

Computational heterogeneous electrocatalysis: How does it work and which questions can be answered at which cost?

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Computational heterogeneous electrocatalysis: How does it work and which questions can be answered at which cost?

Stephan N. STEINMANN

Research interests

Reactivity at (electrified) interfaces

Surface state: Fang, Ding, Zhang, Steinmann, Hu, Mao, Feliu, Tian *J. Am. Chem. Soc*. **2020**, *142*, 9439. **OER:** Curutchet, Colinet, Michel, Steinmann, Le Bahers. *Phys Chem Chem Phys* **2020**, *22*, 7031. **HER:** Abidi, Bonduelle, Steinmann *ACS Appl Mater Interfaces* **2020**, *12*, 31401.

Solid-state

g-CN: Li, Melissen, Le Bahers, Sautet, Masters, Steinmann, Maschmeyer, *Chem. Mater.* **2018**, *30*, 4253. **MoS3:** Sahu, Steinmann, Raybaud, *Cryst. Growth Des.* **2020**, 20, 7750. **MnO2:** Manceau, Steinmann, *ACS Earth Space Chem.* **2023***, 7,* 1459*.*

Method development for solid/liquid interface

Force fields: Clabaut, Beisert, Michel, Steinmann *J Chem. Phys.* **2022***, 157,* 194705*.* **Solvation energy:** Clabaut, Schweitzer, Goetz, Michel, Steinmann *J Chem Theory Comput*. **2020**, 1*6*, 6539. **Electrostatic embedding:** Abidi, Steinmann, *ACS Appl Mater Interfaces* **2023**, *15*, 25009.

Esparza et al., *Revista Matéria*, **2008**, *13*, 579. Steinmann, Seh, *Nature Reviews Materials*, **2021**, *6*, 289.

How do noble metal electrocatalysts look like?

Figure 1: A typical TEM image of the Pt nanoparticles with size distribution histogram.

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Electrified Interface Solution

Abidi, Lim, Seh, Steinmann *WIREs Comput Mol Sci* **2020**, e1499.

Atomistic models for electrocatalysis?

Models in practice

Large nanoparticles

→ Periodic surface model

Solvent

None

Implicit

QM/MM

Electrochemical potential

Implicit: CHE

Explicit: GC-DFT

Grand-Canonical DFT

Mathew, Kolluru, Mula, Steinmann, Hennig, *J. Chem. Phys.* 2019, 151, 234101.

Mathew, Kolluru, Mula, Steinmann, Hennig, *J. Chem. Phys.* 2019, 151, 234101. Abidi, Lim, Seh, Steinmann *WIREs Comput Mol Sci* **2020**, e1499.

Grand-Potential Ω : The energy of GC-DFT

 $\Omega(U) = E(q) - U \times q$ U: potential q: charge E(q): Electronic energy at charge q

Poisson-Boltzmann Equation neuralizes q **Implicit solvent + Electrolyte**

Grand-Canonical DFT

Mathew, Kolluru, Mula, Steinmann, Hennig, *J. Chem. Phys.* 2019, 151, 234101.

Mathew, Kolluru, Mula, Steinmann, Hennig, *J. Chem. Phys.* 2019, 151, 234101. Abidi, Lim, Seh, Steinmann *WIREs Comput Mol Sci* **2020**, e1499.

> Grand-Potential Ω : The energy of GC-DFT

 $\Omega(U) = E(q) - U \times q$ U: potential q: charge E(q): Electronic energy at charge q
 $\frac{4}{0.6}$

Poisson-Boltzmann Equation neuralizes q
 Condutor: A Single parabola Condutor: A Single parabola **Implicit solvent + Electrolyte**

Semi-condutor: A piece-wise parabola

Abidi, Lim, Seh, Steinmann WIREs Comput Mol Sci 2021, 11, e1499.
Curutchet, Colinet, Michel, Steinmann, Le Bahers. Phys Chem Chem Phys 2020, 22, 7031.

Grand-Canonical DFT in practice

The impact of electrode polarization is system dependent

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 $H_2O@Pt(111)$

How to model the water/metal interface?

Diffusion at interfaces is slow: ~500 ps for equilibration

DFT for metals is costly ~140 kCPUh for 10 ps, est. 8 years for 500 ps

Interaction is neither weak nor strong Problem for force fields

Interfaces are amorphous: Large cells required

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Aromatics at Pt(111)/water interface

→ Semi-quantitative agreement between theory and experiment

Données expérimentales de Singh, Campbell *ACS Catal*. **2019**, *9*. 8116.

Abidi, Steinmann *Curr. Opin. Electrochem*. **2022**, *33*, 100940.

