1

Introduction

1.1 General Considerations

1.1.1 The Transition from Electronic to Ionic Conduction

Physical electrochemistry is a branch of physical chemistry. If one were to describe the essence of electrode kinetics in one short phrase, it would be: "*the transition from electronic to ionic conduction*." Naturally, the transfer of charge is influenced by the potential. Conduction in the solution is ionic, whereas in the electrodes and the connecting wires it is electronic. The transition from one mode of conduction to the other requires charge transfer across the interface. The rate of this transfer is controlled by the catalytic properties of the surface and the adsorption on it, the concentration and the nature of the reacting species, and all other parameters that control the rate of heterogeneous chemical reactions. In addition, the potential plays an important role. This is not surprising, since charge transfer is involved, and this process can be accelerated or retarded by the magnitude and the sign of the potential applied across the interface.

Figure 1.1 shows a typical way that the current density would respond to the potential applied, for the case of a dilute (0.01 M) solution of HI in 1.0 M H_2SO_4. The reaction concerned is

$$2\mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I_2} \tag{1.1}$$

There is a lot of information in this simple equation, combined with Figure 1.1. The reaction does not occur spontaneously in the direction shown in Eq. (1.1). Electrical energy is needed to break up molecules of HI into H_2 and I_2. Electrical energy is being converted to chemical energy.

We note that Figure 1.1 has four regions. In the first region there is no current flowing, in other words, the resistance is infinite. It is important to understand that the current flowing here is *exactly zero*, not just very close to zero and too small to be detected experimentally. This follows directly from the first law of thermodynamics, the law of conservation of energy. The minimal electrical energy required to break up the molecules of HI in the particular reaction in Eq. (1.1) is 0.59 V. Above this threshold, the current rises exponentially with potential, along line a. The rate of the reaction is controlled by the rate of charge transfer j_{ct}. Eventually, the mass-transport limitation takes over, as shown by the horizontal part of line b shown in Fig. 1.1. This is the mass-transport-limited

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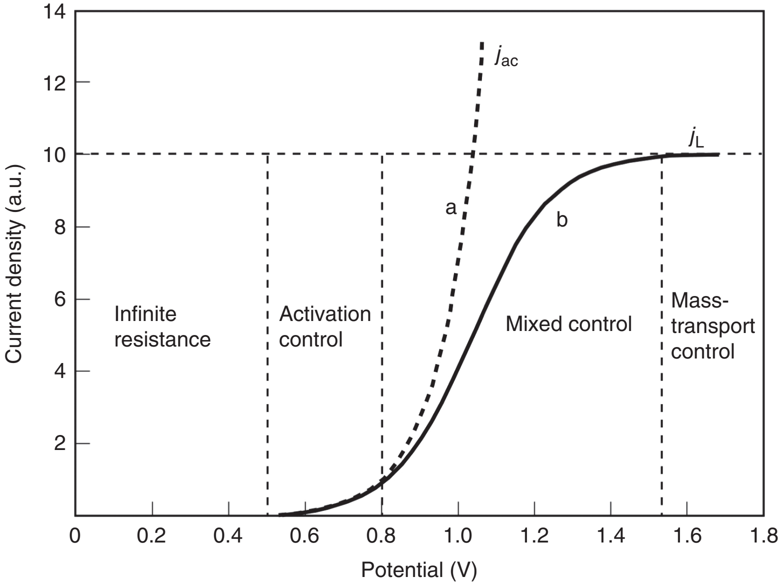

Figure 1.1 Schematic *j/E* plot for the electrolysis of a dilute (0.01 M) solution of HI in 1.0 M H_2SO_4, employing two Pt electrodes. The minimum potential for DC current flow is 0.59 V.

current density, j_L. In the third region, mixed control occurs; the current density is controlled both by activation and by mass transport.

