3D printing and its applications in spectroelectrochemistry

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Abstract

The analytical tools have given not only chemistry but science as a whole, new horizons when it comes to the comprehension of chemical phenomena. With precise information, new possibilities emerged in the identification and characterization of novel compounds and advances in several areas of chemistry. In this context, spectroelectrochemistry (*SEC*) combines complementary tools to that the electrochemistry techniques drive the reactions and spectroscopic methods are focused on species analysis. Thus, this strategy provides a way to monitor what is happening *in situ* or *in operando*, making it a powerful tool for the identification of intermediates of reaction, mechanistic, kinetic studies, and even quantitative analysis. However, *SEC* comes with a somewhat inconvenient drawback: even though it has been rising in popularity, setting up the *SEC* cells might be complicated for newcomers. On the other hand, 3D printing becomes interesting and, at the same time, incredibly effective technology for the user to create customized *SEC* cells to support any necessity. In this review, we will go over the importance of 3D printing in the design and use of spectroelectrochemical cells.

Keywords: Spectroelectrochemistry; 3D printing; Additive Manufacturing; Printed *SEC* Cell

1. Spectroelectrochemistry as a tool for deep investigation in chemistry

Chemical information is the key to understand the processes involved in electrochemistry experiments. Under certain conditions, electrochemical techniques alone are limited in terms of information and in some cases do not allow a full understanding of the chemical phenomena behind the electrochemical processes. For this reason, the combination of electrochemical techniques with spectroscopic analysis is called spectroelectrochemistry (*SEC*) and it allows scientists to observe the details and changes during the chemical transformations and contribute to a deep comprehension of the electrochemical interfacial processes [1], [2], [3], [4].

Spectroelectrochemistry is also known as the hyphenation of electrochemistry and spectroscopy techniques, in other words, an electrochemical reaction (oxidation or reduction) occurs and it is monitored by spectroscopic methods. Although these are fundamentally different methodologies, this concept had been developed in the scientific community since the first optically transparent electrodes (OpTEs) were developed [5]. In this setup, the light can cross the system without any interference and therefore can bring reliable information about the electrochemical processes on the interface of the electrodes [2], [5], [6].

The OpTEs are made of a very thin layer of a conductive material such as Au, Pt, In_2O_3:SnO_2 (ITO – indium tin oxide), or SnO_2:F (FTO – fluorine-doped tin oxide) and they are promptly within the wide array of possibilities for *SEC*. The proposition consists of what is now called a thin layer *SEC* under a semi-infinite diffusion regime, which there is a thin layer of the solution surrounding the electrode, and the optical beam of light directly passes through a conventional cell [6], a scheme can be found in Fig. 1 A. Later, a new type of OpTE was introduced and it is currently known as mini-grid working electrodes. These electrodes consist of a thin plate of metal with small orifices transparent to light in a solution thickness of less than 0.2 mm (see the scheme in Fig. 1 B). Mini-grid working electrodes are less susceptible to artifacts due to the absence of film on their surface [2]. They have surface properties like the bulk Au and present a low internal ohmic resistance. These characteristics contribute to reproducible measurements for current spectroelectrochemical studies.

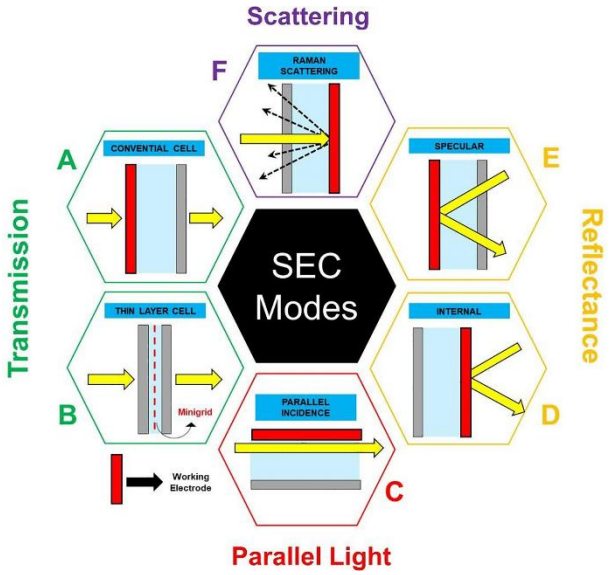


Fig. 1. Overview of the spectrochemistry modes. Minigrid: minigrid working electrode.

SEC brings countless tools of analysis and allows us to study compounds with low molar absorptivity, for example. In this context, a thin layer cell would not be adequate because even in high concentrations absorption spectra cannot be measured. The introduction of the long optical path length spectroelectrochemical cell solves this problem, since the light beam runs parallel to the working electrode in the electrode/solution interface (Fig. 1 C) [7], [8]. Also, it brings the advantage of using any kind of electrode and sensitivity can be modulated according to the optical path. The limitations of this technique are the working regime under static conditions, electrolysis time, and the dynamic of superficial adsorption.

In Raman spectroscopy, the inelastic scattering of incident light over a sample is used to get vibrational information about the samples and help to monitor the presence of functional groups or surface modification, for example. On the other hand, the combination of Raman spectroscopy with electrochemistry experiments allows us to go further and study specific mechanisms of reactions and to follow chemical transformations [9]. The spectroelectrochemistry Raman enables the use of incident and collection modes with backscattering (180°), ATR mode, and Raman confocal microscopy. Each mode has vantages and disadvantages that can be found in the literature. In addition to conventional Raman is possible to perform experiments in resonance regime (Resonance Raman spectroscopy) or probing surface through Surface-enhanced Raman spectroscopy (SERS) [10]. A schematic view of the idea of the spectroelectrochemistry Raman is demonstrated in Fig. 1F.

Although the previously mentioned techniques widely cover the *SEC* analysis, the reflectance modes are essential to complete the set of *SEC* techniques. In specular mode (see

scheme in Fig. 1 E), the light is incident on the reflective surface where it is partly absorbed and reflected. In specular reflection conditions, the reflectance depends on the angle of incidence of the source of light [11], [12]. Because of this, light can be considered anisotropic and polarized. On the other hand, the diffuse reflectance is isotropic and emerges from a rough surface [6], [7]. The most common, but not exclusive, application of these techniques is related to the studies of chemically modified electrodes.

