Versatile Spectroelectrochemical Cell for in Situ Experiments: Development, Applications and Electrochemical Behavior


Submitted date: 09/07/2020 • Posted date: 10/07/2020
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Abstract: (Photo)electrochemical processes are involved in many fields of science and technology. The use of spectroscopic techniques coupled to (photo)electrochemistry, are mandatory to get information about interfacial processes on scale ranges from millimeters to the nanoscale. The development of spectroelectrochemical cells (SEC) contribute to the progress of the field of (photo)electrochemistry and its impact in science and technology. Therefore, in this work, we describe in detail the development of a versatile SEC that can be used for several in situ techniques. We performed electrochemical and computational experiments to analyze the response of our SEC as a function of the working electrode size, position and distance to the window. We found that our SEC behaves as the conventional cell when the electrode is far from the window. However, important differences arise in the thin layer configuration. The computational experiments suggest that to mitigate these problems, it is important to perform in situ experiments in the thin layer configuration using electrodes as small as possible.
Versatile Spectroelectrochemical cell for \textit{in situ} experiments: development, applications and electrochemical behavior

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\textbf{Abstract:} (Photo)electrochemical processes are involved in many fields of science and technology. The use of spectroscopic techniques coupled to (photo)electrochemistry, are mandatory to get information about interfacial processes on scale ranges from millimeters to the nanoscale. The development of spectroelectrochemical cells (SEC) contribute to the progress of the field of (photo)electrochemistry and its impact in science and technology. Therefore, in this work, we describe in detail the development of a versatile SEC that can be used for several \textit{in situ} techniques. We performed electrochemical and computational experiments to analyze the response of our SEC as a function of the working electrode size, position and distance to the window. We found that our SEC behaves as the conventional cell when the electrode is far from the window. However, important differences arise in the thin layer configuration. The computational experiments suggest that to mitigate these problems, it is important to perform \textit{in situ} experiments in the thin layer configuration using electrodes as small as possible.

\textbf{Introduction}

\textit{In situ} coupling between spectroscopic and electrochemical techniques permit a better understanding of the interfacial structures and processes\textsuperscript{[1–10]}. The combination between them allow to develop, test and refine (photo)electrochemical reaction mechanisms, thus providing knowledge of the structure and electronic properties of the materials in function of electrochemical potential.\textsuperscript{[1–15]}

In general, all spectroscopic techniques, including Raman, Infrared (IR), X-ray absorption and diffraction, nonlinear laser spectroscopies (Sum frequency generation spectroscopy, Coherent anti-Stokes Raman spectroscopy, etc.), etc. can be coupled to (photo)electrochemical systems. An essential feature of \textit{in situ} techniques is that the (photo)electrochemical and spectroscopic signals are obtained simultaneously and not sequentially, avoiding erroneous interpretations of the (photo)electrochemical results, since the chemical and surface composition of the electrode is different from the composition at the bulk solution. It is unusual to find in the literature the electrochemical response of a SEC designed for an \textit{in situ} measurement. In general, the (photo)electrochemical results are obtained in conventional three electrodes cells and the spectroscopic data is acquired using the SEC afterwards. This type of approach is several times questionable, especially when the (photo)electrochemical response of the SEC occurs under different conditions compared to the conventional electrochemical cells, making the data unreliable. Thus, in this paper, we show in detail the main components of a SEC that combine the best characteristics of previous contribution\textsuperscript{[10,14]} and add new features that make this SEC more versatile. Besides, we systematically analyze the electrochemical behavior of our SEC using cyclic voltammetry and computational experiments and observe that the ohmic drop in the thin layer can generate the electrochemical reaction to exclusively occur in the electrode edge. These inhomogeneous distribution of current in the electrode surface can seriously compromise the spectroscopic results. Through computational experiments, we show that this problem can be mitigated by using electrodes as small as possible.
Cell Design and Main and Characteristics

Figure 1 shows schematically all the components of our SEC, which combine the best characteristics of mainly two SEC, one proposed by the groups of Prof. Kubota[16] and other by researchers from Argonne National Laboratory[17]. Besides, we added modifications that turn it a very versatile SEC. We describe below the most important component and the main advantages of our SEC.

Figure 1. (A-B) Schematic drawings of the SEC: (1) threaded lip; (2) aperture for passing the radiation beam and, in the case of a photoelectrochemical experiment, to illuminate the electrode with a solar simulator or LEDs, (3) window, (4, 5 and 17) o-ring, (6 and 16) CE, (7) SEC body – part 1, (8) chamber for the electrolyte, the CE and the RE, (9, 11, and 13) electrolyte inlet and outlet, (10) WE inlet, (12) RE inlet, (14) RE, (15) CE inlet, (18) bolt, (19) SEC body – part 2, (20) WE.

SEC body

The SEC body was constructed of poly-ether-ether-ketone (PEEK), a polymer with high mechanical strength and chemical resistance. The SEC is formed by two parts, each having 4 cm in diameter and 2 cm in length, secured by stainless steel 304 bolts (M4-0.7 socket head cap screws), which are highly resistant to corrosion. The SEC holds 3.5 mL of solution. Three electrodes were used in the fabrication of the cell: (i) a working electrode (WE) that can be made of virtually any solid material (e.g. GC, Au, Pt – discs of 5 to 7 mm diameter) in a 10 mm outside diameter PEEK body; (ii) a ring-shaped counter electrode (CE) 5 mm wide and 5 cm long (usually made of Pt or Au); (iii) and a commercial Leak-free® as a reference electrode (RE) that can also be easily substituted. Electrolyte inlet and outlet connections (with M6 thread size) to conduct experiments under flow conditions were also designed. The cell was devised to allow investigation of bulk electrodes and nanostructured materials supported on a substrate (e.g. Pt/C nanoparticles on glassy carbon).

