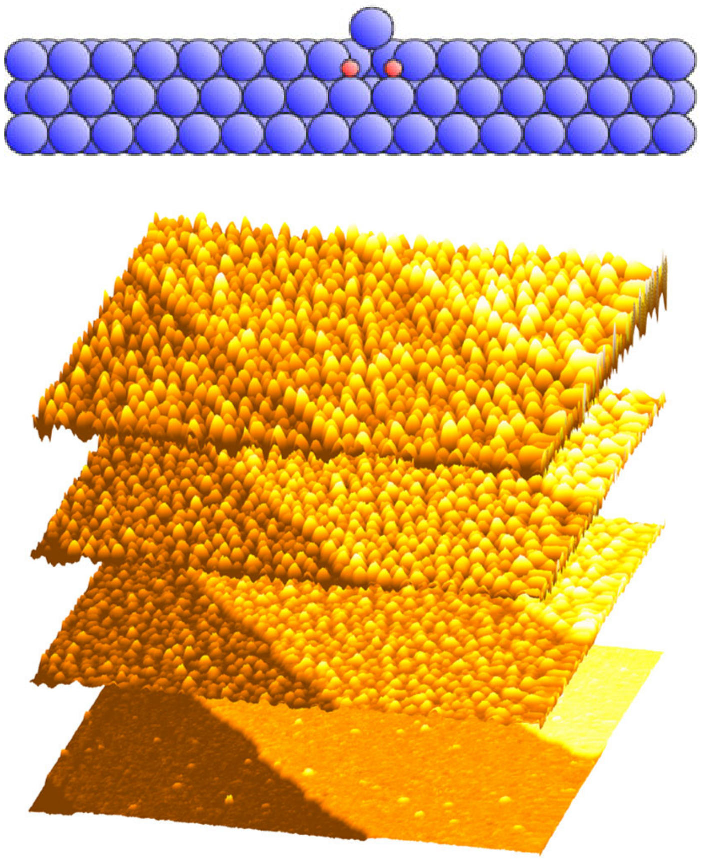
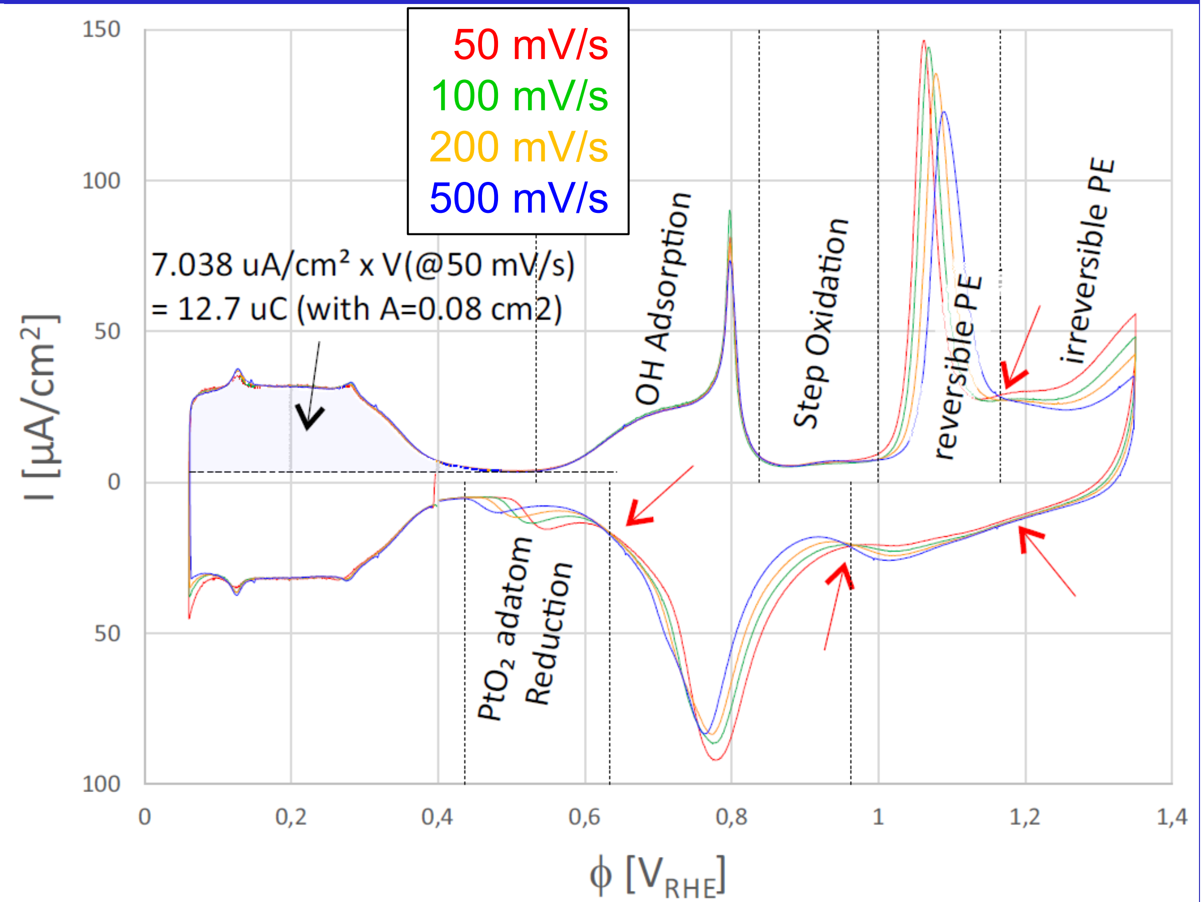
Arrhenius follows Frumkin

to describe Atomic Diffusion involved Peaks in Cyclic Voltammograms: the Reversible Place-Exchange on Pt(111)

M.J. Rost

Kamerlingh Onnes Laboratory, Leiden University (NL)





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www.physics.leidenuniv.nl/rost

Surprising Aspects of Pt(111) Oxidation and Reduction: Unravelling Four Different Oxidation Stages

EN-ROADS (MIT) https://en-roads.climateinteractive.org

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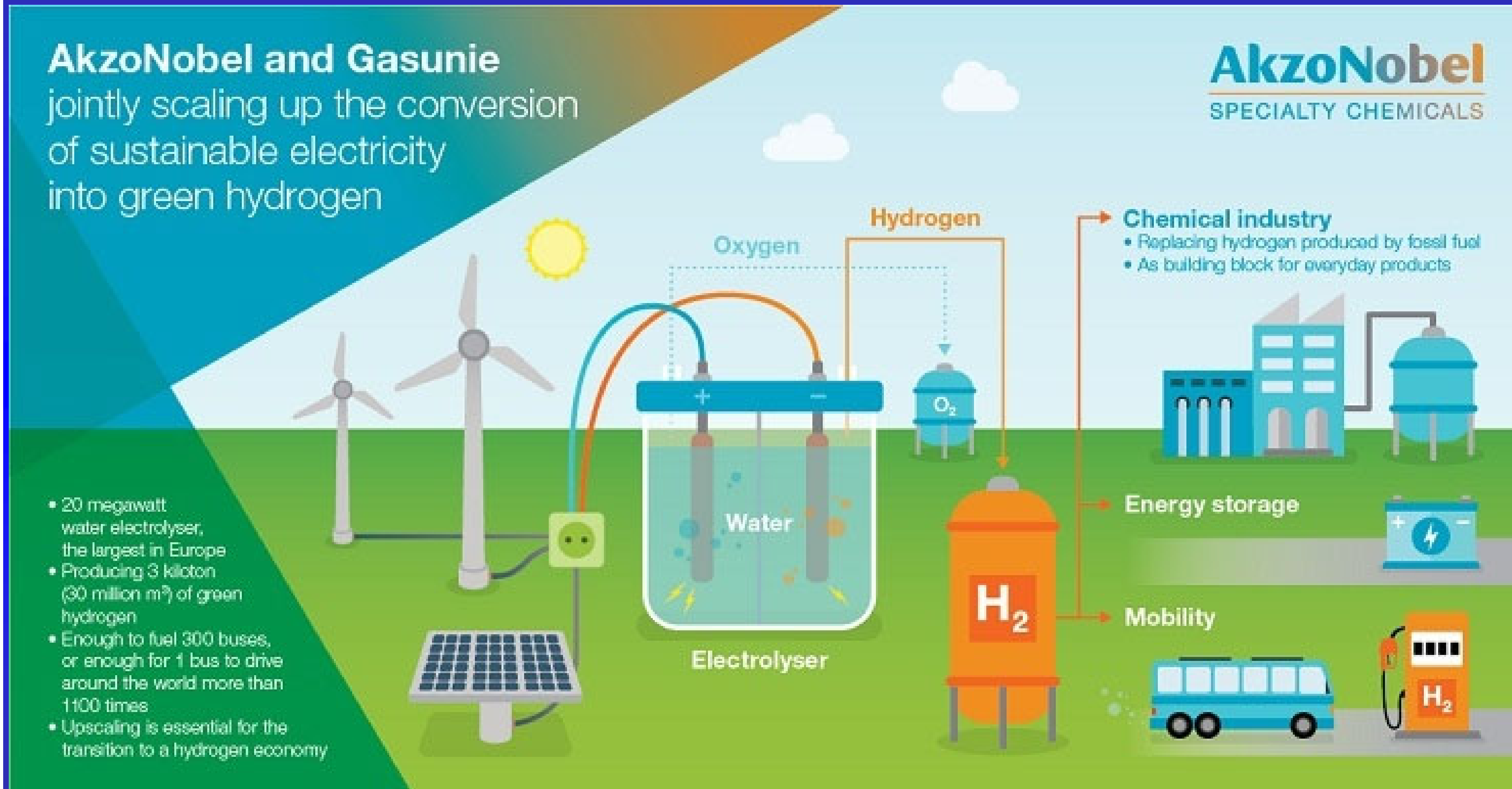
Surprising Aspects of Pt(111) Oxidation and Reduction: Unravelling Four Different Oxidation Stages



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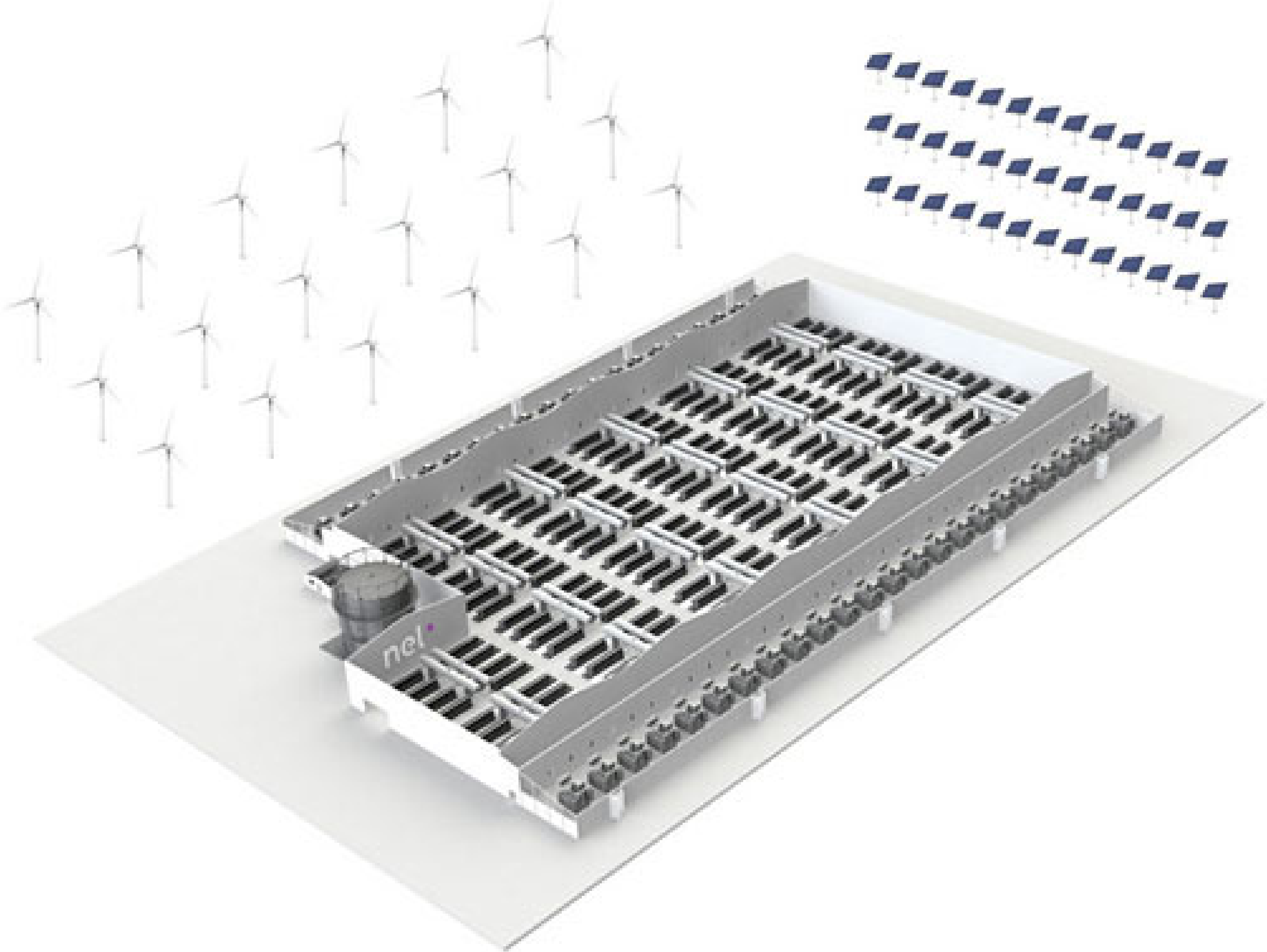
Background / Problem:



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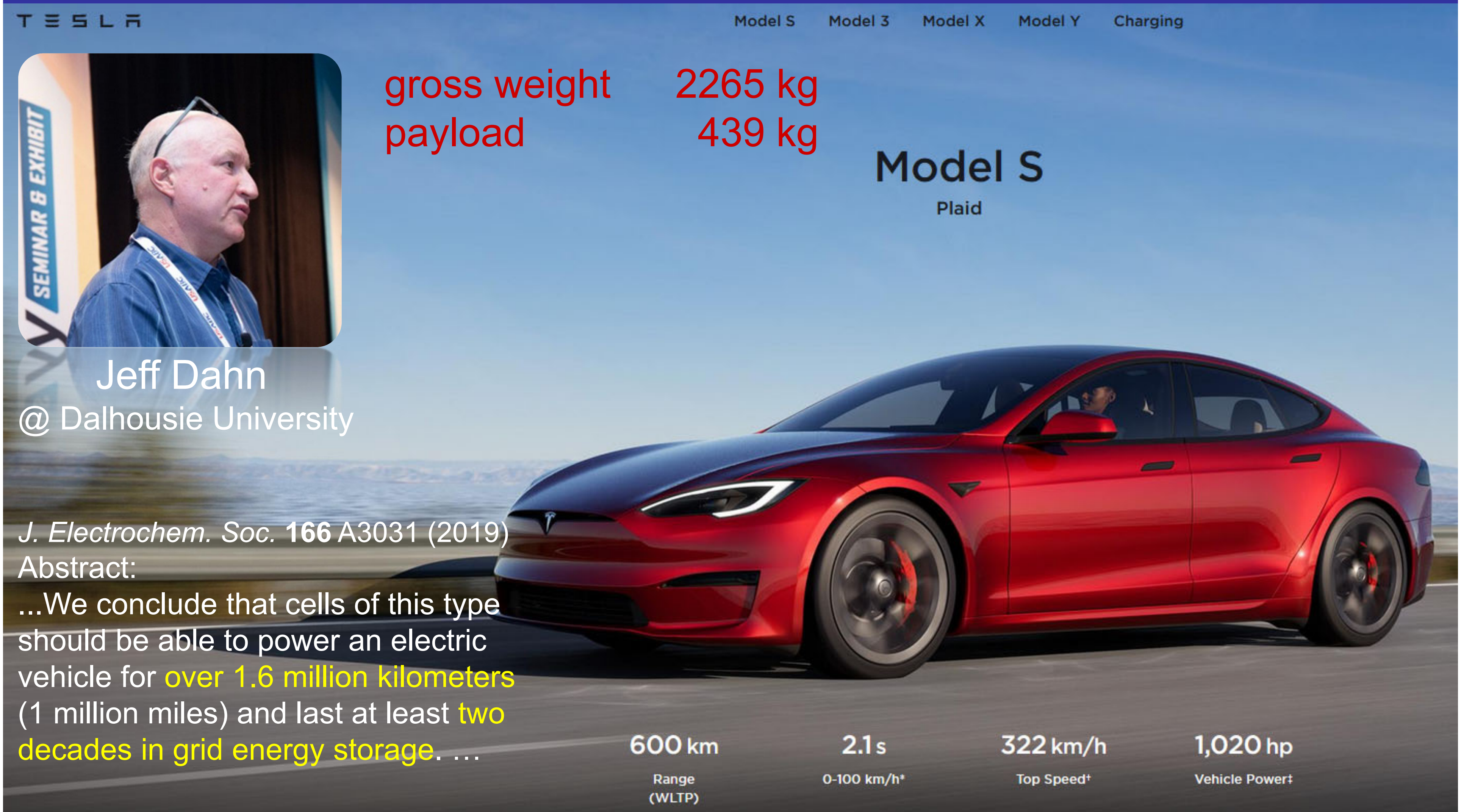
The Future: Fuel Cells



gross weight	2265 kg
payload	439 kg

Jeff Dahn
@ Dalhousie University

J. Electrochem. Soc. **166** A3031 (2019)
Abstract:
...We conclude that cells of this type should be able to power an electric vehicle for over 1.6 million kilometers (1 million miles) and last at least two decades in grid energy storage. …

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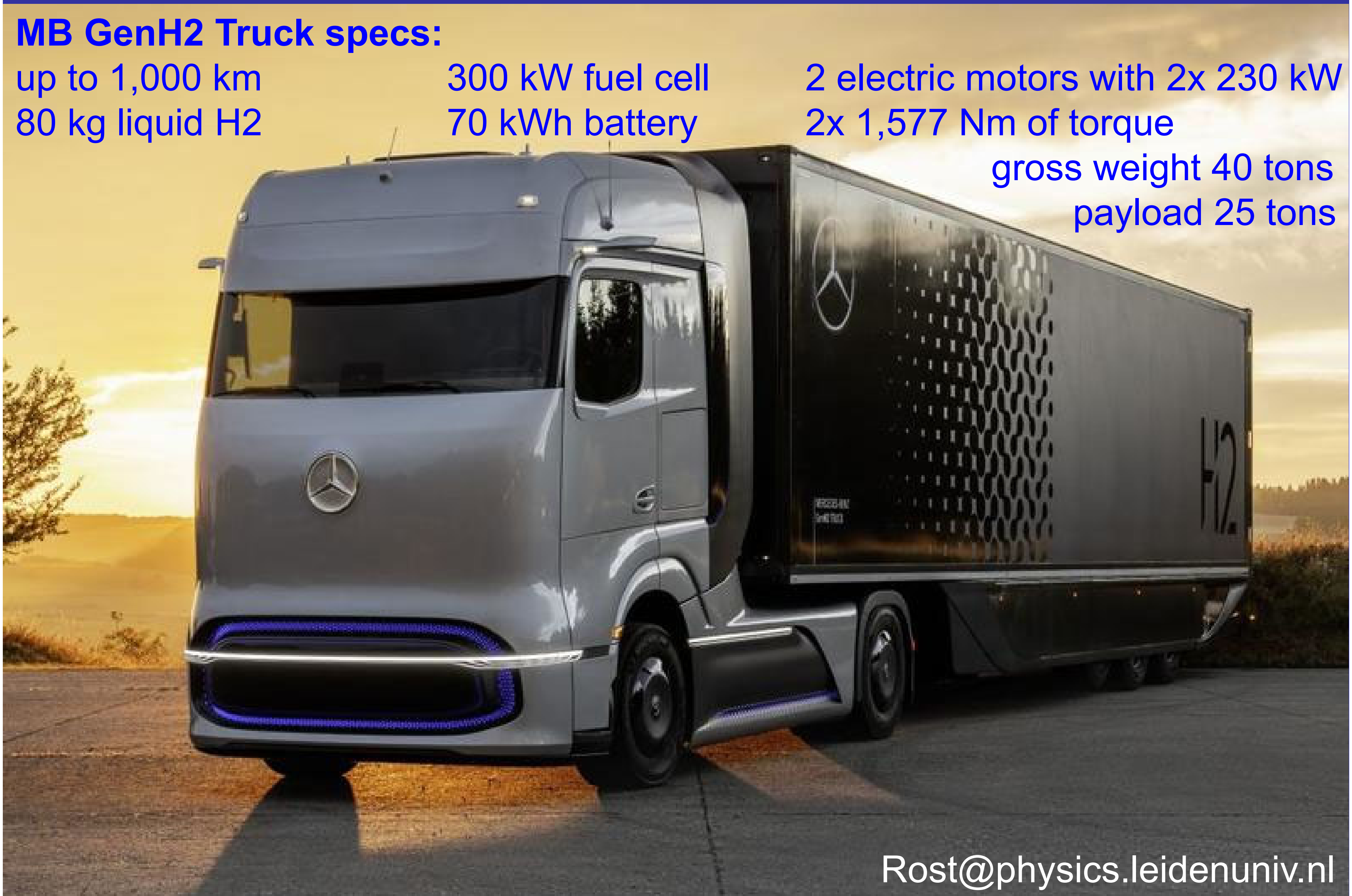
The Future: Fuel Cells

