LIGHT INTENSITY INFLUENCE ON STRONTIUM TITANATE BASED PHOTO- ELECTROCHEMICAL CELLS

D. HERTKORN*, **, #C. MEGNIN**, C. MÜLLER*, T. HANEMANN**, ***, H. REINECKE*

*Laboratory for Process Technology, Department of Microsystems Engineering, 79110 Freiburg, Germany
**Laboratory for Materials Processing, Department of Microsystems Engineering, 79110 Freiburg, Germany
***Institute for Materials Research, Karlsruhe Institute of Technology, 76133 Karlsruhe, Germany

#E-mail: christof.megnin@imtek.de

The influence of light intensity on photo-electrochemical cells (PECs) consisting of an n-type strontium titanate (SrTiO₃) photoanode and nickel cathode in potassium hydroxide electrolyte is studied. The band levels of an electrolyte-metal-semiconductor-electrolyte system are presented and the effect of different light intensities on the energy levels is investigated. Photocurrent density, quantum efficiency, and open circuit potential measurements are performed on the processed PECs under different light intensities (375 nm). It is demonstrated that a threshold value of the light intensity has to be reached in order to obtain positive photo activity and that beyond this value the performance remains nearly constant.

INTRODUCTION

Photo-electrochemical cells (PECs) are an attractive approach for clean hydrogen production. They are based on the splitting of water into hydrogen and oxygen gas under sun light illumination. No additional environmentally harmful by-products are generated, which is a big advantage compared to current hydrogen production methods like steam reforming of methane [1]. There have been investigations on PECs for the last few decades using different approaches and designs with varying cell structures, semiconductor materials, and processing technologies. However, due to numerous requirements in terms of photo-electrochemical and semiconducting properties, finding an optimal material and system is very challenging. Therefore, apart from developing alternative materials with enhanced properties, detailed electrochemical and physical investigations of known materials such as strontium titanate (SrTiO₃) are also important for a better understanding of the behavior of PECs under working conditions.

In this study we present PECs consisting of an n-type SrTiO₃ photoanode and nickel metal cathode in potassium hydroxide electrolyte. SrTiO₃ is a perovskite-type semiconductor and possesses excellent stability properties in alkaline media under illumination [2]. Furthermore, it exhibits adequate band positions and a large band gap to split water into hydrogen and oxygen without any additional bias voltage [3]. At first, we discuss the influence of light intensity on the energy levels of a PEC with electrolyte-metal-semiconductor-electrolyte interfaces and then show photocurrent density, external quantum efficiency (EQE) and open circuit potential (OCP) measurements of the presented PECs under different 375 nm illumination intensities.

THEORETICAL

When an n-type semiconductor photoanode connected with a metal cathode is introduced into an electrolyte containing a redox couple, a charge transfer from the semiconductor and electrolyte occurs until equilibrium is reached. For such a system this results in a depletion of the majority charge carriers (electrons) and in an upwards bending of the valence and conduction band of the semiconductor. As a consequence, under illumination the photo-generated charge carriers are separated in this electric field. On one side the holes move to the semiconductor-electrolyte interface and perform the oxygen evolution reactions (OER), and on the other side the electrons travel to the metal cathode at the metal-electrolyte interface and react with water, causing the hydrogen evolution reaction (HER). The positions of the energy bands at the semiconductor-electrolyte interface are known as flat band levels of the valence and conduction bands. They have to bracket the redox couple potentials for the OER and HER in order to be able to split water without bias voltage. For metal oxide photoanodes the holes exhibit sufficient potential difference for the OER and are therefore not considered to be a limiting factor. In contrast, the position of the

conduction band is usually in the spotlight, since its edge is very close to the HER potential. In the case of SrTiO$_3$ it is only about -200 mV more negative [4]. Figure 1a illustrates that a freely moving electron would not be able to perform the HER, although the semiconductor fulfills the aforementioned requirements.

