Cathode Catalysis in Acid and in Alkaline Fuel Cells

Shimshon Gottesfeld

Cellera Technologies
Caesaria Industrial Park

e-mail: shimshon@cellera.biz

Introductory: 1

- Hydrogen/air fuel cells convert chemical free energy of 1.2 V equivalent , generating max. power at cell voltage around 0.6V
- Out of this loss of 0.6V (conversion efficiency down to 50%) , the air cathode losses are near 0.5V, i.e., 80% of the total voltage loss
- The reason for such high air cathode losses is the slowness of the catalytic oxygen reduction reaction (ORR) at $T_{cell} < 100^0$C

** enhancement of ORR activity is therefore critical
to the operation of low T fuel cells
at higher efficiency /higher power density

Introductory: 2

- The low T fuel cell technology most extensively developed to date (by far) is based on a *proton* conducting membrane electrolyte -- the PEM fuel cell

- The acidic environment of this polymer electrolyte practically forces the use of Pt and Pt alloys as ORR catalysts

- Following extensive R&D , Pt catalyst need per kW generated by a PEM FC stack, is still near 1g (practically all in the air cathode). i.e., 35$ in Pt cost per kW generated

  worse still, Pt price is v. volatile and will jump high on introduction of a new Pt catalyst-based product

*** the ORR catalyst is therefore not only an
important cell performance determinant
it is also a
key FC technology *cost* factor

Introductory: 3

Platinum metal and alloys have been documented to have the highest ORR catalytic activity vs. any alternative catalyst tested

Why Platinum ?

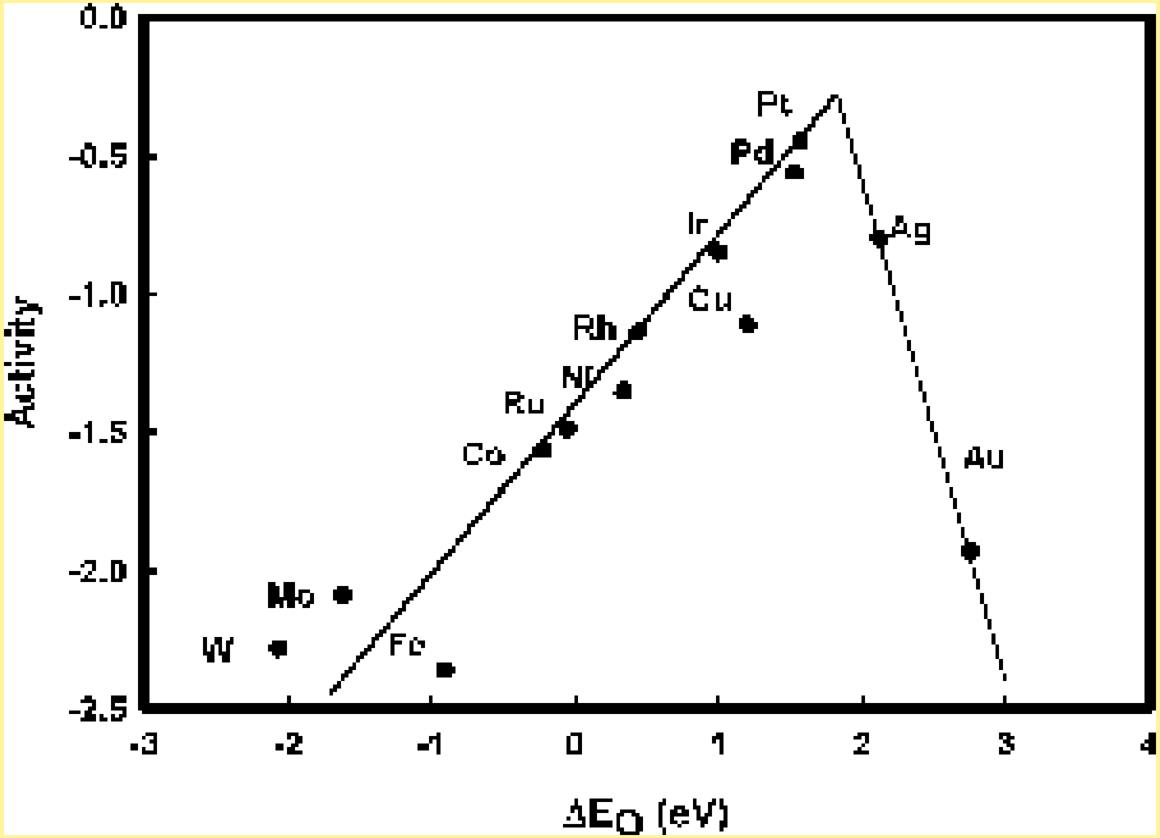
The qualitative argument :

