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Electrochemical NMR spectroscopy: Electrode construction and magnetic sample stirring

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ABSTRACT

The use of nuclear magnetic resonance (NMR) spectroscopy to study electrochemical reactions *in situ* (EC-NMR), in solution, was demonstrated more than four decades ago. Although, the immense potential of EC-NMR has been demonstrated in several applications, this method has been limited to a few specialized groups since there are no commercial EC-NMR cells or cells that can be easily assembled for routine measurements. In most of the proposed EC-NMR cells the electrodes are placed inside the NMR coil, which deteriorates the magnetic field homogeneity and reduces the signal-to-noise ratio. To minimize these interferences, electrochemical cells have been constructed as flow cells, using ultra thin metallic films as electrodes, which are too complex to be produced by non-experts, or use non-metallic electrodes that have limited electrochemical applications. In this paper we report a very simple and efficient way to construct an EC-NMR cell using standard Pt and Ag wires as electrodes. These wires are assembled as coils on capillaries and are inserted into 5 mm NMR tubes and placed approximately 0.5 mm above the NMR coil. During the *in situ* EC-NMR reaction the magnetohydrodynamic effect stirs the solution, homogenizing the concentration of the reagent and the product in the NMR detection region. This effect allows the concentration of the analyte to be measured in real time, even with the electrodes outside the NMR detection region. The electrode materials are not limited to Pt or Ag wires and can be replaced by other materials according to the studied reaction. Details showing how to make the electrodes are presented in a video in the supplementary material. The application and performance of this cell were demonstrated with an *in situ* EC-NMR study of the electro-oxidation of ascorbic acid in solution. In this particular case the magnetic field increased the reaction rate by a factor of approximately two.

1. Introduction

The potential of nuclear magnetic resonance (NMR) spectroscopy to monitor electrochemical reactions *in situ* (EC-NMR) in solution was firstly demonstrated by Richards and Evans in 1975 [1]. The experiments were performed with a 60 MHz tabletop spectrometer using an EC flow cell, with the metallic wire electrodes placed above the NMR coil. This experimental set up was necessary to minimize the deleterious effects in both the spectral resolution and the signal-to-noise ratio (SNR) which are encountered when the electrodes were placed inside the NMR coil. In this EC-NMR cell configuration the EC reaction was performed just above the coil and the analytes were transported to the NMR coil by magnetohydrodynamic flow, allowing real time measurements [1].

In the past decades, several cells designs have been proposed avoiding the flow cell configuration [1-21]. In more recent cells the electrodes were placed inside the NMR coil. To minimize deteriorations in resolution and SNR, these cells were constructed with ultra thin metallic films [4,5] or non-metallic electrodes, such as carbon microfibers [6]. Although all these new cells have performed well, they have

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to be prepared by complex metallic deposition processes, not available in routine electrochemical laboratories, or use carbon microfiber electrodes with limited electrochemical application due to the low achievable currents and the limited number of analytes that can be studied with this material [22].

In the following we are demonstrating a simple EC-NMR cell that is easy to construct. It uses metallic electrodes above the NMR coil, similar to the original cell proposed by Richards and Evans in 1975 [1], but without a flow setup. In our cell the electrochemical medium is strongly stirred by the magnetohydrodynamic (MHD) force [23,24], caused by the electric field of electrochemical cell and the magnetic field of the NMR spectrometer. The stirring by the MHD force homogenizes the concentration of the reagent and the product in the NMR detection region, allowing the concentration of the analytes to be measured in real time, although the electrodes are outside of NMR detection region.

Details on how to make the electrodes are presented in a video in the supplementary material [29 (Data in Brief)]. The application and performance of this cell was demonstrated in an *in situ* EC-NMR study of the electrooxidation reaction of ascorbic acid in solution as a proof of concept.

