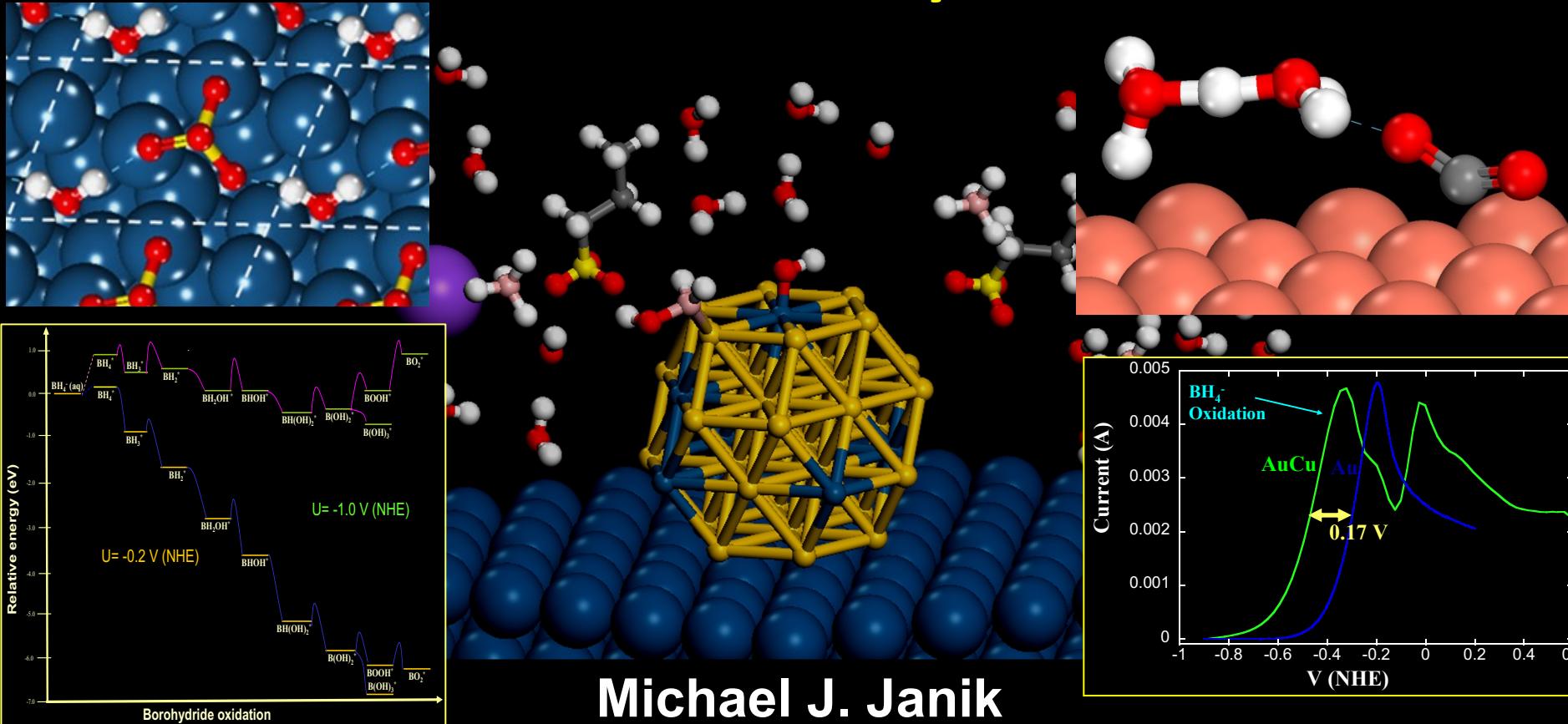


Electronic structure modeling of electrocatalysis at the electrode-electrolyte interface



Michael J. Janik

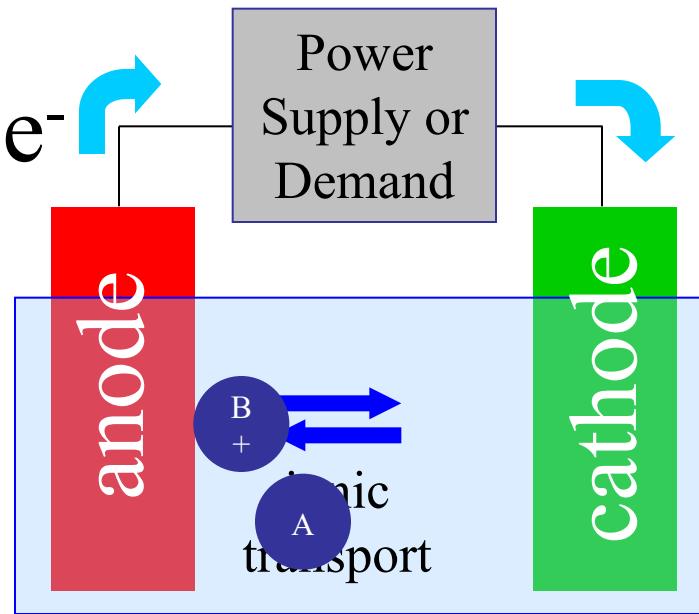
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Mississippi State University – iCOMSE Workshop

June 16, 2022

A general electrochemical cell has an anode, cathode, and electrolyte



Anode – oxidation

Cathode – reduction

Electrochemical Potential (U or V)

- Energy per Charge
- Varies with position in cell
- Cell potential: $U_{\text{cathode}} - U_{\text{anode}}$

What are electrochemical devices/technologies used for?

What are electrochemical devices/technologies currently used for?

Batteries – portable power (alkaline, lead-acid, lithium ion)

Fuel cells – some portable power applications (auxiliary in trucks, forklifts)

Chlor alkali process

electrolysis of water for hydrogen generation

Electroplating – coating metals onto objects (jewelry, car paints)

sensors – redox of ethanol for drunk drivers, glucose measures for diabetes
(and electroanalytic processes in general widely used)

refining – pulling metals out of ores

Photosynthesis, corrosion, supercapacitors, action potentials in neurons, organic electronics,

We learned how to use DFT to calculate the reaction energy (ΔE_{ads}) of



DFT calculations we had to run:

H₂ in the gas phase (E_{H2})

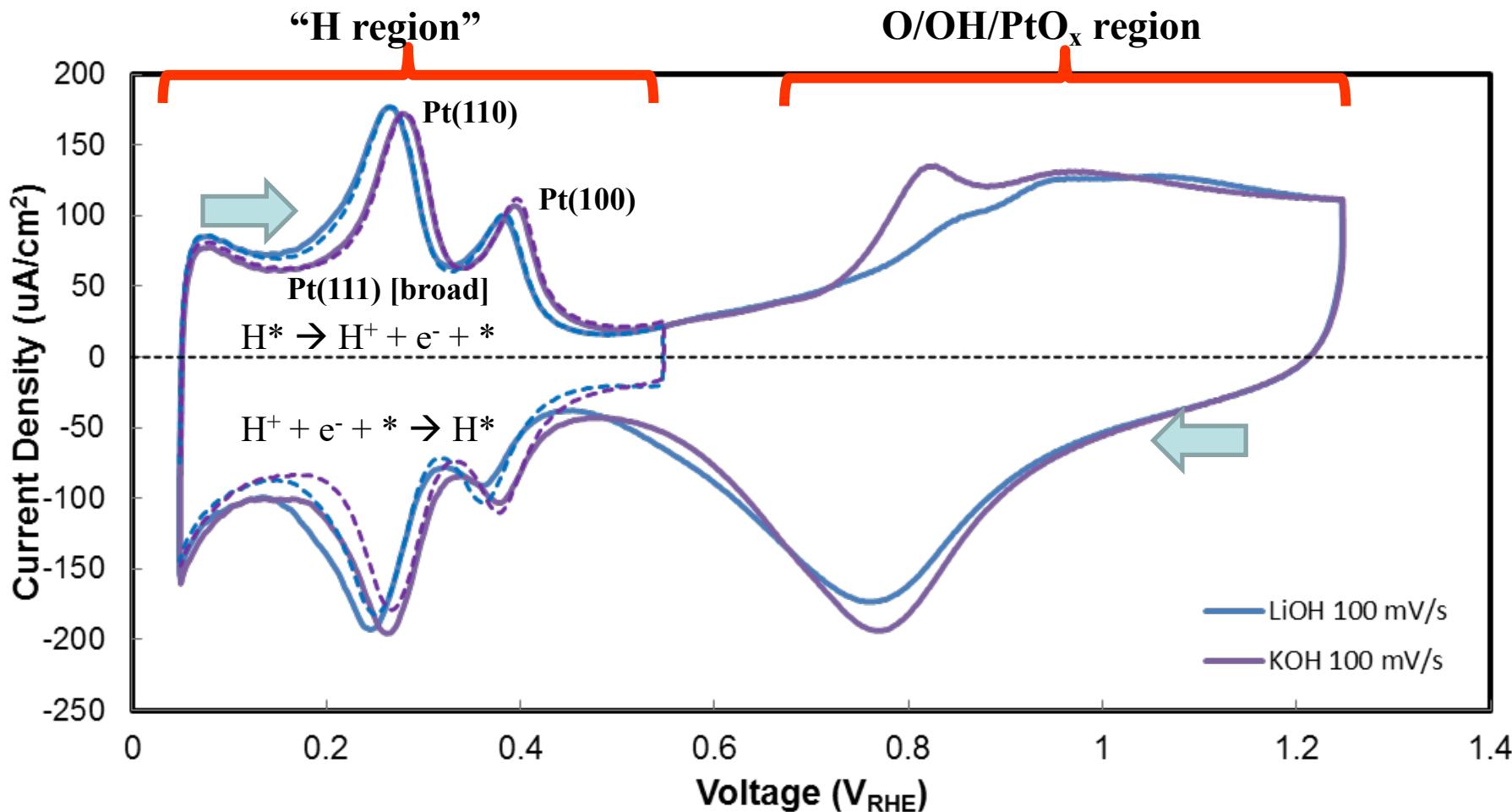
surface without H adsorbed (E_{*})

surface with H adsorbed (E_{H*})

$$\Delta E_{\text{ads}} = E_{\text{H}*} - E_* - \frac{1}{2} E_{\text{H}2}$$

Experimental cyclic voltammogram examines H/OH adsorption/desorption from Pt surfaces

Cyclic voltammetry of a polycrystalline platinum electrode



We learned how to use DFT to calculate the reaction energy (ΔE_{ads}) of



$$\Delta E_{\text{ads}} = E_{\text{H}^*} - E_* - \frac{1}{2} E_{\text{H}_2}$$

How do we calculate the reaction energy of:



We learned how to use DFT to calculate the reaction energy (ΔE_{ads}) of



$$\Delta E_{\text{ads}} = E_{\text{H}^*} - E_* - \frac{1}{2} E_{\text{H}_2}$$

How do we calculate the reaction energy of:



$$\Delta E_{\text{ads}} = E_{\text{H}^*} - E_* - E_{\text{H}^+} - E_e$$

But how do we calculate the energy of an aqueous proton and an electron with DFT?



$$\Delta G_{\text{ads}} = G_{\text{H}^*} - G_* - G_{\text{H}^+} - G_{\text{e}}$$

But how do we calculate the energy of an aqueous proton and an electron with DFT?

Choice 1) “Calculate with DFT” the (free) energy of a gas phase proton, look up an experimental $\Delta G_{\text{solvation}}$. Make sure your code calls 0 energy for an electron = electron in vacuum.

$$\Delta G_{\text{ads}}(U_{\text{abs}}) = G_{\text{H}^*} - G_* - G_{\text{H}^+, \text{gas}} + \Delta G_{\text{H}^+, \text{solv}} + |e| U_{\text{abs}}$$



$$\Delta G_{\text{ads}} = G_{\text{H}^*} - G_* - G_{\text{H}^+} - G_{\text{e}}$$

Choice 1)

$$\Delta G_{\text{ads}}(U_{\text{abs}}) = G_{\text{H}^*} - G_* - G_{\text{H}^+, \text{gas}} + \Delta G_{\text{H}^+, \text{solv}} + |e^-| U_{\text{abs}}$$

U_{abs} = “potential” of an electron relative to an electron in vacuum. Sign convention – more negative = less stable electron

+|e^-|U_{abs} → charge times potential = energy of an electron.



$$\Delta G_{\text{ads}} = G_{\text{H}^*} - G_* - G_{\text{H}^+} - G_{\text{e}}$$

Choice 2)

At 0 V on a “hydrogen electrode scale”

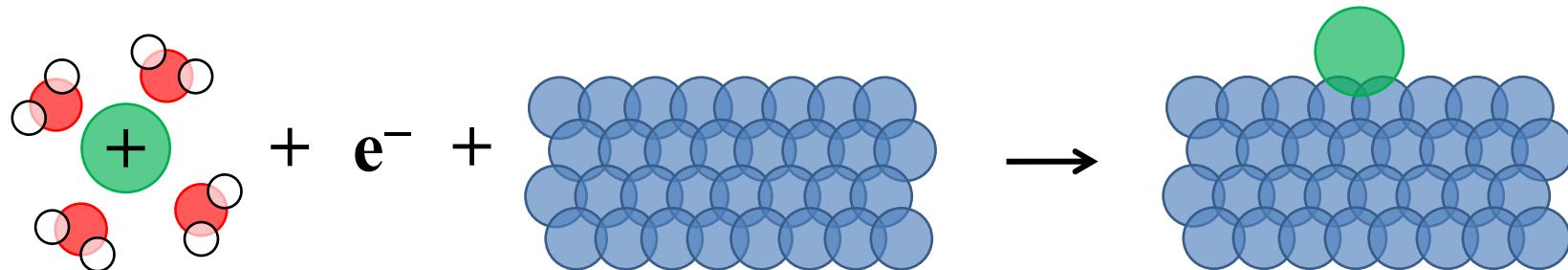
$\text{H}_{2,\text{gas}} \rightarrow 2\text{H}^+ + 2\text{e}^-$ has a $\Delta G = 0$

$G_{\text{H}^+} + G_{\text{e}^-} = \frac{1}{2} G_{\text{H}_2,\text{gas}}$ at 0 V on a CHE scale

$G_{\text{H}^+} + G_{\text{e}^-} = \frac{1}{2} G_{\text{H}_2,\text{gas}} - |e^-|U_{\text{CHE}}$ at any potential relative to the CHE scale

$$\Delta G_{\text{ads}}(U_{\text{CHE}}) = G_{\text{H}^*} - G_* - \frac{1}{2} G_{\text{H}_2,\text{gas}} + +|e^-|U_{\text{CHE}}$$

