

Determination of Linear Tafel Region from Piecewise Linear Regression Analysis

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ABSTRACT: Tafel polarisation method is widely used in corrosion studies but relies heavily on the accurate extrapolation of the linear regions. To eliminate the ambiguity in the linear extrapolation, the present study develops a quantitative method based on piecewise linear regression analysis. In this method, the entire polarisation data is divided into small sub-intervals and variation in the regression coefficient and linearity coefficient values are observed. Consistency in these values serves as a quantitative indicator of the linear Tafel regions. The method described is then demonstrated in potentiodynamic polarisation measurement of Al/NaCl (0.5 M) and Zn/KOH (1.0 M) systems. The piecewise linear regression analysis positively identified the linear regions from the polarisation branches and thus provided more accurate corrosion parameters of the systems.

Keywords: Tafel Linear Region; Regression Analysis; Tafel Equation Constants; Zinc; Aluminium

1. Introduction

Methods used for estimation of corrosion rate of metals include gravimetric method [1,2], colourimetric method (chemical analysis of solution) [3], gasometric technique (quantifying hydrogen evolution) [4], thickness measurement [5], electrical resistance method [5], inner marker method [6], and electrochemical techniques (potentiodynamic or potentiostatic) [7]. Gravimetric method is considered the simplest method for determination of corrosion rate [1,8-11]. However, as cleaning of specimen is often required after exposure to the designated liquid medium, the accuracy of specimen's weight loss or gain is considered less compared to other techniques [1,12]. Among electrochemical methods, potentiodynamic polarisation or commonly referred to as Tafel extrapolation method is most often used for laboratory corrosion testing. It is probably the most commonly used polarisation testing method for measuring corrosion rate and a wide variety of functions. This technique can provide significant information pertaining to corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated media.

Tafel extrapolation method relies greatly on the determination of linear region from cathodic and anodic polarisation branches. As such, non-linearity in the vicinity of corrosion potential is the main concern in this technique. A poor selection of the Tafel slope has led to considerable uncertainty and consequently erroneous values of polarisation resistance [5,13]. To ascertain the accuracy of Tafel extrapolation method, some researchers verified their data obtained with weight loss method [14]. Below are some guides proposed by researchers so as to avoid uncertainties in the Tafel extrapolation method [5]:

1. At least one of the branches of the polarisation curves is under activation polarisation but both are preferable.
2. Well-defined anodic or cathodic Tafel region exist

over at least one decade of current.

3. The extrapolation should start at least 50-100 mV away from E_{corr} .

In all cases, one must first define the linear region from the polarisation branches or before that decide whether a linear region is present. One common misconception is the expectation of the linear region from the polarisation curves [15]. In fact, the Tafel equation is only a special case of the more general Butler-Volmer equation of which most electrode reactions do not obey. As a result, the linear Tafel region is 'shortened' or totally disappeared all together [16,17].

In the absence of linear Tafel region, one approach is to use numerical simulations to elucidate the kinetic parameters of the anodic and cathodic reactions, such as the work of Flitt and Schweinsberg [17]. However, the present study discusses the very core issue in Tafel extrapolation method, that is, on how the linearity of the region is defined. Whether or not the linear region is present, what is the basis of the interpretation? We propose a well-defined quantitative, regression analysis approach in defining the linear Tafel region. The corrosion measurement of Al/NaCl (aq) and Zn/KOH (aq) systems are demonstrated as examples.

2. Theoretical Background

Regression analysis is a statistical process for quantifying the relationship between dependent (x) and independent (y) data pairs. Consider n data pairs (x, y) that are linearly dependent, that is correlated by $y_i = mx_i + c$. Let i index be the observations on the data pairs, while m and c denote the regression coefficient and constant, respectively. On the basis of the least squares method [18], the goodness of the linear model can be measured using R^2 coefficient ($0 \leq R^2 \leq 1$).