Windows and threaded lip

For any spectroscopic experiment, it is imperative to use an inert window that minimizes the adsorption of the radiation. Different window suitable for a specific spectroscopic technique can be easily and quickly assembled/removed from the SEC body thanks to the threaded connections and the seal rings. Our SEC can fit spherical windows with variable radius (from 27 to 32 mm) and thickness (from 1 to 3 mm). This versatility permits to choose between different windows available in the market, made of glass or quartz (for UV, Raman and several laser spectroscopies), and CaF$_2$, ZnSe, etc. (for FTIR). For experiments involving X-rays the windows are made of flexible polymers (typically Mylar and Kapton). Therefore, the polymer can simply be cut to fit in the cell. In this specific case, the diameter must have more than 40 mm to be pressed by the O-ring (all seal rings used are Perfluoroelastomer - FFKM).

Main body

The main body can be easily attached to the lip. It has two compartments, one for the WE at the center and the others for the RE and the CE around the central one. The WE compartment can fit electrodes with cylindrical shape and radio of 10 mm, which are commercially available. Particularly interesting for this cell are electrodes embedded in PTFE or PEEK, as the electrochemical response will come only from the non-covered part at the top of the electrode (it will be thoroughly discussed in the next sections). Vitreous carbon electrodes, which are relatively inert for several applications, are useful as a support of a myriad of electroactive materials, for example, nanoparticles made of metals or semiconductors.

Both, the CE and the RE can be inserted by the side of the body and they can be easily changed accordingly to the system of interest. Figure 1 shows a commercially available Ag/AgCl leak free electrode, but we have also used in the same cell a homemade RHE.

Techniques

To show the versatility of our SEC we have included a section showing how our cell can be adapted to perform several in situ techniques. It is not our aim here to discuss in detail each technique, which have been thoroughly reviewed in the literature. For some techniques, it is important to be aware that the measurements are performed in the thin layer configuration. Thus, we have briefly discussed this concept in the supporting information. Figure 2 displays our SEC positioned in a FTIR, a Raman, a synchrotron Beamline with a X-ray source and in anti-vibration table in front of two lasers to perform ultrafast spectroscopy experiments. Below we will name some details and/or important considerations about the use of the SEC for each technique.

In situ FTIR
Figure 2 shows the SEC positioned on a Specular Reflectance Accessory commercialized by PIKE®. Thus, we can perform in situ FTIR experiments in the reflectance mode. For details about the technique we refer the reader to the vast specialized literature in this field[18–20]. As will be discussed in detail in the next sections, this configuration demands the use of low scan rates to avoid high currents and so, high overpotentials due to the ohmic drop. Apart from this problem, with the aim of obtaining a more intense FTIR signal, usually the measurements are performed holding the electrode potential for several minutes to increase the accumulation of interferograms and the concentration of products in the thin layer. Even if this approach permits to obtain more intense bands, the changes in the thin layer composition could generate unreliable results once that the electrochemical response of the SEC (thin layer) and that of a conventional electrochemical cell will be different. For example, it is common to find bands corresponding to the generation of CO\(_2\) (2343 cm\(^{-1}\)) during the electrooxidation of small organic molecules in alkaline media. Since CO\(_2\) appear as CO\(_3^{2-}\) in alkaline media, it implies that the pH of the thin layer become acid during the experiment due to the concomitant oxidation of the molecule and the generation of H\(^+\). In the supporting information section, figure S1, we show a measurement performed with our SEC during the electrooxidation of glycerol where this phenomenon can be clearly observed.

It is important to note that in situ FTIR measurements can be performed in the ATR (Attenuated Total Reflectance) configuration to avoid all the problems generated by the thin layer. However, unfortunately, the ATR configurations have others limitations that make this approach much less versatile[19].

**In situ RAMAN**

Figure 3 shows the SEC positioned close to the objective lenses of a Raman microscope. For details about the technique we refer the reader to the specialized literature[21,22]. Unlike the FTIR measurement, in this case, the SEC is upside down and the electrode does not need to be pressed onto the quartz windows, as was discussed here and elsewhere[20]. Positioning the electrode far from the windows diminishes the ohmic drop, which is an advantage even knowing that it can be corrected. More importantly, it allows free diffusion of molecules inwards or outwards the electrode surface, minimizing problems related to the change in the solution composition and permitting the use of our SEC as a flow cell. Figure S2 show Raman spectra obtained for a gold electrode in our cell. The results are in agreement with the literature[23].

**In situ XAS and XRD**

Figure 4 shows the SEC in front of a synchrotron X-ray source and close to a fluorescence detector (Vortex), which allows XAS experiments to be carried out in fluorescence mode. Similar to FTIR, as explained in the supporting information, to prevent the X-ray absorption by the solvent, the measurement is performed in the thin layer configuration. Thus, the same precautions taken in FTIR measurements must be considered for these techniques to obtain reliable data.

