Does it have to be Carbon? Metal Anodes in Microbial Fuel Cells and related Bioelectrochemical Systems

SUPPORTING INFORMATION

Preparation of Metal plated graphite electrodes (MPG electrodes)

The manufacturing details were as follows: Silver powder (5 µm – 8 µm, ≥ 99.9% trace metals basis) and copper powder (< 425 µm, 99.5% trace metals basis) were purchased from Sigma-Aldrich. Nickel powder was precipitated from $NiCl_2 \cdot 6\,H_2O$ (Fluka >98%) [21] and gold powder was precipitated from $AuCl_3$ in aqueous solution with hydrazine hydrate (Merck 99%). Graphite plates (CP Graphite GmbH, Germany) were cut into pieces of 10 mm x 10 mm and were polished by rubbing the surface over a sheet of paper. The respective metal powder was transferred into an Al_2O_3 crucible. This was placed in a vacuum vaporizer device (Mini Spectros, Kurt j. Lesker, USA), set at a pressure of $5x10^{-7}$ mbar. Now, the crucible was heated until a deposition of 40 nm metal was archived with a deposition rate of 0.1 nm s^{-1}. The samples where flushed with argon and were removed from the device.

Figure S1: Exemplary scheme of the preparation of metal plated graphite electodes (here: gold electrode). Electrode billet (left), gold plated electrode (center), and electrode connected via stainless steel wire (right).

Each metalized graphite plate was connected via a stainless steel wire. A hole (d = 1.2 mm) was drilled 0.5 cm deep into the graphite plate. The end of the stainless steel wire (d = 0.6 mm) was folded to a double layer and squeezed into the hole leading to a stable mechanical connection and a high conductivity. Here, the immersion of conductive silver paint (Busch silver paint, Busch GmbH & Co. KG, Germany) into the hole improves the conductivity of the connection. All sides of the electrode except the metalized surface were insulated by applying a two-component non-conductive epoxy resin (“5 min Epoxy”, R & G Faserverbundwerkstoffe, Germany). In a final step the stainless steel wire was insulated with a heat shrinking tube (Figure S1).

Dependence of the biofilm formation and the biocatalytic electrode performance on the applied electrode potential

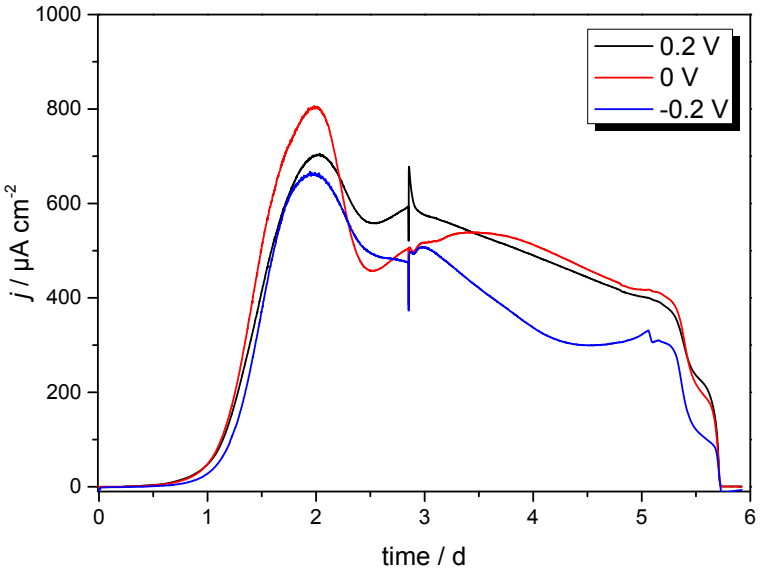

Figure S2: Exemplary cultivation and the resulting bioelectrocatalytic current generation of a secondary, acetate based electrochemically active biofilm at a gold electrode in a batch experiment. The biofilm was cultivated in a half-cell setup under potentiostatic control. The electrode potential was set at constant -0.2, 0 and +.0.2 V (vs. Ag/AgCl).