The techniques of reflectance are very efficient for spectroscopic analysis but for use in *SEC*, there are limitations because they request high-concentration solutions or thick films. To solve this problem the attenuated total reflection (ATR) is an important option. This kind of internal reflectance spectroscopy (see scheme in Fig. 1D), for example, allows analysis in thin films through the interaction of the evanescence wave with the sample. A complete description of the ATR technique can be easily found in textbooks [13] and the important point for *SEC* is that the sample must be in contact with the ATR material, usually germanium or OpTE.

As seen above, the combination of both spectroscopy and electrochemistry opens many doors when it comes to applications to understand electrochemical or interfacial processes. The most noteworthy characteristics are the *in situ* monitoring of a plethora of electrochemical systems that would be otherwise too difficult to evaluate and, at the same time, gain a deeper understanding of mechanisms or their kinetic properties [14], [15], [16], [17], [18], [19].

One of the biggest challenges in *SEC* is the cell design for *SEC* given that, theoretically, any spectroelectrochemical method can be carried out as long as the electrochemical cell can satisfy the requirements of the spectroscopic technique being used. In this context, our goal in this review is to focus on the fact that the cells can be customized in a myriad of ways to fulfill their role using 3D printing [20]. In this sense, additive manufacturing gives the scientist freedom of design to print components, pieces, and even electrodes. In addition, the process is easy to handle, has low cost, and is an incredibly efficient alternative. Given this scenario, we would like to call attention to this subject as a great opportunity for the popularization of spectroelectrochemistry.

2. How can 3D printing assist us in spectroelectrochemistry measurements?

Due to recent technological advances and the popularization of additive manufacturing, 3D printing has increasingly gained space in our laboratory routines, which caused the decentralization of this tool and the modernization of some daily activities [14], [16]. An important area that has benefited from the use of 3D printing is chemistry because its use in the

laboratory has enabled the optimization and/or development of parts, supports, and accessories that can be employed in chemical analysis or monitoring of reactions. Thus, the time and costs involved in the production of specific parts are strongly reduced [14], [21], [22]. As a consequence, 3D printing has permeated different areas and many applications are observed in fields such as energy (both for conversion and storage) [23], [24], adsorption [25], microfluidic devices [26], and the manufacture of electrodes (to use as sensors and biosensors) [27], for example.

In spectroscopic analysis, 3D printing has been a great tool for creating components and even equipment. In addition, 3D printing presents itself as a good quality tool with free design and it is recommended to replace conventional components due to the low cost of prototyping [28]. This reveals to us the potentiality of the application of this technique and its versatility in solving problems.

3D printing has also been widely used in electrochemistry. This is due to the ease of building complex systems, which ultimately contributes to price reduction, presenting great versatility [14], [29], [30]. In this same perspective, the manufacturing of 3D printed electrodes has been widely developed and with the most diverse applications, among which we can mention sensors, biosensors, and energy [27], [31]. Among the 3D Printing processes (Fig. 2), Fused Deposition Modeling (FDM) is the most used for manufacturing these electrodes, due to its good accessibility, low cost, and ease of operation [27], [32], [33].

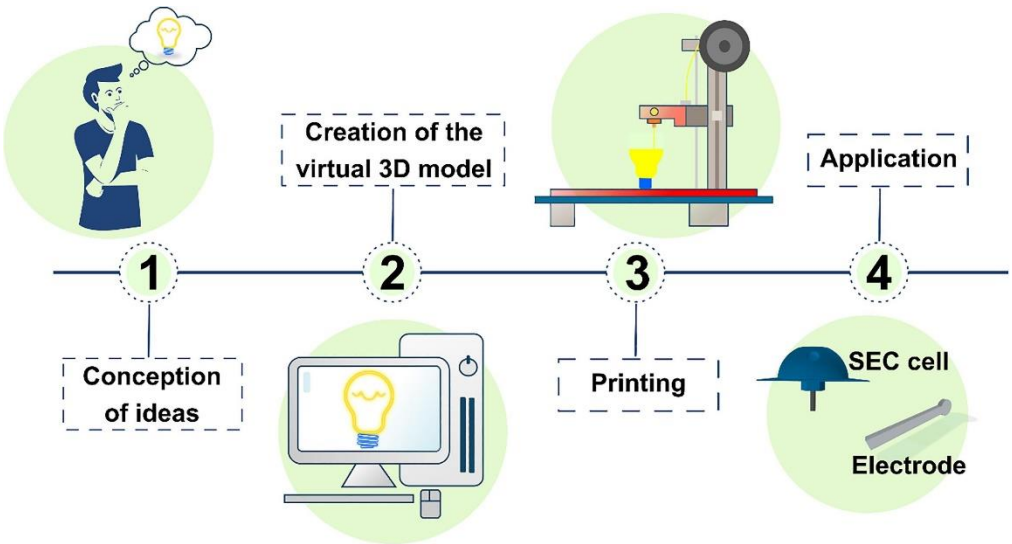


Fig. 2. Steps in the 3D printing process.1) The first step is marked by the conception of ideas; 2) The next step is related to the creation of the virtual 3D model of the part; 3) This step is characterized by the 3D printing of the part that was designed; 4) The last step concerns the numerous possibilities that exist in the use of 3D printing.

Among these features, we believe that 3D printing appears as a tool that makes it possible to assemble personalized *SEC* that can be designed to use different or non-commercial instruments (i. e. synchrotron laboratories). Another advantage that can be considered is the freedom during the creation of the cell by the software, providing the conception of alternative cells to meet the demands. In addition, it allows the analyst to choose the material that will be used for printing the cell so that there is no interference during the analysis (for example, a material that is resistant to basic pH can be chosen). Another interesting aspect is that the cell can be designed in such a way that the volume of sample used during the analysis is reduced [34].

