

Microcalorimetric Determination of the Exchange Current Density and the Reaction Entropy of Fast Electrochemical Processes: Hydrogen Evolution on Pt

Marco Schönig* and Rolf Schuster*



Cite This: *J. Phys. Chem. C* 2024, 128, 14649–14653



Read Online

ACCESS |



Metrics & More

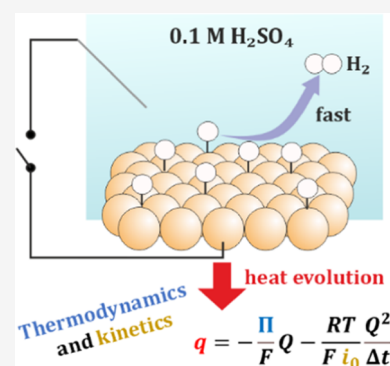


Article Recommendations



Supporting Information

ABSTRACT: A common way to benchmark catalysts is to perform a Tafel analysis on the current-overpotential relationship obtained by potential sweep methods and extract the exchange-current density. However, especially for fast reactions this analysis underestimates the reaction rate. In this contribution, we introduce an alternative way to determine the activation overpotential from the irreversible part of the heat exchanged during the electrode reaction, which was measured with electrochemical microcalorimetry (ECM). In addition, the reversible part of the exchanged heat allows access to the reaction entropy. We evaluate the proposed procedure using the fast hydrogen evolution at platinum in acidic solution as model reaction.



INTRODUCTION

The societal demand for energy storage solutions beyond fossil fuels or batteries drives research in electrocatalysis to develop pathways for storing electrical energy by chemical energy carriers. This demand encourages researchers to develop new and promising electrode materials. However, the diversity of these materials necessitates appropriate ways to determine their catalytic performance. For this purpose, several criteria are used in electrocatalysis research. Examples are the overpotential needed to reach a desired reaction current or vice versa the current density at a certain overpotential, the exchange current density obtained by Tafel analysis or the turnover frequency.^{1,2} While the determination of the turnover frequency might be the most meaningful way to classify the activity of a catalyst,³ it requires the quantification of active sites, which remains experimentally challenging. This leaves scientists with criteria that rely on the determination of the current-overpotential relationship. However, there are several obstacles accompanying experimental procedures to obtain this relationship, e.g., arbitrarily chosen benchmarking values,^{1,4} the questionable applicability of the underlying kinetic model⁵ or the deteriorating influence of mass transport on polarization curves.^{6–8} In general, the Tafel analysis of polarization curves constitutes the most common method, although in cases of fast reactions even at small overpotentials the concentration overpotential becomes dominant for longer current flow and at large overpotentials the current is limited by diffusion.^{9,10} Thus, for reversible reactions like the HER the mass-transport needs to be corrected properly by using the reversible Koutecký–Levich equation.¹¹ All those effects lead to an

inaccurate determination of the activation overpotential and thereby also to an underestimation of the rate constant.^{11–13}

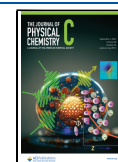
In this contribution we demonstrate an alternative method to obtain the current-overpotential relation and thus the activation overpotential of an electrochemical reaction by using electrochemical microcalorimetry (ECM). With this method, we measure the exchanged heat during a pulsed electrode reaction (typically 10 ms) by monitoring the temperature of a thin working electrode.¹⁴ The irreversible part of the exchanged heat is a direct measure of the deviation from thermodynamic equilibrium, that is, the overpotential. Due to the short current pulses and low conversions the concentration overpotential is kept small. As a consequence of our particular experimental setup, we are insensitive for the heat produced by the IR drop in solution, since this is produced along the millimeter long current path in the electrolyte. In contrast, during the short measurement period heat evolution is probed only up to a distance of about 100 μm from the electrode surface, because of the small thermal conductivity of the electrolyte solution.¹⁵ As model reaction we chose the well-researched HER on polycrystalline Pt in acidic solution. The first part of the paper explains the theoretical background and emphasizes how the activation

Received: June 4, 2024

Revised: August 8, 2024

Accepted: August 14, 2024

Published: August 23, 2024



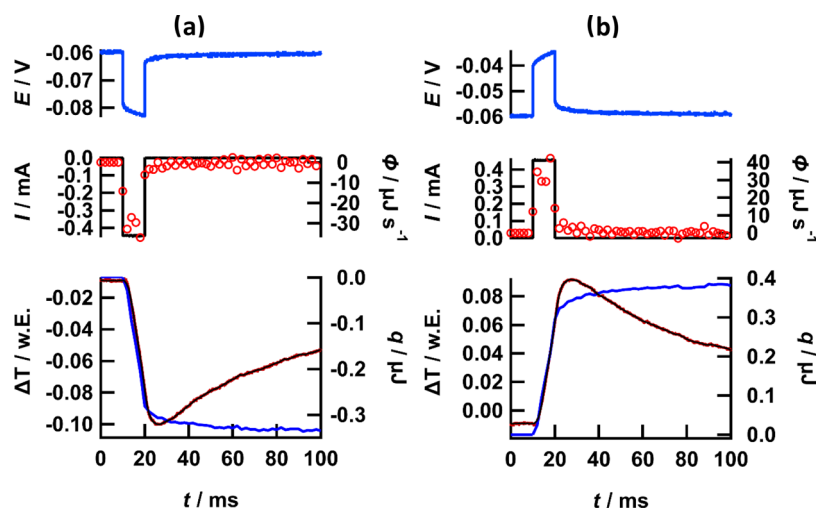


Figure 1. Potential E (blue, left axis), current I (black, left axis) and temperature ΔT (red line, left axis) transients, resulting from (a) a 10 ms, $-450 \mu\text{A}$ current pulse (left panel) and (b) a 10 ms, $+450 \mu\text{A}$ current pulse (right panel), starting at the open circuit conditions of a Pt foil in H_2 -saturated $0.1 \text{ M H}_2\text{SO}_4$. In addition, the heat flux (red circles, right axis) and the heat q (blue, right axis), obtained by deconvolution of the temperature transients, are given.

overpotential is obtained from the irreversible part of the exchanged heat.¹⁶ In the main part of the paper we will discuss the accuracy and limitations of the calorimetric procedure for the HER; first by an intrinsic comparison with results from an analysis of the electrochemical data based on the Butler–Volmer equation and second by a comparison of the obtained kinetic parameters with literature values.

THEORY

Following the remarks in refs 15,17 the exchanged heat δq at a single electrode during an electrochemical reaction, progressing by an infinitesimal extent of reaction $d\xi$, is corresponding to the sum of the reversibly exchanged Peltier heat $\Pi d\xi$ and an irreversible heat contribution, stemming from the application of the overpotential η necessary to drive the reaction

$$\delta q = \Pi d\xi - nF\eta d\xi \quad (1)$$

Thereby Π is the molar Peltier heat, n is the stoichiometric number of electrons involved in the electrode reaction and F is Faraday's constant. According to the thermodynamic conventions δq is negative when heat is transferred to the surrounding. By substituting the extent of reaction $d\xi$ with the charge dQ flowing during the pulse, $d\xi = \frac{-dQ}{nF} = \frac{-I dt}{nF}$, the exchanged heat can be referenced to moles of electrons flowing during the reaction. The reduction reaction corresponds to positive $d\xi$ and thereby negative current. In the case of small overpotentials η is linearly related to the electrochemical current I by the charge transfer resistance R_{CT} .⁹ Thus, substitution and integration of eq 1 at constant current over the duration of the current flow Δt yields¹⁶

$$q = -\frac{\Pi}{F}Q - R_{CT}\frac{Q^2}{\Delta t} \quad (2)$$

It is readily visible that by plotting the exchanged heat versus the charge and fitting the data with eq 2, the Peltier heat and the charge transfer resistance can be extracted.

The Peltier heat corresponds to the molar entropy change at the interface arising from the electrochemical reaction and the transport of ions and electrons across the border of the electrode

boundaries.¹⁷ This entropy change can be used to understand, e.g., charge-neutral side processes,¹⁸ solvation structure of reactants¹⁹ and the local environment of adsorbed species.²⁰

The charge transfer resistance on the other hand is directly correlated to the exchange current density j_0 . For example for an overall reaction obeying simple Butler–Volmer kinetics the exchange current density j_0 is given by^{9,12,21–23}

$$j_0 = \frac{RT}{FR_{ct}A} \quad (3)$$

where A is the unit area of the surface to which the current is referred to.

It is possible to deduce the same quantity j_0 using only the electrochemical data of the pulsed measurement by employing a Butler–Volmer type equation. The corresponding procedure will be discussed in detail in the Results and Discussion section.

EXPERIMENTAL SECTION

The experiments were carried out in a home-built calorimeter, described in detail, e.g., in ref 14 Thin platinum foils ($50 \mu\text{m}$, 99.99% Alfa Aesar Premion) were used as working electrode (WE) and mounted on top of a $25 \mu\text{m}$ LiTaO_3 pyroelectric crystal. Between the WE and the LiTaO_3 a $50 \mu\text{m}$ sapphire sheet was placed to avoid electrostriction. On top of the WE an electrochemical cell (Kel-F) was placed and sealed with a Viton O-Ring. The counter electrode (CE) was a 0.5 mm platinum wire (99.99%, Wieland Edelmetalle) and as reference electrode (RE) a palladium-hydride electrode, prepared from a 0.5 mm palladium wire (99.95%, Advent), was used.²⁴ The solutions were prepared from 96% sulfuric acid (Merck Suprapur) using ultrapure water (Milli-Q, $18.2 \text{ M}\Omega\cdot\text{cm}$). All materials and glassware were submerged in a 3:1 mixture of 96% sulfuric acid and 30% hydrogen peroxide and afterward boiled 3 times in ultrapure water prior to each experiment. The WE and CE were flame annealed before usage, while the RE was charged with hydrogen in $1 \text{ M H}_2\text{SO}_4$ at a current of 0.1 mA for at least 10 min. The electrolyte was purged with Ar for at least 20 min before it was transferred to the electrochemical cell under an Ar stream.

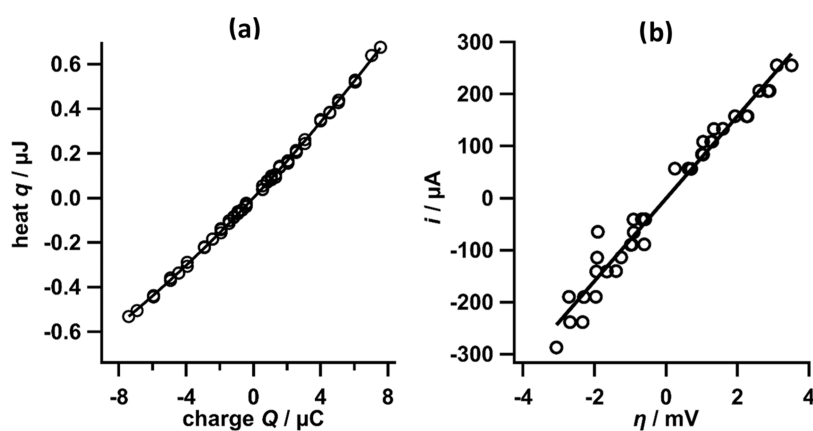


Figure 2. Determination of the charge-transfer resistance of the HER/HOR at a Pt foil in H_2 -saturated 0.1 M H_2SO_4 : (a) by fitting the total heat up to 100 ms (black circles) with eq 2 and (b) by fitting the micropolarization region (between -3 mV and $+3$ mV) obtained from the pulse measurements.

After assembling the electrochemical cell, the setup was closed with a brass lid and sealed with Viton O-rings to prevent oxygen contamination. Using a home-built potentiostat a cyclic voltammogram (CV) was recorded directly after completion of the assembly process to check for impurities and to determine the ECSA. Before the calorimetric measurements, the cell was saturated with hydrogen for at least 15 min at a current of around -1.3 mA. Afterward the cell was switched to open-circuit conditions, that is, no current was allowed to flow through the cell. All calorimetric measurements were started from open-circuit conditions and at the end of the pulse duration (typically 10 ms) the cell was switched back to open-circuit conditions. After the calorimetric measurements, the cell was filled with ultrapure water and the thermal response function of the electrode-sensor assembly was measured by illumination of the electrode surface 100 times with a 2 ms laser pulse.¹⁵ As final step, the electrolyte was exchanged with a 0.1 M $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ solution and calibrated²⁵ using the known Peltier heat of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction of -45.1 kJ mol⁻¹.²⁶

RESULTS AND DISCUSSION

Typical experimental transients of a calorimetric measurement in 0.1 M H_2SO_4 on Pt are shown in Figure 1 for the HER (1a) and hydrogen oxidation reaction (HOR, 1b). The left axis depicts the potential (blue, upper panel) and temperature transients (red, lower panel) originating from short 10 ms current pulses (black, mid panel) with an amplitude of ± 450 μA . During the HER reaction the temperature of the electrode falls almost linearly, while for the HOR it increases during the current pulses. After the current pulses the temperature is relaxing toward its starting values. The right axis shows the heat flux (red dots, mid panel), which is obtained from the temperature transient by disentangling it with the thermal response function of the electrode-sensor assembly as measured by pulsed laser illumination.¹⁵ In addition, the heat as obtained by integration of the heat flux is given (blue, lower panel). The applied current amplitude amounts to a conversion of around 10% of a monolayer with respect to the geometrical surface area of our cell (0.2 cm²). It is readily visible that upon switching off the current pulse at $t = 20$ ms the heat flux drops immediately. The sharp potential drop at the end of the current pulse, originates from switching off the IR-drop in the electrolyte.²⁷ Thus, the potential directly after the end of the current pulse corresponds to the actual overpotential during the 450 μA current pulse. It amounts to only around 7 mV. Although there is a small heat flux

persisting up to around 40 ms, most of the total heat ($>90\%$) is exchanged during the 10 ms of current flow. We attribute the small heat flux after the pulse to the discharge of the interfacial capacitance after stopping the external current flow. It may be quantitatively accounted for with exact knowledge of the interfacial capacitance.¹⁵

To account for the total exchanged heat q , necessary to determine the Peltier heat, the heat flux was integrated up to 100 ms. This quantity was obtained for a series of pulses with varying current amplitudes and is plotted as a function of the pulse charge Q in Figure 2a. Albeit small, the parabolic contribution caused by the irreversible heat in Figure 2a is clearly visible. Using eq 2 to fit the data in Figure 2a, we receive a Peltier heat of 7.9 kJ mol⁻¹ and a charge transfer resistance of about 11.6 Ω . While the charge transfer resistance is a well-defined experimentally accessible quantity, the assignment of an exchange current density j_0 depends on the detailed mechanistic model and the possibility to describe the current-overpotential relationship by a (generalized) Butler–Volmer equation.^{12,22,23} For the HER/HOR on Pt apparently simple Butler–Volmer behavior was found.^{12,21} Thus, from eq 3 at room temperature the measured charge-transfer resistance corresponds to an exchange current density of j_0 of 11.1 mA cm⁻² normalized to the geometrical surface area.

We repeated this procedure 5 times for 4 different cell assemblies. Within one cell assembly the statistical error of j_0 was typically below 15%. It should be noted that a prerequisite for eq 3 is that the reaction current ceases after the end of the current pulse. As mentioned above, in the present case discharging of the interfacial capacitance and thus heat evolution continues after the current pulse but contributes less than 10% to the total heat. Therefore, we refrain from correction for discharging of the interfacial capacitance, which in principle is possible.¹⁵ However, in cases where a significant interfacial capacitance is build-up during the reaction, e.g., by reaction intermediates due to a sluggish reaction step, this contribution needs to be accounted for.

The average Peltier heat amounts to 8.9 ± 1.2 kJ mol⁻¹. At room temperature this corresponds to a reaction entropy of 65.5 J mol⁻¹ K⁻¹ calculated by the procedure outlined in the ESI of ref 28 using the given concentration and a transport entropy of 35.8 J mol⁻¹ K⁻¹. The expected reaction entropy of the hydrogen evolution reaction can be calculated as outlined by Conway et al.,²⁹ and amounts to 67.7 J mol⁻¹ K⁻¹ in 0.1 M H_2SO_4 . Considering the general systematic error of the ECM method of

around $8 \text{ J mol}^{-1} \text{ K}^{-1}$,²⁵ the uncertainty of the calculated activities, and the eventual dependence of the individual Eastman entropies of transport on the activity,¹⁷ the measured and theoretically expected values agree perfectly. This underlines the general accuracy of the employed calorimetric method.

To conduct an analysis of the electrochemical data based on the Butler–Volmer equation at small overpotentials, in Figure 2b the pulse current is shown as a function of the overpotential. As already mentioned above only small activation overpotentials were necessary for achieving reasonable conversions for the calorimetric method. Consequently, only an analysis of the micropolarization region is possible. Such an analysis, based mainly on the linear part of the current-overpotential relation given by the Butler–Volmer equation was shown to yield similar results to the more-frequently used extrapolation of the Tafel slope.²² The overpotential depicted in Figure 2b was extracted from potential transients like the ones in Figure 1. Its value was evaluated directly after the pulse current was switched to zero. At this moment the IR drop in solution immediately drops to zero and the potential at the end of the pulse corresponds to the actual overpotential. In general, the overpotential is composed of activation and concentration overpotential. Nevertheless, since the reaction is probed with short pulses and thus small enough conversions, the concentration overpotential can be neglected.

By fitting simple Butler–Volmer type behavior to the linear relation between the current and the overpotential in Figure 2b, we obtained an exchange current density of $j_{0, \text{MP}} = 9.6 \text{ mA cm}^{-2}$, normalized to the geometrical surface area. This value is close to but slightly less than the result from the calorimetric procedure above. However, as it is clearly visible in Figure 1 the potential slightly increases during the 10 ms duration of the pulse, caused by a change in proton and H_2 surface concentrations. Thus, the overpotential after the pulse is slightly higher than the pure activation overpotential. This results in a lower slope of Figure 2b and thereby an underestimation of j_0 by the electrochemical method.

For comparison of our data with literature values, we determined the ECSA from the hydrogen adsorption/desorption charge measured by cyclic voltammetry (details are shown in the Supporting Information).

The j_0 values referenced to the ECSA obtained in this way by the calorimetric method in $0.1 \text{ M H}_2\text{SO}_4$ fall between 10 and 17 mA cm^{-2} . These values are around 1 order of magnitude higher than values typically obtained using a RDE ($\sim 1 \text{ mA cm}^{-2}$),^{12,30} but in good agreement to results when the mass-transport limit of the HER is properly accounted for ($\sim 20 \text{ mA cm}^{-2}$ without correction for the ECSA).¹¹ This shows that the proposed method indeed overcomes the mass-transport limitations in many studies using classical Tafel analysis on polarization curves.^{12,21} The obtained values are also in good agreement with the results from Bagotzky and Osetrova using a microelectrode to circumvent the mass-transport issues, who obtained values around $15\text{--}18 \text{ mA cm}^{-2}$ that are also one order magnitude higher than those obtained by conventional RDE.¹³

Nevertheless, the variation of our values between different cell assemblies is close to a factor of 1.5, although the data was corrected for the ECSA. Since the statistical error of the data within the same assembly was smaller than 15%, we concluded that this discrepancy is not caused by the presented method, but rather by the surface heterogeneity of the used samples.³¹ Accordingly, our results emphasize that the exchange current density is very sensitive to the real surface conditions and the

exchange current density needs to be taken with great care as an indicator for catalytic activity.

CONCLUSIONS

In this contribution we showed, how kinetic and thermodynamic information can be concomitantly obtained using ECM. By studying the well-investigated HER/HOR at platinum in acidic solution, we obtained reaction entropies, which agree very well with literature values. We were further able to access the overpotential, i.e., the deviation from thermodynamic equilibrium by determining the irreversible part of the heat exchanged during an electrochemical reaction. As this quantity is unaffected by IR-drop in solution and the ECM typically uses small conversions, we could extract the activation overpotential. From the activation overpotential we calculated the exchange current densities, which correspond well to those obtained by an analysis in the micropolarization region of the applied current pulses. The obtained exchange current densities are in good agreement with values obtained using microelectrodes and by accurate consideration of mass-transport. Our results are about an order of magnitude higher than those obtained by classical RDE analysis, which points to the short-comings of this analysis, when not accurately accounting for mass-transport. Thus, measuring the irreversibly exchanged heat of an electrochemical reaction by ECM provides an alternative method for the determination of the overpotential, which is particularly useful for fast electrocatalytic reactions. In principle also slow electrochemical processes may be studied by pulsed ECM, although the discrimination between reversibly and irreversibly exchanged heat contributions will become increasingly difficult due to the high applied overpotential. This might hamper the quantitative determination of the reaction entropy. However, useful mechanistic and kinetic information might be obtained by time-resolved measurements of the heat flux caused by the reaction. For example, from the time dependent heat flux during Na deposition from a battery type electrolyte, a slow chemical process step was inferred, probably slow desolvation of Na^+ while traversing the solid electrolyte interphase during the deposition process.³²

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.4c03723>.

Procedure to determine the electrochemically active surface area (PDF)

AUTHOR INFORMATION

Corresponding Authors

Marco Schönig – *Institute of Physical Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany; Leiden Institute of Chemistry, Leiden University, 2311EZ Leiden, Netherlands; orcid.org/0000-0002-4470-6705; Email: m.schonig@lic.leidenuniv.nl*

Rolf Schuster – *Institute of Physical Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany; orcid.org/0000-0003-3136-6403; Email: rolf.schuster@kit.edu*

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.jpcc.4c03723>

Author Contributions

M.S. conceptualization, data curation, formal analysis, methodology, investigation, visualization, writing—original draft; R.S. methodology, resources, supervision, validation, writing—original draft. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

M.S. and R.S. acknowledge funding from the Deutsche Forschungsgemeinschaft (SCHU 958/7-2). M.S. acknowledges funding from 2023 HORIZON-MSCA-PF program under grant agreement No 101147027.

REFERENCES

- (1) Anantharaj, S.; Kundu, S. Do the Evaluation Parameters Reflect Intrinsic Activity of Electrocatalysts in Electrochemical Water Splitting? *ACS Energy Lett.* **2019**, *4*, 1260–1264.
- (2) Voiry, D.; Chhowalla, M.; Gogotsi, Y.; Kotov, N. A.; Li, Y.; Penner, R. M.; Schaak, R. E.; Weiss, P. S. Best Practices for Reporting Electrocatalytic Performance of Nanomaterials. *ACS Nano* **2018**, *12*, 9635–9638.
- (3) Anantharaj, S.; Karthik, P. E.; Noda, S. The Significance of Properly Reporting Turnover Frequency in Electrocatalysis Research. *Angew. Chem., Int. Ed.* **2021**, *60*, 23051–23067.
- (4) Akbashev, A. R. Electrocatalysis Goes Nuts. *ACS Catal.* **2022**, *12*, 4296–4301.
- (5) Exner, K. S. Why the microkinetic modeling of experimental tafel plots requires knowledge of the reaction intermediate's binding energy. *Electrochem. Sci. Adv.* **2022**, *2*, No. e2100037.
- (6) Anantharaj, S.; Noda, S.; Driess, M.; Menezes, P. W. The Pitfalls of Using Potentiodynamic Polarization Curves for Tafel Analysis in Electrocatalytic Water Splitting. *ACS Energy Lett.* **2021**, *6*, 1607–1611.
- (7) Khadke, P.; Tichter, T.; Boettcher, T.; Muench, F.; Ensinger, W.; Roth, C. A simple and effective method for the accurate extraction of kinetic parameters using differential Tafel plots. *Sci. Rep.* **2021**, *11*, No. 8974.
- (8) Li, D.; Lin, C.; Batchelor-McAuley, C.; Chen, L.; Compton, R. G. Tafel analysis in practice. *J. Electroanal. Chem.* **2018**, *826*, 117–124.
- (9) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley, 2001.
- (10) Hansen, J. N.; Prats, H.; Toudahl, K. K.; Mørch Secher, N.; Chan, K.; Kibsgaard, J.; Chorkendorff, I. Is There Anything Better than Pt for HER? *ACS Energy Lett.* **2021**, *6*, 1175–1180.
- (11) Zheng, J.; Yan, Y.; Xu, B. Correcting the Hydrogen Diffusion Limitation in Rotating Disk Electrode Measurements of Hydrogen Evolution Reaction Kinetics. *J. Electrochem. Soc.* **2015**, *162*, F1470–F1481.
- (12) Sheng, W.; Gasteiger, H. A.; Shao-Horn, Y. Hydrogen Oxidation and Evolution Reaction Kinetics on Platinum: Acid vs Alkaline Electrolytes. *J. Electrochem. Soc.* **2010**, *157*, No. B1529.
- (13) Bagotzky, V. S.; Osetrova, N. V. Investigations of hydrogen ionization on platinum with the help of micro-electrodes. *J. Electroanal. Chem.* **1973**, *43*, 233–249.
- (14) Frittmann, S.; Halka, V.; Jaramillo, C.; Schuster, R. An improved sensor for electrochemical microcalorimetry, based on lithiumtantalate. *Rev. Sci. Instrum.* **2015**, *86*, No. 064102.
- (15) Bickel, K. R.; Etzel, K. D.; Halka, V.; Schuster, R. Microcalorimetric determination of heat changes caused by overpotential upon electrochemical Ag bulk deposition. *Electrochim. Acta* **2013**, *112*, 801–812.
- (16) Schönig, M.; Schuster, R. Sensitive and fast measurement of surface temperature with a thermogalvanic cell. *Appl. Phys. Lett.* **2020**, *116*, No. 091601.
- (17) Agar, J. N. Thermogalvanic Cells. In *Advances in Electrochemistry and Electrochemical Engineering*; Delahay, P., Ed.; Interscience Publishers: London, 1963; Vol. 3.
- (18) Frittmann, S.; Halka, V.; Schuster, R. Identification of Non-Faradaic Processes by Measurement of the Electrochemical Peltier Heat during the Silver Underpotential Deposition on Au(111). *Angew. Chem., Int. Ed.* **2016**, *55*, 4688–4691.
- (19) Karcher, F.; Uhl, M.; Geng, T.; Jacob, T.; Schuster, R. Entropic Contributions to Sodium Solvation and Solvent Stabilization upon Electrochemical Sodium Deposition from Diglyme and Propylene Carbonate Electrolytes. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202301253.
- (20) Botello, L. E.; Schönig, M.; Solla-Gullón, J.; Climent, V.; Feliu, J. M.; Schuster, R. Direct measurement of the hydrogen adsorption entropy on shape-controlled Pt nanoparticles using electrochemical microcalorimetry. *J. Mater. Chem. A* **2023**, *12*, 184–191.
- (21) Marković, N. M.; Grgur, B. N.; Ross, P. N. Temperature-Dependent Hydrogen Electrochemistry on Platinum Low-Index Single-Crystal Surfaces in Acid Solutions. *J. Phys. Chem. B* **1997**, *101*, 5405–5413.
- (22) Weber, D. J.; Janssen, M.; Oezaslan, M. Effect of Monovalent Cations on the HOR/HER Activity for Pt in Alkaline Environment. *J. Electrochem. Soc.* **2019**, *166*, F66–F73.
- (23) Shinagawa, T.; Garcia-Esparza, A. T.; Takane, K. Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion. *Sci. Rep.* **2015**, *5*, No. 13801.
- (24) Vasile, M. J.; Enke, C. G. The Preparation and Thermodynamic Properties of a Palladium-Hydrogen Electrode. *J. Electrochem. Soc.* **1965**, *112*, No. 865.
- (25) Etzel, K. D.; Bickel, K. R.; Schuster, R. A microcalorimeter for measuring heat effects of electrochemical reactions with submonolayer conversions. *Rev. Sci. Instrum.* **2010**, *81*, No. 034101.
- (26) Boudeville, P. Thermometric determination of electrochemical Peltier heat (thermal effect associated with electron transfer) of some redox couples. *Inorg. Chim. Acta* **1994**, *226*, 69–78.
- (27) Notoya, R.; Matsuda, A. Galvanostatic Transient Studies of Platinum Hydrogen Electrode: Application of Periodic Square Current Pulses. *J. Res. Inst. Catal., Hokkaido Univ.* **1967**, *15*, 247–255.
- (28) Schönig, M.; Frittmann, S.; Schuster, R. Identification of Electrochemically Adsorbed Species via Electrochemical Microcalorimetry: Sulfate Adsorption on Au(111). *ChemPhysChem* **2022**, *23*, No. e202200227.
- (29) Conway, B. E.; Angerstein-Kozłowska, H.; Sharp, W. B. A. Temperature and pressure effects on surface processes at noble metal electrodes. Part 1.—Entropy of chemisorption of H at Pt surfaces. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1373–1389.
- (30) Trasatti, S. Work function, electronegativity, and electrochemical behaviour of metals. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *39*, 163–184.
- (31) Alia, S. M.; Pivovar, B. S. Evaluating Hydrogen Evolution and Oxidation in Alkaline Media to Establish Baselines. *J. Electrochem. Soc.* **2018**, *165*, F441–F455.
- (32) Schäfer, D.; Hankins, K.; Allion, M.; Krewer, U.; Karcher, F.; Derr, L.; Schuster, R.; Maibach, J.; Mück, S.; Kramer, D.; Mönig, R.; Jeschull, F.; Daboss, S.; Philipp, T.; Neusser, G.; Romer, J.; Palanisamy, K.; Kranz, C.; Buchner, F.; Behm, R. J.; Ahmadian, A.; Kübel, C.; Mohammad, I.; Samoson, A.; Witter, R.; Smarsly, B.; Rohnke, M. Multiscale Investigation of Sodium-Ion Battery Anodes: Analytical Techniques and Applications. *Adv. Energy Mater.* **2024**, *14*, No. 2302830.