Cyclic voltammetry of electrochemically active biofilms

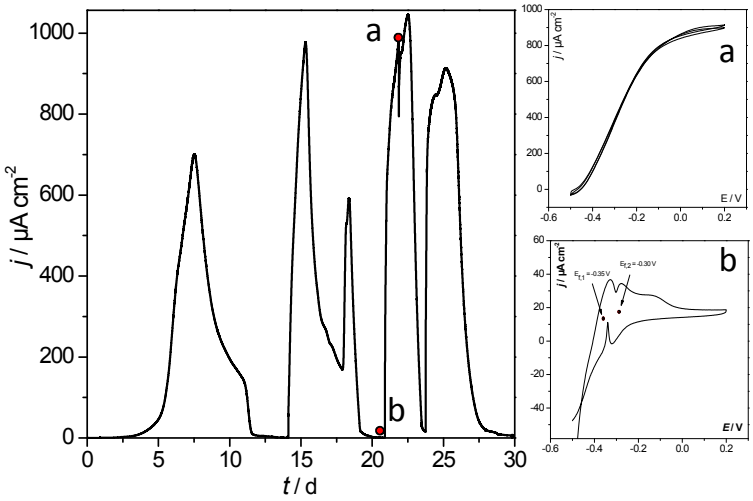

Figure S3. Main Figure: Exemplary cultivation and resulting bioelectrocatalytic current generation of a **secondary**, acetate based electrochemically active biofilm at polycrystalline graphite in a semi-batch experiment. The biofilm was cultivated in a half-cell setup under potentiostatic control. The electrode potential was 0.2 V (vs. Ag/AgCl). Right figure column: **a**: cylic voltammogram recorded under turnover conditions (depicted by the red dot indexed “a” in the main figure). **b**: cylic voltammogram recorded under non-turnover conditions (depicted by the red dot indexed “b” in the main figure).

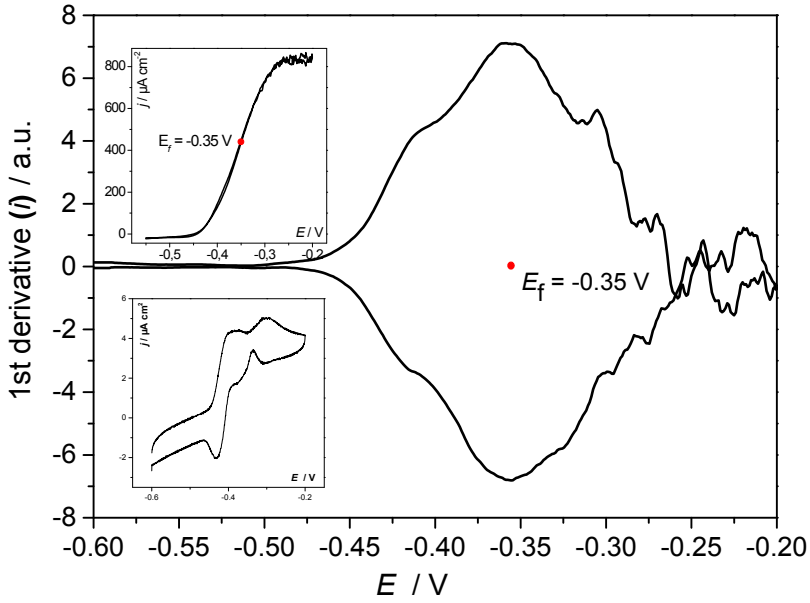

Figure S4: Cyclic voltammogram of a secondary, acetate based electrochemically active biofilm at a copper electrode, recorded under turn-over conditions (upper inset figure) and the corresponding first derivative of the voltammetric curve over the potential (main figure). The lower inset figure depicts a cyclic voltammogram recorded under non-turnover-conditions.

