

New developments in the determination of the rate of electrochemical corrosion

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Introduction

The determination of the rate of corrosion is one of the most important task both in corrosion research and also in industrial corrosion monitoring. While in corrosion research there is quite a long list of the available sophisticated methods (AC methods with small or greater amplitudes, DC polarization methods in wide polarization and sweep rate ranges), under industrial circumstances the most widespread method is the measurement of the Linear Polarization Resistance (LPR) and the calculation of the corrosion current via the following equation:

$$\frac{1}{R_p} = \left. \frac{dJ}{d\eta} \right|_{\eta=0} = J_{\text{corr}} \left(\frac{1}{b_A} + \frac{1}{b_C} \right), \quad (1)$$

where R_p is the polarization resistance, J is the current density, η is the polarization (i.e., the deviation of the potential from the corrosion potential), J_{corr} is the corrosion current density and b_A and b_C are the anodic and cathodic Tafel slopes. The corrosion current density is, consequently, not only a function of the polarization resistance R_p but also the function of the Tafel-slopes. While the polarization resistance can be obtained from AC or DC measurements carried out in a small range around the corrosion potential, the Tafel-slopes can only be obtained from the Butler-Volmer (BV) equation in a wider polarization range:

$$J = J_{\text{corr}} \left(\exp \left[\frac{\eta}{b_A} \right] - \exp \left[-\frac{\eta}{b_C} \right] \right). \quad (2)$$

The assessment of the Tafel slopes can be carried out via non-linear parameter fitting or linearization in the ranges $|\eta| \gg b_A, b_C$. Both methods have technical disadvantages and need careful assessment and, consequently, they are not applicable in automated industrial corrosion monitoring systems. Alternatively, the Tafel slopes can be assessed via harmonic analysis [1, 2], but due to the relatively slow convergence of the Taylor series of Eq. 2 (i.e. the coefficients of all powers are nonzero in the series) the omission of the third and higher order terms can add a significant error also to these methods. Due to these problems, the values of the Tafel slopes are often substituted with hypothetical values which are thought to be common or realistic or frequently measured, but these are basically arbitrary values from about 40 mV up to a few hundred millivolts [3-5]. However, this method adds an inherent and large uncertainty to the corrosion rate figures. In what follows, two new methods are presented for the more accurate estimation of the Tafel slopes via linearized models to provide simple and straightforward computation, also applicable in automated industrial corrosion monitoring technologies.

Quadratic Approximation (QA) Model

This model was first presented in [6] and tested on further corrosion systems in [7]. The final consequence of the Model is that the following approximation is valid:

$$\ln \left(\frac{j}{\eta} \right) \approx \ln \left(\frac{1}{R_p} \right) + A\eta + \frac{S^2}{3!} \eta^2 \quad (3)$$

where $b_A = 1/(S + A)$ and $b_C = 1/(S - A)$. If $|\eta S| < 1$ then the sum leading to Eq. 3 is convergent and the convergence is very fast because – unlike the conventional harmonic analysis models – only the even power addends of the sum are included. If $|\eta S| < 0.5$ then the error of the approximation is less than 1%. Based on Eq. 3 it is feasible to assess the values of all the three parameters (R_p , b_A and b_C) required for determine the corrosion rate according to Eq. 1. The data in the close vicinity of $\eta=0$ are not usable for technical reasons, but with $|\eta| > 10$ mV Eq. (3) gives consistent and reliable results and is applicable for the determination of the corrosion current. The assessment is feasible with a simple quadratic polynomial fitting. The proposed transformation is applicable for studying the kinetics of electrochemical systems in the transition range, hitherto mostly unusable for such purposes because it is not accessible either by the linear polarization fitting (which utilizes the narrow polarization range) nor by the semilogarithmic linear fitting, (using the wide polarization range $|\eta| \gg b_A, b_C$).

