Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information for

New ceramic electrodes allow reaching the target current density in bioelectrochemical systems

Diego Massazza, Rodrigo Parra, Juan P. Busalmen and Hernán E. Romeo [*]

[*] Dr. H. E. Romeo
División Polímeros Nanoestructurados, Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA-CONICET)
Mar del Plata, Buenos Aires (Argentina)
E-mail: hromeo@fi.mp.edu.ar

Dr. D. Massazza, Dr. J. P. Busalmen
Laboratorio de Bioelectroquímica, Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA-CONICET)
Mar del Plata, Buenos Aires (Argentina)

Dr. R. Parra
División Cerámicos, Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA-CONICET)
Mar del Plata, Buenos Aires (Argentina)

Powder X-ray diffraction (XRD) characterization of the Ti_4O_7 electrode material

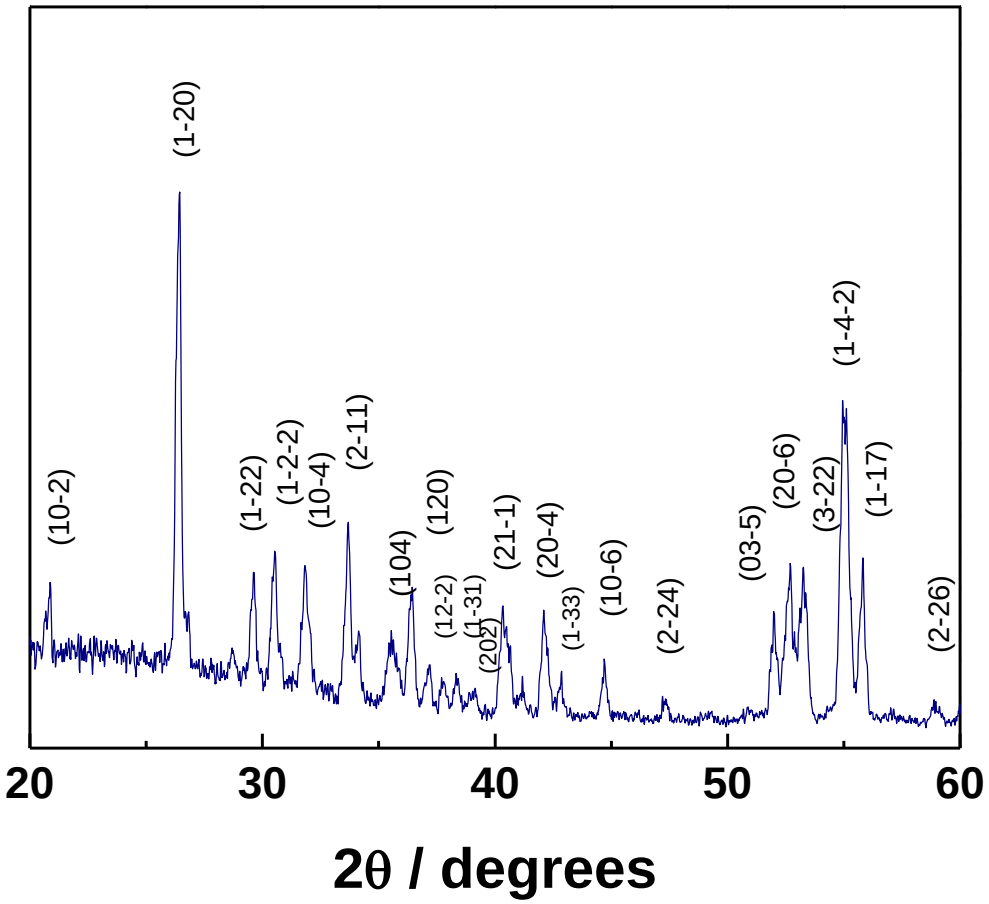


Figure S1.- XRD pattern of the ITTC electrode. *hkl* indexing corresponds to Ti_4O_7 main reflections.

According to the JCPDS 71-1429 file, only Ti_4O_7, the most conducting among the Magnéli phases, was produced after the reducing treatment with metallic Zr.

