

## Fundamental Drivers of Electrochemical Barriers

Xi Chen<sup>1</sup>, Georg Kastlunger<sup>2</sup>, and Andrew A. Peterson<sup>1,\*</sup>

<sup>1</sup>*School of Engineering, Brown University, Providence, Rhode Island 02912, USA*

<sup>2</sup>*Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark*



(Received 2 August 2023; accepted 8 November 2023; published 8 December 2023)

We find that ion creation and destruction dominate the behavior of electrochemical reaction barriers, through grand-canonical electronic structure calculations of proton deposition on transition metal surfaces. We show that barriers respond to potential in a nonlinear manner and trace this to the continuous degree of electron transfer as an ion is created or destroyed. This explains both Marcus-like curvature and Hammond-like shifts. Across materials, we find the barrier energy to be driven primarily by the charge presented on the surface, which, in turn, is dictated by the native work function, a fundamentally different driving force than in nonelectrochemical systems.

DOI: 10.1103/PhysRevLett.131.238003

Electrochemistry is a linchpin technology in the transition from fossil fuels, providing short- and long-duration storage as well as long-distance movement of intermittent electricity [1,2], vehicle power [3,4], and pathways to the defossilization of countless industries, including synthetic fuels [5], cement [6], fertilizers [7], steel [8], aluminum [9], and (nonfossil) petrochemicals [10], either directly or through hydrogen intermediates. While electrochemistry has a rich history in analytical chemistry, our understanding of the controlling reactions at the level of electronic structure calculations is still emerging. Sophisticated electronic-structure approaches have recently gained popularity due to the availability of methods that allow the simulation of reactions at constant applied potential, which naturally occur in the electronically grand-canonical ensemble [11–23]. Advanced simulation methods mimic physical potentiostats to maintain a constant electrical potential by varying the (fractional) number of electrons while allowing for a compensating, screened countercharge as well as a field-free region providing an absolute reference for the electrochemical potential of electrons.

Reaction barriers dictate the rates of elementary reactions and, therefore, are crucial to understanding electrochemical kinetics. In this Letter, we employ the solvated jellium method [18] to understand the basic driving forces behind electrochemical reaction barriers, uncovering their similarities to as well as highly notable dissimilarities from conventional reactions at surfaces, such as those in heterogeneous catalysis. Fundamental electrochemical reactions often involve the creation or destruction of an ion—such as the conversion of  $H^+$  to adsorbed hydrogen (and ultimately  $H_2$  gas), the conversion of graphene-adsorbed lithium to  $Li^+$  in solution, or the conversion of  $CO_2$  to adsorbed  $COO^-$ . Such reactions are inherently coupled to the movement of electrons to reaction sites, and we will show that the barriers for such reactions are strongly affected by

this electron transfer as well as electrostatic interactions—both of which vary along the reaction path—making an understanding distinct from those of conventional surface reactions. We focus on trends in the simplest such reaction: the proton-deposition reaction ( $H^+ + xe^- \rightarrow H^*$ , where  $*$  is the electrode surface and the amount of electron transfer  $x$  is determined *a posteriori* [21,23–25]), but we expect the concepts and trends we develop to hold across ion-creating or -destroying reactions at electrochemical interfaces. For reasons of generality, we neglect tunneling or vibronic effects, which are treated by others [26,27].

In Fig. 1(a), we show converged calculations of a coupled proton-electron transfer to a Pt(111) surface, with all solvent and surface degrees of freedom relaxed, at three different applied potentials  $\phi$ . At each potential, we plot the grand-potential energy versus the reaction coordinate, which starts from the pseudo-initial state (pIS) and proceeds through the transition state (TS) to the final state (FS). We use the term pIS, rather than IS, as the pIS involves a solvated proton ( $H_3O^+$ ,  $H_5O_2^+$ , etc.) localized near and hybridized with the surface; in kinetic models, the pIS should be properly referenced to a thermodynamic initial state, as discussed in depth elsewhere [23,28]. Here, we focus solely on the elementary process. A still image of the TS at  $0.5 V_{SHE}$  is shown in Fig. 1(b). At each potential, the charge transfer—that is, the number of electrons that must be injected by the “computational potentiostat”—is also plotted. The total electron transfer is significantly less than one, a consequence of the prehybridized pIS [28]. The degree of charge transfer at the barrier  $N^\ddagger$  will become an important quantity in the subsequent analysis.

Several overall trends are apparent: As the potential becomes more negative, the reaction becomes more downhill (exothermic), the barrier grows smaller, and the position of the transition state shifts earlier, toward the pIS. These latter observations are consistent with the

