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Determination of kinetic parameters from a new quadratic approximation of the Butler-Volmer equation

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ABSTRACT

The determination of the parameters of the Butler-Volmer equation is a typical nonlinear parameter fitting task. Linear approximations are feasible at high and very low polarizations. However, in both cases the intermediate (transition) potential range, carrying probably the most valuable information on the exchange or corrosion current of an electrochemical system, remains out of scope. The linearization of the Butler-Volmer equation in this intermediate potential range, enabling the determination of both the polarization resistance and the Tafel slopes, can provide a powerful evaluation tool in electrochemical kinetic studies. A simple, robust and accurate method to meet this challenge is proposed, linear in the Tafel slopes and quadratic in the polarization, providing all practical advantages of the linearized systems. The performance of the new model is tested on simulated and experimental data.

1. Introduction

The Butler-Volmer equation is the most basic equation of electrochemical kinetics, establishing the relation between the current density and polarization [1–6]. In corrosion studies it is generally applied in a rather empirical form given by Eq. (1):

$$j = j_{\mathrm{corr}}\left(\exp\frac{\eta}{b_{\mathrm{a}}} - \exp\frac{-\eta}{b_{\mathrm{c}}}\right). \tag{1}$$

Here b_{a} and b_{c} are the so-called anodic and cathodic Tafel constants or Tafel slopes, j_{corr} is the corrosion current and η denotes the polarization, i.e., the difference between the actual electrode potential and the corrosion potential[1]. If $\eta \gg b_{\mathrm{a}}$ or $\eta \ll -b_{\mathrm{c}}$ and, consequently, one of the exponential terms is negligible compared to the other one, then Eq. (1) is transformed into the anodic and cathodic Tafel equations respectively:

$$\ln j = \ln j_{\mathrm{corr}} + \frac{\eta}{b_{\mathrm{a}}} \tag{2a}$$

$$\ln(-j) = \ln j_{\mathrm{corr}} - \frac{\eta}{b_{\mathrm{c}}} \tag{2b}$$

Eqs. (2a) and (2b) are linear in the kinetic parameters $\ln j_{\mathrm{corr}}$, $1/b_{\mathrm{a}}$ and $1/b_{\mathrm{c}}$ and are, therefore, very simply applicable for determining these parameters. It has to be noted that in practice the Tafel slopes are frequently replaced by the decadic Tafel slopes $b_{\mathrm{a},10}$ and $b_{\mathrm{c},10}$ which are defined as $b_{\mathrm{a},10} = b_{\mathrm{a}} \ln 10$ and $b_{\mathrm{c},10} = b_{\mathrm{c}} \ln 10$. With these substitutions, the natural logarithm in Eqs. (2a) and (2b) is replaced with the 10-based logarithm. However, the conditions of their validity restrict their application to the range of relatively high polarization levels where the mechanism of the corrosion process can significantly differ from that established around the corrosion potential.

The reason of the successful application of Eq. (1) for corrosion systems in many cases is that the (surface) concentration relations during anodic and, especially, during cathodic polarization of typical structural steels in typical aqueous solutions exhibits a less significant variability and therefore the agreement between the equation and the measurement data can be much better.

Eq. (1) is found valid for a vast number of corrosion systems with an adequate precision (at least to the practical requirements of determining the corrosion rate) and is therefore widely used in the corrosion research and industrial practice, in spite of the numerous difficulties arising in the process of the application. Theoretically, Eq. (1) cannot be linearized in the form shown here comprising two exponential terms, and the determination of the parameters requires a nonlinear parameter fitting procedure if the linearization at higher polarisation is not applicable (i.e., because the system does not exhibit a Tafel-like behavior at higher polarization). The practical application

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[1] [1] Throughout in this paper, we discuss corrosion systems specifically, and therefore mention *polarization* instead of *overvoltage* and *corrosion current* instead of *exchange current*, but the statements are valid, of course, for all electrochemical systems that obey the Butler-Volmer equation.

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of nonlinear methods has numerous problems and drawbacks, but in this paper we mention only two of them. First, nonlinear parameter fitting requires good initial values and if it does not succeed to find adequately close initial values then the whole fitting procedure may go wrong. For the second, in most cases there is a strong correlation between the parameters. Certainly, if the measurement data were free from any random error or systematic error caused by the approximations in the model, then the nonlinear fitting procedure would return the unbiased, undistorted values of the parameters. However, owing to the correlations between the parameters, the random and systematic errors result in the appearance of local minima of the target function and causes an ambiguity of the determined parameters. These well-known problems of the nonlinear fitting, along with the required relatively complicated mathematical and software apparatus, leads the scientific and engineering community to the search of linear transformations, which are more robust in performance and simpler in application.

