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PEC HOUSE

A COMPETENCE CENTER DEVOTED TO THE PHOTO-ELECTROCHEMICAL SPLITTING OF WATER AND PRODUCTION OF HYDROGEN

Annual Report 2007

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ABSTRACT

Due to the overwhelming need for sources of renewable, portable and storable energy the PECHouse, a photoelectrochemistry centre of competence at the Swiss Federal Institute of Technology of Lausanne (EPFL), has been established for semiconductor-based photoelectrochemical (PEC) water splitting into H_2 and O_2 using sunlight as the energy input. The overall objective of the research is to design and develop novel semiconductor based materials capable of harvesting and converting solar energy into chemical energy by oxidation of water into oxygen and hydrogen. Continuing research on previously reported Fe_2O_3 photoanodes this year has led to a better understanding of their operation mechanism and limiting aspects. Specifically, a photo-inactive layer was identified at the substrate interface, and possible causes were eliminated. Concurrently, the design and fabrication of state of the art deposition equipment has created a platform to allow future optimization and study of the promising Fe_2O_3 as well as new materials. The silicon dopant amount was investigated and the photoanode performance was found to be very sensitive to the doping level. Doping with an insufficient amount of silicon atoms leaves the conductivity of the iron oxide too low for efficient carrier transport while overdoping causes a phase change and the complete drop of photocurrent. The commencement of new research in materials for PEC was also realized this year through the acquisition of equipment for anodization and testing from the University of Bern, and through the gaining of two new members of PECHouse, Dr. Scott Warren (post-doc) and Mr. Florian Le Formal (PhD student).

Goals of the Project

As the world's supply of fossil fuels declines, hydrogen has become the most promising alternative fuel for the new energy economy. Hydrogen can be produced from various sources; however, hydrogen production from renewable sources is highly attractive. The most important renewable source of energy is the sun, which shines in 10 minutes on planet Earth an amount of energy equal to the total yearly human consumption, yet we harness less than 2% of the world's energy demand due to shortness of suitable materials. The *PECHouse*, a photoelectrochemistry centre of competence at the *Swiss Federal Institute of Technology of Lausanne (EPFL)*, has been established for semiconductor-based photoelectrochemical (PEC) water splitting into H_2 and O_2 using sunlight as the energy input.

The PECHouse was established in September 2007 with three separate but related workplans (WPs). The overall objective of the research is to design and develop novel semiconductor based materials capable of harvesting and converting solar energy into chemical energy by oxidation of water into oxygen and hydrogen. The first work plan (WP-1) extends continuing efforts on nanostructured iron oxide (Fe_2O_3) photoanodes developed at EPFL's *Laboratory of Photonics and Interfaces (LPI)*. [1] The specific goals for WP-1 in 2007 concerned the **optimization of deposition techniques for the Fe_2O_3 film**, **analyzing the effects of the silicon doping** and the **investigation of different interfacial thin film layers for the Fe_2O_3/substrate contact**. The second work plan (WP-2) represents a new direction of research in PEC water splitting at LPI and concerns the fabrication of ordered mesoporous oxides as precursors or hosts for new semiconductor photoanodes. The goals of WP-2 for 2007 were **the transfer of all equipment related to the project from the Department of Chemistry and Biochemistry of the University of Bern to the LPI of the EPFL in Lausanne** (Thereafter, the equipment shall be set up in a laboratory), and the **recruitment of an outstanding Ph.D. student**, who is to replace Ilkay Cesar who finished his thesis this fall. The final work plan (WP-3) related to project management and had no specific scientific goals for 2007.

Work accomplished and results achieved

Since the commencement of the PECHouse in September 2007, much effort has been placed on the organization and start-up of this new competency center. The first task for WP-1 was to update the somewhat artisanal thin film deposition system used in the previous research with iron oxide (atmospheric pressure metal-organic chemical vapor deposition). [2] An exhaustive search of Swiss and international companies was performed to locate state of the art deposition equipment. However, since the deposition method developed at LPI for Fe_2O_3 is unique, no third-party supplier was found to be adequate. Subsequently, we embarked on the design and fabrication of a custom start-of-the-art deposition system capable of atmospheric pressure metal-organic chemical vapor deposition from both gaseous and solution-based precursors. The designed system consists of a cold-wall vertical process chamber with a titanium substrate heater capable of temperatures up to 600 °C (see Fig.1). The introduction of precursors to the process chamber is accomplished by volatilizing liquids in bubblers controlled by precise flow controllers, or by entraining solution-based precursors which have been ultrasonically-dispersed into a gas flow by an advanced 120 kHz ultrasonic spray head modified to be capable of pulsed operation mode. This equipment is currently being assembled and tested in our laboratories.

