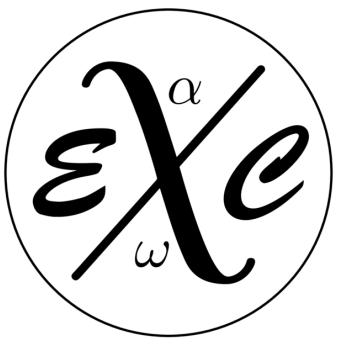
PhotoElectroChemistry for Corrosion

M. Skocic, PhD Electrochemistry and Materials



$\mathcal{E}$lectrochemistry χpertise $\mathcal{C}$orrosion

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.

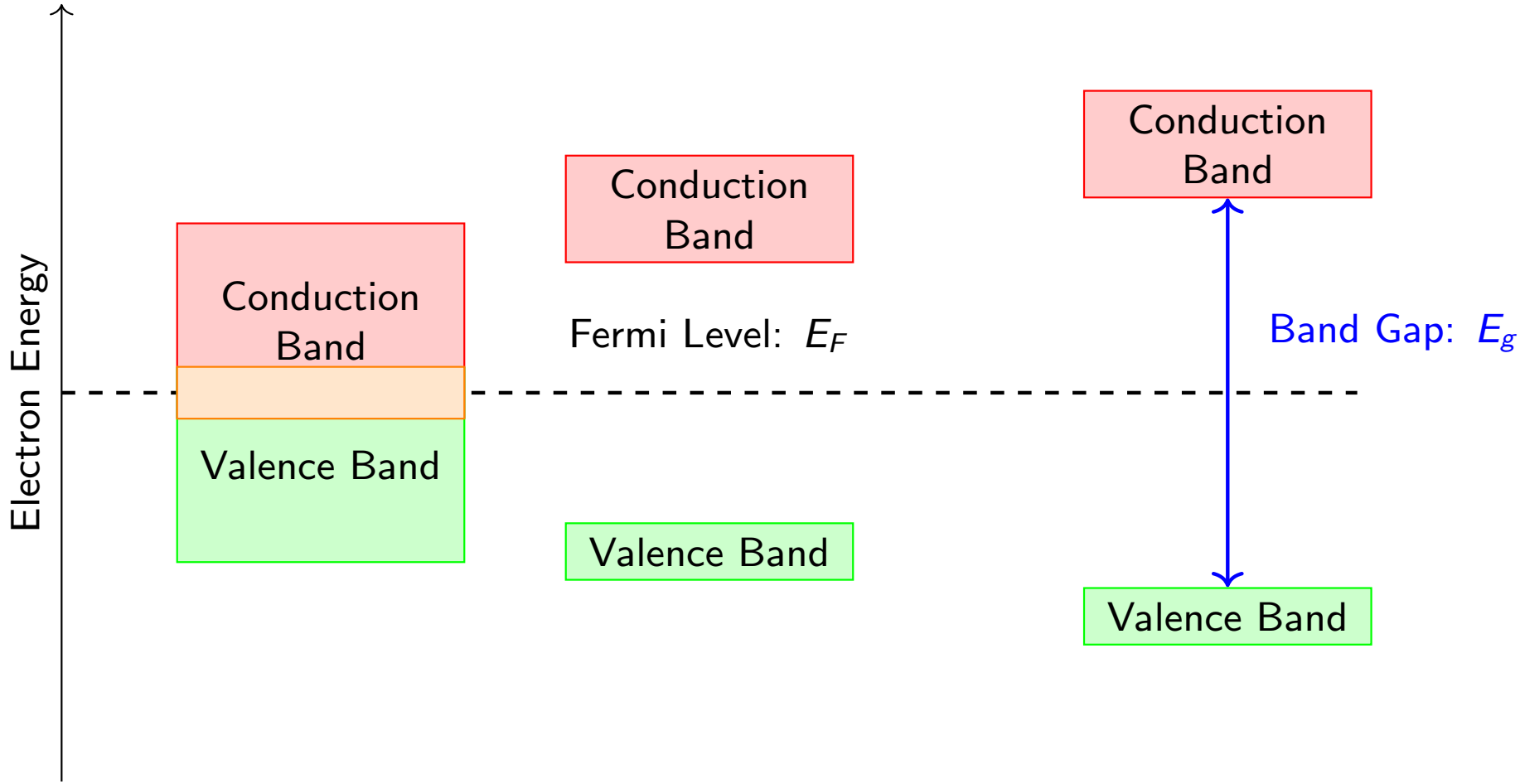
Fermi Level

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.

