Transient phenomenological modeling of photoelectrochemical cells for water splitting — Application to undoped hematite electrodes

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ABSTRACT

A phenomenological model is proposed for a better understanding of the basic mechanisms of photoelectrochemical (PEC) cells. The main assumptions of the one-dimensional transient phenomenological model are: i) bulk recombination of the conduction band electrons with holes in the valence band; ii) the mobile charge transport takes place via diffusion, which arises from the concentration profiles, and migration, caused by a macroscopic electric field; iii) negligible effects of microscopic electric fields in the cell and screening effects, as well as negligible Helmholtz and diffuse layers. For modeling purposes, the photoanode was assumed to be a homogeneous nanocrystalline hematite structure, with thickness L, porosity ε_p and tortuosity τ. The TCO/semiconductor interface was modeled as an ideal ohmic contact, while the electrolyte/platinized TCO interface was described by a Butler–Volmer approach. An alkaline electrolyte solution was used, allowing the transport of the ionic species from the counter-electrode to the photoanode. The continuity and transport governing equations are defined for the mobile species involved: electrons in the conduction band of the semiconductor, holes in the valence band and hydroxyl ions in the electrolyte. Simulated I–V characteristics were computed and the corresponding results compared with the experimental values. The simulated results were in straight agreement with the experimental data.

1. Introduction

It is known that world demand for energy is forecasted to duplicate by 2050 and it is also widely recognized that the existing energy networks are not adequate to supply this demand in a sustainable way [1]. The increasing public awareness concerning the carbon dioxide emissions and the enhanced depletion of fossil fuels motivates the development of alternative technologies based on non-polluting and clean energy sources [2,3]. So far, the sun is our primary source of clean and abundant energy, striking 120 PW of radiation onto the surface of earth at any given moment and is the most powerful resource able to cope with the world's energy needs [1]. However, the present technologies that take advantage of solar energy have a limited ability to store energy due to the variability of daily solar radiation and so an effective method to store energy for later dispatch is therefore needed [4,5]. A practical way to overcome this problem is using sunlight to split water into hydrogen and oxygen — photoelectrolysis [3] — by means of a photoelectrochemical (PEC) cell. The water split phenomenon was first reported by Fujishima and Honda in 1972, but it was only recently that this technology received

special attention from researchers as a potential renewable energy source [3,6–9].

A photoelectrochemical cell is made of a semiconductor, such as iron oxide (Fe_2O_3) — hematite — and a counter-electrode (cathode), both immersed in an aqueous electrolyte solution. When exposed to sunlight, the semiconductor absorbs photons with sufficient energy to inject electrons from the valence band to its conduction band, creating electron-hole pairs. The holes exhibit oxidation potential while the electrons are transferred over the external circuit to the cathode to promote water reduction into hydrogen gas. The energy conversion efficiency of such process is therefore highly determined by the structure and properties of the semiconductor and the electronic junction formed at the semiconductor/electrolyte interface [10,11]. Presently, these devices achieve very low conversion efficiencies since most of the semiconductors used for this application have a large energy bandgap. Furthermore, the band edge potentials of many semiconductors are not suitable for oxygen and hydrogen evolution and the water split reaction can not take place. This is the case of hematite, whose conduction band edge is positioned at a more positive potential than the reduction potential of water. As a result, an additional bias voltage is required to promote the reduction reaction at the cathode side [3].

In the last decade, several studies focusing on promising photoelectrodes were carried out. Doped and undoped semiconductor materials were synthesized and characterized regarding their photoelectrochemical, structural, electrical and optical properties [8,12–14]. Recent studies report hematite as a promising material with several advantages: it has a suitable bandgap energy around 2.0 eV, is able to use 40% of the incident solar spectrum, it is chemically and thermally stable in aqueous solutions and also toward photocorrosion, its valence band is appropriate for oxygen evolution and it is abundant and a low-cost material [3,8,15]. Despite several efforts have been made to develop new more adequate materials for water splitting in photoelectrochemical cells, very few research works focused on the insightful understanding of the working mechanisms of PEC cells. An important work was developed by Gerischer [16,17] on the kinetics and energetics of electron transfer across semiconductor/electrolyte junctions and on the nature of the space-charge layer — the semiconductor layer adjacent to the semiconductor/electrolyte interface. Nozik [18] evaluated the energy level scheme for p–n photoelectrolysis cells in order to demonstrate an enhanced efficiency by simultaneously illuminating the n- and p-type electrodes. Khan and Bockris [19] derived an analytical expression for the resulting photocurrent as a function of the physical properties of an illuminated p-type semiconductor electrode and the neighboring electrolyte solution. Boudjemaa and co-authors [13] studied the transport properties of hematite and its application for hydrogen production. Nevertheless, a global and integrated transient phenomenological model for a better understanding of the phenomena occurring in a PEC cell and how they contribute for its performance has never been presented. Simple models were already developed for other water splitting systems, pointing out some relevant aspects. Choi et al. [20] studied a water electrolysis system with a solid polymer electrolyte by means of a simple model based on the Butler–Volmer kinetics. Also based on the Butler–Volmer approach, Nie et al. [21] modeled a proton exchange membrane water electrolyzer and Marangio et al. [22] studied a high pressure polymer electrolyte membrane water electrolyzer. Ni [23–25] developed an interesting work based on the mathematical modeling of solid oxide steam electrolyzers for hydrogen production.

In the present work, an integrated transient phenomenological model for PEC cells is presented. This model aims at contributing to a better understanding of the phenomena occurring in a PEC cell and how they contribute for its performance. The simulated I–V characteristic curves of the PEC cell allowed the calculation of the cells' performance parameters.

2.   Development of the PEC cell model

Photoelectrolysis of water is the dissociation of water molecules into hydrogen and oxygen by the direct use of light: the conversion of light into electrical current allows the transformation of a chemical entity — water — into another — hydrogen — known to be a preferential energy vector [26]. The principle of operation of a photoelectrochemical cell for water splitting is governed by the kinetics of the charge carriers and reaction mechanisms that take place at the electrodes of the PEC cell. Therefore, the understanding of the electronic processes occurring at the semiconductor nanoparticles level, as well as the dynamics of charge separation/transport and reactive mechanisms in the different interfaces is of great importance. Photons with energy $h \cdot v$ higher than the semiconductor's bandgap generate electron-hole pairs ($e_{CB}^- + h_{VB}^+$) in the conduction and valence bands, respectively:

$$hv + SC \rightarrow SC\left(e_{CB}^- + h_{VB}^+\right) \tag{1}$$

In an alkaline media, holes oxidize water to oxygen in the semiconductor surface (photoanode),

$$2H^+ + 2OH^- \rightarrow H_2O + 1/2O_2 \tag{2}$$

while the photoexcited conduction band electrons, transported to the counter-electrode (cathode) of the PEC cell, reduce water to form hydrogen gas:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{3}$$

The mechanisms behind oxidation of water by photogenerated holes are not completely understood and depend most probably on the interfacial properties of the semiconductor. On the other hand, the reduction of water into hydrogen is a kinetically simple process compared to the water oxidation reaction [27]. In fact, the efficiency of the oxidation process occurring at the semiconductor can be limited by several competing electron loss pathways: bulk recombination via bandgap states or direct electron loss to holes in the valence band; surface recombination; electron loss from the conduction band; photocorrosion of the semiconductor; and dissolution reactions. The last two processes are responsible for the degradation of the electrode and for the consequent stability problems [28].