REVIEW

Fundamental aspects of the polarization resistance technique—the early days

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Abstract The work of Oldham and Mansfeld dealing with the concept of the polarization resistance technique that can be used to determine corrosion rates from potential E—current I curves measured in the vicinity of the corrosion potential E_{corr} has been summarized. In addressing the interpretation of this technique as the "linear polarization (resistance) technique," Oldham and Mansfeld pointed out that curvature of polarization curves in the vicinity of E_{corr} has to occur in order for the Butler–Volmer equation, as modified for corrosion reactions, to be valid. They proposed a modification of the Stern–Geary linear polarization equation and presented a new graphical method for the calculation of corrosion rates from polarization curves. Some of the earliest computer programs for the determination of corrosion current densities, and Tafel slopes from polarization data collected in the vicinity of E_{corr} and examples of their application have been discussed.

Keywords Polarization resistance technique ·
Stern–Geary linear polarization equation · Corrosion rates

Introduction

The year 1970 was the start of a series of papers by Oldham and Mansfeld dealing with some fundamental aspects of the polarization resistance technique and its application for determining corrosion rates [1–5]. In a review article

Dedicated to the 80th birthday of Keith B. Oldham.

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entitled "The Polarization Resistance Technique for Measuring Corrosion Rates" that was published in 1976 [6], Mansfeld pointed out that the theoretical and experimental results contained in the paper entitled "Concerning the Evaluation of Corrosion Reactions by Superposition of Electrochemical Partial Reactions and Concerning the Potential Formation on Mixed Electrodes" [7] by Wagner and Traud form the basis of the polarization resistance technique. An English translation of this classic paper that describes the concept of mixed potential theory has been published recently with comments on its significance for the application of electrochemical techniques in corrosion research by Mansfeld [8]. It was pointed out that Wagner and Traud's paper [7] is a milestone in the history of corrosion—in fact it is the beginning of modern corrosion science as we know it today.

In 1951, Bonhoeffer and Jena, studying the electrochemical behavior of iron samples with different carbon content, found that the slope of the polarization curve at the corrosion potential E_{corr} was correlated to the corrosion rate of these samples [9]. They defined this slope as the polarization resistance R_p according to:

$$R_p = (dE/dI)_{Ecorr} \qquad (1)$$

In 1957, Stern and Geary [10] derived an equation (the Stern–Geary equation) that related quantitatively the slope R_p of a polarization curve in the vicinity of E_{corr} to the corrosion current density i_{corr}:

$$R_p = B/i_{corr} \qquad (2)$$

where $B = b_a b_c / 2.303(b_a + b_c)$. In Eq. 2, b_a and b_c are the anodic and cathodic Tafel slopes, respectively. The dimension of R_p is ohm.cm^2. Figure 1 illustrates the determination of R_p as the slope of the experimental polarization curve at E_{corr}. ASTM G59 "Standard Practice for Conducting
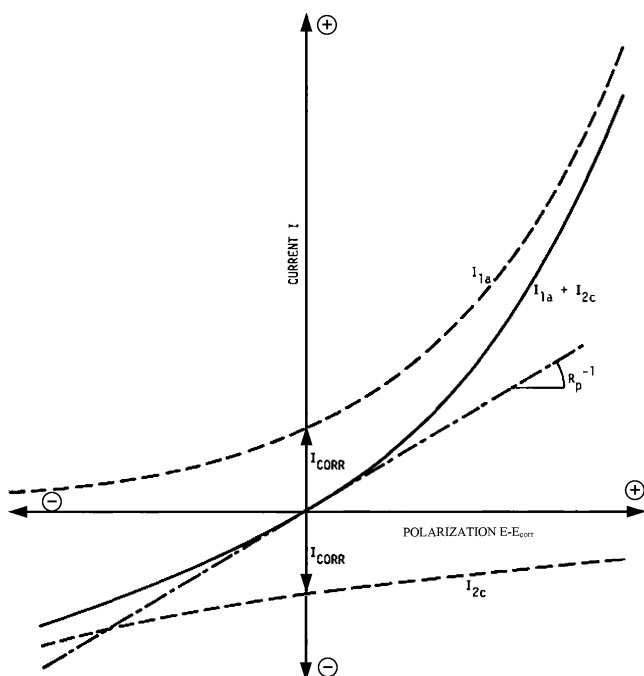
Fig. 1 Linear plot of current as a function of polarization showing superposition of partial anodic and cathodic currents to measured polarization curves and determination of polarization resistance R_p [6]

Potentiodynamic Polarization Resistance Measurements" describes the experimental procedure for determining R_p according to Eq. 1.