2. Experimental

2.1. Chemicals and solutions

2.1.1. Ascorbic acid

L-Ascorbic acid (99% Sigma-Aldrich); H_2SO_4 (95% Vetec), D_2O (99.9% Sigma-Aldrich). The supporting electrolyte solution was H_2SO_4 0.2 mol L^{-1} prepared in D_2O. The ascorbic acid concentration was 0.2 mol L^{-1} prepared with the electrolyte solution.

2.1.2. Adhesive

To prepare the electrodes two types of adhesives were tested: 1) Cyanoacrylate and 2) Caldofix epoxy resin. Cyanoacrylate cures very fast while the epoxy resin takes around 12 h to cure completely. Both can be used but electrodes prepared using epoxy resin last longer without infiltration.

2.2. Electrodes

2.2.1. Glass capillary

Commercial glass capillaries (BLAUBRAND) were employed as support to prepare the electrodes. Different sizes were used (200 and 10 μL).

2.3. Apparatus

The NMR and electrochemical experiments were performed using a Bruker's Ascend 600 NMR spectrometer (600 MHz ^1H NMR frequency) with a PABBO 5 mm probe with z-axis gradient and a potentiostat model SP-150 from BioLogic Science Instruments, respectively.

2.4. Noise attenuation

To reduce the noise in both NMR and electrochemical measurements, radio-frequency filters (chokes) were used (1000 μH) in all three electrode feed lines. The chokes are important because without them the NMR pulses disturb the potentiometry measurements. For example, vertical lines appear in the chronoamperometric measurements [25-27]. A 1.5 m long multiconductor cable with 3 wires, surrounded by copper mesh shielding, connected the cell to the potentiostat, and the chokes were placed between the cable and the electrodes. The cable shield was connected to the potentiostat's ground to reduce the noise.

The developed electrode was tested during the oxidation reaction of ascorbic acid. The electrochemical data (chronoamperometry and cyclic voltammetry) and the acquired real-time NMR spectra are reported in the next section. The effect of the magnetic field of the NMR spectrometer on the electrochemical reaction kinetics is briefly discussed as well [20].

2.5. NMR parameters

The magnetic field was shimmed under computer control. The resultant line width was about 1 Hz. Spectra were acquired at 25 °C using Bruker's zgpr water suppression sequence with 4.55 s acquisition time. D1 was 5 s, 8 scans were used as well as 4 dummy scans.

In situ experiments refer to the measurements performed with the electrochemical cell placed in the NMR spectrometer. As previously mentioned, the electrodes were placed 0.5 mm above the NMR detection region. *Ex situ* measurements, on the other hand, refer to measurements that were performed with the electrochemical cell placed outside the NMR spectrometer. The electrochemical profiles and the NMR spectra acquired in the *in situ* and *ex situ* experiments were compared to determine what effect, if any, the magnetic field has on the reactions.

The NMR spectra of the *ex situ* experiments were acquired after the reaction was finished. Several reactions lasting different times (15, 30, 45 and 60 min) were performed in order to obtain a kinetic curve that could be compared to the curve obtained in the *in situ* measurements.

2.6. Electrochemical parameters

2.6.1. Experimental conditions of the cyclic voltammetry measurements

The potential was swept from −0.5 to 1.5 V (vs. Ag/Ag^+). The sweep velocity was 100 mV s^{-1}. A total of 10 cycles were executed.

2.6.2. Experimental conditions of the chronoamperometry measurements

The following sequence was executed: The applied voltage, E_{app}, was + 1.2 V (vs. Ag/Ag^+) for 20 s (oxidation) and + 0 V (vs. Ag/Ag^+) for 5 s (to clean the electrode surface); this cycle was performed 143 times.

All experiments were performed in triplicate.

