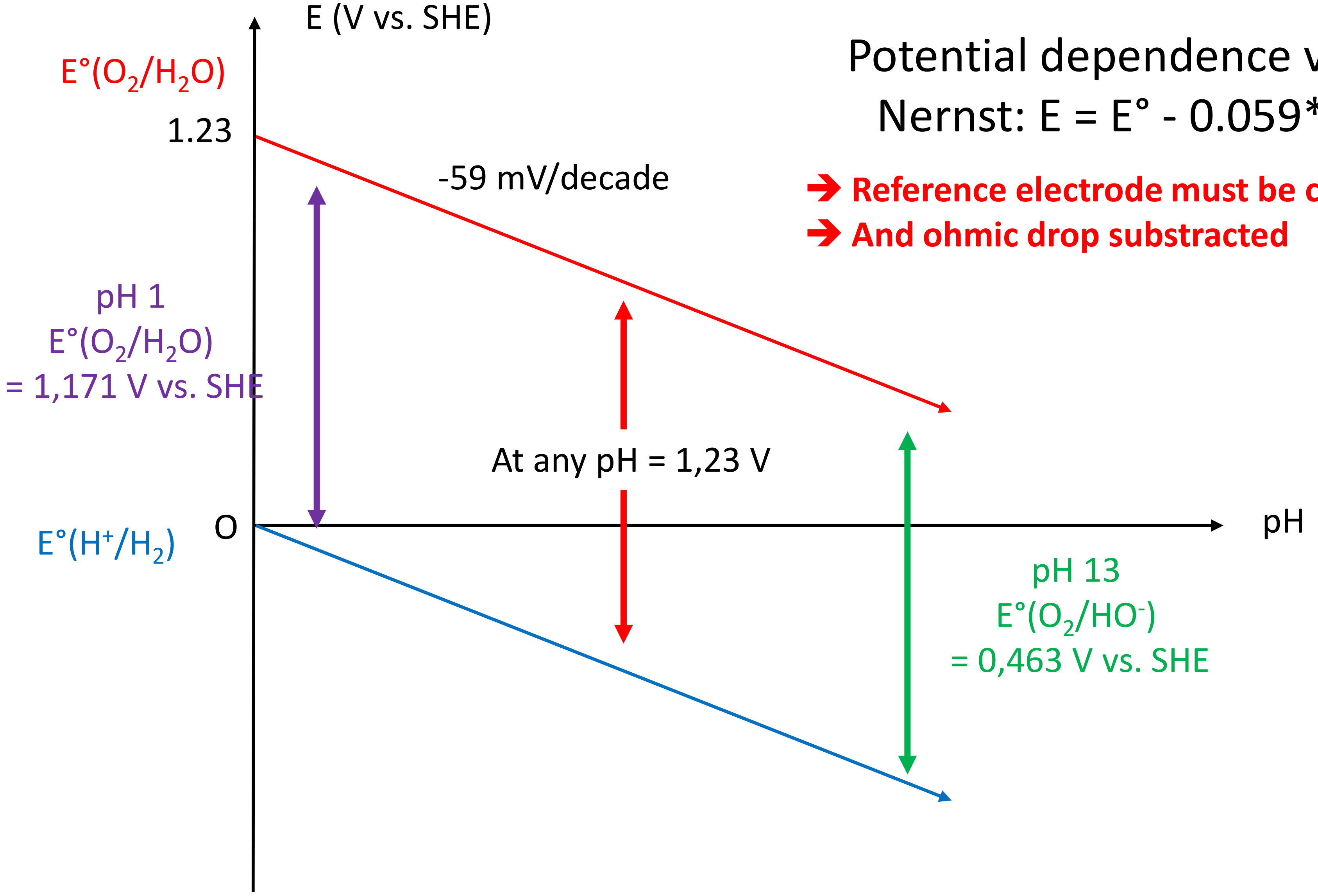
Which potential scale?



Potential dependence vs pH

Nernst: E = E° - 0.059*pH

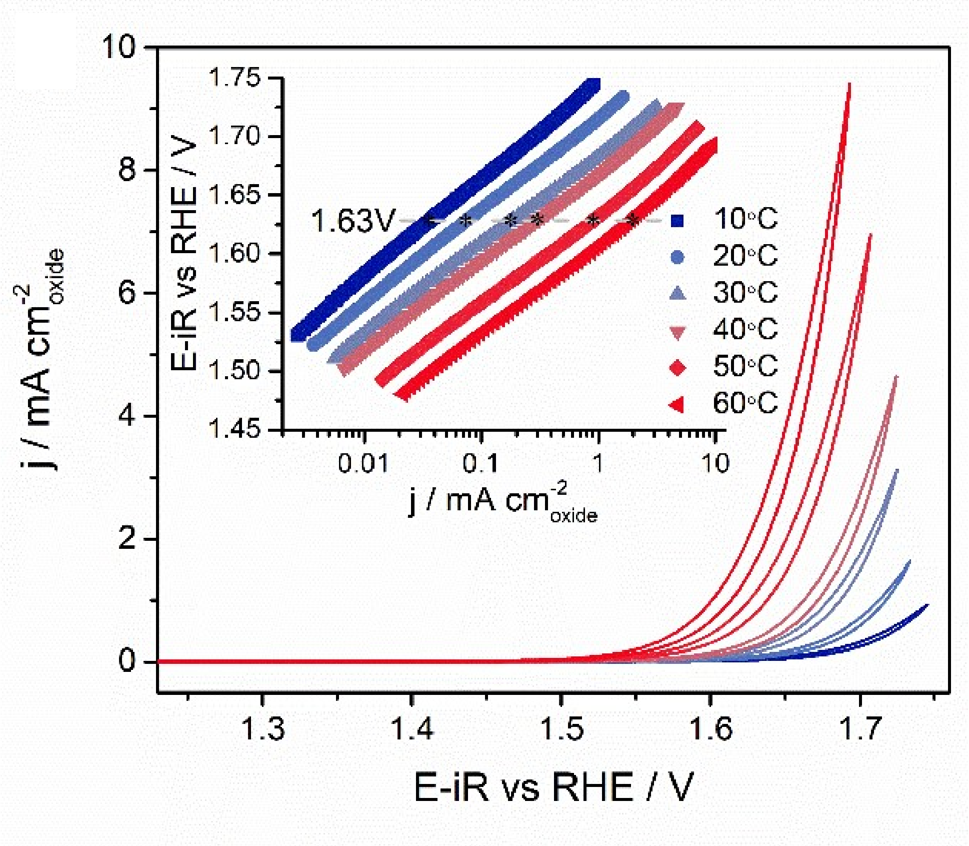
→ Reference electrode must be calibrated

→ And ohmic drop substracted

Activation energy as a function of the catalyst

Reaction rate (transition state theory) $k = \kappa \frac{k_B T}{h} \exp(-\frac{\Delta G^{\ddagger}}{RT})$

Empirically, Arhenius equation can be used: $k = A\, exp(\frac{-E_a}{RT})$



- Measurements in temperature

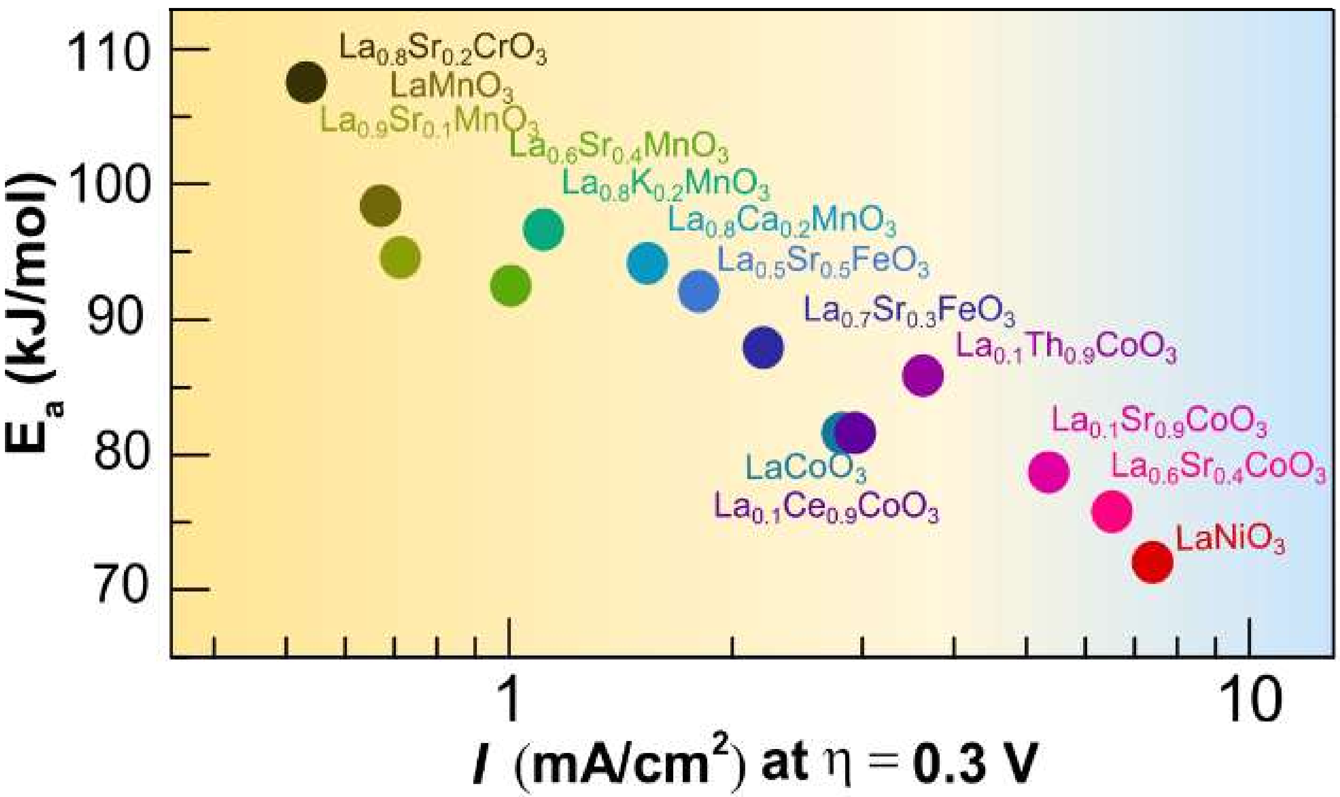
Either at the exchange current density j^0 or at a given overpotential

