

POLYMERIC ELECTROLYTE MEMBRANE PHOTOELECTROCHEMICAL (PEM-PEC) CELL WITH A WEB OF TITANIA NANOTUBE ARRAYS AS PHOTOANODE AND GASEOUS REACTANTS

M.N. Tsampas, T. Stoll, G. Zafeiropoulos

FOM institute DIFFER - Dutch Institute For Fundamental Energy Research,

De Zaale 20, 5612 AJ, Eindhoven, The Netherlands, Email: m.tsampas@diffier.nl

ABSTRACT

A novel photoelectrochemical (PEC) cell design is proposed and investigated for H₂ production with gaseous reactants. The core of the cell is a membrane electrode assembly (MEA) that consists of a TiO₂ photoanode of nanotube arrays, a Pt/C counter and reference electrodes and a polymeric electrolyte membrane (PEM) with proton conductivity, which serves both as compact reactor for water splitting and as gas separator. The design was inspired by PEM electrolysis technology and modified appropriately for allowing illumination and it is also equipped with a third compartment which enables the use of a hydrogen reference electrode.

Photoanodes of titania nanotube arrays, TNTAs, were developed, for the first time, on a Ti-web of microfiber substrates, by electrochemical anodization. The performance of TNTAs/Ti-web photoanodes were evaluated in both gaseous and liquid reactants. Due to the presence of reliable reference electrode in gas phase direct comparison of the results was possible. Gas phase operation with He or Air as carrier gases and only 2.5% of water content exhibits very promising photoefficiency in comparison with conventional PEC cells.

1. INTRODUCTION

Renewable energy sources are highly desirable in this era of dwindling petroleum reserves and increasing environmental concerns. Solar energy can cover a substantial share of global energy needs, but due to the intermittency and dilute nature of sunlight, storage in energy-dense media, such as hydrogen, is essential. Solar hydrogen can be produced using an electrolyzer powered by photovoltaics (PV) [1,2].

Photoelectrochemical (PEC) cells present an alternative to the photovoltaic PV-electrolyzer combination by integration of photoabsorption and photocatalysis in a single unit. The potential advantages of PEC cells over the coupled PV-electrolysis system are that they can enable the use of earth abundant, cheap electrode materials and provide a more compact and integrated reactor design [1,2].

A PEC cell consists of photoactive materials, such as semiconductors, that absorb light and produce charge carriers. Most of the PEC cells, described so far in the literature, are designed to operate in liquid phases, which have a dual role, serving simultaneously both as the electrolyte and as the oxidation/reduction substrate [1,2]. Inspired by the reactor design of polymeric electrolyte membrane (PEM) electrolyzers and fuel cells [3], few research groups [2,4] have attempted to separate the two electrodes of PEC cells (where the two electrochemical half-reactions take place) with an ionically conductive polymeric membrane. In such systems the membrane acts both as electrolyte and as support for the photoelectrodes. This novel strategy seems very promising since it allows the direct separation of the reaction products, while also the polymeric membrane electrolyte does not need to be replenished during long term operation as in the case of liquid electrolytes, which is essential for scaling up PEC devices [1,2].

The viability of PEC cells with PEM electrolyzers designs (PEM-PEC) has been demonstrated in acidic, alkaline and neutral conditions, but examples with gaseous feedstock for the anode remains rare [2,4,5]. Nevertheless the use of solid-state electrolytes in conjunction with gaseous reactants have a series of advantages over liquid-phase reactors such as operation at elevated temperatures and pressures (for improved kinetics), direct production of compressed H₂ and hindering of gas bubbles formation which can impede catalytic reactions [3,4]. The latter is very important especially for space applications where bubble formation leads to more severe performance degradation due to microgravity environment [6].

Another appealing idea where the PEM-PEC water splitting devices can find application is the production of hydrogen from the water contained in ambient air [7]. Air based operation in PEM-PEC cells can decrease maintenance costs, as the possibility of corrosion and poisoning is reduced. In addition, liquid pumping systems are not needed since natural convection of air can feed the water vapor, and the risk of freezing is minimized. Furthermore, capturing water from the air implies that virtually no liquid water is needed for

operation, making it a water-neutral process [7].

