Layered corrugated electrode macrostructures boost microbial bioelectrocatalysis†

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The future success of microbial bioelectrochemical systems like microbial fuel cells inevitably depends on the increase of their performance at decreasing material costs.1–3 One of the key elements and a research priority is the biofuel cell anode. Here we propose layered corrugated carbon (LCC) as an inexpensive but high-performance electrode material produced from the carbonization of one of the most abundant packing materials of our society: corrugated cardboard. In the base configuration of one corrugated layer the projected current density of LCC already reaches 70 A m⁻². Increasing the number of corrugated layers increases the current density linearly. Thus, 200 A m⁻² are achieved at three and 390 A m⁻² at six corrugated layers. These current density values, which were confirmed by experiments in two independent laboratories, represent a performance increase of above one order of magnitude compared to the current state of research.

The last decade has seen tremendous progress in the development of microbial bioelectrochemical technologies. For this development, the concept of directly coupled wastewater treatment and energy (electricity) recovery from wastewater by means of microbial fuel cells (MFCs) is a major application target and driving force.4 Further concepts like microbial electrolysis,5 electrosynthesis,6 reverse-electrodialysis,7 and desalination cells8 strongly expand the spectrum of potential applications for microbial bioelectrochemical systems (BES). During the past decade BES performance has increased remarkably. Especially the exploitation of biofilm anodes, i.e., electrodes based on the activity of electrochemically active (“electrode respiring”) microbial biofilms9,10 made developments towards large scale conceivable.

Yet – despite the recent progress – the further increase of the biofilm anode performance is still a key issue for the future BES success.1–3 The current density of high-performing anodic microbial biofilms at flat, macroscopically smooth, electrode surfaces (e.g., at smooth polycrystalline graphite) reaches about 1 mA cm⁻². A further increase appears to be hampered especially by the rate of substrate and proton transfer within the biofilms.12–14 Several three-dimensional materials were proposed in order to increase the projected current density by increasing the total surface area per electrode footprint area. Examples are carbon felt/paper and carbon brush electrodes,15 carbon fibers16 and foams.17 Recently, we have demonstrated on the example of electrospun carbon fiber networks that an optimized electrode microstructure significantly improves the current densities to values about 3 mA cm⁻².18

In the present study we demonstrate that the development of an optimum material macrostructure, which allows an unhindered substrate supply and product removal, results in a significant boost of the anode performance. The precursor material is available at low costs and in large quantities: corrugated fiberboard. Corrugated

Broader context

The core function of microbial fuel cells (MFCs) and of related microbial bioelectrochemical systems (BES) is based on the ability of their anode to biocatalytically oxidize complex organic matter and to efficiently convert the chemical energy into a current flow. Thereby the anode can be considered as the heart of the bioelectrochemical system. The great majority of BES anodes utilize electroactive bacterial biofilms as the electrocatalytic unit, a concept that has great potential towards a technical realization. The performance of a BES anode decisively depends on the used electrode material. Especially three-dimensional electrodes with optimized microstructures have been shown to increase the electrode performance considerably. In this manuscript we demonstrate that tailoring the electrode macrostructure opens new possibilities to boost the anodes performance. We propose layered corrugated carbon electrode – produced from the cheap resource corrugated fiberboard – as a high-performance electrode material with an optimum macrostructure that allows reaching current densities of up to 40 mA cm⁻² (400 A m⁻²).
fiberboard is a paper-based material that, in the case of a single wall corrugated cardboard, consists of one fluted (corrugated) sheet sandwiched between two flat linerboards. By means of carbonization this insulating material is transformed into a carbon scaffold that retains the original macro-(channel) structure, a structure that we denote here as layered corrugated carbon (LCC, see photographic electrode image in Fig. 1b). A detailed list of the studied electrode materials, their denomination, and their bioelectrochemical performance is provided in Table S2 of the ESI.† Further, an analysis of the morphology and the chemical parameters of the electrode material is provided in the ESI.†

In Fig. 1a the course of the bioelectrocatalytic current generation at a single layer LCC anode (LCC-2.9) is illustrated from the moment of inoculation with preselected, wastewater derived electroactive bacteria, until an electroactive biofilm is formed (Fig. 1d and e) and the electrode reaches a stationary current level.

At comparable electrode thickness the projected current density (i.e., the current normalized to the projected surface area (footprint area) of the electrode) at the corrugated electrodes exceeds all previously reported electrode materials. For instance, an LCC electrode with an electrode thickness of 2.2 mm delivers a current density of \( j_{\text{projected}} \approx 7 \, \text{mA cm}^{-2} \) (LCC-2.2, \( W = 10 \, \text{mm} \)), whereas the current density at conventional carbon felt (2 mm thickness) is \( 1.6 \, \text{mA cm}^{-2} \). This means that the volumetric current density, which refers to the total volume of the 3D electrode, increases four-fold compared to conventional carbon felt. The cyclic voltammograms of the biofilm electrodes (inset figure in Fig. 1a) under turnover and non-turnover conditions are virtually identical in shape and formal potentials to those obtained for Geobacteraceae dominated electroactive biofilms in previous studies.18–22 As shown in Table S2,† the projected current density of the flat liner layer (the non-corrugated part of the electrode material) is \( 1.38 \, \text{mA cm}^{-2} \), a value that does not exceed the average range of common (fibrous) carbon electrodes. The above results demonstrate that it is not the material composition or the microstructure but rather the macrostructure that is responsible for the strongly enhanced electrode performance.

