

# Dynamic tafel factor adaption for the evaluation of instantaneous corrosion rates on zinc by using gel-type electrolytes

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**Abstract.** Electrochemical corrosion measurements allow calculation of the instantaneous zinc corrosion rate via polarization resistances by using tafel factors. However, the determination of the actual tafel factor is problematic since it depends on the state of the formed zinc layers and the corrosion reactions taking place. Therefore, valid tafel factors are either determined in additional experiments via dynamic polarization or estimated by calculation. In most cases a constant value for tafel factors is assumed for simplification, without regard to the real conditions of the corroding system. Since naturally formed zinc layers are unstable using conventional test electrolyte solutions determination of tafel factors is hindered additionally and inaccurate interpretations can result. For some time now, the use of gel-type electrolytes in corrosion research has enabled minimally invasive investigation of zinc surface layers and thus offers new approaches to a scientifically proven determination of tafel factors. The paper presents a new method for the determination and evaluation of tafel factors using gel-type electrolytes and electrochemical frequency modulation technique (EFM). This relatively new electrochemical method offers the possibility to determine both polarization resistances and tafel factors within one measurement and in short measuring intervals. Starting from a comprehensive parameter study it is shown that a direct relationship between the two values exists that can be described mathematically. This contribution presents the determined tafel factors for the system gel-type electrolyte/zinc and discusses their applicability and their limits.

## 1. Introduction

When the tafel factor (B value, Stern-Geary constant) is known, the instantaneous corrosion rate ( $i_{cor}$ ) of an actively corroding system can be described by means of the polarization resistance ( $R_p$ ). This is carried out using the following relationship:

$$i_{cor} = \frac{B}{R_p} \quad (1)$$

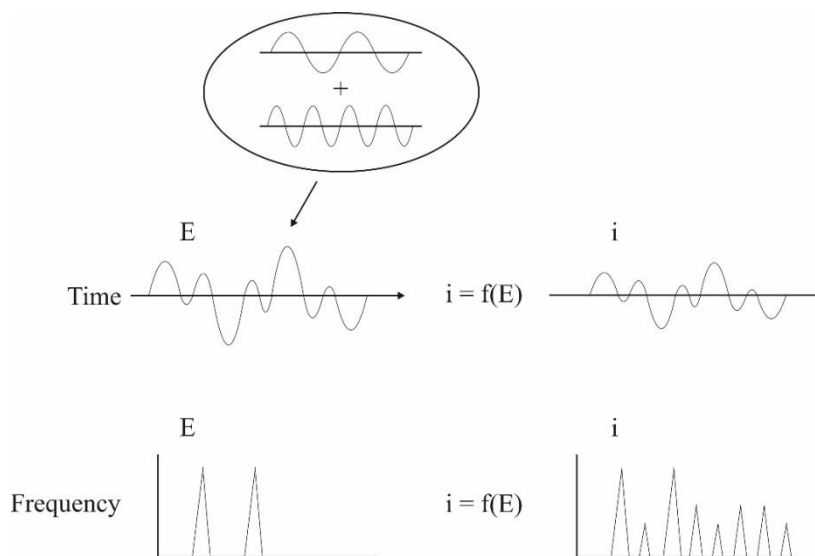
This value can then be used for further calculations to determine mass loss and corrosion loss. Thus, the lifetime of zinc and zinc coatings under atmospheric conditions can be estimated. However, the tafel factor currently valid for the investigated system is not readily accessible. In many cases values for tafel factors are determined by additional experiments (mass loss measurements, tafel relationship) or are taken from the literature. A B value in the range of 5 to 30 mV is described, for example, by Metikos-Hukovic and Zevnik [1] for the system "electrolytically deposited zinc in a neutral 5 % sodium chloride solution". This value determined by means of dynamic polarization was



dependent on the parameters of the zinc deposition and the temperature of the test solution. The investigations proved that the  $B$  value is not a constant value, but is caused by the corrosion processes taking place. It was shown that, as the polarization resistance increases, the  $B$  value decreases statistically. However, in the case of monitoring studies for zinc-coated iron under atmospheric conditions, they used a statistically determined constant  $B$  value of 13.8 mV [2] for simplification.