Despite the positive points of the use of 3D printing in the manufacture of spectroscopic, electrochemical, or spectroelectrochemical cells, it is worth mentioning that there are some limitations regarding its use. One of these limitations concerns the choice of the 3D printing technique used. In general, some techniques present better performance than others, mainly about the finishing of the object or the richness of details, it is up to the user to look for the best option to meet their needs. Another limitation imposed by the use of this tool is related to the degree of knowledge, on the part of the user, in the use of software to create three-dimensional objects. Thus, the analyst should seek knowledge to use these tools or be supported by someone who has the minimum knowledge to operate.

3. Applications of 3D printing in spectroelectrochemistry

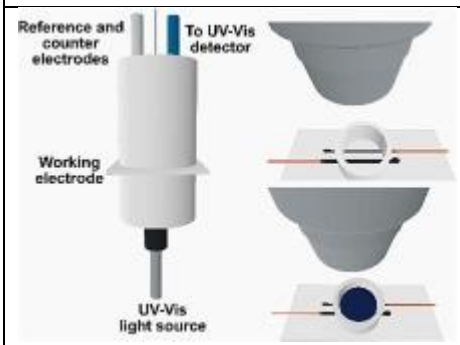
This section presents the main applications and uses of 3D printing to support experiments involving UV/Vis spectroelectrochemistry (UV/Vis-*SEC*), infrared spectroelectrochemistry (IR-*SEC*), Raman spectroelectrochemistry (Raman-*SEC*), and XAS (*X-ray absorption spectroscopy*) spectroelectrochemistry, highlighting some examples found in the literature.

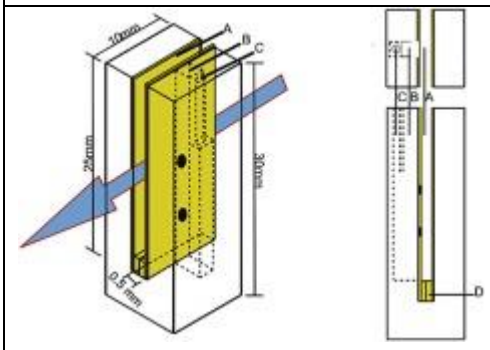
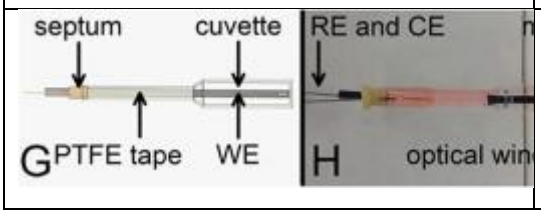
3.1. 3D printing for UV/Vis spectroelectrochemistry (UV/Vis-SEC)

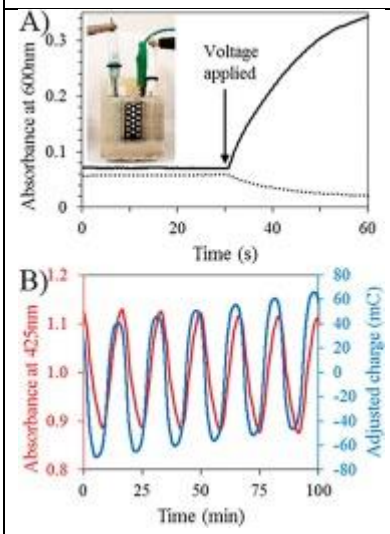
Regarding the application of 3D printing in UV/Vis spectroelectrochemistry, an interesting example is found in the work published by Symes et al. [35]. where a reactionware was printed and used as an electrochemical cell to monitor the reaction, as can be seen in Table 1. The cell was assembled by Ag/AgCl reference electrode, a Pt wire counter electrode, which

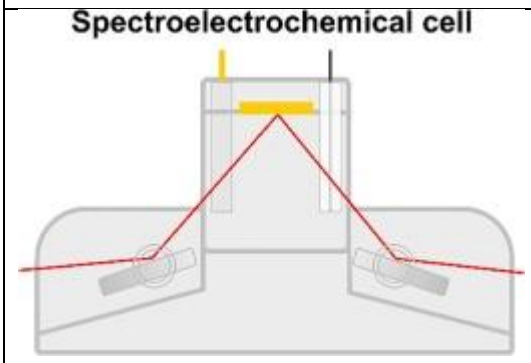
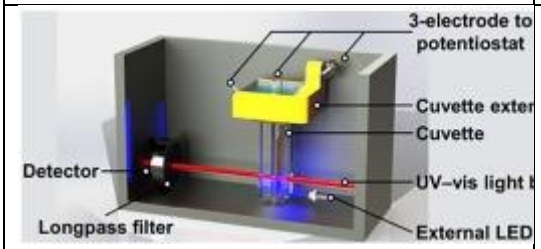
were placed into the cited solution, and the ITO slide was used as the working electrode. It has been observed a color change in the solution from yellow to slightly blue at −0.2 V, which is related to the formation of reduced polyoxomolybdates. To monitor this color change in situ, a fiber-optic cable was put through one of the printed holes located at the top of the reactionware and then connected to the UV/Vis spectrophotometer. A Hg arc lamp was used to provide the input light source in a way that the sample was irradiated from below, allowing the acquisition of the UV/Vis spectra. UV/Vis spectrum was then acquired during the electrochemical and showed the appearance of a new absorbance peak at around 750 nm associated with a slight blue color. Therefore, this study demonstrated that the aforementioned 3D-printed reactionware was suitable for spectroelectrochemical analyses [35].

Table 1. Overview of the 3D printed UV/Vis spectroelectrochemistry cell.