Issues with diffusion current and non-linear slopes

Duan, Grimaud et al, submitted

Activation energy as a function of the catalyst

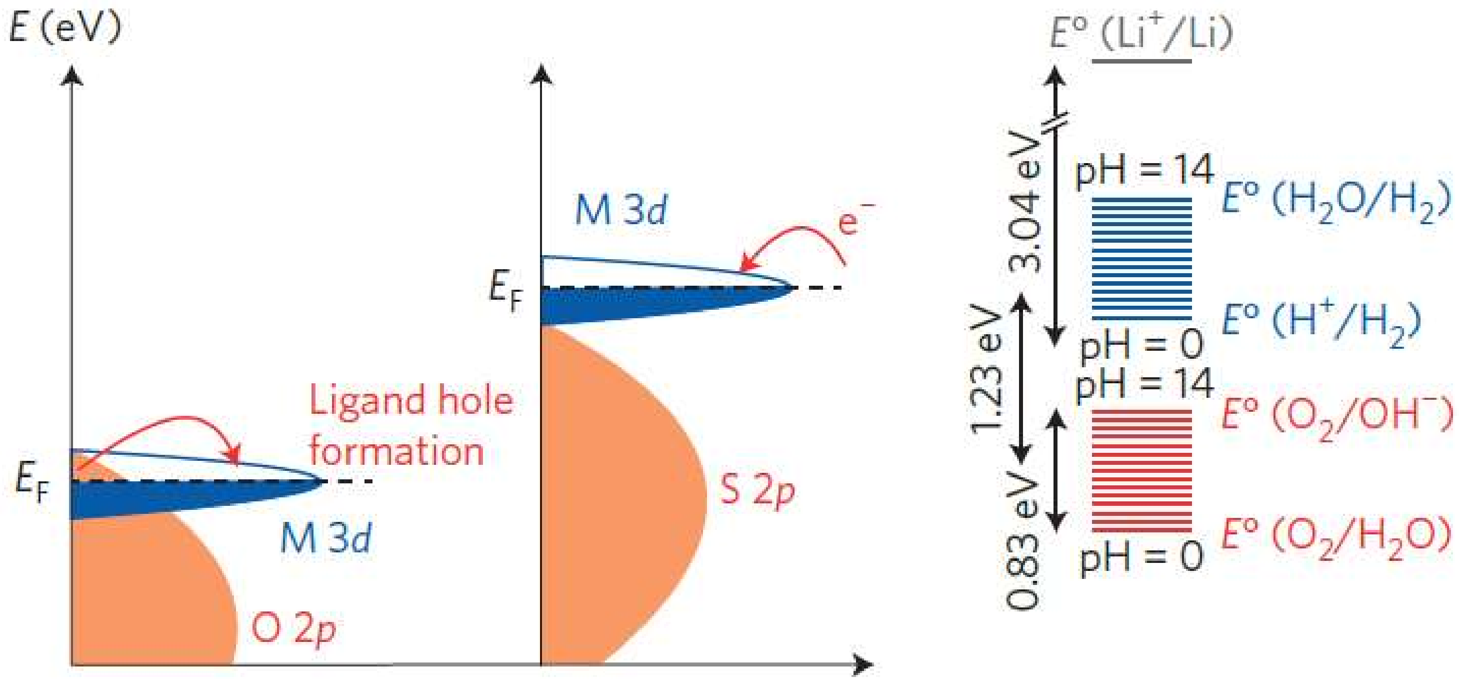
Empirically, Arhenius equation can be used: $k = A\,exp(\frac{-E_a}{RT})$



Zhang, Grimaud et al Chem. Mater. 2019

Our tools as solid-state chemists

Surface of oxides in contact with water cannot be controlled
Only bulk concept can be used



OER = oxidation of O^{2-} into $O_{2(g)}$
Chemical potential of electrons (Fermi level) vs chemical potential of oxygen (ligand)

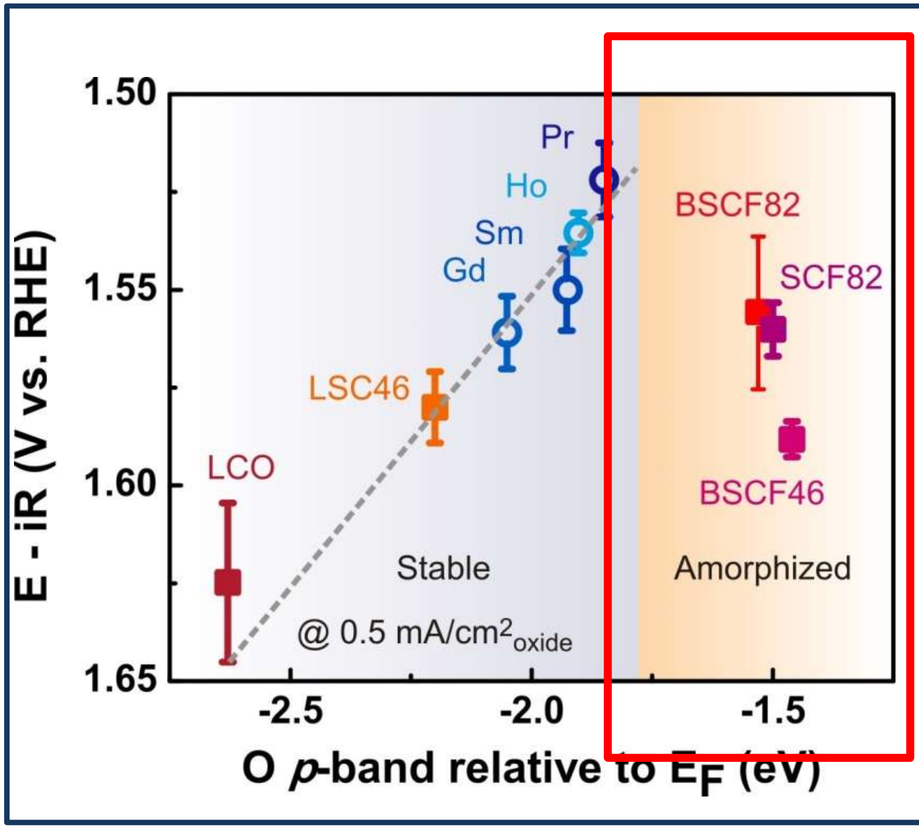
Grimaud, Hong, Shao-Horn and Tarascon, Nature Materials 2016

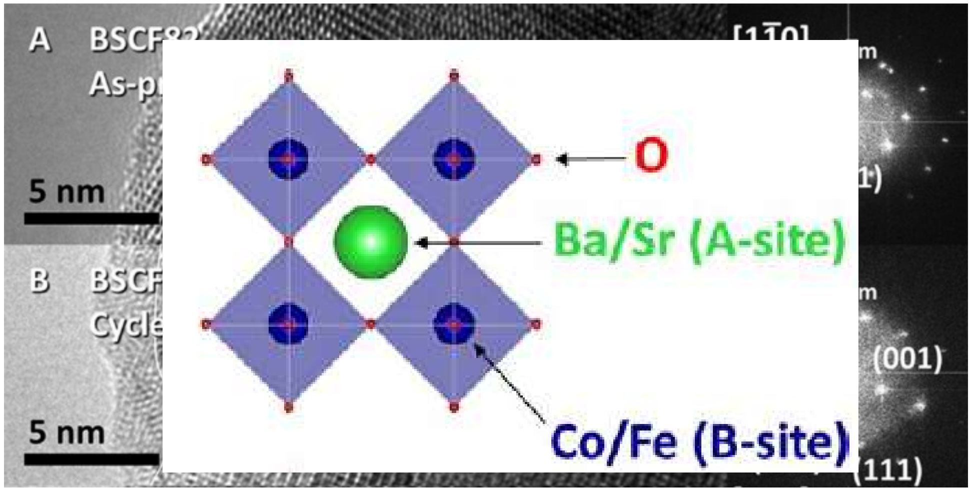
Finding an activity descriptor?

