MRI \textit{in situ} visualization of an electrochemical reaction under forced hydrodynamic conditions

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Magnetic resonance imaging principle

The aim of this section is to provide a simplified overview of the basic elements involved in the process of using nuclear magnetic resonance for imaging. For detailed descriptions of the method, readers may refer to Ref [1] and specific applications in electrochemistry in Ref.[2]. NMR is based on the fact that nuclear spins undergo a precession around the direction of the magnetic field induced by the magnet ($B_0$). MRI relies on the use of an extra set of magnetic fields, which are designed to change linearly with space within the volume of interest. In general three independent gradients are used, each of which encodes an orthogonal direction. These magnetic field gradients ($G$) give rise to a frequency that depends on the position ($r$) as:

$$\omega_0(r) = \gamma (B_0 + r \cdot G),$$  \hspace{1cm} (eq. S1)

where $\gamma$ is the nuclear gyromagnetic ratio of the observed isotope (e.g. $^1$H, $^{19}$F, $^7$Li). If the signal decay is recorded under the action of one of such gradients, a Fast Fourier Transform (FFT) will render a projection of the object in one direction, this is usually referred to as a 1D image. In order to obtain a 3D image of an object two alternative methods can be applied. A set of 2D images, in which different slices of the object are acquired can be used, or a full 3D set of data can be obtained. The former method is in general applied to study a specific region of interest and is chosen in favor of a 3D image as this latter is in general very time consuming.

The MRI sequence used in this work is a 2D Spin-Echo sequence with spin warp sampling (see Fig. S1). A Spin-Echo is generated by a shaped refocusing 180º pulse applied at a time $t_E/2$ after the excitation pulse, and in the presence of a magnetic field gradient ($G_{\text{slice}}$). The phase cycle for the rf pulses is shown in Table S1. The magnetization from a determined region in space is acquired, in this case a Gaussian shaped pulse will refocus the magnetization only from spins located in a Gaussian region of space. Acquisition of $N$-data points is carried out in the presence of a magnetic field gradient ($G_{\text{read}}$), so that an accumulation of phase in one dimension of the $k$-space is achieved (read direction). On the second direction experiments are carried out changing the values of a field gradient orthogonal to $G_{\text{read}}$ ($G_{\text{phase}}$) as shown in the fourth line of Fig. S1. In this way an $N \times M$ data set, representing the $k$-space, is acquired. A 2D FFT algorithm will return a representation of 2D spin density over the selected slice. The direction of read, phase and slice gradients can be chosen arbitrarily.
Figure S1: Schematic representation of the Spin-Echo pulse sequence

Table S1: Phase Cycle used for the rf pulses in the Spin-Echo sequence

| $\Phi_{90}$ | $\Phi_{180}$ | $\Phi_{\text{rec}}$ |
|-------------|-------------|------------------|
| $\pi$       | $\pi/2$     | $\pi$            |
| $0$         | $\pi/2$     | $0$              |

MRI Velocity maps

If the spin bearing molecules are moving during the application of a magnetic field gradient, an extra accumulation in the phases will be produced. In this work a pair of bipolar gradients were applied after the 180º refocusing pulse (see last line in Fig. S1). The application of a pair of gradients imparts a phase proportional to the displacement of the sample in the direction in which the gradients are applied. This phase depends on the gradient intensity ($G_{\text{vel}}$), the pulse time duration ($\delta$) and the spacing between them ($\Delta$). For instance, the phase introduced by a gradient applied in the $z$ direction can be written as:

$$\phi = \int_0^\delta \gamma G_{\text{vel}}(t) z(t) \, dt.$$  \hfill (eq. S2)

