***Operando* electrochemical NMR microscopy of polymer fuel cells**

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1. Materials and Methods

1.1 Membrane preparation. The poly-2,2'-(2,6-pyridine)-5,5'-bibenzimidazole (PBI_5N) polymer was prepared by polycondensation of 3,3'-diaminobenzidine (DAB) and 2,6-pyridinedicarboxylic acid (PDA) in polyphosphoric acid (PPA, 85% P_2O_5), as already reported in details elsewhere.[42] DAB and PDA were dissolved in PPA and polymerized at 200°C under nitrogen atmosphere for 30 h. After the condensation reaction, the polymer was soaked in distilled water, in order to eliminate any residual monomer and PPA, and subsequently treated with a saturated K_2CO_3 solution. The polymer was then washed in boiling water overnight, and finally dried under vacuum for 24 h. The polymer inherent viscosity, η, was 0.7 g dl^{-1}.

A proper amount of polymer powder was dissolved in a sealed flask at 120°C in a DMA/sec-butylamine (8:2) solution. The solution was then sprayed under N_2 flux onto a hot plate (150°C) in a ventilated homemade chamber. The obtained film was peeled out from the cooled plate and washed in deionized water overnight.[43] Two different membranes were prepared for the MRI experiments. The first one was characterized by a thickness of about 250 μm and was used for the experiments reported in Fig.2 (MEA1), whereas the second one, which resulted to have a film thickness of about 340 μm, was used for the MRI studies reported in Figs. 3 and 4 (MEA2). For both films the thickness homogeneity was about 98%.

The membranes were doped in a phosphoric acid (PA) solution (70% w/w) for one day and then dried at 110°C for 2 hours before to be assembled with the electrodes. The doping level (DL) was calculated using the following equation:

$$DL(\%) = \frac{(W_p - W_d)}{W_d} \times 100$$

where W_p and W_d are the weights of the doped and undoped membranes, respectively.

1.2 MEA assembly. The membrane electrode assemblies (MEAs) were prepared by hot pressing the membrane and two gas diffusion electrodes (GDE HT-ELAT, Etek) at 130°C and 1 ton for 10 minutes. The Pt loading was 0.5 mg/cm^2 at both electrodes. Between the gas diffusion electrode, which acts as anode, and the membrane, a Teflon® foil was inserted, in order to avoid the short circuit of the two electrodes (see also Fig. S3). In the Teflon foil was previously realized a small squared hole in order to create the "active part" of the MEA, i.e. where the electrochemical reactions take place, whose area resulted to be 2 cm^2.

MEA1 used for the MRI study reported in Fig. 2 has a total thickness of about 700 μm, while MEA2 used for the studies reported in Figs. 3-4 has a total thickness of 850 μm.

Both the MEAs were used directly, without any specific pre-treatment, but drying at 120°C for 2h in order to remove all water coming from the doping procedure.

1.3 ELMINMR apparatus. A schematic representation of the system is reported in Fig. 1, while a block scheme is reported in Fig. S1.

