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An integral metric for evaluating electrocatalytic activity

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This study introduces an integral metric of electrocatalytic activity, which is based on the comparison of the area under the polarisation curve in current density vs overpotential coordinates over a specific chosen overpotential range. This metric is applied to evaluate and compare several electrocatalysts, allowing for a more comprehensive understanding of electrocatalytic performance. Unlike traditional metrics, which characterise electrocatalyst behaviour under specific conditions (e.g. a particular overpotential or current density), the proposed integral metric provides a broader evaluation over a wide operational range. This approach is particularly useful for electrocatalysts with different Tafel slopes and polarisation characteristics. The metric is shown to be invariant to the shape of the polarisation curve and can be applied even when the exact form of the analytical dependence is unknown. The application of this metric holds promise for both fundamental studies in electrocatalysis and for practical applications in selecting the most efficient electrocatalysts for various technological processes.

Keywords: electrocatalysis, integral metric, electrocatalytic activity, polarisation curve, overpotential

INTRODUCTION

The problem of electrocatalysis is one of the key challenges in theoretical and applied electrochemistry. The concept of electrocatalysis is inherently related to catalysis in ‘conventional’ chemistry, where it is defined as ‘the modification of the rate of a chemical reaction, usually an acceleration, by addition of a substance not consumed during the reaction’ [1]. Since an electrochemical reaction is, by definition, a heterogeneous process occurring on the electrode surface, practically any electrode that serves as the site of electrochemical reactions involving adsorbed intermediates can be considered an electrocatalyst [2]. In this sense, an electrode acts as an electrocatalyst in all cases where the equation of the overall electrochemical process does not include the electrode material itself. Consequently, processes such as anodic dissolution, metal corrosion, and electrodeposition are generally not regarded as electrocatalytic.

Electrocatalytic processes, however, include extremely important reactions for advancing energy, industrial, agricultural, and other critical sectors of human development. These include those involved in renewable energy and the purification of polluted water and industrial waste, such as the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and others (e.g. urea oxidation reaction (UOR), electrochemical reduction of carbon dioxide, alcohol oxidation, electrocatalytic processes for wastewater treatment, fuel cell reactions, etc.) [3–12].

Since the essence of electrocatalysis lies in modifying the rate of an electrochemical process, it is crucial to accurately characterise, compare and select electrocatalysts using appropriate metrics for

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electrocatalytic activity. The following parameters are well-known and widely applied in practice for characterising electrocatalytic performance:

- Exchange current density, j_0 (A m^{-2}).
- Overpotential required to achieve a specific current density (e.g. 1, 10 and 100 mA cm^{-2}, η_1; η_{10} and η_{100}, respectively (mV)).
- Current density of the electrocatalytic process at a specific overpotential.
- Tafel constants (including the Tafel slope).
- Activation energy.
- Faradaic efficiency.
- Turnover frequency (TOF, s^{-1}).
- Mass and specific activities.

The physicochemical meaning, application features, advantages and disadvantages of these and other metrics of electrocatalytic activity have been repeatedly discussed in the literature [13–22]. Therefore, there is no need to delve into these details here. What should be particularly emphasised in the context of this work is that virtually all these quantitative parameters of electrocatalytic performance share a common drawback: they characterise performance 'at a given point', i.e. at a specific overpotential or current density. This limitation arises from the inherent feature of electrochemical reaction kinetics, which significantly differs from that of 'conventional' chemical reactions: the dependence of reaction rate (i.e. current density) on electrode potential (reaction overpotential), which varies for different electrode reactions [2].

As a result, all the above parameters of electrocatalytic performance cannot, in principle, describe the averaged (integral) activity of specific electrocatalysts. This limitation can be illustrated using Fig. 1, which schematically shows polarisation curves for the same electrochemical reaction on two different electrocatalysts, I and II.

Due to the different Tafel slopes of these two reactions (a fairly typical situation), which may also vary along the polarisation curve (i.e. at regions with different overpotentials), these two curves intersect at a certain point. This intersection conditionally divides the entire polarisation curve into two regions: low overpotential and high overpotential. As a result, when comparing the electrocatalytic activity of the two electrocatalysts across different regions of the voltammetric curve, one may arrive at an understandable yet inherently contradictory conclusion: the electrocatalytic activity of electrocatalyst I is higher than that of II in the low-overpotential region, lower in the high-overpotential region, and equal at the polarisation and corresponding current density matching the intersection point.

