13 Solar Photoelectrochemical Production of Hydrogen

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13.1 Introduction

This chapter is focused on photoelectrochemical water splitting using titanium dioxide, TiO$_2$, as the photoelectrode for photoelectrochemical cells (PECs). It is shown that commercial TiO$_2$ may be used as a raw material for processing of well-defined TiO$_2$-based photosensitive oxide semiconductors (POSs) [1,2].

The use of TiO$_2$ for water photolysis has been reported for the first time by Fujishima and Honda [3]. Because of the importance of TiO$_2$ in photoelectrochemical energy conversion, as well as in other environmentally friendly technologies, this chapter provides an extensive outline on its performance-related properties, including electronic structure, charge transport, surface and near-surface properties, and photoreactivity. It is shown that these functional properties are closely related to the disorder of point defects [2]. This relationship applies for all nonstoichiometric compounds. Therefore, defect chemistry may be used as a framework for the formation of oxide semiconductors with enhanced performance in a range of applications. Consequently, the properties of nonstoichiometric oxides must be considered in terms of all lattice species, including the basic lattice elements and lattice imperfections, such as intrinsic and extrinsic defects. This chapter outlines the basic concepts of defect chemistry for nonstoichiometric oxides in general and titanium oxide in particular. It is shown that the performance of oxide semiconductors in energy conversion is closely related to their defect disorder in the bulk phase and at the surface.

The key PEC performance indicator is the energy conversion efficiency (ECE), which is the ratio of the generated chemical energy (e.g., in the form of hydrogen) to the total amount of incoming light energy striking the photoelectrode. It is shown that the performance of PECs should be considered in terms of the multifactorious approach involving all performance-related properties, which are interrelated [4]. Since all these properties are related to defect disorder, this chapter also considers defect chemistry for TiO$_2$ as an example representing POSs.
13.2 Photosensitive Oxide Semiconductors

13.2.1 Development Strategy for Photoelectrochemical Hydrogen Generation

The efforts to develop the high-performance PEC for solar hydrogen production are focused on processing novel materials that are based on binary, ternary, and quaternary oxides as well as their solid solutions, which are needed for photoelectrodes. The most promising candidate for this application is TiO$_2$ for the following reasons:

- TiO$_2$ exhibits an outstanding chemical stability in aqueous environments [5]. While TiO$_2$ is reactive with water, TiO$_2$ itself remains intact and exhibits stable properties over a prolonged period of time.
- The properties of TiO$_2$ (rutile), including its functional properties, may substantially be modified within the stability of the same crystalline structure by changes of its oxygen content and the concentration of foreign ions (anions and cations) introduced into the TiO$_2$ lattice.

One of the key performance-related properties of photoelectrode is electronic structure, which impacts on the amount of the sunlight energy that can be absorbed. The bandgap for TiO$_2$, rutile, is 3.05 eV (Table 13.1 [6–15]). However, the optimal bandgap desired for water splitting is between 1.8 and 2.2 eV.

The reports of Hoffmann et al. [16] and Wang et al. [17] indicated that below a certain critical grain size (10 nm), the bandgap has a tendency to increase as the particle size decreases.

### TABLE 13.1

Bandgap Energy for the Rutile Phase Reported in the Literature

<table>
<thead>
<tr>
<th>Authors</th>
<th>Bandgap (eV)</th>
<th>Method</th>
<th>Specimen (Temperature Range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cronemeyer [6]</td>
<td>3.05</td>
<td>Electrical conductivity</td>
<td>Single crystal (773–1223 K)</td>
</tr>
<tr>
<td></td>
<td>3.05</td>
<td>Electrical conductivity</td>
<td>Single crystal (623–1123 K)</td>
</tr>
<tr>
<td></td>
<td>3.03–3.06</td>
<td>Optical method</td>
<td>Single crystal (room temperature)</td>
</tr>
<tr>
<td>Rudolph [7]</td>
<td>3.12</td>
<td>Electrical conductivity</td>
<td>Ceramic specimen (1125–1300 K)</td>
</tr>
<tr>
<td>Frova et al. [8]</td>
<td>3.0</td>
<td>Optical method</td>
<td>Single crystal (room temperature)</td>
</tr>
<tr>
<td>Vos and Krusemeyer [9]</td>
<td>3.026</td>
<td>Optical method</td>
<td>Parallel to c axis (room temperature)</td>
</tr>
<tr>
<td></td>
<td>3.059</td>
<td></td>
<td>Perpendicular to c axis (room temperature)</td>
</tr>
<tr>
<td>Pascual et al. [10]</td>
<td>3.031</td>
<td>Optical method</td>
<td>Parallel to c axis (1.6 K)</td>
</tr>
<tr>
<td></td>
<td>3.031</td>
<td></td>
<td>Perpendicular to c axis (1.6 K)</td>
</tr>
<tr>
<td>Daude et al. [11]</td>
<td>2.91</td>
<td>Theoretical calculation</td>
<td>Parallel to c axis</td>
</tr>
<tr>
<td></td>
<td>3.05</td>
<td></td>
<td>Perpendicular to c axis</td>
</tr>
<tr>
<td>Vos [12]</td>
<td>3.03</td>
<td>Theoretical calculation</td>
<td>Parallel to c axis (1.6 K)</td>
</tr>
<tr>
<td></td>
<td>3.07</td>
<td></td>
<td>Perpendicular to c axis (1.6 K)</td>
</tr>
<tr>
<td>Gupta and Ravindra [13]</td>
<td>3.0329</td>
<td>Optical method</td>
<td>Single crystal (both perpendicular and parallel to c axis)</td>
</tr>
<tr>
<td>Khan et al. [14]</td>
<td>3.06</td>
<td>Theoretical calculation</td>
<td>Single crystal (both perpendicular and parallel to c axis)</td>
</tr>
<tr>
<td>Nowotny [15]</td>
<td>3.16</td>
<td>Electrical conductivity</td>
<td>High-purity single crystal (1073–1323 K)</td>
</tr>
<tr>
<td>Average</td>
<td>3.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It has been shown, however, that the bandgap is not the only property that controls the photocatalytic performance. Karakitsou and Verykios [18] have shown that the anatase form of TiO$_2$ exhibits the hydrogen production rate that is higher than that of rutile by the factor of 7, despite that its bandgap is larger (3.2 eV). It has been shown that the performance of photoelectrodes depends on several properties, including charge transport, the chemical potential of electrons, as well as surface and near-surface properties, in addition to electronic structure.

### 13.2.2 System Selection

The search for high-performance photoelectrodes for solar hydrogen generation includes a wide range of compounds of different compositions, structure, microstructure, and electronic structure. While the highest conversion efficiency has been achieved for valence semiconductors, such as GaAs, GaInP, and AlGaAs [19,20], these compounds are not promising for practical application because of high costs and poor chemical stability in water. On the other hand, metal oxides (MOs) exhibit much better stability in water and are less expensive than valence semiconductors.

A wide range of oxide materials have been studied for photoelectrochemical properties, including binary oxides (Fe$_2$O$_3$, ZnO, WO$_3$, Cu$_2$O), ternary oxides (SrTiO$_3$, BaTiO$_3$, CaTiO$_3$), as well as quaternary oxides. The most promising compound is TiO$_2$, which exhibits high reactivity with both light and water and is inexpensive. The additional advantage of TiO$_2$ is its high nonstoichiometry and complex defect disorder, which can be used for manipulation with defect-related properties.

The most common strategy in the modification of TiO$_2$ properties includes the following procedures:

- Annealing at different temperatures in air. The resulting changes of properties were considered in terms of either surface area [21] or crystalline structure [22].
- Doping with cations and anions. However, most of the reported systems (discussed in the following) are not compatible because the applied processing procedures are not well defined.
- Formation of nanosize systems. While such systems exhibit outstanding properties [16], most of the reported data are not reproducible and cannot be compared.

The studies of the authors on electrical properties of TiO$_2$ have been recently overviewed [1]. These studies show that properties of TiO$_2$ are closely related to lattice imperfections, such as point defects. Therefore, defect chemistry may be used as a framework in the development of novel TiO$_2$-based oxide semiconductors, which may be modified in a controlled manner using defect engineering [1].

The following sections consider defect chemistry of TiO$_2$ and defect-related properties, including the following matters:

- The reactivity of the TiO$_2$ lattice with oxygen resulting in the formation or removal of point defects (oxidation or reduction)
- Application of defect engineering in the formation of TiO$_2$-based semiconductors with controlled chemical potential of electrons
13.2.3 Point Defects and Defect-Related Properties

It has been documented that properties of nonstoichiometric compounds, such as TiO$_2$, are controlled by point defects and the related defect disorder [23,24]. Therefore, defect chemistry may be used for the conversion of any TiO$_2$, which is not well defined, into a semiconductor with controlled semiconducting properties. The formation of TiO$_2$, which is well defined, requires knowledge of basic concepts of defect chemistry, which are formulated in the following discussion [2].

13.2.4 Summary

The production of solar hydrogen by photoelectrochemical water splitting requires development of a new generation of solar materials, which are free from corrosion and photocorrosion in aqueous environments. The TiO$_2$-based POSs are the most promising candidates for solar water splitting. Their performance-related properties, which are closely related to defect disorder, may be optimized by defect engineering [2]. The concept of defect engineering may be applied for other oxide materials.

13.3 Defect Chemistry for TiO$_2$

13.3.1 Basic Properties

Titanium dioxide exists in three different structures: rutile, anatase, and brookite. The rutile structure, which is the only thermodynamically stable structure, is shown in Figure 13.1. The commercial specimen of Degussa (P25), which is frequently used as a reference TiO$_2$ specimen, contains 20% of the rutile phase and 80% of the anatase phase. The Millennium specimens (PC-10, PC-50, PC-500) exhibit the anatase structure [25].

Wu et al. [22], who studied nanocrystalline TiO$_2$ prepared by solgel, observed that heating of the anatase form of TiO$_2$ in air leads to its transition into the rutile form at approximately 600 K (Figure 13.2). Annealing of TiO$_2$ in extremely reduced conditions results in its transition into a wide range of lower titanium oxides, including Ti$_{20}$O$_{39}$ [26] (Figure 13.3).

![Structure of the rutile phase.](image-url)
Undeﬁected (ideal) TiO$_2$ lattice does not exist. The real TiO$_2$ lattice includes a range of defects, such as point defects, linear, planar, and space defects. This chapter is focused on point defects and their impact on properties. The latter can be explained by defect chemistry [23,24].

TiO$_2$ has been commonly considered as an oxygen-deﬁcient compound of the formula TiO$_{2-x}$, where $x$ is the effective deviation from stoichiometry [2,24,27–33]. The extent of oxygen deﬁcit can be determined by thermogravimetry at elevated temperatures when TiO$_2$ is in equilibrium with the gas phase [27,29–33]. As seen in Figure 13.4,
there is a good agreement between different reports on the effect of oxygen activity on the apparent oxygen deficit.

\( \text{TiO}_2 \) has been commonly considered as an n-type semiconductor [23]. Its valence band is formed of filled 2\( p \) orbitals of doubly valent oxygen ions, and the conduction band is formed of empty 3\( d \) states of four valent Ti ions. The difference between the energies of the top of the valence band, \( E_V \), and the bottom of the conduction band, \( E_C \), forming the forbidden energy gap, is 3.05 eV. The n-type conduction in \( \text{TiO}_2 \) is associated with the transport of electrons, which are formed as a result of ionization of oxygen vacancies, which are the predominant defects in \( \text{TiO}_2 \) [23]. \( \text{TiO}_2 \) also involves titanium interstitials, which are minor-type defects. \( \text{TiO}_2 \) may be reduced or oxidized within a single phase leading to the formation, or removal, of point defects [23].

Reduction results in the formation of donor-type defects: oxygen vacancies and titanium interstitials [2,23]. Their ionization results in the formation of quasi-free electrons, which are the predominant electronic defects in n-type \( \text{TiO}_2 \). Recent studies have shown that prolonged oxidation of pure \( \text{TiO}_2 \) leads to p-type semiconductivity, which is associated with the presence of titanium vacancies [1]. Ionization of these defects results in the formation of electron holes. While the properties of oxides, including \( \text{TiO}_2 \), are closely related to defect disorder, their reactivity and the related charge transfer are determined by the chemical potential of electrons, \( \mu_n \), which is defined as

\[
\mu_n = \mu_n^0 + kT \ln a_n
\]  

(13.1)

where

- \( a_n \) denotes the activity of electrons
- \( \mu_n^0 \) is the standard term
- \( n \) in subscript denotes the terms associated with electrons

Therefore, knowledge of the concentration of the electronic charge carriers is essential in the assessment of the reactivity of \( \text{TiO}_2 \), including the reactivity with water. Defect chemistry may be used in the determination of this quantity.
TiO$_2$ exhibits several interesting properties, such as:

- TiO$_2$ is reactive with both light and water. This reactivity can be attributed to the ease with which the Ti ions (Ti$^{3+}$ and Ti$^{4+}$) alter their valence.
- TiO$_2$ has excellent chemical stability in aqueous environments [5].
- The properties of TiO$_{2-x}$ can be altered by varying the defect chemistry and related electronic structure through alteration of nonstoichiometry [2,23].
- TiO$_2$ is substantially less expensive than other photosensitive materials and, therefore, may be a candidate for a new generation of solar materials.
- TiO$_2$ has several spin-off applications, which are environmentally friendly [34].

The purpose of the following section is to outline the basic concepts of defect chemistry for TiO$_2$ and the impact of point defects on semiconducting properties, reactivity, and photoreactivity. It is shown that defect chemistry may be used as a framework for the processing of TiO$_2$ with controlled properties, including photoreactivity with water and oxygen. Defect disorder models considered in this chapter are based on the most recent studies for pure TiO$_2$ and its solid solutions [2,4,35–60]. The studies aimed to understand the relationship between defect disorder of TiO$_2$ and its performance as photoelectrode for solar hydrogen PEC.

### 13.3.2 Nonstoichiometry and Point Defects of Rutile

The properties of TiO$_2$ can be explained assuming the presence of the following point defects [2,27]:

1. Oxygen vacancies: oxygen ions are missing from their lattice sites.
2. Titanium vacancies: titanium ions are missing in their lattice sites.
3. Titanium interstitials: titanium ions are located in interstitial sites.
4. Electrons: these defects are located on Ti$^{3+}$ ions in their lattice sites.
5. Electron holes: these defects are located on O$^-$ ions in their lattice sites.

Ionization of ionic defects (1)–(3) leads to the formation of electronic defects (electrons and electron holes), which are mainly responsible for the charge transport.

All point defects in MOs, including TiO$_2$, have specific functional properties, which impact on the performance of TiO$_2$-based photocatalysts and photoelectrodes:

- Oxygen vacancies
  - Form adsorption sites for oxygen and water.
  - Their ionization leads to the formation of quasi-free electrons.
- Titanium vacancies
  - Form adsorption sites for water, leading to the formation of an active complex [1].
  - Their ionization leads to the formation of quasi-free electron holes.
- Titanium interstitials
  - Their ionization leads to the formation of quasi-free electrons.
  - Form adsorption sites for acceptor-type molecules, such as oxygen.
• Electrons
These defects are responsible for charge transfer within the conduction band and midgap bands.

• Electron holes
These defects are responsible for charge transfer within the valence band and midgap bands.

The effect of defect disorder on electronic structure is shown schematically in Figure 13.5 for a binary MO (where M is a bivalent metal, such as Ni). The left side of Figure 13.5 represents different types of point defects, including metal vacancies (5b), oxygen vacancies (5c), and metal interstitials (5d). The right side of Figure 13.5 represents ionization of the ionic defects leading to the formation of electronic defects.

**FIGURE 13.5**
Schematic representation of point defects in a binary MO and the related band model: (a) undefected structure, (b) doubly ionized cation vacancy, (c) doubly ionized oxygen vacancy, and (d) doubly ionized interstitial cation. (Reproduced with permission from Bak, T., Oxide Semicond. Res. Rep., Copyright 2010.)
The point defects in Figure 13.5 are represented using the Kröger–Vink notation [24] (this notation allows to assess easily the lattice charge neutrality condition). It has been shown that defect disorder is closely related to reactivity, photoreactivity, and the related charge transfer. Therefore, knowledge of defect disorder is essential to assess the reactivity and photoreactivity. TiO$_2$ is not an exception. Accordingly, defect engineering may be used in processing TiO$_2$ with enhanced photoreactivity with water, oxygen, hydrogen, and alternative species, such as microbial cells.

In equilibrium, the concentration of thermodynamically reversible defects in oxides is a function of temperature and oxygen activity [23]. Quantitative assessment of the effect of defect disorder on properties, such as semiconducting properties, requires knowledge of the related equilibrium constants. These constants may be used for derivation of defect disorder diagrams representing the effect of oxygen activity on the concentration of defects [42].

The following sections report the recent progress in defect chemistry of TiO$_2$. It is shown that photocatalytic properties of nonstoichiometric compounds, such as TiO$_2$, are dependent on defect disorder rather than other commonly studied properties, such as crystal structure, microstructure, and surface area.

Defect chemistry considers point defects in crystalline solids as a solid solution. In the case of dilute solutions, when the concentration of defects is very small, the mass action law may be applied to calculate defect concentrations. At larger concentrations, application of the mass action law requires to use activities instead of concentrations.

The formation of defects in crystals is governed by the general law of thermodynamics, which requires that spontaneous chemical reactions at constant temperature, $T$, and pressure, $p$, result in a decrease of free enthalpy:

$$\left(\Delta G = \Delta H - T\Delta S\right)_{T,p} < 0$$ (13.2)

where $\Delta G$, $\Delta H$, and $\Delta S$ denote the change of free enthalpy, the enthalpy, and the related change of entropy, respectively. When defects are formed in perfect crystals, the change of entropy should be considered in terms of both configuration entropy change and the vibrational entropy change. Therefore, the change of free energy assumes the following form:

$$\Delta G = [d](\Delta H_f - T\Delta S_v) - T\Delta S_{\text{con}}$$ (13.3)

where

- $[d]$ is the concentration of defects
- $H_f$ denote the partial enthalpy of defect formation
- $S_v$ is the partial vibrational entropy
- $S_{\text{con}}$ is configuration entropy

While both the $\Delta H_f$ and $\Delta S_{\text{con}}$ terms are positive, the $\Delta S_v$ term may assume either positive or negative values, depending on defect disorder. Therefore, the equilibrium concentration of point defects is the result of competition between the thermodynamic terms of $\Delta S_{\text{con}}$, $\Delta S_v$, and $\Delta H_f$. Consequently, the following conclusions could be made:

1. Ideal (undefected) crystals are thermodynamically unstable (at any temperature above absolute zero).
2. The equilibrium concentration of thermodynamically reversible defects in oxide crystals depends on equilibrium conditions described by the temperature and oxygen activity.
It is shown in the following sections that photosensitivity of TiO\textsubscript{2} and its performance as photoelectrode are closely related to the concentration and the valence of point defects.