As described in Equation 1, there are several effects and transitions lowering the electron energy level E_e. The energy losses from the flat band level E_{FB} include the band bending E_{BB}, the energy difference E_{CF} of the conduction band E_{CB} and the Fermi level E_F, and the required overpotential η_{CB} for the HER, leading to an energy level of the electron E_e at the metal-electrolyte interface that is too low [5-7]. Note that at the semiconductor-metal interface a charge transfer also occurs, leading to a matching of the work function of the metal and the Fermi level E_F of the semiconductor [1].

$$E_e = |E_{FB}| - |E_{BB}| - |E_{CF}| - |e\,\eta_{CB}| = E_f > E_{HER} \qquad (1)$$
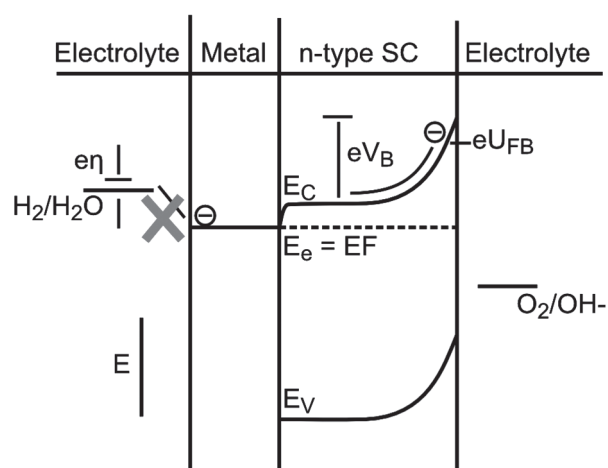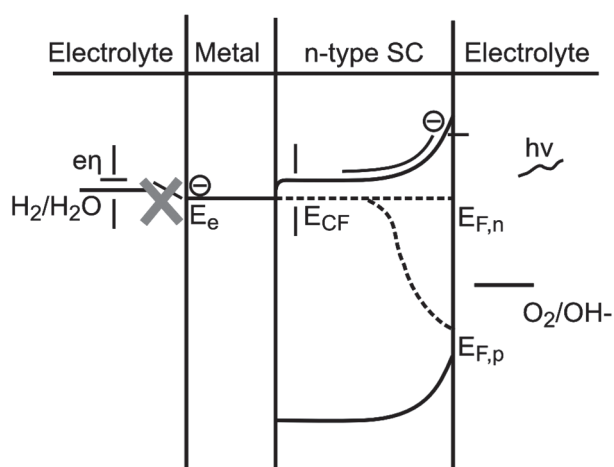
Equation 1 reveals that the Fermi level E_F has to be higher than the HER energy level E_{HER} and not just the flat band level E_{FB}, which is fixed for a given system [8]. The overpotential η_{CB} can be assumed to be fixed, since the density of the light-generated electrons and hence the reaction rates are very low compared to electrolyzers [9]. Therefore, the only way to increase E_F is to decrease the band bending E_{BB} and the difference E_{CF} between E_{CB} and E_F, respectively.

These values change in the presence of photo induced charge carriers as illustrated in Figures 1b and 1c. Under steady-state illumination the use of quasi-Fermi levels for both majority $E_{F,n}$ and minority charge carriers $E_{F,p}$ is introduced, since they are no longer identical for electrons and holes. The quasi-Fermi level for electrons $E_{F,n}$ is defined via the Boltzmann constant k and absolute temperature T. The values Δn and n_0 represent the electron concentration created by the incident light and the intrinsic electron concentration, respectively. As shown in Equations 2 and 3, $E_{F,n}$ increases with increasing light intensity I. However, for an n-type semiconductor n_0 is very high in comparison to Δn, which leads to only a slight shift towards the conduction band [5]. Even for high illumination levels when Δn equals n_0, the $E_{F,n}$ only increases by about 18 meV at room temperature.