In the case of the specific determination of  $B$  values on zinc, zinc alloys and zinc coatings limits may be encountered in certain circumstances. The high reactivity and solubility of the protective layers formed on zinc surfaces under atmospheric conditions are problematic in contact with aqueous test media. As a result, naturally formed protective layers on zinc are stable only for a limited time during the corrosion test with typical aqueous test electrolytes and tend to rebuild or dissolve during the measurement. For this reason,  $B$  values from literature should be considered critically concerning atmospheric corrosion reactions. In order to counter this problem, however, two approaches can be utilized. On the one hand, attempts can be made to shorten the test period by selecting a suitable examination procedure and by adapting the examination parameters. On the other hand, the influence on the naturally formed layers on zinc can be minimized by selecting a suitable test electrolyte (minimally invasive test). New scientific knowledge and results from recent research allow new alternatives for both approaches, which appear promising for the determination of tafel factors on zinc under atmospheric conditions.

In the last 15 years the electrochemical frequency modulation (EFM) was introduced as a monitoring technique in the field of electrochemical investigation methods. Bosch et al. introduced the technique for the first time in [3] and extended it in [4]. It is based on the assumption that a corrosion system is a non-linear system. Thus, a current response at more frequencies (at zero, intermodulation, harmonic frequencies) than the perturbation frequencies is obtained by a potential perturbation with two sine waves of different frequency. The simplified principle of the EFM technique is shown in figure 1.



**Figure 1.** Principle of EFM technique according to [4].

The frequency-dependent current response is modeled (e.g. with Gamry software) by means of a Taylor sequence and the instantaneous corrosion current density as well as the anodic ( $b_a$ ) and cathodic ( $b_c$ ) tafel factors are calculated. A typical measuring routine usually only takes about 1 minute if the suitable examination parameters are chosen. Thus,  $B$  values from  $b_a$  and  $b_c$  and corrosion current densities can be determined in a short period of time. The knowledge of tafel factors is not necessary beforehand, since they are linked to the frequency-dependent current responses. A deri-

variation of this relationship can be found in [3] and will not be explained in this article. In the EFM, the perturbation amplitude and the perturbation frequencies can be varied. The amplitude of the perturbation ( $E_0$ ) should not exceed  $\pm 20$  mV and is subject to the following relationship from [3]:

$$\frac{E_0}{b_{a,c}} \ll 1 \quad (2)$$

Accordingly, the perturbation amplitude should be smaller than the measured tafel factors. However, it is pointed out in [3] that the effective error at a ratio of 1 lies at  $\leq 10\%$  and thus in an acceptable range. According to [4] the choice of perturbation frequencies underlies the following three aspects:

- harmonic and intermodulation frequencies should not influence each other,
- base frequency should be as low as possible to avoid capacitive behavior,
- base frequency should be as high as possible to minimize measurement duration.

These relationships show that the choice of optimal frequencies is not possible and a compromise has to be made. In their studies on steel in sulfuric acid and in a sodium chloride solution with adapted test parameters, Bosch et al. proved that the EFM technique is in good correlation with mass loss, impedance and polarization measurements. In contrast, Mansfeld and Kus [5] offer a critical view of the EFM technique. They utilized EFM measurements for copper, aluminum and stainless steel and were unable to find a satisfactory correlation with established methods. They noted that the accuracy of the technique depends on the accuracy of the current measurement and reaches its limits especially for systems with low corrosion currents. Rauf and Bogaerts, on the other hand, were able to observe the onset of pitting corrosion on stainless steel using EFM [6]. The EFM technique has not been utilized for zinc and zinc coatings so far. However, it appears to be promising as it generates a high amount of information within a short period of time in a minimally invasive way (by small perturbation amplitudes).

The problem that determination of B values on zinc and zinc coatings becomes more difficult due to the high solubility of the formed cover layers under the influence of an aqueous test electrolyte can be countered by using of gel-type electrolytes for electrochemical investigations. This electrolyte variant is a conductive polymerized mass, usually made of agar that can be shaped as desired. Due to the syneresis effect (phase separation of a two-phase system), gel-type electrolytes form a thin moisture film at the gel/metal interface. Thus, an electrochemical instrumentation allows electrochemical corrosion investigations on zinc and zinc coatings. Testing with gel-type electrolytes is minimally invasive since the naturally formed corrosion product layers on zinc coatings are only slightly influenced by the moisture film of the gel-type electrolyte. It has already been demonstrated, that gel-type electrolytes influence zinc corrosion product layers much less than a comparable aqueous test electrolyte [7-9]. Cano et al. could also show this effect for bronze [10]. Due to difficult diffusion conditions in the gel-type electrolyte, dissolution of the corrosion product layers is almost completely inhibited in many applications.