### 13.3.3 Defect Disorder for Undoped TiO\textsubscript{2}

TiO\textsubscript{2} is a nonstoichiometric compound. It has been generally considered that TiO\textsubscript{2} is an oxygen-deficient compound [23]. This picture, which has been supported by gravimetric studies [27–33], suggests that the predominant defects in TiO\textsubscript{2} are oxygen vacancies and/or interstitial titanium ions. Recent studies show, however, that strong oxidation of TiO\textsubscript{2} (at elevated temperatures) leads to the formation of a metal-deficient oxide [39,42]. In this case, TiO\textsubscript{2} may be represented by the formula Ti\textsubscript{1−x}O\textsubscript{2−y} where x > y/2. The properties of the metal-deficient TiO\textsubscript{2} are determined by titanium vacancies, which are formed during a prolonged oxidation leading, in consequence, to p-type properties [39,52].

Figure 13.6 shows a schematic representation of the periodic lattice for defected TiO\textsubscript{2}. The titanium and oxygen ions in their normal lattice sites are represented by the traditional notation using their chemical symbols, and the exponents represent their electrical charge. However, point defects in Figure 13.5, including ion vacancies and the ions located in interstitial sites, are represented according to the Kröger–Vink notation [24]. Introduction of this notation allows representing defect reactions taking into account only their relative electrical charge (compared to the lattice) and ignoring their absolute charge (the classical notation vs. the Kröger–Vink notation is shown in Table 13.2).

#### 13.3.3.1 Definition of Basic Relationships

Description of defect chemistry requires definition of basic relationships, such as defect equilibria, and charge neutralities. These relationships, which have been reported before [1], are briefly outlined in the following.

Using the Kröger–Vink notation [24], the formation of defects at elevated temperatures may be described by the following equilibria [2]:

\[
O_0^\cdot \leftrightarrow V_0^\cdot + 2e^\cdot + \frac{1}{2}O_2
\]

\[
\begin{align*}
\text{Ti}^{3+} & \rightarrow O^{2−} – \text{Ti}^{3+} – O^{2−} – \text{Ti}^{4+} – O^{2−} – \text{Ti}^{3+} – O^{2−} – \text{Ti}^{4+} \\
O^{2−} & \quad \text{Ti}^{3+} \quad O^{2−} \quad O^{2−} \quad O^{2−} \quad \text{Ti}^{4+} \quad O^{2−} \\
\text{Ti}^{3+} & \rightarrow O^{2−} – \text{Ti}^{4+} – O^{2−} – \text{Ti}^{4+} – O^{2−} – \text{Ti}^{3+} – O^{2−} – \text{Ti}^{4+} \\
O^{2−} & \quad O^{2−} \quad O^{2−} \quad O^{2−} \quad O^{2−} \quad O^{2−} \\
\text{Ti}^{4+} & \rightarrow O^{2−} – \text{Ti}^{4+} – O^{2−} – \text{Ti}^{4+} – O^{2−} – \text{Ti}^{4+} – O^{2−} – \text{Ti}^{4+} \\
O^{2−} & \quad O^{2−} \quad O^{2−} \quad O^{2−} \quad O^{2−} \quad O^{2−} \\
\text{Ti}^{4+} & \rightarrow O^{2−} – \text{Ti}^{4+} – O^{2−} – \text{Ti}^{4+} – O^{2−} – \text{Ti}^{4+} \\
O^{2−} & \quad O^{2−} \quad O^{2−} \quad O^{2−} \quad O^{2−} \\
\end{align*}
\]

**FIGURE 13.6**
Schematic representation of thermodynamically reversible point defects in the undoped TiO\textsubscript{2} lattice according to the standard notation showing absolute charges of ions (Table 13.2) [2]. (Reprinted with permission from Nowotny, M.K., Sheppard, L.R., Bak, T., and Nowotny, J., Defect chemistry of titanium dioxide: Application of defect engineering in processing of TiO\textsubscript{2}-based photocatalysts, J. Phys. Chem. C, 112, 5275–5300. Copyright 2008, American Chemical Society.)
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\[ 2\text{O}_2^- + \text{Ti}_1^4 \rightleftharpoons \text{Ti}_1^{+++} + 3e' + \text{O}_2 \]  
(13.5)

\[ 2\text{O}_2^- + \text{Ti}_1^4 \rightleftharpoons \text{Ti}_1^{++++} + 4e' + \text{O}_2 \]  
(13.6)

\[ \text{O}_2 \rightleftharpoons \text{O}_2^- + \text{V}_1^{+++} + 4h^* \]  
(13.7)

\[ \text{Nil} \rightleftharpoons e' + h^* \]  
(13.8)

where \( e' \) and \( h^* \) denote electron and electron hole, respectively.

Any defect disorder must satisfy the charge neutrality condition, which requires that the crystal is electrically neutral. Consequently, the concentration of all charged defects must satisfy the following condition:

\[
2[V_0^{o-}] + 3[Ti_1^{+++}] + 4[Ti_1^{++++}] + [D^*] + p = n + 4[V_{Ti}^{w-}] + [A']
\]  
(13.9)

where

- \( n \) and \( p \) denote the concentrations of electrons and electron holes, respectively
- \([D^*]\) and \([A']\) denote the concentrations of singly ionized donor- and acceptor-type foreign ions, respectively

The condition expressed by Equation 13.9 involves both thermodynamically reversible defects (oxygen vacancies, titanium interstitials, and electronic defects) and also those defects that are thermodynamically irreversible (foreign ions). TiO\(_2\) also includes titanium vacancies, which are thermodynamically reversible (theoretically). These defects, however, are relatively immobile and, therefore, may be considered as quenched in the experimental conditions commonly applied in the determination of defect-related properties. Consequently, these defects may be considered as acceptor-type impurities. Consequently, the titanium vacancies and the impurities (dopants) may be considered as an effective concentration of acceptors:

\[
A = 4[V_{Ti}^{w-}] + [A'] - [D^*]
\]  
(13.10)
For pure TiO$_2$, the quantity $A$ may be directly related to the concentration of titanium vacancies:

$$A = 4 \left[ V_{Ti}^{m} \right]$$  \hspace{1cm} (13.11)

According to equilibria (13.4) through (13.7), the concentrations of intrinsic defects depend on oxygen activity. While equilibria (13.4) through (13.6) may be established relatively fast, the formation and the transport of titanium vacancies, represented by equilibrium (13.7), are extremely slow [39,52]. Therefore, the titanium vacancies in Equations 13.9 and 13.10 may be assumed as acceptor-type dopants, that is, their concentration remains practically independent of oxygen activity. This is the reason why these defects are treated differently than other types of ionic defects. Therefore, the concentration of defects, may also be manipulated by the kinetic factor (equilibration time).

The equilibrium constants for equilibria (13.4) through (13.8) are as follows:

$$K_{V_{O}^{n}} = \left[ V_{O}^{n} \right] n^2 p(O_2)^{1/2}$$  \hspace{1cm} (13.12)

$$K_{2} = \left[ Ti_{i}^{***} \right] n^3 p(O_2)$$  \hspace{1cm} (13.13)

$$K_{3} = \left[ Ti_{i}^{****} \right] n^4 p(O_2)$$  \hspace{1cm} (13.14)

$$K_{4} = \left[ V_{Ti}^{m} \right] p^4 p(O_2)^{-1}$$  \hspace{1cm} (13.15)

$$K_i = np$$  \hspace{1cm} (13.16)

where square brackets represent the concentration of ionic defects (molar fractions) and $p(O_2)$ is the oxygen activity.

Therefore, the concentrations of both electronic and ionic defects may be expressed as follows:

$$\left[ V_{O}^{n} \right] = K_{i} n^{-2} p(O_2)^{-1/2}$$  \hspace{1cm} (13.17)

$$\left[ Ti_{i}^{***} \right] = K_{2} n^{-3} p(O_2)^{-1}$$  \hspace{1cm} (13.18)

$$\left[ Ti_{i}^{****} \right] = K_{3} n^{-4} p(O_2)^{-1}$$  \hspace{1cm} (13.19)

$$p = K_i n^{-1}$$  \hspace{1cm} (13.20)

Knowledge of the equilibrium constants enables the determination of the concentrations of defects. These equilibrium constants have been recently determined using three independently measured defect-related properties (electrical conductivity, thermoelectric...
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**TABLE 13.3**
Equilibrium Constants of Defect Reactions for TiO₂

<table>
<thead>
<tr>
<th>Equilibrium Constant</th>
<th>ΔH⁰ (kJ/mol)</th>
<th>ΔS⁰ J/(mol K)</th>
<th>Specimen</th>
<th>Methods</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₁</td>
<td>493.1</td>
<td>106.5</td>
<td>Undoped TiO₂</td>
<td>Electrical conductivity</td>
<td>Bak et al. [42]</td>
</tr>
<tr>
<td>K₂</td>
<td>334.9</td>
<td>49.9</td>
<td>Nb-doped TiO₂</td>
<td>Electrical conductivity</td>
<td>Bak et al. [42]</td>
</tr>
<tr>
<td>K₃</td>
<td>879.2</td>
<td>190.8</td>
<td>Undoped TiO₂</td>
<td>Thermoelectric power</td>
<td>Kofstad [27]</td>
</tr>
<tr>
<td>K₄</td>
<td>1025.8</td>
<td>238.3</td>
<td>Undoped TiO₂</td>
<td>Thermoelectric power</td>
<td>Kofstad [27]</td>
</tr>
<tr>
<td>K₅</td>
<td>354.5</td>
<td>−202.1</td>
<td>Undoped TiO₂</td>
<td>Electrical conductivity</td>
<td>Bak et al. [42]</td>
</tr>
<tr>
<td>Kᵢ</td>
<td>394.5</td>
<td>−378.7</td>
<td>Nb-doped TiO₂</td>
<td>Electrical conductivity</td>
<td>Bak et al. [42]</td>
</tr>
<tr>
<td>Kⱼ</td>
<td>222.1</td>
<td>44.6</td>
<td>Undoped TiO₂</td>
<td>Electrical conductivity</td>
<td>Bak et al. [42]</td>
</tr>
</tbody>
</table>

K₁, K₂, K₃, K₄, and Kᵢ are defined in text.

Both of these thermodynamic quantities and the associated equilibrium constants represent materials data, which have been reported elsewhere [42,43]. The equilibrium constants and the related data of ΔS⁰ and ΔH⁰ are presented in Table 13.3.

**13.3.3.2 Defect Disorder Diagram**

Using the combination of Equations 13.10, 13.17 through 13.20 and the electroneutrality condition (13.9), the concentration of electronic charge carriers may be described by the relationship, involving p(O₂), equilibrium constants, and the effective concentration of acceptors, A [42]:

\[
\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

Both of these thermodynamic quantities and the associated equilibrium constants represent materials data, which have been reported elsewhere [42,43]. The equilibrium constants and the related data of ΔS⁰ and ΔH⁰ are presented in Table 13.3.

As seen from Equation 13.22, the effect of p(O₂) on the concentration of electronic charge carriers depends on a combination of all defects. Equation 13.22 may be used for derivation of a defect disorder diagram in the form of the plot of concentrations of reversible defects as a function of p(O₂).

Figure 13.7 shows the defect diagram for TiO₂ in terms of the concentration of defects as a function of oxygen activity at 1273 K [42]. As seen, the concentration of electronic charge carriers and the related electrical properties of TiO₂ are closely related to oxygen activity, which may be used for the imposition of either n- or p-type properties or mixed conduction.
In equilibrium, the concentration data represented in the diagram shown in Figure 13.7 are well defined by the equilibrium conditions (temperature and oxygen activity). The changes in the concentrations of defects during cooling from the temperature of processing to room temperature depend on the applied cooling procedure, such as rate of cooling and the associated gas-phase composition.

As seen in Figure 13.7, in the vicinity of the n–p transition regime, the effect of $p(O_2)$ on the concentration of electronic charge carriers in the n- and p-type regimes may be expressed as follows [36]:

$$n = n_0 p(O_2)^{-1/4} \quad (13.23)$$

$$p = p_0 p(O_2)^{1/4} \quad (13.24)$$

where $n_0$ and $p_0$ denote the concentration of electrons and holes in standard conditions. In strongly reducing conditions, when $p(O_2) < 10^{-5}$ Pa, the concentration of electrons is the following function of $p(O_2)$ [36]:

$$n = (2K_1)^{1/3} p(O_2)^{-1/6} \quad (13.25)$$

The ionic defects form donor and acceptor levels in the electronic structure of TiO$_2$. Both oxygen vacancies and titanium interstitials form donor levels and titanium vacancies form acceptors [6,61–63]. The effect of these defects on the concentrations of
electronic charge carriers depends on their ionization degree. At this stage, the following points can be made:

1. TiO$_2$ may exhibit both n-type and p-type properties. Its defect disorder and defect-related properties are closely related to oxygen activity in the TiO$_2$ lattice.
2. The predominant ionic defects in TiO$_2$ at high oxygen activity are oxygen vacancies and titanium vacancies [1]. Recent studies show that nanosize TiO$_2$ exhibits much larger concentrations of these defects than that in the bulk phase [64].
3. Defect disorder diagrams may be used for the processing of TiO$_2$ with controlled properties that are desired for specific performance.

The defect diagrams, such as the diagram in Figure 13.7, may be used to predict the processing conditions in the formation of TiO$_2$ with controlled semiconducting properties, which can be tailored to suit specific applications.

13.3.4 Extended Defects

In strongly reducing conditions, when nonstoichiometry achieves very large values, oxygen vacancies in TiO$_2$ have a tendency to interact leading, in consequence, to the formation of larger defect aggregates and superstructures [23]. When the concentration of point defects surpasses a certain critical value, the crystal structure is stabilized by elimination of isolated oxygen vacancies leading to the formation of extended planar defects, which are known as shear planes. The ratio of titanium to oxygen ions within the shear plane, which is charged positively, is higher than in stoichiometric TiO$_2$. According to Matzke [65], oxygen vacancies aggregate into shear planes when the deviation from stoichiometry exceeds $2 \times 10^{-3}$.

There has been an accumulation of the experimental evidence indicating that point defects are present in equilibrium with shear planes. The planar defects, which have been observed by electron microscopy, lead to the formation of a homologous series of so-called Magneli-type phases. These phases may be represented by the chemical formula Ti$_n$O$_{2n-1}$, where $n$ vary between 38 (TiO$_{1.97}$) and 4 (TiO$_{1.75}$) [66–68]. So far, little is known about the effect of shear planes on photocatalytic properties of TiO$_2$.

13.3.5 Defect Disorder for Donor-Doped TiO$_2$

The properties of TiO$_2$ (rutile) may be modified by the incorporation of foreign ions with a valency that is different from that of the host lattice ions. Incorporation of such ions leads to the formation of donors or acceptors [23]. The defected structure of TiO$_2$, including both donor- and acceptor-type extrinsic defects, is shown in Figure 13.8 (the meanings of symbols are in Table 13.2). This section considers the effect of donor-type ions, such as niobium, on the defect disorder of TiO$_2$. Niobium has been most commonly applied as a donor-type dopant for the modification of semiconducting properties of TiO$_2$ [2,40,43,44,58,69,70]. The studies of electrical properties for Nb-doped TiO$_2$ indicate that at low oxygen activity, niobium incorporation leads to the formation of electrons. This reaction may be represented by the following equilibrium:

$$\text{Nb}_2\text{O}_5 \rightleftharpoons 2\text{Nb}^{\text{III}}_\text{Ti} + 4\text{O}_\text{2}^\text{+} + 2e' + \frac{1}{2}\text{O}_2$$  \hspace{1cm} (13.26)
The defect disorder in this regime is governed by the following (electronic) charge compensation:

\[ n = \left[ \text{Nb}^*_{\text{Ti}} \right] \]  

(13.27)

As seen, the concentration of electrons in this regime is determined by the content of niobium and is practically independent of \( p(O_2) \). It was shown that TiO\(_2\) in this regime exhibits a quasi-metallic conduction [40].

The mechanism of niobium incorporation into TiO\(_2\) at high oxygen activity is entirely different. In this case, niobium incorporation leads to the formation of ionic defects (titanium vacancies) [2, 43]:

\[ 2\text{Nb}_2\text{O}_5 \leftrightarrow 4\text{Nb}^*_{\text{Ti}} + V''''_{\text{Ti}} + 10\text{O}_2^- \]  

(13.28)

In this regime, the defect disorder is governed by ionic charge compensation:

\[ 4\left[ V''''_{\text{Ti}} \right] = \left[ \text{Nb}^*_{\text{Ti}} \right] \]  

(13.29)

Therefore, the concentration of electrons for Nb-doped TiO\(_2\) may be represented by the following function of oxygen activity:

\[ n = K_i \left( \frac{\left[ \text{Nb}^*_{\text{Ti}} \right]}{4K_4} \right)^{1/4} p(O_2)^{-1/4} \]  

(13.30)

As seen, the concentration of electrons in this regime is represented by the slope of log \( n \) versus log \( p(O_2) \) that is equal to \(-1/4\). In conclusion, the effect of niobium on electrical properties of TiO\(_2\) is closely related to oxygen activity in the lattice. It was shown that niobium incorporation into the TiO\(_2\) lattice in extremely reduced conditions leads to a high charge transport [50].
13.3.6 Defect Disorder for Acceptor-Doped TiO$_2$

Chromium has been commonly used as an acceptor-type dopant of TiO$_2$ [59,71]. Its incorporation into the TiO$_2$ lattice at low oxygen activity may be represented by the following equilibrium:

$$\text{Cr}_2\text{O}_3 \Leftrightarrow 2\text{Cr}^+ + 3\text{O}_2^+ + V_o^*$$ (13.31)

where the charge neutrality requires that chromium ions are compensated by oxygen vacancies:

$$\left[\text{Cr}^+\right] = 2\left[V_o^*\right]$$ (13.32)

Therefore, the concentration of electron holes for Cr-doped TiO$_2$ may be represented as the following function of $p(\text{O}_2)$:

$$p = K_i \left(\frac{[\text{Cr}^+]}{2K_i}\right)^{1/2} p(\text{O}_2)^{1/4}$$ (13.33)

The previous relationship has been verified experimentally by Carpentier et al. [71] by using measurements of electrical conductivity.