As we are using a bulk electrode and a diluted sample, in this specific case we are measuring in the fluorescence mode. Figure S3 show the XAFS spectra obtained in the L3 edge of Pt for a commercial Pt/C catalyst in the system show in figure 4. Several books and reviews have discussed the technique in detail. The results obtained with our SEC are in line with those...
thoroughly review by Russell and Rose\textsuperscript{[24]}. However, by changing the carbon vitreous bulk electrode to a hollow one (with carbon paper), the same cell can be used to measure in transmission mode. Alternatively, this same SEC can also be adapted to XRD in reflection mode or grazing incidence to perform measurements of GISAXS, XRR or CDI techniques using a mylar film as the window\textsuperscript{[2,25–27]}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{EC positioned on the XAFS2 beamline of the UVX Synchrotron Light Source of Campinas, São Paulo, Brazil\textsuperscript{[28]}. A result obtained in this system is shown in figure S3.}
\end{figure}

\textbf{In situ Ultrafast Spectroscopy}

Figure 5 shows the SEC positioned in front of two femtosecond lasers in a homemade setup for measurements involving ultrafast spectroscopy\textsuperscript{[29,30]}. As in the case of Raman, the measurements do not need to be performed in the thin layer configuration. However, depending on the specific technique and sample, lasers can operate at high power. Therefore, to check their influence (e.g., raising the electrolyte and electrode temperature), it is important to perform an electrochemical experiment (for example a cyclic voltammetry) turning them on and off. An example of the measurement performed with the system shown in figure 5 was recently published by some of us\textsuperscript{[31]}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{SEC positioned on an antivibration table in front of two femtosecond lasers and forming an angle of 45° with the lasers and the detector. The image shows the beam path (red arrows) and the electrodes connected to a potentiostat. For this experiment, we used a quartz mirror and results obtained with this system can be found elsewhere\textsuperscript{[31]}.}
\end{figure}

\section*{Results and discussion}

\subsection*{Electrochemical response of the SEC}

In order to test the electrochemical behavior of our SEC and how it is influenced by the position and size of the WE, we performed measurements of the electrooxidation of glycerol in alkaline media using a gold electrode, i.e., in the same conditions we used to perform the \textit{in situ} FTIR and Raman measurements showed in the figures S1 and S2. This system was chosen because this reaction has been extensively studied on noble metal electrodes\textsuperscript{[32]} and using \textit{in situ} techniques, mainly FTIR, giving a rich spectra showing several intense bands. The reaction generates relative high currents (and consequently protons), which causes serious problems for measurements in the thin layer configuration, something that it is frequently ignored in the literature as we stated before.

First of all, it is important to emphasize that for currents of the orders of mA, even in conventional systems, the electrolyte conductivity can be low enough to observe a non-negligible ohmic drop. Figure 6 shows the linear sweep voltammetry measurements (LSV) performed in a conventional three electrode cell and in our SEC, comparing the differences in the voltammograms obtained when there is no correction and when the ohmic drop is measured and corrected (details of the ohmic drop measurement and correction can be found in the supporting information section – Figure S4). Under the same conditions, a similar result was obtained for measurements carried out in both conventional cell and our SEC. Thus, we see that both systems are affected by the ohmic drop and that both electrochemical cells behave in a similar way (figures 6B and 6D), as it must be in order to obtain reliable results with any \textit{in situ} technique.
Another extremely important aspect to be considered in these techniques is the absorption of a significant portion of radiation by the electrolyte, as occurs in FTIR and X-rays measurements in aqueous solutions. Under this constraint, the sensitivity is seriously compromised, and the experiments must be performed in the thin layer configuration. To evaluate the influence of this configuration in the performance, the electrochemical response in our cell (Figure 7) was analyzed when the electrode is positioned far from the window (called here conventional design) and when it is pressed against the window to form the thin layer (called here thin layer design). The schemes of the cell configurations are presented in the inset of figure 7 and in figure S5. The results show that the current diminishes about one order of magnitude due to the formation of the thin layer, which happens in any electrochemical cell in this configuration. Besides, the layout in which the WE is projected 1 mm out the inert coating (called here disengaged design) was studied in an attempt to improve the electrochemical response in the thin layer configuration and to analyze if this design allows better diffusion of molecules and ions towards and from the electrode surface. As a result of this analysis, it was observed that the disengaged design shows higher currents and a more similar response to that of the conventional design, where the electrode is far from the window. It is worth to note that these simple measurements, that permit to test the electrochemical behavior of the spectroelectrochemical systems are rarely performed or shown in publication presenting spectroelectrochemical results.

To understand from a fundamental point of view the main parameters affecting the electrochemical behavior of our spectroelectrochemical system, we used the experimental data in figure 7 to perform finite element simulations using the geometric constraints of our SEC. The calculated results are presented as interpolation functions, which allowed the calculation of the current values at each point of the electrode surface as well as the hydroxyl concentration in the entire domain and over the time. We studied the consumption of hydroxyl ions because many important reactions (oxygen and hydrogen evolution and reductions, CO₂ reduction, biomass conversion, etc[33]) generate and consume protons or hydroxyl, generating pH changes near the electrode surface modifying both the catalyst activity and its selectivity[34–37]. Since the interfacial pH is a key parameter in most electrochemical processes, we calculated it as a function of current density (Figure 8) considering that one hydroxyl anion is consumed by every electron that passed through the electric circuit, as it is the case for many important reactions, including the electrooxidation of glycerol, which electrochemical and spectroscopic results are shown here[33].

