Before treating processes at the electrochemical interface, it is useful to re-
view a few basic properties of the adjoining phases, the electrolyte and the
electrode. So here we summarize important properties of metals and semi-
conductors. Liquid electrolyte solutions, which are the only electrolytes we
consider in this book, will be treated in the next chapter. These two chapters
are not meant to serve as thorough introductions into the physical chemistry
of condensed phases, but present the minimum that a well-educated electro-
chemist should known about solids and solutions.

2.1 Metals

In a solid, the electronic levels are not discrete like in an atom or molecule,
but they form bands of allowed energies. In an elemental solid, these bands are
formed by the overlap of like orbitals in neighboring atoms, and can therefore
be labeled by the orbitals of which they are composed. Thus, we can speak of a
1s or a 3d band. The bands are the wider, the greater the overlap between the
orbitals. Therefore the bands formed by the inner electron levels are narrow;
they have low energies and generally play no role in bonding or in chemical
reactions. The important bands are formed by the valence orbitals, and they
are of two types: the s and p orbitals tend to have similar energies, they
overlap well, and they form broad sp bands. In contrast, the d orbitals are
more localized, their overlap is smaller, and they form rather narrow d bands.

At $T = 0$ the bands are filled up to a certain level, the Fermi level $E_F$. It
is a characteristic of metals that the Fermi level lies inside an energy band,
which is therefore only partially filled. This is the reason why metals are good
conductors, because neither empty not completely filled bands contribute to
the conductivity.\footnote{The latter fact may seem a little surprizing. The actual proof is not simple, but,
naively speaking, the electrons cannot move because they have nowhere to go.} At finite temperatures, electrons can be excited thermally
to levels above the Fermi level, leaving behind an unoccupied state or hole. 

The distribution of electrons and holes is restricted to an energy region of a few $k_B T$ around the $E_F$. Quantitatively, the probability that an energy level of energy $\epsilon$ is filled, is given by the Fermi–Dirac distribution depicted in Fig. 2.1:

$$ f(\epsilon) = \frac{1}{1 + \exp\left(\frac{\epsilon - E_F}{k_B T}\right)} $$

(2.1)

Strictly speaking, this equation should contain the electrochemical potential of the electrons instead of the Fermi level, but for metal near room temperature, which we consider here, the difference is negligible.

At room temperature, $k_B T \approx 0.025 \text{ eV}$; often energies of this order of magnitude are negligible, and the Fermi–Dirac distribution can then be replaced by a step function:

$$ f(\epsilon) \approx H(E_F - \epsilon), \quad H(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x \leq 0 \end{cases} $$

(2.2)

For high energies the Fermi–Dirac distribution goes over into the Boltzmann distribution:

$$ f(\epsilon) \approx \exp\left(-\frac{\epsilon - E_F}{k_B T}\right) \quad \text{for} \quad \epsilon \gg E_F $$

(2.3)

We also note the following symmetry between the probability of finding an occupied and an empty state (hole):

$$ 1 - f(\epsilon) = f(-\epsilon) $$

(2.4)

The distribution of the electronic levels within a band is given by the density of states (DOS). In electrochemistry, the DOS at the surface is of primary importance. It differs somewhat from the DOS in the bulk because of the different coordination of the surface atoms. Figure 2.2 shows the DOS at

![Fig. 2.1. Fermi–Dirac distribution.](image-url)
The (111) surface of silver – the notation will be explained in the next section. The $sp$ band is wide and has a pronounced maximum near $−6$ eV below the Fermi level, which is mostly due to the $s$ states. In contrast, the $d$ band is narrow and ends several eV below the Fermi level. We will see later, that this distribution of the $d$ band has a significant effect on the catalytic properties of silver.

![Density of States](image)

**Fig. 2.2.** Densities of state for the $d$ band and the $sp$ band at the Ag(111) surface. Their integrals has been normalized to unity, and the Fermi level has been taken as the energy zero.