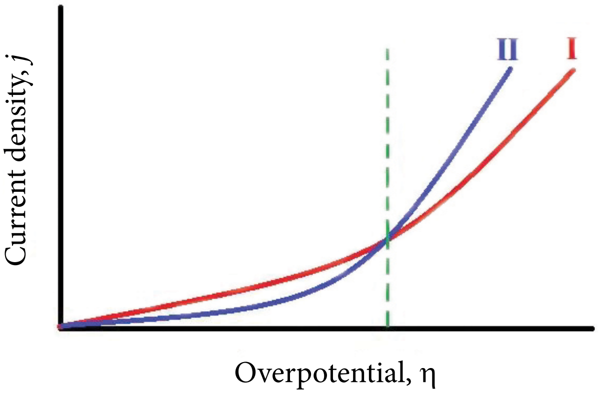

Fig. 1. Schematic polarisation curves of a specific electrochemical reaction using two different electrocatalysts, I and II

Although such a situation is quite typical, in some cases, it complicates the comparison of electrocatalytic activity over a wide range of operational overpotentials (or current densities). On the one hand, any electrocatalyst is generally designed for use within a specific operational range of potentials (overpotentials) or current densities. On the other hand, under real conditions, achieving a uniform current distribution across the electrode surface, which is not equipotential, is challenging. Consequently, different regions of the electrocatalyst operate at different overpotentials (within a certain range of current densities).

In electrocatalytic processes, it is generally desirable to achieve the highest possible specific current density (which inevitably leads to an increase in overpotential) or the lowest possible overpotential (which, for a given polarisation curve, can only be achieved by reducing the current density). This trade-off is crucial for optimising energy efficiency and reducing operational costs. The inherently contradictory nature of this problem necessitates the identification of optimal operating conditions, which, in turn, requires the evaluation of electrocatalytic activity not at a single predefined overpotential or current density but over a specific operational range.

Thus, for the accurate comparison and rational selection of an electrocatalyst, it is advisable to have a clear criterion (metric) of electrocatalytic activity within a specified operational range of overpotentials (current densities). Such a metric has not been described in the literature to date. This study is dedicated to the development and characterisation of this metric.

RESULTS AND DISCUSSION

Basic mathematical model

Consider an electrochemical reaction whose kinetics is described by a certain function of current density as a function of overpotential, $j(\eta)$. In this case, the parameter that characterises electrocatalytic activity over a specific range of overpotentials from η_1 to η_2 is the average current density in this interval, j_{av}. According to the well-known mathematical mean value theorem*, it can be determined using the following equation:

$$j_{av} = \frac{1}{\eta_2 - \eta_1} \cdot \int_{\eta_1}^{\eta_2} j d\eta. \quad (1)$$

Figure 2 provides a geometric interpretation of the quantity j_{av}: it is equal to the height of a rectangle with the width (η_2, η_1), that has the same area as the shaded region under the curve $j(\eta)$ in the interval [η_1, η_2].

If we now need to compare the electrocatalytic (integral) activity of two electrocatalysts (denoted by Roman numerals I and II, respectively) for the same reaction over the overpotential interval (η_1, η_2), where the polarisation dependences are described by the functions $j^{(I)}(\eta)$ and $j^{(II)}(\eta)$ with the upper index indicating the numbering of the electrocatalyst, the ratio of the two integrals should be calculated as follows:

$$\frac{P^{(II)}}{P^{(I)}} = \frac{\int_{\eta_1}^{\eta_2} j^{(II)} d\eta}{\int_{\eta_1}^{\eta_2} j^{(I)} d\eta}. \quad (2)$$

If $P^{(II)} < P^{(I)}$, then the integral electrocatalytic activity is higher for electrocatalyst I; if $P^{(II)} > P^{(I)}$, then the integral electrocatalytic activity is higher for electrocatalyst II; finally, if $P^{(II)} = P^{(I)}$, then the electrocatalysts possess the same integral activity, even if their polarisation dependences do not coincide.

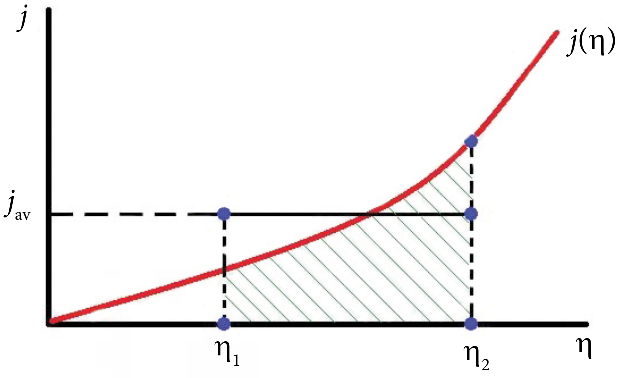

Fig. 2. Schematic geometric interpretation of the quantity j_{av} according to Eq. (1)

The dimension of the quantity $P^{(i)} = \int_{\eta_1}^{\eta_2} j^{(i)} d\eta$ is A V m^{-2} = J s^{-1} m^{-2} = W m^{-2}, so this integral has the dimension of electric current power per unit surface area of the electrode. Thus, this quantity characterises the integrated rate of conversion of electrical energy into other forms of energy (chemical, thermal, and work of gas expansion) in the electrocatalytic process, per unit electrode surface area, within the chosen overpotential range.

