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Highlights

- In electrocatalysis, complex nonlinear and non-monotonic coupling arises in the boundary region between metal and electrolyte
- A recent theoretical framework demonstrates how to handle this coupling
- Approaches in first-principles electrochemical modeling need to be modified to consistently treat nonlinear and non-monotonic charging effects

Approaching the Self-Consistency Challenge of Electrocatalysis with Theory and Computation

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Abstract

This opinion piece centers around challenges involved in developing first-principles electrochemical methods. In recent years, theory and computation have become quintessential tools to navigate the parameter space that controls the activity and stability of electrocatalytic materials and electrochemical devices. Viable methods process as input details on materials structure, composition and reaction conditions. Their output includes metrics for stability and activity, phase diagrams, as well as mechanistic insights on reaction mechanisms and pathways. The core challenge, connecting input to output, is a self-consistency problem that couples the electrode potential to variables for the electronic structure of the solid electrode, solvent properties and ion distributions in the electrolyte as well as specific properties of a boundary region in between. We will discuss a theoretical framework and computational approaches that strive to accomplish this feat.

Keywords: theoretical electrocatalysis, electric double layer, metal charging relation, continuum solvation models, first-principles electrochemistry, electronic density functional theory

1. Introduction

Electrocatalysis is becoming for electrochemical energy technology what semiconductor physics has long been for computer technology: the fundamental discipline to bring forth advances in cost reduction, power performance, durability and lifetime, while submitting to requirements in terms of

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6 safety and materials abundance [1, 2]. Contributions and impact in the field
7 of electrocatalysis exhibit exponential growth, with efforts headed towards
8 new materials and fabrication approaches for next generation electrochemi-
9 cal systems in energy harvesting, water treatment, production of fuels and
10 chemicals, materials processing and biosensing.

11 In addition to maintaining a justified focus on precious metal-based elec-
12 trocatalysts such as Pt and Pt-based alloys [3, 4, 5], escalating efforts strive
13 to harness unusual and opaque properties of transition metal oxides [6, 7], ni-
14 trides [8, 9], phosphides [10, 11, 12, 13, 14], and chalcogenides [15, 16, 17], as
15 well as 2D electronic materials [18, 19] and macromolecular precious metal-
16 free electrocatalysts [20, 21].

17 Finding the best materials for emerging energy, water or sensor technolo-
18 gies demands scientific strategies that (i) utilize materials selection criteria
19 based on a small set of performance and stability descriptors [3, 22, 23],
20 (ii) employ efficient tools to navigate a complex parameter space, and (iii)
21 implement smart approaches in electrode design and fabrication based on
22 knowledge of reaction mechanisms, pathways and conditions.

23 Materials fabrication and characterization increasingly look out to theory
24 and computation for guidance. Theoretical and computational electrocataly-
25 sis strives to relate atomic structure, composition, and electronic structure of
26 electrocatalytic materials to measurable performance and stability descrip-
27 tors, as illustrated in Figure 1. However, to become more than tools for
28 materials screening and comparative analyses, theory and computation must
29 be physically consistent and accurate; utilize a reasonably complex (adap-
30 tive) representation of the real electrochemical interface with a minimal set
31 of assumptions; and provide fundamental mechanistic insight and predictive
32 capabilities.

33 The electrified electrochemical interface as the archetypal electrochemi-
34 cal system is usually a substructure of a porous composite electrode in an
35 electrochemical device, where the interplay of transport and reaction deter-
36 mines distributions of reaction conditions and rates. Well-established models
37 describe the operation of such electrodes [24]. Focusing on theory and mod-
38 eling of the interface itself, the main challenges are to understand how the
39 nature and structure of electrode material, electrolyte and boundary region
40 in-between impact the energetics and dynamics of adsorption and charge
41 transfer processes; how impurities or adsorbed intermediates affect pathways
42 of multistep reactions and reactivity [25]; and how solvent species and ions
43 modulate interfacial properties and reaction conditions [26].

44 Theoretical electrocatalysis is closely interwoven with the quintessential
 45 theories of electrified interfaces [27] and charge transfer [28, 29, 30] and it
 46 draws upon inventories of condensed matter physics, surface science, het-
 47 erogeneous catalysis, and chemical kinetics. Modern developments in this
 48 multidisciplinary field circulate under the label *first-principles electrochem-*
 49 *istry* (FPEC) [31, 32] or alike [33].

50 Computational approaches finding a growing community of users include
 51 the so-called *computational hydrogen electrode* (CHE) based on standard-type
 52 electronic DFT, the *generalized CHE* (GCHE) that employs nonequilibrium
 53 Green's functions and electronic DFT (NEGF+DFT) [34], or implementa-
 54 tions that combine electronic DFT for the electrode region with continuum
 55 mean field theories or classical DFT for the electrolyte region, like JDFTx [35]
 56 or VASPsol [36].

57 "[Figure 1 should be placed here. The basic program for theoretical
 58 electrocatalysis.]"

59 2. Challenges and approaches

60 Figure 2 epitomizes the litmus test and potential pitfall for approaches in
 61 theoretical and computational electrocatalysis. Extracted from a paper pub-
 62 lished in the mid 1970s by Frumkin and Petrii [37], it shows surface excesses
 63 of sodium cations and sulfonate anions near a Pt electrode as a function of
 64 the metal phase potential, ϕ^M . It thus portrays, more or less explicitly, the
 65 metal charging relation, $\sigma^M = f(\phi^M)$, as "seen" by free ions in solution. This
 66 nonlinear and non-monotonic charging relation demonstrates that in general
 67 the effective metal surface charge, and all dependent properties, cannot be
 68 deduced by linear extrapolation from the potential of zero charge with the
 69 double layer capacitance as a proportionality constant.

70 Recent experiments [38, 39, 40] attributed the observations in Figure 2 to
 71 charge polarization effects caused by formation of a (sub-)monolayer oxygen
 72 adatoms at the surface. Existing FPEC approaches fail to reproduce this
 73 charging relation since they have a linear extrapolation of σ^M as function
 74 of ϕ^M built into them or miss certain aspects of the nonlinear coupling of
 75 components and properties that define the interfacial region.

