Electrochemical Kinetics	Động học của các quá trình điện hóa
1. Background	1.Những vấn đề cơ bản
Consider the reaction given below:	Xét phản ứng dưới đây:
(1)	(1)
If kf and kb are the rate constants of the forward and reverse reactions, then the rate of the forward reaction is given by:	Nếu kf và kb là hằng số tốc độ của phản ứng thuận và phản ứng nghịch, thì tốc độ của phản ứng thuận là;
(2)	(2)
And the rate of the backward reaction is given by:	Và tốc độ của phản ứng nghịch là:
(3)	(3)

The net rate of reaction is given by:
(4)

Equilibrium is defined as the point at which the net reaction rate is zero. From equation 4, this condition leads to an equilibrium concentration ratio that is constant, and is called the equilibrium constant (K)
(5)
An equation similar to equation 5 is required of any kinetic theory. In other words, every kinetic theory requires that the kinetic equations collapse to thermodynamic relations at equilibrium. (Constant concentration ratio at equilibrium in the above example). While thermodynamics provides a description of the behaviour at equilibrium and predicts whether a reaction is feasible (spontaneous), it does not provide any information about the reaction rates. This information is provided by kinetic equations. However, for a kinetic expression to be valid, reduction to thermodynamic equations at equilibrium is essential (in some ways, this requirement is similar to a boundary condition).

2.   The Arrhenius Theory
Rate constants vary with temperature (generally increase with T). The most common relationship between rate constant (k) and temperature is of the form:
(6)
where Ea is called the activation energy, and R is the gas constant. A is known as the pre exponential factor. This relationship is called the Arrhenius relationship. The activation energy is the energy barrier that has to
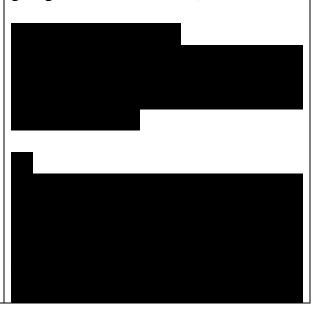
Tốc độ tổng thể (tốc độ toàn phần) của phản ứng là;
(4)
Cân bằng được định nghĩa là điểm tại đó tốc độ phản ứng tổng thể bằng không. Từ phương trình 4, điều kiện này dẫn đến tỷ lệ nồng độ cân bằng không đổi, và được gọi là hằng số cân bằng (K)
(5)
Phương trình tương tự như phương trình 5 rất quan trọng trong bất kỳ lý thuyết động học nào. Nói cách khác, mọi lý thuyết động học đều đòi hỏi rằng các phương trình động học chuyển thành các hệ thức nhiệt động học ở trạng thái cân bằng (Tỷ lệ nồng độ không đổi ở trạng thái cân bằng trong ví dụ trên). Trong khi nhiệt động lực học mô tả các tính chất ở trạng thái cân bằng và dự đoán phản ứng có xảy ra hay không (tự phát), nó không cho chúng ta thông tin về tốc độ phản ứng. Thông tin này được rút ra từ các phương trình động học. Tuy nhiên, để một biểu thức động học có giá trị, nó phải chuyển thành các phương trình động lực học ở trạng thái cân bằng (ở một khía cạnh nào đó, yêu cầu này giống như điều kiện biên).

be surmounted by the reactants before they can be converted to product - the entire exponent therefore is a probabilistic feature in the equation, and represents the probability that the energy barrier will be surmounted. The pre exponential factor represents the number of attempts made at surmounting the barrier, and hence is also called the frequency factor. A reaction path may therefore be represented in terms of energy variation along the reaction co-ordinate (extent to which reactant has progressed) as shown in Fig. 1. The difference between the peak energy and the energy of the reactants represents the activation energy for the forward reaction.
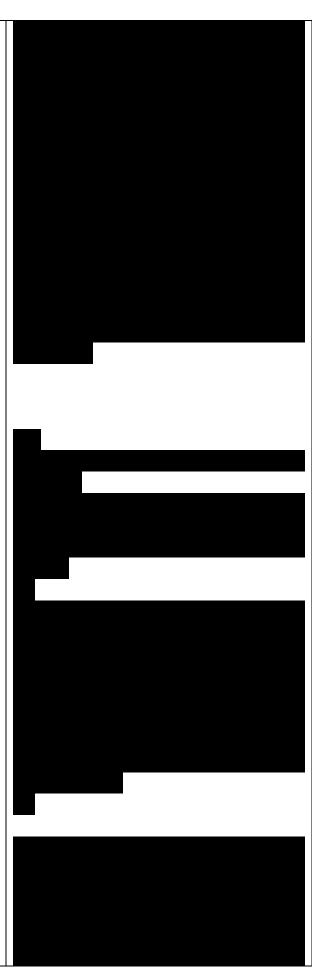
Fig. 1