Pt has an optimized M-O bond strength

An older literature graphical depiction :

"The Volcano Plot"

ORR "activity" vs. formation energy of M-O from water



ORR revisited using Electronic Structure (DFT) Calculations

J. Phys. Chem. B **2004,** *108,* 17886-1789

Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode

J. K. Nørskov,* J. Rossmeisl, A. Logadottir, and L. Lindqvist

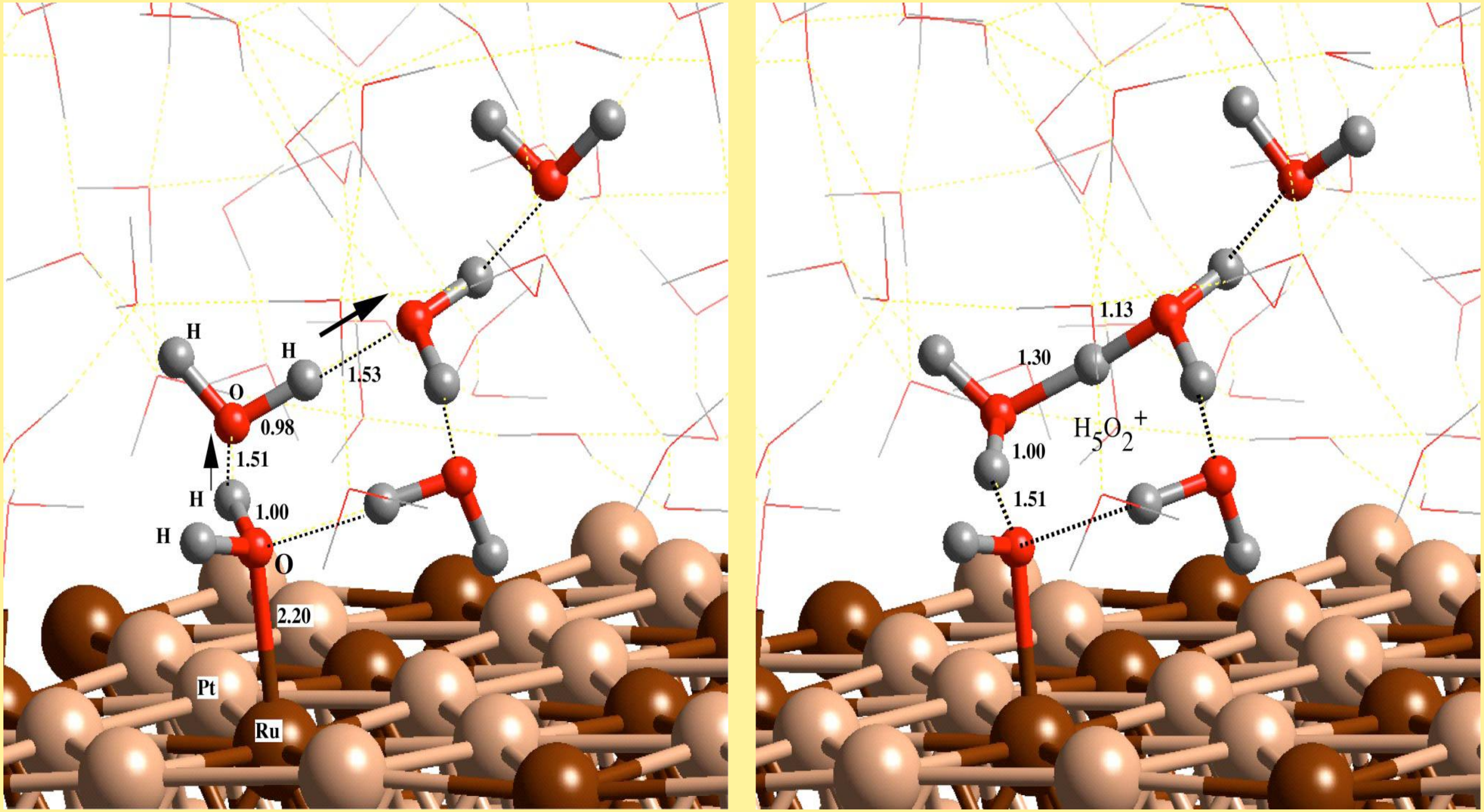
Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark,

