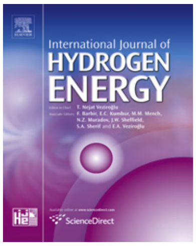
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 37 (2012) 2911–2923

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Modelling and development of photoelectrochemical reactor for H_2 production☆

*C. Carver, Z. Ulissi, C.K. Ong, S. Dennison, G.H. Kelsall, K. Hellgardt**

Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK

ARTICLE INFO

Article history:
Received 24 June 2011
Accepted 5 July 2011
Available online 15 September 2011

Keywords:
Hydrogen
Mathematical model
Oxygen
Photoelectrochemical reactors
Photoelectrolysis
Water splitting

ABSTRACT

Photoelectrolysis of aqueous solutions, using one or more semiconducting electrodes in a photoelectrochemical reactor, is a potentially attractive process for hydrogen production because of its prospectively high energy efficiency, simplicity and potentially low cost. The design requirements and preliminary results of modelling a photoelectrochemical (PEC) reactor are described. Potential and current density distributions, due to ohmic potential losses in thin (non-photo) anodes on poorly conducting fluoride-doped tin oxide coated glass substrates, were modelled. The predicted current densities decayed rapidly from the terminals at the edges, towards the centre of a $0.1 \times 0.1\ m^2$ anode, so limiting scale-up with such substrates. Spatial distributions of dissolved oxygen concentrations were also modelled, aiming to define operating conditions that would avoid forming bubbles, which reflect light specularly decreasing photon absorption efficiencies of photoelectrodes. The implications for the future optimization of the reactor are discussed.

1. Introduction

Hydrogen is perceived as an important future energy carrier, especially for fuel cells, but needs to be produced by sustainable routes, using renewable resources, avoiding CO_2 emissions of the present dominant industrial process: steam reforming of natural gas. Only a few percent of world hydrogen is produced by water electrolysis, causing remote pollution if energised by fossil-fuelled power stations. Using photovoltaic cells to power water electrolysers is a technically-, if not yet economically-viable, environmentally benign option. However, a potentially simpler and lower cost alternative utilises semiconducting photoelectrodes [1–5] to absorb solar photons with energies greater than their band gap, generating electron–hole pairs (excitons):

$$\text{Semiconductor} + h\nu \underset{\text{recombination}}{\overset{\text{absorption}}{\rightleftarrows}} \text{Semiconductor}\left(e^-_{CB}, h^+_{VB}\right) \quad (1)$$

The schematic energetics of the direct photoelectrolysis process are summarized in Fig. 1, for the case of an n-type semiconducting photoanode; photocathodes have also been used, but are generally not sufficiently stable for practical application.

The electric field in the depletion layer at the semiconductor|electrolyte interface separates the photogenerated electron–hole pairs, holes migrating to the photoanode|aqueous solution interface, at which they oxidize water to oxygen:

$$H_2O \rightarrow 1/_2 O_2 + 2H^+ + 2e^- \quad (2)$$

For which the equilibrium electrode potential relative to a standard hydrogen electrode (SHE) at 298 K is defined by the Nernst equation:

$$U_{O_2/H_2O}(SHE)/V = 1.229 - 0.0591 \cdot pH + 0.0148 \log P_{O_2} \quad (3)$$

☆ Paper presented at the 2010 Annual Meeting of AIChE, Salt Lake City, 7–12 November 2010.

* *Corresponding author*. Tel.: +44 20 7594 5577.
E-mail address: k.hellgardt@imperial.ac.uk (K. Hellgardt).