3. Results and discussion

Fig. 1 represents the three electrodes system. Two Pt wires 20 cm long (0.1 mm diameter) as well as an Ag (0.5 mm diameter) wire were used to prepare the working (WE), counter (CE) and reference (RE) electrodes, respectively. To produce the WE, 6 cm were wound around the lower end of a capillary tube (200 μL). The rest of the wire was inserted in the capillary tube and went through it to provide the electrical connection by winding it to a brass contact, without using solder to avoid magnetic field distortions. The CE was made by winding 8 cm of Pt wire around the capillary tube 0.5 cm above the WE. The remainder of the wire was directed to the top of the capillary without bringing it into the capillary tube and brought into contact with another brass connector, again by winding to avoid solder. The part of the wire that stayed outside the capillary was fixated to it with teflon tape. The reference electrode was placed inside a smaller 40 μL capillary which was in turn fixated inside the larger 200 μL capillary with super glue. This setup was chosen because it minimizes the number of components inside the NMR tube, thereby increasing the robustness of the system. Furthermore, the area of the electrodes is increased by winding the wires. More details are shown in the Supplementary material [29 (Data in Brief)].

The use of metallic electrodes is of great interest when coupling electrochemical and NMR studies since they allow larger currents to flow through them than non-metallic electrodes. This is translated into a higher conversion of reagents into products, which is beneficial due to the low sensitivity of NMR. It is worth pointing out that even if the electrodes are shaped as coils, which generate a magnetic field when

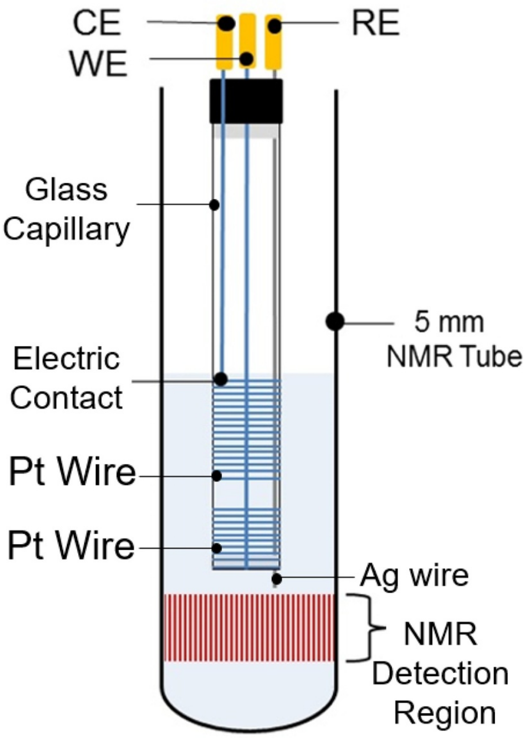

Fig. 1. Electrochemical cell and electrodes. The working, counter and reference electrodes were fixated on a glass capillary tube. The miniaturized electrodes were inserted into a standard 5 mm NMR tube and positioned 0.5 mm above the detection region.

current flows through them, they are oriented parallel to the static magnetic field and, therefore, perpendicular to the radio-frequency field. This means that during the experiments the electrode coil will not be magnetically (or inductively) coupled with the detection coil. As a result, these coils will not interfere with the NMR measurements.

Cyclic voltammetry and chronoamperometry results show that the oxidation potential is shifted to a higher value as well as an increase in the anodic current (Fig. 2) when the reaction is performed *in situ* ($i_{1.2V}$ = 4.6 mA) as opposed to the *ex situ* experiments ($i_{1.2V}$ = 2.7 mA). Both the current increase and the oxidation potential shift occur due to magnetic stirring, which increases the concentration of the analytes in the vicinity of the electrode which, in turn, increases the reaction potential [23,24]. This was verified by performing several cyclic voltammetries *ex situ* using an increasing concentration of ascorbic acid (under the same experimental conditions).

