Kinetics of the Hydrogen Electrode Reaction

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Suggested Citation
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Kinetics of the Hydrogen Electrode Reaction

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It is well recognized that the standard Butler–Volmer equation is lacking in an adequate description of the kinetics of the hydrogen electrode reaction over the complete range of potentials for the alkaline as well as the acid electrolytes. Further, it is unable to explain the asymmetry in current vs potential observed in the hydrogen evolution reaction (HER) vs the hydrogen oxidation reaction (HOR). In fact, even kinetic descriptions via two-step mechanisms (Volmer–Tafel, or Heyrovsky–Tafel) are individually applicable only in limited potential ranges. We present an approach that provides explicit rate expressions involving kinetics of all the three steps (Tafel–Volmer–Heyrovsky) simultaneously, as well as more limiting rate expressions based on two-step pathways. The analysis is based on our recently developed graph-theoretic approach that provides accurate rate laws by exploiting the electrical analogy of the reaction network. The accuracy of the resulting rate expressions, as well as their asymmetric potential dependence, for both HOR and HER is illustrated here based on step kinetics provided in the literature for Pt catalyst in 0.5 M NaOH solution.

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Manuscript submitted January 11, 2010; revised manuscript received March 16, 2010. Published May 21, 2010.

Due to their practical significance, the hydrogen oxidation reaction (HOR), and its inverse, the hydrogen evolution reaction (HER), are by far the most extensively investigated of electrocatalytic reactions. Further, despite being among the simplest of such reactions, their mechanistic and kinetic understanding is still incomplete. The significance of dual-pathway kinetics has recently been shown for the HOR on Pt electrode. However, no general rate expression exists that can simultaneously account for these alternate pathways in terms of the accepted three-step mechanism, namely, the Tafel, Volmer, and the Heyrovsky steps. Further, no realistic first-principles prediction of step kinetics yet exists for the hydrogen electrode reaction, although there is now great interest in ab initio theoretical approaches we recently developed, namely, the reaction route (RR) graph and its electrical analog, along with the notion of intermediate reactions (IRs) for the formation of an intermediate species. It further interrelates the two standard approaches of kinetic analysis, namely, the rate-determining step (RDS)/quasi-equilibrium (QE) approach of Langmuir–Hinshelwood–Houben–Watson (LHHW) and the quasi-steady-state (QSS) analysis of Bodenstein. The resulting rate expression accurately portrays the kinetics of HOR/HER over a broad range of potentials, including their asymmetric potential dependence in both alkaline and acidic media, although in the discussion below we simply use the step rate constants reported for Pt in an alkaline electrolyte. The case of acidic electrolyte, of special interest in fuel cells, will be described in a subsequent publication.

Reaction Mechanism, Network, and Step Kinetics

RRs or pathways.— The hydrogen electrode reaction has been investigated over a long period of time due to its technological and fundamental significance. The most common and well-accepted mechanism involves the Tafel, Volmer, Heyrovsky steps, which have adequately explained the overall reaction (OR) kinetics. This three-step mechanism involves only a single reaction intermediate, H S, where S represents an unoccupied catalyst surface site. However, more recently, other intermediates have been proposed. For instance, intermediates such as adsorbed water (H 2O·S) and adsorbed hydroxyl (OH·S) have been shown to exist on Pt surfaces by Vökeling et al., Bedurftig et al., and Rossmeis et al. Thus, Nørskov et al. consider the OH·S and O·S species to calculate the effect of molecular water on adsorption. Additional intermediates, of course, imply additional elementary steps in the mechanism and would alter the site balance. Nonetheless, because our purpose here is to elucidate an approach that adequately describes the kinetics of the hydrogen electrode reaction, we simply adopt the standard Tafel–Volmer–Heyrovsky mechanism shown below to avoid being distracted by the additional complexities of a more detailed mechanism, which are left for future work

Equation 1 above describes the HOR in an alkaline electrolyte. In an acidic electrolyte, however, the corresponding mechanism is...
The Volmer step, \( s_V \), above describes the electrochemical consumption of the key intermediate, namely, the surface atomic hydrogen, \( \text{H} \), whereas the nonelectrochemical Tafel step, \( s_T \), and the electrochemical Heyrovsky step, \( s_H \), describe the generation of \( \text{H}_2 \) from molecular \( \text{H}_2 \). As indicated by the stoichiometric numbers \( \sigma_{s_V} \), \( \sigma_{s_T} \), and \( \sigma_{s_H} \) above, when these steps are combined in a manner that eliminates the intermediate \( \text{H}_2 \), the OR results. Clearly, this can be accomplished in more than one way, which represents the alternate RRs or pathways. The OR and the elementary steps for the HER are simply the reverse of those written above for the HOR.

More generally, the OR results from a linear combination of the elementary steps \( s_p = \{1, 2, \ldots, m\} \) in a mechanism, i.e., \( \sum_{p} \sigma_{s_p} s_p = \text{OR} \), representing the \( g \)th RR, wherein all the intermediate species \( I_k = \{k=0, 1, 2, \ldots, q\} \) are eliminated to provide the OR in terms of only the terminal species \( T_i = \{i=1, 2, \ldots, n\} \), i.e., the reactants and products of the OR. Here, \( \sigma_{s_p} \) is the stoichiometric number (usually, 0, \( \pm 1 \), or \( \pm 2 \)) of step \( s_p \) in the 9th RR.

The RRs that produce the OR are, in fact, referred to more specifically as full routes (FR). Thus, as shown in Eq. 1 and 2, the three FRs for the HOR are

\[
\begin{align*}
\text{FR}_\text{VH}: (1) s_V + (1) s_H &= \text{OR} \\
\text{FR}_\text{VT}: (2) s_V + (1) s_T &= \text{OR} \\
\text{FR}_\text{HT}: (2) s_H + (1) s_T &= \text{OR}
\end{align*}
\]

Table I. Stoichiometrically distinct direct FRs and ERs for the three-step HER mechanism.