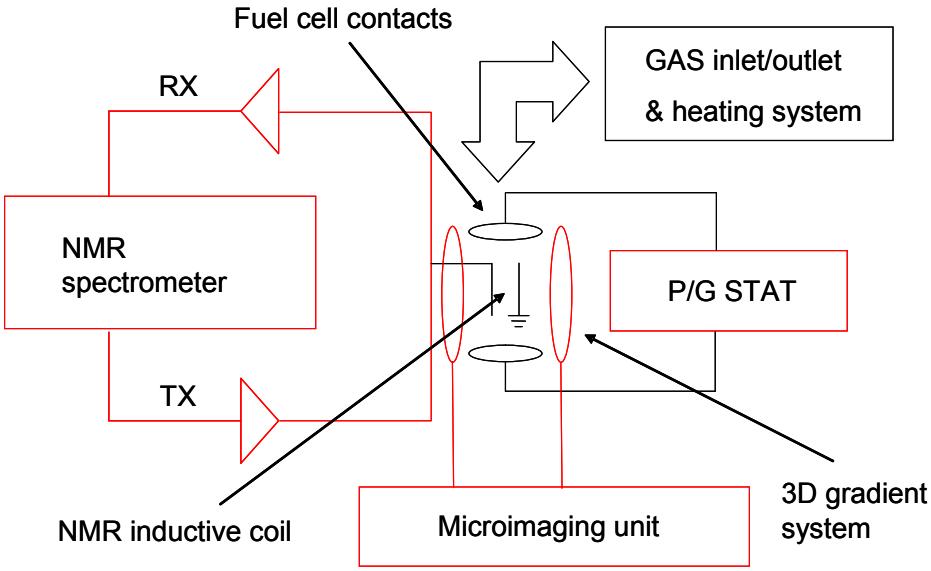

Fig. S1 Block scheme of the ELMINMR instrument. Red: commercially-available parts, black parts: homemade or partially modified parts.

^{1}H MRI images were recorded using a solid-state NMR spectrometer constituted by a 400 MHz wide bore vertical magnet interfaced with a Avance III Bruker console, equipped with Micro2.5 gradient system (40 A, 150 Gauss/cm), a MicWB40 probe and a 30 mm birdcage resonator. For hosting the fuel cell inside the resonator, a Teflon® block was machined in form of two halves of a cylinder, which dimensions were: diameter 28 mm, height 60 mm. In each half a gas-flow channel, a slot for a Viton® o-ring were also prepared, as can be observed in Fig. S2. One half also hosts a hole for inserting the thermocouple, which monitors the fuel cell temperature. As H_2 source was used a H_2 generator (LM-300, Shandong Institute of Chemical Industry JINAN China). H_2 and air were separately supplied to the cell with a pipeline, realized with Teflon® tubes. While the gases flowed through the pipeline, they were heated through a heating bath (Julabo F32, liquid: Thermal H5S Julabo, range T = -50°/+105°CC). The heating bath was thermally isolated with insulating thermosetting foam up to the entering into the ELMI probe. The gas circuit was completed by two tubes, which brought separately the gases outside the magnet. The current was generated with a potentiostat/galvanostat unit (Autolab PGSTAT30 and Booster 20A), which also read the voltage produced by the cell. The unit was connected to the cell by means of standard rf cables. The cables were inserted from the bottom of the magnet into the cell and resulted to be suitable for minimizing artefacts in the MRI measurements. The cables were connected directly to the gas diffusion electrodes through brass screws (see Fig. S3). A copper-constantan thermocouple was inserted into the ELMI probe and connected with an external temperature reader.