- Cobalt-based perovskites as OER catalysts

Relative position of the oxygen electronic states correlate with the OER activity

But also with the stability of transition metal oxides under these conditions

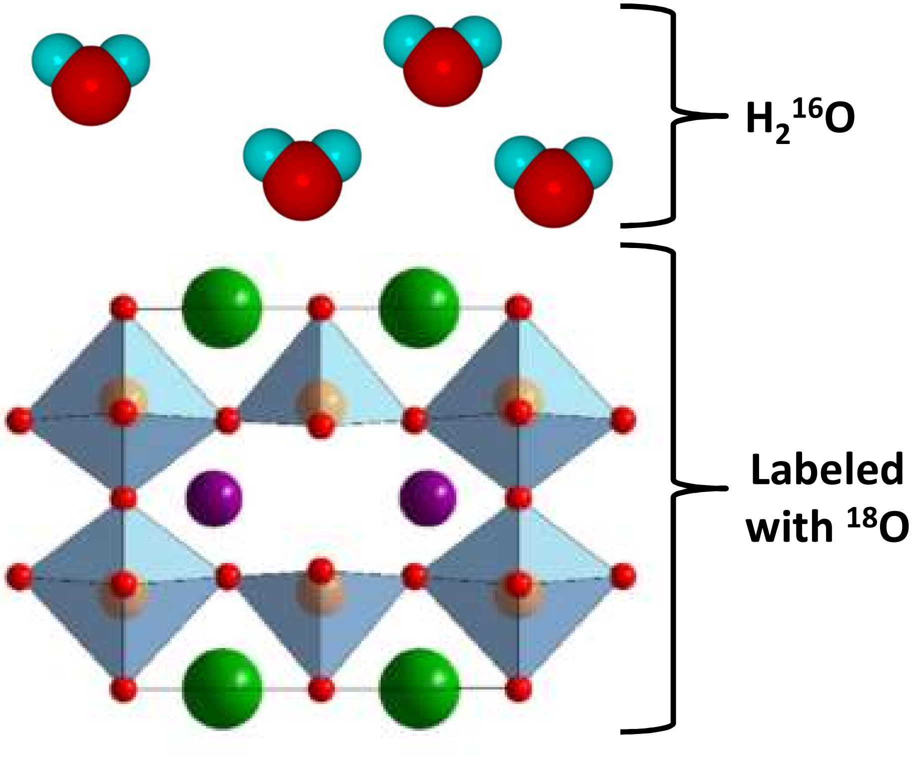




May et al, JPCL (2012)
Risch et al, JPCC (2013)

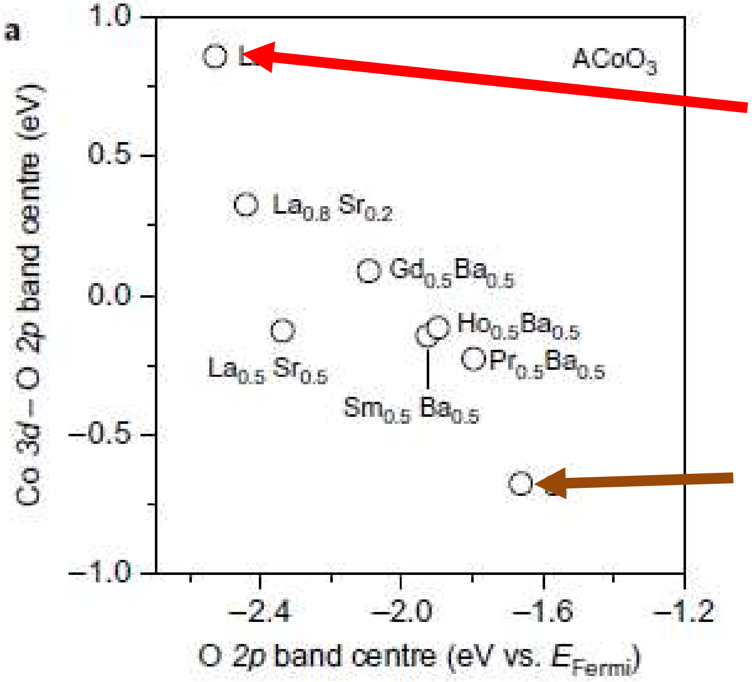
Grimaud et al., Nature Commun. 2013

New OER mechanism for perovskites?

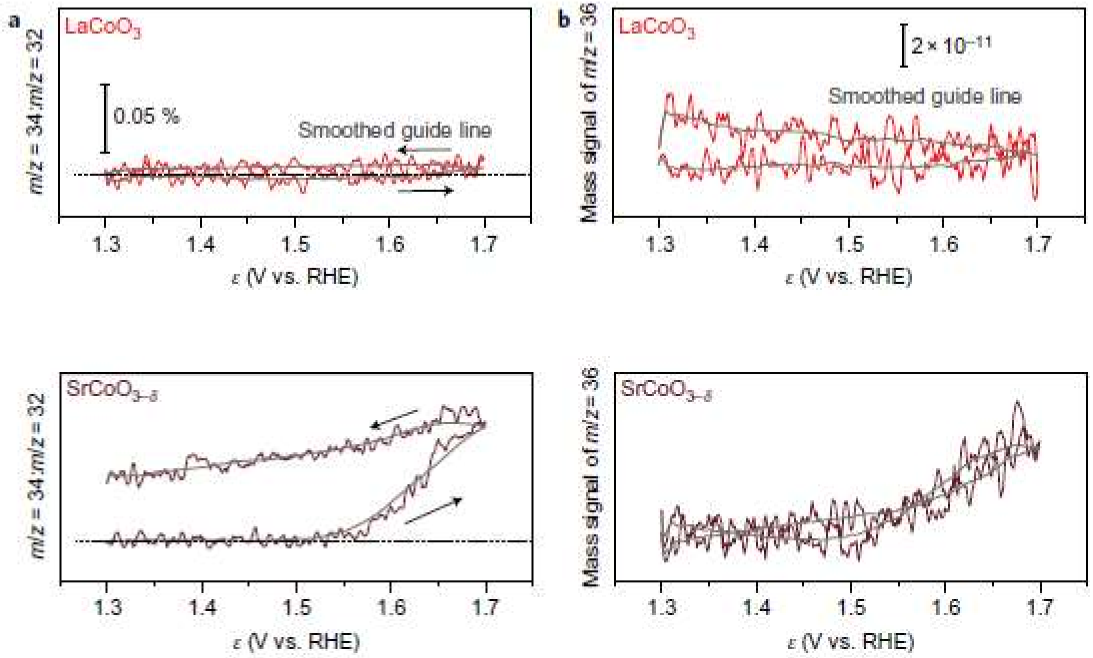


New OER mechanism for perovskites?

Perovskites $La_{1-x}Sr_xCoO_3$
Increasing x lowers the Fermi level closer to oxygen states



$^{18}O - ^{16}O$ $^{18}O - ^{18}O$

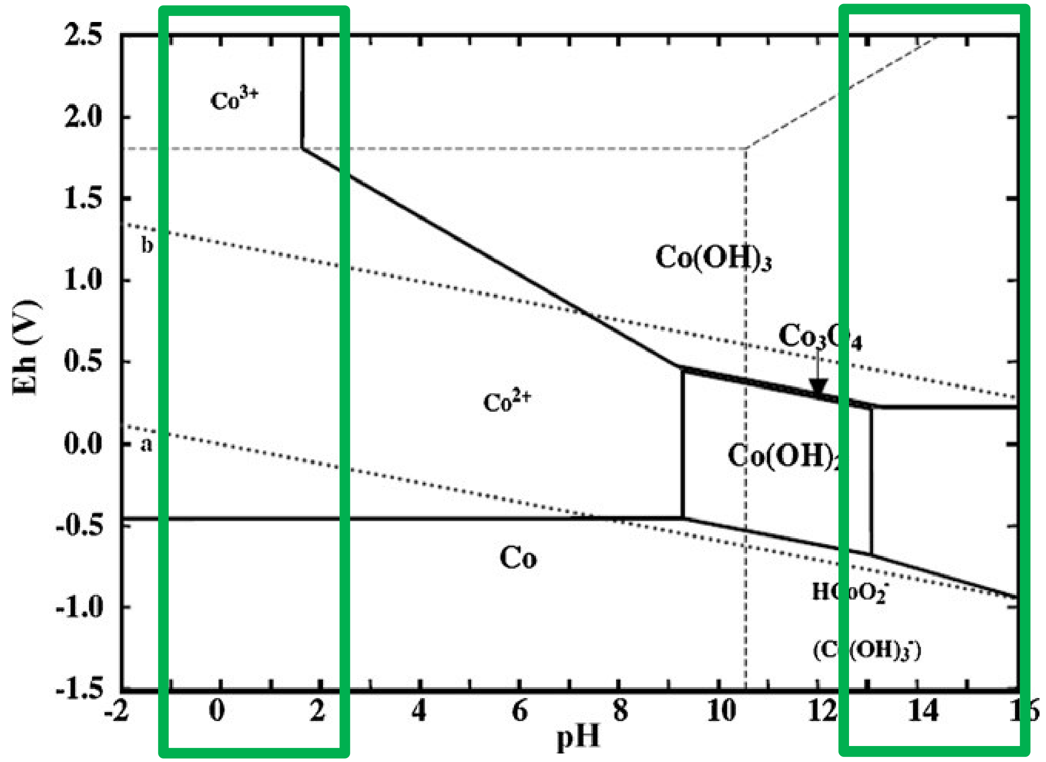


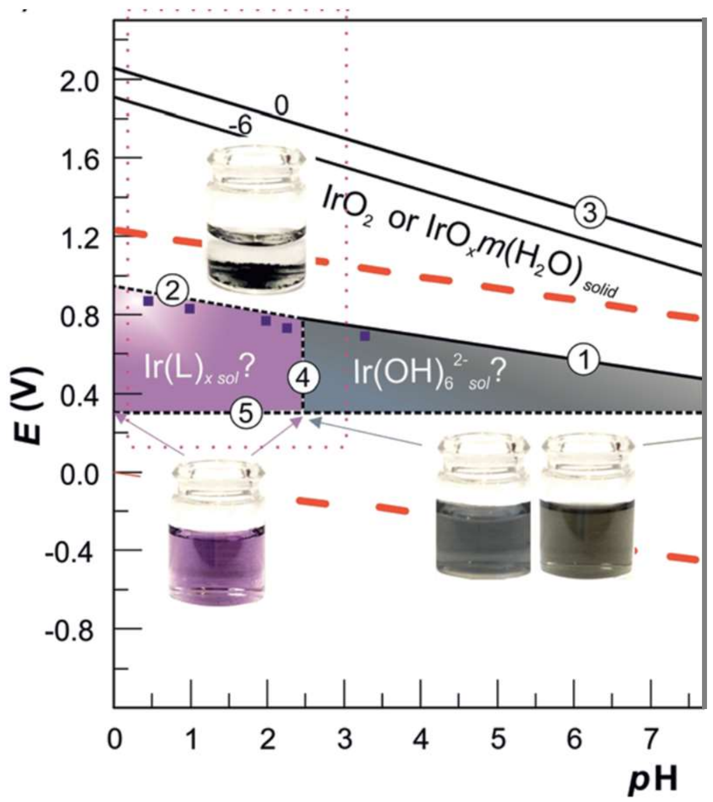
Rong et al, ACS Catalysis (2016)
Mefford et al, Nature Commun. (2016)
Binninger et al, Sci. Rep. 5 (2015)