What about kinetics? Transition states in electrocatalysis

Transition states determine the kinetics of reactions

The number of atoms needs to be conserved from the reactant to the product

Chemical steps: $H^* + CO_2^*$ $\longrightarrow HCOO^*$ \longrightarrow "standard" Electrochemical steps: $H^+ + e^- + CO_2^*$ \rightarrow HCOO* \rightarrow non-standard

Transition states in electrocatalysis

(Electro-)chemical transition states

Transition states determine the kinetics of reactions

Most computational work in electrocatalysis ignore transition states

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Abidi, Steinmann *Curr. Opin. Electrochem*. **2022**, *33*, 100940.

Chemical steps Transition states in electrocatalysis

Abidi, Steinmann *Curr. Opin. Electrochem*. **2022**, *33*, 100940.

Reaction Coordinate

Standard techniques in heterogeneous catalysis

2 weeks to 1 month of real time*

*not 100% of human time

Electrochemical steps Transition states in electrocatalysis

Difficult to identify

1-3 month of real time*

Abidi, Steinmann *Curr. Opin. Electrochem*. **2022**, *33*, 100940.

Reaction Coordinate

*not 100% of human time

Electrochemical steps Transition states in electrocatalysis Abidi, Steinmann *Curr. Opin. Electrochem*. **2022**, *33*, 100940.

lateProduct-like Product-like **Product** Electrolyte 0 **concerted** Reactant-like Reactant-like **early Reactant TS**

Nuclear Reaction Coordinate

Reorganisation of:

- Solvent
- Adsorbate@surface
	- **→ Marcus theory?**
	- **→ Active research**

solution-like TS

Reaction Coordinate

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Transition states in electrocatalysis Goodpaster, Bell, Head-Gordon *J. Phys. Chem. Lett.* 2016, 7, 1471.

Oddly behaving transition states can be found

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HER mechanism on V_s defect

HER over $MoS₂$

Slope: Symmetry factor from GC-DFT

Chemical (Tafel) step Electrochemical (Volmer) step

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Importance of the surface state

EPOC: $CH₄$ activation over Pt

Accelerating CH4 oxidation over Pt via an electrochemical potential

Effective activation energy Surface state as a function of T and U

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Partial take home message

Periodic surface models are most convenient

The effect of the electrochemical potential can be modeled with GC-DFT

Implicit solvents are very practical but have limitations

TS: rarely considered and painful to identify for electrochemical steps

The surface state changes dramatically as a function of the potential

1. Sulfate on Au(111)

2. HER on MoS₂: Screening of dopants

3. Structural complexity

4. Reaction pathways

Fang, Ding, Zhang, Steinmann, Hu, Mao, Feliu, Tian *J. Am. Chem. Soc.* 2020, 142, 9439.
 SO₄ @Au(111)

The gold sulfuric acid interface is prototypical

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Indication of a phase transition \rightarrow What is the structure?

Fang, Ding, Zhang, Steinmann, Hu, Mao, Feliu, Tian *J. Am. Chem. Soc.* 2020, 142, 9439.
 SO₄ @Au(111)

Experimental characterization of ordered phase

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Characterization can barely be better **→ But still, what is the atomic structure of this phase??**

Computational identification of ordered phase

At positive potentials a very ordered water/ SO_4 addlayer becomes most stable

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Fang, Ding, Zhang, Steinmann, Hu, Mao, Feliu, Tian *J. Am. Chem. Soc.* 2020, 142, 9439.
 SO₄ @Au(111)

Experiment and computations agree!

EC-Raman (SHINERS)

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 $SO_4 \cdots W_2$ * **STM** $1.06V$

Partial take home message

Microscopy and spectroscopy for electrified interfaces are challenging

When available: Interpretation not always obvious

Computations can "convert" signals into atomic structures

→ More insights for (electro-)chemists

1. Sulfate on Au(111)

2. HER on MoS₂: Screening of dopants

3. Structural complexity

4. Reaction pathways

MoS₂ as an Hydrogen Evolution Reaction Catalyst Hydrogen evolution reaction on MoS₂ Hinnemann, et al. *J. Am. Chem. Soc*. **2005**, *127*, 5308. Benck et al., *ACS Catal*. **2014**, *4*, 3957. *DK-2800 Lyngby, Denmark* find alternatives to the Pt group metals. the hydrogen evolution process3,4 even though the catalytically active site of the much less noble \mathcal{L} Fe, Ni, and Mo. Recently it has become possible to anchor $n_{\rm U}$ uda genas d proposition on $M \circ C$ free energy of the same as that \sim \mathcal{L} atoms bound to different catalogues bound to different catalogues is then \mathcal{L} found by calculating the free energy with respect to molecular hydrogen Lindranan Lualihar elemental metals is taken from ref 7. The results for hydrogenase are from ref 11. The included result for MoS2 is the free energy required to increase