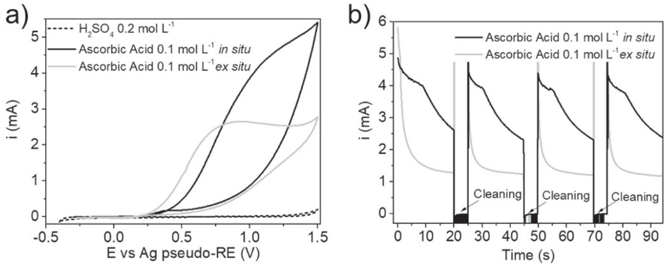

Fig. 2. a) Voltammograms from −0.5 V to 1.5 V (vs. Ag/Ag$^+$) performed on different samples and conditions. Black dotted line: electrolytic solution (*ex situ*). Black solid line: ascorbic acid solution *in situ* (B = 14 T). Grey line: ascorbic acid solution *ex situ* (B = 0 T). Experimental conditions: potential swept from −0.5 to 1.5 V (vs. Ag/Ag$^+$), sweep rate was 100 mV s^{-1}. b) Chronoamperograms of the oxidation of ascorbic acid performed *in situ* (black line) and *ex situ* (grey line). Only the first 90 s are shown. Experimental conditions: E_{app} = +1.2 V (vs. Ag/Ag$^+$) for 20 s (oxidation); E_{app} = +0 V (vs. Ag/Ag$^+$) for 5 s (electrode surface cleaning). The cycle was performed 143 times.

Magnetohydrodynamic force is the effect of an externally applied magnetic field on an electrochemical reaction. The main force acting to create this effect is the magnetic force, $\boldsymbol{F_B}$, which is the result of the cross product between the ionic current density, **j**, and the external magnetic field, **B** [23,24]. This force acts on the bulk of the solution, agitating it and therefore reducing the thickness of the electric double-layer at the electrode surface [23]. Thus, electrochemical reactions analyzed *in situ* by NMR are subjected to this effect and in the case of mass-transport limited reactions, an increase in the reaction rate can be observed since more species are dragged to the electrode surface due to the agitation of the solution, which facilitates the reaction's occurrence [23,24].

Aogaki et al. [28] demonstrated that the diffusion-limited current is proportional to $c^{4/3}\mathbf{B}^{1/3}$, where c is the bulk concentration of the electrolyte. We have estimated that in this experiment the magnetic force that is experienced during electrooxidation of ascorbic acid is nearly 2900 N m^{-3} (the area of the electrode was considered to be 2×10^{-5} m^2, the electric current equal to 4 mA - Fig. 2 - and the magnetic field equal to 14 T) which is more than strong enough to induce turbulent flow in the cell [23].

The effect caused by the magnetic agitation is similar to the one observed when the concentration of the ionic species is increased in the solution. The results prove that, indeed, increasing the concentration of ascorbic acid in the sample has the effect of increasing the current at E = 1.2 V and the peak current as well as shifting the peak oxidation potential. Furthermore, all of these parameters increase linearly with the concentration and Eq. (1) was found to relate the current at E = 1.2 V to the ascorbic acid concentration. Using Eq. (1) and the value of the current at E = 1.2 V found from Fig. 2 we find that performing the *in situ* experiments is equivalent to having an apparent ascorbic acid concentration in the vicinity of the electrodes of approximately 200 mmol L^{-1}, which is consistent with the fact that more species are converted during *in situ* experiments.

$$i_{1.2V}(\text{mA}) = (0.933 \pm 0.036)(\text{mA}) + (0.0184 \pm 0.0004) \times [\text{AA}](\text{mmol}\quad \text{L}^{-1}) \tag{1}$$

Fig. 3 shows the NMR spectra obtained before and after a 1-h reaction performed *in situ* and *ex situ*. The ascorbic acid oxidation generates dehydroascorbic acid (Fig. 3). The different protons are identified by different colors and letters.

Table 1 shows the percentage of the initial and final peak areas of ascorbic acid (AA) and dehydroascorbic acid (DA), the product of the oxidation of AA, in relation to the total spectrum area in both *in situ* and *ex situ* experiments. In the *ex situ* configuration a conversion of 25% of AA is achieved, while the conversion achieved in the *in situ* configuration is 50%. This clearly shows the strong effect that the magnetic field has on the oxidation reaction of AA, by improving the amount that is converted from AA to DA. The advantage of using NMR data is that it is possible to assess the conversion of AA to DA directly through the observation of the peaks of either molecule, while the use of electrochemical data alone does not allow identification of products formed. The complete set of spectra acquired before and after the reaction as well as in intermediate times is shown in the supplementary materials (See Figs. 1 and 2 in Ref. [29]).