$$E_{Fn} = E_{CB} + |E_{FC}| = E_F + kT \ln\left(1 + \frac{\Delta n}{n_0}\right) \qquad (2)$$

$$\Delta n \sim I \qquad (3)$$

Band bending is the result of the equilibrium process of the semiconductor electrons and the redox species in the electrolyte. As a consequence the electron concentration at the surface n_S is lower than the intrinsic electron concentration n_0. This means that in the depletion region the additional photo- generated

a) without illumination

b) with low illumination
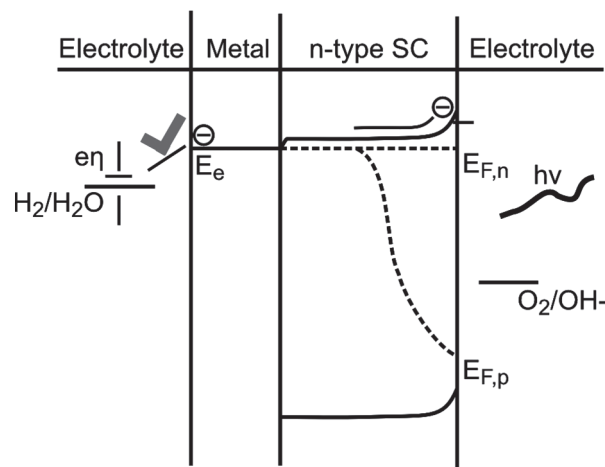
c) with high illumination

Figure 1. Band energy levels for n-type semiconductor-metal PEC in contact with an electrolyte a) without, b) with low, and c) with high illumination; the incident light mainly decreases the band bending EBB leading to a raise of the Fermi level EF,n of the electrons, so that they possess at a certain intensity level sufficient energy to perform the hydrogen evolution reaction.

electrons Δn are significant and clearly cause a potential change. The energy loss of the band bending E_{BB}, i.e. the energy difference of E_{FB} and E_{CB}, can be approximated by a Boltzmann-type relationship [6,7].

$$E_{BB} \approx kT \ln\left(\frac{n_s + \Delta n}{n_0}\right) \approx kT \ln\left(1 + \frac{\Delta n}{n_0}\right) \qquad (4)$$

The surface concentration n_S is very small and can be neglected under illumination. Equation 4 shows that E_{BB} changes significantly with the illumination level [10]. Here, when Δn equals n_0, the band bending vanishes, resulting in a flat band situation. The energy level of the electrons E_e increases with high illumination levels, so that they possess sufficient energy to perform the HER. In other words, there has to be a certain light level, where E_e equals E_{HER}. This value represents a threshold point, below which the HER is blocked and above which the HER is enabled.

EXPERIMENTAL

The PECs investigated in this work consist of an n-type $SrTiO_3$ photoanode and a nickel metal cathode. At first, $SrTiO_3$ nano powder (99 %, Advanced Materials) was electrophoretically deposited on nickel substrates (Nickel 201, Tankii Alloy Material) in order to obtain a porous film with a thickness of approximately 5 μm. Then the samples were sintered in a tube furnace at 1200°C for 20 min with a cooling/heating rate of 10 K/s in reducing gas (95 mol. % N_2 + 5 mol. % H_2, Airliquide, Arcal F5) to induce oxygen vacancies in the $SrTiO_3$ lattice and hence create an n-type semiconductor. A detailed description of the process steps is given in [11]. The samples have an active area of 10×10 mm². The electrochemical measurements were performed under different illumination levels in a two-electrode setup to determine the photocurrent and external quantum efficiency (EQE). They were also characterized in a three-electrode setup to detect the open circuit potential (OCP). The light source (Roithner Laser) has a wavelength of 375 nm, with adjustable intensities ranging from 0.3 to 36.8 mW·cm⁻².

