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Derivative-extremum analysis of current-potential curves showing electrochemical kinetics in the full reversibility range

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ABSTRACT

Derivative-extremum analysis (DEA) of *j*-*E* curves is a newly proposed method of half wave potential ($E_{1/2}$) and activation feature extraction from steady-state voltammetry. Here, the DEA is demonstrated to be valid in the full range of reversibility using numerical simulations with a derived universal electrode equation, providing a novel perspective of electrochemical kinetics in the reversibility domain. The results reveal that $E_{1/2}$ is a better choice of the reference potential instead of equilibrium potential (E_{eq}) in electrode equations, especially since E_{eq} is meaningless in an irreversible case. The equations referenced with standard potential, $E_{1/2}$ and E_{eq}, are summarized in three tables, and their applications in parameter determinations are specified. Finally, reversibility is proved to be a relative measure between kinetic slowness and mass transport of electroactive species, and the reversibility classifications are proposed according to the DEA feature in the reversibility domain. This work, based on the DEA principle, refines the electrode equation forms and generalizes their applicability in the full range of reversibility.

Steady-state current (j)-potential (E) voltammograms provide an easy-to-follow technique for extracting the kinetic information of an electrode reaction because of the simplicity of steady-state kinetic theory. In mathematics, steady-state voltammetry avoids charging current interference [1] and possesses time-independent mass transport processes between the electrode surface and the bulk solution [2].

Reversibility is a basic scale in the recognition of the reactivity of a reaction, and the electrode equations are often divided into reversible, irreversible and *quasi*-reversible types [3]. The electrode equations and their applicability are dependent on the reference potential against which the potential is quantified, *e.g.*, standard (or formal) potential, equilibrium potential (E_{eq}) and half wave potential ($E_{1/2}$). The electrode equations are multifarious in terms of reversibility and reference potential. If possible, it is strongly desired to unify all the electrode equations and elaborately differentiate their applicability in steady-state voltammetry.

"Reversible" and "irreversible" are two extreme cases; the former is only dependent on thermodynamics, while the latter is fully governed by kinetics. The variations in the kinetic features embodied in the steady-state voltammograms between the two cases have long been absent from a quantitative measure. $E_{1/2}$ is an important indicator of reaction occurrence, whereas its physical significance in the full range of reversibility has yet to be clarified.

Recently, we found that the peak point of the derivative of a *j*-*E* curve in irreversible cases corresponded to a special kinetic state, where the peak potential was demonstrated to be $E_{1/2}$ and the peak value designated the activation feature of a reaction driven by potential [4]. Additionally, this derivative extremum analysis (DEA) can be easily demonstrated to be applicable in reversible cases; although, the peak potential and peak value have different expressions. In this work, DEA was further proven to be valid in the full range of reversibility through numerical simulations using a derived universal electrode equation, and it provided a new perspective in understanding the kinetic feature evolution in the reversibility domain. We reorganized the equations referenced with formal potential, E_{eq} and $E_{1/2}$ in the full reversibility scale and elucidated their applicability. Reversibility classifications were proposed according to the variation trends of DEA in the reversibility domain.

To investigate the DEA applicability, we first derived a universal electrode equation in the full range of reversibility with three premises as follows: the uniformly accessible electrode treating the mass transport process, a large excess of supporting electrolyte to

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eliminate the migration effect, and a Nernst diffusion layer with stirring maintaining the bulk concentration constant. The cathodic current is defined as positive, and the anodic current is negative.

The most basic equation describing an elementary reaction $\mathrm{O} + ne^- = \mathrm{R}$ is an original Butler-Volmer form (Eq. 1) [5]:

$$j = nFk^0\left[c_{\mathrm{O}}^* \exp\left(-\alpha nf(E - E^0)\right) - c_{\mathrm{R}}^* \exp\left(\beta nf(E - E^0)\right)\right] \quad (1)$$

where k^0 is the standard rate constant, E^0 is the standard potential and can be replaced by formal potential in practice, c_{O}^* and c_{R}^* are the oxidant and reductant concentrations on the electrode surface, respectively, α and β are the electron transfer coefficients (ETCs), $\alpha + \beta = 1$, F is the Faraday constant, and $f = F/RT$, where R is the ideal gas constant, and T is the temperature in Kelvin. All the symbols are defined in Table S1 (Supporting information).

