FUNDAMENTALS of ELECTROCatalyst MATERIALS and INTERFACIAL CHARACTERIZATION

Energy Producing Devices and Environmental Protection

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Fundamentals of Electrocatalyst Materials and Interfacial Characterization
The unique properties of nanomaterials encourage the belief that they can be applied in a wide range of fields, from medical applications to electronics, environmental sciences, information and communication, heavy industries like aerospace, refineries, automobile, consumer and sports good, etc.

This book series will focus on the properties and related applications of nanomaterials so as to have a clear fundamental picture as to why nanoparticles are being tried instead of traditional methods. Since nanotechnology is encompassing various fields of science, each book will focus on one topic and will detail the basics to advanced science for the benefit of all levels of researchers.

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Fundamentals of Electrocatalyst Materials and Interfacial Characterization

Energy Producing Devices and Environmental Protection

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# Contents

**Preface**

**1 Physics, Chemistry and Surface Properties**

1.1 Introduction 1

1.2 The Electrochemical Interface 2

1.2.1 Conductivity and Electrical Field: Metal Versus Electrolyte 3

1.2.2 Magnitude of Double Layer Capacitance 6

1.3 Energy in Solids and Liquids: Junction Formation 9

1.4 Surface Reactivity of Low-Index Planes 14

1.5 Electron Charge-Transfer Reactions 18

1.5.1 Hydrogen Electrode vs. Oxygen Electrode 21

1.5.2 Organic-Fuels vs. Oxygen Electrode 22

1.6 The Effect of CN- Surface Coordination on Low-Index Pt Surface: ORR 26

References 29

**2 Computational Chemistry for Electro-Catalysis**

2.1 Introduction 35

2.2 Scope and Limitations of Different Models 39

2.2.1 Clusters 40

2.2.2 Slabs 49

2.2.3 Nanoparticles 59

2.3 Influence of the Support in Electrocatalysis 64

References 69

**3 The Hydrogen Electrode Reaction**

3.1 Introduction 75

3.2 Thermodynamics 77

3.3 Hydrogen Evolution Reaction-HER 78

3.3.1 HER on Platinum Catalytic Center 85

3.3.2 HER on Non-Noble Metal Catalyst Centers 90

3.4 Hydrogen Oxidation Reaction-HOR 100

References 101
3.4.1 HOR on Precious Metal Centers 108
3.4.2 HOR on Non-Precious Metal Centers 119
References 124

4 Oxygen Reduction/Evolution Reaction 143
4.1 Introduction 143
4.2 Electrolyzer Thermodynamics 146
4.3 Oxygen Reduction Reaction 148
4.3.1 ORR Pt-Based Nano-Structure Materials 157
4.3.2 Reaction Pathways 159
4.3.3 ORR on Au and Pd-Based Nano-Structure Materials 171
4.4 Oxygen Evolution Reaction 173
References 178

5 Electrochemical Energy Storage 187
5.1 Introduction 187
5.2 Basic Terminology in Batteries 188
5.3 Present Status of Electrochemical Batteries 195
5.3.1 Lead Acid Battery 196
5.3.2 Nickel-Cadmium Battery 197
5.3.3 Nickel-Metal Hydride Battery 198
5.4 Lithium Ion Battery 199
5.4.1 Insertion Electrode Materials 202
5.4.2 Conversion Reaction Electrodes 209
5.4.3 Alloy Electrodes 210
5.5 Post-Li Technologies 210
5.5.1 Na-Ion Batteries 210
5.5.2 Lithium-Sulfur Batteries 212
5.5.3 Metal Air Batteries 215
5.5.3.1 Aqueous Metal Air Batteries 216
5.5.3.2 Non-Aqueous Metal Air Batteries 218
References 220

6 Electrocatalysis and Remediation 225
6.1 Introduction 225
6.2 NOx Reduction 228
6.3 COx Reduction and Methanol Oxidation 240
6.3.1 Methanol Oxidation 246
6.3.2 SOx Reduction 249
6.3.3 Oxidation of Emergent Pollutants 254
6.4 Determination of Nitrate-Based Compounds in DNA 257
References 262

Subject Index 277
Preface

Over the years, numerous books and review articles on electrochemistry have been written because of its applicability linked to the sustainability of society.

This book addresses some essential topics in the science of energy converting devices emphasizing recent aspects of nanodivided materials in the application for the protection of the environment, storage, and energy conversion under the title of *fundamental of electrocatalysts materials and interfacial characterization*. The aim was therefore to provide the basic background knowledge. The electron transfer process and structure of the electric double layer and the interaction of species with surfaces (Chapter I) and the interaction, reinforced by DFT theory for the current and incoming generation of fuel cell scientists to study the interaction of the catalytic centers with their supports (Chapter II). The chief focus in the following chapters is on materials based on precious and non-precious centers for the hydrogen electrode (Chapter III), the oxygen electrode (Chapter IV), energy storage (Chapter V), and in remediation applications (Chapter VI), where the common issue is the rate-determining step in multi-electron charge transfer processes in electrocatalysis. These approaches are used in a large extent in science and technology, so that each Chapter demonstrates the connection of electrochemistry, in addition to chemistry, with different areas, namely, surface science, biochemistry, chemical engineering, and chemical physics.