3.1. Cell performance compared to other literature devices

The performance of the cell developed during this work was compared to the performance of the main electrochemical cells used for EC-

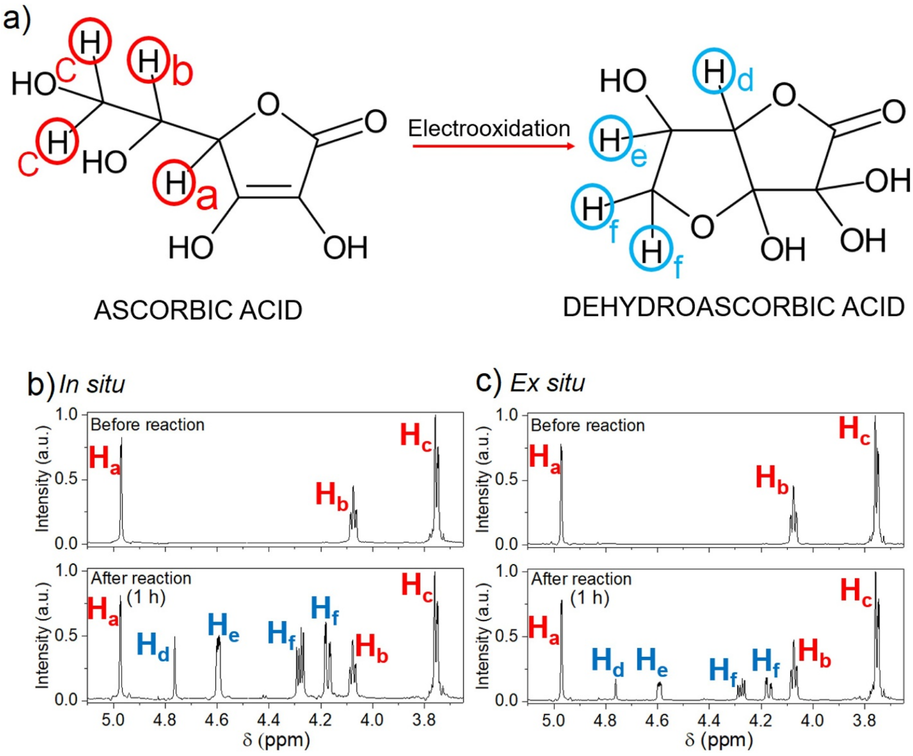

Fig. 3. The different hydrogen atoms which are observed in the NMR spectra are highlighted (a). The ^1H NMR spectra of the oxidation of ascorbic acid *in situ* (b) and *ex situ* (c) are shown. The bottom two spectra were acquired after a 1-h oxidation reaction while the top two spectra were acquired before the reaction.

Table 1
Corresponding concentration for the different chemical groups before and after the reaction. The data are divided into *in situ* and *ex situ* measurements.

Chemical shift (ppm)	Proton	*In situ*		*Ex situ*	
		% Initial	% Final	% Initial	% Final
3.750	H_c	53.6	26.4	52.2	38.7
4.075	H_b	24.7	12.8	25.9	19.3
4.175	H_f	0.9	15.8	0.4	7.1
4.275	H_f	0.6	15.3	0.2	7.1
4.615	H_e	0.4	14.4	0.2	6.5
4.765	H_d	0.3	4.7	0.2	2.7
4.970	H_a	19.5	10.4	20.8	15.7

NMR experiments found in the literature (Table 2). The earliest cells developed for EC-NMR (up until 1990 [1-3]) were either very complex systems, requiring alterations to the NMR probe or a large volume of solvent for the analyses. The devices developed in 2000 [4] and 2004 [5] have the advantage of not significantly affecting the NMR magnetic field, but require some technology not readily available in all laboratories. The cell developed in 2009 [6] is simple to prepare but does not allow large currents to flow and is limited to a small range of potentials and analytes.