In this paper, the EFM technique is linked to a gel-type test electrolyte and applied to pure zinc. At first, suitable test parameters had to be worked out through means of a parameter study, since no EFM parameters were available in literature for the system "pure zinc/gel-type electrolyte". Subsequently, the interdependency between B values and polarization resistances determined by means of EFM was investigated, mathematically described and verified. For this, pure zinc samples were stored for a defined period of time under atmospheric conditions (city atmosphere) in order to form differently stable zinc corrosion product layers and thus to generate a wide range of samples. The interdependency shall allow to calculate the appropriate B value only by means of a measured polarization resistance (from impedance or dynamic polarization) if EFM measurements are not possible.

## 2. Experimental

### 2.1 Sample preparation and test electrolyte

Sample sheets of pure zinc (99.5 % Zn) with a sheet thickness of 0.8 mm were used as specimen for all investigations. At first samples were cleaned and degreased. Then, the samples were pickled with 1 M sodium hydroxide solution for 5 minutes in an ultrasonic bath, cleaned with deionized water and ethanol and dried under a warm airflow. Pickling was conducted to activate the sample surfaces by removing the existing corrosion product layers that formed under undefined atmospheric conditions. Thereby, all samples had the same initial surface conditions. Afterwards, the specimens were stored for different durations with a maximum of 180 days to form a natural zinc corrosion product layer by means of outdoor weathering at city atmosphere (Berlin). During this period, the samples were taken at regular intervals, examined electrochemically and then subjected to the city atmosphere again.

A gel-type electrolyte based on agar was used as test electrolyte. The gel-type electrolyte was shaped as a circular gel pad with a diameter of 19 mm and a pad thickness of 3 mm. From the size of the gel pad, a theoretical electrolyte volume of 0.9 ml was obtained. The measuring area was 2.84 cm<sup>2</sup>. High purity agar powder was dissolved in demineralized water and then polymerized at elevated temperature to produce the gel pads. Afterwards, the gel pads had a gelatinous consistency, a dense surface with no visible porosity and could be brought in the dimensions desired for testing. In the gel pads, a chloride concentration of 260 ppm was determined.

### 2.2 Electrochemical investigations

The gel-type electrolyte in the form of gel pads was first electrochemically instrumented for electrochemical investigations. The typical three-electrode arrangement was used for this purpose. A mixed titanium oxide net was used as counter electrode (CE) and a saturated Ag/AgCl electrode as reference electrode (RE). The samples served as working electrodes (WE). A Potentiostat/Galvanostat Interface 1000 from Gamry Instruments was used for all electrochemical experiments.

The correlations between perturbation frequencies and perturbation amplitude were investigated at two sample states (activated surface before exposure to city atmosphere, after 180 days of exposure) by means of a parameter study. From this the most fitting EFM parameters for the corrosion system zinc/gel pad were derived. Base frequencies of 0.05, 0.1, 0.5 and 1 Hz were varied. Multipliers of the base frequencies were 2 and 5. Thus, for a base frequency of 0.1 Hz a superimposed perturbation with the frequencies 0.2 Hz and 0.5 Hz was obtained in contrast to a perturbation with 2 Hz and 5 Hz for a base frequency of 1 Hz. A measurement included four cycles. In addition, the perturbation amplitude was varied in the range from 5 to 20 mV. After completion of the parameter study, a base frequency of 0.1 Hz (perturbation frequencies 0.2 Hz and 0.5 Hz) with a perturbation amplitude of 5 mV was selected for the remaining sample conditions. Using the Gamry software EchemAnalyst, anodic and cathodic tafel factors as well as corrosion current densities were determined from the EFM data. B values were calculated from the tafel factors using the following relationship:

$$B = \frac{b_a b_c}{2.3 (b_a + b_c)} \quad (3)$$

Polarization resistances  $R_p$  were calculated from the determined corrosion current densities  $i_{cor}$  using the following relationship:

