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Photoelectrochemical Water Splitting

Standards, Experimental Methods, and Protocols

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Preface

The methods and definitions presented herein are the product of an effort supported by the U.S. Department of Energy (DOE) to form a consensus among a number of experienced researchers in the area of photoelectrochemical (PEC) hydrogen production from various DOE-supported laboratories (including national labs and academic institutions) and other international partners. An early result of this effort was the production of a consolidated version of the guide presented here, published in the form of a review paper in the Journal of Materials Research in 2010, [1] and is reprinted in part with permission in this book. The extended guidance in the present work aims to accelerate materials development by establishing standards for methods, definitions, and reporting protocols that will enable direct cross-comparison of materials' properties and performance metrics. The intent is to facilitate knowledge transfer on a global scale.

The authors who have contributed to the writing of this book are members of the PEC Standards Working Group, assembled by the Energy Efficiency and Renewable Energy's Fuel Cell Technologies Office at the U.S. DOE. These authors include:

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The chapters written herein represent many years of collaborative discussion and review, and we hope that their content can enable new researchers in the field of PEC water splitting to rapidly gain traction in their own laboratories towards the development of high efficiency materials.

A number of international researchers participated in providing excellent feedback on the text written in this book, including many affiliated with the International Energy Agency's Hydrogen Implementing Agreement Task 26. In no particular order, we thank Grant Mathieson, Bruce Parkinson, Jennifer Leisch, Theanne Schiros, David Peterson, Ib Chorkendorff, Peter Vesborg, Kendra Kuhl, Blaise Pinaud, Julie Tuttle, Sarah Havig, Berc Kalanyan, Billie Abrams, Candace Chan, Nelson Kelly, Shiwei Lin, Nianqiang Wu, Shane Ardo, Nick Strandwitz, Lorna Jeffery Mingu, Daniel Schaadt, Marie Mayer, Ke Sun, Nikolaos Vlachopoulos, Qiang Huang, Juan Hodelin, Jian Jin, Anna Goldstein, Kevin Sivula, Kazuhiro Sayama, Isabell Thomann, Yue Tak Lai, Ilwhan Oh, and Sonia Juliana Calero.

Reference

1. Z. Chen, T.F. Jaramillo, T.G. Deutsch, A. Kleiman-Shwarsctein, A.J. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E.W. McFarland, K. Domen, E.L. Miller, J.A. Turner, H.N. Dinh, J. Mater. Res. **25**(1), 3–16 (2010)

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Chapter 1
Introduction

One of the most important technical problems facing humanity is the development of a long-term, sustainable energy economy [1]. Although we have the technology and sufficient coal reserves to provide the energy needed for centuries' worth of population growth and economic development, this strategy could come with catastrophic societal costs [2]. Scientific discovery and innovation will be vital to achieving environmentally sound and cost-effective solutions. Technologies are needed that will meet society's increase in annual global energy consumption from the 495 quadrillion British thermal units (Btu) per year we consumed in 2007 to the projected demand of 739 quadrillion Btu/yr by the year 2035 [3]. In terms of power consumption, this corresponds to an increase from 16.6 terawatts (TW) to 24.7 TW. Solar photoelectrochemical (PEC) hydrogen production is one of the promising technologies that could potentially provide a clean, cost-effective, and domestically produced energy carrier by taking advantage of the $\sim$120,000 TW of radiation that continually strikes the earth's surface [4].

The concept of PEC water splitting for hydrogen production has been investigated for decades, with first demonstration in 1972 by Fujishima and Honda [5]. In 1998, Khaselev and Turner [6] demonstrated a PEC solar-to-hydrogen conversion efficiency of 12.4 %, highlighting the great potential for a PEC technology which combines the harvesting of solar energy and the electrolysis of water into a single device. Basically, when a PEC semiconductor device with the right set of properties is immersed in an aqueous electrolyte and irradiated with sunlight, the photon energy is converted to electrochemical energy, which can directly split water into hydrogen and oxygen (chemical energy). Thus intermittent solar energy is converted into an inherently more storable form of energy, that of chemical bonds.

PEC solar water splitting is a powerful, but complex process. For direct photoelectrochemical decomposition of water to occur efficiently and sustainably, several key criteria must be met simultaneously: the semiconductor system must generate sufficient voltage upon irradiation to split water, the bulk band gap must be small enough to absorb a significant portion of the solar spectrum, the band edge potentials at the surfaces must straddle the hydrogen and oxygen redox potentials, the system must exhibit long-term stability against corrosion in aqueous electrolytes, and finally, the charge transfer from the surface of the semiconductor

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to the solution must be facile to minimize energy losses due to kinetic overpotential and selective for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). To date, no cost-effective materials system satisfies all of the technical requirements listed above for practical hydrogen production. While research and development is ongoing to discover materials with bulk and interfacial characteristics that meet these criteria, advances in material science and interfacial electrochemistry are still needed.