Linearized Butler-Volmer (LBV) Model

The Model LBV is based on the observation that the Butler-Volmer equation is, in fact, the solution of a second order, linear, homogeneous differential equation with constant coefficients. The details of the proof are included in a very recent paper [8]. The differential equation, corresponding to Eq. (1), is the following:

$$\frac{d^2J}{d\eta^2} = \left(\frac{1}{b_A} - \frac{1}{b_C}\right) \frac{dJ}{d\eta} + \frac{1}{b_A b_C} J \quad (4)$$

As the derivatives of the current density can be calculated from the $J = J(\eta)$ function, Equation (4) is linear in $(1/b_A - 1/b_C)$ and in $1/b_A b_C$ and, finally, the assessment of the Tafel slopes is reduced to a much simpler linear parameter fitting problem. It has to be mentioned that Equation (4) is invariant to the value of the corrosion current. The generation of the derivative function amplifies the random errors in the function $J(\eta)$ and is not the best way from a technical point of view. Instead of it, the double integral of Equation (4), which, in fact, returns to the BV equation itself, is to be used for the practical applications:

$$J(\eta) = \frac{1}{b_A b_C} \int_0^\eta \int_0^\epsilon J d\epsilon d\epsilon + \left(\frac{1}{b_A} - \frac{1}{b_C}\right) \int_0^\eta J d\epsilon + \frac{\eta}{R_P} \quad (5)$$

Equation (5) includes the integrals of the measured current densities, and these integrals do smoothen the effect of random errors instead of amplifying them. This equation is not only linear in the required parameters, but also contains the value of R_P and is therefore directly applicable for the assessment of the corrosion current density in any polarization range, at least theoretically.

Fitting of synthetic data

In order to prove the validity and applicability of the Models QA and LBV, synthetic $J(\eta)$ vs. η data series were generated with superimposed random errors. The parameters and error levels of the synthetic data are included in Table 1 and the composition of the experimental systems can be found in Table 2. The testing of both methods was carried out on the same experimental data sets. The electrode material was ST-52 low alloyed steel. All further experimental details can be found in [6].

Table 1. Input parameters of the synthetized data series

System code	Simulation parameters					Fitting parameters			
	$b_{A,10} / \text{mV}$	$b_{C,10} / \text{mV}$	$J_{\text{corr}} / \text{mA}$	Rel. error*	Abs. error**	$b_{A,10} / \text{mV}$	$b_{C,10} / \text{mV}$	$J_{\text{corr}} / \text{mA}$	r^2
QA-S1	120	120	1.0	2	0	115.1	116.2	0.964	0.8648
QA-S2	60	120	1.0	2	0	59.7	118.6	0.988	0.9988
LBV-S1***	120	120	1.0	2	2	120.4	120.2	1.007	0.9999
LBV-S2***	60	120	1.0	2	2	62.3/60.0	139.0/120.1	1.062/0.997	0.9997/0.9999

*Percentage of the absolute value of the current

**Percentage of the corrosion current

***Red numbers: fitting in range $\pm 25 \text{ mV}$, blue numbers: fitting in range $-250 \text{ mV} \dots +250 \text{ mV}$ (LBV-S1), $-250 \text{ mV} \dots +130 \text{ mV}$ (LBV-S2).