ABSTRACT:

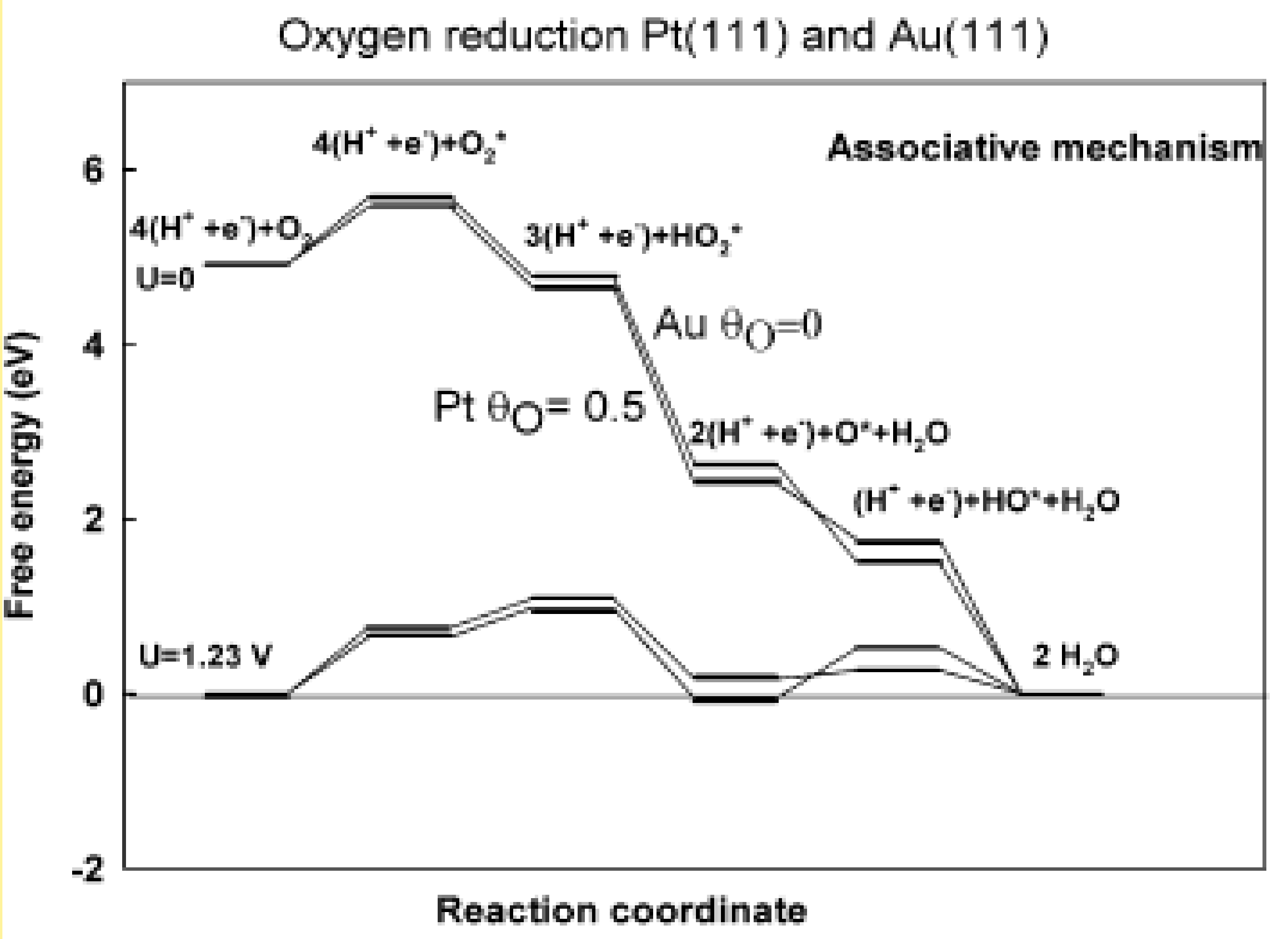
…“(we are) calculating the stability of reaction intermediates of electrochemical processes on the basis of electronic structure calculations”

