

Chapter 2

A Bird's Eye View of Energy-Related Electrochemistry

2.1 Key Concepts

An electrochemical cell is a device capable of either [1] obtaining electrical energy directly from a chemical reaction or [2] of converting electrical energy into chemical transformations. Electrochemical devices where the conversion of the chemical energy (the free energy of a spontaneous chemical reaction) into electrical energy (e.g., combination of molecular hydrogen and oxygen to form water) occurs in fuel cells and batteries. The second type of device, known as an electrolyzer is the class of electrochemical cell where an electrical energy input is supplied to drive an uphill chemical reaction (e.g., water splitting into elementary hydrogen and oxygen).

Now, two questions arise naturally. First, we wonder if a given electrochemical cell will supply or absorb electric energy under a given set of conditions (pressure, concentration, temperature, etc.). The answer to this question has been found by applying the principles of thermodynamics to electrochemical cells. The application of thermodynamic principles to electrochemistry has led to the world famous Nernst equation which, among its many applications, allows the prediction of the maximum energy which may be delivered by a fuel cell or a battery or on the opposite side the minimum energy supply required by an electrolyzer. Second, we may want to know at what rate an electrochemical reaction will proceed and what energy price we will have to pay to have it going at such a given rate. Electrochemical kinetics (sometimes referred to as dynamic electrochemistry) provides the framework for such an understanding. Electrochemical kinetics is truly a “lighthouse” in electrocatalysis, for its deep implications in the design of electrode materials suitable for the exploitation of electrochemical reactions in devices. Indeed, the role of nanotechnology in electrocatalysis comes as a direct consequence of the application of the fundamental laws of electrochemical kinetics. It will become clear throughout the book chapters devoted to electrocatalytic materials [3–8], that for efficient electrochemical processes materials need to be nanostructured in order to have a surface area large enough to allow fast

kinetics. The first two sections of this chapter illustrate the basic principle of electrochemical thermodynamics and kinetics. No derivation for the presented formulas is given, rather we have preferred to discuss their major implications, in the form we feel more appropriate for pursuing the aims of this book.

The discussion is accessible to graduates who have received classes in general chemistry, physical chemistry, or thermodynamics. If the reader feels a need to refresh some fundamental concepts of chemical thermodynamics, they may refer to a variety of textbooks in chemical physics and chemical thermodynamics (see, e.g., [1]). The reader interested in a deeper understanding of both the thermodynamics of the electrochemical cell and electrochemical kinetics is instead referred to excellent specialized monographs [2, 9].

This chapter concludes with a third section describing in detail the electrochemical reactions that are relevant to electrochemical energy conversion, i.e., Hydrogen Evolution Reaction (HER), Hydrogen Oxidation Reaction (HOR), Oxygen Evolution Reaction (OER), and Oxygen Reduction Reaction (ORR). Alcohol oxidation reactions and CO₂ reduction will also be covered. Each of these reactions has been extensively investigated in the literature, leading to an enormous volume of articles and reviews. Making a selection has been necessary. Only major facts and findings have been considered, as the purpose of this section is the illustration of general concepts functional for the understanding of principles and for the design of nanostructured electrode materials. However, here and there across the proceeding chapters of the book which is essentially devoted to materials, a more in-depth discussion essential for a correct understanding of the concepts underlying some specific architectures will also be given.

2.2 Thermodynamics

2.2.1 The Electrochemical Cell

In some sense, we may refer to electrochemistry as the art of splitting reactions. To better understand this concept, let us consider the simple chemical reaction:



Equation (2.1) is the water formation starting from the elements. It is also the overall reaction occurring in fuel cells employing hydrogen as the fuel. It is known that such a reaction is spontaneous ($\Delta G = -237.1 \text{ kJ mol}^{-1}$). According to the thermodynamic definition, ΔG is also the maximum amount of energy delivered by the reaction which can be converted into mechanical work. From general chemistry it is known that both oxygen and hydrogen are in oxidation state 0 when in elementary form. In water they combine in such a way that hydrogen delivers electrons to oxygen. In molecular water, hydrogen is said to be oxidized to +1

having lost one electron in the reaction, while oxygen is reduced to -2 having acquired two electrons. Charge neutrality is fulfilled. Such reactions are called red-ox as one species loses electrons (hydrogen), and the other acquires the electron being reduced (oxygen). The trick of electrochemistry is to separate the oxidation and reduction reactions making them occur in physically distinct regions.

Such a separation is possible thanks to the architecture shown in Fig. 2.1.

The cell consists of two electrodes, an ionic conductor and an electronic conductor. An electrode is denoted as the anode if the oxidation occurs there. If a reduction reaction occurs the electrode is defined as the cathode.

Now let us consider again the reaction of Eq. (2.1). It can be formally split in the following way:



Equation (2.2) is the HOR, hence, according to our above considerations this takes place at the anode, while Eq. (2.3) is the ORR and takes place at the cathode. There is a substantial difference between this set of equations and Eq. (2.1). Charged species are explicitly considered here. Particularly at the anode we observe the formation of hydrogen ions and electrons, while at the cathode oxygen

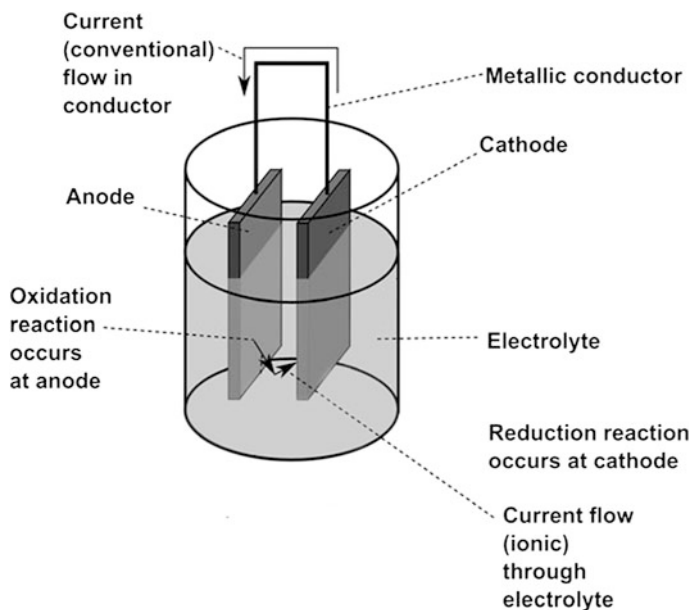


Fig. 2.1 Sketch of a simple electrochemical cell reporting the four essential components, the anode (oxidation electrode), the cathode (reduction electrode), the electrolyte (ion conductor), and the metal connection between the electrodes (electronic conductor)

is reduced to negative ions and electrons are consumed. Since the reaction occurs in physically separated regions there is the need to allow the transport of such charged species. Furthermore, we have to avoid the same path for ions and electrons. Fortunately, it is known that the transport of ions and electrons need different kinds of conductors. Generally what conducts electrons does not conduct ions and vice versa. Electrons need the so-called first type conductors (e.g., metals, a variety of conducting oxides and compounds), while ions need second type conductors, namely electrolytes (e.g., liquid solutions containing significant amounts of dissolved ions or ceramic materials at high temperature). Therefore, in order to close the circuit and start the reaction, there is the need to have an electron conductor connecting the anode and the cathode and an electrolyte allowing ions to freely move across the cell. If in the middle of the electron conductor an electrical load (e.g., a lamp, a radio, or any other electrical device) is applied, it consumes part of the energy of the electrons which uses this for its functioning. This is the way that chemical energy can be transformed into electrical energy without passing through thermo-mechanical cycles with their known efficiency limitations.

In principle all this could seem a bit artificial, but the implications of this approach are incredibly important. Indeed, as just seen, it is this art of splitting reactions which allows the existence of fuel cells and batteries, the only devices where chemical energy is directly transformed into electrical energy without the need of heat and mechanical work. The same is the basis for the electrolytic generation of hydrogen, electro-synthesis of chemical compounds, and electrolytic metal production and refining.

2.2.2 Electrochemical Reaction and the Nernst Equation

It is now clear how electrochemistry splits redox reactions into half reactions. What is still not defined is how to predict if under a given set of conditions (temperature, pressure, concentrations) the reaction will produce energy or energy will be required to keep it going. For chemical reactions such a prediction is possible thanks to the concept of free energy. Basically a chemical transformation is, in principle (the kinetics may however be so slow to completely hamper the course of the reaction), said possible or spontaneous if its associated free energy is negative.

Furthermore, it is essential to have the chance of a priori prediction of the potential of an electrochemical reaction. The last task is accomplished calculating the cell potential according to Eq. (2.4).

$$E^0 = -\frac{\Delta G^0}{nF} \quad (2.4)$$

Let us consider again the reaction of Eq. (2.1). We have seen that the associated standard Gibbs free energy is $-237.1 \text{ kJ mol}^{-1}$. The application of Eq. (2.4) leads to a cell standard potential of 1.23 V. Hence, a cell with HOR as anode reaction and ORR as cathode reaction is capable of delivering at maximum 1.23 V when hydrogen and oxygen are fed in standard conditions (1 atm and 298 °C). This is the theoretical cell potential of a hydrogen fuel cell. From Eq. (2.4), we also notice that as the potential gets more positive the reaction will become more spontaneous.

The prediction of the cell potential in nonstandard conditions is possible through the application of the Nernst equation (Eq. 2.5). The Nernst equation explicitly accounts for the dependence of the cell potential on parameters such as partial products and reactants activity (in a first approximation and for diluted solutions or gas activity may be replaced by concentrations or partial pressure) and temperature.

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{\text{products}}^{v_i}}{\prod a_{\text{reactants}}^{v_j}} \quad (2.5)$$

With the Nernst equation, we are able to predict the thermodynamic potential of an electrochemical cell under a given set of operating conditions. For the water formation reaction reported in Eq. (2.1) the Nernst equation takes the form of Eq. (2.6).

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}}}{a_{\text{H}_2} a_{\text{O}_2}^{1/2}} \quad (2.6)$$

As water is liquid under 100 °C its activity is conventionally fixed as 1. In a first approximation, we may also consider the activity of hydrogen and oxygen equal to their partial pressures (for practical purposes the activity is replaced by concentrations for liquid solutions and partial pressures for gases), leading to Eq. (2.7) which may be used in practice for rough estimations:

$$E = E^0 - \frac{RT}{2F} \ln \frac{1}{p_{\text{H}_2} p_{\text{O}_2}^{1/2}} \quad (2.7)$$

From Eq. (2.7), we notice that as we increase the partial pressure of both hydrogen and oxygen the potential gets more positive indicating that the reaction is more energetically favored.

It is worthy to spend some more words on the dependence of the cell potential on the temperature. Such a dependence is more subtle than what is suggested by Eq. (2.5). Basically this is because even the term E^0 is affected by the temperature. The dependence of E^0 on the temperature may be accounted for by applying Eq. (2.8).

$$E = E^0 + \frac{\Delta S}{nF} (T - T^0) - \frac{RT}{nF} \ln \frac{\prod a_{\text{products}}^{v_i}}{\prod a_{\text{reactants}}^{v_j}} \quad (2.8)$$

Nevertheless the temperature dependence may often be neglected, at least in practical technologies, as such dependence is usually small. Values of the order of

0.1–1 mV/°C are common. For low temperature systems (operating between 20 and 100 °C), such variations are not relevant as compared to the overall cell potential and for rough calculations this may be neglected.

Very often in aqueous systems chemical reactions include the production or the consumption of H^+ or OH^- species. The concentration of such species, hence, the pH of the electrolyte, affect the cell potential. Again such a dependence can be calculated using the Nernst equation.

As an example, let us consider the partial oxidation of ethanol in alkaline environments, a reaction exploited for energy production by Direct Ethanol Fuel Cells (DEFC).