***SEC* Cell (Technique)**	**Application**	**Main feature**	**Ref.**
 Figure was drawn based on information from reference [35].	The device was used to monitor the color change in situ of the phosphomolybdic acid (PMA) solution in 0.1 M H2SO4, which is associated with the generation of polyoxomolybdates from the reduction of this compound.	Reactionware was printed using a robust and quick-curing acetoxysilicone polymer. The light from the Hg arc lamp passes through the solution contained in this apparatus from below to the UV/Vis detector located at the top of it, allowing the detection of the polyoxomolybda	[35], [40]

		tes derived from the reduction of PMA.	
 Reprinted with permission from ref. [34]. © 2013 Elsevier B.V. All rights reserved.	The cell was used to determine the reduction midpoint potential of Safranine O, protein HH, and horse heart cytochrome. Absorbance spectra of the samples were taken between each potential step for building both a kinetic profile and Nernst curve data with a unique titration.	This 3D printed *SEC* was placed into a standard cuvette, allowing fast spectroelectrochemical titrations of protein or small molecules. Its design maximizes the ratio of the WE surface area to the solution volume while keeping the full path length of the cuvette. A similar system can be used in spectroelectrochemistry experiments related to redox-responsive self-assembled monolayers [41].	[34], [41]
	*SEC* cell fabricated to monitor three-	In this cell, 3D printed electrode made of	[36]

Reprinted with permission from ref. [36]. © 2019 Elsevier B.V. All rights reserved.	wavelength values during the reduction and re-oxidation of the [Ru(acac)$_3$]. Using for investigation of the product formation and the reactant depletion.	composites of PLA and CNT has an optical window (quartz cuvette), which allowed the acquisition of UV/Vis absorbance spectra during the cyclic voltammetric reduction and re-oxidation of [Ru(acac)$_3$].	
 Reprinted with permission from ref. [37]. Copyright © 2019, American Chemical Society	UV/Vis *SEC* used to monitor changes in pH during bulk electrolysis.	The working electrode is porous and printed from the conductive filament of PLA. This kind of 3D-printed electrode must be activated to remove the insulating PLA from the surficial layer. This process improves the electrochemical activity of	[37]

		printed electrodes.	
 Drawn based on information from ref. [38].	This device was applied to investigate *in situ* the Prussian blue (PB) growth at the homemade platinum disc working electrode surface.	*SEC* cell manufactured with black color PETG filament and inside it a quartz window was placed to interact between the radiation and electrode surface. Continuous absorbance measurements were carried out at 700 nm, thus monitoring *in situ* the PB growth.	[38]
 Reprinted with permission from ref. [39] Copyright © 2021 Wiley-VCH GmbH.	Printed setup for UV/Vis spectroscopy studies of $ZnFe_2O_4$ water oxidation intermediates.	The printed setup can be used for UV/Vis spectroelectrochemistry to understand the interfacial reaction and intermediates of the $ZnFe_2O_4$ in water oxidation	[39], [42]

The work carried out by Brisendine *et al.* [34] demonstrated the application of 3D printing technology to make a microchannel that can be inserted inside of standard cuvettes (1 cm^2) used in conventional spectrometers in transmission mode, in which the cell design is depicted in Table 1. The electron transfer kinetics was measured by monitoring the reduction and oxidation of the potassium ferricyanide. Moreover, protein titrations were made using a small molecule mediator mixture responsible for mediating electron transfer in the −500 to + 300 mV range. Complete visible spectra of the samples were taken between each potential step for building both a kinetic profile and Nernst curve data with a unique titration. This spectroelectrochemical cell was employed to track the safranine O reduction and oxidation at 522 nm and the potentiometric titration of this compound.

Vaněčková *et al.* have reported the utilization of FDM based 3D printing to produce electrodes from composites of polylactic acid (PLA) as the binder and carbon nanotubes (CNT) as the conductive filler. These electrodes were designed to have an optical window, which enabled them to be used in UV/Vis absorption spectroscopic to detect the electrogenerated reaction products [36].

The goal was then to develop electrochemically active electrodes from PLA/CNT composite filament for spectroelectrochemical experiments. Besides, since the authors embedded an optical window on these electrodes, they were employed to carry out UV/Vis absorption spectroelectrochemical measurements. It is also worth mentioning that this work was the first reported application of 3D printed electrodes in UV/Vis spectroelectrochemistry. Such electrodes for UV/Vis spectroelectrochemistry experiments presented a cuboid shape with dimensions of 0.75 mm × 3.4 mm × 110.0 mm and involved a rectangular (0.8 mm × 4.0 mm) optical window placed at one end and they were manufactured in batches of five pieces. The assembled *SEC* cell can be seen in Table 1. Spectroelectrochemical experiments were carried out in the cyclic voltammetry regime and UV/Vis absorbance spectra were obtained in time intervals of 20 s, this condition is necessary for the chemical system to reach equilibrium before the experiment.

In addition, they compared the electrochemical response of 3D printed PLA-CNT electrodes to the filament not processed by 3D printing. In this scenario, 3D printing of the filament decreased the values of the separation of cathodic and anodic faradaic maximum, pointing out that the intrinsic kinetic barrier is considerably reduced. The developed electrodes were described as fast and cheap to produce because the PLA-CNT composite filament used to manufacture one 3D printed electrode just cost 0.04 USD and the fabrication procedure took only 6 min. The described experiment was useful to confirm that $[Ru(acac)_3]$ used as an

electroactive probe reversibly transfers electrons at the interface of the 3D printed PLA-CNT electrode and the aqueous electrolyte. Besides, the activated 3D printed electrodes presented electron transfer characteristics similar to those obtained for electrodes manufactured from conventional carbon-based materials.

Wirth *et at.* have described the use of 3D printed electrodes through the FDM technique for UV/Vis spectroelectrochemistry [37]. The working electrodes were obtained from the conductive filament of PLA. An important point for this kind of printed electrode is the introduction of the activation process, which is the removal of the insulating PLA from the surficial layer. This process improves the electrochemical activity of printed electrodes. The setup presented in this work allows the use of a three-component electrochemical cell where the working electrode is printed and spectroscopically monitored by a conventional UV/Vis spectrophotometer.

Print electrodes remove limitations of the design and introduce the numberless possibilities of setup and applications. For example, the authors focused on their studies to observe the pH change during the water electrolysis using a UV/Vis-*SEC* with a printed working electrode.

Another application of 3D printing in UV/Vis spectroelectrochemistry is found in an interesting paper written by da Silva Junior *et al.* in which the authors described in detail the fabrication of 3D printed *SEC* for *in situ* UV/Vis measurements [38]. The electrochemical setup was made using a system composed of three electrodes, in which the working electrode was a homemade platinum disc electrode, an Ag/AgCl as a reference electrode, and a platinum wire as an auxiliary electrode.