It is thus obvious that gas phase operation in PEM-PEC cells is a promising research approach for photoelectrochemistry which deserves further investigation. The transition from aqueous to solid state electrolytes is a challenging process due to the different reactor configurations and electrode requirements. In conventional PEC cells with aqueous electrolytes the photoelectrodes generally consist of semiconductor modified conductive glass substrates that are immersed in the liquid phase [1,2]. This configuration cannot be directly transferred to PEM-PEC cells, where high porosity of the substrate is required in order to optimize the reactants supply to the electrode/electrolyte interfaces [3].

The aim of our efforts is to develop an integrated PEM-PEC system with gaseous reactants for unassisted water splitting operation based on the Z-scheme approach [1], where nanostructured n-type and a p-type photocatalyst drives for the oxygen and hydrogen evolution reaction respectively. Our present work is focused on the following aspects:

- (i) development of a novel PEM-PEC cell reactor equipped with reference electrode compartment for allowing comparison between PEC studies,
- (ii) fabrication of a photoanode composed of TiO₂ nanotube arrays on a high surface area Ti-web of microfibers porous substrate and investigation of the correlation between anodization time and nanotube length,
- (iii) evaluation and comparison, for the first time, of the fabricated photoanode performance in liquid and gas phase (with He and Air as carrier gases) operation.

Our ultimate goal is to load those TNTAs with visible light sensitive photocatalysts and to examine the effect of nanostructuring on the photoelectrode performance.

2. EXPERIMENTAL

Prior to anodization, Ti-webs (gas diffusion layer, Bekinit, 20 μ m microfibers, 80% porosity, Figure 2) were cleaned by sonication in acetone and in ethanol for 20 min, respectively and rinsed with deionized water. All the experiments were performed in the electrolyte containing ethylene glycol, 0.3 wt% ammonium fluoride and 2% vol% deionized water.

In Figure 1 is illustrated the anodization setup, i.e. typical two-electrode configuration with Ti-web as the counter electrode, along with SEM images of the Ti-web before and after the anodization process. Titania nanotube arrays TNTAs were generated by potentiostatic anodization under a constant applied potential of 30V for 1h. After the anodization, the samples were properly rinsed with deionized water to

remove the occluded ions and then were calcined at 450°C for 5h under air to increase the crystallinity

Surface morphologies of the TNTAs were characterized with a Scanning electron microscope (FEI Quanta 3D FEG instrument). The crystal phases were analysed by X-ray diffraction (PanAnalytical X'pert PRO MRD) using a Cu K α tube.

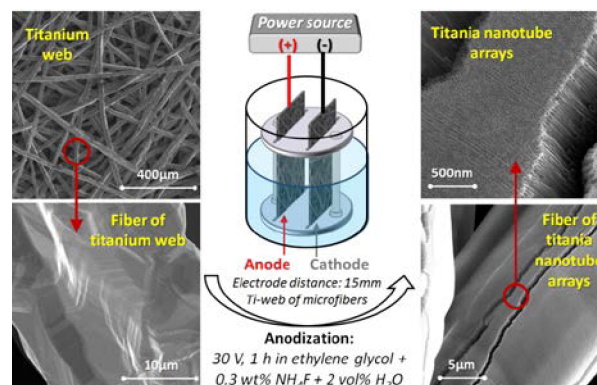


Figure 1. Basic setup and fabrication process of titania nanotube arrays on a Ti-web of microfibers, by potentiostatic electrochemical anodization.

Ti-web photoanode was placed on the top side of a Nafion® perfluorinated membrane (180 μ m thick, Alfa Aesar) while on the bottom side of the membrane a Pt counter-electrode (supported on carbon cloth, with 0.5mg/cm² loading) was placed. The reference electrode which is also Pt/C electrode (with the same characteristics) is deposited on the top of the membrane as presented in Figure 2. MEA was pressed between two graphitic flow-fields plates.