It is clear that the dependences $j(\eta)$ are determined either based on experimental data or through theoretical formulations and modelling. The overpotential interval (η_1, η_2) is chosen arbitrarily and is determined by the operating overpotential ranges (or corresponding current densities) for the electrocatalysts under consideration.

It should be emphasised that the average current density on the overpotential range (η_1, η_2), as defined by Eq. (1), is not a kinetic parameter of the electrochemical reaction and, by itself, is not a measure of electrocatalytic activity. In our opinion, the value and practical significance lie in the ratio of the average current densities in the overpotential range, which are calculated using Eq. (2) for the two electrocatalysts being compared. Thus, integral electrocatalytic activity is a relative quantity, not an absolute one, used for comparing the efficiency of different electrocatalysts for the same electrode process. This approach corresponds to the fundamental meaning of this quantity, as electrocatalysis (like any catalysis) pertains to changing the rate rather than its absolute values. Therefore, any characteristic

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[*] Note that for real electrochemical systems, all the following conditions for the mean value theorem are usually met: $j(\eta)$ is differentiable on (η_1, η_2); it is continuous on [η_1, η_2]; and it is real-valued.

of electrocatalytic activity should, in essence, be a parameter of comparison (the ratio) of the performance of several electrocatalysts relative to each other.

Theoretical analysis for the case where the Butler–Volmer equation is valid

For further theoretical analysis, it is convenient to take the zero value of overpotential (which corresponds to the equilibrium potential of the electrochemical reaction) as the lower bound of the integration interval in Eqs. (1) and (2): $\eta_1 = 0$. Then, we can introduce the simplified notation for the upper bound of the integration interval as $\eta_2 = \eta$.

Assume that the rate-determining step of the electrochemical process is charge transfer. To describe the polarisation dependences, it is appropriate to use Butler–Volmer-type equations [2].

It is important to note that the use of relatively simplified Butler–Volmer equations may initially appear inappropriate for electrocatalysis, as these equations are strictly valid for an outer-sphere electron transfer step, whereas electrocatalysis typically involves an inner-sphere mechanism and can be limited by adsorption or chemical steps. In such cases, the pre-exponential term often includes a potential-dependent surface coverage of certain adsorbed species, which is evidently not accounted for in the Butler–Volmer equations. However, our objective in this study is not to provide a detailed mechanistic description of electrocatalytic reactions but rather to develop a kinetic model. This implicit assumption is common in electrocatalysis research, where Tafel plots are widely used to assess electrocatalytic performance by determining exchange current densities and apparent transfer coefficients without delving into the reaction mechanism details. Therefore, the application of Butler–Volmer equations for further analysis is justified.

For the region of small deviations from the equilibrium (small overpotentials), the polarisation dependence, as is well known, has a linear character

$$j = j_0 \frac{zF}{RT}\eta, \tag{3}$$

where j_0 is the exchange current density, z is the number of electrons transferred during the charge transfer stage, F is Faraday's constant, R is the universal gas constant, and T is the absolute temperature.

Substituting Eq. (3) into Eq. (2) and integrating, we obtain

$$\frac{P^{(II)}}{P^{(I)}} = \frac{j_0^{(II)}}{j_0^{(I)}}. \tag{4}$$

Thus, in the region of small overpotentials near the equilibrium potential, the only and exhaustive criterion of electrochemical activity is the exchange current density: the higher it is, the greater the electrochemical activity of the electrocatalyst.

For the region of relatively high overpotentials, when the reverse electrochemical process can be neglected, the Butler–Volmer equation simplifies to[**]

$$j = j_0 \exp\left(\frac{\alpha z F \eta}{RT}\right), \tag{5}$$

where α is the transfer coefficient.

Then, the mean current density over the overvoltage interval from 0 to η, according to Eq. (1), will be determined as follows:

$$j_{av} = \frac{1}{\eta}\cdot\int_0^{\eta} j_0 \exp\left(\frac{\alpha z F \eta}{RT}\right) d\eta =$$
$$= \frac{1}{\eta}\cdot j_0 \cdot \frac{RT}{\alpha z F}\cdot\left[\exp\left(\frac{\alpha z F \eta}{RT}\right) - 1\right]. \tag{6}$$

Substituting Eq. (6) into Eq. (2), we get

$$\frac{P^{(II)}}{P^{(I)}} = \frac{j_0^{(II)}}{j_0^{(I)}}\cdot\frac{\alpha^{(I)}}{\alpha^{(II)}}\cdot\frac{\exp\left(\frac{\alpha^{(II)} z F \eta}{RT}\right) - 1}{\exp\left(\frac{\alpha^{(I)} z F \eta}{RT}\right) - 1}. \tag{7}$$

It is clear that in the case of identical values of the transfer coefficients $\alpha^{(I)} = \alpha^{(II)}$, Eq. (7) simplifies significantly and transforms into Eq. (4), meaning that the exchange current density is the sole criterion that unequivocally characterises the electrocatalytic activity of the two compared electrocatalysts. However, if the transfer coefficients are not identical (indicating differences in Tafel slopes), then in addition to the exchange current density, the transfer coefficients start to have a significant influence

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[**] Obviously, the kinetic equations are here written for the case of an anodic reaction.

on the electrocatalytic activity, as emphasised by Bokris [23].

