

3D-printed Photo-Spectroelectrochemical devices for *in situ* and *in operando* X-Ray Absorption Spectroscopy investigation

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Abstract

3D printed multi-purpose electrochemical devices for X-Ray Absorption Spectroscopy are presented in this paper. The aim of this work is to show how 3D printing can be a strategy for the creation of electrochemical cells for in situ and in operando experiments by means of synchrotron radiation. As a case study, we present the description of two cells which have been employed in experiments on photoanodes for photoelectrochemical water splitting. The main advantages of these electrochemical devices are associated to their compactness and to the precision of the 3D printing systems which allows to achieve details that otherwise would be difficult to obtain. Thanks to these systems it was possible to combine synchrotron-based methods to complementary techniques in order to study the mechanism of the photoelectrocatalytic process.

1. INTRODUCTION

Synchrotron radiation has nowadays grown into an essential tool for the study of the changes in terms of charge state, local geometric and electronic environment of target elements during the occurrence

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of particular physico-chemical phenomena, which are in turn triggered by variations in temperature, pressure or by electrochemical perturbations (Filez *et al.*, 2014; Tian *et al.*, 2014; Mansour *et al.*, 2012; Hillman *et al.*, 2011). One of the main limitations lies in the adaptation of the beamlines to the different experimental needs: in many cases, it is difficult to create adequate setups to monitor and control the physicochemical conditions of the sample. In addition, there is an increasing need for detailed study of systems in their real working conditions: this is particularly true in the field of catalysis where *in situ* and *in operando* techniques are gaining increasing attention (Frenkel *et al.*, 2012). The purpose of this work is to show how 3D printing can be an effective tool for the construction of multi-purpose cells for *in-situ* and *in-operando* experiments with synchrotron radiation. As a case study, here we describe two different types of cells (A and B, respectively) for X-Ray Absorption Spectroscopy (XAS) experiments on photoanodes for photoelectrochemical water splitting. This is in turn a challenging topic since these devices represent in principle the ideal energy conversion systems, allowing the direct production of hydrogen from sunlight. The photoanodes we investigated are composed of an electrocatalytic domain (IrO_x), which is characterized by high activity as catalyst for the oxygen evolution reaction – OER – in the water splitting process (Yamanaka, 1989; Steegstra & Ahlberg, 2012; Blakemore *et al.*, 2011), coupled to a semiconductor part (hematite, $\alpha\text{-Fe}_2\text{O}_3$), which is sensitive to UV-Vis light. The investigation of photoelectrochemical water splitting represents a step of a more complete research plan, aimed at studying the mechanism and the kinetics of electrocatalytic reactions (Minguzzi *et al.*, 2013, Minguzzi *et al.*, 2014; Achilli *et al.*, 2014; Minguzzi *et al.* 2015). The study of photoelectrochemical architectures (Fujishima & Honda, 1972) would shed light onto the role of the electrocatalyst when coupled to a semiconductor, providing a link between electrochemistry and photochemistry. It is important to note that the coupling between the semiconductor domain and the electrocatalytic moiety implies limits on the illumination by both X rays and UV-Vis light.

Fig. 1 shows the scheme of the photoanode: it is composed of a bilayer architecture with the semiconductor part deposited onto a FTO (Fluorine-doped Tin Oxide) substrate, which is transparent