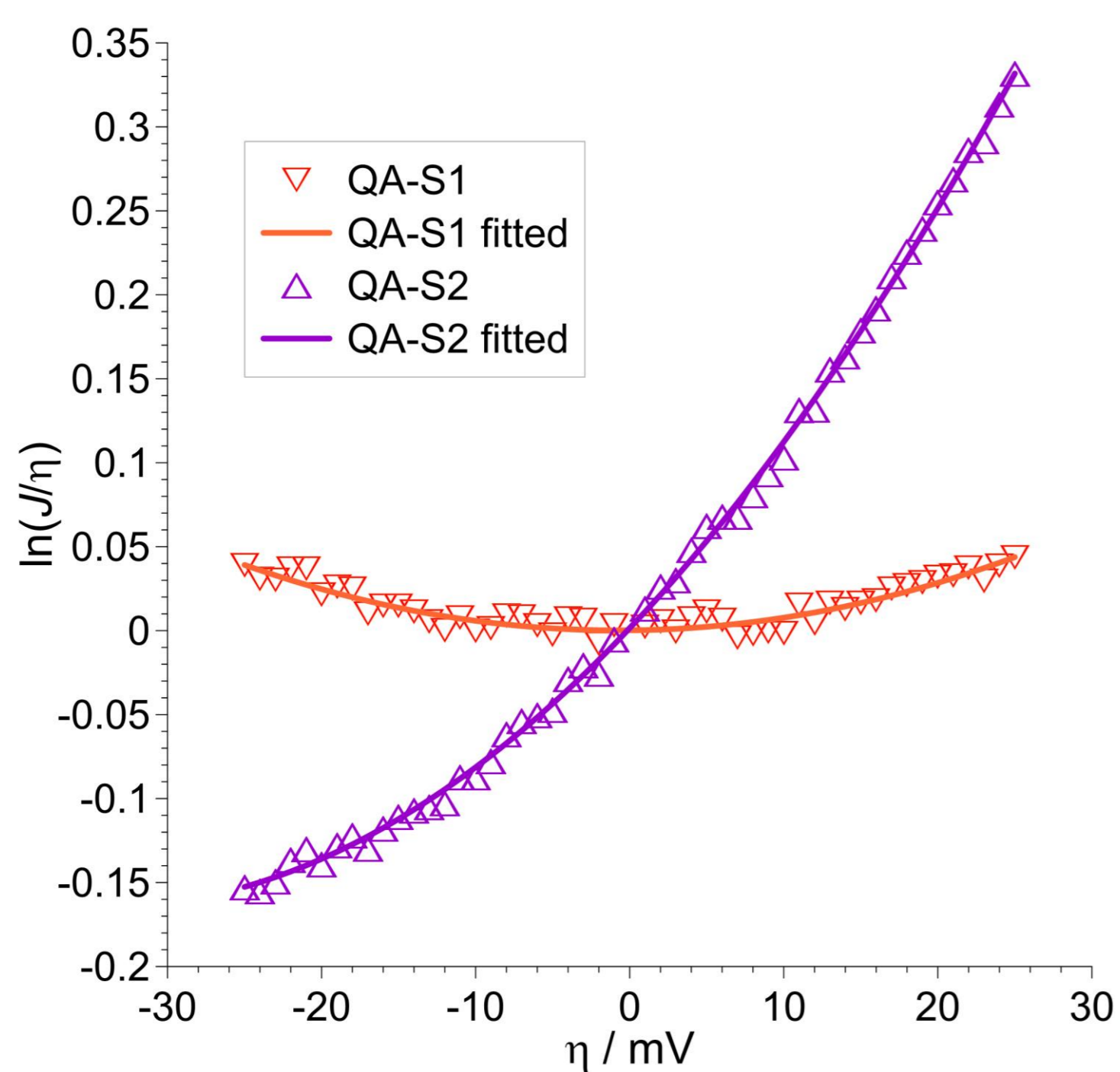


Figure 1. Fitting of synthetized data with Model QA.