76 "[Figure 2 should be placed here. Frumkin.]"

77 Figure 3 illustrates schematically the typical modeling domain and the
 78 fundamental theoretical challenge. The Galvani potential, ϕ^M , in the bulk
 79 of the metal phase (at point A) is specified relative to a reference Galvani

80 potential in the bulk electrolyte phase (at point B), ϕ^S , with A and B lo-
81 cated far away from the interfacial region. The solution phase potential thus
82 establishes a reference for the potential scale, which can be fixed as $\phi^S = 0$,
83 without having to invoke a thermodynamic construction that is strictly valid
84 only at a certain equilibrium condition of the interfacial system, as is the
85 case for the CHE. Complete solution of the interface problem must fulfill
86 two essential conditions: (1) it must generate a continuous potential profile
87 between A and B; (2) it must account self-consistently for the coupling of
88 relevant variables that define the properties of different interface regions *en*
89 *route* from A to B.

90 Figure 3 resolves the different components of the interfacial system, in-
91 cluding electrode material, chemisorbed surface species, a structured region
92 of interfacial solvent molecules, and a diffuse electrolyte region extending
93 towards the bulk. The coupled variables in the system include the electro-
94 chemical potential of electrons in the electrode, the electrode surface state
95 represented by the surface atom configuration and chemisorbed species, an or-
96 der parameter for the preferential orientation of interfacial solvent molecules,
97 solvent dielectric or polarization properties, and the ion density in the elec-
98 trolyte. The main function to solve for is the electrostatic potential profile
99 along the path from A to B, as a function of ϕ^M and pH (and ion concentra-
100 tions) in the bulk electrolyte.

101 For the electrode region, Kohn-Sham DFT (KS-DFT) at the level of the
102 generalized gradient approximation (GGA) is used to calculate ground state
103 electronic densities, energy contributions and forces [41]. Systems with on-
104 site Coulomb interaction of strongly localized electrons (typically, d- or f-
105 electrons) require addition of a Hubbard-like interaction term [42]. Inter-
106 action parameters for this DFT+U approach [43] are obtained from linear
107 response theory [44]. This correction is required for calculating the properties
108 of transition metal oxides [45]. Needs and challenges involved in extending
109 DFT approaches towards treatment of electron dispersion interactions were
110 discussed in Ref. [46]. The accuracy of various dispersion-corrected DFT func-
111 tionals was assessed in Ref. [47, 48] for the Pt-water system.

112 The electrolyte region, consisting of solvent molecules and ions, deter-
113 mines the system's capacity to store charge at the electrochemical interface.
114 The size of the electrolyte region relevant for electrochemical studies de-
115 pends on the Debye length. This length could lie in the range of 10 nm
116 or more, rendering a quantum mechanical treatment infeasible. Theoretic-
117 al approaches to describe this region must deal with solvent polarization,

118 steric effects and Coulomb interactions. Due to reactive events and ther-
119 mal effects, the electrolyte region reorganizes dynamically. Thermodynamic
120 sampling of electrolyte configurations is thus needed for the calculation of
121 thermodynamic averages. This statistical sampling can be done using contin-
122 uum solvation models (CSM), surveyed in Refs. [49, 50], in conjunction with
123 mean field approaches like Poisson-Boltzmann (PB) or modified Poisson-
124 Boltzmann (MPB) theory [51, 52, 53]. An alternative to continuum theories
125 is the rigorous classical density functional theory of liquids [54]; it calculates
126 thermodynamic functions by variational free energy minimization, render-
127 ing it computationally more efficient than molecular dynamics simulations.
128 As for the latter, there are currently no reports on explicit simulations of
129 electrochemical interfaces based on QM/MM, as are widely popular in other
130 fields [55].

131 Combination of electronic structure calculations for the electrode region
132 with different treatment of the solvent region results in three main classes
133 of FPEC approaches, which are (i) the computational hydrogen electrode
134 (CHE) of Nørskov, Rossmeisl and others [56, 57, 58], (ii) a standard ap-
135 proach (DFT-CSM/MPB) that combines electronic DFT with mean field
136 theories for the electrolyte region, pioneered by Otani and Sugino [59] and
137 developed further by Jinnouchi and Anderson [49] as well as Dabo, Bon-
138 net and Marzari [60], and (iii) joint density functional theory (JDFT) that
139 combines electronic and classical DFT for the respective regions [35, 61].

140 All of these approaches and their numerous derivatives (too many to
141 cite) are heavily preoccupied with two crucial questions: how to fix a po-
142 tential scale and how to maintain electroneutrality in the system? As for
143 the first point, in principle, this must be done by adding or deleting a suffi-
144 cient number of electrons to the system - meaning that electrons are treated
145 grand-canonically, as proposed originally by Lozovoi et al. [62] - to tune the
146 electrochemical potential of electrons to a desired value [63]. Next, in order
147 to maintain electroneutrality countercharge must be added. This has been
148 done in different ways. In the CHE protons and electrons are added pairwise;
149 this incurs a problem of an unphysical discreteness of charge amounts that
150 could be addressed by increasing and extrapolating cell size. Lozovoi and
151 Alavi employed a Gaussian charge sheet to add counter charge [64], whereas
152 Taylor *et al.* added a uniform charge background [65].

153 These *ad hoc* approaches to the charging problem encountered the diffi-
154 culty of adjusting to the correct value of the electric field at the interface.
155 Otani and Sugino [59] tried to overcome this problem by combining KS-DFT

156 with MPB theory to calculate distributions of ion density and electric field in
157 the interfacial region. Jinnouchi and Anderson [49] as well as Dabo *et al.* [60]
158 refined this approach by connecting DFT and MPB approaches through a
159 smooth dielectric continuum model for the solvent polarization that had been
160 developed by Fattbert and Gygi [66]. The JDFT approach calculates the
161 ion distribution self-consistently [61].