In conventional cell design (8C and 8D), simulations show that there are no significant pH changes at these current densities. On the other hand, the results are completely different in the thin layer (Figure 8A and B) and the disengaged (Figure 8E and F) designs, since the electrode is pressed against the window. In these two configurations, as the current increases, the pH of the entire thin layer changes considerably. Although this variation is not dependent on the axial direction, the change is significant comparing the center of the electrode with its edge. In the thin layer design, the pH nearby the electrode edge changes more than in the center, in agreement with a diffusion controlled process in a disk-shape electrode[38]. However, in the disengaged design, the pH variation in the same regions is not so substantial as the ions can more easily diffuse into the solution bulk. For the same reason, the pH at the uncovered side
of the electrode in this design is not very marked, and this region can be regarded as a bulk cell design.

Since our results show that in the thin layer design most of the current density comes from the electrode edges, we repeated the simulations shown in figures 8 and 9 maintaining the current density, reducing the electrode diameter to 2mm and reducing the PTFE thickness to 1mm (figure S6). The simulation suggests that the decrease in the electrode diameter provides a better current and pH uniformity in the thin layer. On the other hand, the decrease in the inert layer did not change the pH profile, but it generates a decrease in the ohmic drop due to the smaller confinement of the field lines.

**Conclusion**

We developed a versatile spectroelectrochemical cell able to perform several in situ experiments: FTIR, Raman spectroscopy, X-ray spectroscopies and diffraction, Ultrafast Spectroscopy, among other techniques. Besides, the measurements can be done in transmission and reflection mode and in a stagnant or flowing electrolyte.

By comparing electrochemical results obtained with our cell and with a conventional three electrodes electrochemical cell, it was possible to show that the observed discrepancies are mainly caused by the ohmic drop, which can be corrected in most of the modern potentiostats.

The analyses of finite element method simulations suggest that the main issues in any SEC arise for experiments performed in the thin layer configuration. These simulations permit us to understand the main parameters affecting the electrochemical behavior of the system in this configuration, indicating that it is important to use electrodes as small as possible but always being aware that the WE design must allow the radiation beam to easily hit its surface.
Experimental Section

Electrochemical experiments

The electrochemical tests were carried out in a potentiostat/galvanostat (Autolab PGSTAT101, Metrohm®). A gold disk (7 mm diameter) was used as working electrode (WE) and a gold foil as counter electrode (CE). The reference electrode (RE) was a leak free Ag/AgCl electrode or a reversible hydrogen electrode (RHE). All potentials mentioned in this work are referred to the RHE scale. When necessary, the ohmic resistance was determined by electrochemical impedance spectroscopy (EIS). The electrooxidation of glycerol was performed in 0.1 M NaOH + 0.1 M glycerol with and without correction of the ohmic drop. Electrochemical experiments were performed in the SEC and the results were compared to those obtained in a conventional three-electrode cell. More details are described in the supplementary material.

Finite element simulations

A tertiary current distribution model was proposed to better understand the ionic transport in the thin layer configuration. Three different geometries were analysed (Figure S2): i) a disk electrode 5 mm from the window, ii) a disk electrode 10 μm from the window, and iii) an electrode projected 1 mm out the inert coating also at 10 μm from the window. The same current density observed experimentally for each configuration was projected 1 mm out the inert coating also at 10 μm from the window. The geometries were analysed (Figure S2): i) a disk electrode 5 mm from the window, ii) a disk electrode 10 μm from the window, and iii) an electrode projected 1 mm out the inert coating also at 10 μm from the window. The same current density observed experimentally for each configuration was defined on the electrode surface for each simulation with the corresponding configuration. From this, it was possible to evaluate the pH variation throughout the solution and the double layer potential considering the ohmic drop between each point on the electrode surface and the counter electrode. Further details about the proposed model are described in the supplementary material.

Acknowledgements

Financial support from the Brazilian agencies: PSF, ECP and JLB thanks FAPESP (grants: 2013/07296-2, 2014/50249-8, 2015/12851-0, 2016/01365-0, 2018/24383-0, 2018/20952-0, 2019/07449-0, 2020/12851-0, 2016/01365-0, 2017/11986-5, 2018/24383-0, 2018/20952-0, 2019/07449-0) and Shell and the strategic research supported by LNLSBrazilian Synchrotron Light Natural Gas and Biofuels Agency) through the R&D levy importance of the support given by ANP (Brazil’s National Oil, Gas and Biofuels Agency) through the R&D levy (EIS). The electrooxidation of glycerol was performed in 0.1 M NaOH + 0.1 M glycerol with and without correction of the ohmic drop. Electrochemical experiments were performed in the SEC and the results were compared to those obtained in a conventional three-electrode cell. More details are described in the supplementary material.