1.1.2 The Resistance of the Interface can be Infinite

The potential is mostly measured with respect to a suitable reference electrode, and instead of the current, one refers to the current density j. Replacing the platinum electrodes with two copper electrodes and adding some $CuSO_4$ instead of HI changes the situation dramatically. Passing a current between the electrodes causes no net chemical change (copper is dissolved off the positive anode and is deposited on the negative cathode). In this case, current is observed as soon as a potential, small as it may be, is applied between the electrodes.

1.1.3 Mass-Transport Limitation

The rate of charge transfer can be greatly increased by increasing the potential, but charge can be transferred across the interface only over a very short distance (of the order of 1 nm). Another process is required to bring the reacting species close enough to the surface and to remove the species formed at the surface into the bulk of the solution. This process is called *mass transport*.

Mass transport and charge transfer are two consecutive processes. It is therefore always the slower of the two that determines the overall rate observed experimentally. When the potential applied is low, barely above its minimum value needed to pass a current, charge transfer is slow and one can ignore mass-transport limitation. The bottleneck is in transferring the charge across the interface to the electroactive species, not in getting the species to the surface. At high potentials, charge transfer becomes the faster process and ceases to influence the overall rate. Increasing the potential further will increase the rate of charge transfer, but this will have no effect on the observed current density, which will be limited by mass transport. The result is a current density that is independent of potential, which is referred to as the *limiting current density*, j_L, as seen in Figure 1.1. For the observed current density j, one can write the simple equation

$$\frac{1}{j} = \frac{1}{j_\mathrm{ac}} + \frac{1}{j_\mathrm{L}} \tag{1.2}$$

Clearly, the smaller of the two currents is dominant. In a stirred solution, a steady state is reached when the concentration inside the diffusion layer varies linearly with distance. Under such conditions we can express the current density by

$$j = \frac{nFD(c_\mathrm{b} - c_\mathrm{s})}{\delta} \tag{1.3}$$

where n is the number of electrons transferred, F is the Faraday constant ($96\,485\,\mathrm{C\,mol^{-1}}$), nF is the charge transferred per mole, D is the diffusion coefficient of the species ($\mathrm{cm^2\ s^{-1}}$), c_b is the concentration ($\mathrm{mol\,cm^{-3}}$) of the electroactive species in the bulk of the solution, c_s is its surface concentration ($\mathrm{mol\,cm^{-3}}$), and δ is the thickness of the Nernst diffusion layer (cm). Thus, the unit of current density is $\mathrm{A\,cm^{-2}}$. The current density reaches its mass-transport-limited value, j_L, when $c_\mathrm{s} = 0$, thus

$$j_\mathrm{L} = \frac{nFDc_\mathrm{b}}{\delta} \tag{1.4}$$

The corresponding equation for the activation-controlled current density is

$$j_\mathrm{ac} = nFkc_\mathrm{b} \tag{1.5}$$

where the rate constant k is a function of the potential. From a comparison of the last two equations it is seen that the ratio D/δ in Eq. (1.4) has the same role as the rate constant k in Eq. (1.5), except that it is independent of potential. This ratio may be regarded as the specific rate of diffusion. From Eq. (1.4) it is also evident that the limiting current density increases as c_b is increased, the temperature is raised (thus, D increases), or the solution stirring is enhanced (thus, δ is decreased, as explained later).

Now, the essence of mass transport is the quantity δ. In certain favorable cases it has been calculated theoretically, in others it can only be determined experimentally. Sometimes, it is a function of time, while under different circumstances it is essentially constant during an experiment. Stirring the solution and transporting it toward, past, or through the electrode, all decrease the value of δ, hence, increase j_L. Moving the electrode (e.g. by rotation or vibration) has a similar effect. In quiescent solutions, δ increases linearly with $t^{1/2}$, hence j_L can be increased by taking measurements at short time.