Eq. 1 is difficult to use since c_{O}^* and c_{R}^* can hardly be defined and measured. However, c_{O}^* and c_{R}^* can be replaced by introducing the mass transport relationships of reactants (O and R). In the steady state, the reaction rate equals the mass transport fluxes of O and R between the electrode surface and bulk solution (Eqs. 2) and 3:

$$\frac{j}{nF} = m_{\mathrm{O}}\left(c_{\mathrm{O}}^b - c_{\mathrm{O}}^*\right), \text{ with } m_{\mathrm{O}} = D_{\mathrm{O}}/\delta_{\mathrm{N,O}} \quad (2)$$

$$\frac{j}{nF} = m_{\mathrm{R}}\left(c_{\mathrm{R}}^* - c_{\mathrm{R}}^b\right), \text{ with } m_{\mathrm{R}} = D_{\mathrm{R}}/\delta_{\mathrm{N,R}} \quad (3)$$

where $c_{\mathrm{O}}^{\mathrm{b}}$ and $c_{\mathrm{R}}^{\mathrm{b}}$ are the concentrations in bulk solution, m is the mass transport coefficient, D is the diffusion coefficient, and δ is the diffusion layer thickness. The maximum transport fluxes of O and R are expressed as the cathodic and anodic limiting current densities ($j_{\mathrm{l,c}}$ and $j_{\mathrm{l,a}}$), which are obtained at c_{O}^* and c_{R}^* reaching zero (Eq. 4):

$$j_{\mathrm{l,c}} = nFm_{\mathrm{O}}c_{\mathrm{O}}^{\mathrm{b}} \text{ and } j_{\mathrm{l,a}} = -n_{\mathrm{s}}Fm_{\mathrm{R}}c_{\mathrm{R}}^{\mathrm{b}} \quad (4)$$

Introducing Eq. 4 into Eqs. 2 and 3 obtains (Eq. 5):

$$c_{\mathrm{O}}^* = \frac{j_{\mathrm{l,c}} - j}{nFm_{\mathrm{O}}} \text{ and } c_{\mathrm{R}}^* = \frac{j - j_{\mathrm{l,a}}}{nFm_{\mathrm{R}}} \quad (5)$$

Finally, introducing Eq. 5 into Eq. 1 derives the following equation with the potential referenced against E^0 (Eq. 6):

$$j = \frac{\frac{k^0}{m_{\mathrm{O}}} j_{\mathrm{l,c}} \exp(-\alpha nf(E - E^0)) + \frac{k^0}{m_{\mathrm{R}}} j_{\mathrm{l,a}} \exp(\beta nf(E - E^0))}{1 + \frac{k^0}{m_{\mathrm{O}}} \exp(-\alpha nf(E - E^0)) + \frac{k^0}{m_{\mathrm{R}}} \exp(\beta nf(E - E^0))} \quad (6)$$

This equation is a universal form in consideration of the concentration polarization in the full range of reversibility, which excludes any simplification of kinetic factors. The electrode geometric size information can be introduced to the equation by using the analytical expressions of the diffusion layer thickness [6]. All other equation forms, such as reversible and irreversible, in the presence of only O or R, and with equal mass transport coefficients, can be simplified from this equation. For example, in the presence of only O, $j_{\mathrm{l,a}} = 0$, Eq. 6 can be simplified to the following well-known equation proposed by Mirkin and Bard (Eq. 7) [2]:

$$\frac{j}{j_{\mathrm{l,c}}} = \frac{1}{1 + \frac{m_{\mathrm{O}}}{k^0} \exp(\alpha nf(E - E^0)) + \frac{m_{\mathrm{O}}}{m_{\mathrm{R}}} \exp(nf(E - E^0))} \quad (7)$$

Under the premise of equal mass transport coefficients ($m_{\mathrm{O}} = m_{\mathrm{R}}$), Eq. 6 can be transformed to the following form as reported by Molina *et al.* (Eq. 8) [6]:

$$\frac{j}{j_{\mathrm{l,c}}} = \frac{\bar{k}^0 \exp(-\alpha\eta)(1 - \mu \exp(\eta))}{1 + \bar{k}^0 \exp(-\alpha\eta)(1 + \exp(\eta))} \quad (8)$$

where $\eta = nf(E - E^0)$, $\bar{k}^0 = k^0/m_{\mathrm{O}}$ and $\mu = c_{\mathrm{R}}^{\mathrm{b}}/c_{\mathrm{O}}^{\mathrm{b}}$.

If specifying the electrode geometric size in m_{O} and m_{R}, more detailed electrode equations hold for hemispherical and disc microelectrodes [3,7]. Here, the electrode equations referenced with E^0 in the full range of reversibility are summarized in Table S2 (Supporting information).

The DEA derivation in reversible case is shown as follows. To obtain the reversible equations, Eq. 6 is transformed to the following form (Eq. 9):

$$\begin{aligned} j = &\frac{j_{\mathrm{l,c}}}{1 + \frac{m_{\mathrm{O}}}{m_{\mathrm{R}}} \exp(nf(E - E^0)) + \frac{m_{\mathrm{O}}}{k^0} \exp(\alpha nf(E - E^0))} \\ &+ \frac{j_{\mathrm{l,a}}}{1 + \frac{m_{\mathrm{R}}}{m_{\mathrm{O}}} \exp(-nf(E - E^0)) + \frac{m_{\mathrm{R}}}{k^0} \exp(-\beta nf(E - E^0))} \end{aligned} \quad (9)$$