Acceptor-type doping may be used for the imposition of p-type properties of TiO$_2$, which are required for application of TiO$_2$ as photocathodes.

13.3.7 Real Chemical Formula for Nonstoichiometric TiO$_2$

The defect disorder models derived previously indicate that the TiO$_2$ lattice involves a number of point defects. These defects may be grouped according to their location in the TiO$_2$ lattice, including [2] the following:

1. The titanium sublattice, $A_T$
2. Interstitial sites, $B_i$
3. The oxygen sublattice, $C_O$

Accordingly, the TiO$_2$ lattice may be represented by the following general formula:

$$A_T B_I C_O$$ (13.34)

where $A_T$, $B_I$, and $C_O$ can be considered as modules of the TiO$_2$ lattice. These modules are expressed by the following specific formulas:

$$A_T = \left(\text{Ti}^{4+}_T\right)_a \left(\text{Ti}^{3+}_T\right)_b \left(M_1^{5+}\right)_c \left(M_2^{5+}\right)_d \left(V_T\right)_f$$ (13.35)

$$B_I = \left(\text{Ti}^{3+}_I\right)_g \left(\text{Ti}^{4+}_I\right)_h \left(M_I^+\right)_j$$ (13.36)

$$C_O = \left(\text{O}_O^{2+}\right)_k \left(\text{O}_O\right)_l \left(A_O\right)_m \left(A_O^{2+}\right)_r$$ (13.37)
where the indexes \(a, b, c, d, f, g, h, j, k, l, m, o, \) and \(r\) correspond to the amount of the related lattice species (in molar ratio), which are outlined in Table 13.2; \(M\) denote foreign cations in the cation sublattice; and \(A\) are foreign anions in the oxygen sublattice. The concentrations of these species are interdependent. A wide range of their combinations may be imposed in a controlled manner by appropriate processing conditions at elevated temperatures. The resulting properties are then determined by (i) oxygen activity in the gas phase and (ii) the content of foreign ions forming donors and acceptors. Each combination, however, requires that the following conditions are satisfied:

- The sum of concentrations of all species in the titanium sublattice must be equal to unity:
  \[a + b + c + d + f = 1\]  
  \(13.38\)

- The sum of concentrations of all species in the oxygen sublattice must be equal to two.

Consequently,

\[k + l + m + o + r = 2\]  
\(13.39\)

The lattice charge neutrality condition can be easily derived when the defects and their electrical charge are expressed in the Kröger–Vink notation \([24]\). Therefore, Equations 13.35 through 13.37 may be expressed in the following forms:

\[A_T = (Ti_{Ti}^\circ)_a (Ti_{Ti}^\prime)_b (M_{Ti}^\circ)_c (M_{Ti}^\prime)_d (V_{Ti}'''')_f\]  
\(13.40\)

\[B_i = (Ti_{i}^{***})_g (Ti_{i}^{****})_h (M_{i}^\prime)_i\]  
\(13.41\)

\[C_O = (O_{O}^\circ)_k (V_{i}^{*})_l (O_{O}^\prime)_m (A^\circ)_o (A^\prime)_r\]  
\(13.42\)

The charge neutrality condition requires that the charges associated with all lattice species are fully compensated electrically. Consequently,

\[c + 3g + 4h + j + 2l + m + o = b + d + 4f + r\]  
\(13.43\)

The defects indexed by \(a\) and \(k\) are electrically neutral with respect to the lattice and, therefore, are not taken into account in the charge neutrality condition.

The diagram in Figure 13.7 shows the effective deviation from stoichiometry, \(x\), which can be expressed as follows:

\[x = \frac{2(g + h - f) + l}{1 + g + h - f}\]  
\(13.44\)

The concept of defect engineering is based on the imposition of desired properties by controlled combination of the concentration of the lattice species, which are a function of the following variables:

1. Temperature
2. Oxygen activity
3. Concentration of aliovalent ions
The reactivity and photoreactivity of TiO$_2$-based oxide semiconductors and the related photocatalytic properties are closely related to their electroactivity, which is determined by defect disorder. The defect disorder diagrams (see Figure 13.7) may be used for assessment of the electroactivity and prediction of optimized processing conditions.

The incorporation of aliovalent ions into the TiO$_2$ lattice (deliberately and incidentally) has a substantial impact on the semiconducting properties. Correct understanding of the effects of these ions imposes the following requirements:

1. Basic characterization of TiO$_2$ specimens should include the determination of the concentration of incidentally introduced foreign defects (impurities), which have a substantial impact on properties already at the level of parts per million.
2. The formation of TiO$_2$-based solid solutions leads to well-defined systems only when the doping procedure is well defined in terms of (1) oxygen activity, (2) time of processing, and (3) cooling procedure.

In conclusion, the formula TiO$_2$ is not reflective of the complex composition of this non-stoichiometric compound that involves a wide range of ionic and electronic point defects. The real chemical formula of TiO$_2$, which is reflective of specific properties, is more complex.

13.3.8 Summary

TiO$_2$ of unknown defect disorder may be used as a raw material for the processing of well-defined POSs, which are required for photoelectrodes of PECs. Therefore, the promising research strategy in the development of TiO$_2$-based semiconductors for high-performance photoelectrodes is the processing at elevated temperatures in controlled oxygen activity and the subsequent cooling procedure.

13.4 Electrical Properties

13.4.1 General

The electrical properties are defect sensitive if the defects are electrically charged [23]. Therefore, the electrical properties have been most commonly applied in the verification of defect disorder models. The most commonly studied electrical properties are as follows:

1. Electrical conductivity
2. Thermoelectric power (Seebeck effect)
3. Work function (WF)

The electrical properties may easily be determined experimentally at room temperature (during the performance) and also at elevated temperatures (during processing in the gas phase of controlled oxygen activity). Finally, the electrical properties may be used for monitoring the chemical reactions associated with charge transfer at gas/solid and liquid/solid interfaces.
13.4.2 Electrical Conductivity

13.4.2.1 Definition

The measurements of electrical conductivity can be used to assess the charge transport involving the components related to both electrons and electron holes [23,36]:

\[
\sigma = e n \mu_n + e p \mu_p
\]  

(13.45)

where

- \(e\) is the elementary charge
- \(\mu\) is the mobility
- \(n\) and \(p\) denote the concentration of electrons and holes
- the subscripts \(n\) and \(p\) correspond to specific charge carriers

Usually one type of charge carriers is predominant. However, for amphoteric oxides, such as TiO\(_2\), the electrical conductivity in the \(n\)–\(p\) transition regime involves the components related to both charge carriers. Taking into account Equations 13.23 and 13.24, Equation 13.45 in equilibrium assumes the following form:

\[
\sigma = \sigma_n^0 \rho(O_2)^{-1/4} + \sigma_p^0 \rho(O_2)^{1/4}
\]  

(13.46)

where \(\sigma_n^0\) and \(\sigma_p^0\) are the parameters related to the conductivities of electrons and holes in standard conditions. However, in strongly reducing conditions, the electrical conductivity exhibits the dependence, which is consistent with Equation 13.25 [36]:

\[
\sigma = \sigma_n^p p(O_2)^{-1/6}
\]  

(13.47)

The defect disorder models, represented by Equations 13.46 and 13.47, have been verified against well-defined experimental data of electrical conductivity for high-purity TiO\(_2\) single crystal (TiO\(_2\)-SC), which are shown in Figure 13.9 [36], and also for high-purity TiO\(_2\)-SC.

![Figure 13.9: Effect of oxygen activity on electrical conductivity for undoped TiO\(_2\)-SC in the 1073–1323 K range within both extremely reducing conditions and the n–p transition regime. (Reproduced with permission from Nowotny, M.K., Bak, T., and Nowotny, J., Electrical properties and defect chemistry of TiO\(_2\) single crystal. I. Electrical conductivity, J. Phys. Chem. B, 110, 16270–16282. Copyright 2006, American Chemical Society.)](image-url)
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Polycrystalline TiO$_2$ (TiO$_2$-PC) [51]. As seen, the electrical conductivity of TiO$_2$, determined as a function of oxygen activity in oxidizing and reducing conditions, is consistent with Equations 13.46 and 13.47, respectively. The difference between the electrical conductivity data for TiO$_2$-SC and TiO$_2$-PC may be used to assess the local semiconducting properties of grain boundaries [55].

The electrical conductivity at elevated temperatures includes a substantial contribution of ions to the charge transport. Then the ionic conductivity component, $\sigma_i$, cannot be ignored, especially in the n–p transition regime. Therefore,

$$\sigma = \sigma_n^0 P(\text{O}_2)^{1/4} + \sigma_p^0 P(\text{O}_2)^{1/4} + \sigma_i$$

(13.48)

The individual electrical conductivity components outlined in Equation 13.48, which were determined from the experimental data shown in Figure 13.9, are shown in Figure 13.10. As seen, these data allow the determination of the n–p transition point.

The defect disorder models for Nb–TiO$_2$ and Cr–TiO$_2$, outlined by Equations 13.30 and 13.33, have been verified using the measurements of the electrical conductivity versus oxygen activity. These data indicate the following:

1. Doping with niobium results in a substantial increase of the electrical conductivity of TiO$_2$. The effect of niobium on the electrical conductivity depends on oxygen activity and the content of niobium.

2. At low concentrations, chromium doping results in a decrease of electrical conductivity within the n-type regime. However, at higher concentrations, chromium results in a transition of semiconducting properties from n- to p-type.

13.4.2.2 Mobility of Electronic Charge Carriers

Equation 13.45 involves both concentration and mobility terms. The latter term can be determined using the concentration terms derived from defect disorder diagrams and the
experimental data of electrical conductivity. For high-purity TiO\textsubscript{2}-SC, the mobility terms for electrons and holes assume the following respective forms [60]:

\[
\mu_n(TiO_2-SC) = (6.7 \pm 0.3) \times 10^{-6} \text{ (m}^2/\text{V s)}
\]

\[
\mu_p(TiO_2-SC) = (1.5 \pm 0.7) \times 10^{-1} \exp\left(\frac{-94 \pm 4 (\text{kJ/mol})}{RT}\right) \text{ (m}^2/\text{V s)}
\]

The observed independence of the mobility of temperature for electrons suggests that their transport can be described by the band model and mobility of holes, which is thermally activated, is described by the hopping model. The transport in TiO\textsubscript{2}-PC is similar. However, absolute values of the mobility terms are different, indicating that grain boundaries have an effect on the charge transport. Figure 13.11 shows the effect of temperature on the mobility of electrons for Nb-doped TiO\textsubscript{2} in reducing conditions. As seen, a metallic-type charge transport is observed in the range 900–1230 K [40].

### 13.4.2.3 Bandgap

The bandgap, \(E_g\), may be expressed as the following function of temperature [72,73]:

\[
E_g = E_g^0 - \beta T
\]

where \(\beta\) is the temperature coefficient. According to Becker and Frederikse [73], the component \(E_g^0\) may be determined from the temperature dependence of the minimum value of the electrical conductivity versus \(p(O_2)\), \(\sigma_{\text{min}}\), which corresponds to the n–p transition:

\[
\sigma_{\text{min}} = 2e\sqrt{\mu_n\mu_p}N_nN_p \exp\left(\frac{\beta}{2k}\right)\exp\left(-\frac{E_g^0}{2kT}\right)
\]

where

\(N_n\) and \(N_p\) are the densities of states for electrons and electron holes, respectively

\(k\) is the Boltzmann constant

**FIGURE 13.11**

Both $\beta$ and $E_g$ may also be determined from the Jonker analysis that is based on the isothermal plot of $S$ versus $\log \sigma$ [74]. The bandgap determined from the plot of $\log \sigma_{\text{min}}$ as a function of $1/T$ for undoped TiO$_2$-SC at elevated temperatures results in the following value:

$$E_g = 3.16 \pm 0.02 \text{ eV} \quad (13.52)$$

Doping with aliovalent ions may lead to the reduction of the effective bandgap required for ionization. This is the case when doping results in imposition of midgap levels as it is schematically represented in Figure 13.12 [75].

### 13.4.2.4 Effect of Cooling

The processing procedures of nonstoichiometric oxides, which aim at imposition of controlled oxygen activity, take place at elevated temperatures at which the gas/solid kinetics is relatively fast. On the other hand, the performance of TiO$_2$ as photoelectrode and photocatalyst takes place at room temperature. The changes of TiO$_2$ properties during cooling may be considered in terms of the following effects [23]:

1. The changes in the concentration of ionic defects, which are electrically charged. These changes are related to the formation term for defects, $\Delta H_f$.
2. The changes of the mobility term, $\Delta H_m$.
3. The changes of the ionization degree of ionic defects.

The effect of cooling on the electrical conductivity of oxide semiconductors is schematically represented in Figure 13.13. As seen, the activation energy of the electrical conductivity at higher temperatures (above the $T_c$ point) involves both $\Delta H_m$ and $\Delta H_f$ terms. Then

$$\sigma = \text{const} \cdot \exp \left( \frac{- (2/m_\sigma) \Delta H_f - \Delta H_m}{RT} \right) \quad (13.53)$$

where $m_\sigma$ is the slope of the following dependence:

$$\frac{1}{m_\sigma} = \frac{\partial \log \sigma}{\partial \log p(\text{O}_2)} \quad (13.54)$$
Below a certain critical temperature, $T_c$, the ionic transport in the lattice is quenched and the activation energy is determined by the $\Delta H_m$ term:

$$\sigma = \text{const} \cdot \exp\left(-\frac{\Delta H_m}{RT}\right) \quad (13.55)$$

13.4.2.5 Measurements

The electrical conductivity is relatively easy to measure in laboratory conditions. Therefore, this property is frequently reported in studies of defect disorder of MOs.

There is a wide range of approaches for the determination of electrical conductivity at elevated temperatures. The basic principle is shown in Figure 13.14. The external (current)
probes, consisting commonly of platinum plates, are attached to both sides of rectangular-shaped specimen. A spring mechanism, located outside the high-temperature zone, is used to maintain effective galvanic contact between the electrodes and the specimen. In the case of four probe method [36], the voltage electrodes formed of two platinum wires are wrapped around the specimen and welded to the platinum wires connected to a voltmeter. The sample holder, placed in an alumina tube, is connected to a gas-flow system that aims to impose the gas phases of controlled oxygen activity in the reaction chamber [76].

The required oxygen activity, \( p(\text{O}_2) \), in the reaction chamber can be imposed using gas mixtures of appropriate compositions. The \( p(\text{O}_2) \) can be imposed using mixtures of hydrogen and water vapor or argon/oxygen mixtures to achieve lower and higher oxygen activities, respectively. The oxygen activities can be determined using a zirconia-based electrochemical oxygen sensor. Measurements of electrical conductivity, \( \sigma \), can be used for monitoring semiconducting properties during both oxidation and reduction. Details of the experimental procedures used to determine the electrical conductivity have been reported elsewhere [36,76].

Figure 13.15 shows a standard sheet for monitoring the equilibration kinetics during oxidation of CaTiO\(_3\) at 1223 K. Figure 13.15a shows that imposition of a new gas phase results in a very rapid increase in the \( p(\text{O}_2) \) to the level of \( \sim 95\% \) of its final value within seconds, followed by adoption of the final equilibrium value within 10 min. Figure 13.15b shows that the temperature during the experiment remains constant within \( \pm 0.3 \) K. The observed fluctuations in temperature have a negligible effect on the measured electrical resistance data. Figure 13.15c shows that constant resistance is reached within \( \sim 1 \) h and then remains constant for the following 20 h. These kinetics data can be used to determine the chemical diffusion coefficient [38,39].

**FIGURE 13.15**
Typical record for the measurements of electrical resistivity for CaTiO\(_3\) during two cycles of isothermal oxidation at 1223 K, showing the time dependence of (a) oxygen activity, (b) temperature at both sides of the specimen, and (c) resistance corresponding to the dc current passing in both directions. (Reproduced with permission from Springer Science+Business Media: J. Mater. Sci.: Mater. Electron., Charge transport in CaTiO\(_3\): Electrical conductivity, 15, 2004, 635, Bak, T., Nowotny, J., Sorrell, C.C., Zhou, M.F., and Vance, E.R.)
13.4.3 Thermoelectric Power

The thermoelectric power, also termed the Seebeck coefficient or thermopower, is an electrical property that may be used to characterize semiconducting properties at elevated temperatures. Specifically, the thermoelectric power may be used to assess the concentrations of electronic charge carriers. Since the electrical conductivity is the product of the concentration and mobility terms, the combination of the electrical conductivity and thermoelectric power data can be used to determine both terms [60].