For the bipolar pulses sketched in Fig. S1, this equation reduces to:

$$\phi = \gamma G_{\text{vel}} \left[ \int_0^\delta z(t) \, dt - \int_\Delta^{\delta+\Delta} z(t) \, dt \right].$$  \hfill (eq. S3)
Evidently, if the nuclei are static the total accumulated phase is zero, however, if nuclei are moving with a stationary velocity \( \mathbf{v} \), the net phase can be written, in a general case as:

\[
\phi = \gamma \delta \Delta \mathbf{G}_{\text{vel}} \cdot \mathbf{v} \tag{eq. S4}
\]

It must be noted that even though this gradient is plotted in a different line in Fig. S1, it will be applied in one of the imaging directions. Velocity maps in a given spatial direction are obtained by calculating the phase difference between a reference image measured without velocity gradients and a second image measured with the bipolar gradient pair applied along the desired spatial direction\(^3\). The phase of the signal of both images is subtracted and the pixel by pixel phase difference is converted to velocities using Eq. S4, where the velocity of the nuclei contained in a volume element, or voxel, is considered to be stationary.

There are a series of considerations to be taken into account for the optimum determination of velocities, as described in the main text. A full description for this particular setup may be found in Ref. 3. For the rotation speed of 6.3 Hz used for the velocity and imaging parameters are set such that the limiting velocity before blurring occurs during acquisition (read gradient) is 35 m/s.

**Relaxation weighted MRI**

The Saturation-Recovery pulse sequence is one of the most convenient methods to determine the relaxation time \( T_1 \). It consists in a series of 90° pulses that initially cancel the longitudinal magnetization. Then, it evolves freely for a time \( \tau \), which is varied from experiment to experiment. The pulse sequence and the phase cycle for the rf pulses required to eliminate unwanted signals are shown in Fig. S2 and Table S2 respectively.

![Figure S2: Schematic representation of Saturation-Recovery pulse sequence.](image)

**Table S2**: Phase Cycle used in the Saturation-Recovery sequence
In order to study the reaction process in real time, a calibration of the relaxation time $T_1$ with a given concentration of Cu$^{2+}$ ions is needed. Different solutions of CuSO$_4$ were prepared at different concentrations between 0 mM and 25 mM. $T_1$ was measured and the reported value corresponds to the average value of three independent measurements.

These experiments were carried out in a superconducting magnet with a field intensity of 7.05 T. Finally, the relaxivity $R_1 = \frac{1}{T_1}$ of the solution was calibrated as a function of the concentration of Cu$^{2+}$. Figure 2a shows that there is a linear dependency between the relaxivity $R_1$ and the concentration of paramagnetic ions. Performing a minimum squares fitting, the following calibration curve was obtained:

$$R_1 = 0.607\frac{mM}{s} - 1\left[\text{Cu}^{2+}\right] + 0.413\frac{s}{s}$$

(eq. S5)

The relaxivity of Cu$^{2+}$ ions in water at 7.05 T can be determined by the slope of the previous calibration curve, being equal to $(0.607 \pm 0.007) \frac{mM}{s}$.

In order to obtain a contrast by the $T_1$ value in a MRI, a preparation period ($\tau^* + \tau$) with pulses similar to the Saturation Recovery is followed by the Spin Echo sequence (Fig S3).
**Figure S3:** Schematic representation of the Saturation Recovery weighted Spin Echo MRI pulse sequence.

The preparation period provides a contrast given by $T_1$ and $T_2$ in the signal used for the images. In this way, each pixel of the acquired image is weighted by the relaxation times associated with that voxel. The relaxation values of the explored reaction goes from the Zn$^{2+}$ solution ($T_1 = 1.9$ s and $T_2 = 750$ ms) to the highest CuSO$_4$ concentration ($T_1 = 76$ ms and $T_2 = 71$ ms). Several solutions were prepared and images were acquired under the same experimental parameters without the Zn plate and rotating at 1 rps. Then, the signal intensity of the pixel can be expressed as

$$S = S_0 \left(1 - \exp \left(-\frac{\tau}{T_1}\right)\right) \exp \left(-\frac{t_E}{T_2}\right)$$

where $S_0$ is the signal when the magnetization is fully recovered. Figure S4 shows the image intensity as a function of the CuSO$_4$ concentration, which is used as a calibration curve.