Band Model III

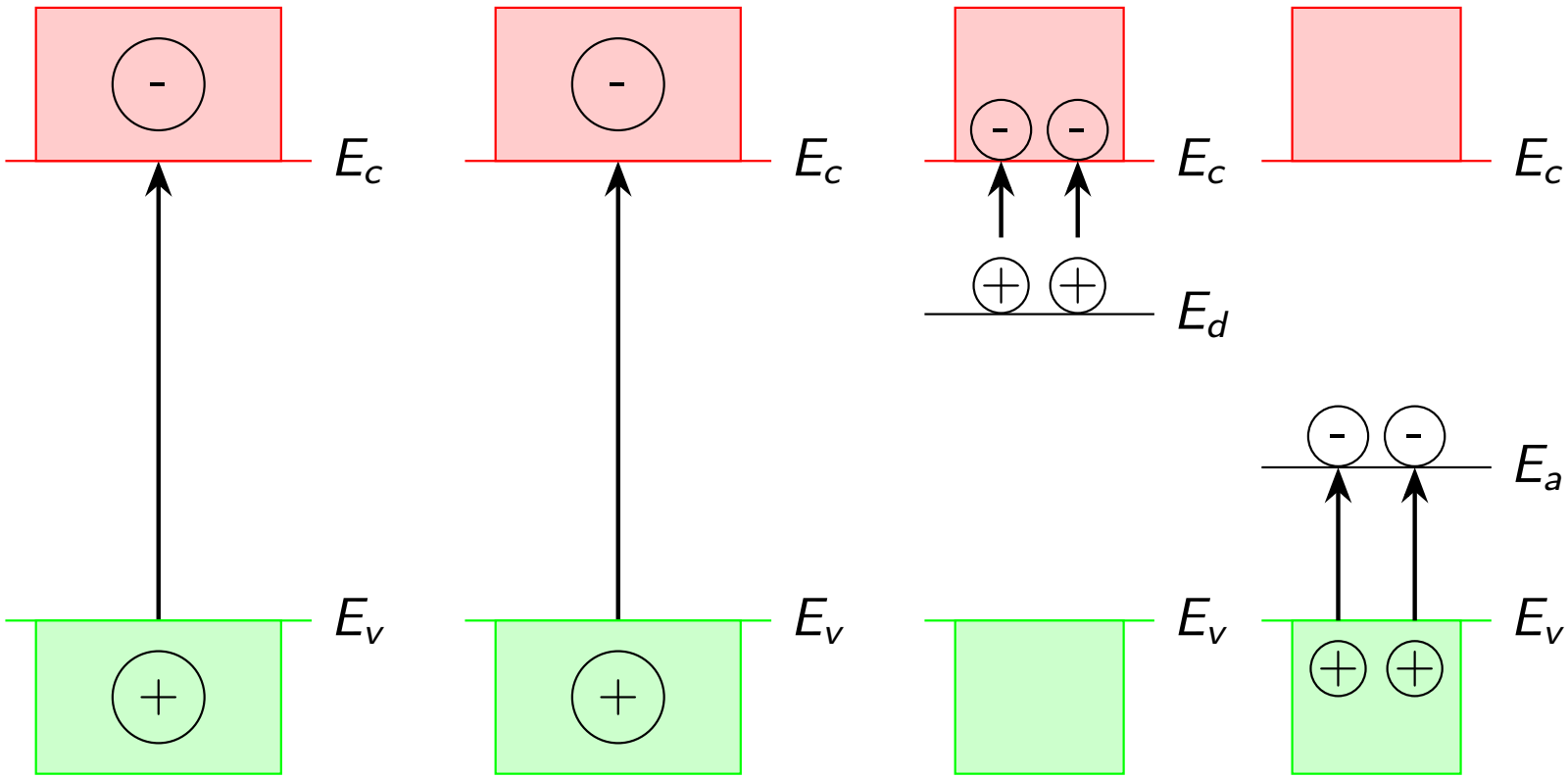


Excitation carrier I

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

- thermal excitation: in the case of very low band gaps, thermal excitation can be enough in order to eject an electron from the valence band to the conduction band.
- photoexcitation: ejects electrons from the valence band to the conduction band when an incident photon, with energy greater than the band gap, is absorbed.
- doping: introduces additional energy level located in between the conduction and valence bands.