$$R_p = \frac{B}{i_{cor}} \quad (4)$$

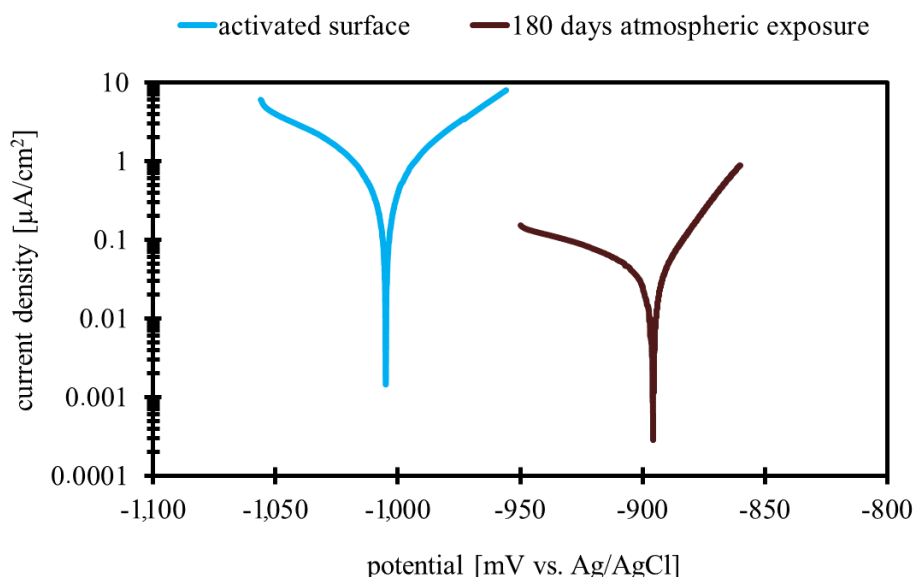
Current density-potential curves were determined by means of dynamic polarization at the two sample states of the EFM parameter study in order to evaluate the EFM results. After 10 minutes of potential measurement, the samples were polarized in anodic direction in a potential range from -50 mV to +50 mV vs.  $E_{cor}$ . The sweep rate was 1 mV/s. In a potential range with only slight distance from the

free corrosion potential ( $\pm 5$  mV vs.  $E_{\text{cor}}$ ), linear polarization resistances (LPR) were subsequently determined as a characteristic value for the instantaneous protection ability of the zinc layer. In addition, the corrosion current density at the free corrosion potential was determined via tafel relationship. Anodic and cathodic tafel factors were determined at a distance of 5, 10, 15 and 20 mV from the free corrosion potential by using the Gamry software EchemAnalyst.

### 3. Results

#### 3.1 Dynamic polarization for evaluation of EFM results

By means of an EFM parameter study at two sample states, the best fitting parameters for the selected corrosion system should be derived. In order to be able to evaluate the EFM results, current density-potential curves and their specific characteristic values were determined using dynamic polarization. In the following figure 2, the current density-potential curves for the activated surface state and for a sample after 180 days of exposure to city atmosphere are shown.



**Figure 2.** Current density-potential curves on pure zinc with pickled (activated) surface and after 180 days of exposure to city atmosphere, determined by using gel-type electrolyte.

The curves and the position of the free corrosion potentials differ depending on the sample state. The free corrosion potential is approximately 100 mV more negative when the surface is activated than after 180 days of exposure to city atmosphere during which a surface layer of corrosion products could form on the surface. This inhibits the partial reactions so that after 180 days of exposure lower current densities are measured overall. However, typical potential ranges for a zinc surface are measured for both states. The following table 1 compiles the corrosion-relevant tafel factors and the characteristic kinetic values determined by using the current density-potential curves. The determined linear polarization resistances (LPR) and corrosion current densities ( $i_{\text{cor}}$ ) as characteristic values provide an overview of the state of the zinc surface. A stable zinc corrosion product layer was formed after 180 days of exposure to city atmosphere. A low polarization resistance and thus a high corrosion current density were measured on the activated surface. The anodic and cathodic tafel factors determined at defined distances from the free corrosion potential become larger with increasing distance to the free corrosion potential for both sample states. The cathodic tafel factors are larger than the anodic. The tafel factors for the sample exposed to city atmosphere for 180 days tend to be smaller than when the surface is activated.

**Table 1.** Corrosion-relevant tafel factors and kinetic values on pure zinc determined by means of dynamic polarization and gel-type electrolyte.

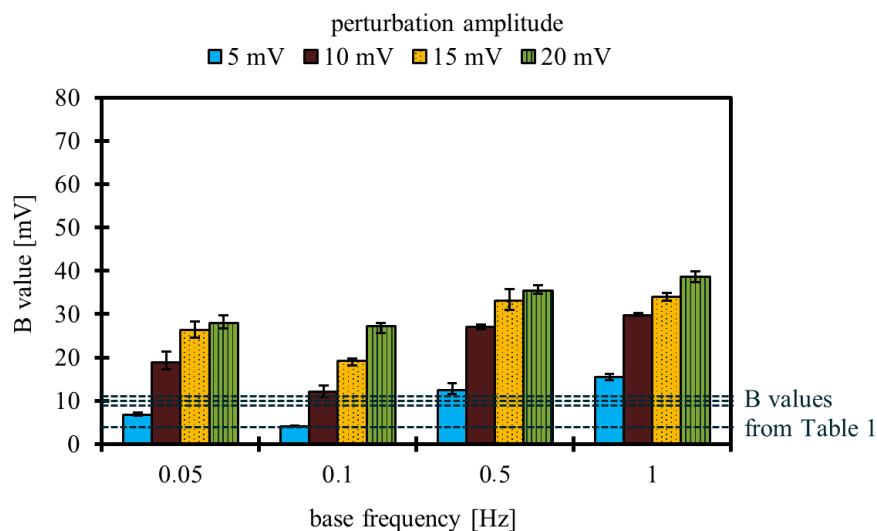
Sample	Tafel factors calculated at ... vs. $E_{\text{cor}}$	Tafel factors			corrosion relevant values	
		$b_c$ (mV/dec)	$b_a$ (mV/dec)	$B$ (mV)	$i_{\text{cor}}$ ( $\mu\text{Acm}^{-2}$ )	LPR ( $\Omega\text{cm}^2$ )
activated surface	5 mV	18	17	4	0.7	12,936
	10 mV	44	36	9		
	15 mV	53	43	10		
	20 mV	59	47	11		
180 days of atmospheric exposure	5 mV	12	11	3	0.03	158,580
	10 mV	37	26	7		
	15 mV	54	34	9		
	20 mV	59	36	10		