Each of the systems presented has both its advantages and drawbacks but we highlight the simplicity, practicality and low cost of our system as its main advantages for EC-NMR studies. Furthermore, the electrodes can be produced with a wide variety of metals that enable high currents to flow through the system, which is of great importance to both NMR and electrochemistry, which makes this an attractive electrochemical cell for initial or quick tests where speed and simplicity are required and even for more complex studies.

4. Conclusion

The results of this study demonstrate that the MHD can be an ally when preparing suitable, simple and reliable plug-in electrochemical cells for *in situ* EC-NMR studies. With the stirring effect produced by the MHD forces during the *in situ* EC-NMR experiments, it is not necessary to place the electrodes inside the NMR coil, but just in its vicinity. This condition minimizes the electrodes' interference with the NMR signals even when they are constructed with regular metallic wires. Therefore, we are also demonstrating that a very simple and efficient EC-NMR cell can be constructed using common Pt and Ag wires assembled in capillary tubes. This electrode device is plugged into a 5 mm NMR tube and the wires are approximately 0.5 mm above the NMR coil. During a reaction the medium is stirred by the MHD effect, homogenizing the concentration of the reagent and product in the NMR detection region. The proposed electrode device is not limited to Pt, Ag wires. The application and performance of this cell were demonstrated in an *in situ* EC-NMR study of the electro-oxidation of ascorbic acid in solution, and it was noticed that the magnetic field increased the reaction rate by approximately a factor of two. It is expected that this homogenization will work at lower (and higher) magnetic field strengths, which has been shown by Hinds in 2001 as well as in studies from Gomes et al. from 2014, 2015 and 2017, using a low field NMR spectrometer. However, for this effect to be noticed at lower magnetic field strengths the concentration, c, of the electrolyte must also be high enough, as the limiting current in the electrochemical experiments is proportional to $c^{4/3}\mathbf{B}^{1/3}$.

Table 2
Summary of the main electrochemical cells for EC-NMR including the one from this work.

Author/year	Electrodes	Reaction studied	Coupling mode	Advantages	Disadvantages
Richards and Evans [1]	Pt/Hg wire	Reduction of trans-1-phenyl-1-buten-3-one	*In situ* online	No modifications to the NMR probe required	Use of Hg, Complex cell design, Line broadening
Albert et al. [2]	Pt melted wire	2,4,6-Tri-*tert*-butylphenol electrolysis	Online	No line broadening	*in situ* NMR and electrochemical measurements not possible simultaneously, Need flow analysis NMR probe, Solvent consumption
Mincey et al. [3]	Sb-SnO_2 film	Benzoquinone reduction	*In situ*	Magnetic field homogeneity practically unaffected	Spinning system, NMR probe requires modification
Prenzler et al. [4]	Au thin-film	Benzoquinone reduction	*In situ*	Magnetic field homogeneity practically unaffected	Complex electrode building process, Requires a 10 mm NMR tube
Webster [5]	Au thin-film	Reduction of 9-bromoanthracene, 9-chloroanthracene, and 4-bromobenzophenone	*In situ*	Suitable for routine operation	Complex electrode building process, Requires a 10 mm NMR tube
Klod et al. [6]	C microfibers	Benzoquinone reduction	*In situ*	Low-cost, Disposable electrodes, Easy construction	Low current, Limited analytes can be studied, Long reaction times
Coaxial electrode cell	Pt coil	Ascorbic Acid oxidation	*In situ*	Low-cost, Disposable electrodes, Easy construction, High currents can be achieved, Other metals can be used as well, No need to alter the NMR probe	Electrodes placed above the detection region

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2019.01.010.

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