in the visible range but strongly absorbs in the near UV. On the other hand, IrO_x strongly absorbs in the visible region. Then, in each experiment, UV-Vis illumination could occur on different sides of hematite according to the best opportuneness. The X-Ray probe is then used for the investigation of local electronic changes in the IrO_x overlayer triggered by illumination of Fe₂O₃. The main limitation of the X-Ray probe lies here in the attenuation coefficient by the other materials present. The presence of the hematite and FTO on the back-side of the electrocatalytic film prevents us from irradiating the system with X-Rays from the back-side, and in addition forbids the use of transmission geometry. Consequently, XAS investigation should take place at the other side of the IrO_x film, which is in direct contact with the electrolytic solution, and in fluorescence mode. In respect to the water attenuation coefficient at the Ir –L_{III} edge, the solution layer cannot be thicker than 1 mm. A photo-spectroelectrochemical cell for hosting such a photoanode should also allow a three-electrodes assembly where the working electrode (at which the process of interest takes place) is combined to a counter electrode (a Pt foil) and a reference (usually Ag/AgCl). It is important to point out that in these small-sized electrochemical cells small channels and holes are present that difficult to obtain manually or with conventional tools. These channels and holes should guarantee the electrical contact between the electrodes via the electrolyte. Another requirement for these devices is the resistance against X-Rays in order to avoid the formation of holes in the material and the subsequent loss of contents. The employment of a 3D printer based on the use of photopolymers represents the easiest and fastest way to produce efficient photo-spectroelectrochemical devices characterized by details that would be difficult to obtain using standard subtractive manufacturing technologies.

The first example of the use of 3D printing of a [cell](#) for spectroscopy dates back to few years ago (Symes *et al.* (2012)), but, to our best knowledge, 3D printing has not been yet employed for building photoelectrochemical devices for *in situ* and *in operando* experiments with synchrotron radiation.

2. Design of the photo-spectroelectrochemical devices

Commentato [E1]:

The photo-spectroelectrochemical devices described in this work are entirely made of a photopolymer resin.

2.1 Cell type A

As shown in the scheme presented in Fig. 2A, the device is composed of two parts. Side 1 in Fig. 2A is the cell main body, while side 2 is a rectangular cover. The two parts are assembled by means of screws and bolts, inserting an O-ring ensuring tightness against electrolyte leakage. The frontal circular window is used for illumination by both UV-Vis and X-rays. The internal cell volume is then filled with the electrolyte as explained below. In this case, the thickness of the frame defined by the two arrows in Fig. 2A is limited to 1 mm, due to the absorption of water at the energy of the Ir-L_{III} edge (the absorption length for water at 11200 eV is 2.5 mm).

The rectangular shape is ideal for adding an upper external part that in turn allows a stable lodging of the reference electrode. The lodging is constituted by a rectangular block with two cylindrical holes, of which one is used for housing the reference electrode and the other for filling the cell, once assembled, with the electrolyte by means of a syringe, and also works as electrolyte reservoir. Both holes are connected to the inner part of the cell by means of small canals, whose diameter is 500 μm (Fig. 2B): this diameter is in turn dictated by the thickness of the 1 mm frame as detailed above. The counter electrode consists of a mylar square film, half of which is covered with a Pt/C+Nafion mixture. The latter is deposited by dropcasting over the mylar while it is kept on a laboratory hot plate. The electrical contact is ensured by Ag epoxy (EPO-TEK[®] H20E) and a Cu wire. The electrode is glued onto the frontal face of the cell using melted Parafilm[®]. The counter electrode thus also works as a closure of the whole internal cell volume.

The electrochemical device with and without the three-electrode assembly is shown in Fig. 3. The stable architecture achieved by means of this design allows to obtain the best conditions to perform photo-electrochemical measurements. In this case the working electrode is the photoanode made of two parts, namely the electrocatalytic domain, IrO_x , which is subjected to the XAS investigation, and a semiconductor part Fe_2O_3 , which is illuminated by an UV-Vis diode. The cell contains the electrolyte solution with a controlled thickness and presents a frontal window that allows illuminating on by X-Ray photons.

2.2 Cell Type B

The scheme of Cell B, that is clearly a modification of Cell A, is illustrated in Fig. 4A (front side) and 4B (back side). Two are the main differences of this cell if compared to Cell A. The first lies in the presence of an additional electrolyte reservoir (D) in the main body of the device. This part is open at the upper side and is electrically connected with the photoanode by the electrolyte. The design of this feature is aimed at: i) obtaining room devoted to the lodging of the counter electrode in direct electrical contact with the photoanode; ii) having a larger static reservoir for the electrolyte to cope with possible radiation damages (local heating, radical formation, etc.) induced by the X-ray beam. The second important characteristic of this electrochemical cell is represented by the circular hole generated in the rectangular cover. This feature provides a window on the working electrode and is accomplished in order to perform UV-vis illumination at the back side of the hematite, thus avoiding the absorption in the visible region by the IrO_x layer.