![Image Intensity vs. Cu$^{2+}$ concentration](image.png)

**Figure S4:** Image intensity vs. Cu$^{2+}$ concentration.

The value of $\tau$ is chosen in order to get the best possible contrast between the $T_1$ values of the sample. Additionally, $t_E$ is chosen so that the image intensity is not greatly affected by $T_2$. The experimental parameters were set as follows: $t_E = 8$ ms; soft 90° pulse duration = 700 μs, hard 90° and 180° pulses duration = 250 μs, $\tau^* = 100$ ms; $\tau = 240$ ms, Read direction = z, Phase direction =
Numerical Simulations

Numerical simulations were performed using the finite element method as implemented in COMSOL Multiphysics. The simulations were carried out in a 2D model representing a 3D system with cylindrical symmetry. The geometry of the cell matched the experimental cell geometry. Two coupled processes were incorporated: in a first stage, a time-dependent computational fluid dynamics (CFD) simulation is carried out in order to obtain the fluid velocity field, $\mathbf{u}$. This is accomplished by solving the continuity and Navier–Stokes equations for an incompressible, isothermal flow at low Mach number. Viscosity and density parameters corresponding to pure water were used unless otherwise mentioned. In this CFD model the flow is laminar. No-slip boundary conditions are imposed at the boundaries corresponding to the cell walls and bottom. Rotational boundary conditions are considered at the bottom of the rod and at the shaft of the cylinder. The CFD simulation is carried out until a stationary state is observed (typically 100 s or less). In a second stage, mass transport for $\text{Cu}^{2+}$ is solved by solving the combined diffusion-convection equation

$$\frac{\partial C_{\text{Cu}^{2+}}}{\partial t} + \nabla \cdot (\mathbf{u} C_{\text{Cu}^{2+}}) - D \nabla^2 C_{\text{Cu}^{2+}} = 0$$  \hspace{1cm} (eq. S7)

where $C_{\text{Cu}^{2+}}$ and $D$ are the concentration and the diffusion coefficient of $\text{Cu}^{2+}$, and $\mathbf{u}$ is the stationary velocity field. No-flux boundary conditions were imposed on the walls of the cell and in order to emulate a mass-transport limited reaction, $C_{\text{Cu}^{2+}}$ was fixed at 0 at the bottom of the rod. Grid and time step independence of the results was checked. The first-order rate constant was calculated by averaging the concentration over the whole of the solution, linearizing and fitting a linear function. In all cases the fit was very satisfactory ($r^2 \geq 0.9999$), which corroborates that the reaction is first-order with respect to $C_{\text{Cu}^{2+}}$.

In order to validate eq. 5, simulations were carried out for different rotational velocities, kinematic viscosities and diffusion coefficients. Then $k$ was plotted as a function of $\Omega^{1/2}$, $\nu^{-1/6}$ and $D^{2/3}$ (figure S5). As can be seen, the linear behaviour of these plots validates the use of the Levich equation for this system.
Figure S5: Simulation results for the rate constant used to validate the use of eq. 5 and corresponding linear fit results. (a) As a function of $\Omega^{1/2}$, for $\nu = 1.0097 \cdot 10^{-6}$ $m^2 s^{-1}$ and $D = 1.0 \cdot 10^{-9}$ $m^2 s^{-1}$. (b) As a function of $\nu^{-1/6}$, for $\Omega = 62.8$ $rad$ $s^{-1}$ and $D = 1.0 \cdot 10^{-9}$ $m^2 s^{-1}$. (c) As a function of of $D^{2/3}$ for $\Omega = 62.8$ $rad$ $s^{-1}$ and $\nu = 1.0097 \cdot 10^{-6}$ $m^2 s^{-1}$.

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