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Uncertainties of Corrosion Measurement Method Based on Tafel Equation

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ABSTRACT

A method to interpret corrosion current based on an electro chemical reaction is dominated by Tafel equation. However, this equation is still left uncertainties. Tafel method is valid for any certain conditions; the electron transfer is fast, reversible reaction, similar accessibility, and equal diffusion coefficients. Calculating model uncertainty is important to give correction factors to the theoretical calculations. It can be also useful to indicate the true values compared to prediction values. To investigate the Tafel uncertainties, it was conducted experiments involving CO_2 *pressure, pH, and HAc as independents variables using different polarization methods and different Tafel coefficients to measure corrosion rate. The results showed that the deviation has occurred. A numerical calculation resulted an absolute error was about 30%. If the other erroneous that comes from several Tafel assumptions and experiment data were accounted, the uncertainty will become more than 40%.*

Introduction

Tafel equations are method to calculate corrosion rate based on electrochemical process which relates to electron flow and over potential. Although this method has been applied intensively, but theoretically it contains problems openly to discuss. So far, researchers have applied a different assumption regarding calculating corrosion rate based on LPR technique. Even more, Streeter[1] stated that Tafel equation is only valid at the tubular flow electrode when axial and radial diffusion are insignificant. An uncertainty also arises from the Tafel experiment error, i.e., systematic and stochastic error. Fritz[2] calculated an un-acceptable absolute error of 27% -30%.

Linear Polarisation absolute Error

Tafel's method is considering the correlation between current density versus over-voltage. By using linear polarization technique (LPR), corrosion rate for mild steel is calculated by the formula (1):

$$CR = 0.503 \cdot \frac{\beta_a \beta_c}{(\beta_a + \beta_c)} * \frac{1}{R_p} \qquad (1)$$

Thus, relative deviation of corrosion rate calculation due to component variable can be expressed as (2):

$$\frac{\delta CR}{CR} = \left[\frac{\delta(CR)}{\delta T}\right]\frac{\delta T}{CR} + 2\left[\frac{\delta(CR)}{\delta E}\right]\frac{\delta E}{CR} + 2\left[\frac{\delta(CR)}{\delta I_{app}}\right]\frac{\delta I_{app}}{CR} + 2\left[\frac{\delta(CR)}{\delta a}\right]\frac{\delta a}{CR}$$

...(2)

Then Fritz[2] made a derivation expression above to become Equation 3:

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$$\frac{\delta CR}{CR} = \left[\frac{m_1}{\beta_a} + \frac{m_2}{\beta_c}\right]\delta T - \frac{2}{E}\delta E + \frac{2}{I_{app}}\delta I_{app} - \delta_a \quad \text{....(3)}$$

This formula means that overall uncertainty variable in corrosion calculation by LPR technique is due to instrumentation (potential, applied current, working electrode surface area) and Tafel slope(β). By making an assumption that Tafel slope is in certain value, Fritz accounted an error of 27%. In additional to effect of preparation solution and changing of specimen surface, he recorded a total error of 34%. Such LPR technique has uncertainties as descried below.

Tafel Slope Uncertainties

Refer to Equation (3) which Fritz calculated an absolute errors, it seems still to have an un-considered of uncertainty. The other uncertainties are erroneous from deviation due to an assumption of an exact value of Tafel slope (β). So far, this slope is under discussion intensively. As presented in Figure 1, Mokhtar[3] and Veloz[4] shows a different perception of slope that bring an addition to uncertainty corrosion rate calculation of 20%.

Tafel slope in LPR equation demonstrate a calculation instantaneous corrosion rate. There are two slopes which consist of anodic and cathodic slope to calculate corrosion rate.

$$\beta_a = \frac{2.303RT}{\alpha_a F}$$

$$\beta_c = \frac{2.303RT}{\alpha_c F} \qquad (4)$$

Where β_a and βc is anodic and cathodic Tafel slope, respectively, and α is coefficient of electron transfer. Quoted from the corrosion competent handbook created by KR Trethewey and Camberlain[5], coefficient of transfer electron of α is usually taken about 0.5. While cathodic and anodic Tafel slope (β_{anodic}, $\beta_{cathodic}$) is about 30 mV/decade to 100 mV/ decade, respectively. They did not give an alternative value of those constants.