To evaluate the effects of the macrostructure, different electrode geometries were systematically investigated (see Table S2† for details). The results show that the height of the flute layer (\( H_f \)) has a decisive impact on the LCC performance (Fig. 2a). Thus, \( j_{\text{projected}} \) increases by a factor of 1.5 from \( H_f = 1.4 \, \text{mm} \) (4.68 mA cm\(^{-2} \)) to \( H_f = 2.2 \, \text{mm} \) (7.02 mA cm\(^{-2} \)) – most likely caused by an improved substrate supply into the wider channels. Above a flute height of \( H_f = 2.2 \, \text{mm} \) the projected current density levels off, which leads to a decreasing volumetric current density at further increasing \( H_f \) values (Fig. 2b).

A close look at Table S2† reveals that the geometric current density (i.e., the current normalized to the geometric surface area of all electrode parts that face the electrolyte solution and thus allow biofilm settlement) of the LCC materials is comparable to data of carbon paper electrodes, at which current densities between 1.0 and 1.5 mA cm\(^{-2} \) are achieved.16 This strongly supports the finding that the LCC microstructure plays only a minor role for the high electrode performance.

The most remarkable feature of the new electrode design is its stackability. The assembling of multiple cardboard layers on top of
each other (sandwiching) before carbonization leads to a respective multi-layer LCC with a scaled current output. As can be seen in Fig. 3a, a triple layer electrode achieves a projected current density of nearly 20 mA cm$^{-2}$. As shown for up to six layers (Fig. 3b), the linear current increase with the number of layers can be described with $I_{\text{projected}} = (6.4n + 1.37)$ mA cm$^{-2}$ with $n$ being the number of corrugated layers. The constant 1.37 mA cm$^{-2}$ represents the contribution of the respective upper surface of the terminal liner layer of the multilayer system. The value is in agreement with the current density of the pure LCC liner of 1.38 mA cm$^{-2}$ (Table S2†). A six-layer LCC electrode (hexa-LCC, $W = 42$ mm $L = 9.5$ mm, $H_e = 18$ mm) achieved an absolute current of 151 mA (illustrated in Fig. S5†), corresponding to a projected current density of 39 mA cm$^{-2}$ (Fig. 3b).

The linearity of the current density increases and the only slightly decreasing volumetric current densities of the stacked electrodes emphasize the efficiency of the layer concept. They illustrate that the maximum possible number of layers and thus the maximum projected current density are certainly not yet achieved.

In summary, the proposed layered corrugated electrode structure represents an important advancement in the design of anodes for the exploitation of microbial bioelectrocatalysis (e.g. microbial fuel cells or in microbial electrosynthesis). The importance of the macrostructure of the electrode has been clearly proven and it has been demonstrated that such efficient macrostructures can be achieved using a low-cost electrode precursor. The forthcoming work will now concentrate on proving the presented electrode concept under application oriented conditions. The material will be studied using different types of real wastewater, issues like long term performance, up-scaling and mechanical stability will be addressed.

Materials and methods

The results in this study are based upon independent sets of experiments in two laboratories: at the Jiangxi Normal University (JNU), China and the Technische Universität Braunschweig (TUBS), Germany.

Electrode material and its preparation

Single wall corrugated cardboard (Licheng Paper Products Co., Ltd, China), produced from recycled paper and consisting of one flute layer, sandwiched between two liner layers was used as the precursor for electrode preparation. Four cardboard materials were used differing in their flute heights: $H_e = 1.4$ mm, 2.2 mm, 2.9 mm and 3.2 mm. As Fig. 1c depicts by means of an energy-dispersive X-ray spectroscopy (EDX) analysis no potential electrocatalytic impurities such as iron were found in the material, hence, the material was processed as received, without purification.