Ion adsorption free energies are calculated using a combination of DFT calculations, statistical mechanics, and experimental data



$$\Delta G_{ads} = \sum G_{products} - \sum G_{reactants}$$

$$\Delta G_{ads}(U) = G_{H^*} - G_{H_{(aq)}^+} - G_* - e^-(U - U_{ref})$$

$$G_{H_{aq}^+} = G_{H_g^+} + \Delta G_{sol}^\circ + RT \ln[H^+] \quad \text{Or reference through H}_2 \text{ gas and U}_{\text{RHE}}$$

$$G_{H_g^+} = E_{DFT} + E(T) + PV - (S_{vib} + S_{translation} + S_{rotation}) T$$

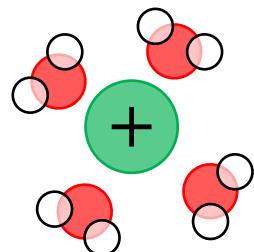
$$G_* = E_{DFT}$$

$$G_{H^*} = E_{DFT} + ZPVE - S_{vib}T$$

DFT
DFT _{VIB}
Stat Mech
Expt/Set

$$\Delta G_{ads}(U_0) = 0 \rightarrow \text{equilibrium potential } U_0$$

Choices to determine the chemical potential of the ion and electron



$$G_{H_{aq}^+} = G_{H_g^+} + \Delta G_{sol}^\circ + RT \ln[a_{H^+}]$$

$$G_{H_g^+} = E_{DFT} + E(T) + PV - (S_{vib} + S_{translation} + S_{rotation}) T$$

ΔG_{sol}° from experiment or DFT continuum solvent model
 $e^- (U - U_{ref})$ - reference is “vacuum electrode”

Or jointly reference ion and electron:

$$\frac{1}{2} H_2 \rightarrow H^+ + e^- \quad \Delta G = 0 \text{ at } U_{RHE}$$

G_{H_2} from ab initio thermo as for $G_{H_g^+}$ above

$$G_{H_2} = E_{DFT} + ZPVE + E(T) + PV - (S_{vib} + S_{translation} + S_{rotation}) T$$

$$G_{H_{aq}^+} + G_e = \frac{1}{2} G_{H_2} + e^- (U - U_{RHE})$$

DFT
DFT_{VIB}
Stat Mech
Expt/Set

Similar approaches to reference other ions based on gaseous or solid species and known experimental equilibrium potentials

Electrochemical reaction mechanisms – ion transfer and chemical steps:

Hydrogen oxidation (anode of a hydrogen fuel cell) [this not only possible mechanism]



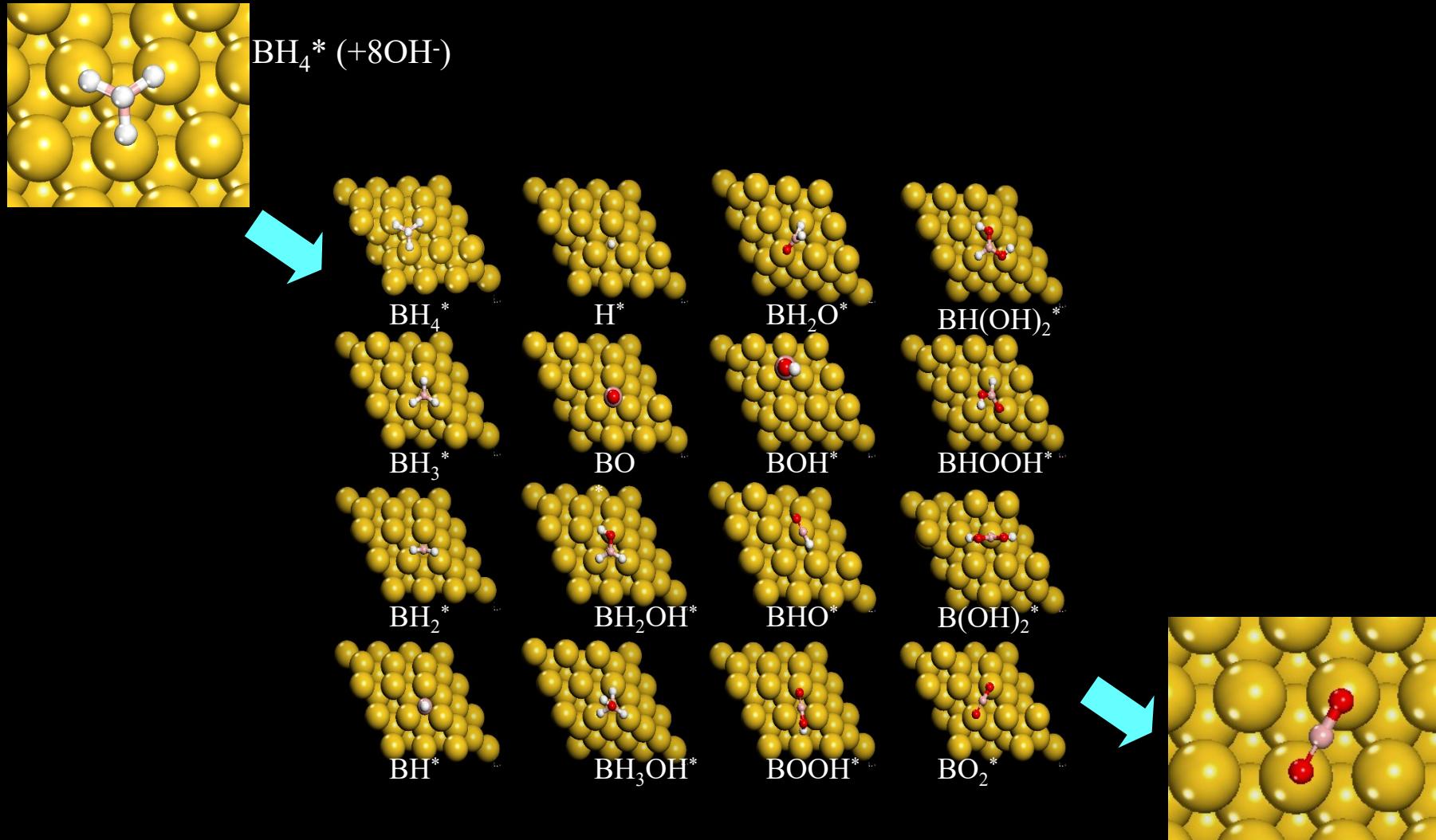
$$\Delta G_{\text{rxn}}(U_{\text{CHE}}) = - [\text{G}_{\text{H}^*} - \text{G}_* - \frac{1}{2} \text{G}_{\text{H}_2,\text{gas}} + + |\text{e}^-| U_{\text{CHE}}]$$

Oxygen reduction (the cathode of a hydrogen fuel cell) [not the only possible mechanism]



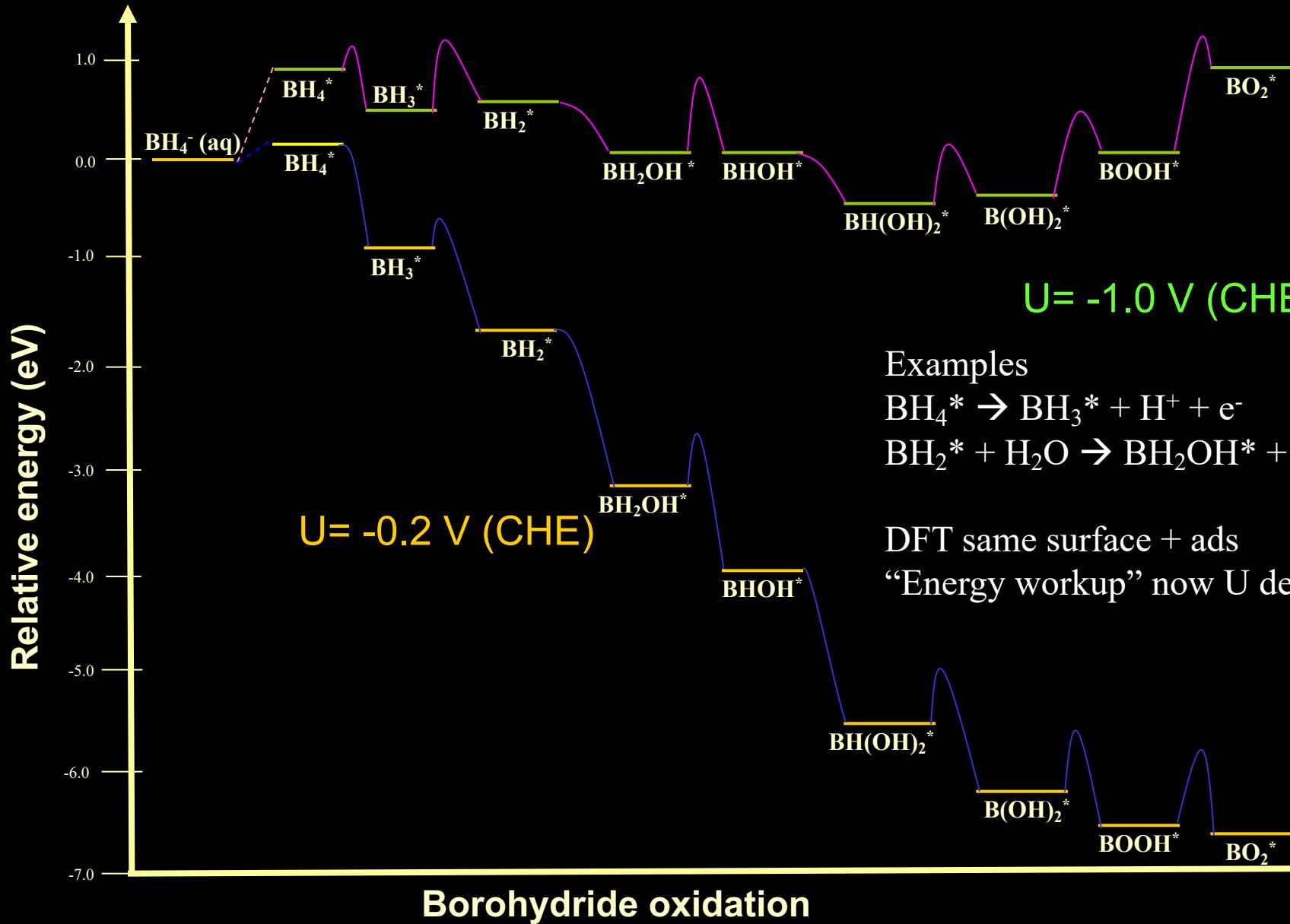
Note the only difference versus the “adsorption” energy we calculated previously is that the proton/electron “adsorb” to an O* (ie, a surface that already has O on it) rather than a bare surface (*)

Reaction Intermediates and Adsorption Sites



Assumption – all adsorbates can access there most stable configuration

Minimum Energy Path over Au(111)



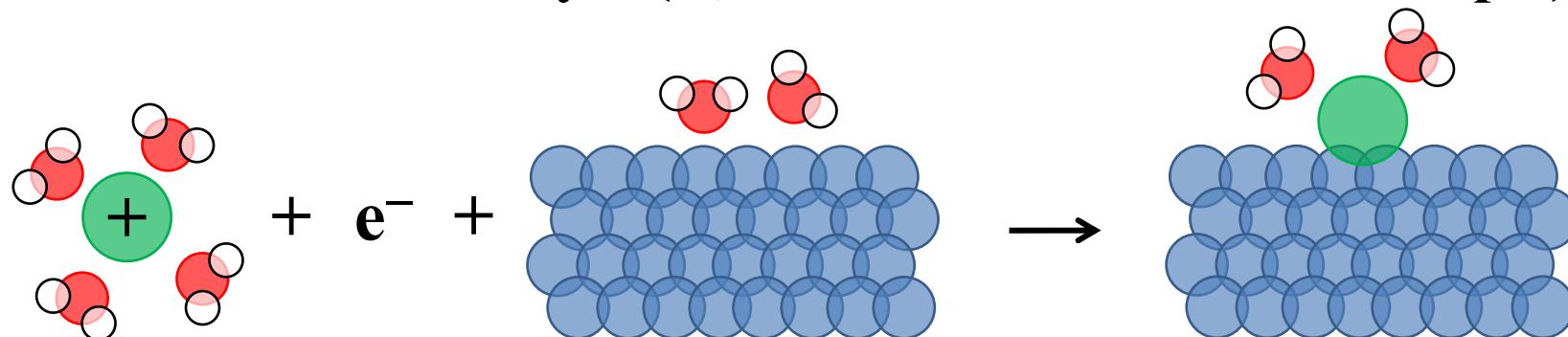
Examples



DFT same surface + ads

“Energy workup” now U dependent

BUT – the reaction does not occur at a solid-gas interface, it occurs as a solid-electrolyte (ie, water with ions in our example)



$$\Delta G_{ads} = \sum G_{products} - \sum G_{reactants}$$

$$\Delta G_{ads}(U) = G_{H^*} - G_{H_{(aq)}^+} - G_* - e^-(U - U_{ref})$$

$$G_{H_{aq}^+} = G_{H_g^+} + \Delta G_{sol}^\circ + RT \ln[H^+] \quad \text{Or reference through H}_2 \text{ gas and U}_{\text{RHE}}$$

$$G_{H_g^+} = E_{DFT} + E(T) + PV - (S_{vib} + S_{translation} + S_{rotation}) T$$