A short list of books giving account of the fundamental progress from an academic (experimentally and theoretically) and
practical point of view is given at the end of the book to complement it.

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Physics, Chemistry and Surface Properties

1.1 Introduction

This chapter outlines, in a simplified manner, the current knowledge, regarding the electrochemical interface, and the surface-electrochemistry, surface-chemistry necessary to favor multi-electron charge transfer of most common reactions of interest for the energy conversion: chemical-electrical; electrical-chemical. This principle can be applied, e.g., to the water cycle, as well as to the carbon cycle. The interplay is very complex, since the site where the charge transfer takes place is defined by the energy fluctuating principle (Gerischer-Marcus Theory) [1, 2] between two dissimilar phases, namely, solid-liquid [3]. Similar principles can be applied to solid-solid; liquid-liquid interfaces. We will focus on the solid-liquid interface, where factors like structure, chemical nature, composition, catalytic activity, support interaction, strain,
coverage, stability conjugated with the theory assess the surface science approach to grasp the physical and chemical essentials of electrochemical generators from a fundamental point of view.

### 1.2 The Electrochemical Interface

Electrochemical energy, and storage devices have in common the electrical double layer formed between two dissimilar phases, e.g., a solid and a liquid. The former one is constituted of surface atoms with a broken symmetry (low coordination number) with respect to the underlaying atoms forming the bulk of the material capable of transporting electrons, whereas in the latter, the species responsible for such charge transportation are the anions, and cations species certainly solvated by the solvent molecules, generally water. This solid/electrolyte junction is known as the electrochemical interface, Figure 1.1. This interface is a region where the properties of each phase at the junction of two phases change with

![Figure 1.1](image)

**Figure 1.1** The electrode/electrolyte electrochemical interfaces. OHP, outer Helmholtz plane; IHP, inner Helmholtz plane.
respect to their bulk. The figure illustrates, at the junction, the well-known concept that the electrical double layer is constituted of two charged layers, namely, IHP (Inner Helmholtz Plane) a layer of adsorbed ions, and the OHP (Outer Helmholtz Plane) a layer of solvated ions. The understanding of this electrochemical interface has been done since the 1940’s, e.g., by Grahame [4, 5], and important pieces of work (experimental and theory) developed so far were recently summarized by Schmickler and Santos [3]. Considering the scheme in Figure 1.1, the immersed electrode in an electrolyte develop a potential difference as a result of a charge transfer across the two phases as a result a charge accumulation is found at the solid counter balanced by an opposite charge at the liquid phase of the interface. The solid phase, i.e., the electrode is usually a metal or an alloy, whereas the electrolyte is usually a liquid (i.e., ionic liquids, molten salts, neutral solutions). Moreover, the charge-transfer process is usually linked to phenomena such as adsorption-desorption, mass-transfer mechanisms, surface diffusion, crystallization, and so on. However, the main driving force for the charge transfer at the interface is the internal potential difference between the electrode and the electrolyte, which is associated to the double layer capacitance, therefore, to the electrode surface. The double layer at the electrode/electrolyte interface possesses electrical, compositional and structural properties, which depend on the excess of charge density and the distribution of ions, electrons, dipoles and neutral molecules at the interface.

1.2.1 Conductivity and Electrical Field: Metal Versus Electrolyte

The metal. The solid in a solid/liquid interface is generally a metal surface that carries an excess of charge. In Figure 1.1 the solid electrode, after charge transfer, presents a deficit of electrons (positive charge) and the solution an excess of electrons (negative charge). On metals the excess of charge is confined at the surface at ca. 1 Å (10⁻⁸ cm), i.e., there is no depletion layer unlike semiconductor materials. The face centered cubic (fcc) metals, such as,
Ag, Cu, Au, possess a conductivity of $0.62 \cdot 10^6$, $0.59 \cdot 10^6$, $0.44 \cdot 10^6$ $\Omega^{-1} \text{ cm}^{-1}$, respectively, whereas 1M of KCl (considered a strong concentrated electrolyte) has a conductivity of $0.11 \cdot 10^{-1} \Omega^{-1} \text{ cm}^{-1}$. There is a huge difference in the conductivity of ca. 7 orders of magnitude. The mobility of charges, $\mu$ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), in each phase, can be determined by Equation (1.1).

$$\mu = \frac{\sigma}{nq}$$

(1.1)

Where $n$ is the concentration per unit volume ($\text{cm}^{-3}$) of charge; $q$ the elementary charge ($\text{C}$), and $\sigma$ ($\Omega^{-1} \text{ cm}^{-1}$) the conductivity. The metals like Ag, Cu, and Au possess an electron concentration ($\text{cm}^{-3}$) of $5.85 \cdot 10^{22}$, $8.45 \cdot 10^{22}$, $5.90 \cdot 10^{22}$, respectively, whereas the aqueous electrolyte containing 1M KCl has a concentration of ions/$\text{cm}^3$ of $1.2 \cdot 10^{21}$. When imposing an electric field in a metal, the electrons travel opposite to this field and they can occupy these empty states with the flux of electrons, $j$, defined by equation (1.2).

$$j = \sigma E$$

(1.2)

Where, $j$ is the current density ($\text{A cm}^{-2}$), $\sigma$ is the conductivity ($\Omega^{-1} \text{ cm}^{-1}$), and $E$ is the electrical field ($\text{V cm}^{-1}$). In the electronic structure of fcc metals (i.e., Ag, Cu, Au), their conduction takes place in the $sp$-band, that is wide and quite free-electron-like. The electron-electron scattering can occur with the $d$-band. Moreover, the $4d$-electrons of Ag are ca. 4 eV away from the Fermi level, as compared to $3d$ bands in Cu, and $5d$ bands of Au that are closer to the Fermi level. This is the reason why Ag is a very good conductor of electricity.