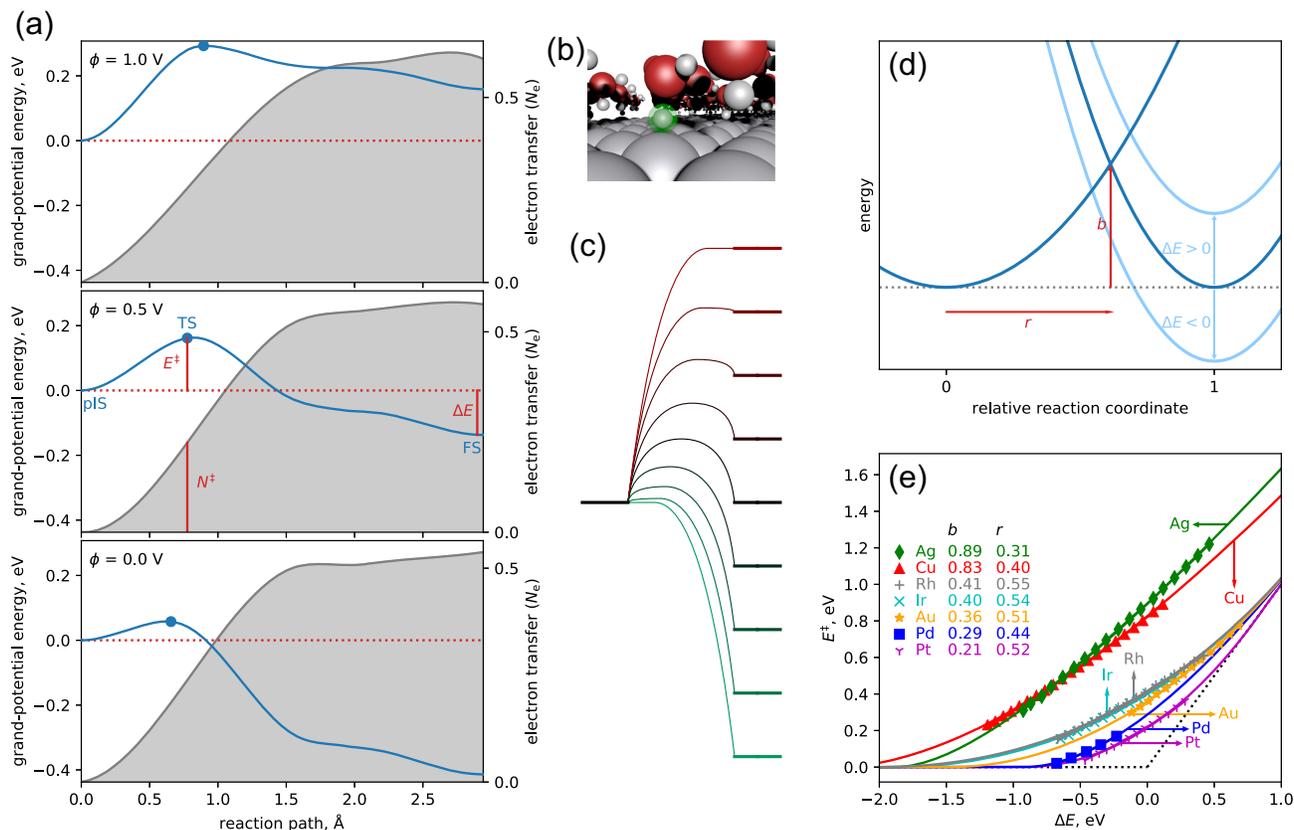


FIG. 1. Potential-dependent behavior of reaction barriers. (a) Reaction barriers and electron transfer on Pt(111) at three fixed potentials versus standard hydrogen electrode ( $V_{\text{SHE}}$ ). Constant-potential reaction paths were found by pairing the solvated jellium method [18] to calculate grand-canonical forces with the DyNEB method [29] to search for the saddle point. Potentials are referenced assuming SHE is 4.44 V versus vacuum, as suggested by Trasatti [30]. (b) Atomic figure of the transition state on Pt(111) at 0.5  $V_{\text{SHE}}$ . (c) Schematic of the Hammond-Leffler postulate, which can be interpreted to mean that strongly downhill reactions have barriers similar in structure and energy to the initial state (or the final state for strongly uphill reactions). (d) Two-parameter model for curved barrier scaling. (e) Barrier heights as a function of the energy change for several transition metals.

Hammond-Leffler postulate [31,32] [shown qualitatively and described for general reactions in Fig. 1(c)], and later we will derive quantitatively why this behavior holds for electrochemical reactions. We employ a simple model to correlate the barrier height  $E^\ddagger$  to the energy change  $\Delta E$ , shown in Fig. 1(d). In this two-parameter expansion of a previous model [33],  $b$  represents the barrier height at  $\Delta E = 0$ , while  $r$  indicates the degree of skew (i.e., asymmetry of parabola widths), with a symmetric response given by  $r = \frac{1}{2}$ . (While this bears a superficial resemblance to Marcus theory, we employ it solely to match the limiting behavior of the Hammond-Leffler postulate.) The full form and derivation of this model are shown in Supplemental Material [34]. In Fig. 1(e), we show the results of extensive grand-canonical barrier calculations across several transition metals and potentials; full results are shown in Supplemental Material [34]. From this figure, a curvature in the barrier height is clear, in contrast to predictions of the conventional Brønsted-Evans-Polanyi, transition-state, and linear free-energy scaling relations conventionally employed in catalysis and organic chemistry [35–41].

What drives the barrier to change with potential, and what is responsible for the curvature? In Supplemental Material [34], we show that a simple thermodynamic relationship exists:

$$\left(\frac{\partial E^\ddagger}{\partial \phi}\right)_{\{\bar{x}_i\}} = eN^\ddagger, \quad (1)$$

where  $N^\ddagger$  indicates the amount of electron transfer at the barrier and  $e$  is the (positive) electronic charge. This relationship is exact, in the limit of fixed atomic positions  $\{\bar{x}_i\}$ . Thus, to a first approximation, we can consider the barrier height to change in proportion to the amount of electron transfer at the barrier. With grand-canonical methods, this quantity is unambiguous: It is simply the difference in the number of excess electrons at the barrier minus those at the reference initial state; this is indicated on the middle panel of Fig. 1(a).