### 2.2 Single crystal surfaces

The structure of electrode surfaces is of primary importance for electrochemistry. Fundamental research is nowadays mostly done on single crystals, which have a simple and well-defined surface structure. Many metals that are used in electrochemistry (Au, Ag, Cu, Pt, Pd, Ir) have a *face-centered cubic* (fcc) lattice, so we will consider this case in some detail. For other lattice structures we refer to the pertinent literature and to Problem 1.

Figure 2.3 shows a conventional unit cell of an fcc crystal. It consists of atoms at the eight edges of a cube and at the centers of the six sides. The length of the side of the cube is the *lattice constant*; for our present purpose we may assume that it is unity. The lattice of an infinite, perfect solid is obtained by repeating this cubic cell periodically in all three directions of space.
Fig. 2.3. Conventional unit cell of a face-centered cubic crystal. The lattice contains the points at the corners of the cube and the points at the centers of the six sides.

Fig. 2.4. The principal lattice planes of a face-centered cubic crystal and the principal lattice planes.

A perfect surface is obtained by cutting the infinite lattice in a plane that contains certain lattice points, a lattice plane (Fig. 2.4). The resulting surface forms a two-dimensional sublattice, and we want to classify the possible surface structures. Parallel lattice planes are equivalent in the sense that they contain identical two-dimensional sublattices, and give the same surface structure. Hence we need only specify the direction of the normal to the surface plane. Since the length of this normal is not important, one commonly specifies a normal vector with simple, integral components, and this uniquely specifies the surface structure.

For an fcc lattice a particularly simple surface structure is obtained by cutting the lattice parallel to the sides of a cube that forms a unit cell (see Fig. 2.5a). The resulting surface plane is perpendicular to the vector (1,0,0); so this is called a (100) surface, and one speaks of Ag(100), Au(100), etc., surfaces, and (100) is called the Miller index. Obviously, (100), (010), (001) surfaces have the same structure, a simple square lattice, whose lattice constant is $a/\sqrt{2}$. Adsorption of particles often takes place at particular surface sites, and some of them are indicated in the figure: The position on top of a
lattice site is the atop position, fourfold hollow sites are in the center between the surface atoms, and bridge sites (or twofold hollow sites) are in the center of a line joining two neighboring surface atoms.

The densest surface structure is obtained by cutting the lattice perpendicular to the [111] direction (see Fig. 2.5b). The resulting (111) surface forms a triangular (or hexagonal) lattice and the lattice constant is $a/\sqrt{2}$. Important sites for adsorption are the atop, the bridge, and the threefold hollow sites (Fig. 2.5b).

The (110) surface has a lower density than either the (111) or the (100) planes (Fig. 2.5c). It forms a rectangular lattice; the two sides of the rectangle are $a$ and $a/\sqrt{2}$. The resulting structure has characteristic grooves in one direction.

The three basal planes, (100), (111) and (110), define the vertices of a stereographic triangle [2]. When these surfaces are appropriately treated by annealing, they show large, highly uniform terraces. However, the catalytic activity is sometimes better at defect sites. The simplest example of a defect is a vacancy or its opposite, an adatom. In addition, dislocations in the bulk propagating outside of the crystal produce mesoscopic defects, which appear as steps at the surface.

An interesting method to systematically investigate mesoscopic defects is to cut the crystal at a small angle $\theta$ with respect to one of the basal planes to expose a high index plane consisting of terraces of low index planes, with constant width, linked by steps often of monoatomic height. The terraces can extend to large distances in a given direction of the crystal. These surfaces are called vicinal surfaces and the terrace/step geometry is determined by the cutting angle. In Fig. 2.6 we show three different stepped surfaces, the (997),

Fig. 2.5. Lattice structures of single crystal surfaces: (a) fcc(100), (b) fcc(111), (c) fcc(110).
Fig. 2.6. Examples of vicinal surfaces. A bar across a Miller index indicates a negative number.