Keywords: Electrochemistry, in situ Spectroscopy, Synchrotron, Ultrafast Spectroscopy, Consol simulations


We describe in detail the main components of our spectroelectrochemical cell (SEC), which can be used to perform several *in situ* experiments. We also compare the electrochemical behaviour of our SEC with that of a conventional cell. Besides, computational experiments show that the inhomogeneous distribution of current in the electrode surface in experiments in the thin layer configuration can be mitigated by using electrodes as small as possible.
Versatile Spectroelectrochemical cell for in situ experiments: development, applications and electrochemical behavior

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Introduction

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**In situ FTIR**

Figure 2 shows the SEC positioned on a Specular Reflectance Accessory commercialized by PIKE®. Thus, we can perform **in situ** FTIR experiments in the reflectance mode. For details about the technique we refer the reader to the vast specialized literature in this field. As will be discussed in detail in the next sections, this configuration demands the use of low scan rates to avoid high currents and, thus, high overpotentials due to the ohmic drop. Apart from this problem, with the aim of obtaining a more intense FTIR signal, usually the measurements are performed holding the electrode potential for several minutes to increase the accumulation of interferograms and the concentration of products in the thin layer. Even if this approach permits to obtain more intense bands, the changes in the thin layer composition could generate unreliable results once that the electrochemical response of the SEC (thin layer) and that of a conventional electrochemical cell will be different. For example, it is common to find bands corresponding to the generation of CO$_2$ (2343cm$^{-1}$) during the electrooxidation of small organic molecules in alkaline media. Since CO$_2$ appear as CO$_3^{2-}$ in alkaline media, it implies that the pH of the thin layer become acid during the experiment due to the concomitant oxidation of the molecule and the generation of H$^+$. In the supporting information section, figure S1, we show a measurement performed with our SEC during the electrooxidation of glycerol where this phenomenon can be clearly observed.

It is important to note that **in situ** FTIR measurements can be performed in the ATR (Attenuated Total Reflectance) configuration to avoid all the problems generated by the thin layer. However, unfortunately, the ATR configurations have others limitations that make this approach much less versatile.

**In situ RAMAN**

Figure 3 shows the SEC positioned close to the objective lenses of a Raman microscope. For details about the technique we refer the reader to the specialized literature. Unlike the FTIR measurement, in this case, the SEC is upside down and the electrode does not need to be pressed onto the quartz windows, as was discussed here and elsewhere. Positioning the electrode far from the windows diminishes the ohmic drop, which is an advantage even knowing that it can be corrected. More importantly, it allows free diffusion of molecules inwards or outwards the electrode surface, minimizing problems related to the change in the solution composition and permitting the use of our SEC as a flow cell. Figure S2 show Raman spectra obtained for a gold electrode in our cell. The results are in agreement with the literature.

**In situ XAS and XRD**

Figure 4 shows the SEC in front of a synchrotron X-ray source and close to a fluorescence detector (Vortex), which allows XAS experiments to be carried out in fluorescence mode. Similar to FTIR, as explained in the supporting information, to prevent the X-ray absorption by the solvent, the measurement is performed in the thin layer configuration. Thus, the same precautions taken in FTIR measurements must be considered for these techniques to obtain reliable data.
As we are using a bulk electrode and a diluted sample, in this specific case we are measuring in the fluorescence mode. Figure S3 show the XAFS spectra obtained in the L3 edge of Pt for a commercial Pt/C catalyst in the system show in figure 4. Several books and reviews have discussed the technique in detail. The results obtained with our SEC are in line with those thoroughly review by Russell and Rose[24]. However, by changing the carbon vitreous bulk electrode to a hollow one (with carbon paper), the same cell can be used to measure in transmission mode. Alternatively, this same SEC can also be adapted to XRD in reflection mode or grazing incidence to perform measurements of GISAXS, XRR or CDI techniques using a mylar film as the window[1,25–27].

Figure 4. EC positioned on the XAFS2 beamline of the UVX Synchrotron Light Source of Campinas, São Paulo, Brazil[28]. A result obtained in this system is shown in figure S3.

In situ Ultrafast Spectroscopy

Figure 5 shows the SEC positioned in front of two femtosecond lasers and forming an angle of 45° with the lasers and the detector. The image shows the beam path (red arrows) and the electrodes connected to a potentiostat. For this experiment, we used a quartz mirror and results obtained with this system can be found elsewhere[31].

Results and discussion

Electrochemical response of the SEC

In order to test the electrochemical behavior of our SEC and how it is influenced by the position and size of the WE, we performed measurements of the electrooxidation of glycerol in alkaline media using a gold electrode, i.e., in the same conditions we used to perform the in situ FTIR and Raman measurements showed in the figures S1 and S2. This system was chosen because this reaction has been extensively studied on noble metal electrodes[32] and using in situ techniques, mainly FTIR, giving a rich spectra showing several intense bands. The reaction generates relative high currents (and consequently protons), which causes serious problems for measurements in the thin layer configuration, something that it is frequently ignored in the literature as we stated before.