The *SEC* cell, all accessories, and sample holders were manufactured using black color PETG (polyethylene terephthalate glycol) filament to substitute the original spectrometers, as represented in Table 1. Inside the cell, the sample surface of the working electrode was vertically disposed and a quartz window was placed to interact between the radiation and electrode surface. Besides, 18 h were approximately spent to print this UV/Vis *SEC* with an estimated cost of about 15 USD.

To evaluate the performance of this *SEC* cell, electrodeposition of Prussian Blue film in the working electrode was made by applying a potential of + 0,3 V against the reference electrode with the use of a potentiostat for 200 s, allowing the reaction between potassium ferricyanide and ferric chloride. Meanwhile, the continuous absorbance measurements were carried out at 700 nm, which is the intervalence charge-transfer band for the Prussian Blue (PB), allowing the *in situ* observation of the PB film growth. This 3D printed spectroelectrochemical

cell demonstrated the capacity of the 3D printing technology to manufacture bespoke accessories for spectroelectrochemistry analysis [38].

The interesting printed setup presented by Yongpeng Liu and collaborators [39] can be used for spectroelectrochemistry-UV/Vis to understand the interfacial reaction and intermediates produced during the photochemical water oxidation by $ZnFe_2O_4$. The comprehension of the interfacial processes and recombination can be used to improve the properties of the catalyst;

3.2. 3D printing infrared spectroelectrochemistry

The 3D printed modules presented by Silva Junior et al. and Baumgartner et al. are objects used in conventional spectroscopic analysis. Fig. 3A shows the impression of a specular reflectance module for ex-situ experiments. The support was designed to couple two mirrors and it can be used in UV/Vis-NIR and FT-IR analysis. Another interesting project is presented in Fig. 3B where the attenuated total reflection module was designed and printed in a 3D printer - FDM. This object was projected for ATR-IR analysis and can be adapted for different equipment. Both projects have low-cost, fast production and might be adjusted for any setup. Although these proposals do not contemplate the use of FT-IR *SEC*, the coupling of the original projects with an electrochemical cell might be possible.

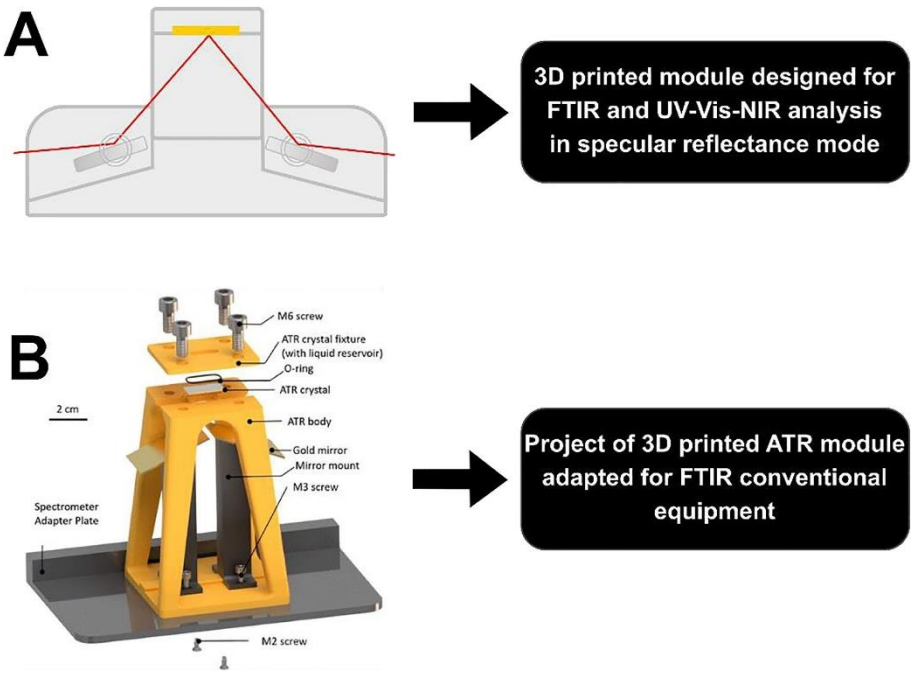
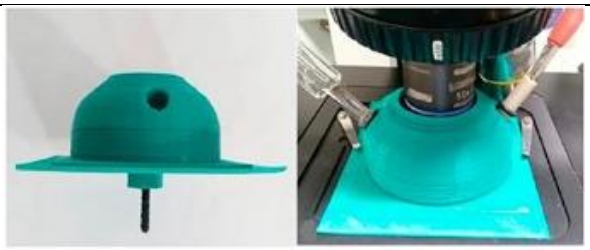


Fig. 3. A) 3D printed accessory for spectroscopic analysis (FTIR) by specular reflectance, a figure drawn based on information from reference [38]; B) 3D printed ATR module adapted for FT-IR analysis Copyright © 2020, American Chemical Society.

3.3. 3D printing for Raman spectroelectrochemistry (Raman-SEC)

3D printing technology's use for manufacturing a spectroelectrochemical cell and a working electrode to carry out *in situ* Raman measurements was demonstrated in the paper written by dos Santos *et al.* [9]. Raman spectroelectrochemistry has some limitations that are related to the elevated cost and the complexity of the commercial spectroelectrochemical cells used in this technique. However, such drawbacks can be circumvented by the introduction of 3D printing technologies, which they offer an alternative to designing such a system in a much cheaper, simpler, and more versatile way in a short period. In this context, the authors have shown the fabrication of a dome-shaped *SEC* using acrylonitrile − butadiene − styrene (ABS) filament to fit the Raman objective lens in the center hole of the spectroelectrochemical cell above the working electrode's surface and two other holes were added to fit the reference electrode (Ag/AgCl, 3 mol.L^{-1}) and Pt counter electrode, as it is depicted in Table 2. Apart from that, the working electrode with a screw shape was printed using a conductive graphene-based PLA filament. Both the *SEC* and the 3D-printed electrode were printed within 3.5 h with a very low cost of materials used, which was estimated at less than 2 USD [9].

Table 2. Overview of the *SEC* – Raman cell.