The electrolyte. The difference of charge carriers’ concentration of ions in the electrolyte with respect to electrons in metals allows a charge space confinement that can be extended from 5 to 20 Å in the electrolyte side from the electrode surface. This thickness separating the opposite charges is known as the electrical double layer, symbolized by an electric analog symbol: a capacitor (provided with two plates of charge separated by some distance, $d$) e.g., $C_{dl}$ in Figure 1.2(d). Physically,
if we consider that, between the metal and the solution (double layer), a potential drop $\Delta \varphi$ of 1 V within the region of 5 to 20 Å will create an electrical field, $E = \frac{\Delta \varphi}{d} \approx 10^7$ V cm$^{-1}$. Moreover, under physical-chemically considerations, this electrical field can be estimated taking into consideration the interaction of

![Energy diagram of a metallic conductor showing the main parameters.](image)

![Energy diagram of a redox species in an electrolyte showing the Gaussian distribution function for the unoccupied lowest state (LUMO) and the highest occupied state (HOMO).](image)

![Solid/liquid interface at equilibrium.](image)

![Equivalent electrical circuit corresponding to a kinetic model.](image)

**Figure 1.2** (a) Energy diagram of a metallic conductor showing the main parameters. The Fermi level, $E_F$, the energy between the conduction band (CB) and the valence band (VB) overlapping. The reference energy is the vacuum (0 eV); I – The ionization energy; $\varphi$ – The work function; A – The electron affinity. (b) The energy diagram of a redox species in an electrolyte showing the Gaussian distribution function for the unoccupied lowest state (LUMO) and the highest occupied state (HOMO). The "$E_F$" corresponds to the $E_{Ox/Red}$ potential. (c) The solid/liquid interface at equilibrium ($E_F = E_{Ox/Red}$). (d) The equivalent electrical circuit corresponding to a kinetic model $C_{dl}$: double layer capacitance; $R_{ct}$: charge transfer resistance.
water molecules at the surface of a metal electrode: We start considering the length of a water dipole molecule of \( l \approx 2 \, \text{Å} \approx 2 \times 10^{-8} \, \text{cm} \), its dipole moment \( \mu \approx 1.87 \, \text{D} \approx 6 \times 10^{-28} \, \text{C} \, \text{cm} \). Therefore, the charge, \( Q \), of the dipole is: \( Q = \frac{\mu}{l} = 3 \times 10^{-20} \, \text{C} \).

With the calculated surface of water \( (A = \pi (l/2)^2) \), the number of water molecules per unit surface is \( n = 3.1 \times 10^{15} \, \text{cm}^{-2} \). Now, assuming that 1% of water dipoles are oriented, we will have \( 0.31 \times 10^{15} \, \text{cm}^{-2} \). The charge density at the interface will be: \( q = Q \cdot n = 9.3 \, \mu\text{C} \, \text{cm}^{-2} \).

Per definition, one can relate this charge and the capacitance via the equation (1.3):

\[
Q = CV = A\varepsilon\varepsilon_0 \frac{V}{d}
\]  

Since the electrical field is \( V/d \), then,

\[
E = CV = \frac{q}{\varepsilon\varepsilon_0}
\]  

Where, \( E \) is the electrical field, \( \varepsilon_0 \) the vacuum permittivity constant \( (8.85 \times 10^{-14} \, \text{F/cm}) \), and \( \varepsilon \) the water permittivity taken as 10 as a good approximation in the first layer at the surface of the electrode [6]. The permittivity of bulk water at room temperature (RT) is 80. This simple calculation also delivered an electrical field of \( E \approx 10^7 \, \text{V/cm} \).