Under reversible conditions, $m_{\mathrm{O}}/k^0 \to 0$ and $m_{\mathrm{R}}/k^0 \to 0$. We proved that $m_{\mathrm{o}}/k^0 \exp(\alpha nf(E - E^0))$ in the first term and $m_{\mathrm{R}}/k^0 \exp(-\beta nf(E - E^0))$ in the second term are negligible; the detailed derivation is shown in Supporting information. Thus, a reversible equation form can be simplified from the above equation:

$$j = \frac{j_{\mathrm{l,c}}}{1 + \frac{m_{\mathrm{O}}}{m_{\mathrm{R}}} \exp\left(nf(E - E^0)\right)} + \frac{j_{\mathrm{l,a}}}{1 + \frac{m_{\mathrm{R}}}{m_{\mathrm{O}}} \exp\left(-nf(E - E^0)\right)} \quad (10)$$

By solving for the extremal solution of the derivative of Eq. 10, we derived the expressions of the peak potential (E_{P}) and peak vale (PV) in the dj/dE curve and demonstrated that E_{P} was identical to $E_{1/2}$. The detailed derivation process is shown in the Supporting information.

$$E_{1/2} = E^0 + \frac{1}{nf} \ln \frac{m_{\mathrm{R}}}{m_{\mathrm{O}}} \quad (11)$$

$$\mathrm{PV} = 0.25nf(j_{\mathrm{l,c}} - j_{\mathrm{l,a}}) \quad (12)$$

The DEA derivation in irreversible case is shown here. To date, the reported irreversible equations have basically applied the forms using E_{eq} as the reference potential. Eq. 6 can be transformed to a E_{eq}-referenced form. The exchange current density (j_0) is an equilibrium current at the initial state where $c_{\mathrm{O}}^* = c_{\mathrm{O}}^{\mathrm{b}}$ and $c_{\mathrm{R}}^* = c_{\mathrm{R}}^{\mathrm{b}}$ and has the following expressions (Eq. 13):

$$\begin{aligned} j_0 &= nFk^0 c_{\mathrm{O}}^{\mathrm{b}} \exp(-\alpha nf(E_{\mathrm{eq}} - E^0)) \\ &= nFk^0 c_{\mathrm{R}}^{\mathrm{b}} \exp(\beta nf(E_{\mathrm{eq}} - E^0)) \end{aligned} \quad (13)$$

In combination with the expressions of j_0, $j_{\mathrm{l,c}}$ and $j_{\mathrm{l,a}}$, the cathodic and anodic terms in Eq. 6 can be rearranged as follows (Eqs. 14 and 15):

$$\frac{k^0}{m_{\mathrm{O}}} \exp(-\alpha nf(E - E^0)) = \frac{j_0 \exp(-\alpha nf(E - E_{\mathrm{eq}}))}{j_{\mathrm{l,c}}} \quad (14)$$

$$\frac{k^0}{m_{\mathrm{R}}} \exp(\beta nf(E - E^0)) = \frac{j_0 \exp(\beta nf(E - E_{\mathrm{eq}}))}{j_{\mathrm{l,a}}} \quad (15)$$

Please note that the above transformations are only valid at $c_{\mathrm{O}}^{\mathrm{b}}$ and $c_{\mathrm{R}}^{\mathrm{b}}$ are not zero. Based on the above relationships, Eq. 6 can be transformed to the following form referenced with E_{eq} (Eq. 16):

$$j = \frac{j_0 \exp(-\alpha nf(E - E_{\mathrm{eq}})) - j_0 \exp(\beta nf(E - E_{\mathrm{eq}}))}{1 + \frac{j_0}{j_{\mathrm{l,c}}} \exp(-\alpha nf(E - E_{\mathrm{eq}})) - \frac{j_0}{j_{\mathrm{l,a}}} \exp(\beta nf(E - E_{\mathrm{eq}}))} \quad (16)$$

In the irreversible case, j_0 is so small that a very high overpotential is required to drive the reaction occurrence. Thus, the term $\exp(\beta nf(E - E_{\mathrm{eq}}))$ for the cathode reaction is negligible, and $\exp(-\alpha nf(E - E_{\mathrm{eq}}))$ for the anode reaction is negligible. Eq. 16 can be simplified to the following cathodic and anodic irreversible equations (Eqs. 17 and 18):

Cathode:

$$j = \frac{j_0 \exp\left(-\alpha nf(E - E_{\mathrm{eq}})\right)}{1 + \frac{j_0}{j_{\mathrm{l,c}}} \exp\left(-\alpha nf(E - E_{\mathrm{eq}})\right)} \; (E \le E_{\mathrm{eq}}) \quad (17)$$