For the convenience of further mathematical analysis of Eq. (7), let us consider cases of a significant deviation from the equilibrium ($\eta >> 0$), where both in the numerator and denominator of the right-hand side of Eq. (7), the term 1 can be neglected compared to the diminishing exponential. In this case, to the first approximation, we get

$$\frac{P^{(II)}}{P^{(I)}} = \frac{j_0^{(II)}}{j_0^{(I)}} \cdot \frac{\alpha^{(I)}}{\alpha^{(II)}} \cdot \exp\left(\frac{\left[\alpha^{(II)} - \alpha^{(I)} \right] zF\eta}{RT} \right). \quad (8)$$

The right-hand side of Eq. (8) consists of two factors: $\frac{j_0^{(II)}}{j_0^{(I)}}$ and $\frac{\alpha^{(I)}}{\alpha^{(II)}} \cdot \exp\left(\frac{\left[\alpha^{(II)} - \alpha^{(I)} \right] zF\eta}{RT} \right)$. The first factor, $\frac{j_0^{(II)}}{j_0^{(I)}}$, reflects the influence of changes in the exchange current density on electrocatalytic activity. It is clear that the integral electrocatalytic activity is directly proportional to the exchange current density of the considered reaction.

The second factor on the right-hand side of Eq. (8), $\frac{\alpha^{(I)}}{\alpha^{(II)}} \cdot \exp\left(\frac{\left[\alpha^{(II)} - \alpha^{(I)} \right] zF\eta}{RT} \right)$, reflects the influence of changes in the transfer coefficient when transitioning from one electrocatalyst to another. As seen from the structure of this expression, the nature of this influence strongly depends on the applied overpotential, and this dependence is ambiguous. Indeed, when the value of the transfer coefficient increases ($\alpha^{(II)} > \alpha^{(I)}$), on the one hand, the exponential term in this expression will become greater than 1, which will promote an increase in electrocatalytic activity. On the other hand, at the same time, the fraction $\frac{\alpha^{(I)}}{\alpha^{(II)}}$ will decrease, which will lead to a decrease in electrocatalytic activity. Therefore, there are two factors influencing in opposite directions. To highlight the nature of this dependence, values of the factor $\frac{\alpha^{(I)}}{\alpha^{(II)}} \cdot \exp\left(\frac{\left[\alpha^{(II)} - \alpha^{(I)} \right] zF\eta}{RT} \right)$ were calculated for the cases where $\alpha^{(I)} = 0.5$ remains constant, and the transfer coefficient $\alpha^{(II)}$ changes, becoming either smaller or larger compared to $\alpha^{(I)}$. The calculations were carried out for several values of the overpotential, and the results are summarised in Table 1.

It trivially follows that when the transfer coefficient does not change when transitioning from one electrocatalyst to another ($\alpha^{(II)} = \alpha^{(I)}$), the value of $\frac{\alpha^{(I)}}{a^{(II)}} \cdot \exp\left(\frac{\left[\alpha^{(II)} - \alpha^{(I)} \right] zF\eta}{RT} \right)$ equals 1 for any overpotential, indicating no effect on the integral electrocatalytic activity.

However, if the transfer coefficient increases ($\alpha^{(II)} > \alpha^{(I)}$), the dominant effect is due to the corresponding exponential term in the expression for $\frac{\alpha^{(I)}}{a^{(II)}} \cdot \exp\left(\frac{\left[\alpha^{(II)} - \alpha^{(I)} \right] zF\eta}{RT} \right)$, leading to an increase in the integral electrocatalytic activity. This enhancement becomes more pronounced as the overpotential increases.

On the other hand, if the transfer coefficient decreases ($\alpha^{(II)} < \alpha^{(I)}$) when moving from one electrocatalyst to another, a decrease in the integral electrocatalytic activity is observed (again, due to the exponential term, which in this case takes values less than 1). This decrease becomes more pronounced as the overpotential increases. However, in this case, at a significant reduction of the transfer coefficient for very low overpotentials, there may be a situation where the integral electrocatalytic activity even slightly increases (as seen in Table 1, the value of $\frac{\alpha^{(I)}}{\alpha^{(II)}} \cdot \exp\left(\frac{\left[\alpha^{(II)} - \alpha^{(I)} \right] zF\eta}{RT} \right)$ equals 1.053 at $\eta = 0.1$ V and $\alpha^{(II)} = 0.1$). This is the result of the exponential term approaching unity, and the dominant effect on the final result comes from the fraction $\frac{\alpha^{(I)}}{\alpha^{(II)}}$.