The XRD analyses were conducted by means of an X`Pert Pro PANalytical diffractometer, employing the $K_{\alpha 1}$ line of Cu (wavelength 1.54059 Å). The electrical voltage and current were 40 kV and 30 mA, respectively. Data were collected for 2θ angles ranging between 20º and 80º, with a step size of 0.02º and 0.5 s acquisition time per step.

Electrical characterization of ITTC compared to a typical carbon electrode

The current-voltage curves show an increase in material resistance with temperature. This is a typical feature displayed only by Ti_4O_7 compared to the other Magnéli phases, which evidences its metallic conductivity.

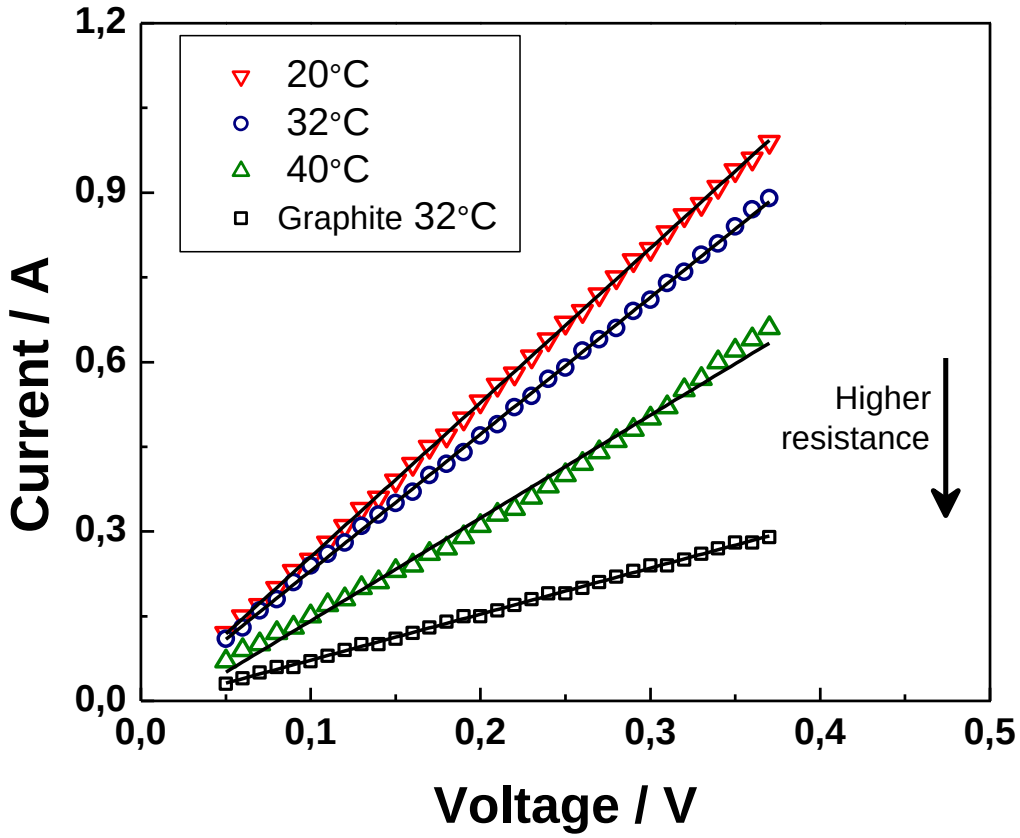


Figure S2.- Current-voltage curves as a function of temperature corresponding to ITTC, compared to a typical graphite electrode.

Electrical resistance values of 0.37 Ω (20ºC), 0.41 Ω (32ºC) and 0.55 Ω (40ºC) were calculated from the reciprocal of the slopes of the curves, which were registered for a porous ITTC electrode (85% porosity) and dimensions of 2 cm in length and 1 cm in diameter. A graphite bar with the same dimensions as those of the ITTC electrode was employed as a control material. The comparison was made at 32ºC, a temperature corresponding to that of the bioelectrochemical tests.

For the electrical characterization, silver electrodes were painted on both (parallel) faces of the samples (ITTC and graphite). Current-voltage curves were registere by means of a Siglent SPD 3303 source/measure unit and a sample holder equipped with Ingun GKS-113 test probes. Electrical

characterization as a function of temperature was conducted by placing the sample holder inside a glass receptacle modified by electrical resistances.