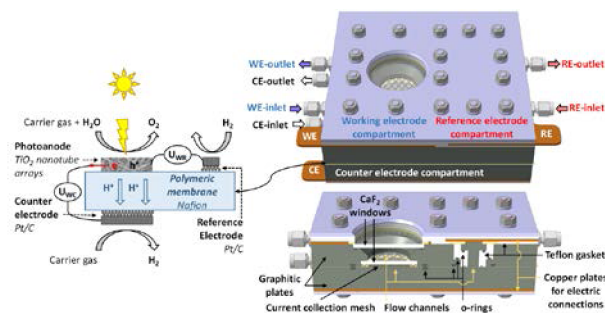


Figure 2. (Left) Configuration and operation of the membrane (photo)electrode assembly. (Right) Novel PEM-PEC reactor design with three compartments for accommodating anode, cathode and reference electrodes.

The three different compartments (sealed with rubber rings) of the novel PEM-PEC cells are illustrated in Figure 2. Teflon gaskets are used to electrically isolate anodic and reference current collection which are in the same side of the cell and are presented with the brown plates. Two Ca₂F windows are used for allowing illumination and ensuring sealing in the anodic compartment and an Au mesh for the current collection.

Each compartment was fed with gaseous streams, made by bubbling He or Air or H₂ through thermostated gas saturators containing H₂O. The cathode was always fed with 2.5 vol% H₂O in He (100 ml/min) and reference with 2.5 vol% H₂O in H₂ (30 ml/min).

The photoelectrochemical studies were carried out using an electrochemical work station (Vertex, Ivium) under the irradiation of a UV-LED lamp (M365LP1, 365±15nm, ThorLabs, 10mW/cm² at the photoanode) equipped with pulse modulator (DC2200, ThorLabs) to perform the chopped irradiation linear sweep voltammetry.

3. RESULTS AND DISCUSSION

3.1. PEM-PEC electrode design

The electrodes used in PEM devices typically consist of carbon supports loaded with the electrocatalytically active phase (usually in powder form) which is also in contact with the polymeric membrane, as depicted in Figure 3a [3].

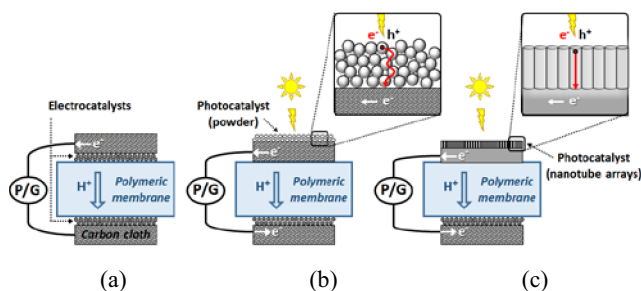


Figure 3. Schematic diagram of the PEM cell (a), PEM-PEC with power photocatalyst (b) and nanotube arrays photocatalyst (c). In all cases the cell is connected to a potentiostat-galvanostat, P/G.

The current gas phase PEM-PEC studies are focused on a very similar design where the electrocatalyst is replaced by a photocatalyst (e.g. TiO₂, WO₃), which however is deposited on the opposite side of the substrate (Figure 1), for allowing light absorption [4,5]. This solution presents two main disadvantages: (i) it provides many recombination pathways of photogenerated species at the powder grain boundaries and (ii) long term stability issues occur, since the photocatalytic powder eventually falls away from the substrate after prolonged operation [3].

To overcome the aforementioned issues we hereby propose in this study an alternative design for PEM-PEC photoelectrodes, which is investigated for the first time in conjunction with gaseous reactants. This design is based on the fabrication of titania nanotubes arrays (TNTAs) photoanode obtained by electrochemical anodization of a titanium porous substrate (composed of a web of Ti-microfibers). This substrate was recently proposed in PEM-electrolysis studies as alternative material due to the vulnerability of carbon to electro-oxidation [8].

This strategy allows to obtain an unidimensional ordered nanotube architecture that offers a wide specific surface and an excellent electrical channel for charge transfer facilitating this way the separations of the photogenerated electron-hole pairs (Figure 1c).