First of all, it is important to emphasize that for currents of the orders of mA, even in conventional systems, the electrolyte conductivity can be low enough to observe a non-negligible ohmic drop. Figure 6 shows the linear sweep voltammetry measurements (LSV) performed in a conventional three electrode cell and in our SEC, comparing the differences in the voltammograms obtained when there is no correction and when the ohmic drop is measured and corrected (details of the ohmic drop measurement and correction can be found in the supporting information section – Figure S4). Under the same conditions, a similar result was obtained for measurements carried out in both conventional cell and our SEC. Thus, we see that both systems are affected by the ohmic drop and that both electrochemical cells behave in a similar way (figures 6B and 6D), as it must be in order to obtain reliable results with any in situ technique.
Another extremely important aspect to be considered in these techniques is the absorption of a significant portion of radiation by the electrolyte, as occurs in FTIR and X-rays measurements in aqueous solutions. Under this constraint, the sensitivity is seriously compromised, and the experiments must be performed in the thin layer configuration. To evaluate the influence of this configuration in the performance, the electrochemical response in our cell (Figure 7) was analyzed when the electrode is positioned far from the window (called here conventional design) and when it is pressed against the window to form the thin layer (called here thin layer design). The schemes of the cell configurations are presented in the inset of figure 7 and in figure S5. The results show that the current diminishes about one order of magnitude due to the formation of the thin layer, which happens in any electrochemical cell in this configuration. Besides, the layout in which the WE is projected 1 mm out the inert coating (called here disengaged design) was studied in an attempt to improve the electrochemical response in the thin layer configuration and to analyze if this design allows better diffusion of molecules and ions towards and from the electrode surface. As a result of this analysis, it was observed that the disengaged design shows higher currents and a more similar response to that of the conventional design, where the electrode is far from the window. It is worth to note that these simple measurements, that permit to test the electrochemical behavior of the spectroelectrochemical systems are rarely performed or shown in publication presenting spectroelectrochemical results.

To understand from a fundamental point of view the main parameters affecting the electrochemical behavior of our spectroelectrochemical system, we used the experimental data in figure 7 to perform finite element simulations using the geometric constraints of our SEC. The calculated results are presented as interpolation functions, which allowed the calculation of the current values at each point of the electrode surface as well as the hydroxyl concentration in the entire domain and over the time. We studied the consumption of hydroxyl ions because many important reactions (Oxygen and hydrogen evolution and reductions, CO₂ reduction, biomass conversion, etc.⁴⁻³⁷) generate and consume protons or hydroxyl, generating pH changes near the electrode surface modifying both the catalyst activity and its selectivity⁴⁻³⁷. Since the interfacial pH is a key parameter in most electrochemical process, we calculated it as a function of current density (Figure 8) considering that one hydroxyl anion is consumed by every electron that passed through the electric circuit, as it is the case for many important reactions, including the electrooxidation of glycerol, which electrochemical and spectroscopic results are shown here⁴³.

In conventional cell design (8C and 8D), simulations show that there are no significant pH changes at these current densities. On the other hand, the results are completely different in the thin layer (Figure 8A and B) and the disengaged (Figure 8E and F) designs, since the electrode is pressed against the window. In these two configurations, as the current increases, the pH of the entire thin layer changes considerably. Although this variation is not dependent on the axial direction, the change is significant comparing the center of the electrode with its edge. In the thin layer design, the pH nearby the electrode edge changes more than in the center, in agreement with a diffusion controlled process in a disk-shape electrode⁴⁸. However, in the disengaged design, the pH variation in the same regions is not so substantial as the ions can more easily diffuse into the solution bulk. For the same reason, the pH at the uncovered side of the electrode in this design is not very marked, and this region can be regarded as a bulk cell design.
The analysis of the current density distribution at the electrode surface explains the pH profiles (Figure 9), local currents at 550s and 700s are also available in 2D plot (Figure S7). For the conventional design, the current is uniformly distributed, which means that the consumption rate of hydroxyl ions is the same for the entire electrode surface. Consequently, the pH is not affected by the position in the radial direction. Otherwise, the scenario changes when the WE is pressed against the window. In this case, the current distribution is not homogeneous along the electrode surface; instead, most of the current comes from the electrode edge and, for the disengaged design, from the electrode side. This lack of homogeneity is a serious problem for in situ techniques because the result becomes dependent on the region of the electrode that was hit by the radiation, which sometimes is randomly chosen. Also, the simulation results show that the disengaged design does not represent a significant improvement for in situ techniques. The increase in the current density, which could be in principle an indication that this configuration could bring some advantage, results from higher reaction rates on the electrode side, where usually there is no monitoring by the spectroscopic technique.

Since our results show that in the thin layer design most of the current density comes from the electrode edges, we repeated the simulations shown in figures 8 and 9 maintaining the current density, reducing the electrode diameter to 2mm and reducing the PTFE thickness to 1mm (figure S6). The simulation suggests that the decrease in the electrode diameter provides a better current and pH uniformity in the thin layer. On the other hand, the decrease in the inert layer did not change the pH profile, but it generates a decrease in the ohmic drop due to the smaller confinement of the field lines.

