

Supporting Information

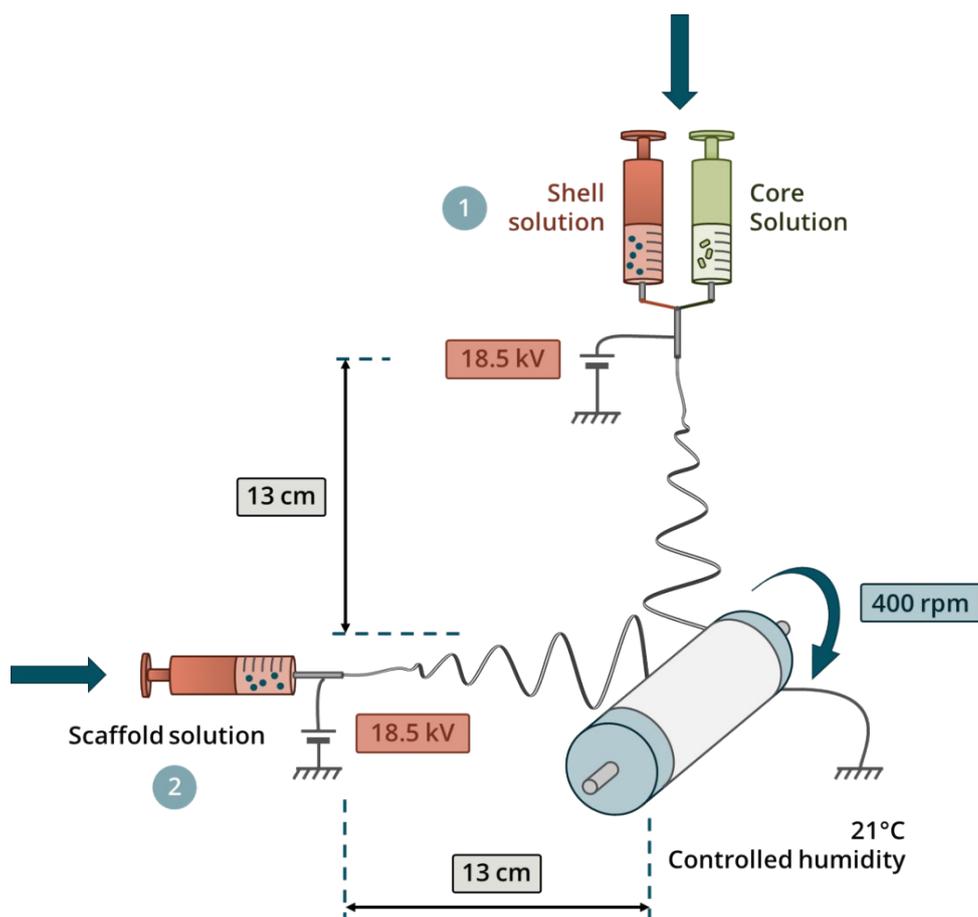


Figure S1. Schematic representation of a dual electrospinning set-up designed to produce a mixed electrospun mat of two networks: (1) core-shell fibers encapsulating bacteria inside a porous carbon black-containing shell (core syringe driver speed of $0.5 \text{ mL}\cdot\text{h}^{-1}$; shell syringe driver speed of $3.5 \text{ mL}\cdot\text{h}^{-1}$; glass syringe) and (2) conductive carbon black-rich scaffold fibers (syringe driver speed of $3.5 \text{ mL}\cdot\text{h}^{-1}$; glass syringe). 13 kV applied between the stainless-steel needle/coaxial nozzle and a grounded roller covered with an aluminum foil at 400 rpm. This set-up is adapted from an Electrospinz (Blenheim, New Zealand) ES1™ lab-scale generator and apparatus and a custom coaxial nozzle. Temperature and humidity are controlled at 21 °C and between 30 and 35 %RH.

Table S1. Formulations of the core, shell & conductive scaffold solutions for the dual electrospinning of the bioanode.