The reaction Eq. (2.9) occurs in alkaline environments and the OH^- species is a reactant. In a first approximation, we can substitute the activity with the concentration, furthermore considering that four electrons are exchanged in Eq. (2.9), we obtain the following Nernst relationship:

$$E = E^0 - \frac{RT}{4F} \ln \frac{C_{CH_3COO^-}}{C_{CH_3CH_2OH} C_{OH^-} p_{O_2}} \quad (2.10)$$

Then considering the ionic water product and the pH definition this equation together with some algebraic workout results in Eq. (2.11):

$$E = E^0 + \frac{RT}{4F} pH - \frac{RT}{4F} \ln \frac{C_{CH_3COO^-}}{C_{CH_3CH_2OH} p_{O_2}} \quad (2.11)$$

Hence, the higher will be the pH, the higher will be the potential and the higher the reaction will be spontaneous.

The use of the Gibbs free energy for the calculation of the standard cell potential can be avoided introducing the concept of the standard reduction potential for half reactions. As previously calculated water formation in an electrochemical cell under standard conditions produces a potential difference of 1.23 V. The cell potential may hence be considered as the contribution of the sum of a potential contribution coming from the half cell anode (Eq. 2.2) and the half cell cathode reactions (Eq. 2.3), respectively. As in physical systems only potential differences matter, there is no chance to define an absolute potential scale for half reactions. Nevertheless for practical purposes the problem can be solved tabulating all half cell potentials with respect to the same standard electrode providing a practical working framework. The role of reference for the potential scale is assigned to the so-called standard hydrogen electrode (SHE) to which a conventional value of 0 V is assigned. A further convention is that each half reaction in the standard potential table is reported in such a way that the direct reaction is the reduction one. Table 2.1 lists values for a variety of reduction half reactions. According to Table 2.1, the standard electrochemical cell potential for water formation can be calculated as follows:

Table 2.1 Table of standard reduction potential for selected half cell reactions

Reduction half reaction	Standard reduction potential E° (V)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.38
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.41
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.23
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.04
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{aq})$	0.16
$\text{ClO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{ClO}_3^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.17
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	0.22
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{ClO}_2^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.35
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.52
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	0.54
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l})$	0.80
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$	0.85
$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.90
$2\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}(\text{aq})$	0.90
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.96
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	1.36
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	1.44
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.49
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.78
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Co}^{2+}(\text{aq})$	1.82
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}(\text{aq})$	2.01
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	2.87

$$E_{\text{H}_2\text{O}}^0 = E_{\text{H}_2\text{O}}^0 - E_{\text{H}_2}^0 = 1.23 \text{ V} - 0.00 \text{ V} = 1.23 \text{ V} \quad (2.12)$$

The term related to hydrogen is negative in sign as hydrogen is actually oxidized. Furthermore, the term concerning hydrogen is 0 V as the hydrogen oxidation in standard conditions is our actual reference.

In summary, we have seen how thermodynamics considerations allow us to make predictions of the maximum energy we may extract from spontaneous chemical reactions. In turn, we can also predict the minimum potential we have to supply to a given system to drive an uphill reaction (this is the case in electrolysis).

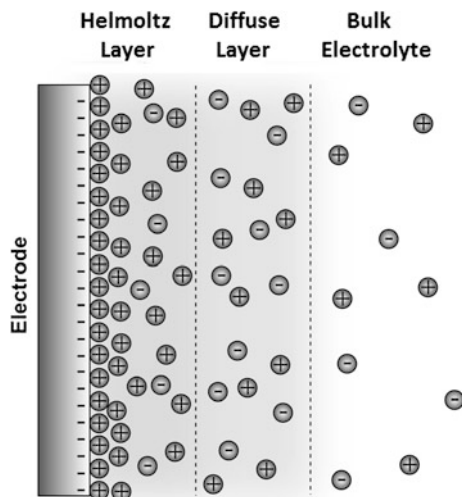
2.3 Electrochemical Kinetics

Electrochemical kinetics is a complex subject and its comprehensive description is out of the scope of the present book. Nevertheless as pointed out before a review of its fundamental concepts is essential for the understanding of the major implications that the theory of the rate of electrochemical reactions has in the design of efficient electrocatalysts.

In order to understand electrochemical kinetics we have to rely on the actual picture of what an electrochemical interface is. Conventionally, we refer to the electrochemical interface as the spatial region including the electrode and the portion of the electrolyte where the “most important” things for determining the rate of an electrochemical reaction occur. This commonly accepted vision of the electrochemical interface is actually sketched in Fig. 2.2.

Three distinct sections are identified in the electrolyte. The first one, directly in contact with the electrode surface, is the so-called Helmholtz layer. In such a portion, positive ions accumulate as a result of the electrostatic attraction with the negative charge accumulated at the surface of the electrode. The Helmholtz layer may divide in the so called inner Helmholtz layer and outer Helmholtz layer. The inner Helmholtz layer consists of the molecules or ions directly adsorbed at the electrode surface. The outer Helmholtz layer is formed by the ion electrostatically attracted by the electrode

Fig. 2.2 Pictorial view of a negatively polarized electrochemical interface



but still being coordinated by a shell of solvent molecules. Specific adsorption of chemical species may also occur. Specific adsorption, also called chemisorption, is the result of strong covalent interactions between chemical species and the electrode surface. It will be clear when describing in detail some electrochemical reactions that adsorption may play a very important role in the determination of the rate of an electrochemical reaction. Sometimes, as in the case of CO for platinum adsorption, this may also result in the most relevant poisoning pathway for electrocatalysts.

There is also another essential step in electrochemical reactions which occurs here and that has to be considered. As we know electrons cannot directly flow through the electrolyte. In order to guarantee a current flow through the cell, we need the electrons to *hop on* or *hop off* from chemical species such as ions. The stage where the electrons *hop on* or *hop off* the ions is the so-called charge transfer. The order of magnitude for the spatial size of the Helmholtz layer is less than 1 nm as it is identified as the order of magnitude of an atomic distance. Charge transfer mainly occurs here because it has been demonstrated to be the result of a quantum tunneling effect whose probability quickly drops as the distance from the electrode surface increases. The second section of the electrolyte consists in the diffuse layer. In such a portion of the electrolyte, only coulombic interactions and polarization effects occur. In the bulk or third section of the electrolyte, we may have what is called bulk diffusion which may also produce limitations to the rate, especially for low reactant concentrations or high polarizations of the interface. A mathematical description of the model reported here has been attained so the dependence of the value of the potential across the interface can be calculated.

2.3.1 Charge Transfer

A key quantity for electrochemical kinetics is the overpotential which is defined as the potential difference between the reduction potential, as determined by thermodynamic considerations, and the actual half cell potential.

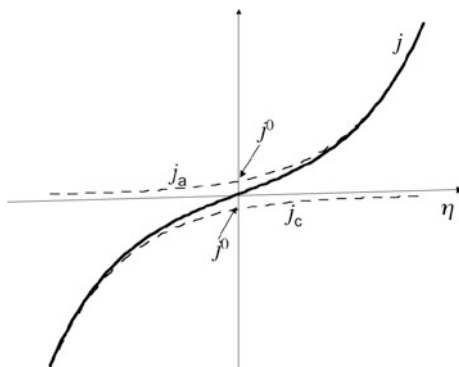
$$\eta = E - E^0 \quad (2.13)$$

The overpotential is the true driving force for a half cell reaction. The definition of the overpotential is the first step in the determination of the rate of an electrochemical reaction. The equation linking the rate (current density) of an electrochemical reaction where only charge transfer limits the rate is the so-called Butler–Volmer equation which takes the name from the scientists who independently derived it.

$$j = j^0 (e^{\alpha_a n F \eta / RT} - e^{-\alpha_c n F \eta / RT}) \quad (2.14)$$

In Eq. (2.14) j^0 is the exchange current density and it is the common absolute value of the anodic and cathodic current densities when the system is at the equilibrium (no net current flowing through the electrochemical cell). This is

Fig. 2.3 Plot for the Butler–Volmer equation showing anodic current density j_a (upper dashed curve), cathodic current density j_c (lower dashed curve), and net current density j (solid curve) dependence on the overpotential



probably the most determining quantity in electrochemical kinetic, as the current for overpotential away from zero is directly proportional to it. Basically the larger is the exchange current density the faster the reaction will occur. In other words, large values of j^0 will require small polarization, absorbing only a limited fraction of energy as compared to systems with smaller j^0 . It is also worth noticing that such a density is usually referred to the geometric area only and does not account for the real surface area of the electrode. According to this we can have an immediate taste of why nanotechnology is so important in electrocatalysis. Indeed, nanotechnology provides an approach to increase j^0 through the increase of the real surface area while keeping the geometric area constant.

Other essential quantities for electrocatalysis are the coefficients α_a and α_c . Such coefficients define how large is the increment in the rate of the reaction for a given variation of the overpotential shows a typical shape for the Butler–Volmer curve (Fig. 2.3). The curve may be divided into two distinct regions. The first one is the closest to the equilibrium ($\eta = 0$). Here the shape is approximately linear. This region does not invest much interest in electrocatalysis as reaction rates are usually very small and unpractical for devices. On the contrary this is very important in the investigation of metal corrosion. The second region is where the potential significantly departs from 0 showing an exponential dependence of j on η . In this region, only the cathodic or anodic terms of the Butler–Volmer equation may be considered, as the entity of the reverse reaction can be neglected. At large overpotential deviation from the Butler–Vomer behavior occurs. This is because mass transfer limitation due to the diffusion of the electroactive species occurs. When mass transport controls the reaction rate nothing else matters. Even if the overpotential rises we will never see our reaction going faster. A current density increase may be eventually observed, but that is generally due to the onset of other parasitic electrochemical reactions. The second region is worthy of more consideration as it allows, in principle, the determination of the cathodic and anodic coefficients. Equations (2.15) and (2.16) show the dependence of α_c and α_a on the current density and the overpotential when $|\eta| \gg 0$ (absolute value is used to include in the relationship both anodic and cathodic region).

$$\alpha_c = -\left(\frac{RT}{nF}\right) \left(\frac{d \ln j_c}{d \eta}\right) \quad (2.15)$$

$$\alpha_a = \left(\frac{RT}{nF}\right) \left(\frac{d \ln j_a}{d \eta}\right) \quad (2.16)$$

At first glance one could also be tempted to use Eqs. (2.15) and (2.16) to estimate the number of exchanged electrons before the rate determining step of an electrochemical reaction. By the way as it is going to be pointed out by a specifically addressed IUPAC commission, drawing mechanistic conclusion from this is not allowed. Indeed IUPAC is proposing the following definitions for α_c and

$$\alpha_c = -\left(\frac{RT}{F}\right) \left(\frac{d \ln j_c}{d \eta}\right) \quad (2.17)$$

$$\alpha_a = \left(\frac{RT}{F}\right) \left(\frac{d \ln j_a}{d \eta}\right) \quad (2.18)$$

This simply requires the removal of the factor n from the denominator of Eqs. (2.15) and (2.16). Such a definition is based directly on a experimental quantity and avoids any possible attempt to draw mechanistic conclusions. Hence the two following relationships can be derived

$$j_a = j^0 \exp[\alpha_a F \eta / RT] \quad (2.19)$$

$$|j_c| = j^0 \exp[-\alpha_c F \eta / RT] \quad (2.20)$$

The above relationships may be passed to logarithms returning the following equations:

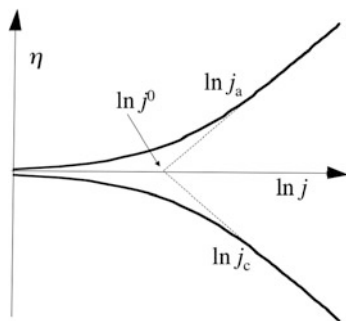
$$\ln j_a = \ln j^0 + \frac{\alpha_a F}{RT} \eta \quad (2.21)$$

and

$$\ln |j_c| = \ln j^0 - \frac{\alpha_c F}{RT} \eta \quad (2.22)$$

From Eqs. (2.21) and (2.22) it is clear that plotting η versus $\ln j$ returns a straight line whose slope is proportional to the anodic or cathodic coefficients. The intercept provides a tool for determining the value of j_0 . Such plots are referred to as Tafel plots (Fig. 2.4). Deviation from linearity of the Tafel plot at low overpotentials is due to the rising contribution of the inverse reaction. It is important to mention that a linear Tafel plot might eventually not be encountered in practice. This may be the consequence of a variety of reasons, such as the onset of other electrochemical reactions, variation in the mechanism as a result of the variation of the overpotential, adsorption of poisoning species, etc.