RESULTS

Figure 2 shows the photocurrent densities and the EQEs under illumination with different intensities. The photocurrent density increases linearly with increasing intensity (light power density) beyond an intensity of 0.8 mW cm⁻².

This threshold intensity is quite low, but still in the resolution range of the used optical sphere (Coherent PS19Q). Below this value no current is measured. In this case the intensity is too low to sufficiently raise the energy level of the electrons E_e, and hence the HER

cannot proceed. A higher light intensity and hence a higher energy level is needed to allow the generated electrons to react with the electrolyte. Beyond the threshold point the EQE plateau is in the range of 54 % to 60 % and independent of the light intensity. This can be expected, since the photocurrent density depends linearly on the photon flux. The OCP behaves similar to the EQE for different illumination levels.

As illustrated in Figure 3, once the threshold value is reached the redox reactions proceed and the OCP drops steeply. With increasing intensity the OCP further decreases approaching the flat band potential which is approximately -1.09 V vs. Ag/AgCl [12]. However, although the electrons possess a higher potential at high illumination levels, the EQE remains the same. This also means that the overall efficiency is independent of the light level beyond the threshold point. This is the main difference between solar cells and PECs. The electrons and holes in PECs have to perform the water splitting reaction and therefore need to possess the E_{HER} and E_{OER}, respectively. This automatically defines the required
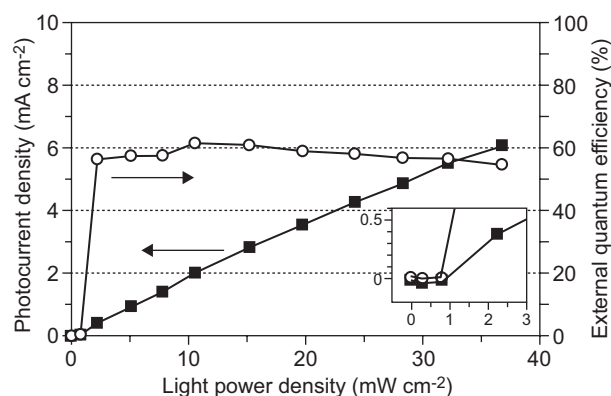
Figure 2. Photocurrent densities and quantum efficiencies under different light powder densities (intensities); a threshold intensity has to be reached to obtain a measurable response.
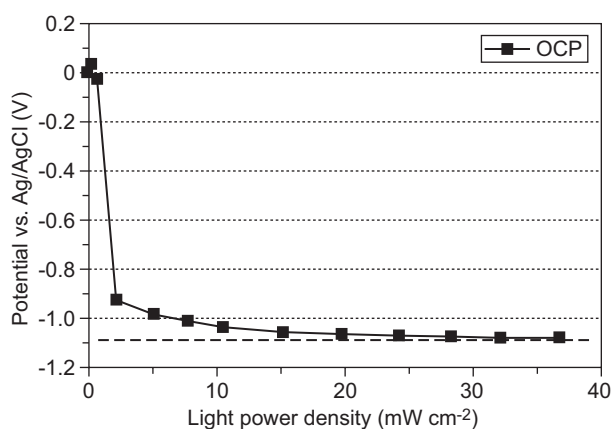
Figure 3. Open circuit potentials under different light power densities; at the threshold intensity the potential drops steeply and further decreases with increasing intensity approaching the flat band potential [12].

potential and hence the operation point of the device. In contrast, solar cells are set to work at the optimal operation point. This corresponds to the maximum power point, where the product of the photocurrent and voltage is highest. Thus, the light-induced voltage increase can be exploited in solar cells to get a higher overall efficiency, but not in PECs.