<table>
<thead>
<tr>
<th>RR</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full RRs</td>
<td>( s_V + s_H = \text{OR} )</td>
</tr>
<tr>
<td>( \text{FR}_\text{VH} = \text{Volmer–Heyrovsky} )</td>
<td>( s_V + s_H = \text{OR} )</td>
</tr>
<tr>
<td>( \text{FR}_\text{VT} = \text{Volmer–Tafel} )</td>
<td>( 2s_V + s_T = \text{OR} )</td>
</tr>
<tr>
<td>( \text{FR}_\text{HT} = \text{Heyrovsky–Tafel} )</td>
<td>( 2s_H - s_T = \text{OR} )</td>
</tr>
</tbody>
</table>

Zero). In fact, because subtracting one FR from the other, e.g., \( \text{FR}_\text{VT} - \text{FR}_\text{HT} \), would eliminate all species, it can provide an ER, namely, \( (1)s_V + (1)s_H + (1)s_T = 0 \), is an ER, \( \text{ER}_1 \).

In general, thus, \( \text{ER}_1: \sum_{p} \sigma_{s_p} s_p = 0 \) represents an ER.

Finally, let us consider another linear combination of FRs, e.g., \( \text{FR}_\text{VT} + \text{FR}_\text{VH} - \text{FR}_\text{HT} \), which simply results in another FR, namely, \( \text{ER}_2: \sum_{p} \sigma_{s_p} s_p + (3) s_V + (2) s_T - (1) s_H = 0 \). In fact, because new RRs may be obtained simply by linearly combining others, one may, in principle, obtain an infinite set, if no further restrictions are placed on their definition.

This is avoided by the concept of “directness” proposed by Milner,\(^{42}\) i.e., the number of steps involved in an RR must be minimal. In other words, a “direct” FR must not contain any cycles or ERs. Such a direct FR contains no more than \( q + 1 \) steps, whereas a direct ER contains no more than \( q + 2 \) steps,\(^{23,24,26}\) selected from among the given mechanism of \( p \) steps. Here, \( q \) is the number of linearly independent intermediate species, typically 1 less than the number of intermediates due to intermediates conservation, e.g., site conservation. For the three-step \( p = 3 \) HOR/HER reaction mechanism considered here, \( \text{H}_2 \) is, in fact, the only independent intermediate, so that \( q = 1 \) simply.

For the hydrogen electrode reaction, thus, a direct FR must not contain more than any two of the three steps, whereas a direct ER must be restricted to less than three steps. As a result, the FR obtained above from the combination of other RRs may include both FRs and ERs, so long as they include among themselves all of the steps in the mechanism. Moreover, the number of linearly independent ERs is given by \( p - (q + 1) = 3 - 2 = 1 \) for the reaction mechanism considered.\(^{23}\) Thus, a set of two linearly independent RRs may be readily determined by identifying one independent ER and one FR by a simple inspection of the HER/HOR mechanism, as done above, thus avoiding the stoichiometric enumeration of RRs used for complex mechanisms.\(^{23,24,26}\)

Let us consider \( \text{FR}_\text{VH} \) and \( \text{ER}_1 \), mentioned above as the independent set of RRs for the considered HOR/HER mechanism, from which the remaining set of unique RRs can be obtained. Thus, a linear combination of \( \text{FR}_\text{VH} \) and \( \text{ER}_1 \) results in \( \text{FR}_\text{VT} \) and \( \text{FR}_\text{HT} \) (Table I).

These RRs or pathways may, in fact, be simply traced as walks on the RR graph of a mechanism for an OR. The construction of
Figure 1. (Color online) RR graph construction for the three-step HER mechanism.

such a graph is discussed in detail by us elsewhere \cite{23,24,26} and is described below briefly with regard to the hydrogen electrode reaction, as done elsewhere.\cite{26}

**RR graph.**— An RR graph is a graph-theoretical depiction of the mechanism of an OR, in which the elementary steps are represented individually by directed branches or edges, interconnected at nodes or vertices, such that all possible RR graphs enumerable, for instance, from stoichiometric considerations, \cite{23,24,26,43} can be traced on it simply as walks between terminal nodes (TNs) across which the OR is connected. These RR graphs further follow Kirchhoff’s laws of flow graphs rooted in the species conservation principle along with the state properties of thermodynamic functions, which provide the topological constraints on the individual step rates. Of course, Kirchhoff’s laws are central to the analysis of electrical networks. For this reason, RR graphs are completely analogous to electrical networks. In fact, a QSS rate expression of Ohm’s law form, \(\text{i.e., OR rate = driving force/overall network resistance},\) can be derived by exploiting the analogy to electrical circuits. This property is used below to obtain a general rate law for the kinetics of HOR/HER.

With the independent set of RRs (\(\text{i.e., FR}_V\text{ and ER}_y\)) at hand, the construction of the RR graph is straightforward and is illustrated in Fig. 1.\cite{2} We start by assembling the ERs, only ER 1 in this case, into a cycle graph. It is further noted that there exists nonunit stoichiometric \((\sigma_{ij} = \pm 2)\) numbers in some of the RRs in the unique set (Table I), \(\text{i.e., in FR}_V\text{ and in FR}_H\). This implies that every elementary reaction step \(s_p\) as well as the OR must occur twice in the RR graph, which must furthermore be symmetrical.\cite{20,21} This can be accomplished by fusing two ERs, as shown in Fig. 1a. Next, the remaining RR in the independent set, namely, \(\text{FR}_H\), can be included in the graph by simply connecting the OR (also twice) across TNs, yielding the final RR graph (Fig. 1b). All of the four unique RRs (Table I) for HOR can be traced on the resulting RR graph as walks between the TNs. In fact, every RR in the graph is involved twice. This is a consequence of the fact that the mechanism is nonminimal,\cite{28} \(\text{i.e., the elementary steps are involved more than once in a FR. Nonetheless, the affinity (or any other thermodynamic potential change across it) and the rate of a step (e.g., } s_H, s_V, \text{ or } s_H\) remain unchanged regardless of their placement because of the network symmetry. For HER, the FR walks are simply in the opposite direction.