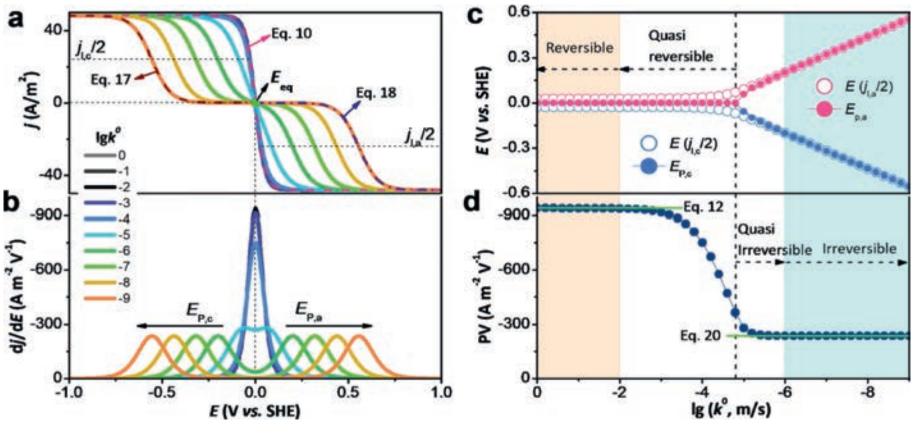

Fig. 1. Calculation results of Eq. 6 with lgk^0 varying from 0 to –9, c_O^b=c_R^b=10 mol/m^3, and $m_O = m_R = 5\times10^{-5}$ m/s, $n = 1$, $E^0 = 0$ V, $\alpha = 0.5$ and T = 25 °C: (a) j-E curves, the dashed lines were calculated from the reversible equation (Eq. 10) with lg$k^0 = 0$ and irreversible equations (Eqs. 17 and 18) with lg$k^0 = -9$, (b) associated dj/dE curves, (c) peak potential (E_P) and potentials at $j_{l,c}/2$ and $j_{l,a}/2$ plotted *vs.* lgk^0, and (d) PV plotted *vs.* lgk^0, the lines were calculated from the reversible and irreversible expressions of PV.

Anode:

$$j = \frac{-j_0 \exp\left(\beta nf(E - E_{\mathrm{eq}})\right)}{1 - \frac{j_0}{j_{\mathrm{l,a}}}\exp\left(\beta nf(E - E_{\mathrm{eq}})\right)}\ (E \ge E_{\mathrm{eq}}) \tag{18}$$

These equations have similar forms to those derived from the multielectron and multistep irreversible process with one sole rate-limiting step [4]. The DEA applicability in irreversible cases has been demonstrated by solving for the extremal solution of the derivatives of Eqs. 17 and 18 in a previous work [4]. The expressions of $E_{1/2}$ and PV in irreversible cathodic reactions are shown as follows (Eqs. 19 and 20):

$$E_{1/2} = E_{\mathrm{eq}} + \frac{1}{\alpha nf}\ln\frac{j_0}{j_{\mathrm{l,c}}} = E^0 + \frac{1}{\alpha nf}\ln\frac{k^0}{m_{\mathrm{O}}} \tag{19}$$

$$\mathrm{PV} = 0.25 nf\alpha\, j_{\mathrm{l,c}} \tag{20}$$

In both reversible and irreversible cases, E_p is identical to $E_{1/2,}$ and PV has a unit of A m^{-2} V^{-1} and can serve to characterize the kinetic slowness of a reaction driven by potential. However, $E_{1/2}$ and PV have different expressions in the two cases.

Furthermore, the DEA simulations in the full range of reversibility using Eq. 6 are calculated to show the DEA in the transition range between reversible and irreversible cases, because mathematically solving for the derivatives of Eq. 6 is too difficult. In a given scenario, a set of j-E curves with k^0 values varying from 0 m/s to 10^{-10} m/s are calculated first, then the dj/dE curves are calculated, and the E_p and PV values are extracted from the peak points of dj/dE curves. Finally, the plots of E_p and PV *vs.* lgk^0 are obtained. For all the calculations, $n = 1$, $\alpha = \beta = 0.5$, $E^0 = 0$ V *vs.* SHE and T = 25 °C. The other parameter values (m_O, m_R, c_O^b and c_R^b) are presented in the figure titles. The calculations were performed using MATLAB 2012a.

The calculation results in the presence of both O and R are shown in Fig. 1. Figs. 1a clearly presents the variation trend of the j-E curves from the reversible to irreversible case: in the condition of $k^0 > 10^{-4}$ m/s, the curves approached the calculation result of the reversible equation (Eq. 10) with $k^0 = 1$ m/s; once k^0 was small enough, namely, $k^0 = 10^{-9}$ m/s, the curves were consistent with the results of irreversible equations (Eqs. 17 and 18). In Fig. 1b, the associated dj/dE curves show that the peak point gradually shifts from one point in the reversible case to two peak points. The isolation degree between the cathode and anode reactions can be characterized by the distance between the two points and is intensified as k^0 decreases.