MB GenH2 Truck specs:

up to 1,000 km
80 kg liquid H2

300 kW fuel cell
70 kWh battery

2 electric motors with 2x 230 kW
2x 1,577 Nm of torque
gross weight 40 tons
payload 25 tons



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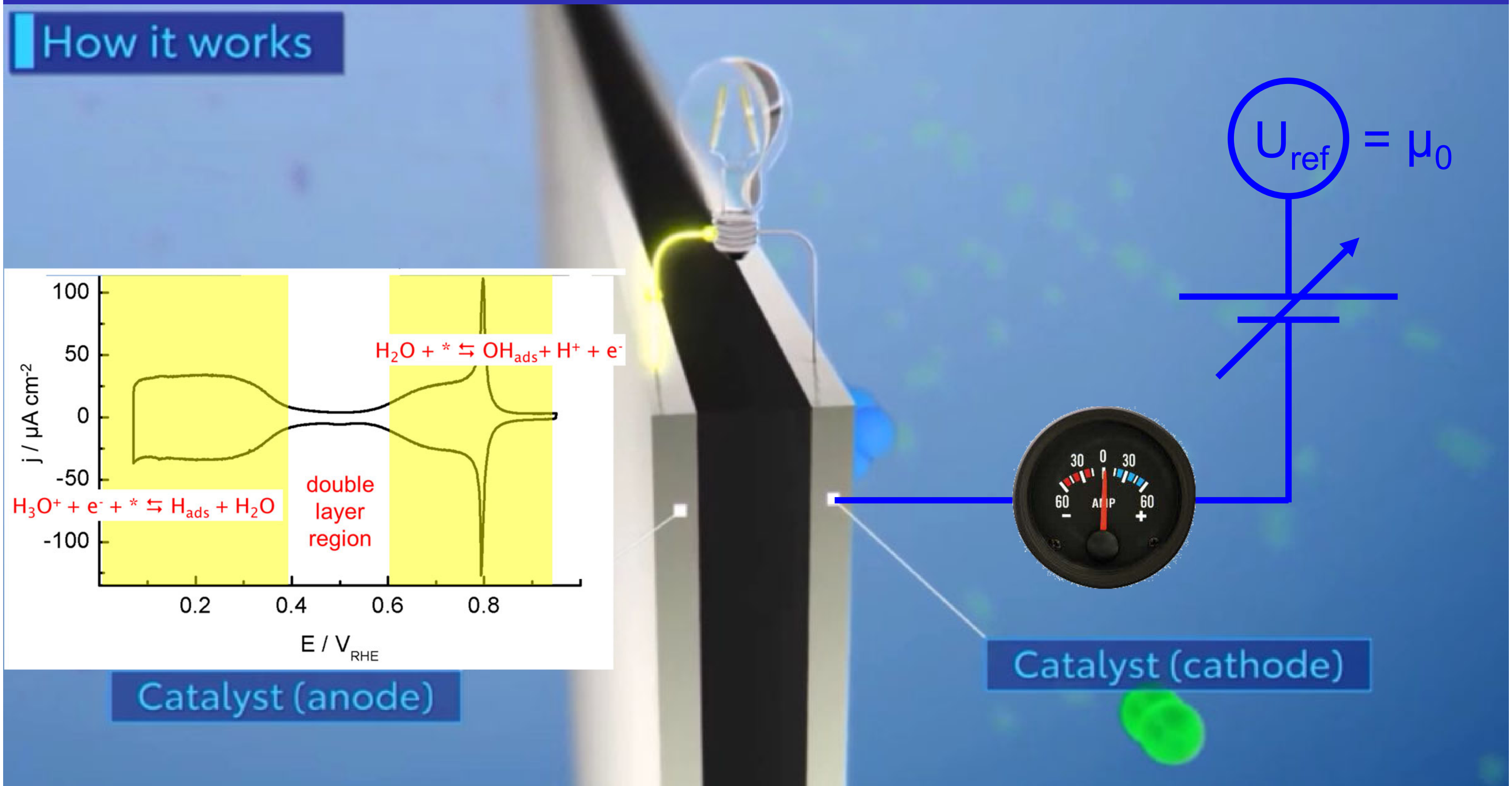
The Future: Fuel Cells

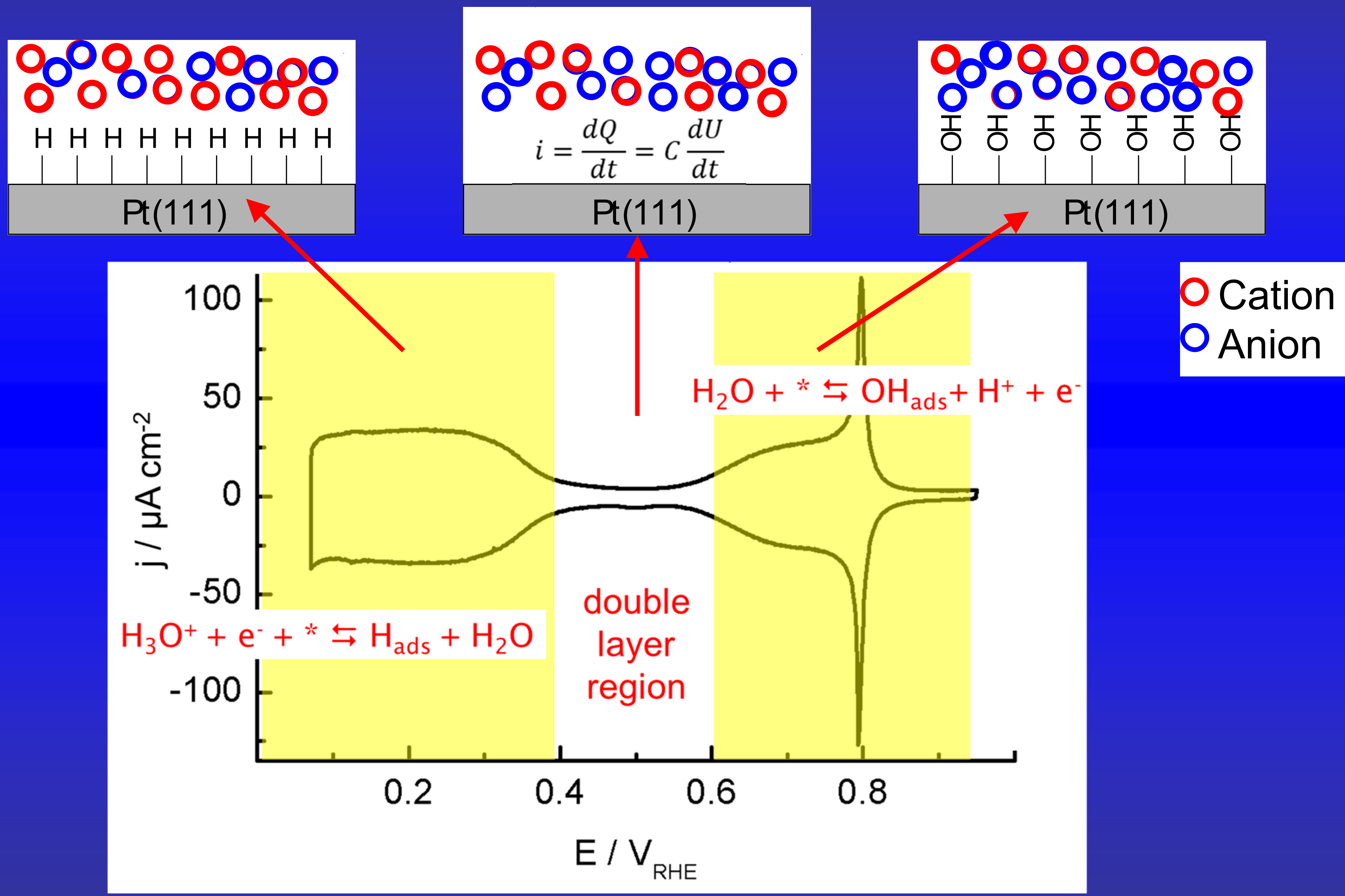
YouTube: 2021 Toyota Mirai - how it works and what's changed

The Future: Fuel Cells



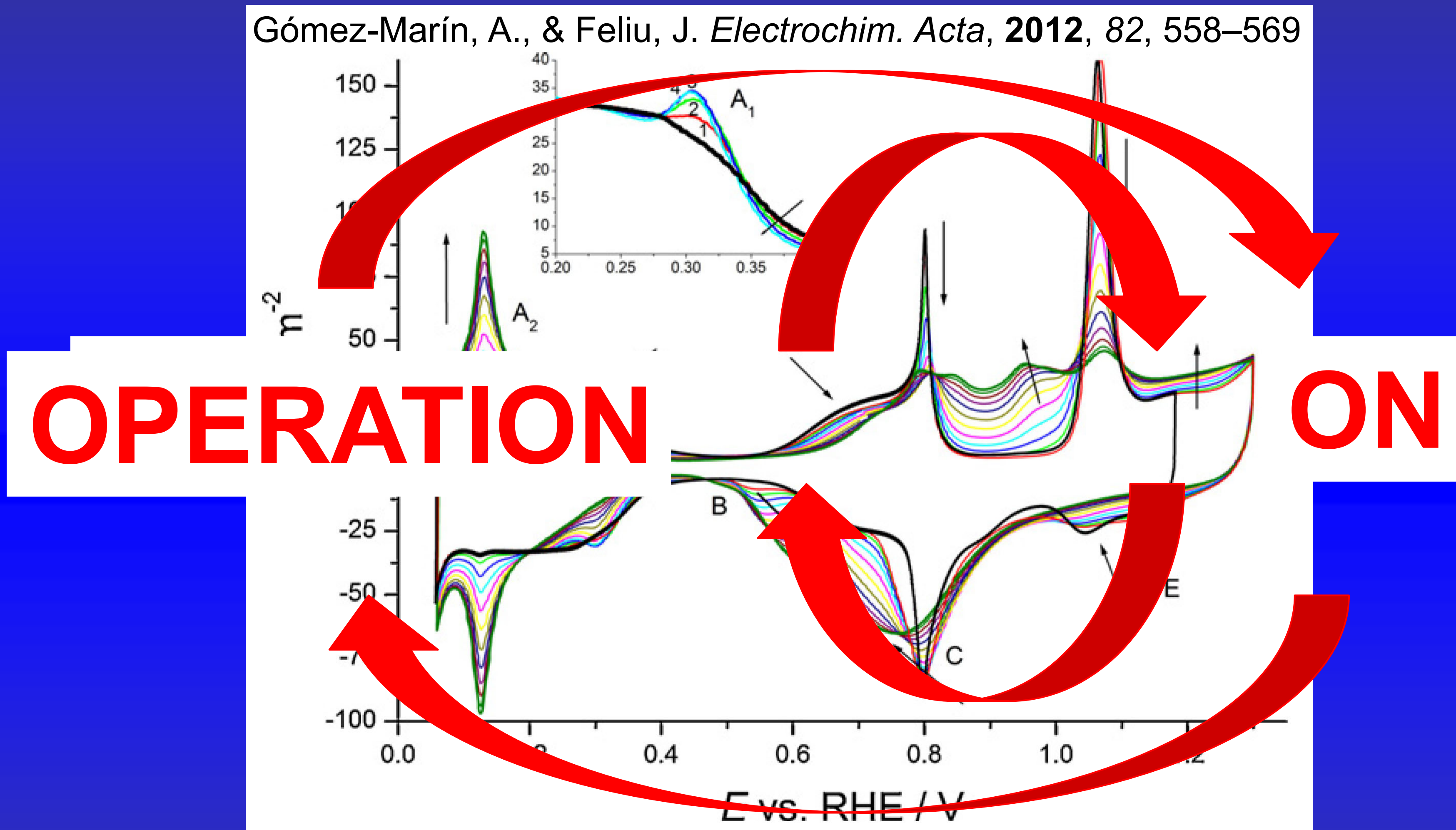
YouTube: 2021 Toyota Mirai - how it works and what's changed

Pt(111) Electrochemistry in 0.1 M $HClO_4$:



Adapted from M.T.M. Koper, *Electrochim. Acta,* **2011**, *56,* 10645

Problem: Deterioration of Electrode



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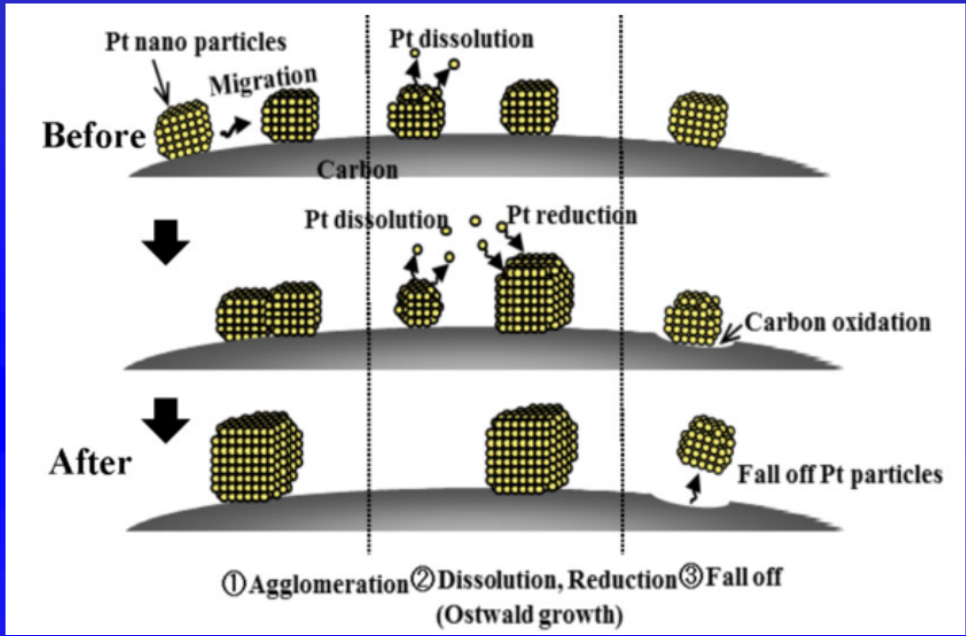
Background / Problem:

Green Car Congress

Energy, technologies, issues and policies for sustainable mobility

Toyota details design of fuel cell system in Mirai; work on electrode catalysts

While other major automakers have either introduced (Hyundai, Honda) or are in serious development of new hydrogen fuel cell vehicles for the market, Toyota continues to take the point in not just promoting, but also supporting the broader technical (and infrastructure) development required for a large-scale realization of hydrogen-based electromobility.



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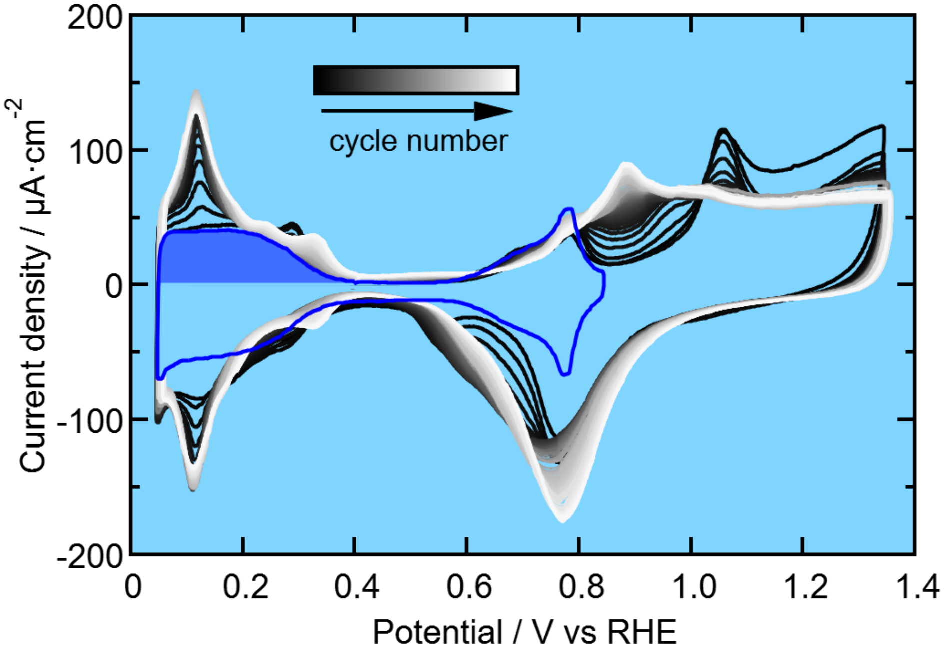
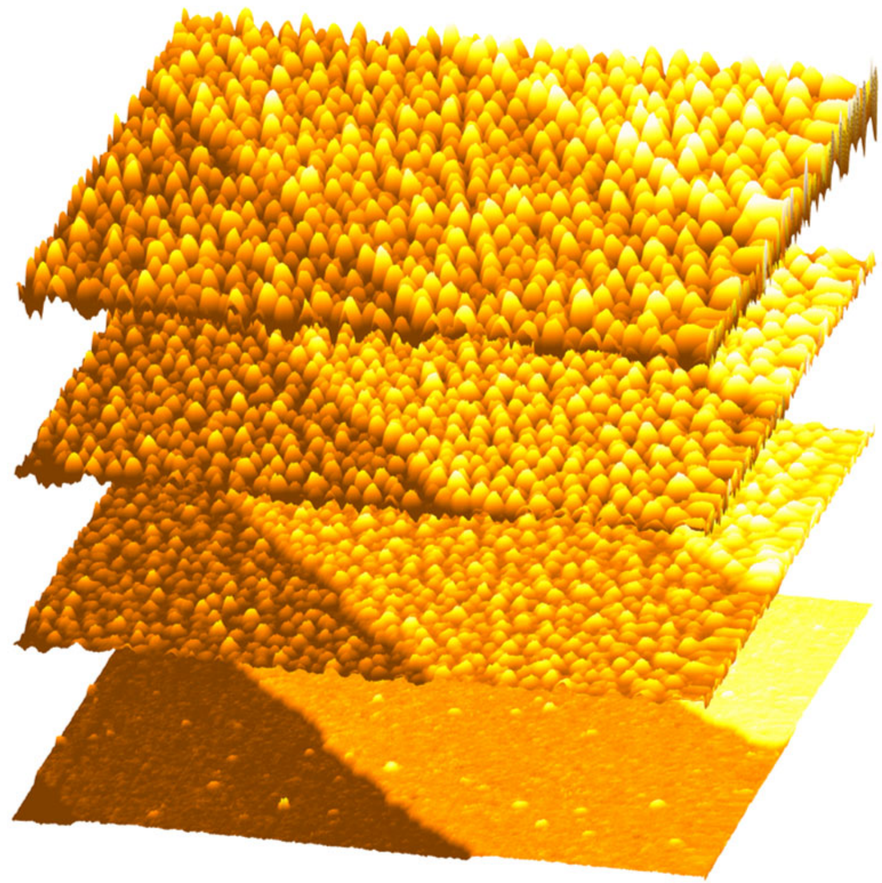
Atomic-Scale Identification of the Electrochemical Roughening of Platinum:





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Surface & Electrochemical Evolution:

Correlation of Surface Site Formation to Nanoisland Growth in the Electrochemical Roughening of Pt(111)