Chronoamperometric comparison between ITTC electrodes, Ti_4O_7 dense electrodes and a typical dense graphite bar

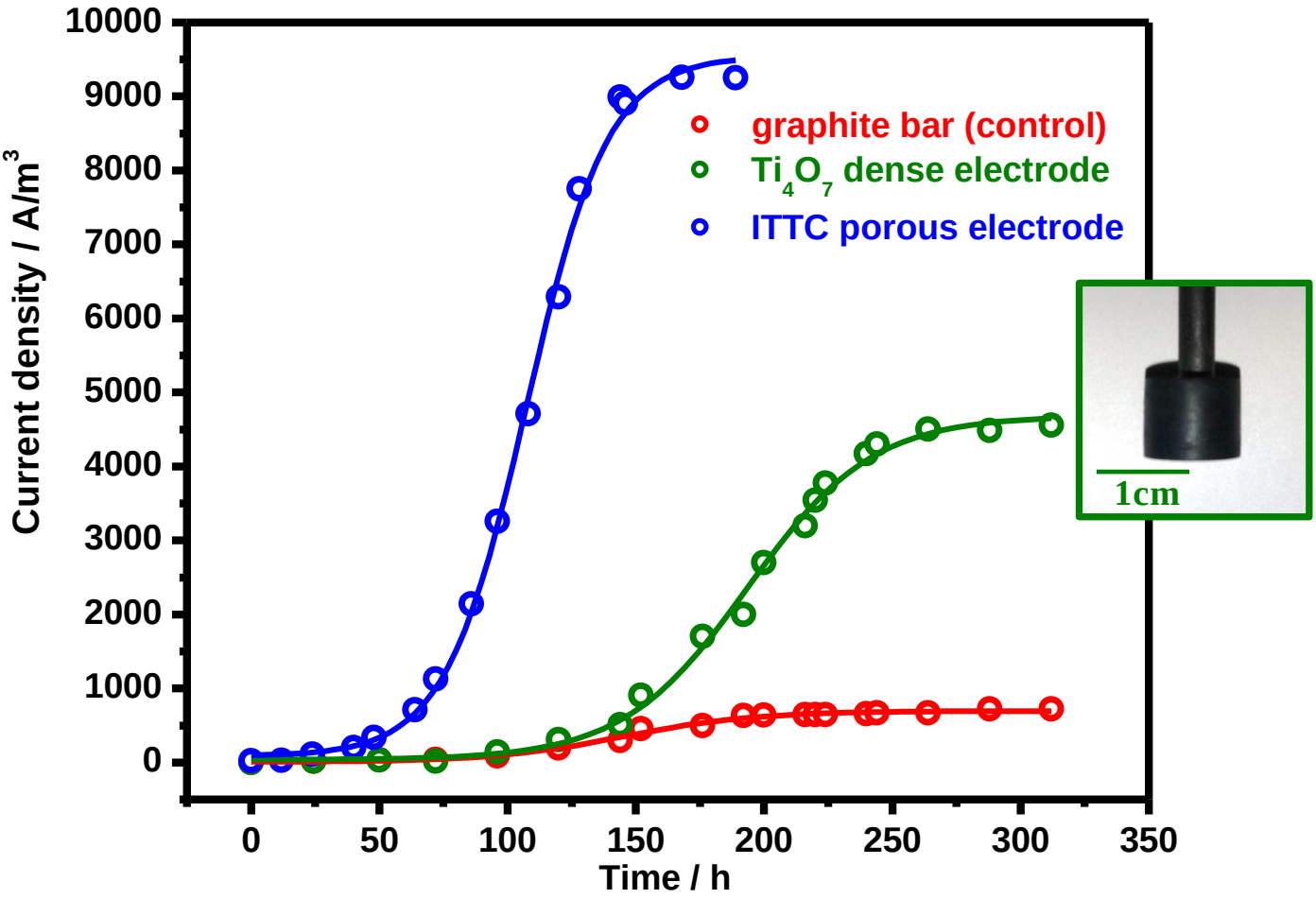


Figure S3.- Chronoamperometry illustrating the growth and electrocatalytic activity of *G. sulfurreducens* biofilms on ITTC porous electrodes and Ti_4O_7 dense electrodes compared to a typical graphite bar, used as a control substrate. Tests were all performed in the same bioelectrochemical cell.