To further investigate the relationship between E_p and $E_{1/2}$, the E_p and the potentials of $j_{l,c}/2$ and $j_{l,a}/2$ were plotted in Fig. 1c. E_p changed suddenly from the reversible $E_{1/2}$ feature, namely, the potential of $(j_{l,c} + j_{l,a})/2$, to the irreversible $E_{1/2}$ feature, namely, the potentials of $j_{l,c}/2$ and $j_{l,a}/2$. In Fig. 1d, the PV gradually shifts from the reversible case, as designated by the line calculated from Eq. 12 to the irreversible case designated by the line calculated from Eq. 20. These results confirmed that DEA is applicable in most cases in the presence of both O and R, except for a narrow transition range between reversible and irreversible cases where the

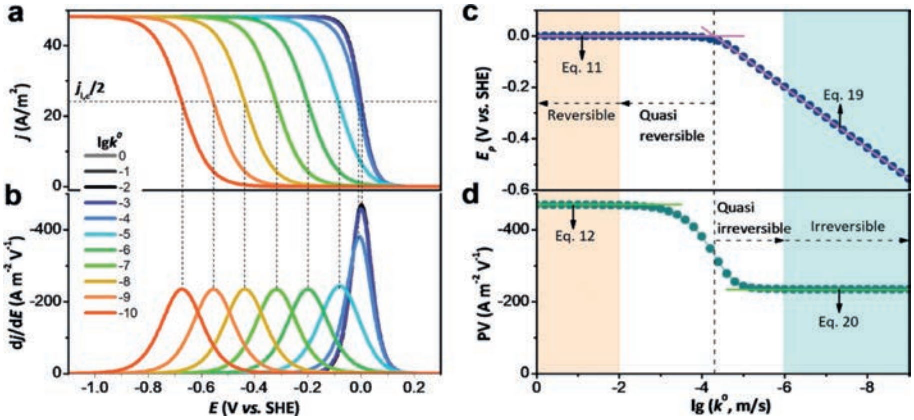

Fig. 2. Calculation results of Eq. 6 with lgk^0 varying from 0 to –10, c_O^b = 10 mol/m^3, c_R^b = 0, $m_O = m_R = 5\times10^{-5}$ m/s, $n = 1$, $E^0 = 0$ V, $\alpha = 0.5$ and T = 25 °C: (a) j-E curves, (b) associated dj/dE curves, (c) E_p *vs.* lgk^0 and (d) PV *vs.* lgk^0, the lines were calculated from the reversible and irreversible expressions of E_p and PV.

Table 1

Electrode equation forms referenced with $E_{1/2}$ in the full range of reversibility.

	Presence of both O and R	Presence of only O
Reversible	Electrode equation: Eq. 21 $E_{1/2}$: Eq. 11, PV: Eq. 12	Eq. 21 with $j_{\mathrm{l,a}} = 0$
Quasi-reversible	Equation is not available, $E_{1/2}$ approaches to the reversible $E_{1/2}$	
Quasi-irreversible	Equation is not available, $E_{1/2}$ approaches to the irreversible $E_{1/2}$	
Irreversible	Cathode: Eq. 22 $E_{1/2}$: Eq. 19, PV: Eq. 20 Anode: Eq. 23 $E_{1/2} = E_{\mathrm{eq}} - \frac{1}{\beta nf} \ln \frac{j_0}{-j_{\mathrm{l,a}}} = E^0 - \frac{1}{\beta nf} \ln \frac{k^0}{m_{\mathrm{R}}}$ $\mathrm{PV} = -0.25 nf\beta j_{\mathrm{l,a}}$	

Table 2

Electrode equation forms referenced with E_{eq} in the full range of reversibility.

	Presence of both O and R	Presence of only O
Reversible	Eq. 25	Not available
Quasi-reversible/ irreversible	Eq. 16	Not available
Irreversible	Cathode: Eq. 17 Anode: Eq. 18	

exact $E_{1/2}$ can hardly be defined. In light of the variation features of E_{p} and PV, the exact reversible and irreversible ranges can be defined as shown by the colored regions.

The DEA simulation results in the presence of only O are shown in Fig. 2. Figs. 2a and b demonstrate that the E_{p} in the dj/dE curves corresponded to the potential of $j_{\mathrm{l,c}}/2$ in the j-E curves in the full range of reversibility. Thus, E_{p} is invariably identical to $E_{1/2}$ in this case. The E_{p} *vs.* lgk^0 plot in Fig. 2c also presented a sudden change from the reversible $E_{1/2}$ feature to the irreversible $E_{1/2}$ feature. In Fig. 2d, PV gradually shifts from the reversible case to the irreversible case.

Finally, the above DEA simulation results confirmed that $E_{1/2}$ is a kinetically special potential corresponding to the positions of the half limiting current in the j-E curves and the peak point in the dj/dE curve. DEA is a general method to extract $E_{1/2}$ as well as PV in the full range of reversibility. The variation trends of $E_{1/2}$ and PV along the k^0 axis can give a classification criterion of *quasi*-reversible and *quasi*-irreversible regions, namely, (i) *quasi*-reversible: $E_{1/2}$ is approximate to the reversible $E_{1/2}$ value; (ii) *quasi*-irreversible: $E_{1/2}$ is approximate to the irreversible $E_{1/2}$ value.