Although titania nanotubes can be formed by other routes, the electrochemical anodization method is regarded as one of the relatively simple techniques to synthesize TiO₂ nanotubes with large surface area [9]. Moreover, the one-dimensional and highly ordered nanotube architecture offers an excellent electrical channel for vectorial charge transfer so that photoinduced electron-holes pairs can be effectively separated, resulting in an obvious improvement in the photoelectrochemical performance. Anodization of Ti-web of microfibers has been very recently reported as a template for loading Pd nanoparticles for alcohol electro-reforming [10], however to our knowledge is the first time that this material is evaluated as photoanode. The unique characteristics of this structure, i.e. high surface area and porosity, make them ideally compatible with membrane electrolytes.

3.2. Reference electrode considerations

While the use of reference electrodes in aqueous phase electrochemistry research is well established, there are only few reports on their application to PEM systems [11]. Among the different possibilities we decided to create a third compartment in our cell which interface a Pt/C electrode deposited on an uncoated area of the polymeric membrane as depicted on the Figure 2a. This compartment is fed by (humidified) hydrogen and thus a reversible hydrogen electrode, RHE is established.

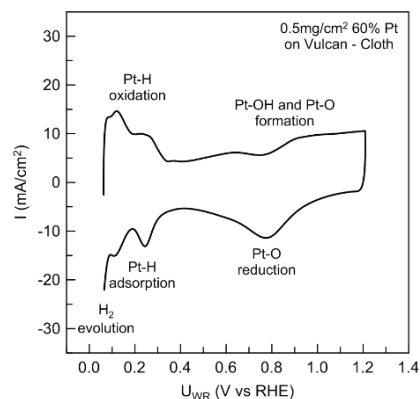


Figure 4. Cyclic voltammetry curves with scan rate of 50mV/s of commercial Pt on Vulcan electrocatalyst obtained in our PEM-PEC device with feed of 2.5% H₂O in He.

In order to validate the reliability of the reference electrode we performed cyclic voltammetry (CV) measurements in commercial carbon supported Pt electrocatalyst. Figure 4 shows that all the features of CV on Pt were observed, i.e. the well-known hydrogen adsorption and desorption peaks in the potential region

of 0 to 0.3V vs RHE, as well as the Pt oxide formation and its counterpart reduction peak at ~ 0.75 V. These results are in good agreement with literature reports obtained in aqueous phase [12], indicating that the PEM-PEC developed in this study is equipped with a reliable reference electrode.

3.3. Photoelectrochemical characterization

The use of gaseous reactants as feed for future PEC installations could be a way to reduce complexity and cost because water supply management can be very simple. Additionally, air based PEM-PEC systems could be used to capture water molecules from ambient air for H_2 production, in this case humidified air supply could be achieved by natural convection [7]. Therefore, in order to investigate this possibility in our study, air was also used as a carrier gas apart from He. The present studies are focused, for the first time, on the comparison of a conventional PEC with aqueous electrolyte (0.1M H_2SO_4) and our gas phase PEM-PEC system operating at 2.5% H_2O vapour pressure which corresponds to 22°C with 100% relative humidity.

Figure 5a and b depicts the linear sweep voltammetry (LSV) measurement of the TNTAs electrodes for water oxidation in a conventional PEC cell with and in our home made PEM-PEC reactor, respectively. Using the PEM-PEC reactor, apart from the gas phase experiments (with He and Air as carrier gas for H_2O steam), water was also poured as droplets on the anode in order to resemble operation with liquid reactants. As one can see by comparing Figure 5a (for 1h anodization) with the dashed line in Figure 5b, the obtained performance with liquid H_2O in the PEM-PEC (apart from the dark current) is almost identical.

Figure 5b shows also that the effect of carrier gas is important only below 0.3V while above 0.4V the photoanode performance is only 8-10% lower when Air is used as carrier gas instead of He. In the low applied potential region the presence of oxygen molecules (when Air is used as carrier gas) act as mediators for recombination [11] and thus cause back reactions which deteriorate photoefficiency. Oxygen-related side reactions are initiated by electron capture by molecular oxygen. To minimize the detrimental impact of oxygen, electrons should be rapidly extracted from the semiconductor to a conducting back contact. The fact that for applied potential higher than 0.4V the presence of oxygen has low impact on the photoefficiency implies that our TNTAs are capable of fast electron injection inside the TiO_2 valence band that limits the possible recombination pathway due their nanostructure. The photocurrent in gas phase is 0.43 mA and 0.40mA at 1.23V when He and Air are used as carrier gas respectively. These values correspond to 50% and 47% of the current obtained at the same potential in liquid phase, which is very interesting taking into account that only 2.5% of water in the gas phase can give half of the

photocurrent.

