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New Transparent Laser-Drilled Fluorine-doped Tin Oxide covered Quartz Electrodes for Photo-Electrochemical Water Splitting

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ABSTRACT

A new-designed transparent, conductive and porous electrode was developed for application in a compact laboratory-scale proton exchange membrane (PEM) photo-electrolyzer. The electrode is made of a thin transparent quartz sheet covered with fluorine-doped tin oxide (FTO), in which an array of holes is laser-drilled to allow water and gas permeation. The electrical, morphological, optical and electrochemical characterization of the *drilled* electrodes is presented in comparison with a *non-drilled* one. The drilled electrode exhibits, in the visible region, a good transmittance (average value of 62%), a noticeable reflectance due to the light scattering effect of the hole-drilled internal region, and a higher effective surface area than the non-drilled electrode. The proof-of-concept of the applicability of the drilled electrode was achieved by using it as a support for a traditional photocatalyst (i.e. commercial TiO_2 nanoparticles). The latter, coupled with a polymeric electrolyte membrane (i.e.Nafion 117) and a Pt counter electrode, forms a transparent membrane electrode assembly (MEA), with a good conductivity, wettability and porosity. Electrochemical impedance spectroscopy (EIS) was used as a very powerful tool to gain information on the real active surface of the new *drilled* electrode and the main electrochemical parameters driving the charge transfer reactions on it. This new electrode architecture is demonstrated to be an ideal support for testing new anodic and cathodic photoactive materials working in tandem configuration for solar fuels production by water photo-electrolysis.

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1. Introduction

Also known as "artificial photosynthesis", the photo-electrochemical water splitting offers a promising way for clean, low-cost, environmentally friendly and virtually inexhaustible fuel production from solar energy. The appealing idea is to use the light from the sun, together with appositely designed semiconducting and catalytic materials, to obtain the water dissociation into elemental hydrogen and oxygen, and eventually the production of hydrocarbon fuels if the generated hydrogen is employed to reduce CO_2. Since 1972, when this concept was firstly developed using a TiO_2 photoelectrode by Fujishima and Honda [1], a lot of efforts have been devoted to obtain materials and devices with the stability, cost and efficiency requirements needed for large-scale applications. On the one hand the research focuses on improving the photocatalyst properties, suggesting nanostructured materials, easy to prepare and highly stable in aqueous solutions and oxygen evolving conditions, generally based on n-type metal oxides [2–6]. On the other hand, the aim is to develop low-cost integrated devices, designing photo-electrochemical cells with high solar power to fuel conversion efficiencies [7–10].

The generally proposed architecture for water splitting devices is based on the presence of separate compartments for the water oxidation and the reduction reactions. The reaction chambers are separated by a proton exchange membrane (PEM), similar to the ones already in use for hydrogen fuel cells (FC) [11,12] and for water-electrolyzers [13,14], as proposed in some recent EU-projects [15–17] and by different research groups [7–10,13–20]. This PEM approach also enables gases generation under pressure, tightening the electrolyser, which brings about an increased level of safety [21]. Both PEM electrolyzers and PEM photo-electrolyzers are constituted by three principal components [22]: the membrane electrode assembly (MEA) with the anode, the cathode and the polymeric electrolyte membrane (usually made in Nafion [23]); two reaction chambers (respectively anodic and cathodic) where water flows, and the housing system, that in PEM photo-electrolyzers has to contain transparent windows for solar light illumination.

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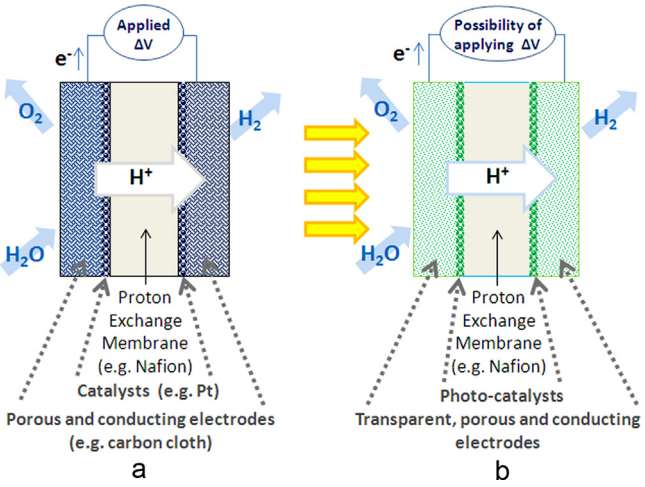

Fig. 1. MEA assemblies for PEM electrolyzer (a) and PEM photo-electrolyzer (b).