Solution	Solvent	Polymer	Additives
Core	PBS 0.5X	PEO 5 wt%	<i>S. oneidensis</i> at $\text{OD}_{600} = 1$
Shell	90/10 wt chloroform + DMF	PCL 6 wt%	PEG 1.5 wt% + CB 2 wt%
Scaffold	DMF	PAN 7 wt%	CB 7 wt%

The coaxial electrospinning apparatus adapted to the laboratory electrospinning platform was developed for the production of coelectrospun fibers. The spinneret (**Figure S2.**) polymer parts were designed on the Autodesk® Fusion 360 software and printed on a Formlabs Form 2 3D-printer in the FLGPGR04 photopolymer resin. The resin is easily cleanable and resistant to the usual electrospinning solvents.

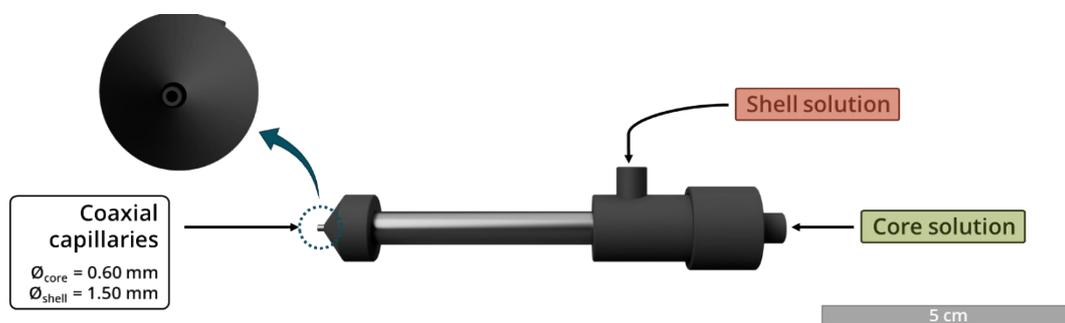


Figure S2. Render of the 3D-printed coaxial electrospinning spinneret.

The spinneret is composed of 5 pieces (**Figure S3**):

1. 3D-printed nozzle ($\varnothing_{\text{shell}} = 1.50 \text{ mm}$);
2. 3D-printed fluted centering piece;
3. Steel tube ($\varnothing = 6 \text{ mm}$);
4. 3D-printed main body with shell solution entry;
5. Blunt-end needle ($\varnothing_{\text{core}} = 0.60 \text{ mm}$);
6. 3D-printed cap with core solution entry.

During its assembly, the various parts were sealed together and electrically isolated with tape. The internal needle is set to slightly protrude from the external nozzle.

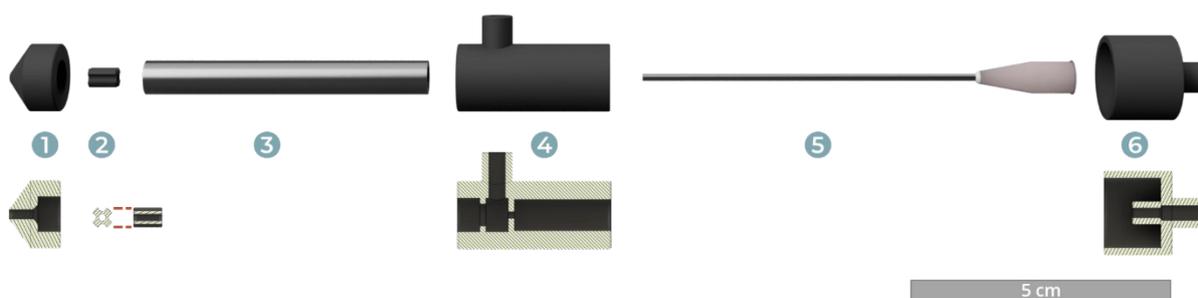


Figure S3. Individual render and radial cuts of the spinneret 3D-printed parts.