***SEC* Cell (Technique)**	**Application**	**Main feature**	**Ref.**
 Reprinted with permission from ref. [9]. Copyright 2019 American Chemical Society.	It was used to study structural changes in Prussian Blue during electrochemical measurements. *In situ* Raman spectra of this	This *SEC* cell was printed using ABS filament in a dome shape in order to fit Raman objective lens in the center	[9]

	compound were acquired to investigate the shifts in the frequency of the CN stretching band as a function of the applied potential.	hole of the cell, enabling the obtainment of Raman spectra while the electrochemical measurements were made. In addition, the working electrode was also printed in a screw shape and after modified with Prussian blue.	
 Figure drawn based on information from ref. [38].	It was applied to track the Prussian blue growth film process. Raman spectra were obtained continuously, allowing the characterization of the PB forms. Moreover, this system was also used to real-time accompany the electrochemical conversion of PB film into the	It was made using black color PETG filament and its design enabled it to receive three or more electrodes to perform dynamic flux measurements. Raman spectra were obtained using 633 nm laser every 20 s during the reaction	[38]

	Prussian white and Berlin Green.	between potassium ferricyanide and ferric chloride in order to monitor the presence of CN bands.	

These facts emphasize the advantages of using additive manufacturing, its simplicity, fast prototyping capabilities, and the possibility of designing any type of device with the desired shape and dimension make it suitable for a wide variety of applications, such as the monitoring of reactions *in situ* or *modus operandi*. This system was then employed to study structural changes in Prussian Blue (PB) during electrochemical measurements. *In situ* Raman spectra of this compound were acquired in the electrode potential range from −0,4 to + 1.2 V vs Ag/AgCl, which enabled the investigation of the shifts in the frequency of the CN stretching band as a function of the applied potential. According to the results, the printed electrode proved to be good support for anchoring the PB particles, besides it showed a comparable electrochemical behavior to the commercial glassy carbon electrode [9].

Another example regarding the application of 3D printing technology in Raman spectroelectrochemistry can be found in the paper published by da Silva Junior *et al*. mentioned before [38]. In this work, 3D printed accessories were developed to unite *ex situ* or *in situ* electrochemical and spectroscopic techniques to study dynamic interfacial and surface phenomena, including the *SEC* for Raman microspectroscopy analysis able to work in flux or a stationary regime. The design of the cell allowed its use with the available equipment and compatibility with common commercial electrodes was achieved, besides it involved a simple, cheap, sustainable, and low-time production process.

The spectroelectrochemical cell was made utilizing PETG filament due to its good chemical and high impact resistance, ease of printing, and outstanding durability. The design of the printable parts was performed using an online 3D app such as *Tinkercad*^{TM} in a way to obtain the working electrode surface facing upwards, enabling it to receive an array of three or more electrodes to carry out dynamic flux measurements, as can be visualized in Table 2.

The time spent printing the Raman-*SEC* was about 6 h with an estimated cost of around 15 USD. The performance of this 3D-printed device was evaluated by tracking the Prussian Blue growth film over the Pt working electrode using 0.1 mol.L^{-1} KCl electrolyte. A potential of + 0.3 V vs Ag/AgCl (3 M KCl) was applied for 200 s to drive the reaction between potassium ferricyanide and ferric chloride, the Raman-*SEC* cell was then used to obtain a spectrum in the wavenumber range from 1600 to 2600 cm-1 using 633 nm laser every 20 s.

This experiment permitted the characterization of the PB forms by the change of CN stretch bands between 2000 and 2200 cm^{-1}. Over again, the possibilities and application depend on the problem, creativity, and ability to design/print cells for Raman equipment.

3.4. XAS spectroelectrochemistry (XAS-SEC)

Fabrication of 3D-printed multi-purpose electrochemical devices for X-ray absorption spectroscopy (XAS) is well described in the paper written by Achilli *et al.*.It demonstrated the use of 3D printing for the development of electrochemical cells to be employed in experiments with *in situ* and *in operando* characteristics using synchrotron radiation, which allows a detailed investigation of systems in their real working conditions [43].

It is worth mentioning that the use of synchrotron radiation as a characterization tool requires the connection of the beamlines to distinct experimental setup demands, which means that the creation of a suitable arrangement to control the physicochemical conditions of the sample is often difficult. In this context, advantages that arise from the use of this technology to create the mentioned electrochemical devices are underlined, such as the precision of the 3D printing system, which enables the manufacture of the cells with the required details, making the combination of synchrotron-based methods with electrochemical techniques viable. It is reported in this paper the design of two different types of spectroelectrochemical cells for XAS experiments on photoanodes for photoelectrochemical water splitting [43].

Photoanodes studied for water oxidation were composed of the catalytic domain made of IrOx and hematite. The main objective was to investigate the mechanism and the kinetics of electrocatalytic reactions. In this case, limits on the illumination by X-rays and UV/Vis light exist due to the coupling between the hematite and IrOx. In their structure, hematite is deposited over the FTO substrate which strongly absorbs wavelengths in the range of near-UV, and the IrOx layer which absorbs in the visible region is placed upon the hematite layer. The aim of using the X-ray probe in each experiment was to investigate the local electronic changes in the IrOx overlayer caused by the illumination of hematite and because of the attenuation coefficient

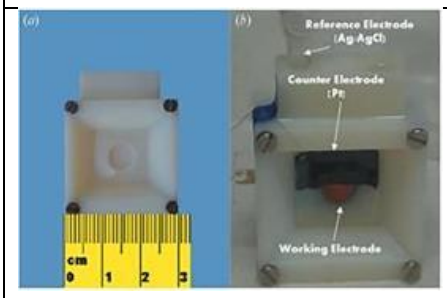
of the materials present, XAS investigation was carried out on the side of the IrOx film and in fluorescence mode.