Alternatively to Eqs. (2a) and (2b), another plausible linearization process of Eq. (1) results in the determination of the polarization resistance R_p by means of the serial expansion of the exponential terms and omitting the second- and higher order members [6,7]:

$$\frac{1}{R_p} = \frac{dj}{d\eta}\bigg|_{\eta=0} = j_{corr}\left(\frac{1}{b_a}+\frac{1}{b_c}\right). \tag{3}$$

Note that the signs of b_a and b_c are equal.

Eq. (3) and the concept of the polarization resistance has a great practical importance; the industrial application of the LPR (Linear Polarization Resistance) corrosion monitoring method is an important and useful tool in assessing fast changes in the corrosion rate which facilitates identification of factors influencing the corrosion rate. However, it is much more problematic to assess the absolute rate of corrosion by the LPR method because the values of b_a and b_c are required for the calculation of the corrosion current. Generally, this problem is handled by substituting the (decadic) Tafel slopes with some frequently measured, but basically arbitrary values, 100 to 120 mV [8] or 40, 60 or 80 mV for the anodic and 120 mV for the cathodic reaction [9], or some value above 30 mV [10]. Typically, if $b_{a,10} = 60\mathrm{mV}$ and $b_{c,10} = 120\mathrm{mV}$ then an acceptable approximation of the different proposals is given. In some cases, one of the processes is strongly diffusion-controlled and the reciprocal Tafel slope becomes negligible and/or the linearity of the curve can be severely distorted. However, this method can lead to erroneous corrosion rate figures, as it will be shown below, owing to the fact that the corrosion rate determination via the polarization resistance carries an inherent uncertainty.

The accurate and unbiased assessment of the basic corrosion parameters (j_{corr}, b_a and b_c) at or around the corrosion potential (E_{corr}) is of utmost importance. According to Mansfeld [9], "… one could accurately determine j_{corr} as a function of time, electrolyte composition, temperature, or other parameters. A determination of j_{corr}, E_{corr}, b_a and b_c as a function of such parameters[2] *in a potential range where no changes in the surface structure*[3] of the test electrode due to polarization are to be expected is of additional interest…". This claim justifies all efforts to determine these critical parameters from the polarization range as narrow as possible around the corrosion potential.

A frequently applied method to increase the accuracy of the determination of the corrosion rate, called harmonic analysis, is the modification of the EIS (Electrochemical Impedance Spectroscopy) transfer function by means of taking the higher order terms of the expansion of the exponential expressions in Eq. (1) into account [11,12]. These procedures lead to the determination of the coefficients of higher order polynomials arising in the series expansion of the exponential terms in Eq. (1) and, consequently, the Tafel slopes, required for the more accurate corrosion current assessment, in the less polarized, i.e. transition potential range, where neither the linear approximation of the low polarization range nor the linear extrapolation of the Tafel-slopes in the high polarization range is applicable [13]. The common difficulty with all these methods is that if the anodic and cathodic Tafel slopes are not exactly equal (and in most cases they are not) then all powers appear in the series and this causes convergence problems; if too many terms are included then the respective target function can be overdetermined, if too few members are considered then the fit may be inadequate.

The possible variations of the electrochemical parameters at higher levels of polarization and the uncertainties of the calculation of the corrosion current from the polarization resistance both emphasise the importance of the transition polarization range. In this paper we propose a transformation of Eq. (1), *linear* in the Tafel slopes and *quadratic* in the polarization, which treats all these problems at a technically satisfactory level and significantly reduces the required mathematical apparatus using this transition polarization range.

2. Theoretical discussion

Let us write Eq. (1) decomposing the reciprocal of both Tafel slopes into a symmetric and an asymmetric component:

$$j = j_{corr}\exp[\eta A](\exp[\eta S] - \exp[-\eta S]) \tag{4}$$

where $b_a = 1/(S+A)$ and $b_c = 1/(S-A)$.

Upon dividing both sides, the following expression is obtained:

$$\frac{j}{\eta} = j_{corr}\exp[\eta A]\frac{\exp[\eta S] - \exp[-\eta S]}{\eta} \tag{5}$$

This division, while facilitates proceeding to well-conditioned expressions, also limits the applicable polarization range excluding the $\eta = 0$ value and increasing the noise of the data around zero. This step, i.e. division of the current with the polarization, was carried out earlier by Guzmán et al. [14]. They continue with a relatively simple polynomial expansion of Eq. (1), stating that a fourth order polynomial approximation returns a perfect fit. Here we have to note that any polynomial (or other) approximation applying more than three parameters makes the original three-parameter model of Eq. (1) overdetermined, causing a strong correlation between the parameters. The work of Mészáros et al. [11] is correct in this respect, but e.g. the approximation of Slepski et al. [12] uses more than three parameters in a Taylor expansion. The division with the polarization is applied by Reeve and Bech-Nielsen [15], too, but they do not proceed with an expansion of the governing equation.