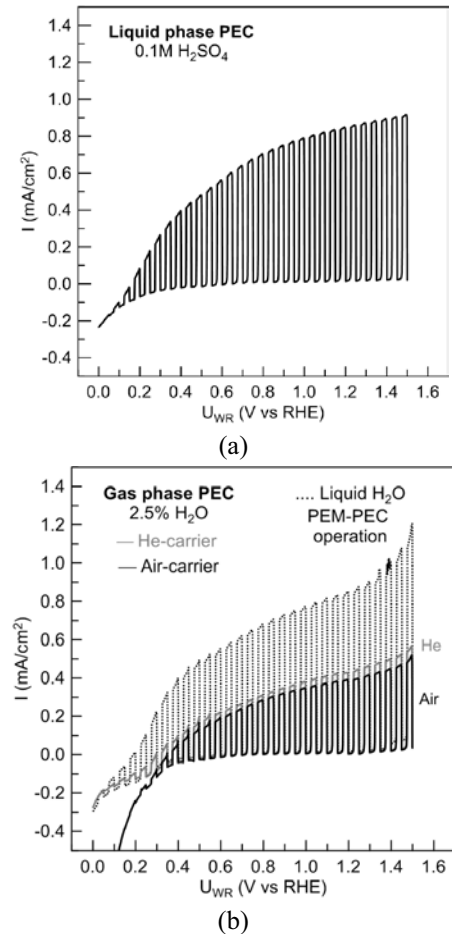


Figure 5. Linear voltammetry sweeps (2.5mV/s) on the photoanode (anodized for 1h) under chopped illumination for water splitting (a) in aqueous electrolytes pH=1 and (b) in polymeric electrolyte with He (top) and Air (bottom) carrier gases for 2.5% H_2O . The dashed line corresponds to operation when the photoanode was poured with droplets of water before assembling the PEM-PEC cell.

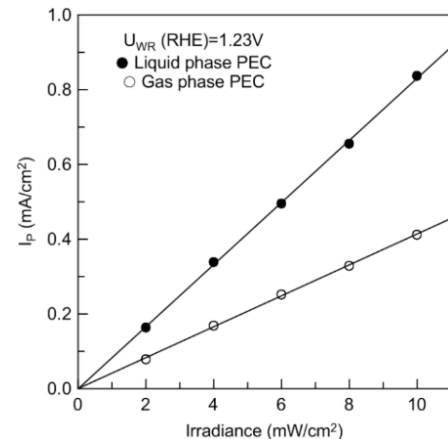


Figure 6. Effect of irradiation on the photocurrent in both aqueous and gas phase PEC.

These results give, for the first time, a comparison of the photoactivity of a photoelectrode in an air-based PEM-PEC vs a conventional PEC cell. The shape of the LSVs in both environments are very similar which illustrates that our proposed PEM-PEC cell design is equipped with a reliable reference electrode, that allows comparison of photoelectrodes in liquid or gas operation.

Figure 6 presents the effect of irradiation on the photocurrent in liquid and gas phase PEC operation. In both cases a linear relationship is observed, showing that photocurrent level reflects the amount of photogenerated charge carriers, limited by the number of photons and efficiency of the photocatalyst. Taking into account the AM1.5 Global and the AM0 which are the standard solar irradiance spectra that are used for terrestrial and space applications, the irradiance in the UV region is 3.9 and 9.1mW/cm² respectively [1]. Therefore the expected photocurrent at 1.23V during gas phase operation will be around 0.34mA/cm² for terrestrial and 0.16mA/cm² for space applications.