The use of rate anodic and cathodic Tafel constants were assumed of 60 and 120 mV, was also used by Bill Hedges[6] during the experiments of solution contained different Acetic Acid concentration. This value was also followed by many other researchers. Denny A.Jones[7], 1996, an author of corrosion handbook, gave a range of 60 – 120 for both cathodic and anodic Tafel slope in activation regime. Further, he mentioned a similarity factor of α which is the difference value of β_{anodic} and $\beta_{cathodic}$. In his discussion, it is analyzed that the maximum error will occur in the greatest difference of α.

Mokhtar, 2005, used a constant value of 25 mV for B value in his solution experiment contained CO_2 gas and Acetic species. He did not consider of β_{anodic}, $\beta_{cathodic}$ individually and effects of α for different temperature and different composition concentration, as well as different flow rate regime. It, so far, seems to be acceptable.

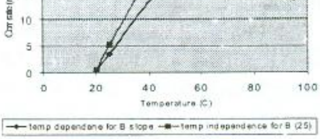

Figure 1- Effect of Tafel slope assumptions (B) on corrosion rate

Approximation of Tafel slope by Mokhtar is in contrast with **Keith George**[8] **and Srdjan Nesic** observations. These opponent researchers suggested that Tafel slope must change according to degree of temperature, composition and concentration. They found that when no HAc was present, the value of ba=40 mV/dec and bc=120 mV/dec. But in solution with HAc, ba is 80 mV/dec. Jean Louis and Crolet[9] observed an anodic slope pattern. He found that different composition of Acetic Acid and CO_2 caused different value of anodic Tafel slope. In general, Tafel slope increased with increasing of pH and decrease with increasing species concentration. The range value of anodic slope was 25 mV/dec to 120 mV/dec.

The role of other species such as H_2S in solution contained HAc and CO_2 was presented by Veloz and Gonzales[4], 2002. According to them, Tafel slope value increase with the presence of 0.104 M H_2S. Tafel anodic slope goes up from 93 mV/dec to 135 mV/dec and from 262 mV/dec to 235 mV/dec for cathodic slope.

Temperature is also contributed to change Tafel slope behavior as reported by Fransson[10]. They noted that the increased of temperature from 20°C to 95°C had given an increase result of ba=50 mV/dec -56 mV/dec (anodic slope) and bc=15 mV/dec - 207 mV/dec (cathodic slope).

Polarization Plot Limitation

Anodic and cathodic Tafel slopes to calculate corrosion rate is obtained by Tafel plot. By conducting a potentio-dynamic sweeps from ± 10 mV refer to open circuit potential, polarization curves is plotted. Potential and current relationship regime is governed by a corrosion reaction. Then, the free corrosion potential and potential corrosion (E_{corr} and I_{corr}) point occurs at the mixed point of intersection of anodic and cathodic current. Accuracy of polarization plot is predominantly influenced by scan rate and solution dynamics.

A effect of scan rate

Because of un-stability composition solution and dynamics electro-chemical reaction, the Tafel plot results an un-hopefully linearity region - what Tafel want. There has been, sometimes, more than one possibility for Tafel slope line (Figure2). One of the factors influenced Tafel plot is scan rate. Effect of different scan rate makes a different potential and current plot (Figure3). These feature plots are under user control. Conducting a very slow of scan rate will cause an unstable plot. While, the fast scan will result an un-complete electro-chemical reaction process, the specimen is not allowed time to reach a stable potential.