Voltammetric behaviour of selected electrode materials in the absence of a microbial biofilm

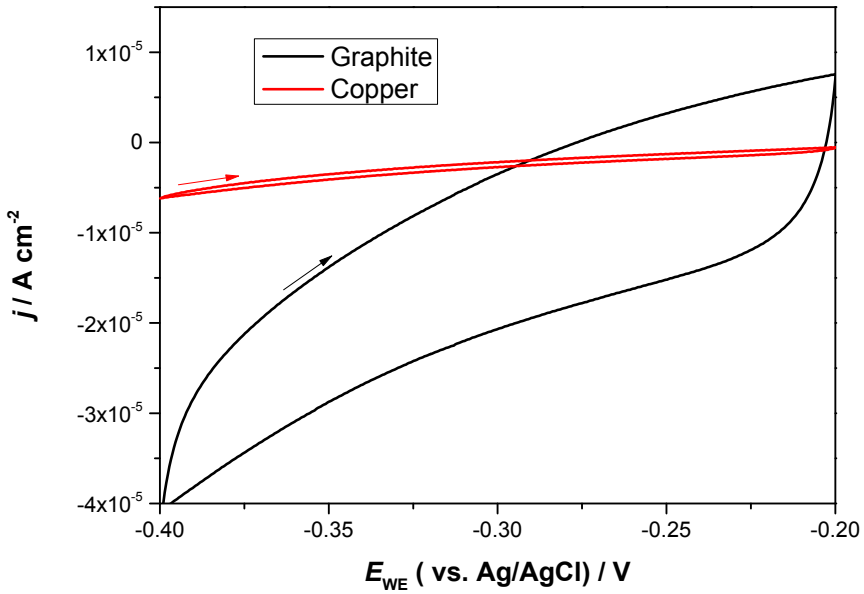

Figure S5. Comparison of the cyclic voltammograms of copper and graphite in sterile bacterial growth medium ("artificial wastewater"). The scan rate was 10 mV s^{-1}. No voltammetric/redox features of the electrode materials or of the growth medium are visible. The polycrystalline graphite electrode exhibits significantly larger capacitive currents than copper due to its porous structure.

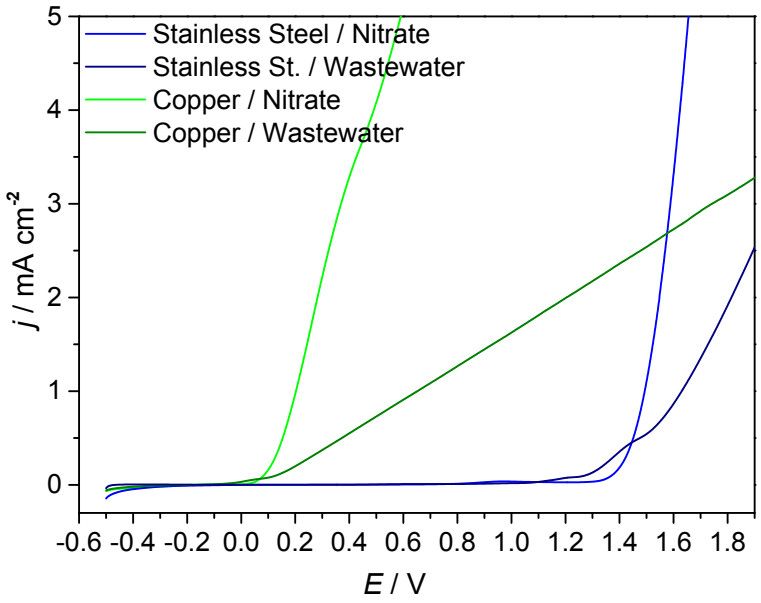

Figure S6. Oxidative linear sweep voltammograms of blank copper and stainless steel (metal sheets), recorded in 0.1 M potassium nitrate solution, as well as in filtrated primary wastewater (Scan rate 1 mV s^{-1}. The wastewater had a pH of 7 and a conductivity of 1.21 $mScm^{-1}$.