3. Requirements of Kinetic Theories

Consider the general reversible electrode reaction (eqn. 7), with kf and kb as the forward and reverse reaction rate constants:

(7)

This is a typical redox reaction. For such a reaction, the equilibrium state is governed by the Nernst equation (derived in the section on thermodynamics). This equation relates the equilibrium potential of the electrode (E) to the concentration of the reactants and products as follows:

(8)

Where the terms within the parentheses represent bulk concentrations. Therefore, any electrode kinetics theory must reduce to this equation when equilibrium conditions are placed upon it. An additional requirement of

any kinetic theory is that it must provide an accurate prediction about the dependence of current on electrode potential. Typically, when a current is passed, some electrochemical change is taking place at the electrode. Since all real processes are irreversible, sustaining a given current requires that a penalty be paid in terms of electrode potential. This penalty is often called overpotential or overvoltage. The overvoltage may be defined as:

(9)

where Eeq is the expected (equilibrium) electrode potential, and E is the actual electrode potential. It has been experimentally observed that at low currents, the current is exponentially related to the overpotential. This was postulated by Tafel as follows:

(10)

Where a and b are constants. This equation is called the Tafel equation. Any successful electrode kinetic theory must also explain Tafel behaviour.

4. Kinetics of Electrode Reactions

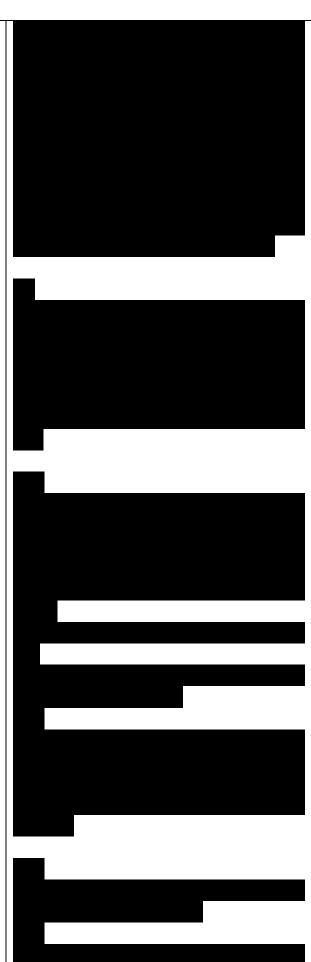For the reaction in equation 7, one can write:

(11)

The rate of the forward reaction (Rf) is proportional to the surface concentration of o and the cathodic current (since it is a reduction reaction). Similarly, for the backward reaction, one can write:

(12)

The net reaction rate (and hence the net current) is given by:

(13)

In an electrochemical reaction, both kf

and kb are potential dependent functions. Since the forward reaction (a reduction) is an electron accepting process, the rate increases as the electrode potential becomes more negative (the electrode can give away electrons more easily). The opposite trend is seen for the reverse (oxidation) reaction. This is illustrated in Fig. 2. This potential dependence needs to be qualified to obtain a true picture of electrochemical kinetics.

Fig. 2

It is possible to adjust the electrode potential and O and R concentrations to such a value that the net reaction rate is zero. At this point:

(14)

In other words:

(15)

Rearranging this equation, and taking logarithms on both sides we have:

(16)

Since equation 16 is stated under conditions of equilibrium, the equality can be extended by applying the Nernst equation (8) as follows:

(17)