Fighting the thermodynamics – Pourbaix diagram

- ❑ Pourbaix diagram (potential-pH diagram) of transition metal
  - ➢ The Nickel Pourbaix diagram
  - ➢ The Iridium Pourbaix diagram

Soluble **Hydroxides**





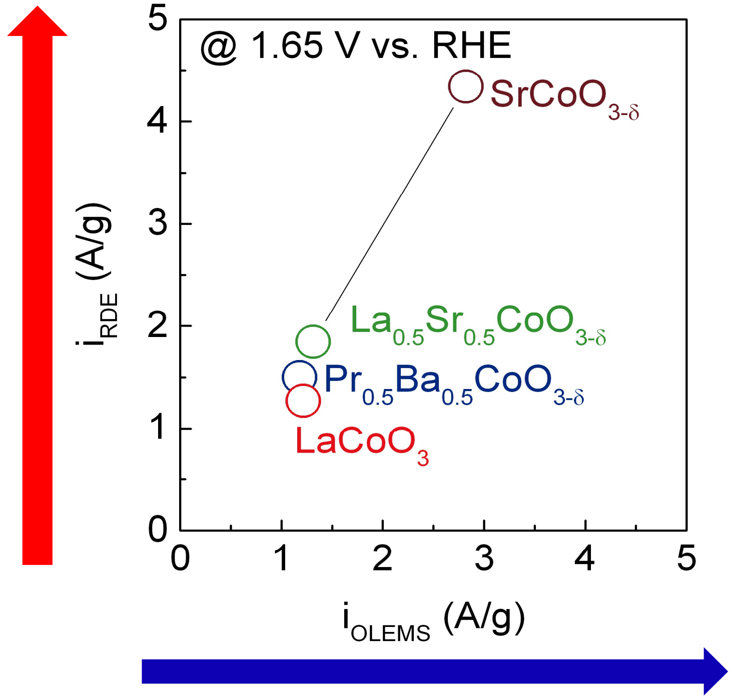
Zhang, Grimaud et al., Angewandte 2019

- ☐ Catalysts/Surfaces are often out of thermodynamical equilibrium
- ☐ Surfaces can reconstruct
- ☐ Make sure that the surface you think of is the one you are measuring
- ☐ Increased of OER activity can simply come from the formation of a new surface with more active sites

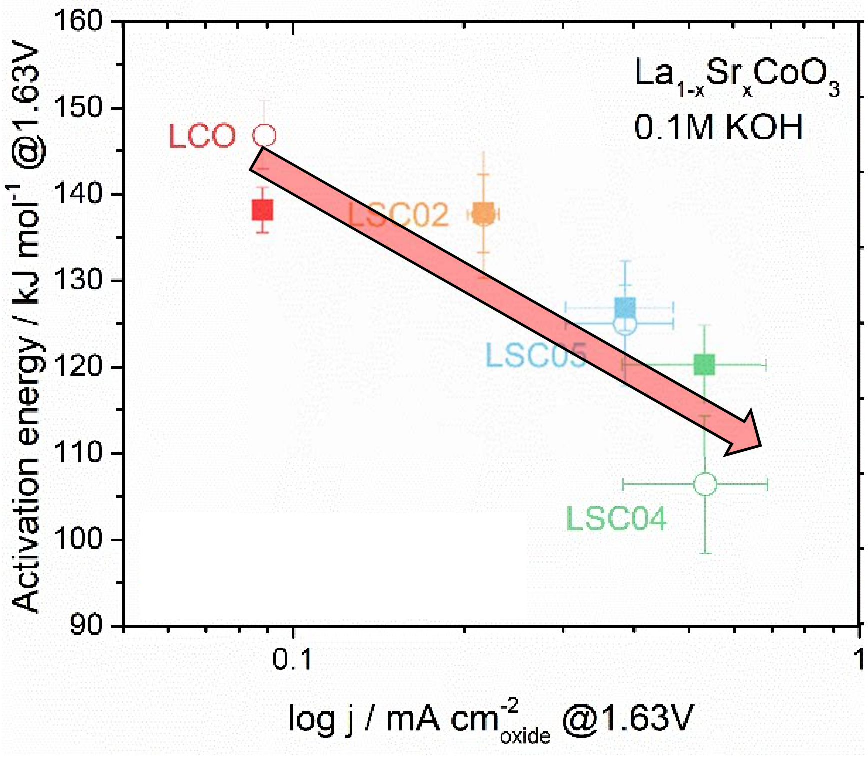
Additional effect related to the electrolyte

- OER activity increases with the involvment of lattice oxygen
- Decrease of the activation energy ➔ optimization of the intermediates energy

OER activity



Amount of lattice oxygen

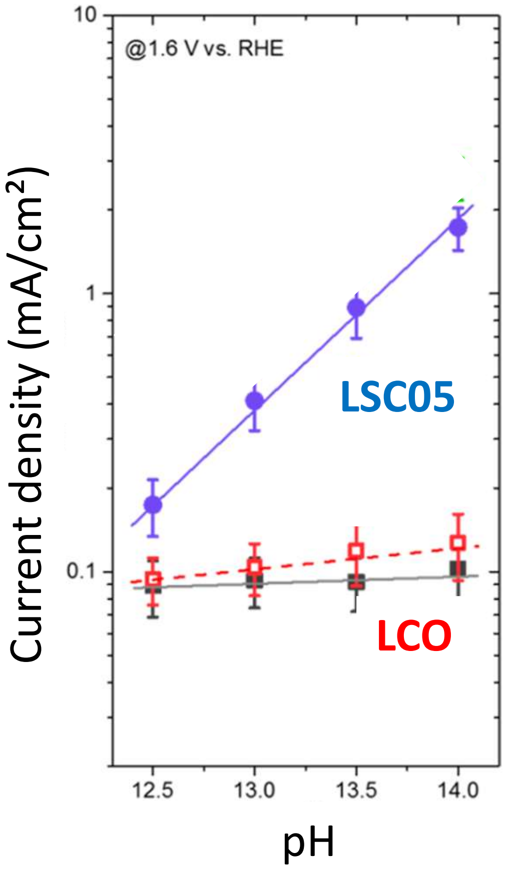


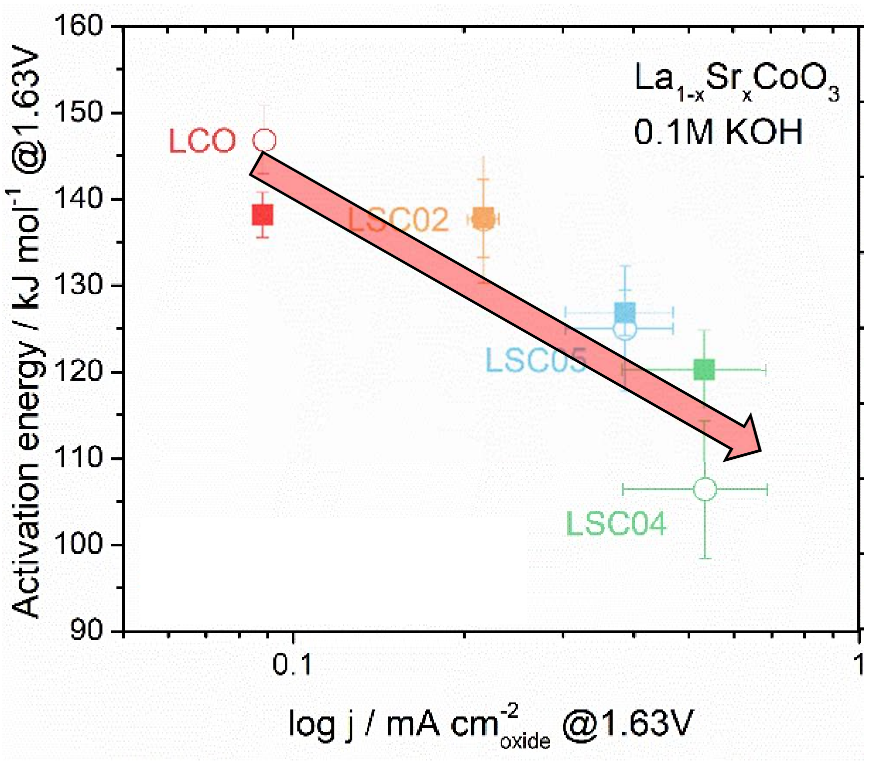
Grimaud et al., Nature Chemistry 2017

Duan, Grimaud et al, submitted

Additional effect related to the electrolyte

- OER activity increases with the involvment of lattice oxygen
- Decrease of the activation energy ➔ optimization of the intermediates energy
- The OER activity becomes dependent on the pH