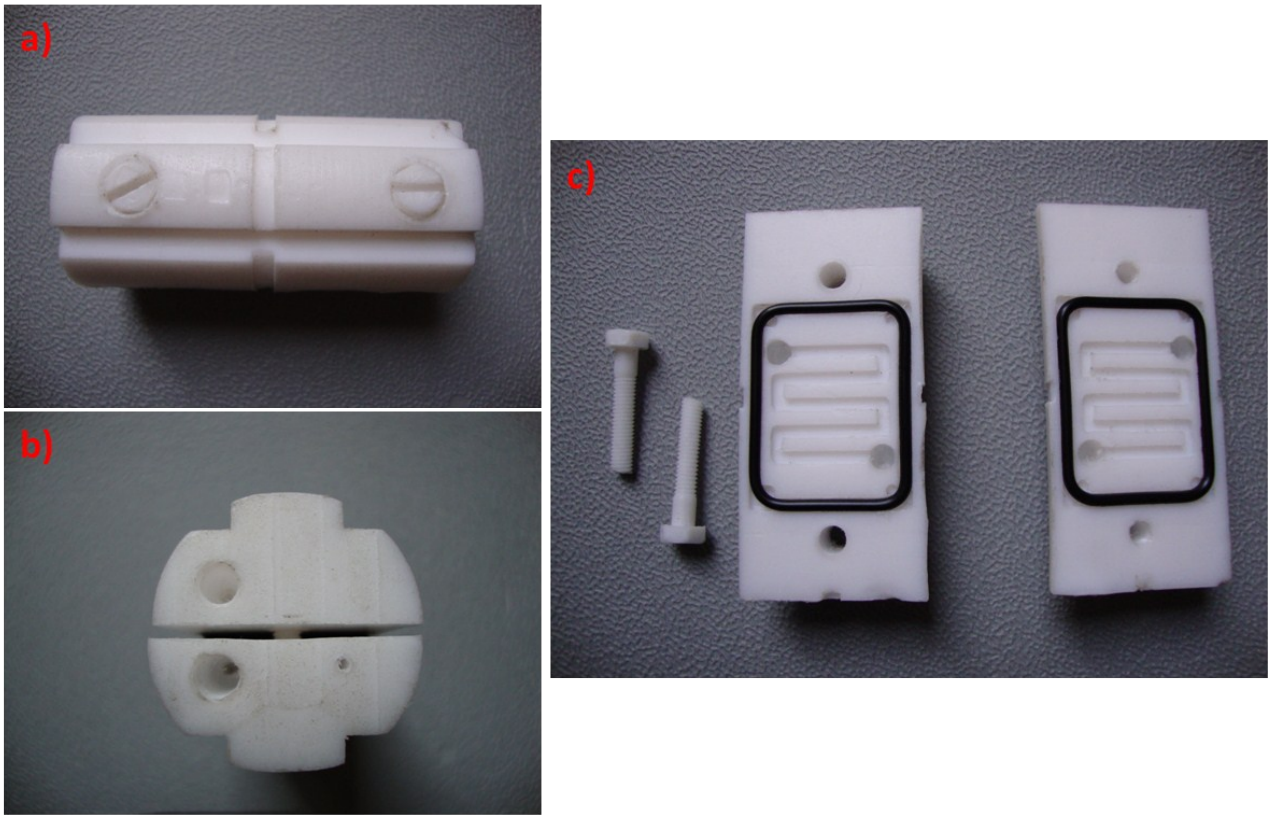

Fig. S2 Teflon housing for MEA: a) lateral view; b) sectional view, where the two big holes are gas inlets, whereas the small hole is the thermocouple inlet; c) exploded view of the housing with the gas-flow channels and the o-rings.

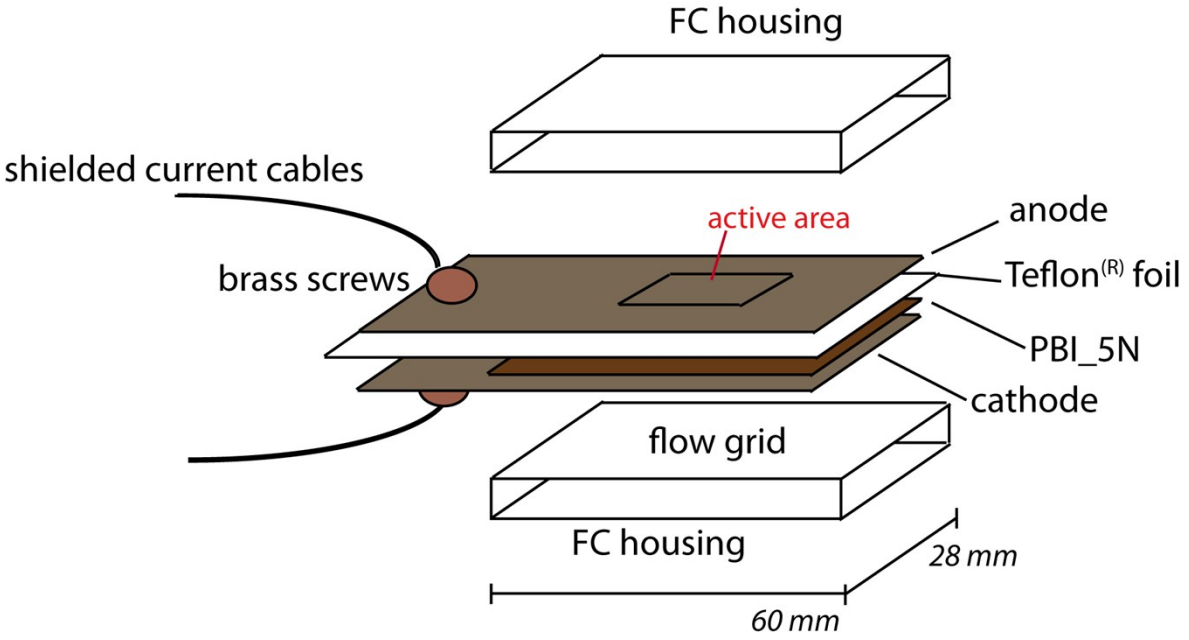

Fig. S3 Exploded view of the MEA inside the FC housing. The MEA is constituted by four foils in this order from up to bottom: anode, Teflon® foil, PBI_5N membrane and cathode. The two electrodes are longer than the Teflon® cylinder in order to allow a direct connection with the