Upon differentiation with respect to E (first and last terms only), this yields:
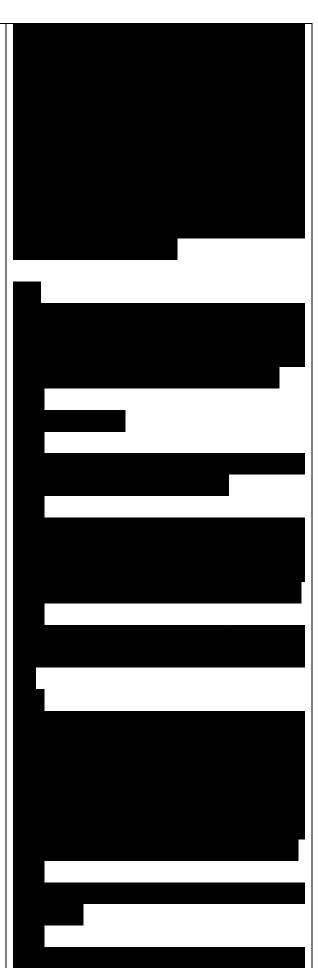
(18)

The two terms on the left hand side sum up to one, and are called symmetry factors in the case of an one electron transfer reaction. The reductive symmetry factor (associated with the forward reaction) is frequently represented by the Greek alphabet a

(19)

The oxidative symmetry factor therefore becomes 1- a.

(20)

The term a is a measure of the

symmetry of the energy barrier - if the effect of changing the potential is identical on both sides of the barrier, then a = 0.5 = 1- a. Any asymmetry results in other values of a. This is illustrated in Fig. 3

Equation 19 on integration gives:
 (21)
If kf = kf° @ E = E° (where kf° is termed the standard (or conditional) rate constant), we have:
 (22 - a)

Similarly, one can derive an expression for kb:
 (22 -b)
Now, if we consider a case where the concentrations of O and R are equal, , and the potenial is maintained at E° to prevent current flow. Then, from equation 15, kf° = kb°. Therefore, it can be replaced by a single symbol k°.
5.   The Butler - Volmer Theory
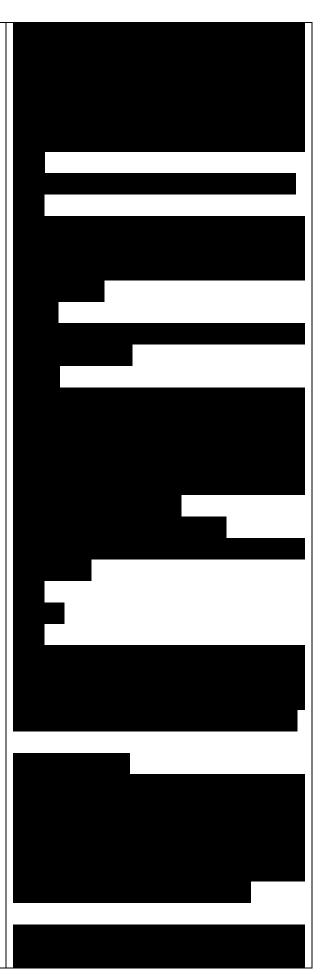Writing an expression for net reaction rate:
(23)
Thus:
 (24)

substituting the values for the rate constants from 22 in 23 (with a factor of n present in the numerator of the exponent to cover multi - electron transfer rections):

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This formulation is called the Butler - Volmer formulation of electrode kinetics. This formulation links the four important parameters - faradaic current, electrode potential, concentration of reactant and concentration of product.

Now, equation 25 can be rewritten (after some arithmetic) as:

(26)

Now for very fast reactions, $k° \sim$ infinity. Therefore, the right hand side goes to zero. The equation then becomes merely a statement of the Nernst equation - Another way of obtaining the Nernst equation is to consider equilibrium conditions (I = 0). Under these conditions, equation 25 directly yields the Nernst equation. Therefore, the B-V theory fulfils one requirement for a successful kinetic theory - i.e. it collapses to the Nernst equation at equilibrium (or if the reaction is reversible).

Furthermore, if we consider a case of very large overpotential (E-E° = H), then one or the other of the exponents on the right hand side of equation 25 goes to zero (depending on whether the overpotential is positive or negative). If the concentration is taken to be a constant, then the B-V formulation reduces to the form:
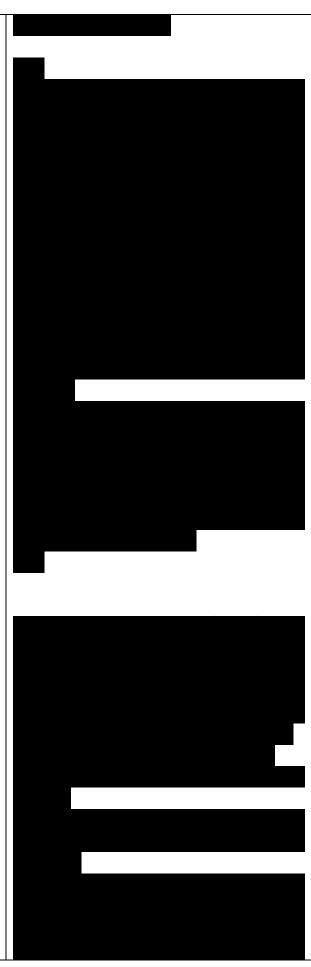
(27)