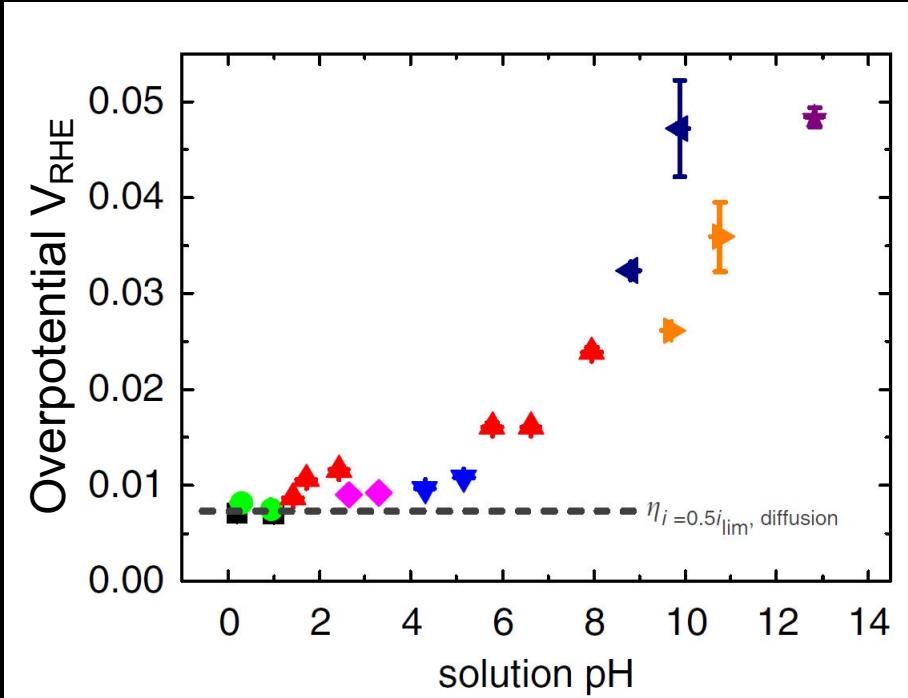
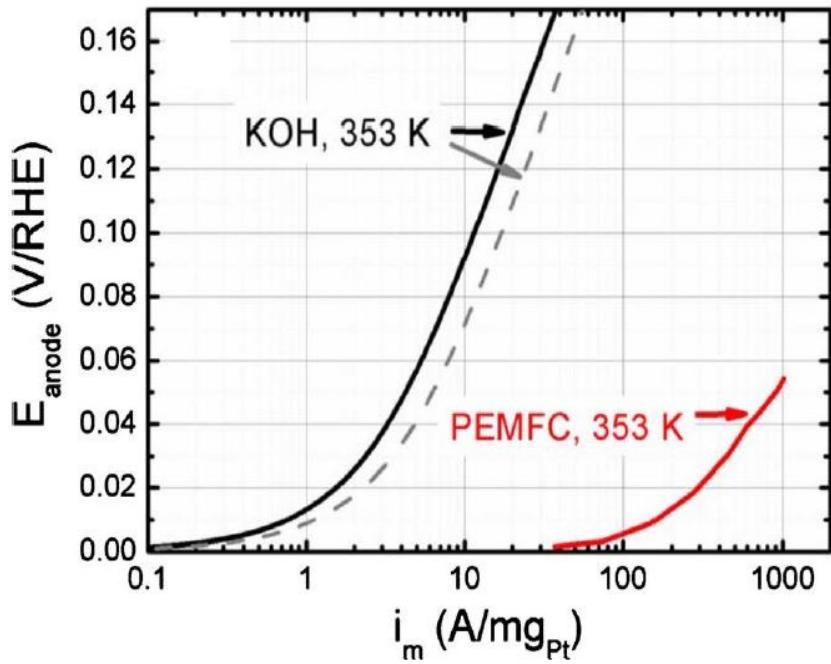
$$G_* = E_{DFT}$$

$$G_{H^*} = E_{DFT} + ZPVE - S_{vib}T$$

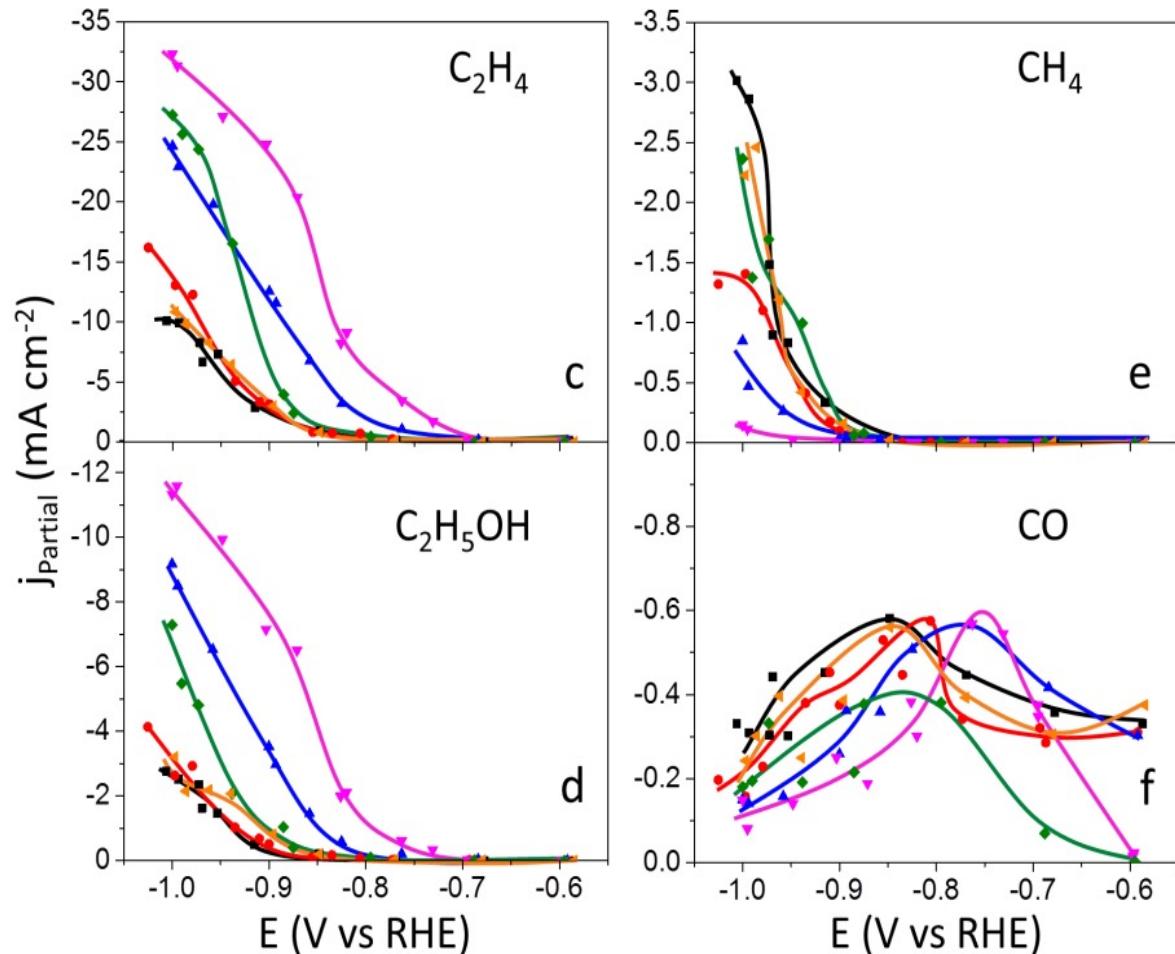
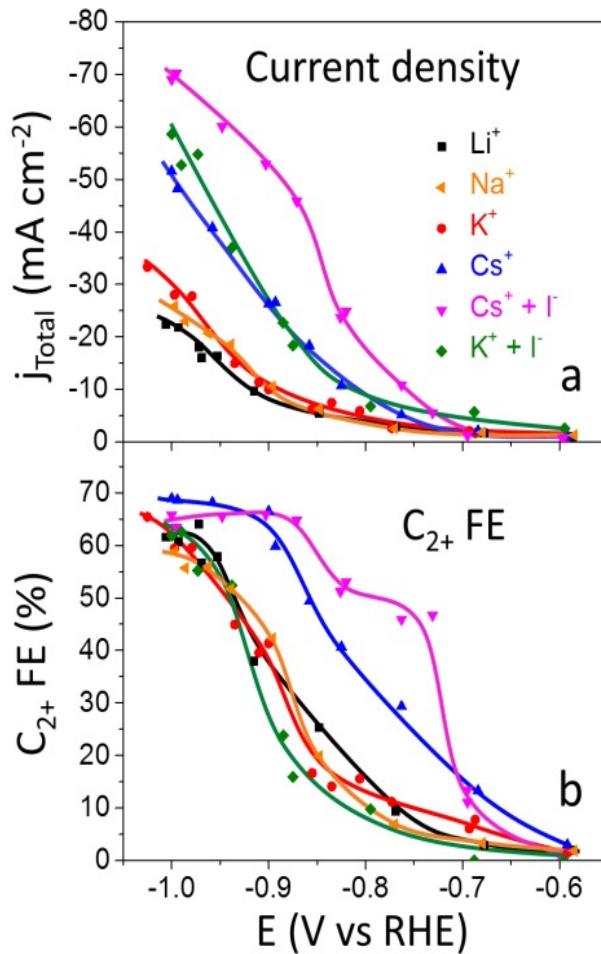
DFT
DFT _{VIB}
Stat Mech
Expt/Set

$$\Delta G_{ads}(U_0) = 0 \rightarrow \text{equilibrium potential } U_0$$

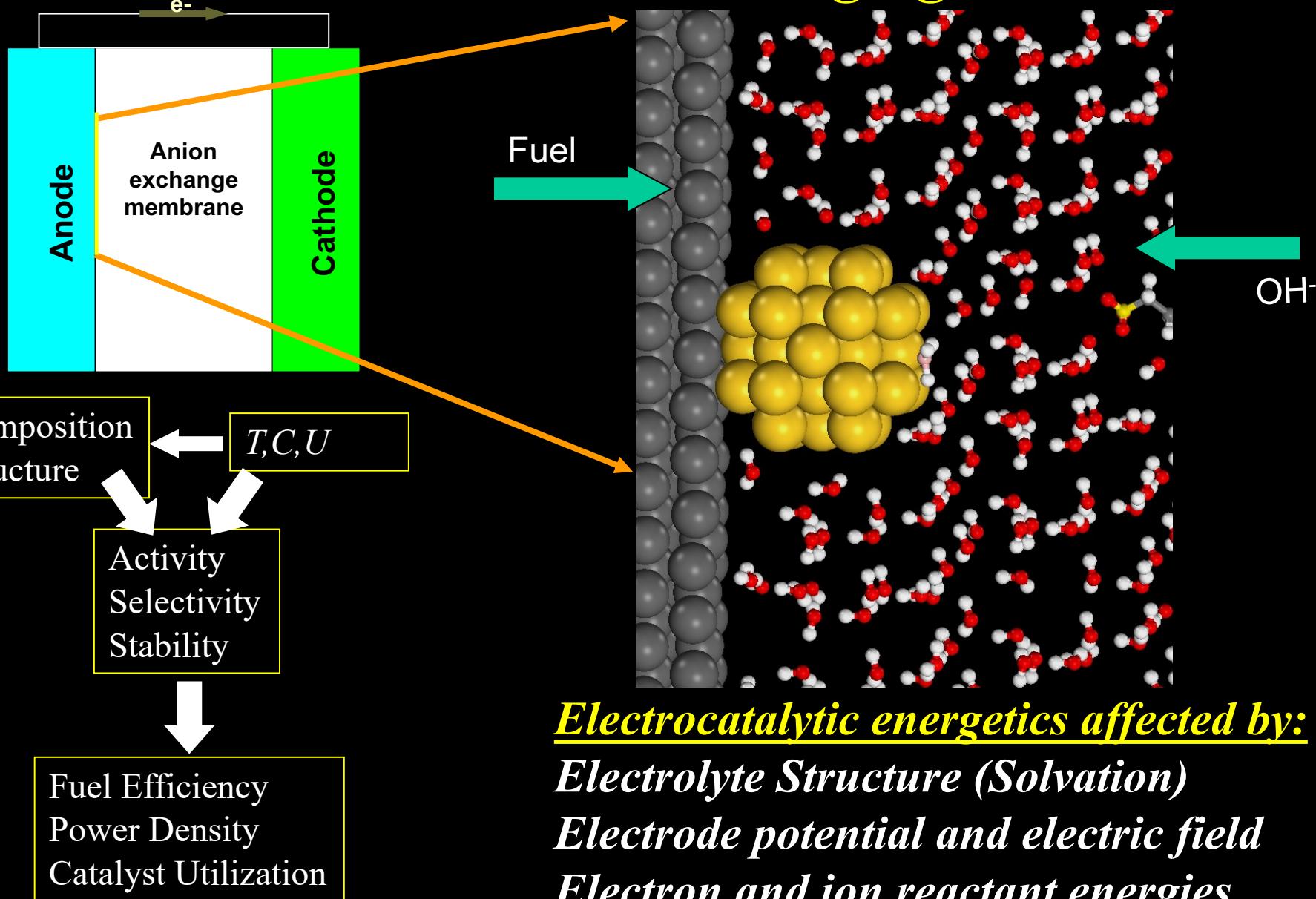
Both electrode and electrolyte impact electrocatalytic rates: pH on HOR



Ions in electrolyte alter CO₂ RR activity and selectivity



DFT representation of the complex electrochemical interface is challenging



The electrolyte (solvent, counterions) structure varies on length and time scales beyond DFT simulations

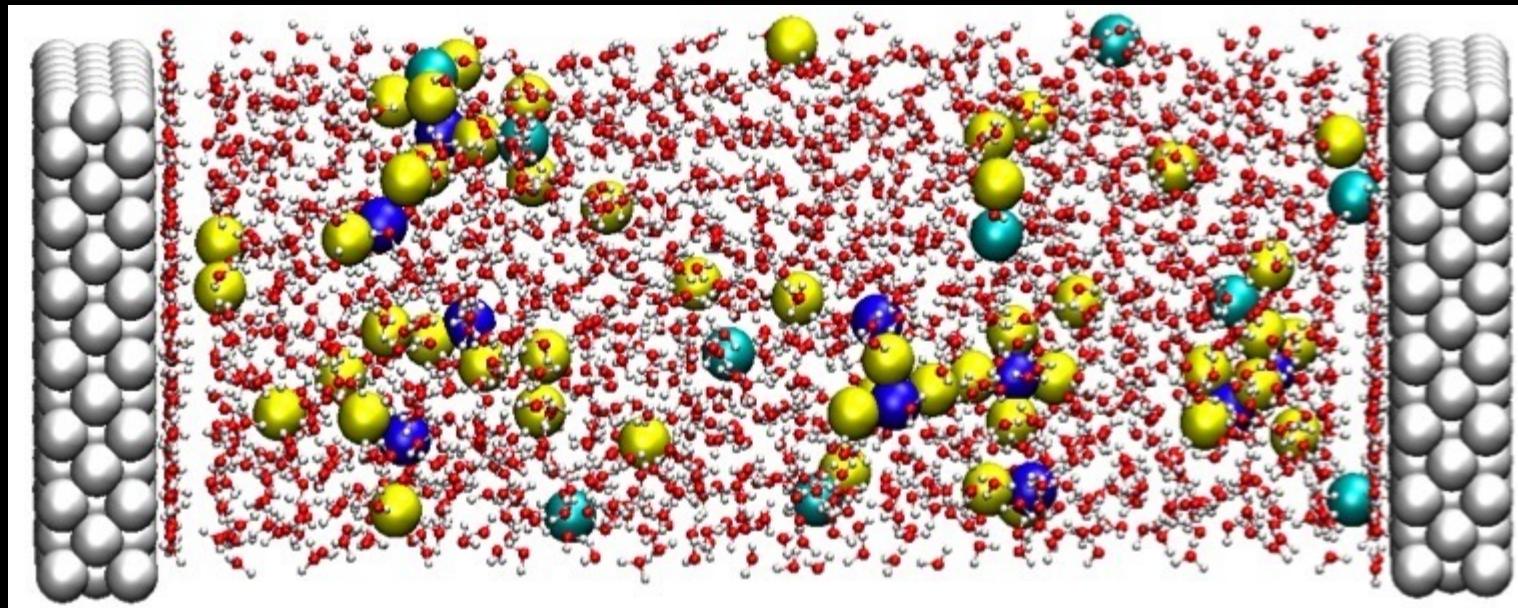


Image from Madden and Chandler, Berkeley

1 M KOH = 1800 H₂O per 32 ion pairs

0.03 M KOH = 11000 H₂O per 6 ion pairs

Water relaxation times on the order of 10 ps, ion diffusion/dissociation
much longer

How to charge surface, periodic charges, etc..