### 1.2.2 Magnitude of Double Layer Capacitance

With the concepts outlined above, we can consider the electrical double layer as a place where no electrochemical reaction takes place, so-called an inert or an ideally polarizable interface, which is easily found experimentally as the electrode potential window where the solvent or any electrochemical process do not interfere. The solid/electrolyte interface accumulates charge on the metal, \( q_M \), and at the electrolyte, \( q_S \), so that the electroneutrality condition is fulfilled: \( q_M = -q_S \), under an applied electrode potential difference, \( \Delta\phi = \phi^M - \phi^S \), leading to the double layer capacitance:
This model was first put forward in the 1850's by Hermann von Helmholtz. The interactions between the ions and the electrode’s surface were assumed to be electrostatic in nature because of the presence of a charge density \( q_M \). The distance of approach of the ions is limited to their radius within a sphere of solvation on each ion. The potential drop between the two plates occurring linearly, allows to model electrochemical systems in terms of capacitive elements. It is clear that the model of Helmholtz could explain the existence of a capacitance, moreover, it cannot explain the capacitance variation with the applied electrode potential, nor the numerical experimental value of \( C_{dl} \). Indeed, for this latter, the experimentally observed capacitance data in a solid/electrolyte interface lies between 10–40 \( \mu F \) cm\(^{-2}\). Now, the calculated capacitance, \( C \), from equation (1.3), with \( \varepsilon(H_2O) \) of 10 and 80, is 8.85 \( \mu F \) cm\(^{-2}\) and 88.5 \( \mu F \) cm\(^{-2}\), respectively. It shows that using \( \varepsilon(H_2O) = 80 \) the numerical capacitance value is higher than the experimental one. Furthermore, the Helmholtz-model does not take into account other factors such as, diffusion/mixing in solution, adsorption at the surface and the interaction between solvent dipole moments and the electrode. This is the reason that various models were put forward to address these limitations, e.g., a model considering a diffuse layer region, as well as the use of numerical modelling to follow the redistribution effects as the electrode potential is changed. Herein, it is worth to mention succinctly the various important models regarding the electrical double layer. The historical and mathematical development are thoroughly described in electrochemistry text books, which list is given at the end of this chapter.

In the model of Gouy-Chapman (1910), the double layer is not as compact as in the Helmholtz rigid layer. The fundamental condition of this theory was to model the ions as points surrounded in the dielectric continuum of the solvent, combining
the principles of electrostatics (Poisson equation, Gauss theorem), and thermodynamics (Boltzmann equation). The resulting differential capacitance in the diffuse layers is:

\[ C_d = \left( \frac{2e^2e \varepsilon_0 C^0}{k_BT} \right)^{1/2} \cosh \left( \frac{ze \Delta \varphi}{2k_BT} \right) \]  

(1.6)

Or

\[ C_d = \frac{\varepsilon \varepsilon_0}{L_D} \cosh \left( \frac{ze \Delta \varphi}{2k_BT} \right) \]  

(1.7)

Where \( \Delta \varphi = E - E_{pzc} \), and \( L_D \) (Å) is the Debye length considered as the effective plate separation. Clearly, at high electrolyte concentrations, \( C^0 \), e.g., 0.1M of a 1:1 electrolyte one has an \( L_D = 9.6 \) Å, compared to 0.001 M, \( L_D = 304 \) Å. Equations (1.6) or (1.7) predicts correctly the minimum in the capacity at pzc (point of zero charge); otherwise it predicts an unlimited rise of the capacity. The solution to this capacity “catastrophe” was a further refinement of the model that takes into account that ions have a finite size, so that a close approach was not possible, since the ions are stopped from approaching the electrode at a distance corresponding to their radii. The Stern model (1924) accounts for the finite size of ions, and combines the Helmholtz and Gouy-Chapman models, so that the electrical layer is constituted of two parts, namely, (i) the rigid one, where the ions are found at a closest distance of the electrode surface \( (x < x_H) \) where the linear variation of the potential takes place, and (ii) the diffuse layer. Mathematically this model consists of two capacitors in series, so that the total capacitance is the double layer capacitance, \( C_{dl} \):

\[ \frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_d} \]  

(1.8)

Clearly, if \( \Delta \varphi = E - E_{pzc} \) is large, \( C_{dl} \approx C_H \); if \( \Delta \varphi = E - E_{pzc} \) is small, \( C_{dl} \approx C_d \).

Further refinement of these models was brought by the Grahame’s model (1947). This model considers that some ions (those with smaller radii), usually anions lose the solvation
shell and could approach more the electrode surface. Therefore, 
this model considers three different regions: Inner Helmholtz 
plane (IHP) having as centers the small partially solvated 
anions.; the Outer Helmholtz Plane (OHP) having as centers 
the fully solvated ions; and the outside OHP, or diffuse layer, 
cf. Figure 1.1.

1.3 Energy in Solids and Liquids: Junction 
Formation

In Solids. In a metal the Fermi level is the energy that separates 
occupied states (valence band – VB) from the empty states 
(conduction band – CB) at the absolute temperature \( T = 0 \) K, 
Figure 1.2(a). The number of electrons, \( n \), at thermal equilib-
rium is dictated by the Fermi-Dirac equation:

\[
n(E) = g(E)f(E) \tag{1.9}
\]

Where, \( g(E) \) is the density of states, \( f(E) \) is the Fermi-Dirac 
statistics obeyed by electrons.

\[
f(E) = \frac{1}{1 + e^{(E-E_F)/k_BT}} \tag{1.10}
\]

Whereas the Boltmann statistics, equation (1.11) works for 
system of non-interacting particles, electrons have a strong 
repulsive interaction.

\[
p(E) = Ae^{\left(-\frac{E}{k_BT}\right)} \tag{1.11}
\]

At absolute zero all energies below \( E_F \) have an occupa-
tion probability of 1; and above \( E_F \) are empty, so that \( f(E)=0 \).
Therefore, at any temperature \( f(E) \) at \( E_F \) is 0.5, Figure 1.2(a). 
The number of occupied states, \( n(E) \), can be calculated from 
density of states, \( g(E) \), and the probability of occupation, \( f(E) \).
Integrating equation (1.9) from the bottom of the band to \( E_F \), 
with \( f(E)=1 \), results equation (1.12) [7].
Electrocatalyst Materials and Interfacial Characterization

\[ n(E) = 8\pi\sqrt{2} \left( \frac{m_e}{\hbar^2} \right)^\frac{3}{2} \frac{2}{3} E_F^2 \frac{E}{E_F} \] (1.12)