It will be noticed that for accurate determination of i_{corr}, the value of the parameter B has to be known for the system at the time of the measurement of R_p (Eq. 2). As discussed by Mansfeld [6], numerical values of the parameter B in Eq. 2 have usually been determined by one of the following methods:

1. The Tafel slopes b_a and b_c are calculated from the Tafel lines obtained in separate experiments for the same material and under identical test conditions.
2. Tafel slopes are taken from literature values for the same or similar corrosion systems.
3. Theoretical values of Tafel slopes are assumed.
4. Tafel slopes are obtained from the same polarization curve that was used to determine R_p.
5. The parameter B is determined by calibration using weight loss data.

The work of Oldham and Mansfeld

In addressing the concept of the polarization resistance technique, Oldham and Mansfeld noticed a shift from the original concept of the technique as discussed by Wagner and Traud and others [7, 9–11] to the concept of the "linear polarization (resistance) technique" and warned against the

expectations that straight-line relationships between potential and current have to be found for all corroding systems [2]. In a discussion of the data presented by Indig and Groot [12], Mansfeld and Oldham [1] used a modification of the Stern–Geary equation [3] to include more than one oxidation and reduction reactions as was assumed in the original treatment. Indig and Groot [12] had determined corrosion rates of stainless steel in an alkaline solution at 288 °C by a weight loss technique and by use of the Stern–Geary "linear polarization" method. The rates measured by the two techniques differed by almost a factor of 10, i_{corr} calculated from the weight loss data being much less than that calculated from the Stern–Geary Eq. (2). Indig and Groot suggested that the Stern–Geary formula by neglecting the reverse of the cathodic reaction, i.e.

$$1/2H_2 + OH^- \leftrightarrow H_2O + e- \qquad (3)$$

would overestimate i_{corr}. Based on a modified value of i_{corr} calculated from the exact polarization resistance theory and that obtained from the Stern–Geary Eq. (2), it was shown by Mansfeld and Oldham [1] that the approximation inherent in the Stern–Geary treatment leads to an overestimate in i_{corr} of about 45% which goes a small way to explain the tenfold discrepancy with the i_{corr} values obtained from weight loss data [12].

In addressing the question of the linearity of polarization curves in the vicinity of E_{corr}, Oldham and Mansfeld [2] demonstrated that not only is there no theoretical reason for polarization curves to be linear at E_{corr}, the non-linearity possibly being severe, but that the polarization curves must display curvature in the vicinity of E_{corr} for the Stern–Geary treatment to be valid. Figure 2a–d shows polarization curves that have been calculated for a variety of Tafel slopes in a plot of the dimensionless parameter I/I_{corr} vs. polarization $E-E_{corr}$ [6]. These plots have been calculated based on the Butler–Volmer equation modified for corroding electrodes:

$$I/I_{corr} = \exp[2.3(E - E_{corr})/b_a] - \exp[-2.3(E - E_{corr})/b_c] \qquad (4)$$