Starting from Eq. (5), we propose taking the logarithm of both sides and we get a sum from the product of the right side, rendering the term related to j_{corr} and A linear:

$$\begin{aligned}\ln\frac{j}{\eta} &= \ln j_{corr} + \eta A + \ln\frac{\exp[\eta S] - \exp[-\eta S]}{\eta}\\ &= \ln j_{corr} + \eta A + \ln\left(\frac{2}{\eta}\frac{\exp[\eta S] - \exp[-\eta S]}{2}\right)\\ &= \ln j_{corr} + \eta A + \ln\left(\frac{2}{\eta}\mathrm{sh}[\eta S]\right)\end{aligned} \tag{6}$$

The linearization of the last term is still to be solved. In order to do this, we notice that the Taylor-series of the sh function is convergent for $|\eta S < 1|$:

$$\mathrm{sh}[\eta S] = \eta S + \frac{(\eta S)^3}{3!} + \frac{(\eta S)^5}{5!} + \frac{(\eta S)^7}{7!} + \cdots \tag{7}$$

Substituting Eq. (7) into Eq. (6), we obtain:

$$\ln\frac{j}{\eta} = \ln j_{corr} + A\eta + \ln\left(2S\left(1 + \frac{(\eta S)^2}{3!} + \frac{(\eta S)^4}{5!} + \frac{(\eta S)^6}{7!} + \cdots\right)\right) \tag{8}$$

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[2] ^{2} Notation in this citation is transcripted into the conventions of this paper.

[3] ^{3} Italics ours.

Considering that $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \cdots \approx x$ if $|x| \ll 1$, this equation can be transformed into a polynomial of ηS. Assuming a first-order approximation of the logarithmic function:

$$\ln\frac{j}{\eta} = \ln 2j_{corr}S + A\eta + \frac{S^2}{3!}\eta^2 + \frac{S^4}{5!}\eta^4 + \frac{S^6}{7!}\eta^6 + \cdots \quad (9)$$

It is important to note that according to Eqs. (3) and (4) $\ln 2j_{\mathrm{corr}}S = \ln 1/R_{\mathrm{p}}$.

Alternatively, considering a second-order approximation of the logarithmic function, it is obtained that.

$$\begin{aligned}\ln\frac{j}{\eta} &= \ln 2j_{\mathrm{corr}}S + A\eta + \frac{S^2}{3!}\eta^2 + \left(\frac{S^4}{5!} - \frac{S^4}{2(3!)^2}\right)\eta^4 + \cdots \\ &= \ln 2j_{\mathrm{corr}}S + A\eta + \frac{S^2}{3!}\eta^2 - \frac{S^4}{180}\eta^4 + \cdots \end{aligned} \quad (10)$$

If $|\eta S| < 0.5$ then the contribution of the order 4 member in Eq. (10) is less than 1% of that of the order 2 member and is considered negligible. It is interesting that the sign of the order 4 member changes compared to Eq. (9) (this also improves the convergence of the second order approximation). If a fitting procedure gives a positive value, then it can be an indication of a systematic (model) error. Omitting the order 4 term, the expression is linear in parameters $\ln 2j_{\mathrm{corr}}S$, A and $S^2/3!$. It is important to note that in Eq. (10) the higher-order terms are all even, and they decrease very fast. Consequently, the quadratic approximation of Eq. (10) is adequate and three parameters, similarly to Eq. (1), can correctly describe the model. Also, if $A = 0$, i.e., Eq. (1) is symmetric in b_{a} and in b_{c} then Eq. (10) can be further simplified by means of the $x = \eta^2$ substitution.

Another way of further simplification can be made via the observation that the constant term $\ln 2j_{\mathrm{corr}}S$ in Eq. (10) gives the linear polarization resistance R_{p}. In this way the constant term is eliminated, the count of parameters to be determined is decreased, also decreasing the extent of correlations between the coefficients of the polynomial. The value of the polarization resistance can generally be accurately assessed (e.g., from a polynomial fit of the current–potential curve around the corrosion potential). Thus, with the appropriate rearrangement the following dimensionless form is obtained:

$$\ln\left(\frac{j}{\eta}R_{\mathrm{p}}\right) \approx A\eta + \frac{S^2}{3!}\eta^2 \quad (11)$$

Eq. (11) is probably the simplest approximation of Eq. (1), but is, as it will be demonstrated below, surprisingly accurate. However, as η is included in the denominator of the left side, around$\eta \approx 0$ the accuracy and robustness of the function may be significantly worse than at greater absolute values. Accordingly, a further division of both sides with η, which would give a linear relationship with the intercept A and the slope $S^2/3!$ and might be very elegant, is impractical. Obviously, the convergence of Eq. (11) is fast decreasing as $|\eta S| \to 1$, therefore such range of $|\eta S|$ should be avoided in the application of the theory.