Chronoamperometries clearly show that Ti_4O_7 *dense* electrodes generate higher volumetric current densities (7 times higher) compared to those from typical graphite bars. By employing ITTC *porous* platforms, the volumetric current density displays an extra 2-fold increase with respect to that corresponding to the Ti_4O_7 *dense* material.

The picture accompanying the figure depicts a typical Ti_4O_7 *dense* bar used as electrode under the same experimental conditions as those reported in the Experimental section.

SEM characterization on Ti_4O_7 dense electrodes

Figure S4 shows the SEM characterization corresponding to Ti_4O_7 *dense* platforms after 300 h of culture. Images confirm typical bacterial (*G. sulfurreducens*) adhesion and proliferation features.

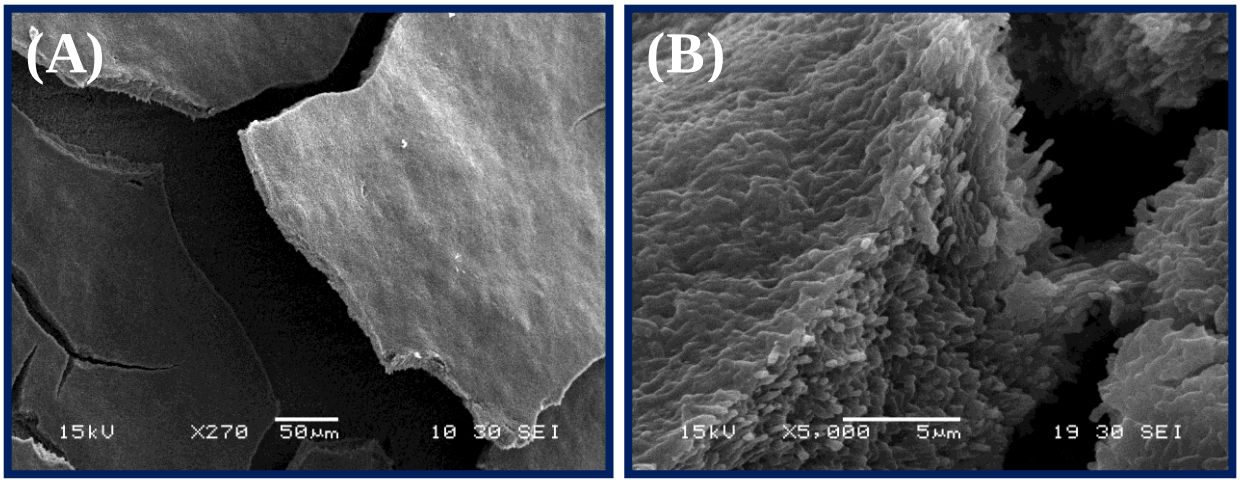


Figure S4.- Compact biofilms comprising numerous bacterial layers are observed, totally covering the electrode surface. Observed cracks correspond to typical shrink processes occurred when the biofilms are dehydrated with ethanol.

Cyclic voltammetry tests on the ITTC electrode during *G. sulfurreducens* biofilm evolution with time