162 Having deposited a certain number of extra electrons on the metal sur-
163 face and balanced it out with ionic charges on the solvent side, another
164 problem arises: properties of the boundary region will respond to the elec-
165 trode charging conditions, and this response could be highly nonlinear, in-
166 validing simple potential extrapolation schemes and not accounted for in
167 approaches discussed to this point. A shift in ϕ^M and σ^M , will induce changes
168 in the chemical surface configuration. These may involve modification of sur-
169 face electronic states, short range electronic interactions with near surface
170 species, bond formation (chemisorption), or orientational ordering of polar
171 solvent molecules. For instance, in the case of a Pt electrode, a shift to
172 high ϕ^M induces oxygen chemisorption and oxide layer growth [67, 68, 69].
173 For Ni oxyhydroxide under alkaline conditions, deprotonation of the surface
174 occurs [70]. Such changes disturb the interfacial electric field, as seen in pro-
175 nounced work function shifts [71], which cannot be handled by any of the
176 FPEC approaches developed to date.

177 Potential-dependent surface configurations, e.g., involving chemisorbed
178 species formed during reactive events, must be accounted for, necessitating
179 in principle dynamic (or reactive) simulation approaches. Moreover, correct
180 treatment of the properties of interfacial solvent molecules demands exten-
181 sive thermodynamic sampling of configurations of near-surface solvent layers
182 using *ab initio* MD [71, 72]. It turns out that the boundary region is indeed
183 the most complex part of the electrochemical interface and its description
184 is highly specific for particular electrode material, electrolyte composition,
185 environmental conditions and potential regime. Next, we will briefly review
186 a theoretical framework that illustrates the intricacies introduced by this re-
187 gion, to provide a proper basis for discussing current limitations and future
188 needs to be addressed by next-generation FPEC approaches.

189 ”[Figure 3 should be placed here. Interface.]”

190 3. Theoretical framework

191 A theoretical approach to solve the interface problem, depicted in Figure
192 3, was developed in Ref.[73] and refined in Ref.[74]. This mean field ap-
193 proach focuses on interfacial charging effects and it was developed for the Pt-
194 electrolyte interface. It considers the metal as an interface with an effective
195 potential-dependent σ^M and covered by a (sub-)monolayer of chemisorbed
196 oxygen, which is treated with a thermodynamic submodel. A water layer
197 submodel accounts for ordering of water dipoles relative to the surface with
198 an Ising-like two-state approach. PB or MPB theory [51, 52, 53] are used to
199 solve for ion and potential distributions in the electrolyte. The submodels
200 for the different system components are self-consistently coupled resulting
201 in two equations for the variables σ^M and X , where X is the dimensionless
202 adsorption energy of interfacial water molecules.

203 For the Pt-electrolyte system, the oxide layer submodel is the crucial
204 link that connects metal and electrolyte regions. The experimental relation
205 between oxide species coverage and ϕ^M is used to pin the potential scale to
206 an experimentally accessible scale, such as the SHE scale. For other potential
207 ranges and other materials, different experimental relations for the interfacial
208 configuration must be used to pin the potential scale, e.g., the degree of
209 surface deprotonation of Ni oxyhydroxide. Parameters that define the dipolar
210 field generated by the layer of chemisorbed oxygen are calculated with KS-
211 DFT.

212 The fully parameterized model reproduces the non-monotonic charging
213 relation as shown in Figure 2 and predicts a negative capacitance in the
214 high potential region [78]. Moreover, it predicts the impact of pH on the
215 metal charging behaviour [73]. It was applied to rationalize electrochemical
216 processes in a water-filled nanopore with Pt plated walls [75], the particle
217 proximity effect in nanoparticle electrocatalysis [76], and induced charge ef-
218 fects by an ionomer skin layer in catalyst layers of PEM fuel cells [77]. In
219 combination with microkinetic modeling and input of basic boundary layer
220 and reaction parameters from electronic DFT, the model allowed the oxygen
221 reduction reaction to be deciphered and effective electrode parameters to be
222 calculated [78], as explained in Figure 4. The utility of this approach remains
223 to be demonstrated for other materials and conditions.

224 ”[Figure 4 should be placed here. Coupling scheme of theory.]”

225 4. First-principles electrochemistry: status and path ahead

226 How well do current FPEC approaches address the fundamental challenge
227 of electrocatalysis, depicted in Figure 1? What contributions to understand-
228 ing basic electrocatalytic phenomena, deciphering reaction mechanisms, and
229 developing advanced materials can they make? What methodical improve-
230 ments will be needed in the future?

231 The CHE has been the most versatile and successful computational ap-
232 proach to date. It relates the potential scale to a thermodynamic reference
233 and postulates a linear free energy relationship for the electrochemical poten-
234 tial (LFER-EP) of electrons. The CHE enforces a strict coupling of electron
235 and proton transfer [80]. It gets by without explicitly treating solvent and
236 electrolyte phenomena, then again implying that it blinds out the impact
237 of electrode potential on bond strengths, adsorbate formation, and solvent
238 polarization in the boundary layer. Generalizations using thermodynamic ex-
239 trapolation schemes [81] or *ab initio* molecular dynamics for the near-surface
240 solvent region [82] strive to address these shortcomings.

241 The CHE has proven useful in comparative evaluation of mechanisms and
242 pathways of electrocatalytic reactions in fuel cells, batteries, electrolyzers,
243 fuel production and CO₂ reduction. It demonstrated sufficiency of a single
244 descriptor approach, rooted in scaling laws [84], to screen transition metal al-
245 loys for electrocatalytic activity [83] and enabled calculation of surface Pour-
246 baix diagrams [85]. These outcomes are largely owed to the capabilities of
247 KS-DFT to accurately reproduce electronic properties of metals.