Excitation carrier II

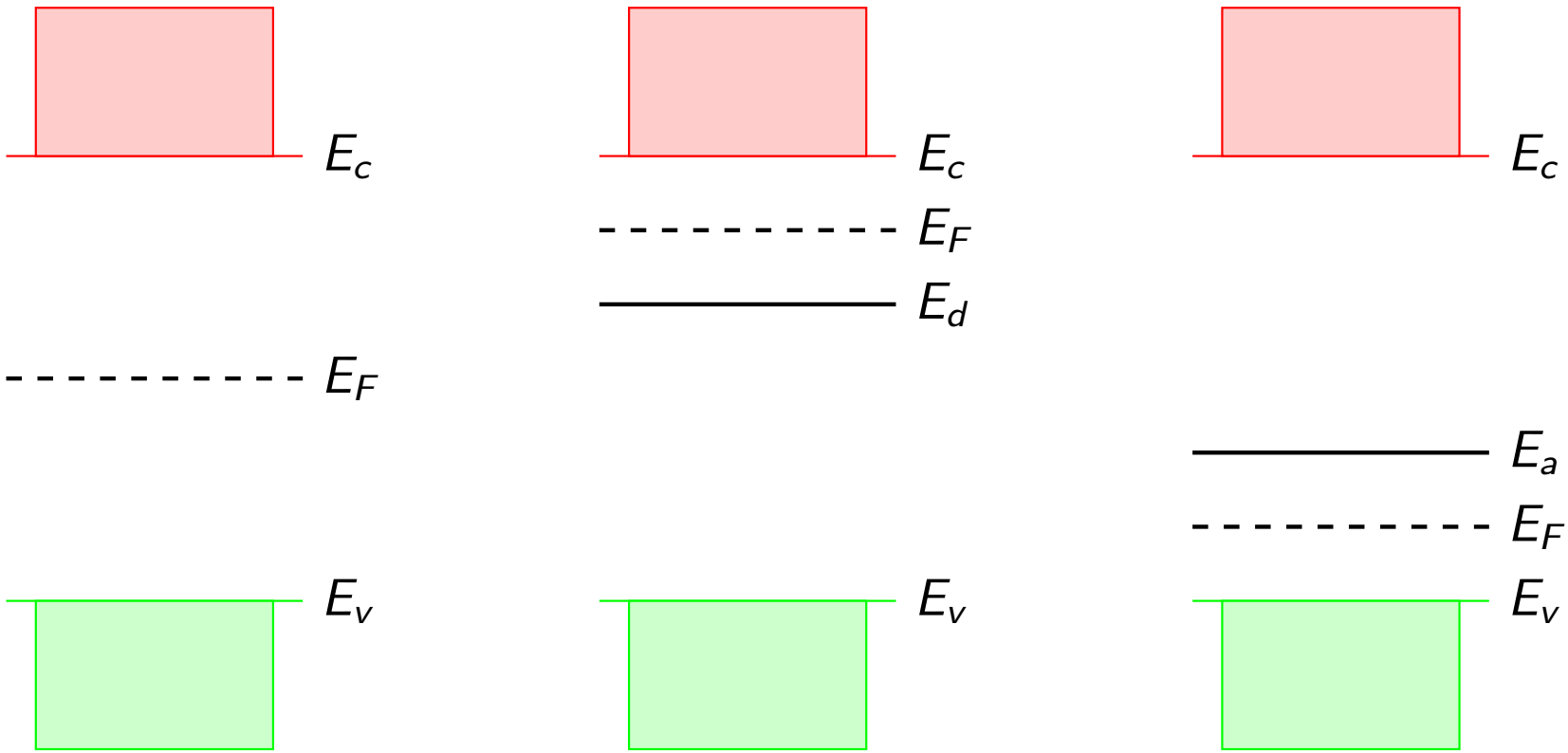


a) Thermal Excitation

b) Photoexcitation

c) Doping

Fermi Position