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - m - cx_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (\text{Eq. 1})$$

where,

$$m = \bar{y} - c\bar{x} \quad (\text{Eq. 2})$$

$$c = \frac{\sum_{i=1}^n (x_i y_i - m - n\bar{y}\bar{x})}{\sum_{i=1}^n (x_i^2 - n\bar{x}^2)} \quad (\text{Eq. 3})$$

The higher the value of R^2 , the better the linear fit.

Let the n data pairs (x, y) that make up the linear region be divided into equal k sub-intervals. Assuming independent residuals or random statistical data deviation over the entire data range, the linear regression model of the n data pairs (x, y) is then applicable to all k sub-intervals. Accordingly, each sub-interval possesses the same regression parameters, such as the regression coefficient, regression constant, R^2 value and so on.

Now suppose a section of a potentiodynamic polarisation curve constitutes a linear region. Let the entire data region (inclusive of linear and non-linear parts) be divided into equally small n sub-intervals and ascribed with their respective m and R^2 values (calculated from Eq. 1 and Eq. 2). The sub-intervals that make up the linear region are anticipated to possess high R^2 values and consistent m values. Conversely, the sub-intervals that originated from the non-linear region are expected to show varying m values and low R^2 values. Therefore, by observing the variation in these two parameters against the equally divided n sub-intervals, the linear region of the Tafel slope could be established more accurately.

3. Materials and Method

The potentiodynamic polarisation of aluminium in sodium chloride electrolyte (0.5 M) and zinc in potassium hydroxide electrolyte (1.0 M) were measured. Aluminium and zinc specimens were of 99.9 % purity. The specimens were cold mounted in acrylic resin and then subjected to grinding (600, 800, 1000 and 1500 grit) and polishing (alumina sizes of 1.0 μm , 0.3 μm and 0.05 μm) processes. Before and after surface polishing, the specimens were cleansed with methanol in an ultrasonic bath. The exposed specimen area measured 1 cm x 1 cm. A platinum foil was used as the counter electrode. Reference electrode was placed in close proximity to the surface of working electrode via Luggin capillary, that is, Ag/AgCl (saturated KCl) for Al/NaCl cell and Hg/HgO (1.0 M) for Zn/KOH cell. The experiments were performed in a 100-cm³ volume Pyrex glass cell, at ambient room temperature of 28 °C. An AUTOLAB PGSTAT302N potentiostat/

galvanostat (Eco Chemie B.V.) instrumentation was used. The measurement was performed in the scan range of 2 V to -2 V at a rate of 0.1 Vs⁻¹.

4. Results and discussion

In Tafel analysis, the anodic and cathodic polarisation curves are fitted to the Tafel equation

$$\eta = E - E_{eq} = a + b \log \frac{i}{i_0} \quad (\text{Eq. 4})$$

where E is the electrode potential, E_{eq} is the equilibrium electrode potential, i is the electrode current density, i_0 is the exchange current density, and a and b are called the Tafel equation constants. By extrapolating the linear regions of the anodic and cathodic profiles on a semi logarithmic plot, the corrosion kinetic parameters can be elucidated and subsequently the corrosion rate of the metallic sample determined. However, often times, the determination of the linear regions is rather ambiguous. Hence, this current study presents a piecewise linear regression approach in consideration of the anodic and cathodic linear regions.

The entire polarisation data obtained were initially converted into voltage-logarithm of current data pairs $(V - \log i)$. These data pairs were then divided into sub-intervals of 10 data points each. For each sub-interval, the linear regression coefficients of m and R^2 were calculated (Eq. 1 and Eq. 2). The results were finally summarised as a bar chart to observe the variation in these two parameters. Consistency in m and R^2 values will be reflected as brief plateau profiles on the bar chart.