doi:10.1016/j.ijhydene.2011.07.012

Notation

A_i	cross sectional area of material i, m^2
c_i	concentration of species i, mol m^{-3}
C_i^S, C_i^B	surface and bulk concentrations of species i, mol m^{-3}
D_i	diffusion coefficient, $m^2\,s^{-1}$
d_i	distance, m
e	electronic charge, C
E_C	conduction band edge energy, eV
E_F	Fermi energy of semiconductor, eV
E_V	valence band edge energy, eV
F	Faraday constant, C mol^{-1}
I	current flowing through photoanode to current collector, A
j, j_A, j_C	current density, at anode and cathode, A m^{-2}
j_0	exchange current density, A m^{-2}
N_D	dopant density in semiconductor, m^{-3}
N_i	molar flux of species i, mol $m^{-2}\,s^{-1}$
n	electron stoichiometry of reaction
O	oxidised species
P_{H_2}	partial pressure of hydrogen, Pa
P_{O_2}	partial pressure of oxygen, Pa
R	gas constant, J $mol^{-1}\,K^{-1}$
R	reduced species
T	temperature, K
U_A	anode potential, V
U_C	cathode potential, V
ΔU	total cell potential difference, V
U_{fb}	flatband potential of semiconductor, V
$U_{O/R}$	equilibrium potential for anode/cathode reaction, V
$u_{m,i}$	mobility of species i, m s^{-1} J kg^{-1}
U	electrolyte flow velocity, m s^{-1}
β	Tafel coefficient, V^{-1}
ε_0	permittivity of vacuum, F m^{-1}
ε	relative permittivity
η	overpotential at electrode, V
η_A	overpotential for anode reaction, V
η_C	overpotential for cathode reaction, V
κ_i	conductivity, S m^{-1}
μ	dynamic viscosity of electrolyte, Pa s
ϕ	potential, V
ϕ_A	potential in anolyte, V
ϕ_C	potential in catholyte, V
ϕ_M	potential in membrane, V
ρ	density of electrolyte, kg m^{-3}

In this example, the photogenerated electrons are driven into the bulk of the semiconductor and are transported via an external circuit to the cathode, at which they reduce water to hydrogen:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (4)$$

for which the Nernst equation at 298 K is:

$$U_{H_2O/H_2}(SHE)/V = -0.0591 \cdot pH + 0.0296 \log P_{H_2} \qquad (5)$$

Hence, addition of reactions (2) and (4) gives the overall water decomposition reaction:

$$H_2O \rightarrow H_2 + 1/_2 O_2 \qquad (6)$$

Since the first publication on the photoelectrolysis of water by TiO_2 [1], most photoelectrochemical research has aimed to develop materials with increased stability and energy conversion efficiency, minimising the rate of electron–hole recombination by the reverse of reaction (1), with little attention paid to the development of photoelectrochemical reactors for hydrogen generation. Hence, the design requirements, fabrication, performance characterisation and modelling of a practical photoelectrochemical (PEC) reactor are described below, in anticipation of the future development of optimized photoelectrode materials.

1.1. *Energetic and materials requirements for the photoelectrode*

Fig. 1 shows a schematic energy diagram for a PEC reactor consisting of an n-type semiconducting photoanode and metal cathode, with anolyte and catholyte separated by an ion-permeable membrane to prevent hydrogen–oxygen recombination and oxygen and hydrogen reaching the cathode and anode, respectively. For a Fe_2O_3 photoanode, an additional bias has to be applied because its conduction band edge does not otherwise lie above the energy level for decomposing water to hydrogen; hence, the process is restricted to photo-assisted electrolysis of water. Photoelectrolysis would be spontaneous with an ideal semiconductor, if the properties of which met all the criteria arising from thermodynamic, kinetic and solid state physics constraints of the process [4,6,7], inter alia:

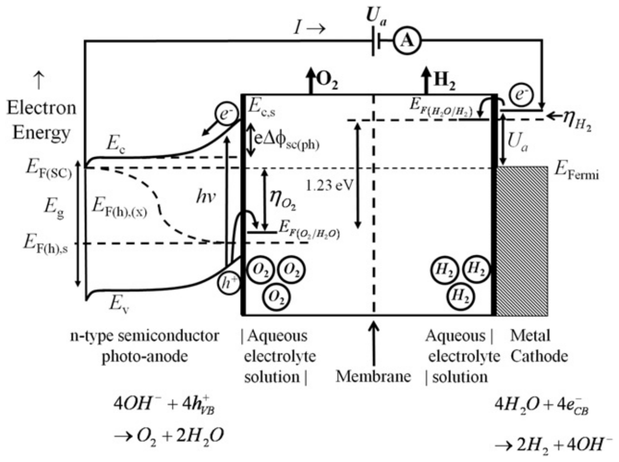


Fig. 1 – Schematic energy level diagram for operation of photoelectrochemical cell using an n-type semiconducting photoanode for water photoelectrolysis.