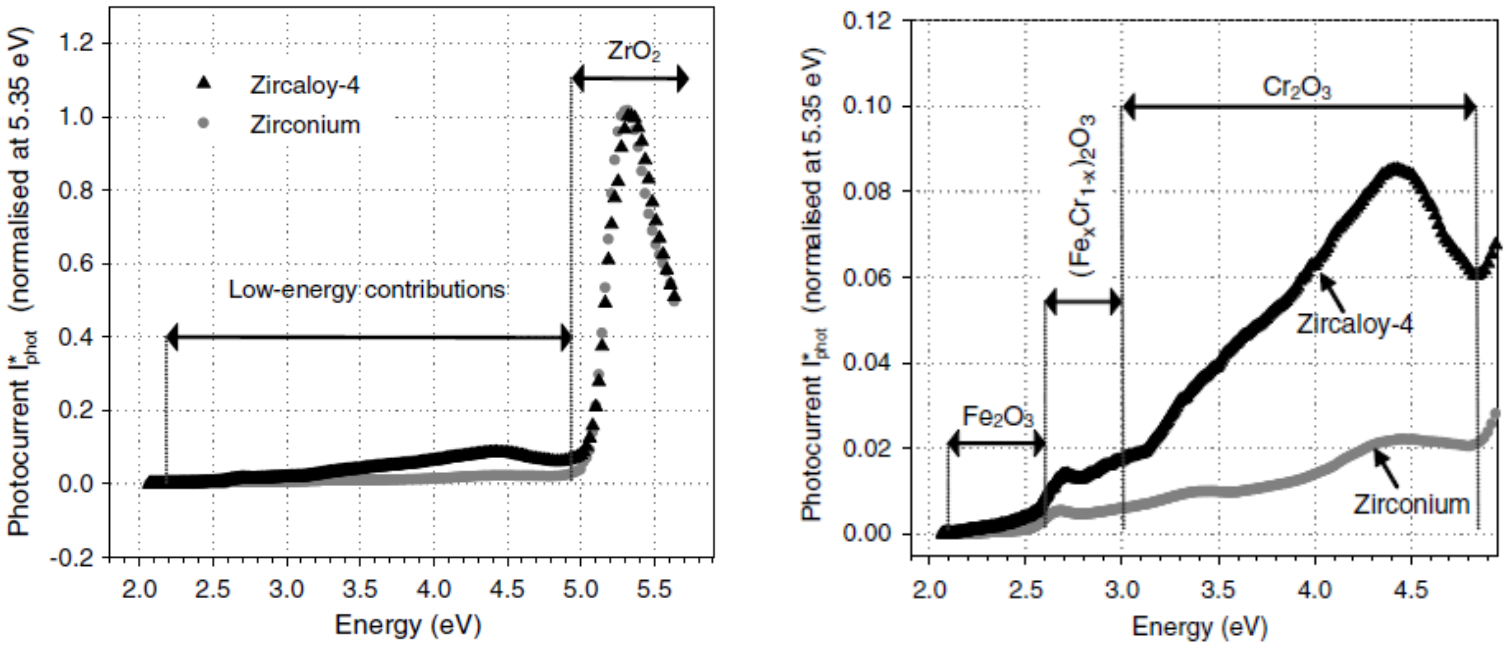
a) Intrinsic b) n-type b) p-type

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.