…“(we) identify the origin of the overpotential found for this reaction”

…“the calculated rate constant for the activated proton/electron transfer to adsorbed oxygen or hydroxyl can account quantitatively for the observed kinetics”



Neurock et al , 2003



Free Energy Map of ORR Reactants ,Intermediates and Products

Norskov et al, 2004

Most quoted mechanism of O_2 electro-reduction on Pt

(1) 1st electron & proton transfer to O_2 activating the O-O bond:

$$O_2 + (H^+ + e) + Pt_{SS} = HOO\text{-}\ Pt_{SS}$$

(2) O-O bond cleavage and formation of adsorbed O atom:

$$HOO\text{-}\ Pt_{SS} + (H^+ + e) = O\text{-}\ Pt_{ss} + H_20$$

(3) Reduction of adsorbed O to adsorbed OH:

$$O\text{-}\ Pt_{SS} + (H^+ + e) = HO\text{-}\ Pt_{ss}$$

(4) Reduction of adsorbed OH to water:

$$OH\text{-}\ Pt_{ss} + (H^+ + e) = Pt_{ss} + H_20$$

The Mechanism of O_2 electro-reduction

(1) $O_2 + (H^+ + e) + Pt_{SS} = HOO\text{-}\ Pt_{SS}$

(2) $HOO\text{-}\ Pt_{SS} + (H^+ + e) = O\text{-}\ Pt_{ss} + H_20$

(3) $O\text{-}\ Pt_{SS} + (H^+ + e) = HO\text{-}\ Pt_{ss}$

(4) $OH\text{-}\ Pt_{ss} + (H^+ + e) = Pt_{ss} + H_20$

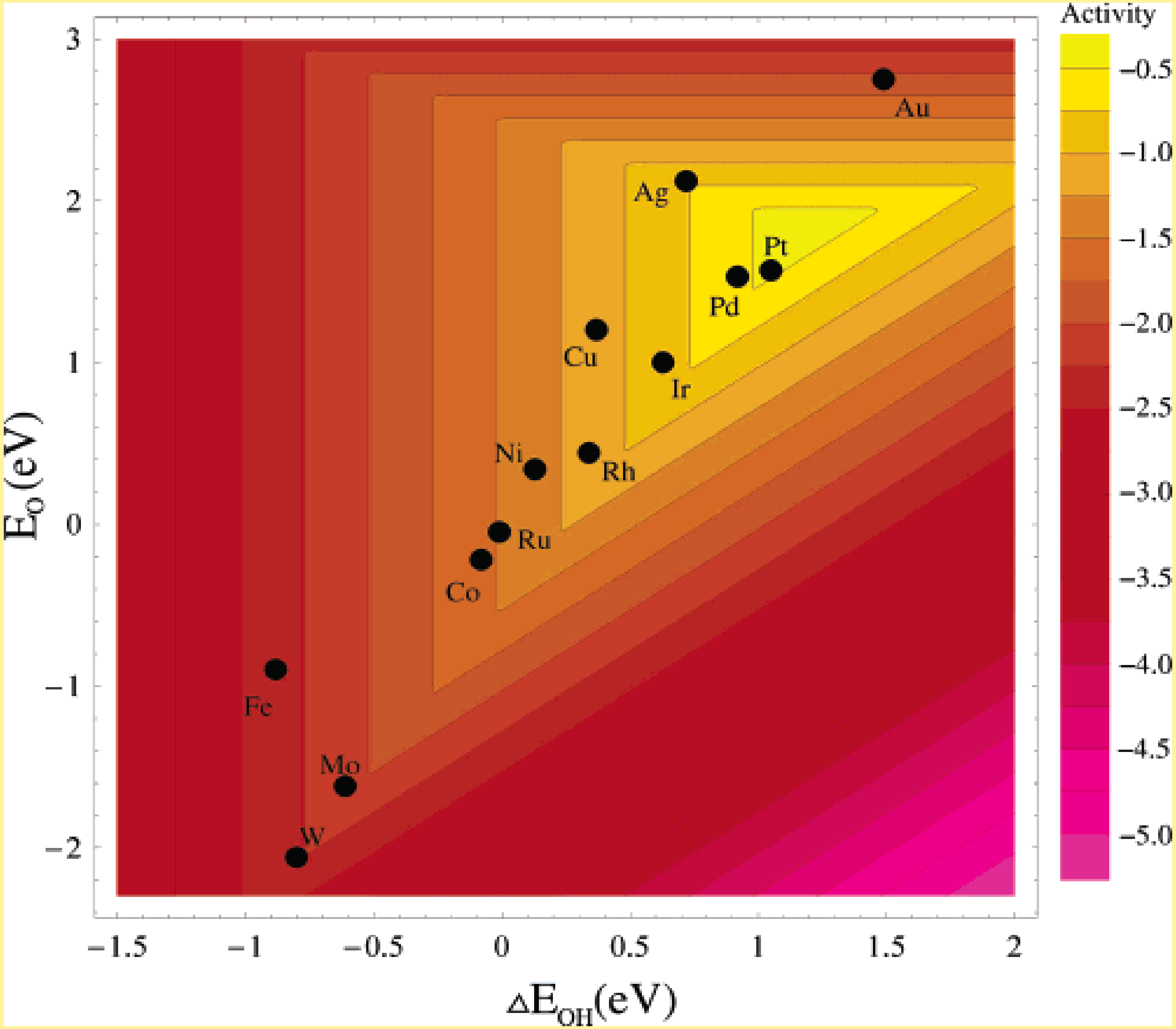
2004 paper :