The main body of the device and the rectangular cover are held together by means of screws and bolts and an O-ring is inserted in order to ensure tightness against solution leakage. The rectangular shaped electrolyte chamber presents an upper slot, ideal for the insertion of the Pt counter electrode. The

lodging for the reference electrode is achieved by a hole generated in the upper part. This is connected to the electrolyte chamber by means of a curved canal with a diameter equal to 500 μm as one can see in the cross section illustrated in Fig. 4C. In addition, this second cell has a 100 μm thick window for X-ray illumination that is directly printed on the front side, ensuring a proper sealing versus the back pressure of the electrolyte solution. The realization of such details would not be possible (or very difficult to realise) with the traditional and manual instrumentation.

Fig. 5 shows a picture of the electrochemical device with the three-electrodes assembly mounted in the experimental hutch of the LISA beamline (BM08) at ESRF, where all the experimental results described in this paper were obtained: UV-vis illumination is carried out on the left side by means of a solar simulator lamp whereas the X Ray illumination takes place on the other side of the cell.

Commentato [E2]:

3. Cell fabrication

The photo-spectroelectrochemical devices are manufactured using a photopolymer based printer (Objet 30 Pro, Objet-Stratasys). This technology was selected among different 3D printing solutions available on the market because of its ability to print very small parts with high resolution and using a material that is resistant to chemicals. The printer uses photopolymeric resins that are laid down on the printing bed in a liquid form and polymerized using a UV lamp. The device is printed at a layer resolution of 28 μm , that is the height of each deployed layer, while the in-plane printing error is about 1 $\mu\text{m}/1\text{ mm}$. This is well appropriate to the diameter of the channels for the reference electrode and for the electrolyte reservoir (500 μm , as mentioned above).

The printer can deploy one material at a time, in combination with a support material that can be removed using a water jet machine and a sodium hydroxide solution. The presence of the support material in all the inner cavities was taken into account during the device design. Actually, all the

inner channels have been designed with the minimum level of curved parts, in order to facilitate the cleaning process.

The devices are printed using the VeroWhite (<http://usglobalimages.stratasys.com>) material, an opaque rigid photopolymeric polyacrylic resin characterised by an adequate stiffness and resistance to chemicals.

An adequate resistance to temperatures and mechanical stresses forced by the experimental conditions characterizes this material. Actually, the resin has a softening temperature of 52-54 °C (measured with ASTM standard DMA) and has a Heat Deflection Temperature (HDT) of about 45-50 °C (measured with ASTM standard D-648-06 and D-648-07). Since the experimental procedure is carried out in contact with a liquid, water absorption represents an another important feature to be considered: actually, the prototyped object has always a little porosity, because of the layering process that builds it. The water absorption parameter ranges from 1.1% - 1.5% within 24 hours. Since each experimental test last for less than 8 hours, the devices can be considered as waterproof for this application.

The printer is able to realize an entire set in about 2 hours. After printing, the devices components are cleaned first using a water jet machine, paying attention in not damaging the thin walls. After that, the parts are immersed in a solution of water (90%) and sodium hydroxide (10%) to facilitate the removal of the support material. A thin wire has been used to ensure a good cleaning of the inner channels.

4. XAS results

The capabilities of the photo-spectroelectrochemical cells described are illustrated in this section.

Before discussing the X-ray Absorption results, it is important to show that the 3D printed electrochemical devices actually work. A comparison between a cyclic voltammetry obtained by

means of a 3D printed XAS cell and one obtained by means of a standard electrochemical cell is illustrated in Fig. 6. These electrochemical measurements were performed between -0.2 and 0.4 V vs Ag/AgCl (KCl 1M) at 20mV/s in ferrocene methanol 1mM in KClO₄ 0.1M. The working electrode was a Pt foil. The signals clearly show that the cell response is very similar in the two cases, thus probing the conformity between the electrochemical behaviours.