Fig. 2.4 Tafel plot. A line fit for the high overpotential region allows the estimation of the anodic and cathode coefficients, while the intercept provides a tool for the determination of the exchange current density j_0



By the way, for practical purposes only, a fully empirical knowledge of the relationship between the overpotential and the current density may be enough, at least for defining the energy of a given electrochemical reaction.

2.3.2 Mass Transfer

When electrochemical reactions are driven far from the equilibrium depletion of reactants at the electrochemical interface may occur. On the other hand, difficulties in the removal of the reaction products may lead to accumulation in close proximity of the electrode surface. In still electrolyte the mass transfer usually only occurs for diffusion even if local variation of the concentration of chemical species may drive variation in the density leading to buoyant convection. Mass transfer may affect both thermodynamics and kinetic reactions. The way diffusion affects thermodynamics is intuitive as in the Nernst equation only depends on the actual value of the concentration at the electrode surface. So reactant depletion and product pile up may slow down the reactions rates departing from the value expected from bulk concentration. Kinetics also is significantly altered by variation in the concentration. Indeed the Butler–Volmer equation can be modified to account for the actual concentration value at the electrode–electrolyte interface leading to

$$j = j^0 \left[\frac{c_R}{c_R^0} \exp(\alpha_a n F \eta / RT) - \frac{c_P}{c_P^0} \exp(-\alpha_c n F \eta / RT) \right] \quad (2.23)$$

Under complete diffusion control the Butler–Volmer equation loses its validity and the current density becomes independent of the overpotential, in the sense that further polarization of the interface does not provide any further increment in the current, which in turn will diminish with the increasing time. The effect of diffusion may be limited by applying convection. Under convection it is possible to replenish (or remove) chemical species from the electrode–electrolyte interface. Controlled convection conditions are sometimes employed for expanding the possibility of electrochemical characterization as, e.g., in the case of the rotating disk experiments which will be discussed later.

It is worthy to mention that diffusion phenomena may significantly be hampered in certain nanoarchitectures. This will be discussed in some detail in [Chap. 4](#).

2.3.3 Adsorption

We have seen that adsorption occurs within the Helmholtz layer. Such a stage is often determining for the rate of electrochemical reactions. Conventionally, we may discriminate between various kinds of adsorption interaction between the electrode surface and the molecules or ions in the solutions. The first one is the previously encountered chemisorptions. It occurs when between the electrode surface and the molecules or ions in the solution a covalent interaction subsists. We will see later that this is truly an issue of outstanding importance, as the extent of the specific adsorption interaction may heavily determine the effectiveness of a material as an electrocatalyst. Particularly it is usually necessary to find a good compromise between the strength of the adsorption which is accompanied by a high adsorption rate and the ability of the adsorbed species to be removed from the surface. Practically the adsorption interaction has to be “just right.” Right enough to guarantee high adsorption rate and low enough to guarantee a quick desorption. If the adsorbed species sticks strongly to the surface it will hamper the catalytic activity of the site. This is the basis of the Sabatier principle [10] whose pictorial view are the volcano plots which will be discussed in some detail for the hydrogen and oxygen oxidation and reduction. A case of very strong adsorption interaction is that of CO with platinum [3–6]. The adsorption of carbon monoxide may determine the deactivation of the platinum catalyst, leading, e.g., to overall efficiency losses of the polymer electrolyte fuel cells fuelled with methanol.

Adsorption may also be aspecific when due to weak dispersive interaction. Under such circumstances adsorption is usually denoted as physisorption. The interactions are much weaker than in chemisorptions and such phenomena is not as relevant as chemisorptions is. A third kind of adsorption may also result from the interaction of charged surface with ions of the opposite sign. In some cases adsorption may be the rds of an electrochemical reaction. As an example, we may cite the case of the alcohols oxidation on palladium in an alkaline environment. It is known and it will be discussed later that in such cases the formation $\text{Pd}(\text{OH})_{\text{ads}}$ is the rate determining step for the reaction at least at low overpotential [7]. To circumvent the problem palladium may be mixed with materials (e.g., CeO_2 , NiO , etc.) [8, 11] which have a stronger tendency to form hydroxide species at the surface. In such oxides, such species are also very mobile and can be transferred to the metal affecting the rate of the rate determining step. Such a phenomenon is known as “spillover of the primary oxide” [12, 13] and involves the adsorption of hydroxide at both an oxide and the palladium metals. It has been demonstrated that the primary oxide spillover can be exploited enhancing the efficiency of the DEFCs. Analogous phenomena may also occur with hydrogen. If palladium

particles are deposited onto a gold support they can collect hydrogen at their surface and transfer it to the surface of the gold support. Such a phenomenon has been investigated in electrochemistry and it is a well-known case of “hydrogen spillover.” Spillover phenomena are sometimes considered when designing catalysts, as they may significantly enhance the rate of electrochemical reactions.

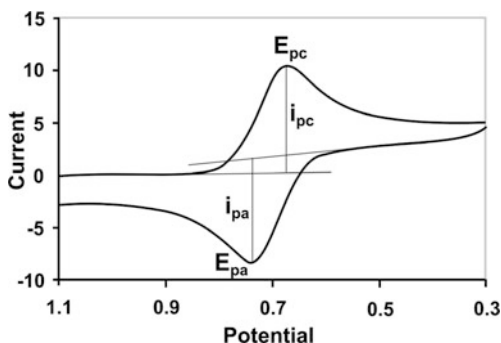
2.4 Electrochemical Techniques

Phenomena occurring at the electrochemical interface may be investigated by means of the so-called three-electrode cell or half cell. This electrochemical cell arrangement allows the identification of phenomena occurring at a single interface. The experimental setup consists in a cell containing a working electrode, a counter electrode, and a reference electrode. The working electrode is the one where the interface subject of the investigation is located. The counter is where reactions necessary to close the circuit occur. The reference is indeed a kind of “spectator” which allows only a negligible current flow, keeping its potential constant during the measurement (usually this condition is referred to as nonpolarized). The three electrodes are connected to a potentiostat. With the potentiostat the operator is allowed to directly control the potential difference between the reference and the working electrode. Once this potential has been set, the instrument adjusts the potential between the working and the counter electrode so that the potential difference between the reference electrode and the working electrode sticks to the value set by the operator. Historically, the potentiostat is the instrument which produced a true “quantum leap” in electrochemical characterization. Most of the present understanding of electrochemical kinetics we owe to the potentiostat.

2.4.1 *Voltammetry*

Voltammetry is one of the major experiments in dynamic electrochemistry. In a voltammetric experiment, the potential at the working electrode interface is scanned with the time using a three-electrode cell arrangement and a potentiostat. If the scan is performed with the potential varying linearly with the time and just in one direction, while recording the current passing through the cell, the experiment takes the name of Linear Sweep Voltammetry (LSV). If the same scan is performed at very low scan rate (e.g., 1 mV s^{-1} this condition is usually referred to as potentiostatic), it may allow the acquisition of Tafel plots, described in the section devoted to mass transport. More commonly scans are performed both in the forward and backward directions and eventually repeated many times, leading to the so-called cyclic voltammetry (CV) (Fig. 2.5). Cyclic voltammetry is possibly the most widespread experiment for evaluating the effectiveness of an electrocatalyst. At least is the first performed by electrochemists when they want to have a

Fig. 2.5 A cyclic voltammetry curve. Amongst the information which can be obtained from the CV, there are the degree of reversibility of electrochemical reactions, the on-set potential, and the peak current densities for anodic and cathodic processes



preliminary understanding of the electrochemical behavior of systems. CV has been the subject of entire books and its deep understanding would require much more space than this book can accommodate. We limit the treatment to the set of information which can be obtained by a cyclic voltammogram, inviting the reader to refer to the excellent book from Bard and Faulkner for a comprehensive review of CV basic principles.

Cyclic voltammetry provides a wide variety of relevant information about the electrocatalytic properties of materials, the following list reports some of them:

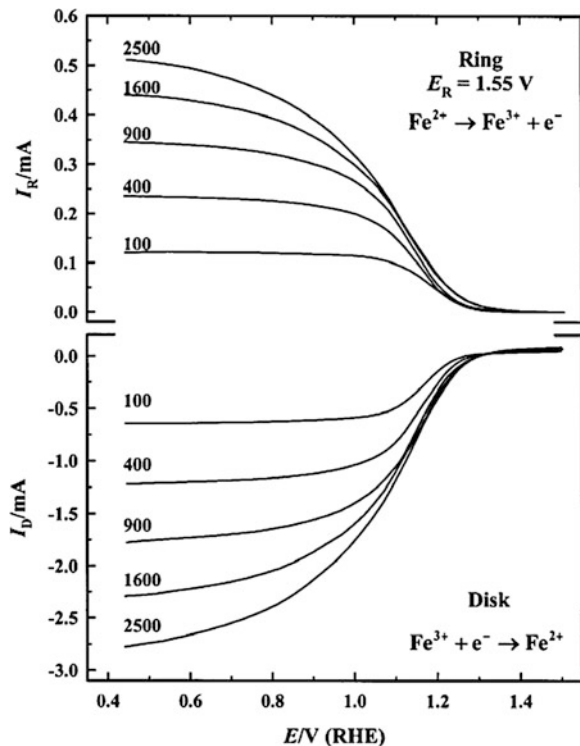
- (1) Onset potential (it is the potential at which the reaction current density significantly departs from the background) for a given electrochemical reaction.
- (2) Determination of the diffusion coefficient of the reactants.
- (3) Oxidation, dissolution, and electrochemical behavior of the active catalyst phase.
- (4) Determination of the electrochemically active surface area of the catalyst.
- (5) Direct comparison of the electrocatalytic activity of various materials.

The obtainment of this set of information may require the acquisition of CV varying parameters such as the potential span (minimum and maximum potential), the scan rate, and eventually the nature of the electrolyte.

2.4.2 Rotating Disk and Rotating Ring-Disk Methods

Controlled mass transport conditions may be employed to design electrochemical experiments helpful to elucidate electrochemical reaction mechanisms. The rotating disk electrode consists of a disk electrode embedded in an inert non-conductive cylinder. The cylinder is then connected to the shaft of an electric motor with a precise control of the rotation rate (usually between 100 and 3,000 r.p.m.). The disk rotation provides the instauration of a laminar flow which is the result of a centrifugal force pushing the electrolyte away from the center of the electrode in the radial direction and a liquid movement from the bulk of the electrolyte to the electrode surface in the axial direction. For large overpotentials complete mass transport control of the electrochemical reaction occurs and

Fig. 2.6 Classical representation for a rotating ring disk experiment for the electrochemical couple $\text{Fe}^{3+}/\text{Fe}^{2+}$. The ring partially collects the products generated at the disk as a result of the rotation-induced convection



formulas describing the resulting convection–diffusion problem can be obtained. The resulting Levich equation (Eq. 2.24) [14] provides a reliable method for estimating the number of exchange electrons in a electrochemical reaction.

$$j_l = 0.62 n F D^{2/3} \omega^{1/2} \nu^{-1/6} C. \quad (2.24)$$

When the control of the reaction is mixed kinetic and convective–diffusive the Koutecky–Levich (Eq. 2.25) equation may be used [2]. Such an equation allows the determination of the kinetic current density for a given overpotential and has been widely applied for extracting electrocatalytic parameters for reactions relevant to electrochemical energy conversion. By the way, its application is not straightforward and questions regarding the quality of the information that can be obtained may arise [14, 15].

$$1/j = 1/j_l + 1/j_k \quad (2.25)$$

If a second working electrode in the form of a ring is embedded in the nonconductive cylinder in such a way that it encircles the disk, a rotating ring-disk electrode is obtained. As two working electrodes are present, to operate the RRDE a special potentiostat capable of controlling four electrodes is necessary (bi-potentiostat).

The current at both electrodes is recorded and the most common data representation correspond to that is shown in Fig. 2.6.