DFT electrocatalysis models make approximations

No model is “right”

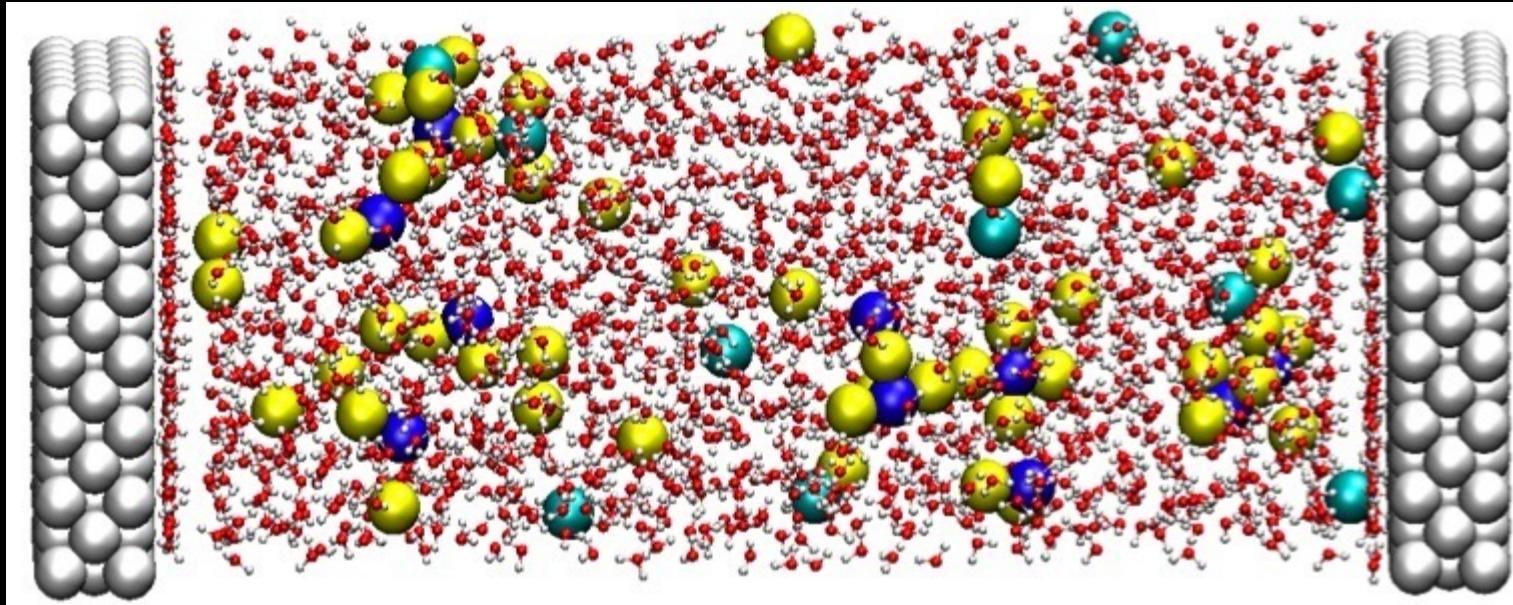


Image from Madden and Chandler, Berkeley

1 M KOH = 1800 H₂O per 32 ion pairs

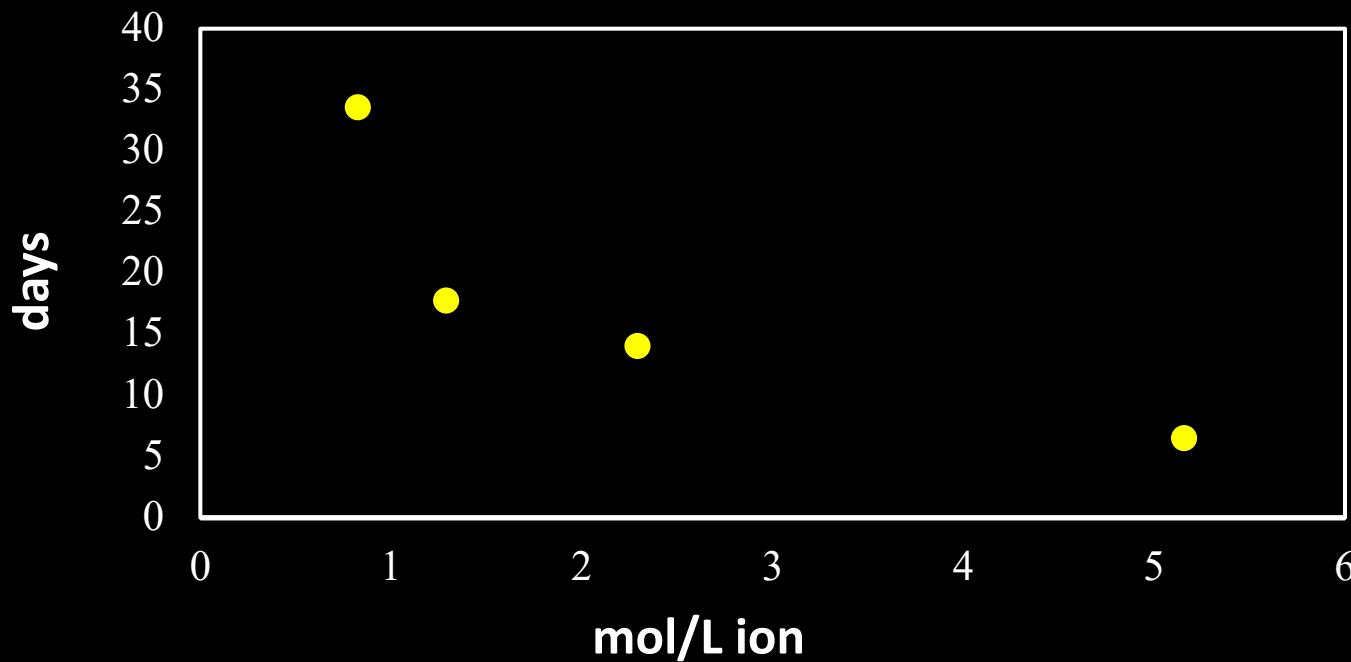
0.03 M KOH = 11000 H₂O per 6 ion pairs

Water relaxation times on the order of 10 ps, ion diffusion/dissociation
much longer

How to charge surface, periodic charges, etc..

Ab initio MD does not provide a viable solution to handle electrochemical interfacial length and time scales

Time for a 15 ps MD simulation with 1 ion and 1 nm water layer

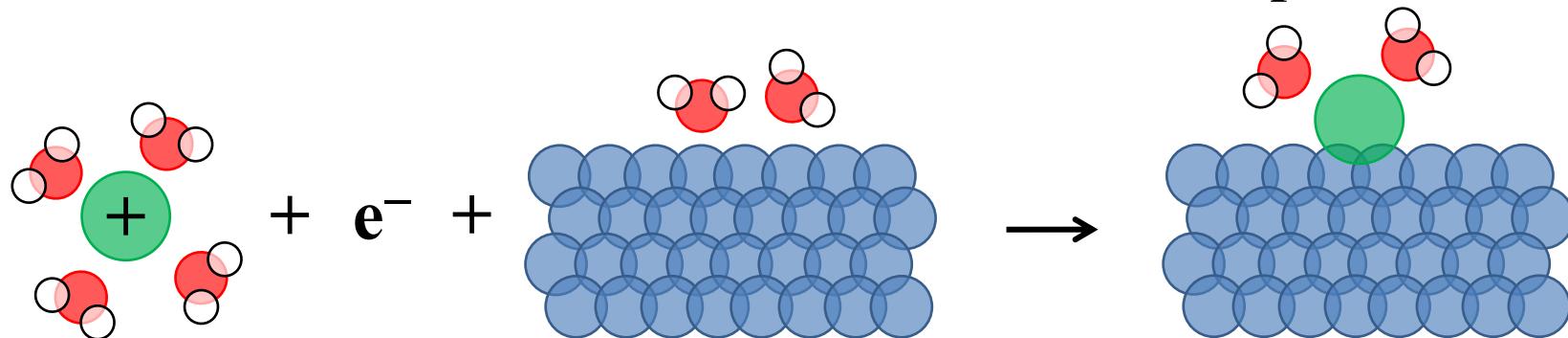


Approximate wall time for a 15 ps AIMD simulation on 32 cores, including 4 water bilayers (1 nm) and 1 ion

Any DFT model of electrode/electrolyte interface will be approximate

Accurate enough to answer/inform research questions
Tested for sensitivity versus model choices

Ion adsorption free energies are calculated using a combination of DFT calculations, statistical mechanics, and experimental data



$$\Delta G_{ads} = \sum G_{products} - \sum G_{reactants}$$

$$\Delta G_{ads}(U) = G_{H^*} - G_{H_{(aq)}^+} - G_* - e^-(U - U_{ref})$$

$$G_{H_{aq}^+} = G_{H_g^+} + \Delta G_{sol}^\circ + RT \ln[H^+] \quad \text{Or reference through H}_2 \text{ gas and U}_{\text{RHE}}$$

$$G_{H_g^+} = E_{DFT} + ZPVE + E(T) + PV - (S_{vib} + S_{translation} + S_{rotation}) T$$

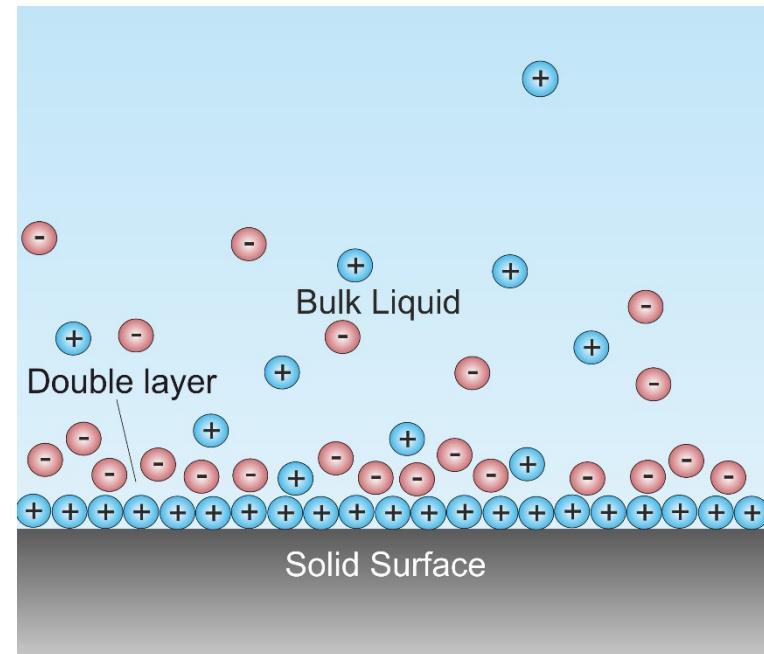
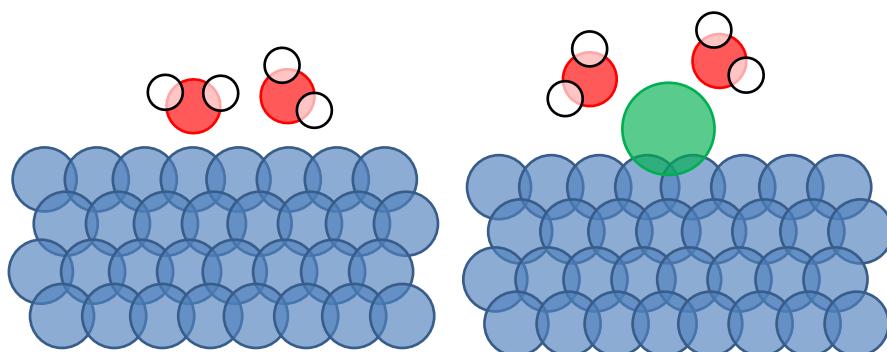
$$G_* = E_{DFT}$$

$$G_{H^*} = E_{DFT} + ZPVE - S_{vib}T$$

DFT
DFT _{VIB}
Stat Mech
Expt/Set

$$\Delta G_{ads}(U_0) = 0 \rightarrow \text{equilibrium potential } U_0$$

How to include the electrochemical interface in the model?