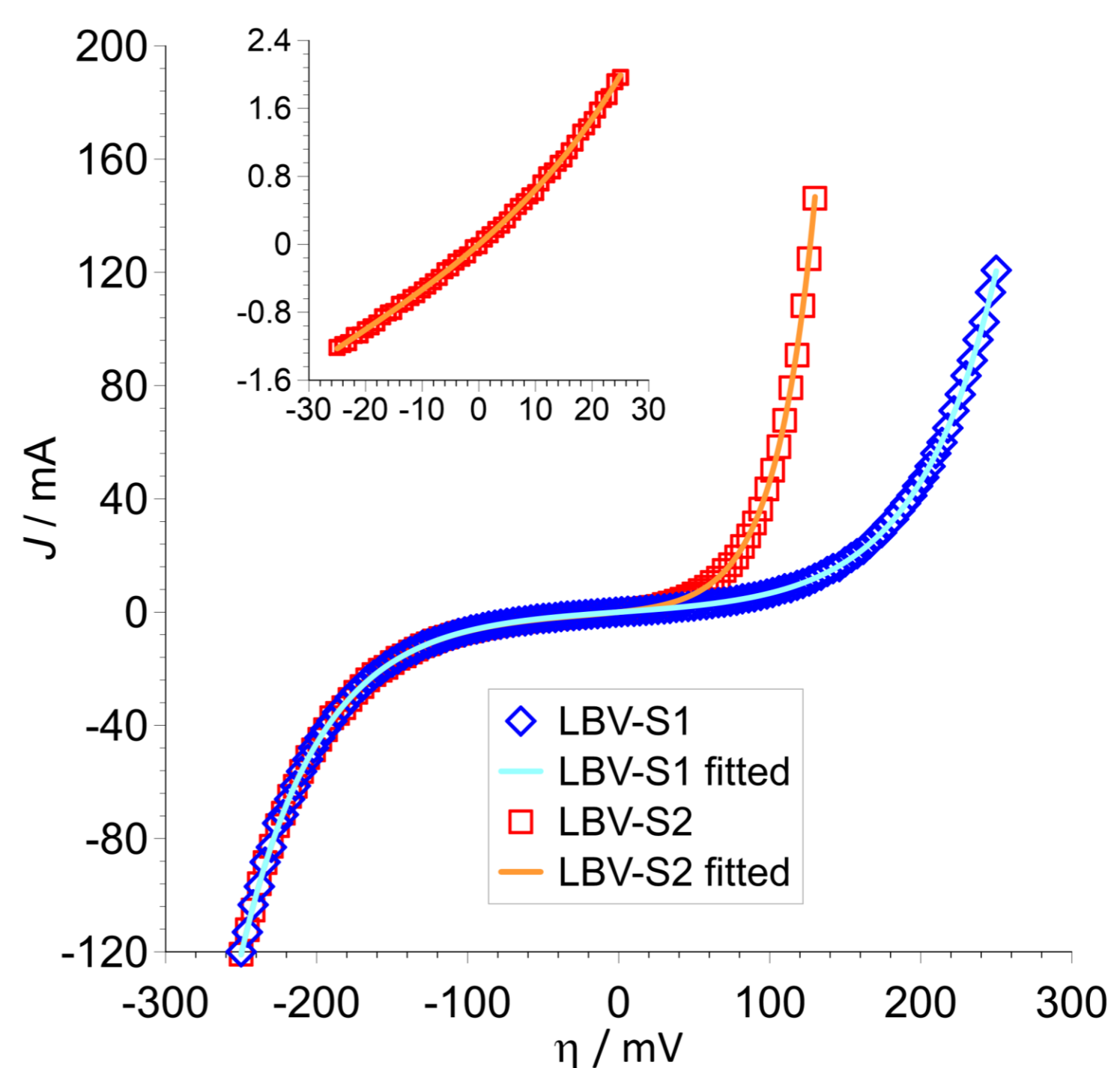


Figure 2. Fitting of synthetized data with Model LBV.

Fitting of experimental data

In order to collect further evidence of the applicability of models in the assessment of corrosion kinetic parameters, they were tested on two frequently used experimental systems, too. All polarization data are corrected for the ohmic potential drop. The detailed description of the experimental conditions is included in the original publications [6,8]. Obtained kinetic parameters are shown in Table 2 and Figures 3,4.

Table 2. Fitted parameters of the experimental data series

System code	Solution composition	b_A / mV		b_C / mV		$J_0 / \mu\text{A}/\text{cm}$	
		QA/LBV	Semilog**	QA/LBV	Semilog**	QA/LBV	Semilog**
QA-HCL	1% HCl	76.2	63.4	92.1	85.3	37.3	27.2/27.5
LBV-HCl±25mV		76.5		92.9		37.3	
LBV-HCl*		62.5		83.9		23.1	
QA-NaCl	5% NaCl + 0.5% Acetic acid	58.1	45.2	87.4	159.9	31.0	14.8/48.5
LBV-NaCl±25mV		65.8		99.6		28.5	
LBV-NaCl*		42.2		145.4		39.3	

*Polarization in uncompensated potential range -200 ... +100 mV.

**Conventional semilogarithmic fitting, corrosion current is obtained from extrapolation to the corrosion potential, anodic polarization, cathodic polarization.