steps (3) ,(4) are the slow step(s) by reasoning of calculated energy changes associated with these steps

In contrast, earlier experimental diagnostics revealed:

*ORR reaction order vs. O_2 =1 , and
* $dV_{cath}/dlogJ_{orr}$ =120 mV/decade for ORR on oxide-free Pt

leading to assignment of ***step (1)*** as the slowest step in the process



From Norskov et al 2004

The Mechanism of O_2 electro-reduction

(1) $O_2 + (H^+ + e) + Pt_{SS} = HOO\text{-}\ Pt_{SS}$

(2) $HOO\text{-}\ Pt_{SS} + (H^+ + e) = O\text{-}\ Pt_{ss} + H_20$

(3) $O\text{-}\ Pt_{SS} + (H^+ + e) = HO\text{-}\ Pt_{ss}$

(4) $OH\text{-}\ Pt_{ss} + (H^+ + e) = Pt_{ss} + H_20$

2004 paper :

steps (3) ,(4) are the slow step(s) by reasoning of calculated energy changes associated with these steps

In contrast, earlier experimental diagnostics revealed:

*ORR reaction order vs. O_2 =1 , and

* $dV_{cath}/dlogJ_{orr}$ =120 mV/decade for ORR on oxide-free Pt

leading to assignment of ***step (1)*** as the slowest step in the process

The mechanism of O_2 electro-reduction

$$(1)\ O_2 + (H^+ + e) + Pt_{SS} = HOO\text{-}\ Pt_{SS}$$

$$(2)\ HOO\text{-}\ Pt_{SS} + (H^+ + e) = O\text{-}\ Pt_{ss} + H_20$$

$$(3)\ O\text{-}\ Pt_{SS} + (H^+ + e) = HO\text{-}\ Pt_{ss}$$

$$(4)\ OH\text{-}\ Pt_{ss} + (H^+ + e) = Pt_{ss} + H_20$$

ORR kinetics at Pt is generally written , with step 1 in mind, as:

$$\mathbf{J_{ORR}(E) = k\ P_{O2}\ \exp\{-\Delta H^*_{act}/RT\}\exp\{-(E-E^0_{O2/H2O})\ /b\ \}}$$

with:

k-frequency factor

ΔH^*_{act} - chemical component of E_{act} for the slow step

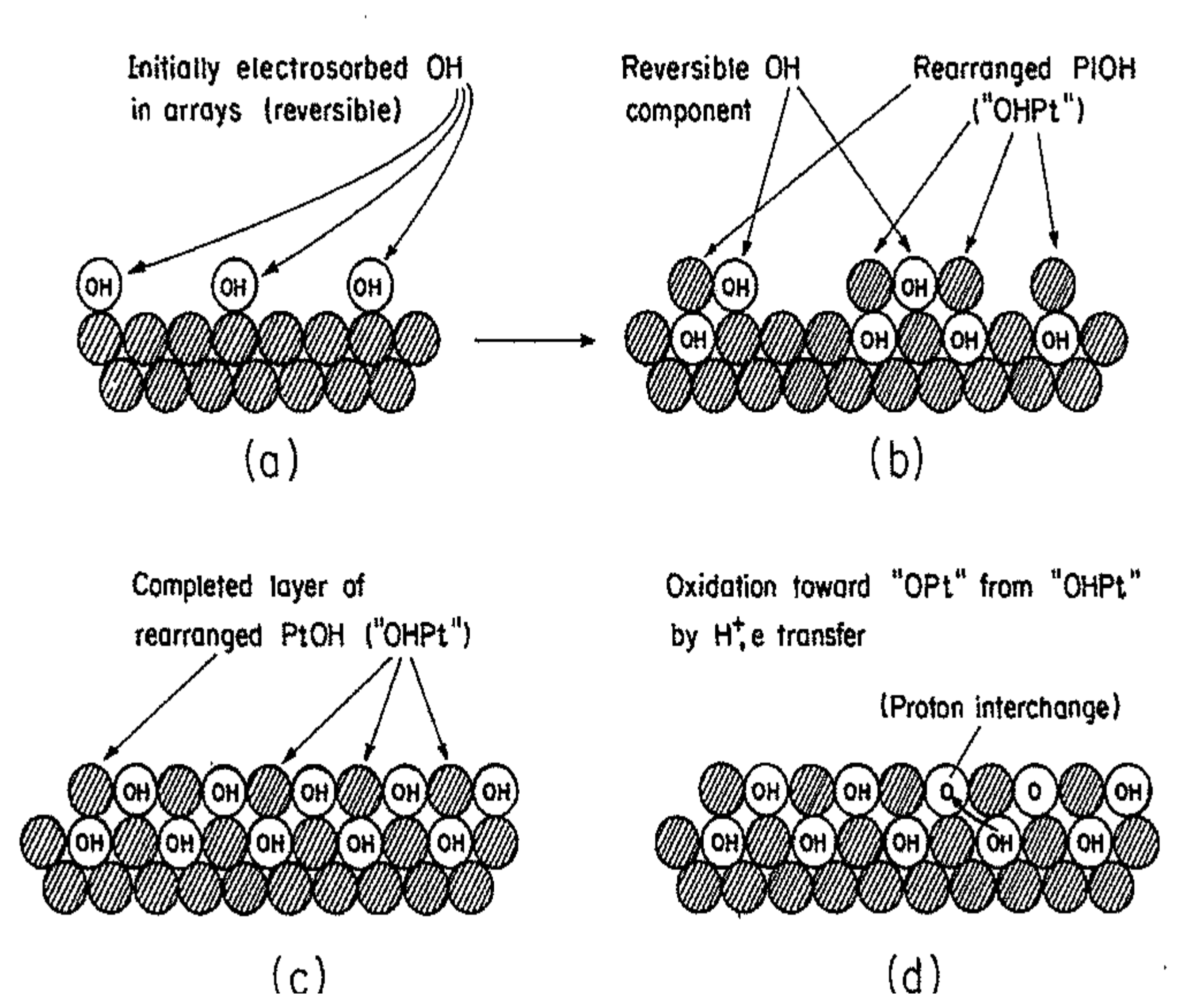
b - $d\log J\ /d(E-E^0_{O2/H2O})$ (“Tafel slope”)

Why would slow step 1 lead to a strong correlation of J_{ORR} with M-O bond energy ??

Could step (3) actually be the slow step ?

Is there something else that could explain the volcano correlation ?