Thus, the results of the numerical modelling generally confirm the trend that has been repeatedly pointed out in the literature [9, 13, 19, 20]: the electrocatalytic activity (in this case, integral) increases with the transfer coefficient, i.e. with the decrease in the corresponding Tafel slope, and

Table 1. **Calculated values of the factor $\frac{\alpha^{(I)}}{\alpha^{(II)}} \cdot \exp\left(\frac{\left[\alpha^{(II)}-\alpha^{(I)}\right]zF\eta}{RT}\right)$ from Eq. (8) for the case where α(*I*) = 0.5 = const, *z* = 1 and *T* = 298 K**

η/V	$\frac{\alpha^{(I)}}{\alpha^{(II)}} \cdot \exp\left(\frac{\left[\alpha^{(II)}-\alpha^{(I)}\right]zF\eta}{RT}\right)$				
	α(*II*) = 0.1	α(*II*) = 0.25	α(*II*) = 0.5	α(*II*) = 0.75	α(*II*) = 0.9
0.10	1.053	0.755	1.000	1.765	2.638
0.15	0.483	0.464	1.000	2.871	5.748
0.20	0.222	0.285	1.000	4.673	12.524
0.25	0.102	0.175	1.000	7.603	27.291
0.30	0.047	0.108	1.000	12.370	59.467

this enhancement becomes more pronounced as the overpotential increases. However, this regularity is not unambiguous, and, as seen from the results of the calculations, there can be an opposite situation for small overpotentials.

Use of the developed model for evaluating the electrocatalytic activity of nickel anodically treated in a deep eutectic solvent

As a specific example of applying the proposed criterion for integral electrocatalytic activity, let us consider the case of the electrocatalytic behaviour of a nickel electrode anodically treated in a deep eutectic solvent concerning the hydrogen evolution reaction in an alkaline medium [24]. In this context, it should be noted that, as is well known, the electrocatalytic activity of metals and alloys can be significantly enhanced by anodic treatment in various aqueous and non-aqueous solutions [25–28]. Among these, systems based on representatives of the new generation of low-temperature ionic liquids, the so-called deep eutectic solvents, seem particularly promising. Their use in various electrochemical processes and technologies is being intensively studied in recent years due to a number of technological, ecological and economic advantages [29–34].

Figure 3 shows linear voltammograms characterising the electrocatalytic activity of the nickel surface before and after anodic treatment in reline,

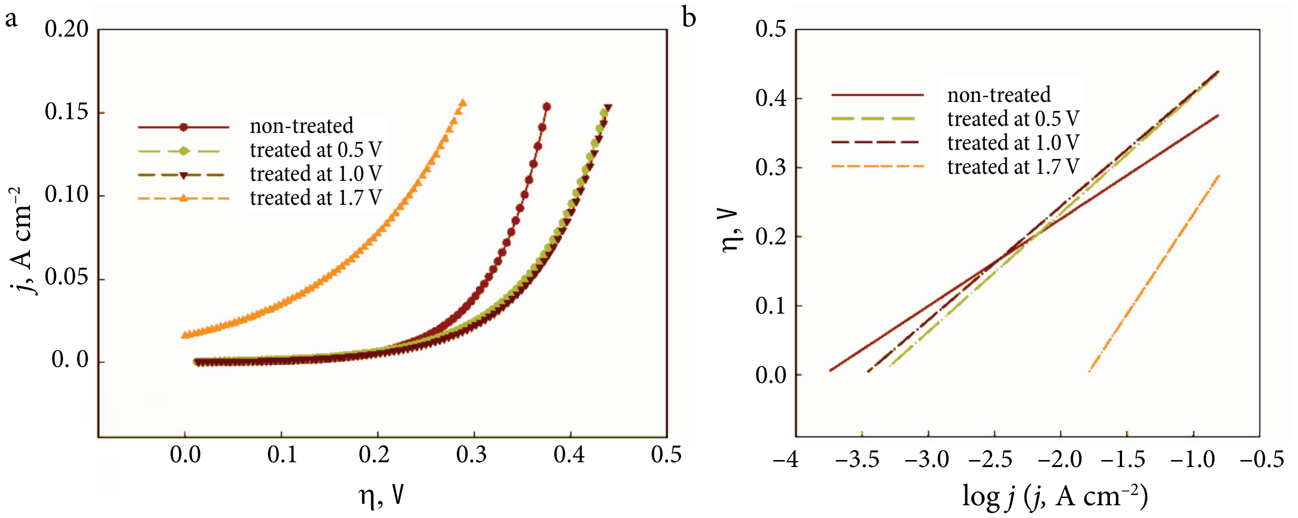

Fig. 3. Cathodic polarisation curves (a) and the corresponding Tafel transforms (b) in Tafel equation coordinates for the HER in a 1 M NaOH solution at 298 K on a nickel electrode, both untreated and anodically treated in reline at different potentials (potentiostatic treatment duration of 2.5 h at 298 K) (data reproduced from Ref. [24] under the Creative Commons Attribution License (CC BY))

a typical representative of deep eutectic solvents, which is an eutectic mixture of choline chloride and urea [24]. It should be noted that the methodology for conducting these experimental studies was described in detailed elsewhere [24].