The above calculations indicate that $E_{1/2}$ is a good choice of reference potential because it can be steadily determined in the full range of reversibility. Here, the electrode equations referenced with $E_{1/2}$ in the full range of reversibility are summarized in Table 1. The reversible equation form (Eq. 21) can be obtained by combining Eqs. 10 and 11:

$$j = \frac{j_{\mathrm{l,c}}}{1 + \exp\left(nf(E - E_{1/2})\right)} + \frac{j_{\mathrm{l,a}}}{1 + \exp\left(-nf(E - E_{1/2})\right)} \tag{21}$$

The $E_{1/2}$-referenced equations of irreversible cathode and anode reactions can be derived by introducing the irreversible expression of $E_{1/2}$ (Eq. 19) into Eqs. 17 and 18, respectively (Eqs. 22 and 23):

Cathode:

$$j = \frac{j_{\mathrm{l,c}}}{1 + \exp\left(\alpha nf(E - E_{1/2})\right)} \tag{22}$$

Anode:

$$j = \frac{j_{\mathrm{l,a}}}{1 + \exp\left(-\beta nf(E - E_{1/2})\right)} \tag{23}$$

In irreversible cases, it is not necessary to distinguish the equations in the presence of both O and R and in the presence of only O because the anode and cathode reactions are evidently separated from each other.

In *quasi*-reversible/irreversible cases, $E_{1/2}$-referenced equations are not available because the exact expression of $E_{1/2}$ and PV can hardly be derived. Nonetheless, DEA is still applicable.

Furthermore, the electrode equations referenced with E_{eq} in the full range of reversibility are summarized in Table 2. The reversible equation is derived as follows. Simultaneously, dividing by j_0 in the numerator and denominator of Eq. 16, it becomes (Eq. 24):

$$j = \frac{\exp(-\alpha nf(E - E_{\mathrm{eq}})) - \exp(\beta nf(E - E_{\mathrm{eq}}))}{\frac{1}{j_0} + \frac{1}{j_{\mathrm{l,c}}}\exp(-\alpha nf(E - E_{\mathrm{eq}})) - \frac{1}{j_{\mathrm{l,a}}}\exp(\beta nf(E - E_{\mathrm{eq}}))} \tag{24}$$

In the reversible case, j_0 is so large that $1/j_0$ is negligible. The above equation can be transformed to the following reversible form (Eq. 25):

$$j = \frac{1 - \exp(nf(E - E_{\mathrm{eq}}))}{\frac{1}{j_{\mathrm{l,c}}} - \frac{1}{j_{\mathrm{l,a}}}\exp(nf(E - E_{\mathrm{eq}}))} \tag{25}$$

Although irreversible E_{eq}-referenced equations are derived and are as given in Table 2, users should be highly cautious about their applications. The applications of E_{eq} and j_0 are introduced in the following part. The E_{eq} used as a reference potential in kinetics is the open circuit potential of an electrode reaction, which satisfies the Nernst relationship (Eq. 26):

$$E_{\mathrm{eq}} = E^0 + \frac{1}{nf}\ln\frac{c_{\mathrm{O}}^b}{c_{\mathrm{R}}^b} \tag{26}$$

At this potential, the cathodic and anodic rates reach balance and are expressed as exchange current density (j_0) (Eq. 27):

$$j_0 = nFk^0 (c_{\mathrm{O}}^b)^{\beta} (c_{\mathrm{R}}^b)^{\alpha} \tag{27}$$

It is obvious that E_{eq} and j_0 are relevant only in the presence of both O and R. Once c_{O}^b or c_{R}^b approaches zero, E_{eq} and j_0 in Eqs. 26 and 27 become an infinite problem without explicit value. Moreover, E_{eq} is experimentally indeterminable in irreversible cases because the zero current is not a point but a wide gap between the cathode and anode reactions (Fig. 1). Thus, E_{eq} and j_0 are applicable for the kinetically fast reactions in the presence of both O and R.

Despite this, E_{eq} and j_0 are still frequently applied in irreversible cases. Here, we demonstrate that E_{eq} and j_0 are an interdependent pair in irreversible cases. Choosing any potential in the zero current stage as a formal equilibrium potential (E_{eq}^*), the deviation of E_{eq}^* from the theoretical E_{eq} can be described by $E_{\mathrm{eq}} = E_{\mathrm{eq}}^* + \Delta E$. Introducing it to the irreversible equation (Eq. 17) obtains Eq. 28:

$$j = \frac{j_0^* \exp(-\alpha nf(E - E_{\mathrm{eq}}^*))}{1 + \frac{j_0^*}{j_{\mathrm{l,c}}} \exp(-\alpha nf(E - E_{\mathrm{eq}}^*))} \text{ with } j_0^* = j_0 \exp(\alpha nf \Delta E) \qquad (28)$$

It revealed that the application of E_{eq}^* only results in the variation of j_0. In irreversible cases, E_{eq} is indeterminable and is usually determined as the onset potential, the lowest potential where the faradaic current is observed [8]. Therefore, the j_0 value has little physical significance in irreversible cases. If selecting the same E_{eq} value, j_0 is still useful to compare the activity of a reaction between different conditions or catalysts.