The other characteristic that an appropriate RR graph must satisfy is that the connectivity at the intermediate nodes (INs) and the TNs must be consistent with the QSS condition for the intermediate and terminal species. Thus, INs interconnect mechanistic steps \(s_p\) only, with the incidence of steps being consistent with the QSS conditions for intermediates or their linear combination, along with the condition of minimality. The TNs, however, interconnect mechanistic steps \(s_p\) to the OR, with the incidence of steps being consistent with QSS equations for terminal species as well as with minimality of incidence.\cite{23,24,26}

Because there is only one linearly independent intermediate here, H·S, its QSS condition is

\[
Q_H: (-2)r_T + (+1)r_V + (-1)s_H = 0
\]

which is consistent with the connectivity, \(\sum_j m_{ij} s_j = 0\), where the incidence coefficient \(m_{ij} = +1\), if a branch leaves the node \(j\), and \(m_{ij} = -1\), if a branch is coming into the node \(j\), of the only one IN (although present twice) in the RR Graph, that is

IN\(_1\): \((-2)s_T + (+1)s_V + (-1)s_H = 0\) \[7\]

Similarly, the QSS condition for the terminal species \((\text{H}_2\text{O}^+, \text{H}_2\text{O},\text{e}^-)\) for the HOR in alkaline electrolyte (Eq. 1) are

\[
\begin{align*}
Q_H: & (-1)r_{OH} + (-1)r_T + (-1)s_H = 0 \\
Q_{H2O}: & (+2)r_{OR} + (+1)r_V + (+1)s_H = 0 \\
Q_e: & (+2)r_{OR} + (+1)r_V + (+1)s_H = 0 \\
Q_{OR}: & (-2)r_{OR} + (-1)r_V + (-1)s_H = 0
\end{align*}
\]

The QSS condition for \(\text{OH}^+, \text{e}^-, \text{and H}_2\text{O}\) is the same and is represented by the TN\(_i\) (represented twice) in the RR Graph, namely

TN\(_1\): \(2\text{OR} - s_V - s_H = 0\) \[9\]

Thus, the resulting RR graph satisfies all of the conditions imposed on the RR graph, \(\text{i.e., all nodes are balanced in that they satisfy the QSS conditions of one or more surface intermediates (in case of INs) and of one or more terminal species (in case of TNs). Further, all the RRs can be traced as walks or paths on the RR graph. The network includes the commonly considered Volmer–Heyrovsky and Volmer–Tafel pathways, along with the not so common Heyrovsky–Tafel pathway.\cite{3} Thus, this is an appropriate RR graph for the hydrogen electrode reaction.

Finally, a curious observation by Gennero de Chialvo and Chialvo\cite{12,36} that two distinct sets of alternate parameters provide identical HOR/HER kinetics can be explained simply from the topology of the RR graph. Thus, it is clear from the symmetry of the RR graph in Fig. 1b that the Volmer and the Heyrovsky steps can be interchanged without affecting the properties of the circuit. As a result, interchanging the kinetic parameters of the Volmer and the Heyrovsky steps does not alter the current density vs overpotential predictions, as found by Gennero de Chialvo and Chialvo,\cite{12,36} even though it changes the dependence of surface coverage on \(\eta\) from \(\theta_H(s)\eta) \text{ to } 1 - \theta_H(s)\eta)\).

We will use the RR graph in Fig. 1b below for deriving a QSS rate law based on its electrical analog, which would include the flux along all the three pathways (FRs), so that one need not select a pathway individually for kinetic analysis, as is the usual practice. Earlier, we had used this RR graph for a numerical QSS kinetic analysis.\cite{3}

**Step kinetics.**— The net rate of a generic elementary step, \(r_p\) \(= \dot{r}_p - \dot{r}_p^o\) may be written as
Table II. Reaction rate constants for HER on Pt in 0.5M NaOH at 296 K.  

<table>
<thead>
<tr>
<th>Reaction step, (s_p)</th>
<th>(\tilde{\kappa}_{p,0}) (mol cm(^{-2}) s(^{-1}))</th>
<th>(\tilde{\kappa}_{p,\Phi_0}) (mol cm(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_y: H_2 + 2S = 2H-S)</td>
<td>(\tilde{\kappa}_T = 8.8 \times 10^{-10})</td>
<td>(\tilde{\kappa}_T = 8.8 \times 10^{-8})</td>
</tr>
<tr>
<td>(x_y: H_2 + S + OH^- \rightleftharpoons H_2O + S + e^-)</td>
<td>(\tilde{\kappa}_V = 4.4 \times 10^{-7})</td>
<td>(\tilde{\kappa}_V = 4.4 \times 10^{-8})</td>
</tr>
<tr>
<td>(x_y: H_2 + S + OH^- \rightleftharpoons H_2O + H-S + e^-)</td>
<td>(\tilde{\kappa}_H = 2.4 \times 10^{-10})</td>
<td>(\tilde{\kappa}_H = 2.4 \times 10^{-9})</td>
</tr>
</tbody>
</table>

This clearly shows the nature of the pre-exponential factor, \(\tilde{\lambda}_p\), as \(\kappa (k_B T/h) \exp (\Delta G_{p,\Phi_0}^\ddagger /RT)\), the activation energy that explains the temperature dependence in the usual Arrhenius form with the activation energy being related to the enthalpy of activation in the absence of potential, \(E_{F,\Phi_0 = 0} = \Delta H_{p,\Phi_0}^\ddagger\), and the potential dependence via the usual Butler–Volmer form. Clearly, both temperature and potential have a substantial effect on the rate constant of an electrochemical step. However, for the nonelectrochemical steps, e.g., the Tafel step, the potential dependence is clearly zero, and the rate constant simplifies to the Arrhenius expression, \(\tilde{\kappa}_T = \tilde{\lambda}_T \exp (-E_{F,\Phi_0 = 0}/RT)\). It should further be apparent that the pre-exponential factor is the same for both chemical and nonelectrochemical steps. Further, any conclusions about the RDS, and the importance of different pathways, etc., are temperature- and potential-dependent.