The obtained voltammograms in Fig. 3 reflect the kinetics of the hydrogen evolution reaction in an aqueous solution of 1 M NaOH on the studied electrocatalytic materials at a temperature of 298 K. Also, in Fig. 3, the corresponding Tafel transforms are shown, plotted in the coordinates of the Tafel equation (overpotential of hydrogen evolution, η, vs decimal logarithm of the cathodic current density, log j). As seen, the experimental data linearise excellently in Tafel coordinates ($R^2 \geq 0.9999$), which indicates that the Butler–Volmer equation is valid and allows for the calculation of the corresponding Tafel slopes and exchange current densities (Table 2).

Analysis of the obtained data indicates the ambiguous nature of the conclusions drawn from applying various 'point' criteria of electrocatalytic activity. Specifically, when considering the regions corresponding to relatively high overpotentials (here, the value of η_{100}, i.e. the overpotential at a current density of 100 mA cm^{-2}, can be used here as a criterion for electrocatalytic activity towards the HER), it turns out that nickel treatment in a DES at potentials of 0.5 and 1.0 V leads to a decrease in electrocatalytic activity (an increase in overpotential), while the use of a treatment potential of 1.7 V, on the contrary, results in a significant increase in the electrocatalytic activity (a noticeable decrease in overpotential). These effects are likely related to the complex influence of the anodic treatment potential of nickel in reline on the surface morphology, and consequently on the activity and concentration of catalytic sites on the surface.

However, anodic treatment of nickel in a DES results in an increase in Tafel slopes (compared to the untreated surface). As a consequence of the different slopes, the Tafel lines intersect, and the exchange current densities, determined by extrapolating the Tafel curves to zero overpotential, show an increase after anodic treatment in reline compared to the original untreated nickel surface.

Thus, 'point' characteristics of electrocatalytic behaviour give different, sometimes diametrically opposed, pictures for different regions of the polarisation curve (regions of a relatively high polarisation and regions of a low polarisation near the equilibrium potential). Therefore, in this case, it is necessary and appropriate to use an integral characteristic of electrocatalytic activity that encompasses data about the catalytic performance of the electrode not at a specific overpotential value, but over a sufficiently wide range of values. Such an integral characteristic $P = \int_{\eta_1}^{\eta_2} j d\eta$ was calculated by numerically integrating the experimental data using the trapezoidal rule over the η interval from 0 to 0.288 V (Table 2).

If the electrocatalytic activity of the untreated DES nickel surface is taken as a reference point for comparison (arbitrary unit), the effect of anodic treatment of Ni on the integral electrocatalytic activity can be calculated according to Eq. (2).

From the obtained results (Table 3), it is evident that the anodic potentiometric treatment of

Table 2. **Electrochemical parameters of untreated and anodically treated nickel at different anodic potentials in reline for the cathodic hydrogen evolution reaction in 1 M NaOH at 298 K**

Potential of anodic treatment of Ni in *reline*, V	**Constants in the Tafel equation*** $\eta = a + b \log j$		**Calculated exchange current density, j_0, A cm^{-2}**	**η_{100}, V**	$P = \int_0^{0.288} j d\eta$, **A V cm^{-2}**
	***a*, V**	***b*, V dec^{-1}**			
– (non-treated)	0.478	0.126	1.61×10^{-4}	0.350	1.691×10^{-3}
0.5	0.576	0.171	4.28×10^{-4}	0.404	1.578×10^{-3}
1.0	0.573	0.165	3.37×10^{-4}	0.407	1.301×10^{-3}
1.7	0.522	0.290	1.59×10^{-2}	0.232	1.761×10^{-2}

* For simplicity in the analysis, the cathodic overpotential of the hydrogen evolution reaction, Tafel constants, and cathodic current density are conditionally indicated with 'plus' signs, contrary to the commonly used traditional notation.

Table 3. **Integral electrocatalytic activity of untreated and anodically treated nickel at different anodic potentials in reline for the HER in 1 M NaOH at 298 K. Integration was performed over the overpotential range from 0 to 0.288 V**

Potential of anodic treatment of Ni in *reline,* V	$\frac{P^{(II)}}{P^{(I)}}=\frac{\int_{\eta_1}^{\eta_2} j^{(II)}d\eta}{\int_{\eta_1}^{\eta_2} j^{(I)}d\eta}$
– (non-treated)	1
0.5	0.93
1.0	0.77
1.7	10.41

nickel in reline at the lowest of the studied potentials (0.5 V) leads to a slight decrease in integral electrocatalytic activity (93% of the activity of the untreated material), treatment at 1.0 V results in a noticeable decrease in activity (77%), while at the highest potential used (1.7 V), the integral electrocatalytic activity increases more than tenfold (1041% compared to the untreated nickel surface). Interestingly, this dependence somewhat correlates with the changes in the other 'point' metrics of electrocatalytic activity (primarily, j_0 and η_{100}). However, unlike them, the metric proposed in this work characterises the behaviour of the electrocatalyst not under certain specific conditions of its operation but over a sufficiently wide range of operational overpotentials (and corresponding current densities), which is its unique feature and advantage.