The (755) and the (911). They were obtained cutting the crystal at 6.5° and 9.5° with respect to the (111) plane for the two first, but towards different directions, and at 9.0° with respect to the (100) plane for the latter. The (997) and the (755) have (111) terraces of different lengths, and monoatomic (111) and (100) steps, respectively. A more convenient nomenclature for these high index faces, which indicates better their structures, is that proposed by Lang et al. [1] and it is also given in the figure. This is equivalent to a high Miller index and has the form: \([m(hkl) \times n(h'k'l')]\), where the first part designates a terrace of Miller index \((hkl)\) with \(m\) infinite atomic rows and the second part indicates a step of Miller index \((h'k'l')\) and \(n\) atomic layers high. Obviously, this are nominal structures; depending on their thermal stability, they may undergo reconstruction (see Chap. 16).

### 2.3 Semiconductors

Electronic states in a perfect semiconductor are delocalized just as in metals, and there are bands of allowed electronic energies. In semiconductors the current-carrying bands do not overlap as they do in metals; they are separated by the band gap, and the Fermi level lies right in this gap (see Fig. 2.7).

The band below the Fermi level, which at \(T = 0\) is completely filled, is known as the valence band; the band above, which is empty at \(T = 0\), is the conduction band. In a pure or intrinsic semiconductor, the Fermi level is close to the center of the band gap. At room temperature a few electrons
are excited from the valence into the conduction band, leaving behind electron vacancies or holes (denoted by $h^+$). The electric current is carried by electrons in the conduction band and holes in the valence band. Just like in metals, the concentrations $n_c$ of the conduction electrons and $p_v$ of the holes are also governed by Fermi statistics. Denoting by $E_c$ the lower edge of the conduction band, and by $N_c$ the effective density of states at $E_c$, the concentration of electrons is:

$$n_c = N_c f(E_c - E_F) \approx N_c \exp\left(-\frac{E_c - E_F}{kT}\right) \quad (2.5)$$

The last approximation is valid if $E_c - E_F \gg kT$ (i.e., if the band edge is at least a few $kT$ above the Fermi level), and the Fermi–Dirac distribution $f(\epsilon)$ can be replaced by the Boltzmann distribution. Similarly, the concentration of holes in the valence band is:

$$p_v = N_v [1 - f(E_v - E_F)] \approx N_v \exp\left(-\frac{E_F - E_v}{kT}\right) \quad (2.6)$$

where $E_v$ is the upper edge of the valence band, and $N_v$ the effective density of states at $E_v$. The last approximation is valid if $E_F - E_v \gg kT$. If the Fermi level lies within a band, or is close (i.e. within $kT$) to a band edge, one speaks of a degenerate semiconductor.

The band gap $E_g$ of semiconductors is typically of the order of 0.5–2 eV (e.g., 1.12 eV for Si, and 0.67 eV for Ge at room temperature), and consequently the conductivity of intrinsic semiconductors is low. It can be greatly enhanced by doping, which is the controlled introduction of suitable impurities. There are two types of dopants: Donors have localized electronic states with energies immediately below the conduction band, and can donate their
electrons to the conduction band; in accord with Eq. (2.5) this raises the Fermi level toward the lower edge of the conduction band (see Fig. 2.8a). Semiconductors with an excess of donors are \textit{n-type}, and the electrons constitute the \textit{majority carriers} in this case, and the holes are the \textit{minority carriers}. In contrast, \textit{acceptors} have empty states just above the valence band, which can accept an electron from the valence band, and thus induce holes. Consequently, the Fermi level is shifted toward the valence band (see Fig. 2.8b); we speak of a \textit{p-type} semiconductor, and the holes constitute the majority, the electrons the minority carriers.