Figure 1 depicts the bar chart distribution for m and R^2 values across the entire polarisation curve of aluminium in 0.5 M NaCl. As anticipated, a brief plateau region denoting consistent m regression coefficient is observed for both anodic and cathodic branches. We attribute this trend to the onset of Tafel linear region, that is, the voltage-current response in this region was under activation polarisation. The R^2 linearity coefficients are also very close to unity in those regions. However, most of the sub-intervals recorded $R^2 > 0.9$, which is in fact a pseudo-linearity indication. This phenomenon occurred due to the small sub-interval size but it will not lead to erroneous determination of the Tafel region. The consistency in the gradient m values is used as the main indicator supported by the R^2 linear coefficient. **Figure 2** shows the corresponding interval of linearity on the anodic and cathodic polarisation curves as located from the bar chart distribution of m and R^2 coefficients of **Figure 1**. The linearity factor for the entire region was almost unity. Subsequently, the following parameters were obtained for the aluminium sample in 0.5 M NaCl:

Corrosion current, I_{corr} : 26.7 μA

Corrosion potential, E_{corr} : -558 mV

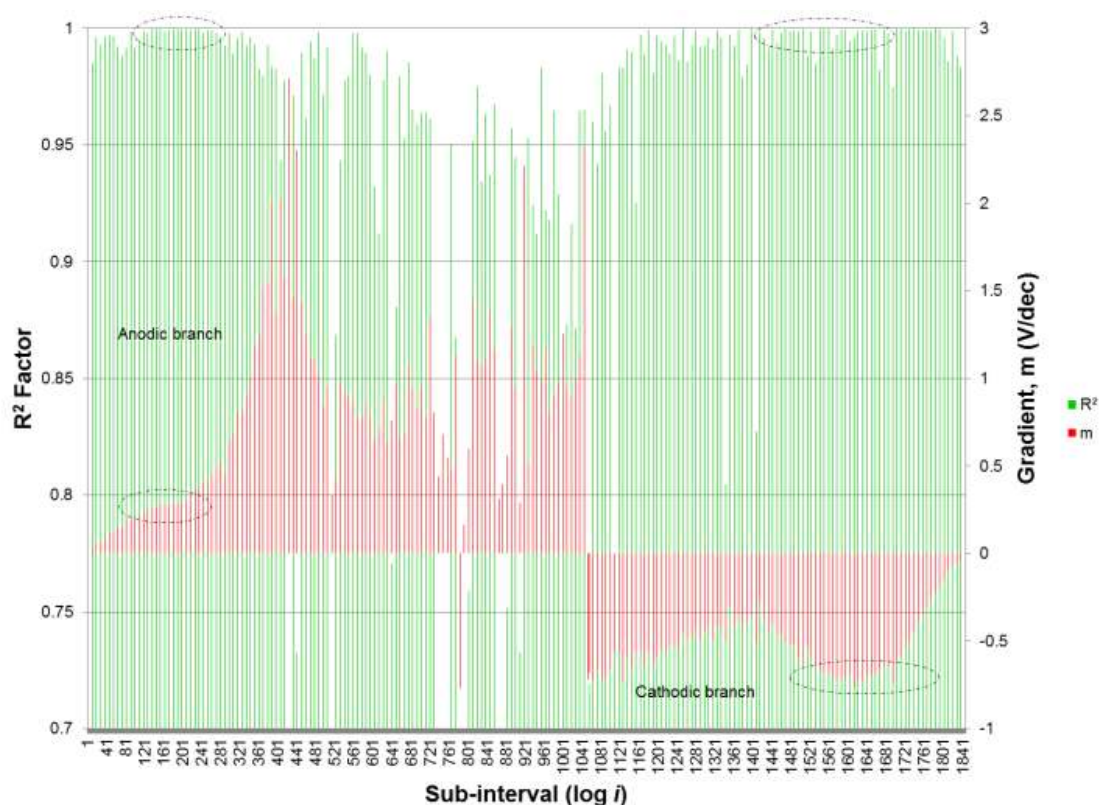


Figure 1: Bar chart distribution for m and R^2 values across the entire polarisation curve of aluminium in 0.5 M NaCl