In addition, the activation overpotential (η_{act}) in the irreversible case is also meaningless because it is dependent on the j_0 and E_{eq} values. Nonetheless, the overpotential analysis of the mass transport effect is feasible, *viz.*, the concentration overpotential assigned to reactant mass transport [9] and the pH overpotential assigned to H$^+$/OH$^-$ transport [10], because the overpotential part $E - E_{\mathrm{eq}} - \eta_{\mathrm{act}}$ has excluded the E_{eq} value.

Currently, the E_{eq}-referenced equations are typically used to fit the *j-E* curves for parameter determinations, such as the Tafel fitting method and a recently reported nonlinear fitting method [11]. The Tafel method either directly ignores the mass transport effect by fitting a narrow *j-E* curve range [12,13] or corrects the mass transport current part to improve the accuracy of parameter values [14–16]. The nonlinear fitting method is performed based on Eqs. 17 or 18 to fit the entire *j-E* curve range, which overcomes the disadvantages of the Tafel method to obtain reliable ETC, j_0 and j_{l} values.

The $E_{1/2}$-referenced equations are more significant for quantifying the activity of irreversible reactions. The information of E_{eq} and j_0 is involved in $E_{1/2}$ (see Eq. 19) to reveal the priority of reaction occurrence. The nonlinear fitting method can also be performed using the irreversible $E_{1/2}$-referenced equations and obtain the values of ETC, $E_{1/2}$ and j_{l}. In Fig. S1 (Supporting information), the nonlinear fitting results of the two types of equations (Eqs. 17 and 22) showed that the fitting lines were totally identical and could well fit the entire *j-E* curve. All the parameter values (Table S3 in Supporting information) determined from Eq. 22 have a narrow 95% confidence interval, and the intervals of ETC, $E_{1/2}$ and $j_{\mathrm{l,a}}$ are less than 1.10%, 0.06% and 0.25%, respectively. This confirms that the nonlinear fits based on the irreversible $E_{1/2}$-referenced equations are a reliable parameter determination method of irreversible reactions.

Moreover, the irreversible $E_{1/2}$-referenced equations are also applicable in conditions deviating from the irreversible case, wherein the ETC reveals reversibility variations. The reversible $E_{1/2}$-referenced equations are the special form of irreversible $E_{1/2}$-referenced equations with ETC equal to 1. With the aid of micro- and nanoscale electrode techniques to measure steady-state voltammograms [17], the practical application scope of irreversible $E_{1/2}$-referenced equations can be greatly extended.

Importantly, the variation trends of $E_{1/2}$ and PV in DEA in the reversibility domain provide classification criteria of reversible, irreversible, *quasi*-reversible and *quasi*-irreversible cases. Here, the influences of transport coefficients (m_{O} and m_{R}) and concentrations ($c_{\mathrm{O}}^{\mathrm{b}}$ and $c_{\mathrm{R}}^{\mathrm{b}}$) on the reversibility classifications are investigated. In the presence of only O, the effect of m_{O} with a k^0 scale is shown in Figs. 3a–c. The reversible and irreversible ranges presented by the colored regions gradually shift toward the decreasing direction of lgk^0 as m_{O} decreases from 10^{-4} m/s to 10^{-6} m/s. The transition region can be divided into *quasi*-reversible and *quasi*-irreversible parts bounded by lgm_{O} as indicated by the dashed lines in Figs. 3a–c.

The E_{p} *vs.* lgk^0 plots in Figs. 3a–c were redrawn using a logarithmic k^0/m_{O} scale as shown in Fig. 3d, and the results at different m_{O} conditions were the same. It revealed that k^0/m_{O} was a dimensionless parameter and the most basic scale for reversibility classification. Hence, reversibility was a relative measure between reaction kinetics and mass transport of electroactive species. Roughly,