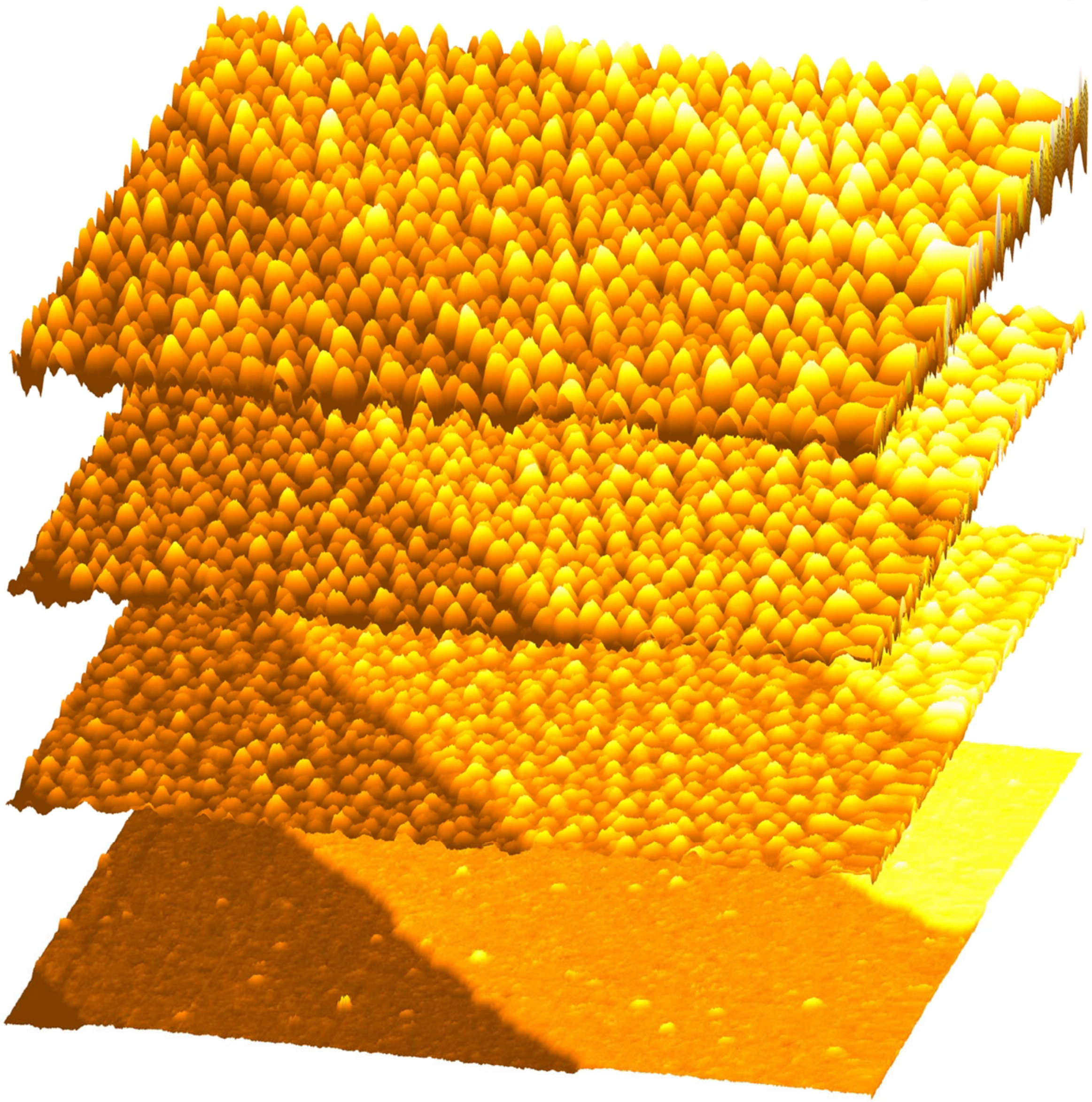
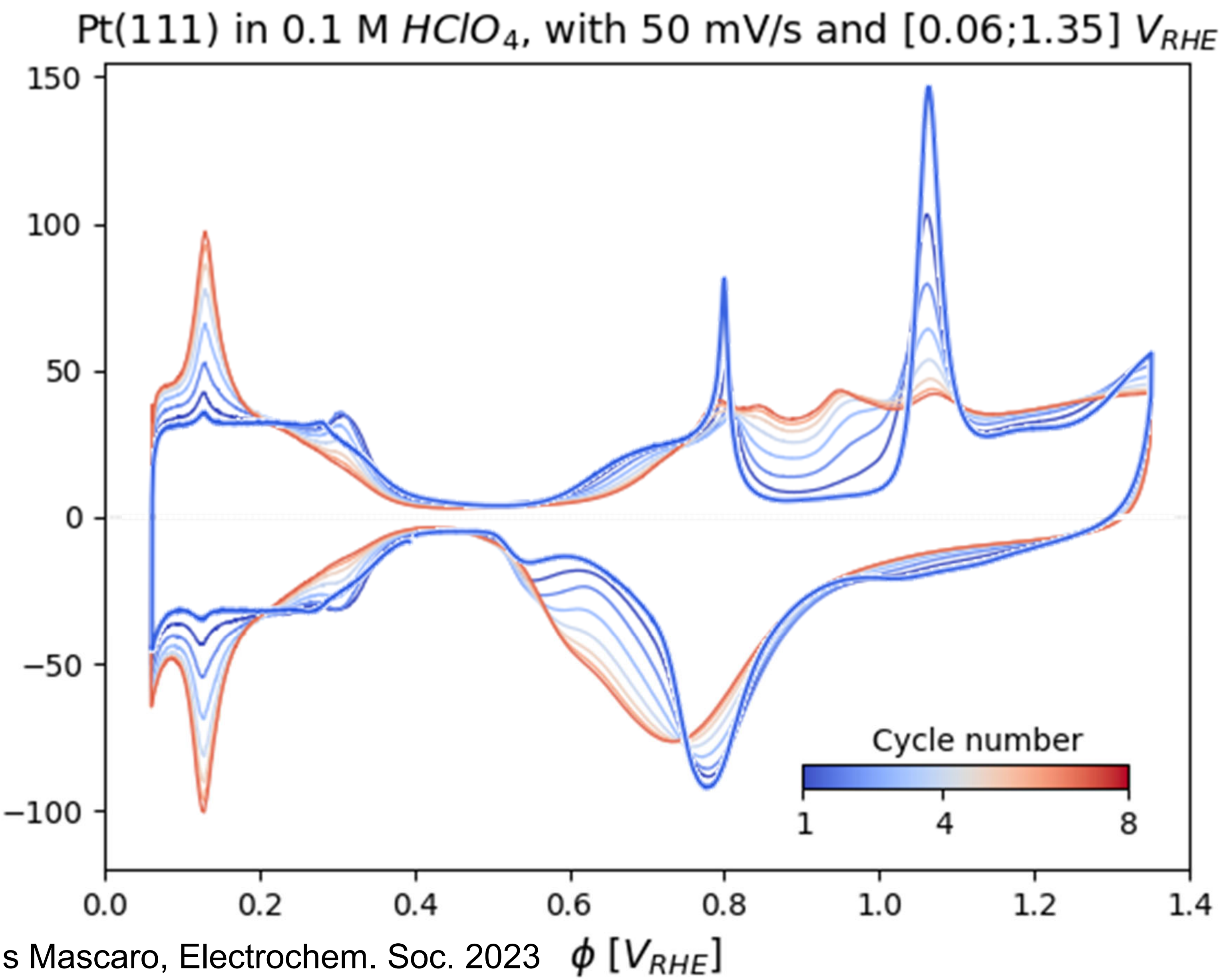


Image size: 230 x 230 nm^2
Measured in the double layer region:
U_s = 0.4 V and U_t = 0.45 V (vs. RHE)
after one or more CVs to 1.35 V

L. Jacobse, Y.-F. Huang, M.T.M. Koper, and M.J. Rost, Nature Materials, doi: 10.1038/s41563-017-0015-z

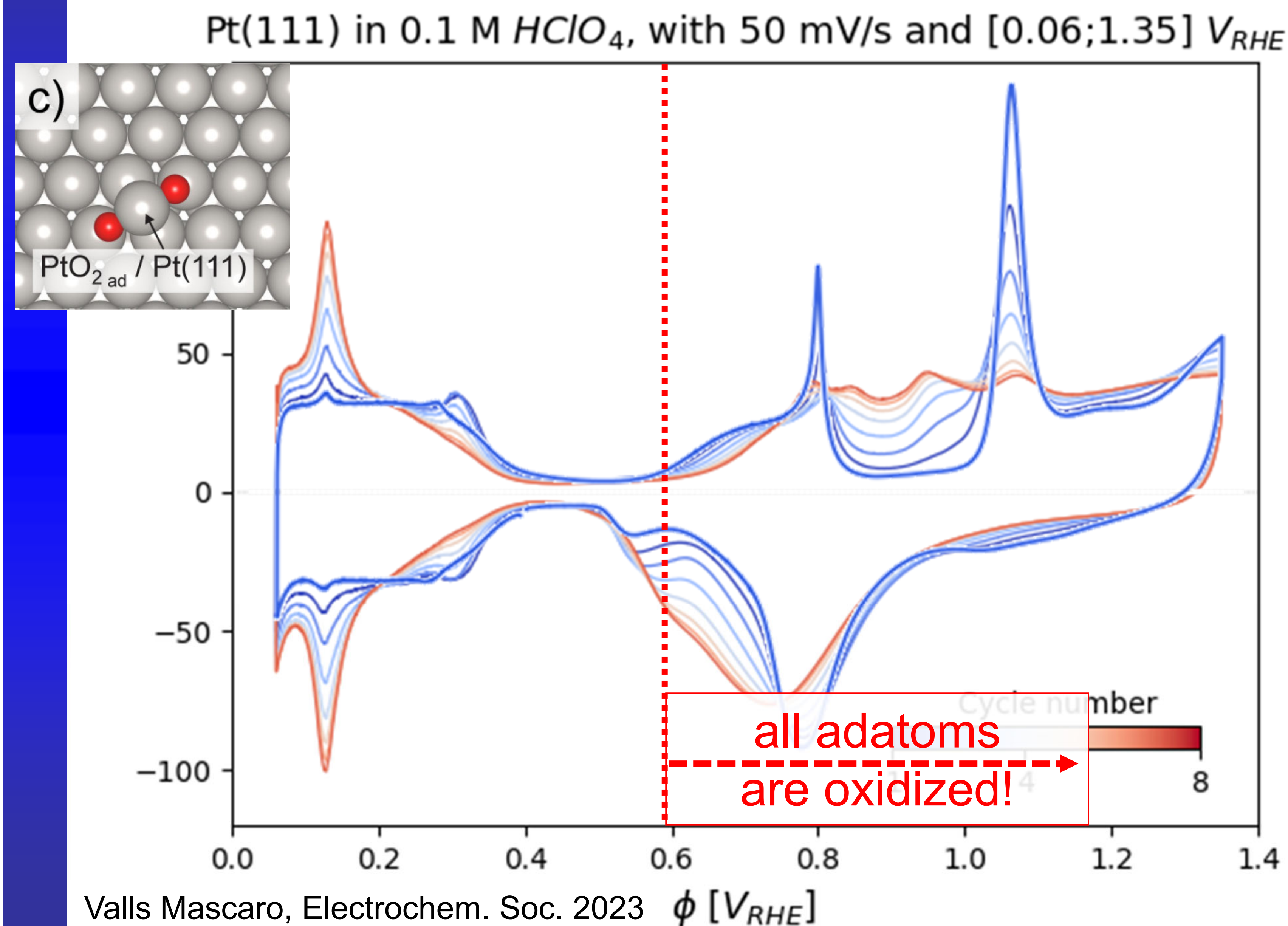
Roughening Process:

All the Oxides…



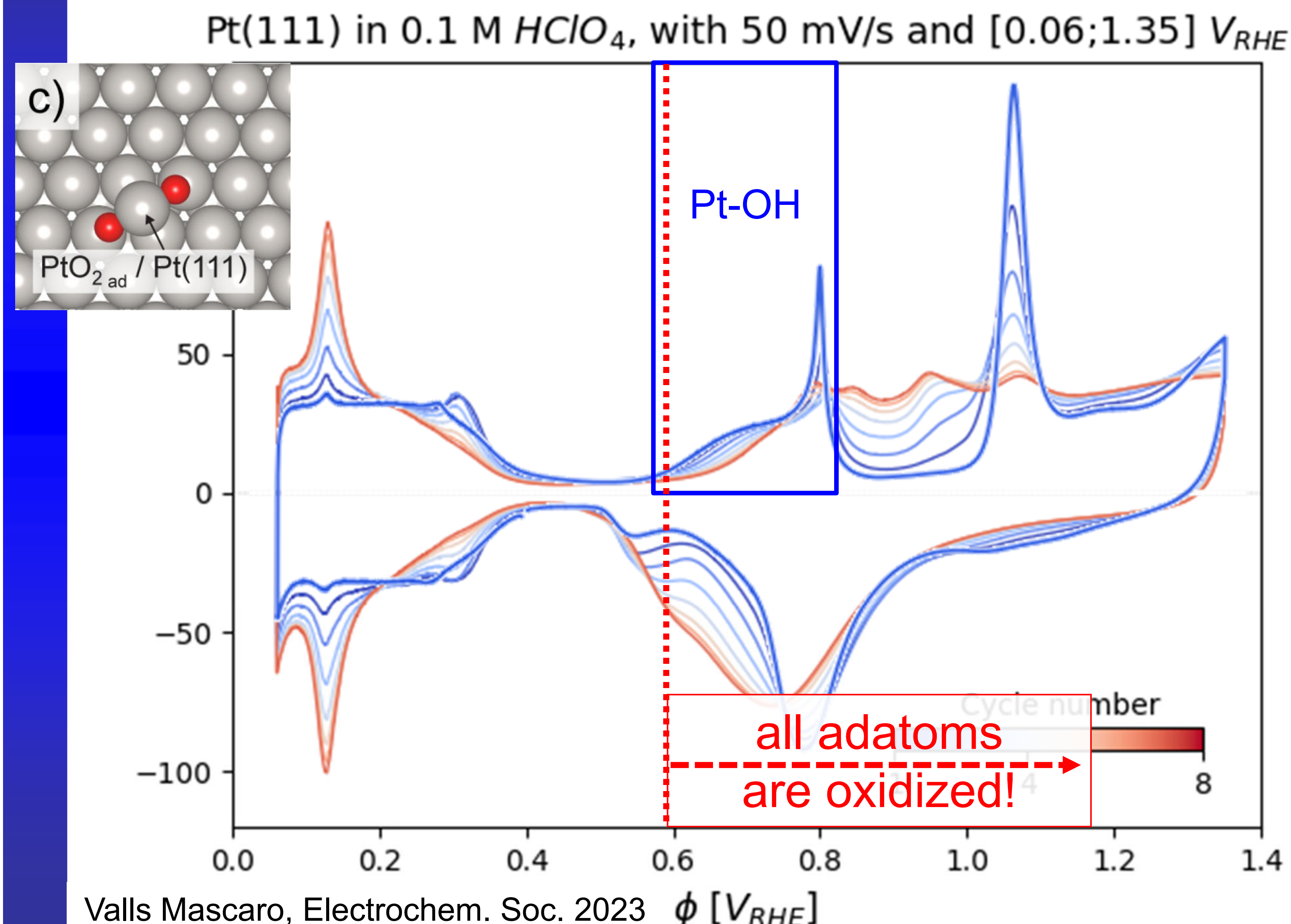
Valls Mascaro, Electrochem. Soc. 2023

All the Oxides…



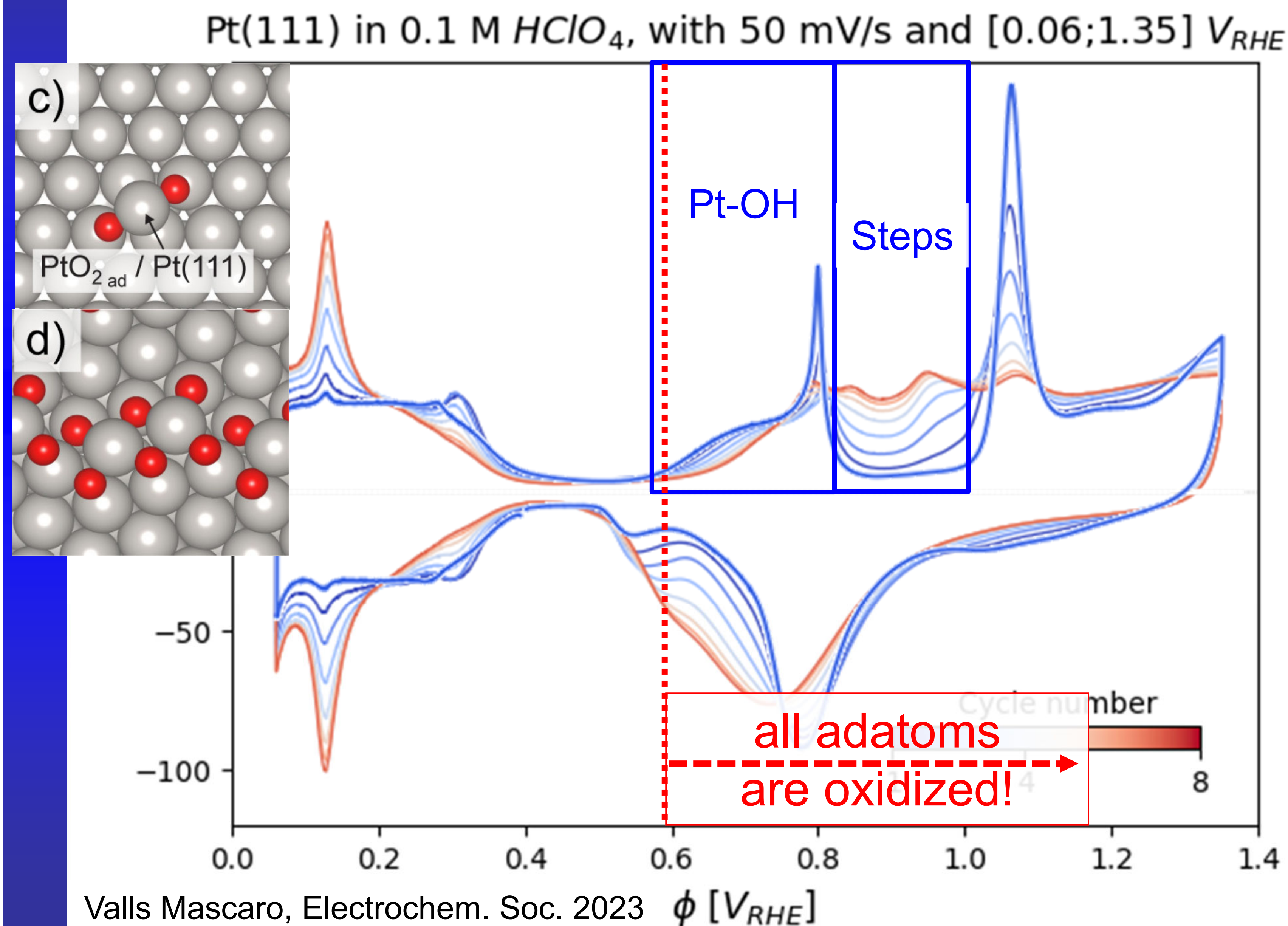
Valls Mascaro, Electrochem. Soc. 2023

All the Oxides…



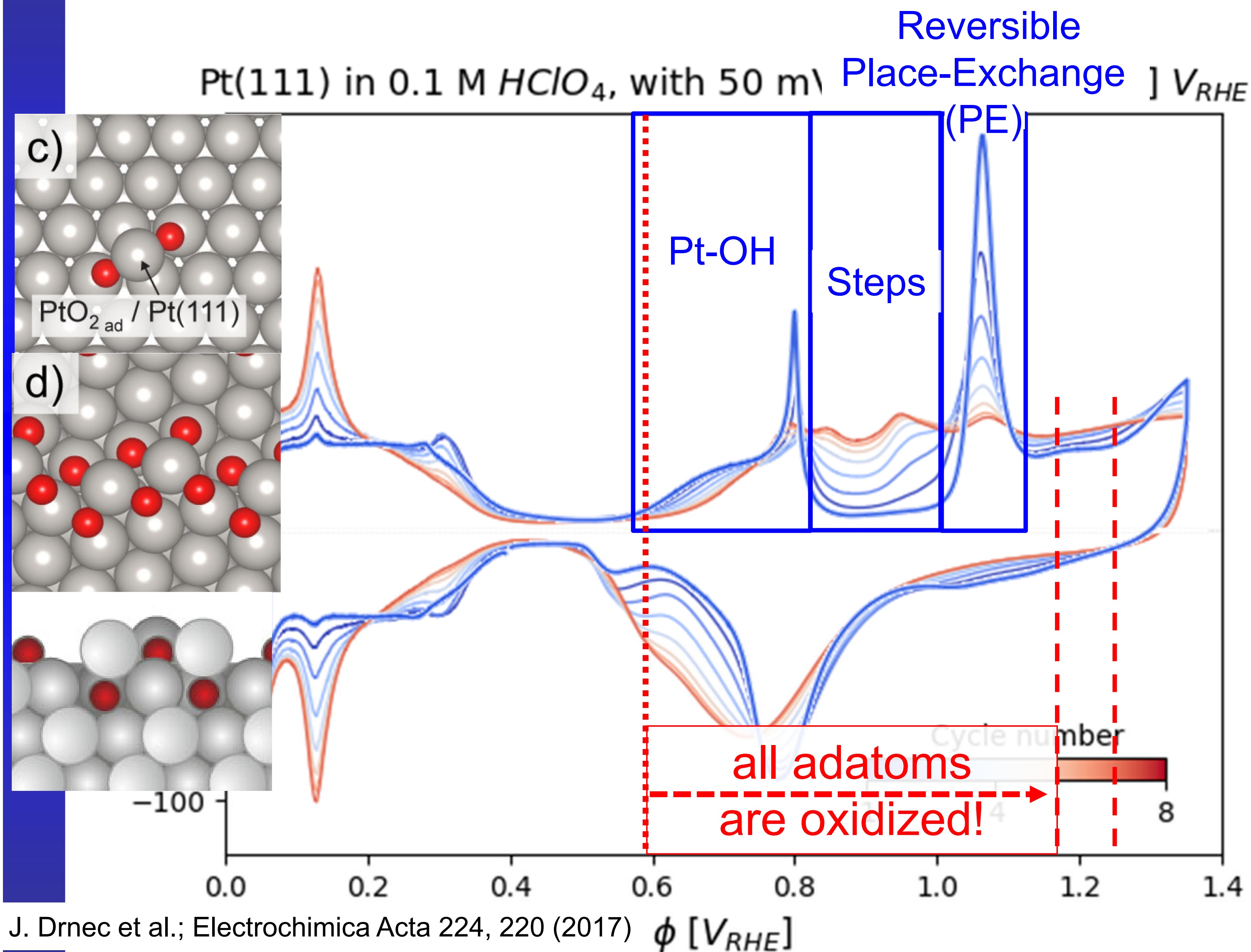
Valls Mascaro, Electrochem. Soc. 2023

All the Oxides…



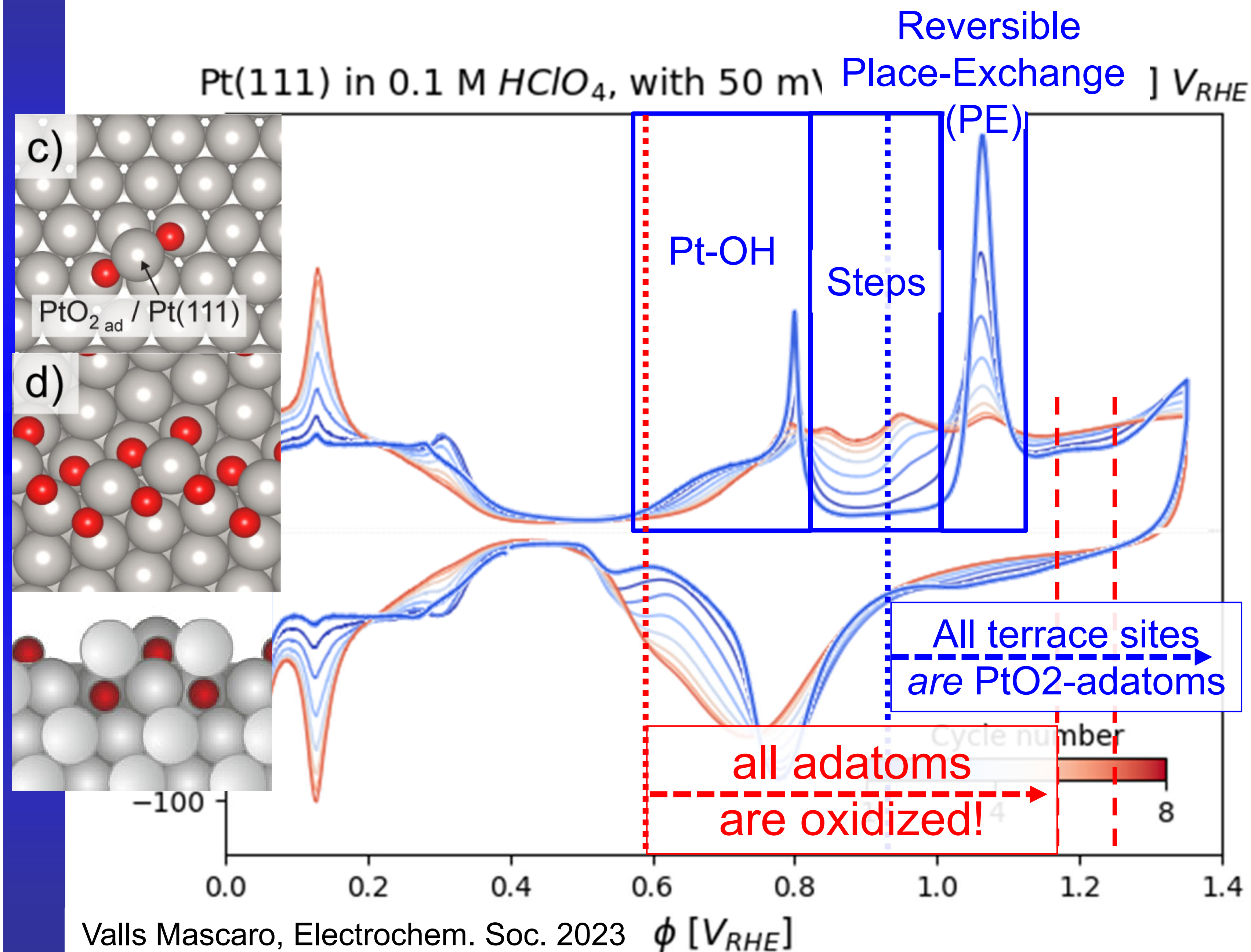
Valls Mascaro, Electrochem. Soc. 2023

All the Oxides Structures…



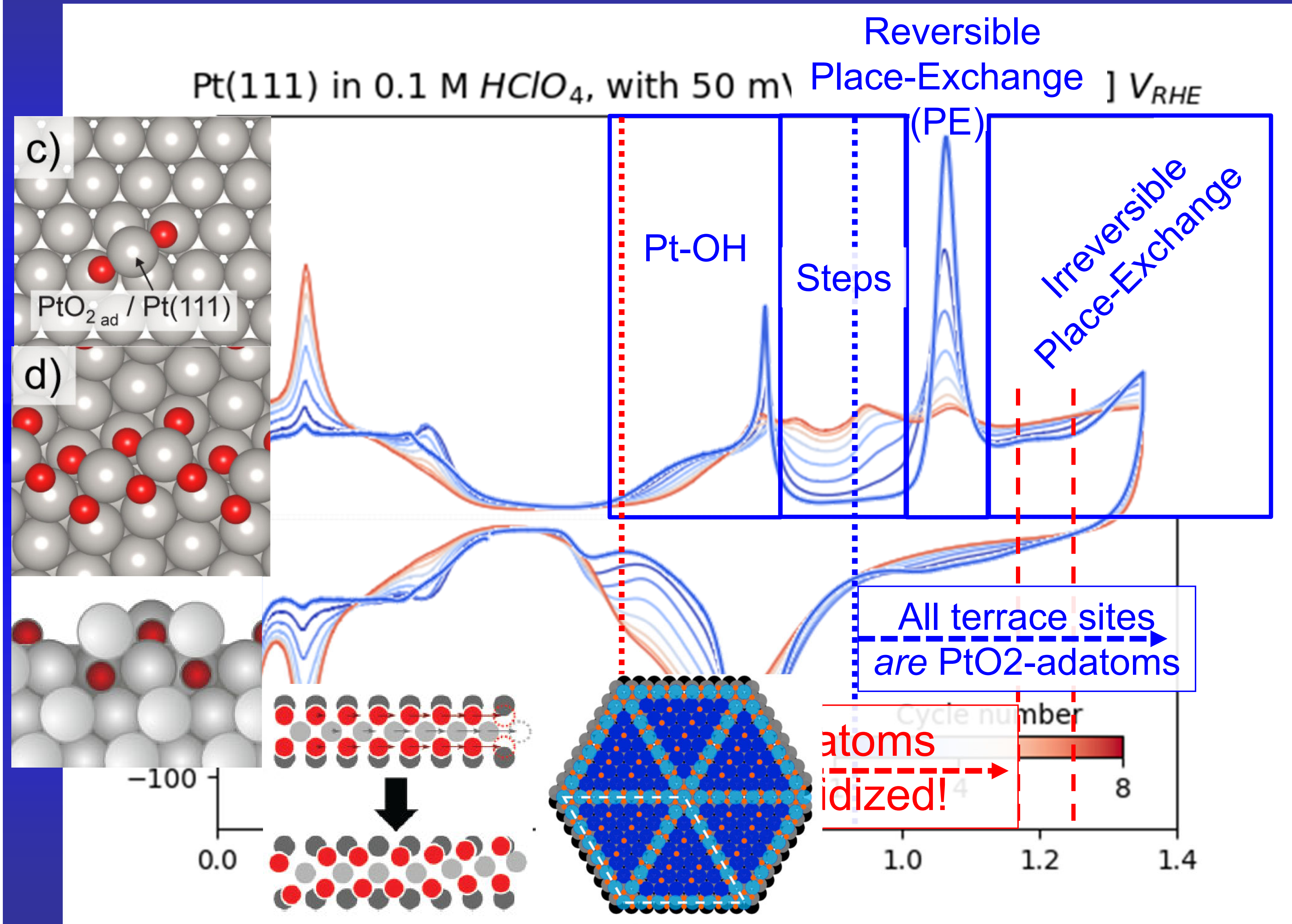
J. Drnec et al.; Electrochimica Acta 224, 220 (2017)

All the Oxides Structures…

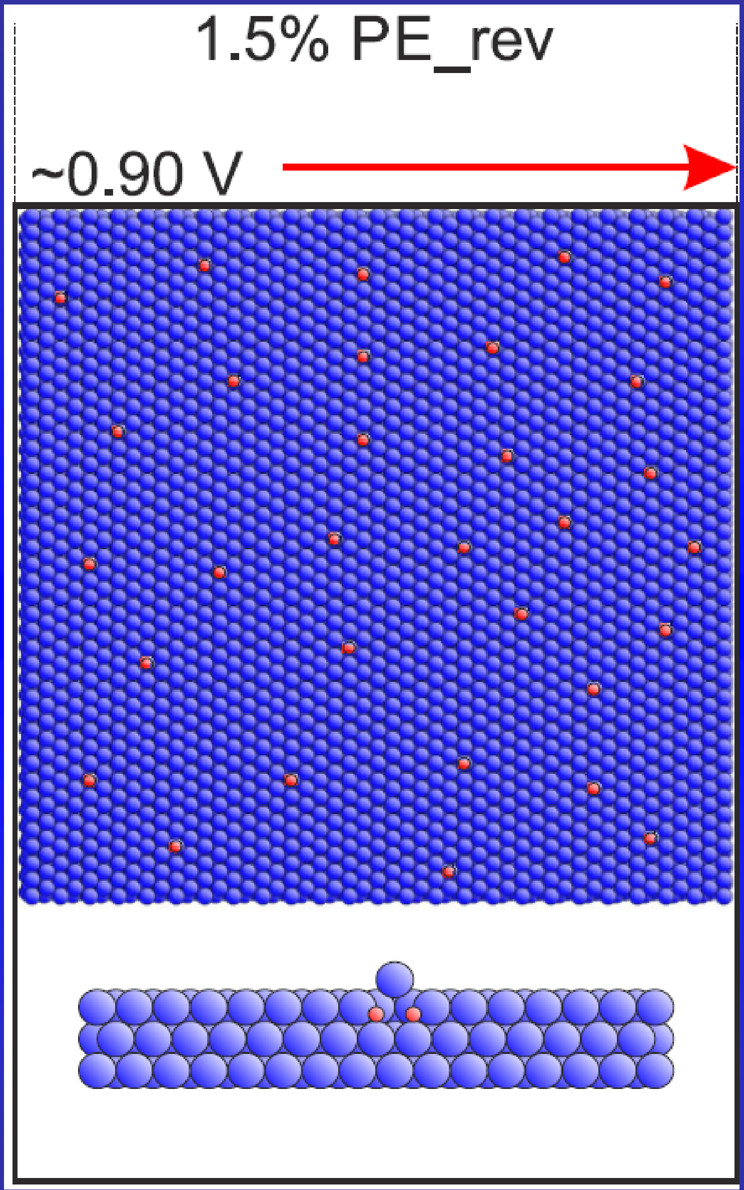


Valls Mascaro, Electrochem. Soc. 2023

All the Oxides Structures…



Pt(111) Oxidation: Reversible PE Adatom Gas



repulsive interaction

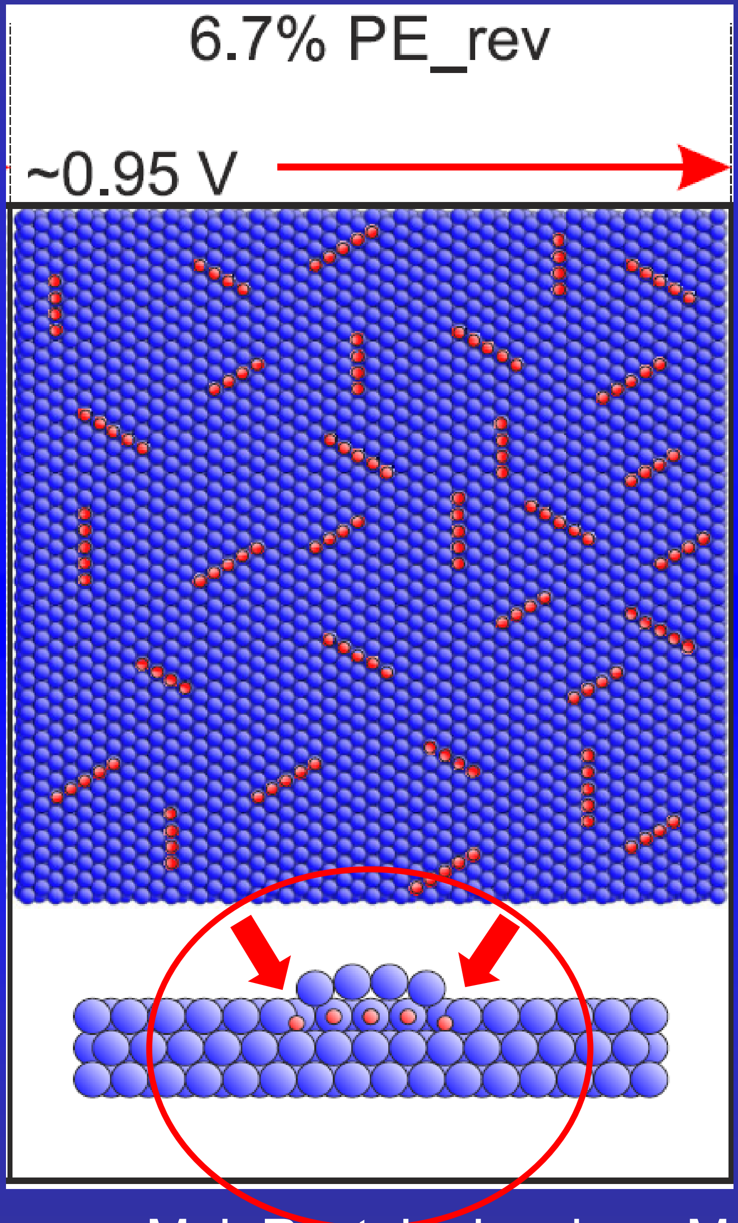
=>

reversible *Place Exchange Atoms*

maximize distances

M.J. Rost, L. Jacobse, M.T.M. Koper, Angewandte Chemie 2023

Pt(111) Oxidation: Formation of 1D Chains / Spokes



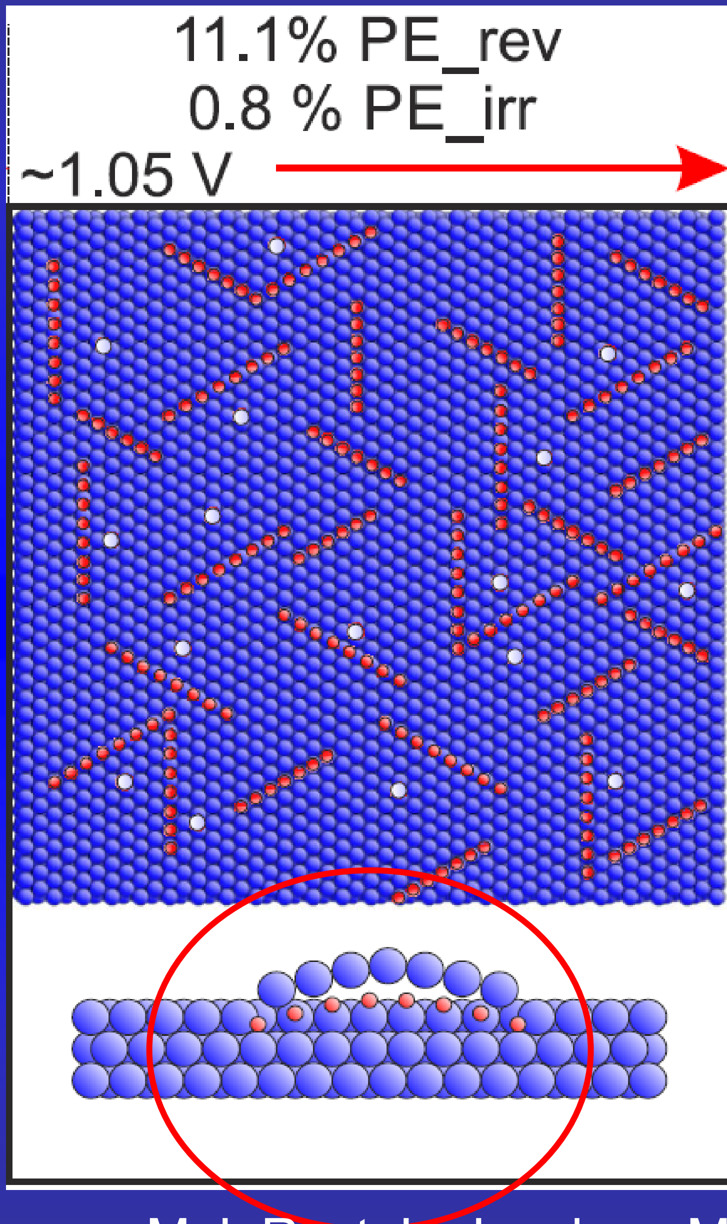
Reversible PE atom density high
=>
energetically more favorable to form
1D rows (or spokes).