 M_{\odot} Ω is an a of the speak le free energy of the same NIOS_2 is one of the dest io conditions. The free energy of H atoms bound to different catalysts is then to different catalysts is then then then the following the conditions in the following catalysts is the following catalysts in the conditions of t found by calculating the free energy with respect to molecular hydrogenergy with \sim including zero-point energies and energies and energies and energies and energies and different of different $\mathbf{h} \mathbf{h} \cdot \mathbf{C}$ catalyst, one can compare different metal surfaces as catalysts. For a chemical process to proceed at or around room temperature, no reaction step can be associated with large changes in the free energy. This immediately excludes the metals that form strong bonds to explain available experimental observations regarding metals as MoS_2 is one of the best low-cost HER catalysts in acidic conditions It is interesting the same analysis to apply the same analysis to the active sites in $\mathcal{L}_\mathcal{S}$ \blacksquare nitrogenases and hydrogenases. For \blacksquare the model of the active site, the FeMo cofactor (FeMoco) shown $a_n = \frac{1}{2}$ standard conditions, which corresponds to a thermodynamic to a thermodynamic $\frac{1}{2}$ P a more of the best", but not a good one ers have performed computational studies of $\mathsf{D}\mathsf{H}\mathsf{H}\mathsf{H}\mathsf{H}\mathsf{H}$ $t_{\rm eff}$ allow us to calculate the atomic use of α Our findings suggest that we can begin searching for new catalytic materials using quantum chemical methods. The MoS2 nanoparticles supported on graphite may be an example of a new not a good c **Acknowledgment.** M. Brorson is gratefully thanked for provid-(Right) STM images of MoS2 nanoparticles on modified graphite.

atomic hydrogen (Ni and Mo in Figure 1) as good catalysts because

 $t = -t$ step will be the thermodynamically uphill be the thermodynamically uphill be the thermodynamical values of \mathcal{L}

the hydrogen coverage from 25 to 50%; see Figure 2.50%; see

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Received January 24, 2005; E-mail: norskov@fysik.dtu.dk

has been made in the synthesis of compounds in solution resembling

Hydrogen Evolution Reaction on $MoS₂$

Abidi, Bonduelle, Steinmann, *Electrochim. Acta* **2023**, *439*, 141653*.*

Can We Activate the Basal Plane?

Mo: Element to substitute Element: Better stabilized on Mo-edge **Element:** Better stabilized on S-edge Edge substitution strongly preferred Basal plane substitution possible

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Doping stability is one of the key issues

Hydrogen Evolution Reaction on $MoS₂$

Abidi, Bonduelle, Steinmann, *Electrochim. Acta* **2023**, *439*, 141653*.*

Can We Activate the Basal Plane?

At -0.2 V vs SHE:

few dopants create active sites:

Mo/P via $OH/H₂O$ cycling Ti₂/S, Hf₂/S and $Zr₂/S$ via Volmer-Heyrovsky

> **~1 year**
12 de **PhD**

Partial take home message

Material screening

Computers are patient and non-intelligent

Strong and necessary assumptions limit the scope

Do not forget about stability

➙Computationally expensive and not always that useful

1. Sulfate on Au(111)

2. HER on MoS₂: Screening of dopants

3. Structural complexity

4. Reaction pathways

Alloy Re-Organization under Reactive Conditions

In-plane Island formation

 $C_2H_2@Ag_xPd_{1-x}(111)$

Random

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Ordered

Vertical Segregation

Vignola, Steinmann, Le Mapihan, Vandegehuchte, Curulla, Sautet, *J. Phys. Chem. C* **2018**, 122, 15456.

(111) surface; 5 parameters; *R*² = 0.756 (111) surface; 12 parameters; *R*² = 0.861

 Ω

0.5

CE Energy/eV

CE Energy/eV

1

1.5

Cluster expansion of alloy arrangement $C_2H_2@Ag_xPd_{1-x}(111)$

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Refined model: quantitative improvement, but same trends

226 DFT configurations bare alloy 150 configurations with 1 C_2H_2 52 configurations with 2 C_2H_2

0 0.5 1 1.5

DFT Energy/eV

Typical Configuration of Ag_{0.76}Pd_{0.24} @ 1 bar of C₂H₂ Dense packing: Lateral Interaction are key

Pd: Covered with C₂H₂ Ag: Acts as spacer

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 $C_2H_2@Ag_xPd_{1-x}(111)$

Vignola, Steinmann, Le Mapihan, Vandegehuchte, Curulla, Sautet, *J. Phys. Chem. C* **2018**, 122, 15456.