The RRDE is a fundamental tool for determining properties of electrocatalysts for fuel cells. As an example, it has been widely employed in the characterization of the ORR as cathode reaction for PEMFC. This is mainly because partial ORR may result in the production of hydrogen peroxide a specie harmful in fuel cell for its significant contribution to carbon support corrosion. Experiments are performed coating the disk with a thin layer of electrocatalyst and then driving a potential scan to the reduction of oxygen. Any product generated at the disk electrode is removed from the disk in virtue of the flow regime above described and reaches the ring electrode. In the case of the ORR, the potential of the ring electrode is poised to detect any hydrogen peroxide that may have been generated at the disk leading to quantitative information about the amount of partially reduced oxygen species.

2.5 Major Energy-Related Electrochemical Reactions

2.5.1 Hydrogen Oxidation and Evolution Reactions

As hydrogen has been recognized as a possible energy vector for the future, much attention has been devoted to both its production through water electrolysis and oxidation in fuel cells.

As a consequence the major energy-related hydrogen reactions are the HER and the molecular HOR.

As previously seen in the section devoted to thermodynamics, hydrogen reduction is taken as a reference for the standard potential table and its reduction potential is by convention set to 0 V at standard conditions (pH = 0, T = 25 °C, H₂ partial pressure 101,325 Pa). To drive the reaction far from equilibrium and having hydrogen oxidation or reduction proceeding at a given rate we have hence to force the potential away from 0. Namely positive potentials provide oxidation and while negative evolution. At present hydrogen evolution and oxidation are not the main concern in electrocatalysis. Indeed, their kinetics is fast as compared to the more sluggish OER and ORR. The kinetic of hydrogen oxidation and reduction is known to be relatively fast on noble metals. Indeed, at present, best candidate electrocatalysts for such reactions for application in devices are metals such as, e.g., Pt, Pd, and Ru in pure form or in alloys. In our description, all the considered mechanisms refers to platinum without loss of generality. Indeed, analogous mechanisms apply to a wide variety of metal electrocatalysts.

Hydrogen evolution reaction

HER is reported in Eq. (2.26). Equation (2.26) shows the way that hydrogen ions are oxidized to produce H₂ in acidic environment.

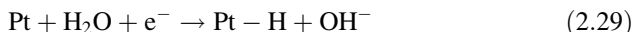


In alkaline environment the HER takes the form of Eq. (2.27).



A glance at the HER reactions immediately reveals that the reduction potential of hydrogen reduction depends on the pH. Indeed, as previously pointed out the potential for pH = 0 is 0 V, while the Nernst equation shows that at pH 14 the potential is -0.83 V.

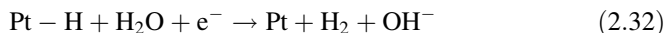
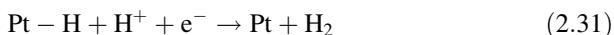
HER has been thoroughly investigated, leading to a generally accepted mechanistic scheme. Nowadays, it is widely recognized that the HER occurs through two main pathways, the Vomer–Tafel and the Volmer–Heyvrosky. For both pathways the first step is the adsorption of hydrogen on platinum through the so-called Volmer reactions which for acidic and alkaline conditions take the form of Eqs. (2.28) and (2.29), respectively [16]



The Volmer reaction is essentially a combined charge transfer and adsorption step. Then adsorbed hydrogens atoms may react together according to the Tafel (Eq. 2.30).



Alternatively the Heyvrosky reactions for acidic and alkaline environment (Eqs. 2.31 and 2.32) may occur again leading to H_2 evolution

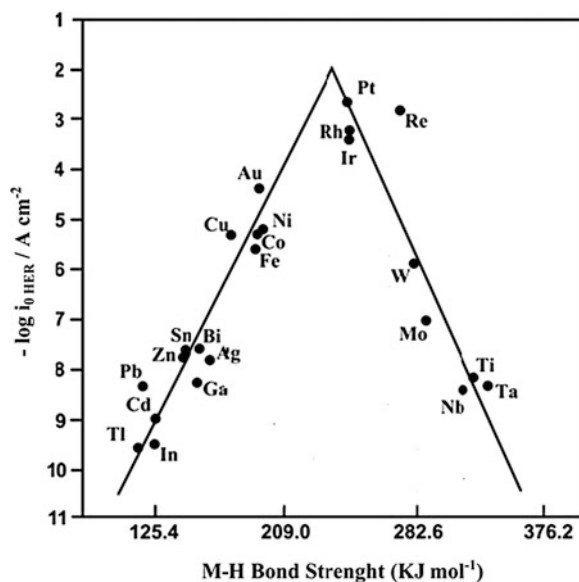


It has been demonstrated that the Volmer–Heyvrosky mechanism dominates for large overpotentials, while at low overpotentials the Volmer–Tafel is the preferred pathway [16].

Both hydrogen evolution pathways show charge transfer, adsorption and desorption steps. The search for good catalysts for such reactions need to account for all these elements, but adsorption and desorption definitely play the major role. The interaction of adsorbed hydrogen with the catalyst has to be strong enough to guarantee a sufficient adsorption rate, while on the other side, has not to be too strong to allow fast desorption of the product. The most widely accepted figure to elucidate the relationships between material fundamental properties and its activity is the so-called volcano plot (Fig. 2.7). The volcano plot provides a graphical representation of the dependence of the exchange current density on the strength of the bond between the catalyst surface and hydrogen. Indeed, volcano plots are a pictorial view of the Sabaltier principle previously discussed in the section dedicated to adsorption.

The plot peaks just around platinum (Fig. 2.7). This is because platinum has a good tendency to adsorb hydrogen at high rate, but at the same time doesn't form a

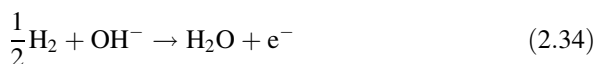
Fig. 2.7 Volcano plot for hydrogen evolution exchange current density



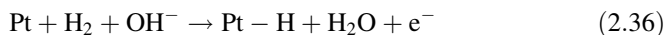
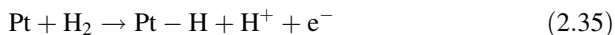
bond whose strength hamper desorption and mobility of atoms. The volcano plot justifies why platinum is the most performing, at least among all the pure metals, for both hydrogen evolution and oxidation reaction. By the way other metals even not noble, may be used to reduce or oxidize hydrogen. This is the case of Ni a transition metal scoring pretty well in the plot. In virtue of its position in the volcano plot and its stability in alkaline environment, Ni has found application as a catalyst for hydrogen evolution in electrolytic water splitting.

Hydrogen oxidation reaction

HOR is the anode reaction occurring in hydrogen fuel cells. It's existence is one of the foundations of the hydrogen economy paradigm. Most of the consideration for the HER also holds for the HOR [16, 17]. The mechanism is the same, but the reaction has to be viewed as the reverse. Next, the HOR for acidic (Eq. 2.33) and alkaline (Eq. 2.34) environments are reported.



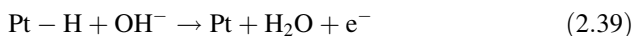
Hydrogen oxidation reaction takes place in similar way indeed the oxidation of hydrogen to protons may occur through the acidic and (Eq. 2.35) alkaline (Eq. 2.36) Heyrovsky reactions



Alternatively the Tafel reaction (Eq. 2.37) may occur



Then hydrogen adsorbed on Pt can release produced hydrogen ions in acidic environment or water in alkaline through the Volmer reactions (Eqs. 2.38 and 2.39)



2.5.2 Oxygen Evolution and Reduction Reaction

Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER) are the cathode and the anode reactions in fuel cells and electrolyzers, respectively. Despite the fact that oxygen is a powerful oxidizing agent, its complete reduction is still a major issue in electrocatalysis. Actually ORR limits the energy efficiency of fuel cells.

A list of the main reactions involved in ORR and OER is shown in Table 2.2 for both the acidic and the alkaline environments. The list also reports the value for the thermodynamic potentials reported against the Normal Hydrogen Electrode (NHE).

Oxygen reduction reaction

At present, the best catalyst for ORR is platinum. Because these Pt-based catalysts are too expensive for making commercially viable fuel cells, extensive research over the past several decades has focused on developing alternative catalysts, including non-noble metal catalysts. Damjanovic in [18] summarizes the following:

- (1) Few materials (only noble metals and alloys) can withstand the highly positive potential associated with the oxygen reduction (or evolution) without undergoing dissolution themselves and hence contributing to the overall current.

Table 2.2 Table of the reactions related to the ORR with the relative reduction potentials

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.229 V (NHE)
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.682 V (NHE)
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.77 (NHE)
$\text{O}_2 + 4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.401 (NHE)
$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{OH}^- + \text{HO}_2^-$	-0.427 (NHE)
$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-$	0.942 (NHE)

- (2) The mechanistic analysis of oxygen–reduction reactions is relatively complex owing to the numerous reaction steps and reaction intermediates with the energy of adsorption varying with the electrode potential and coverage. Furthermore, the reduction of O_2 may proceed either by a two-electron process to hydrogen peroxide or by a four-electron process leading to water. Hydrogen peroxide may, at least partially, reduce to water, or it may catalytically decompose.
- (3) In the potential range in which oxygen dissolution occurs, the electrode surface may be covered with oxide or relatively bare, so meaningful conclusions on the catalysis may be drawn.
- (4) Due to the low-exchange current densities, the electrode reactions may become potential controlling, particularly at low current densities. So even traces of impurities can profoundly affect the overall kinetic.

It is known that ORR in aqueous electrolytes may occur via four or two electron reaction pathways. The four electron pathway results in the formation of water, while the two electron pathway leads to the formation of hydrogen peroxide. There are a variety of reasons why the four electron pathway is preferred to the two electron one. First, the production of H_2O_2 in a fuel cell delivers less energy according to the reduction potential table. Second, the formation of H_2O_2 may be dangerous for the materials of the fuel cells. Indeed, hydrogen peroxide is a powerful oxidizing agent (this is again shown by the potential table) and may lead to the oxidation of the carbonaceous materials on the cathode side. That is one of the major reason for the performance degradation in PEMFC. Hence, the search for electrocatalysts for the O_2 reduction need to account for such an aspect and the number of exchanged electrons is a major criterium for the definition of the quality of a suitable electrocatalyst for ORR.

A sketch of the ORR mechanism on metal (Pt) catalyst is reported [wroblòwa 76] as follows:

As shown in Scheme 2.1 the first stage for the ORR is the O_2 adsorption onto the surface of the metal. Such an adsorbed oxygen may directly react to form water. Alternatively oxygen may be oxidized to the adsorbed hydrogen peroxide which either may be further oxidized to H_2O or may be released from the electrode surface. As for HER and HOR adsorption plays a fundamental role. A volcano plot reporting the activity of a variety of metals against the oxygen adsorption energy is shown in Fig. 2.8. Again just as the case of HER and HOR platinum is on top of the diagram indicating that among the transition metals platinum is the most active.

The effectiveness of a variety of other catalysts for the ORR has been demonstrated. Indeed, macrocycles of iron and cobalt (Chap. 10) as well as metal oxides have been proved to be effective for the ORR, providing a cheap alternative route to platinum and noble metals. Nevertheless, apart from a few examples reported in the literature, are stable in alkaline conditions only. It is worth remembering that PEMFCs for automotive and general high power applications operate in acidic conditions preventing the use of such materials. The state of the art for electrocatalysis in commercial PEMFCs is still platinum. The required

Scheme 2.1 Scheme of the possible pathways for the ORR

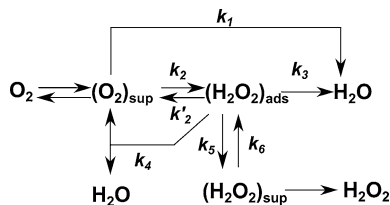
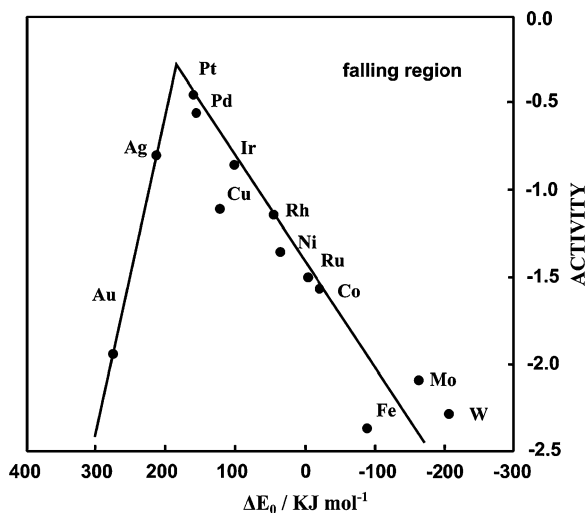


Fig. 2.8 Volcano plot for ORR



platinum loading at the cathode is larger than that required at the anode as the kinetic of the HOR is much faster than that of ORR.