### 2.4 Comparison of band structures

Figure 2.9 shows schematically the band structure of a few typical electrode materials, three metals (platinum, gold and silver) and a semiconductor (silicon). All three metals possess a wide \textit{sp} band extending well above the Fermi level. However, the \textit{d} bands are different. The position of the \textit{d} band of silver is lower than that of gold, and both lie lower than that of platinum. In the latter case the \textit{d} band even extend about 0.5 eV above the Fermi level. As we shall see later, these differences are crucial for the electrocatalytical properties of these materials.

According to the Fermi distribution, all electronic states below the Fermi level are occupied for the four materials, although for the metals a small numbers of electrons can be excited thermally within an energy range of about \( kT \) around the Fermi level. This effect is represented by the shadowing near the \( E_F \). In the case of the semiconductor, the band gap of undoped silicon is too large to allow the electrons to be excited thermally into the conduction band, since the band gap \( E_g \) is much wider than the thermal energy.
2.4 Comparison of band structures

Fig. 2.9. Band structures of a semiconductor and a few metals (schematic). The energies are not to scale.

Fig. 2.10. One-dimensional model for few typical band structures as a function of the wave-vector $k$.

Figure 2.9 just shows the allowed energy levels, but contains no information about the wave-functions. In a solid, the electronic wavefunctions depend on the wavenumber $k$. In the simple free electron model, the corresponding wavefunctions are simply plane waves of the form $\exp(ikx)$, with momenta $\hbar k$ and energy $E_k = \hbar^2 k^2 / 2m$. However, in a real crystal the electrons experience the three-dimensional periodic potential of the nuclei. While the vector $k$ can still be used as a quantum number, the expression for the energy is no longer simple. We shall need this $k$ dependence of the energy only in Chap. 11, when we consider optical excitations. For a basic understanding it is sufficient to consider a one-dimensional case, in which the electrons experience a periodic
potential with lattice constant $a$. The periodicity in space induces a corresponding periodicity in $k$, and it is sufficient to consider values of $k$ in the range $[0, \pi/a]$, and plot $E(k)$ in this range.

Figure 2.10 shows a few typical cases. Note that the minimum of the conduction band and the valence band need not coincide, as in the second figure from the left. This can also happen in semiconductors, and will be treated in Chap. 11.

Problems

1. (a) Consider the second layer beneath an fcc(111) surface and verify, that there are two different kinds of threefold hollow sites on the surface. (b) The conventional unit cell of a body-centered cubic (bcc) lattice consists of the corners and the center of a cube. Determine the structures of the bcc(111), bcc(100), and bcc(110) surfaces.

2. One-dimensional free electron gas We consider a simple model for a one-dimensional solid. It is represented by a box extending between $x = 0$ and $x = L$ with infinite walls. This is a well-known problem in quantum mechanics. Show that the wavefunctions have the form:

$$\phi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin(n\pi x/L), \quad n \in \mathbb{N} \quad (2.7)$$

with an energy:

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n}{2L}\right)^2 \quad (2.8)$$

Let $N$ be the total number of electrons in the solid, which we can take to be an even number. Using the fact, that each level $n$ can be occupied by two electrons of opposite spin, show that the Fermi energy is:

$$E_F = \frac{\hbar^2}{2m}\left(\frac{N}{4L}\right)^2 \quad (2.9)$$

Calculate the Fermi energy for the case where the density per length is $N/L = 0.5$ electrons per Å. Show that for sufficiently large $N$ the total energy of the ground state (at $T = 0$) is given by:

$$E_0 = \frac{1}{3}NE_F \quad (2.10)$$

In the limit of $L \to \infty$, the quantum number $n$ becomes continuous. The density of states $\rho(\epsilon)$ is the number of electron states per unit of energy. Using Eq. (2.8), show that:

$$\rho(\epsilon) = 2\frac{dn}{d\epsilon} = \frac{4L}{h} \left(\frac{m\epsilon}{2}\right)^{1/2} \quad (2.11)$$

References

Interfacial Electrochemistry
Schmickler, W.; Santos, E.
2010, XII, 270 p., Hardcover
ISBN: 978-3-642-04936-1