rows resemble a α-PtO_2 structure
with larger lattice constant than Pt
=> stress is generated

stress partially reduced by a buckling,
but at ends rows push into surface

M.J. Rost, L. Jacobse, M.T.M. Koper, Angewandte Chemie 2023

Pt(111) Oxidation: Growth of Rows / Spokes



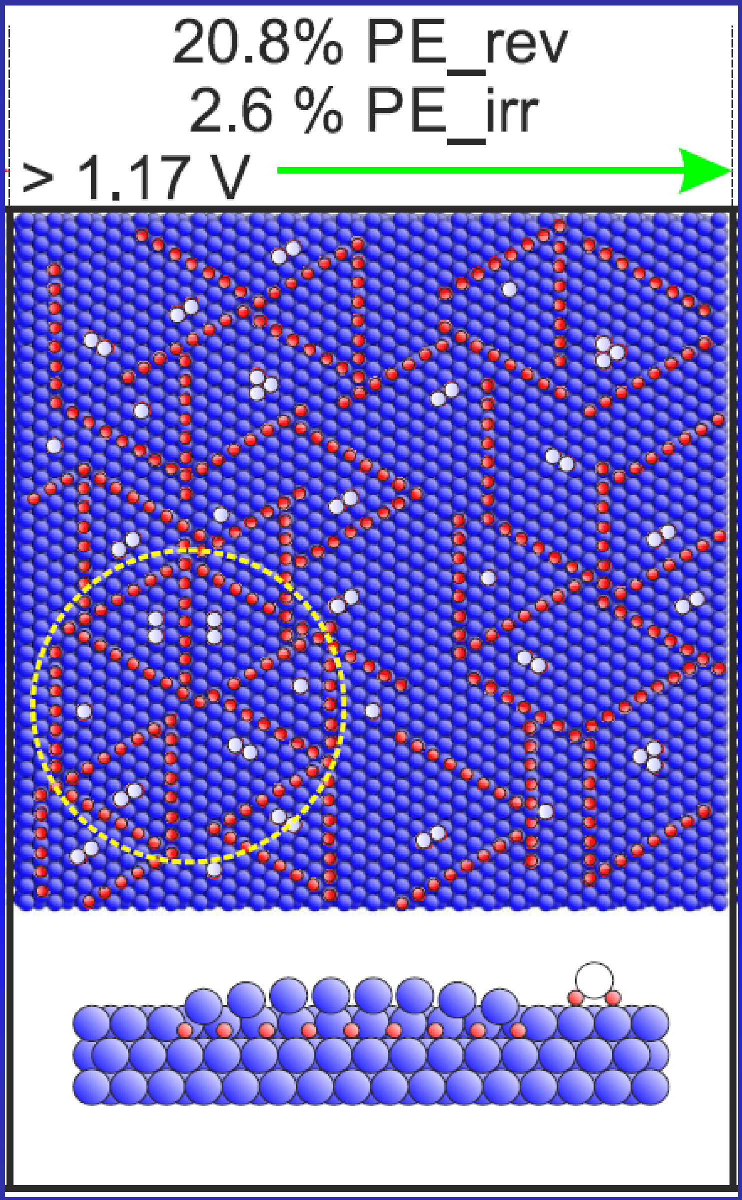
7 α-PtO_2 units exactly match 8 platinum units
=> stress relaxed by pushing out one atom

cross section still shows stressed row

entropy
=> rows align along all 3 orientations

M.J. Rost, L. Jacobse, M.T.M. Koper, Angewandte Chemie 2023

Pt(111) Oxidation: Creation of Irreversible PE Atoms



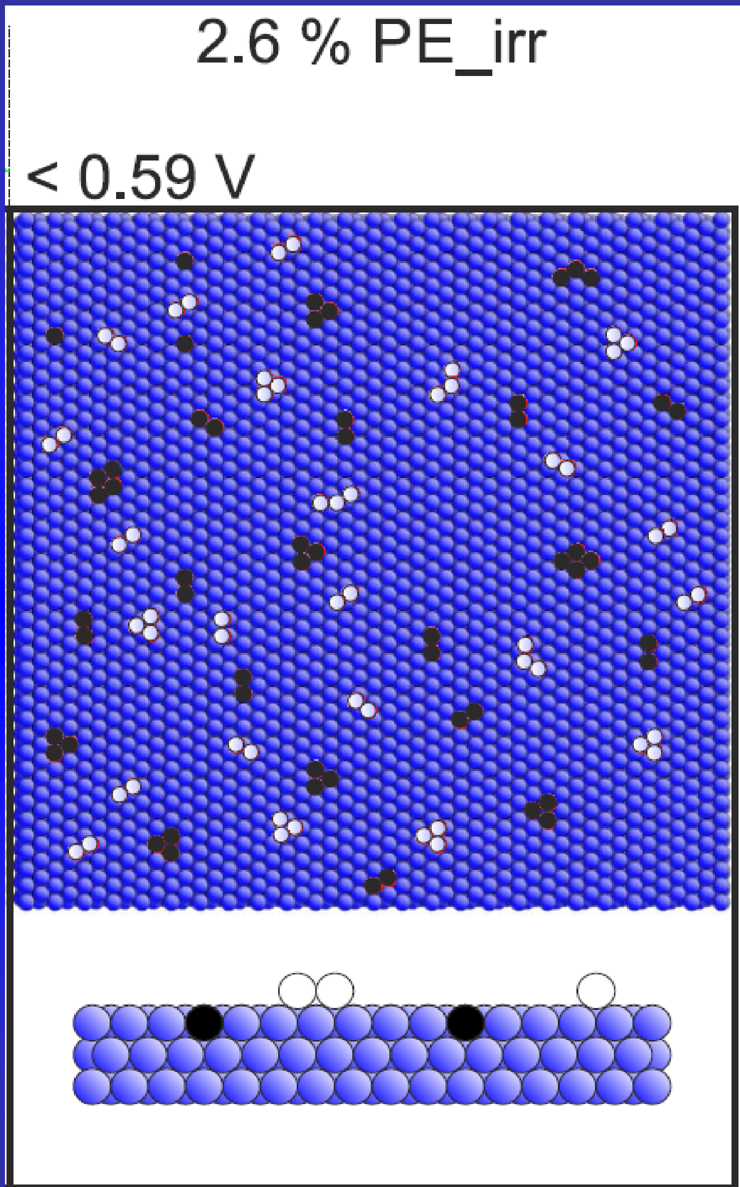
all rows reached critical lengths,
all rows pushed out one atom

disordered network of rows appears
type of spoke wheel structure
=> serves as the nucleation sites
that *a priori* did not exist

cross section shows a relaxed row
one platinum atom is pushed onto surface

M.J. Rost, L. Jacobse, M.T.M. Koper, Angewandte Chemie 2023

Pt(111) Reduction: Adatoms & Vacancies



reduction: oxygen atoms are removed
reversible Place Exchange Atoms fall back into their holes

pushed out atoms remain as well as their holes

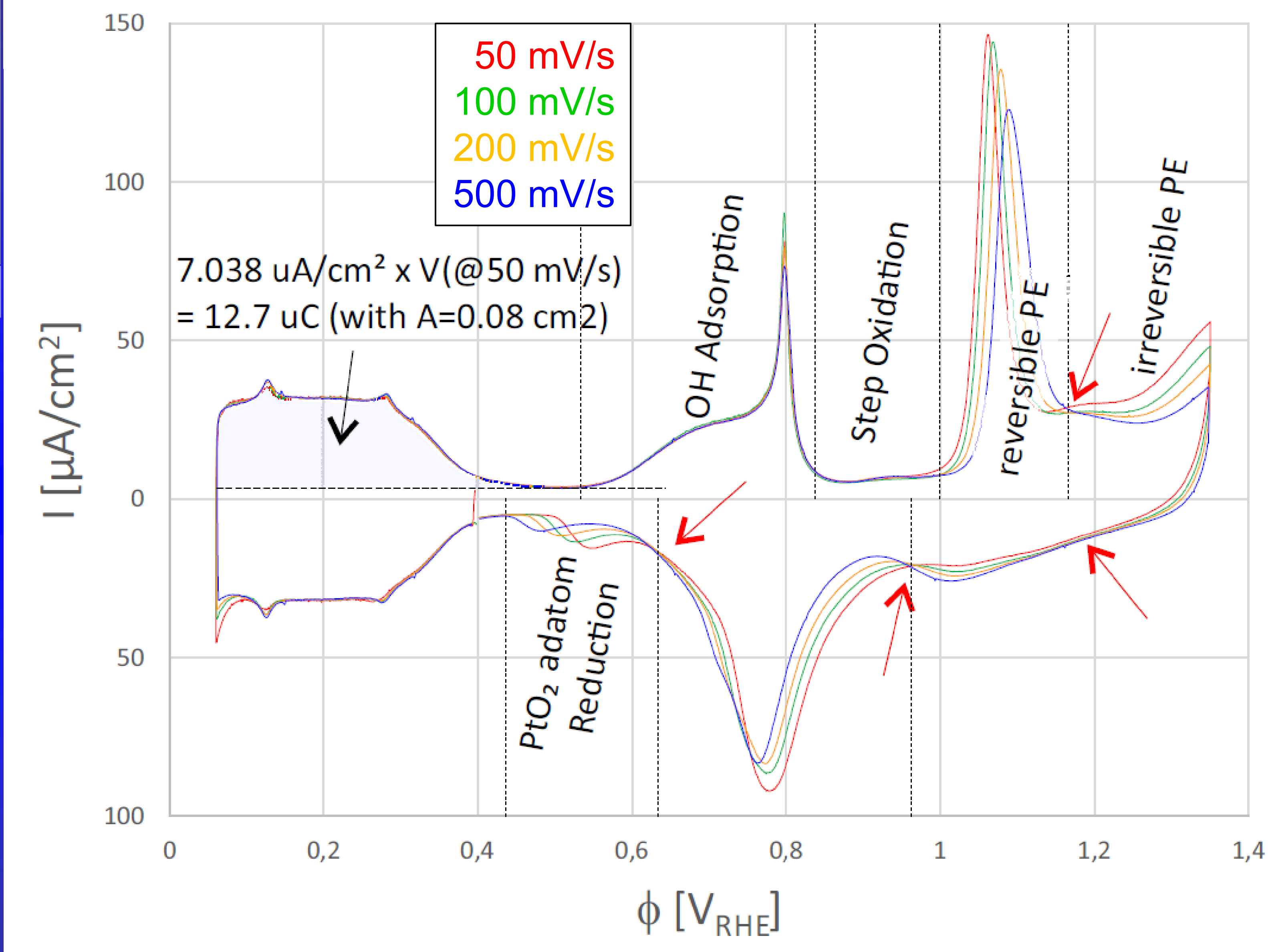
Nucleation and growth occurs
=> surface changes,

which is (one of) the reasons for the deterioration of the electrode in a fuel cell.

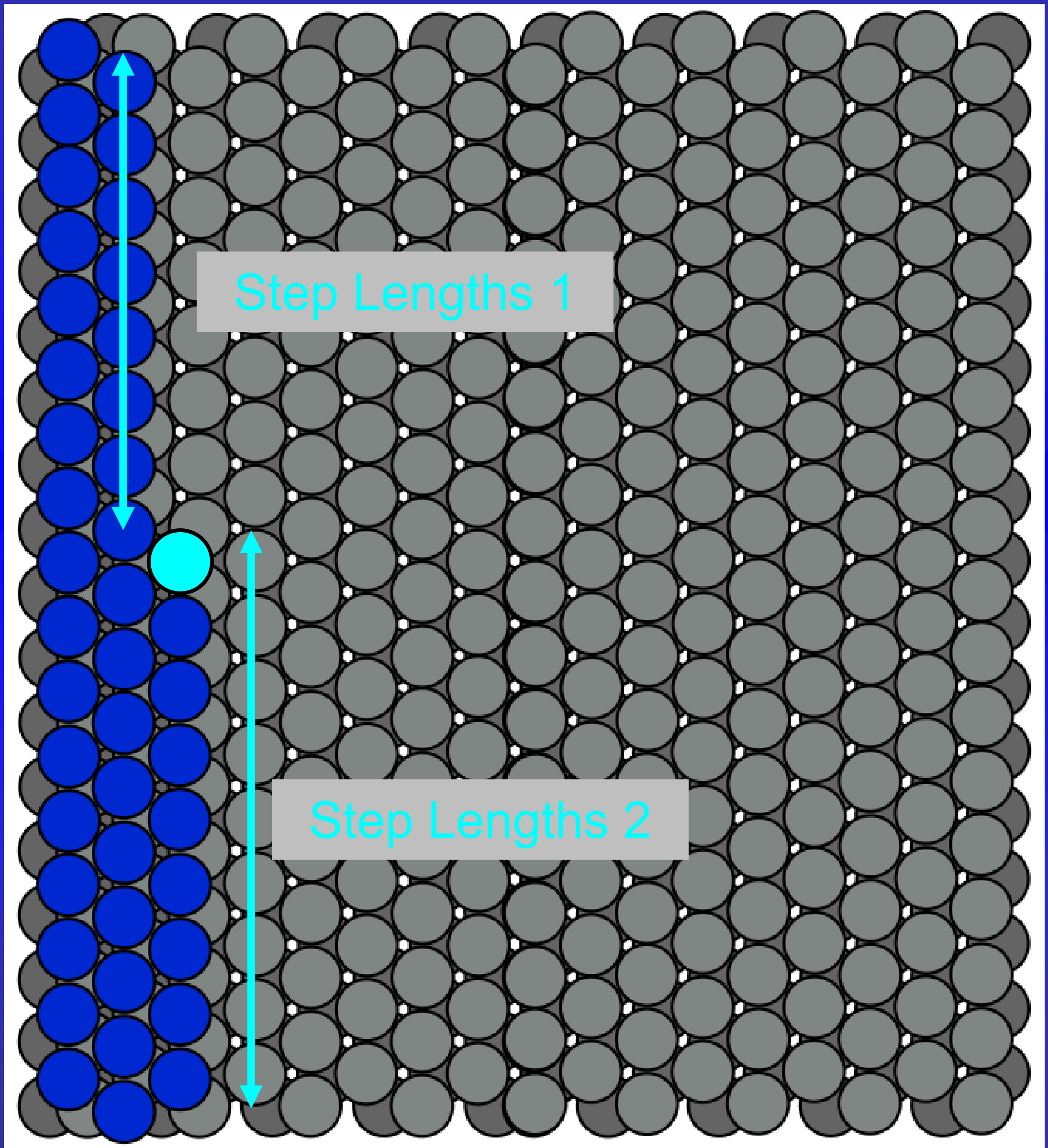
M.J. Rost, L. Jacobse, M.T.M. Koper, Angewandte Chemie 2023

What to Learn from Scan Rate Dependent Measurements ?

B.Valbæk Mygind

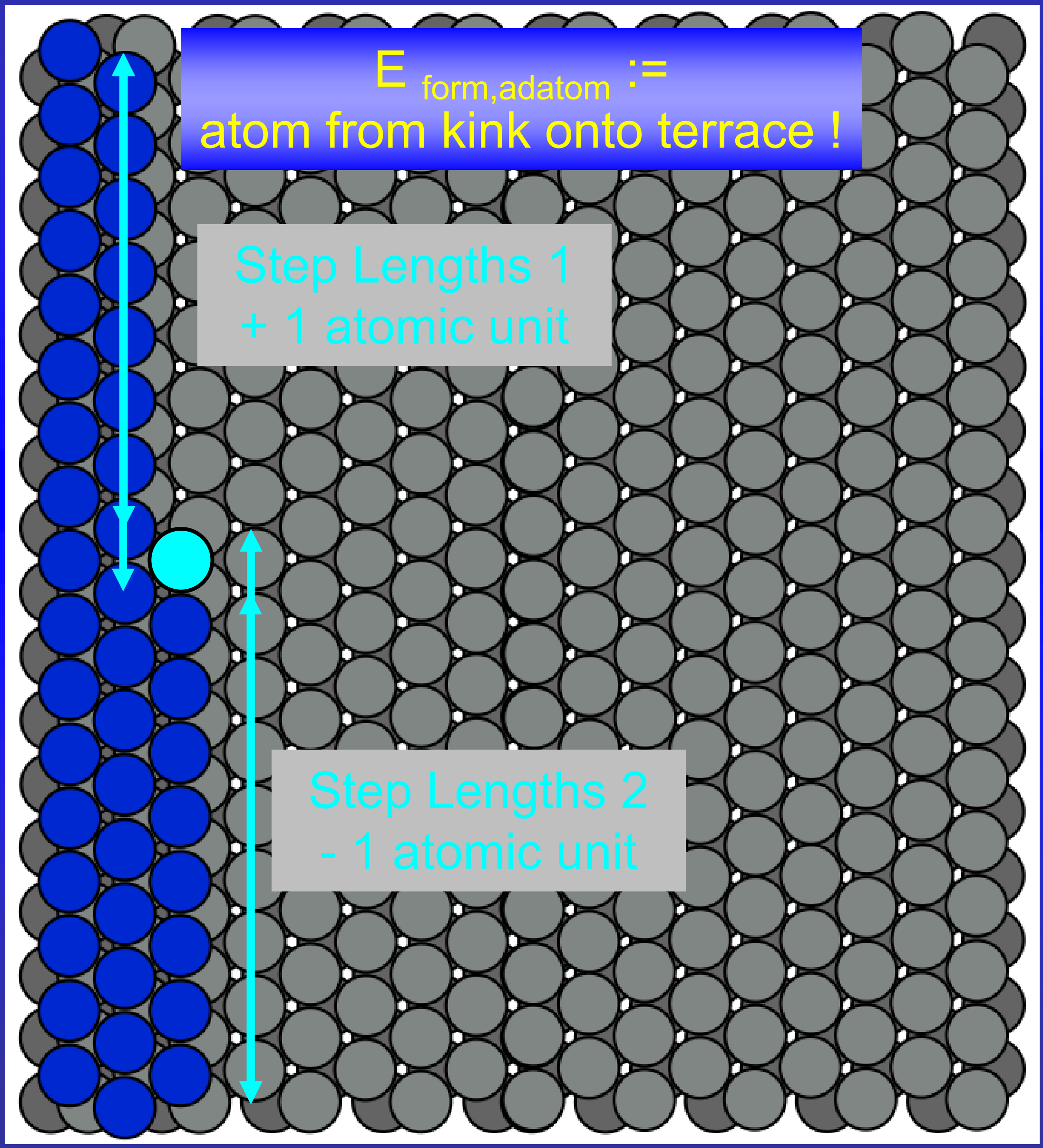


Kink = Very Special Site!



Kink Defines Adatom Formation Energy!

Step Lengths = Step Energy = const.



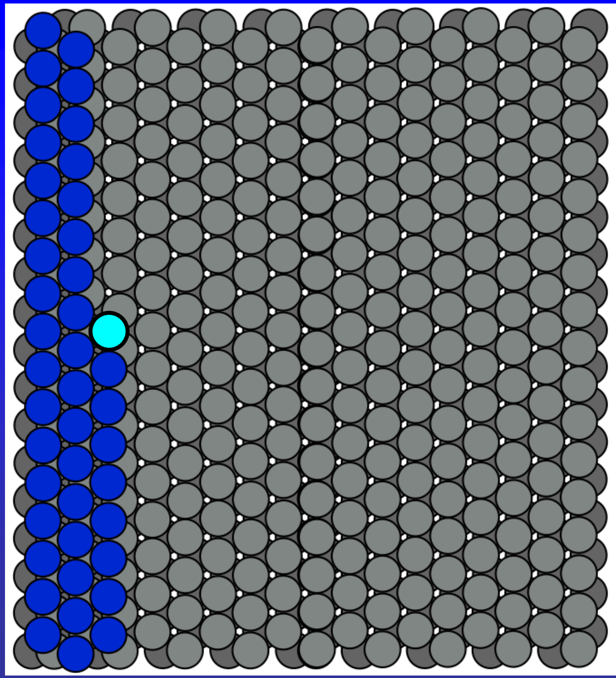
Chemical Potentials & Adatom Pressure:

$$\mu_{ad} = \mu_0 + k_B T\, ln\left(\frac{\theta_{ad}}{1-\theta_{ad}}\right) + W(\theta_{ad}) \approx \mu_{ad} = \mu_0 + k_B T\, ln(\theta_{ad}$$

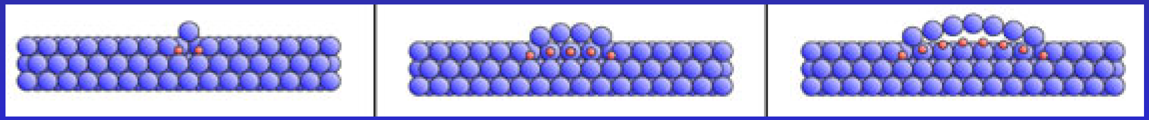
E $_{form,ad.}$ Entropy Interaction

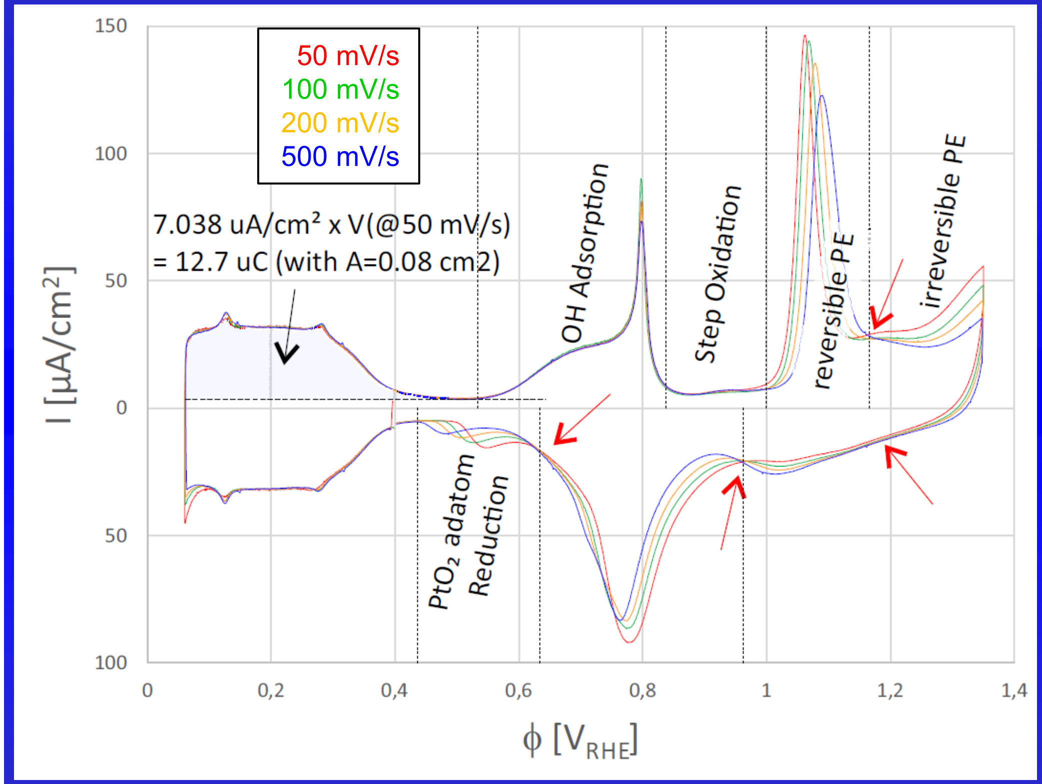
Adatom Pressure follows Boltzmann Distribution