Where a and b are constants. This is nothing but the Tafel equation (details of which will be discussed later). In this manner, the B-V theory fulfils the other requirement for a successful electrode kinetic theory.

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6.   The Standard Rate Constant and the Exchange Current 10 h 30

The standard rate constant $k°$ is a very important parameter in electrode kinetics.

It is a measure of the "kinetic facility" of the redox couple - in other words, the larger the value of $k°$, the faster equilibrium will be attained. Systems

with small rate constants are typically sluggish. The standard rate constant is large for simple redox couples (such as the ones involving a single electron transfer - such as Hydrogen oxidation is a PEM fuel cell). The largest measured values of these constants are on the order of 1-10 cm/s. These values drop rapidly with increasing reaction complexity, and can be as lower as 10 9 cm/s in certain cases. The oxygen reduction reaction, being a 4 electron process, ==will have a lower value of== $k°$ than the hydrogen oxidation reaction - this is why cathode kinetics in a PEM fuel cell are very sluggish compared to anode kinetics.
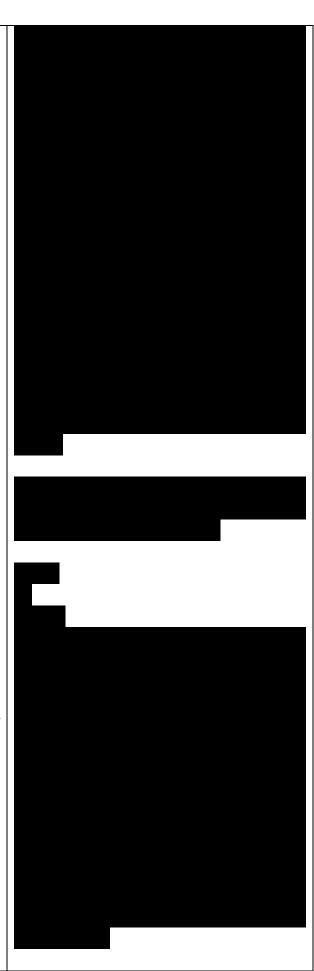
Note however, that the forward and reverse rate constants can still be large (even though the value of $k°$ is small. Recall that:

(22-a)

and

(22-b)

Thus, by suitably increasing the value of the overpotential, once can obtain large reaction rates. The reaction in this case is driven by the electrical energy supplied - i.e. the activation energy of the reaction is provided by electrical energy. In a fuel cell, this is what happens at large reaction rates. The only difference is that since the fuel cell reaction is Galvanic in nature, electrical energy is not supplied externally - what happens is that the voltage output of the cell is lower than normal due to the larger than normal overpotential.

Recall that at equilibrium, the net current is zero. Also, the surface concentrations of O and R are identical to the bulk concentrations. In this case, equation 25 becomes:
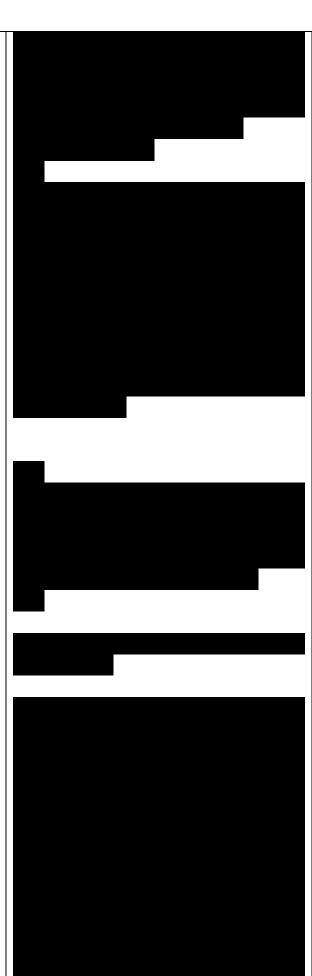
(28) which reduces to:

(29)

Where Eeq is the voltage corresponding to equilibrium. As discussed earlier, this is merely a restatement of the Nernst equation (8). Even though the net current is zero, what is envisaged is that faradaic activity is still in progress at the electrode surface, with an equal magnitude of anodic and cathodic current flowing. This current is referred to as the exchange current (Io). Thus the exchange current may be written as:

(30)

Where io is called the exchange current density. If we raise both sides of equation 29 to the power -a, we can substitute for the term e{- [anF/RT] (Eeq-E)} to yield:

(31)

In the case where $C_O^* = C_R^* = C$, we have:

In both cases, it is evident that the exchange current density is directly proportional to the standard rate constant $k°$. Indeed, the exchange current density is frequently used as an important kinetic parameter in place of $k°$, and is an important indicator for the facility of an electrochemical reaction. Ideally, one would like to have as high an exchange current density as possible for fast kinetics. The effect of exchange current and the symmetry factor (transfer coefficient) on electrode

kinetics will be seen in the next section, after discussing the current-overpotential equation.

7. The Current - Overpotential Equation:

If we divide the current density (eqn. 25) by the exchange current density (eqn.31), we have:

(33)

Now substituting for $[CO*/CO*]_a$ and $[CO*/CO*]'(1'a)$ using equation 29, we get:

(34)

where $\wedge = E - E_{eq}$. This equation is termed the current - overpotential equation, and is especially convenient because it provides a direct relationship between the current and the overpotential (which is $E - E_{eq}$). This is unlike the earlier formulation, where the relationship was between the current and the quantity $E - E°$. It is for this reason that it is preferred to work with exchange currents rather that standard rate constants while reporting and analyzing electrode kinetic data. A typical current - overpotential curve is shown in Fig.4. The lessening significance of the contribution of one or the other of the components (cathodic or anodic) as the overpotential is pushed either to large positive or large negative overpotentials is clearly illustrated.

Fig. 4

The effect of exchange current density on electrode kinetics (as obtained from the current - overpotential equation) for a constant value of a (0.5) is shown in Fig.5. The effect of the transfer coefficient (a) for a constant value of exchange current density (10 -6 A/cm2) is shown in Fig. 6.
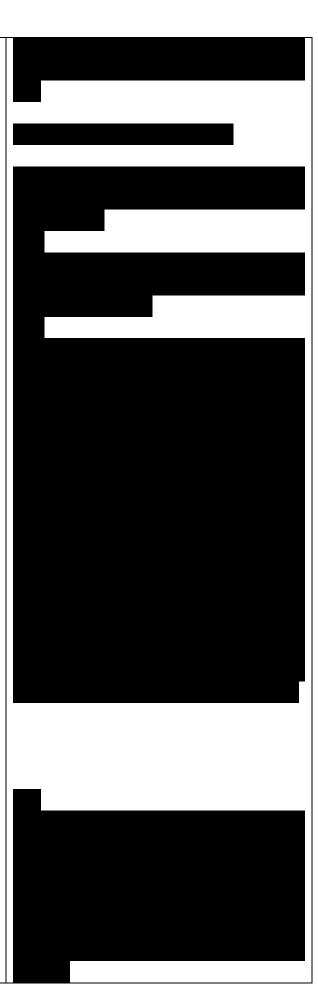
Fig. 5

Fig. 6

We can now consider limiting cases in eqn. 34. If there are no mass transport effects (i.e the solution is well stirred), then the surface and bulk concentrations are identical, and their ratio equals unity. In this case, eqn. 34 may be rewritten as:

(35)

Traditionally, this equation is known as the Butler - Volmer equation. It can be used as a good approximation to equation 34 when the current density i is smaller than 10% of the smaller of the anodic or cathodic limiting currents (recall definition of limiting current from electrochemistry notes). Evidently, the smaller the value of io, the larger will be the overpotential required to generate a given current.