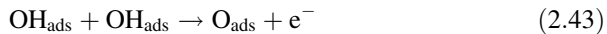
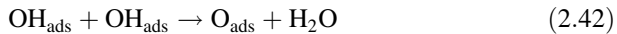
Oxygen evolution reaction

The OER occurs as the anode reaction in water electrolysis. The mechanism of such a reaction is indeed very complex and involves many steps with high energy intermediates explaining the need for large overpotentials. Consequently, the OER is the reaction absorbing most of the overpotentials required for water electrolysis [19]. The first step of the ORR for the acidic and the alkaline environment is as follows:



These reactions are the rate determining steps for the OER on materials where the affinity toward the hydroxyl adsorption is weak. Materials with this characteristic are unpractical for application in electrolysis. On the other hand, materials strongly adsorbing OH, the rate determining step may become OH_{ads} desorption, suggesting again that the behavior of materials may be explained with the volcano plot reported in Fig. 2.8.

From the volcano plot is clear that, among all the pure metals platinum is the most active metal. After OH has been adsorbed according to Eqs. (2.40) or (2.41) for the acid and alkaline conditions, respectively, the following cascade of reactions occurs (Eqs. 2.42, 2.43 and 2.44).



This is the so-called chemical oxide pathway which in principle should result in Tafel slopes of the order of 30 mV. Alternatively, the electrochemical pathway may occur, consisting in the hydroxyl adsorption (Eq. 2.40) followed by Eq. (2.45) :



According to this scheme the formation of the surface oxide occurs electrochemically. A cascade of two successive electron transfer is observed with an estimated Tafel slop of 40 mV for low OH coverage. In some cases, larger slope of around 60 mV may be observed leading to the so-called acid base equilibrium path. The Path's first step is again the hydroxyl adsorption (Eq. 2.40). Adsorbed hydroxyl gets then deprotonated according to Eq. (2.46).



Deprotonated adsorbed oxygen can then release one electron according to Eq. (2.47):



Once O_{ads} has been produced it may react producing molecular oxygen.

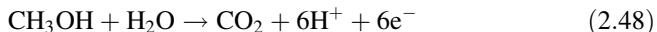
Whatever the mechanism is of a given material OER is a complex and essential task. Since the formation of oxides is involved in the mechanism this imply that not only bare metals may be active but also the corresponding oxide. Indeed this is the case. It is known and even commercially exploited that in alkaline environment NiO is a good material for the OER also in virtue of its stability in alkaline environment.

2.5.3 Methanol Oxidation

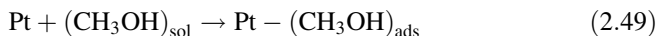
Since 1990 methanol has been investigated as a possible fuel for direct fuel cells. Methanol shows some principle advantages over hydrogen, above all the fact of being a liquid is definitely the most relevant. Nevertheless a full exploitation of methanol oxidation in fuel cells has not yet been achieved. As compared to HOR, MOR electrocatalysis is still an challenge and the existence of poisoning pathways

strongly hampers the diffusion of such devices. Again the most effective catalysts for the MOR are noble metals, with Pt and its alloys (e.g., Pt–Ru) being the best. Next a short survey of the mechanism for the MOR is reported. The treatment only refers to acidic conditions as at present this is the state of the art for the DMFC.

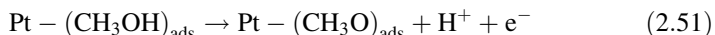
The complete oxidation of methanol to CO_2 proceeds according to Eq. (2.48):



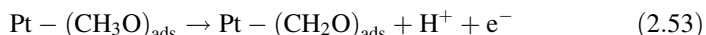
Despite the fact that only simple molecules are involved in the reaction, the mechanism is rather complex and it involves eleven possible steps. We present here the mechanism by Leger [20]. According to Leger, the first step of the reaction is the adsorption of a methanol molecule according to Eq. (2.49).



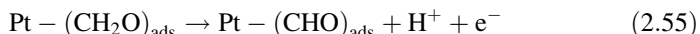
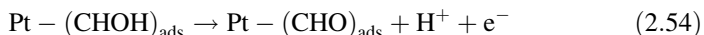
Adsorption is then followed by dissociation of several species which may lead to a variety of reaction pathways. The first step after adsorption is the formation of radical species with the release of 1e^- according to Eqs. (2.50) or (2.51).



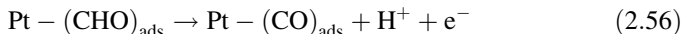
Further monoelectronic oxidation occurs, leading to the Eqs. (2.52) or (2.53)



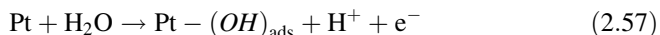
Both the products of Eqs. (2.52) or (2.53) are then oxidized to adsorbed reactive intermediate $\text{Pt} - (\text{CHO})_{\text{ads}}$ through Eqs. (2.54) or (2.55).



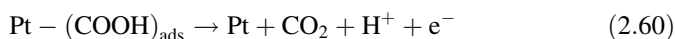
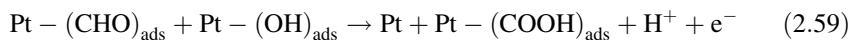
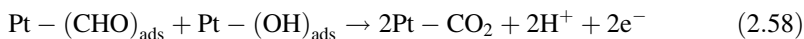
$\text{Pt} - (\text{CHO})_{\text{ads}}$ may then be oxidized to $\text{Pt} - (\text{CO})_{\text{ads}}$ according to Eq. (2.56). Such a reaction is responsible for the poisoning of Pt-based catalysts in DMFCs as CO is so strongly adsorbed that it may hamper further oxidation.



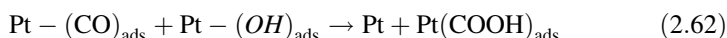
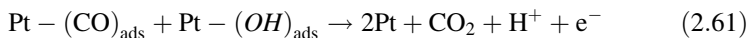
In parallel with the formation of the formyl like species and CO adsorption of OH at the Pt surface also occurs according to Eq (2.57).



Adsorbed OH species may then react with the adsorbed formyl to directly render CO_2 (Eq. 2.58) or to form adsorbed COOH groups (Eq. 2.59) which according to Eq. (2.60) are successively oxidized to CO_2 .



To oxidize CO larger overpotentials are required. Under such conditions, production of CO_2 occurs directly via Eq. (2.61) or indirectly via Eq. (2.62) followed by Eq. (2.60).

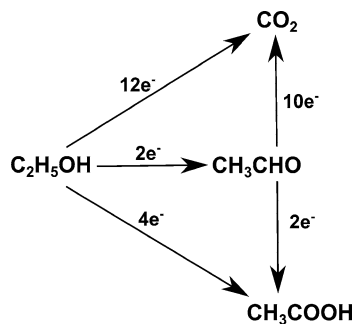


Discussion on the mechanism is limited to the acidic environment, as in these conditions platinum and ruthenium alloys exhibit the lowest overpotentials for the MOR. Low overpotential operation prevents catalyst poisoning prolonging the life of the catalyst. Platinum ruthenium effectiveness in the MOR reaction is due to a synergistic effect between the two metals. Indeed, platinum is very active for the dissociative chemisorptions of methanol, while the oxidation of the carbonaceous adsorbate to CO_2 is favored by the presence of oxidized form of ruthenium [21]. At present platinum ruthenium alloys are the state of the art catalysts for the MOR.

2.5.4 Ethanol Electrooxidation

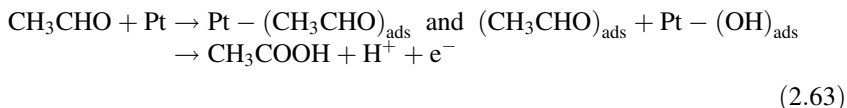
Ethanol is receiving much attention for exploitation in DEFCs, largely for its renewable nature, its well-established distribution infrastructure and lower toxicity as compared to methanol. Scheme 2.2 reports the variety of oxidation products in principle attainable through electrocatalysis. Complete oxidation to CO_2 would render 12e^- but it is hard to obtain requiring a breakage of the C–C bond. Alternative products can be acetic acid and acetaldehyde delivering 4e^- and 2e^- , respectively [22].

Scheme 2.2 Possible oxidation reaction products for ethanol electrooxidation

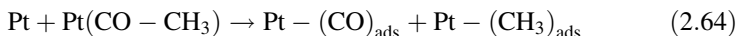


As pointed out complete oxidation is difficult to obtain. Next a description of the complex mechanism leading to the formation of the above-mentioned products is reported.

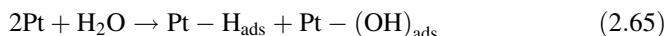
Aldehydes may react through the following pathway to render acetic acid:



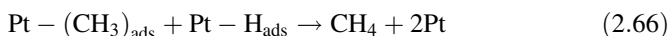
Obtaining CO_2 requires a difficult pathway which also may lead to the formation of methane.



Equation 2.64 illustrates the dissociation of the adsorbed aldehyde into adsorbed CO and CH_3 .



Hence, the adsorbed methyl may recombine with adsorbed hydrogen to produce methane and refresh catalytic metal sites.

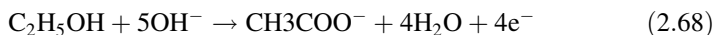


On the other side, CO may react with the hydroxyl adsorbed at the platinum surface to produce CO_2 .



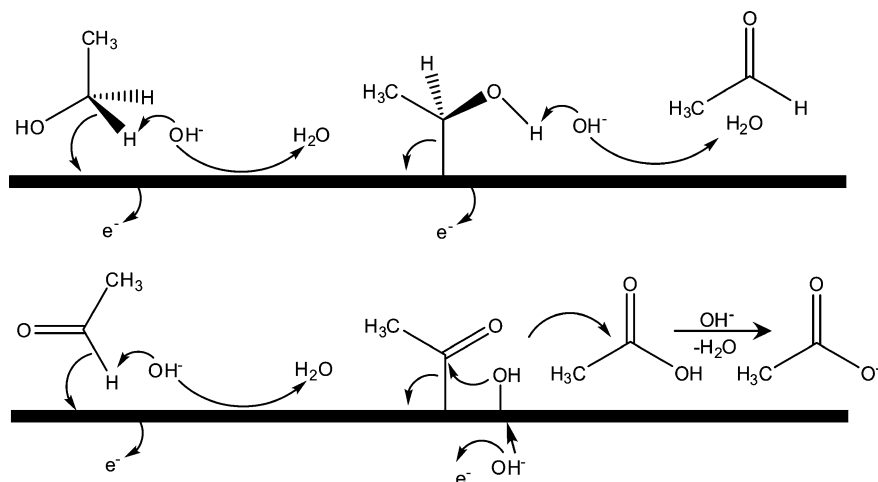
It is worthy to spend a few words on the role that the adsorbed hydroxyl species play in the oxidation of ethanol. As we have learnt for the oxidation of methanol, the presence of adsorbed CO species at the platinum surface may hamper the catalytic activity. Nevertheless its occurrence is essential to produce a full oxidation to CO_2 . Indeed, it is the presence of adsorbed hydroxyl which allows CO to be oxidized to CO_2 . Coupling materials capable of increasing the rate of formation of the adsorbed hydroxyl at the platinum surface is indeed a key for increasing the effectiveness of the ethanol electrooxidation.

Lately, ethanol electrooxidation has been widely explored in alkaline media mainly because Pt can be effectively substituted by Pd indeed leading to even better performance. Nevertheless the C–C bond cleavage in alkaline environments has been proved to not occur for ethanol at pHs larger than 13 [23], acetate being the only oxidation product according to Eq. (2.68)



which proceeds according to the mechanism illustrated in Scheme 2.3.