The main difference of a PEM photo-electrolyzer with respect to a PEM electrolyzer stands in the MEA, which has to allow the H^+ transfer to the membrane, the collection of the electrons and the support of the catalysts (see Fig. 1). In PEM electrolyzers, MEAs are generally made in porous and electron conducting materials such as carbon cloth, which is highly conductive, water permeable (so to permit the wetting of the Nafion membrane) and can easily host Pt or other nanoparticle catalysts (see Fig. 1-a) [24,25]. In PEM photo-electrolyzers, the electrodes have also to support the light harvester material, able to capture the solar photons and to further reduce the bias potential, and the carbon cloth cannot be employed. As shown in Fig. 1-b, the MEA of photo-electrolyzers should be transparent to the light on both the anodic and cathodic side, so that also the cathodic electrode can absorb and take advantage of the part of the solar spectrum not exploited by the anodic material. In PEM electrolyzers the employed MEAs are generally fabricated following the consolidated and well established technology of the gas diffusion electrodes for PEM fuel cells, but in PEM photo-electrolyzers new technological solutions have to be searched. The PEM photo-electrolyzer electrode support has to be electrically conductive (at least on the photocatalyst side), transparent to the visible light, porous, mechanically robust and permit an easy attachment of catalysts and/or bio-molecules, q-dots, or other photo-active nanoparticles. Despite the fast growing literature on artificial photosynthesis, few papers have till now focused on this subject. Goretex membranes have been employed for "breathable" electrodes providing a good separation of the two gas chambers and decreasing the gas cross-over [26]. Nafion membranes in which photocatalyst (e.g. TiO_2 powder) and Pt powders have been embedded with a suitable amount of conductive carbon black powder [27] have been demonstrated to be a valid alternative when catalysts materials are easily mixable in a Nafion monomer suspension. Also, some novel electrode architectures at the nano- or micro-scopic scale have recently been suggested, even if not yet employed in photo-electrolyzers: 3D-branched nanowires [28], nano-crystalline and macroporous antimony-doped Tin Oxide [29], nano-ITO films with high surface area [30] and free-standing, very thin films of hierarchically porous N-doped graphene [31]. Finally, it has to be observed that, in the impressive number of papers that propose new photocatalytic materials, the characterizations are generally done in electrolytic cells and the materials are generally deposited on a glass substrate, covered by a transparent conductive oxide (TCO) (see for instance: [32–34]). Such transparent electrodes are also used in dye sensitized or thin films solar cells: they are made of glass slides covered with a thin film of a TCO, i.e. ITO (Indium-doped Tin Oxide) or FTO (Fluorine-doped Tin Oxide). However, they cannot be employed in PEM photo-electrolyzers, since they are not porous and hence the gases (O_2, H_2) produced during the water splitting reaction and the water cannot permeate.

The main aim of this paper is to propose a new design of transparent, conductive and porous electrodes to be employed as support for photo-active materials. These new electrodes offer all the advantages of the TCO/glass substrates: good transparency, low electric resistance and easy adhesion of photocatalysts, moreover they permit the passage of water and gases and can be employed in a MEA assembly for PEM photo-electrolyzers. They have been made with very thin (250 μm) quartz slides in which an array of holes has been obtained by laser drilling for permitting water and gas flow. An FTO thin film has been deposited on the laser-treated quartz slides to guarantee electrical conductivity. The results of morphological, optical and electrochemical characterization of the electrodes are reported. Moreover, the MEA has been integrated and tested in a simple and easy-to-handle PEM photo-electrolyzer device appositely designed for testing different photo-activated materials. The first water splitting results obtained on laser-drilled FTO/quartz electrodes covered with a traditional photocatalyst (*i.e.* commercial available TiO_2 nanoparticles) are also presented. Electrochemical impedance spectroscopy (EIS) results, modeled though an equivalent circuit allowing the determination of the electrochemical parameters that can help in the optimization of both the photo-electrode and the device, are finally reported and discussed.

2. Experimental

2.1. Electrodes Preparation

Very thin quartz plates (250 μm-thick, 2.5×2.5 cm^2) were laser-drilled and subsequently covered by an FTO layer. By using an electronically pulsed Model L48-1 Synrad CO_2 10 W laser source (driven by a UC-1000 Synrad controller) mounted on a modified Deltatech D700 X-Y table (by Solaronix) an array of 1659 holes was drilled over the central region (1×1 cm^2) of the quartz plates. The holes dimensions and spacing were carefully chosen in order to guarantee robustness, electrical conductivity and permeation to water and gas molecules. The drilled quartz sheets were spin-coated with a thin TiO_2 buffer-film (thickness of about 25 nm) in order to guarantee good adhesion. They were then covered on one side with an FTO layer (thickness of 150 nm), deposited by atmospheric pressure chemical vapor deposition at a temperature of 500 °C. A non-drilled quartz slide was covered with a continuous FTO film with the same procedure and used as a reference for comparison purposes. Below, these two electrodes will be called "*drilled*" and "*non-drilled*" respectively.

Photo-electrodes were prepared by depositing a thick film of TiO_2 nanoparticles on the FTO-side of drilled electrode. The substrates were firstly cleaned for 3 min in acetone and 3 min in ethanol in an ultrasonic bath and then a titania film was spread by the doctor blade method using a commercial paste (DSL 18NR-T by Dyesol). The film was annealed in a programmable furnace at 450 °C for 30 min in calm Air, using a heating rate of 5 °C/min, and then cooled down naturally. Below, these electrodes will be referred to as "*TiO_2/drilled*".

Cathodes were fabricated by depositing a thin and dense film of Pt (thickness of about 110 nm) on FTO-drilled electrodes. The drilled substrates were first cleaned with a pre-sputtering procedure in Ar plasma at 20 mA for 5 min and then Pt was deposited by sputtering (Quorum Q150TES) at 30 mA for 320 s. Below, these electrodes will be called "*Pt/drilled*".

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