

Fuel Cells

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Interfacing Electrocatalysis and Biocatalysis with Tungsten Carbide: A High-Performance, Noble-Metal-Free Microbial Fuel Cell**

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Microbial fuel cells (MFCs) produce electricity by utilizing the metabolism of living microorganisms to catalyze the oxidation of organic or inorganic substrates for electricity generation. Different concepts and mechanisms for electron transfer from the biocatalyst to the anode of the fuel cell have

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been proposed.^[1] Thus, direct electron transfer to the fuel-cell anode via membrane-bound cytochromes (for example, *Geobacter* species,^[2] *Rhodospirillum rubrum*^[3]) is possible (Figure 1a); however, this method so far delivers current

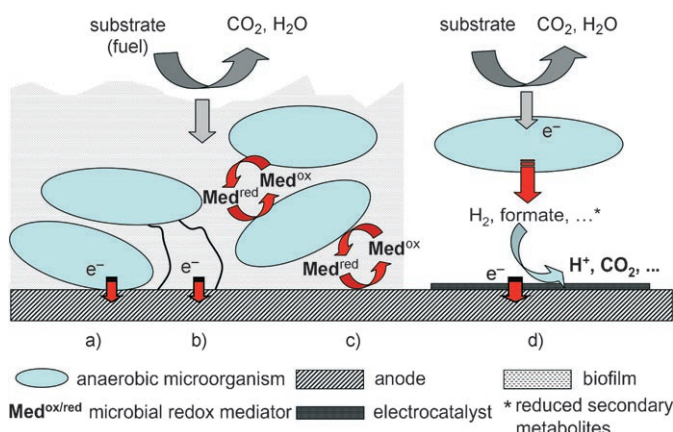


Figure 1. Identified electron-transfer mechanisms in MFCs. Electron transfer via a) cell-membrane-bound cytochromes, b) electrically conductive pili (nanowires), c) microbial redox mediators, and d) oxidation of reduced secondary metabolites.

densities as low as $3 \mu\text{A cm}^{-2}$.^[3] Alternatively, direct electron transfer can also take place through conductive bacterial pili (“nanowires”), as was recently demonstrated for *Shewanella oneidensis* MR-1 (Figure 1b).^[4] Electrochemically enriched microbial biofilm consortia show a very promising performance.^[5–7] Herein, bacterial redox mediators are assumed to enhance electron transport to the anode and between multiple cell layers^[8] (Figure 1c). For high MFC performance, however, selection procedures of over 70 days seem necessary.^[9]

We have focused our research on the exploitation of electron-rich microbial metabolites as fuels (electron shuttles) for electricity generation (Figure 1d). For this approach, we have developed robust and yet highly effective electrocatalytic anode catalysts based on platinum–polyaniline^[10] and platinum–poly(tetrafluoroaniline)^[11] sandwich materials that allow the efficient in situ oxidation of microbial hydrogen, that is, in the microbial cultures. Current densities up to 1.5 mA cm^{-2} , short lag times, and a great versatility to exploit fermentative,^[12,13] photofermentative,^[14] and even purely photosynthetic^[15] microbial activity set new standards for MFC performance.

So far the expensive electrocatalyst, the lack of suitable oxygen reduction cathodes, and the use of bacterial monocultures have been the main disadvantages of this promising approach. We now present a MFC that overcomes these problems. The major cornerstone is a noble-metal-free and yet highly efficient MFC anode based on tungsten carbide (WC) that allows current densities of presently up to 3 mA cm^{-2} to be reached. By combining this electrocatalytic anode with an oxygen reduction cathode based on pyrolyzed Fe^{III} phthalocyanine (pyr-FePc)^[16,17] and hydrogen-producing soil bacteria that serve as biocatalysts,^[18] we can report herein

a fully noble-metal-free high-performance MFC that reaches a maximum power density of $585 \mu\text{W cm}^{-2}$ (5.85 W m^{-2}).