Thus, the net rates, \(\tilde{r}_T = \tilde{r}_T - \tilde{r}_p\), of the three elementary steps in the HOR/HER mechanism may be written as

\[
\begin{align*}
\tilde{r}_T &= \tilde{\omega}_T (1 - \theta_H) - \tilde{\omega}_H \theta_H S \\
\tilde{r}_V &= \tilde{\omega}_V (1 - \theta_H) - \tilde{\omega}_V (1 - \theta_H) \\
\tilde{r}_H &= \tilde{\omega}_H (1 - \theta_H) - \tilde{\omega}_H \theta_H S
\end{align*}
\]

where the site balance, namely, \(\theta_H + \theta_H S = 1\), has been incorporated.

The step weights in the above may be written as

\[
\begin{align*}
\tilde{\omega}_T &= \tilde{\kappa}_T \Theta_1 \\
\tilde{\omega}_V &= \tilde{\omega}_V \exp (\tilde{E}_{V,0}^\ddagger /RT) \\
\tilde{\omega}_H &= \tilde{\omega}_H \exp (\tilde{E}_{H,0}^\ddagger /RT)
\end{align*}
\]

where the dimensionless electrode overpotential, \(\psi = (1/2) \times (F\eta/RT)\). Further, for the alkaline electrolytes, the parameters above, in terms of the rate constants at equilibrium electrode potential and the activities of the terminal species, are

\[
\begin{align*}
\tilde{\omega}_V &= \tilde{\kappa}_V, \tilde{\omega}_H = \tilde{\kappa}_H, \\
\tilde{\omega}_H S &= \tilde{\kappa}_V, \tilde{\omega}_V S = \tilde{\kappa}_H
\end{align*}
\]

Furthermore, in these expressions, the activity of water is usually assumed to be unity, i.e., \(\alpha_{H2O} = 1\), for saturated conditions, whereas the activity of hydrogen is written as its partial pressure, i.e., \(\alpha_{H2} = p_{H2}\) in atm.

Unfortunately, the rate constants for electrocatalytic elementary reactions are not yet available from first-principles predictions, although important progress is being made in this direction.9,11,13,16 Therefore, for our analysis, we adopt rate constants obtained in the literature by fitting experimental rate data. Thus, the set of rate constants used here for the Pt catalyst in 0.5 M NaOH solution at 296 K is provided in Table II.36,45

The kinetic analysis given below is,
sary, of course, because Kirchhoff’s laws apply for nonlinear elements, e.g., diodes as well as intuitively appealing. It results from the following definitions for the net rate of a reaction step \( s_p \) and its affinity \( A_p \):

\[
    r_p = \bar{r}_p - \bar{r}_p \quad A_p = \frac{\bar{r}_p}{RT} = \ln \frac{\bar{r}_p}{\bar{r}_p} \quad (p = 1, 2, \ldots, p)
\]

The step resistance, \( R_p \), is defined as the mean value of the \( 1/r_p \) between its limiting values, i.e., \( \bar{r}_p \) and \( r_p \):

\[
    R_p = \frac{1}{\bar{r}_p - r_p} \int_{\bar{r}_p}^{r_p} \frac{1}{r_p} dr_p = \frac{\bar{r}_p}{r_p} = \frac{A_p}{r_p} \quad (p = 1, 2, \ldots, p)
\]

which, thus provides a linear relation between \( A_p \) and \( r_p \), in the form of ohm’s law. This, however, does not represent a linearization of kinetics but may be construed as simply the definition of step resistance, which clearly is not a constant but rather changes with reaction conditions, especially temperature and potential. Thus, using its definition \( R_p = \ln \frac{(\bar{r}_p)}{(r_p)} \), the step resistance may be calculated from step kinetics. The resistance remains unchanged whether a step is written for HOR or HER, i.e., whether the reaction is proceeding in the forward or reverse direction.

**Kinetic Analysis via Kirchhoff’s Network Laws**

*The electrical analogy.*— Any quantitative network involving flow (e.g., reaction network or a piping network) must be consistent with two basic laws (Kirchhoff’s laws) of networks, i.e., (i) consistency with conservation principle (e.g., of mass) at the nodes along with (ii) the thermodynamic constraint, i.e., path independence of thermodynamic potentials, e.g., pressure drop in a piping system. As another example, Gibbs free energy, or enthalpy or entropy change over the network elements of a process graph must add up to that of the overall process, and it must be zero for a cycle. Thus, the corresponding laws in electrical networks are Kirchhoff’s current law (Kirchhoff’s flux law) in the electrical circuit analysis, it is conceptually useful, although it is not essential, to draw an analogy of the RR graphs to electrical networks. In fact, an RR graph can be directly converted into an equivalent electric circuit,3,23,24,26,27 thus facilitating its analysis by allowing use of the vast array of techniques available for electric circuit analysis.46 Thus, each branch in the RR graph may be replaced by its equivalent impedance, or “resistance” \( R_p \), for the steady-state analysis, whereas the branch representing the OR is replaced by a “voltage” source, \( A_{\text{OR}} \), i.e., the affinity (or \( -\Delta G_{\text{OR}} \), the Gibbs free energy change) of the OR. On the other hand, the branch voltage in electrical networks is equivalent to \( A_p \) (\( A_p = -\Delta G_p \)) i.e., the reaction step affinity,23,24,26 Figure 2, thus, represents the electrical analog for the HER/HOR mechanism, obtained directly from the RR graph in Fig. 1b. In doing this, the elementary steps are viewed as resistances, whereas the OR is viewed as a power source.3

Finally, to complete the electrical analogy, the step kinetics may also be cast in the form of Ohm’s law.23,24,26 This step is not necessary, independent of the HOR/HER conducted in alkaline or acid electrolyte and how the rate constants might have been obtained.