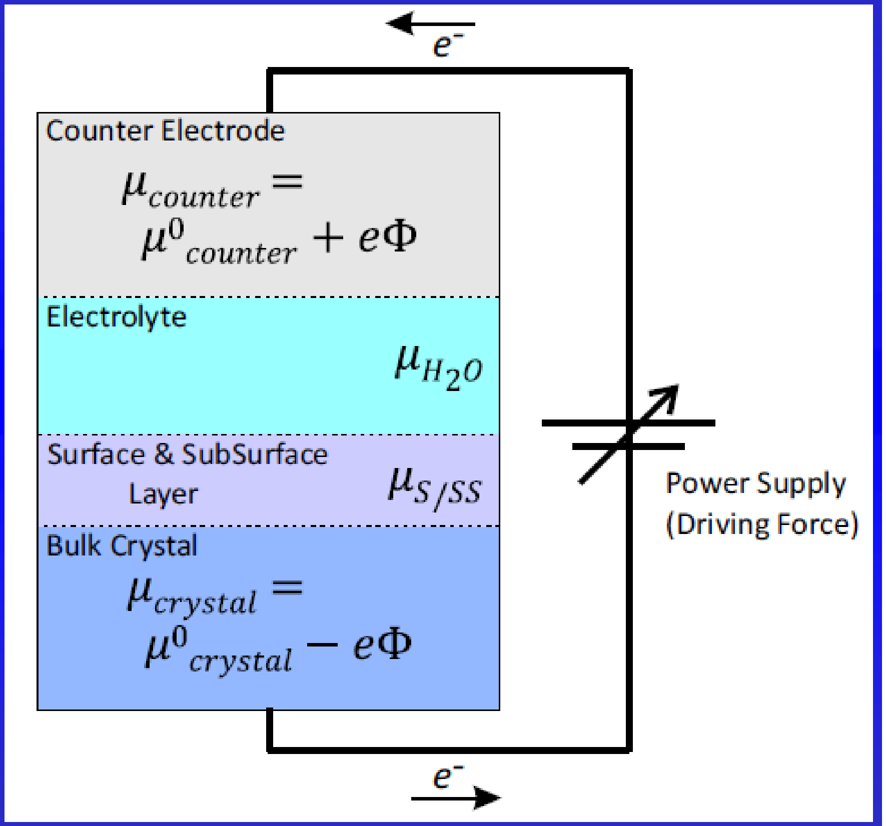
$$\theta_{ad} \approx \exp(-E_{form,ad.}/k_B T)$$



Arrhenius follows Frumkin to describe Atomic Diffusion involved Peaks CVs:







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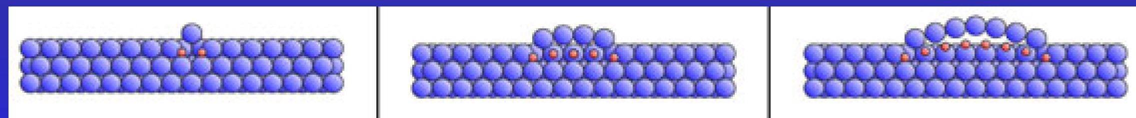
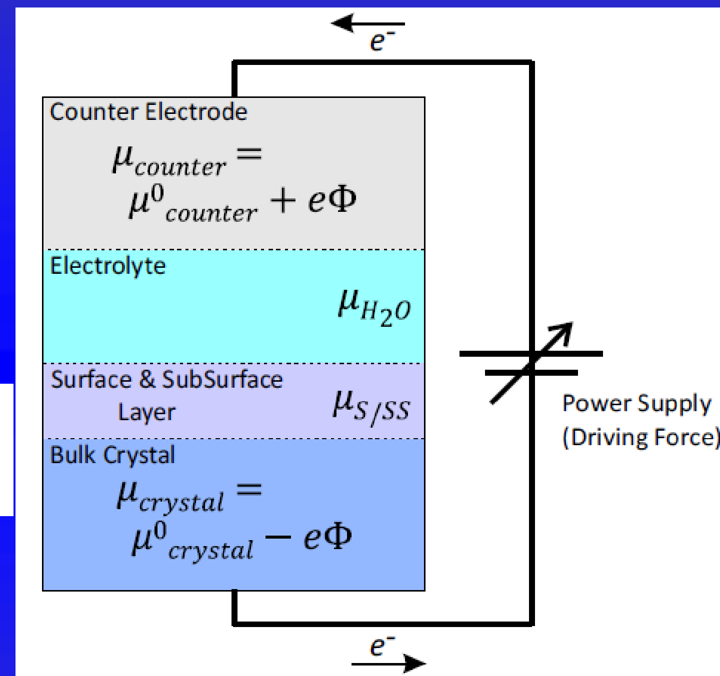


$$\mu_{H_2O} = \mu_{S/SS} = \mu_{crystal}$$

$$\mu_{H_2O} = \mu^0_{H_2O}(T) + k_B T \; ln\left(\frac{c_{H_2O}}{c_O}\right)$$

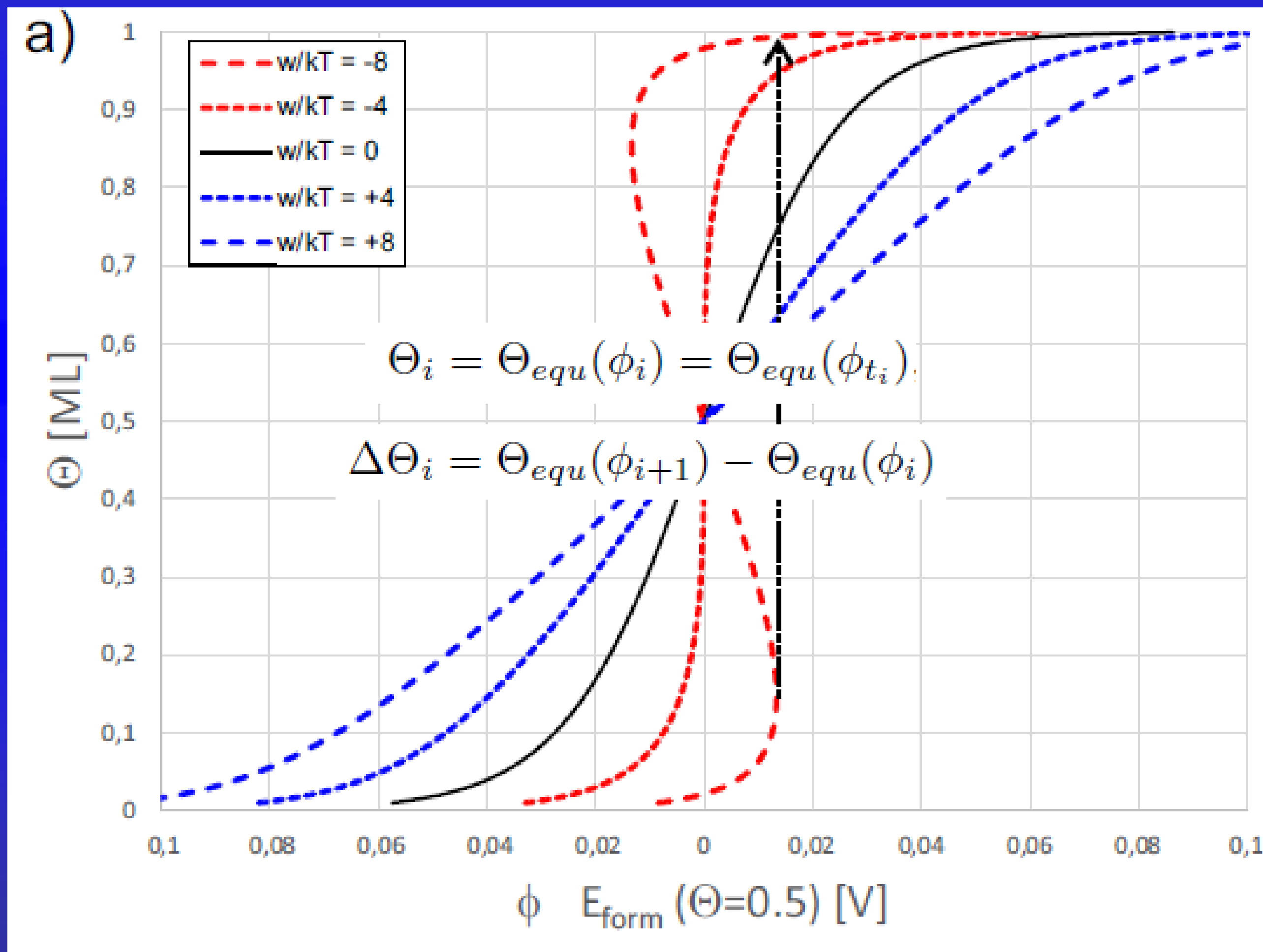
$$\mu_{S/SS} = \mu^0_{S/SS}(T) - ze(|\phi - \phi_{PZC}|) + w\Theta + k_B T \; ln\left(\frac{\Theta}{1-\Theta}\right)$$

$$\mu_{crystal} = \mu^0_{crystal}(T) - ze(\phi - \phi_{PZC})$$



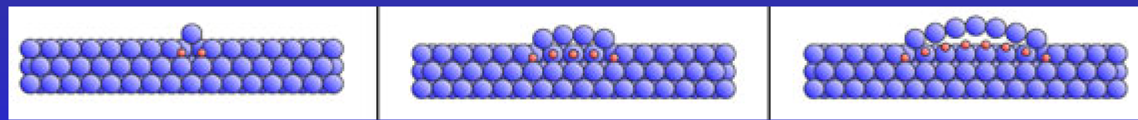
Arrhenius follows Frumkin to describe Atomic Diffusion involved Peaks CVs:

$$\mu_{S/SS} = \mu^0_{S/SS}(T) - ze(|\phi - \phi_{PZC}|) + w\Theta + k_B T\, ln\left(\frac{\Theta}{1-\Theta}\right)$$



Delay due to Atomic Diffusion:

Pt atom has to diffuse up, while 2 oxygen's diffuse subsurface



$$\Theta_i = \Theta_{equ}(\phi_i) = \Theta_{equ}(\phi_{t_i}),$$

$$\Delta\Theta_i = \Theta_{equ}(\phi_{i+1}) - \Theta_{equ}(\phi_i)$$

$$\Delta\Theta_i = (\Theta_{equ}(\phi_{i+1}) - \Theta_{act}(\phi_i)) \times \Delta t * \nu_0 * exp(-E_{diff}/kT),$$

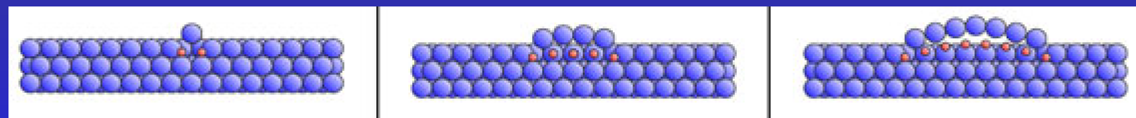
$$\Theta_{act} = \sum_i \Delta\Theta_i$$

4 fit parameters:

E^0_{form}, w, ν_0, E^0_{diff}

Delay due to Atomic Diffusion:

Pt atom has to diffuse up, while 2 oxygen's diffuse subsurface



$$\Theta_i = \Theta_{equ}(\phi_i) = \Theta_{equ}(\phi_{t_i})$$

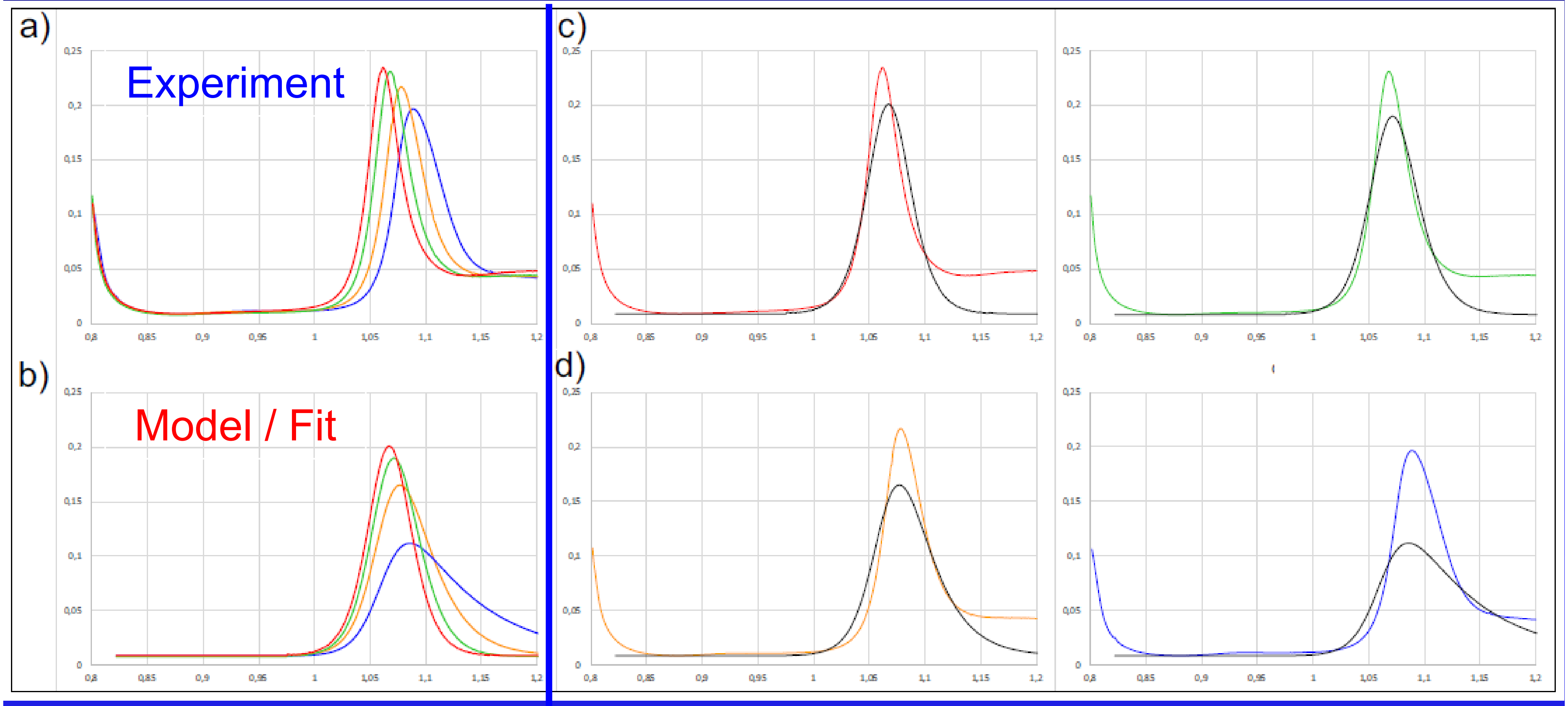
$$\Delta\Theta_i = \Theta_{equ}(\phi_{i+1}) - \Theta_{equ}(\phi_i)$$

$$\frac{d\Theta}{dt} = \left(\Theta_{equ}(\phi(t)) - \int_0^t \frac{d\Theta}{dt}\right) \times \Delta t \; \nu_0 \; exp\left(-\left(E_{diff}\right)/kT\right)$$

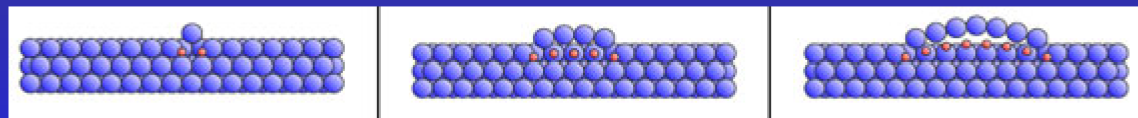
4 fit parameters:

E^0_{form}, w, ν_0, E^0_{diff}

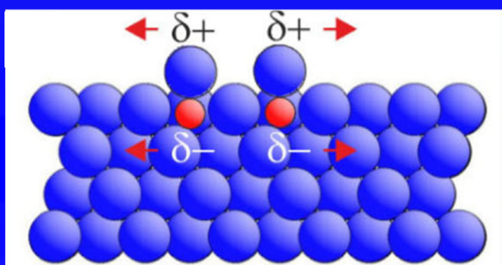
4 parameter numerical fit: E^0_{form}, w, ν_0, E^0_{diff}



Accounting for Dipole Moments thus Potential Dependence: Brønsted–Evans–Polanyi (BEP)



$$\frac{d\Theta}{dt} = \left(\Theta_{equ}(\phi(t)) - \int_0^t \frac{d\Theta}{dt}\right) \times \Delta t\ \nu_0\ exp\left(-\left(E_{diff}\right)/kT\right)$$

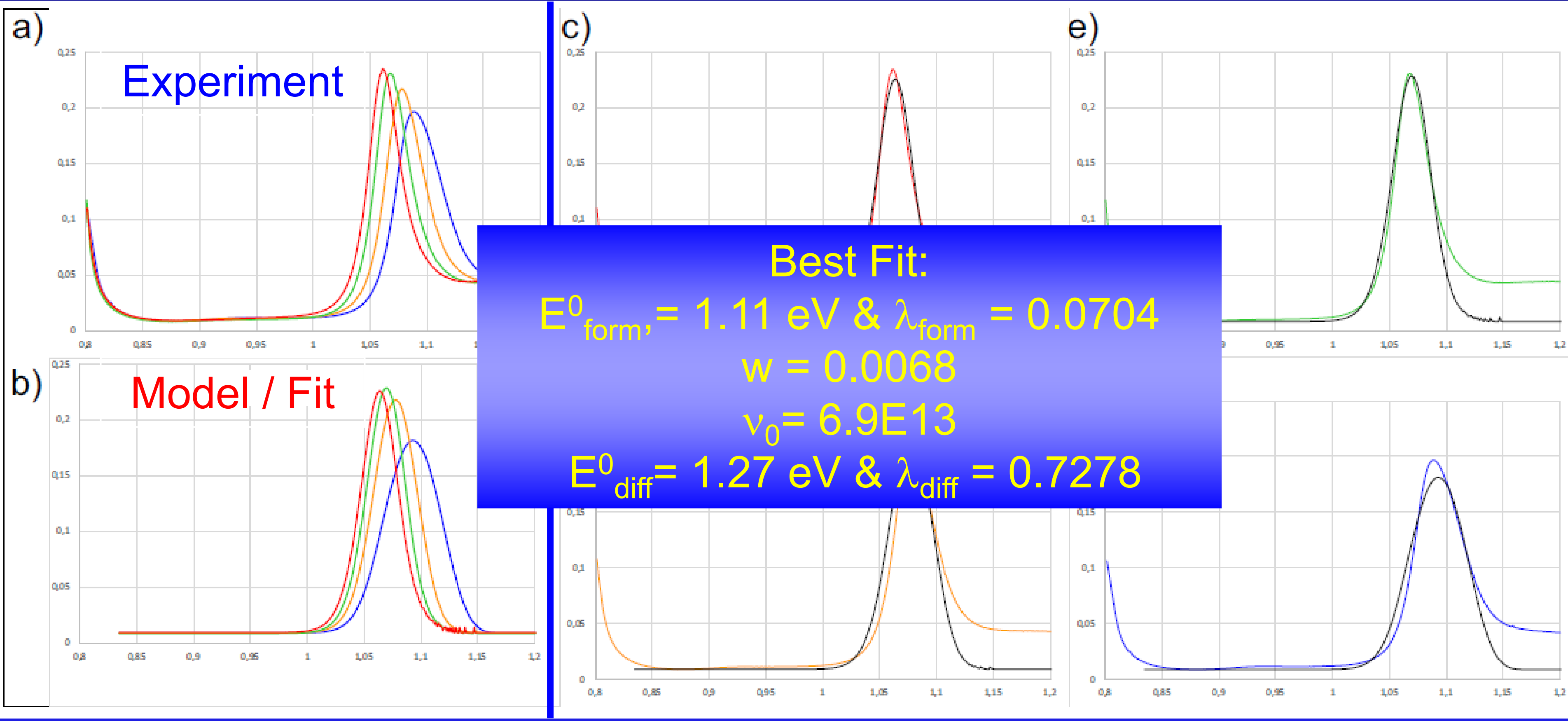


$$E_{form} = E^0_{form} - e\lambda_{form}\left(\phi - \phi_{PZC}\right)$$
$$E_{diff} = E^0_{diff} - e\lambda_{diff}\left(\phi - \phi_{PZC}\right),$$