Many previously published books [7–9] and review articles [10–12] include excellent discussions of the fundamental principles of PEC. Still, a brief summary of the basic operations of PEC devices is instructive here. Figure 1.1a illustrates fundamental processes in a PEC device for the example of a two-electrode system containing a single absorber photoanode. Incoming photons ($h\nu$) generate electrons (e^-) and holes (h^+) with an efficiency labeled η_{e^-/h^+}. The photogenerated electrons and holes then separate and travel through the semiconductor in opposite directions; the efficiency associated with the charge transport process is labeled $\eta_{transport}$. The holes drive the OER at the surface of the semiconductor working electrode. Simultaneously, the electrons are driven to the rear ohmic contact and through an electrical connection to the surface of the counter electrode to drive the HER. The combined efficiency of the charge transfer at the solid–liquid interface for both electrons and holes is labeled $\eta_{interface}$. An important discussion of how these processes affect calculations of PEC device efficiencies is contained in Chapter "Efficiency Definitions in the Field of PEC": Figure 1.1a also depicts the minimum thermodynamic voltage for splitting water ($\Delta E^0 = 1.23$ V).

A more extensive illustration of the energetic requirements for a PEC water splitting device is shown in Fig. 1.1b. In addition to the thermodynamic requirement, there are overpotentials associated with driving the kinetics of the hydrogen evolution reaction (OP_{HER}) and oxygen evolution reaction (OP_{OER}) at the solid–liquid interface. Minimizing these overpotentials through the development of efficient catalysts for each half-reaction is a key step in making highly efficient water splitting devices.

Entropic losses associated with the photogenerated electrons and holes must also be considered [13, 14]. The actual driving force for water splitting is represented as a photovoltage (V_{ph}) which, as a result of losses (arising from factors such as spontaneous emission, incomplete light trapping, and non-radiative recombination) [13], is always less than the band gap of the semiconductor. Additional factors such as non-ideal band structure alignment can further reduce available photovoltage. The photovoltage in the semiconductor is the potential difference between the quasi-Fermi levels of electrons ($E_{F,n}$) and holes ($E_{F,p}$) under illumination, although the accuracy of this formalism, particularly in the vicinity of semiconductor-liquid interface, remains an active area of discussion within the PEC community. A more conservative requirement for unassisted water splitting is that the photovoltage (compensated for overpotential losses) must enable the quasi-Fermi levels under illumination to straddle the OER and HER redox potentials.

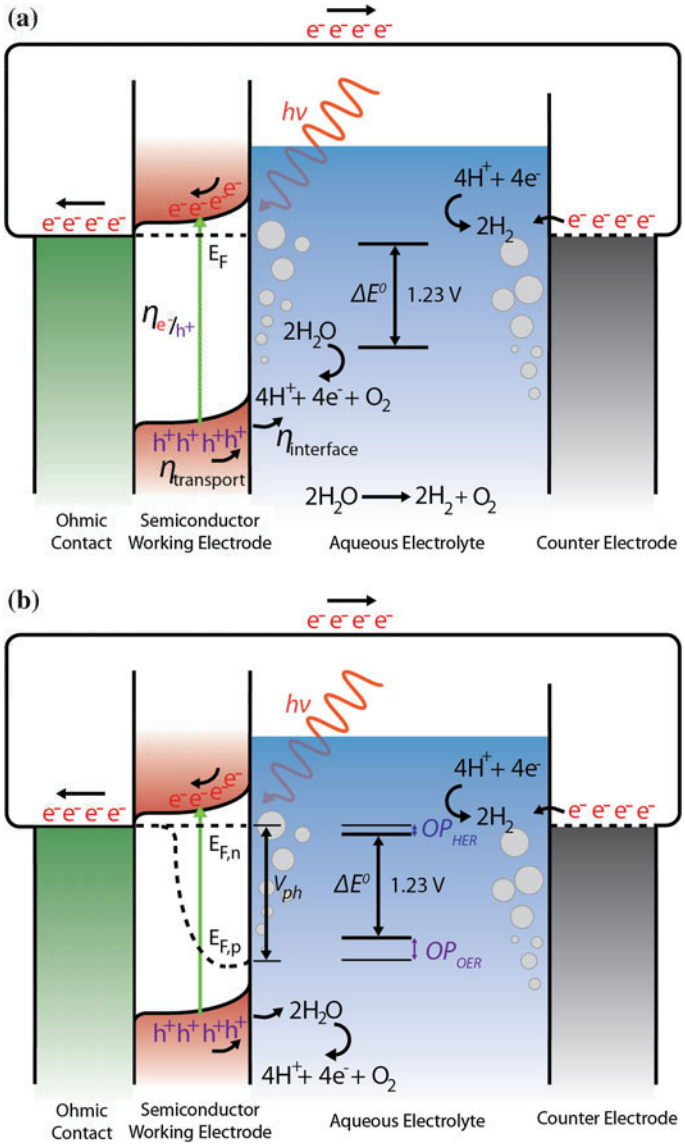

Fig. 1.1 Band structure of an n-type photoanode water splitting device, (**a**) Illustrating the various processes of photon irradiation, electron–hole pair formation, charge transport, and interfacial reactions, (**b**) Illustrating the energetic requirements associated with the minimum thermodynamic energy to split water, catalytic overpotentials for the HER and OER half-reactions, and photovoltage