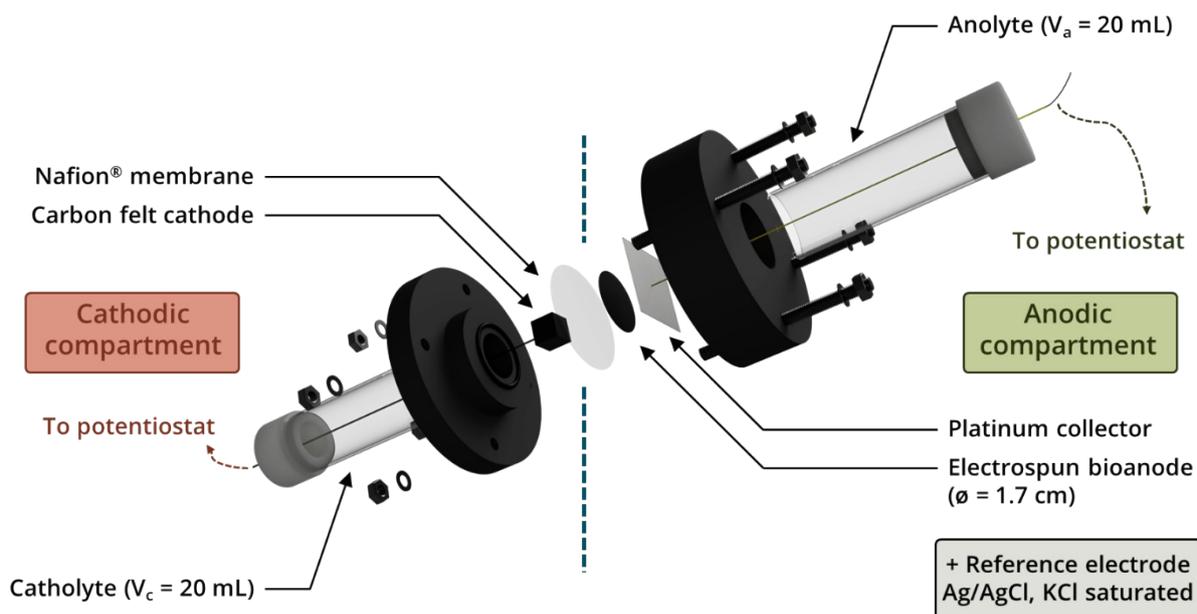


Figure S4. Lab-scale two-compartment microbial fuel cell setup.

The MFC lab-scale setup main body has been custom made in polyethylene, with silicone O-ring ensuring the sealing of the cell (**Figure S4**., radial cut in **Figure S5**.).

The 20 mL anodic and cathodic compartments are fabricated from the bodies of Terumo® 30cc syringes. The Nafion® proton exchange membrane (Nafion® NRE-212, 50 μm thick, Sigma-Aldrich) is cut to the setup dimensions ($\varnothing \approx 2.5 \text{ cm}$) and pretreated with concentrated HNO_3 overnight and subsequently rinsed with distilled water until its neutralization. The platinum mesh collector connected to the denuded part of a WCT30 wire (Radiospire) isolated from the anolyte with 3M™ polyimide 1218 electrical tape and is inserted with the help of a needle through a silicon folding skirt sealing the anodic compartment. The skirt is pierced to allow the insertion of a reference electrode. The carbon felt cathode is connected to a Terumo® hypodermic needle which passes through a silicon folding skirt sealing the cathodic compartment. The assembly is sealed by tightening 4 screws passing through the two parts of the body, ensuring the contact of the platinum mesh with the anode.

All the assembly is conducted under sterile conditions in a biosafety cabinet from sterilized parts (UV light for 30 minutes for the Nafion®, 70 % ethanol in water for the reference electrode and autoclaving at 120°C for 20 minutes for the other parts).

Anode and cathode sides are loaded through the skirts with hypodermic needle with the corresponding electrolytes (catholyte: 150 mM of NaCl (supporting electrolyte) and 100 mM of $K_3[Fe(CN)_6]$; anolyte: MR-1/L sterile medium).