Choice 1 - ignore electrochemical interface entirely – use vacuum

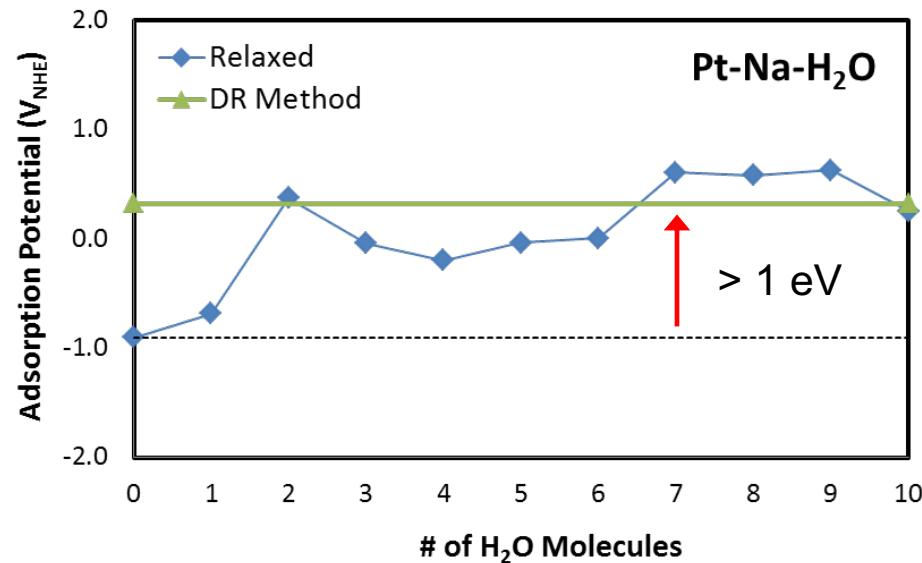
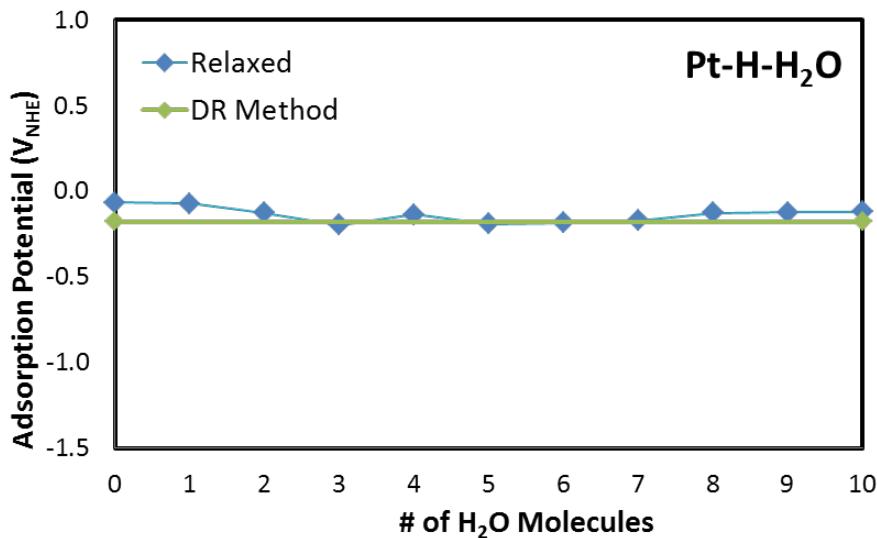
Choice 2 – add solvation, ignore electrification

Choice 3 – add electrification through external field, ignore solvation

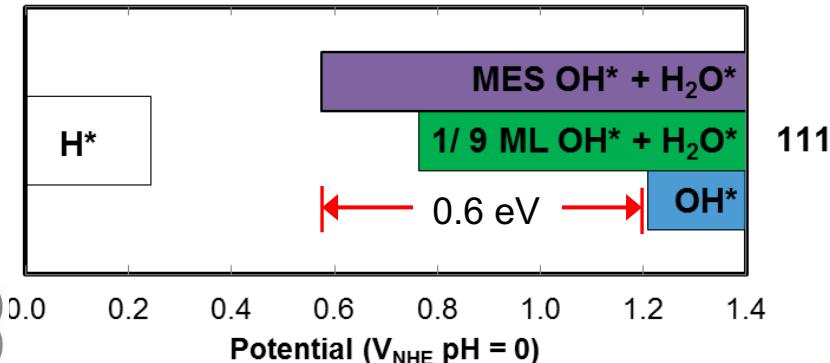
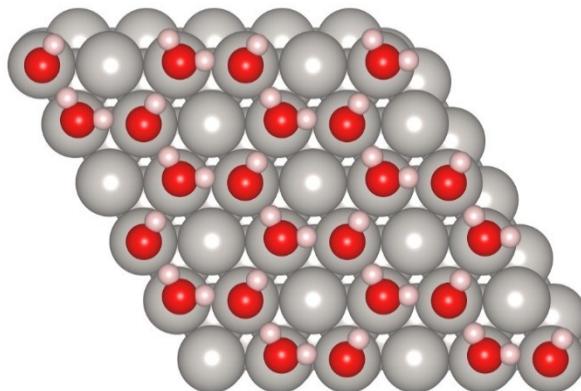
Choice 4 – add coupled solvation and electrification

For all of these, we can try putting the feature in the DFT model, or use an “analytical” model to include the interaction of the electronic system with solvent/electrification “post-hoc”

Solvation modeled through explicit H₂O molecules



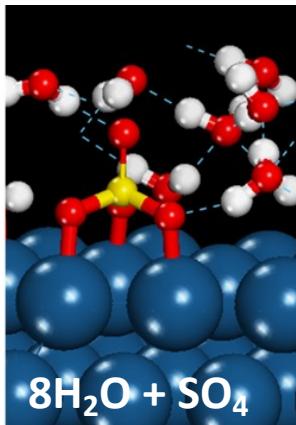
Dipole Moment (eÅ)	
H*	-0.016
Na*	-0.83
OH*	0.052



Large dipoles, propensity for specific solvation dictate solvent inclusion
 Solvation can vary from inconsequential to a 1 eV choice
 Goal is to get “relative solvation energy” between initial, transition, final states

All solvent models have their pros and cons, and inherent imperfections will limit absolute accuracy

Micro-solvation



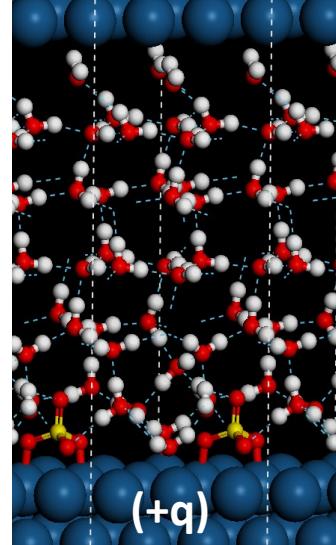
Pros:

- Can capture differences in strong hydrogen bonds
- Computationally facile

Cons:

- Water structure unrestricted in density (surface normal)
- Referencing between structures challenging
- Static, local minima

Fully explicit solvation



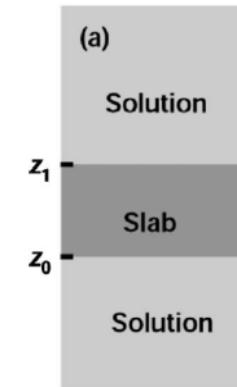
Pros:

- Can vary density

Cons:

- Computationally more intense
- Still a local minima (ice-like) and now there are more minima

Continuum solvation



$$\varepsilon(\mathbf{r}) = 1 + \frac{\varepsilon_\infty(\mathbf{r}) - 1}{2} \left\{ 1 + \frac{1 - [\rho_{na}(\mathbf{r})/\rho_0]^{2\beta}}{1 + [\rho_{na}(\mathbf{r})/\rho_0]^{2\beta}} \right\}$$

Pros:

- Not “static” (averaged), not only local

Cons:

- requires parameterization
- specific solvation dilemma

R. Jinnouchi and A. B. Anderson
Phys. Rev. B77, 2454170-24541718 (2008)

Dabo (Penn State)
Arias (Cornell)
Sundararaman (RPI)

DFT Models can capture electrification of the electrocatalytic interface

Post-hoc electric field:

$$G_{A^*}(U) = E_{DFT} + ZPVE - S_{vib} T + \mu_{A^*} E_{field}(U)$$

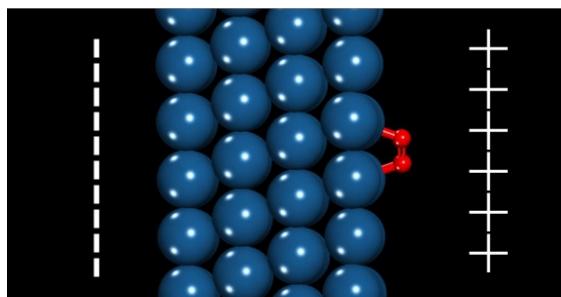
$$E_{field}(U) = \frac{U - U_{PZC}}{d} \text{ or from non-Helmholtz model}$$

Pros: Picks up leading term of adsorbate/field interaction

Cons: Need field versus potential model

No adsorbate polarizability

Applied electric field:



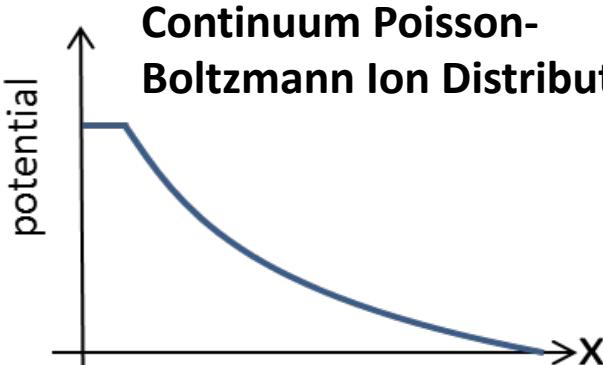
$$G_{A^*}(E_{field}) = E_{DFT}(E_{field}) + ZPVE - S_{vib} T$$

$$E_{field}(U) = \frac{U - U_{PZC}}{d} \text{ or from non-Helmholtz model}$$

Pros: Adds polarizability

Cons: Now need a series of optimizations for each A^*

Continuum Poisson-Boltzmann Ion Distribution:



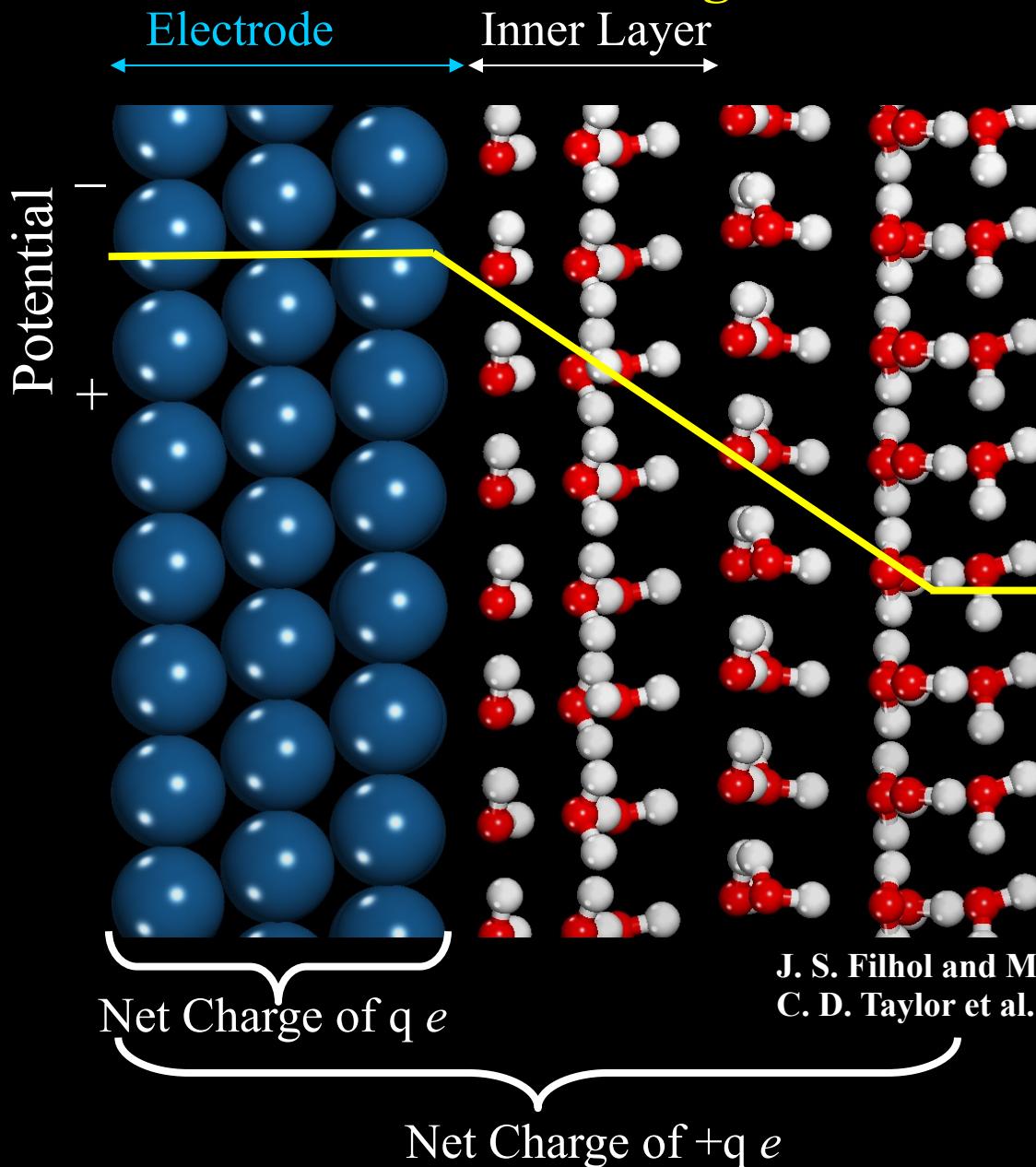
$$\rho_{\pm}(\mathbf{r}) = \mp \frac{c_b e^{[\pm \phi(\mathbf{r}) - \phi_{rep}(\mathbf{r})]/k_B T}}{1 - 2a^3 c_b + 2a^3 c_b \cosh[\phi(\mathbf{r})/k_B T] e^{-\phi_{rep}(\mathbf{r})/k_B T}}.$$

$$G_{A^*}(U) = E_{DFT}(U) + ZPVE - S_{vib} T$$

Pros: More physical ion distribution

Cons: Still a continuum approximation
Explicit/continuum dilemma

Double-Reference Method: include explicit charge and counter-charge in the unit cell