In typical electrochemical measurements, the thickness of the Nernst diffusion layer attains values in the range of 10^{-3}–10^{-1} cm. Since in aqueous solutions at room temperature the diffusion coefficient of ions in aqueous solutions is on the order of 10^{-5} cm^2 s^{-1}, this yields limiting current densities in the range of 0.01–1.0 mA cm^{-2} when $n = 1$ and the concentration of the electroactive species in solution is 10^{-6} mol cm^{-3}. The two most important things to notice in Eq. (1.4) are that: (i) the limiting current density is independent of the potential, and (ii) it depends linearly on the bulk concentration. A less obvious, but equally important, consequence of this equation is that j_L is independent of the kinetics of the reaction (i.e. of the nature of the surface and its catalytic activity). These characteristics make it an ideal tool for probing the concentration of species in solution. This is why most electroanalytical methods depend in one way or another on measurements of the mass-transport-limited current density.

1.1.4 The Capacitance at the Metal/Solution Interphase

When a metal is dipped in solution, a discontinuity is created. This affects both phases to some degree, so that their properties near the contact are somewhat different from their bulk properties. The exact position of the interface on the atomic scale is hard to define. “Where does the metal end?” we may ask. Is it the plane going through the centers of the outermost layer of atoms, is it one atomic radius farther out, or is it even farther out where the charge-density function of the free electrons in the metal has decayed to essentially zero? Fortunately, we do not need to know the position of this plane, for most purposes, when we discuss the properties of the interface.

One distinct property of the metal/solution interphase is a capacitance, called *the double-layer capacitance*, C_{dl}. It is a result of the charge separation between the two phases in contact. The double-layer capacitance observed depends on the structure of a very thin region near the interface, extending to about 1–10 nm, called *the double layer*. If the surface is rough, the double layer will follow its curvature down to atomic dimensions, and the capacitance measured under suitably chosen conditions is proportional to the *real* surface area of the electrode.

The double-layer capacitance is rather large, on the order of 10–30 μF cm^{-2}. This presents a serious limitation on our ability to study fast electrode reactions. Thus, a 10 μF capacitor coupled with a 10 Ω resistor yields a time constant $\tau_c = R \times C_{dl} = 0.1$ ms. It is possible to take measurements at shorter times by applying special techniques, but even so, the lower limit at present seems to be about 0.05 μs, seven orders of magnitude slower than that currently achievable in the gas phase.

The double-layer capacitance depends on the potential, the composition of the solution, the solvent, and the metal. It has been the subject of numerous investigations, some of which are discussed later (e.g. in Chapter 8).

1.2 Polarizable and Nonpolarizable Interfaces

1.2.1 Phenomenology

When a small current or potential is applied, the response is in many cases linear. The effective resistance may, however, vary over a wide range. When this resistance is high, we have a polarizable interface, meaning that a small current generates a high potential across it (i.e. the interface is polarized to a large extent).

When the effective resistance is low, the interface is said to be nonpolarizable. In this case, a significant current can be passed with only minimal change of the potential across the interface. A nonpolarizable electrode is, in effect, a reversible electrode. The reversible potential is determined by the electrochemical reactions taking place and the composition of the solution, through the Nernst equation. For example, for a copper electrode in a solution containing $CuSO_4$ it is

$$E_{\mathrm{rev}} = E^0 + \left(\frac{2.3RT}{nF}\right)\log\left(\frac{a_{\mathrm{Cu}^{2+}}}{a_{\mathrm{Cu}^0}}\right) \tag{1.6}$$

where $E^0 = +0.34\,\mathrm{V}$ is the standard potential for the $\mathrm{Cu}^{2+}/\mathrm{Cu}$ couple, on the scale of the Standard Hydrogen Electrode (SHE), and $a_{\mathrm{Cu}^{2+}}$ is the activity of the cupric ions in solution. In aqueous solutions that are not very concentrated ($c_b \leq 1.0\,\mathrm{M}$), the error introduced when replacing the activity by the concentration is rather small and often considered negligible.

A good reference electrode, which exhibits a constant and stable potential, is always a reversible electrode. The inverse is not necessarily true. Not every reversible electrode is suitable as a reference electrode. For example, the correct thermodynamic reversible potential of a metal/metal-ion electrode may be hard to reproduce, because of impurities in the metal or complexing agents in the solution, even when the interface is highly nonpolarizable.