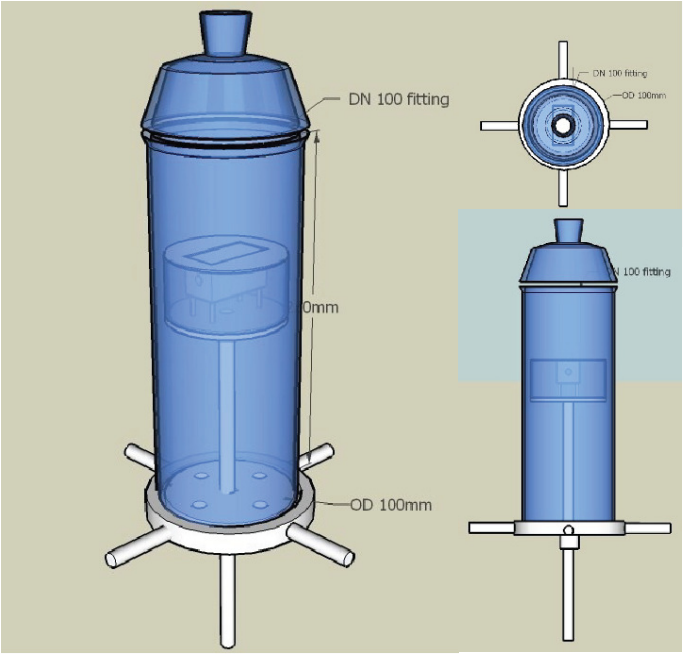

Figure 1. Design of new cold wall chemical vapor deposition system chamber currently being assembled at EPFL. The chamber consists of a borosilicate glass cylinder (OD 10 mm) with a standard DN 100 fitting. The titanium substrate heater (rectangular prism, center of chamber) resides inside a protected and movable platform. Gaseous or sprayed liquid precursors will be introduced though the top and subsequently flow downwards to the heated substrate.

Despite the unanticipated slow process of assembling new deposition equipment our work has continued on optimizing deposition process parameters including the investigation of new variables with the current deposition. An increased understanding of the current system will decrease the optimization time of the new deposition equipment. We have thus spent considerable effort investigating the effect of the silicon doping parameter on the performance of the iron oxide photoanodes. This is also the first step in gaining a further understanding of the silicon doping optimizing the dopant species and amount.

While the silicon doping amount has been optimized in the past, the effects of varying the silicon doping level were not systematically scrutinized. An obvious first step is to vary the amount of silicon precursor (TEOS) in the deposition. This was done by changing the mass flow controller setting for separate iron oxide depositions. Since the TEOS and its carrier gas (argon) flowrate (20 mL/min) is small compared to the overall carrier gas flowrate (2 L/min) this variation should have a limited effect on the other experimental parameters. The photocurrent of photoanodes made with different TEOS flowrates are shown as function of the mass flow controller setting in Fig. 2. The data show the performance of the iron oxide photoanodes is highly sensitive to the silicon precursor flowrate; when the TEOS flowrate is halved from optimum the performance drops by a factor of about 10. This is presumably due to the decreased carrier conductivity but is also, in part, due to morphological effects as previously shown. Interestingly, the performance of the photoanodes drops suddenly at higher concentrations of TEOS. In addition, a change in the UV-Vis properties are also seen in these over doped films and this suggests presence of a new (photoinactive) crystalline phase. Finally, by comparing the photocurrents at the different bias voltages the optimum doping level is seen to shift to higher levels at higher bias voltages. This implies that lesser doped films have better onset behavior. While no explain yet exists for this behavior, we will continue investigation as lowing the photocurrent onset is a major performance goal.