Also included is the tangent of a polarization curve at E_{corr} from which R_p can be determined using Eq. 1. It is apparent from these curves that the curvature of the polarization curve is determined by the ratio of the Tafel slopes b_a/b_c as can be seen by going from Fig. 2a to d. For equal Tafel slopes, a straight-line relationship is observed over a wider range of $E–E_{corr}$ (Fig. 2c). Figure 2a refers to neutral, aerated solutions, while Fig. 2b is characteristic for iron in deaerated acids. Figure 2c describes the system stainless steel 430/1 N H_2SO_4, and Fig. 2d refers to a passive metal on which reduction of H^+ (acid media) or oxygen (neutral media) occurs. These examples show that
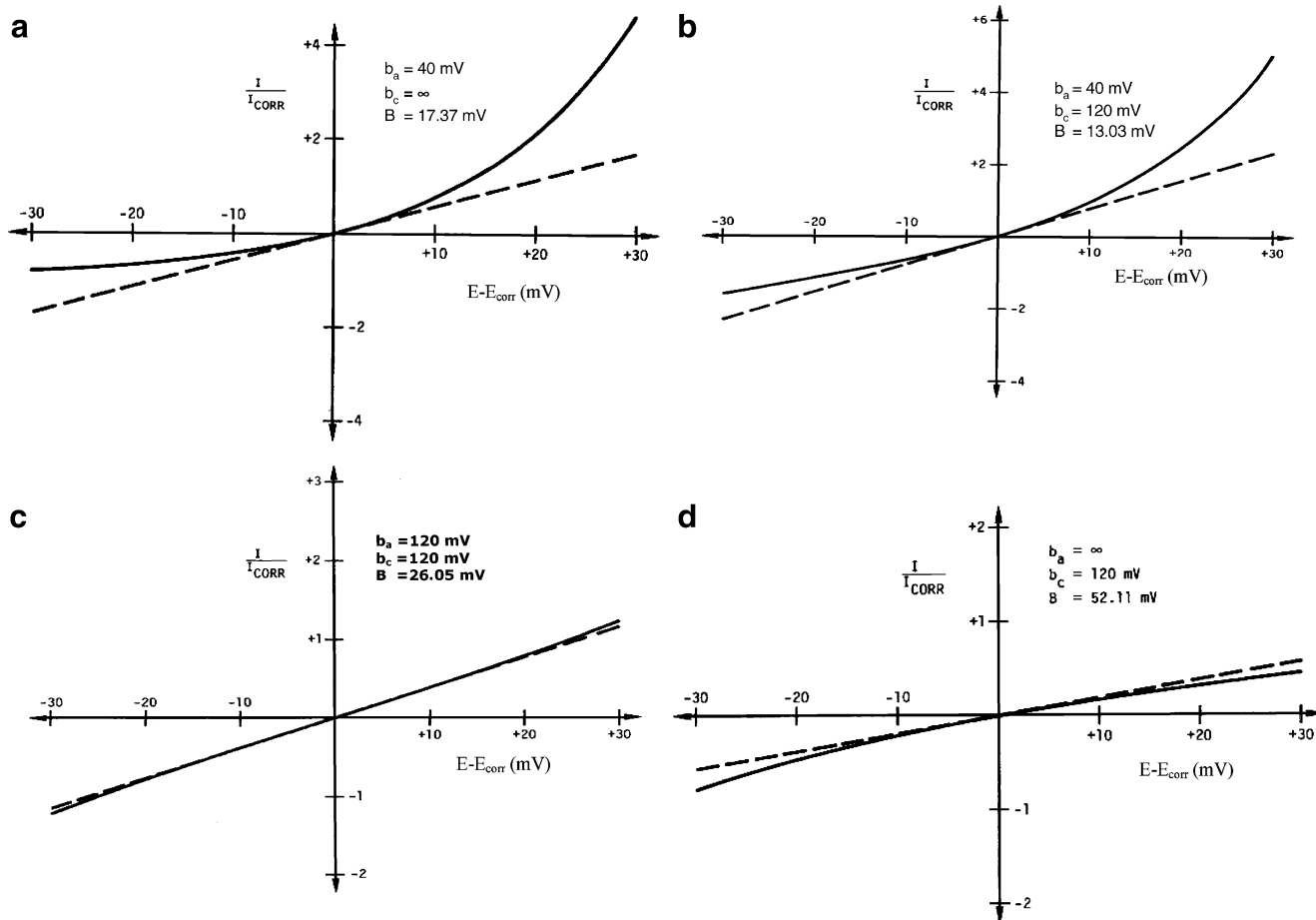
Fig. 2 Current–polarization plots for various combinations of Tafel slopes [6]

the experimenter has to expect a wide variety of polarization curves of different shape even in close vicinity of E_{corr}. The shape of a polarization curve might change with time as Tafel slopes change due to changes of the corroding electrode surface and/or the corrosive environment [6].

Oldham and Mansfeld's conclusions were as follows [2]:

1) Only exceptionally will the polarization curve of a corroding metal be linear at E_{corr}.
2) Whether or not the polarization curve is linear at E_{corr}, its gradient there may be employed to determine i_{corr} by application of the Stern–Geary method or its extension [3].
3) The gradient of the polarization curve should vary significantly over a range of about ±26 mV from E_{corr}, and perceptible non-linearity should be apparently close to E_{corr}. The absence of such non-linearity should be treated with suspicion, since it probably reflects the presence of ohmic control and invalidates the measurement of corrosion currents by the Stern–Geary method.