Figure 2a shows the current generation at a WC-modified graphite electrode immersed in a glucose substrate solution freshly inoculated with heat-treated soil. The electrode was potentiostatically poised at a potential of 0.2 V (vs Ag/AgCl) to allow the anode performance to be studied unaffected by the cathode performance. The small size of the anode (0.19 cm^2) in relation to the large volume of the substrate solution (0.25 L) in these experiments guarantees that there is only a negligible feedback of the electrode reaction on the microbiological processes. This condition is important as, in contrast to biofilm-based MFCs, the use of microbial suspensions allows the electrochemical and biocatalytic performances to be separated. In experiments with biofilms on

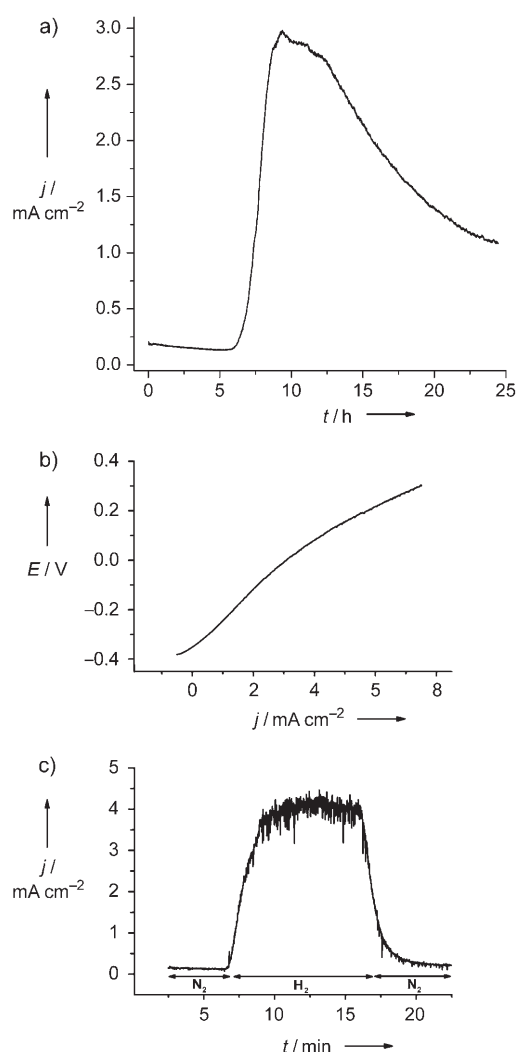


Figure 2. a) Current generation in an anaerobic glucose substrate solution (5 g L^{-1}) inoculated with heat-treated soil. The working electrode was a WC-modified graphite disk poised at a potential of 0.2 V and the temperature was 37°C . b) Galvanodynamic experiment performed in the fermenting medium of (a). The scan rate was $10 \mu\text{A s}^{-1}$. c) Current–time measurement as in (a), but performed in sterile phosphate buffer (100 mM, pH 7) and hydrogen/nitrogen purged.

electrodes, the amount of biocatalyst is inextricably dependent on the size of the anode. As can be seen in Figure 2a, the current flow starts after a lag time of only seven hours. The current is caused by the electrocatalytic oxidation of reduced metabolic products (mainly hydrogen and formate) of the commencing fermentation of glucose by the anaerobic culture that develops from the soil inoculum. The current reaches a maximum density of 3 mA cm^{-2} (geometric surface area). Such a large peak current density has never been reported before, and it even exceeds our results with platinum–polyaniline sandwich electrodes.^[10,11] After about 12 hours the current density decreases because of substrate exhaustion in the medium. The excellent performance of the WC-modified graphite disk electrode can also be derived from galvanodynamic polarization experiments (see Figure 2b), which show that high current densities are achieved even at rather negative potentials. Thus, at a potential of -0.1 V the current density still exceeds 2 mA cm^{-2} . By feeding hydrogen gas into the medium the measured current density even went up to 4 mA cm^{-2} (Figure 2c). The oxidation of formate (0.2 M) in phosphate buffers yielded current densities of 1.9 mA cm^{-2} (data not shown).

Since the studies of Böhm in the early 1970s,^[19] WC has been discussed as a possible replacement for platinum as an electrocatalyst for hydrogen oxidation.^[20–22] It has also been shown to possess good electrocatalytic properties toward the oxidation of formate,^[23,24] but it could not fulfill the demands of chemical fuel cells. MFCs do not require this high oxidation performance, as the power generation is limited by the rate of bacterial metabolism, but they do require cheap, robust, and biocompatible anode materials. As the results described above indicate, WC fulfills these prerequisites for an excellent MFC anode catalyst. It also possesses the ability to catalyze several different pathways for the oxidation of inorganic and organic metabolites, for example, hydrogen and formate. This is of prime importance for achieving high conversion efficiencies.

MFC polarization experiments confirm the results of the half-cell measurements. In combination with an oxygen reduction cathode based on pyr-FePc,^[16,17] an open-circuit potential of 864 mV is achieved (Figure 3). The maximum power point (MPP) of $585 \text{ } \mu\text{W cm}^{-2}$ (5.85 W m^{-2}) at a current density of 1.6 mA cm^{-2} represents the highest power density measured in a MFC thus far.