Fig. 7 illustrates XAS results obtained *in situ* and *in operando* by means of the 3D printed electrochemical devices previously described. Two different types of sample have been considered: electrodes onto which the IrO_x film was electrodeposited (Fig. 7A, 7B, 7C) and electrodes onto which the IrO_x film was photodeposited (Fig 7D)

Fig. 7A shows Ir-L_{III} XANES spectra obtained at two different potential values: 0.4 and 1.4 V (in the latter case oxygen evolution takes place) by means of the A type cell. The spectra of IrCl₃ and IrO₂ standard materials are added as better references for Ir(III) and Ir(IV) respectively. Transitions from the Ir 2*p* levels to continuum states and to 5*d* localized states give rise to steps and peaks (white lines). The energy position of the peak maximum is directly associated to Ir oxidation state: a shift to a larger potential value corresponds to an oxidation process.

When the applied potential is 0.4 V the peak maximum is situated between that of IrCl₃ and IrO₂ thus indicating that the mean oxidation state is between (III) and (IV). In oxygen evolution conditions, when the potential is equal to 1.4 V, the peak maximum is shifted towards larger energy values. This suggests that the oxidation state of the photo-absorber is very close to Ir(IV). This corresponds, after corrections for the ohmic drops in the □-Fe₂O₃ layer, to what previously described by some of us (Minguzzi et al., 2015; Minguzzi et al 2014) by using a much larger volume cell.

In Fig. 7B and 7C the response of the IrO_x layer to the illumination of □-Fe₂O₃ by UV-Vis light is shown for two different applied potentials: 0.4 V (Fig. 7B) and 0.8 V (Fig. 7C). The normalized

XANES spectra acquired in UV-Vis light (red line) and dark conditions (blue line) are illustrated. Their differences (represented by the black lines), resulting from the subtraction of the spectrum acquired in dark conditions from that observed in light conditions, are different in the two cases but very small. However, taking into account that the signal is recorded *in situ* by means of a photo-spectroelectrochemical device, these differences can be considered as significant. For applied potential equal to 0.4 V the difference is positive: the only reasonable explanation to this is a larger hole density in the iridium *5d* orbitals occurring under UV-Vis irradiation. For applied potential equal to 0.8 V the difference is negative: this trend accounts for a smaller hole density in the iridium *5d* states in presence of UV-Vis light. These results show that the experimental setup provides a key tool for monitoring the UV-Vis light driven variations in the hole density of iridium *5d* states under different applied potentials. A more detailed discussion of the mechanism and the kinetics of the photo-electrochemical process investigated will be presented in a future work.

Finally, Fig. 7D shows the response of the photoanode to the illumination by UV-Vis light when the electrodic layer is prepared via photo-electrochemical deposition. In this case, measurements were performed by means of the electrochemical cell of type B. The red line and the blue line are the XANES spectra acquired in presence and in absence of UV-Vis light illumination respectively. The difference between them is indicated as a black line. Its trend clearly accounts for a peak shift towards lower energy values under UV-Vis illumination: the only reasonable explanation to this is a reduction process of iridium.

These results show that the experimental setup provides a key tool for monitoring the UV-Vis light driven variations in the hole density of iridium *5d* states under different applied potentials. A more detailed discussion of the mechanism and the kinetics of the photo-electrochemical process investigated will be presented in a future work. However, it should be noted that IrOx overlayer prepared by different methods (by electrochemical or photoelectrochemical deposition) respond differently to UV-Vis illumination.

5. Conclusions

In the current research work we designed and built multi-purpose photo-spectroelectrochemical devices for *in situ* and *in operando* X-Ray Absorption Spectroscopy by means of a 3D printer. Thanks to these systems it was possible to combine synchrotron-based methods to complementary techniques. In particular we created two types of photo-spectroelectrochemical cell for investigating the photoelectrochemical water splitting providing a key link between spectroscopy and electrochemistry and photochemistry.