Conclusion

We developed a versatile spectroelectrochemical cell able to perform several in situ experiments: FTIR, Raman spectroscopy, X-ray spectroscopies and diffraction, Ultrafast Spectroscopy, among other techniques. Besides, the measurements can be done in transmission and reflection mode and in a stagnant or flowing electrolyte. By comparing electrochemical results obtained with our cell and with a conventional three electrodes electrochemical cell, it was possible to show that the observed discrepancies are mainly caused by the ohmic drop, which can be corrected in most of the modern potentiostats. The analyses of finite element method simulations suggest that the main issues in any SEC arise for experiments performed in the thin layer configuration. These simulations permit us to understand the main parameters affecting the electrochemical behavior of the system in this configuration, indicating that it is important to use electrodes as small as possible but always being aware that the WE design must allow the radiation beam to easily hit its surface.
**Experimental Section**

**Electrochemical experiments**

The electrochemical tests were carried out in a potentiostat/galvanostat (Autolab PGSTAT101, Metrohm®). A gold disk (7 mm diameter) was used as working electrode (WE) and a gold foil as counter electrode (CE). The reference electrode (RE) was a leak free Ag/AgCl electrode or a reversible hydrogen electrode (RHE). All potentials mentioned in this work are referred to the RHE scale. When necessary, the ohmic resistance was determined by electrochemical impedance spectroscopy (EIS). The electrooxidation of glycerol was performed in 0.1 M NaOH + 0.1 M glycerol with and without correction of the ohmic drop. Electrochemical experiments were performed in the SEC and the results were compared to those obtained in a conventional three-electrode cell. More details are described in the supplementary material.

**Finite element simulations**

A tertiary current distribution model was proposed to better understand the ionic transport in the thin layer configuration. Three different geometries were analysed (Figure S2): i) a disk electrode 5 mm from the window, ii) a disk electrode 10 μm from the window, and iii) an electrode projected 1 mm out the inert coating also at 10 μm from the window. The same current density observed experimentally for each configuration was defined on the electrode surface for each simulation with the corresponding configuration. From this, it was possible to evaluate the pH variation throughout the solution and the double layer potential considering the ohmic drop between each point on the electrode surface and the counter electrode. Further details about the proposed model are described in the supplementary material.

**Acknowledgements**

Financial support from the Brazilian agencies: PSF, ECP and JLB thanks FAPESP (grants: 2013/07296-2, 2014/50249-8, 2015/12851-0, 2016/01365-0, 2017/11986-5, 2018/24383-0, 2018/20952-0, 2019/07449-0) and Shell and the strategic importance of the support given by ANP (Brazil’s National Oil, Natural Gas and Biofuels Agency) through the R&D levy regulation. MVFR thanks the Capes/CNPEN fellowship. Research supported by LNLS-Brazilian Synchrotron Light Laboratory, CNPEM/MCTIC under proposals 20180571 and 20171115. Authors thanks Renan Picoreti (ACO-LNLS) for the picture at XAFS2 and Dr. Patricia V. Santiago and Rafael Vicentini for Raman measurements.

**Keywords:** Electrochemistry, in situ Spectroscopy, Synchrotron, Ultrafast Spectroscopy, Consol simulations


We describe in detail the main components of our spectroelectrochemical cell (SEC), which can be used to perform several in situ experiments. We also compare the electrochemical behaviour of our SEC with that of a conventional cell. Besides, computational experiments show that the inhomogeneous distribution of current in the electrode surface in experiments in the thin layer configuration can be mitigated by using electrodes as small as possible.
Versatile Spectroelectrochemical cell for in situ experiments: development, applications and electrochemical behavior

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Supplementary Information

Figure S1. In situ FTIR spectra obtained during glycerol electro-oxidation on polycrystalline gold electrode in 0.1 M NaOH solution + 0.1 M glycerol. The 2342 cm⁻¹ band attributed to CO₂ production suggests the acidification of the thin layer. The band at 1580 cm⁻¹ can be due to the superimposition of several bands (glycerate, formate, etc.). The broad band at 1400 cm⁻¹ is due to carbonate. Besides, two characteristics bands for formate can be clearly advertised in the same region. The assignment of these bands was discussed in detail in our previous papers[1,2].

Figure S2. The Raman spectra were obtained using a Renishaw Raman Spectrometer equipped with 785 nm wavelength laser and gratings of 1200 l/mm. A lens of 50x was used to focus the laser beam on electrode surface. The Raman spectra was obtained using 1 accumulation of 50 second with 10% of laser power. We used similar conditions to the in situ FTIR experiment, i.e., a polycrystalline gold electrode in 0.1 M NaOH. The in situ Raman spectra were obtained at constant potentials: i) 0.75 V is a potential below the Au oxide formation and reduction, then we observe the signal coming from the adsorption of the HO⁻ around 400 cm⁻¹ on Au. On the other hand, 1.35 V is above the onset of the oxide formation, thus, the spectra is dominated by the broad AuO feature centered at 565 cm⁻¹. The assignment of these bands was based on the literature[3].

Figure S3. In situ XAFS measurement in 0.1 M NaOH for Pt/C (a Pt foil used as a reference is also plotted). Differences in the results are due to both, electronic and structural differences. For a detailed discussion about XAFS of Pt/C see the paper of Russel and Rose[4]. These results were obtained with the set up of figure 4 in the Pt-L₃ edge (from 11400 to 12500 eV) using a double crystal monochromator of Si(111). The measurement was performed in the fluorescence mode using a Ge-15 detector (Camberra®). The beamline details could be found elsewhere[5].

Figure S4. Impedance spectra obtained in 0.1 M NaOH + 0.1 M glycerol: (A) conventional electrochemical cell, (B) SEC with WE at 5 mm from the window, (C) SEC with WE at 10 μm from the window and projected 1 mm out the inert coating, (D) SEC with WE at 10 μm from the window.