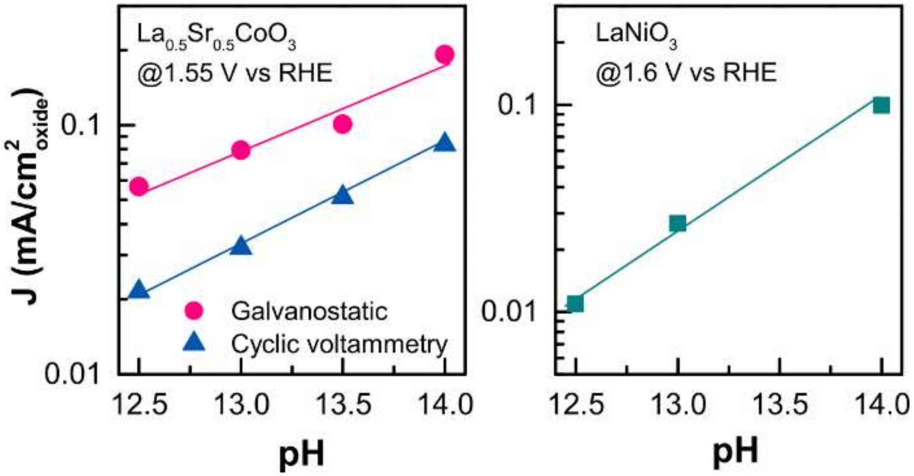


Yang, Grimaud et al., JPCL 2017

Duan, Grimaud et al, submitted

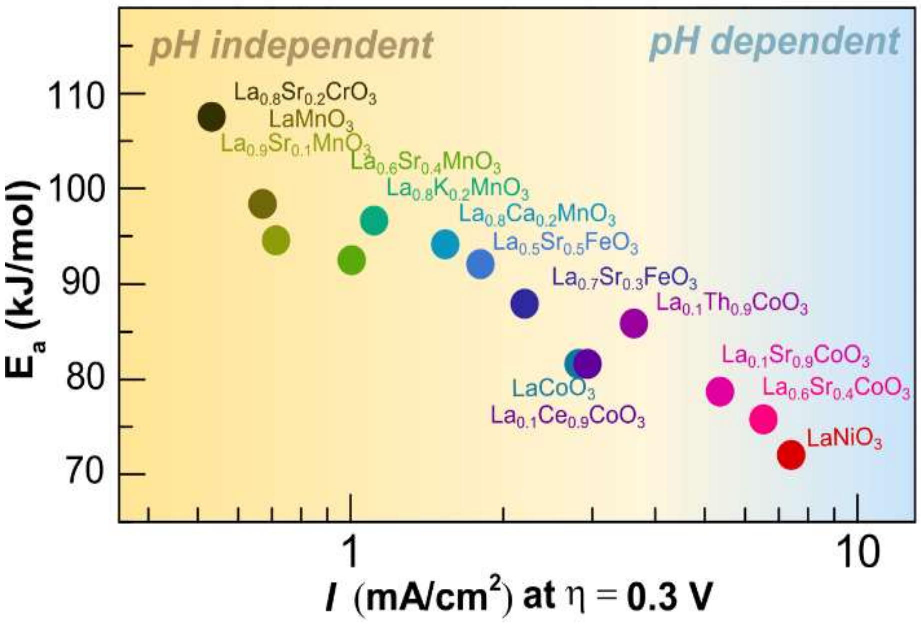
What is the role of the electrolyte structuration on the kinetics?

- **For the best OER catalysts, the electrocatalytic activity is dependent on the pH**



Grimaud, Shao-Horn et al, Nature Chem. 2017

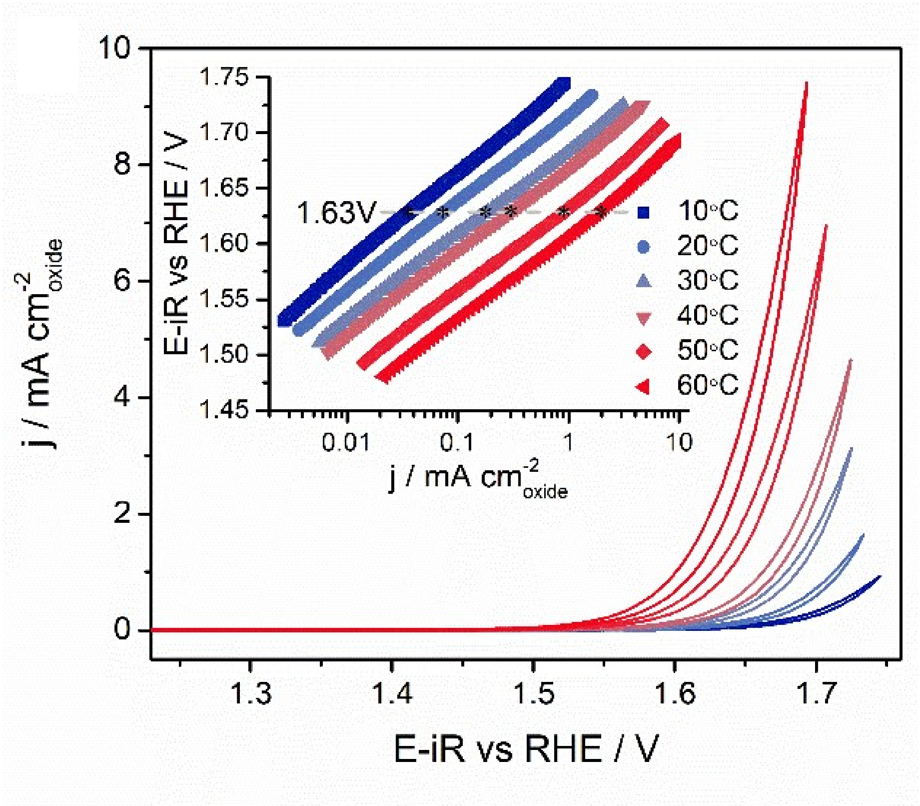
Yang, Grimaud et al, ACS Energy Lett. 2018



Zhang, Pearce, Duan, Dubouis, Marchandier and Grimaud, Chem. Mater. 2019

Going back to the Arhenius relationship

Empirically, Arhenius equation can be used: $k = \boxed{A}\, exp(\boxed{\frac{-E_a}{RT}})$



The reaction rate (OER current) can increase by:

1) a decrease of E_a

2) an increase of the pre-exponential factor *A*

$$\exp(-\frac{\Delta S^{\ddagger}}{R})$$

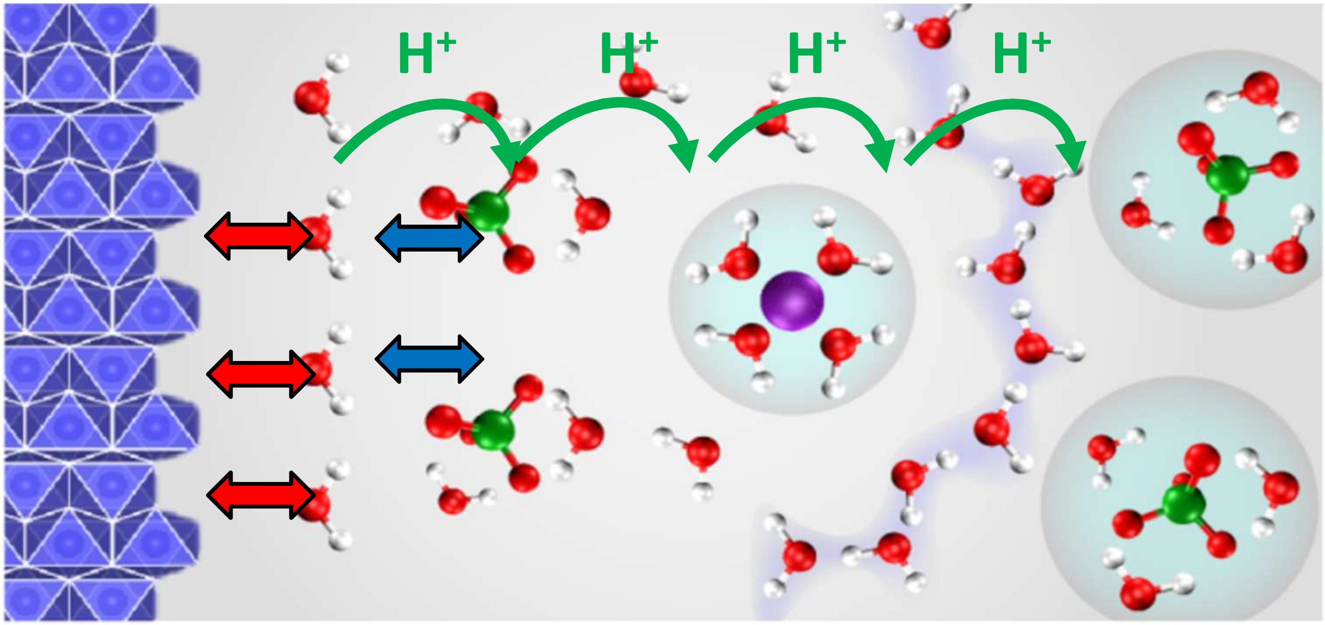
Modification of the concentration of active sites

Duan, Grimaud et al, submitted

What is the role of the electrolyte structuration on the kinetics?