### 3.2 EFM parameter studies for determination of test parameters

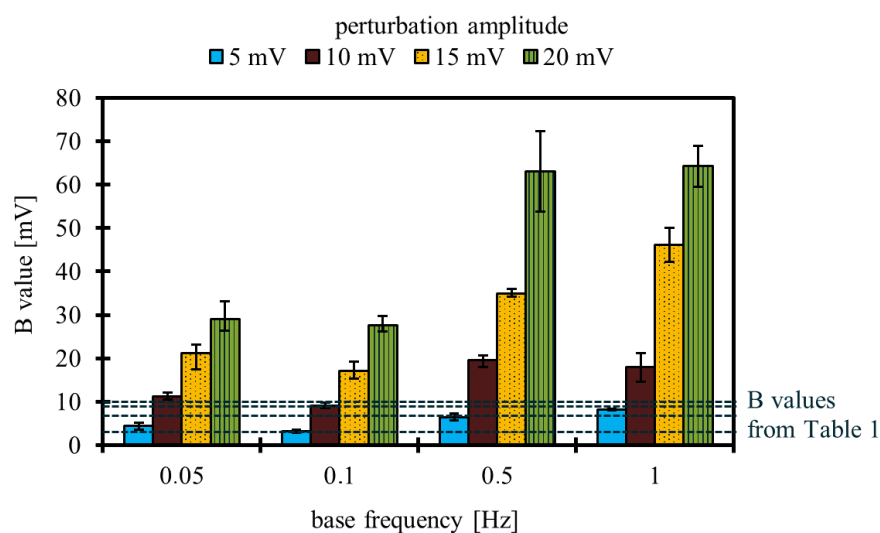
The results of the EFM parameter study are presented below. In the following figure 3, the  $B$  values determined on the activated (pickled) sample by means of EFM are depicted as a function of the base frequency and the perturbation amplitude. In addition,  $B$  values from the current density-potential curves from table 1 are shown for comparison purposes.

The  $B$  values show a strong dependence on the perturbation amplitude and a lower dependence on the base frequency of the perturbation. With higher perturbation amplitude, the  $B$ -value is also increased. With a higher base frequency, the  $B$  value tends to increase slightly. Compared to the  $B$  values from the dynamic polarization, the  $B$  values from the EFM measurements at perturbation amplitudes greater than 10 mV are in some cases significantly higher than the comparative values. The same dependencies can be also seen at the sample state after 180 days of exposure to city atmosphere. The results are summarized in figure 4. The  $B$  values also show a strong dependence on the perturbation amplitude and a dependence on the base frequency, especially at higher perturbation frequencies. Compared to the  $B$  values from the dynamic polarization, there is an even higher deviation to the  $B$  values from the EFM measurements at perturbation amplitudes greater than 10 mV than when the surface is activated. In addition, the  $B$  values tend to be higher than when the surface is activated. The interdependencies between polarization resistances determined by means of EFM and the chosen test parameters are shown in figure 5 at the example of the activated (pickled) surface.