shielded current cables coming from the potentiostat/galvanostat. Two small brass screws were used for connecting electrodes to the cables. For preventing short circuits between the two electrodes, a Teflon® foil was inserted for separating them, where prior to the hot pressing step a squared hole in was prepared. In this way we reduced the effective active area to a square of about 2 cm^2.

1.4 MRI images acquisition. The images were acquired using a 3D imaging protocol called ZTE (Zero Time Echo) *(30-32)* with T_R= 4 ms, N_A= 4, bandwidth = 200 kHz. The field of view (FOV) was a coronal cube 4 x 4 x 4 cm. A 192 x 192 x 192 pixel matrix was used, resulting in a spatial resolution of 0.208 mm/pixel. To record one image required 17 minutes.

The ZTE protocol is only available for Bruker Avance II and III spectrometers equipped with a DRU receiver (see Bruker Imaging Manual). It is based on a non-selective excitation and a signal acquisition in the presence of a constant gradient. ZTE operates in a steady state of magnetization. For efficient scanning, usually a very short T_R and a small flip angle are used. ZTE is a 3D radial acquisition method, performing centre-out readouts according to the schemes as shown in Fig. S4. Because this is a 3D acquisition method, it allows only isotropic FOV centered on the centre of the birdcage. Due to its extreme sensitivity also to short T_2 protons, the samples support (in our case the FC housing) should be proton-free. Furthermore, it must be avoided that proton sources exceed the FOV in order to prevent aliasing artifacts.

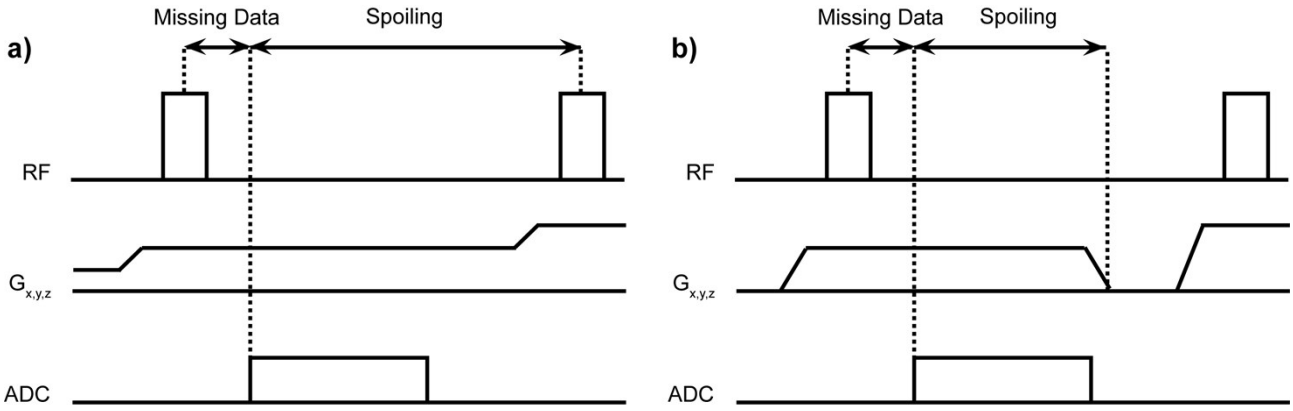

Fig. S4 Schemes of the ZTE acquisition protocol. If the minimum T_R is used the gradient are always on (case a), otherwise they are switched on and off like in spin echo sequence (case b). [Scheme courtesy from Bruker Biospin GmbH].

1.5 Data processing. For obtaining axial slices from the 3D ZTE dataset, the Jive 3D visualization application provided with the Paravision 5.1 software (Bruker Biospin GmbH), was employed. An

area of 27.5 mm was divided in 12 axial slices spaced of 0.25 mm. Each slice has an area 26 x 26 mm (pixel dimension 0.135 x 0.135 mm).