248 The CHE approach does not pretend to mimic structure and properties
249 of real electrochemical interfaces. Strictly speaking it is not an FPEC ap-
250 proach. In principle, FPEC approaches like DFT-CM/MPB or JDFT should
251 provide equal capabilities as the CHE in comparative materials evaluation,
252 analyses of reaction mechanisms and pathways, and determination of phase
253 equilibria, since they rely on electronic DFT as well. However, these complex
254 FPEC approaches strive to establish a potential reference self-consistently,
255 which as yet cannot be achieved with sufficient accuracy. Not employing a
256 fixed reference frame for the potential, the potential scale will experience an
257 uncontrollable drift caused by electric field effects in the boundary region,
258 which are structure sensitive and highly non-linear. If the FPEC approach
259 does not adequately project the configuration of the boundary region, it will
260 fail at reproducing the correct double layer properties. Recent works sug-
261 gest that FPEC approaches capture the capacitive response of the interface

262 only close to the potential of zero charge and even there the agreement is
263 qualitative at best [86].

264 Consistent treatment of the boundary region in Figure 3 transpires as
265 the crucial challenge of computational approaches. Consequently, none of
266 the existing approaches reproduces the non-monotonic relation in Figure 2.
267 JDFT, which relies on the formulation of a free energy functional for the elec-
268 trochemical interface, offers the best prospects for addressing this challenge.
269 The approach must be extended with functionals for the boundary region to
270 account for specific surface states and local solvent polarization effects. The
271 theoretical framework discussed in the previous section should provide guid-
272 ance in this regard. It suggests that (at least) two additional field-dependent
273 variables must be considered in variational free energy minimization: a vari-
274 able for the surface configuration of the catalyst and a variable for the order-
275 ing of near-surface solvent molecules. These functionals could be determined
276 self-consistently, demanding dynamic or reactive versions of JDFT, or they
277 must be parameterized empirically using experimental data.

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285 **Figure Captions**

Figure 1: General schematic outline for theoretical-computational methodologies in electrocatalysis. The central challenge is to solve a self-consistency problem for pre-set electrode potential and electrolyte composition (represented symbolically by the pH). Other macroscopic operating parameters and external conditions must be controlled as well. The problem involves a non-linear coupling of phenomena in three regions, viz. electrode region, electrolyte region and a boundary region in-between.

Figure 2: “Free” metal surface charge density at a Pt electrode vs. electrode potential, as seen by ions in electrolyte solution. (a) shows surface excesses of sodium and sulfate ions as function of ϕ^M , obtained from radiotracer measurements. In the normal region on the left, cation concentration decreases with increasing ϕ^M in response to the decrease in electronic charge on the metal. Above the first potential of zero charge, at $\approx 0.5 V_{SHE}$, chemisorbed oxygen species form. An inverted charging region occurs for $\phi^M > 0.9 V_{SHE}$, with a transition to negative excess “free” charge. Adapted with permission [37]. Copyright 1975, Elsevier. Part (b) shows the electrode charging relation calculated in the model of Huang *et al.* [73], which reproduces the nonlinear and non-monotonic trends in (a). Reprinted with permission [73]. Copyright 2016, American Chemical Society.

Figure 3: Schematic of the electrode-electrolyte interface, showing electrode region, electrolyte region and boundary region in-between. Simulation methodologies for different regions are indicated at the lower edge. Different flavours of first-principles approaches to study the electrochemical interface are indicated along the bottom rail.

Figure 4: Deciphering the oxygen reduction reaction [78]. A reaction mechanisms is identified and the reaction pathway is parameterized using basic KS-DFT calculations (bottom, left). Microkinetic modeling (bottom, centre) gives an expression for net reaction rate (equation in the centre). Separately, the electrochemical interface model can be solved (bottom, right), using the theory in Ref. [73], to obtain the metal charging relation. The fully parameterized approach provides as output mechanistic insights, e.g., rate-determining term in the net reaction rate; descriptor-based activity assessment for materials screening; and effective parameters like Tafel-slope or exchange current density to use in porous electrode models.

286 References

287 References

- 288 [1] Y. Shao, N. M. Markovic, *Prelude: The renaissance of electrocatalysis*,
289 *Nano Energy* 29 (2016) 1–3.
- 290 [2] G. Wittstock, M. Eikerling, N. Alonso-Vante, M. B. Vukomirovic, H.
291 Uchida, *Electrocatalysis: holding the keys to advanced energy materials*
292 *and systems*, *ChemElectroChem* 3 (2016) 1518–1519.
- 293 [3] F. Calle-Vallejo, M. T. M. Koper, A. S. Bandarenka, *Tailoring the cat-*
294 *alytic activity of electrodes with monolayer amounts of foreign metals*,
295 *Chem. Soc. Rev.* 42 (2013) 5210–5230.
- 296 [4] V. R. Stamenkovic, B. Simon Mun, M. Arenz, K. J. J. Mayrhofer, C. A.
297 Lucas, G. Wang, P. N. Ross, N. M. Markovic, *Trends in electrocatalysis*
298 *on extended and nanoscale Pt-bimetallic alloy surfaces*, *Nature Mat.* 6
299 (2007) 241–247.
- 300 [5] D. Strmcnik, P. Papa Lopes, B. Genorio, V. R. Stamenkovic, N. M.
301 Markovic, *Design principles for hydrogen evolution reaction catalyst*
302 *materials*, *Nano Energy* 29 (2016) 29–36.
- 303 [6] S. Sreekantan, E. P. San, L. C. Wei, W. Kregvirat, *Nanotubular transi-*
304 *tion metal oxide for hydrogen production*, *Adv. Mater. Res.* 364 (2011)
305 494–499.
- 306 [7] T. L. Tan, L.-L. Wang, D. D. Johnson, K. Bai, *A comprehensive search*
307 *for stable PtPd nanoalloy configurations and their use as tunable cata-*
308 *lysts*, *Nano Lett.* 12 (2012) 4875–4880.