The principles of the determination of thermoelectric power are given elsewhere [76]. The imposition of a temperature gradient ($\Delta T$) across a specimen results in the generation of a potential difference ($\Delta \Psi$), which is termed the Seebeck voltage or thermovoltage. Knowledge of both $\Delta \Psi$ and $\Delta T$ is required to determine the thermoelectric power ($S$), which can be expressed as follows:

$$S = \lim_{\Delta T \to 0} \frac{\Delta \Psi}{\Delta T} = \frac{d\Psi}{dT}$$

(13.56)

For non-degenerated semiconductors thermoelectric power can be related to the concentration of electronic charge carriers according to the following expressions for n- and p-type regimes, respectively [78]:

$$S_n = -\frac{k}{e} \left( \ln \frac{N_n}{n} + A_n \right)$$

(13.57)

$$S_p = \frac{k}{e} \left( \ln \frac{N_p}{p} + A_p \right)$$

(13.58)

where

- $e$ is the elementary charge
- $k$ is the Boltzmann constant
- $N_n$ and $N_p$ denote the densities of states for electrons and electron holes, respectively
- $n$ and $p$ denote their respective concentrations
- $A_n$ and $A_p$ are the kinetic constants associated with the scattering of electrons and electron holes, respectively

The common way to verify the defect disorder models of MOs is based on the dependence of $S$ as a function of $p(O_2)$:

$$\frac{1}{m_S} = \frac{k}{e} \frac{\partial S}{\partial \log p(O_2)}$$

(13.59)

where

- $m_S$ is a parameter related to the specific defect disorder
- the subscript $S$ refers to the case when the parameter is obtained using thermoelectric power data

The equivalent equation allows the assessment of the effect of oxygen activity on the electrical conductivity, which is expressed by Equation 13.54. Both sets of data may be used for the confirmation of the effect of oxygen activity on the concentration of electronic charge carriers (when the mobility term remains independent of oxygen nonstoichiometry).
It is well known that in the case of symmetrical semiconductors thermoelectric power achieves a critical value at the n–p transition, namely, \( S = 0 \). Figure 13.16 shows a schematic representation of the effect of the \( p(O_2) \) on both the electrical conductivity (\( \sigma \)) and the thermoelectric power (\( S \)) for an amphoteric oxide semiconductor, which exhibits both n- and p-type regimes. It can be seen that the slope of the logarithm of electrical conductivity versus \( \log p(O_2) \) dependence in the n- and p-type regimes adopts negative and positive values, respectively, and that the electrical conductivity at the n–p transition point reaches a minimum. The n- to p-type transition point occurs at

\[
\sigma_n = \sigma_p
\]  

(13.60)

It also can be seen in Figure 13.16 that the thermoelectric power versus \( \log p(O_2) \) dependencies in the n- and p-type regimes are linear. In these two regimes, the formalism is to present the slopes \( (1/m_s) \) as positive values. The parameter \( 1/m_s \) is well defined when thermoelectric power corresponds to pure n- or p-type regime. Then the thermoelectric power data reflect the effects of the majority charge carriers (in this case the effects of the minority charge carriers are negligible). However, in the n–p transition regime, where two charge carriers are present in comparable concentrations, the meaning of \( 1/m_s \) is more complex.

The principle of the measurement of thermoelectric power according to Equation 13.56 is shown in Figure 13.17. Figure 13.18 represents the circuit for simultaneous determination

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**FIGURE 13.16**
Schematic representation of the effect of oxygen activity on both electrical conductivity (\( \sigma \)) and thermoelectric power (\( S \)) within p-type, n–p transition and p-type regimes (the subscripts \( n \) and \( p \) are related to n-type and p-type regimes, respectively). (Reproduced with permission from Nowotny, M.K., Bak, T., and Nowotny, J., Electrical properties and defect chemistry of TiO\(_2\) single crystal. II. Thermoelectric power, *J. Phys. Chem. B*, 110, 16283–16291. Copyright 2006, American Chemical Society.)
FIGURE 13.17
The principle of measurements of thermovoltage along the temperature gradient imposed by microheaters on both sides of the specimen. (Reproduced with permission from Nowotny, M.K., Bak, T., and Nowotny, J., Electrical properties and defect chemistry of TiO$_2$ single crystal. II. Thermoelectric power, J. Phys. Chem. B, 110, 16283–16291. Copyright 2006, American Chemical Society.)

FIGURE 13.18
The circuit for simultaneous determination of electrical conductivity (four probes) and thermoelectric power. (Reproduced with permission from Nowotny, M.K., Bak, T., and Nowotny, J., Electrical properties and defect chemistry of TiO$_2$ single crystal. I. Electrical conductivity, J. Phys. Chem. B, 110, 16270–16282. Copyright 2006, American Chemical Society.)
of electrical conductivity and thermoelectric power. The temperature gradient required for the determination of thermoelectric power is imposed by microheaters located close to external (current) probes. The internal voltage electrodes wrapped around the specimen and welded to the platinum wires served for the measurements of the electrical conductivity. The sample holder is placed in tube furnace that is connected to a gas-flow system that imposes the gas phase of controlled oxygen activity.

The experimental data of thermoelectric power for TiO$_2$-SC in reducing conditions, over the temperature range 1073–1323 K, are represented in Figure 13.19. As seen, the data exhibit a continuous change of the $S$ versus log $p$(O$_2$) slope from 1/6 at extremely reduced conditions to lower 1/$m_S$ values. The gradually decreasing slope indicates increasing influence of the minority charge carriers. This figure also includes the thermoelectric power data for high-purity TiO$_2$-PC determined at 1273 K using the same equipment and following the same experimental procedure.

As seen in Figure 13.19, the slope of the thermoelectric power versus log $p$(O$_2$) dependence for TiO$_2$-PC at 1273 K is ~1/10 in the entire low $p$(O$_2$) regime (similar slope was determined at other temperatures as well). Since in both cases of TiO$_2$-PC and TiO$_2$-SC the specimens were of high purity, the only difference between the two is the presence of grain boundaries for TiO$_2$-PC. Therefore, the difference between the $S$ versus log $p$(O$_2$) slope for these two specimens is reflective of the local properties of grain boundaries of the polycrystalline material.

13.4.4 Work Function

WF is the electrical property that is selectively sensitive to the outermost surface layer and is defined as the work required for removing an electron from its Fermi level (at the surface) to the energy level outside the surface [76,79]. Consequently, the WF measurements may be used for in situ monitoring of the charge transfers during chemical reactions at the gas/solid interface, such as chemisorption of gases.
The WF of oxide semiconductors involves several components, including the internal WF, $\Phi_{in}$, the WF component related to band bending, $\Phi_s$, and the external WF, $\chi$ [80] (Figure 13.20):

$$\Phi = \Phi_{in} + \Phi_s + \chi$$  \hspace{1cm} (13.61)

Oxidation and reduction of oxide semiconductors within a single-phase regime result in WF changes that are determined by the components $\Phi_{in}$ and $\Phi_s$ while the external WF, $\chi$, remains constant. Therefore,

$$\Delta\Phi = \Delta\Phi_{in} + \Delta\Phi_s$$  \hspace{1cm} (13.62)

Equation 13.62 represents the case when oxidation of an MO leads to both oxygen chemisorption and oxygen incorporation.

Oxidation of oxides at elevated temperatures results in a change of the component $\Delta\Phi_{in}$ while the component $\Delta\Phi_s$ is negligibly small and, therefore, may be ignored. Conversely, oxidation of oxides at room temperature results mainly in the WF changes due to the component $\Delta\Phi_s$ while the component $\Delta\Phi_{in}$ may be ignored since the bulk phase is quenched. Then the WF changes may be considered in terms of chemisorptions equilibria.

The WF changes may also be used in studies of segregation-induced effects, where segregation refers to adsorption of species derived from the solid phase. Therefore, it is important to recognize that WF changes at elevated temperatures may also include a component related to segregation. However, the changes of WF at room temperature are determined mainly by the component $\Delta\Phi_s$ because the lattice transport is quenched.

The external WF, $\chi$, is determined by the surface structure [76,79]. Consequently, during chemisorption, leading to changes of $\Delta\Phi_s$, the component $\chi$ remains constant. Also during oxidation, leading to oxygen incorporation without structural changes, the WF component $\chi$ remains constant. In certain cases, however, a change in the concentration of defects may lead to structural changes, which are induced by strong interactions between the defects [55].

The effect of oxygen on WF of titanium dioxide has been reported by Figurovskaya et al. [81] and Bourasseau et al. [82–87] at room temperature and by Odier et al. [88,89] at elevated temperatures. These WF data allow assessing the reactivity of oxygen with the surface of $\text{TiO}_2$. 

![Figure 13.20](https://example.com/fig13.20.png)

**FIGURE 13.20**
Band model of n-type semiconductor without surface charge (a) and at the presence of oxygen chemisorption-induced surface charge (b).
The effect of oxygen activity on WF of oxide semiconductors may be expressed by the following equation [79]:

\[
\frac{1}{m_\Phi} = \frac{1}{kT} \frac{\partial \Delta \Phi}{\partial \ln p(O_2)}
\]  

(13.63)

where \(m_\Phi\) is the exponent of the \(p(O_2)\) dependence that is related to the WF changes, which are determined by changes of the Fermi level of the outermost surface layer:

\[
\Delta \Phi = -\Delta E_F
\]  

(13.64)

The relationship between the surface coverage by oxygen-chemisorbed species and the WF changes may be expressed by the following expression:

\[
\frac{1}{m_\Phi} = \frac{1}{z} \left[ 1 - \frac{\alpha}{x_{a,z}} \frac{\partial x_{a,z}}{\partial \ln p(O_2)} \right]
\]  

(13.65)

where the component \(x_{a,z}\), related to the activity of the specific chemisorbed species, is given by

\[
x_{a,z} = \frac{\Theta_{a,z}}{1 - \Theta_1 - \Theta_2}
\]  

(13.66)

where

- \(\alpha\) is the number of chemisorbed species formed from a single oxygen molecule
- \(z\) is the number of electrons involved in chemisorption
- \(\Theta\) is the degree of surface coverage with chemisorbed oxygen species

WF may be determined by the dynamic condenser method, which has been developed by Kelvin [90]. The high-temperature Kelvin probe (HTKP), which allows WF measurements at elevated temperatures in controlled gas-phase composition, may be used for in situ monitoring of surface reactions at the gas/solid interface and the related charge transfer [76,91].

The main part of the Kelvin probe is the vibrating capacitor, which is formed of a lower electrode (involving the studied specimen) and an upper reference platinum electrode (Figure 13.21). The HTKP allows determining the WF changes with an accuracy of 0.5 meV, if the external noise level is minimized.

The WF changes can be determined by the measurements of the contact potential difference (CPD), which is equal to the difference between the WF values of the studied specimen and of the reference electrode, \(\Phi_R\):

\[
\text{CPD} = \frac{1}{e} (\Phi - \Phi_R)
\]  

(13.67)

The formation of the CPD according to Wagner is shown in Figure 13.22 [93]. Platinum can be applied as the reference electrode. It was shown that oxidation of platinum leads to the formation of a PtO\(_2\) layer on surface [76]. Therefore, the WF changes of platinum should be considered in terms of the electrical properties of the PtO\(_2\) surface layer, which can be expressed by Equation 13.63.
According to Equation 13.67, the WF changes of the studied specimen may be determined from the CPD data only when the WF changes of the reference electrode are known:

\[ \Delta \Phi = e \Delta \text{CPD} + \Delta \Phi_R \]  \hspace{1cm} (13.68)

**Figure 13.23** represents the WF data during oxidation for high-purity TiO$_2$, which was equilibrated in different conditions, including annealing at 1173 K at $p(\text{O}_2) = 10$ Pa (Figure 13.23a) and reduction at 1173 K at $p(\text{O}_2) = 10^{-10}$ Pa (Figure 13.23b) [79]. In both cases, the subsequent oxidation experiments were performed at $p(\text{O}_2) = 75$ kPa after cooling the specimen to room temperature. As seen, oxidation of the specimen initially reduced in moderate conditions (Figure 13.23a) leads to WF increase within different stages, including oxygen chemisorption (rapid WF changes within 5 h by 0.38 eV) and subsequent slow changes related to oxygen incorporation over the period of 130 h (by $\sim$0.22 eV). These data represent the reactivity of TiO$_2$ reduced in moderate conditions with oxygen. As seen in Figure 13.23b, oxidation of strongly reduced TiO$_2$ results in a rapid WF decrease by 0.78 eV. The sign of the
WF changes during oxidation of this specimen, which is opposite to that for the specimen reduced in moderate conditions, indicates that oxidation in this case results in the formation or removal of a low-dimensional surface structure of outstanding properties, which is formed when the specimen was exposed to the gas phase involving hydrogen.

13.4.5 Surface Photovoltage Spectroscopy

The concept of surface photovoltage spectroscopy (SPS) is based on the measurements of WF of a photosensitive semiconductor (using the Kelvin probe [76,80]) versus incident photon energy. In this method, the reference electrode is made of a mesh (platinum or gold) that allows light access to the surface of the studied specimen. The SPS provides information on the effect of light on surface semiconducting properties [93,95]. Figure 13.24 represents the plot of the surface photovoltage signal versus photon energy in the range 0.4–4.5 eV for TiO₂ specimens annealed at 1273 K in oxidizing conditions, p(O₂) = 21 kPa.
(upper part), and in reducing conditions at $1273 \text{ K}, p(O_2) = 10^{-10} \text{ Pa}$ (lower part) \[95\]. As seen, at the bandgap illumination ($h\nu > 3 \text{ eV}$), the photovoltage signals are positive and negative for oxidized and reduced TiO$_2$, respectively, indicating that the photoinduced electrons are transferred toward the surface and the bulk, respectively. Therefore, the SPS signal informs of the effect of light on the charge transfer and the related photoreactivity.

### 13.4.6 Effect of Impurities

The effect of dopants on properties, which usually concerns high concentrations of donors or acceptors, has been widely reported. It has been generally assumed that the effect of impurities on properties can be ignored when their concentration is low. The recent studies indicate that this is not the case \[57\]. Defect disorder diagrams may be used to predict the effect of aliovalent ions (donors and acceptors) in titanium dioxide on the concentration of electronic charge carriers (electrons and electron holes) and the related electrical properties. Such effect of both donors and acceptors, considered in terms of the effective concentration of acceptors \[57\], is shown in Figure 13.25. These data indicate the following:

- The effect of aliovalent ions on properties may be ignored below certain critical values. The effect of temperature and oxygen activity on the critical value $A_{cr}$ below which the concentration of electronic charge carriers is independent of $A$, is shown in Figure 13.26. As seen, the effect of aliovalent ions on the electrical conductivity above this value becomes substantial and cannot be ignored.

**FIGURE 13.24**
Surface photovoltage spectra at 300 K in air for TiO$_2$ both oxidized and reduced at 1273 K. (Reprinted with permission from Tributsch, H. et al., *Energy Mater.*, 3, 158. Copyright 2009, Institute of Materials, Minerals & Mining and Maney Publishing.)
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FIGURE 13.25
Effect of acceptors, $A$, at the ppm level on the concentration of electronic charge carriers at 1173 K for both reduced and oxidized TiO$_2$. (Reprinted with permission from Nowotny, J., Bak, T., Nowotny, M.K., and Sheppard, L.R., Defect chemistry and electrical properties of titanium dioxide. 2. Effect of aliovalent ions, J. Phys. Chem. C, 112, 602–610. Copyright 2008, American Chemical Society.)

FIGURE 13.26
Isobaric plots of the critical values of the effective concentration of acceptors, above which the effect on electrical conductivity becomes substantial, as a function of temperature for TiO$_2$. (Reprinted with permission from Nowotny, J., Bak, T., Nowotny, M.K., and Sheppard, L.R., Defect chemistry and electrical properties of titanium dioxide. 2. Effect of aliovalent ions, J. Phys. Chem. C, 112, 602–610. Copyright 2008, American Chemical Society.)
• The effect of aliovalent ions, added intentionally (dopants) or unintentionally (impurities), on the concentration of electronic charge carriers and related electrical properties depends on temperature and oxygen activity.

• The observed effect of aliovalent ions increases with the decrease of temperature.

• Aliovalent ions may have a substantial effect on properties already at the level of several parts per million and, therefore, cannot be ignored.

13.4.7 Summary

The electrical techniques are sensitive to defect disorder of MOs. Simultaneous measurements of electrical conductivity and thermoelectric power may be used for the determination of several semiconducting quantities, such as the mobility and concentration terms. The measurements of both electrical conductivity and WF provide information about surface versus bulk semiconducting properties. The light-induced WF data may be used for the determination of the effect of light on reactivity. The measurements of the electrical properties may also be used for in situ monitoring of processing at elevated temperatures. The experimental approach for in situ monitoring is shown in Figure 13.27.

13.5 Collective and Local Factors in Reactivity and Photoreactivity

13.5.1 TiO$_2$/H$_2$O Interface

The prerequisite of the reactions between TiO$_2$ and water (and its solutes) is adsorption of the reacting species on the TiO$_2$ surface and the subsequent charge transfer. The reactivity is determined by the ability of TiO$_2$ to donate or accept electrons and the chemical
affinity or ionization potential of the adsorbed species. There has been a general perception that the reactivity of TiO$_2$ (with water and organic solutes in water) is closely related to collective properties of TiO$_2$. So far, little is known about the effect of local surface properties, which are closely related to the presence of point defects, on reactivity.

### 13.5.2 Collective Factor

The collective factor is related to collective properties in a macroscale, which are reflective of the entire bulk phase, or its surface layer, as a continuum. An important collective factor controlling the reactivity of oxide semiconductors and their ability to charge transfer is the chemical potential of electrons, which is related to the Fermi level. There is a perception that the charge transfer at the TiO$_2$/liquid interface is determined by collective properties, such as the chemical potential of electrons and the flat-band potential (FBP). According to the electronic theory of chemisorption and catalysis [97], the charge transfer between the surface of a semiconductor and the adsorbed molecule is determined by the Fermi level at the surface and the ionization potential of the molecule.

The ability of the semiconductor to donate or accept electrons, and the related chemical potential of electrons, may be modified by the incorporation of either donors or acceptors. The schematic representation of the effect of donor versus acceptor doping on the Fermi level is shown in Figure 13.28. The effect of acceptors and donors on the concentration of electrons in TiO$_2$ at 1073 K is shown in Figure 13.29 [57]. The doping procedure may be used for shifting up or down the chemical potential of electrons in TiO$_2$, compared to the energy levels of the electrochemical couples H$^+$/H$_2$ and O$_2$/H$_2$O, in order to allow spontaneous charge transfer. Therefore, the collective properties have an essential effect on reactivity of TiO$_2$.

### 13.5.3 Local Factor

While the collective factor is the driving force of the charge transfer within the PEC, it has been shown that photoreactivity at the TiO$_2$ surface, and the related charge transfer, must be considered in terms of both the collective factor and a local factor [35].