Identification of minor oxides I

- Benaboud et al. [8] showed that the photoelectrochemical characterization is robust for detecting the presence of minor oxides.
- Alloying elements Fe, Sn and Cr, present in Zircaloy4, form precipitates which can be oxidized into minor oxides during the oxidation process.
- The strong photocurrent observed at around 5 eV reveals the major oxide i.e. monoclinic zirconia.
- The photocurrent at energy lower than 5 eV is not null and reveals the presence of minor oxides even in "pure" zirconium despite the very low concentration of impurities.
- The slope changes provided an estimation of the band gaps where the author identified the presence of hematite, chromia and a solid solution of $(Fe_x Cr_{1-x})O_3$.

Identification of minor oxides II



(a) (b)

Figure: Photocurrent spectra measured on zirconia oxide layer formed on Zircaloy4 and "pure" zirconium oxidized for 1h at 470°C in oxygenated atmosphere[8]: a) complete spectrum b) close-up view on the minor contributions.

Identification of minor oxides

References I

[1] S. R. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*. New York: Plenum Press, 1980.

[2] A. K. Vijh, "Correlation between bond energies and forbidden gaps of inorganic binary compounds," *Journal of Physics and Chemistry of Solids*, vol. 30, pp. 1999–2005, 1969.

[3] U. Stimming, "Photoelectrochemical studies of passive films," *Electrochimica Acta*, vol. 31, no. 4, pp. 415–429, 1986.

[4] F. Di Quarto, C. Sunseri, S. Piazza, and C. Sunseri, "Semiempirical Correlation between Optical Band Gap Values of Oxides and the Difference of Electronegativity of the Elements. Its Importance for a Quantitative Use of Photocurrent Spectroscopy in Corrosion Studies," *Journal of Physical Chemistry*, vol. 101, pp. 2519–2525, 1997.

[5] Y. Wouters, A. Galerie, and J.-P. Petit, "Photoelectrochemical Study of Oxides Thermally Grown on Titanium in Oxygen or Water Vapor Atmospheres," *Journal of The Electrochemical Society*, vol. 154, no. 10, pp. C587–C592, 2007.

[6] W. W. Gärtner, "Depletion-Layer Photoeffects in Semiconductors," *Physical Review*, vol. 116, no. 1, pp. 84–87, 1959.

[7] M. Butler, "Photoelectrolysis and physical properties of the semiconducting electrode WO_3," *Journal of Applied Physics*, vol. 48, no. 5, p. 1914, 1977.

[8] R. Benaboud, P. Bouvier, J.-P. Petit, Y. Wouters, and A. Galerie, "Comparative study and imaging by PhotoElectroChemical techniques of oxide films thermally grown on zirconium and Zircaloy-4," *Journal of Nuclear Materials*, vol. 360, no. 2, pp. 151–158, 2007.

[9] A. Srisrual, J.-P. Petit, Y. Wouters, C. Pascal, and A. Galerie, "Photoelectrochemical investigations on individual ferritic and austenitic grains of a duplex stainless steel oxidized in water vapour.," *Materials at High Temperatures*, vol. 28, no. 4, pp. 349–354, 2011.

[10] M. Bojinov, P. Kinnunen, T. Laitinen, K. Mäkelä, T. Saario, and P. Sirkiä, "Photocurrent response of the passive film on iron in a high-temperature aqueous electrolyte," *Electrochemistry Communications*, vol. 4, pp. 222–226, 2002.

[11] M. Skocic, "Etude (photo)-électrochimique en réacteur simulé du phénomène de shadow corrosion des alliages de zirconium," Ph.D. dissertation, Université de Grenoble Alpes, Grenoble, May 2016.

[12] A. J. Bard and M. Stratmann, *Fundamentals of Semiconductors Electrochemistry and Photoelectrochemistry*. Wiley-VCH, 2002.