- 309 [8] W.-F. Chen, K. Sasaki, C. Ma, A. I. Frenkel, N. Marinkovic, J. T.
310 Muckerman, Y. Zhu, R. R. Adzic, *Hydrogen evolution catalysts based*
311 *on non-noble metal nickel-molybdenum nitride nanosheets*, *Angew.*
312 *Chem. Int. Ed.* 51 (2012) 6131–6135.
- 313 [9] X.-H. Tan, L. Wang, B. Zahiri, A. Kohandehghan, E. Memarzadeh
314 Lotfabad, M. H. Eikerling, D. Mitlin, *Titanium Oxynitride Interlayer to*
315 *Influence Oxygen Reduction Reaction Activity and Corrosion Stability*
316 *of Pt and PtNi Alloy*, *Chem. Sus. Chem.* 8 (2015) 361–376.
- 317 [10] J. Kibsgaard, T. F. Jaramillo, *Molybdenum phosphosulfide: an active,*
318 *acid-stable, earth-abundant catalyst for the hydrogen evolution reac-*
319 *tion*, *Angew. Chem. Int. Ed.* 53 (2014) 14433–14437.
- 320 [11] J. Tian, Q. Liu, N. Cheng, A. M. Asiri, X. Sun, *Self-supported Cu₃P*
321 *nanowire arrays as an integrated high-performance three-dimensional*
322 *cathode for generating hydrogen from water* *Chem. Int. Ed.* 53 (2014)
323 9577–9581.
- 324 [12] L. Feng, H. Vrubel, M. Bensimon, X. Hu, *Easily-prepared dinickel phos-*
325 *phide (Ni₂P) nanoparticles as an efficient and robust electrocatalyst for*
326 *hydrogen evolution*, *Phys. Chem. Chem. Phys.* 16 (2014) 5917–5921.
- 327 [13] E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M.
328 Wiltrout, N. S. Lewis, R. E. Schaak, *Nanostructured nickel phosphide*
329 *as an electrocatalyst for the hydrogen evolution reaction*, *J. Am. Chem.*
330 *Soc.* 135 (2013) 9267–9270.
- 331 [14] Z. Xing, Q. Liu, A. M. Asiri, X. Sun, *High-efficiency electrochemical*
332 *hydrogen evolution catalyzed by tungsten phosphide submicroparticles*,
333 *ACS Catal.* 5 (2015) 145–149.
- 334 [15] B. Konkana, J. Masa, W. Xia, M. Muhler, W. Schuhmann, *MoSSe@*
335 *reduced graphene oxide nanocomposite heterostructures as efficient and*
336 *stable electrocatalysts for the hydrogen evolution reaction*, *Nano Energy*
337 29 (2016) 46–53.
- 338 [16] D. Merki, X. Hu, *Recent developments of molybdenum and tungsten*
339 *sulfides as hydrogen evolution catalysts*, *Energy Environ. Sci.* 4 (2011)
340 3878–3888.

- 341 [17] D. Kong, J. J. Cha, H. Wang, H. R. Lee, Y. Cui, *First-row transition*
342 *metal dichalcogenide catalysts for hydrogen evolution reaction*, *Energy*
343 *Environ. Sci.* 6 (2013) 3553–3558.
- 344 [18] L. Qu, Y. Liu, J. B. Baek, L. Dai, *Nitrogen-doped graphene as efficient*
345 *metal-free electrocatalyst for oxygen reduction in fuel cells*, *ACS Nano*
346 4 (2010) 1321–1326.
- 347 [19] J. Sun, H. W. Lee, M. Pasta, H. Yuan, G. Zheng, Y. Sun, Y. Li, Y. Cui,
348 *A phosphorene–graphene hybrid material as a high-capacity anode for*
349 *sodium-ion batteries*, *Nature Nanotechnol.* 10 (2015) 980.
- 350 [20] J. Jaouen, J. Herranz, M. Lefevre, J.-P. Dodelet, U. I. Kramm, I.
351 Herrmann, P. Bogdanoff, J. Maruyama, T. Nagaoka, A. Garsuch, J.
352 R. Dahn, T. Olson, S. Pylypenko, P. Atanassov, E. A. Ustinov, *Cross-*
353 *laboratory experimental study of non-noble-metal electrocatalysts for the*
354 *oxygen reduction reaction*, *ACS Appl. Mater. Interfaces* 1 (2009) 1623–
355 1639.
- 356 [21] Z. Chen, J. -P Dodelet, J. Zhang, *Non-noble metal fuel cell catalysts*,
357 Wiley-VCH, Weinheim, Germany, 2014.
- 358 [22] J. Greeley, T. F. Jaramillo, J. Bonde, I. Chorkendorff, J. K. Nørskov,
359 *Computational high-throughput screening of electrocatalytic materials*
360 *for hydrogen evolution*, *Nat. Mater.* 5 (2006) 909–913.
- 361 [23] A. Jain, K. A. Persson, G. Ceder, *Research Update: The materials*
362 *genome initiative: data sharing and the impact of collaborative ab ini-*
363 *tio databases*, *APL Materials* 4 (2016) 053102.
- 364 **Aiming at reducing time and cost of materials research, the**
365 **authors discuss three different databases developed with the**
366 **help of density functional theory calculations to guide data-**
367 **driven discovery and design of functionally optimized electro-**
368 **catalytic materials.**
- 369 [24] M. Eikerling, A. Kulikovskiy, *Polymer Electrolyte Fuel Cells: Physical*
370 *Principles of Materials and Operation*, CRC Press, New York, 2014.
- 371 [25] M. J. Eslamibidgoli, M. Eikerling, *Electrochemical formation of reactive*
372 *oxygen species at Pt (111): a density functional theory study*, *ACS*
373 *Catal.* 5 (2015) 6090–6098.

374 [26] M. J. Eslamibidgoli, J. Huang, T. Kadyk, A. Malek, M. Eikerling, *How*
375 *theory and simulation can drive fuel cell electrocatalysis*, *Nano Energy*
376 29 (2016) 334–361.