3. Experimental

In order to prove the validity of Eq. (11) and the considerations leading to it, we carried out simulations and also verified the application on two typical corrosion systems. In the simulations current-potential curves were generated with no added random error and also with zero-centred, evenly distributed absolute error of order 0.01 and 0.02, superimposed on the dimensionless left side of Eq. (11) (this corresponds to a relative error of the current of 1% and 2% respectively). A similar range of random error was applied by Shen et al. [16] in their synthetic data fitting procedure. The simulation parameters are shown in Table 1.

The experimental conditions of the measurements were the same as published earlier for similar low-carbon steel electrodes [17]. The working electrode was a DIN St-52 type cylindrical steel electrode of 30 mm length and 6 mm diameter in a Teflon holder, and the geometrical electrode surface was 5.94 cm^2. Saturated Ag/AgCl electrode was used as a reference electrode and a platinum net with an approximate surface area of 20 cm^2 was used as a counter electrode. Electrolyte compositions are included in Table 2. The reference electrode was fixed in a Luggin-capillary to provide a well-defined geometry. The experiments were carried out in a conventional three-electrode electrochemical cell of a volume of approximately 700 cm^3. The working electrodes were polished with #400, #600 and finally #1000 emery paper and were then degreased in acetone and etched in 10% HCl for 5 min. EIS measurements were carried out in order to assess the solution resistance, which was compensated in the potential values of the polarization experiments. All measurements were carried out with a METROHM AUTOLAB PGSTAT 302 N type potentiostat using a NOVA 1.11 type software. All potential figures published below are compensated with the ohmic potential drop using the measured current value and the ohmic resistance obtained from the EIS data. The current-potential characteristics was determined from potentiodynamic measurements with a sweep rate of 1 mV/s, starting at the corrosion potential with a 200 mV sweep first in the negative and then with a 100 mV sweep in the positive direction. The points used for the determination of the polarisation resistance R_{p} and also the parameters j_{corr}, $b_{\mathrm{a,10}}$ and $b_{\mathrm{c,10}}$ via Eq. (11) were taken from the cathodic-anodic transition range of the curves. The (decadic) Tafel slopes and the corrosion currents of the polarization curves were also assessed by the linear fitting of the semilogarithmic representation of the measurement data; the Tafel slope values were determined from the apparently best-fit sections of the respective curves at higher polarizations. The polarisation resistance was assessed from an order 3 polynomial fitting in the subject potential range (-25 mV … + 25 mV). These data are published in the tables and figures below for a direct comparison of the conventionally obtained data with the ones received via Eq. (11). All calculations were carried out with Excel, demonstrating the simplicity and easy applicability of the proposed procedures.

4. Results and discussion

The results of the simulation experiments are shown in Figs. 1 and 2, the parameters are summarized in Table 3. In Fig. 1 and in Fig. 2 the symmetric S1 and asymmetric S2 simulation data sets are shown, respectively, and the polynomial fits. In case of the S3 (simulated) and E1, E2 (experimental) systems only the transition range (i.e. transition from linear to semilogarithmic) was fitted and the central potential range between -10 mV … + 10 mV was omitted. The advantage of the applied transition potential range is that it is relatively close to the corrosion potential and the electrochemical parameters are presumably not changed significantly with this minor polarization. Although according to Eq. (11) the constant term of the quadratic model function is negligible, in the fitting procedure also this parameter is calculated, resulting in extremely low values both for the S1 and the S2 data series.

In Figs. 1 and 2 the apparent extent of the deviations seems to be very different but in fact the deviations are of the same size; the range of the data is different in the two figures. The obtained parameters, shown in Table 3, are fairly accurate in the S1 and S2 series. In the Series S3 extremely large errors are superimposed on the theoretical curve and, still, the deviation of the parameters from the theoretical ones differs only a few percent. In conclusion, it can be stated that the applied transformation of Eq. (1), linear in the parameters and quadratic in the polarization, can be fitted in a robust way even in case of relatively large random errors. Consequently, if a kinetic system obeys Eq. (1) then it can be fitted properly with Eq. (11) and, *vice versa*, if it can

Table 1
Simulation parameters according to Eq. (1).