Analysis for the case of complicated electrochemical kinetics

In real-life situations, the Butler–Volmer equation does not always strictly describe experimentally obtained polarisation dependences. There may be several reasons and explanations for this. Specifically, the electrochemical kinetics may be complicated by transport (diffusion) limitations (mixed kinetics), various adsorption stages, the presence of several consecutive charge transfer steps, etc. All of this can lead to changes in the Tafel slope $\frac{\partial\eta}{\partial\log j}$ with the change in overpotential (nonlinear dependences in the Tafel equation coordinates) or to the appearance of breakpoints in the polarisation curve (formation of regions with different Tafel slopes). As a result, situations may arise where, when transitioning from one electrocatalyst to another, crossing points are formed on the corresponding polarisation curves (as shown in Fig. 1).

Moreover, an important factor is the conditions for recording the polarisation dependence, particularly the potential scan rate. At high scan rates, the obtained curves may become complicated due to non-stationary diffusion. At slow scan rates, this risk is eliminated, but in the results of sufficiently prolonged polarisation curve registration, the surface state of the electrode may evolve during the recording process, which will also affect the obtained results.

In all cases of complicated kinetics, there are no limitations when using the general formula (2), that is, integrating the experimental polarisation dependence for evaluating the integral electrocatalytic activity. The only condition here is the necessity of obtaining experimental data under identical conditions.

CONCLUSIONS

In this work, for the first time, an integral metric of electrocatalytic activity was proposed based on the comparison of the area under the polarisation curve in current density vs overpotential coordinates over a specific chosen overpotential range for several evaluated electrocatalysts. Unlike previously proposed metrics of electrocatalytic activity, which characterise the behaviour of the electrocatalyst under specific operational conditions (e.g. a particular overpotential or current density), the integral electrocatalytic activity allows for the evaluation and comparison of the electrocatalytic performance over a sufficiently wide operational range, which is the key feature and advantage of this metric.

The integral electrocatalytic activity metric is an effective and accurate tool for comparing the activity of electrocatalysts characterised by different Tafel slopes in polarisation dependences. Moreover, the proposed integral metric is invariant to the shape of the polarisation dependence j vs η, and it can be successfully applied even when the exact form of the corresponding analytical dependence is unknown.

Hopefully, the use of this integral metric of electrocatalytic activity can be valuable not only for addressing fundamental theoretical problems in electrocatalysis but also for solving practical tasks related to comparing and selecting the most efficient electrocatalyst for specific technological processes. Future research could explore the application of this metric to a wider range of electrocatalysts and in diverse conditions, potentially enhancing its robustness and applicability in various fields.