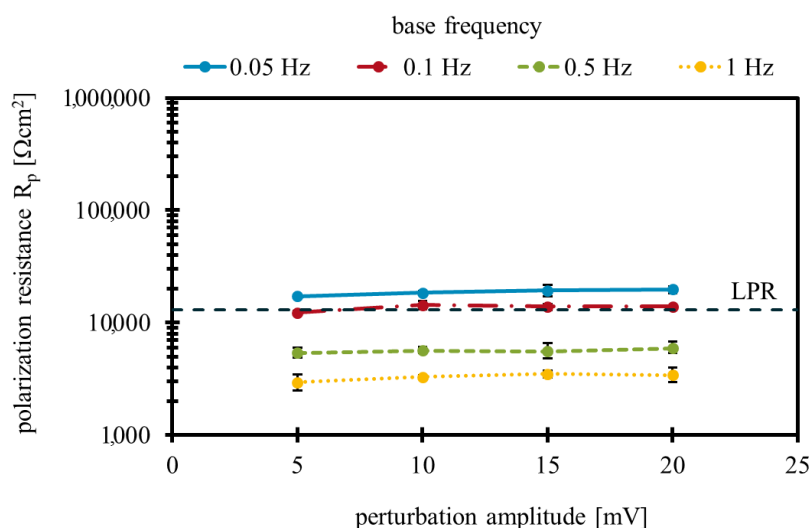
The polarization resistances show an indirect dependence on the base frequency of the perturbation. If a higher base frequency is chosen, a lower polarization resistance is measured. The perturbation amplitude has no significant influence on the magnitude of the polarization resistance. The polarization resistance of the EFM measurements corresponds to the determined linear polarization resistance from table 1 at a base frequency of 0.1 Hz. The polarization resistances of the sample after 180 days of exposure to city atmosphere are shown in figure 6 as a function of the test parameters.



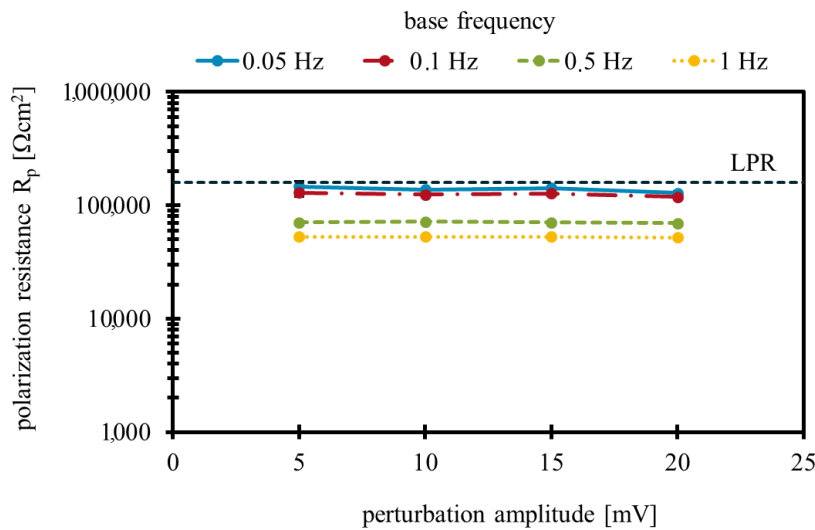
**Figure 3.** B values in function of base frequency and perturbation amplitude determined by EFM and B values from dynamic polarization (Table 1), pure zinc with activated surface, gel-type electrolyte.



**Figure 4.** B values in function of base frequency and perturbation amplitude determined by EFM and B values from dynamic polarization (table 1), pure zinc after 180 days of exposure to city atmosphere, gel-type electrolyte.



**Figure 5.** Polarization resistances in function of base frequency and perturbation amplitude determined by EFM, pure zinc with activated surface, gel-type electrolyte.



**Figure 6.** Polarization resistances in function of base frequency and perturbation amplitude determined by EFM, pure zinc after 180 days of exposure to city atmosphere, gel-type electrolyte.

The polarization resistances comprise the same interdependencies between the test parameters as with the activated surface. The perturbation amplitude also has no significant influence on the magnitude of the polarization resistance. The polarization resistances are higher than with the activated surface caused by the protective zinc corrosion product layer. At a base frequency of 0.1 and 0.05 Hz, the polarization resistance of the EFM measurements corresponds sufficiently to the determined linear polarization resistance from table 1. From the results of the EFM parameter study with regard to the results of dynamic polarization, the following test parameters are obtained for subsequent studies:

- a base frequency of 0.1 Hz (= perturbation frequencies 0.2 Hz and 0.5 Hz) in correlation with the LPR,
- a perturbation amplitude of 5 mV in good correlation with results of dynamic polarization and in accordance to equation (2).

### 3.3 Interdependency between $B$ value and polarization resistance

A large number of sample states after atmospheric exposure were examined by means of a gel type electrolyte to investigate the correlation between  $B$  values and the calculated polarization resistances via EFM measurements on pure zinc. These samples differed in the duration they were subjected to city atmosphere and thus in the state of the formed corrosion product layer. Thereby, it was possible to obtain a wide spectrum of different polarization resistances and  $B$  values on pure zinc samples. The determined  $B$  values as well as the corresponding polarization resistances are shown in figure 7. In addition, the figure shows two regressions with their corresponding equation and the coefficient of determination ( $R^2$ ), respectively.