Typical Configuration of Ag_{0.76}Pd_{0.24} @ 1 bar of C₂H₂ Dense packing: Lateral Interaction are key **~1 year**
hp

Pd: Covered with C₂H₂ Ag: Acts as spacer

PhD

 $C_2H_2\omega$ Ag_xPd_{1-x}(111)

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Increasing the Number of Edge Sites?

Highly dispersed, amorphous $MoS₂ - or - MoS₃$ has many edge-sites

Amorphous, building block look like:

Wu, Longo, Dzade, Sharma, Hendrix, Bol, De Leeuw, **EN-Mose Films corrected by unconstructed resistance with scan rates of the Hensen, Hofmann,** *ChemSusChem* **2019,** *12***, 4383.**

Sahu, Steinmann, Raybaud, *Cryst. Growth Des. 2020, 20,* 7750*.*

36 **The CV and 5 mV statel slopes of CV and 5 mV statel slopes of CV** curves in (b). The contract of \mathbf{r} . The contract of \mathbf{r} . Hydrogen Evolution Reaction on $MoS₃$

Abidi, Sahu, Raybaud, Steinmann, *ACS Catalysis* **2023**, *13*, 15290*.*

How Stable is MoS₃ under HER Conditions?

Figure 2: GC-DFT reaction energy profile on Mo3S⁹ at 0 V vs SHE. The first two steps α corresponding to the next four four four steps and α are hydrogen and α Desorption of at least 1 H₂S is easy, even at 0 V vs SHE, pH 0

Adhikari, Steinmann, Arunachalam, Kang, Kim *Small* **2024**, *20*, 2311548.

OER on hybrid material

Hybrid material for oxidation of water and urea

Ni foam is not very active $Ni₃S₂$ (NS3) overlayer \longrightarrow Small improvement manganese cobalt oxide (MCO) overlayer \rightarrow improvement Covering MCO with Ni_3S_2 \longrightarrow even better, but why?

-
-
-

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OER on hybrid material

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Reaction energy profile of OER

Conductivity and active surface area explain high experimental performance

OER on hybrid material

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Adhikari, Steinmann, Arunachalam, Kang, Kim *Small* **2024**, *20*, 2311548.

120 kCRUh ~5000 €

Reaction energy profile of OER

Conductivity and active surface area explain high experimental performance

Partial take home message

Structural complexity

Each system is different

Models, scope and confidence vary a lot

Amorphous structures are the worst for computational (electro-)chemists

Computations do not always lead to the expected insight

1. Sulfate on Au(111)

2. HER on MoS₂: Screening of dopants

3. Structural complexity

4. Reaction pathways

Revisited mechanism for alkaline OER with GC-DFT

Considering barriers and overpotentials, mechanism III is likely

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Revisited mechanism for alkaline OER with GC-DFT

HER over $MoS₂$

HER mechanism on V_S defect

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Activation energies from Grand-Canonical DFT

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HER over $MoS₂$

Activation energies from Grand-Canonical DFT

HER over $MoS₂$

Partial take home message

Reaction pathways

Time consuming

Detailed insight, sometimes hard to (in-)validate by experiments

Activation energies are necessary for detailed mechanisms

Symmetry factors can be computed - but with which precision?

Delicate competition between "chemical" vs "electrochemical" reactions **→ Can be addressed by GC-DFT**

Amorphous or ill-characterized materials \rightarrow Structural complexity = major bottleneck

In many cases computational studies are neither cheap nor fast

→ Developments are necessary for modelling solid/liquid interfaces

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Collaborators

Elena Baranova Zhi Wei Seh Andreas Goetz

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Vignola, Steinmann, Le Mapihan, Vandegehuchte, Curulla, Sautet, *J. Phys. Chem. C* **2018**, 122, 15456.

Cluster Expansion of Adsorption Energy

Refined model:

 $C_2H_2\omega$ Ag_xPd_{1-x}(111)

150 DFT configurations

Spreads between ensembles is important for Pd_2Ag and Pd_3 **DE CHIMIE**

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Cluster Expansion of Lateral Interaction Energy $C_2H_2@Ag_xPd_{1-x}(111)$ Vignola, Steinmann, Le Mapihan, Vandegehuchte, Curulla, Sautet, *J. Phys. Chem. C* **2018**, 122, 15456.

52 DFT configurations

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