PhotoElectroChemistry for Corrosion

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Electrochemistry Xpertise Corrosion

Contents

Introduction

- Photoelectrochemical techniques have been shown to be useful tools for characterizing oxidation layers.
- Interdisciplinary theoretical underpinnings were built [1–5] such as the Gärtner-Butler model [6, 7] which has been proven to be a simple and robust model for the photocurrent generation.
- Technical progresses were achieved, allowing to study oxide layers at macroscopic, mesoscopic, and microscopic scales [8, 9], or in-situ in high temperature corrosion conditions [10, 11].

Hypotheses

Several hypotheses are needed in order to apply the theoretical concepts:

- semiconductors are considered to be ideal i.e. crystallized and homogeneous
- the dielectric constant of the semiconductor is independent of the light wavelength
- the capacity of the Helmholtz layer is greater than the capacitance of the space charge capacitance
- the potential drop in the Helmholtz layer is independent of the applied potential and is negligible

Warning

The hypotheses are rarely fully respected in the case of oxides or passive films formed on industrial alloys. Nonetheless, the literature shows that the developed models can be applied to non-ideal systems such as oxides and passive films.

Band Model I

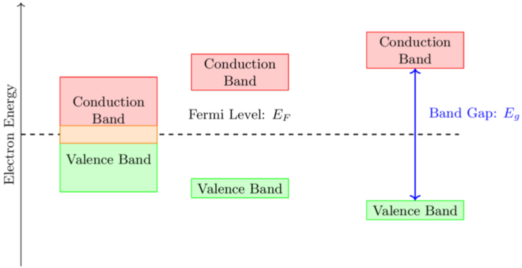
- Solids: conductors, semiconductors and insulators.
- Valence and conduction bands correspond to allowed energy states for the electrons.
- E_c is the lowest energy level of the conduction band.
- E_v is the highest energy level of the valence band.
- E_g is the band gap with no allowed energy states.
- E_F is the Fermi Level which describes the distribution of the electrons among both bands.

Fermi Level

The Fermi Level represents the highest energy state that can be occupied level at 0K. It is equivalent to the electrochemical potential in solid phases.

Band Model II

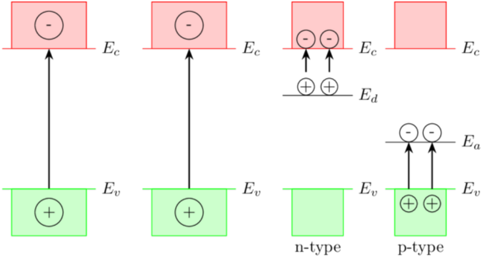
- The electronic conduction = movement of electrons and/or holes in conduction/valence band.
- The conduction depends on the number of available charge carriers in the conduction band and in the valence band.
- In conductors: overlap of the conduction and the valence bands occurs.
- In semiconductor and insulator: the conduction depends on the band gap and the energy provided by the environment to the electrons from the valence band in order to jump into the conduction band.



Excitation carrier I

In semiconductors, charge carriers can be generated by three mechanisms:

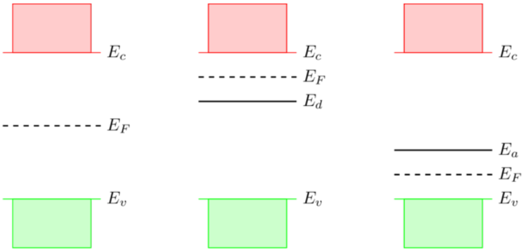
- thermal excitation: in the case of very low band gaps, it can be enough in order to eject an electron from E_v to E_c.
- photoexcitation: ejects electrons from E_v to E_c band when an incident photon $(h\nu > 5eV)$ is absorbed.
- doping: introduces additional energy level located in between E_v to E_c.



a) Thermal Excitation b) Photoexcitation c) Doping

Fermi Position

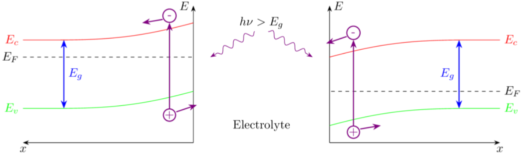
The Fermi level E_F in intrinsic semiconductors is located at the mid-gap. The n-type and p-type doping shift the Fermi level towards band edges E_c and E_v.



