PhotoElectroChemistry
Theoretical Background

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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].

Basics

PEC takes advantage of the photovoltaic effect, discovered by Becquerel [12] in 1839, that occurs at the interface of a semiconductor and an electrolyte. In fact, the first experience showed the occurrence of a photopotential and a photocurrent under illumination when a silver electrode, covered with an oxide layer, was immersed in an acidic medium and connected to a platinum electrode. Nonetheless, the first studies focused on the understanding of the interfacial processes were performed much later [3, 13, 14].

The basics of photoelectrochemistry and application examples are presented in the following sections and they are largely described in the literature [1, 15–19]. Several hypotheses are needed in order to apply the theoretical concepts:

- semiconductor are considered to be ideal i.e. crystallized and homogeneous
- the dielectric constant of the semiconductor is independent of

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.

References II

[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] 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.

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

[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. 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.

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

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

References III

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

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

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

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

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