Where, \( m_e \) is the free electron mass, \( h \), the Planck’s constant. Electrons in the outer shell of Ag are delocalized and are free to move in the material. Implementing in equation (1.5) the Fermi energy of Ag \( (E_F = 5.5 \text{ eV}) \), \( n(E) = 5.08 \cdot 10^{22} \text{ cm}^{-3} \), a value very close to the number of atoms per unit volume of Ag metal \( (5.85 \cdot 10^{22} \text{ cm}^{-3}) \). Each atom of Ag contributes with one electron, so that \( n(E) \) is the number of electrons that fills the states below \( E_F \); and above the Fermi level (empty states), there are the same available states to be occupied by electrons.

A comparison of the occupation probability using equations (1.10) and (1.11) is made in Table 1.1. This Table shows when \( (E - E_F) >> k_B T \) \( (0.0256 \text{ eV at } T = 298 \text{ K}) \) the behavior of the Fermi function approaches that of the Boltzmann function. Then, for \( 10 \cdot k_B T = 0.256 \text{ eV} \), this energy is low compared to the band-gap of one of the most technologically advanced semiconductors: Si \( (E_g = 1.1 \text{ eV}) \), meaning that a nice approximation to the electron occupation in semiconductors can be calculated by the Boltzmann function.

**Table 1.1** \( f(E) \) Versus \( p(E) \) at \( x \cdot k_B T \).

<table>
<thead>
<tr>
<th>((E - E_F))</th>
<th>(P(E))</th>
<th>(F(E))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 \cdot k_B T)</td>
<td>0.367</td>
<td>0.26</td>
</tr>
<tr>
<td>(2 \cdot k_B T)</td>
<td>0.135</td>
<td>0.12</td>
</tr>
<tr>
<td>(10 \cdot k_B T)</td>
<td>(4.5 \cdot 10^{-5})</td>
<td>(4.5 \cdot 10^{-5})</td>
</tr>
</tbody>
</table>

In electrolyte. The energy of a redox couple (Ox/Red) in an electrolyte is defined by the thermodynamic potential, \( E_{O/R}^0 \), with respect to a reference: The Standard Hydrogen Electrode (SHE). Just like the model in the solids, see above, the empty, and occupied states are given by the Ox, and Red species, respectively, and in equimolar concentration \([\text{Ox}] = [\text{Red}]\), the equilibrium potential, \( E \), after the Nernst
equation is \( E = E^{0}_{O/R} = E_{F,\text{redox}} \). These empty and occupied states extend over a range of energies dictated by the reorganization energy, \( \lambda \), see Figure 1.2(b). The electrochemical reaction can be represented by equation (1.13). This simple representation of the redox reaction shows that the molecular structure of the solvent in the vicinity of ions is different from that of pure solvent due to the ion-ion interactions. The solvation layer differs significantly for the two types of ions, i.e., the charged ion is always more strongly solvated due to the more important ion-dipole interactions.

\[ \text{Ox}_{\text{solv}} + e^{-} \rightleftharpoons \text{Red}_{\text{solv}} \quad (1.13) \]

In addition, the structure of the solvation shell permanently fluctuates due to the thermal movement. Considering that an electronic transition is very fast compared to the thermal vibration of the molecules of solvation (Franck-Condon principle), the redox reaction can be separated into two consecutive steps, namely, (i) transfer by tunneling of electron through the solvation layer, which remain unchanged, and (ii) the reorientation of the molecules of the solvation with release of energy consumption or reorganization, \( \lambda \), in other words, during the reorganization of the solvation, the reorganization energy \( \lambda_{\text{Ox}} \), and \( \lambda_{\text{Red}} \), is released, Figure 1.2(b). This simplified picture shows the energy as a function of the density of states (DOS) of the reactive species in the electrolyte. Their corresponding density of states, \( D \), for Ox and Red can be represented by the equations (1.14) and (1.15).

\[ D_{\text{Ox}} (E) = C_{\text{Ox}} W_{\text{Ox}} (E) \quad (1.14) \]
\[ D_{\text{Red}} (E) = C_{\text{Red}} W_{\text{Red}} (E) \quad (1.15) \]

Where \( C \) is the concentration of the respective species in the electrolyte, \( W \) is the probability to find an empty state (Ox) or occupied state (Red). As shown in the Figure 1.2(b) the energy
The level of the species possesses a Gaussian distribution shape for $W(E)$, mathematically defined as:

$$W(E) = \left(\frac{\pi 4k_B T}{\lambda}\right)^{-1/2} \exp\left(-\frac{(E-E_0)^2}{4\lambda k_B T}\right)$$  \hspace{1cm} (1.16)

One recognizes that $\lambda$ in the exponential term is the reorganization energy. The energy levels on solid (metal or semiconductor) combined with those of the electrolyte containing active species provide hints to the electrochemical processes understanding and constitutes the basis of the fluctuating energy Gerischer-Marcus theory [1, 2].