CONCLUSION

The influence of light intensity on the performance of *n*-type $SrTiO_3$ based photo-electrochemical cells has been investigated. The photo induced charge carriers decrease the band bending of the semiconductor and hence raise the quasi-Fermi level and the energy level of the electrons, respectively. Reaching a certain light intensity enables the hydrogen evolution reaction to be performed. The convergence of the quasi-Fermi level towards the conduction band is small and can be neglected. Photocurrent density measurements reveal that $SrTiO_3$-Ni PECs have a light intensity threshold value that must be met for water splitting to occur. Once this value is reached, the photocurrent density increases linearly with the photon flux and constant quantum efficiencies are exhibited. The open circuit potential drops steeply at the threshold value and further decreases with increasing intensity. However, PECs do not work better with higher intensities beyond the threshold point, since the operation point is defined by the required water splitting potential. In contrast, solar cells are set to work at the maximum power point exploiting the light induced voltage increase.

REFERENCES

1. Bak T., Nowotny J., Rekas M., and Sorrell C.C. (2002): Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects. *International Journal of Hydrogen Energy, 27*, 991-1022. doi:10.1016/S0360-3199(02)00022-8

2. Wrighton M.S., Ellis A.B., Wolczanski P.T., Morse D.L., Abrahamson H.B., Ginley D.S. (1976): Strontium Titanate Photoelectrodes. Efficient Photoassisted Electrolysis of Water at Zero Applied Potential. *Journal of the American Chemical Society, 98*, 2774-2779. doi:10.1021/ja00426a017

3. Mavroides J.G., Kafalas J.A., Kolesar D.F. (2016): Photoelectrolysis of water in cells with $SrTiO_3$ anodes. *Applied Physics Letter, 28*, 241-243. doi:10.1063/1.88723

4. Maruska H.P., Gosh A.K. (1979): Transition-metal dopants for extending the response of titanate photoelectrolysis anodes. *Solar Energy Materials, 1*, 237-247. doi:10.1016/0165-1633(79)90042-X

5. Tomkiewicz M., Fay H. (1979): Photoelectrolysis of Water with Semiconductors. *Applied physics, 18*, 1-28. doi:10.1007/BF00935899

6. Gomes W.P., Cardon F. (1982): Electron energy levels in semiconductor electrochemistry. *Progress in Surface Science, 12*, 155-215. doi:10.1016/0079-6816(82)90002-8

7. Walter M.G., Warren E.L., McKone J.R., Boettcher S.W., Mi Q., Santori E.A., Lewis N.S. (2010): Solar Water Splitting Cells. *Chemical Reviews, 110*, 6446-6473. doi:10.1021/cr1002326

8. Carp O., Huisman C.L., Reller A. (2004): Photoinduced reactivity of titanium dioxide. Progress in Solid State Chemistry, 32, 33-177. doi:10.1016/j.progsolidstchem.2004.08.001

9. Suffredini H.B., Cerne J.L., Crnkovic F.C., Machado S.A., Avaca L.A. (2000): Recent developments in electrode materials for water electrolysis. *International Journal of Hydrogen Energy, 25*, 415-423. doi:10.1016/S0360-3199(99)00049-X

10. Sanchez C., Sieber K.D., Somorjai G.A. (1988): The photo-electrochemistry of niobium doped α-Fe_2O_3. *Journal of Electroanalytical Chemistry and Interfacial Electro-chemistry, 252*, 269-290. doi:10.1016/0022-0728(88)80216-X

11. Hertkorn D., Elsenheimer H.C., Bruch R., Paul F., Müller C., Hanemann T., Reinecke H. (2013): Thickness variation of electrophoretically deposited strontium titanate films for photoelectrochemical energy conversion. *Journal of Applied Physics, 114*, 027020. doi:10.1063/1.4811817

12. Chen Z., Jaramillo T.F. Deutsch T., Shwarstein A., Forman A., Gaillard N., Garland R., Takanabe K., Heske C., Sunkara M., McFarland R., Domen K., Miller E., Turner J., Dinh H. (2010): Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols. *Journal of Materials Research, 25*, 3-16. doi:10.1557/JMR.2010.0020