Satpati[11] observed a different scan rate that has caused a different result on his data. When lowest scan rate was applied to zircaloy in NaCl solution, pit initiated at edges. It initiates at the scratch at intermediate scan rate. But, uniform distribution of pits was seen at higher scan rates. He correlated this behavior with thickness of passive film formed and its changes of potential during scanning.

ASTM recommends a standard test (G59) for potentio-dynamic polarization test with the scan rate of 0.6 V/h (0.16 mV/s) from ? E = –30 mV to ? E = +30 mV and back to ? E = –30 mV.

The plot should be linear, go through the origin. The curves recorded for the forward and reverse scans should be identical. However, with any reasons, researchers did not conduct that recommended rate. Papavinasan[12], Bill Hedges[6], and R De Marco, for examples, those who run scan rate of 0.5 mV/s, 1 mV/s, 0,1 mV/s respectively. Keith and George[8] did a sweep of 0.2

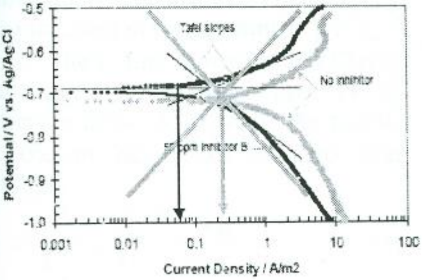

Figure 2-An ambiguous of I_{corr}[9]

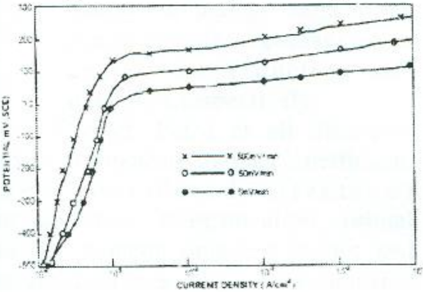

Figure3-Effect of scan rate on Potential and Current density[11]

B Charger transfer reaction effect on Tafel Plot

An ideal curve is reached when relationship both of E and log (i) in a linear curve. When $\alpha = 0.5$, this value gives a symmetry plot at a corrosion potential or zero over-voltage (figure 4).

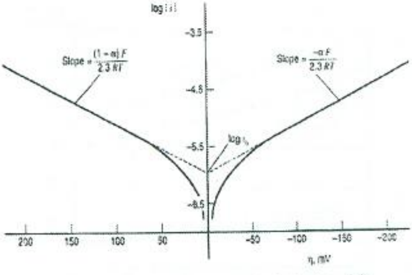

Figure 4-An ideal Tafel plot[13]

The fact that an ideal of Tafel plot is quite difficult to obtained. It has to have stable reaction kinetics and both reduction and oxidation energy barrier is identical. Such that the total of α must be one. When standard free energy is not the same, bring the shift of Tafel slope to asymmetry plot. **Tafel slope described by Fenton[13] (Figure 5) show** the case of a one-electron transfer reaction is asymmetry:

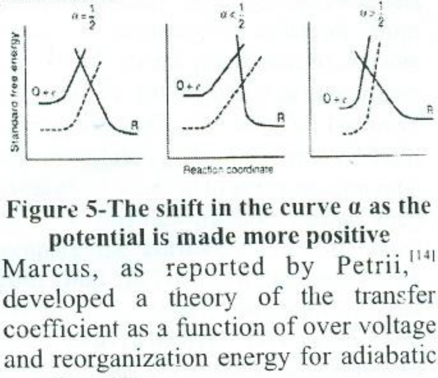

Figure 5-The shift in the curve α as the potential is made more positive

Marcus, as reported by Petrii,[14] developed a theory of the transfer coefficient as a function of over voltage and reorganization energy for adiabatic reactions (5).

$$\alpha = \frac{1}{2} - \frac{F\eta}{2\lambda} \qquad (5)$$

For diabatic reaction, homogenous electron transfer and over potential near to zero , Marcus wrote a more simple equation as following (6).

$$\alpha \approx 1 - n(\acute{\varepsilon}) \qquad (6)$$

Where, έ is the effective energy level. If έ in the significantly lower than Fermi level, the condition is called as an activation-less discharge which is near to zero for α value. According to Marcus equation, a prediction of 0.5 value of α for zero over-voltage has a maximum error in the interval of ~ $0.05\lambda/F$.