**Creating the junction.** For a given metal, Figure 1.2(a) the Fermi energy, $E_F$, represents the free energy per electron or the electrochemical potential for electrons, $\mu_e$. This factor is a measure of the potential of an electron to perform electrical work (e∙V) over an electrochemical reaction process, see Chapters III-VI.

The solid/solid junction between two metals will be brought through their different work functions, $\phi_M$, with respect to the vacuum to build a difference named chemical potential, $\Delta \mu$, meaning that the system can deliver an external work. Moreover, this is not possible, since electrons are immediately transferred from one metal to another, until thermodynamic equilibrium is reached, or the free energy per electron $\mu_e$ for the whole system is minimized, and uniform across the two metals, in other words, $\Delta \mu = 0$ or $\Delta E_F = 0$. Therefore, an electrical work in this kind of junction can only be obtained by applying an external energy source (i.e., heat, potential) to rise the Fermi level of one metal with respect to the other one. Just like the metal/metal junction, the metal/electrolyte junction can be formed, as schematically represented in Figure 1.2(c). Clearly, this junction is established after the thermodynamic equilibrium is attained, i.e., $E_F = E_{F,\text{redox}}$, with the consequence that the electrical double layer at the metal/electrolyte interface is established, (see section 1.2.2). The metal and redox species density of states overlaps, meaning that if the
Fermi level of the metal is moved by a change in the applied electrode potential (bias), electronic states in the electrolyte must be available at the same energy as that of electrons in the metal, and as a consequence tunneling of electrons (radiationless process) takes place. This phenomenon takes place with the necessary energy to support the electrochemical rates of reactions and finds its principle through the “fluctuating energy model” of Gerischer-Marcus [1, 2, 8–11].

The bias potential to carry out the reaction: \( \text{Ox}_{\text{solv}} + e^{-M} \rightarrow \text{Red}_{\text{solv}} \) changes the probability function \((0, 1)\), cf. Equations (1.10).

\[
\begin{align*}
N_{\text{occ}} (E) &= f (E) \rho (E) \quad (1.17) \\
N_{\text{empt}} (E) &= [1 - f (E)] \rho (E) \quad (1.18)
\end{align*}
\]

\( \rho(E) \) (cm\(^{-2}\) eV\(^{-1}\)) is the density of states. Resulting in the distributions of the occupied metal states, eq. (1.17) and \( \text{Ox}_{\text{solv}} \) states:

Where;

\[
W_{\text{Ox}} (\lambda, E) = \left(4\pi\lambda k_B T\right)^{-1/2} \exp \left[\frac{-(E - E^0 - \lambda)^2}{4\lambda k_B T}\right] \quad (1.20)
\]

\( N_A \), is the Avogadro number. The application of equations (1.17) and (1.19) leads to the determination of the rate of electron transfer dictated by the law of mass action:

\[
\text{Rate} = \nu \int_{-\infty}^{+\infty} \varepsilon_{\text{red}} (E) D_O (\lambda, E) AN_{\text{occ}} (E) \, dE \quad (1.21)
\]

Where \( \varepsilon_{\text{red}} \) (cm\(^3\) eV) is a constant, and \( A \) (cm\(^2\)) is the area. Rearranging (1.21), one obtains the cathodic rate constant, \( k_f \).

\[
k_f = \nu \int_{-\infty}^{+\infty} \varepsilon_{\text{red}} (E) W_O (\lambda, E) f (E) \rho (E) \, dE \quad (1.22)
\]

Since the cathodic overpotential, \( \eta_c = -(E-E^0) \) is sufficiently large, the rate constant, \( k_b \), for the oxidation current is zero.

\[
k_b = \nu \int_{-\infty}^{+\infty} \varepsilon_{\text{ox}} (E) W_R (\lambda, E) [1 - f (E)] \rho (E) \, dE \approx 0 \quad (1.23)
\]
1.4 Surface Reactivity of Low-Index Planes

Surface science studies of well-defined systems have provided interesting information as to the surface atoms reactivity, and stability bridging the ideal material’s gap science with the real-world materials, namely, nano-derived materials. Of special interest to catalysis and/or electrocatalysis concerns the dissociative adsorption energetics involved in the rate-limiting step in a catalytic and/or electrocatalytic cycle. This aspect is strongly related to the electronic factors that favor the surface chemical bond formation. Herein, the key word is the “interfacial reaction based on strong interactions”. Unlike the fluctuating energy model described above, the bond formation through coordination chemistry is accompanied by a shift of the energy levels, i.e., bonding and antibonding orbitals [12], so that one can assume that the broad bell-shaped distribution of redox species, Figure 1.2(c), can change to a narrow δ-shape-like distribution. One of the tasks in surface electrochemistry is to establish the relation between surface structure and reactivity of species, with special regards on the electrocatalytic processes discussed so far in the next chapters.