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References

1. H. S. Taylor, *Catalysis*, Encyclopedia Britannica [https://www.britannica.com/science/catalysis].
2. J. O'M. Bockris, A. K. N. Reddy, M. Gamboa-Aldeco, *Modern Electrochemistry: Fundamentals of Electrodics*, 2nd edn., New York, Kluwer Academic Publishers (2002).
3. G. Squadrito, G. Maggio, A. Nicita, *Renew. Energy*, **216**, 119041 (2023) [https://doi.org/10.1016/j.renene.2023.119041].
4. A. J. Shih, M. C. O. Monteiro, F. Dattila, et al., *Nat. Rev. Methods Primers*, **2**, 84 (2022) [https://doi.org/10.1038/s43586-022-00164-0].
5. M. A. Qadeer, X. Zhang, M. A. Farid, et al., *J. Power Sources*, **613**, 234856 (2024) [https://doi.org/10.1016/j.jpowsour.2024.234856].
6. A. Raveendran, M. Chandran, R. Dhanusuraman, *RSC Adv.*, **13**, 3843 (2023)[https://doi.org/10.1039/D2RA07642J].
7. S. Paygozar, A. S. R. Aghdam, E. Hassanizadeh, R. Andaveh, G. B. Darband, *Int. J. Hydrogen Energy*, **48**, 7219 (2023) [https://doi.org/10.1016/j.ijhydene.2022.11.087].
8. X. Sun, R. Ding, *Catal. Sci. Technol.*, **10**, 1567 (2020) [https://doi.org/10.1039/C9CY02618E].
9. M. Tahir, L. Pan, F. Idrees, et al., *Nano Energy*, **37**, 136 (2017) [https://doi.org/10.1016/j.nanoen.2017.05.022].
10. M. Plevová, J. Hnát, K. Bouzek, *J. Power Sources*, **507**, 230072 (2021) [https://doi.org/10.1016/j.jpowsour.2021.230072].
11. J. Jayabharathi, B. Karthikeyan, B. Vishnu, S. Sriram, *Phys. Chem. Chem. Phys.*, **25**, 8992 (2023) [https://doi.org/10.1039/D2CP05522H].
12. S. Farissi, G. A. Abubakar, K. A. Akhilghosh, A. Muthukumar, M. Muthuchamy, *Environ. Monit. Assess*, **195**, 1447 (2023) [https://doi.org/10.1007/s10661-023-12083-y].
13. S. González-Poggini, *Int. J. Hydrogen Energy*, **59**, 30 (2024) [https://doi.org/10.1016/j.ijhydene.2024.01.362].
14. S. Anantharaj, P. E. Karthik, S. Noda, *Angew. Chem. Int. Ed.*, **60**, 23051 (2021) [https://doi.org/10.1002/anie.202110352].
15. O. van der Heijden, S. Park, R. E. Vos, J. J. J. Eggebeen, M. T. M. Koper, *ACS Energy Lett.*, **9**, 1871 (2024) [https://doi.org/10.1021/acsenergylett.4c00266].
16. T. Shinagawa, A. T. Garcia-Esparza, K. Takanabe, *Sci. Rep.*, **5**, 13801 (2015) [https://doi.org/10.1038/srep13801].
17. A. R. Zeradjanin, P. Narangoda, J. Masa, *ChemCatChem*, **16**, e202400634 (2024) [https://doi.org/10.1002/cctc.202400634].
18. Z. P. Wu, X. F. Lu, S. Q. Zang, X. W. Lou, *Adv. Funct. Mater.*, 1910274 (2020) [https://doi.org/10.1002/adfm.201910274].
19. C. V. M. Inocêncio, Y. Holade, C. Morais, K. B. Kokoh, T. W. Napporn, *Electrochem. Sci. Adv.*, e2100206 (2022) [https://doi.org/10.1002/elsa.202100206].
20. N. T. Suen, S. F. Hung, Q. Quan, N. Zhang, Y. J. Xu, H. M. Chen, *Chem. Soc. Rev.*, **46**, 337 (2017) [https://doi.org/10.1039/c6cs00328a].
21. C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.*, **137**, 4347 (2015) [https://doi.org/10.1021/ja510442p].
22. D. Voiry, M. Chhowalla, Y. Gogotsi, et al., *ACS Nano*, **12**, 9635 (2018) [https://doi.org/10.1021/acsnano.8b07700].
23. J. O'M. Bockris, *J. New Mat. Electrochem. Systems*, **7**, 67 (2004).
24. V. S. Protsenko, D. O. Makhota, T. E. Butyrina, S. A. Korniy, F. I. Danilov, *Voprosy Khimii i Khimicheskoi Tekhnologii*, (1), 89 (2024) [https://doi.org/10.32434/0321-4095-2024-152-1-89-98].
25. S. A. Korniy, S. A. Halaichak, M. R. Chuchman, V. A. Vynar, B. M. Datsko, *Colloids Surf. A Physicochem. Eng. Asp.*, **705**, 135677 (2025) [https://doi.org/10.1016/j.colsurfa.2024.135677].
26. M. Kim, Y. T. Kim, J. Choi, *Electrochem. Commun.*, **117**, 106770 (2020) [https://doi.org/10.1016/j.elecom.2020.106770].
27. V. S. Protsenko, T. E. Butyrina, D. O. Makhota, S. A. Korniy, F. I. Danilov, *Port. Electrochim. Acta*, **41**, 29 (2023) [https://doi.org/10.4152/pea.2023410103].
28. V. Protsenko, T. Butyrina, D. Makhota, S. Korniy, F. Danilov, *Arch. Metall. Mater.*, **68**, 477 (2023) [https://doi.org/10.24425/amm.2023.142425].
29. A. Kityk, V. Pavlik, M. Hnatko, *Int. J. Hydrogen Energy*, **48**, 39823 (2023) [https://doi.org/10.1016/j.ijhydene.2023.07.158].

30. R. Al-Farsi, M. Hayyan, *J. Energy Chem.*, **92**, 357 (2024) [https://doi.org/10.1016/j.jechem.2023.12.021].
31. A. Kityk, V. Pavlik, M. Hnatko, *Adv. Colloid Interface Sci.*, **334**, 103310 (2024) [https://doi.org/10.1016/j.cis.2024.103310].
32. E. L. Smith, A. P. Abbott, K. S. Ryder, *Chem. Rev.*, **114**, 11060 (2014) [https://doi.org/10.1021/cr300162p].
33. B. B. Hansen, S. Spittle, B. Chen, et al., *Chem. Rev.*, **121**, 1232 (2021) [https://doi.org/10.1021/acs.chemrev.0c00385].
34. A. P. Abbott, *Curr. Opin. Green Sustainable Chem.*, **36**, 100649 (2022) [https://doi.org/10.1016/j.cogsc.2022.100649].

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