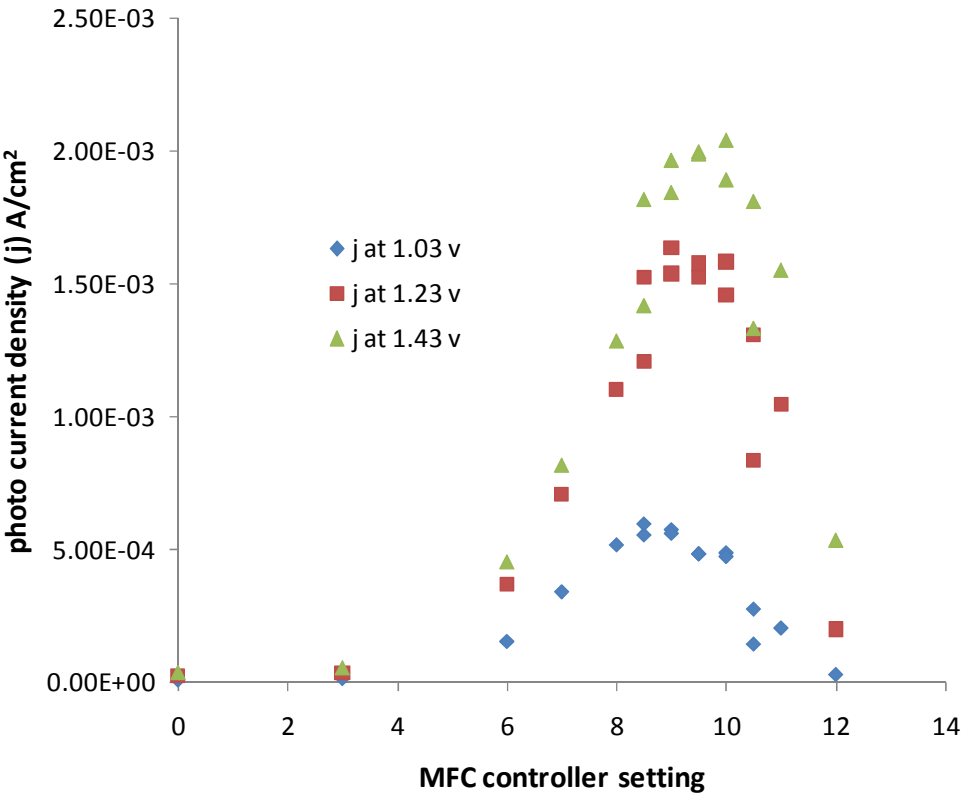

Figure 2. measured photocurrent density under AM 1.5G simulated sunlight at different bias voltages presented as a function of the mass flowcontroller setting (MFC 10 = 0.32 mg TEOS/min).

In addition to the deposition system design, construction, and optimization, continuing work in alignment with the goals outlined in WP-1 of the PECHouse proposal has been performed to gain insight on the nature of the interface between the Fe_2O_3 and the transparent conducting substrate. By calculating the absorbed-photon conversion efficiency of thin films of the photoactive Fe_2O_3 we found that the light absorbed by a very thin film was not as effective as a thicker film at creating the desired photocurrent (see Fig. 3). The poor photoresponse of the thinnest film (~45nm) deposited for 48 sec can be ascribed to an increased recombination rate compared to thicker films and suggests that a photo-inactive dead-layer exists at the interface. The poor performance cannot be attributed to a mismatch between feature size and hole diffusion length as the top morphology and feature size are independent of deposition time. Nor does its Raman spectrum (not shown) contain any anomalies other than enhanced intensities of substrate bands. The same trend was observed for samples prepared by spray pyrolysis as well as ultrasonic spray pyrolysis. To further understand the origin of this dead layer, the photoactive layer was also deposited on gold coated substrates and the dead-layer was found to still be present. Since gold is an excellent conductor with a large work function, an electronic explanation alone is not enough to account for the dead-layer. Structural defects due to the fast deposition and the mismatch of crystal structures are a more likely explanation. As such, current efforts are underway involving underlayer materials with matching crystal structures to α-Fe_2O_3.