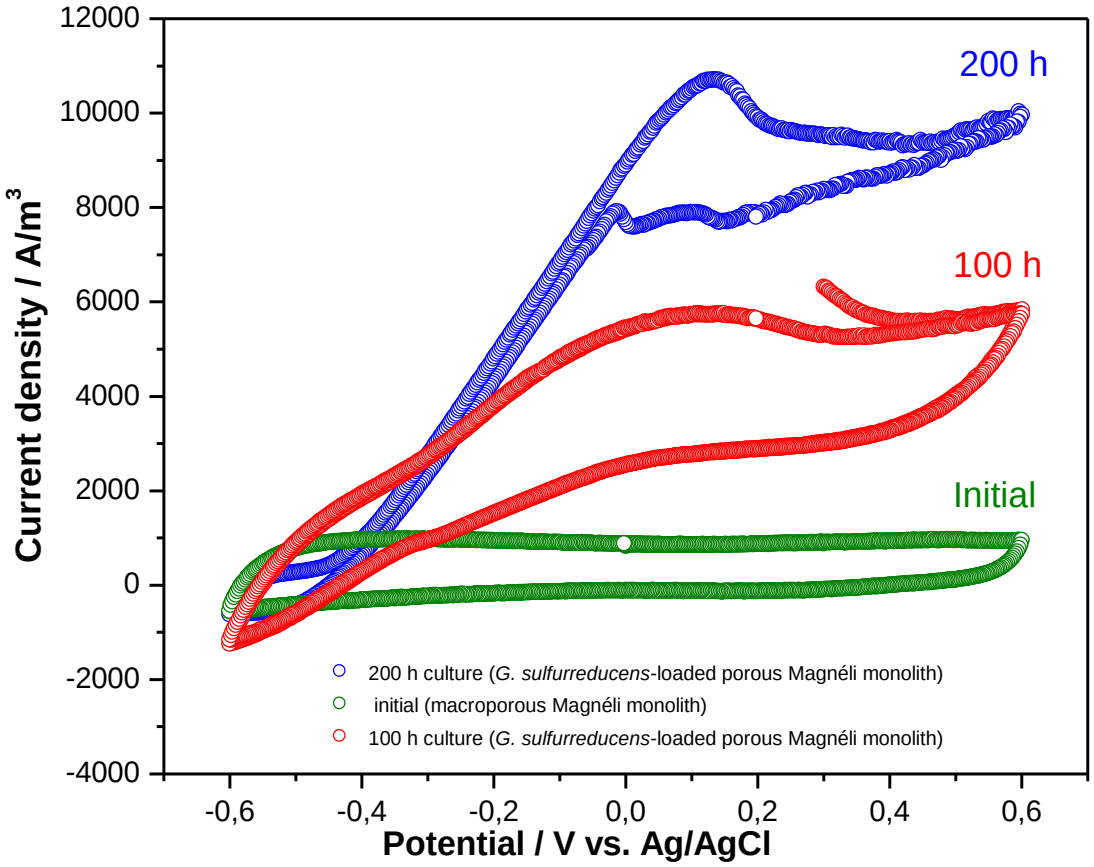


Figure S5.- Cyclic voltammetry tests performed on the ITTC electrode at different stages during *G. sulfurreducens* biofilm growth. Tests were conducted by scanning a -0.6 V/0.6 V potential range, using a scanning rate of 0.01 V/s.

Comparison of cyclic voltammetry tests between ITTC and a typical graphite bar after biofilm growth

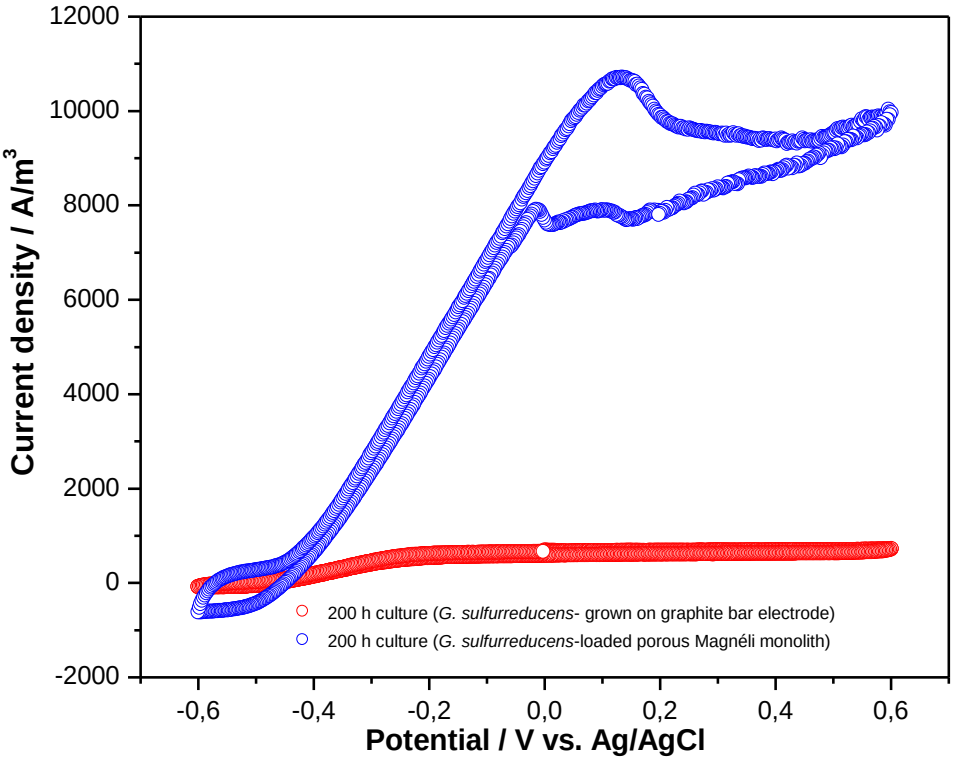
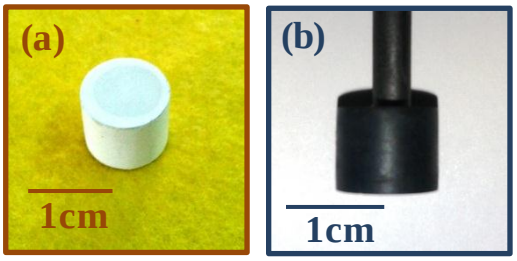