It turns out that the  $B$ -value decreases with increasing polarization resistance. This interdependency can be described adequately by a logarithmic function or via a power regression. With high polarization resistances above  $200,000 \Omega\text{cm}^2$ , only a small decrease in the  $B$  value is observed. In contrast, with low polarization resistances below  $10,000 \Omega\text{cm}^2$  there is a strong dependency between polarization resistance and  $B$  value. The interdependency can be described by the following regressions:

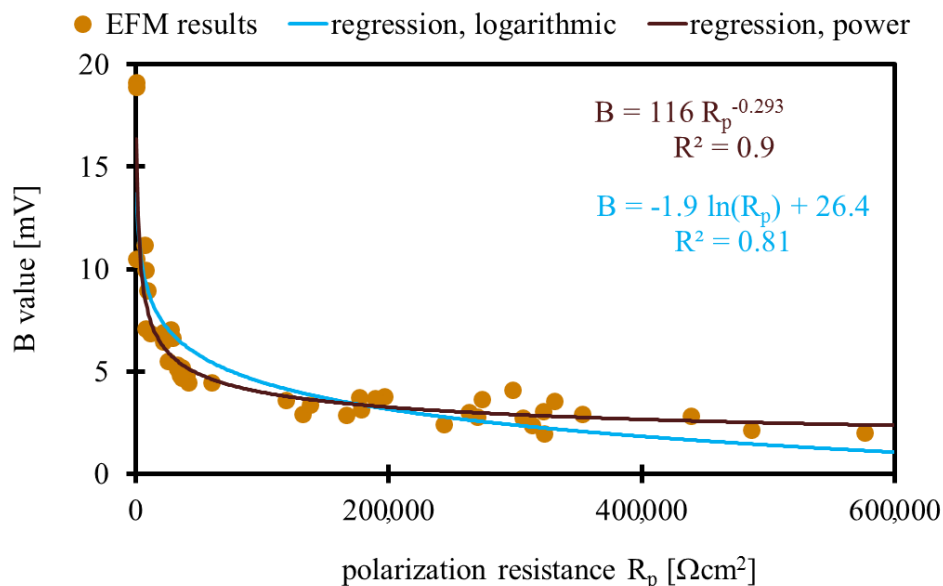
$$B = -1.9 \cdot \ln R_p + 26.4 \quad (5)$$

$$B = 116 \cdot R_p^{-0.293} \quad (6)$$

The  $B$  values calculated by means of equations (5) and (6) are compiled for predetermined polarization resistances in table 2. Subsequently, the corrosion current density was calculated by means of



the B value via the equation (4). Corrosion current densities calculated with a constant B value from literature [2] are also shown.



**Figure 7.** Interdependency between B value and polarization resistance in EFM measurements on pure zinc with different exposure times to city atmosphere, gel-type electrolyte.

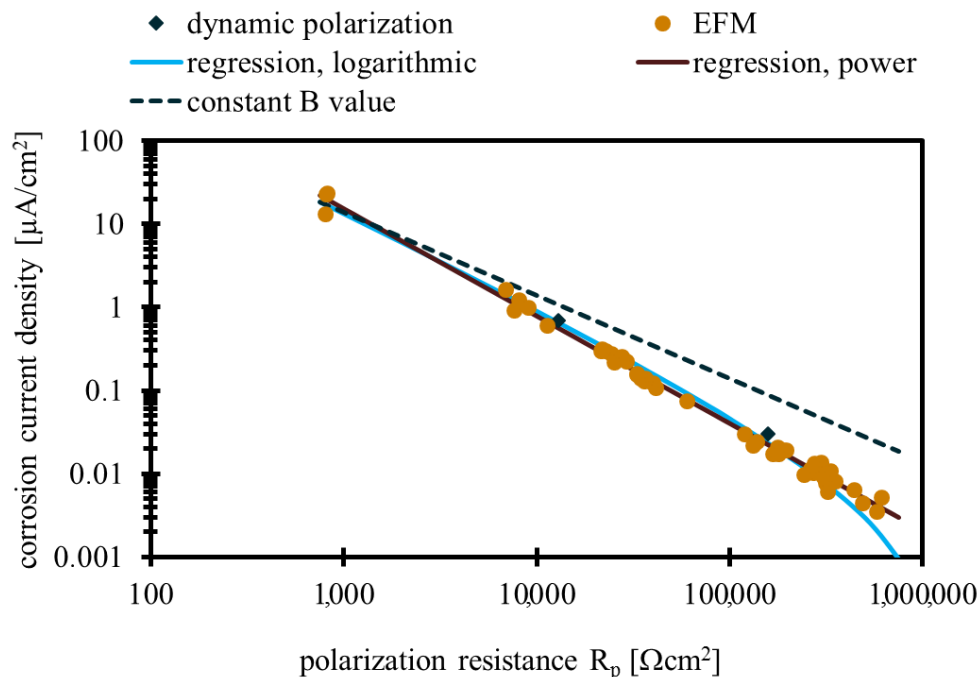
**Table 2.** Calculated B values from regression and literature and corrosion current densities for pure zinc, gel-type electrolyte.