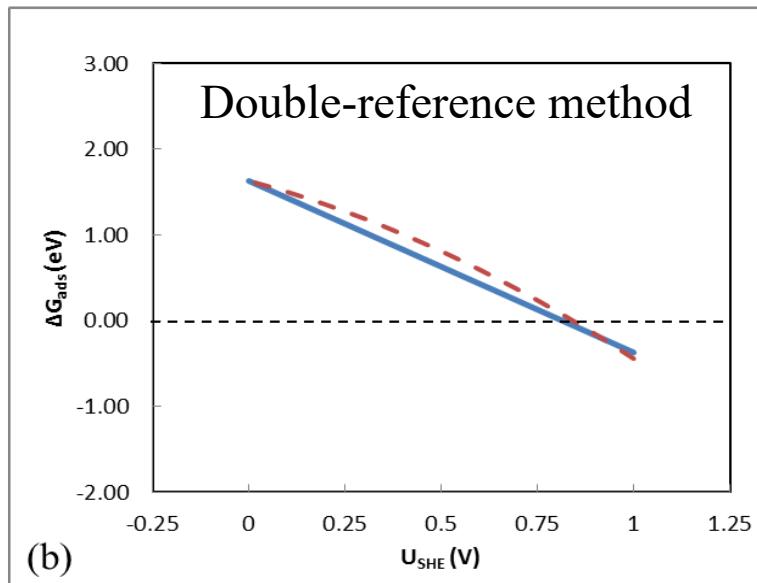
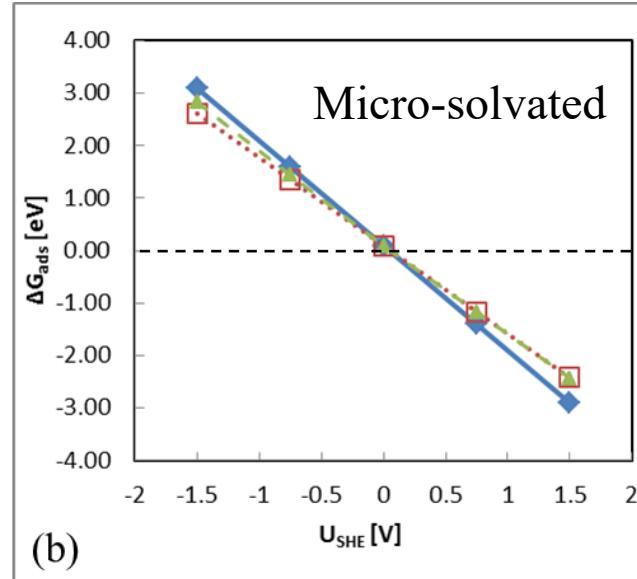
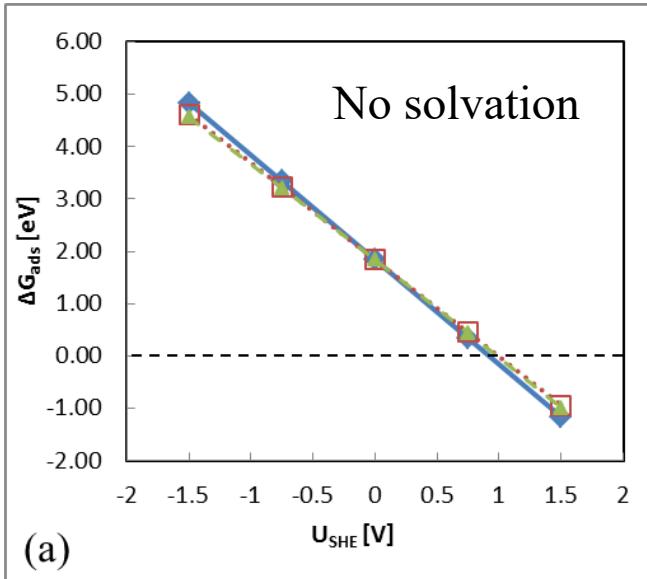


Quantum Chemical “Potentiostat”

Change # electrons (q):
-charges metal, shifts E_F
-countercharge added
-potential drop across interface
-vary q , tune potential

The subtle details:
Referencing the potential
Deriving proper energy

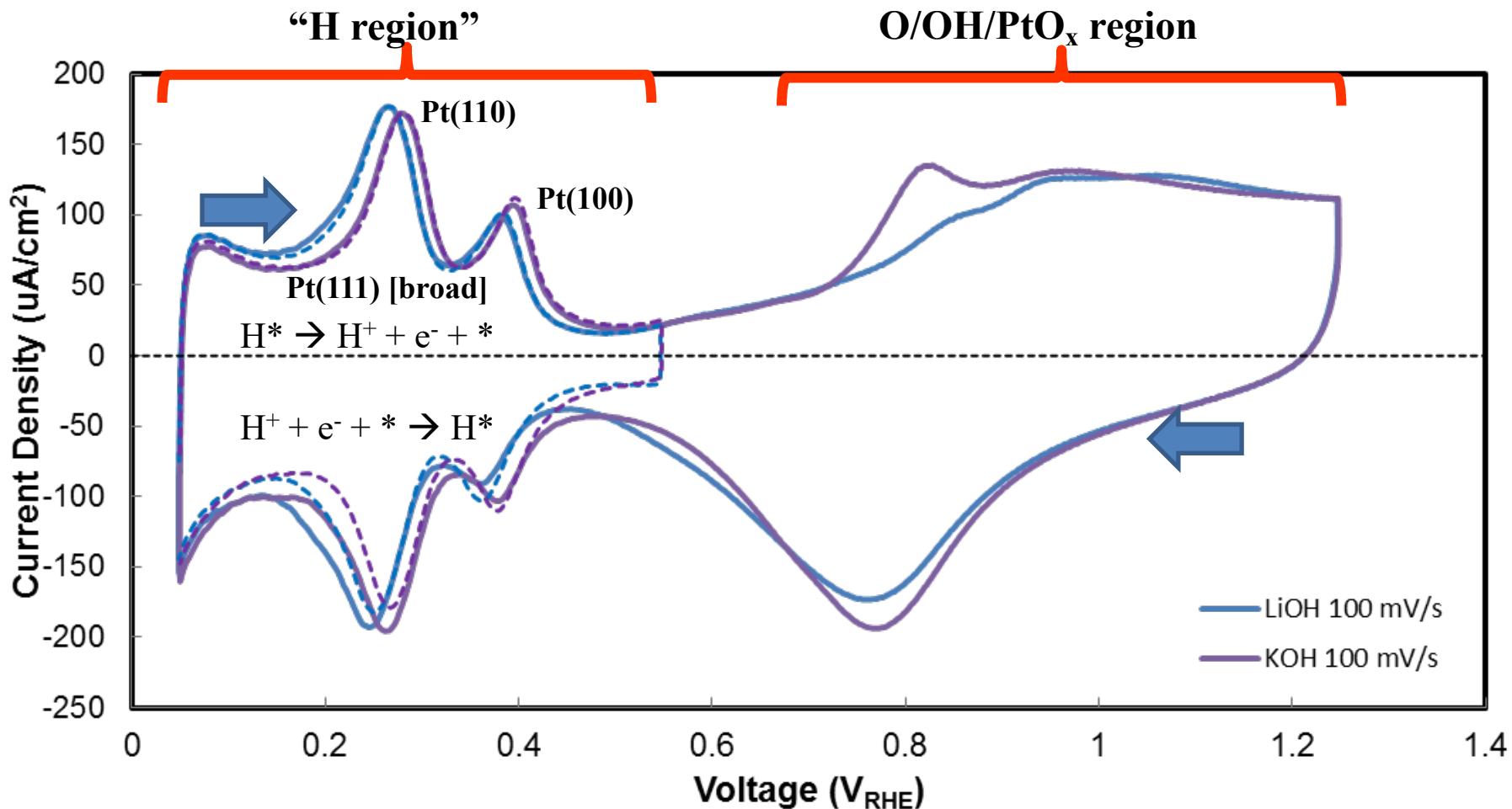
An “electrified interface model” gives minor differences in sulfate adsorption behavior (will be more significant for cations that retain charge)



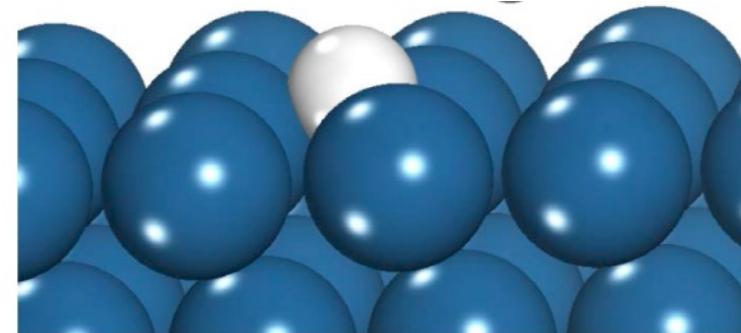
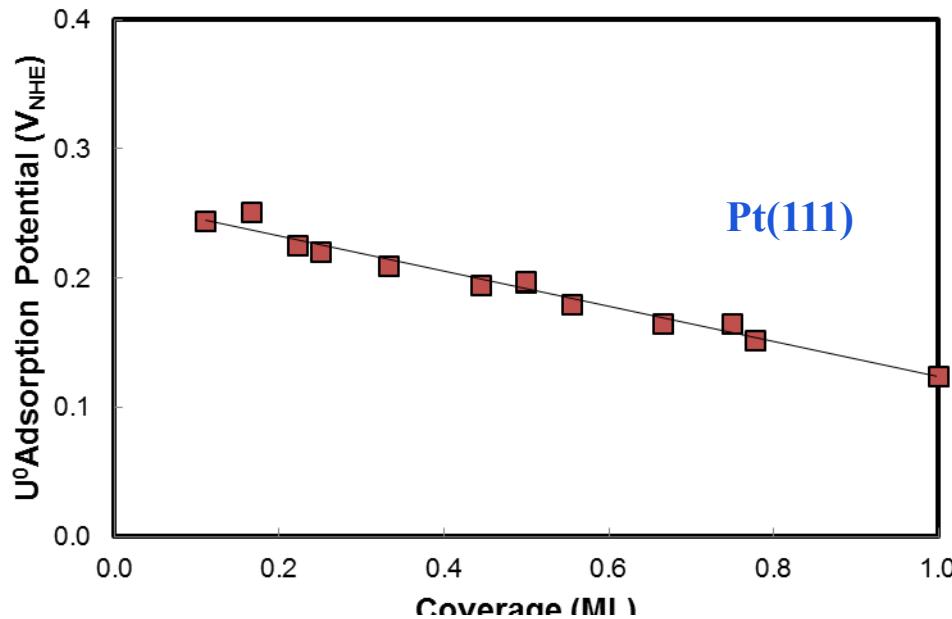
- Solvation:
- shifts adsorption potential by >0.1 eV
- Electrification:
- shifts adsorption potential by <0.05 eV

Experimental cyclic voltammogram examines H/OH adsorption/desorption from Pt surfaces

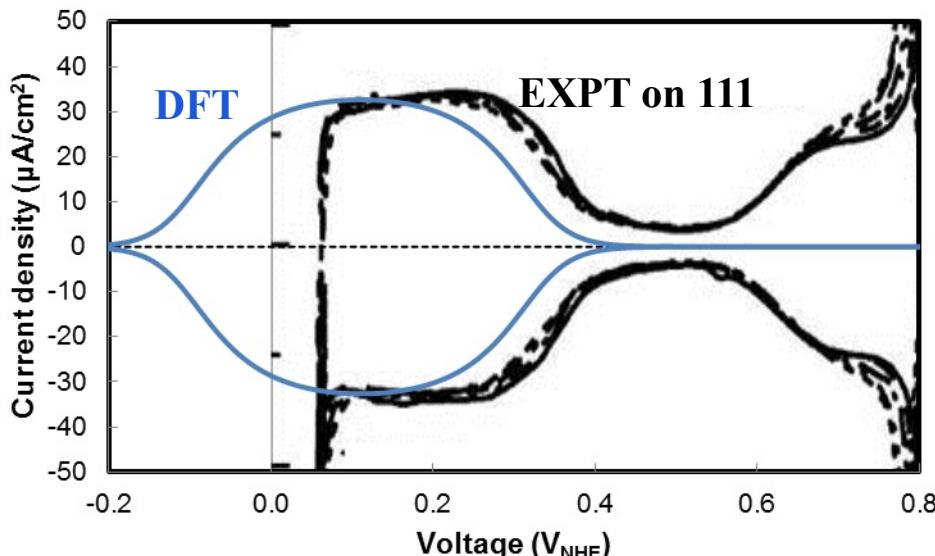
Cyclic voltammetry of a polycrystalline platinum electrode



Vacuum interface model DFT for $\text{H}^* \rightarrow \text{H}^+ + \text{e}^-$ on Pt(111) matches experiment



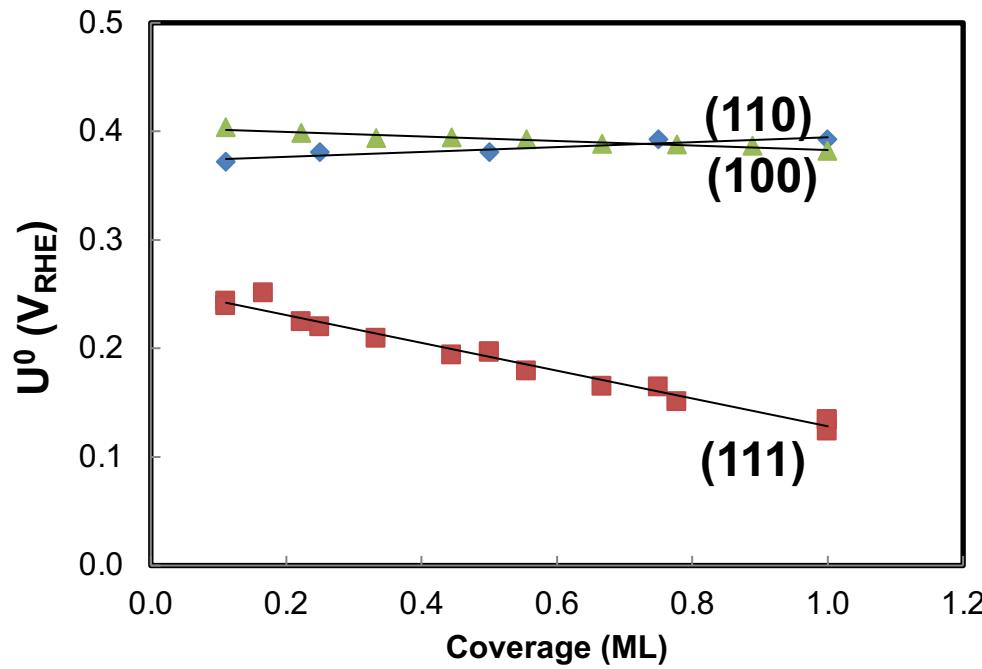
H^{*} adsorption on Pt(111)
- coverage dependent
~ no surface dipole (0.0008 e⁻ Å)



Simulated CV matches experiment
-breadth
-height
-location

Experimental data is CV on Pt(111) at 50 mV/s in 0.1 M perchloric acid from V. Climent, R. Gómez, J. Orts, J.M. Feliu. *J. Phys. Chem. B* **2006**, 110, 11344-11351

