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An Algorithm for the Extraction of Tafel Slopes

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Abstract

The Tafel equation, which serves as a linearized representation of the Butler-Volmer expression, permits the extraction of fundamental parameters of electrochemical systems, such as exchange current densities and Tafel slopes. However, the application of these linear fitting procedures become problematic in the cases of experimental data featuring non-linearities in the Tafel ($\log(J)$ - V) response. This is especially troubling in low-overpotential regimes, where charge transfer kinetics generally dominate electrode behavior (as opposed to diffusion-limited currents at higher overpotentials) and linearization is expected to be most applicable. As a response to this complication, and the ad-hoc forms of fitting that may arise from it, this report outlines a systematic method for the determination of Tafel slopes through a rigorous, quantitative framework. The algorithm's performance is benchmarked using electrochemical measurements of well-characterized reactions for water splitting, hydrogen evolution and dioxygen reduction at iridium and platinum electrodes. As a final validation test, we show that the exchange currents extracted through this automated fitting procedure, used in conjunction with the Butler-Volmer model, are capable of reproducing the original electrochemical data in kinetically-controlled regimes.

Keywords: electrochemistry, Tafel, Butler-Volmer, electrokinetic, electrocatalysis

36 **Introduction**

37 Evaluation of electrocatalytic properties through the use of Tafel analysis has proven itself invaluable,
38 allowing for the determination of fundamental quantities such as exchange currents, charge transfer
39 resistances and perhaps most crucially, quantitative measurement of intrinsic catalyst activity through
40 the report of Tafel slopes. While measures such as catalyst mass activity are commonly used as
41 alternative methods for rating catalyst performance, the use of mass activity as a comparative metric
42 requires standardizing either the overpotential or current at which the current density used for mass
43 activity calculation is determined. Furthermore, specific and mass activities cannot ~~not~~ provide
44 information on more fundamental measures of catalyst behavior, such as the exchange current
45 density/interfacial electron transfer rates, charge transfer resistances or electrode mechanisms,
46 information that may be gained through the measurement of Tafel slopes. However, employ of the Tafel
47 method assumes sufficient linearity in the voltage/log(current) response to permit unambiguous fitting
48 to a linear equation^{1,2}. Clearly, this assumption is not universally valid, particularly for Tafel data
49 acquired over a broad range of potentials, where non-linearities in the log(current)-potential (log(J)-V)
50 response curves may become prominent³. In such cases, selection of a sufficiently narrow potential
51 window that may be approximated as linear is left to the discretion of the researcher. However, selection
52 of a sufficiently small interval will allow for the approximation of *any* region on a curve as linear,
53 resulting in a Tafel fit that may be dangerously arbitrary, with subsequently extracted Tafel slopes and
54 exchange currents potentially marking inaccurate representations of electrocatalyst activity^{1,2}. Here, a
55 systematic approach for conducting Tafel analysis that removes the need for qualitative guesswork in
56 selecting the proper fitting region, is described.

57 Current efforts to quantitatively determine Tafel slopes have largely fallen in the domain of
58 microkinetic analyses of electrochemical data, with kinetic models derived through application of a
59 suitable reaction mechanism (i.e., Volmer, Heyrovsky, Tafel, etc) being used to reproduce
60 voltammograms and corresponding Tafel plots. This effort has largely been motivated by an
61 understanding that the Butler-Volmer model is not a broadly-applicable descriptor of electrochemical
62 charge flows but rather, a particular description of electrode kinetics, valid only under a highly-
63 constrained set of conditions^{4,5}. In general, the more detailed microkinetic models require prior
64 knowledge of which mechanism dominates electrode kinetics to allow for their application, although
65 promising work by Kucernak and Zalitis yielded a generalized (Heyrovsky-Tafel-Volmer) kinetic model

66 that was demonstrated to converge to the Tafel-Volmer and Heyrovsky-Tafel mechanisms as particular
67 limiting cases⁴. However, such models often require knowledge or at least, intelligent estimates of,
68 electrode adsorbate surface coverages, values which are difficult to determine experimentally^{4,5}.

69 In an effort to circumvent these limiting aspects of microkinetic modeling, we sought a semi-
70 empirical approach towards the goal of reliably extracting Tafel parameters from experimental data. In
71 particular, we test the hypothesis that the proper electrochemical parameters for the best possible
72 microkinetic description of a system under study would be information implicitly contained in the
73 experimental electrochemical data. If accurate, this idea opens up the possibility of conducting Tafel fits
74 through the application of some physically-relevant set of constraints to the data itself. This theory
75 derives from an observation that many electrochemical kinetics models include rate constant
76 expressions acting as substitutions to the exchange current term (J_0) in the B-V model, while leaving the
77 general form of the B-V equation intact.^{4,5}. Such an observation suggested that a semi-empirical
78 approach, while not suited for reproducing entire J-V polarization and Tafel curves or yielding
79 information on adsorbate concentrations, may still permit the determination of some relevant
80 electrochemical parameters, particularly the Tafel slope. We outline the precise nature of these physical
81 constraints and the datasets on which they operate below. In addition, we emphasize this fitting strategy
82 as a tool for the quantitative extraction of experimental Tafel slopes, which may serve as a complement
83 to kinetic models of electrode polarization.

84 Verification of this approach is achieved by pairing the theory with experiment, as we test the
85 algorithm using experimentally acquired data of three different electrochemical reactions: platinum-
86 catalyzed hydrogen evolution (HER), iridium-catalyzed oxygen evolution (OER), and platinum-
87 catalyzed dioxygen reduction (ORR). For each of these cases, the algorithm predicts a Tafel slope
88 similar to those reported in long-established bodies of electrochemical literature. The ability of our
89 method to achieve this, despite the fact that each reaction we examine is distinct, and each may proceed
90 by a variety of unique mechanisms, strongly suggests the general applicability of this method for
91 determining electrocatalyst Tafel slopes.

92

93 **Fitting Methodology – Quantitative Framework**

94 Broadly, the approach employed consists of three critical parts. The first comprises the core of the
95 algorithm and involves expression of the exchange current density, J_0 – a quantity derived from a Tafel

fit – as a function of the differential $dJ/d\eta \sim \Delta J/\Delta\eta$, a value readily accessed by quantifying the slopes of linear sweep voltammograms (LSVs). The terms J and η are the electrode current and overpotential, respectively. The relationship between these terms is determined through Taylor expansion of the Butler-Volmer equation using the power series definition of the function $f(x) = e^x$; retention of the 0th and 1st order expansion terms give the following relation:

$$J(\eta) = J_0 \left[\left(1 + \frac{nF\eta\alpha}{RT} \right) - \left(1 - \frac{nF\eta(1-\alpha)}{RT} \right) \right] = J_0 \frac{nF\eta}{RT} \quad (1),$$

with differentiation of the R.H.S. of eq (1) with respect to η yielding:

$$\frac{dJ(\eta)}{d\eta} = J_0 \frac{nF}{RT} \quad (2a),$$

where R is the ideal gas constant (8.3145 J mol⁻¹ K⁻¹), F is Faraday's constant (96485 C mol⁻¹), J_0 is the exchange current density, n is the number of electrons transferred and T is the cell temperature (293 K). Using eq (2a), in concert with experimental Tafel and voltammetry data, the R.H.S. and L.H.S. of eq (2a) are determined independently for a range of overpotentials (the R.H.S. through standard Tafel fitting and the L.H.S. by taking the slopes of voltammograms with the aim of minimizing the absolute difference between the two sides of eq (2a). That is, the best fit is achieved for a quantity given by:

$$\min \left| \frac{dJ(\eta)}{d\eta} - J_0 \frac{nF}{RT} \right| \quad (2b).$$

We term this quantity the Tafel residue.

In this approach, an ideal Tafel fit results in the discovery of some overpotential region where the LSV slope (L.H.S., equation 2a) equals the R.H.S. of equation 2a, which is a function of the J_0 resulting from a Tafel slope measured over the same range of overpotentials as done for the LSV. In the ideal limit, this pair-wise fitting process yields total equality between the R.H.S. and L.H.S. of equation 2a, forcing the Tafel residue to zero, though in practice we find that even minimized residues almost always assume

123 non-zero, though small, values. Although this procedure significantly reduces the number of possible
 124 optimal fits for a given set of input parameters, its application alone is not enough to determine the
 125 proper region for determining Tafel slopes.

126

127

128

Figure 1.

A block diagram of the algorithm's process flow. Data inputs consist of a linear sweep voltammogram and a corresponding Tafel trace over the same range of overpotential values. User-defined overpotential windows and lower bounds for acceptable R^2 's set the operating parameters for the fitting method.

129 linearity of the region. The voltage width is referred to as the overpotential fit width, $d\eta$ hereon. It
 130 should be expected that a proper fit will not be a function of the width of the overpotential window size
 131 chosen for fitting, as this is a completely arbitrary parameter on which eq. (2a), unlike the case of
 132 residue minimization or R^2 constraints, has no explicit or implicit dependence. However, Tafel fitting
 133 may be viewed as the application of calculating function differentials, with the selection of a suitable
 134 overpotential region of a sufficiently small width, $d\eta$, enabling the approximation of the Tafel data in

the chosen region as linear. As a result, progressively shrinking $d\eta$ in this region should continue to yield similar linear fits (similar Tafel slopes). In other words, an additional criterion for a good Tafel fit should include a requirement that the measured Tafel slope will remain nearly constant over a range of voltage widths $d\eta$, if the proper overpotential region has been selected; good fits should be expected to span a wider range of $d\eta$ s than poor fits. This concept of $d\eta$ -span optimization forms the second aspect of the fitting algorithm and is illustrated in Figure 2.

Figure 2.

(Top, left) A depiction of Tafel fitting. Arbitrarily chosen regions 1 and 2 represent potential areas for conducting a linear fit. In each region, window sizes ($d\eta$) of 10, 20 and 40 mV are tested. In the case of region 1, fits with different overpotential widths result in disparate Tafel slopes. However, using the same fit widths in region 2 produce linear fits that yield very similar Tafel slopes. (Top, right) A depiction of $d\eta$ -span optimization. For region 2, the fits for $d\eta = 10, 20$ and 40 mV yield similar Tafel slopes (red bin); i.e., the Tafel slope of 60 spans the widest range of explored overpotential fit widths. Region 1 fits are not maximally spanning, suggesting this region is a poor candidate for fitting. Having found the optimal bin, the fit(s) within it exhibiting the highest R^2 are selected, indicating the optimal Tafel fit.

Both the linear response between the quantities $\log(J)$ and η assumed by the Tafel relation, and the fact that Tafel fits can be viewed as linear, differential elements of an overall Tafel curve, suggest the physical relevance of imposing linearity (R^2) constraints in the refinement of fits generated through Tafel residue minimization and subsequent $d\eta$ -span optimization procedures. Imposing requirements on R^2 for regions being tested for Tafel fitting help ensure that the regions under examination are indeed linear or near-linear, as demanded by the Tafel approximation, forming the third tier of this fitting

method. In the data examined here, minimum R^2 constraints between 0.900 and 1.000 are examined. As expected, fits conducted with successively stringent R^2 values approaching unity, following residue and $d\eta$ -span optimization, are shown to yield Tafel slopes that agree with literature values of well-characterized, electrode systems. This is verified through tests of the algorithm on platinum hydrogen evolution (HER), platinum oxygen reduction (ORR) and iridium water oxidation/oxygen evolution (OER) datasets.

Avoidance of user bias is managed through an algorithm that performs the initial step of residual minimization by recursively computing fits for a given range of $d\eta$ and R^2 values. Fits are first performed for a given $d\eta$ for all specified minimum R^2 thresholds, over all possible intervals in the dataset of width $d\eta$. The algorithm described here starts by exploring $d\eta$ s defined by the interval $[\eta_i, \eta_i + d\eta]$ for $i = 0$ to $l/(1/r)d\eta$, where η_0 is the point of zero overpotential, l is the length of the Tafel/LSV datasets and r is the voltage resolution of the acquisition. The process is then repeated for all $d\eta$ values specified by the user, over each R^2 threshold value. This systematic variation of R^2 and $d\eta$ parameters generates the set of residue-minimized fits. From this set, $d\eta$ -span optimization is then performed by conducting a search for the Tafel slopes computed in the residue-minimized set that span the largest number of unique overpotential fit widths. From this $d\eta$ -optimized subset, the fit(s) exhibiting the highest measured R^2 (s) are then selected. This member or members represent the fully optimized Tafel fit(s).

Handling Datasets with Diffusion-Limited Current

Even with the multi-tiered approach outlined above, for data collected at sufficiently high overpotentials, where LSVs often display current plateaus caused by diffusion-limited currents, equality may be observed between both sides of eq (2a), despite the fact that at high overpotentials, BV kinetics generally do not control electrode behavior. Given that the BV equation is really only a description of interfacial charge transfer at electrode donor/acceptor interfaces^{1,2}, deviation from this relation is commonly observed in cases where diffusion-limited effects are manifested. In such instances, stark deviations from the exponential current-potential scaling predicted by the BV equation are evidenced by current plateaus at high-overpotentials. Fitting such datasets properly, without having to arbitrarily truncate them in attempts to prevent accidental fitting of diffusion-limited regimes, requires a clear way of determining the point of transition between interfacial/surface-limited charge transfer and diffusion-

179 limited kinetics. In service of this goal, we leverage the observation that diffusion-limited
180 voltammograms are marked by changes in the curve's inflection during the transition from interfacial to
181 transport-limited kinetics. Precise determination of these inflection changes may therefore be found by
182 numerical differentiation of voltammetry data (dLSVs), with the exact inflection point manifested as a
183 local minimum or maximum in the dLSV dataset. Knowledge of the potential at which this transition
184 occurs provides the researcher with a useful threshold value, below which (low overpotentials) kinetics
185 are governed primarily by BV scaling relations and above which (high overpotentials), kinetics become
186 a partial or total function of diffusional (or other) effects. Given the assumptions implicit in the Tafel
187 equation, we know to use data in the low-overpotential regime to conduct fits according to relation (2b).
188 Finer points of this fitting procedure, such as the importance of dLSV analysis in preventing over-fitting
189 in diffusion-limited systems, and the use of R^2 thresholds for assuring sufficient linearity, are addressed
190 in the Discussion.

191

192 **Methods**

193 *Experimental*

194 Electrochemical characterization was performed in a typical, three-electrode, electrochemical glass cell.
195 An Ag/AgCl reference electrode, and Pt counter electrode were used in all experiments; all reference
196 potentials in this paper are corrected to the reversible hydrogen electrode (RHE) scale. The electrolyte
197 used was 0.1 M HClO₄ (Sigma Aldrich), and a Biologic potentiostat was used for electrochemical
198 measurements alongside a Pine rotator. Pt supported on vulkan carbon (46 wt% Pt, TKK) and
199 unsupported IrO_x (TKK) were used as electrocatalysts for HER, ORR and OER, respectively^{6,7}. The
200 procedure and ink formulations developed by NREL were used to prepare and deposit the
201 electrocatalyst inks onto 5 mm glassy carbon disks^{6,7}. The electrodes were immersed, without potential
202 control, into a solution saturated with Ar for initial break in and measurement of CVs. Subsequently, the
203 solution was exchanged and saturated with H₂ for HER/HOR measurements and O₂ for ORR
204 measurements, under potential control (0.05 V vs RHE). For Pt and Ir measurements, the respective
205 break in procedures were used^{6,7}. The sweep rate for CVs were 50 mV sec⁻¹, while for potentiodynamic
206 (HOR, HER, ORR, OER) measurements the sweep rates were 10 mV sec⁻¹ at a rotation rate of 1600
207 rpm. Potentiodynamic and potentiostatic experiments were obtained with iR compensation typically 18-
208 20 Ohms. Each experiment was measured in triplicate (Supporting Information, S1).

209

210

211 *Computational*

212 Tafel traces were generated through logarithmic transforms of linear sweep voltammetry data. Tafel
213 fitting, slope extraction and data visualization were performed using custom scripts composed in the
214 Python programming language with Scipy, Pandas, Matplotlib and Numpy libraries. Least squares
215 fitting of dLSV data were conducted with the `numpy.poly1d` and `numpy.polyfit` routines using a 15th-
216 order polynomial. Data inputs for the main fitting procedure consisted of a three column chart
217 containing the overpotentials in column 0, electrode current (LSV) in column 1, and the logarithm of
218 the electrode current (Tafel trace) in column 2. Fitting was performed one Tafel branch at a time,
219 starting from the point of zero overpotential to the end of the (anodic or cathodic) current series. For the
220 datasets used in this study, overpotential windows of 10-50 mV widths in 1 mV increments, along with
221 overpotential windows of 1-10 mV with 1 mV increments, were tested. For each overpotential window
222 tested, R^2 values were varied from 0.900 and 1.000, and tested with a step increment (ΔR^2) of 0.001.
223 Prior to fitting, all datasets were converted to the relevant overpotential scale. For slope optimization
224 and extraction, generated fits were grouped by their Tafel slopes (binned) in 1-10 mV decade⁻¹
225 increments, to inspect any effect that bin size had on the determined Tafel slope. Success of this
226 algorithm was measured by benchmarking its prediction of Tafel slopes against the known literature
227 values for the Pt-catalyzed, hydrogen evolution reaction (HER), Pt-catalyzed oxygen reduction reaction
228 (ORR) and Ir-catalyzed oxygen evolution (OER).

229

230 *Interpreting the Program Output*

231 For each fit test conducted during the program recursion, a chart consisting of the residue-minimized
232 fits satisfying both the overpotential fit width ($d\eta$) and R^2 constraints provided by the user, is generated.
233 A plot is also generated for each residue-minimized fit that is found for a particular $d\eta$ - R^2 pair
234 (Supporting Information, S2). From this set, a secondary chart reporting the relevant parameters for the
235 optimal fit (fit with the lowest Tafel residue). Repeating this process for all user-defined $d\eta$ and R^2 values
236 results in a master chart, which tabulates the entire set of residue-optimized Tafel fits generated from
237 every compliant (yielding a fit) $d\eta/R^2$ test performed during program recursion (Figure 3).

238 The residue-optimized fits contained in the master chart are then used to generated the primary
239 visual output, consisting of 6 subplots. The top three subplots (1, 2 & 3) display the dependence of the
240 raw, extracted Tafel slopes on the magnitude of $d\eta$ used for fitting, R^2 of the Tafel fit, and the
241 overpotential value (η_o) marking the lower-bound of the overpotential interval defining a particular fit
242 (the position of the fit on the Tafel curve defined by the interval $[\eta_o, \eta_o + d\eta]$). In the top three subplots,
243 color bars are used to indicate the number of times the automated procedure yields a particular fit
244 (measured in counts).

245 The lower three subplots (4, 5 & 6) illustrate the result of refining these residue-minimized fits,
246 with the colormap in the 6th subplot summarizing the optimal Tafel fit (red dot) and its position on the
247 Tafel curve, defined through its x,y coordinate. Refinement is achieved by the sequential application of
248 $d\eta$ spanning and R^2 constraints, which are conducted on the generated set of Tafel residue-minimized
249 fits. The $d\eta$ -span of a Tafel slope is illustrated in subplots 1&4, marked by the number of *unique* values
250 of overpotential fit widths that yield some particular Tafel slope; a fit that yields the same Tafel value for
251 multiple overpotential fit widths (e.g., $d\eta=10, 15, 20, 25$ mV etc.) is preferred over a Tafel slope that
252 simply occurs at a single or few overpotential fit width(s), even if the slope has several counts at that
253 single overpotential fit width. As described earlier, this condition arises naturally from the definition of
254 a curve differential, where the best approximation of a function's derivative occurs in the differential
255 limit of $d\eta \rightarrow 0$. In practice, the process generally yields Tafel slopes that are close, but not exactly
256 the same value. As a result, it is necessary to group (bin) similar Tafel slopes together to enable
257 determination of the Tafel fit that maximally-spans the range of $d\eta$ s that were explored by the user. In
258 general, binning size should be kept as small as possible, so that bin values are as close to the individual
259 Tafel slopes they contain, minimizing any distortion to the original (unbinned) set of residue-minimized
260 data. Given the 1 mV voltage fit resolution used for these studies and the fact that Tafel slope accuracies
261 are typically meaningful to within ± 10 mV decade⁻¹, bin sizes no larger than 10 mV decade⁻¹ were
262 tested. We are able to show that, while binning can result in significant losses in data resolution, even
263 binning sizes large as 10 mV decade⁻¹ are shown, in almost all cases explored, to yield consistent values
264 of the Tafel slope that agree with both lower-binning tolerances (1-3 mV decade⁻¹) and literature-
265 reported values of the reactions examined. Tafel slopes that are $d\eta$ -span-optimized are highlighted in
266 cyan circles in subplots 4, 5 and 6. Optimization of the R^2 parameter is conducted following $d\eta$ -span

optimization, as described earlier. The fully optimized (Tafel residue, $d\eta$ -span and R^2) fits are plotted as red circles in subplots 4, 5 and 6.

Results

Iridium Oxygen Evolution Reaction (OER) Benchmarking

In the case of data acquired for iridium catalysts functioning in water oxidation, this method predicts a Tafel slope of 62 mV decade⁻¹ for a bin tolerance of 1 mV decade⁻¹. These results agree well with reported Tafel slopes of 59-64 mV decade⁻¹ reported in studies of iridium oxygen evolution catalysts^{5,8-17}. Exploring binning at sizes large as 10 mV decade⁻¹ does not significantly alter the extracted Tafel slope (Supporting Information, S5) in most cases. However, as the residue-minimized dataset gets distorted by increased binning, a spurious Tafel value can be observed for an 8 mV decade⁻¹ bin size (Tafel slope = 24 mV decade⁻¹; Supporting Information, S5), illustrating the potential limitations of over-binning. Despite this potential for binning to warp results, we still find that an average of extracted Tafel slopes for bin sizes between 1 and 10 mV decade⁻¹ (done at 1 mV decade⁻¹ increments; 10 independent fits) yields 60±12 mV decade⁻¹ for Ir-catalyzed water oxidation. Omission of the outlier at the 8 mV bin size yields an average slope of 64±3 mV, a small standard deviation demonstrating that user binning choice, while arbitrary, may only marginally impact the extracted Tafel slope, even over this broad range of bin sizes tested for the analysis of Ir OER anodes. While smaller bin sizes should improve accuracy of this fitting procedure, it is generally advisable to check that similar Tafel slopes are found for various bin sizes.

For the fully optimized fit, the overpotential region between 52 and 99 mV is found to yield this optimal fit. Furthermore, this region exhibits good linearity, with an R^2 of 0.993 being found for the Tafel plot and an $R^2=0.977$ resulting for the LSV in this overpotential region (the minimum R^2 threshold during program recursion was 0.977 for this fit). The fitting procedure displays a distinct sensitivity to the linearity threshold, with significantly different slopes occurring with variations to the R^2 parameter (Figure 4, subplots 2 and 5). As a measure of linear correlation, the R^2 should be expected to strongly influence the values yielded by the fitting process, even when Tafel residues are minimized, as the Tafel

297 approximation is a linearization of electrode current-overpotential response. We should therefore expect
298 that proper Tafel fits should exhibit high degrees of linearity (high R^2). Furthermore, these results
299 confirm our expectation that, while arbitrary, the range of potentials should not cause the extracted Tafel
300 slope to vary significantly (so long as the chosen fitting range is not so wide that it is appreciably non-
301 linear). This is evidenced by the observed convergence of various fits where the region size varied
302 between 10 and 49 mV in width, to a common Tafel slope value of 62 mV decade⁻¹.

303

Figure 3.

Tafel fitting results for Ir OER. Fits were conducted by varying R^2 lower bounds between 0.900 and 1.000 at overpotential fit widths between 10-50 mV in 1 mV increments; $n=1$. Data in lower subplots binned at 1 mV decade⁻¹. Fully optimized fit (red dot in subplots 4, 5 and 6) reveal an optimal Tafel fit of 62 mV decade⁻¹ for this sample. The optimal region for fitting is found to lie between 52 and 99 mV overpotential ($dV=47$ mV), inclusive. This region displays a high degree of linearity (minimum R^2 threshold = 0.977; measured Tafel R^2 = 0.993, LSV R^2 = 0.977 result for the fully-optimized fit). Raw input LSV and Tafel data are shown in the bottom panel; optimized fit shown as black line in Tafel subplot.

Platinum Hydrogen Evolution Reaction (HER) Benchmarking

Automated fitting of Pt-catalyzed, proton reduction (2500 rpm electrode rotation) predicts a Tafel slope of -30 mV decade⁻¹ for a bin tolerance of 1 mV decade⁻¹ (Figure 5). This -30 mV decade⁻¹ slope is consistent with the Tafel mechanism and for that has been widely reported for low-overpotential,

311 platinum hydrogen evolution in acid, conditions similar to those used in this study^{5,18–22}. This lies in
312 contrast to the slopes of -40 and -120 mV decade⁻¹ theoretically expected for the respective cases of
313 Heyrovsky and Volmer mechanisms of hydrogen evolution. Lower rotation speeds of 1600 and 900 rpm
314 resulted in predicted Tafel slopes of -33 and -43 mV decade⁻¹ respectively (Supporting Information, S6).
315 This trend suggests a progressive deviation from the Tafel mechanism towards the Heyrovsky
316 mechanism at lower angular velocities, where reactant (proton) diffusion becomes more apparent⁵. In
317 the case of Pt HER, changes to binning size are found to influence the optimized Tafel slope even less
318 than in the case of Ir OER, with an average extracted Tafel slope of -30 ± 0.2 mV decade⁻¹ resulting for
319 HER on Pt cathodes, for bin sizes between 1 and 10 mV decade⁻¹ (done at 1 mV decade⁻¹ increments;
320 10 independent fits total). Again, the small standard deviation observed, despite the broad range of bin
321 sizes tested, illustrate the minor influence of binning choice on the extracted Tafel slope. For the fully
322 optimized fit, the region between -14 and -24 mV overpotential is found to yield this optimal fit.
323 Furthermore, this region exhibits good linearity in both the Tafel plot ($R^2 = 0.988$) and LSV ($R^2 =$
324 0.985) in the overpotential region yielding these results (the minimum R^2 threshold during program
325 recursion was 0.985 for this fit).

Figure 4.

Tafel fitting results for Pt HER shown (2500 rpm). Fits were conducted by varying R² lower bounds between 0.900 and 1.000 at overpotential fit widths between 10-50 mV in 1 mV increments; $n=1$. Data in lower subplots are binned at 1 mV decade⁻¹. Fully optimized fit (red dot in subplots 4, 5 and 6) reveal an optimal Tafel fit of 30 mV decade⁻¹ for this sample. The optimal region for fitting is found to lie between -14 and -24 mV overpotential (dV=10 mV). Selection of this region demonstrates occurs for an R² threshold = 0.985. Actual measured Tafel R² = 0.988; an LSV R² = 0.985 results for the optimized fit in this overpotential window. Raw input LSV and Tafel data are shown in the bottom panel; optimized fit shown as black line in Tafel subplot.

342 Figure 5 shows the results of fitting Pt-catalyzed dioxygen reduction (ORR) using this procedure. In
 343 Figure 6, the derivative linear sweep voltammogram for this electrode process reveals a distinct local
 344 maximum, corresponding to the onset of transport-limited effects at higher overpotentials. A least-
 345 squares fit was conducted to determine the local maximum of the calculated dLSV, yielding a value of -
 346 413 mV. Using the $\eta \leq -413$ mV region as an exclusion cutoff, Tafel fitting was then conducted over
 347 the range $-413 \leq \eta \leq 0$. After selection of the regions where ORR is under kinetic (rather than
 348 diffusion-limited) control, application of the fitting procedure predicts a Tafel slope of $-119 \text{ mV decade}^{-1}$
 349 ¹ for a bin tolerance of 1 mV decade^{-1} (Figure 5). Notably, program recursion yields fits 40 unique
 350 overpotential intervals (of widths ranging from 10 to 49 mV), falling in the region between -364 and -
 351 413 mV overpotential. Again, this result demonstrates the expectation that rigorous fits in the proper
 352 region should exhibit a constant or near-constant slope, as the magnitude of the differential, $d\eta$, varies.
 353 Changes to binning size are found to influence the optimized Tafel slope to some degree, however, the
 354 effect remains negligible, with an average of extracted Tafel slope of $-120 \pm 2 \text{ mV decade}^{-1}$ for bin sizes
 355 between 1 and $10 \text{ mV decade}^{-1}$ (1 mV increments used for a total of 10 independent fits). These
 356 numbers compare favorably to literature-reported values for platinum ORR^{7,23–25}, which are typically
 357 estimated to lie around $-120 \text{ mV decade}^{-1}$. The small standard deviation observed, despite the broad
 358 range of bin sizes tested, illustrate the minor influence of binning choice on the extracted Tafel slope.
 359 Furthermore, this overpotential region exhibits high degrees of linearity in both the Tafel ($R^2 = 0.995$)
 360 and LSV data ($R^2 = 0.997$), when the program's recursion reaches an R^2 threshold of 0.995. The mixing
 361 of mass-transport effects with kinetically-controlled electrode processes in the case of ORR were
 362 further explored by investigating any dependence of the extracted Tafel slope on electrode rotation rate.
 363 For this purpose, additional RDE angular velocities of 900 and 1600 rpm were examined (Supporting
 364 Information, S6). Fits of these data result in Tafel slopes that increase with rotation rate, with mixing at
 365 900 and 1600 rpm yielding respective slopes of 93 and $111 \text{ mV decade}^{-1}$. Notably, rotation at the three
 366 speeds tested show a steady trend approaching the commonly reported value of $-120 \text{ mV decade}^{-1}$ for
 367 oxygen reduction on platinum, as diffusional effects are dampened through increased rotation^{5,23}. These
 368 results suggest that our approach for determining the kinetically-controlled regime of the electrode
 369 through inspection of the derivative LSV is indeed effective, permitting the deconvolution of diffusion
 370 limitations that would typically complicate manual Tafel fitting. While in this study, the low-
 371 overpotential diffusion effects seen in ORR were managed by employing higher electrode rotation rates,

372 it should also be possible to use this method in fitting data featuring diffusion-limited currents after the
 373 application of Koutecky-Levich corrections to the input polarization curves²⁶.

Figure 5.

Tafel fitting results for ORR at a Pt rotating disk electrode (2500 rpm data shown). Fits were conducted by varying R^2 thresholds from 0.900 to 1.000 at overpotential fit widths between 10-50 mV in 1 mV increments. Data in shown the lower subplots are binned at 1 mV decade⁻¹; $n=1$. Fully optimized fit (red dot in subplots 4, 5 and 6) reveal an optimal Tafel fit of 119 mV decade⁻¹ for this sample. The optimal region includes fits falling in the -364 to -413 mV overpotential region (optimal Tafel slope found for $d\eta=10-49$ mV). Selection of this region occurs for an R^2 threshold = 0.995. Actual measured Tafel R^2 = 0.995; an LSV R^2 = 0.997 results for the optimized fit in this overpotential window. Raw input LSV and Tafel data are shown in the bottom panel; optimized fit shown as black line in Tafel subplot.

Figure 6.

(Top): The inflection change in the polarization response (red dot) is a result of an electrode current that transitions from being controlled by interfacial (B-V) kinetics where the curve is concave (-) at low overpotentials ($\eta \geq -413$ mV) to O_2 diffusion control at higher overpotentials ($\eta \leq -413$ mV), where the curve is convex (+). As the B-V Equation is a description of charge transfer kinetics at a substrate-electrode interface, the information given by the dLSV is essential, indicated which regions should be included (low overpotentials) and excluded (high overpotentials) from fitting.

(Bottom): The 1st derivative linear sweep voltammogram (dLSV) for Pt ORR at 2500 rpm indicates the precise point of the curve's transition between diffusion and kinetic regimes, manifested here as a local maximum at -413 mV. A polynomial fit (red line, 15th-order shown) of the dLSV data is used to determine the dLSV peak position (red line).

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391 *Modeling J-V Response at Low Overpotentials*

392 As a final check of fit accuracy, attempts were made to reproduce our experimental LSV and Tafel data
 393 by using the exchange currents generated from our Tafel fits as inputs to the B-V equation^{1,27}:
 394

$$395 \quad J(\eta) = J_0 \left[\exp\left(\frac{nF\eta\alpha}{RT}\right) - \exp\left(-\frac{nF\eta(1-\alpha)}{RT}\right) \right] \quad (3).$$

396

397 Proper fits should be able to reproduce the exponential current-potential relationship described by B-V
 398 kinetics in the low-current, low-overpotential regimes, where mass-transport limitations do not
 399 significantly influence the electrode response. Application of the exchange currents determined by this
 400 fitting methodology to the B-V model, are shown to reproduce our Ir OER ($i_0 = 95 \mu\text{A}$) and Pt ORR (i_0
 401 $= 187 \text{ nA}$) data (Figure 7) for $T=293 \text{ K}$. The transfer coefficient (α) is commonly assumed to be 0.5 but
 402 may assume any value between 0 and 1^{1,2,28}, however its actual value is unknown in our particular cases.
 403 We therefore treated α as an adjustable parameter in efforts to model our experimental data. In the case
 404 of OER, $\alpha=0.97$; an $\alpha=0.49$ is found to provide the best agreement between modeled and experimental
 405 ORR curves. The B-V description of charge transfer was insufficient for modeling platinum-catalyzed
 406 proton reduction using the measured HER exchange current ($285 \mu\text{A}$), even though the fit process
 407 extracted Tafel slopes that agree well with literature precedent. Such a finding is consistent with
 408 established work detailing the inadequacy of the B-V treatment in modeling Pt-catalyzed hydrogen
 409 evolution^{4,5,29}. While we have been able to use the B-V equation to reproduce our original data here, it
 410 must be emphasized that in many cases, this model will not be sufficient for predicting polarization
 411 behavior, as a result of its assumption of a constant transfer coefficient, potential-independent exchange
 412 current and exclusion of mass-transport effects^{1,2,4,5,24,30,31}.

413 This approach may be viewed as a complement to techniques such as those developed by
 414 Compton et al., where models of entire polarization curves (both the kinetic and diffusion-limited
 415 regions) are produced through analytical descriptions that effectively combine the B-V formalism with a
 416 substrate diffusion model³⁰.

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Figure 7.

(Top Panels) Left: The predicted experimental LSV for Ir-catalyzed OER using the exchange current ($i_0=95$ μA) generated from automated Tafel fitting (binned at 1 mV decade⁻¹) applied to the B-V model (blue). Measured OER data in black. Other B-V input parameters used to generate the modeled curve include temperature ($T=293\text{K}$), and number of electrons transferred at the electrode surface ($n = 1$). The transmission coefficient (α) is treated as a fit parameter and set at 0.95. Right: Tafel curve modeled using the B-V equation. Non-ideal behavior at low overpotentials results in deviations between the predicted and experimental curves. However, overlap between the two is observed in the region (bounded by dotted lines) used for Tafel fitting.

(Bottom Panels) Left: Predicted experimental LSV for Pt-catalyzed ORR using the exchange current in blue ($i_0 = 187$ nA, $T=293\text{K}$, $n=1$, fitting binned at 1 mV). In the low-overpotential region where Tafel analysis is relevant, using the i_0 derived from fitting as an input to the B-V model is sufficient for reproducing the J-V response. The α term is treated as a fitting parameter and set at 0.51. As predicted by analysis of the differential LSV, deviation of the predicted LSV from the acquired data occurs at overpotentials beyond -0.413 mV (dotted line), as diffusion effects start to impede electrode kinetics. Right: The predicted Tafel curve displays overlap with the experimental data in the fit region (dotted lines) calculated by the algorithm, despite diffusional and non-ideal deviations at high and low overpotentials.

428 Discussion

429 *Fit Optimization*

430 Although residue minimization alone is not sufficient for determining Tafel slopes, the procedure is
431 responsible for paring down the universe of total possible fits by several orders of magnitude. In general,
432 the maximum number of possible fits (T) for a user-specified range of R^2 s and j $d\eta$ s is given by eq (4):

$$433 \quad T = \frac{R_f^2 - R_i^2}{\Delta[R^2]} \sum_j l - \left(\frac{1}{r}\right) d\eta_j \quad (4),$$

435 where $R_{i,f}^2$ are the respective initial and final R^2 bounds that set the range, $[R_i^2, R_f^2]$, of linearity
436 thresholds to be tested by the user; $\Delta[R^2]$ is the R^2 increment used during fitting, l is the length (number
437 of points) of the dataset and r is the resolution at which the data were acquired, in volts; $d\eta_j$ is the j^{th}
438 overpotential fit width in the range $[d\eta_o, d\eta_i]$ set by the user. As an example, in the particular case of
439 fitting of our OER data, where R^2 thresholds were varied between 0.900 and 1.000 in 0.001 increments,
440 and overpotential fit widths were varied between 10 and 50 mV in 1 mV increments, the number of
441 possible fits is found to total 354900 during the program recursion (of these potential fits, 316309 of
442 them yielded actual fits to the data). Application of the residue minimization procedure alone, reduces
443 these 354900 possibilities to 3535 potential fits, prior to $d\eta$ and R^2 optimizations. Considering this
444 dramatic reduction to the space of potential fits, it is clear that Tafel residue minimization is a key
445 feature of this fitting algorithm, serving an outsize role in the extraction of Tafel slopes using this
446 approach. Continued processing over the set of residue-minimized fits through $d\eta$ -span optimization is
447 generally found to reduce the set of fits by up to two orders of magnitude. The final step of fitting, R^2
448 optimization, usually occurs over a minimal set of fits (~ 10 -100) and is typically able to reduce the
449 original set of fits down to a single Tafel slope.

451 While initially, it may seem that the best Tafel fit might be that occurring with the greatest
452 frequency for a given set of input parameters, we find this is not the case. Slope selection using mere
453 frequency (counts) as a criterion generally results in spurious values for the Tafel slope, evidenced by
454 comparing the fits with the highest numbers of counts in the plots for the catalysts studied, with the
455 actual known value of the catalysts Tafel slope.

Although the manner in which we automate $d\eta$ -span and R^2 optimizations only allow for unique solutions to the Tafel slope, we also recognize that possibility that multiple distinct Tafel regimes may exist for a given dataset, such as in the cases of CO₂ reduction cathodes, where multiple products may be produced, and so multiple Tafel slopes may exist^{5,32}. To address such possibilities, we note that visualizing the space of residue-minimized fits by inspecting trends in the Tafel slope vs $d\eta$ (subplots (1) & (4) in figures 3, 4, and 5) yields useful information on whether multiple slope regimes are likely to be present. Specifically, such cases would be manifest in subplots (1) & (4) as multiple distinct areas where the $d\eta$ span is the maximized. Having determined these regimes and the overpotentials over which they can be found, the user may then break up the dataset accordingly and proceed with R^2 optimizations separately for each segment. Similarly, the original input data could be divided in a similar manner, and the entire fitting procedure applied to each individual segment. As an example of this, we note that, while the algorithm tested here was designed to seek out a single Tafel slope, our ORR data contains two very obvious regimes where a large number of compliant fits span a broad range of overpotential fit widths (a ~ -90 to -150 decade⁻¹ region and a ~ -10 to -50 mV decade⁻¹ Tafel region, Figure 5). Performing $d\eta$ -span and R^2 optimizations on the residue-minimized data for our 2500 rpm ORR curve in the -10 to -50 mV decade⁻¹ region, reveals an optimal Tafel slope of 42 mV decade⁻¹, in a lower overpotential region than the 120 mV decade⁻¹ slope that is extracted overall (Supporting Information, S7). This agrees with previous work, which has reported the possibility of observing a low-overpotential, 40 mV decade⁻¹ Tafel slope, along with a 120 mV decade⁻¹ slope at higher overpotentials, in ORR⁵.

Advancing Algorithm Performance

As noted earlier, the approach taken here has largely been predicated on the idea that complex microkinetic models commonly act as modifiers to the exchange current, while retaining the general form of the B-V equation, and that this composition of functions allows us to treat the measured exchange current density as an implicit function of some unknown microkinetic model and its associated parameters. Such an outlook implies that in the most generalized case, where the exchange current is potential-dependent, $J_0 \rightarrow J_0(\eta)$. In this case, derivation of the Tafel residue starting from eq (1) yields a generalized form given by:

$$\min \left| \frac{dJ(\eta)}{d\eta} - \frac{nF}{RT} (J_0(\eta) + \eta \frac{dJ_0(\eta)}{d\eta}) \right| \quad (5),$$

which reduces to the particular residue case explored by this manuscript where $dJ_0/d\eta = 0$ (expression 2b). While not used here, the application of such a residue may improve the algorithm's accuracy, as it factors in the possibility of a potential-dependent exchange current, as suggested by several kinetics studies. However, our ability to automate the Tafel fitting process using the simplified residue in (2b) as opposed to its general form, while successfully extracting slope values for well-characterized reactions, suggests that (at least in the cases of our HER, OER, and ORR benchmarks) the differential exchange term in expression (5) is small, permitting the use of eq. (2b) as a reasonable approximation of the generalized residue in slope calculations.

Sensitivity to User Input – Binning, R^2 Thresholds, and Overpotential Fit Widths ($d\eta$ s)

Given that the motivations for developing this algorithm were rooted in a desire to conduct Tafel fitting in a manner that is not susceptible to user bias, it is necessary to consider any changes that arbitrary selection of R^2 thresholds or overpotential windows can have on the resulting fit. While it is apparent, from subplots 1 and 2 of Figures 3, 4 and 5, that the set of residue-minimized Tafel slopes show a weak dependence on the size of the overpotential window (subplot 1) and a strong dependence on the fit linearity (subplot 2), the algorithm's behavior clearly illustrates that performing recursive fits over a range of both R^2 thresholds and overpotential window sizes is enough to remove the opportunities for this type of user bias. For this reason, inputs provided by the user must span a range of overpotential window sizes and R^2 values. Bracketing R^2 thresholds between 0.9 and 1.0 with sufficiently small ($\Delta R^2 \leq 0.01$) are found to be more than sufficient to ensure that the user input does not skew fit results. Attempts to conduct fitting with low R^2 small thresholds yield fit results that deviate substantially from literature reports, a reflection on the crucial role played by linearity thresholds in this fit procedure. For example, fitting Ir OER data using relaxed minimum R^2 thresholds between 0.500 and 0.600 ($\Delta R^2 = 0.001$) yielded a Tafel slope of 19 mV decade⁻¹ (binning=1 mV decade⁻¹), a value far from the 62 mV decade⁻¹ slope extracted when a high degree of linearity (threshold $R^2 = 0.900$ -1.000) is enforced on the fit process (Supporting Information, S3).