$R_p$ ( $\Omega\text{cm}^2$ )	regression, logarithmic (5)		regression, power (6)		constant B value	
	B (mV)	$i_{\text{cor}}$ ( $\mu\text{Acm}^{-2}$ )	B (mV)	$i_{\text{cor}}$ ( $\mu\text{Acm}^{-2}$ )	B (mV)	$i_{\text{cor}}$ ( $\mu\text{Acm}^{-2}$ )
750	14	18	17	22	13.8	18
1,000	13	13	15	15	13.8	14
2,500	12	5	12	5	13.8	6
5,000	10	2	10	2	13.8	3
7,500	9	1	8	1	13.8	2
10,000	9	0.9	8	0.8	13.8	1
25,000	7	0.3	6	0.2	13.8	0.6
50,000	6	0.1	5	0.1	13.8	0.3
75,000	5	0.07	4	0.06	13.8	0.2
100,000	5	0.05	4	0.04	13.8	0.1
250,000	3	0.01	3	0.01	13.8	0.06
500,000	1	0.003	2	0.005	13.8	0.03
750,000	1	0.001	2	0.003	13.8	0.02

The regression based on a power (6) gives a good agreement with the measured values at polarization resistances below  $1,000 \Omega\text{cm}^2$  (figure 7). For higher polarization resistances with a value above  $500,000 \Omega\text{cm}^2$  current densities calculated by means of both regressions differ slightly from each other. In comparison to the regressions the effect of a constant B value on the calculated corrosion current density is shown. Being in good agreement with the regressions for very low polarization resistances, a higher corrosion current density is determined for polarization resistances above  $2,500 \Omega\text{cm}^2$ .

#### 4. Discussion

The investigated parameters from the EFM parameter study are in good correlation with the results from dynamic polarization. An adequate correlation between polarization resistance and B value was possible by means of the selected test parameters. It was possible to confirm the relation described in [1] that the B value decreases with increasing polarization resistance. This relation can be described mathematically by means of regressions. Figure 8 visualizes the values from table 2 and the results from EFM measurements in contrast to the results of dynamic polarization (from table 1) in order to evaluate whether the regressions based on the EFM results or a constant value of  $13.8 \text{ mV}$  from [2] describe the investigated corrosion system more adequate. The regression on the basis of a power describes the studied system the most accurate, for the EFM results as well as for the kinetic parameters from the dynamic polarization. The regression on the basis of a logarithm describes the system sufficiently accurate up to a polarization resistance of  $250,000 \Omega\text{cm}^2$ . For higher polarization resistances a lower corrosion current density is calculated.



**Figure 8.** Interdependency between polarization resistance and corrosion current density from EFM measurements on pure zinc with different exposure times to city atmosphere, gel-type electrolyte, verification of results by comparison to values from dynamic polarization (table 1).

If a constant B value is used, the calculated corrosion current densities deviate too much from the measured values and no agreement can be found with values from dynamic polarization.

## 5. Conclusion

The results of the electrochemical investigations using EFM technique and gel-type electrolyte show that determination of B values and polarization resistances on pure zinc samples with differently stable corrosion product layers is possible. It has to be considered that these B values are only valid for the described corrosion system. These values have to be confirmed and adapted for other zinc coatings and variants as well as gel-type electrolytes with a different composition (e.g. higher chloride content in the pad). It was shown that the B value is not a constant value, but is strongly dependent on the corrosion system, the condition of the surface layer on the surface, and the corresponding polarization resistance. However, a determination of a valid B value is possible by means of the presented mathematical equations and regressions. These provide the possibility to calculate a B value by means of a measured polarization resistance, e.g. from impedance measurements or linear polarization resistances, without additional measurements. The B value can be used for the calculation of instantaneous corrosion current densities via the polarization resistance.

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