Answer: The accepted expression for J_{ORR} assumes a metal surface fully available for the process, however



there is high chemisorbed O/OH coverage *derived from water on Pt* in the operating cathode :

formed by: $Pt_{ss} + H_20 = OH\text{-} Pt_{ss} + (H^+ + e)$ (“water discharge”)

Consideration of Metal Site Availability in the expression for ORR:
The pre-exponential factor

(1) J_{0RR} dependence on $N_{ss,\ total}$ and θ_{OX} :

- $J_{ORR}(E) = k\, N_{total}\, P_{O2}\, (1- \theta_{OX})\, \exp\{-\Delta H^*_{act}/RT\}\exp\{-(E-E^0_{O2/H2O})\, /b\}$

(2) θ_{OX} dependence on E_{cath} :

- $\theta_{OH} /(1-\theta_{OH})= \exp\{\, (RT/F)\, (E - E^o{}_{Pt(H2O)/Pt\text{-}OHads})\}$

(1) +(2) :

- $J_{orr}(E)= kP_{O2}\, N_{total}\, (1/Z+1)\, \exp\{-\Delta H^*act/RT\}\exp\{-(E-E^0_{O2/H2O})\, /b\}$

where $Z= \exp\{\, (F/RT)\, (E - E^o{}_{Pt(H2O)/Pt\text{-}OHads})\}$

$E-E^0_{O2/H2O}$ =1.23V vs. hydrogen

$E^o{}_{Pt(H2O)/Pt\text{-}OHads}$ = 0.80V vs. hydrogen

The extra redox potential in the J_{ORR} expression

A “deeper meaning” of the involvement of

$\mathbf{E^{o}}_{\mathbf{Pt(H2O)/Pt\text{-}OHads}}$ as determinant of the ORR rate

O_2 interaction with the Pt catalyst surface is enabled by interaction with the reduced form of a surface site

The reduced form become available only when $\mathbf{E_{cath}}$ approaches $\mathbf{E^{o}}_{\mathbf{Pt(H2O)/Pt\text{-}OHads}}$

This is strongly reminiscent of electroredution

by “***Redox Couple Mediation***”

further details on the science and practicality of the ORR
and on bridging apparent gaps between ORR reports:

“Electrocatalysis of Oxygen Reduction
in Polymer Electrolyte Fuel Cells:
A Brief History and
Critical Examination of Present Theory and Diagnostics”

Shimshon Gottesfeld, Cellera Technologies

in: “Fuel Cell Catalysis: a Surface Science Approach”
Ed. M.T.M Koper (Leiden University) , John Wiley ,in press

oxygen reduction redox mediated by an active $Co^{+3}/^{+2}$ surface system

- (A) $4Co^{+3}_{surface} + 4e = 4Co^{+2}_{surface}$

  active reduced site generation

- (B) $4Co^{+2}_{surface} + O_2 + 4H^+ = 4Co^{+3}_{surface} + 2H_2O$

  faradaic reaction of O_2 at/with the reduced site

- (C) $4Co^{+3}_{surface} + 4e = 4Co^{+2}_{surface}$

  active site regeneration

oxygen reduction “redox mediated” by the Pt/Pt-OH redox system

- (A) $4Pt\text{-}OH_{surface} + 4H^+ + 4e = 4Pt_{surface} + 2H_2O$
  active reduced site generation

- (B) $4Pt_{surface} + O_2 + 4e + 4H^+ = 4Pt\text{-}OH_{surfac}$
  faradaic reaction of O_2 at/with the reduced site

- (C) $4Pt\text{-}OH_{surface} + 4H^+ + 4e = 4Pt_{surface} + 2H_2O$
  active site regeneration

Good general principle for searching an active ORR catalyst

"A Pourbaix guide for electrocatalysis galaxy travel":