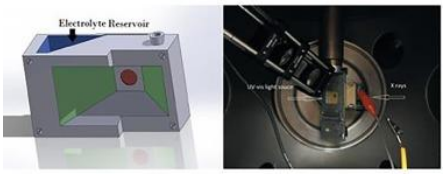
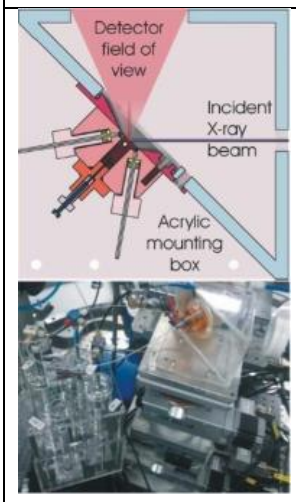
Given these boundary conditions, the authors developed photo-spectroelectrochemical cells for containing the photoanodes, and besides they were designed to have three electrodes, a reference electrode, a counter electrode, and the working electrode, which is the photoanode. Their design and fabrication made the importance and practicality of 3D printing evident, because these devices have small channels and holes, which should ensure the electrical contact between the three electrodes by the electrolyte, something extremely hard to be obtained using conventional tools or manually.

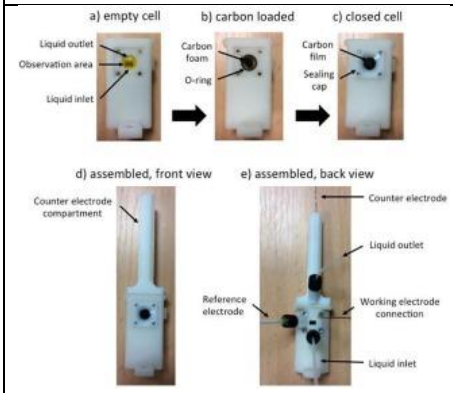
These photo-spectroelectrochemical devices should also be resistant to X-rays, otherwise, they would suffer from the formation of holes and consequently loss of mass. Thus, the application of a 3D printer with the use of photopolymers resin was able to meet all the material requirements, being the easiest and fastest way to manufacture efficient photo-spectroelectrochemical cells with the necessary details compared to the conventional subtractive manufacturing technologies.

The two photo-spectroelectrochemical apparatuses demonstrated in this article were called cell types A and B (see Table 3). Both cells were fabricated using a photopolymer-based 3D printer. Cell type A is composed of two parts linked by screws and bolts and a frontal circular window was put in for illumination by UV/Vis and X-ray photons (Table 3). In the working electrode, XAS investigation was carried out in the electrocatalyst IrOx and the hematite part of the electrode was illuminated by UV/Vis light.

Table 3. Overview of the *SEC* – XAS.

***SEC* Cell (Technique)**	**Application**	**Main feature**	**Ref.**
 Reprinted with permission from ref. [43]. Copyright 2016,	**Cell type A** was developed to investigate electrodeposited IrOx overlayers in the working electrode. Local electronic changes in this overlayer were	*SEC* cell made of photopolymers resin is composed of two parts and a frontal circular window that allows the illumination by UV/Vis and X-ray photons.	[43]

International Union of Crystallography.	studied by using the X-ray probe.	XAS investigation was performed in the electrocatalyst IrOx in fluorescence mode while the hematite part of the working electrode was illuminated by UV–vis light.	
 Reprinted with permission from ref. [43]. Copyright 2016, International Union of Crystallography	**Cell type B** was fabricated to study photoelectrodeposited IrOx overlayers upon the working electrode. With its use of it, a better understanding of the mechanism and the kinetics related to the photoelectrocatalytic process of water splitting was achieved.	This cell has a circular hole providing a window to the working electrode. Its left side was illuminated by UV/Vis while the right side received X-ray illumination, enabling the study of the different responses of the catalyst under UV/Vis light and dark conditions	[43]
 Reprinted with permission from [44]. Copyright 2021,	X-ray absorption spectra were obtained from copper (II) solutions by using this XAS-*SEC* cell to show that electrochemical together with flow control can enable a repeated analysis of solutions sensitive to photoreduction without	XAS-*SEC* cell is made of a rigid UV-cured Polymer. A Ag/AgCl reference electrode and porous reticulated vitreous carbon working electrode were employed. The cupper solutions were transferred to gas-tight syringes and valves in a	[44]

International Union of Crystallography.	considerable change to the XANES. Open circuit potential was altered in the absence and presence of illumination during the spectra acquisition to evaluate the susceptibility of the sample to oxidation and reduction.	glove box. Afterward, the syringes were connected to the cell, ensuring precise control of the solution flow. It was developed for controlling redox state and photoreduction from solutions of species sensitive to photodamage.	
 Reproduced with permission from ref. [45]. Copyright 2019, International Union of Crystallography.	XAS-*SEC* cell for time-resolved X-ray absorption spectroelectrochemistry experiments in a homogeneous medium	This printed cell was used in time-resolved X-ray spectroelectrochemistry experiments. The object of this research is to probe transient species produced during the electrochemical experiment. Thus, it is possible to investigate the local and electronic structure of redox-active species in solution through time-resolved X-ray spectroscopy.	[45]

The cell type B was designed with a circular hole in the rectangular cover, providing a window on the working electrode to perform UV/Vis spectroscopy. This cell has also a

rectangular-shaped electrolyte chamber which presents an upper slot, making the insertion of the Pt counter electrode easier, as depicted in Table 3.

More importantly, according to the results collected these 3D-printed cells worked. It was made a comparison between cyclic voltammetry obtained employing a 3D-printed XAS cell and one obtained using a standard electrochemical cell, in both cases, the cell response was very similar. With the use of these photo-spectroelectrochemical cells was possible to study the different responses of the catalyst under UV–Vis light and dark conditions, which resulted in a better understanding of the mechanism and the kinetics associated with the photoelectrocatalytic process of water splitting.

The paper published by Best *et al.* describes CAD-based design and 3D printed XAS-*SEC* cells, as can be seen in Table 3. The work aimed to control the redox state and the photoreduction of species sensitive to photodamage in solution. This article highlighted the benefits of coupling CAD design with 3D printing, which allows the accomplishment of more difficult designs and low-cost units [44].

A problem to be overcome during the measuring of X-ray absorption spectra of the first-row transition metals at the K edge is photoreduction. A possible solution was the development of methods that enable the acquisition of XAS spectra at energies higher than 4 KeV from small volumes of solution samples at room temperature under potentiostatic control. Additive manufacturing guided by CAD packages was used in this work to manufacture highly optimized 3D printed XAS-*SEC* cells at a low-cost, in which the quality of the data obtained using this system was demonstrated.