System ID	Corrosion current[*] (j_{corr})	Anodic decadic Tafel slope/mV ($b_{a,10}$)	Cathodic decadic Tafel slope/mV ($b_{c,10}$)	Superimposed absolute error[**]
S1-0	1.0	120	120	0
S1-1%				0.01
S1-2%				0.02
S2-0	1.0	60	120	0
S2-1%				0.01
S2-2%				0.02
S3-1%-5%[***]	1.0	60	120	0.01

[*] Arbitrary unit.
[**] Centralized, even distribution, added to the current values on the left side of Eq. (11).
[***] 1% absolute error added to the current on the left side of Eq. (11) plus 5% centralized, even distribution error of the corrosion current added to the current values.

Table 2
System identification and solution composition of the experimentally tested systems.

System ID	Solution composition
E1	1% HCl
E2	5% NaCl + 0.5% Acetic acid

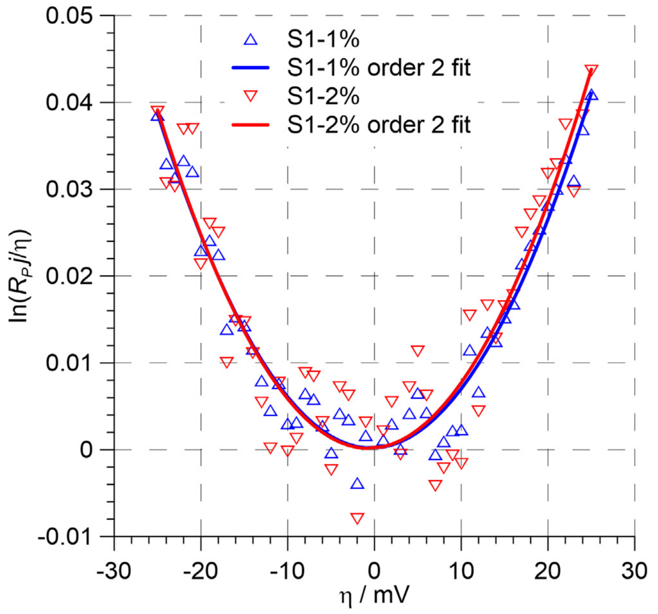

Fig. 1. Symmetric polarization data simulations according to Table 1 and Table 3.

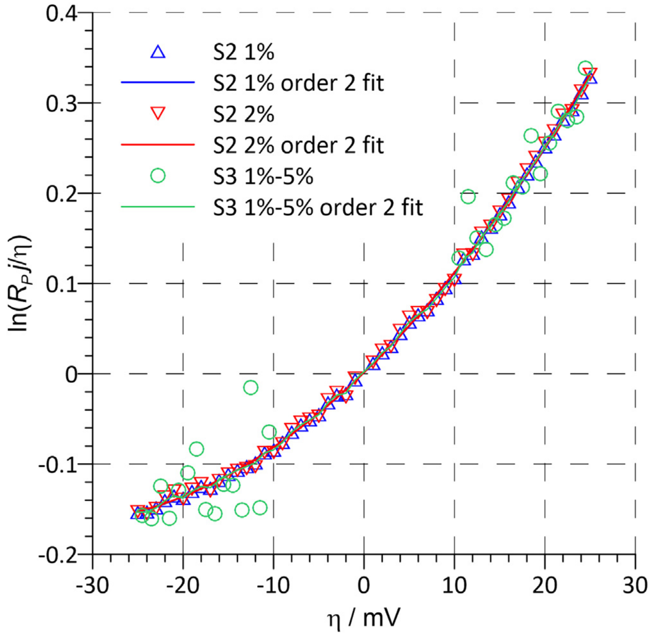

Fig. 2. Asymmetric polarization data simulations according to Table 1 and Table 3.

be fitted with Eq. (11) then it is likely to follow the kinetics formulated in Eq. (1). This conclusion will be strongly exploited in the following evaluation of the measured polarization curves.

The semilogarithmic potentiodynamic curves are shown in Figs. 3 and 4 for the systems E1 and E2 respectively, and the assessed parameters are summarized in Table 4. The potential range applied in the quadratic fitting is also marked in the figures. The transformed (quadratic) representations, according to Eq. (11), are shown in Fig. 5. The linear potentiodynamic curves, assessed in the same potential range as the transformed ones (-25 mV… + 25 mV), are included in Fig. 6.