The E_{corr} value of -558 mV obtained is much noble than the high purity aluminium (normally in the order of 99.999% purity), which is normally around -1.45 V [19]. Subsequently the high purity aluminium specimen is expected to register a much higher corrosion current I_{corr} . Commercial aluminium foil, as used in this study, was of technical grade, that is, less than 99.99 % purity. Using the technical grade aluminium specimen, El-Wahab et al. [20] also reported a much higher E_{corr} of -672 mV (versus SCE) with its corresponding I_{corr} value of $45.9 \mu\text{A cm}^{-2}$ in 0.5 M NaCl. Their higher corrosion current than $26.7 \mu\text{A cm}^{-2}$ observed in this study is most likely due to its lower E_{corr} value.

The potentiodynamic polarisation measurement was also performed on zinc metal in 1.0 M KOH. **Figure 3** illustrates the bar chart distribution of m and R^2 linear regression coefficients over all sub-intervals formed. The plateau regions indicating consistent gradient m coefficients can be easily noticed and supported by the high linearity factor. The entire sub-intervals of the anodic branch possessed very high linearity coefficient. **Figure 4** shows the corresponding linear intervals on the anodic and cathodic branches as determined from **Figure 3**. The linearity coefficient for both intervals was also 0.99. Finally, the corrosion parameters for Zn in 1.0 M KOH were obtained as:

Corrosion current, I_{corr} : $176.3 \mu\text{A}$

Corrosion potential, E_{corr} : -1.444 V

For the same Zn/KOH (1.0 M) system, El-Sayed [21] reported E_{corr} of -1.439 V (versus SCE) and I_{corr} of $1635 \mu\text{A cm}^{-2}$, while Ravindran and Muralidharan [22] reported values of -1.340 V (versus Hg/HgO) and $2600 \mu\text{A cm}^{-2}$, respectively. In both reports, they used high purity (99.999%) zinc specimen as opposed to the technical grade zinc specimen used in the current study. This could possibly be the reason for the presence of I_{corr} value of a lower order of magnitude observed here.

Basic data pertaining to zinc corrosion, as well as aluminium, are not in consensus. There are a number of contributing factors, among others the purity and preparation of specimens, surface pre-treatment and also the corrosion measurement itself, that is, the issue addressed in the current study. For instance, looking at the potentiodynamic polarisation curves of **Figures 2** and **4**, should the intervals of linearity be determined from merely qualitative visual inspection, one may define different intervals and this consequently will result in different corrosion parameters. There will be numerous other possibilities but with no concrete justifications. Thus, the current study offers a quantitative justification - the piecewise linear regression analysis - in consideration of the Tafel linear regions, if they exist.