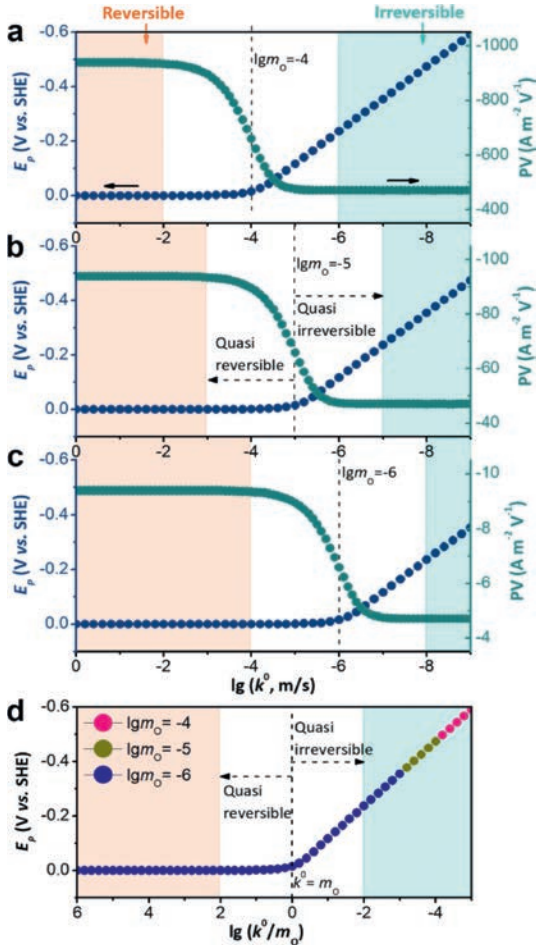

Fig. 3. E_{p} and PV *vs.* lgk^0 plots in the presence of only O calculated from Eq. 6 with c_{O}^{b}=10 mol/m^3, $n = 1$, $\alpha = 0.5$, $E^0 = 0$ V and T = 25 °C: (a) lg$m_{\mathrm{O}} = -4$, (b) lg$m_{\mathrm{O}} = -5$, and (c) lg$m_{\mathrm{O}} = -6$; (d) plots of E_{p} in Fig. (a–c) *vs.* lg(k^0/m_{O}).

$k^0/m_{\mathrm{O}} \gg 1$: reversible
$k^0/m_{\mathrm{O}} \ll 1$: irreversible

In theory, the full "reversible" and "irreversible" are two extreme cases that can hardly be reached, and all the reactions may be regarded as *quasi*-states [3]. Here, a detailed classification of the effectively *quasi*-reversible and *quasi*-irreversible cases was proposed, as listed in Table 3, namely,

100 $> k^0/m_{\mathrm{O}} >$ 1: *quasi*-reversible, where $E_{1/2}$ approaches the reversible $E_{1/2}$ value

0.01 $< k^0/m_{\mathrm{O}} <$ 1: *quasi*-irreversible, where $E_{1/2}$ approaches the irreversible $E_{1/2}$ value

The k^0 scale for the reversibility classification is dependent on the m_{O} and/or m_{R} values. In practice, the diffusion coefficient or

Table 3
Reversibility classifications in terms of k^0/m_{O} and k^0 in the presence of only O.

	Reversible	*Quasi*-reversible	*Quasi*-irreversible	Irreversible
k^0/m_{O}	$> 10^2$	10^2-1	1-10^{-2}	$< 10^{-2}$
k^0 (m/s)[a]	$> 10^{-3}$	10^{-3}-10^{-5}	10^{-5}-10^{-7}	$< 10^{-7}$

[a] The k^0 scale is determined from Fig. 3b with $m_{\mathrm{O}} = 10^{-5}$ m/s.

mass transport coefficient values of most solutes rarely differ by more than one order of magnitude. The diffusion coefficient usually has a magnitude of 10^{-9} m^2/s [18,19], and the mass transport coefficient has a magnitude of 10^{-5} m/s [20]. The reversibility classification in terms of the k^0 scale with $m_O = 10^{-5}$ m/s (see Fig. 3b) is listed in Table 3.

In addition, $j_{0,}$ in comparison to the transport limiting current ($j_{l,c}$ or $j_{l,a}$), is also frequently applied to the quantification of reversibility in electrochemistry [21]. The ratio between j_0 and $j_{l,c}$ can be derived from Eqs. 4 and 27 as follows (Eq. 29):

$$\frac{j_0}{j_{l,c}} = \frac{k^0}{m_O}\left(c_R^b/c_O^b\right)^{\alpha} \tag{29}$$

This indicates that $j_0/j_{l,c}$ is an extended form of k^0/m_O that involves an extra concentration term. Obviously, $j_0/j_{l,c}$ is applicable in the presence of both O and R and is identical to k^0/m_O in the condition of $c_O^b = c_R^b$. The DEA calculation result under the condition of $c_O^b = c_R^b$ is shown in Fig. S2 (Supporting information), confirming that the reversibility scale is independent of the concentration extent. Under the condition of $c_O^b \neq c_R^b$ (Fig. S3 in Supporting information), the reversible and irreversible regions can be well identified but the *quasi*-state regions for anode and cathode reactions become very complicated.

In this work, numerical simulations of DEA using a derived universal electrode equation successfully verified the validity of DEA in the full range of reversibility and gained panoramic insight into electrochemical kinetics. The equations referenced with E^0, $E_{1/2}$ and E_{eq} in conjunction with their applicability were reorganized in three tables in terms of the reversibility scale. Reversibility classifications in terms of the variation features of DEA in the reversibility domain were proposed.

The outcomes of this work are especially important for reactions suffering from mass transport limitations. One can apply the DEA method to extract $E_{1/2}$ and PV from the steady state *j-E* curves. $E_{1/2}$ is a potential feature parameter pronouncing the priority of reaction occurrence on a potential scale. PV is an activation feature parameter revealing the kinetic slowness driven by potential. Alternatively, the nonlinear fitting method of *j-E* curves using the irreversible $E_{1/2}$-referenced equations can obtain reliable ETC, $E_{1/2}$ and j_l values. In summary, the $E_{1/2}$-referenced equations have wide application scope in the presence of only O, while the E_{eq}-referenced equations are primarily useful for the kinetically fast reactions in the presence of both O and R. Users should be highly cautious about the applications of E_{eq} and j_0 in irreversible cases because they are an interdependent pair and have little physical significance.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.01.078.

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