Besides, the design of an integrated stepper motor syringe pump was also shown. Measurements of copper(II) complexes were made to show that electrochemistry together with flow control can permit repeated analysis of a defined volume of the solution of samples sensitive to photoreduction without significant change to the X-ray absorption near-edge structure (XANES). During the data acquisition of the XANES, the open circuit potential (OCP) was varied in the absence and presence of illumination to evaluate the susceptibility of the sample to oxidation or reduction during measurement.

X-ray absorption spectra of copper solution (2 mM in phosphate buffer under an inert atmosphere) were acquired using the I20-Scanning wiggler beamline of Diamond Light Source. Ag/AgCl reference electrode and porous reticulated vitreous carbon working and counter electrode were used in the XAS spectroelectrochemical cell. Its design was implemented by employing the open-source software OpenSCAD. Besides, a Connex3 Objet350 3D printer with

UV-cured ink and water-soluble support was used to fabricate objects with high geometric precision appropriate for working with aqueous solutions.

In terms of the material used, although the UV-cured polymer is rigid, it's brittle and its compatibility with non-aqueous solvents is poor. Thus, this 3D printed cell had the limitation in repeated use due to the material's characteristics, but it is compensated by its low unit cost. Regarding the electrochemical cell, it had porous reticulated vitreous carbon WE and CE with Ag/AgCl reference placed close to the WE. Moreover, the space between the electrodes was filled with glass beads to minimize the mixing of the solution in the WE and CE. A graphite rod was also used to establish electrical connections to the working and counter electrodes. The cell was connected to the syringes, in which fine control over the volume and rate of the solution was made to guarantee a successful cell's operation. XAS-*SEC* cell was placed into an acrylic box to decrease air scatter and fix the angle between the incident beam and the surface of the working electrode positioned at 45°.

The authors have reported that the optimization of the flow rate parameters and beam intensity allows the attainment of high-quality XAS spectra from small solution volumes. Furthermore, thanks to the advances in 3D printing, and more accessibility to commercial printing, considerable improvements have been made in the electrochemical performance and reliability, leading to the minimization of sample volume and XAS spectra with better quality.

Another example of XAS-*SEC*, presented by Khaled Cheaib and collaborators, describes the design and construction of a spectroelectrochemical cell (transmission mode) for time-resolved X-ray absorption spectroscopy in the homogeneous medium. This cell allows studies of the electronic structure and identification of active species or oxidation states in solution through time-resolved spectroscopy [45].

4. Final remarks about using 3D printing in spectroelectrochemistry

Additive manufacturing introduces new possibilities to spectroelectrochemistry due to the low cost and fast prototyping to create spectroelectrochemical cells. Moreover, the freedom of design allows us to create printed *SEC* for any type of equipment for spectroscopy analysis and facilitates the coupling with a potentiostat. In this way, existing equipment can deliver even more in characterization and understanding of chemical reactions, identification of intermediates of reaction, mechanistic analysis, kinetic studies, and even quantitative analysis.

These features of 3D printing enable the user to manufacture bespoke accessories and electrodes rapidly to meet the requirements of a given experimental setup, without the need of

using expensive materials and drastically reducing the generation of waste during the fabrication of the *SEC* cell in comparison with the conventional subtractive manufacturing technologies. The examples cited in section 3 highlighted the advantages of additive manufacturing, making it possible to create devices able to monitor several reactions *in situ* and *in operando* by coupling spectroscopic and electrochemical techniques.

Although 3D printing brings great freedom in the development and creation of objects that can be used in spectroelectrochemical analyses, some limitations must be considered. One of the main limitations is related to the type of polymer used during 3D printing, because depending on the solvent or pH of the medium, the durability of the cell will be affected, considering the behavior of the polymer against these factors. As has also been reported, it is sometimes necessary to print more than once of the same cell, to make the experiment reproducible. However, it is interesting to note that even printing several repeated accessories, the cost involved in this process is very low, making this path viable.

FDM and digital light processing (DLP) are nowadays the main additive manufacturing techniques used to print *SEC*. The FDM technique uses ABS and PLA as polymeric filaments. ABS has excellent stability in acid and alkaline conditions but resists organic-based solvents poorly (either suffers from considerable swelling or outright solubilization), while PLA struggles with swelling for most solvents except for water and cannot stand very acidic or alkaline systems. 3D-printed objects from resin with UV cure through the DLP technique usually are stable in mild acid and alkaline conditions and they are relatively stable in organic solvents. However, stability can change depending on the type of resin used.

Another visible limitation is related to the time established for optimizing the 3D printing parameters. Optimizing the 3D printing parameters is very important as they will determine the quality of the print, so in some cases, it takes considerable time. However, once these parameters are adjusted, they can be saved as soon as the same object is printed, it will only be necessary to keep the parameters that were established previously as optimal.

3D printing is still influenced by the material used and there can be many possibilities. Certainly, it depends on the richness of details that the object/accessory will have to use spectroelectrochemical analyses. But in general, among the techniques used, FDM stands out for its cost, speed, and ease of use. Besides, the use of 3D printing by DLP techniques is increasing due to the reduced cost observed for UV cure resins and the quality of the final piece.

3D printed electrodes can be an alternative to conventional electrodes mainly when some restriction of size or setup is required. They can also be printed fastly and at a low cost. Finally, we believe that 3D printing using different techniques can be a turning point in the

popularization of spectroelectrochemistry analysis and we acknowledge the huge potential that 3D-printed electrodes have due to their versatility and cost, making them pair incredibly well with the number of experiments that can be done.

Finally, we observe that 3D printing allows freedom for the printing project of an *SEC* to most of the equipment available in a research lab. Moreover, it would be an unparalleled opportunity to produce very specific *SEC* to solve relevant problems and a starting point to popularize spectroelectrochemical techniques.

CRediT authorship contribution statement

Mateus V. Pereira: Conceptualization, Investigation, Writing – original draft. **Evandro Datti:** Investigation, Writing – original draft. **Gabriel R. Alvarenga:** Investigation, Writing – original draft. **Bruno C. Janegitz:** Conceptualization, Writing – review & editing. **J.A. Bonacin:** Supervision, Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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