6 fit parameters:

E^0_{form}, λ_{form} w, ν_0, E^0_{diff}, λ_{diff}

6 parameter num. fit: E^0_{form}, λ_{form} w, ν_0, E^0_{diff}, λ_{diff}



Best Fit:

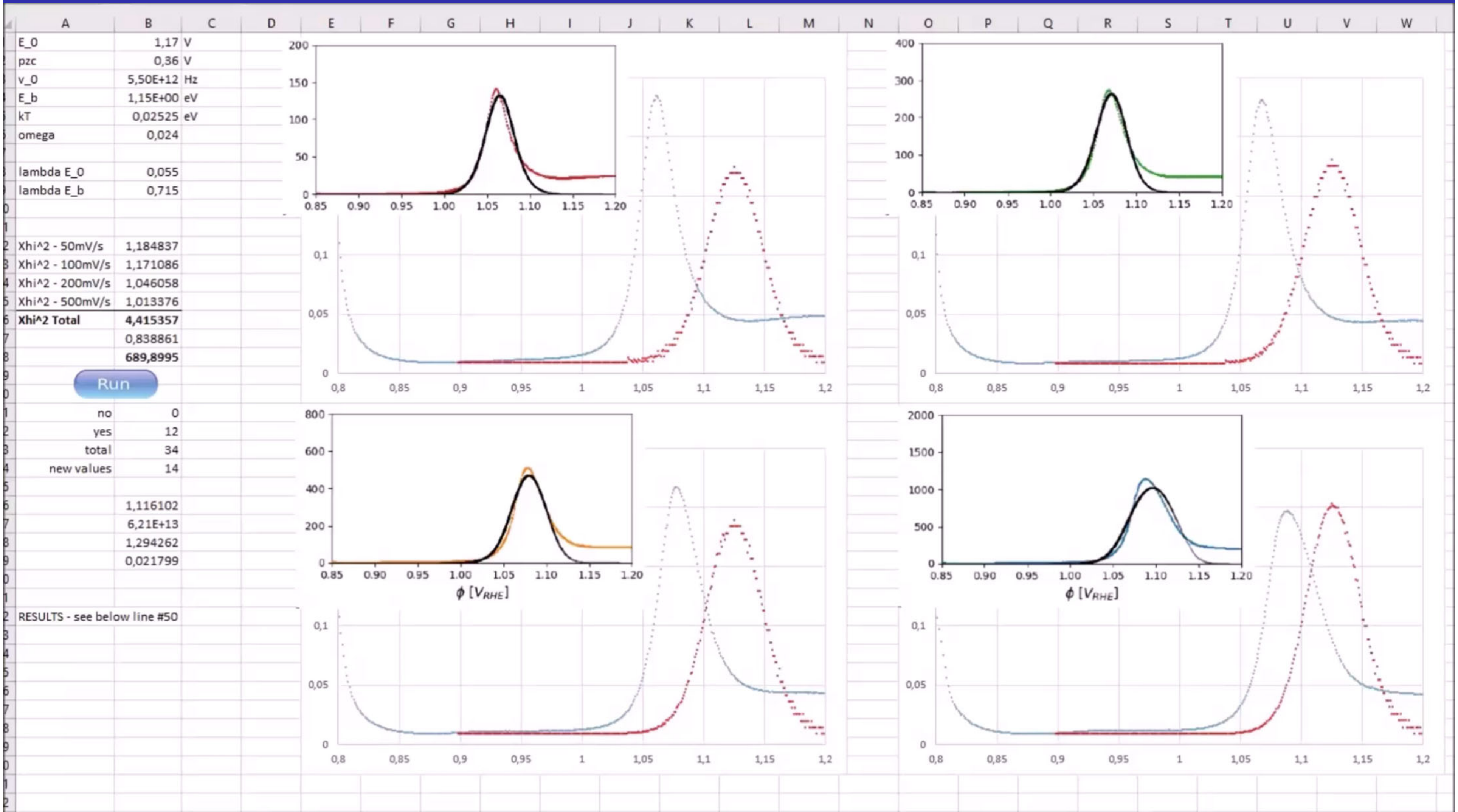
E^0_{form},= 1.11 eV & λ_{form} = 0.0704

w = 0.0068

ν_0= 6.9E13

E^0_{diff}= 1.27 eV & λ_{diff} = 0.7278

Kinetic Monte Carlo Approach on χ^2:



6 parameter fit: E^0_{form}, λ_{form} w, ν_0, E^0_{diff}, λ_{diff}

Best Fit:

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How to cite: doi.org/10.1002/anie.202216376

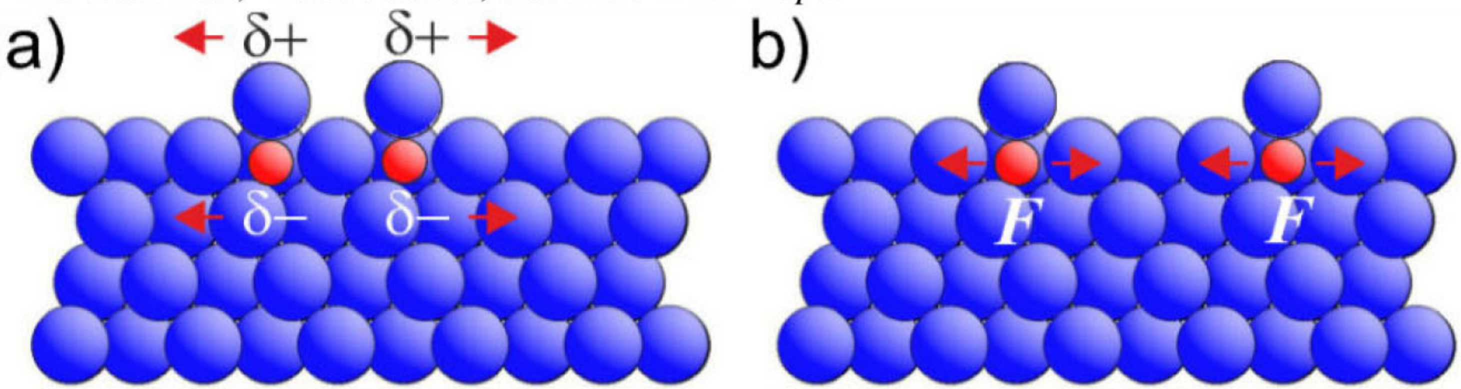
Electrochemistry

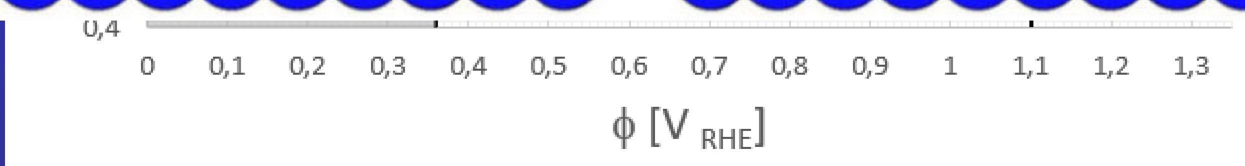
Non-Random Island Nucleation in the Electrochemical Roughening on Pt(111)

Marcel J. Rost, Leon Jacobse, and Marc T. M. Koper*

relaxed surface
y between un-

94)





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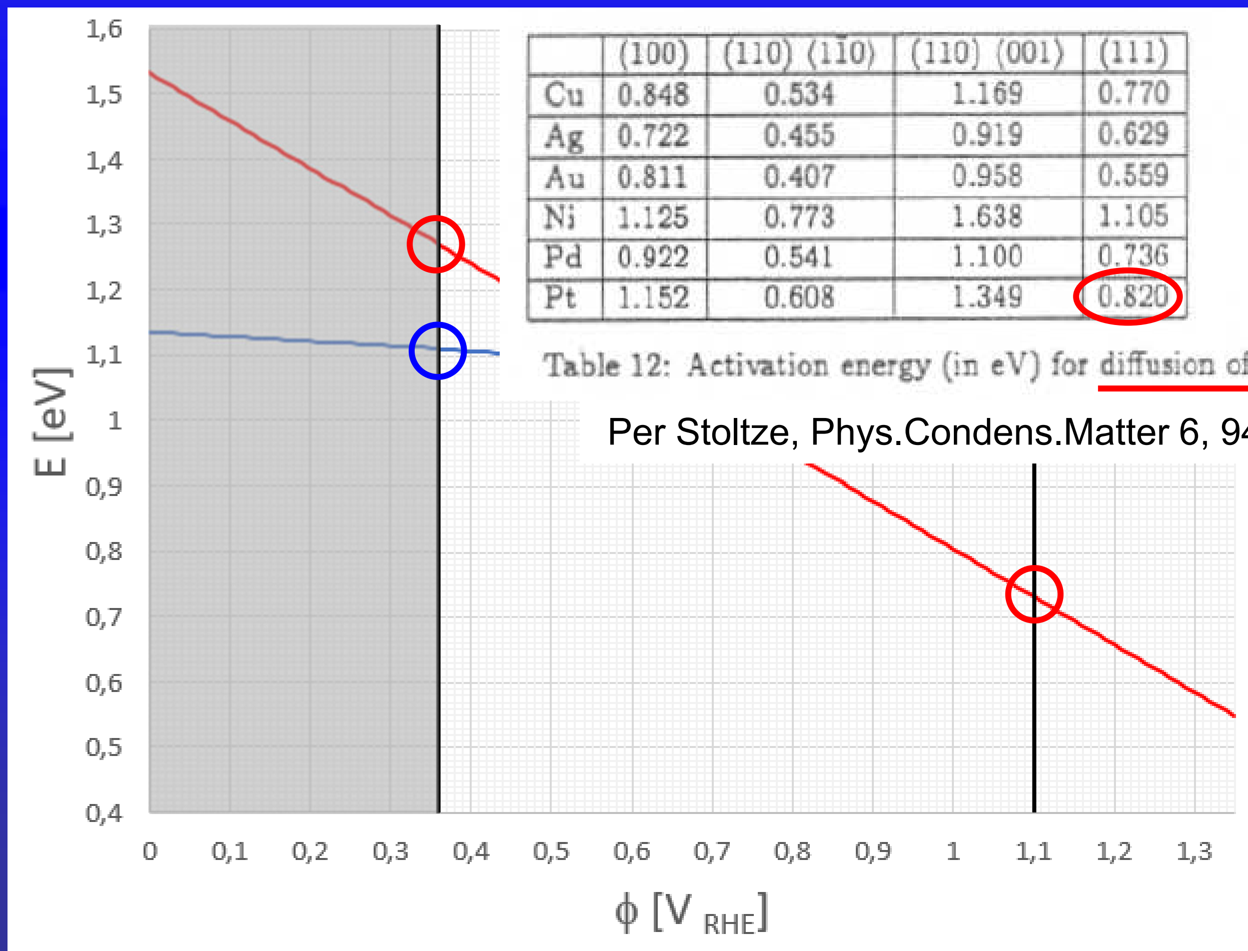


	(100)	(110) $(1\bar{1}0)$	(110) (001)	(111)
Cu	0.848	0.534	1.169	0.770
Ag	0.722	0.455	0.919	0.629
Au	0.811	0.407	0.958	0.559
Ni	1.125	0.773	1.638	1.105
Pd	0.922	0.541	1.100	0.736
Pt	1.152	0.608	1.349	0.820

Table 12: Activation energy (in eV) for diffusion of an atom out of a step

Per Stoltze, Phys.Condens.Matter 6, 9495 (1994)

6 parameter fit: E^0_{form}, λ_{form} w, ν_0, E^0_{diff}, λ_{diff}

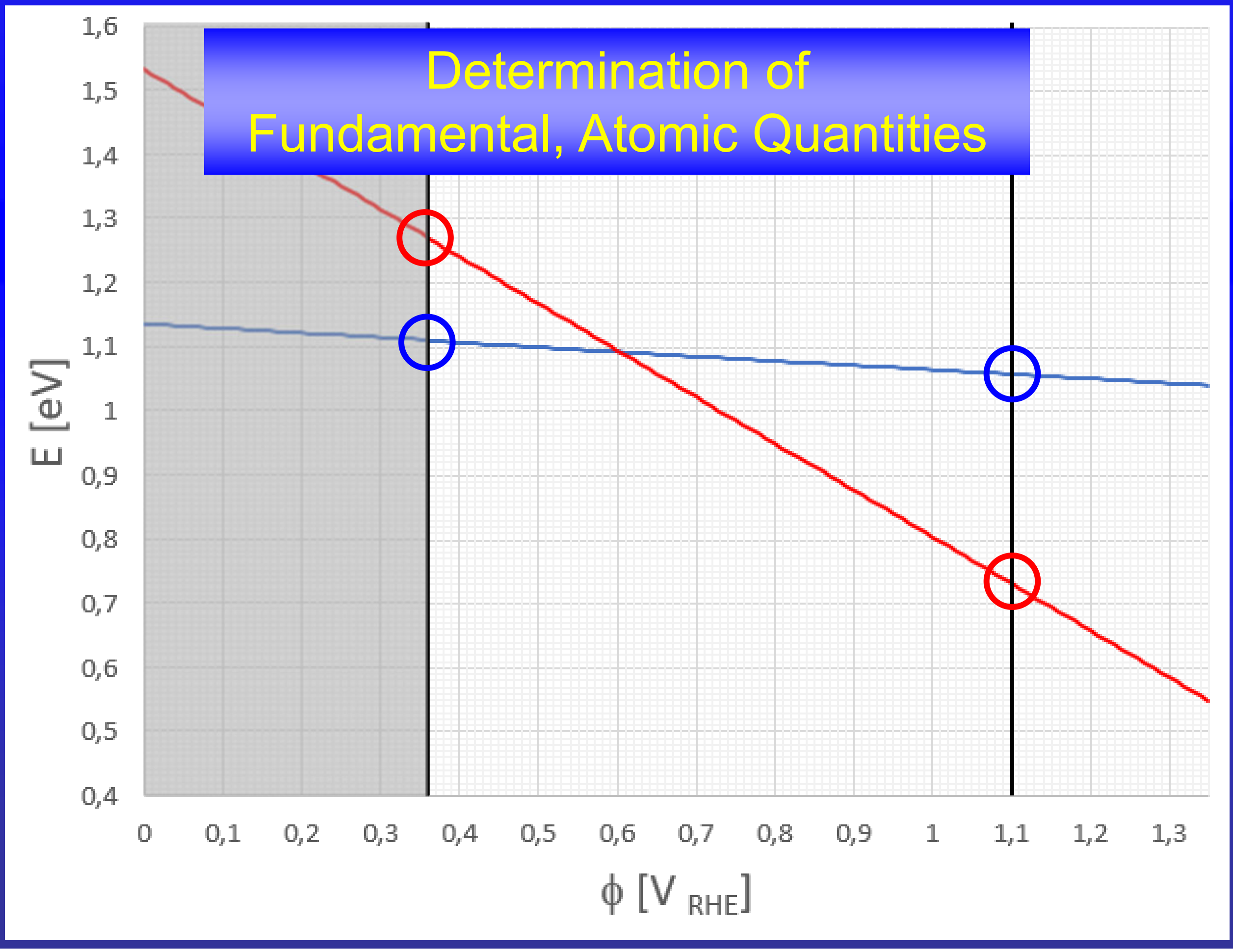
Best Fit:

E^0_{form},= 1.11 eV & λ_{form} = 0.0704

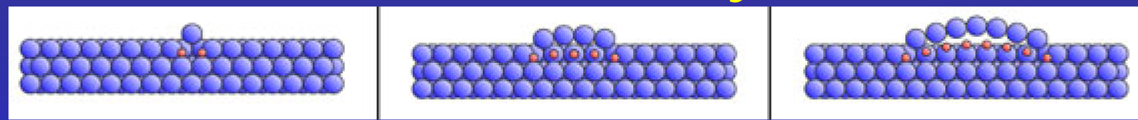
w = 0.0068

ν_0= 6.9E13

E^0_{diff}= 1.27 eV & λ_{diff} = 0.7278



towards an analytical fit:



$$\frac{d\Theta}{dt} = \left(\Theta_{equ}(\phi(t)) - \int_0^t \frac{d\Theta}{dt}\right) \times \Delta t\ \nu_0\ exp\left(-\left(E_{diff}\right)/kT\right)$$

$$E_{form} = E^0_{form} - e\lambda_{form}\left(\phi - \phi_{PZC}\right)$$
$$E_{diff} = E^0_{diff} - e\lambda_{diff}\left(\phi - \phi_{PZC}\right),$$

6 fit parameters:

E^0_{form}, λ_{form} w, ν_0, E^0_{diff}, λ_{diff}

$$0 = \mu^0_{S/SS}(T) - \mu_{S/SS} - ze(|\phi - \phi_{PZC}|) \quad + w\Theta + k_B T\ ln\left(\frac{\Theta}{1-\Theta}\right)$$

$$0 = E_{form} \quad + w\Theta + k_B T\ ln\left(\frac{\Theta}{1-\Theta}\right)$$

$$0 = E^0_{form} - e\lambda_{form}\left(\phi - \phi_{PZC}\right) \quad + w\Theta + k_B T\ ln\left(\frac{\Theta}{1-\Theta}\right)$$

$$\Theta_{equ} = \gamma/(1+\gamma) - \frac{w}{k_B T} \times \gamma^2/(1+\gamma)^3$$
$$\gamma := exp\left(-E_{form}(\phi)/kT\right)$$

after quite some math…:

$$\lambda e \phi = \underbrace{\mu^\circ_{*/ss}(T) - \mu^\circ_{H_2O}(T)}_{\equiv E_{form}} + w\theta + k_B T \ln\left(\frac{\theta}{1-\theta}\right)$$

$\Rightarrow$

$\Rightarrow$

$$-\frac{1}{k_B T} E_{form}(\phi) = \ln\left(e^{w\theta/k_B T}\right) + \ln\left(\frac{\theta}{1-\theta}\right)$$

, where $E_{form}(\phi) = E_{form} - \lambda e \phi$

$\Rightarrow$

$$\exp\left(-E_{form}(\phi)/k_B T\right) = \left(e^{w\theta/k_B T}\right)\left(\frac{\theta}{1-\theta}\right)$$

, here we assume $w/k_B T < 0.1$ and $0 \leq \theta \leq 1$.
Then we can make a Taylor expansion on the right hand side:

$$e^{w\theta/k_B T} \simeq 1 + \frac{w\theta}{k_B T} + \mathcal{O}(\theta^2)$$

$\Rightarrow$

and denote: $\gamma = \exp\left(-E_{form}(\phi)/k_B T\right)$

$\Rightarrow$

$$(1-\theta)\gamma = \left(1 + \frac{w\theta}{k_B T}\right)\theta$$

$\Rightarrow$

$$\left(\frac{w}{k_B T}\right)\theta^2 + (1+\gamma)\theta - \gamma = 0$$

$\Rightarrow$

quadratic in θ, thus solvable, which gives:

$$\theta = \frac{-(1+\gamma) \pm \sqrt{(1+\gamma)^2 + 4\left(\frac{w}{k_B T}\right)\gamma}}{\left(2w/k_B T\right)}$$

, only the solution with the + sign is physical.
Moreover, as $w/k_BT < 1$, we can make a Taylor expansion of the root: $\sqrt{1+\alpha} \cong 1 + \frac{\alpha}{2} - \frac{\alpha^2}{8} + O(\alpha^3)$

$\Rightarrow$

$$\left(\frac{2w}{k_BT}\right) \cdot \theta \cong -(1+\gamma) + (1+\gamma)\left[1 + \left(\frac{2w}{k_BT}\right)\gamma/(1+\gamma)^2 - 2\left(\frac{w}{k_BT}\right)^2\frac{\gamma^2}{(1+\gamma)^4}\right.$$

$$= \left(\frac{2w}{k_BT}\right)\gamma/(1+\gamma) - 2\left(\frac{w}{k_BT}\right)^2 \gamma^2/(1+\gamma)^3$$

$\Rightarrow$

$$\theta_{eq} = \gamma/(1+\gamma) - (w/k_BT)\,\gamma^2/(1+\gamma)^3$$

This is the equilibrium coverage.