![Figure 2](image)

**Figure 2.** (Color online) The equivalent electrical circuit for the three-step HER mechanism.
The other root of the quadratic equation does not provide a value between 0 and 1. This may be used to obtain the surface coverage of adsorbed hydrogen for a given set of kinetic parameters, using which the step rates as well as step affinities and step resistances may be calculated.

The OR rate can next be calculated from the application of KFL at the TN, namely

\[ \text{TN}_i: (−2)\theta_{\text{OR}} + (+1)\theta_{\text{V}} + (+1)\theta_{\text{H}} = 0 \]  

Thus, although an explicit OR rate expression that contains all the three mechanistic steps cannot be obtained, numerical calculations of the OR rate can be readily performed for a variety of conditions, as shown in Fig. 3. Such QSS analysis is performed for the HOR/HER by many authors, for instance, by Gennero de Chialvo and Chialvo, although we interpret this as KFL applicable to the RR graph. Consequently, the results are similar.

One can similarly compute the QSS (KFL) rate for each of the individual limiting cases of the two-step mechanisms, namely, the Volmer–Heyrovsky, Volmer–Tafel, and Heyrovsky–Tafel mechanisms. Of course, the QSS (KFL) condition changes for each such limiting case, as does the dependence of \( \theta_{\text{HS}} \) on overpotential. Figure 3, thus, also provides QSS rates obtained numerically for each of the three two-step mechanisms. Figure 3 shows that the Heyrovsky–Tafel mechanism is not a significant contributor over any part of the range of overpotentials considered here for the alkaline system. In fact, even the Volmer–Heyrovsky and Volmer–Tafel mechanisms are individually applicable only in limited potential ranges.

A specific advantage of the RR graph approach, however, is that once the step rates, affinities, and resistances are hence obtained via KFL, a robust identification of the dominant reaction pathways may be accomplished based on a comparison of the flux (current) along different branches in the RR graph or via a comparison of pathway resistance. Moreover, comparison of resistance enables us to bottleneck the rate-limiting steps (RLS) without making any ad hoc assumptions, which in a sequence is defined as step(s) that contribute most significantly to the overall resistance of the sequence. In general, there can be more than a single RLS, the latter being distinct from the RDS. We previously presented such an analysis for the HER on Ni in alkaline electrolyte.29

However, the KFL/QSS approach discussed above is entirely numerical. We show next that, in fact, following the electrical analog of Ohm’s law description of kinetics, an approximate, albeit accurate, explicit rate law for the general case involving all three steps can be obtained, as well as explicit rate expressions for limiting two-step mechanisms.

**Ohm’s Law Kinetics**

The overall resistance of a reaction network may be calculated in terms of branch resistances using standard electrical circuit methods.30 For the HOR/HER, the overall rate may be written as

\[ 2\theta_{\text{OR}} = \frac{A_{\text{OR}}}{R_{\text{OR}}} \]  

where, for the circuit shown in Fig. 2, the overall resistance \( R_{\text{OR}} \) can be obtained by employing, e.g., a \( Δ − Y \) conversion utilized in electrical circuits.5,30 The rate \( \theta_{\text{OR}} \) on the left side of Eq. 28 has been doubled because the network involves the OR twice (Fig. 2). The overall network resistance for HOR/HER may be shown to be equal to

\[ \theta_{\text{HS}} = \frac{1}{4\left(\hat{\omega}_{\text{T}} - \hat{\omega}_{\text{v}}\right)}\left(\left[4\hat{\omega}_{\text{T}} + (\hat{\omega}_{\text{v}} + \hat{\omega}_{\text{H}}) + (\hat{\omega}_{\text{H}} + \hat{\omega}_{\text{H}})\right] + \sqrt{\left[4\hat{\omega}_{\text{T}} + (\hat{\omega}_{\text{v}} + \hat{\omega}_{\text{H}}) + (\hat{\omega}_{\text{H}} + \hat{\omega}_{\text{H}})\right]^2 + 8(\hat{\omega}_{\text{T}} - \hat{\omega}_{\text{v}})(2\hat{\omega}_{\text{T}} + \hat{\omega}_{\text{v}} + \hat{\omega}_{\text{H}})}\right) \]  

We have shown earlier that such a representation of the reaction rate is entirely consistent with the numerical results obtained from the conventional KFL/QSS analysis discussed in the last section. Unfortunately, the step resistances in Eq. 29 as defined above by Eq. 19 involve step kinetics including the activity of the intermediate species \( \theta_{\text{HS}} \), which is, of course, not known a priori, the determination of which is, in fact, the key goal of kinetic analysis. We have, thus, recently proposed an alternate Ohm’s law representation of Eq. 28 of the form

\[ 2\theta_{\text{OR}} = \frac{E_{\text{OR}}}{R_{\text{OR}}} \]  

in which the network resistance \( R_{\text{OR}} \), of a form similar to Eq. 29 as described below, can, in fact, be determined a priori. Here, the thermodynamic driving force is defined as

\[ E_{\text{OR}} = 1 - \zeta_{\text{OR}} \]  

whereas the reversibility of the OR

\[ \zeta_{\text{OR}} = \tilde{r}_{\text{OR}}/\tilde{r}_{\text{OR}} = \exp(-A_{\text{OR}}) = \frac{1}{K_{\text{OR}}} \prod_{i=1}^{n} a_{i}^{r_{i}} \]  