The local factor is related to local interactions in an atomic scale between the adsorbed species and specific surface-active sites, which are formed by individual lattice species (ions and defects) at the surface. These defects, which are directly involved in the reactivity

![FIGURE 13.28](Reproduced with permission from Bak, T., Oxide Semicond. Res. Rep., Copyright 2010.)
between H\textsubscript{2}O and TiO\textsubscript{2}, play an essential role in the charge transfer, such as the transfer of electron holes from the TiO\textsubscript{2} surface to the adsorbed H\textsubscript{2}O molecules. Different sites have different ability for the charge transfer. Recent studies have shown that titanium vacancies at the outermost surface layer are the favorable active surface sites that allow effective charge transfer between the H\textsubscript{2}O molecule and the TiO\textsubscript{2} surface. The proposed reactivity model, involving the reaction between the H\textsubscript{2}O molecule and the TiO\textsubscript{2} surface site, leading to the formation of an active complex, is shown schematically in Figure 13.30 [35].

The photoreactivity between the TiO\textsubscript{2} surface and water may be considered in terms of the following reactions:

- Adsorption of water molecule on the active site, such as titanium vacancy (V\textsubscript{Ti})

\[
2\text{H}_2\text{O} + V\text{Ti} \rightarrow (2\text{H}_2\text{O} - V\text{Ti})
\]

(13.69)

- The charge transfer between the TiO\textsubscript{2} lattice and adsorbed water species resulting in the formation of a photocatalytically active complex

\[
(2\text{H}_2\text{O} - V\text{Ti}) \rightarrow (2\text{H}_2\text{O}^{2+} - V_{\text{Ti}}^{4+})^\ast
\]

(13.70)

- Decomposition of the activated complex into oxygen, proton, and titanium vacancies

\[
(2\text{H}_2\text{O}^{2+} - V_{\text{Ti}}^{4+})^\ast \rightarrow \text{O}_2 + 4\text{H}^\ast + V_{\text{Ti}}^{4-}
\]

(13.71)

where \((2\text{H}_2\text{O}^{2+} - V_{\text{Ti}}^{4+})^\ast\) is a metastable surface-active complex.
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Light-induced ionization over the bandgap leading to the formation of an electron–hole pair

\[ O_2^- + Ti^{4+}\stackrel{hv}{\longrightarrow} O + Ti^{3+} \]  \hspace{1cm} (13.72)

Reactivation of the surface sites that is associated with the following charge transfer

\[ 4O^- + V_{Ti}^{3+} \rightarrow 4O_2^- + V_{Ti} \]  \hspace{1cm} (13.73)

In analogy, oxygen vacancies and the associated trivalent Ti ions may be considered as local active sites for the formation of chemisorbed oxygen species, which are important in photocatalytic water purification. The related reactivity model is represented in Figure 13.31.

**FIGURE 13.30**

**FIGURE 13.31**
The development of high-performance photoelectrodes for water splitting and photocatalysts for water purification requires that both collective and local factors are optimized to the level required for maximum performance.

13.5.4 Summary

The photoreactivity of photoelectrode with water should be considered in terms of both the collective and the local reactivity factors. The typical collective properties include electrical conductivity and Fermi level. The local component is related to local structure in the atomic scale.

13.6 Reactions at the Water/TiO₂ Interface

The reactivity of water with TiO₂ should be considered in terms of all species present in water, including oxygen (dissolved in water), hydrogen (in the form of protons), and the dissolved ions. The reactivity includes adsorption and chemisorption of species derived from the liquid phase as well as diffusion and segregation in the solid phase. The latter process leads to the imposition of surface composition that is different from the bulk phase.

13.6.1 Effect of Oxygen

Since oxygen is a part of the oxide lattice, the properties of oxides, such as TiO₂, are closely related to oxygen activity in the lattice and that in the surrounding gas phase. The effect of the gas phase on properties depends critically on temperature.

At lower temperatures, when the lattice transport is quenched, the changes in gas-phase composition lead to changes in chemisorption equilibria. In other words, oxidation of oxides at lower temperatures is limited to the adsorption layer. Then oxygen activity in the oxide lattice is independent of the gas-phase composition.

As temperature increases, oxidation leads to the imposition of strong concentration gradients within the gas/solid interface. Then changes of oxygen activity in the gas phase result in the propagation of the newly imposed oxygen activity into the bulk phase leading, ultimately, to the imposition of new gas/solid equilibrium.

The rate of the gas/solid equilibration reactions is determined by the chemical diffusion coefficient, which can be considered as the rate constant of the diffusion of defects under chemical potential gradient [23,41]. Therefore, knowledge of the diffusion data is essential for understanding the reactivity between oxygen in the gas phase and the oxide lattice.

The following section considers the following phenomena related to the O₂/TiO₂ interface:

1. Oxygen chemisorption leading to the formation of oxygen-chemisorbed species
2. Oxygen lattice diffusion leading to imposition of controlled oxygen activity within the entire O₂/TiO₂ system

13.6.2 Oxygen Chemisorption

Oxygen chemisorption on oxide semiconductors may be considered in terms of the following equilibria [79]:

\[ \text{O}_2 + e^- \leftrightarrow \text{O}_2^* \]  \hspace{1cm} (13.74)
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$$\text{O}_2 + e^' \leftrightarrow 2\text{O}^- \quad (13.75)$$

$$\text{O}^- + e^' \leftrightarrow \text{O}^{2-} \quad (13.76)$$

Reaction (13.74) represents the formation of singly ionized molecular species, which is considered a weak type of oxygen chemisorption. In dark conditions, these species have the tendency to be transformed into singly ionized atomic species, represented by reaction (13.75), which is considered a strong form of oxygen chemisorption. Imposition of light leads to the transition of these species back to the singly ionized molecular species, which are formed as a result of leftward shift of equilibrium (13.75) [83–86]. According to Henrich and Cox [98], oxygen may also be chemisorbed in the form of doubly ionized atomic species, which are formed according to reaction (13.76). This claim, however, is in conflict with the energy-related data indicating that these species may only be stable within the crystal field, that is, after the incorporation into the oxide lattice [95].

The mechanism of oxygen chemisorption on the surface of TiO$_2$, leading to the formation of several oxygen species, is represented in Figure 13.31. The active sites for oxygen chemisorption are the donor sites formed by oxygen vacancies or interstitial titanium ions.

The charge transfer related to the reactivity of TiO$_2$ with oxygen was studied using WF measurements by Bourasseau et al. [82–87] and Nowotny et al. [79].

13.6.3 Oxygen Propagation (Equilibration)

The reaction of TiO$_2$ with oxygen at elevated temperatures, involving oxidation and reduction, results in shifts of defect equilibria that are represented by Equations 13.4 through 13.7. Then defects are formed or removed at the gas/solid interface. The newly imposed defects diffuse into the bulk phase leading to the imposition of new equilibrium state. The change of the concentration of defects versus distance from the surface (1) before isothermal oxidation and reduction of the oxide lattice, (2) during equilibration, and (3) after equilibration is shown schematically in Figure 13.32. At this point, it is important to note that knowledge of the diffusion data is essential to predict the time required for uniform imposition of oxygen activity over the specimen.

In most cases, the mass transport may be considered in terms of a single diffusion coefficient when the diffusion involves only type of species. However, when the mass transport proceeds via two types of species with different diffusion rates, then the equilibration may be considered in terms of two kinetic regimes [39,52]. This is the case of TiO$_2$. It has been shown that mass transport in TiO$_2$ involves both oxygen vacancies and titanium interstitials, which are very fast, and titanium vacancies, which are extremely slow. In this case, the following two kinetic regimes have been identified [49]:

1. Kinetic Regime I. This regime corresponds to the transport of fast defects (oxygen vacancies and titanium interstitials) that exhibit high diffusion rates.

2. Kinetic Regime II. The kinetics in this regime is determined by the diffusion rate of titanium vacancies, which is exceptionally slow (it takes 3–4 months at 1323 K to impose an equilibrium concentration of titanium vacancies in a TiO$_2$ disk that is 1 mm thick).
The effects of isothermal oxidation of TiO$_2$ at 1123 and 1323 K on electrical conductivity during the Kinetic Regime I (the left-hand side) and the Kinetic Regime II (the right-hand side) are shown in Figure 13.33 [49]. This figure also includes the change in the concentration of titanium vacancies during both kinetic regimes. These data indicate that prolonged oxidation results in a measurable change of the concentration of titanium vacancies (the Kinetic Regime II).

### 13.6.4 Reactivity of TiO$_2$ with Water

The reactivity of TiO$_2$ with water leads to the incorporation of hydrogen into the TiO$_2$ lattice even at room temperature. The most recent studies indicate that hydrogen may result in substantial changes of semiconducting properties of TiO$_2$ [100].

The reactivity of TiO$_2$ with water may be considered in terms of the defect reaction resulting in removal of oxygen vacancies and the formation of protons (Figure 13.34):

$$\text{H}_2\text{O} + V_\text{O}^* \rightleftharpoons 2\text{H}^+ + \text{O}_\text{O}^-$$  \hspace{1cm} (13.77)

Alternatively, the incorporation of hydrogen may lead to the formation of titanium vacancies (Figure 13.35):

$$2\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + V_{\text{Ti}}^{''''} + 2\text{O}_\text{O}^-$$  \hspace{1cm} (13.78)

FIGURE 13.32
Schematic representation of defect concentration during isothermal oxidation and reduction (the propagation of defects at different stages of oxidation is represented by isoconcentration curves). (Reproduced with permission from Bak, T., Oxide Semicond. Res. Rep., Copyright 2010.)
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![Graph showing equilibration kinetics for TiO\textsubscript{2}-SCs during oxidation, represented by the time dependence of the electrical conductivity and the concentration of Ti vacancies at 1123 and 1323 K, within the short- and long-time regimes (Kinetic Regimes I and II, respectively). (Adapted from Bak, T., Nowotny, M.K., Sheppard, L.R., and Nowotny, J., Effect of prolonged oxidation on semiconducting properties of titanium dioxide, J. Phys. Chem. C, 112, 13248–13257. Copyright 2008, American Chemical Society.)](image1)

**FIGURE 13.33**

Equilibration kinetics for TiO\textsubscript{2}-SCs during oxidation, represented by the time dependence of the electrical conductivity and the concentration of Ti vacancies at 1123 and 1323 K, within the short- and long-time regimes (Kinetic Regimes I and II, respectively). (Adapted from Bak, T., Nowotny, M.K., Sheppard, L.R., and Nowotny, J., Effect of prolonged oxidation on semiconducting properties of titanium dioxide, J. Phys. Chem. C, 112, 13248–13257. Copyright 2008, American Chemical Society.)

![Reaction of proton incorporation resulting in the removal of oxygen vacancies. (Reprinted with permission from Nowotny, J., Norby, T., and Bak, T., Reactivity between titanium dioxide and water at elevated temperatures, J. Phys. Chem. C, 114, 18215–18221. Copyright 2010, American Chemical Society.)](image2)

**FIGURE 13.34**

Reaction of proton incorporation resulting in the removal of oxygen vacancies. (Reprinted with permission from Nowotny, J., Norby, T., and Bak, T., Reactivity between titanium dioxide and water at elevated temperatures, J. Phys. Chem. C, 114, 18215–18221. Copyright 2010, American Chemical Society.)
where the charge neutrality requires that

\[ [H^+] + 2[V^*_{O}] = n + 4[V^*_{Ti}] \]  

(13.79)

Consequently, hydrogenation of the TiO\(_2\) lattice favors the incorporation of protons. Exposure of n-type TiO\(_2\) to hydrogen at room temperature may lead to the formation of a low-dimensional surface layer of the H\(_2\)TiO\(_4\) structure [100].

### 13.6.5 Summary

The performance of TiO\(_2\)-based photoelectrode for PEC is closely related to the reactivity of TiO\(_2\) with water, oxygen, and hydrogen.

### 13.7 Segregation

#### 13.7.1 Segregation-Induced Effects

The chemical composition and the related properties of materials interfaces are different from those of the bulk phase as a result of segregation [101,102]. Therefore, knowledge of the effect of segregation on surface properties is crucial in correct interpretation of catalytic and photocatalytic reactions.

The driving force for segregation is the excess of interfacial energy. Such segregation is termed *equilibrium segregation* or, equivalently, *thermodynamic segregation*. Details of the physical meaning of segregation and the main driving forces involved are outlined elsewhere [101,102].

Segregation is a diffusional process and so may take place at elevated temperatures at which the mobilities of lattice elements are sufficiently high. However, it is important to recognize that sufficient time also is required to reach the segregation equilibria.

It is clear that segregation-induced concentration gradients at interfaces, such as external surfaces and grain boundaries, have a substantial impact on the functional properties of photoelectrodes. This impact may be beneficial or detrimental. The imposition of segregation-induced concentration gradients in a controlled manner may be used to...
engineer interfaces in order to achieve specific properties desired for defined applications. Thus, it is clear that there is a need to understand both the impact of segregation on the functional properties of materials and the theoretical underpinning of this phenomenon. At present, the level of knowledge on segregation in ionic-covalent compounds is limited, although there is a large body of literature on segregation in metals [103]. This limitation is due largely to experimental difficulties in the determination of well-defined data on segregation.

The solid remains in continuous interaction with the gas phase, and so the effect of the gas phase on segregation must be taken into account, particularly when comparing different segregation data.

The study of nonstoichiometric compounds, such as binary MOs, requires consideration of several issues that impact the generation of well-defined data on segregation, including (1) impurities, (2) low-dimensional surface structures, and (3) nonstoichiometry.

Segregation results in the formation of both chemical and electrical potential barrier layers within the near-surface layer. Segregation impacts on the surface and grain boundary composition of both undoped TiO$_2$ and its solid solutions. It has been shown that grain boundaries of undoped TiO$_2$ are enriched with donor-type defects, such as oxygen vacancies and titanium interstitials [55]. Surface versus bulk analysis of Nb-doped TiO$_2$ indicates that the surface is enriched with niobium as it is shown in Figure 13.36 [104].

The phenomenon of segregation may be used as a technology for the imposition of controlled surface composition and chemically induced electric field, $F$. The latter may be used for charge separation. Figure 13.37 represents the WF component related to the surface charge and the related electric field.

**13.7.2 Summary**

Segregation results in a change of the local properties at interfaces, including chemical composition and the associated semiconducting properties. These properties have a substantial effect on reactivity and photoreactivity of oxide semiconductors.
13.8 Defect Engineering of TiO$_2$

13.8.1 Concept of Defect Engineering

Defect engineering allows the imposition of controlled defect-related property through the modification of defect disorder. Therefore, defect engineering allows imposition of controlled reactivity of the surface with adsorbed species, such as oxygen, hydrogen, water, and its solutes. Consequently, defect engineering offers an innovative approach for the processing of high-performance TiO$_2$-based photoelectrodes and photocatalysts with desired properties through the imposition of controlled defect disorder.

It is essential to note at this point that the performance of photoelectrodes and photocatalysts concerns room temperature. On the other hand, most of the processes leading to the modifications of defect disorder require annealing at elevated temperatures, which allow the diffusion transport of defects from the surface into the bulk or vice versa. Consequently, the studies on the development of oxide semiconductors with controlled properties may include the following procedures:

- The formation of oxides with desired oxygen activity. This may be achieved by the imposition of controlled oxygen activity at elevated temperatures.
- The formation of solid solutions by the incorporation of aliovalent ions (cations and anions) at elevated temperatures.
- Surface processing leading to imposition of surface versus bulk controlled concentration gradients of oxygen and aliovalent ions.
- The formation of polycrystalline specimens of controlled grain size.

Defect chemistry may be used in the development of high-performance photoelectrodes. While the concept of defect engineering is described in this chapter for titanium dioxide as an example, its principal approach is valid for all nonstoichiometric oxides.
13.8.2 Summary

Defect engineering may be used for the processing of TiO$_2$-based photosensitive semiconductors with desired functional properties, which are defect-related.

13.9 Effects of Light

13.9.1 Solar Energy Spectrum

The spectrum of electromagnetic waves ranges between kilometers (radio frequency) and fractions of picometers (gamma radiation), including the UV range (100–400 nm), the visible range (400–700 nm range), and the infrared range (>700 nm), as seen in Figure 13.38. The energy of photons is related to their wavelength by the following expression:

$$ E = \frac{hc}{\lambda} $$

where

- $c$ is the speed of light
- $h$ is the Planck constant
- $\lambda$ is the wavelength

The energy provided by the Sun on Earth is substantial and exceeds the present global energy needs by the factor of $3 \times 10^4$. This supply of energy has been the support of life. The resulting photosynthesis over billions of years led to the accumulation of the resources of fossil fuels. In order to reverse the effects of climate change, which are already apparent, there is now a need to use solar energy in the formation of fuel that is

![Electromagnetic wave spectrum in terms of energy and wavelength. (Reproduced with permission from Bak, T., Oxide Semicond. Res. Rep., Copyright 2010.)](image-url)
environmentally clean. The promising clean fuel is the hydrogen fuel, which can be generated by photoelectrochemical water splitting.

The most critical functional element in the development of solar hydrogen fuel is the photoelectrode. The key functional property of the photoelectrode is its ability to efficiently absorb sunlight.

The solar energy spectrum is frequently considered in terms of radiation energy versus wavelength, as shown in Figure 13.39. The area under this spectrum is the incidence of solar irradiance, $I_r$.

$$I_r = \int_{\lambda_i}^{\lambda_f} E(\lambda) \, d\lambda$$  \hspace{1cm} (13.81)

The bandgap is the key functional property of a photocatalyst as it has a critical impact on the ECE [2,4,105]. Since only the photons of energy equal to and larger than the bandgap may be absorbed and used for conversion, there is a need to select the semiconductors with an optimized bandgap that allow to achieve maximized conversion.