Kinetics for electrocatalytic processes can be controlled by:

- Surface intermediates energy
- Solvation structure of the reactant in the vicinity of the active sites

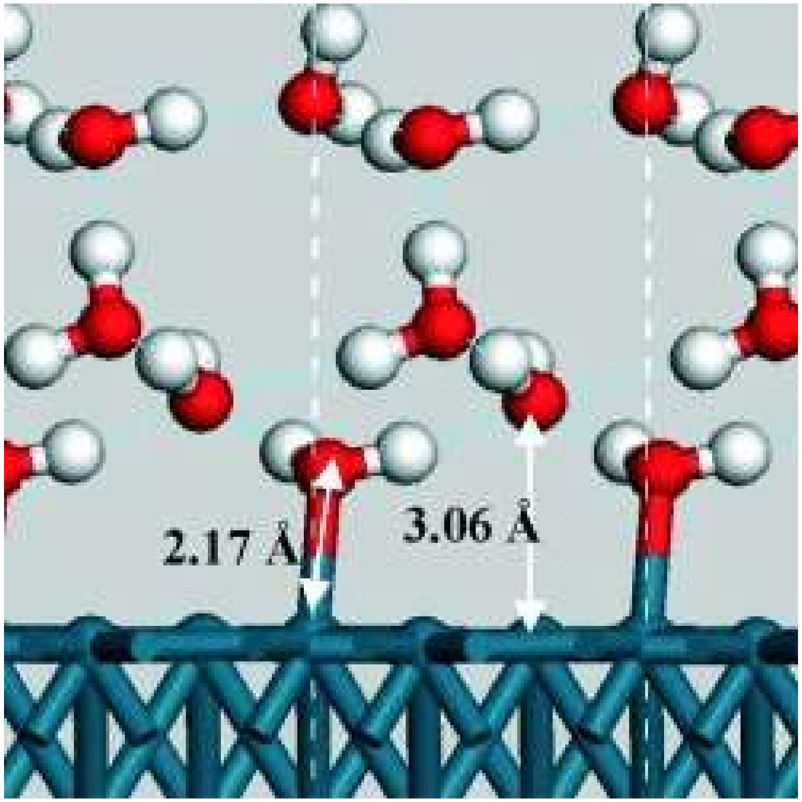


Formation of surface intermediates

Interaction of intermediates with electrolyte

Proton diffusion from the IHP to the diffusion layer

The triple role of water



3) H^+ diffusion layer (Grotthuss)

2) H^+ acceptor layer

1) OH^- donor layer

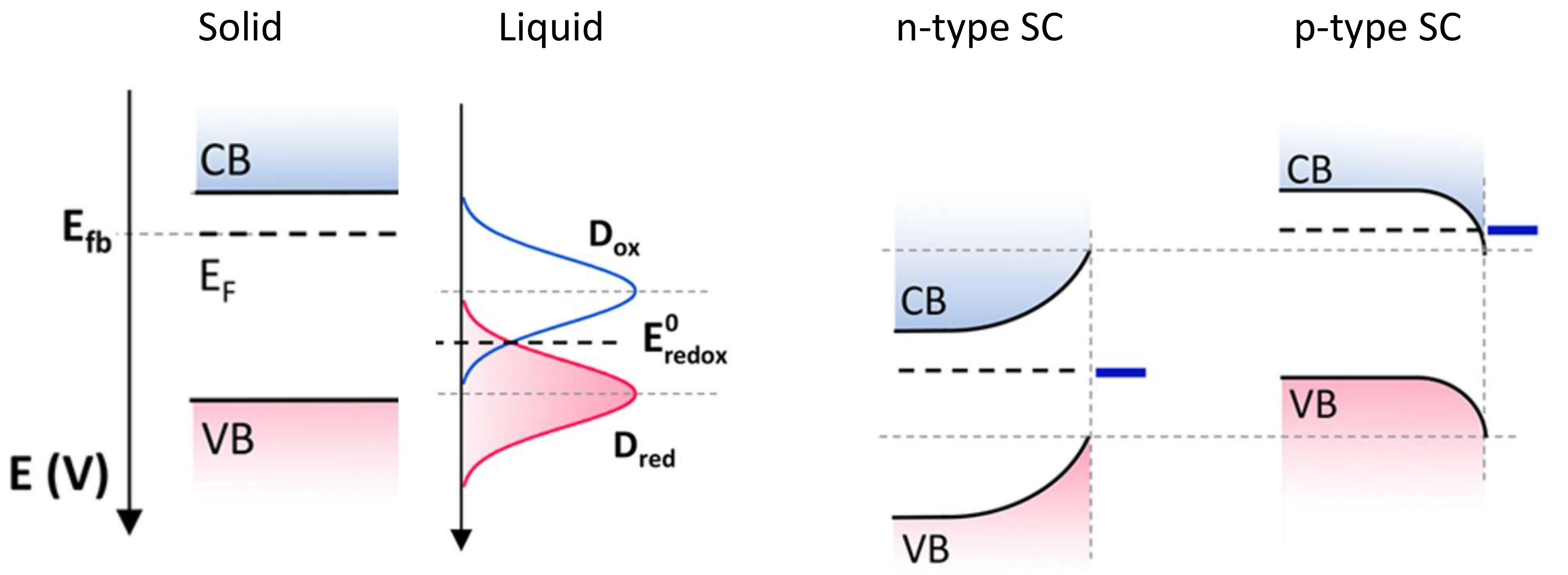
Oxygen Evolution Reaction (OER):
$2\ H_2O \rightarrow O_{2(g)} + 4\ H^+ + 4\ e^-$

Filhol and Neurock, Angewandte 2006

Dubouis and Grimaud et al, Chem. Sci. 2019

Formation of the double layer

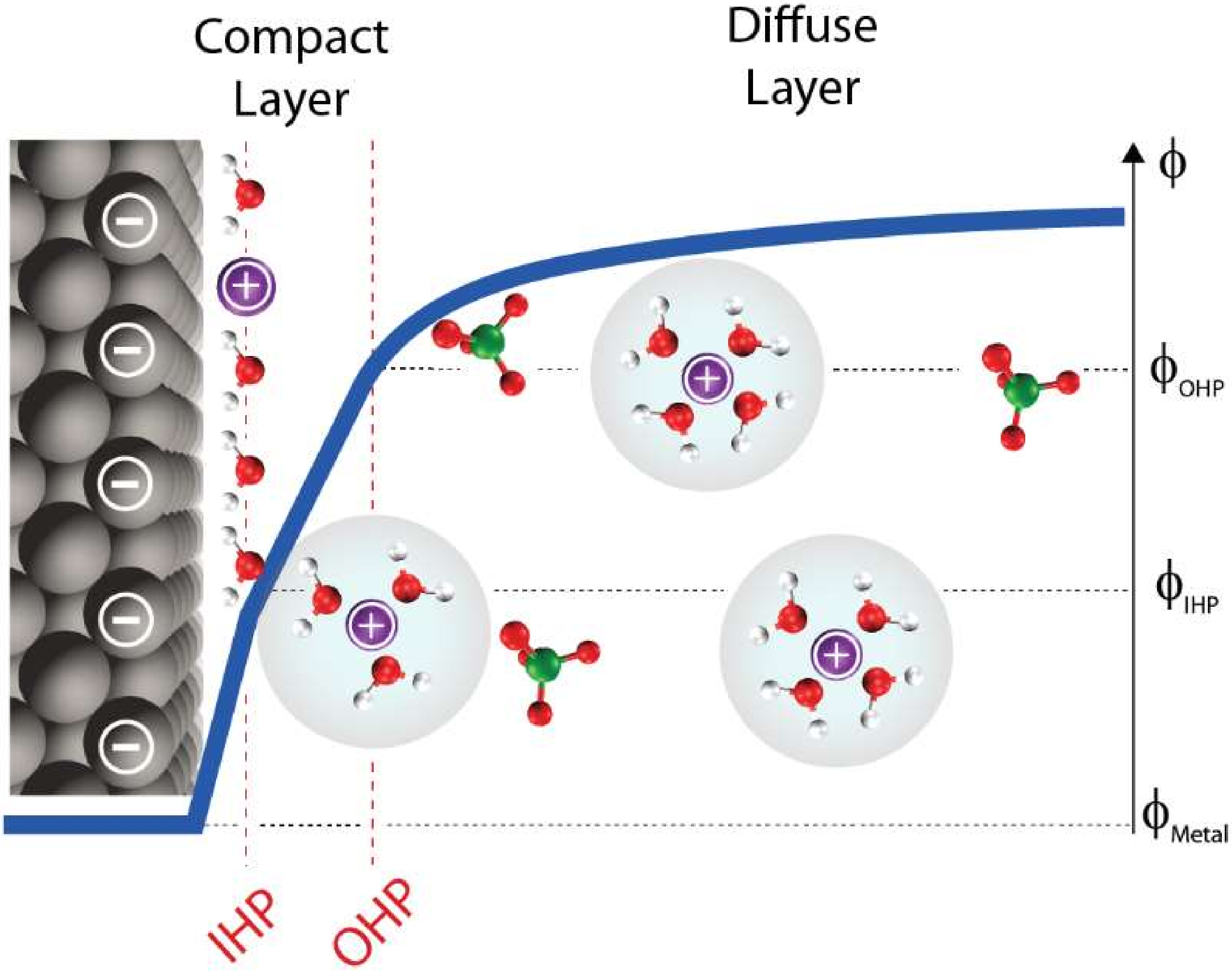
- Solid in contact with a liquid:



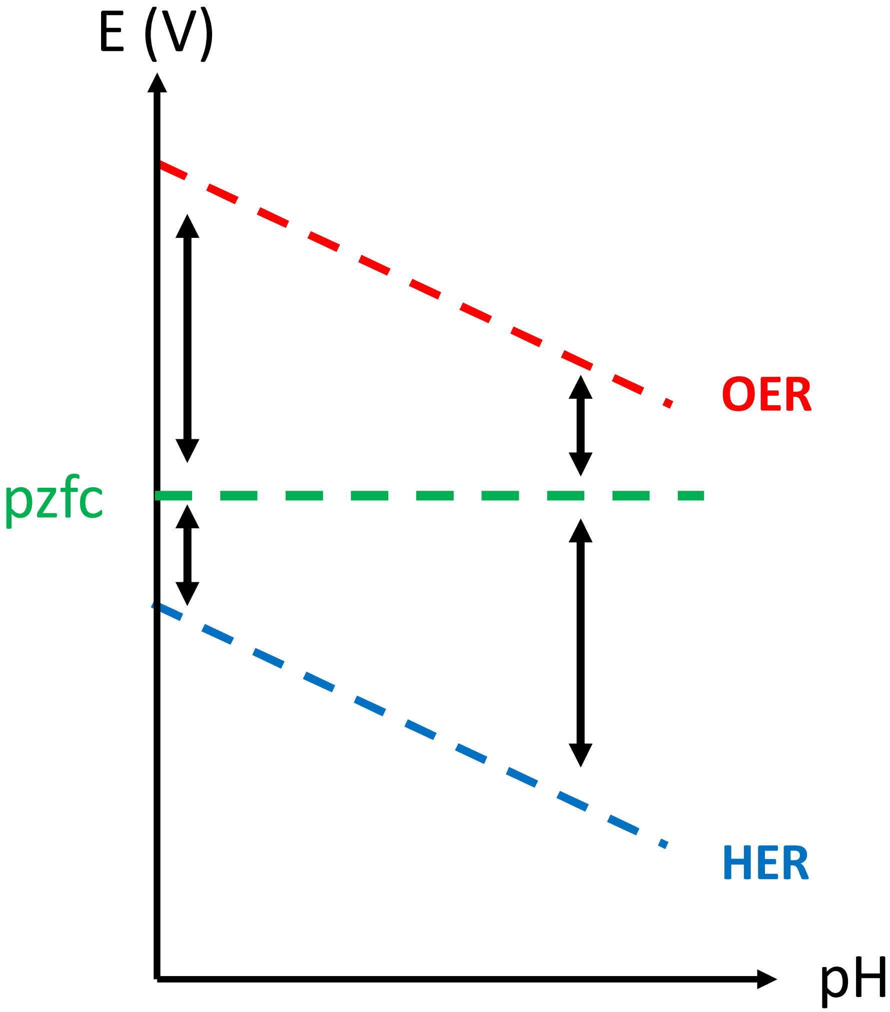
- Equilibrium of the chemical potential of electrons
- Redistribution of charges for the solid (band bending) and the liquid
- Length of the redistribution depends on the density of charge

Azcarate, Grimaud et al, JPCC 2018

Formation of the double layer



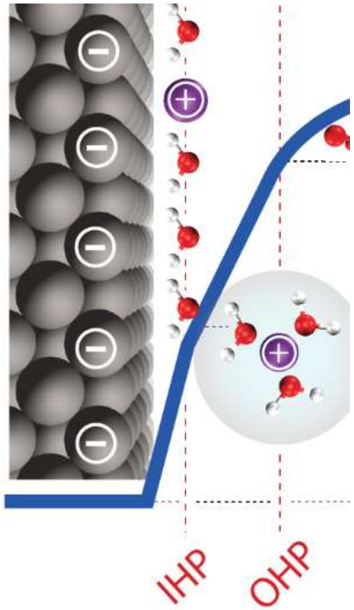
Stiffeness/density of the double layer



Potential of zero free charge
Electrical charge on the surface = 0

Close to the pzfc ➔ soft double layer

Far from the pzfc ➔ rigid double layer



Dubouis and Grimaud et al, Chem. Sci. 2019

☐ Be critical regarding the origin for any increase in electrocatalytic activity

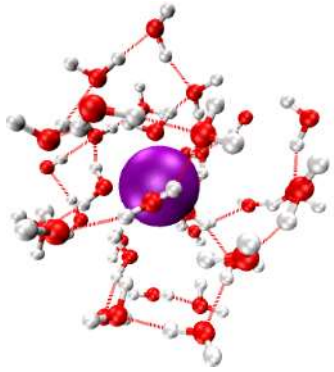
☐ Go beyond simply thinking of surface intermediates

☐ Develop experimental strategies to study complex processes

Ions in solution – effect on hydrogen bond network?

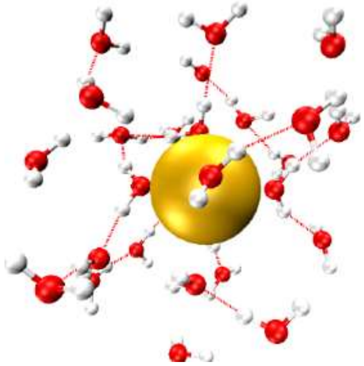
❑ Ions can be ranked depending on their effect on water

Kosmotropic



- Water structuring
- B > 0
- Li^+, F^-, etc.

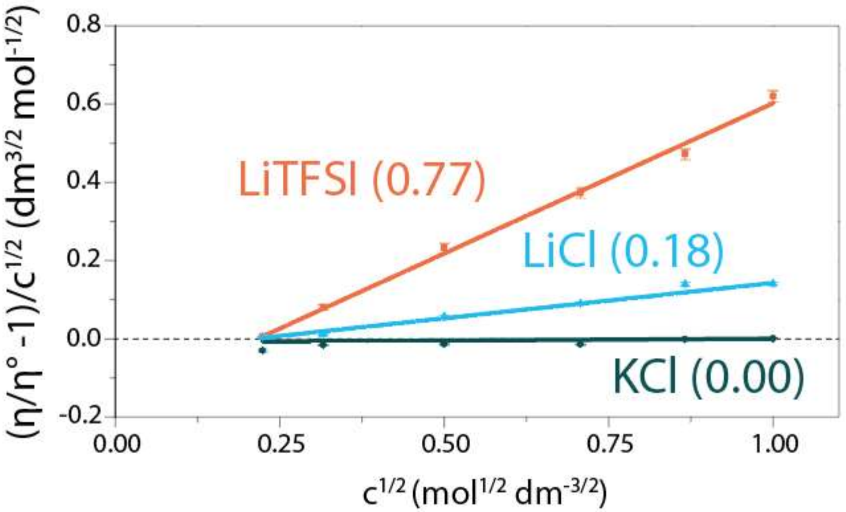
Chaotropic



- Water destructuring
- B < 0
- Cs^+, SCN^-, etc.

Jones-Dole equation

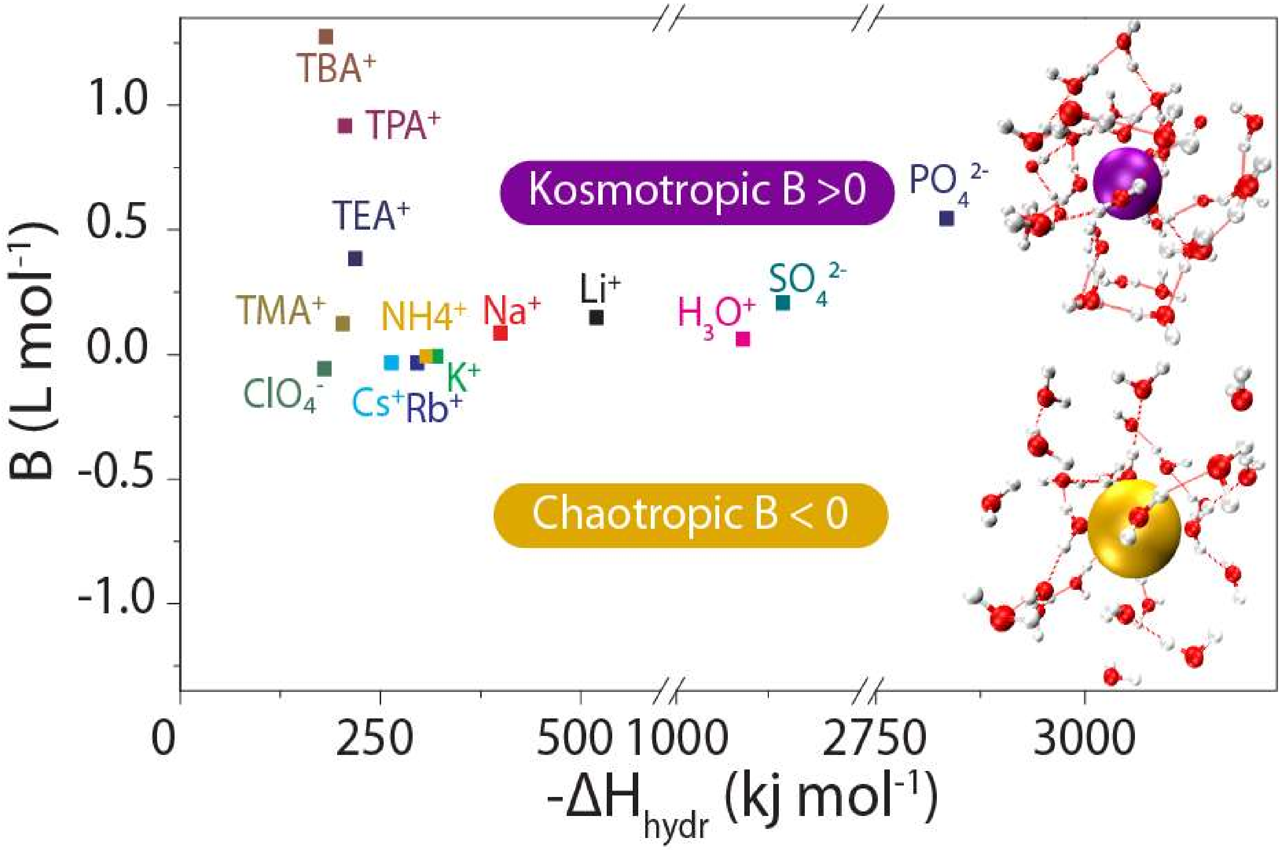
$$\frac{\eta}{n^{\circ}} - 1 = Ac^{1/2} + Bc + \cdots$$



Dubouis, Grimaud, Rotenberg et al., ACS Central Science 2019

Ions in solution – effect on hydrogen bond network?