The electrochemical reactivity investigations of low-index planes started with the pioneering work of Clavilier et al., [13] Platinum was the material of choice. This material has an fcc structure, as well as others like, Ag, Au, Cu, Pd, etc. The atoms in a single crystal are arranged in a three-dimensional periodic lattice. The faces of a single crystal are characterized by Miller indices (hkl), representing the reciprocal intercepts of the plane under consideration with x-, y- and z-axes. The three low-index planes are: (100, 110) and (110). Figure 1.3 (a) summarizes the ideal three low-indexes, together with computer generated respective surfaces in a Ball model representation. Moreover, real surfaces present inhomogeneities and defects, e.g., adatoms, islands, vacancies, holes, monoatomic steps and
screw dislocations. Considering all these factors, though, it was possible to obtain high-resolution images thanks to the application of the scanning tunneling microscopy (STM) technique on the low-index surfaces of Au [14], see Figure 1.3(b). Due to surface energy, the surface atoms can take different positions from those expected from the bulk structure termination. As pointed out by Dakkouri et al., [14] the gold single crystal surface shows surface reconstruction after flame-annealing, a phenomenon observed when the materials are submitted to ultra high vacuum (UHV) studies. Platinum single crystals, on the other hand, behave differently under flame-annealing, as compared to samples studied in UHV. Experiments under low pressure (<10⁻³ mbar), summarized by Imbihl and Ertl [15], pointed out that the surface reconstruction of platinum single crystals takes place on the open surfaces (100) and (110) only, as shown in Figure 1.3(c). The (111) surface is more stable with the bulk 1 × 1 termination. The (100) and (110) turns to a “quasi”

Figure 1.3 (a) Low-index (100, 110) and (111) fcc surfaces; (b) The high-resolution TEM images of Au surfaces; (c) The surface reconstruction on (100) and (110) surfaces.
hexagonal surface, and to $1 \times 2$ missing row geometry, respectively. The critical control of an adsorbate coverage, e.g., CO, can revert the surface reconstruction in a reversible manner, in other words phase transition takes place: $1 \times 1 \rightleftharpoons \text{hex}$; and $1 \times 1 \rightleftharpoons 1 \times 2$ phases. This is the basis to understand the surface dynamics because of the difference of the surface energy of one phase with respect to the other, otherwise, a difference in the adsorption energy must be the driving force. Unlike the solid/gas interface, the solid/liquid interface, in electrochemical processes, can present one more degree of complexity. However, similar thermodynamic and kinetic principles prevail. To show the richness of the structure-activity relation, the next paragraph is devoted to discuss succinctly the electrochemical response of low-index surface of single crystals based on platinum recorded in different containing anions acid media via the cyclic voltammetry technique [16]. Other examples on other noble transition metal surfaces have been summarized elsewhere [17, 18].

Striking effects of the electrolyte composition are generated on ($hkl$) surfaces, since these surfaces present a long-range atomic order and are sensitive to the anion adsorption, see Section 1.6. Figure 1.4 shows the fingerprints of $hkl$-Pt submitted to a scan rate of 50 mV/s in acid-containing sulfate ($\text{SO}_4^{2-}$ or $\text{HSO}_4^-$), and perchlorate ($\text{ClO}_4^-$) anions. The responses of (111, 110), and (100) correspond to the $\text{H}_{\text{upd}}$ region (potential interval within 0.5 to 0 V/RHE). The H-coverage takes place on surfaces with different symmetries, since each $hkl$ has different adsorption energies. Pt atoms are arranged in different unit cells, Figure 1.3 (a), with a difference in the overlapping between the electronic local density of a “Site” with the adsorbed hydrogen. We can then perceive that the strong adsorbed hydrogen peak corresponds to the electrochemical response at the (100) surface, whereas the weakly adsorbed peaks are generated on (110) and (111) surfaces. Table 1.2, summarizes the number of atoms per unit surface, $n$, as well as the charge density, $q$,
The table indicates that the charge density is well-suited in all surfaces, so that the average charge density is 197 μC cm$^{-2}$.

**Figure 1.4** Cyclic voltammograms at 50 mV/s of (hkl) Pt recorded in acid (H$_2$SO$_4$, and HClO$_4$). Adapted from reference [21].

**Table 1.2** Charge density on hkl surface of Pt (fcc).

<table>
<thead>
<tr>
<th>Surface (hkl)</th>
<th>$N$ atom/cm$^2$</th>
<th>Surf. conc. mol/cm$^2$</th>
<th>q μC/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>1.28·10$^{15}$</td>
<td>2.13·10$^{-9}$</td>
<td>205</td>
</tr>
<tr>
<td>(110)</td>
<td>0.92·10$^{15}$</td>
<td>1.53·10$^{-9}$</td>
<td>147</td>
</tr>
<tr>
<td>(111)</td>
<td>1.50·10$^{15}$</td>
<td>2.49·10$^{-9}$</td>
<td>240</td>
</tr>
</tbody>
</table>
This data approaches the value used for a polycrystalline surface, i.e., 210 μC cm\(^{-2}\) [19]. This charge density corresponds to a full H monolayer coverage, a parameter that is commonly used to determine the real surface area of nanoparticulated platinum, see Chapters III-IV. Another important aspect shown in Figure 1.4 is that the H monolayer coverage is affected by the specific adsorption of anions present in the acid electrolyte. The interesting phenomenon observed on (111) surface was unraveled combining electrochemistry with UHV experiments [20]. The peculiar spike, in sulfuric acid, on Pt (111) surface was named the “butterfly” feature. Such spike reveals the transition of the SO\(_4^{2-}\) (or HSO\(_4^{-}\)) adlayer between disordered and ordered states [21, 22].