Taking into account the amount of solar energy that can be absorbed and the energy losses, the solar energy spectrum can be subdivided into several segments, which are represented in Figure 13.40 [106,107]. Consequently, for standard TiO$_2$, with the bandgap, $E_{g'}$, equal to 3.05 eV [6–15], only the most energetic segment is available for conversion. As seen, this is a very small part of the entire solar energy spectrum. Therefore, there have been efforts to reduce the bandgap of TiO$_2$ from 3 to 2 eV in order to increase the amount of the absorbed energy. This may be achieved, for example, through the imposition of midgap bands [2]. Asahi et al. [108] reported that the bandgap reduction may also be achieved by
lifting the $E_V$ energy level through mixing $2p$ states of oxygen and $s$ states of dopant, such as nitrogen. The same effect was reported by Kudo et al. [109].

The effect of the Earth’s atmosphere on solar radiation is considered in terms of the so-called air mass (AM) which can be expressed in a simplified form as:

$$AM = \frac{1}{\cos \alpha} \quad (13.82)$$

where $\alpha$ is the angle between the overhead and actual positions of the Sun. At the Earth’s surface, the AM assumes values between unity ($\alpha = 0$) and infinity ($\alpha = 90^\circ$). The AM characterizes the effect of the atmosphere on solar radiation, which depends on geographical position, local time, and date. By definition, outside the Earth’s atmosphere, the AM is zero. The radiation standard assumes an AM of 1.5, which corresponds to $\alpha = 0.841$ rad or 48°. Of course, the solar energy available for conversion depends also on local atmospheric conditions, such as cloudiness, air pollution, airborne dust particles, and relative humidity.

The solar energy spectrum for the common case of an AM 1.5 is shown in Figure 13.41 in terms of radiation energy versus the wavelength. Since the energy required for splitting the water molecule is 1.23 eV, the solar radiation with the wavelength greater than 1 μm is not available for conversion.

### 13.9.2 Light Source

The ECE data reported in the literature have been determined for different light sources, which exhibit a wide range of spectral distributions, usually different from that of the
sunlight [106,107]. Therefore, the related ECE data may differ substantially from those corresponding to sunlight. Consequently, the ECE data for artificial light sources should be considered only as indicative.

13.9.3 Summary

Most of light-related data of oxide semiconductors are reported for artificial light sources, which are not well defined in terms of their energy spectrum. On the other hand, the key criterion for the evaluation of the performance is their response to sunlight. Therefore, while artificial light sources may be used to compare sample to sample within the same laboratory, the final test should be performed under sunlight.

13.10 Photoelectrochemical Water Splitting

13.10.1 Photoelectrochemical Cell

The concept of photoelectrochemical water splitting is represented schematically in Figure 13.42. Fujishima and Honda [3] reported their pioneering experiment with the PEC, which was formed of a TiO$_2$ single crystal as a photoanode and platinum as a cathode. The PEC performance includes water oxidation at photoanode, leading to the formation of gaseous oxygen, hydrogen ions (protons), and electrons. The electrons and protons are transported to cathode (via the external circuit and the electrolyte, respectively) where protons are reduced to hydrogen gas.
Solar Photoelectrochemical Production of Hydrogen

Water is a very stable compound. Therefore, high temperature is required to split water into oxygen and hydrogen gas:

$$2\text{H}_2\text{O} \Leftrightarrow \text{O}_2 + 2\text{H}_2$$ \hspace{1cm} (13.83)

At 3773 K, 30% of water is decomposed. However, both hydrogen and oxygen recombine during cooling.

The key reaction associated with water splitting, which requires a substantial amount of energy, is the removal of electrons from water molecules [2,4,35]:

$$\text{H}_2\text{O} \Leftrightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \hspace{1cm} E = -1.23 \text{ eV}$$ \hspace{1cm} (13.84)

Light-induced water splitting at room temperature by a PEC equipped with a single photoelectrode (photoanode), which is an n-type semiconductor, and a metallic cathode involves the following reactions [4]:

1. Adsorption of water molecules at the photoanode. This primary reaction leads to the formation of an active complex consisting of the water molecule and the adsorption site, such as surface lattice ion or a defect. In the dark, the reactivity of oxide semiconductors with water is limited to physical adsorption. The formed adsorbed species have a weak tendency to exchange charge.
2. Absorption of light by photoanode. Absorption of a photon of energy, which is equal to or larger than the band energy, leads to electron excitation over the bandgap resulting in the formation of electron holes in the valence band and electrons in the conduction band. These light-induced electronic charge carriers are very reactive but usually quickly recombine.

3. Charge separation. The light-induced charge carriers have the tendency to recombine what leads to energy loses. The light-induced ionization and subsequent recombination of electrons and holes are shown in Figure 13.43a. The recombination-related energy losses may be reduced when the light-induced electronic charge carriers are separated in an electric field that is formed by the surface charge, resulting in the formation of a space charge within the surface layer (Figure 13.43b). The charge separation at the photoanode leads to the transport of electrons and holes toward the bulk and the surface, respectively.

4. Photoreactivity of photoanode. The newly imposed chemical potential of electrons and holes leads to enhanced surface reactivity of photoanode promoting the charge transfer between the adsorbed water molecules and the surface. The resulting multielectron charge transfer leads to water splitting into oxygen gas, hydrogen ions, and electrons.

5. Reduction of hydrogen ions. The hydrogen ions are transported to cathode via electrolyte, and the electrons removed from water molecules are transferred to cathode via the external circuit. Both hydrogen ions and electrons combine into hydrogen molecules at the cathode.

The most important aspect of effective water splitting concerns the photocatalytic material, which must exhibit the following key functional properties:

1. Availability of appropriate surface-active sites for adsorption of water molecules
2. Ability to absorb sunlight
3. Ability for multielectron charge transfer

The studies on the development of high-performance PECs are focused on TiO$_2$-based oxide semiconductors, which are the most promising candidates for photoelectrochemical

![FIGURE 13.43](Image)  
Schematic representation of recombination (a) and the effect of band bending on charge separation (b).
water splitting. It will be shown later that commercially available TiO$_2$ may be used as a raw material for the processing of well-defined TiO$_2$, which exhibits the desired performance as photoelectrode for solar hydrogen cells [2].

**13.10.1.1 Anodic Reactions (Oxidation)**

The light-induced electron holes diffuse to the surface where they oxidize water at the photoanode/electrolyte interface:

$$2h^* + H_2O_{(liquid)} \rightarrow 2H^* + \frac{1}{2}O_2(gas)$$ (13.85)

Gaseous oxygen evolves at the photoanode and the hydrogen ions migrate to the cathode through the internal circuit (electrolyte), while electrons travel to the cathode through the external circuit where they are available for reduction reaction.

The charge transfer at the semiconductor/electrolyte interface is influenced by the structure of the solid/liquid interface and the related potential distributions within the layers forming this interface, including the Gouy layer and the Helmholtz layer on the liquid side, as well as the space charge layer on the solid side (Figure 13.44).

**13.10.1.2 Cathodic Reactions (Reduction)**

The cathodic reaction between protons and electrons results in the formation of hydrogen gas, which evolves at the cathode:

$$2H^* + 2e' \rightarrow H_2(gas)$$ (13.86)

![FIGURE 13.44](image_url)  
Schematic representation of the solid/liquid interface structure.
Taking into account the reactions (13.85) and (13.86), the overall reaction of the PEC may be expressed as follows:

$$2h\nu + H_2O_{(liquid)} \rightarrow \frac{1}{2}O_2(gas) + H_2(gas)$$

(13.87)

where

- $h$ is the Planck constant
- $\nu$ is the light frequency

Accordingly, the overall reaction 13.87 takes place when the energy of the photons absorbed by the photoanode is equal to or greater than the energy $E_t$ that is needed to split water molecule:

$$E_t = \frac{\Delta G^0}{N_A} = 1.23 \text{ eV}$$

(13.88)

where

- $\Delta G^0$ is the standard free enthalpy per mole of reaction (13.87)
- $N_A$ is the Avogadro number

The economic feasibility of the photoelectrochemical hydrogen generation technology depends on the following criteria:

- The ECE and the related rate of hydrogen formation are above the level required for commercial viability. According to the DOE, such level in 2002 was 10% [111].
- The photoelectrode is chemically stable in an aqueous environment that is used in the PEC as electrolyte.

### 13.10.2 PEC Circuit

A typical cell involves a photoanode and cathode immersed in an aqueous solution of a salt (electrolyte). The cell reaction results in oxygen and hydrogen evolution at the photoanode and cathode, respectively. The band energy models of both electrodes, including the photoanode formed from an n-type semiconductor, such as TiO$_2$, and metallic cathode, are shown schematically in Figures 13.45 through 13.48 at different stages of performance. The related performance is represented by several energy-related quantities, including WF, band levels of the electrodes, and band bending.

#### 13.10.2.1 Open Circuit

Figure 13.45 shows the open circuit and the flat-band model, with the two electrodes. The ability to charge transfer between the electrodes is determined by their WFs. The WF
values for TiO$_2$ and platinum are in the range 2.9–3.9 eV and 5.12–5.93 eV, respectively [112–114]:

$$\Phi_{\text{Pt}} > \Phi_{\text{TiO}_2}$$  \hspace{1cm} (13.89)

This difference indicates that electrons have a tendency to be transferred from the TiO$_2$ semiconductor (higher $E_F$) to platinum (lower Fermi level).
13.10.2.2 Closed Circuit

Figure 13.46 represents the PEC circuit, involving the electrodes that are connected both internally (via electrolyte) and externally (via the external circuit). As seen, the electrons are transferred from the phase of the higher $E_F$ (TiO$_2$) to the phase of lower $E_F$ (Pt), leading to an upward band bending of the TiO$_2$ semiconductor. The charge transfer results in the formation of the CPD (CPD = $V_g$), which prevents further charge transfer:

$$\text{CPD} = \frac{1}{e} (\Phi_{\text{Pt}} - \Phi_{\text{TiO}_2})$$

(13.90)
13.10.2.3 Effect of Light

The effect of light on the PEC’s band model is shown in Figure 13.47. As seen, illumination results in the following effects:

1. Light-induced ionization over the bandgap
2. Split of the Fermi level leading to the formation of quasi-Fermi levels related to electrons and holes
3. Charge separation in the electric field within the space charge layer

As seen in Figure 13.47, the energy level of the electrochemical couple H⁺/H₂ is above the Fermi level of the cathode (E_F(2)). The difference is responsible for the formation of an electrical potential barrier preventing spontaneous charge transfer at the Pt/electrolyte system.

13.10.2.4 Effect of Light and Electrical Bias

The retarding barrier shown in Figure 13.47 may be removed by the imposition of an electrical bias resulting in lifting the (E_F(2)) level above that for the electrochemical couple H⁺/H₂. Then potential distribution within the electrochemical chain becomes favorable for spontaneous charge flow within the PEC circuit as it is represented in Figure 13.48.

13.10.3 Light-Induced Reactions

13.10.3.1 Light-Induced Ionization over the Bandgap

An essential part of the PEC is the semiconducting photoelectrode. The light-induced ionization over the bandgap results in the formation of an electron–hole pair:

\[ 2h\nu \rightarrow 2e^+ + 2h^+ \]  \hspace{1cm} (13.91)

The effect of light on the photoactivity may be considered in terms of splitting the Fermi level, \( E_F \), into two quasi-Fermi levels related to electrons, \( (E_F)_e \), and holes, \( (E_F)_h \), as it is schematically represented in Figure 13.49 [115]. As seen, the effect of light on changes of \( E_F \) related to electrons for n-type semiconductors, such as n-type TiO₂, is very small. However, the effect

![FIGURE 13.49](image-url)

Light-induced split of the Fermi energy for (a) n-type and (b) p-type semiconductors. (Reproduced with permission from Bak, T., Oxide Semiconductors Res. Rep., Copyright 2010.)
on the minority charge carriers (holes) is substantial. Therefore, the photon-induced ionization for n-type semiconductors results in a large increase of the oxidation potential induced by electron holes. The picture for the p-type semiconductor is similar but the final result is an increase in the reduction potential.

The effect of light on the quasi-Fermi levels of electrons and holes can be considered in terms of the associated increase of the concentrations of electrons ($\Delta n$) and electron holes ($\Delta p$), which can be expressed by the following dependencies, respectively [115]:

$$E_F^* = E_C + kT \ln \frac{n_0 + \Delta n}{N_n}$$ (13.92)

$$E_F^* = E_V - kT \ln \frac{p_0 + \Delta p}{N_p}$$ (13.93)

where

- $(E_F)_n^*$ and $(E_F)_p^*$ are the ionization-induced quasi-Fermi levels related to electrons and electron holes, respectively
- $E_C$ and $E_V$ are the energies of the bottom of the conduction band and the top of the valence band, respectively
- $k$ is the Boltzmann constant
- $T$ is the absolute temperature
- $n_0$ and $p_0$ denote the concentrations of electrons and electron holes, respectively, before irradiation
- $\Delta n$ and $\Delta p$ denote the changes in the concentrations of electrons and electron holes, respectively, after irradiation
- $N_n$ and $N_p$ are the densities of states in the conduction band and valence band, respectively

### 13.10.4 Structures of Photoelectrochemical Cells

The PECs frequently require the imposition of an external electrical bias in order to perform. This is not required when PEC consists of two photoelectrodes [116,117]. In that configuration a substantial increase of the ECE may be achieved. The advantage of such a system is that the photovoltages are generated on both electrodes, resulting, in consequence, in the formation of an overall photovoltage that is sufficient for water decomposition without the application of a bias. In this case, light energy is absorbed by two photoelectrodes, including photoanode and photocathode, which are formed of n- and p-type semiconductors, respectively. The performance concept of the PEC equipped with two photoelectrodes, its photoelectrochemical chain, and the related band model are shown in Figures 13.50 through 13.52.

The efficient operation of PEC equipped with two photoelectrodes requires that both the collective and the local factors are optimized. The collective factor is related to the n- and p-type photoanode and photocathode, respectively. The local factor is related to specific point defects, which form surface-active sites. Figure 13.53 shows the surface defect disorder models for the photoanode and the photocathode, involving acceptor- and donor-type defects, respectively:

1. Titanium vacancies act as acceptor sites at the surface of photoanode. These sites form an active complex with adsorbed water molecule.
2. Oxygen vacancies act as donor sites at the surface of photocathode. These sites provide electrons to protons and reduce them to hydrogen gas.
Solar Photoelectrochemical Production of Hydrogen

![Diagram](attachment:image.png)

**FIGURE 13.50**

![Diagram](attachment:image.png)

**FIGURE 13.51**
FIGURE 13.52
Band model of the PEC involving two photoelectrodes. (Reproduced with permission from Bak, T., Oxide Semicond. Res. Rep., Copyright 2010.)

FIGURE 13.53
Schematic representation of the reactivity of two TiO₂-based photoelectrodes with water and the related charge transfer.
According to Nozik [116], application of two photoelectrodes (n–p PEC) leads to a substantial increase of the light-induced cell current. As seen in Figure 13.54, the performance of the PEC equipped with two photoelectrodes is substantially enhanced compared to that of single photoelectrode PECs since the energy required for water splitting is derived from two photoelectrodes that are exposed to light, instead of one. According to Nozik [116], the theoretical efficiency of such cells is 45%. However, the p-type photoelectrodes reported so far, such as p-GaP and p-InP, exhibit fast photocorrosion in aqueous environments leading to a substantial deterioration of the PEC performance [112]. This will not be the case when the PEC is equipped with both photoanode and photocathode made of TiO$_2$. The recent discovery of a p-type semiconductor made of pure TiO$_2$ [39,42] paves the way for high-performance solar cells involving two TiO$_2$ photoelectrodes: n-type TiO$_2$ photoanode and p-type TiO$_2$ photocathode. The platinum-free high-performance solar hydrogen cells, based entirely on TiO$_2$, are expected to pave the way for commercialization of solar hydrogen.

Better performance may also be achieved by integrating a photovoltaic system into the PEC. The ECE for the system based on the GaAs/GaInP$_2$ system is 12.4% [19]. The efficiency reported for the system including the tandem cell GaInP and GaInAs and the polymer electrolyte membrane (PEM) electrolyzer is 18% (Figure 13.55) [118]. While these systems exhibit a high ECE level, their relatively high costs are the main concerns.

Morisaki et al. [119] reported a PEC involving a hybrid photoelectrode (HPE), which is formed of a silicon cell and TiO$_2$ layer on the top. The advantage of this structure is that only the TiO$_2$ layer is exposed to the aqueous environment, while the silicon solar cell, forming a sublayer, is not in contact with the electrolyte. The purpose of the silicon solar cell is to generate photovoltage that provides an internal electrical bias. This type of solar cell exhibits spontaneous performance in the absence of an external bias. The HPE cell allows very efficient use of solar energy. As the external layer of TiO$_2$ absorbs only the
photons of energy greater than 3 eV, the remaining part of the solar spectrum is transmitted to the silicon solar cell (beneath the TiO$_2$ layer), which has $E_g = 1.2$ eV. Consequently, the silicon cell absorbs the low-energy part of the solar spectrum, involving the photons of energy between 3 and 1.2 eV. Figure 13.56 shows the electrochemical chain of the HPE invented by Morisaki et al. [119].
A wide range of approaches have been applied to enhance the performance of photoelectrodes, including sensitization by incorporation of foreign ions; formation of HPEs involving the components that exhibit different functions [119]; incorporation of noble metals in micronized particles, such as Ag and Pt [120]; and dye deposition [121].

Another kind of cells uses dye sensitization [121]. The photosensitizer, which is an organic dye, is attached to the surface of the photoelectrode. Light absorption by the dye leads to excitation of the dye molecules, which may be represented by the following reaction:

\[
\text{Dye} + h\nu \rightarrow \text{Dye}^* \quad (13.94)
\]

The excited dye state (Dye*) may be oxidized releasing electrons:

\[
\text{Dye}^* \rightarrow \text{Dye}^- + e^- \quad (13.95)
\]

The reaction between the oxidized dye molecule and I\(^-\) ions in the electrolyte results in the formation of I\(_3\)\(^-\) ions at the photoanode:

\[
2\text{Dye}^+ + 3\text{I}^- \rightarrow 2\text{Dye} + \text{I}_3^- \quad (13.96)
\]

The I\(_3\)\(^-\) ions are transported to the cathode where they are reduced:

\[
\text{I}_3^- + 2e^- \rightarrow 3\text{I}^- \quad (13.97)
\]

The dye-sensitized semiconducting photoelectrode exhibits two functions: (1) absorption of light by the dye and (2) charge transport by the semiconductor. Such dye-sensitized cells allow conversion of light into electricity.