377 **This perspective article presents an overview of parametric**
378 **effects in electrocatalyst systems for polymer electrolyte fuel**
379 **cells. It discusses approaches in theory and modeling to un-**
380 **derstand fundamental phenomena in electrocatalysis, guide**
381 **efforts in materials design, and rationalize the impact of ma-**
382 **terials modification on performance and stability.**

383 [27] A. A. Kornyshev, *Double-layer in ionic liquids: paradigm change?*, *J.*
384 *Phys. Chem. B* 111 (2007) 5545–5557.

385 [28] A. M. Kuznetsov, *Charge Transfer in Physics, Chemistry and Biology:*
386 *Physical Mechanisms of Elementary Processes and an Introduction to*
387 *the Theory*, Gordon and Breach, Amsterdam, 1995.

388 [29] A. M. Kuznetsov, J. Ulstrup, *Theory of electron transfer at electrified*
389 *interfaces*, *Electrochim. Acta* 45 (2000) 2339–2361.

390 [30] M. C. Henstridge, E. Laborda, N. V. Rees, R. G. Compton, *Marcus–*
391 *Hush–Chidsey theory of electron transfer applied to voltammetry: a*
392 *review*, *Electrochim. Acta* 84 (2012) 12–20.

393 [31] F. Calle-Vallejo, M. T. M. Koper, *First-principles computational elec-*
394 *trochemistry: achievements and challenges*, *Electrochim. Acta* 84
395 (2012) 3–11.

396 [32] M. Nielsen, M. E. Björketun, M. H. Hansen, J. Rossmeisl, *Towards*
397 *first principles modeling of electrochemical electrode–electrolyte inter-*
398 *faces*, *Surf. Sci.* 631 (2015) 2–7.

399 [33] N. Lespes, J.-S. Filhol, *Using implicit solvent in ab initio electrochemi-*
400 *cal modeling: investigating Li^+/Li electrochemistry at a $\text{Li}/\text{solvent}$ in-*
401 *terface*, *J. Chem. Theor. Comput.* 11 (2015) 3375–3382.

402 [34] M. H. Hansen, C. Jin, K. S. Thygesen, J. Rossmeisl, *Finite bias calcu-*
403 *lations to model interface dipoles in electrochemical cells at the atomic*
404 *scale*, *J. Phys. Chem. C* 120 (2016) 13485–13491.

405 **This article presents a generalized computational hydrogen**

406 electrode model as an efficient DFT-based approach for sim-
407 ulating electrochemical interfaces. It presents the thermody-
408 namic underpinnings for studying electric double layer at con-
409 stant electrode potential and pH, considering equilibrium of
410 the interface with a reservoir of electrons and a reservoir of
411 protons.

412 [35] R. Sundararaman, K. Letchworth-Weaver, K. A. Schwarz, D. Gunceler,
413 Y. Ozhabes, T. A. Arias, *JDFTx: software for joint density-functional*
414 *theory*, *SoftwareX* 6 (2017) 278.

415 **The authors present their fully-featured open source imple-**
416 **mentation of joint density functional theory as a tool to study**
417 **the properties of electrochemical systems.**

418 [36] K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias,
419 R. G. Hennig, *Implicit solvation model for density-functional study of*
420 *nanocrystal surfaces and reaction pathways*, *J. Chem. Phys.* 140 (2014)
421 140.

422 [37] A. Frumkin, O. Petrii, *Potentials of zero total and zero free charge of*
423 *platinum group metals*, *Electrochim. Acta* 20 (1975) 347–359.

424 [38] N. Garcia-Araez, V. Climent, J. Feliu, *Potential-dependent water ori-*
425 *entation on Pt (111), Pt (100), and Pt (110), as inferred from laser-*
426 *pulsed experiments. Electrostatic and chemical effects*, *J. Phys. Chem.*
427 *C* 113 (2009) 9290–9304.

428 [39] R. Martínez-Hincapie, V. Climent, J. M. Feliu, *Peroxodisulfate reduc-*
429 *tion as a probe to interfacial charge*, *Electrochem Commun.* (2018) in
430 press.

431 [40] V. A. Safonov, M. A. Choba, O. A. Petrii, *The difference between in-*
432 *terfaces formed by mechanically renewed gold and silver electrodes with*
433 *acetonitrile and aqueous solutions*, *J. Electroanal. Chem.* 808 (2018)
434 278–285.

435 [41] J. P. Perdew, K. Burke, M. Ernzerhof, *Generalized gradient approxi-*
436 *mation made simple*, *Phys. Rev. Lett.* 77 (1996) 3865.

437 [42] A. J. Cohen, P. Mori-Sanchez, W. Yang, *Insights into current limita-*
438 *tions of density functional theory*, *Science* 321 (2008) 792–794.

- 439 [43] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A.
440 P. Sutton, *Electron-energy-loss spectra and the structural stability of*
441 *nickel oxide: An LSDA+U study*, Phys. Rev. B: Condens. Matter
442 Mater. Phys. 57 (1998) 1505.
- 443 [44] M. Cococcioni, S. De Gironcoli, *Linear response approach to the cal-*
444 *culatation of the effective interaction parameters in the LDA+U method*,
445 Phys. Rev. B: Condens. Matter Mater. Phys. 71 (2005) 035105.
- 446 [45] Z. Zeng, M. K. Y. Chan, Z.-J. Zhao, J. Kubal, D. Fan, J. Greeley, *To-*
447 *wards first principles-based prediction of highly accurate electrochemical*
448 *Pourbaix diagrams*, J. Phys. Chem. C 119 (2015) 18177–18187.
- 449 [46] J. Klimes, A. Michaelides, *Perspective: Advances and challenges in*
450 *treating van der Waals dispersion forces in density functional theory*,
451 J. Chem. Phys. 137 (2012) 120901.
- 452 [47] K. Tonigold, A. Gross, *Dispersive interactions in water bilayers at*
453 *metallic surfaces: A comparison of the PBE and RPBE functional in-*
454 *cluding semiempirical dispersion corrections*, J. Comput. Chem. 33
455 (2012) 695–701.
- 456 [48] S. Sakong, K. Forster-Tonigold, A. Gross, *The structure of water at a*
457 *Pt (111) electrode and the potential of zero charge studied from first*
458 *principles*, J. Chem. Phys. 144 (2016) 194701.
459 **The authors present extensive ab initio molecular dynamics**
460 **simulations to understand the structure of water at a Pt(111)**
461 **surface. They determined the amount of water necessary to**
462 **simulate liquid water properties.**
- 463 [49] R. Jimnouchi, A. B. Anderson, *Electronic structure calculations of*
464 *liquid-solid interfaces: combination of density functional theory and*
465 *modified Poisson-Boltzmann theory*, Phys. Rev. B 77 (2008) 245417.
- 466 [50] O. Andreussi, I. Dabo, N. Marzari, *Revised self-consistent contin-*
467 *uum solvation in electronic-structure calculations*, J. Chem. Phys. 136
468 (2012) 064102.
- 469 [51] J. J. Bikerman, *Structure and capacity of electrical double layer*, The
470 London, Edinburgh, and Dublin Philosophical Magazine and Journal
471 of Science 33 (1942)384–397.