At very small values of x, the exponent e^x is approximately equal to $1+x$. In this case, The B-V equation can be written in a linear form as:
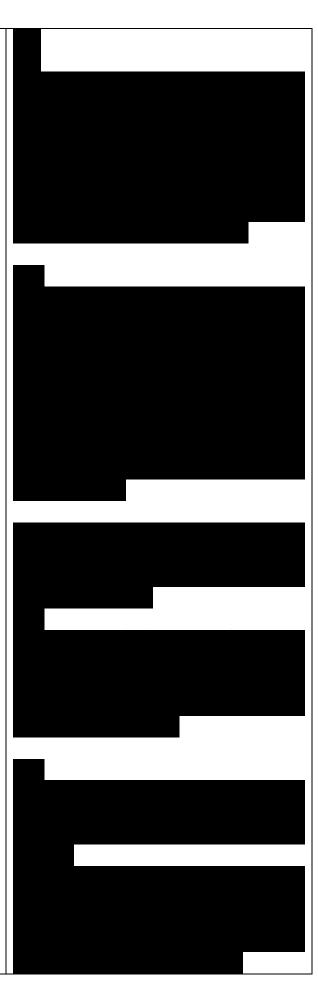
(36)

Therefore, at E very close to Eeq, the relation between current and overpotential is linear. The ratio of the two has units of resistance, and is called the charge transfer resistance (Rct).

(37)

This parameter is the negative reciprocal of the slope of the i - ^ curve (Fig. 4), and approaches 0 for very fast kinetics (large io).

At very large values of ^, one of the exponents in eqn 35 goes to 0, depending on whether the large ^ is negative or positive. For example, at large positive values of "n, we have:

(38)

which becomes:
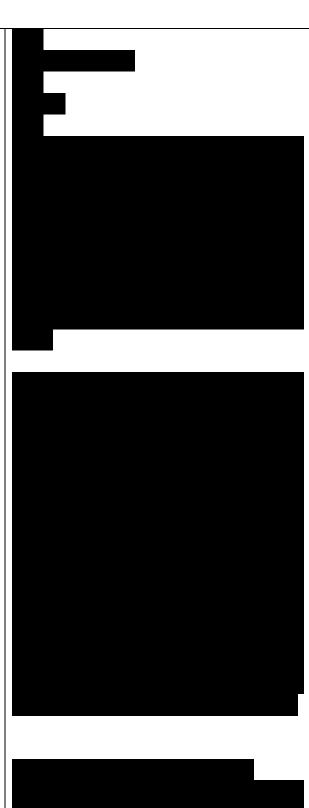
(39)

which reduces to:

(40)

This equation fits the Tafel formulation (eqn. 10), with a = - [RT/(1-a)nF] ln io and b = [RT/(1-a)nF]. Thus, systems that obey this equation are said to display Tafel behaviour. Such an approximation is only valid for a given oxidation or reduction component when the other component contributes 1% or less to the total current.

A plot of log i vs. "n is called a Tafel plot. Typically, it comprises an anodic branch and a cathodic branch, with slopes of (1- a)nF/2.3 RT and - anF/2.3 RT respectively (2.3 - conversion factor - ln to log).A Tafel plot is shown in fig. 7. It is seen that the extrapolated intercepts of both components of the plot occurs at log io. Furthermore it is seen that both components deviate sharply from linearity as "n approaches zero. This occurs because the approximation made above (insignificant contribution of one of the components) falls apart under these conditions.

Fig. 7

8. Effect of Mass Transport

The above equations (35 - 40) assumed that there were no mass transport effects complicating the system. Unfortunately, mass transport effects are often seen in electrochemical systems. In this case, the above equations will need to be modified to account for mass transport. Recall from the electrochemistry notes (eqn. 40)

that:

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Where il is the limiting current. This can be incorporated into equation 34 to yield:

(41)

This equation is the current - overpotential equation corrected for mass transfer effects. For very small overpotentials, this equation can be linearized (usig the Taylor expansion), and yields (derivation omitted):

(42)

If RT/Fio represents the resistance to charge transfer (37), the other two terms in the brackets can be thought of as representing the mass transfer resistances. Therefore, eqn. 42 can be expressed as:

(43)

From 42 and 43, we can understand that when io >> il>c and il>a, then the overpotential occurs mainly due to mass transport effects even very close to equilibrium. In this case, the kinetics of the system are very fast. On the other hand, if the reverse is true, then the kinetics of the reaction is so slow that the overpotential close to equilibrium is due to poor charge transfer.

Similarly, for very large values of r, a Tafel like expression can be obtained. For insignificant anodic overpotential, this may be written as:

(44)

This may be rearranged to give:

(45)

This expression can be used to obtain kinetic parameters in systems having mass transport effects.