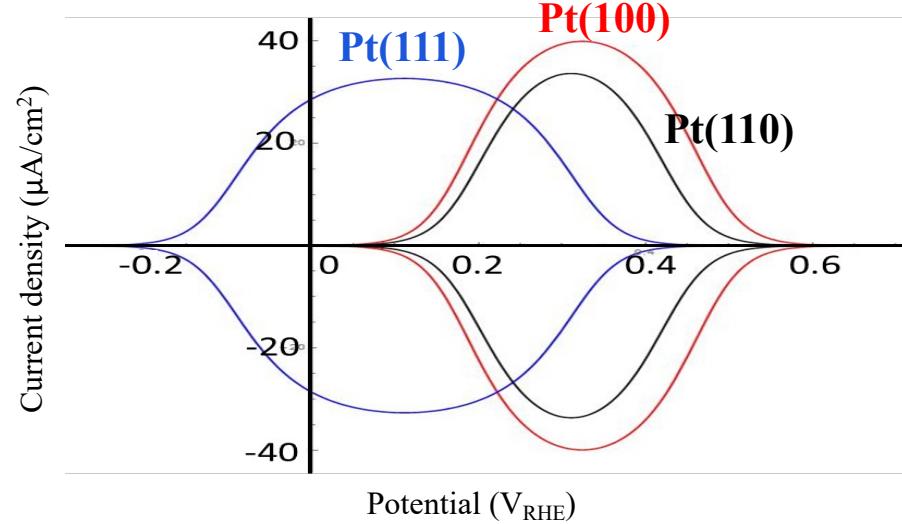
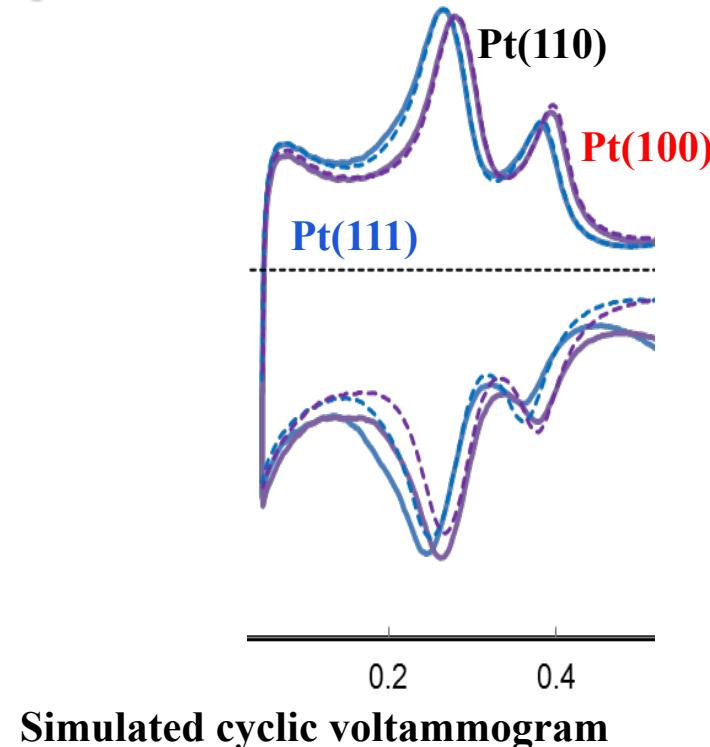
Peak order based on H* desorption does not match experiment



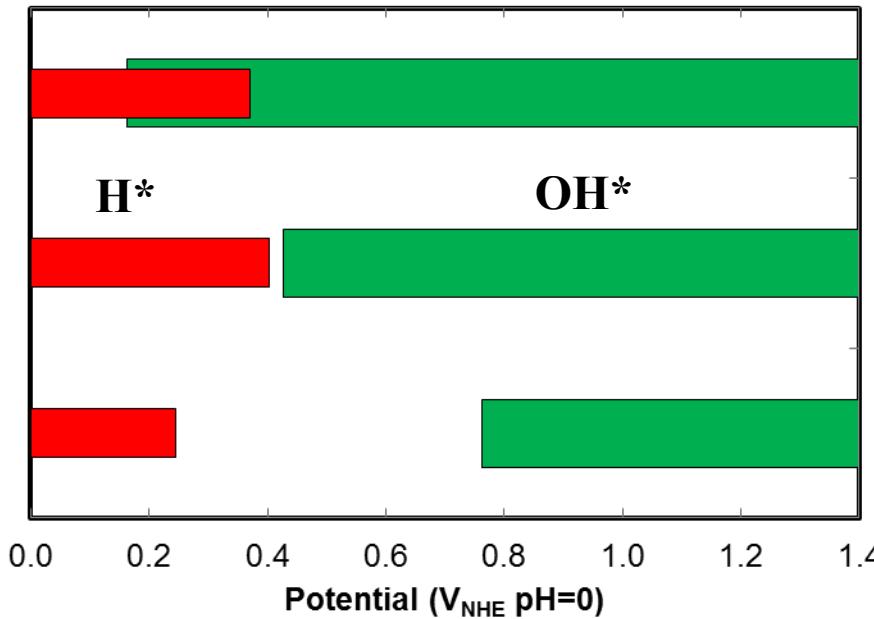
111 coverage dependence explains broader peak

Simulation – 111 desorption before 110 and 100

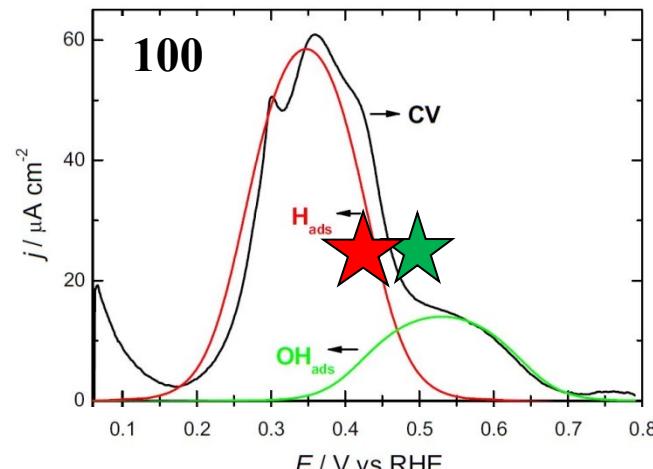
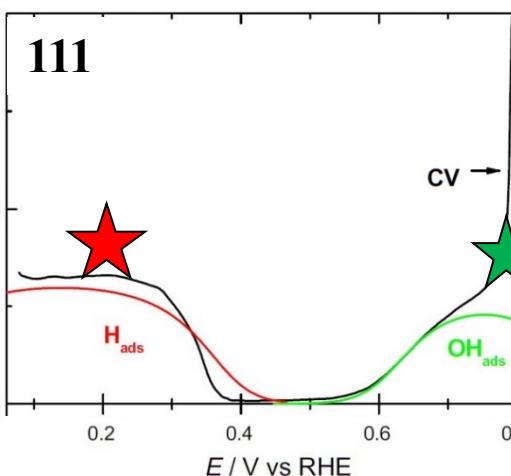
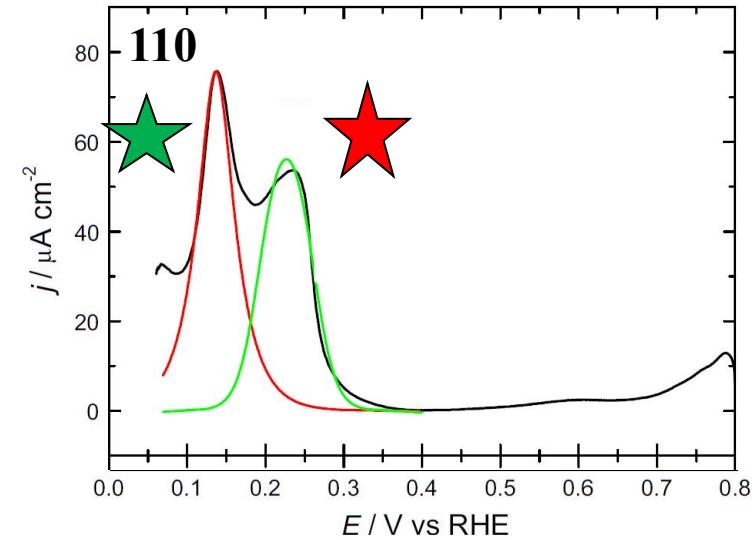
Experiment – 110 and 111 before 100



Pt(110) and Pt(100) peaks represent an H* to OH* exchange reaction



110
100
111

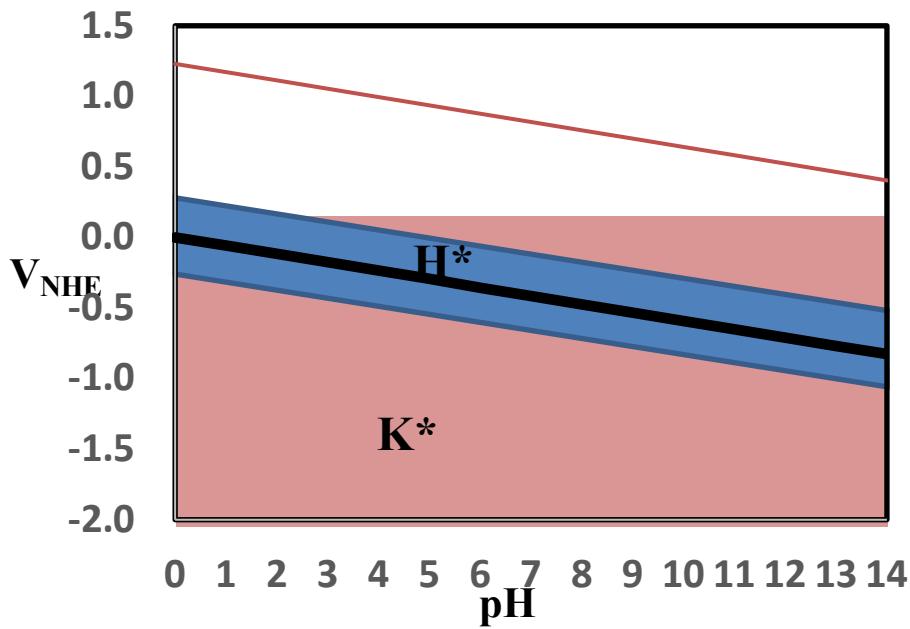
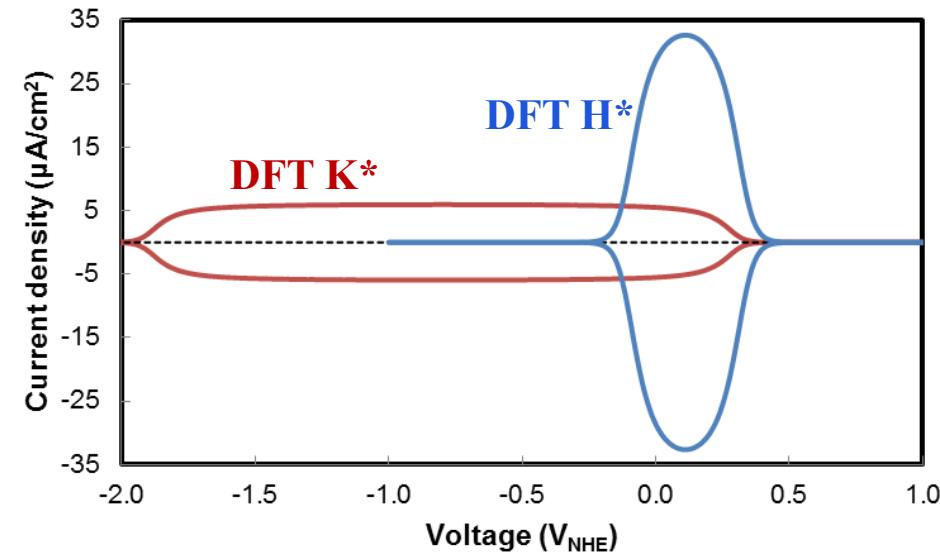


110 and 100 peaks involve exchange reaction



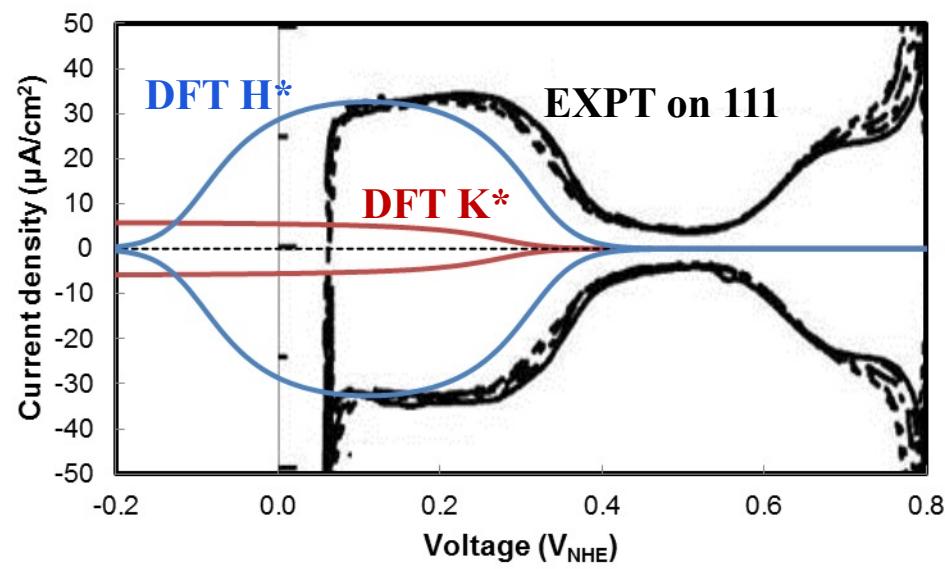
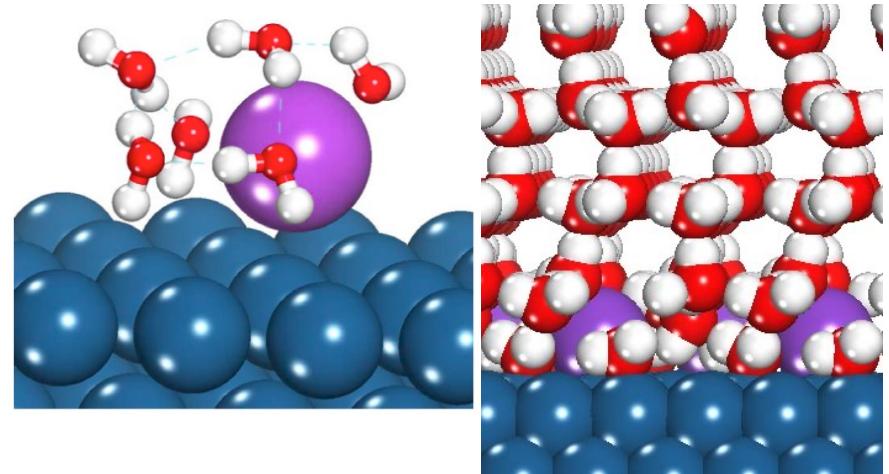
Pushes 110 peak to left, agrees with experimental peak order