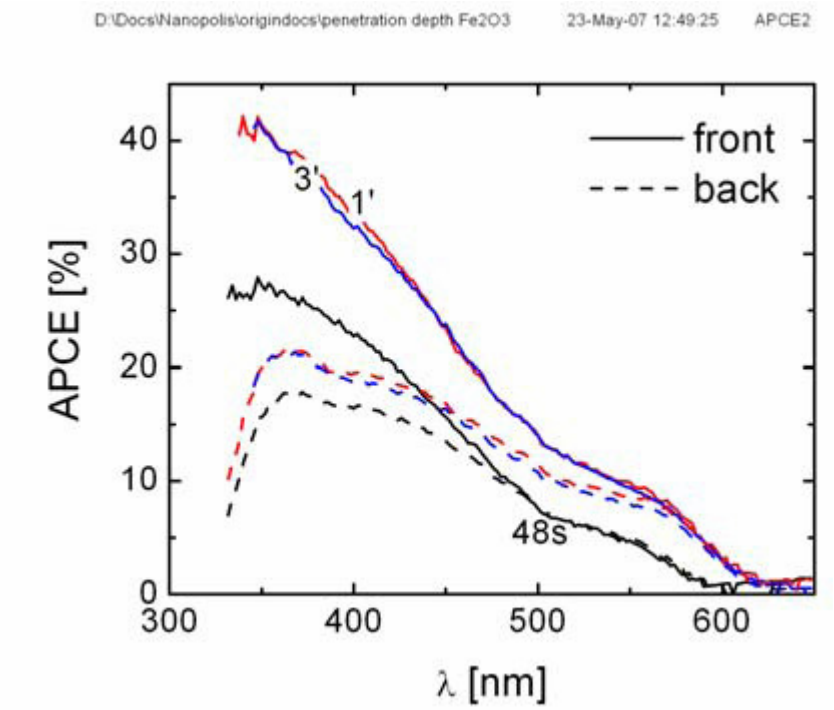

Figure 3. Absorbed photon to current efficiency (quantum yield) of meso-porous silicon doped hematite films on conductive SnO_2:F deposited during 48 sec, 1 and 3 min.

To begin the new research outlined in WP-2 of the PECHouse proposal we first transported the laboratory equipment used by Dr. Antonio Currao at the University of Bern to the EPFL. This equipment will facilitate the anodization of metal films to oxide nanostructures as well as the automatic and precise testing of these films. Dr. Antonio Currao also provided an explanation of the equipment's operation. Laboratory space was allocated for the equipment at EPFL. Its assembly is currently underway and will be completed by Dr. Scott Warren. To assist Dr. Warren in the research outlined in WP-2 a PhD student was sought to fill the vacancy left by the graduation of Ilkay Cesar. An outstanding candidate, Florian le Formal (Masters of engineering materials from EECMP, Strasbourg), was chosen and he has started research on the first tasks in WP-2.

National collaborations

None declared

International collaborations

Members of PECHouse are actively collaborating with international groups. The Marie Curie Research Training Networks is currently providing financial assistant for the stipend of Mr. Le Formal according to contract number MRTN-CT-2006-032474. In addition, the Marie Curie Research Training Network manages the Hydrogen network. The Hydrogen network brings together leading researchers from different disciplines and sectors with a combined expertise that maximizes the chance of achieving scientific breakthroughs in production and storage of hydrogen, while guaranteeing the successful training of a new generation of scientists for tackling scientific problems standing in the way of the hydrogen economy. An important industrial collaboration for PECHouse is with Hydrogen Solar, Ltd. of the United Kingdom. In addition to their financial support (80 kFrs. p.a.), ongoing technical discussions and collaboration prove to be very valuable. Supplementary financial support for PECHouse research also comes from ESF Hydrogen (European program) 60 kFrs p.a. and Portugese Science Foundation (post doc Monica Barroso) 80 KFr p.a.

Evaluation of year 2007 and outlook for 2008

The last few months of 2007 have seen the successful start of the PECHouse center of competency at EPFL. The ongoing research on the promising Fe_2O_3 photoanodes has lead to the further understanding of the limitations of this material and offered possible solutions which will undoubtedly allow the increase in material performance in the coming year. The tasks outlined for 2007 in WP-1

were achieved as expected despite the difficulty in locating commercial deposition equipment. The new custom equipment, once fully operational, will provide a powerful and reliable platform for the rapid testing of materials and fabrication conditions and facilitate the research tasks outlined for 2008.

This year also saw the commencement of a new research program of LPI as outlined by WP-2. The basic start-up tasks for 2007 for this research were completed as planned. The recent arrival of Dr. Scott warren and Mr. Florian Le Formal and the equipment from the University of Bern will provide the path to complete the research tasks for 2008. Specifically, during the first half of 2008, Scott and Florian will begin by gaining experience in preparation techniques and characterization methods present at the LPI, getting to know the PEC water oxidation and water splitting experimental setups present at the LPI, and testing synthesis procedures relevant to the project, in particular electrochemical anodization, hydrothermal synthesis and sol-gel process. In addition, an additional graduate student will be hired as specified by the PECHouse budget proposal. The search for this outstanding canadate is underway. These initial tasks are important to form a basis for the rigorous preparation and characterization of ordered mesoporous ternary and multinary compounds, as outlined by WP-2 for the remainder of 2008.

References

[1] Kay, Andreas; Cesar, Ilkay; Graetzel, Michael. **New Benchmark for Water Photooxidation by Nanostructured a-Fe2O3 Films**. *Journal of the American Chemical Society* (2006), *128*(49), 15714-15721.

[2] Cesar, Ilkay; Kay, Andreas; Gonzalez Martinez, Jose A.; Graetzel, Michael. **Translucent Thin Film Fe2O3 Photoanodes for Efficient Water Splitting by Sunlight: Nanostructure-Directing Effect of Si-Doping**. *Journal of the American Chemical Society* (2006), *128*(14), 4582-4583.