The deviation of charge transfer coefficient from 0.5 can be explained by modern theory. Refer to Oleg A[14]. Petrii prediction, there are some source that causes transfer coefficient behavior deviate from 0.5. Firstly, effect of intra-molecular reorganization energy as can be expressed in the equation (7). If $\lambda_{in} / \lambda_s << 1$, then the transfer coefficient exceeds 0.5 at zero over-voltage. For the opposite limit $\lambda_{in} / \lambda_s >> 1$, the transfer coefficient below 0.5 at zero over-voltage.

$$\alpha \approx \frac{1}{2}\left(1 \pm \frac{\overleftarrow{\lambda}_{in}}{\lambda_s}\right) - \frac{F\eta}{2\lambda_s} \qquad (7)$$

Where, λs is the solvent reorganization energy λ and $\overleftarrow{\lambda}$ refer to the intramolecular reorganization energy for reduction and oxidation, respectively.

Further, Petrii et all discussed factors influenced transfer coefficient. They considered effects of intramolecular reorganization, orbital overlap, reactant quantum modes and solvent dynamics. The main conclusion is that majority α can be near to 0.5 and over-voltage independence at *η equal to 0*. However, there are many examples which transfer coefficient falling beyond 0.45-0.55.

Effect of α assumption ranged from 0.44-0.56 make a different value of B Tafel slope as pictured at figure 6 below. This different assumption of α has increased an uncertainty of corrosion rate about 5%.

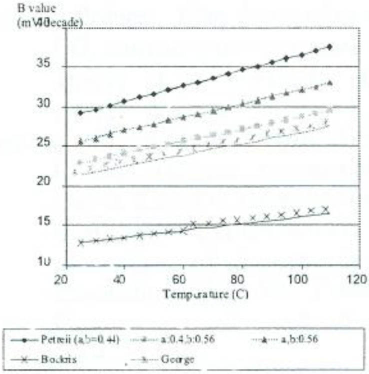

Figure 6- Effect of electron transfer coefficient (α)on Tafel slope of B

B an alternative of polarisation plot

A new method had been introduced by Xianming Shi[15] ,Shizhe Song. They purpose a quite complicated method. They gave an alternative to determine Tafel slope. Studying corrosivity of chemical deicers, they used polynomials fitting in polarization behavior from E_{corr}±70 mV (weak polarization). Anodic and cathodic Tafel slope was taken from a derivative of E_{corr} at ±60 mV. The next, they calculate i_{corr} from the rule of Tafel linear extrapolation to get corrosion rate. To verify this new method, further, they compare the corrosion rate calculated from that polynomial method with weight loss methods. The result was that the relationship between the instantaneous corrosion rate (expressed as i_{corr}) and the average corrosion rate (stated as percentage of corrosion area), was linear with log weight loss.

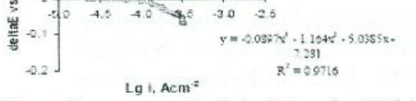

Figure 7- a new method to determine Tafel slope(15)

Conclusion

Based on the LPR error calculation, it is impossible to recommend the use of the method which is very unsatisfied statistically. Statisticians normally accept an experiment data error of 5% rather than 30% what LPR reached. This discussion of uncertainty corrosion calculation based on LPR technique reminds the need of further interpretation of the corrosion data. Corrosion calculation is not only study about the rate of material attached but also knowledge of mechanism and kinetics. Factors influence real corrosion rate is very complicated. It is more likely that other factors may have a prime role, and be more important than these uncertainties. Therefore, to conclude a corrosion phenomena is important to understand not only electrochemical process involved in corrosion process but also history of operating condition without neglecting an inevitable error that creating a deviation.

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