As will be discussed below, development of appropriate software programs allows determination of the experimental

b_a, b_c and i_{corr} values based on a fit of the measured polarization curve to Eq. 3 without the need for calculation of R_p according to Eq. 1 unless the R_p values are to be compared with values obtained from others techniques such as electrochemical impedance spectroscopy (EIS) [13, 14] or the noise resistance R_n obtained from electrochemical noise data [14].

In a paper entitled "Corrosion Rates from Polarization Curves," [5] Oldham and Mansfeld pointed out that methods such as the Tafel extrapolation or intercept method suffer from the drawback of requiring data obtained from regions far from E_{corr}. In such regions, the net current flow is large, as a result of which ohmic voltage drops and concentration polarization might distort the polarization curve which leads to erroneous values of i_{corr}. In addition, large changes in the surface structure might result especially from anodic polarization. In order to complement the polarization resistance technique and the Tafel extrapolation technique, Oldham and Mansfeld [5] suggested a third method which had the advantage of not requiring a priori knowledge or estimation of the Tafel slopes b_a and b_c. Because this new method did not involve taking data far

from E_{corr}, it ran less danger than does the intercept method of problems occurring due to ohmic drop and concentration polarization, changes of surface activity, or the influence of secondary electrochemical reactions. The new method proposed by Oldham and Mansfeld [5] enables those regions of the polarization curve that are useless for either the Stern–Geary or the intercept method to be used to determine i_{corr}.

Reference to Fig. 3 illustrates the different stages of the method that are described in more detail in the original paper [5]. First, points A and C are selected, and the currents i_a and i_c are determined. By drawing tangents at points A and C, the potential differences $|\Delta_a|$ and $|\Delta_c|$ are determined. Based on this set of experimental data, i_{corr} can be determined [5]. Experimental results obtained with the new graphical method were presented for the system Fe/1 N H_2SO_4 [5]. Figure 4 shows good agreement between the i_{corr} data obtained with the new graphical method over a 24-h period and the average corrosion current density calculated from the amount of iron found in the test solution after the 24-h test (analysis by atomic absorption).
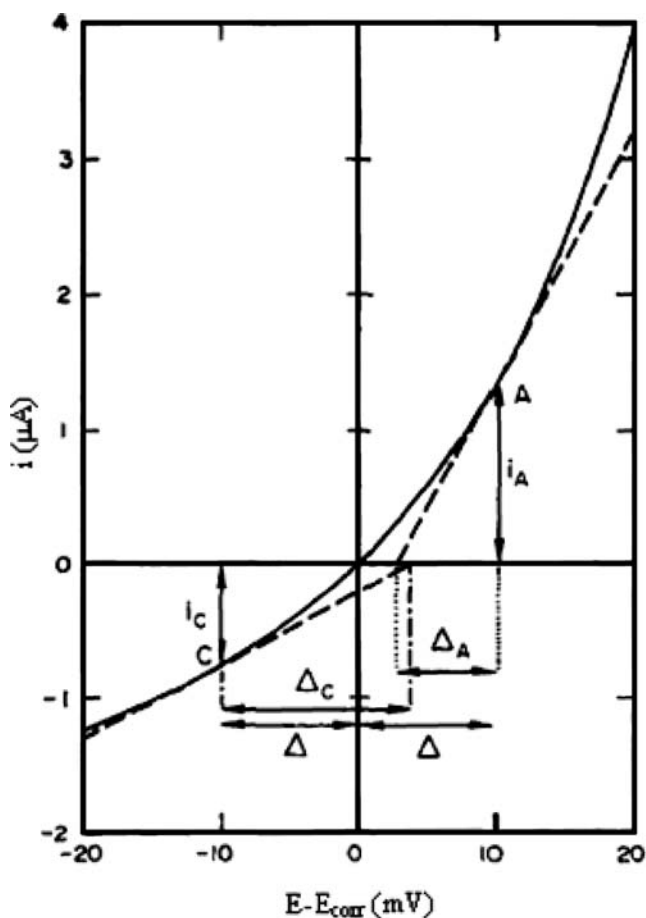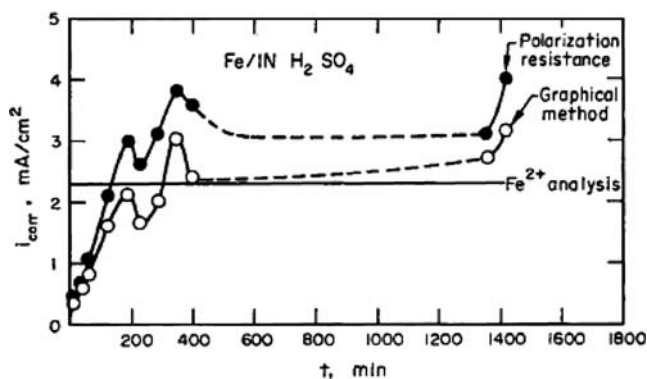

Fig. 4 Corrosion c.d. I_{corr} as a function of time for Fe/1 N H_2SO_4 obtained with the graphical method determination of R_p and from chemical analysis of the test solution [5]

Data obtained with the polarization resistance technique are also shown in Fig. 4 for comparison.