References II

[13] E. Becquerel, "Mémoire sur les effets électriques produits sous l'influence des rayons solaires," *Comptes Rendus des Séances Hebdomadaires*, vol. 9, pp. 561–567, 1839.

[14] A. W. Copeland, O. D. Black, and A. B. Garrett, "The Photovoltaic Effect," *Chemical Reviews*, vol. 31, no. 1, pp. 177–226, 1942.

[15] H. Finklea, "Photoelectrochemistry: Introductory concepts," *Journal of Chemical Education*, vol. 60, no. 4, p. 325, 1983.

[16] H. Gerischer, "Electrochemical Behavior of Semiconductors under Illumination," *Journal of The Electrochemical Society*, vol. 113, no. 11, pp. 1174–1182, 1966.

[17] H. Gerischer, "Semiconductor electrodes and their interaction with light," in *Photoelectrochemistry, Photocatalysis and Photoreactor*, M. Schiavello, Ed., Dordrecht: D. Reidel Publishing Company, 1985, pp. 39–106.

[18] P. Marcus and F. Mansfield, *Analytical Methods in Corrosion Science and Engineering*. Boca Raton, FL: CRC Press, 2006.

[19] J.-F. Marucco, *Chimie Des Solides*. Paris: EDP Sciences, 2006.

[20] R. Memming, *Semiconductor Electrochemistry*. Weinheim: WILEY-VCH Verlag GmbH, 2008.

[21] N. Sato, *Electrochemistry at Metal and Semiconductors Electrodes*. Amsterdam: Elsevier Science, 1998.

[22] W. Plieth, *Electrochemistry for Materials Science*. Amsterdam: Elsevier, 2008.

[23] P. R. Bevington and D. K. Robinson, *Data Reduction and Error Analysis for Physical Sciences*, Third. New York: McGraw Hill, 2003.

[24] J. D. Hunter, "Matplotlib: A 2D graphics environment," *Computing In Science and Engineering*, vol. 9, no. 3, pp. 90–95, 2007.

[25] E. Jones, T. Oliphant, P. Peterson, et al., *SciPy: Open source scientific tools for Python*, http://www.scipy.org/, 2020.

[26] J. Kiusalaas, *Numerical Methods in Engineering with Python*, Second. Cambridge: Cambridge University Press, 2010.

[27] H.-P. Langtangen, *A Primer on Scientific Programming with Python*, Third. Berlin Heidelberg: Springer, 2012.

[28] K. J. Millman and M. Aivazis, "Python for Scientists and Engineers," *Computing in Science & Engineering*, vol. 13, no. 2, pp. 9–12, 2011.

References III

[29] J. Nocedal and S. J. Wright, *Numerical Optimization*, Second. New York: Springer, 2006.

[30] T. E. Oliphant, "Python for Scientific Computing," *Computing in Science & Engineering*, vol. 9, no. 3, pp. 10–20, 2007.

[31] J.-P. Petit, R. Boichot, A. Loucif, A. Srisrual, and Y. Wouters, "Photoelectrochemistry of Oxidation Layers: A Novel Approach to Analyze Photocurrent Energy Spectra," *Oxidation of Metals*, vol. 1, pp. 1–11, 2013.

[32] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes: The Art of Scientific Computing*, Third. Cambridge: Cambridge University Press, 2007.

[33] A. Srisrual, "Caractérisation photoélectrochimique d'oxydes thermiques développés sur métaux et alliages modèles," Thèse de Doctorat, Université de Grenoble, 2013.

[34] S. Van der Walt, S. C. Colbert, and G. Varoquaux, "The NumPy Array: A Structure for Efficient Numerical Computation," *Computing in Science & Engineering*, vol. 13, no. 2, pp. 22–30, 2011.

[35] A. Loucif, J.-P. Petit, and Y. Wouters, "Semiconducting behavior and bandgap energies of oxide films grown on alloy 600 under PWR simulated primary water conditions with different dissolved hydrogen contents," *Journal of Nuclear Materials*, vol. 443, no. 1–3, pp. 222–229, 2013.