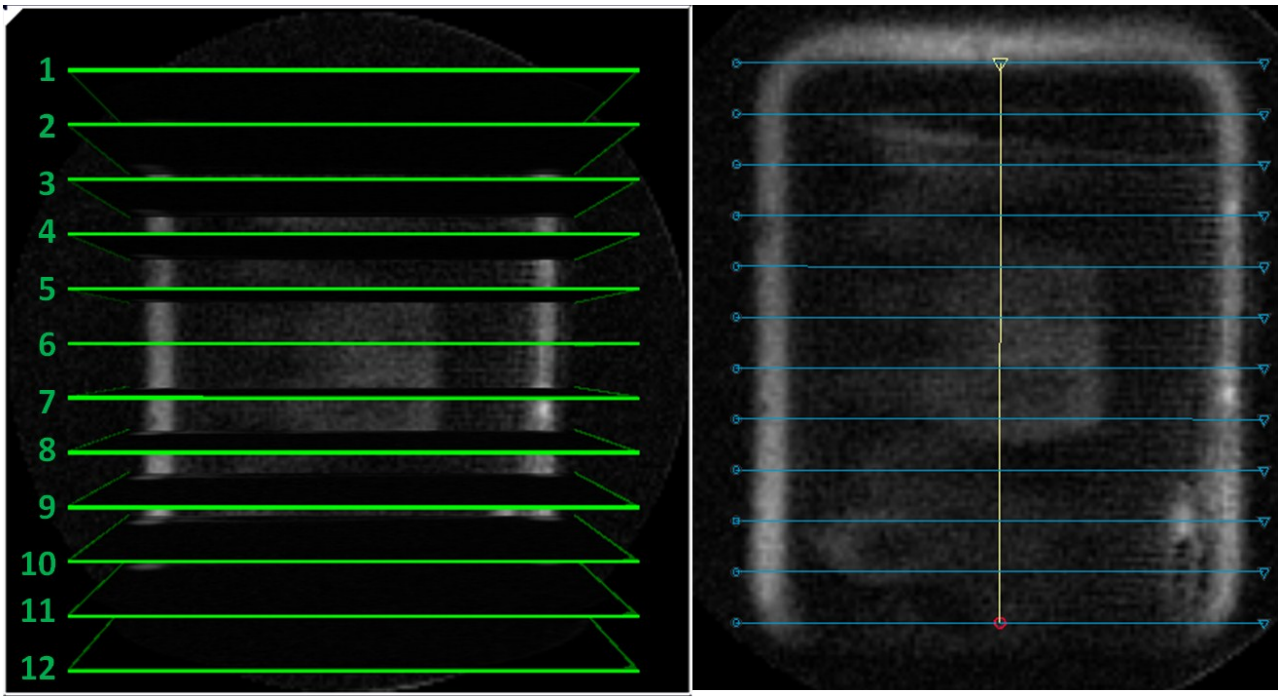

Fig. S5 Scheme of the positioning of the 12 axial slices obtained from the 3D ZTE dataset using the Jive 3D visualization package. For studying in detail the active area of the MEA we selected slices 5, 6, 7 and 8, which are reported for each acquired ZTE reported in Figs. 2-3-4.

2. Brief summary of the development of the ELMINMR apparatus

As the NMR resonator, we initially developed a surface coil, which could work as a volume one due to the relatively small depth of the MEA (400-900 μm). In order to reduce possible interferences with the electrochemical d.c. signals, the RF NMR coil was inductively coupled with another coil, which in turn was connected with the signal descending cables through a proper capacity. The two NMR coils were printed on a vetronite plastic support, and faced to the electrochemical current collectors (interdigitated electrodes, see electrical scheme in Fig. S6). The two plastic supports were sandwiched with MEA inside and inserted in a Teflon® housing, with separate gases inlets and outlets and temperature sensing. All these parts were fitted in a custom microimaging probe (see Fig. S7). As far as concerns the thermal dissipation under operating conditions (i.e. max 150° C of fuel cell working temperature), we estimated that the Teflon®

thermal housing would be enough to insulate the NMR gradient subsystem, which is the only thermo-critical part of the instrumentation. Furthermore, for a more safety work environment, instead of inserting a heating system inside the housing, we planned to raise the cell temperature by heating the gas flows, so avoiding direct Joule heating of the gases.