Further developments—analysis of polarization curves by computer programs

As discussed by Mansfeld in a paper entitled "Tafel Slopes and Corrosion Rates Obtained in the Pre-Tafel Region of Polarization Curves" [15], a more accurate determination of R_p and Tafel slopes can be performed by computer analysis of polarization curves obtained in the vicinity of E_{corr}. The analysis based on the computer program CORFIT [16] has the advantage that Tafel slopes can be determined in the pre-Tafel region and that b_a and b_c can be calculated even if only a cathodic or anodic polarization curve has been obtained. The calculated errors of b_a, b_c R_p, and i_{corr} indicate how much experimental scatter is involved. If CORFIT cannot find a solution of an experimental polarization curve, the scatter of the data is too large, or the basic equation that relates I to $\Delta E = E - E_{corr}$ (Eq. 4) is not obeyed due to excessive IR-drop or other complications discussed by Oldham and Mansfeld [1–5]. The method has been used to explain the observed changes of corrosion rates with exposure time based on the relative changes of the rates of the anodic and cathodic reactions occurring on iron in 1 N H_2SO_4 [16]. Contrary to the usual procedure, Tafel lines were constructed from the calculated values of b_a, b_c, and i_{corr} that were obtained using CORFIT near E_{corr}. The calculated Tafel lines illustrated these changes [16].

In 1992, Shih and Mansfeld [17] published a paper dealing with the software program POLFIT for quantitative analysis of polarization curves. This program provides full graphics functions and has both simulation and fitting procedures based on Eq. 2. Electrochemical parameters such as b_a, b_c, i_{corr}, R_p, and E_{corr}, the errors for each of these parameters and the results of the statistical analysis are displayed in tabular form. A unique feature of POLFIT is

Fig. 3 Illustration of graphical method. The polarization curve has been drawn for b_a=30 mV, b_c=120 mV, and i_{corr}=1.00 μA; Δ= 10 mV [5]
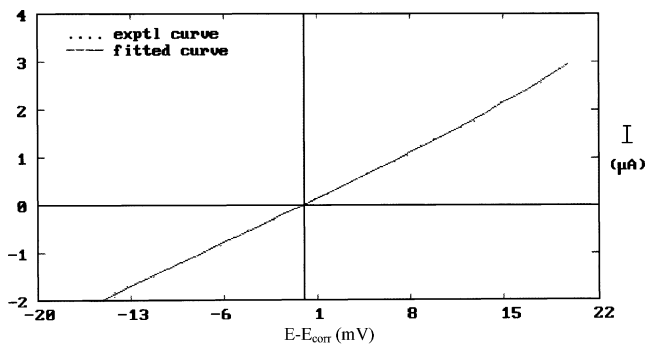
the possibility of eliminating the uncompensated resistance R_u in the data analysis based on the modified Eq. 4:

$$i = i_{corr}\{\exp[2.3(\Delta E - iR_u)/b_a] - \exp[-2.3(\Delta E - iR_u)/b_c]\}$$

(5)

Inspection of the deviation between the experimental and fitted current data points at each potential allows elimination of data points with excessive scatter and detection of systematic errors such as those arising from the neglect of R_u in the data analysis. The performance of POLFIT has been evaluated for theoretical data with various random noise levels [17].

Figure 5 shows a potentiodynamic polarization curve recorded in the vicinity of E_{corr} for Cu exposed to 0.5 N NaCl and the results of the analysis using POLFIT [17]. The table in Fig. 5 lists the fit parameters b_a, b_c, and I_{corr} and their errors as well as the calculated values of B and R_p. Also displayed are E_{corr} and the normalized values i_{corr} and R_p^o. Additional statistical data are included in the table.