The main characteristics of these electrochemical devices are summarized below:

- (i) The devices are compact and small enough to allow an easy and fast experimental set up in the beamline hutch.
- (ii) Thanks to the precision of the 3D printing system, it is possible to achieve details that otherwise would be difficult to obtain. For example, it is possible to control the thickness of the electrolytic solution avoiding problems associated to X-Ray attenuation coefficient by water. Furthermore, we can obtain small and curved canals for the counter and reference electrodes ensuring electric contact between the different parts of the cell.
- (iii) The cell geometry is easily adaptable for other experiments, for example for studying different materials or for performing RIXS or XRD. In particular, the experiments here described were performed at the Ir-LIII edge (11215 eV). However, the design of cell B allows to use softer X-rays thanks to the fact that the X-ray window is printed and can be in principle made thinner to cope with the lesser penetration depth at low

energies, still ensuring a proper stiffness for sustaining the back pressure of the electrolyte.

Experiments carried out by means of these photo-spectroelectrochemical devices allowed performing measurements at different potential values, including those where oxygen evolution is expected to occur. Furthermore, thanks to specific details above mentioned, it was possible to study the different responses of the catalyst in UV-Vis light and dark conditions. Results obtained led to a better understanding of the mechanism and the kinetics associated to the photoelectrocatalytic process of water splitting.

As a final remark, we note that the small volume parts of the photo-spectroelectrochemical devices here described could hardly be fabricated without the 3D printing technology. It is quite straightforward to expect that this technology will be of increasing importance in the creation of environmental chambers for *in situ* and *in operando* synchrotron radiation experiments.

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Figures captions

Figure 1. Photoanode architecture: the IrO_x film is in contact with the Fe₂O₃ deposited onto the FTO (Fluorine-doped Tin Oxide) substrate.

Figure 2. Design of cell type A: rectangular plate and cover with hole (A) and schematic representation of the canals connecting the reference and counter electrodes holders to the inner part of the cell (B).

Figure 3. Image of the assembled photo-spectroelectrochemical cell of type A without (A) and with (B) the three-electrode setup.

Figure 4. Scheme of the photo-spectroelectrochemical cell of type B showing the electrolyte reservoir (A), the rectangular cover with circular hole (B), the curved canal connecting the reference electrode to the inner part of the cell (C) and the working electrode lodging (D)

Figure 5. Picture of the assembled photo-spectroelectrochemical cell of type B, mounted in the experimental hutch. UV-vis illumination is carried out on the left side by means of a solar simulator lamp whereas the X Ray illumination takes place on the other side of the cell.

Figure 6. Comparison between a cyclic voltammetry obtained by means of a 3D printed XAS cell (blue line) and one obtained by means of a standard electrochemical cell (red line). These were performed between -0.2 and 0.4 V vs Ag/AgCl (KCl 1M) at 20mV/s in ferrocene methanol 1mM in KClO₄ 0.1M. Working electrode: Pt foil

Figure 7. XAS results obtained with electrodes onto which the IrO_x film was electrodeposited (Fig. 7A, 7B, 7C) and electrodes onto which the IrO_x film was photodeposited (Fig 7D). 7A: Ir L_{III} XANES spectra acquired *in situ* at two different potential values: 0.4 V (red line) and 1.4 V (green line). The spectra of IrCl₃(black line) and IrO₂ (blue line) standard materials are plotted as references for Ir(III) and Ir(IV) respectively. 7B: Ir L_{III} XANES spectra acquired in presence (red line) and in absence (blue line) of UV-Vis illumination at a constant potential equal to 0.4 V. The

light-dark difference is indicated as a black line. 7C: Ir L_{III} XANES spectra acquired in presence (red line) and in absence (blue line) of UV-Vis illumination at a constant potential equal to 0.8 V. The light-dark difference is indicated as a black line. 7D: Ir L_{III} XANES spectra acquired in presence (red line) and in absence (blue line) of UV-Vis illumination at a constant potential equal to 0.7 V. The light-dark difference is indicated as a black line.