- 472 [52] I. Borukhov, D. Andelman, H. Orland, *Steric effects in electrolytes: a*
473 *modified Poisson-Boltzmann equation*, Phys. Rev. Lett. 79 (1997) 435.
- 474 [53] M. Bazant, B. Storey, A. Kornyshev, *Double layer in ionic liquids:*
475 *overscreening vs. crowding*, Phys. Rev. Lett. 106 (2011) 046102.
- 476 [54] J. Wu, *Classical density functional theory for molecular systems*,
477 in Variational Methods in Molecular Modeling, Springer, Singapore,
478 201765–99.
- 479 [55] H. Lin, D. G. Truhlar, *QM/MM: what have we learned, where are we,*
480 *and where do we go from here?*, Theor. Chem. Acc. 117 (2007) 185?–
481 199.
- 482 [56] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin,
483 T. Bligaard, H. Jonsson, *Origin of the overpotential for oxygen reduc-*
484 *tion at a fuel-cell cathode*, J. Phys. Chem. B 108 (2004) 17886.
- 485 [57] J. Rossmeisl, E. Skulason, M. Björketun, V. Tripkovic, J. K. Nørskov,
486 *Modeling the electrified solid-liquid interface*, Chem. Phys. Lett. 466
487 (2008) 68.
- 488 [58] V. Tripkovic, M. E. Björketun, E. Skulason, J. Rossmeisl, *Standard*
489 *hydrogen electrode and potential of zero charge in density functional*
490 *calculations*, Phys. Rev. B 84 (2011) 115452.
- 491 [59] M. Otani, O. Sugino, *First-principles calculations of charged surfaces*
492 *and interfaces: a plane-wave nonrepeated slab approach*, Phys. Rev. B
493 73 (2006) 115407.
- 494 [60] I. Dabò, Y. Li, N. Bonnet, N. Marzari, *Ab initio electrochemical proper-*
495 *ties of electrode surfaces*, in Fuel Cell Science: Theory, Fundamentals,
496 and Biocatalysis, edited by A. Wieckowski and J. Nørskov (2010) 415–
497 431.
- 498 [61] K. Letchworth-Weaver, T. A. Arias, *Joint density functional theory of*
499 *the electrode-electrolyte interface: application to fixed electrode poten-*
500 *tials, interfacial capacitances, and potentials of zero charge*, Phys. Rev.
501 B 86 (2012) 075140.

- 502 [62] A. Y. Lozovoi, A. Alavi, J. Kohonoff, R. M. Lynden-Bell, *Ab initio*
503 *simulation of charged slabs at constant chemical potential*, J. Chem.
504 Phys. 115 (2001) 1661.
- 505 [63] N. Bonnet, T. Morishita, O. Sugino, M. Otani, *First-principles molec-*
506 *ular dynamics at a constant electrode potential*, Phys. Rev. Lett. 109
507 (2012) 266101.
- 508 [64] A.Y. Lozovoi, A. Alavi, *Reconstruction of charged surfaces: general*
509 *trends and a case study of Pt (110) and Au (110)*, Phys. Rev. B 68
510 (2003) 245416.
- 511 [65] C. D. Taylor, S.A. Wasileski, J.-S. Filhol, M. Neurock, *First principles*
512 *reaction modeling of the electrochemical interface: consideration and*
513 *calculation of a tunable surface potential from atomic and electronic*
514 *structure*, Phys. Rev. B 73 (2006) 165402.
- 515 [66] J.-L. Fattebert, F. Gygi, *Density functional theory for efficient ab initio*
516 *molecular dynamics simulations in solution*, J. Comput. Chem. 23
517 (2002) 662.
- 518 [67] M. J. Eslamibidgoli, M. Eikerling, *Atomistic mechanism of Pt extrac-*
519 *tion at oxidized surfaces: insights from DFT*, Electroanalysis 7 (2016)
520 345–354.
- 521 **This article presents a detailed mechanistic explanation of sur-**
522 **face atom extraction and formation of a place-exchanged state**
523 **at an oxidized Pt(111) surface. It establishes local selection**
524 **criteria for elementary reaction steps that could be general-**
525 **ized to surfaces of nanostructured or nanoparticle-based cat-**
526 **alysts.**
- 527 [68] S. G. Rinaldo, J. Stumper, M. Eikerling, *Mechanistic principles of plat-*
528 *inum oxide formation and reduction*, Electroanalysis 5 (2014) 262–272.
- 529 [69] H. Baroody, G. Jerkiewicz, M. Eikerling, *Modelling oxide formation*
530 *and growth on platinum*, J. Chem. Phys. 146 (2017) 144102.
- 531 [70] O. Diaz-Morales, D. Ferrus-Suspedra, M. T. M. Koper, *The impor-*
532 *tance of nickel oxyhydroxide deprotonation on its activity towards elec-*
533 *trochemical water oxidation*, Chem. Sci. 7 (2016) 2639–2645.