The semilogarithmic polarization curves in Fig. 3 display a quite ordinary electrochemical behaviour of a typical corrosion system. Both the cathodic and the anodic curves have typical linear sections at higher levels of polarization, which intersect at the corrosion potential, determining the corrosion current in a fairly accurate way. The anodic and cathodic Tafel slopes are 63.4 and 85.3 mV respectively. The corresponding quadratic fitting is included in Fig. 5. The fitting is fairly good and leaves no doubt that the quadratic model function is realistic, in agreement with the regular 'double exponent' behaviour represented in Eq. (1). It is appearing that this transition potential range is just that intermediate one which cannot be used either for the conventional linear fitting of the polarization resistance or for the semilogarithmic Tafel fit in the higher polarization range. The choice of the range might be critical; it must be wide enough to allow the contribution of the second-order term to the overall variance, on the one hand, and narrow enough to avoid the divergence over $|\eta S| \geq 1$ on the other hand. The holding this second condition is not trivial; while the range of η must be decided before the evaluation, the fulfilment of the condition can be checked after the evaluation only, thus an iterative approach may be required.

The results obtained on the experimental system E2 are fairly different. The semilogarithmic presentation in Fig. 4 reveals that the anodic and the cathodic polarization curves do not intersect on the corrosion potential and, consequently, provide significantly different values of corrosion current. This anomaly is observed frequently in practice (e.g. [18,19]) and is very critical in itself, because makes the determination of the corrosion current (and the corrosion rate) inaccurate (the ratio of the cathodic and anodic corrosion current is

Table 3

Table 3A. Polynomial coefficients fitted to simulation data sets via Eq. (11).

System ID	Constant term*	A/mV^{-1}	$S^2/3!/\mathrm{mV}^{-2}$	Correlation coefficient R^2
S1-0	1.952E-4	−2.97E-19	6.09E-05	1.000
S1-1%	1.92E-4	4.71E-5	6.35E-5	0.9587
S1-2%	1.81E-4	9.37E-05	6.61E-05	0.8648
S2-0	1.44E-3	9.59E-03	1.36E-04	1.000
S2-1%	1.34E-03	9.64E-03	1.39E-04	0.9997
S2-2%	1.41E-3	9.69E-03	1.41E-04	0.9988
S3-1%-5%	6.66E-3	9.76E-3	1.28E-3	0.9728

Table 3B. Transformed electrochemical parameters of simulation data.

System ID	Corrosion current (j_{corr})	Anodic decadic Tafel Slope/mV ($b_{\mathrm{a,10}}$)	Cathodic decadic Tafel Slope/mV ($b_{\mathrm{c,10}}$)	S/mV^{-1}
S1-0	1.003	120.41	120.41	0.0191
S1-1%	0.982	117.67	118.24	0.0195
S1-2%	0.964	115.12	116.21	0.0199
S2-0	1.006	60.34	121.38	0.0286
S2-1%	1.001	59.85	119.98	0.0288
S2-2%	0.9879	59.37	118.64	0.0291
S3-1%-5%	1.02	61.41	128.12	0.0277

* Not included explicitly in Eq. (11), but fitted with full quadratic polynomials, including the constant term, too.

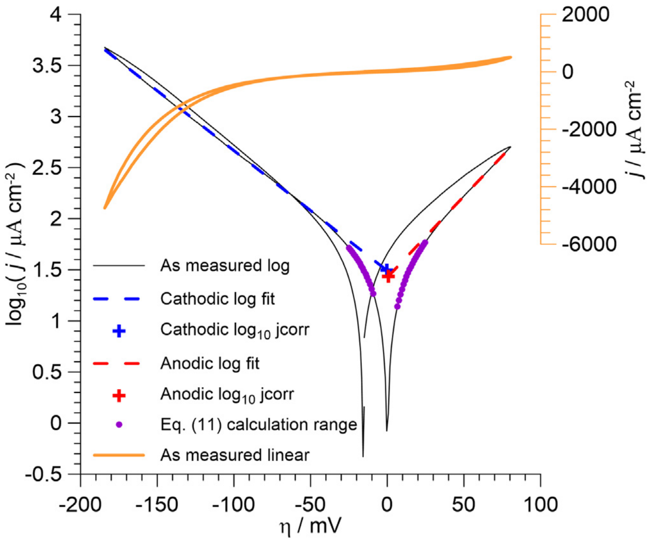

Fig. 3. System E1 semilogarithmic potentiodynamic polarization curves (left side vertical axis) with the linear fits of the Tafel sections of the curves and with the corrosion current values as the intercepts of the fitted lines. See also the linear current-potential curve (right axis) and the range of points used for the calculation via Eq. (11) (purple points). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