From the mechanistic scheme, it is clear that in order to produce full oxidation to acetate the adsorption of hydroxyl is essential. Indeed, it has been demonstrated

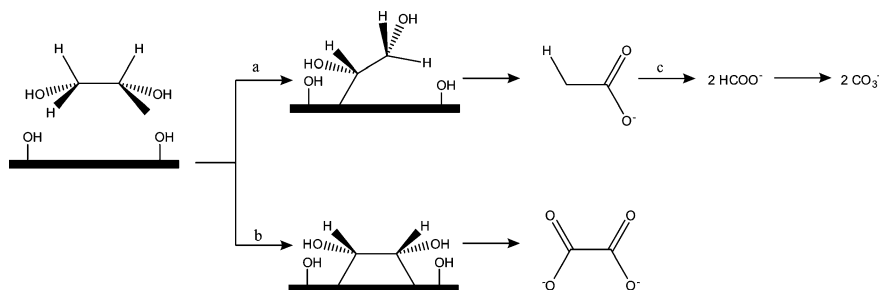


Scheme 2.3 Ethanol electrooxidation mechanism for alkaline environment

that with palladium hydroxyl adsorption is the rate determining step [7], at least at low over potentials. The addition of materials which may increase the hydroxyl adsorption rate on palladium has been proved to be effective in enhancing ethanol electrooxidation. This is the case of Ceria, which is capable of improving kinetics via spillover of the primary oxide [8].

2.5.5 Other Alcohols

Alcohols with a higher molecular weight than ethanol are now arousing great interest as fuels in direct alcohol fuel cells (DAFC). That is for a variety of reasons, including relatively low toxicity, low vapor pressure, high energy density, and the fact, at least for some of them, of being renewable. Included in this group are ethylene glycol (EG) and glycerol (G) [24]. Again, as in the case of ethanol and even more so here, the complete oxidation of these species has not yet been achieved and appears to be a very challenging task. To the best of our knowledge, all known Pd- or Pt-based electrocatalysts cannot promote the complete oxidation of EG or G to CO_2 both in acidic and alkaline media. EG or G may eventually undergo C–C bond scission with formation of CO_2 or carbonate. By the way this is a minor reaction pathway as compared to the oxidation to various carboxylic acids and carboxylates. Such reactions are, in turn, not completely selective. The subject is extensive and for the sake of illustrating the peculiar feature of electrocatalysis for such complex process we describe the oxidation of EG and G only in alkaline environments. The selection has been made as there are many more reports of alkaline fuel cells employing these fuels as compared to the acidic.



Scheme 2.4 Proposed mechanism for the electrooxidation of EG on Pd in alkaline media

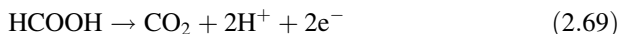
As shown in Scheme 2.4, in the case of EG on Pd-based anodes in alkaline media, carbonate can be produced by oxidation of glycolate (route c), whereas the major product, oxalate, is produced by the direct oxidation of EG (path b).

The oxidation of G is more complex than that of EG. Scheme 2.5 illustrates the possible reaction mechanisms proposed for G oxidation on Pd-, Pt-, and Au-based anode electrocatalysts.

Glycerol on Pd-based anodes is first oxidized to aldehyde (path a), which in turn is quickly oxidized to glycerate in a subsequent two-electron transfer step. Glycerate is further oxidized to tartronate and, by cleavage of C–C bond, into glycolate and formate. The latter species lead to carbonate and glycolate is oxidized to oxalate [25–28]. G is also oxidized directly to tartronate (path b) by chelating adsorption on catalytic surfaces. However, the oxidation of G yields significant amounts of carbonate. Since oxalate is very slowly oxidized on Pd-based electrodes [25, 26, 29, 30] CO_2 is prevalently a by-product of the oxidation of either glycerate or glycolate.

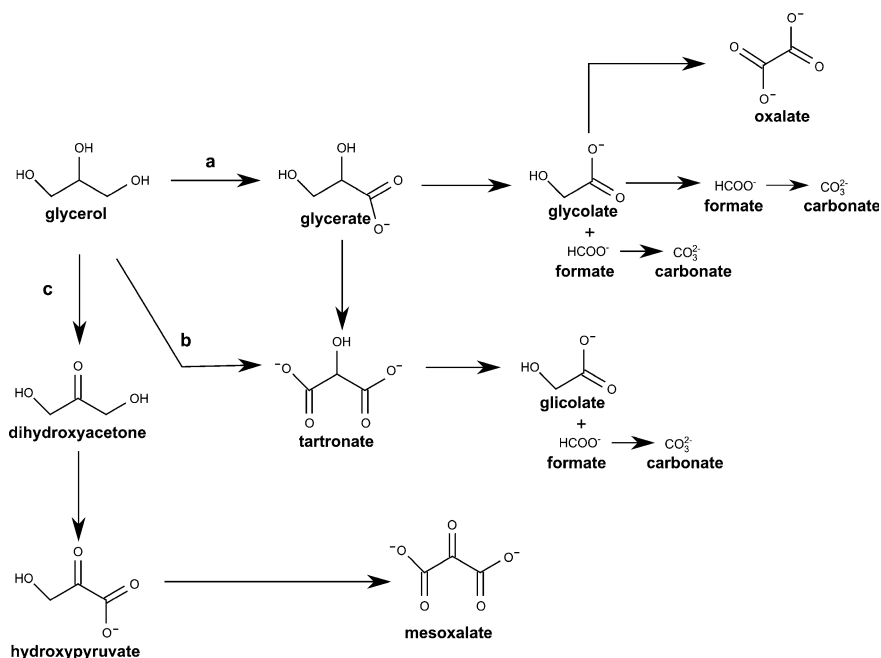
2.5.6 Formic Acid

Formic acid has been proposed as a liquid fuel for powering fuel cells [31]. It shares the advantage of high energy density with alcohols. Further its oxidation in acidic environment is favorable ($E^0 = -0.25$) and combined to oxygen reduction ($E^0 = 1.23$ V) leads to a cell potential of 1.48 V.

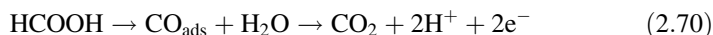


On the other hand, complete oxidation produces only two electrons which is much less as compared to methanol (6e^-) or ethanol (12e^-).

The so-called “parallel or dual pathway” is the recognized mechanism for formic acid oxidation. Direct oxidation (pathway 1) occurs via a dehydrogenation reaction, without forming CO as a reaction intermediate Eq. (2.69) [32] Alternatively, adsorbed carbon monoxide (CO) may form as a reaction intermediate by dehydration leading to Eq. (2.70):



Scheme 2.5 Main oxidation products of glycerol oxidation



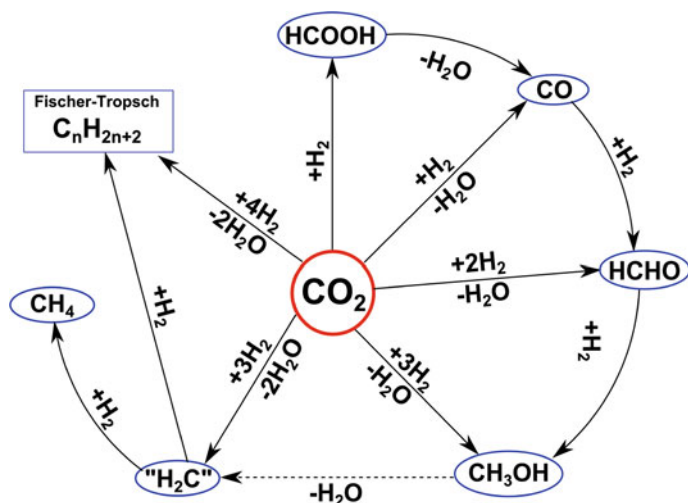
For direct formic acid fuel cells, dehydrogenation is the desired reaction pathway, to enhance overall cell efficiency and avoid poisoning of the catalyst. Anode catalyst selection is pivotal in directing formic acid oxidation to proceed via Eq. (2.69).

Recently, oxidation of formate (the deprotonated form of formic acid) has also been investigated in alkaline environment. Under such conditions, the oxidation leads to carbonate as major oxidation product and catalysts such as palladium have been proved to be effective [33].

2.5.7 CO_2 Electoreduction reaction

The steady increase in the atmospheric CO_2 concentration is a pressing global environmental issue; as a consequence, the reduction of carbon dioxide is currently investigated by many scientists as one of the most promising ways to convert waste CO_2 to useful materials and products (Scheme 2.6).

CO_2 is very stable (standard free energy of formation $\Delta G^\circ = -394,359 \text{ kJ mol}^{-1}$) and is the most oxidized form of carbon; therefore, the only chemical transformation



Scheme 2.6 Reduction of CO_2 to industrial products

possible at normal energies should be its reduction which can be performed using different approaches such as: (a) radiochemical methods [34, 35]; (b) chemical reduction by metals [36]; (c) Thermo-chemically [37]; (d) Bio-chemically [38]; (e) Bio-photochemically [39]; (f) Photo-electrochemically [40]; and (g) Bio-photo-electrochemically [41];

A bibliometric analysis of the scientific literature concerning CO_2 reduction published in the Science Citation Index (listed periodicals from 1999 to 2009) was presented by C.-M. Shu in 2011 (see Table 2.3) to highlight the emerging nature of this research issue worldwide [42]. The subject categories which deal with CO_2 reduction include Material Science, Electrochemistry, and Environmental Science.

Regarding the electrochemical reduction of CO_2 , a status report on metal-based cathodes was published in 2004 and various factors which influence the process efficiency and selectivity were critically evaluated [43].

In order to exploit the electroreduction of CO_2 an understanding of the chemistry of CO_2 activation is fundamental. Carbon dioxide electroreduction to useful fuels is the reverse electrochemical process with respect to the anode reactions which occur in direct fuel cells. From the thermodynamic point of view, the Gibbs free energy of this reduction process is always positive at medium and high pHs and the theoretical potentials are negative; therefore, CO_2 reduction is an electrolysis process that requires an electrical energy input. Concerning the kinetic aspect, the over-potential needed to electrochemically reduce CO_2 is always >1.0 V (in order to obtain a high yield of products, i.e., methane, ethylene, etc.). In addition, when using an aqueous electrolyte, at these potentials water reduction will always occur and as a consequence H_2 is a major by-product of the process.

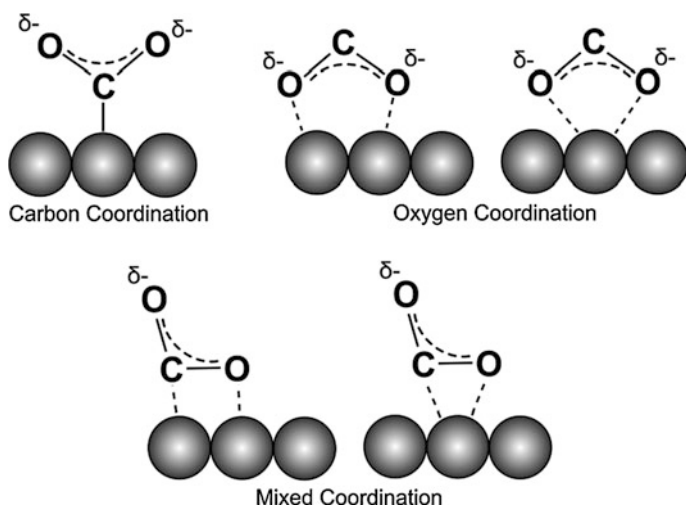
The reactions that occur on the electrode in an aqueous solution at pH 7 at 25 V (E^0 vs. SHE) are shown in Table 2.4 [44, 45]:

Table 2.3 Journals that publish articles on CO₂ reduction

Journal	Articles in the field (%)	Subject category
Abstracts of Papers of the American Chemical Society	33 (3.9)	–
Journal of the American Chemical Society	19 (2.2)	Chemistry, multidisciplinary
Journal of Electroanalytical Chemistry	18 (2.1)	Chemistry, analytical electrochemistry
Energy Policy	16 (1.87)	Energy and fuels, Environmental sciences
Inorganic Chemistry	12 (1.4)	Chemistry, inorganic and nuclear
Catalysis today	11 (1.28)	Chemistry, Applied Chemistry, Physical, Engineering, Chemical
Electrochimica Acta	11 (1.28)	Electrochemistry
Industrial and Engineering Chemistry Research	11 (1.28)	Engineering, Chemical
Tetrahedron Letters	11 (1.28)	Chemistry, organic
Carbon Dioxide Utilization for Global Sustainability	10 (1.17)	–
Chemical Communications	10 (1.17)	Chemistry, multidisciplinary
European Journal of Inorganic Chemistry	10 (1.17)	Chemistry, inorganic and nuclear
Journal of the Electrochemical Society	10 (1.17)	Electrochemistry
Studies in Surface Science and Catalysis	10 (1.17)	–
Green Chemistry	9 (1.05)	Chemistry, multidisciplinary
Applied Catalysis B—Environmental	8 (0.94)	Chemistry, Physical, Engineering, Environmental Engineering, Chemical
Chemistry Letters	8 (0.94)	Chemistry, multidisciplinary
Journal of Applied Electrochemistry	8 (0.94)	Electrochemistry
Angewandte Chemie-International Edition	7 (0.82)	Chemistry, multidisciplinary
Applied Catalysis A-General	7 (0.82)	Chemistry, Physical, Environmental science

Table 2.4 Reactions related to carbon dioxide reduction with relative reduction potentials

$\text{CO}_2 + 4\text{e}^- + 3\text{H}_2\text{O} \rightarrow \text{HCHO} + 4\text{OH}^-$	$E^0 = -0.48 \text{ V}$
$\text{CO}_2 + 2\text{e}^- + \text{H}_2\text{O} \rightarrow \text{CO} + 2\text{OH}^-$	$E^0 = -0.52 \text{ V}$
$\text{CO}_2 + 2\text{e}^- + \text{H}_2\text{O} \rightarrow \text{HCOO}^- + \text{OH}^-$	$E^0 = -0.43 \text{ V}$
$\text{CO}_2 + 8\text{e}^- + 6\text{H}_2\text{O} \rightarrow \text{CH}_4 + 8\text{OH}^-$	$E^0 = -0.25 \text{ V}$
$2\text{CO}_2 + 12\text{e}^- + 8\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4 + 12\text{OH}^-$	$E^0 = -0.34 \text{ V}$
$3\text{CO}_2 + 12\text{e}^- + 9\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^-$	$E^0 = -0.33 \text{ V}$
$3\text{CO}_2 + 18\text{e}^- + 13\text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_7\text{OH} + 18\text{OH}^-$	$E^0 = -0.32 \text{ V}$
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$	$E^0 = -0.41 \text{ V}$



Scheme 2.7 Proposed structures for adsorbed $\text{CO}_2^{\delta-}$ on metals

CO_2 reduction on various metal-based electrodes has been extensively investigated, even if the reaction mechanism is only partially understood. The rate determining step is represented by the single electron reduction of CO_2 to $\text{CO}_2^{\delta-}$ occurring at the standard potential of -1.90 V through $\text{CO}_2^{\delta-}$ adsorption. The five possible molecular structures for adsorbed $\text{CO}_2^{\delta-}$ are shown in Scheme 2.7. It is not clear which is the actual geometry as the expected molecular vibrations can be easily affected by the surface geometry (we know that $\text{CO}_2^{\delta-}$ is most easily produced at surface defects).

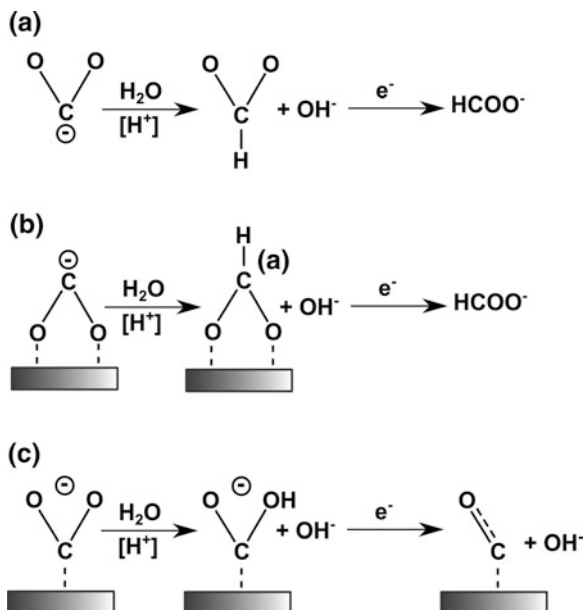
In addition, the adsorbed state of $\text{CO}_2^{\delta-}$ is also influenced by the type of metal on the electrode surface.

Scheme 2.8 shows the main reaction pathways for the electroreduction of CO_2 .

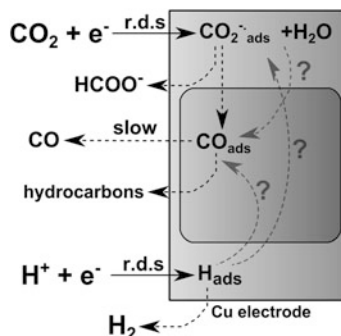
In case (a): (i.e., Hg, Cd, Pb, Tl, In, and Sn), high hydrogen overvoltage electrodes with weak adsorption of CO, there is also a high overvoltage for CO_2 reduction to $\text{CO}_{2\text{ads}}^-$ and as a consequence these metals generally produce predominantly formate (or oxalate in nonaqueous CO_2 electrolysis); in case (b) (i.e., Pt, Ni, and Fe) these low hydrogen overvoltage metals also reduce CO_2 at low overpotentials to form tightly adsorbed CO; and in case (c) (i.e., Au, Ag, Zn, and Cu) metals with a low hydrogen overvoltage that reduce CO_2 at medium overpotentials form more loosely held CO. Scheme 2.9 shows a schematic overview of CO_2 reduction on a Cu electrode. Two pathways are shown, one leading to formate and the other to CO and hydrocarbon products. Both CO_2 reduction and hydrogen evolution occur on unblocked areas of the electrode surface, with CO being the primary cause of surface inhibition.

The development of Cu-based or Cu-coated metallic electrodes for the preparation of hydrocarbons and/or alcohols from CO_2 in aqueous media has been a major breakthrough in this area.

Scheme 2.8 Proposed reaction pathways for the reduction of adsorbed CO_2^- on different metals



Scheme 2.9 CO_2 reduction reaction pathways on a Cu electrode surface



The electrocatalytic activity of Cu-based alloys, such as Cu-Sn and Cu-Zn in addition to elemental Cu, Sn, and Zn cathodes, at low temperatures has also been studied (275 K) [46].

The highly selective reduction of CO_2 to C2 compounds such as CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$, and C_2H_4 on Cu-Hg alloy electrodes by employing pulsed electroreduction has been reported [47]. The Faradic efficiencies (rf) for the production of C2 compounds produced on Cu-Ag alloy electrodes were found to vary with the atomic ratio of Cu and Ag. The total rf for C2 compounds was 54.2 % for the pulsed reduction on a Cu-Ag alloy electrode (Cu/Ag = 28/72) with an anodic bias of $V_a = -0.4$ V and a cathodic bias of $V_c = -2.0$ V versus Ag/AgCl. It was found that the formation of an oxide layer on Cu and the desorption of

intermediates on Ag under anodic bias were key factors for the product selectivity. The products were found to be formic acid, methanol, and CO. These reductions were performed at ambient temperature and pressure and at high current density. When neutral supporting electrolytes were used the rf was quantitative. The major limitation of these copper-based electrodes lies in their quick deactivation (within 20–30 min. of electrolysis). A periodic anodic activation procedure can be used and this has allowed high hydrocarbon yields over prolonged electrolysis, which has been confirmed by Cook et al. [48] who found that the electrocatalytic activity of Cu depends on the renewal of the electrode surface. The clean Cu surface allowed for the achievement of rf values of 73 % for CH₄ and 25 % for C₂H₄. Li and Prentice 1997 [47], synthesized MeOH (rf = 40 %) via the electroreduction of CO₂ under aqueous high pressure conditions with a LiCl electrolyte using a Cu electrode, at a current density of 9 mA/cm² at −1.1 V versus Ag/AgCl. These researchers used a rotating disk electrode in order to achieve hydrodynamic conditions.

The mechanism of CO₂ electroreduction on Cu remains not yet fully understood [44]. Generally, for the electrochemical reduction of CO₂ in water, hydrogen formation competes with the CO₂ reduction reaction. Therefore, the depression of hydrogen formation is very important because the applied energy is wasted on hydrogen evolution instead of being used for the reduction of CO₂. In a recent example using a Na⁺/methanol-based electrolyte, the faradic efficiency for hydrogen formation on a Cu electrode at 243 K was suppressed to 17.9 %. An efficiency below 1 % was achieved when sodium hydroxide and thiocyanate salts were used. Only in a CH₃COONa/electrolyte hydrogen-formation efficiency was relatively high (34.0 %), as with other acetates, also, the efficiency was very high. The hydrogen formation roughly decreased with a decreasing cation size [49].

Numerous studies have been carried out with the objective of elucidating the reaction mechanisms. However, liquid phase CO₂ electrocatalytic reduction suffers from serious problems which are difficult to overcome, such as sluggish reaction kinetics, low selectivity of CO₂ reduction formation of various by-products (nonselectivity), the low solubility of CO₂ in aqueous solutions, and the deactivation of the electrode catalysts.

For these reasons, an alternative to CO₂ reduction in aqueous electrolytes has been developed and is represented by the use of GDEs (Gas Diffusion Electrodes) and solid polymer electrolytes such as cation exchange membranes as well as anion exchange membranes (AEM) for CO₂ reduction to formic acid or methane as well as ethylene in devices similar to that developed for fuel cell technology, usually composed of Teflon-bonded catalyst particles and carbon blacks [50–68].

The electroreduction of CO₂ promoted by molecular complexes will be described in [Chap. 10](#).