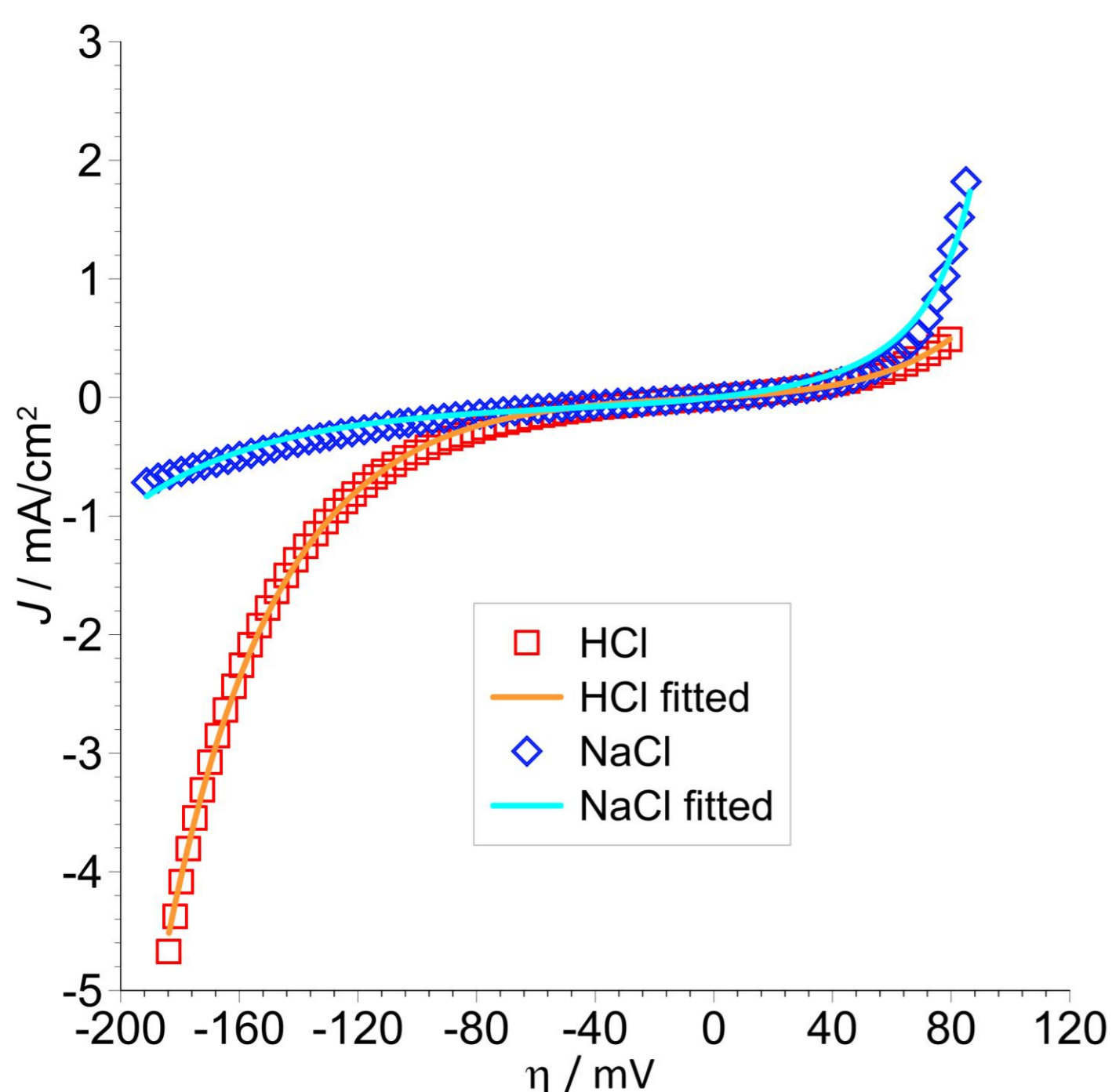


Figure 3. Fitting of experimental data with Model LBV in the wide potential range.