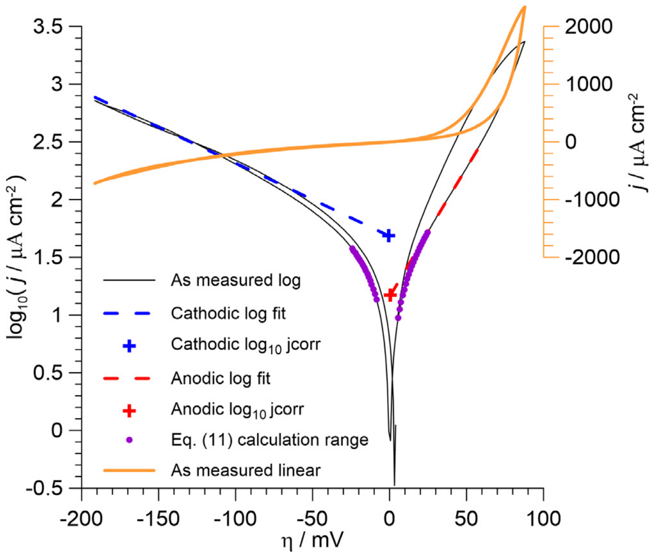

Fig. 4. System E2 semilogarithmic potentiodynamic polarization curves (left side vertical axis) with the linear fits of the Tafel sections of the curves and with the corrosion current values as the intercepts of the fitted lines. See also the linear current-potential curve (right axis) and the range of points used for the calculation via Eq. (11) (purple points). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.27, which adds an intolerably high uncertainty to the corrosion rate determination). This large difference is presumably related to the similarly large difference in the Tafel slopes (45.2 mV and 155.9 mV for the anodic and the cathodic process, respectively), which are also unusually low and high values. The Tafel slopes obtained from the quadratic fitting (58.1 and 87.4 mV) are significantly closer to each other and to the values obtained in the rather similar experimental system E1. Not surprisingly after all, the logarithm of the corrosion current obtained from the R_{P} value assessed from the linear polarization curve (see Fig. 6) and the S value from the quadratic fitting is between the anodic and the cathodic values, namely 1.493. With all these strange features, observing the shape of this polarization curve (E2, red curve), one might think it to be a quite ordinary one, very much resembling to the other one which, as it was discussed above, shows quite ordinary electrochemical behavior. And this case shows the real

Table 4
Summary of parameters obtained in the experimental systems E1 and E2.

Property	System E1 value	System E2 value	Reference
$b_{\mathrm{a,10}}/\mathrm{mV}$	63.4	45.2	Figs. 3 and 4
$b_{\mathrm{a,10}}/\mathrm{mV}$	76.7	58.1	Fig. 5 and Eq. (11)
$b_{\mathrm{c,10}}/\mathrm{mV}$	85.3	159.9	Figs. 3 and 4
$b_{\mathrm{c,10}}/\mathrm{mV}$	92.1	87.4	Fig. 5 and Eq. (11)
$\log_{10}\left(\frac{j_{\mathrm{corr}}}{\mu\mathrm{A/cm}^2}\right)$	1.572	1.493	Fig. 6 and Eq. (11)*
Anodic $\log_{10}\left(\frac{j_{\mathrm{corr}}}{\mu\mathrm{A/cm}^2}\right)$	1.435	1.171	Figs. 3 and 4
Cathodic $\log_{10}\left(\frac{j_{\mathrm{corr}}}{\mu\mathrm{A/cm}^2}\right)$	1.439	1.686	Figs. 3 and 4

* Using the value of S obtained from the fitting of Eq. (11) and the value of R_{P} obtained from the fitting of current vs. potential data of Fig. 6.

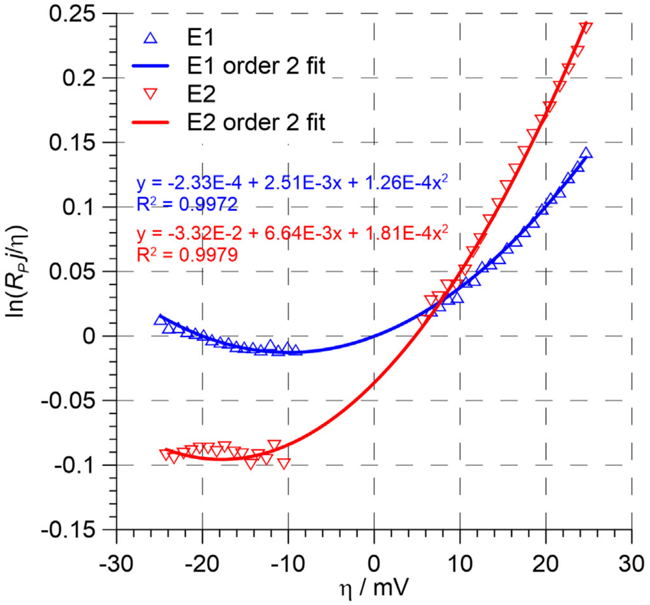

Fig. 5. Experimental measured curves (triangles) and quadratic fittings (lines) of the E1 and E2 systems.