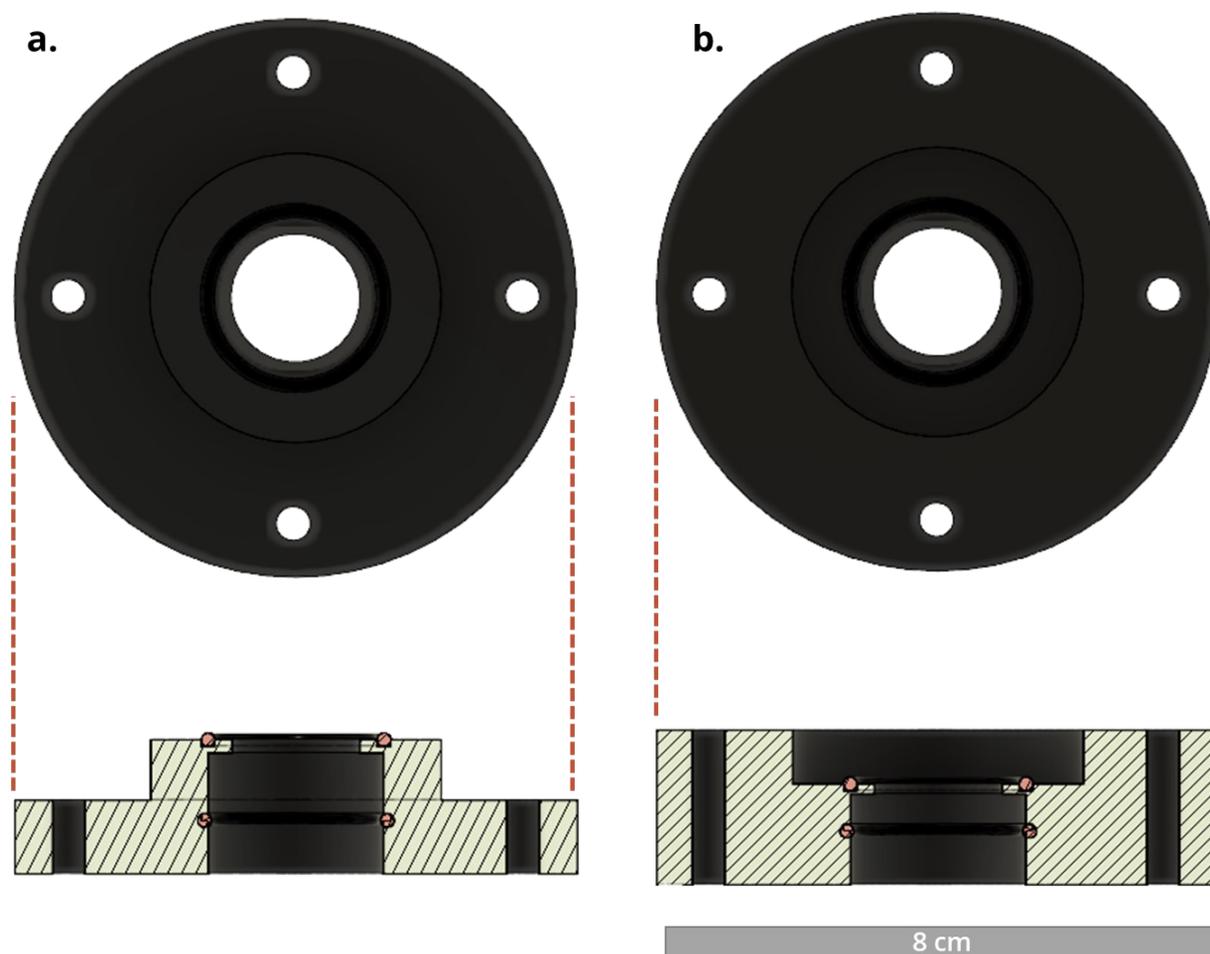


Figure S5. Radial cut of the 2 parts of the MFC reactor body: **a.** cathodic side; **b.** anodic side.