a) Intrinsic b) n-type b) p-type

Electron/hole pairs I

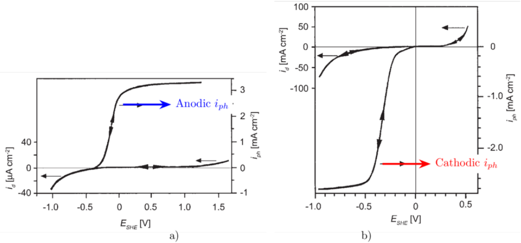
- The illumination of the semiconductor/electrolyte interface, with photons having an energy greater than the band gap, E_g, creates electron/hole pairs in the semiconductor.
- By applying the adequate potential the pairs can be separated.
- As a consequence, the majority charge carriers are attracted to the semiconductor bulk whereas the minority charge carriers are drawn to the semiconductor/electrolyte interface where they can be transferred to a RedOx species creating an additional current called photocurrent.



a) n-type b) p-type

Electron/hole pairs II

- The photocurrent is significant when the semiconductor/electrolyte junction is in depletion.
- n-type (p-type) semiconductors generate anodic (cathodic) photocurrents where the electrons (holes) move towards the external circuit whereas the holes (electrons) move towards the interface.
- The applied potential on n-type (p-type) semiconductors is greater (lower) than the flat band potential.

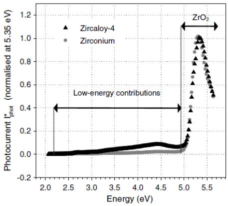


Linear transform I

- The linear transform with respect to the energy is used for determining the band gaps.
- The linear transform with respect to the potential is used for determining the semiconducting type, the flat band potential, and the number of majority charge carrier.

Identification of minor oxides I

- Benaboud et al. [8] showed that the photoelectrochemical characterization is robust for detecting the presence of minor oxides.
- The strong photocurrent observed at around 5 eV reveals the major oxide i.e. monoclinic zirconia.
- The photocurrent $h\nu < 5eV$ reveals the presence of minor oxides even in "pure" zirconium.
- The slope changes provided an estimation of the band gaps: hematite, chromia and a solid solution of $(Fe_x Cr_{1-x})O_3$.



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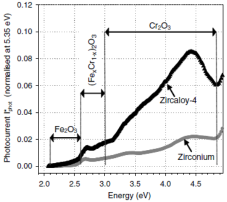

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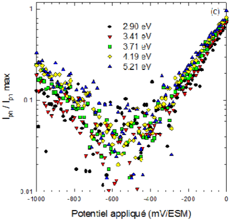
Semiconduction type I

- Loucif et al. [12] showed the effect of hydrogen pressure on the semiconduction type on Ni-based alloy 600 oxidized in simulated PWR.
- The "V-shape" of the normalized photocurrent reveals an isolating behavior of the oxide layer at high hydrogen pressure.
- The monotonous increase of the normalized photocurrent towards more anodic potentials reveals n-type semiconduction.



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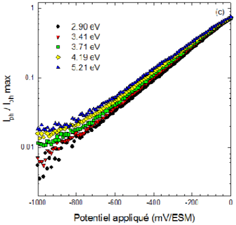

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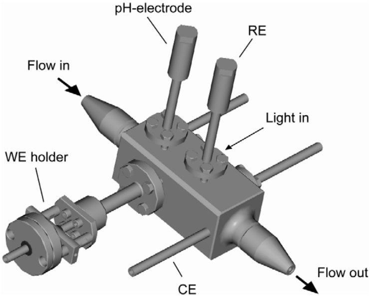
High temperature PEC I

- The majority of photoelectrochemical characterizations are performed at room temperature in simple glass/Plexiglas cells where the signal/noise ratio is very good.
- High temperature photoelectrochemical characterizations require sophisticated metallic cells and transparent windows able to withstand the arch environment.
- Despite the need to improve the signal/noise ratio, the feasibility of the in-situ photoelectrochemical characterizations was demonstrated by Bojinov et al. [10] in 2002 and more recently by Skocic [11] in 2015

High temperature PEC II



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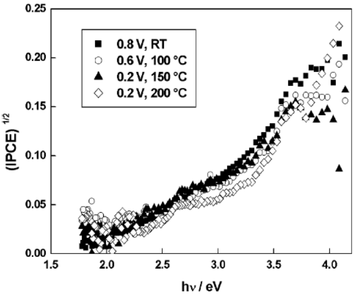

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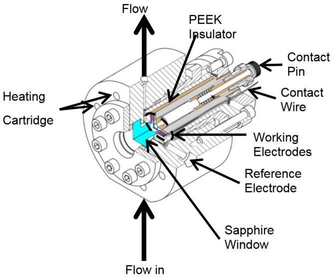
High temperature PEC III



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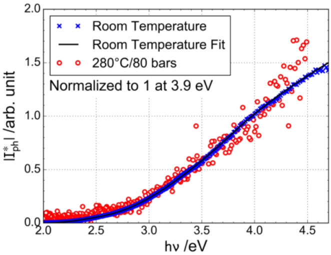

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