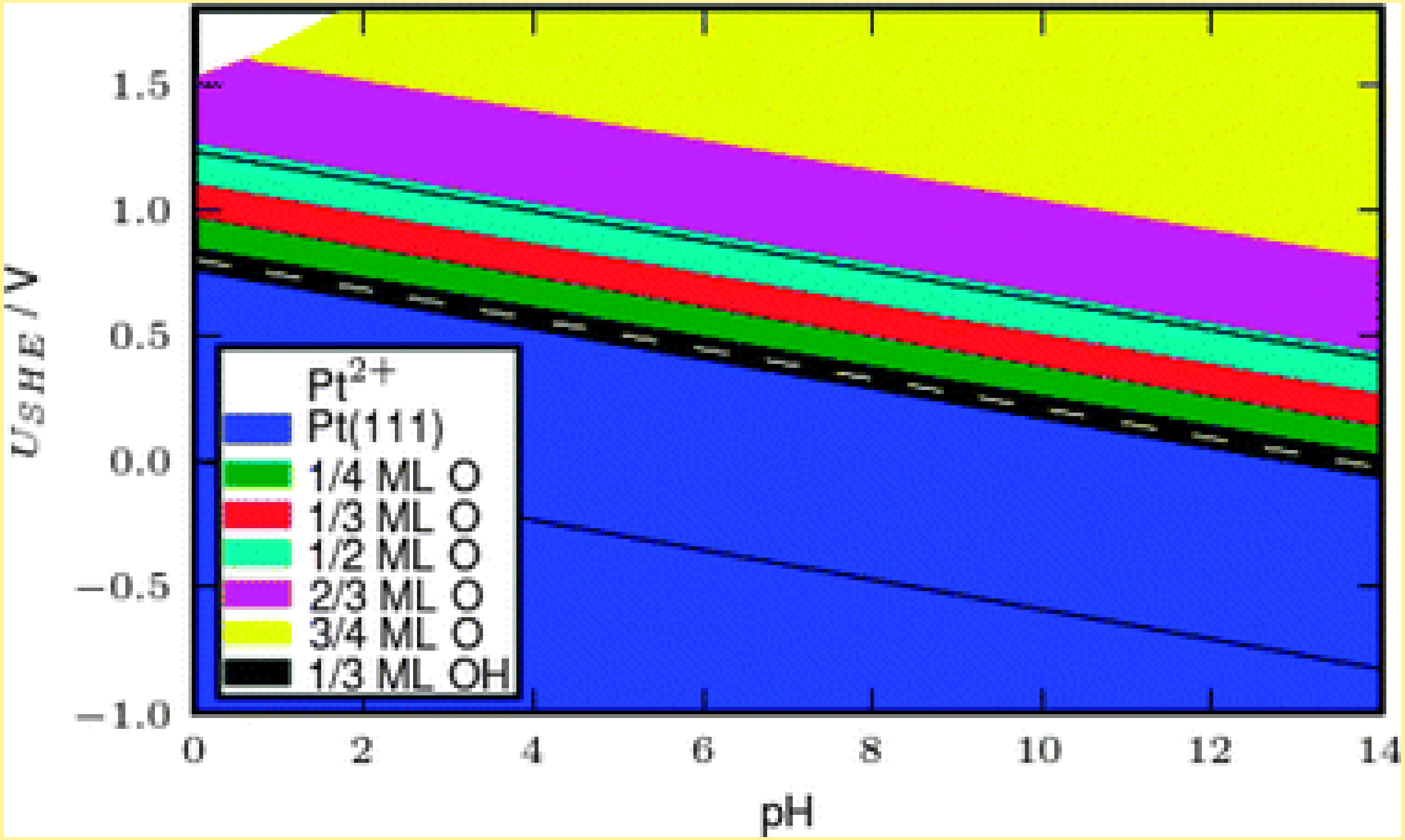
" **match the target electrode potential in the operating fuel cell with :**

the $M/M\text{-}OH_{ads}$ standard potential of the metal , or metal alloy catalyst at the relevant pH ,

or with:

the $M^{+2/+3}$ standard potential of an active surface redox couple at the relevant pH"

$Pt/Pt\text{-}OH_{ads,1/3\ ML}$; E^0 = 0. 8V , (stable in air pH 0-14)



Some Conclusions Offered :

- ORR at Pt in a fuel cell cathode takes place at a surface partly covered by various adsorbed oxygen species and the oxygen molecule can react only with metal sites

- The result can be an apparent Tafel slope lower than 120 mV/decade at V>0.75V, although the intrinsic Tafel slope for oxygen reduction at Pt metal does not necessarily change at all as function of potential

Some Conclusions Offered :

- The M/M-OH “surface redox” couple determines the pre-exponential factor in the ORR and has as important an effect as the exponential factor. *In the beginning there has to be the active site*

- Complete consideration of the pre-exponential factor and it’s exponential dependence on an Eo of the relevant surface redox system, is prerequisite for a complete description of the ORR and other electrocatalytic processes

Some Conclusions Offered :

- The guiding parameter of M-OH bond strength proposed most recently by Norskov et al, may indeed be a good gauge for ORR rate to large degree through the important function of the "surface redox" system.
- **Alkaline systems open the door to highly active/very inexpensive fuel cell catalysts – particularly so in the Alkaline Membrane Fuel Cell**

Acknowledgements

- **Israel Cleantech Ventures**
- **Office of the Chief Scientist**