K* specific adsorption at low coverage occurs in H* potential range

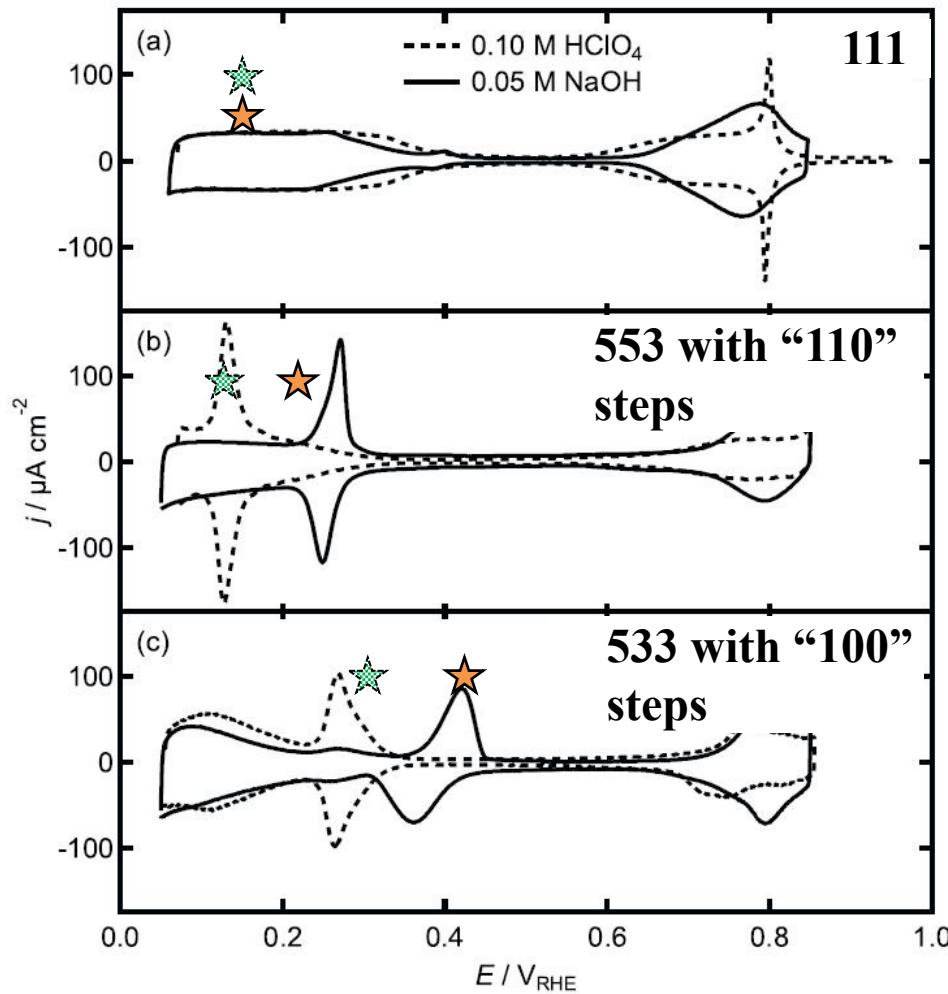
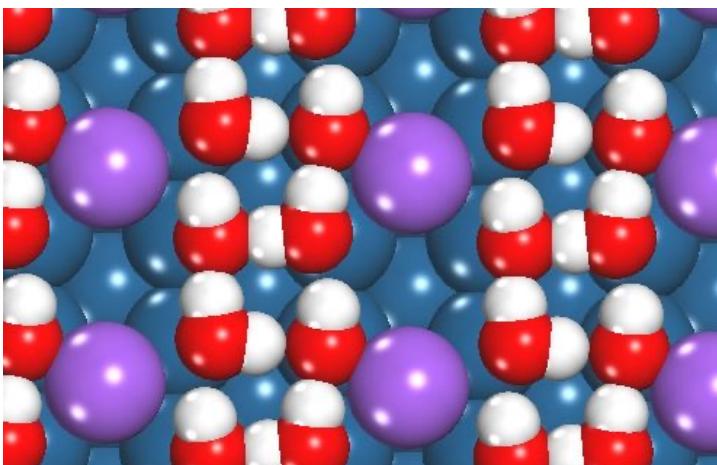
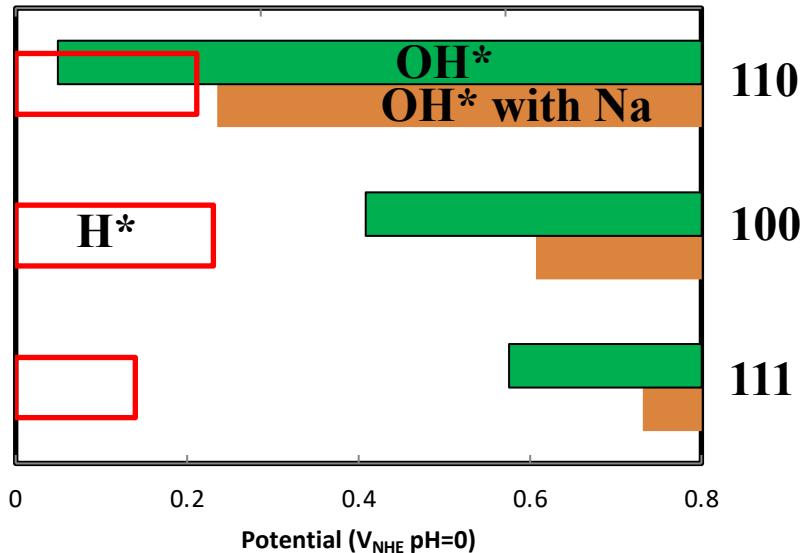


K* adsorption on Pt(111)

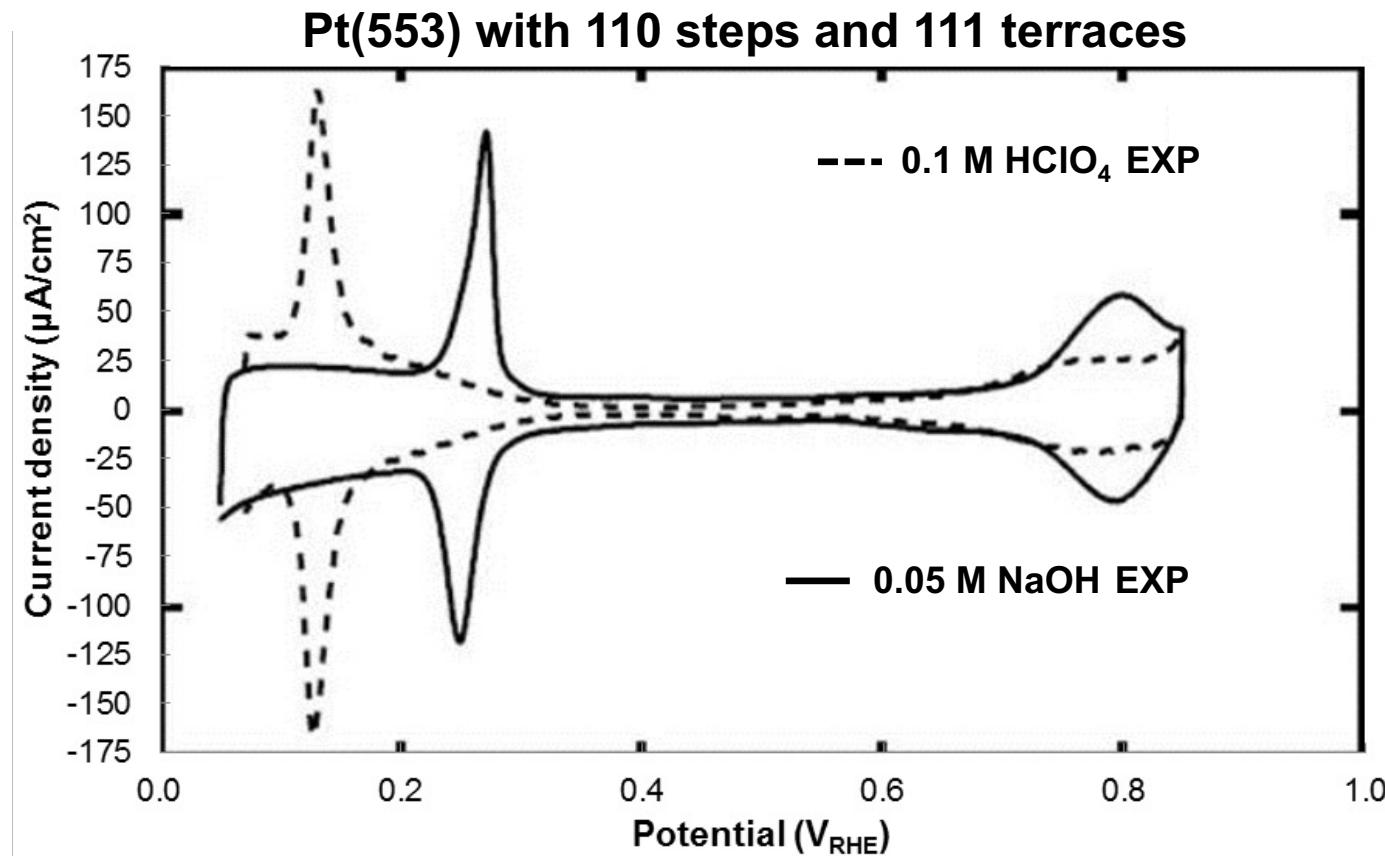
- extreme coverage dependence
- ~ large surface dipole ($-1.06 \text{ e}^- \text{ \AA}$)



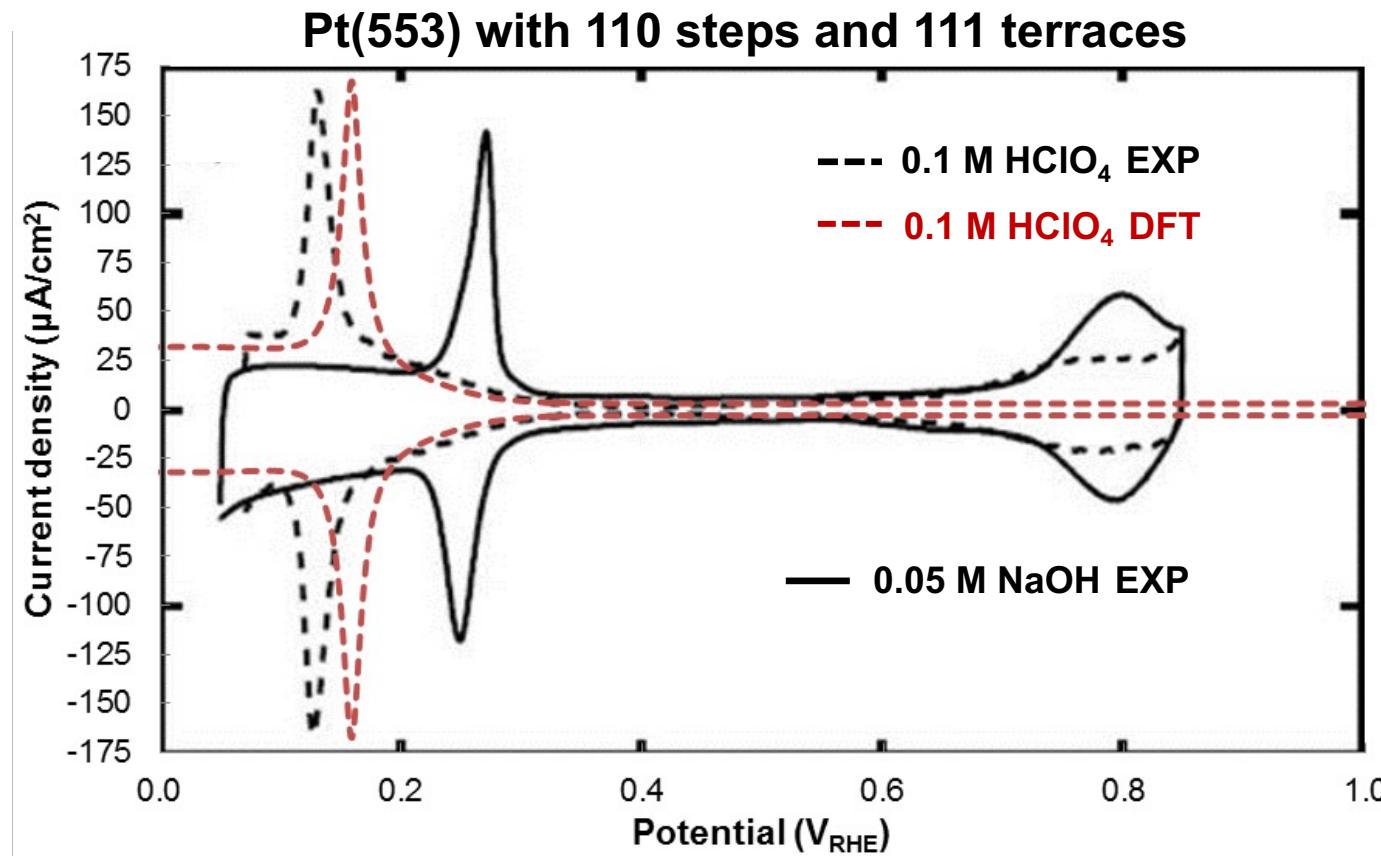
Experiment – 110 and 100 peaks shift right in base DFT – alkali “steals the solvation shell” making OH* adsorption less favorable



H^* on the terrace and $H^*/(OH^*+H_2O^*)$ on the step simulated CV's match experiment



H^* on the terrace and $H^*/(OH^*+H_2O^*)$ on the step simulated CV's match experiment



H^* on the terrace and $H^*/(OH^*+H_2O^*)$ on the step simulated CV's match experiment