This simplifies the analysis of free-energy diagrams: Over small perturbations, the barrier changes in an analogous fashion to how reaction end states have long been

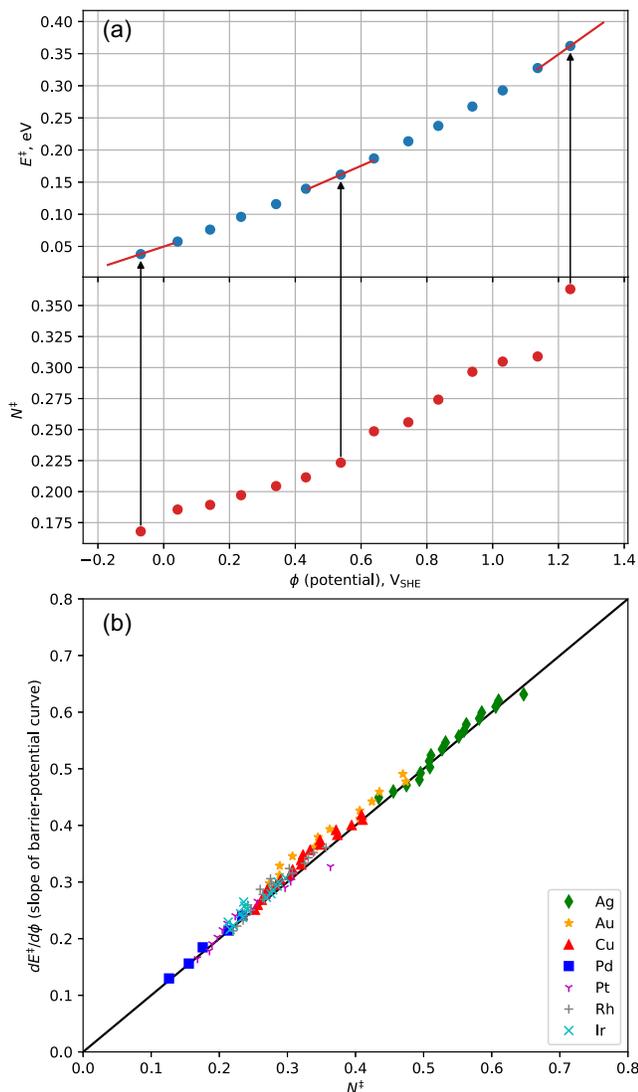


FIG. 2. Electron transfer drives the local potential response of barriers. (a) Reaction barrier ( $E^\ddagger$ ) and electrons transferred at the barrier ( $N^\ddagger$ ) both plotted versus potential ( $\phi$ ). The slopes on the upper figure are those calculated from  $N^\ddagger$  in the bottom figure. (b) The local slope of the barrier height versus potential ( $dE^\ddagger/d\phi$ ) curve (calculated by fitting the curve to a parabola and taking an analytical derivative) versus  $N^\ddagger$  for each surface and potential combination.

assumed to change, that is, consistent with the widely used computational hydrogen electrode [21,33,42–44] approach, as  $\Delta E^\ddagger \approx eN^\ddagger \Delta\phi$ . However, since  $N^\ddagger$  itself is a function of the potential  $\phi$ , this predicts the local slope only, with the ultimate expression exhibiting curvature. This differs from models based on capacitance [44], which predict linear behavior. In Fig. 2(a), we show that this thermodynamic relation holds locally for Pt (111), and in Fig. 2(b) we also show that it holds locally for each metal surface we report in this study, across their full range of potentials.

We can use the relationship of Eq. (1)—which holds for any two fixed geometries—to analyze this behavior in more

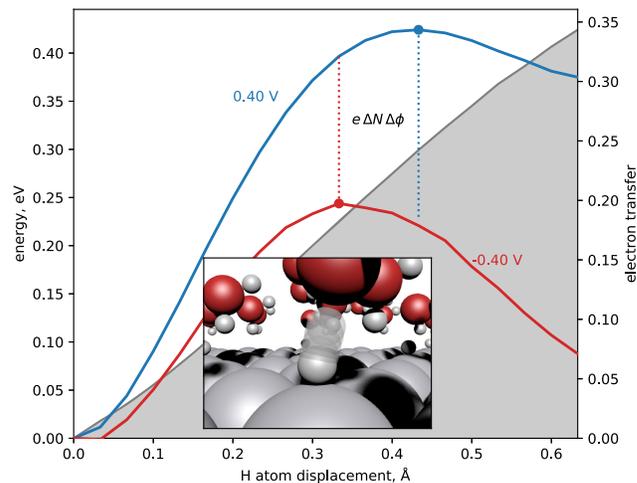


FIG. 3. Electron transfer drives barrier movement. The degree of charge transfer along the reaction path drives the barrier to move earlier and become smaller as the potential is made more negative. The top (blue) curve shows the barrier of a fixed path at +0.40 V<sub>SHE</sub>, while the shaded curve shows the charge transfer at each image along the path. The vertical lines coming down show quantitative predictions of the energy change, at each image, based upon  $e\Delta N\Delta\phi$ . The bottom (red) curve shows the density-functional-theory-calculated barrier of the same fixed path at -0.40 V<sub>SHE</sub>.

depth. To do this, we contrive a simple one-dimensional system shown in Fig. 3, where the proton is constrained to move along a one-dimensional interpolation between the water layer and the surface. All other atoms were fixed at their pIS positions, to ensure only a single reaction path is possible regardless of potential. The energy of each state along this path is shown in the top curve at 0.4 V<sub>SHE</sub>, and the peak of this path can be considered the barrier height  $E^\ddagger$  for this system. The shaded curve shows the corresponding electron transfer for this system. From Eq. (1), we can predict that the energy of any state along this curve will be reduced by  $e\Delta N\Delta\phi$ , where  $\Delta N$  is the electron transfer relative to the start of the curve. We quantitatively predict this change for the barrier and one earlier image in the figure, shown by the dashed vertical lines. Since more electrons have transferred at the barrier, the barrier energy decreases more rapidly with potential, relative to the earlier state; this shifts the maximum earlier while the energy decreases. Thus, this, predicts how the barrier shifts in both magnitude and position as the potential is changed, and we see this prediction is a near-exact match to grand-canonical electronic structure calculations carried out at the lower potential of -0.4 V<sub>SHE</sub>.

Thus, the charge transfer along a reaction path, in combination with Eq. (1), predicts and explains a multitude of related effects: the observed Hammond-Leffler behavior of barrier movement, the energetic shifts of barriers with potentials, and the curved Marcus-like behavior of barrier energies. This is fundamentally due to the creation or

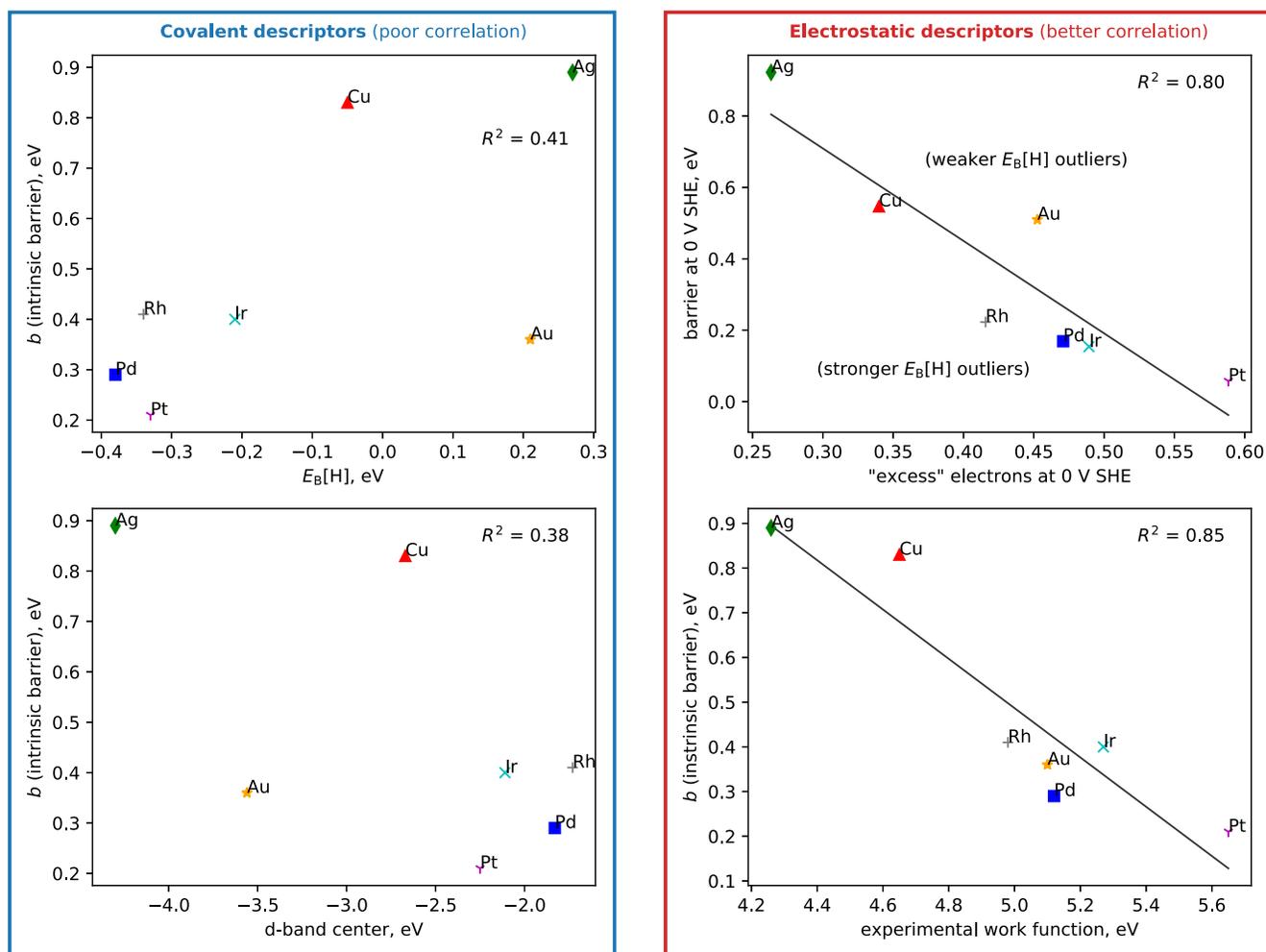


FIG. 4. Correlation of barriers with various material properties. The barrier exhibits a strong correlation with electrostatic descriptors and only a weak correlation to covalent descriptors.

destruction of ions that accompanies elementary electrochemical reactions.

We next turn our attention to trends among materials, attempting to understand if electrochemical barriers follow the general trends developed for catalytic systems. These commonly used trends include correlations of the reaction barrier to the binding energies of reactants and products [36,39] and—for late transition metals—correlation of adsorption energies, in general, to the central moment of the material's d band [45,46]. In our system, the FS is a hydrogen bound to a metal surface, while the TS is a hydrogen loosely bound to the same surface, so we would naïvely expect the TS energy to correlate to the FS energy across metals.

In Fig. 1(e), we showed the relationship between  $E^\ddagger$  and  $\Delta E$  for a range of late transition metals. We can use the parameter  $b$  to make comparisons between materials, as it corresponds to the barrier height with zero local driving force; we refer to this as the intrinsic barrier. Interestingly, we see that Pt has an abnormally low intrinsic barrier,

perhaps contributing to the many proposed reasons for platinum's excellence in catalyzing the hydrogen evolution reaction. Conversely, we see relatively high intrinsic barriers for Ag and Cu.

In Fig. 4, we first attempt to correlate the intrinsic barriers to the materials' hydrogen binding energies and d-band centers. We see no strong correlation of the intrinsic barrier to either of these quantities. This suggests a different factor may be driving the barrier energetics.

A key differentiating feature of electrochemistry is that reactions typically involve creating or destroying an ion, and, thus, the ionic nature of the transition state may play a crucial role, which we next explore. Each material requires a different amount of electronic charging to reach a particular voltage; therefore, at any particular voltage each material expresses a different surface charge. In the top-right panel in Fig. 4, we focus on the 0 V<sub>SHE</sub> condition and plot the barrier versus the charge presented on each electrode; we now observe a strong correlation—suggesting an electrostatic driving force. Interestingly, we

see that the hydrogen binding energy trends predict the deviation from the correlation. For example, Au, Rh, Pd, and Ir all have similar excess electrons at 0 V<sub>SHE</sub> and to first order have similar barriers. However, Au binds hydrogen weakly and deviates positively from the correlation, while Rh, Pd, and Ir bind hydrogen strongly and deviate negatively from the correlation. A similar argument can be made regarding the relative deviations of Ag and Cu. This shows an interplay between covalent and ionic interactions in driving the barrier energetics, with the ionic interactions stronger.

We can consider the primary driver of the differences in surface-charge density to be the (native) work function of each material, with secondary contributions from capacitances and solvation [47]. Indeed, we found a striking correlation between experimentally tabulated work functions [48] and our excess-electron parameter (shown in Supplemental Material [34]). As a simplified, readily obtainable descriptor, we also plot in Fig. 4 the intrinsic barriers versus these experimentally measured work functions for each metal. We again see an excellent correlation.

This indicates that, while the end-state energetics are driven by the formation of covalent bonds, the transition-state energetics are driven more strongly by the electrostatics. Thus, different material properties can drive the behavior of these two states: Covalent descriptors such as the d-band center may more strongly drive end-state binding energies, while the (native) material work function may be a larger driver of barrier energies due to their ionic nature. Indeed, for many decades, the experimental rates of reactions such as hydrogen evolution have been observed to correlate not only with binding energies, but also with material work functions [49–55], with the physical reason remaining elusive [54]. Our relation between reaction barrier and work function offers a clear and compelling explanation for these experimental trends. While surface electrostatic effects can affect all adsorbates [56–60], we can generally expect that, for reactions that create or destroy ions, electrostatic effects will be more significant at the transition state than the bound end state (or vice versa in some systems such as CO<sub>2</sub> → \*COO<sup>-</sup>). This offers a second degree of control in electrochemical systems.

In summary, we show unique aspects of electrochemical barriers, as opposed to barriers at nonelectrified interfaces. First, the degree of charge transfer at the barrier drives many aspects of the barrier behavior, including its potential response, its adherence to the Hammond-Leffler postulate, and the curved Marcus-like behavior apparent over wide ranges in driving force. Second, the interaction of the transition state with the specific electrode surface appears to be driven largely by electrostatic interactions with the surface rather than the typical covalent descriptors involved in catalysis. While we expect the degree of covalent versus ionic nature of each class of transition state to differ, we nonetheless expect that this identifies a different

fundamental material driving force for electrochemical barriers. These aspects are both driven by the creation or destruction of ions that accompany elementary electrochemical reactions.

*Methods.*—The solvated jellium method [18] was used to perform electronic structure calculations. Full details and parameters are available in Supplemental Material [34], which contains additional references [61–70]. Data are available from the corresponding author upon reasonable request.

The authors acknowledge funding by the U.S. National Science Foundation under Grant No. 1553365. Calculations were performed at Brown’s Center for Computation and Visualization. G. K. acknowledges funding from V-Sustain: The VILLUM Centre for the Science of Sustainable Fuels and Chemicals of VILLUMFONDEN (Grant No. 9455).

A. A. P. conceived of this study. X. C. conducted the calculations with guidance from G. K. A. A. P., X. C., and G. K. developed the conclusions. G. K. and A. A. P. developed the curved scaling model. A. A. P. wrote the manuscript, and all authors contributed to the ideas within and its final form.

The authors declare no competing interests.

---

\*Corresponding author: andrew\_peterson@brown.edu

- [1] Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, and J. Liu, Electrochemical energy storage for green grid, *Chem. Rev.* **111**, 3577 (2011).
- [2] B. Miao, L. Giordano, and S. H. Chan, Long-distance renewable hydrogen transmission via cables and pipelines, *Int. J. Hydrogen Energy* **46**, 18699 (2021).
- [3] A. Hoekstra, The underestimated potential of battery electric vehicles to reduce emissions, *Joule* **3**, 1412 (2019).
- [4] C. Cunan, M.-K. Tran, Y. Lee, S. Kwok, V. Leung, and M. Fowler, A review of heavy-duty vehicle powertrain technologies: Diesel engine vehicles, battery electric vehicles, and hydrogen fuel cell electric vehicles, *Clean Technol.* **3**, 474 (2021).
- [5] M. Dietsch and M. Anderson, Vision of the U.S. biofuel future: A case for hydrogen-enriched biomass gasification, *Ind. Eng. Chem. Res.* **46**, 8863 (2007).
- [6] L. D. Ellis, A. F. Badel, M. L. Chiang, R. J.-Y. Park, and Y.-M. Chiang, Toward electrochemical synthesis of cement—an electrolyzer-based process for decarbonating CaCO<sub>3</sub> while producing useful gas streams, *Proc. Natl. Acad. Sci. U.S.A.* **117**, 12584 (2019).
- [7] O. Westhead, R. Jervis, and I. E. L. Stephens, Is lithium the key for nitrogen electroreduction?, *Science* **372**, 1149 (2021).
- [8] D. V. Lopes, M. J. Quina, J. R. Frade, and A. V. Kovalevsky, Prospects and challenges of the electrochemical reduction of