References

1. P.W. Atkins, J. De Paula, *Physical Chemistry*, 9th edn. (W.H. Freeman, New York, 2010), pp. xxi, 1139 p
2. A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd edn (Wiley, New York, 2001), pp. xxi, 833 p
3. C.A. Lucas, N.M. Markovic, B.N. Grgur, P.N. Ross, Structural effects during CO adsorption on Pt-bimetallic surfaces I. The Pt(100) electrode. *Surf Sci* **448**, 65 (2000)
4. C.A. Lucas, N.M. Markovic, P.N. Ross, Structural effects during CO adsorption on Pt-bimetallic surfaces II. The Pt(111) electrode. *Surf. Sci.* **448**, 77 (2000)
5. C.A. Lucas, N.M. Markovic, P.N. Ross, Structural effects induced by CO adsorption on Pt-bimetallic surfaces. *Surf. Rev. Lett.* **6**, 917 (1999)
6. M. Hachkar, T. Napporn, J.M. Leger, B. Beden, C. Lamy, An electrochemical quartz crystal microbalance investigation of the adsorption and oxidation of CO on a platinum electrode. *Electrochim. Acta* **41**, 2721 (1996)
7. Z.X. Liang, T.S. Zhao, J.B. Xu, L.D. Zhu, Mechanism study of the ethanol oxidation reaction on palladium in alkaline media. *Electrochim. Acta* **54**, 2203 (2009)
8. M. Bevilacqua et al., Improvement in the efficiency of an OrganoMetallic Fuel Cell by tuning the molecular architecture of the anode electrocatalyst and the nature of the carbon support. *Energy Environ. Sci.* **5**, 8608 (2012)
9. J.O.M. Bockris, A.K.N. Reddy, M.E. Gamboa-Aldeco, *Modern Electrochemistry*, 2nd edn. (Plenum Press, New York, 1998)
10. A.B. Laursen et al., Electrochemical hydrogen evolution: Sabatier's principle and the Volcano plot. *J. Chem. Educ.* **89**, 1595 (2012)
11. C.W. Xu, P.K. Shen, Y.L. Liu, Ethanol electrooxidation on Pt/C and Pd/C catalysts promoted with oxide. *J. Power Sour.* **164**, 527 (2007)
12. J.A. Jaksic et al., Spillover of primary oxides as a dynamic catalytic effect of interactive hypo-d-oxide supports. *Electrochim. Acta* **53**, 349 (2007)
13. J. M. Jaksic, D. Labou, G. D. Papakonstantinou, phenomena and significance of intermediate spillover in electrocatalysis of oxygen and hydrogen electrode reactions. *Chem. Ind.* **66**, 425 (2012)
14. S. Treimer, A. Tang, D.C. Johnson, A consideration of the application of Koutecky-Levich plots in the diagnoses of charge-transfer mechanisms at rotated disk electrodes. *Electroanalytical* **14**, 165 (2002)
15. F.J. Vidal-Iglesias, J. Solla-Gullon, V. Montiel, A. Aldaz, Errors in the use of the Koutecky-Levich plots. *Electrochem. Commun.* **15**, 42 (2012)
16. W.C. Sheng, H.A. Gasteiger, Y. Shao-Horn, Hydrogen oxidation and evolution reaction kinetics on platinum: acid vs alkaline electrolytes. *J. Electrochem. Soc.* **157**, B1529 (2010)
17. B.E. Conway, B.V. Tilak, Interfacial processes involving electrocatalytic evolution and oxidation of H₂, and the role of chemisorbed H. *Electrochim. Acta* **47**, 3571 (2002)
18. A. Damjanovic, in *Modern Aspects of Electrochemistry*, vol. 5, ed. by B.E. Conway, J.O'M. Bockris (Plenum, New York, 1965)
19. E. Guerrini, S. Trasatti, *Electrocatalysis in water electrolysis* ed. by C. Bianchini, P. Barbaro. *Catalysis for Sustainable Energy Production* (John Wiley and Sons, 2009), p. 235 (2009)
20. J.M. Leger, Mechanistic aspects of methanol oxidation on platinum-based electrocatalysts. *J. Appl. Electrochem.* **31**, 767 (2001)
21. H.A. Gasteiger, N. Markovic, P.N. Ross, E.J. Cairns, Methanol electrooxidation on well-characterized Pt-Rn alloys. *J. Phys. Chem.-Us* **97**, 12020 (1993)
22. C. Lamy et al., Recent advances in the development of direct alcohol fuel cells (DAFC). *J. Power Sources* **105**, 283 (2002)
23. X. Fang, L.Q. Wang, P.K. Shen, G.F. Cui, C. Bianchini, An in situ fourier transform infrared spectroelectrochemical study on ethanol electrooxidation on Pd in alkaline solution. *J. Power Sources* **195**, 1375 (2010)

24. A. Marchionni et al., Electrooxidation of ethylene glycol and glycerol on Pd-(Ni-Zn)/C anodes in direct alcohol fuel cells. *Chemosuschem* **6**, 518 (2013)
25. V. Bambagioni et al., Ethylene glycol electrooxidation on smooth and nanostructured pd electrodes in alkaline media. *Fuel Cells* **10**, 582 (2010)
26. V. Bambagioni et al., Ethanol oxidation on electrocatalysts obtained by spontaneous deposition of palladium onto nickel-zinc materials. *Chemosuschem* **2**, 99 (2009)
27. Y. Kwon, K.J.P. Schouten, M.T.M. Koper, Mechanism of the catalytic oxidation of glycerol on polycrystalline gold and platinum electrodes. *Chem. Cat. Chem.* **3**, 1176 (2011)
28. C. Bianchini, P.K. Shen, Palladium-Based electrocatalysts for alcohol oxidation in half cells and in direct alcohol fuel cells. *Chem. Rev.* **109**, 4183 (2009)
29. P.A. Christensen, A. Hamnett, The oxidation of ethylene glycol at a platinum electrode in acid and base: an in situ FTIR study. *J. Electroanal. Chem. Interfacial Electrochem.* **260**, 347 (1989)
30. F. Hahn, B. Beden, F. Kadirgan, C. Lamy, Electrocatalytic oxidation of ethylene glycol: Part III. In-situ infrared reflectance spectroscopic study of the strongly bound species resulting from its chemisorption at a platinum electrode in aqueous medium. *J. Electroanal. Chem. Interfacial Electrochem.* **216**, 169 (1987)
31. X. Yu, P.G. Pickup, Recent advances in direct formic acid fuel cells (DFAFC). *J. Power Sources* **182**, 124 (2008)
32. J.M. Feliu, E. Herrero, *Handb. Fuel Cells* **2**, 679 (2003)
33. A.M. Bartrom, J.L. Haan, The direct formate fuel cell with an alkaline anion exchange membrane. *J. Power Sources* **214**, 68 (2012)
34. A. Voss, The future-role of nuclear and renewable forms of energy. *Brennst-Warme-Kraft* **42**, 579 (1990)
35. C. Willis, A.W. Boyd, Excitation in the radiation chemistry of inorganic gases. *Int. J. Radiat. Phys. Chem.* **8**, 71 (1976)
36. E.L. Quinn, C.L. Jones, *Carbon Dioxide*. American Chemical Society Monograph series (Reinhold Publishing Corporation, New York, 1936), pp. 294, 6 p. incl. illus., tables, diagrs
37. C.E. Bamberger, P.R. Robinson, Thermochemical splitting of water and carbon dioxide with cerium compounds. *Inorg. Chim. Acta* **42**, 133 (1980)
38. J.M. Lehn, R. Ziessel, Photochemical generation of carbon monoxide and hydrogen by reduction of carbon dioxide and water under visible light irradiation. *Proc. Natl. Acad. Sci. USA* **79**, 701 (1982)
39. D. Mandler, I. Willner, Photochemical fixation of carbon dioxide: enzymic photosynthesis of malic, aspartic, isocitric, and formic acids in artificial media. *J. Chem. Soc. Perkin Trans. 2* **0**, 997 (1988)
40. I. Taniguchi, B. Aurian-Blajeni, J.O.M. Bockris, The reduction of carbon dioxide at illuminated p-type semiconductor electrodes in nonaqueous media. *Electrochim. Acta* **29**, 923 (1984)
41. B.A. Parkinson, P.F. Weaver, Photoelectrochemical pumping of enzymatic CO₂ reduction. *Nature* **309**, 148 (1984)
42. T.J. Wan, S.M. Shen, A. Bandyopadhyay, C.M. Shu, Bibliometric analysis of carbon dioxide reduction research trends during 1999–2009. *Sep. Purif. Technol.* **94**, 87 (2012)
43. M.A. Scibioh, B. Viswanathan., Electrochemical reduction of carbon dioxide: a status report. *Proc. Indian Natn. Sci. Acad* **70**, 65 (2004)
44. M. Gattrell, N. Gupta, A. Co, A review of the aqueous electrochemical reduction of CO₂ to hydrocarbons at copper. *J. Electroanal. Chem.* **594**, 1 (2006)
45. J.A. Dean, N.A. Lange, *Handbook of Chemistry* (McGraw-Hill, New York, 1973), p. v
46. M. Watanabe, M. Shibata, A. Katoh, H. Uchida, M. Tomkiewietz, H. Yoneyami, Y. Hori, R. Haynes, Eds. (1993)
47. J.W. Li, G. Prentice, Electrochemical synthesis of methanol from CO₂ in high-pressure electrolyte. *J. Electrochem. Soc.* **144**, 4284 (1997)
48. R.L. Cook, R.C. MacDuff, A.F. Sammells, Electrochemical reduction of carbon dioxide to methane at high current densities. *J. Electrochem. Soc.* **134**, 1873 (1987)

49. S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, Electrochemical reduction of CO₂ to methane at the Cu electrode in methanol with sodium supporting salts and its comparison with other alkaline salts. *Energ. Fuel* **20**, 409 (2006)
50. K. Hara, A. Kudo, T. Sakata, M. Watanabe, High-Efficiency electrochemical reduction of carbon-dioxide under high-pressure on a gas-diffusion electrode containing Pt catalysts. *J. Electrochem. Soc.* **142**, L57 (1995)
51. K. Hara, A. Kudo, T. Sakata, Electrochemical reduction of carbon-dioxide under high-pressure on various electrodes in an aqueous-electrolyte. *J. Electroanal. Chem.* **391**, 141 (1995)
52. N. Furuya, T. Yamazaki, M. Shibata, High performance Ru-Pd catalysts for CO₂ reduction at gas-diffusion electrodes. *J. Electroanal. Chem.* **431**, 39 (1997)
53. J. Lee, Y. Kwon, R.L. Machunda, H.J. Lee, Electrocatalytic recycling of CO₂ and small organic molecules. *Chem-Asian J* **4**, 1516 (2009)
54. T. Yamamoto, D.A. Tryk, A. Fujishima, H. Ohata, Production of syngas plus oxygen from CO₂ in a gas-diffusion electrode-based electrolytic cell. *Electrochim. Acta* **47**, 3327 (2002)
55. C.M. Sanchez-Sanchez, V. Montiel, D.A. Tryk, A. Aldaz, A. Fujishima, Electrochemical approaches to alleviation of the problem of carbon dioxide accumulation. *Pure Appl. Chem.* **73**, 1917 (2001)
56. D.A. Tryk et al., Recent developments in electrochemical and photoelectrochemical CO₂ reduction: involvement of the (CO₂)(2)(.-) dimer radical anion. *Appl. Organomet. Chem.* **15**, 113 (2001)
57. T. Yamamoto, D.A. Tryk, K. Hashimoto, A. Fujishima, M. Okawa, Electrochemical reduction of CO₂ in the micropores of activated carbon fibers. *J. Electrochem. Soc.* **147**, 3393 (2000)
58. Y. Hori et al., "Deactivation of copper electrode" in electrochemical reduction of CO₂. *Electrochim. Acta* **50**, 5354 (2005)
59. S. Komatsu, M. Tanaka, A. Okumura, A. Kungi, Preparation of Cu-solid polymer electrolyte composite electrodes and application to gas-phase electrochemical reduction of Co₂. *Electrochim. Acta* **40**, 745 (1995)
60. C. Delacourt, P.L. Ridgway, J.B. Kerr, J. Newman, Design of an electrochemical cell making syngas (CO + H₂) from CO₂ and H₂O reduction at room temperature. *J. Electrochem. Soc.* **155**, B42 (2008)
61. D. Dewulf, A. Bard, The electrochemical reduction of CO₂ to CH₄ and C₂H₄ at Cu/Nafion electrodes (solid polymer electrolyte structures). *Catal. Lett.* **1**, 73 (1988)
62. R.L. Cook, R.C. Macduff, A.F. Sammells, High-rate gas-phase Co₂ reduction to ethylene and methane using gas-diffusion electrodes. *J. Electrochem. Soc.* **137**, 607 (1990)
63. R.L. Cook, R.C. Macduff, A.F. Sammells, Gas-phase Co₂ reduction to hydrocarbons at metal solid polymer electrolyte interface. *J. Electrochem. Soc.* **137**, 187 (1990)
64. M. Shibata, N. Furuya, Electrochemical synthesis of urea at gas-diffusion electrodes Part VI. Simultaneous reduction of carbon dioxide and nitrite ions with various metallophthalocyanine catalysts. *J. Electroanal. Chem.* **507**, 177 (2001)
65. M. Shibata, N. Furuya, Simultaneous reduction of carbon dioxide and nitrate ions at gas-diffusion electrodes with various metallophthalocyanine catalysts. *Electrochim. Acta* **48**, 3953 (2003)
66. Y. Hori, A. Murata, S.-Y. Ito, Y. Yoshinami, O. Koga, Nickel and Iron Modified Copper Electrode for Electroreduction of CO₂ by In-situ Electrodeposition. *Chem. Lett.* **18**, 1567 (1989)
67. Y. Hori, H. Ito, K. Okano, K. Nagasu, S. Sato, Silver-coated ion exchange membrane electrode applied to electrochemical reduction of carbon dioxide. *Electrochim. Acta* **48**, 2651 (2003)
68. S. Ikeda, T. Ito, K. Azuma, K. Ito, H. Noda, Electrochemical mass reduction of carbon-dioxide using Cu-loaded gas-diffusion electrodes .I. Preparation of electrode and reduction products. *Denki Kagaku* **63**, 303 (1995)

Nanotechnology in Electrocatalysis for Energy

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2013, XIII, 331 p. 131 illus., 48 illus. in color., Hardcover

ISBN: 978-1-4899-8058-8