Furthermore, because this is a thermodynamic property using KPL, Eq. 20 for the \( A_{\text{OR}} \), along with Eq. 18 for step affinities and the definition of step reversibility, \( \zeta_{i} = \tilde{r}_{i}/\tilde{r}_{i} = \exp(-A_{i}) \), we have

\[ \text{Figure 3. (Color online) Semilog plot of overpotential, } \eta \text{ vs absolute value of kinetic current, } i. \text{ Solid lines represent data obtained from solving QSS equation for the three-step Tafel–Volmer–Heyrovsky mechanism and each of the two-step mechanism, namely, Volmer–Heyrovsky, Volmer–Tafel, and Heyrovsky–Tafel mechanism, while symbols represent calculations from ohm’s law. (○) Three-step mechanism Eq. 52. (▲) two-step Volmer–Heyrovsky mechanism Eq. 59. (▲) two-step Volmer–Tafel mechanism Eq. 62.} \]
As mentioned above, $R'_n$ in the above relations is the total network resistance, which may be written in terms of step resistance in the same form as Eq. 29, that is

$$R'_n = \frac{R'_p R'_n + R'_n (R'_s + 4 R'_n)}{2 (R'_p + R'_s + R'_n)}$$

where $R'_p$ is defined as the resistance of the step $s_p$ when it is considered as the RDS, with all other steps at QE, i.e., $R'_p = R'_p (1 - z_{OR})$, when the entire affinity drop of the OR occurs across the RDS step, that of the QE steps approaches zero. Thus

$$R'_p = \frac{1}{r_p}$$

The bullet in the superscript denotes the step as the RDS. Thus, $r'_s (F'_s)$ is the rate (current) of the branch (resistor) $s_p (R_p)$ if all other resistors in the circuit were short-circuited, i.e., if the entire motive force $E_{OR} (\Delta_{OR})$ occurred across a chosen step (resistor) $s_p (R_p)$, which, of course, would be the maximum step rate (current) in the step (resistor) for the given motive force.

By the same token, because the driving force (i.e., affinity, $A_s$) drop across the remaining steps is virtually zero, they may be considered to be at QE. The RDS and QE hypothesis (also called pseudoidealization hypothesis) go hand in hand. It is thus, possible to explicitly determine $R'_s$ a priori following the LHWH algorithm.

Equation 38, hence, provides an explicit rate expression for the QSS rate. We have shown before that this alternate form of Ohlm’s law kinetics provides exact results for the linear kinetics mechanisms (i.e., step kinetics linear in intermediates), whereas it provides an approximate, albeit, accurate results in other cases (i.e., when step kinetics are nonlinear in intermediates). Furthermore, Eq. 38 is in a form that is readily amenable to comprehension as well as pruning via comparison of resistances. We next show how to obtain the $R'_s$ employing the LHWH approach along with the notion of IRRs.

\textit{LHWH methodology for reaction resistance, $R'_s$}—Recall that an IRR, $\Sigma_{IRR} I_{IRR} = I_{IRR}$, is an RR in which all intermediate species, except the given species $I_k$ (along with a reference intermediate, say surface site, $S$), are eliminated, resulting in the $I_{IRR} \gamma_S I_k + (\gamma_S) S + \sum_{i=1}^{n-1} (\gamma_{I_i}) T_i = 0$. From KPL, the affinity of the $I_{IRR}$, thus, is

$$\sum_{I_{IRR}} \sigma_{I_{IRR}} A_{I_{IRR}}$$

Using the definition of step reversibility, as before, the IR reversibility

$$z_{I_{IRR}} = \prod_i (z_i)^{n_i} = \prod_i \left( \frac{r_i}{r_{i0}} \right)^{n_i}$$

Using this in the step kinetics in terms of step weights and noting that all intermediates but $I_k$ and the vacant surface site $S$ are eliminated by the stoichiometric numbers chosen to produce the IR

$$z_{I_{IRR}} = \left( \frac{\theta_{I_k}}{\theta_{I_k}} \right)^{\gamma_S} \prod_{I_{IRR}} \left( \frac{\omega_{I_{IRR}}}{\omega_{I_{IRR}}} \right)^{n_{I_{IRR}}}$$

Further, if we select all the steps $s_j$ in IRR, $\Sigma_{IRR} I_{IRR} = I_{IRR}$, such that it does not include the step $s_j$ under consideration as RDS or all the selected steps are among the QE steps, $z_{I_{IRR}} = 1$, we have

$$\theta'_{s_j} \left[ \prod_{I_{IRR}} \left( \frac{\omega_{I_{IRR}}}{\omega_{I_{IRR}}} \right)^{n_{I_{IRR}}} \right]^{1/\gamma_S}$$

We use the notation $\theta'_{s_j}$ to represent site fraction of $I_k$ when $s_j$ is considered as the RDS. Finally, the site fractions thus calculated are used in the site balance, $1 = \sum_{s_j} \theta'_{s_j}$ written in the form
For the kinetic data provided in Table II, this relation provides an exchange current density of $10^{-4}$ \( \text{A cm}^{-2} \) on Pt for alkaline M NaOH at $T = 296$ K. This value compares well with that predicted using the correlation provided by Gennero de Chialvo and Chialvo based on an extension of the Temkin development for a single RR. Many others have also suggested $i_0$ to be $10^{-4}$ \( \text{A cm}^{-2} \) on Pt for alkaline electrolytes.

The last two expressions can be further combined to alternately express the current density in terms of exchange current density.
Although the above expressions are approximate, they are highly accurate as shown in comparison with the QSS numerical results over the entire range of potentials of interest for both HOR and HER, as shown in Fig. 3. Moreover, they quite nicely explain the asymmetry between the kinetics in the HER region vs that in the HOR region (Fig. 3).