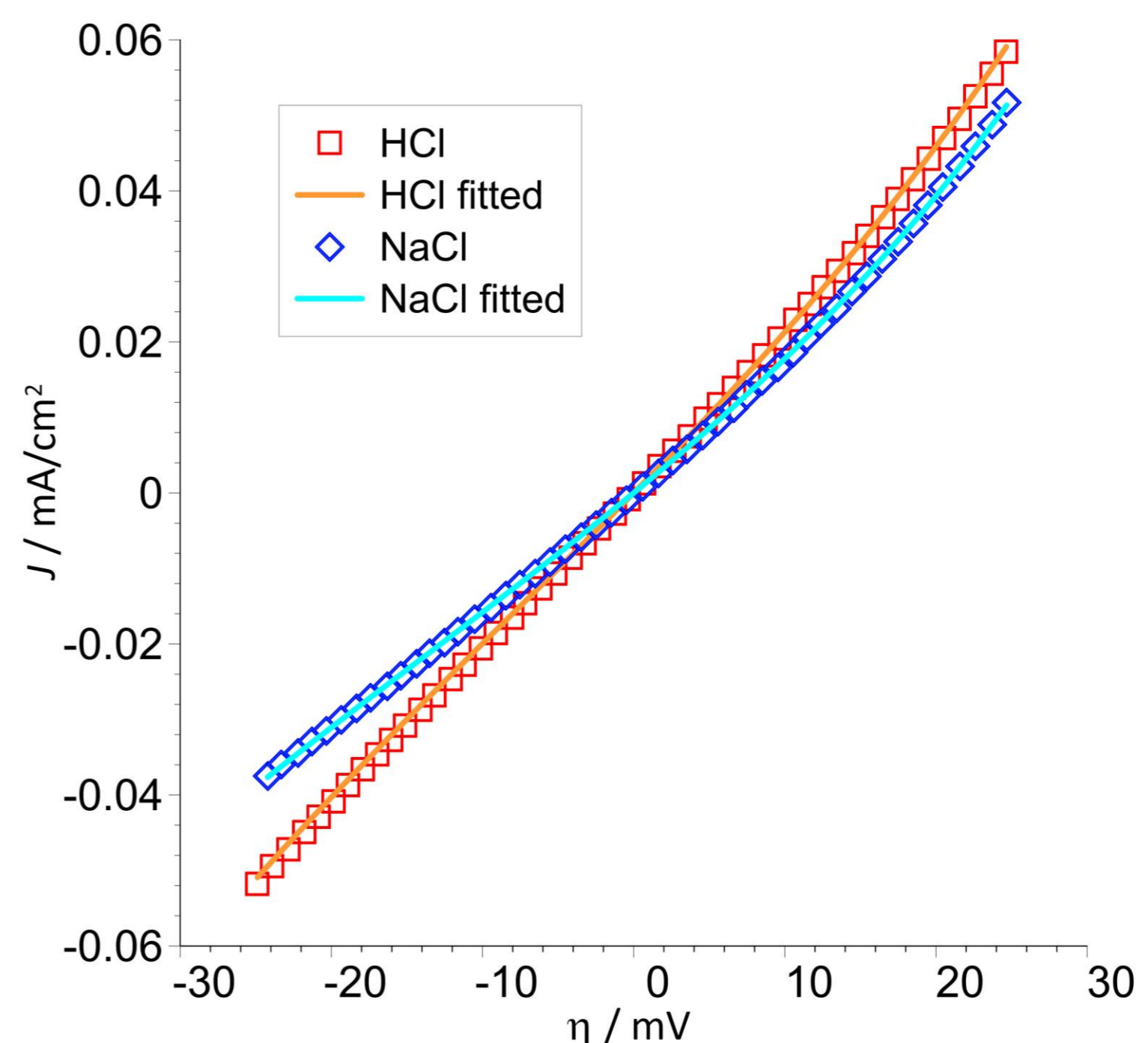


Figure 4. Fitting of experimental data with Model LBV in the narrow potential range.

Conclusion

Two new and robust mathematical models were developed for the assessment of corrosion kinetic parameters. The LBV model is applicable in the whole polarization range and the QA model is applicable in the transition range, which hitherto could not be utilized for the determination of kinetic parameters. These new developments facilitate the determination of the Tafel slopes, too, via relatively simple linear parameter fitting, and therefore they increase the accuracy of corrosion rate assessment in industrial corrosion monitoring systems.

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