The coverage will be driven by:

$$\dot{\theta} = [\theta_{eq}(\phi) - \theta]\, \nu_0\, e^{-[E_d^0 - \alpha\phi]\beta}$$

, where $\beta = 1/k_BT$

, now $\phi = \phi_0 + s \cdot t$ with sweep rate s.
$d\phi = s \cdot dt$

$$\Rightarrow \frac{\partial\theta}{\partial\phi} \cdot \frac{\partial\phi}{\partial t} = [\theta_{eq}(\phi) - \theta]\, \nu_0\, e^{-[E_d^0 - \alpha\phi]\beta}$$

$\Rightarrow$

$$\frac{\partial \theta}{\partial \phi} \cdot s = \left[\theta_{eq}(\phi) - \theta \right] v_0 \, e^{-[E_d^0 - \alpha\phi]\beta}$$

$$= \left[\theta_{eq}(\phi) - \theta \right] \tilde{v}_0 \, e^{+\alpha\beta\phi}$$

$$\tilde{v}_0 = v_0 \, e^{-\beta E_d^0}$$

$$\theta_{eq} = \gamma/(1+\gamma) - (w/k_B T)\, \gamma^2/(1+\gamma)^3$$

with $\gamma = \exp\left(-E_{form}(\phi)/k_B T\right)$

$$= \exp\left(-\beta E_{form}^0 + \alpha' \beta \phi\right)$$

$$u = e^{\eta\phi} \Rightarrow du = \eta e^{\eta\phi} d\phi = \eta u \, d\phi$$

$$\phi = \frac{1}{\eta} \ln(u)$$

$$\Rightarrow \frac{\partial \theta}{\partial \phi} = \frac{\partial \theta}{\partial u} \cdot \frac{\partial u}{\partial \phi} = \eta u \frac{\partial \theta}{\partial u}$$

$$e^{\alpha\beta\phi} = e^{\frac{\alpha\beta}{\eta}\ln(u)} = u^{\alpha\beta/\eta}$$

$$e^{\alpha'\beta\phi} = e^{\frac{\alpha'\beta}{\eta}\ln(u)} = u^{\alpha'\beta/\eta}$$

$$\gamma = \tilde{\gamma}_0 \cdot u^{\alpha'\beta/\eta} \quad \text{with} \quad \tilde{\gamma}_0 = e^{-E_{form}^0 \cdot \beta}$$

$$\Rightarrow \eta u \frac{\partial \theta}{\partial u} s = \left[\gamma/(1+\gamma) - (w/k_B T)\, \gamma^2/(1+\gamma)^3 - \theta \right] \cdot \tilde{v}_0 \cdot u^{\alpha\beta/\eta}$$

choice: $\eta = \alpha\beta$

Hence, we obtain the following differential equation:

$$\frac{\partial\theta}{\partial u} = \left[\frac{\gamma}{1+\gamma} - \left(\frac{\omega}{k_B T}\right)\frac{\gamma^2}{(1+\gamma)^3} - \theta\right]\cdot\frac{\tilde{v}_0}{\alpha\beta s}$$

let us have a closer look at the γ parameter:

$\gamma = \tilde{\gamma}_0 \, u^{\alpha'/\alpha}$, yet realize that $\alpha'/\alpha \ll 1$.

which allows us to use the following approx.:

$$\gamma = \tilde{\gamma}_0 \, u^{\alpha'/\alpha} \cong \tilde{\gamma}_0 \left[1 + \underbrace{\left(\frac{\alpha'}{\alpha}\right)}_{\tilde{\alpha}} \log(u)\right]$$

, thus we find:

$$\frac{\gamma}{1+\gamma} \cong \frac{\tilde{\gamma}_0\left[1 + \tilde{\alpha}\log(u)\right]}{\left[1+\tilde{\gamma}_0\right]\left[1 + \left\{\frac{\tilde{\gamma}_0}{1+\tilde{\gamma}_0}\right\}\tilde{\alpha}\log(u)\right]}$$

$$\cong \left[\frac{\tilde{\gamma}_0}{1+\tilde{\gamma}_0}\right]\left(1 + \tilde{\alpha}\log(u)\right)\left(1 - \left\{\frac{\tilde{\gamma}_0}{(1+\tilde{\gamma}_0)}\right\}\tilde{\alpha}\log(u)\right)$$

$$\cong \left[\frac{\tilde{\gamma}_0}{1+\tilde{\gamma}_0}\right]\left\{1+\tilde{\alpha}\log(u)\left\{1-\frac{\tilde{\gamma}_0}{1+\tilde{\gamma}_0}\right\}\right\}$$

$\rightarrow$

$$\frac{\gamma}{1+\gamma} \cong \frac{\tilde{\gamma}_0}{1+\tilde{\gamma}_0}\left\{1+\frac{\tilde{\alpha}\log(u)}{1+\tilde{\gamma}_0}\right\}$$

$$\frac{\gamma^2}{(1+\gamma)^3} \cong \frac{\tilde{\gamma}_0^{\,2}\left[1+\tilde{\alpha}\log(u)\right]^2}{\left(1+\tilde{\gamma}_0\left[1+\tilde{\alpha}\log(u)\right]\right)^3}$$

$$= \frac{\tilde{\gamma}_0^{\,2}\left(1+2\tilde{\alpha}\log(u)\right)}{\left(\left[1+\tilde{\gamma}_0\right]\left\{1+\frac{\tilde{\gamma}_0\tilde{\alpha}}{1+\tilde{\gamma}_0}\log(u)\right\}\right)^3}$$

$$= \frac{\tilde{\gamma}_0^{\,2}}{(1+\tilde{\gamma}_0)^3}\cdot\frac{\left(1+2\tilde{\alpha}\log(u)\right)}{\left\{1+3\frac{\tilde{\gamma}_0\tilde{\alpha}}{1+\tilde{\gamma}_0}\log(u)\right\}}$$

$$\cong \frac{\tilde{\gamma}_0^{\,2}}{(1+\tilde{\gamma}_0)^3}\left(1+2\tilde{\alpha}\log(u)\right)\left(1-3\frac{\tilde{\gamma}_0\tilde{\alpha}}{1+\tilde{\gamma}_0}\log(u)\right)$$

$$\cong \frac{\tilde{\gamma}_0^{\,2}}{(1+\tilde{\gamma}_0)^3}\left(1+\tilde{\alpha}\log(u)\left[2-\frac{3\tilde{\gamma}_0}{1+\tilde{\gamma}_0}\right]\right)$$

$\Rightarrow$

$$\frac{\gamma^2}{(1+\gamma)^3} \simeq \frac{\tilde{\gamma}_0^2}{(1+\tilde{\gamma}_0)^3}\left[1+\left(\frac{2-\tilde{\gamma}_0}{1+\tilde{\gamma}_0}\right)\tilde{\alpha}\log(u)\right]$$

$\Rightarrow$ We can rewrite the differential equation:

$$\frac{\partial\theta}{\partial u} = \left[\frac{\gamma}{1+\gamma} - \left(\frac{w}{k_BT}\right)\frac{\gamma^2}{(1+\gamma)^3} - \theta\right]\cdot\frac{\tilde{v}_0}{\alpha\beta S}$$

$\Rightarrow$

$$\frac{\partial\theta}{\partial u} = \left[\frac{\tilde{\gamma}_0}{1+\tilde{\gamma}_0} - \left(\frac{w}{k_BT}\right)\frac{\tilde{\gamma}_0^2}{(1+\tilde{\gamma}_0)^3} - \theta\right]\frac{\tilde{v}_0}{\alpha\beta S}$$

$$+\left[\frac{\tilde{\gamma}_0}{(1+\tilde{\gamma}_0)^2} - \left(\frac{w}{k_BT}\right)\frac{\tilde{\gamma}_0^2(2-\tilde{\gamma}_0)}{(1+\tilde{\gamma}_0)^4}\right]\frac{\tilde{\alpha}\tilde{v}_0}{\alpha\beta S}\cdot\log(u)$$

for simplicity in writing, let us introduce two functions of $\tilde{\gamma}_0$:

$$f_0 = \frac{\tilde{\gamma}_0}{1+\tilde{\gamma}_0} - \left(\frac{w}{k_BT}\right)\frac{\tilde{\gamma}_0^2}{(1+\tilde{\gamma}_0)^3}$$

and:

$$f_1 = \frac{\tilde{\gamma}_0}{(1+\tilde{\gamma}_0)^2} - \left(\frac{W}{a_D \tau}\right) \frac{\tilde{\gamma}_0^2 (2-\tilde{\gamma}_0)}{(1+\tilde{\gamma}_0)^4}$$

as well as:

$$1/\tau = \tilde{v}_0 / \alpha p S$$

$\Rightarrow$ the differential equation thus becomes:

$$\frac{\partial \theta}{\partial u} = [f_0 - \theta]/\tau + f_1 \frac{\tilde{\alpha}}{\tau} \log(u)$$

using wolfram alpha, we can solve this differential equation and find:

$$\theta(u) = f_1 \tilde{\alpha}\, e^{-u/\tau}\, \mathrm{Ei}\left(\frac{u}{\tau}\right) + k_1 e^{-u/\tau} + f_0 - f_1 \tilde{\alpha} \log(u)$$

, where k_1 is an integration constant.

We can now substitute back $u = e^{\alpha p \phi}$, with ϕ the actual electric potential.

$\Rightarrow$

$$\theta(\phi) = f_1 \tilde{\alpha}\, e^{-e^{\alpha\beta\phi}/\tau}\, Ei\left(\frac{e^{\alpha\beta\phi}}{\tau}\right)$$

$$+ k_1\, e^{-e^{\alpha\beta\phi}/\tau} + f_0 - f_1 \alpha' \beta \phi$$

, where k_1 should be found from a boundary condition, for example a potential at which the coverage is known.

The elliptic integral can cause problems in the (numerical) evaluation of the solution.

$\Rightarrow$ $Ei(e^{\alpha\beta\phi}/\tau)$ diverges if $e^{\alpha\beta\phi}/\tau \to 0$.

$\Rightarrow$ we can rewrite the equation back into the time domain:

$$\phi = \phi_0 + s \cdot t$$

$\Rightarrow$

$$\theta(t) = f_1 \tilde{\alpha}\, e^{-e^{\alpha\beta(\phi_0+st)}/\tau}\, Ei\left(\frac{e^{\alpha\beta(\phi_0+st)}}{\tau}\right)$$

$$e^{-e^{\alpha\beta(\phi_0+st)}/\tau}$$

$$+ k_1 e \qquad + f_0 - f_1 \alpha' \beta (\phi_0 + st)$$

$\theta(t=0)$ should be the equilibrium coverage at ϕ_0, hence:

$$\theta(t=0) = f_1 \tilde{\alpha}\, e^{-e^{\alpha\beta\phi_0}/\tau}\, Ei\left(\frac{e^{\alpha\beta\phi_0}}{\tau}\right)$$

$$+ k_1 e^{-e^{\alpha\beta\phi_0}/\tau} + f_0 - f_1 \alpha' \beta \phi_0$$

$$\equiv \underbrace{\gamma/(1+\gamma) - (w/k_BT)\, \gamma^2/(1+\gamma)^3}_{\text{define: } f_2(\phi_0)} \quad [@ \gamma \phi_0]$$

$\Rightarrow$

$$f_1 \tilde{\alpha}\, e^{-e^{\alpha\beta\phi_0}/\tau}\, Ei\left(\frac{e^{\alpha\beta\phi_0}}{\tau}\right) + k_1 e^{-e^{\alpha\beta\phi_0}/\tau}$$

$$+ f_0 - f_1 \alpha' \beta \phi_0 = f_2(\phi_0)$$

$\Rightarrow$

$$k_1 = \left[f_2(\phi_0) - f_0 + f_1 \alpha' \beta \phi_0\right] e^{e^{\alpha\beta\phi_0}/\tau}$$

$$- f_1 \tilde{\alpha}\, Ei\left(\frac{e^{\alpha\beta\phi_0}}{\tau}\right)$$

we do have a solution…:

, which results in the following final solution for $\Theta(\phi)$:

Till now
not capable of plotting….

$$+ k_1 e^{-e^{\alpha\beta\phi}/\tau} + f_0 - f_1 \alpha' \beta \phi$$

$$\theta(\phi) = f_1 \tilde{\alpha} \left[E_i\left(\frac{e^{\alpha\beta\phi}}{\tau}\right) - E_i\left(\frac{e^{\alpha\beta\phi_0}}{\tau}\right) \right] e^{-e^{\alpha\beta\phi}/\tau}$$

$$+ \left[f_2(\phi_0) - f_0 + f_1 \alpha' \beta \phi_0 \right] e^{\left[e^{\alpha\beta\phi_0} - e^{+\alpha\beta\phi}\right]/\tau}$$

$$+ f_0 - f_1 \alpha' \beta \phi_0$$

, which is only valid for $\phi \geq \phi_0$!

=

ϕ is the potential you want to know θ

ϕ_0 is the starting potential

S is the sweep rate of the potential

$\beta = 1/k_B T$, k_B Boltzmann's constant, and T temperature

$\tilde{\gamma}_0 = e^{-E^\circ_{form} \cdot \beta}$ where E°_{form} is the formation energy

$\tilde{\nu}_0 = \nu_0 e^{-\beta E_d^0}$, where ν_0 is the attempt frequency and E_d^0 is the diffusion energy.

α = correction to diffusion energy with potential

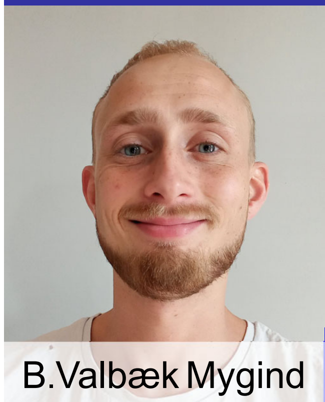
α' = correction to formation energy with potential

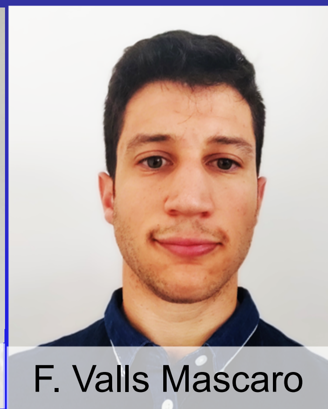
Question:

Unless you do temperature dependent measurements, I do not think ν_0 and the diffusion energy E_d^0 are independent fitting parameters, as they come together in:

$$\tilde{\nu}_0 = \nu_0 \exp(-\beta E_d^0)$$

Acknowledgments:

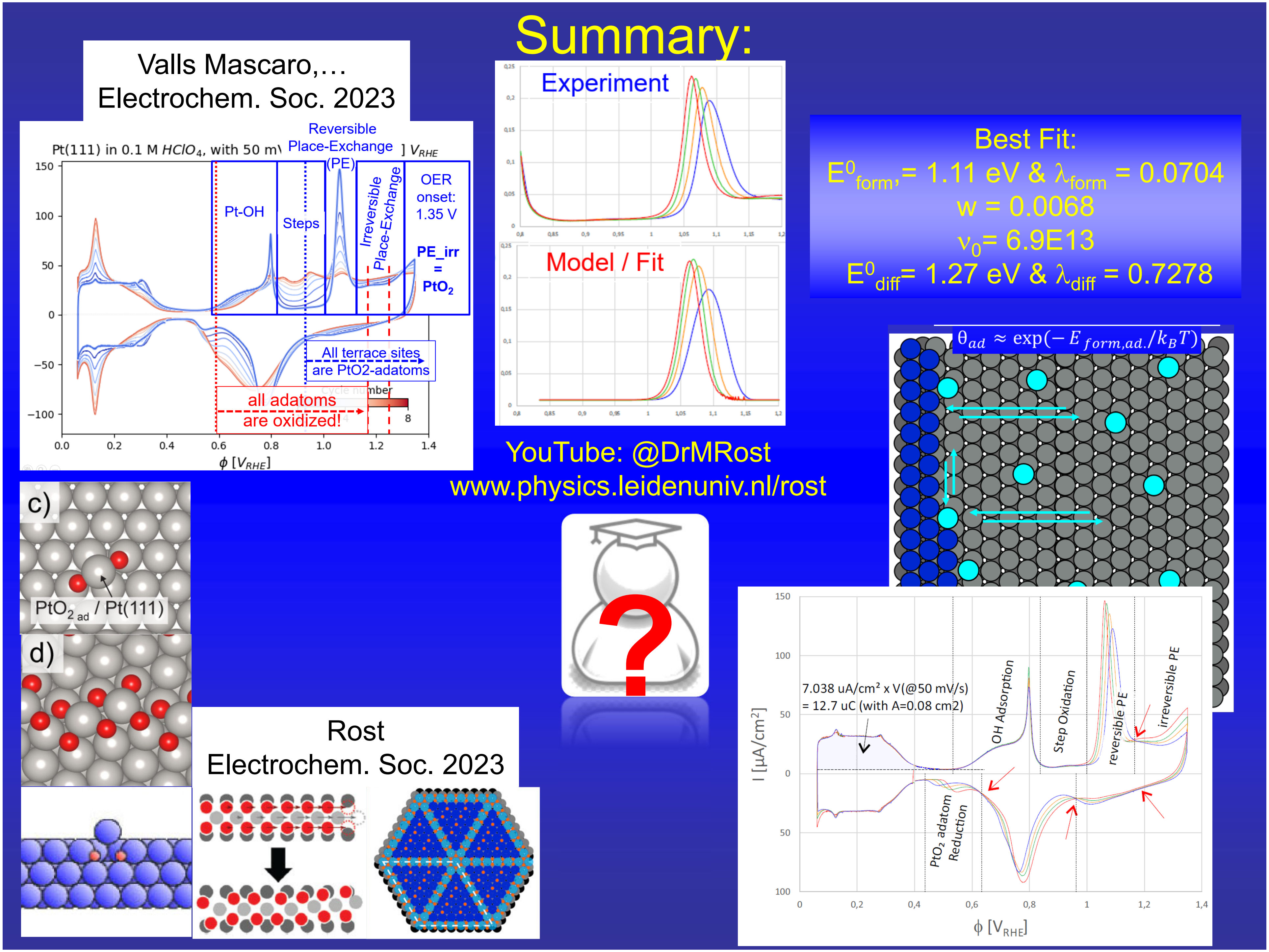

B.Valbæk Mygind


F. Valls Mascaro


Prof. G. Verbiest


Prof. M. Koper

Leiden Institute of Physics & Leiden Institute of Chemistry


Summary:
Valls Mascaro,… Electrochem. Soc. 2023
Pt(111) in 0.1 M HClO4, with 50 m\ ] VRHE
Reversible Place-Exchange (PE)
Pt-OH
Steps
Irreversible Place-Exchange
OER onset: 1.35 V
PE_irr = PtO2
All terrace sites are PtO2-adatoms
all adatoms are oxidized!
Cycle number
ϕ [VRHE]
Experiment
Model / Fit
Best Fit:
E0form,= 1.11 eV & λform = 0.0704
w = 0.0068
ν0= 6.9E13
E0diff= 1.27 eV & λdiff = 0.7278
θad ≈ exp(− Eform,ad./kBT)
YouTube: @DrMRost
www.physics.leidenuniv.nl/rost
c)
PtO2 ad / Pt(111)
d)
Rost Electrochem. Soc. 2023
7.038 uA/cm² x V(@50 mV/s)
= 12.7 uC (with A=0.08 cm2)
OH Adsorption
Step Oxidation
reversible PE
irreversible PE
PtO2 adatom Reduction
I [μA/cm²]
ϕ [VRHE]