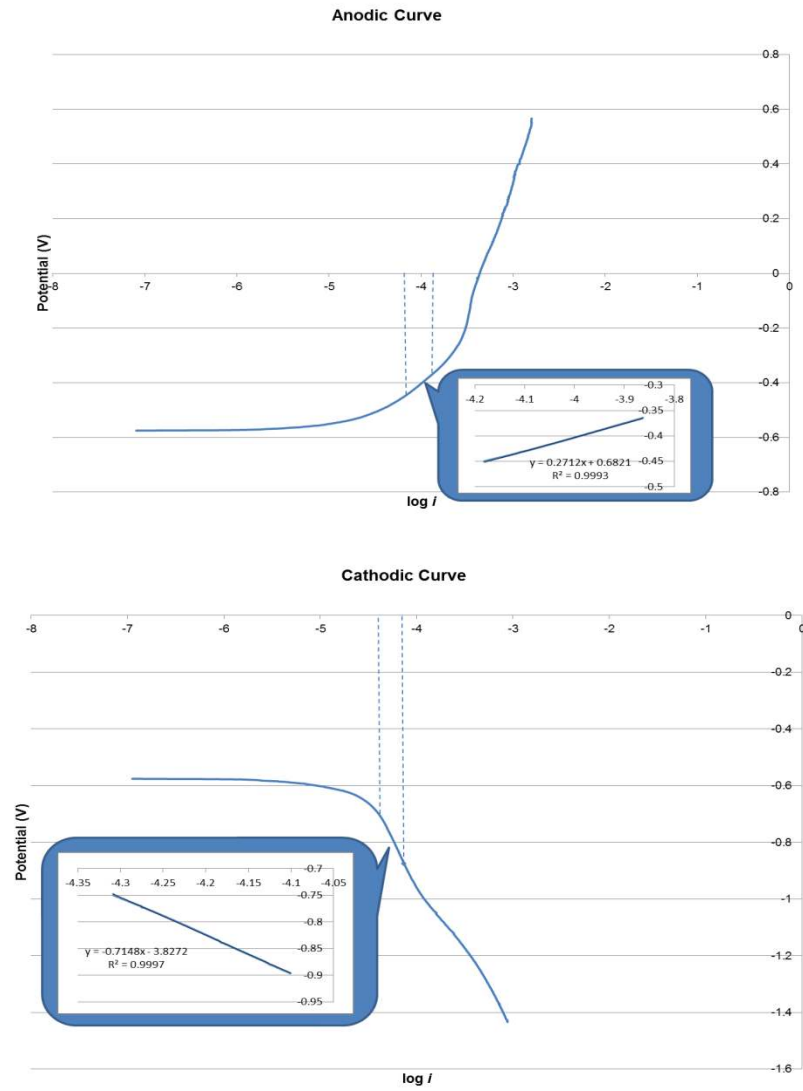


Figure 2: Corresponding interval of linearity on the anodic and cathodic polarisation branches as located from the bar chart distribution of m and R^2 coefficients for Al/NaCl (aq) system

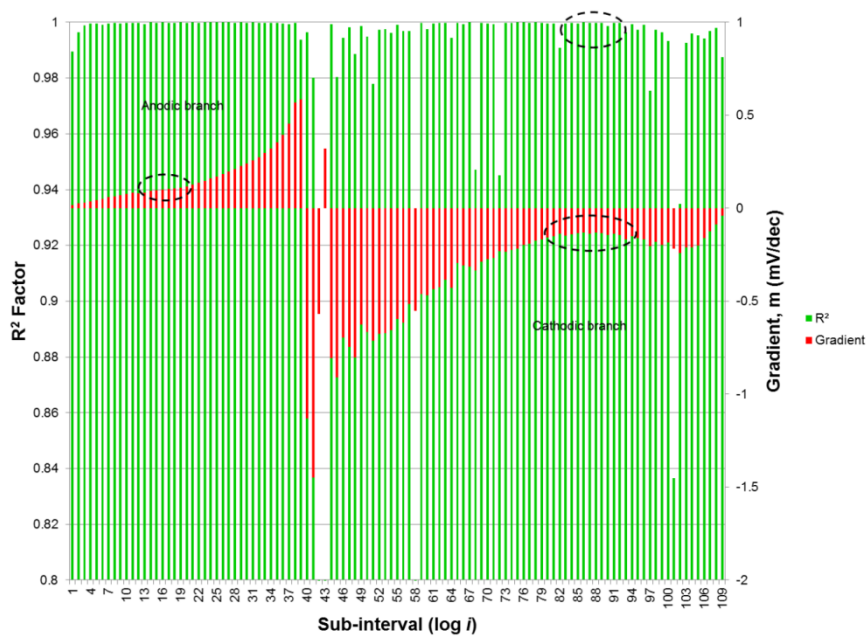


Figure 3: Bar chart distribution for m and R^2 values across the entire polarisation curve of zinc in 1.0 M KOH