- iron oxides in alkaline media for steel production, *Front. Mater.* **9** (2022).
- [9] R. P. Pawlek, Inert anodes: An update, in *Essential Readings in Light Metals* (Springer International Publishing, New York, 2016), pp. 1126–1133.
- [10] IEA, The future of petrochemicals, technical report, International Energy Agency, (2018), <https://www.iea.org/reports/the-future-of-petrochemicals>.
- [11] A. Y. Lozovoi, A. Alavi, J. Kohanoff, and R. M. Lynden-Bell, *Ab initio* simulation of charged slabs at constant chemical potential, *J. Chem. Phys.* **115**, 1661 (2001).
- [12] M. Otani and O. Sugino, First-principles calculations of charged surfaces and interfaces: A plane-wave nonrepeated slab approach, *Phys. Rev. B* **73**, 115407 (2006).
- [13] C. D. Taylor, S. A. Wasileski, J.-S. Filhol, and M. Neurock, First principles reaction modeling of the electrochemical interface: Consideration and calculation of a tunable surface potential from atomic and electronic structure, *Phys. Rev. B* **73**, 165402 (2006).
- [14] R. Jinnouchi and A. B. Anderson, Electronic structure calculations of liquid-solid interfaces: Combination of density functional theory and modified Poisson-Boltzmann theory, *Phys. Rev. B* **77**, 245417 (2008).
- [15] K. Letchworth-Weaver and T. A. Arias, Joint density functional theory of the electrode-electrolyte interface: Application to fixed electrode potentials, interfacial capacitances, and potentials of zero charge, *Phys. Rev. B* **86**, 075140 (2012).
- [16] J. D. Goodpaster, A. T. Bell, and M. Head-Gordon, Identification of possible pathways for C–C bond formation during electrochemical reduction of CO<sub>2</sub>: New theoretical insights from an improved electrochemical model, *J. Phys. Chem. Lett.* **7**, 1471 (2016).
- [17] R. Sundararaman, W. A. Goddard, and T. A. Arias, Grand canonical electronic density-functional theory: Algorithms and applications to electrochemistry, *J. Chem. Phys.* **146**, 114104 (2017).
- [18] G. Kastlunger, P. Lindgren, and A. A. Peterson, Controlled-potential simulation of elementary electrochemical reactions: Proton discharge on metal surfaces, *J. Phys. Chem. C* **122**, 12771 (2018).
- [19] A. Bouzid and A. Pasquarello, Atomic-scale simulation of electrochemical processes at electrode/water interfaces under referenced bias potential, *J. Phys. Chem. Lett.* **9**, 1880 (2018).
- [20] M. M. Melander, M. J. Kuisma, T. E. K. Christensen, and K. Honkala, Grand-canonical approach to density functional theory of electrocatalytic systems: Thermodynamics of solid-liquid interfaces at constant ion and electrode potentials, *J. Chem. Phys.* **150**, 041706 (2019).
- [21] N. G. Hörmann, N. Marzari, and K. Reuter, Electrosorption at metal surfaces from first principles, *npj Comput. Mater.* **6**, 136 (2020).
- [22] N. G. Hörmann and K. Reuter, Thermodynamic cyclic voltammograms based on *ab initio* calculations: Ag(111) in halide-containing solutions, *J. Chem. Theory Comput.* **17**, 1782 (2021).
- [23] P. Lindgren, G. Kastlunger, and A. A. Peterson, Electrochemistry from the atomic scale, in the electronically grand-canonical ensemble, *J. Chem. Phys.* **157**, 180902 (2022).
- [24] Y.-H. Fang, G.-F. Wei, and Z.-P. Liu, Constant-charge reaction theory for potential-dependent reaction kinetics at the solid–liquid interface, *J. Phys. Chem. C* **118**, 3629 (2014).
- [25] A. Ge, G. Kastlunger, J. Meng, P. Lindgren, J. Song, Q. Liu, A. Zaslavsky, T. Lian, and A. A. Peterson, On the coupling of electron transfer to proton transfer at electrified interfaces, *J. Am. Chem. Soc.* **142**, 11829 (2020).
- [26] Y.-C. Lam, A. V. Soudackov, and S. Hammes-Schiffer, Theory of electrochemical proton-coupled electron transfer in diabatic vibronic representation: Application to proton discharge on metal electrodes in alkaline solution, *J. Phys. Chem. C* **124**, 27309 (2020).
- [27] M. M. Melander, Grand canonical rate theory for electrochemical and electrocatalytic systems I: General formulation and proton-coupled electron transfer reactions, *J. Electrochem. Soc.* **167**, 116518 (2020).
- [28] L. D. Chen, M. Bajdich, J. M. P. Martinez, C. M. Krauter, J. A. Gauthier, E. A. Carter, A. C. Luntz, K. Chan, and J. K. Nørskov, Understanding the apparent fractional charge of protons in the aqueous electrochemical double layer, *Nat. Commun.* **9**, 3202 (2018).
- [29] P. Lindgren, G. Kastlunger, and A. A. Peterson, Scaled and dynamic optimizations of nudged elastic bands, *J. Chem. Theory Comput.* **15**, 5787 (2019).
- [30] S. Trasatti, The absolute electrode potential: An explanatory note (recommendations 1986), *J. Electroanal. Chem. Interfacial Electrochem.* **209**, 417 (1986).
- [31] J. E. Leffler, Parameters for the description of transition states, *Science* **117**, 340 (1953).
- [32] G. S. Hammond, A correlation of reaction rates, *J. Am. Chem. Soc.* **77**, 334 (1955).
- [33] P. Lindgren, G. Kastlunger, and A. A. Peterson, A challenge to the  $G \sim 0$  interpretation of hydrogen evolution, *ACS Catal.* **10**, 121 (2020).
- [34] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.131.238003> for a mathematical description of the curved scaling model as well as an associated python class, the derivation of Eq. (1), full barrier calculation results, the relationship between work function and excess electrons, and detailed methodology.
- [35] M. G. Evans and M. Polanyi, Inertia and driving force of chemical reactions, *Trans. Faraday Soc.* **34**, 11 (1938).
- [36] T. Bligaard, J. Nørskov, S. Dahl, J. Matthesen, C. Christensen, and J. Sehested, The Brønsted-Evans-Polanyi relation and the volcano curve in heterogeneous catalysis, *J. Catal.* **224**, 206 (2004).
- [37] S. Wang, V. Petzold, V. Tripkovic, J. Kleis, J. G. Howalt, E. Skúlason, E. M. Fernández, B. Hvolbæk, G. Jones, A. Toftelund, H. Falsig, M. Björketun, F. Studt, F. Abild-Pedersen, J. Rossmeisl, J. K. Nørskov, and T. Bligaard, Universal transition state scaling relations for (de)hydrogenation over transition metals, *Phys. Chem. Chem. Phys.* **13**, 20760 (2011).
- [38] S. Wang, B. Temel, J. Shen, G. Jones, L. C. Grabow, F. Studt, T. Bligaard, F. Abild-Pedersen, C. H. Christensen, and J. K. Nørskov, Universal Brønsted–Evans–Polanyi relations for C–C, C–O, C–N, N–O, N–N, and O–O dissociation reactions, *Catal. Lett.* **141**, 370 (2011).

- [39] J. E. Sutton and D. G. Vlachos, A theoretical and computational analysis of linear free energy relations for the estimation of activation energies, *ACS Catal.* **2**, 1624 (2012).
- [40] E. Rosta and A. Warshel, Origin of linear free energy relationships: Exploring the nature of the off-diagonal coupling elements in  $S_N2$  reactions, *J. Chem. Theory Comput.* **8**, 3574 (2012).
- [41] N. M. Hoffmann, X. Wang, and T. C. Berkelbach, Linear free energy relationships in electrostatic catalysis, *ACS Catal.* **12**, 8237 (2022).
- [42] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, and H. Jonsson, Origin of the overpotential for oxygen reduction at a fuel-cell cathode, *J. Phys. Chem. B* **108**, 17886 (2004).
- [43] A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, and J. K. Nørskov, How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels, *Energy Environ. Sci.* **3**, 1311 (2010).
- [44] K. Chan and J. K. Nørskov, Potential dependence of electrochemical barriers from *ab initio* calculations, *J. Phys. Chem. Lett.* **7**, 1686 (2016).
- [45] B. Hammer and J. K. Nørskov, Electronic factors determining the reactivity of metal surfaces, *Surface Sci.* **343**, 211 (1995).
- [46] F. Abild-Pedersen, J. Greeley, F. Studt, J. Rossmeisl, T. Munter, P. Moses, E. Skúlason, T. Bligaard, and J. Nørskov, Scaling properties of adsorption energies for hydrogen-containing molecules on transition-metal surfaces, *Phys. Rev. Lett.* **99**, 016105 (2007).
- [47] S. R. Kelly, H. H. Heenen, N. Govindarajan, K. Chan, and J. K. Nørskov, OH binding energy as a universal descriptor of the potential of zero charge on transition metal surfaces, *J. Phys. Chem. C* **126**, 5521 (2022).
- [48] H. B. Michaelson, The work function of the elements and its periodicity, *J. Appl. Phys.* **48**, 4729 (1977).
- [49] J. O. Bockris, Electrolytic polarisation—I. The overpotential of hydrogen on some less common metals at high current densities. influence of current density and time, *Trans. Faraday Soc.* **43**, 417 (1947).
- [50] B. E. Conway and J. O. Bockris, Electrolytic hydrogen evolution kinetics and its relation to the electronic and adsorptive properties of the metal, *J. Chem. Phys.* **26**, 532 (1957).
- [51] H. Kita, Periodic variation of exchange current density of hydrogen electrode reaction with atomic number and reaction mechanism, *J. Electrochem. Soc.* **113**, 1095 (1966).
- [52] S. Trasatti, Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions, *J. Electroanal. Chem. Interfacial Electrochem.* **39**, 163 (1972).
- [53] A. R. Zeradjanin, A. Vimalanandan, G. Polymeros, A. A. Topalov, K. J. J. Mayrhofer, and M. Rohwerder, Balanced work function as a driver for facile hydrogen evolution reaction—comprehension and experimental assessment of interfacial catalytic descriptor, *Phys. Chem. Chem. Phys.* **19**, 17019 (2017).
- [54] F. C. Østergaard, A. Bagger, and J. Rossmeisl, Predicting catalytic activity in hydrogen evolution reaction, *Curr. Opin. Electrochem.* **35**, 101037 (2022).
- [55] A. H. Shah, C. Wan, Y. Huang, and X. Duan, Toward molecular level understandings of hydrogen evolution reaction on platinum surface, *J. Phys. Chem. C* **127**, 12841 (2023).
- [56] M. T. Koper and R. A. van Santen, Electric field effects on CO and NO adsorption at the Pt(111) surface, *J. Electroanal. Chem.* **476**, 64 (1999).
- [57] M. P. Hyman and J. W. Medlin, Theoretical study of the adsorption and dissociation of oxygen on Pt(111) in the presence of homogeneous electric fields, *J. Phys. Chem. B* **109**, 6304 (2005).
- [58] G. S. Karlberg, J. Rossmeisl, and J. K. Nørskov, Estimations of electric field effects on the oxygen reduction reaction based on the density functional theory, *Phys. Chem. Chem. Phys.* **9**, 5158 (2007).
- [59] K. Chan, A few basic concepts in electrochemical carbon dioxide reduction, *Nat. Commun.* **11**, 5954 (2020).
- [60] S. Ringe, The importance of a charge transfer descriptor for screening potential  $CO_2$  reduction electrocatalysts, *Nat. Commun.* **14**, 2598 (2023).
- [61] A. Khorshidi, J. Violet, J. Hashemi, and A. A. Peterson, How strain can break the scaling relations of catalysis, *Nat. Catal.* **1**, 263 (2018).
- [62] C. Zeng, T. A. Maark, and A. A. Peterson, Strain in catalysis: Rationalizing material, adsorbate, and site susceptibilities to biaxial lattice strain, *J. Phys. Chem. C* **126**, 20892 (2022).
- [63] G. Kastlunger, P. Lindgren, and A. A. Peterson, Controlled-potential simulation of elementary electrochemical reactions: Proton discharge on metal surfaces, *J. Phys. Chem. C* **122**, 12771 (2018).
- [64] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, Real-space grid implementation of the projector augmented wave method, *Phys. Rev. B* **71**, 035109 (2005).
- [65] J. Enkovaara *et al.*, Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method, *J. Phys. Condens. Matter* **22**, 253202 (2010).
- [66] A. H. Larsen, M. Kuisma, J. Löfgren, Y. Pouillon, P. Erhart, and P. Hyldgaard, libvdwxc: A library for exchange–correlation functionals in the vdW-DF family, *Model. Simul. Mater. Sci. Eng.* **25**, 065004 (2017).
- [67] S. Schnur and A. Groß, Properties of metal–water interfaces studied from first principles, *New J. Phys.* **11**, 125003 (2009).
- [68] S. Sakong, K. Forster-Tonigold, and A. Groß, The structure of water at a pt(111) electrode and the potential of zero charge studied from first principles, *J. Chem. Phys.* **144**, 194701 (2016).
- [69] A. H. Larsen *et al.*, The atomic simulation environment—a python library for working with atoms, *J. Phys. Condens. Matter* **29**, 273002 (2017).
- [70] S. R. Bahn and K. W. Jacobsen, An object-oriented scripting interface to a legacy electronic structure code, *Comput. Sci. Eng.* **4**, 56 (2002).