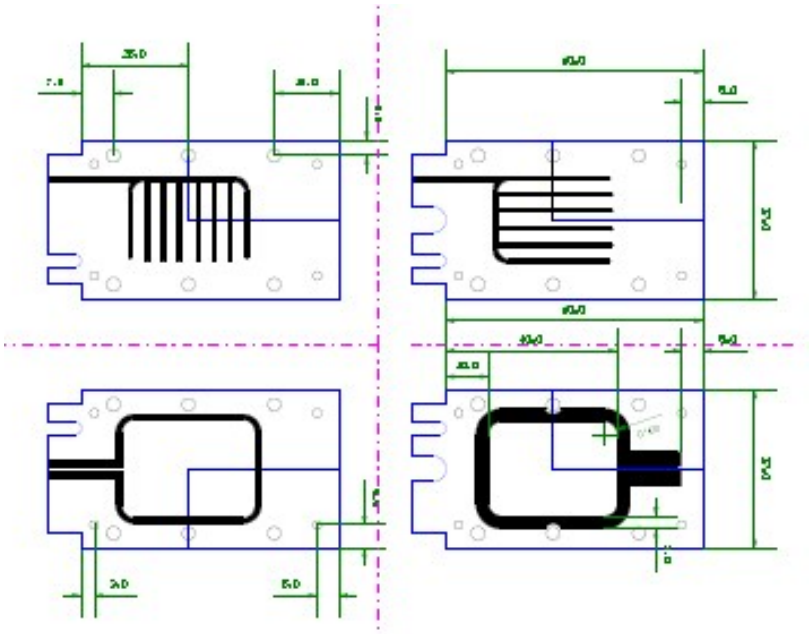

Fig. S6 Electrical scheme of the two vetronite layers facing interdigitated current collectors and the NMR surface coil.

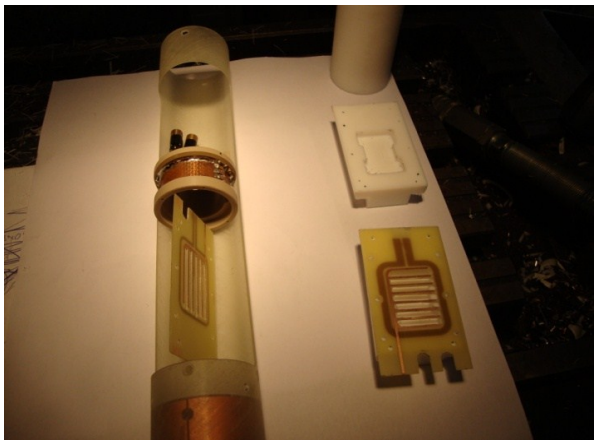

Fig. S7 First prototype of an ELMI probe with the surface coil and the integrated current collectors. A first prototype of the FC housing is also included in the picture.

Preliminary tests showed that the surface coil generated some artifacts and did not offer enough signal-to-noise ratio to fulfill the stringent requirements of the proton acquisition in the PBI

membrane. Figure 8 showed an image obtained with a standard spin echo (SE) sequence of the FC housing filled with a wet filter paper phantom, cut in the same dimensions of a potential MEA. The interdigitated assembly is evident. Some additional artifacts due to gradients (tooth-saw lines at the left side) can also be observed. Furthermore, strong detuning effects were observed during wobbling.

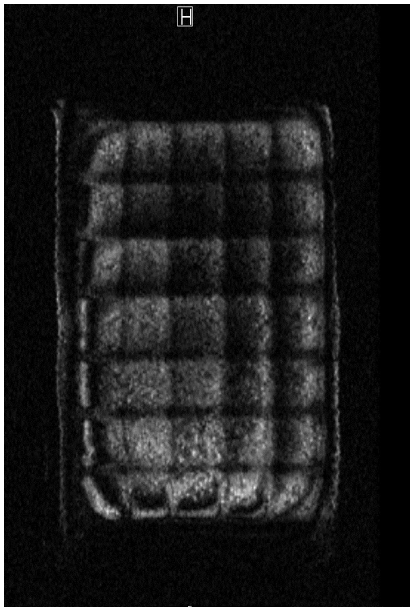

Fig. S8 Preliminary test with a phantom of the surface coil: MRI image obtained for a rectangle of wet filter paper (2D spin echo sequence, coronal slice (3 x 4 cm, thickness 1 mm, T_R = 0.6s, T_E= 14ms, matrix 256 x 256).