Preparation of layered corrugated carbon, LCC. The cardboard material was cut into pieces of the desired size (e.g., $1 \times 1$ cm$^2$). For experiments involving single face LCC and for the preparation of multiple layer LCC the upper liner layer was removed and the respective number of corrugated layers were assembled using a corn starch glue (5 g of corn starch dissolved in 10 mL of distilled water at room temperature to form a suspension that was heated to boiling to form a viscous solution before usage). The resulting cardboard materials were carbonized for 1 hour in a high temperature furnace (Yuandong Instrument and Meter Plant, China) at 1000 $^\circ$C under N$_2$ atmosphere, with a N$_2$ flow rate of about 100 cm$^3$ min$^{-1}$. Subsequently, the LCC samples were glued onto same sized graphite plates serving as the current collector (see Fig. 1b), using a conductive two-component epoxy resin mixed with carbon black powder (Vulcan XC-72). All exposed sides of the current collector were insulated by pure epoxy resin. The resulting LCC electrodes served as habitat for the preparation of biofilm electrodes, i.e., electrodes modified by an electroactive biofilm.

Sample denomination. For the electrode denomination two parameters are important: the number of flute layers and the flute height. Thus, single-LCC-2.9 denotes a single flute layer material with a flute height of 2.9 mm. Single-flute electrodes were often also abbreviated as, e.g., LCC-2.9 (see also Table S2†).

Bioelectrochemical experiments

The bioelectrochemical experiments were conducted under anoxic conditions and under potentiostatic control. The electroactive microbial biofilms were grown and studied in half-cell semi-batch experiments at a potential of 0.2 V vs. Ag/AgCl and a temperature of

![Fig. 3](image-url)
35 °C. To assure comparability and reproducibility across the biofilm electrodes usually six electrodes were prepared and tested simultaneously in one 500 mL electrochemical cell. Besides the working electrodes the electrochemical cells contained one reference electrode (Ag/AgCl, sat. KCl, 0.195 V vs. standard hydrogen electrode; JNU: Tianjing Aida Electronic Co., Ltd, China; TUBS: Sensortechnik Meinsberg, Germany) and a carbon felt (JNU) or carbon rod (TUBS) counter electrode. The following potentiostats were employed: JNU – CHI1040B (Shanghai Chenhua Instrument Co., Ltd, China) and TUBS – Autolab 30 (Ecology, Netherlands), each equipped with six working electrode channels allowing individual working electrodes to be addressed. As internal standards polycrystalline graphite rods (JNU: Hunan Jiuhua Carbon High-tech Co., Ltd, China; TUBS: CP Graphite GmbH, Germany) and graphite felt (JNU: Hunan Jiuhua Carbon High-tech Co., Ltd, China) were used as working electrodes together with the LCC-materials.

All experiments were conducted under continuous stirring in aerated artificial wastewater (NaH$_2$PO$_4$ $\times$ 2H$_2$O (2.69 g L$^{-1}$), Na$_2$HPO$_4$ (4.33 g L$^{-1}$), NH$_4$Cl (0.31 g L$^{-1}$), KCl (0.13 g L$^{-1}$), 12.5 mL trace metal and 12.5 mL vitamin solution$^9$ containing 20 mM acetate as the electron donor (substrate). The bacterial source for the primary biofilm formation was primary wastewater from the local wastewater treatment plants QingShan (Nanchang, China) and Steinhof (Braunschweig, Germany), respectively. For the electrode tests, pre-selected bacterial cultures based on primary electroactive biofilms were used, as described in ref. 26.

The current–current density data reported in this paper correspond to the maxima of the respective semi-batch cycles. The data are based on at least three independent biofilm replicates with at least three to seven semi-batch feeding cycles per biofilm. The standard deviation values for the performance data are provided in Table S2.$^+$ Cyclic voltammograms were performed for turn-over and non-turnover conditions according to ref. 19.

**Bioelectrocatalytic electrode material characterization**

The following parameters were used to evaluate the material performance: the *projected current density*, $j_{\text{geometric}}$, denotes the current related to the projected surface area (footprint area) of the electrode. The footprint area is of great technical relevance and is gained by the geometric dimensions (length \times width) of the electrode. The *geometric current density*, $j_{\text{geometric}}$, denotes the current related to the total geometric area, $A_{\text{geometric}}$, of the electrode. Here, $A_{\text{geometric}}$ comprises the geometric surface area of all electrode parts that face the electrolyte solution (i.e., LCC outer and inner liner and flute areas) and thus allow biofilm settlement. Here we assessed $A_{\text{geometric}}$ by two means (i) using a trigonometry based approximation procedure approved by (ii) digital photography (TESCAN vega 3, Czech Republic) and subsequent digital image measuring. Both approaches showed a deviation of less than 3%. The *volumetric current density*, $j_{\text{volumetric}}$, denotes the current related to the volume of the LCC, V.$^\circ$ The volume is gained from the geometric dimensions (width \times length \times height) of the LCC material and comprises the carbon material and void space (Fig. 1b).

**Biofilm imaging**

The biofilm morphology was characterized by scanning electron microscopy (SEM). The preparation of biofilm samples for SEM characterization was performed as follows:$^{27}$ biofilm samples were fixed by 5 wt% glutaric aldehyde dehydrated in a graded series of ethanol aqueous solution and naturally dried at room temperature, coated with gold and subsequently examined under a TESCAN vega SEM.

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