### 13.10.5 Summary

The performance of TiO\(_2\)-based PECs for water splitting is relatively well defined in terms of light-induced electrode reactions and the related charge transfer. A wide range of approaches have been reported in the development of high-performance PECs with reduced energy losses. The most promising approach includes the development of PECs equipped with two photoelectrodes.

### 13.11 Functional Properties

The research strategy on the development of a TiO\(_2\)-based PEC with high performance involves maximization of light absorption and minimization of all energy losses. In order to achieve high efficiency, there is a need to optimize the key performance-related properties, such as electronic structure, FBP, charge transport, concentration of surface-active sites, and charge separation. These may be achieved through the imposition of bulk versus interface properties in a controlled manner.

#### 13.11.1 Electronic Structure

The electronic structure for metals, semiconductors, and insulators is schematically represented in Figure 13.57. The most critical quantity of electronic structure of semiconductors
is the bandgap, $E_g$. The light is effectively absorbed by semiconductors when the photon energy is equal to or higher than the width of forbidden bandgap. Then light absorption leads to ionization i.e. generation of electron-electron hole pairs. Since the energy required for water splitting is 1.23 eV, the optimum value of the bandgap is the sum of 1.23 eV and the amount of energy losses (approximately 0.5–1 eV). Therefore, the optimal bandgap for water splitting is between 1.8 and 2 eV, depending on the extent of energy losses.

The bandgap of TiO$_2$, rutile, is 3.05 eV (Table 13.1 [6–15]). Therefore, intensive research aims to process TiO$_2$ with reduced bandgap. The electronic structure of oxides, including TiO$_2$, is closely related to defect disorder, which may be modified by varying oxygen content as well as through doping with aliovalent ions [2].

The main research strategy in reducing the bandgap of TiO$_2$ includes the following approaches:

1. Elevation of the edge of valency band
2. Imposition of midgap bands so that the effective bandgap required for ionization is reduced

Figure 13.58 is an estimated representation of the effect of $E_g$ on the ECE for a single photoelectrode PEC, including both conservative and optimistic scenarios.

Wilke and Breuer [122] reported that incorporation of Cr$^{3+}$ and Mo$^{5+}$ results in reduction of the bandgap to 2 and 2.8 eV, respectively. According to Khan et al. [123], doping TiO$_2$ with carbon results in bandgap reduction to 2.3 eV. This effect, however, was not confirmed by Barnes et al. [124].

There is no agreement on the reported effect of vanadium doping on electrochemical properties of TiO$_2$. Phillips et al. [125] reported that addition of 30 mol% V to TiO$_2$-SC results in bandgap reduction to 1.99 eV; however, the formation of Ti$_{0.7}$V$_{0.3}$O$_2$ has detrimental effects on photoactivity. On the other hand, Zhao et al. [126,127] observed that increased amount of vanadium in TiO$_2$ thin films results in an increase in the ECE.

There have been some studies on the reduction of the bandgap by manipulation the grain size of TiO$_2$. Hoffmann et al. [16] reported that below a certain critical grain size (~10 nm), the bandgap increases. This effect has been confirmed by Wang et al. [17] who observed that the bandgap of the 2.72 nm grain size TiO$_2$ is 3.32 eV, while the bandgap for TiO$_2$-SC is 3.05 eV (Table 13.1 [6,8–15]). On the other hand, there are several experimental and theoretical evidences indicating that TiO$_2$ nanotubes exhibit reduced bandgap [128–132]. These studies indicate a relationship between the surface shape and bandgap. Namely, the concave curvatures at surfaces result in a decrease of bandgap, while convex curvatures lead to increase of bandgap.
The bandgap is not always the key property, controlling the photocatalytic performance. Karakitsou and Verykios [18] observed that the hydrogen production rate by anatase form of TiO$_2$ is higher than that of rutile by the factor of 7.

There are several experimental approaches to assess the width of the bandgap, including the optical reflection spectra and the temperature dependence of the electrical conductivity corresponding to the n–p transition point [2].

13.11.2 Flat-Band Potential

When a semiconducting photoelectrode is immersed in an aqueous electrolyte, the charge transfer at the photoelectrode/electrolyte interface results in the formation of an electrical potential barrier, which causes the band bending. This barrier, which helps with the charge separation, is an important property of photoelectrode. The voltage needed to straighten the bands is termed the FBP. It may be determined experimentally by the imposition of an external potential compensating the surface charge and flattening the band bending.

Figure 13.59 shows the FBP relative to the vacuum level and the normal hydrogen electrode (NHE) level, and the bandgap values for several oxide materials [33]. The FBP may be determined from the Mott–Schottky equation:

$$\frac{1}{C^2} = \frac{2}{\varepsilon_s \varepsilon_0 N_{A,D}} \Delta V_{SC}$$  \hspace{1cm} (13.98)

where

- $C$ is the measured interfacial capacitance
- $\varepsilon_s$ and $\varepsilon_0$ denote the dielectric constant of the specimen and dielectric permittivity of vacuum, respectively
- $N_{A,D}$ is the concentration of donors or acceptors
- $\Delta V_{SC}$ is the applied external potential

The FBP is the intercept on the voltage axis (Figure 13.60) of the extrapolated linear dependence between $1/C^2$ and the voltage, $V$. 
FIGURE 13.59
FBP of different oxide semiconductors versus energy gap and normal hydrogen energy level in electrolyte of pH = 2. (Reproduced with permission from Bak, T., Oxide Semicond. Res. Rep., Copyright 2010.)

FIGURE 13.60
Graphical determination of the FBP from the Mott–Schottky relationship (plot of $1/C^2$ vs. potential). (Reproduced with permission from Bak, T., Oxide Semicond. Res. Rep., Copyright 2010.)
13.11.3 Charge Transport

The energy losses related to charge transport may be substantial. These may be minimized when the charge transport is maximized and the ohmic resistance is minimized. The charge transport is closely related to the concentration of charge carriers and their mobility. Consequently, the charge transport may be enhanced by the modification of defect disorder in order to enhance the concentration of electronic charge carriers with high mobility.

The amount of hydrogen generated within the PEC is related to the charge transported through the PEC over time. Under the influence of electric field, $F$, randomly moving quasi-free electrons would have acceleration in the direction opposite to the field. The mobility of electrons is

$$\mu_n = \frac{\nu}{F} \quad (13.99)$$

where $\nu$ is the drift velocity:

$$\nu = \frac{et_r}{m^*_n} F \quad (13.100)$$

where
- $t_r$ is the relaxation time
- $m^*_n$ is the effective mass of electron
- $F$ is the electric field
- $e$ is the elementary charge

The corresponding electrical current densities for electrons and holes may be expressed by the following respective equations:

$$J_n = e\mu_n n F$$
$$J_p = e\mu_p p F \quad (13.101)$$

The conductivity is then the sum of both conductivity components for electrons and holes:

$$\sigma = \frac{J}{F} = e\mu_n n + e\mu_p p \quad (13.102)$$

However, the physical meaning of $F$ is more complex in the case when a PEC is equipped with a TiO$_2$ photoelectrode that exhibits a segregation-induced electric field, $F_s$. Then $F$ involves two components: one is related to $F_s$ and the second is the cell component related to the electric field imposed by the electromotive force (EMF) induced by light, $F_c$. The effective electric field will then be a superimposition of these two electric fields that are localized in the surface layer of the photoelectrode. Consequently, the charge transport within a PEC may be enhanced when the direction of $F_s$ is the same as that of $F_c$. In analogy, the field $F_s$ has a retarding effect on the charge transport when its direction is opposite to that of $F_c$.

An important electrical property is electrical conductivity, which must be maximized. In situ monitoring of the electrical conductivity, thermoelectric power, and work function during processing provides a mean to achieve optimal properties [78,134].
The electrical resistance of the TiO$_2$ photoelectrode may be reduced by reduction of TiO$_2$ at high temperatures in a hydrogen/argon mixture. In nonstoichiometric TiO$_{2-x}$, the higher the $x$ value, the lower the resistance [36]. An alternative method of reducing the resistance is through minimization of the thickness of the photoelectrode by fabricating it in the form of a thin film. This method has the advantage that the substrate can be made of titanium metal, which imposes a strong reduction potential, thereby possibly obviating the need for postreduction.

### 13.11.4 Surface Properties

Undefeeted surface of oxides, including TiO$_2$, is not reactive [98]. In other words, efficient photoreactivity between the adsorbed water molecules and TiO$_2$ requires the presence of defects. Lo et al. [130] reported that oxygen vacancies are the active sites for oxygen and water adsorption. These active sites may be considered in terms of either point defects in the outermost surface layer or traces of another phase deposited on the TiO$_2$ surface, such as platinum. High performance requires optimal population of the surface-active sites, able to form photocatalytically active complexes with water, which ultimately leads to its splitting.

An important surface property is the Schottky barrier, which is formed as a result of concentration gradients, surface states, and adsorption states. Such barrier plays an important role in preventing recombination of the charge formed as a result of photoionization. An electrical potential barrier across the surface layer can be formed as a result of structural deformations within the near-surface layer due to an excess of surface energy and segregation-induced chemical potential gradients of aliovalent ions across the surface layer imposed during processing [101,135]. Accordingly, the formation of these gradients may be used for the modification of the Schottky barrier in a controlled manner. The use of this procedure requires in situ monitoring of the surface versus bulk electrochemical properties during the processing of the electrode materials [78,134].

Surface reactivity of TiO$_2$, including the reactivity with water, is closely related to the concentration and the charge of point defects in the outermost surface layer. Recent studies show that effective water splitting on the surface of TiO$_2$, which requires multielectron charge transfer, takes place at titanium vacancies, which are strong acceptor sites able to remove electrons from water molecules [35]. Consequently, high reactivity of TiO$_2$ with water requires an optimal surface population of these active sites.

The concentration of titanium vacancies may be estimated from full defect disorder diagram, which may be derived from defect-related data for TiO$_2$ exposed to prolonged oxidation [39]. An alternative way to determine their concentration is by using the spectroscopy of soft positrons [136].

### 13.11.5 Corrosion Resistance

Photoelectrodes may exhibit stable performance when resistant to corrosion and photocorrosion in aqueous environment [4]. Any form of reactivity results in a change in the chemical composition and the related properties. Therefore, this property is critical for the selection of materials for photoelectrodes. Certain oxide materials, such
as TiO$_2$ and its solid solutions, are particularly resistant to these reactivity types [5]. Therefore, they are suitable candidates for photoelectrodes for electrochemical water decomposition.

A large group of valence semiconductors, which exhibit suitable semiconducting properties for solar energy conversion (width of bandgap and direct transition within the gap), are not resistant to these types of reactivity. Consequently, their exposure to aqueous environments during the photoelectrochemical process results in the deterioration of their performance.

### 13.11.6 Property Limitations

Figure 13.61 shows the positions of band edges for several oxide materials, which are the candidates for photoelectrodes, compared to the energy levels of the electrochemical couples H$^+$/H$_2$ and O$_2$/H$_2$O [135]. Unfortunately, the most promising materials from the viewpoint of the bandgap width, such as GaP ($E_g = 2.23$ eV [128]) and GaAs ($E_g = 1.4$ eV [135]), are not stable in aqueous environments and so suffer from a significant corrosion. Therefore, these materials are not suitable as photoelectrodes in solar cells for water decomposition. The most promising oxide materials, which are corrosion resistant, include TiO$_2$ and SrTiO$_3$ [137–139].

### 13.11.7 Summary

The key performance-related properties for PECs include electronic structure (bandgap), FBP, charge transport, and surface properties. These properties are closely related to defect disorder and, therefore, may be modified in a controlled manner by defect engineering.

**FIGURE 13.61**
Diagram showing bandgap width of different oxide materials and relative positions of band edges with respect to vacuum level and NHE level in electrolyte of pH = 2. (Reproduced with permission from Chandra, S., *Photoelectrochemical Solar Cells* (Electrocomponent Science Monographs), Routledge, New York, 1985.)
13.12 Solar Energy Conversion Efficiency

13.12.1 Basic Relationships

The overall efficiency of a PEC unit, which is known as the solar conversion efficiency $\eta_c$, can be defined according to the following formula [136]:

$$\eta_c = \frac{\Delta G_{\text{H}_2\text{O}}^0 R_{\text{H}_2} - V_{\text{bias}} I}{I_r A}$$  \hspace{1cm} (13.103)

where

$\Delta G_{\text{H}_2\text{O}}^0$ is the Gibbs free energy of formation for 1 mol of liquid H$_2$O = 237.141 (kJ/mol)

$R_{\text{H}_2}$ is the rate of hydrogen generation (mol/s)

$V_{\text{bias}}$ is the bias voltage applied to the cell (V)

$I_r$ is the current within the cell (A)

$I_r$ denotes the incidence of solar irradiance, which depends on geographical location, time, and weather conditions (W/m$^2$)

$A$ is the irradiated area (m$^2$)

Assuming that $R_{\text{H}_2} = I/2F$, Equation 13.103 assumes the following form [140]:

$$\eta_c = \frac{I(1.23 - V_{\text{bias}})}{I_r A}$$  \hspace{1cm} (13.104)

The overall efficiency $\eta_c$ is the following function of the property-related components [136]:

$$\eta_c = \eta_g \eta_{ch} \eta_{QE}$$  \hspace{1cm} (13.105)

where

$\eta_g$ denotes the solar irradiance efficiency

$\eta_{ch}$ is the chemical efficiency

$\eta_{QE}$ is the quantum efficiency

The $\eta_g$ is defined as the fraction of the incident solar irradiance with photoenergy $\geq E_g$ and may be expressed as

$$\eta_g = \frac{J_g E_g}{E_s}$$  \hspace{1cm} (13.106)

where

$J_g$ is the flux density of absorbed photons

$E_s$ is the incident solar irradiance (W/m$^2$)

The chemical efficiency is defined as the fraction of the excited state energy effectively converted to chemical energy and may be expressed as

$$\eta_{ch} = \frac{E_g - E_{\text{loss}}}{E_g}$$  \hspace{1cm} (13.107)

where $E_{\text{loss}}$ is the energy loss per molecule in the overall conversion process. For ideal systems, $E_{\text{loss}}$ is defined as the difference between the internal energy and Gibbs free energy of the excited states. For real systems, $E_{\text{loss}}$ assumes considerably larger values.
The quantum efficiency is defined as the following ratio:

\[ \eta_{QE} = \frac{N_{\text{eff}}}{N_{\text{tot}}} \]  

(13.108)

where

- \( N_{\text{eff}} \) is the number of effective incidents leading to the generation of photoelectron/photohole pairs
- \( N_{\text{tot}} \) is the total number of absorbed photons

### 13.12.2 Energy Losses

The key performance indicator of PECs is the ECE, which may be defined as the ratio of the energy output, \( E_{\text{out}} \), to the energy input, \( E_{\text{in}} \):

\[ \text{ECE} = \eta_c = \frac{E_{\text{out}}}{E_{\text{in}}} \]  

(13.109)

where \( E_{\text{out}} \) is the difference between the \( E_{\text{in}} \) and all kinds of energy losses:

\[ E_{\text{out}} = E_{\text{in}} - E_{\text{loss}} \]  

(13.110)

These losses are related to a range of properties/phenomena, including (1) optical reflection, \( E_{\text{OPT}} \); (2) recombination, \( E_{\text{REC}} \); (3) electrical resistance, \( E_{\text{R}} \); (4) charge transfer, \( E_{\text{CT}} \); and (5) heat, \( E_{\text{H}} \). Therefore,

\[ E_{\text{loss}} = E_{\text{OPT}} + E_{\text{REC}} + E_{\text{R}} + E_{\text{CT}} + E_{\text{H}} \]  

(13.111)

**Figure 13.62** shows the optical processes within PEC associated with different types of reflection and absorption. The \( E_{\text{REC}} \) component may be reduced by the imposition of an electric field leading to enhanced charge separation. Recent reports indicate that the electric field may be imposed in a controlled manner by surface and near-surface engineering, leading to the formation of concentration gradients and the related potential barriers. The electrical resistance-related losses, \( E_{\text{R}} \), may be decreased by the increase of the concentration of charge carriers and/or their mobility. The energy losses related to charge transfer at the surface, \( E_{\text{CT}} \), may be reduced by appropriate engineering of the outermost surface layer, where the charge transfer between the solid and the adsorbed molecules takes place. The heat-related energy losses, \( E_{\text{H}} \), are caused by light absorption of the energy lower and also larger than the width of bandgap.

### 13.12.3 Interdependence of Functional Properties

It has been a general perception that the width of the forbidden gap is the most important property of the photoelectrode. Indeed, it has been shown previously that the amount of the light energy being absorbed is determined by the bandgap. It has been shown, however, that the amount of the energy output is substantially lower due to energy losses.

The key performance-related properties are interdependent. Therefore, the modification of one property also results in a change of other properties. For example, while a
particular dopant ion introduced into the lattice results in reduction of the band gap, the same dopant may lead to a decrease of charge transport. When the earlier or the latter term predominates, the ECE will increase or decrease, respectively. Therefore, ECE should be maximized using a multivariant approach of all performance-related properties, which are closely related to defect disorder. Therefore, the performance of oxide semiconductors may be modified by using defect chemistry as a framework to enhance the performance. This approach is based on the fact that all functional properties, and the associated energy losses, are related to defect disorder. However, since the effects of defect disorder on these losses are interdependent, the system should be considered as multivariant. Consequently, each variable leading to the modification of the system is expected to have an effect on all properties.

It is difficult to make a graphical representation of the effect of all functional properties, and the related energy losses, on ECE. An attempt to make the 3D representation of the effect of the bandgap, along with the effect of the electric field, on the ECE is shown in Figure 13.63c.