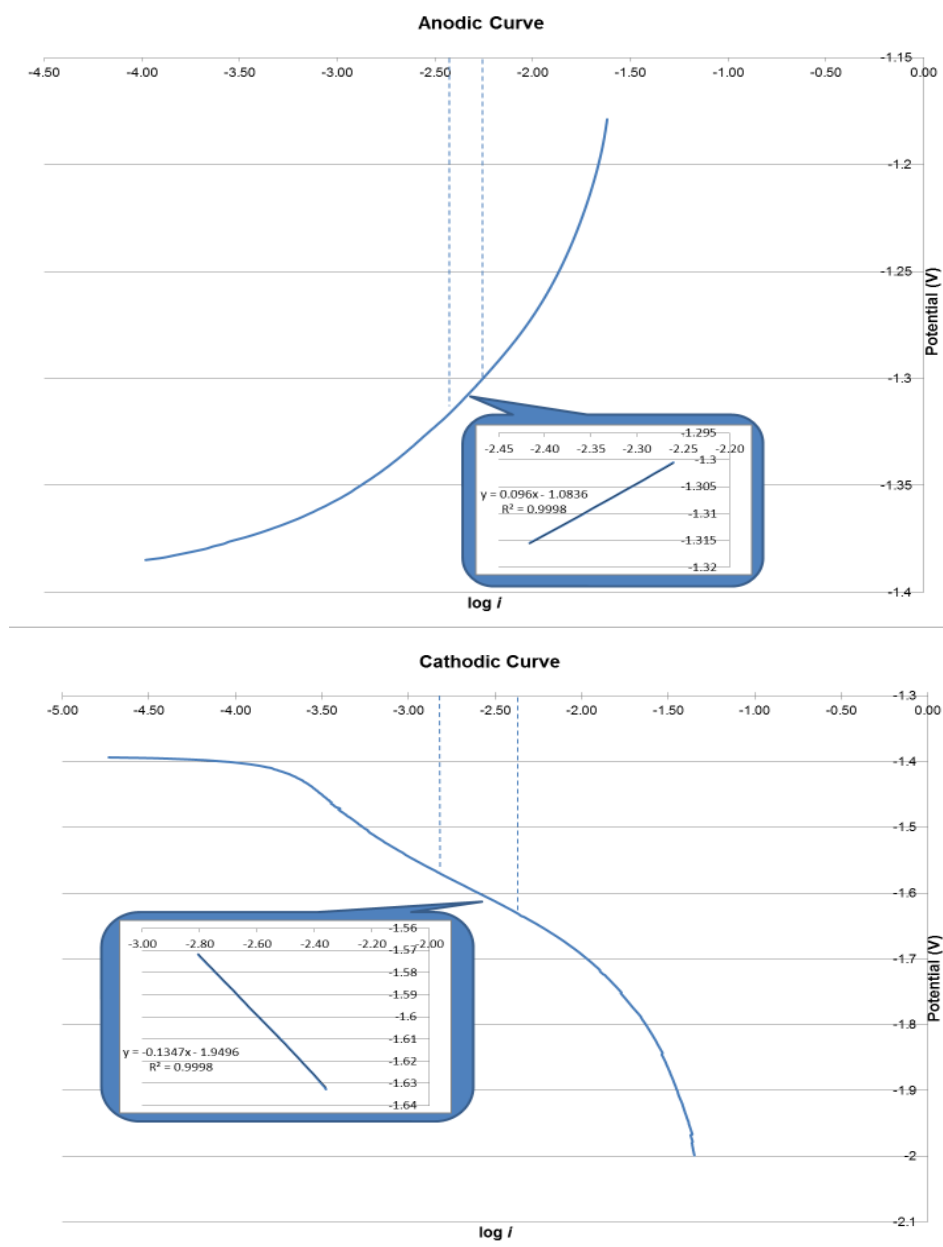


Figure 4: Corresponding intervals of linearity on the anodic and cathodic polarisation branches as located from the bar chart distribution of m and R^2 coefficients for Zn/KOH (aq) system

5. Conclusion

The current study presented a systematic and quantitative approach in determining the Tafel linear regions. Using the piecewise linear regression analysis, the ambiguity in which the linear region is determined could be minimised, if not eliminated. The method has been applied in Al/NaCl (aq) and Zn/KOH (aq) corrosion cells and proven to be very useful in defining the 'true' Tafel linear regions.

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