**Limiting Cases of Dual-Step Kinetics**

When one of the two-step mechanisms (Volmer–Heyrovsky or Volmer–Tafel) is dominant, the third step may be removed from the RR graph and the corresponding simplified $R'_{OR}$ computed for the hence reduced circuit (Fig. 5). The Heyrovsky–Tafel mechanism is not considered here further based on the QSS results in Fig. 3. Thus, the overall resistances of the two-step pathways involved in HER/HOR are

$$R'_{VH} = \left( R'_V + R'_H \right) / 2 \quad \text{[57]}$$

which may be used for $R'_{OR}$ in Eq. 38-40, i.e., in $r_{OR} = E_{OR}/(2R'_{OR}) = E_{OR}/(2R'_{FR})$.

**Volmer–Heyrovsky mechanism.**—For the Volmer–Heyrovsky mechanism, using the expressions for the Volmer and Heyrovsky resistances in Eq. 57 and rearranging

$$i_{VH} = \frac{4i_{OR,e}r_{OR}(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})(e^\psi - e^{-2\psi})}{(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0}) + (\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})} \quad \text{[58]}$$

This rate expression can, in fact, be derived via the KFL/QSS analysis as well, which provides an explicit solution in this case because the kinetics for both the Volmer and Heyrovsky steps are linear in the unknown surface intermediate concentration.

This is plotted in Fig. 3 for the HER/HOR in an alkaline system and is compared to the QSS result as well as the complete kinetic expression provided above. The expression is clearly adequate in the overpotential range of $-0.3 \text{ V} < \eta < -0.24 \text{ V}$ for HER and $0.13 \text{ V} < \eta < 0.3 \text{ V}$ for HOR in the alkaline system. Further, the asymmetry between the kinetics in the HER region vs that in the HOR region is a result of the coefficient of the tanh term in the denominator. For small $\psi$, this would be small, and the result would be a simple symmetric behavior as described by a Butler–Volmer kinetic expression.

**Volmer–Tafel Mechanism.**—For the Volmer–Tafel mechanism, using the expressions for the Volmer and Tafel resistances, along with $\omega_{V,0}\rho_{H,0} = \omega_{V,0}\rho_{V,0}$, and Eq. 57 in Eq. 39 and rearranging provides the exchange current density

$$i_{VT,0} = \frac{|v_{OR,e}|r_{OR}(\omega_{V,0}^2)}{(\omega_{V,0} + \tilde{\omega}_{V,0})^2} \left[ 1 + \frac{4\omega_{V,0}r_{OR}}{(\omega_{V,0} + \tilde{\omega}_{V,0})^2} \right] \quad \text{[62]}$$

which may be combined with Eq. 40 to provide

$$\text{[56]}
\left[ \frac{\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0}}{\tilde{\omega}_{V,0} + \tilde{\omega}_{V,0}} \left[ 1 + \frac{4\omega_{V,0}r_{OR}}{(\omega_{V,0} + \tilde{\omega}_{V,0})^2} \right] \right] \left[ \frac{\omega_{V,0}^2}{\omega_{V,0} + \tilde{\omega}_{V,0}} \right] \left[ 1 + \frac{4\omega_{V,0}r_{OR}}{(\omega_{V,0} + \tilde{\omega}_{V,0})^2} \right]
$$

$$\text{[57]}
\left[ \frac{R'_V + R'_H}{2} \right] \left[ \frac{2R'_V + R'_H}{2} \right]
$$

$$\text{[58]}
\frac{4i_{OR,e}r_{OR}(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})(e^\psi - e^{-2\psi})}{(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0}) + (\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})}
$$

$$\text{[59]}
\frac{4i_{OR,e}r_{OR}(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})(e^\psi - e^{-2\psi})}{(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0}) + (\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})}
$$

$$\text{[60]}
\frac{|v_{OR,e}|r_{OR}(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})}{(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0}) + (\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})} \left[ 1 + \frac{4\omega_{V,0}r_{OR}}{(\omega_{V,0} + \tilde{\omega}_{V,0})^2} \right] \left[ \frac{\omega_{V,0}^2}{\omega_{V,0} + \tilde{\omega}_{V,0}} \right]
$$

$$\text{[61]}
\frac{|v_{OR,e}|r_{OR}(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})}{(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0}) + (\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})} \left[ 1 + \frac{4\omega_{V,0}r_{OR}}{(\omega_{V,0} + \tilde{\omega}_{V,0})^2} \right] \left[ \frac{\omega_{V,0}^2}{\omega_{V,0} + \tilde{\omega}_{V,0}} \right]
$$

$$\text{[62]}
\frac{|v_{OR,e}|r_{OR}(\tilde{\omega}_{V,0} + \tilde{\omega}_{H,0})}{(\tilde{\omega}_{V,0} + \tilde{\omega}_{V,0})^2} \left[ 1 + \frac{4\omega_{V,0}r_{OR}}{(\omega_{V,0} + \tilde{\omega}_{V,0})^2} \right] \left[ \frac{\omega_{V,0}^2}{\omega_{V,0} + \tilde{\omega}_{V,0}} \right]
$$
which can alternately be written in terms of hyperbolic functions as above

\[
i_{VT} = \frac{4i_{VT,0} \left[1 + \frac{4\dot{\omega}_V - \dot{\bar{\omega}}}{\omega_V(\dot{\omega}_V + \dot{\bar{\omega}})}\right]}{\cosh \psi \left[1 + \frac{2 - 4\dot{\omega}_V - \dot{\bar{\omega}}}{\omega_V(\dot{\omega}_V + \dot{\bar{\omega}})}\right] + \frac{4\dot{\omega}_V \dot{\omega}_V}{\omega_V(\dot{\omega}_V + \dot{\bar{\omega}})}}\sinh \psi
\]

which may be used in Eq. 15 for calculating the OR rate via the.