### 1.5 Electron Charge-Transfer Reactions

The electron charge transfer can be represented with the general electrochemical equation (1.24), cf. equation (1.13).

\[
\nu_{ox} Ox + ne^- \xrightarrow{k_f} \nu_{red} Red
\]  

(1.24)

Where, \(\nu\) is the stoichiometric factor, and \(n\) is the number of electrons exchanged to form the species \(Red\). Moreover, the electrochemical reactions of technological interest are multielectronic, \(n > 1e^-\), e.g., equations (3.5) (4.1).

Conjugating all the concepts discussed in sections 1.2 to 1.4, the overlapping degree of the occupied states (electrons in the metal) versus the empty states (Ox species in the electrolyte), within the fluctuating energy model of Gerischer-Marcus, will favor the reaction reduction kinetics of the reaction in eq. (1.24). Herein, for the sake of simplification, we do not consider the adsorption nor the diffusion processes. Equation (1.22) can be linked to the Arrhenius equation:

\[
k_f = A_f e^{-\frac{\Delta E}{k_B T}}
\]  

(1.25)
Where, $A_f$ is a constant term related to the transition theory and frequently assumed as $10^4 \ \text{cm s}^{-1}$, $\Delta E$ is the activation energy dictated by the potential energy surfaces and electron-transfer probability [2, 9] of the Ox/Red species in the solution, cf. Figure 1.2(b). This activation energy $\Delta E$ within the Marcus’ theory is given by:

$$\Delta E = \frac{(\Delta G + \lambda)}{4\lambda} = \frac{\lambda}{4} \left(1 + \frac{\Delta G}{\lambda}\right)^2 \quad (1.26)$$

Where, $\Delta G = e \cdot \eta \ \text{(eV)}$; the overpotential, $\eta = E_{eq} - E^0$; $\lambda$ is the reorganization energy. Substituting (1.26) in (1.25) and rearranging for $n = 1$, we have:

$$k_f = A_f e^{\frac{\lambda}{4k_BT}} e^{-\frac{\alpha e\eta}{k_BT}} \quad (1.27)$$

$$k_f \approx k^0 e^{-\frac{\alpha e\eta}{2k_BT}} \quad (1.28)$$

Where, $k^0$ is the reduction and the oxidation rate constant at the standard potential, $E^0$. From equation (1.28) $\frac{1}{2} = \alpha_c$ has to be related to the cathodic charge transfer coefficient of the Butler-Volmer equation. Usually for a simple charge transfer process $\alpha_a$ and $\alpha_c$ are constants with values of 0.5, therefore, at any electrode potential $\alpha_a + \alpha_c = 1$, to account for a reduction and oxidation symmetric electrochemical process. Per definition, the kinetic current is $I_k = nFAkC$. The total kinetic current, $I_k = I_a + I_c$, can be then expressed as:

$$I_k = I_a + I_c = nFACk_bC_{Red}(0, t) - k_fC_{Ox}(0, t) \quad (1.29)$$

Where $A$ is the electrode surface area, $F$ is the Faraday constant (for one mol of species), $C(0, t)$ the species concentration at the surface of the electrode. With the substitution of the corresponding rate constants (i.e., equation (1.28)) we obtain the general Butler-Volmer equation:

$$I_k = nFAl^0 \left[ C_{Red}(0, t) e^{-n\frac{F}{RT}(1-\alpha_c)(E-E^0)} - C_{Ox}(0, t) e^{n\frac{F}{RT}\alpha_a(E-E^0)} \right] \quad (1.30)$$
Or expressed in terms of current density, $j_k$, a pure charge transfer process. The Nernst equation at equilibrium is:

$$\frac{C_{Ox}(0,t)}{C(0,t)} = e^{\frac{F}{RT}(E_{eq} - E^0)}$$  \hspace{1cm} (1.31)

At equilibrium the corresponding concentration in the bulk of the solution, $C^*$, can be used in the equation (1.31). In the pure kinetic regime, the ratio of the species concentration at the surface with respect to the concentration of the same species in the bulk of the solution, $C(0,t)/C^*$ is ca. 1, and applying $E = E^0 + \eta$ in equation (1.30) we obtain the kinetic Butler-Volmer equation:

$$j_k = j_0 \left[ e^{(1-\alpha a)n\frac{F}{RT}\eta} - e^{-\alpha c n\frac{F}{RT}\eta} \right]$$  \hspace{1cm} (1.32)

The graphical representation of equation (1.32) is shown in Figure 1.5. With a large overpotential, $\eta \to \infty$, eq. (1.32) simplifies to the well-known Tafel equation:

$$\pm \eta(j) = a + b \ln |j|$$  \hspace{1cm} (1.33)

Where, $b$ is the Tafel slope ($\pm 2.303 \frac{RT}{\alpha F}$). Equation (1.33) is graphically presented in Figure 1.5(b). The extrapolation to $\eta = 0$ gives the exchange current density, $j_0$. Its magnitude is a metric of the electrocatalytic power of electrode materials.