534 **Authors demonstrated the important effect of the electrolyte**
535 **pH on the degree of surface deprotonation of NiOOH, which**
536 **crucially affects the activity for the oxygen evolution reaction.**

537 [71] S. Schnur, A. Gross, *Properties of metal–water interfaces studied from*
538 *first principles*, *New J. Phys* 11 (2009) 125003.

539 [72] M. J. Eslamibidgoli, A. Gross, M. Eikerling, *Surface configuration and*
540 *wettability of nickel (oxy) hydroxides: a first-principles investigation*,
541 *Phys. Chem. Chem. Phys.* 19 (2017) 22659–22669.

542 [73] J. Huang, A. Malek, J. Zhang, M. Eikerling, *Non-monotonic surface*
543 *charging behavior of platinum: a paradigm change*, *J. Phys. Chem. C*
544 120 (2016) 13587–13595.

545 **This article presents a new structural model of the electrified**
546 **interface that self-consistently accounts for the formation of**
547 **chemisorbed oxygen species and the orientational ordering of**
548 **interfacial water molecules. Analytical solution of the model**
549 **finds the non-monotonic charging behavior of Pt that agrees**
550 **with experimental data of Frumkin and Petrii [37]. The the-**
551 **oretical framework could serve as a blueprint for refinements**
552 **of joint density functional theory in order to properly account**
553 **for boundary layer phenomena.**

554 [74] J. Huang, T. Zhou, J. Zhang, M. Eikerling, *Double layer of platinum*
555 *electrodes: non-monotonic surface charging phenomena and negative*
556 *double layer capacitance*, *J. Chem. Phys.* 148 (2018) 044704.

557 [75] J. Huang, J. Zhang, M. Eikerling, *Theory of electrostatic phenomena*
558 *in water-filled Pt nanopores*, *Faraday Discuss.* 193 (2016) 427–446.

559 [76] J. Huang, J. Zhang, M. Eikerling, *Particle proximity effect in*
560 *nanoparticle electrocatalysis: surface charging and electrostatic inter-*
561 *actions*, *J. Phys. Chem. C* 121 (2017) 4806–4815.

562 [77] T. Muzaffar, T. Kadyk, M. Eikerling, *Physical modeling of the proton*
563 *density in nanopores of PEM fuel cell catalyst layers*, *Electrochim Acta*
564 245 (2017) 1048–1058.

565 [78] J. Huang, J. Zhang, M. Eikerling, *Unifying theoretical framework for*
566 *deciphering the oxygen reduction reaction on platinum*, *Phys. Chem.*

567 Chem. Phys. in press (2018).

568 **This article presents a theoretical framework for deciphering**
569 **the ORR, based on a unified treatment of the formation of**
570 **chemisorbed oxygen intermediates, surface charging effects,**
571 **thermodynamics and kinetics of the ORR. It sheds light on**
572 **the roles of oxygen intermediates and yields Tafel slope and**
573 **exchange current density as continuous functions of electrode**
574 **potential.**

575 [79] B. Hammer, J. K. Nørskov, *Theoretical surface science and catalysis:*
576 *calculations and concepts*, Adv. Catal. 45 (2000) 71–129.

577 [80] J. Rossmeisl, K. Chan, R. Ahmed, V. Tripkovic, M. E. Björketun, *pH*
578 *in atomic scale simulations of electrochemical interfaces*, Phys. Chem.
579 Chem. Phys. 15 (2013) 10321–10325.

580 [81] K. Chan, J. K. Nørskov, *Electrochemical barriers made simple*, J.
581 Phys. Chem. Lett. 6 (2015) 2663–2668.

582 **A simple and elegant method is presented to study constant**
583 **potential reaction energetics for simple charge transfer re-**
584 **actions. Using a single barrier calculation as well as surface**
585 **charges at initial, transition, and final states, this method al-**
586 **lows for a tremendous reduction in the costs of DFT-based**
587 **kinetic analysis of electrochemical reactions.**

588 [82] M. H. Hansen, J. Rossmeisl, *pH in grand canonical statistics of an elec-*
589 *trochemical interface*, J. Phys. Chem. C 120 (2016) 29135–29143.

590 **A DFT-based atomic-scale model of the electrochemical in-**
591 **terface is presented, which treats effects of pH and electrode**
592 **potential with the generalized computational hydrogen elec-**
593 **trode approach, and accounts for solvent effects using exten-**
594 **sive sampling based on ab initio molecular dynamics.**

595 [83] Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov,
596 T. F. Jaramillo, *Combining theory and experiment in electrocatalysis:*
597 *insights into materials design*, Science 355 (2017) eaad4998.

598 [84] F. Calle-Vallejo, J. I. Martínez, J. M. García-Lastra, J. Rossmeisl,
599 M. T. M. Koper, *Physical and chemical nature of the scaling relations*

- 600 *between adsorption energies of atoms on metal surfaces*, Phys. Rev.
601 Lett. 108 (2012) 116103.
- 602 [85] H. A. Hansen, J. Rossmeisl, J. K. Nørskov, *Surface Pourbaix diagrams*
603 *and oxygen reduction activity of Pt, Ag and Ni (111) surfaces studied*
604 *by DFT*, Phys. Chem. Chem. Phys. 10 (2008) 3722–3730.
- 605 [86] R. Sundararaman, K. Schwarz, *Evaluating continuum solvation mod-*
606 *els for the electrode-electrolyte interface: challenges and strategies for*
607 *improvement*, J. Chem. Phys. 146 (2017) 084111. **The authors dis-**
608 **uss and compare methods of first-principles electrochem-**
609 **istry. They calculate charging curves for a simple electrode-**
610 **electrolyte interface using KS-DFT combined with various sol-**
611 **vation models and thereby unveil shortcomings and challenges**
612 **that the field must overcome in order to provide an accurate**
613 **representation of electrochemical interfaces.**