According to Fig. 3 based on this explicit rate expression, there is a great asymmetry in the Volmer–Tafel mechanism, described by the form of the denominator in the above expression. This mechanism is important for HER in an alkaline system in the overpotential range of ~0.1 V < P < 0 V. For HER in an alkaline system, the Volmer–Tafel mechanism is only applicable in a narrow overpotential range of 0 < P < 20 mV.

Note that this is the first such explicit expression for the Volmer–Tafel mechanism, as the corresponding QSS analysis cannot be written explicitly in such a form due to the nonlinearity of the kinetics. Thus, the QSS site coverage for the Volmer–Tafel kinetics is

\[
\theta_{HS} = \frac{1}{4(\dot{\omega}_T - \dot{\bar{\omega}})} \left[\frac{4\dot{\omega}_T + \dot{\bar{\omega}}}{\dot{\omega}_T + \dot{\bar{\omega}}}\right] - \frac{1}{2} \left[\frac{4\dot{\omega}_T + \dot{\bar{\omega}}}{\dot{\omega}_T + \dot{\bar{\omega}}}\right]^2 - \frac{8(\dot{\omega}_T - \dot{\bar{\omega}})(2\dot{\omega}_T + \dot{\bar{\omega}})}{\dot{\omega}_T + \dot{\bar{\omega}}}
\]

which may be used in Eq. 15 for calculating the OR rate via the KFL/QSS approach.

**Conclusions**

The RR graph approach has been applied here to the hydrogen electrode reaction to obtain explicit rate expressions involving all three steps (Volmer–Heyrovsky–Tafel) as well as for more limiting two-step (Volmer–Heyrovsky and Volmer–Tafel) mechanisms. These expressions agree completely with the QSS analysis and nicely explain the asymmetry in current vs potential observed in the HER vs the HOR. Our topological approach is revealing and intuitive in depicting all possible reaction pathways as walks or paths on the RR graph and by visualizing the steps as resistances in an electrical circuit analog involving series and parallel pathways. Thus, the RR graph approach can be effectively used to identify the dominant reaction pathways. The approach further provides a link between the more rigorous but complex QSS kinetics and the LHHW analysis, which is simpler but arbitrary in its assumptions.

Thus, for the three-step hydrogen electrolyte reaction mechanism on Pt in 0.5 M NaOH at T = 296 K, we find that the Volmer–Heyrovsky pathway is dominant in the potential region ~0.3 V < P < ~0.24 V for HER and in the range 0.13 ~ P < 0.3 V for HOR, whereas the Volmer–Tafel mechanism dominates in the potential region ~0.1 V < P < 0 V for HER and in 0 < P < 20 mV for HOR. All three steps, however, need to be retained over the complete range of potentials of interest.

The above implications regarding the significance of the mechanism and kinetics of the HER reaction are limited to the three-step mechanism considered. Moreover, the conclusions are limited to a constant temperature of 298 K and liquid water (unit activity), corresponding to the given rate constants. However, the described approach is more general and can also be adapted to investigate additional steps in the mechanism when their kinetics as a function of temperature and potential become available. Further, of course, the hydrogen electrode reaction in an acid electrolyte is also of great interest in connection with fuel cells and can also be analyzed via this approach.

Worcester Polytechnic Institute assisted in meeting the publication costs of this article.

**List of Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units or Dimension</th>
</tr>
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<tbody>
<tr>
<td>A_i</td>
<td>affinity of elementary reaction ( \rho )</td>
<td></td>
</tr>
<tr>
<td>A_k</td>
<td>dimensionless reaction affinity of elementary reaction ( \rho )</td>
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</tr>
<tr>
<td>E_k</td>
<td>activation energy for step ( s_i )</td>
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</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
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<tr>
<td>\Delta G_k</td>
<td>Gibbs free energy change of the elementary reaction</td>
<td>\rho</td>
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<tr>
<td>\Delta G^\circ_k</td>
<td>Gibbs free energy of activation</td>
<td>\rho</td>
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<tr>
<td>\hbar</td>
<td>Planck’s constant</td>
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<tr>
<td>\Delta H^\circ_k</td>
<td>enthalpy of activation</td>
<td>\rho</td>
</tr>
<tr>
<td>I'_m</td>
<td>maximum branch current</td>
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<tr>
<td>k_d</td>
<td>adsorbed intermediate species ( k )</td>
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<tr>
<td>k_i</td>
<td>rate constant of the elementary reaction ( \rho )</td>
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<td>k_d</td>
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<td>K_k</td>
<td>equilibrium constant of the elementary reaction</td>
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<tr>
<td>m_s</td>
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<td>n</td>
<td>number of terminal species</td>
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<tr>
<td>n</td>
<td>number of elementary reactions</td>
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<td>q</td>
<td>number of linearly independent intermediate species</td>
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<td>r'_m</td>
<td>maximum rate of the elementary reaction ( \rho )</td>
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<td>R</td>
<td>gas constant</td>
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<td>R'_k</td>
<td>resistance of elementary reaction ( s_i ) when ( s_i ) is the RDS</td>
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<tr>
<td>s_i</td>
<td>elementary reaction ( \rho )</td>
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<tr>
<td>s_p</td>
<td>entropy of activation</td>
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<tr>
<td>\theta</td>
<td>reaction affinity of elementary reaction ( \rho )</td>
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<tr>
<td>T</td>
<td>temperature, K</td>
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<tr>
<td>T_i</td>
<td>terminal species ( i )</td>
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<tr>
<td>\psi</td>
<td>reversibility of reaction ( \rho )</td>
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**Greek**

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<td>\eta_e</td>
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<td>\sigma_k</td>
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<td>stoichiometric number for the elementary reaction ( \rho )</td>
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<tr>
<td>\Phi_s</td>
<td>standard electrode potentials</td>
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<td>dimensionless electrode overpotential, 0.5F\eta/RT</td>
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<tr>
<td>\omega</td>
<td>step weight for reaction ( s_i )</td>
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References