- ❑ Ions can be ranked depending on their effect on water
  - ➢ This effect is entropic and does not follow the hydration enthalpy of ions

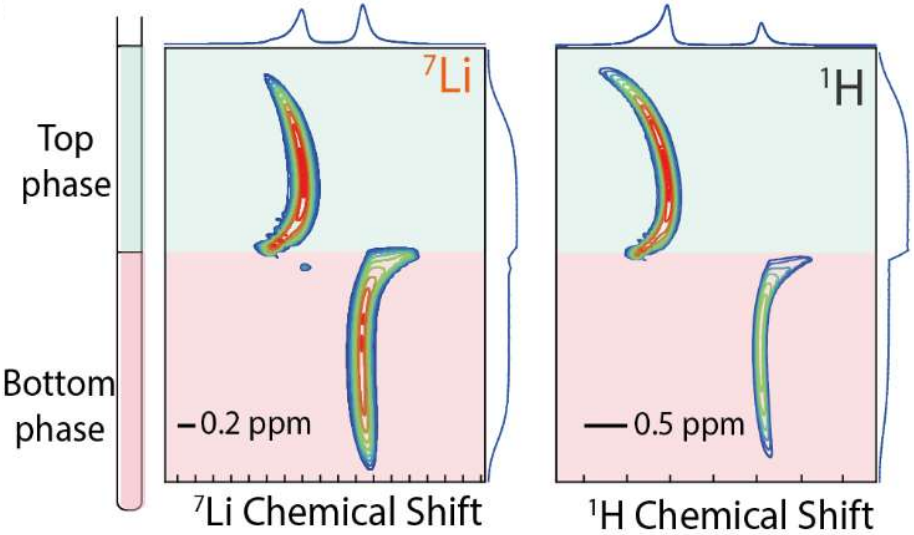


Dubouis, Grimaud, Rotenberg et al., ACS Central Science 2019

Effect can be used to prepare aqueous biphasic solutions

12 m LiTFSI + 5 m LiCl in H_2O

Different environments for H_2O and Li^+



Creation of a liquid/liquid interface in aqueous solutions

- ➔ How can we control this effect to structure H-bonding around the active sites?
- ➔ Can we boost the OER activity?
- ➔ Is the cationic effects enthalpic or entropic in nature?

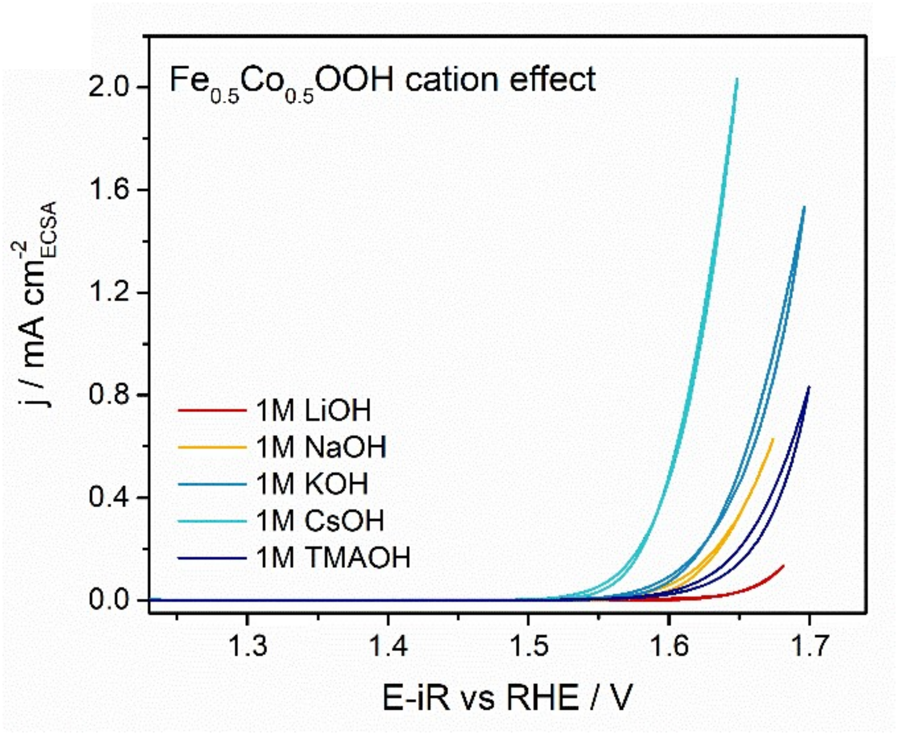
Dubouis, Grimaud, Rotenberg et al., ACS Central Science 2019

Cations effect on the OER

- OER activity for amorphous Co,FeOOH (or Ni,FeOOH) films is dependent on cations

Yang, Grimaud et al, Angewandte 2017
Koper et al, Angewandte 2019

$Cs^+ > K^+ > Na^+ > TMA^+ > Li^+$

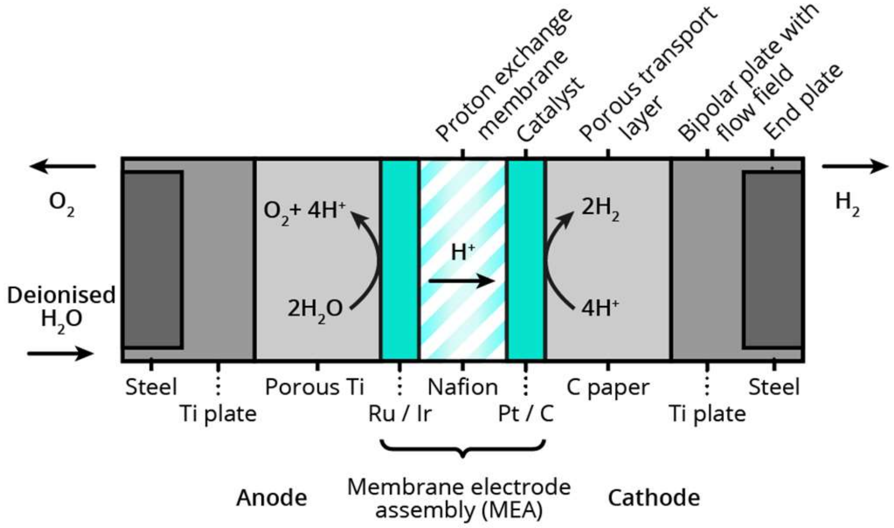


Duan, Grimaud et al, submitted

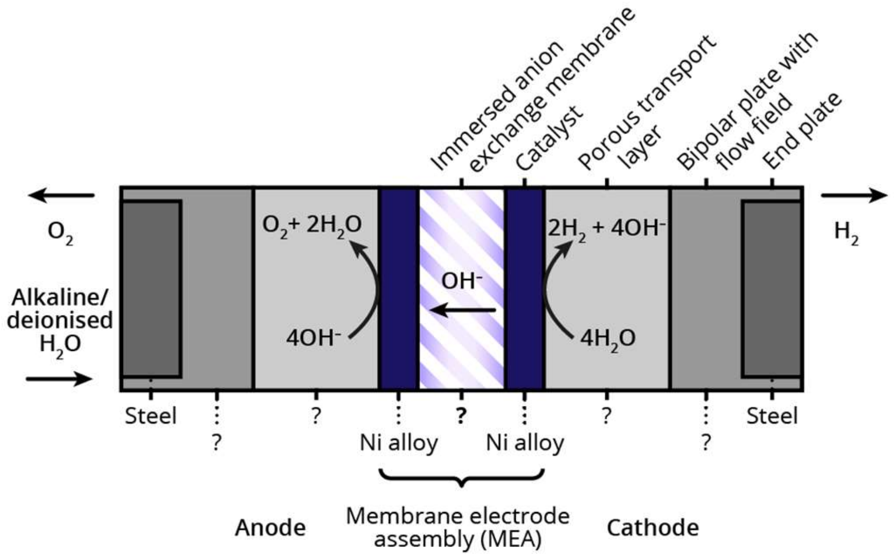
Bridging the gap from fundamental to the application

- Practical electrolyzers are way more complex

Proton exchange membrane water electrolyser



Anion exchange membrane water electrolyser



Role of these effects of solution structure when using an ion selective membranes?

Lagadec and Grimaud, in preparation

Bridging the gap from fundamental to the application

☐ OER (and HER for now) catalysts for alkaline WE are not yet an issue since there is no good membrane !!

☐ OER (and HER) activity measured at lab must be benchmarked in real conditions (MEA)

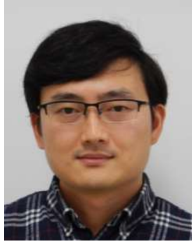
☐ Ir price is not an issue right now for PEMWE
(price is mostly governed by all the other elements of the WE)

→ Abundance is the real issue: need to increase the intrinsic activity as well as the mass activity

Thank you for your attention

Dr. Ronghuan Zhang

Nicolas Dubouis



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PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR