

Polarization Curves Demystified

by **Thomas A. Zawodzinski**

It is occasionally the case that certain types of work produce results that seem completely obvious in hindsight. A common example of a case where this effect is observed is for papers that provide a synthesis of several ideas. The elegance, simplicity, and power of such analyses, while critical to the consolidation of scientific ideas, leads us to forget the state of confusion or piecemeal understanding that existed prior to their elaboration. Such works also open the door to revisionist interpretations that champion certain of the contributors in the “piecemeal phase.” Stern and Geary’s

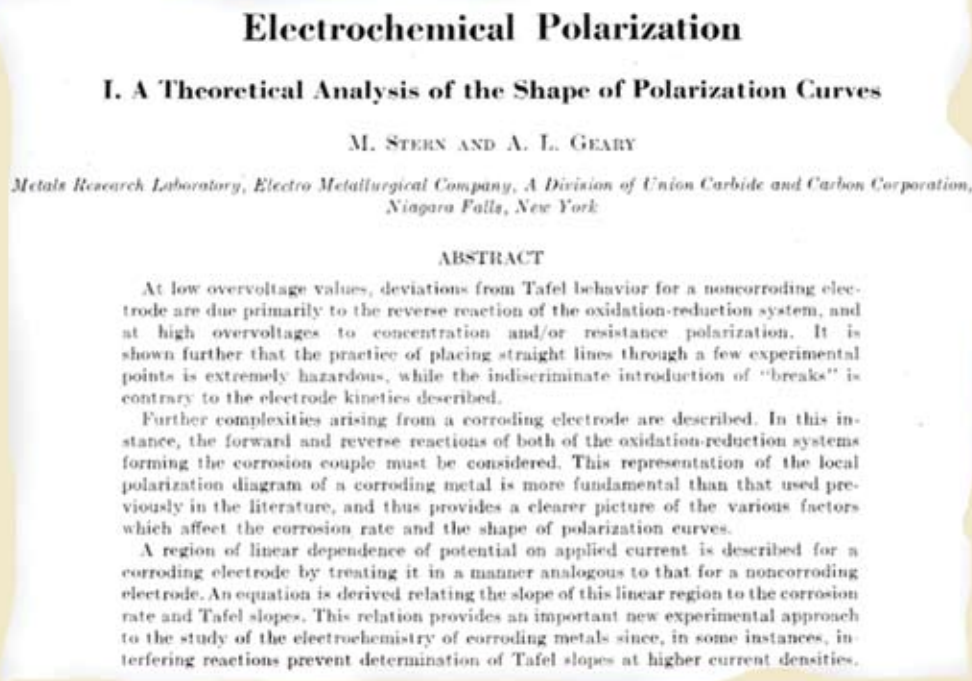
Once again, this work has formed a significant portion of the background presumed in all dissections of the electrochemical processes studied by polarization measurements.

Context and Content of the Paper

As evident from the discussion in the Stern-Geary paper, common practice in the analysis of polarization curves up to the late 1950s among most electrochemists included linearization of the curves or of portions of the curves, the assumption that

FROM:

M. Stern and L. Geary, “The Shape of Electrochemical Polarization Curves,” *JES*, **104**, 56 (1957).



paper (citation given in the illustration) is one such piece of work. Several notions that even beginning electrochemists are aware of today (and take for granted) were synthesized in this work to produce a description of the shape of the polarization curve. These notions include (1.) the superposition of anodic and cathodic currents under certain polarization conditions; (2.) the smooth transitioning and overlap between polarization losses arising from various sources; and (3.) the identification of the series of mechanistic contributions from kinetics, concentration polarization and mass transfer losses, and IR losses with specific regions of the observable curves.

In this “Perspective,” we will present an overview of the context and content of the paper and explore some of the broad implications of this work across electrochemistry. The paper has been especially influential in corrosion circles but the primary discussion—of the underlying processes occurring in various regions of an electrochemical polarization curve—is relevant to fuel cell research, metal deposition, and other areas.

sharp “breaks” occurred in the polarization curve and a general lack of clarity with respect to the processes determining the observed shape of the curve.

Many papers published in the 1950s focused on analyzing polarization in terms of abrupt changes in slope of the overvoltage-log *I* plot. Examples cited by Stern and Geary include papers by Logan,¹ Schwerdtfeger and McDorman,² and Johnson and Babb.³ Various theoretical concepts were used to justify the existence and analysis of these supposed “breaks.” As we shall see, Stern and Geary showed that such breaks were really smooth transitions. They took their cue from the experimental data provided by Parsons⁴ and by Bockris and Conway,⁵ considering dual mechanisms and the pH dependence of reactions, respectively. These studies clearly indicated smooth transitions.

Stern and Geary discuss the behavior of non-corroding and corroding electrodes. The initial discussion of non-corroding systems provides a foil for highlighting distinctive features of the corroding electrode.

Non-corroding Electrodes

This section of the paper develops and analyzes a specific example describing the effects of kinetics, IR-drop and concentration polarization, and mass transfer limitations on the shape of the polarization curve for the simple case of a redox reaction at a non-corroded reaction. The goals of this section would appear to be twofold: (1.) to illustrate conditions under which the polarization curve can be analyzed to reliably extract kinetic parameters in the face of other losses and possible simultaneous contributions of both anodic and cathodic branches of the reaction; and (2.) to set up a corresponding and contrasting analysis of observed polarization in corroding systems once the authors have presented the effects of different loss mechanisms for the simple case.

The approach taken is to calculate a series of polarization curves, in Tafel (overvoltage vs. log i) format, using a basic set of parameters, adding phenomena to successive calculations. First, Butler-Volmer kinetics are used to determine the shape of the curve at low polarization. Both anodic and cathodic branches are explicitly included in the calculation. The authors show that one branch rapidly dominates the observed curve as the overpotential is increased. Concentration polarization effects (also commonly referred to as mass transfer limitations in present-day parlance) are then introduced, producing marked curvature in the overvoltage vs. log i plot at high currents. Introducing ohmic losses further exacerbates this deviation. The authors use their calculated curves to clearly define conditions under which accurate analyses of kinetics can be derived, using as criteria the isolation of a single branch of the redox reaction and, at high overvoltage, the onset of concentration polarization effects.

A key point is succinctly made in the following remark, "Note here again that it is not only a simple matter to draw a break in this curve but that there is considerable latitude in the choice of the break position." Thus Stern and Geary demolish the analysis of "breaks" in the curve, indicating the arbitrary nature of identification of breaks as well as showing that the polarization curve naturally exhibits transitions in the curve. Occam's razor indeed!

Corroding Electrodes

This section is responsible for the status of this article as a classic of corrosion literature. The authors proceed to extend the analysis to a corroding system, positing the existence of two simultaneous reactions, the redox reaction discussed above and a metal corrosion reaction. The analysis of the kinetics proceeds by adding the rates of the two reactions and by noting that at the corrosion potential the anodic and cathodic currents must be equal. Frankel has provided a simplified version of this analysis, reproduced below with minor changes.⁶

Our starting point is the Tafel equation

$$i = i_0 \exp(\eta/b) \quad (1)$$

where i_0 is the exchange current density, $\eta = E - E_{\text{rev}}$, b is the Tafel slope, and $b' = b/2.3$. Consider the case of metal M dissolving in acid. The Tafel equations for the anodic and cathodic reactions occurring at a mixed potential (for instance, metal dissolution and hydrogen evolution at the corrosion potential) are given by

$$i_a = i_{0,a} \exp\left(\frac{E - E_a^{\text{rev}}}{b'_a}\right) \quad (2)$$

$$|i_c| = i_{0,c} \exp\left(\frac{E_c^{\text{rev}} - E}{|b'_c|}\right) \quad (3)$$

The net current that would be measured by a potentiostat during a polarization experiment is then given by

$$i_{\text{net}} = i_a - |i_c| = i_{0,a} \exp\left(\frac{E - E_a^{\text{rev}}}{b'_a}\right) - i_{0,c} \exp\left(\frac{E_c^{\text{rev}} - E}{|b'_c|}\right) \quad (4)$$

But at $E = E_{\text{corr}}$, $i_a = |i_c| = i_{\text{corr}}$

$$i_{\text{corr}} = i_{0,a} \exp\left(\frac{E_{\text{corr}} - E_a^{\text{rev}}}{b'_a}\right) = i_{0,c} \exp\left(\frac{E_c^{\text{rev}} - E_{\text{corr}}}{|b'_c|}\right) \quad (5)$$

Solving for $i_{0,a}$ and $i_{0,c}$ and substituting into Eq. 4

$$\begin{aligned} i_{\text{net}} &= i_{\text{corr}} \left[\exp\left(\frac{E - E_{\text{corr}}}{b'_a}\right) - \exp\left(\frac{E - E_{\text{corr}}}{b'_c}\right) \right] \\ &= i_{\text{corr}} \left[10^{\left(\frac{E - E_{\text{corr}}}{b_a}\right)} - 10^{\left(\frac{E - E_{\text{corr}}}{b_c}\right)} \right] \end{aligned} \quad (6)$$

Eq. 6 is identical in form to the Butler-Volmer equation but replaces the standard potential with the corrosion potential, shifting the reference current to i_{corr} instead of i_0 .

A non-linear least-squares fit of this equation to the experimental data provides values of E_{corr} , i_{corr} , b_a , and b_c with the assumption that perfect Tafel behavior is observed for both the anodic and cathodic reactions, and that the extrapolations of the Tafel portions of the curves both intersect at the corrosion potential. This is one of the most utilized approaches for determination of corrosion rate.

A further step in the analysis given by Stern and Geary considers the case of small deviations from the corrosion potential. Then, the exponentials in Eq. 6 can be linearized

$$\exp\left(\frac{2.3(E - E_{\text{corr}})}{b}\right) \cong 1 + \frac{2.3dE}{b} \quad (7)$$

For small differences in potential from E_{corr} , dE , the measured net currents will be small, and can be considered to be di. Substituting into Eq. 6

$$di = 2.3i_{\text{corr}} dE \left(\frac{1}{b_a} + \frac{1}{|b_c|} \right) \quad (8)$$

Polarization resistance, R_p , can be defined as the slope of the linear polarization curve at the corrosion potential

$$R_p \equiv \frac{dE}{di} \Big|_{E=E_{\text{corr}}} \quad (9)$$

Rearranging Eq. 8, what is now known as the Stern-Geary Equation² is generated

$$i_{\text{corr}} = \frac{b_a |b_c|}{(b_a + |b_c|) 2.3 R_p} \quad (10)$$

This expression shows that the corrosion rate can be determined by a small polarization from the corrosion potential, unlike Tafel extrapolation, which requires large potential changes from the corrosion potential.

Thus, Stern and Geary provide the machinery for two analysis approaches to corrosion rates via fits to Eq. 6 for the full curve and via linearized expressions (Eq. 10) for the low current range.

Concluding Remarks

This paper provided, via a clear-cut analysis, a succinct and well-defined synthesis of ideas concerning the shape of the polarization curve, with the added practical benefits of practical criteria for accurate analysis and means of separating various phenomena occurring simultaneously under the surface of the polarization curve.

It is perhaps fitting to conclude this appreciation of their contribution by quoting Stern and Geary at length, from their conclusion, to illustrate their clear-eyed apprehension of what they had presented:

This analysis has illustrated several important concepts which are worth listing for emphasis.

1. The representation of a corroding metal by polarization diagrams should be extended to include the reverse reaction of the various oxidation reduction systems which are operative.
2. Deviations from Tafel behavior may be caused by local action currents, concentration polarization, and IR drop effects, and by a change in the predominant electrode reaction.
3. An experimental polarization curve may show a linear dependence of potential on applied current for small amounts of polarization.
4. An equation has been derived which relates the slope of the linear region of a polarization measurement to the corrosion rate and the Tafel slopes. This equation will prove valuable (!) when interfering reactions prevent the determination of the Tafel constants at higher currents.
5. The shape of the experimental electrochemical polarization curve, either cathodic or anodic, can be analyzed if sufficient data are obtained to permit an accurate description of the curve. Placing straight lines through four or five experimental points is hazardous, while the indiscriminate introduction of "breaks" is contrary to modern electrochemical concepts. Sufficient information concerning the system should be available to estimate whether concentration polarization or resistance drop effects have been included in the measurements.

The authors then go on to promise a study of these principles in action in experimental studies. The electrochemical world has continued this program ever since. ■

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About the Author

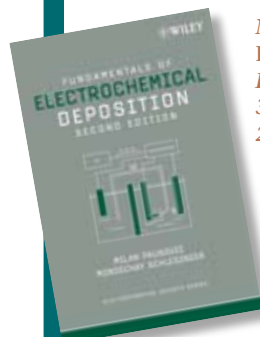
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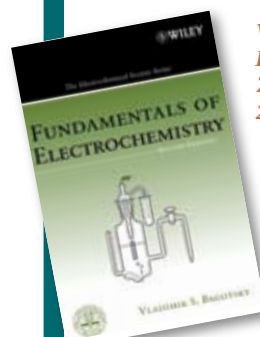
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