Figure S6.- Cyclic voltammetry tests on ITTC and a graphite bar after 200 h of biofilm formation. Tests were performed in the same bioelectrochemical cell, and were conducted by scanning a -0.6 V/0.6 V potential range, using a scanning rate of 0.01 V/s.

Preparation of Ti_4O_7 dense electrodes

For preparing Ti_4O_7 bars, the same TiO_2 paste used to build up the macroporous scaffolds (see the Experimental section) was first dried at 50-70 ºC. The obtained powder was uniaxially pressed at 2.8 Tn/cm^2, and the resulting cylinder (1.3 cm in length, 1 cm in diameter) was finally sintered at 1000 ºC for 3 h with a dwell step of 30 min at 500 ºC (heating and cooling rates of 5 ºC/min). A rutile phase-dense bar was obtained (picture (a) below) which was subsequently heat-treated in the presence of Zr in order to promote its reduction to Ti_4O_7, employing the same experimental conditions described in the Experimental section. A graphite bar was finally glued to the Ti_4O_7 dense bar as connection to the external circuit (picture (b)).



Economic considerations on the ITTC electrode manufacturing

The evaluation of the suitability of an electrode should take into account, at least, an estimate on economic considerations. In our case, our analysis relied on the material prices (TiO_2 nanoparticles, Zr turnings to perform the reducing treatment) and processing costs (mainly associated to the employed cryogenic source and the power supply for high temperature treatments).

It has to be mentioned that a lab-bench electrode was developed in our study, so the costs involved in each processing stage are not the lowest ones that could be found in the market (thinking, for instance, of an industrial scale). Nevertheless, a rough calculation was made.

We have calculated (per electrode):

- **Mass of TiO_2: 0.785 g (for an electrode of 1 cm diameter, 2 cm length and a density of 0.5 g/cm^3)**, equivalent to **US$ 0.0016** (on the base of US$ 2000/tn TiO_2 nanoparticles, according to Evonik Argentina).
- **Mass of Zr turnings: 0.157 g**, equivalent to **US$ 0.28** (on the base of US$ 1787/kg Zr, in Buenos Aires, Argentina at the time of manuscript preparation).
- **Volume of liquid nitrogen: 0.5 L**, equivalent to **US$ 1** (on the base of US$ 2/L $N_{2(l)}$ in Mar del Plata, Argentina at the time of manuscript preparation).
- **Energetic considerations: 16.5 h** of thermal treatment (at 1000ºC), equivalent to 66 kW.h=**US$ 5.9** (on the base of 4 kW power supply corresponding to the Indef 332 high temperature furnace, and US$ 0.09/kW.h in Mar del Plata, Argentina at the time of manuscript preparation).

Estimated ITTC electrode cost ~ US$ 7