In summary, the research strategy in the development of high-performance oxide semiconductors should lead to minimization of the energy losses by a multifactorious approach:

$$\nabla E_{\text{loss}}(x_1, x_2, \ldots, x_n) = 0$$  \hspace{1cm} (13.112)

where $x_1$, $x_2$, and $x_n$ are independent variables, such as dopant concentration and oxygen activity.
13.12.4 Overview of Progress

The increasing recognition of the impact of greenhouse gas emissions on climate change is expected to intensify the development of the technology of hydrogen production from water using solar and other renewable energy sources. Awareness is growing that hydrogen generated by water splitting using solar energy (solar hydrogen) is the most promising clean fuel of the future.

At present, the most common way of solar hydrogen generation is by water electrolysis using photovoltaic electricity. Tani et al. [141] reported that efficiency of the experimental PV-based solar hydrogen systems is 4.47%. The conversion efficiency of the most recently reported home fueling solar system, involving high-efficiency PV modules (16%) and high-pressure (44.8 MPa) electrolyzer, is 9.3% [142]. The two-device approach, however, requires application of two different devices: the silicon-based photovoltaic panel to harness solar energy for the production of electricity and the water electrolyzer, which converts the photovoltaic electricity into hydrogen.

There have been efforts to develop a PEC, which absorbs solar energy and splits water within a single device [2–4,78,80,105,113,116,117,119–121,126,127,137–139,143–179]. This technology has a substantial advantage over the PV technology due to the following reasons:

- The key component of the PEC is expected to be an oxide semiconductor, which is much less expensive than silicon and, first of all, exhibits stable performance when immersed in water.
- The PEC allows generating hydrogen within a single step.

FIGURE 13.63
A 3D representation of the dependence of ECE on both bandgap and the FBP (represented by electric field), the latter in arbitrary units.
While the advantage of the PEC technology is clear, its performance is still not satisfactory because so far its ECE is below the level that is economically feasible.

The simplest approach for photoelectrochemical hydrogen generation is using a photocatalyst, such as TiO$_2$, dispersed in aqueous solution. Then water splitting leads to the formation of the gas mixture involving both hydrogen and oxygen. This approach, however, requires energy for gas separation.

For a long time, the ECE for photoelectrochemical water splitting by using TiO$_2$ has remained below the level required for commercialization [4]. However, the recent progress in solid-state science and materials engineering is expected to allow the development of high-performance photoelectrodes for the production of hydrogen fuel with high efficiency. The most recent progress in defect chemistry for TiO$_2$ indicates that it is possible to process TiO$_2$ with controlled properties that are desired for specific applications.

Owing to the promising properties of TiO$_2$, this compound has been investigated in many laboratories. The research project initiated by the National Space Development Agency (NADA), Japan, and the Institute for Laser Technology (ILT) aims to generate solar hydrogen using a space-based solar unit harvesting solar energy and transferring this energy (by laser) to a TiO$_2$-based electrochemical device located on Earth [180].

The future production scale of hydrogen using different technologies will be determined by their production costs. Solar hydrogen can be expected to be a long-distance winner as the ultimate fuel for the following reasons:

- Large parts of continents have an abundance of solar energy.
- Solar energy may be captured by MoS$_2$, which are relatively inexpensive.
- Solar hydrogen production technology could be adapted easily to the needs of individual households. The technology of domestic PECs may provide a driving force for mass production of small units.

The focal points of the research on photosensitive compounds for photo-assisted water splitting include the determination of the effects of composition on their performance in water splitting. There has been an accumulation of data indicating that the incorporation of foreign ions may lead to the reduction of the bandgap [122,123,140,181]. However, there are substantial hurdles, which must be overcome. For example, in the case of chromium incorporation, the observed reduction of the bandgap of TiO$_2$ even to 2 eV [122] leads to a decrease of ECE [182]. The latter data have been considered in terms of the effect of Cr on an (1) increase of the recombination-related energy losses due to reduced lifetime of light-induced electron–hole pairs from 90 μs for undoped TiO$_2$ to 30 μs for Cr-doped TiO$_2$ [122] and an (2) increase of the ohmic-resistance-related energy losses.

The majority of performance-related data on photoelectrochemical water splitting are reported in terms of arbitrary units that are related to specific experimental conditions. These data cannot be compared.

Mavroides et al. [138] reported quantum energy conversion efficiencies for different TiO$_2$ specimens, including single crystals, polycrystals, thin films, and thin layers formed on metallic titanium by oxidation. These data indicate that the TiO$_2$ layers formed by oxidation on metallic titanium exhibit the best performance.

The use of hybrid PECs, involving inner photovoltaic tandem systems that are covered with a thin layer of corrosion resistance TiO$_2$, represents a promising research strategy in the development of solar hydrogen technology [118,119].
Photosensitizers made of organic compounds may be used to increase the energy conversion efficiencies up to 10% [121]. The key issue in the development of the dye-sensitized systems is their durability.

Very high total energy conversion efficiencies (in the range 12%–18%) have been reported for photoelectrodes made of GaAs and Al-doped GaAs [19,118]. However, their stable performance in aqueous environments is limited.

The key issues, which must be addressed in the development of a commercial solar hydrogen PEC, include maximization of the ECE and the related hydrogen generation rate and maximization of the lifetime of photoelectrode. The latter impacts on the maintenance cost. Taking this into account, the thick line in Figure 13.64 seems to represent the expected commercial viability line.

While the technology of solar hydrogen has not been commercialized so far, there have been efforts toward installation of pilot plants. A US company, Nanoptek, Maynard, MA, claims to have achieved success in the processing of titania photocatalyst to be photoactive well into the visible blue and so is 6× more efficient in sunlight than native titania [183]. The company disclosure, however, neither provides the definition of the native titania nor specifies its ECE. Therefore, it is difficult to compare the performance of their photocatalysts with other systems reported in the literature. J. Guerra, the company’s CEO, claims that this has been achieved by coating titania on domelike plastic nanostructure surface resulting in the pulling of atoms apart [184].

The solar hydrogen technology has not been commercialized so far. One may expect that the approach to develop a commercial unit will include (1) the solar cell exposed to sunlight and (2) two water circulation units including gas collection cylinders and water pump enforcing the circulation in the unit.

**FIGURE 13.64**
Schematic representation of critical requirements for the solar hydrogen commercial viability in terms of the ECE and the lifetime of photoelectrode along with selected ECE data reported in the literature. (Reproduced with permission from Int. J. Hydrogen Energy, 32, Nowotny, J., Bak, T., Nowotny, M.K., and Sheppard, L.R., Titanium dioxide for solar-hydrogen 1. Functional properties, 2609–2629. Copyright 2007, International Association for Hydrogen Energy. Published by Elsevier Ltd.)
The key function of the solar cell is to absorb solar energy. Therefore, the cell should be flat in order to achieve maximum surface area for the photoelectrode. As shown in the cross section in Figure 13.66, the cell has a layered structure including (from the top) (1) a sunlight transparent window, (2) photoanode deposited on a support, (3) water permeable membrane that allows rapid proton transport between the electrodes, and (4) cathode.

The aqueous electrolyte circulation system aims to remove the gases from both PEC compartments as well as collection of gases. The system includes both oxygen and hydrogen circuits connected to photoanode and cathode spaces, respectively. These gases are initially collected in the gas collection cylinders under atmospheric pressure and are subsequently pumped into storage tanks.

TiO$_2$ is also a promising candidate for photocatalytic water purification. The performance model of TiO$_2$-based photocatalyst is shown in Figure 13.65. Such a photocatalyst may be considered as a micro-PEC involving anodic and cathodic sites, which are contained to a single TiO$_2$ grain. The primary anodic reaction product is hydroxyl radical, OH*, formed according to the following reaction:

$$H_2O + h^* \rightarrow H^+ + OH^*$$  \hspace{1cm} (13.113)

The most important cathodic reaction is the formation of superoxide species [185,186]:

$$O_2 + e^- \rightarrow O_2^-$$  \hspace{1cm} (13.114)

Alternatively, cathodic reduction may be represented by the following reaction:

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$$  \hspace{1cm} (13.115)

The species OH*, O$_2^-$, and H$_2$O$_2$ then react with toxic organic compounds and bacteria leading ultimately to their oxidation and the formation of stable molecules. An efficient photocatalytic process requires that both cathodic and anodic reactions take place with the same rate, leading to efficient removal of the excess of both charge carriers at both anodic and cathodic sites. In the photocatalytic process, both oxidation and reduction
occur on the surface of the photocatalyst, which exhibits the functions of both anode and cathode as it is shown in Figure 13.65.

### 13.12.5 Summary

The solar-to-chemical ECE of PECs is determined by several performance-related properties, which are interrelated. Therefore, the modification of the ECE requires applying a multivariant approach. The most promising is the PEC equipped with two photoelectrodes, photoanode and photocathode, which are made of oxide semiconductors that exhibit stable performance in water.

### 13.13 Summary

This chapter provided a comprehensive overview of several aspects of hydrogen generation using solar energy. The focus is on several aspects of hydrogen generation by photoelectrochemical water splitting using TiO$_2$-based POSs. It is shown that these materials are the promising candidates for photoelectrochemical solar cells due to an outstanding corrosion and photocorrosion resistance.

The key performance-related properties of TiO$_2$-based oxide semiconductors have been considered, including the following:

- **Electronic structure.** This property, and specifically the bandgap, is responsible for the absorption of solar energy. The optimal bandgap of TiO$_2$ that is required for maximized absorption of sunlight is in the range of 1.8–2.2 eV.

- **Charge transport.** Minimization of the energy losses related to charge transport requires minimizing the ohmic resistance.

- **FBP.** An optimal value of the FBP is required for effective charge separation and reduction of recombination-related energy losses in photoelectrodes.

- **Surface defect disorder.** The ECE critically depends on the presence of surface-active sites for water splitting. These sites should be identified and their surface population should be optimized.

All these performance-related properties are closely related to defect disorder. Therefore, the performance of TiO$_2$ may be tailored using defect engineering.

### 13.14 Conclusions

There is an increasingly urgent need to develop renewable energy-related technologies. Since solar energy is available in abundance, this energy is expected to be the most attractive option in the development of the modern energy system, including photovoltaic electricity and solar fuel. Therefore, there have been efforts to harness solar energy for a wide range of applications. A spectacular achievement in the race to increase the solar ECE is a triple-junction solar PV panel with ECE at the new record level of 40.8% [187].

There is a general consensus that fossil fuels will be replaced by hydrogen as the fuel in the near future. However, the economical consequences of climate change dictate the need
to abandon the present steam reforming technology and develop the technology of hydrogen generation using renewable energy, such as solar hydrogen. Therefore, the future of hydrogen economy must be considered in terms of the development of hydrogen generation technologies using renewable energy. While solar power is universally available, equally attractive alternatives are wind, tide, hydroelectric, hydrothermal, and geothermal power that are more regionally based.

Hydrogen generated from solar energy does not contribute to the emission of greenhouse gases and climate change. Awareness is growing that hydrogen generated from water as a raw material using solar energy as the renewable energy is the most promising option for generation of hydrogen (solar hydrogen).

While at present solar hydrogen is generated by water electrolysis using photovoltaic energy, one of the most promising methods of hydrogen generation, which is environmentally friendly, is photoelectrochemical water splitting using PEC. This method allows hydrogen generation in a single step. The concept of a PEC—equipped with one photoelectrode—for solar hydrogen, involving a planar solar unit, the water flow system, and the gas collection system, is represented schematically in Figure 13.66. There are several advantages of solar hydrogen, including the following:

- Solar hydrogen will assist in reducing the levels of greenhouse and pollutant gases.
- Solar hydrogen encompasses both the production and utilization of a fuel that is 100% environmentally clean.
- Solar hydrogen will reduce the reliance on fossil fuels.
- Solar hydrogen will allow its producers to export solar energy.
- When this technology matures, it will allow developing countries to have access to cheap energy.
13.15 Historical Outline

1839: The Becquerel effect. The discovery of the photovoltaic effect by Becquerel [188] was the first observation of the chemical reaction induced by radiation.

1954: Theory of photoelectrochemistry. Brattain and Garret [189] first explained the charge transport during the photoelectrochemical effect in terms of the band model. Subsequent studies of Gerischer [190], Memming [191], and Morrison [192] led to a better understanding of the impact of the semiconducting properties of photoelectrodes on the photoelectrochemical effect.


1975: Bi-photoelectrode PEC. Yoneyama et al. [117] first reported PEC equipped with two semiconducting photoelectrodes, involving a photoanode and a photocathode made of n-type and p-type semiconductors. The performance of the bi-PEC was subsequently explained by Nozik [116].

1976: Hybrid PEC. Morisaki et al. [119] first reported an HPE consisting of the inner Si-based photovoltaic cell and external TiO$_2$-based photoanode. This concept subsequently led to the construction of high-efficiency cells reported by Khaselev and Turner [19] and Peharz et al. [118].

1978: Modification of TiO$_2$. Ghosh and Maruska [193] reported the effect of doping on semiconducting and photoelectrochemical properties of TiO$_2$ (the effect of doping was then confirmed by Houlihan et al. [181] and others).


2006: Derivation of defect disorder for TiO$_2$. First derived defect diagram that allows to determine the effect of oxygen activity, temperature, and the concentration of aliovalent ions on the chemical potential of electrons [42]. This diagram may be used to predict the reactivity and photoreactivity of TiO$_2$ with water.

Nomenclature

- $a$: Activity
- $A$: Effective concentration of acceptors (atomic ratio)
- $c$: Chemical concentration (atomic ratio)
- CPD: Contact potential difference (V)
- $d$: Thickness of the depleted layer (m)
- $D_{chem}$: Chemical diffusion coefficient ($\text{m}^2/\text{s}$)
- $e$: Elementary charge ($1.602 \times 10^{-19}$ C)
- $e'$: Quasi-free electron
- $E_C$: Energy of the bottom of the conduction band (eV)
- $E_F$: Fermi level (eV)
- $\Delta E_F^*$: Change in Fermi level after irradiation (eV)
- $(E_F)_n$: Light-induced quasi-Fermi level associated with electrons (eV)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>((E_F)^*)_p</td>
<td>Light-induced quasi-Fermi level associated with electron holes (eV)</td>
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<td>(E_g)</td>
<td>Bandgap (eV)</td>
</tr>
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<td>(E_V)</td>
<td>Energy of the top of the valence band (eV)</td>
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<td>(E(\text{H}^+/\text{H}_2))</td>
<td>Energy level of the redox couple (\text{H}^+/\text{H}_2) (eV)</td>
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<td>(E(\text{O}_2/\text{H}_2\text{O}))</td>
<td>Energy level of the redox couple (\text{O}_2/\text{H}_2\text{O}) (eV)</td>
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<td>(E_a)</td>
<td>Activation energy of electrical conductivity (kJ/mol)</td>
</tr>
<tr>
<td>(F)</td>
<td>Electric field (V/m)</td>
</tr>
<tr>
<td>(h)</td>
<td>Planck constant ((6.626 \times 10^{-34} \text{ J s}))</td>
</tr>
<tr>
<td>(h^*)</td>
<td>Quasi-free electron hole</td>
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<tr>
<td>(\Delta H_f)</td>
<td>Activation enthalpy of defect formation (kJ/mol)</td>
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<tr>
<td>(\Delta H_m)</td>
<td>Activation enthalpy of defect motion (kJ/mol)</td>
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<td>(j)</td>
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<td>Equilibrium constant</td>
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<td>(m_\sigma)</td>
<td>Parameter related to defect disorder</td>
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<td>Concentration of electrons ((\text{m}^{-3}))</td>
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<td>Distribution of photons with respect to energy ((1/\text{s m}^2 \text{ eV}))</td>
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<td>Density of states in the conducting band ((\text{m}^{-3}))</td>
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<tr>
<td>(N_p)</td>
<td>Density of states in the valence band ((\text{m}^{-3}))</td>
</tr>
<tr>
<td>(p)</td>
<td>Concentration of electron holes ((\text{m}^{-3}))</td>
</tr>
<tr>
<td>(p_0)</td>
<td>Concentration of electron holes before irradiation ((\text{m}^{-3}))</td>
</tr>
<tr>
<td>(p(\text{O}_2))</td>
<td>Oxygen activity (Pa)</td>
</tr>
<tr>
<td>PEC</td>
<td>Photocell photoelectrochemical cell</td>
</tr>
<tr>
<td>(R)</td>
<td>Universal gas constant ((8.3144 \text{ J/mol K}))</td>
</tr>
<tr>
<td>(S)</td>
<td>Thermoelectric power ((\text{V/K}))</td>
</tr>
<tr>
<td>SPS</td>
<td>Surface photoelectron spectroscopy</td>
</tr>
<tr>
<td>(T)</td>
<td>Absolute temperature (K)</td>
</tr>
<tr>
<td>(\text{TiO}_2)-PC</td>
<td>Polycrystalline titanium dioxide</td>
</tr>
<tr>
<td>(\text{TiO}_2)-SC</td>
<td>Single-crystal titanium dioxide</td>
</tr>
<tr>
<td>WF</td>
<td>Work function (eV)</td>
</tr>
<tr>
<td>(x)</td>
<td>Distance (m)</td>
</tr>
<tr>
<td>(z)</td>
<td>Valence</td>
</tr>
<tr>
<td>(\beta)</td>
<td>Temperature coefficient of the bandgap (eV/K)</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Electrochemical potential (eV)</td>
</tr>
<tr>
<td>(\Theta)</td>
<td>Surface coverage (ratio)</td>
</tr>
<tr>
<td>(\mu)</td>
<td>Chemical potential (eV)</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Electrical conductivity ((1/\Omega \text{m}))</td>
</tr>
<tr>
<td>(\nu)</td>
<td>Frequency of light (Hz)</td>
</tr>
<tr>
<td>(\rho(\chi))</td>
<td>Charge distribution ((\text{C/m}))</td>
</tr>
<tr>
<td>(\Psi)</td>
<td>Electrical potential (V)</td>
</tr>
<tr>
<td>(\chi)</td>
<td>External work function (eV)</td>
</tr>
<tr>
<td>(\Phi)</td>
<td>Work function (eV)</td>
</tr>
<tr>
<td>(\Phi_s)</td>
<td>Work function component related to surface charge (eV)</td>
</tr>
<tr>
<td>(\Phi_{in})</td>
<td>Internal work function component (eV)</td>
</tr>
</tbody>
</table>
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