514 In the case of overpotential fit widths, tests using randomly-selected overpotential fit widths
515 ranging from either 1-10 mV in 1 mV increments or 10-50 mV at 1 mV increments, were found to yield
516 the same Tafel slope, illustrating that fit results are not readily influenced by user-defined overpotential
517 windows. As a result, it is clear that with this approach, the user-defined input parameters do not
518 significantly affect fitting results, and that the measured fit is primarily influenced by the datasets on
519 which the algorithm operates (Supporting Information, S4).

520 The assignment of fits with particular Tafel slopes to a narrow range of Tafel slopes – a Tafel
521 slope “bin” – is essential to the execution of $d\eta$ -span optimization, and represents a potential
522 opportunity for user input to bias the fitting results. For this reason, binning must be performed with
523 care. As a rule, the dataset produced from residue minimization should be altered as little as possible
524 during the binning process. This points to the use of bins that are small as possible. As a general rule,
525 bin sizes cannot be smaller than the voltage resolution of the input data, and should be no larger than 10
526 mV decade⁻¹, as the error associated with Tafel fits typically limits any meaningful accuracy of
527 experimental Tafel slopes to within ± 10 mV decade⁻¹. Excessive binning results in significant data
528 distortion, causing subplots (1) & (4) to deviate from each other significantly; ideally, these should look
529 similar (the case of narrower binning). As a general rule of thumb, if the general shape of subplots (1)
530 & (4) change significantly, the binning width is too broad and should be reduced. However, we note that
531 even over a wide range of bin sizes (1-10 mV decade⁻¹) we extract optimized fits that fall well within the
532 range of literature-reported Tafel slopes for each of the reactions tests here, showing that this method is
533 even robust to moderate data distortions (Supporting Information, S5). Applying such binning criteria
534 to our test data yield Tafel slopes at bin values of 1-10 mV decade⁻¹ that are similar in all cases. The
535 greatest deviation observed was in the OER dataset, where a bin value of 8 mV yielded a fully-
536 optimized fit of 24 mV decade⁻¹ (Supporting Information, S5). A good practice may include the
537 averaging of Tafel slopes for bin values between 1 and 10 mV decade⁻¹. Whether using small bin values
538 or considering the average over a range of bin sizes, binning operations should be reported when using
539 this fitting method, to ensure reproducibility by other researchers.

540

541 **Conclusions**

542 The difficulty of reliably fitting Tafel data where the semi-logarithmic current/potential response
543 contains pronounced curvatures, demands a refined method for extracting electrochemical parameters

544 free of researcher bias. While earlier work successfully implemented the minimization of Tafel residuals
545 to manually fit and reproduce data from metalloenzyme ORR cathodes^{33,34}, that process marked the
546 protoform of the strategy outlined in this manuscript, omitting the additional constraints needed to
547 automate Tafel parameter extraction with high fidelity. A comprehensive fitting methodology has been
548 outlined here and successfully applied to canonical datasets for platinum HER, ORR, and iridium OER,
549 with recursive, pair-wise fitting of experimental Tafel and LSV data being used to determine the
550 optimum regions for conducting linear Tafel analysis. Notably, while this fitting procedure is essentially
551 an optimization problem, we have been able to ground each step of the optimization itself in a physical
552 understanding of the Butler-Volmer equation and its linearized form, rather than simply being the result
553 of empirical observations that were found to yield Tafel slopes in agreement with literature values.
554 Furthermore, the limited scope of user input largely eliminates the danger that Tafel fitting becomes a
555 subjective exercise, mitigating the potential for researcher bias influencing the fit process.

556 The method outlined here employs a definition of the Tafel residue that only invokes the use of
557 0th and 1st order Taylor-expanded terms of the B-V equation. The algorithm's scope has been limited to
558 these early terms for two critical reasons. First, since Tafel fitting is the process of drawing linear fits to
559 Tafel data, it makes physical sense to only use the linear (0th and 1st order) terms of the Taylor-expanded
560 Tafel equation. In addition, while a possible improvement on this algorithm may include the definition
561 of a Tafel residue that incorporates 2nd or even 3rd -order expansion terms (i.e., η^2 , η^3) that could permit
562 the fitting of non-linear functions to the full curvature of experimental Tafel plots, doing this first
563 requires the provision of a solid, physical basis for using these terms. However, it is presently unclear
564 whether such non-idealities are actually caused by partial contributions of quadratic and/or cubic
565 dependencies of the current differential on the electrode overpotential. In fact, work on this subject has
566 demonstrated that Tafel curvatures may find root in any number of causes, including potential-
567 dependent exchange currents (unlike the constant exchange term assumed by the traditional B-V model),
568 and potential-dependent symmetry factors^{3,4,30,35}. Such ambiguities must be resolved before attempting
569 to employ these higher order terms in a generalized fit process related to what we've outlined here, as
570 failure to do so increases the likelihood of over-fitting Tafel data. However, if a rigorous physical
571 justification can be found to justify the use of quadratic or cubic expansion terms, the application of
572 non-linear regressions to fit experimental Tafel data may indeed enhance the performance of the fitting
573 procedure even beyond the capabilities of this first generation algorithm.

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579 **Supporting Information**

580 Raw data collected for this study, complete fitted datasets are available free of charge, for use and
581 modification as needed, in the Supporting Information. Python codes for automated Tafel fitting can be
582 found at http://github.com/MEG-LBNL/Tafel_Fitter.

583

584 **Author Contributions**

585 P.A. conceived and developed the Tafel fitting methodology described here, wrote the fitting software
586 and performed the data analysis. N.D. acquired the experimental voltammetry data used for algorithm
587 validation in this paper.

588

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