Figure S5. Scheme of the cell configuration with the ring electrode (CE) around the disk electrode (WE). Two main configurations of the WE were studied, with the top of the electrochemically active part (A) aligned with the inert coating and (B) projected 1 mm out the inert coating. Based on these configurations, three different geometries were analysed in the finite element simulations: (C) a disk electrode at 5 mm from the window, (D) a disk electrode at 10 μm from the window, and (E) an electrode projected 1 mm out the inert coating also at 10 μm from the window.

Figure S6. Simulation of pH profile at the thin layer after 700 s for electrodes with radius 1 mm (A and C) and 3.5 mm (B and D). The PTFE inert layer length is 1.5 mm in A and B and 1.0 mm in C and D. For a better visualization of the thin layer, the vertical aspect ratio was set to 1:250.

Figure S7. Local current density along the electrode surface for conventional and thin layer configurations at different times (main current xx mA/cm²) and 700 s (main current: yy mA/cm²).
**Thin layer configuration**

*In situ* FTIR measurements are performed mainly using the external reflection (also called attenuated total reflection, ATR) or internal reflection configuration. In the ATR configuration, an electrocatalyst with a high refractive index is deposited directly on the IR prism forming a thin film. This approach restricts the use of some working electrodes (WE), because the type of materials and deposition methods are limited⁶. On the other hand, the external reflection configuration has been widely used in situ FTIR experiments, because WE does not need to be deposited on the IR prism, so that a wide variety of materials and types of electrodes (such as single crystal electrodes) can be investigated. In a thin layer spectroelectrochemical cell, a transparent window is placed at one end of the cell. The WE, which is usually a flat metal disc polished to a mirrored finish, is positioned near the window. During the experiments, WE is pressed against the window and a thin layer of solution with a few micrometers thick (1 to 100 µm) between the surface of the WE and the window is formed⁷. The incident infrared radiation through the window, the thin electrolyte layer, reaches the electrode surface, and is reflected out of the cell towards the detector (as shown in the figure below).

The thin layer configuration is important *in situ* FTIR experiments, because it minimizes the absorption of infrared radiation by the solvent (water), while maximizing the absorption signal due to the species present in the thin layer⁸. Therefore, this approach hinders the free ion exchange with the rest of the solution⁹. As the species are essentially trapped in the thin layer between the working electrode and the window, there is an accumulation of products and intermediates, as well as the depletion of reagents in the thin film of the electrolyte⁹. Consequently, pH changes in the thin layer are quite common in this type of experiment, which can compromise electrochemical processes. However, as demonstrated in this work, some changes in the configuration of the cell, such as the use of an electrode with a small area, reduce these disturbances in the thin layer. The same concepts can be applied to other techniques when this configuration is used.

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**In situ FTIR results:**

![Electrode](image)

The solution layer (1-100 µm) between the electrode and the window shows the incident and reflected beams.
In situ FTIR spectra obtained during glycerol electro-oxidation on polycrystalline gold electrode in 0.1 M NaOH solution + 0.1 M glycerol. The 2342 cm\(^{-1}\) band attributed to CO\(_2\) production suggests the acidification of the thin layer. The band at 1580 cm\(^{-1}\) can be due to the superimposition of several bands (glycerate, formate, etc.). The broad band at 1400 cm\(^{-1}\) is due to carbonate. Besides, two characteristics bands for formate can be clearly advertised in the same region. The assignment of these bands was discussed in detail in our previous papers\[^1,2\].

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**Determination of ohmic resistance**

The ohmic resistance was determined by the electrochemical impedance spectroscopy (EIS). The impedance spectra were collected in the range of 10\(^5\) to 20 Hz, at open circuit potential and applying a sinusoidal perturbation with amplitude of 10 mV (20 points of number of frequency). The ohmic resistance equals the interception of the spectra with the real part of the impedance (horizontal axe) at high frequencies. The compensation of the ohmic resistance was done using 90 % of the determined value.
Figure S4. Impedance spectra obtained in 0.1 M NaOH + 0.1 M glycerol: (A) conventional electrochemical cell, (B) SEC with WE at 5 mm from the window, (C) SEC with WE at 10 μm from the window and projected 1 mm out the inert coating, (D) SEC with WE at 10 μm from the window.
Figure S5. Scheme of the cell configuration with the ring electrode (CE) around the disk electrode (WE). Two main configurations of the WE were studied, with the top of the electrochemically active part (A) aligned with the inert coating and (B) projected 1 mm out the inert coating. Based on these configurations, three different geometries were analysed in the finite element simulations: (C) a disk electrode at 5 mm from the window, (D) a disk electrode at 10 µm from the window, and (E) an electrode projected 1 mm out the inert coating also at 10 µm from the window.
Simulation of different electrode configurations:

Figure S6. Simulation of pH profile at the thin layer after 700 s for electrodes with radius 1 mm (A and C) and 3.5 mm (B and D). The PTFE inert layer length is 1.5 mm in A and B and 1.0 mm in C and D. For a better visualization of the thin layer, the vertical aspect ratio was set to 1:250.
Local current density at 550 and 700s:

![Diagram showing local current density along the electrode surface for conventional and thin layer configurations at 550 s (main current 0.080 mA/cm²) and 700 s (main current: 0.28 mA/cm²).]

Figure S7. Local current density along the electrode surface for conventional and thin layer configurations at 550 s (main current 0.080 mA/cm²) and 700 s (main current: 0.28 mA/cm²).

References