4. CONCLUSIONS

TiO₂ nanotubes arrays photoanodes were fabricated on a Ti-web of microfibers by electrochemical anodization.. These novel photoanodes were first evaluated for water splitting and ethanol reforming in conventional PEC cells with liquid electrolytes and then in our novel PEM-PEC cell with gaseous reactants. This solid state electrolyte cell is equipped with a reliable reference electrode that made possible to compare, for the first time, the performance of the fabricated TNTAs/Ti-web in liquid and gas phase operation. It is demonstrated that gas phase PEC operation with only 2.5 % H₂O results to photocurrent close to the 50% in comparison with the liquid operation. Taking into account the cost reduction of air based PEM-PEC cell operation arising from the lack of a liquid pumping system (which is essential for conventional PEC systems), one can conclude that this performance is very promising. The one-dimensional (1D) nanostructures, which provide high electron mobility, specific surface area and mechanical strength, in addition with the porous nature of the Ti-web substrate, makes the fabricated photoanodes ideal for interfacing polymeric membrane electrolytes. Furthermore, this architecture plays a key role in the performance of the TNTAs during gas phase operation since similar results were obtained when either Air or He was used as a carrier gas for water splitting.

5. REFERENCES

1. Van de Krol, R. & Grtzel, M. (2012). Photoelectrochemical Hydrogen Production, Springer, New York.
2. Bosserez, T., Rongé, J., van Humbeeck, J., Haussener, S. & Martens, J. (2015). Design of compact photoelectrochemical cells for water splitting. *Oil & Gas Science and Technology – Rev. IFPEN*. 70(5), 877-889.
3. Carmo, M., Fritz, D.L., Mergel & J., Stolten D. (2013). A comprehensive review on PEM water electrolysis. *Int. J. Hydrogen Energy*. 38, 4901-4934.
4. Iwu, K.O., Galeckas, A., Kuznetsov, A.Y. & Norby, T. (2013). Solid-state photoelectrochemical H₂ generation with gaseous reactants. *Electrochim. Acta*. 97, 320-325.
5. Iwu, K.O., Galeckas, A., Diplas, S., Seland, F., Kuznetsov, A.Y. & Norby, T. (2014). Effects of temperature, triazole and hot-pressing on the performance of TiO₂ photoanode in a solid-state photoelectrochemical cell. *Electrochim. Acta*. 115, 66-74.
6. Matsushima H., Nishida T., Konishi Y., Fukunaka Y., Ito Y. & Kuribayashi K., (2003). Water electrolysis under microgravity: Part 1. Experimental technique, *Electrochim. Acta*. 48, 4119–4125.
7. Ronge J., Deng S., Pulinthanathu Sree S., Bosserez T., Verbruggen S.W., Kumar Singh N., Dendooven J., Roeffaers M.B.J., Taulelle F., De Volder M., Detavernier C. & Martens J.A., (2014). Air-based phototelectrochemical cell capturing water molecules from ambient air for hydrogen production, *RSC Adv*. 4, 29286–29290.
8. S.A. Grigoriev, P. Millet, S. S. Volobuev, V. N. Fateev, (2009). Optimization of porous current collectors for PEM water electrolyzers, *Int. J. hydrogen Energy*. 34, 4968-4973.
9. Grimes, C.A. & Mor, G.K. (2009). TiO₂ Nanotube Arrays: Synthesis, Properties and Applications, Springer, Berlin
10. Chen Y.X., Lavacchi A., Miller H.A., Bevilacqua M., Filippi J., Innocenti M., Marchionni A., Oberhauser W., Wang L. & Vizza F., (2014). Nanotechnology makes biomass electrolysis more energy efficient than water electrolysis, *Nat. Commun.*, 5, 4036, 1-6.
11. Brightman E., Dodwell J., van Dijk N. & Hinds G., (2015) In situ characterisation of PEM water electrolyzers using a novel reference electrode, *Electrochem. Commun.* 52, 1–4
12. Ji W., Qi W., Tang S., Peng H. & Li S., (2015) Hydrothermal Synthesis of Ultrasmall Pt Nanoparticles as Highly Active Electrocatalysts for Methanol Oxidation, *Nanomaterials*. 5(4), 2203-2211.