Therefore, we modified the project and the ELMI probe was designed starting from a standard 30 mm birdcage resonator. The current collectors were planned outside the FC housing, which was then rebuilt as already described in section 1.3.

We tried to collect MRI images with different sequences, but the ZTE 3D acquisition method gave the better results. For comparison a 2D SE image and a ZTE collected for the same MEA are reported in Fig. S9. With the ZTE we were able to get a detailed image of the system, while in the SE image, obtained using the minimum attainable echo time (3.1 ms), most of the signal was cut away due to fast T_2 relaxation times of the proton species, leading to a consistent loss of details. In the central part of the image, the S/N ratio was 3.4 for the ZTE and 1.9 for the SE image.

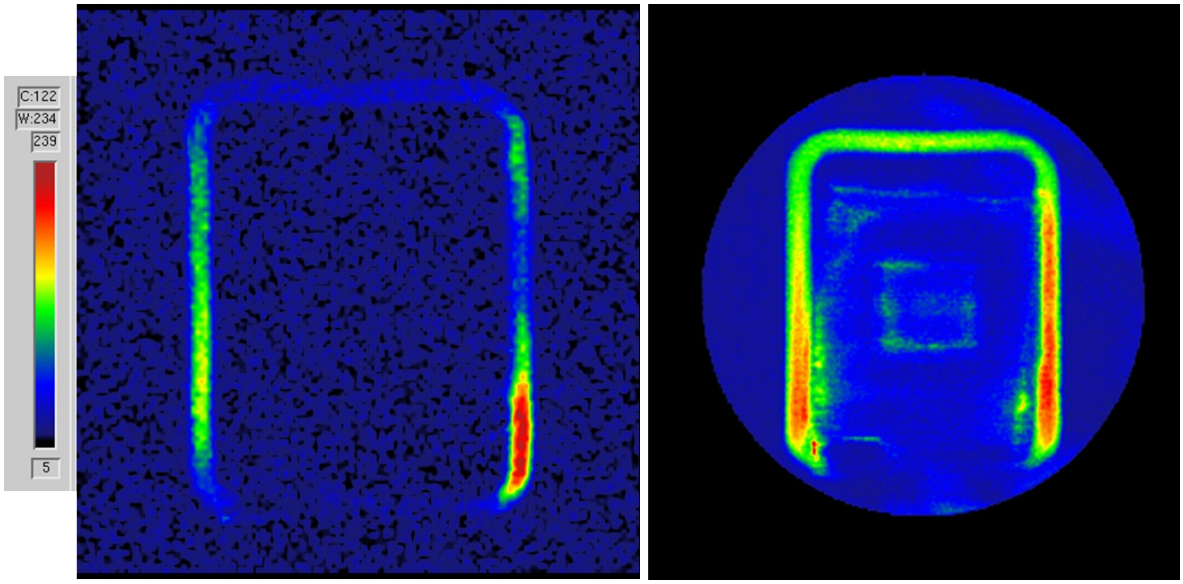

Fig. S9 Preliminary tests with a MEA: left) a 2D spin echo image (coronal 4x4cm, thickness 5 mm, T_E=3.1ms, T_R=1s, N_A=4, 128x128 matrix, 0.312 mm/pixel); right) ZTE image (coronal 4x4x4cm, T_R=4ms N_A=4, 192x192x192 0.208 mm/pixel).

The heating bath was finally implemented with a low-boiling oil and this limited the maximal temperature attainable to 100°C. A further optimization of this system, including a heating bath with a high-boiling oil, such silicon oil, could allow to perform measurement above 120°C, i.e. in the optimal operational range of PBI-based fuel cells for automotive.