In summary, we have introduced a high-performance, noble-metal-free MFC, and have shown that the cheap and yet effective catalyst WC allows electrocatalysis to be effectively interfaced with biocatalysis. By using a WC anode, pyr-FePc as cathode catalyst (oxygen reduction), and soil-based bacteria as biocatalysts, the performance of MFCs can be significantly increased with concurrently improved robustness and low costs.

Experimental Section

Catalyst synthesis: WC powder was prepared from $\text{WO}_3 \cdot \text{H}_2\text{O}$ in a tube oven under a CO stream for 10 h at 800°C .^[25] CO was provided by dropping dry HCOOH into hot oleum at a rate of two to three drops per minute.^[26]

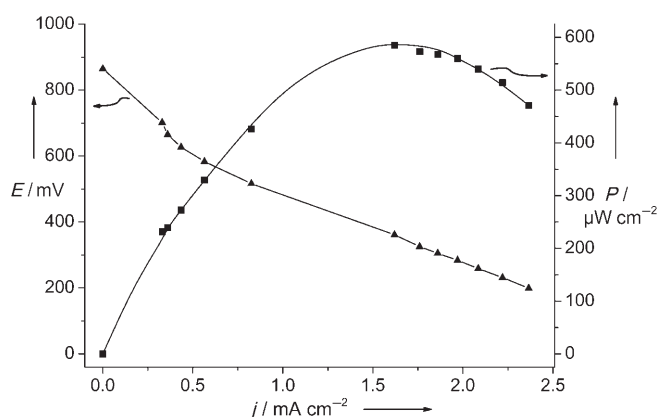


Figure 3. Polarization (■) and power (▲) curves of a MFC experiment using a WC-modified graphite disk as the anode. The substrate was glucose (5 g L^{-1}) and the biocatalyst inoculum was heat-treated soil.

Electrode preparation: For anode preparation, WC powder was mechanically pressed onto a carbon support (10 mg cm^{-2} ; graphite disk electrodes, paraffin impregnated,^[27] $\varnothing 4.9 \text{ mm}$, geometrical surface area 0.19 cm^2 , Elektrokohle, Lichtenberg) using 5% Nafion solution as binder. Anodes based on platinum–poly(tetrafluoroaniline) catalyst were prepared by the electrodeposition of platinum black and subsequent polymer coating as described elsewhere.^[11] The cathode was prepared by coating graphite foil (geometrical surface area 55 cm^2) with pyrolyzed iron(III) phthalocyanine^[16]/polytetrafluoroethylene (pyr-FePc/PTFE). The catalyst load was 1 mg cm^{-2} .

Biocatalyst: Foliage/dung soil from the botanical garden (University of Greifswald) was pretreated for 2 h at 120°C to select spore-forming microbes. Sieved soil (2 g) was inoculated into culture medium (250 mL): at the beginning, mineral medium as in reference [18] containing glucose (5 g L^{-1}) was used; later only glucose (5 g), NH_4HCO_3 (2 g), and aqueous KH_2PO_4 (3.6 g L^{-1}) were employed. The culture medium was purged with nitrogen for 15 min prior to inoculation and cultivated anaerobically at 37°C .

Electrochemical systems: Experiments were conducted in a batch-type two-chamber model fuel cell.^[14] The cathode compartment was filled with phosphate buffer (250 mL , 50 mM , $\text{pH } 4.4$) and was purged with air using a fish pump. The anode compartment was filled with the soil bacterial solution. The anode and cathode compartments were separated by a Nafion 117 proton-exchange membrane. The monitoring of redox potentials and currents under different external resistance loads was performed with a data acquisition system (Keithley Integra 2700 digital multimeter) interfaced to a personal computer. The electrochemical (half-cell) characterization of the WC anodes was carried out galvanostatically or potentiostatically in a conventional three-electrode arrangement, with a graphite rod as counter electrode and a Ag/AgCl electrode (saturated KCl, 0.197 V vs normal hydrogen electrode (NHE)) as the reference electrode. All electrode potentials refer to this reference electrode. The experiments were carried out with PSTAT10, PGSTAT20, and PGSTAT30 potentiostats (Ecochemie, Netherlands). The PGSTAT30 was equipped with five array modules that allowed multiple working electrode measurements. The counter electrode was separated from the working electrode(s) by a Nafion 117 perfluorinated membrane.

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