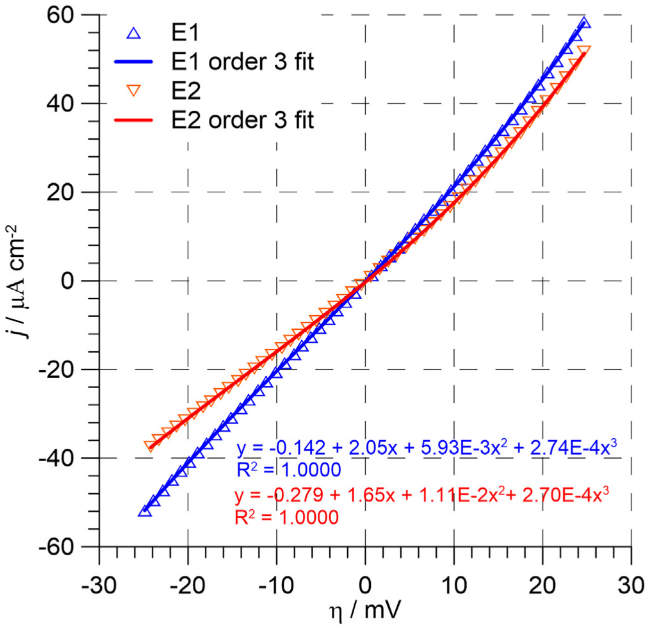

Fig. 6. Current vs. polarization curves in the experimental systems with order 3 polynomial fittings.

practical significance of the quadratic fit; while in the conventional corrosion current assessment methods the values of the Tafel slopes, assessable only from the high-polarization range, are necessary for the accurate calculation of the corrosion current both via the polarization resistance and also via the Tafel extrapolation, the quadratic fit uses only a relatively narrow polarization range (in this case ± 25 mV) for getting the same parameters. Considering that during extensive polarisation the surface conditions can change significantly and the Tafel slopes obtained from these potential ranges do not necessarily agree with the energetics of the reactions around the corrosion potential, the accuracy of the corrosion current obtained from the quadratic fit may be much better. The abnormal behavior of E2 is also indicated by the offset in Fig. 5 (the curve does not pass through the origin of the coordinate system). Irrespective of this conclusion, it is important to note that the measurement data curve of system E2 is not that typical parabolic shape as the one of E1; both the negative and the positive parts seem to be rather linear sections than parts of a parabola. In spite of this slight but observable destruction of the shape, the correlation coefficient R^2 of the system E2 is somewhat better than that of the system E1. This phenomenon needs further investigation in other corrosion systems in order to get a more general and more reliable picture on the applicability of the quadratic fit as a method for the assessment of the corrosion current and other electrochemical parameters. However, the inconsistencies in the evaluation of system E2 may also point to the fact that the Butler-Volmer equation does not describe the kinetics of the system accurately for this system. Consequently, the quadratic fit can be a method to quantify the deviations from the Butler-Volmer equation in the narrower range around the corrosion potential.

5. Conclusions

A transformation, linear in the parameters and quadratic in the polarization (overvoltage), was proposed for the determination of the Tafel slopes and, finally, the corrosion (exchange) current of systems obeying the Butler-Volmer equation. The theoretical considerations lead to the conclusion that in case of a perfect agreement with the Butler-Volmer equation the constant term of the resultant quadratic relationship (Eq. (11)) is zero. The performance of the transformation was tested on simulated data series with preset levels of random error and also on two experimental corrosion systems. The method utilizes the transition potential range around the corrosion potential that exceeds the linear range used for the assessment of the polarisation resistance but does not reach out to the range applicable for the determination of Tafel slopes from the semilogarithmic transformation of the current vs. potential relationship. The simulated data fittings showed that the method returned the electrochemical parameters with minor errors, roughly proportional to the data error levels. The fittings on experimental system polarization data revealed that if the system showed a regular Butler-Volmer behavior at high polarization levels then the subject transformation also returned regularly the quadratic dependence of the model function on the polarization, with a negligible constant term. Further research is required to investigate the correspondence between the anomalies of the Tafel slopes (giving different extrapolated values for the anodic and the cathodic slope) and the anomalies of the quadratic fit. The method provides an alternative way to determine the corrosion current and the corrosion rate, from a narrower range than the Tafel slope extrapolations and without the ambiguity of the conventional polarization resistance method. It seems that the proposed transformation is applicable for studying the kinetics of electrochemical systems in the transition range which was hitherto mostly unusable for such purposes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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