Polarizable interfaces behave differently. Their potential is not fixed by the solution composition, and it can be changed over a certain range depending on the metal and the composition of the solution in contact with it. For such a system, the potential may be viewed as an additional degree of freedom in the thermodynamic sense, as used in the Gibbs phase rule. To be sure, a so-called nonpolarizable interface can be polarized by passing a significant current through it. This, however, alters the concentration of both the reactant and the product *at the electrode surface* (without changing significantly their bulk concentrations). The potential developed across the interface will be in agreement with the Nernst equation as long as the concentrations used are the surface concentrations, which depend on the current passing across the interface.

We may summarize the difference between perfectly polarizable and perfectly nonpolarizable electrodes as follows. A perfectly polarizable electrode (e.g. Pt electrode) is an electrode in which no charge crosses the electrode/electrolyte interface when a current is applied. Such an electrode behaves like a capacitor. In contrast, a perfectly nonpolarizable electrode (e.g. Ag/AgCl/KCl reference electrode) is an electrode in which current passes freely across the interface, requiring no energy to make the transition.

1.2.2 The Equivalent Circuit Representation

We have already seen that the metal/solution interphase has some capacitance C_{dl} associated with it, as well as a (non-Ohmic) resistance R_{F} (also referred to as charge-transfer resistance, R_{ct}). Also, the solution has a finite resistance R_{S} that

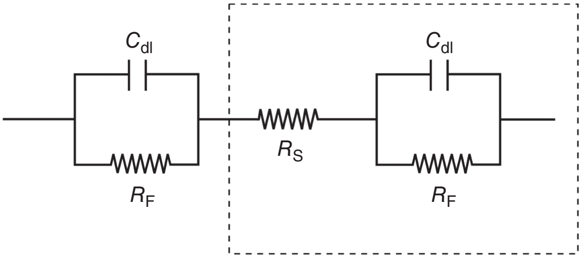

Figure 1.2 The equivalent circuit for a two-electrode cell. A single interface is usually represented by the elements inside the dashed rectangle (the Randles equivalent circuit). C_{dl}, R_F, and R_S represent the double-layer capacitance, the faradaic resistance, and the solution resistance, respectively.

must be taken into account. Thus, a cell with two electrodes can be represented by the equivalent circuit shown in Figure 1.2. Usually, one considers only the part of the circuit inside the dashed line, since the experiment is set up in such a way that only one of the electrodes is studied at a time. This part is known as the Randles equivalent circuit.

The equivalent circuit shown in Figure 1.2 represents a gross oversimplification, and interfaces rarely behave exactly like it. It does, nevertheless, help us gain some insight concerning the properties of the interface.

The combination of the double-layer capacitance and the faradaic resistance represents the interphase. How do we know that C_{dl} and R_F must be put in a parallel rather than in a series combination? Simply because we can observe a steady direct current flowing when the potential is high enough (above the minimum prescribed by thermodynamics (see Figure 1.1)). Also, when the resistance is effectively infinite under DC conditions, we can still have an AC signal going through (keep in mind that a capacitor does not transfer DC, only AC).

The equivalent circuit just described also makes it clear why conductivity measurements are routinely conducted by applying a small AC signal. If the appropriate frequency is chosen, the capacitive impedance associated with C_{dl} can be made negligible compared to the faradaic resistance, R_F, which is thus effectively shorted, leaving the solution resistance R_S as the only measured quantity.

The equivalent circuit shown in Figure 1.2 is meant to represent only the simplest situation. It does not take into account factors such as mass transport, heterogeneity of the surface, and the occurrence of reaction intermediates absorbed on it. Some of these factors are discussed later. Even in the simplest cases, in which this circuit does represent the response of the interphase to an electrical perturbation reasonably well, one should bear in mind that both C_{dl} and R_F depend on potential and, in fact, R_F depends on potential exponentially over a wide range, as will be discussed later.

The difference between polarizable and nonpolarizable interfaces can be easily understood in terms of this equivalent circuit. A high value of R_F is associated with a polarizable interface, whereas a low value of R_F represents a nonpolarizable interface.

Further Reading

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