Figure 6 gives another example for the application of POLFIT for electroplated Zn–Ni exposed to 0.5 N NaCl. These data were obtained as part of a larger effort to develop chromate-free conversion coatings for galvanized steels [18]. The deviation between the measured and fitted data is very small except in the vicinity of E_{corr} which is
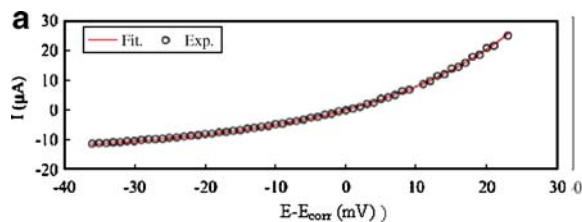

Initial Potential: -814mV   Final Potential: -745mV
Estimated Solution Resistance R_u: 0
Number of Iterations: 10

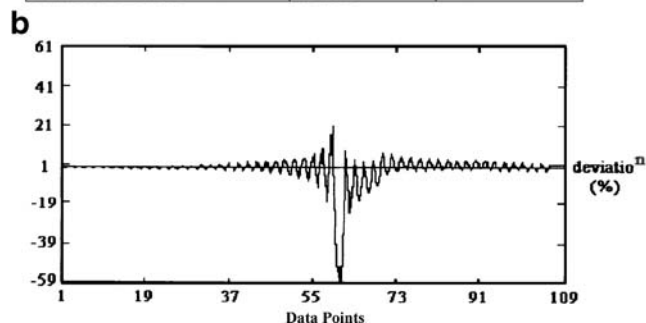|	Results	Error
I_{corr} (μA)	11.2	0.4
b_a (mV)	46.1	0.9
b_c (mV)	481	95
R_p (ohm)	1633	7
B (mV)	18.3	
i_{corr} (μA/cm^2)	2.29	0.09
R_p^o (ohm.cm^2)	8003	37
E_{corr} (mV)	-784.1	379
Sum of Squared Observation	12457	
Sum of Squared Deviation	5.2	
R-squared	0.99958	
Correlation	0.99979	
Standard deviation	0.22572	

Fig. 6 Potentiodynamic polarization curve for Zn-Ni exposed to 0.5 N NaCl (**a**), deviation between experimental and fit data (**b**), and results of data analysis using POLFIT [15]

due to the difficulty of an accurate determination of E_{corr} as E at $i=0$ using POLFIT (Fig. 6b).

Since the development of the CORFIT and POLFIT programs, many other computer programs that can be used for the determination of corrosion current densities and Tafel slopes from polarization data obtained in the pre-Tafel region have been discussed. Some of these programs are available as part of commercial instrumentation for the collection of electrochemical data. It has to be noted that some of these computer programs are based on the "linear polarization" concept, i.e., the polarization data determined in the vicinity of E_{corr} are fit to a straight line, the slope of which is assumed to be equal to R_p.

Initial Potential = -255 mV; Final Potential = -215 mV

Estimated Solution Resistance R_u = 0.0 ohms
Number of iterations: 5

	Results	Error
I_{corr} (μA)	2.13	0.21
b_a (mV)	68.4	5.7
b_c (mV)	80.7	8.2
R_p (ohms)	7535	62
B (mV)	16.1	
i_{corr} (μA/cm^2)	0.426	0.042
R_p^o area (ohm.cm^2)	37677	312
E_{corr} (mV vs. SCE)	-235.8	0.15

Sum of squared observations = 126.1
Sum of squared deviations = 0.102
R-squared = 0.999
Correlation = 0.999
Standard Deviation = 0.0486 with 43 d.f.

Fig. 5 Potentiodynamic polarization curve for Cu exposed to 0.5 N NaCl and results of data analysis using POLFIT [15]

Summary

The papers by Oldham and Mansfeld [1–5] have provided a thorough discussion of the background of the polarization resistance technique and the experimental conditions that have to be met for the correct application of the technique.

Curvature of a polarization curve in the vicinity of E_{corr} has to be expected. The degree of curvature depends on the ratio of the Tafel slopes b_a/b_c. Absence of curvature might be due to excessive ohmic drop and/or concentration polarization. The graphic method proposed by Oldham and Mansfeld [5] has the advantage that it doe not require a priori knowledge or estimation of b_a and b_c to calculate i_{corr} from R_p values (Eq. 2). Computer programs such as CORFIT [16] and POLFIT [17] or more recent version can be used to determine i_{corr} and the Tafel slopes in the pre-Tafel region of a polarization curve.

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