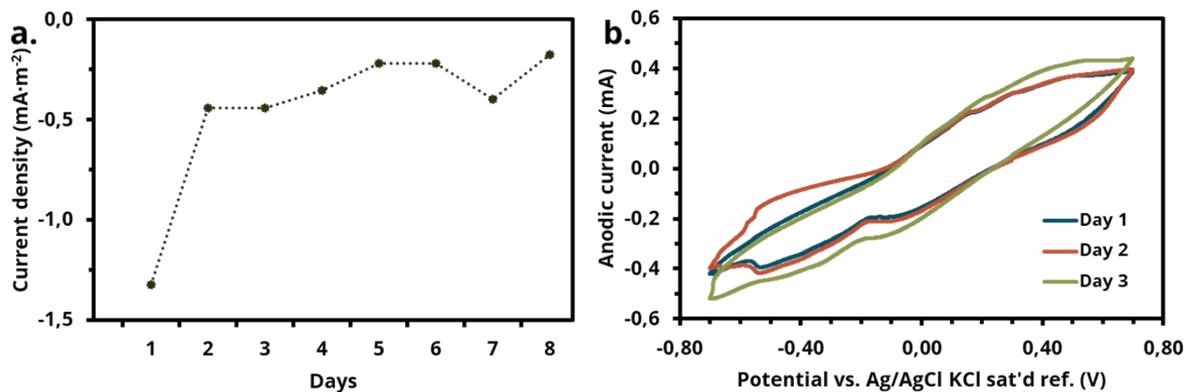


Figure S6. Electrochemical characterization of a control two-compartment MFC including a sterilized dual bioanode polarized at +0.3 V vs. the reference (electrospun from a 10 wt% PAN in DMF solution, stabilized under air at 280 °C, carbonized under argon at 940 °C, thickness of 81 μm). **a.** Evolution of the average current density. **b.** Evolution of cyclic voltammetry as a function of; sweep rate of $1 \text{ mV}\cdot\text{s}^{-1}$; 3 cycles are acquired, here is the second one. Current and power are normalized by the geometric surface area of the electrospun carbon electrode (anode diameter is 1.7 cm; geometrical surface area is approximately 2.27 cm^2). The anolyte is MR1-L medium; the catholyte is 150 mM of NaCl (supporting electrolyte) and 100 mM of $\text{K}_3[\text{Fe}(\text{CN})_6]$.

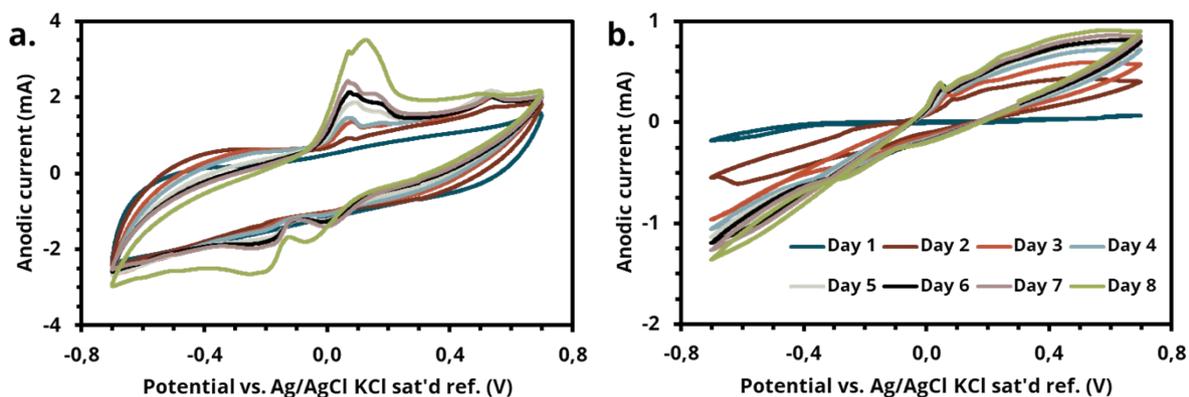


Figure S7. The integrated bioanode as a microbial fuel cell anode **a.** Evolution of cyclic voltammetry at $1 \text{ mV}\cdot\text{s}^{-1}$ for a fresh bioanode ($h \approx 293 \mu\text{m}$), **b.** For a bioanode cryodesiccated prior to MFC integration ($h \approx 410 \mu\text{m}$).