Developing Cheap and Mass-Prodicable Graphite-Filled Paper as an Anode Material for Microbial Electrochemical Technologies

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This study details, in-depth, the development of graphite paper as electrodes, specifically anodes, for microbial electrochemical technologies. Processed natural graphite powders were used as an active filler substance in paper composites. Mechanical and electrical properties were balanced during development. Graphite papers with 80 wt% natural graphite content had tear lengths of 730 ± 58 m and resistivities of 0.014 ± 0.001 Ω cm. Electrochemically active biofilms on these materials, cultivated from biomass taken from the bioanodes of an already running bioelectrochemical reactor, were fed with acetate and yielded an average maximum current density of 0.855 ± 0.135 as well as 0.489 ± 0.148 mA cm⁻² with a complex substrate mixture. All anodes exhibited similar performance to commonly used carbonaceous electrodes fed the same substrates. This places them as flexible and cheap electrode materials suitable for large-scale microbial electrochemical technologies.

1. Introduction

Primary microbial electrochemical technologies (MET)[1] share a common core component: electrochemically active bacteria (EAB), which in microbial fuel cells or electrolysis cells participate in the transformation of the chemical energy contained in organic wastewater substances into electrical energy or chemical energy carriers. In a MET, EAB utilize the electrode i.e. anode as an electron sink by performing extracellular electron transfer (EET) using e.g. membrane-bound cytochromes or pili.[2] EAB use these interactions to form biofilms at the solid-liquid interface of the electrode. In addition to requirements such as biocompatibility or chemical and mechanical stability, anode materials must have low a resistivity and be easy as well as cheap to produce, in order to be considered for large-scale applications.[3,4]

Much effort has been invested into designing 3-D anodes,[5–8] developing carbon-based polymer composites, coatings as well as conductive hydrogels[9–11] and by selecting new graphite grades[12] which could sustain high performance in scaled-up applications.

One of the major challenges to effectively scaling up MET is reduced to about 5 m² for at least 100 m² anode per m³ of anode chamber, while maintaining a high treatment capacity around 1 mA cm⁻² to make MET competitive versus other treatment options.[5]

As such, the undertaken research aims to provide a high quality and cheap bioanode material, which can be formed into high anode surface area to anode volume-ratio electrodes.

Paper is a product, which is manufactured by the millions of tons each year and is present in many areas of daily life. With retail prices for 200 gm⁻² copier paper being under 1 € m⁻² (incl. 19% VAT, Germany), for example, paper is potentially a good base material for MET bioanodes. The main component of paper or paper pulp, used for production, is cellulose with small amounts of hemicellulose and lignin. Cellulose is a biopolymer that is highly accessible and has been successfully employed as structural component in graphite composite electrodes for Li-ion batteries.[13–15] Its ability to absorb electrolytes and good ionic conduction in wet environments makes its also interesting for development of new electrode materials for energy storage e.g. super capacitors.[16]

In order to get from a non-conductive paper to a viable bioanode material, a conductive filler in the form of graphite flakes are added. The resulting papers are specialty papers with “filler” contents up to 80 wt% (weight percent). In this study, we present an in depth characterization of graphite papers, which were produced using conventional paper production techniques as the first step in the development of potential alternative anode materials for large-scale MET. The novel materials were evaluated for their potential application in large scale MET based on mechanical, electrical and bioelectrochemical performance indicators.

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Experimental Section

All chemicals used in this study were, if not otherwise stated, purchased from Sigma Aldrich or Carl Roth, Germany, and were of analytical grade purity.

Graphite Paper Preparation and Evaluation Methods

The graphite papers were developed as part of the “ElektroPapier” Project (BMBF-MachWas Grant nr: 03XP0041) and were produced by the Papiertechnische Stiftung (PTS - Heidenau, Germany). Filtered and heated treated natural graphite (SC 20 OS; S-type) and expanded flakes thereof (EXG 98 25/50, E-type) were used as the conductive filler in the paper matrix. The graphite was supplied to the PTS by another project partner Graphit Kropfmühl (AMG Graphit Kropfmühl, Germany). These two graphite types were chosen for further research based on the resistivity of graphite papers, shown in Figure SI-1, which were produced and measured as the initial part of this study.

Circular sheets of graphite paper were formed using the “Rapid Köthen” process. The resulting sheets had an area density of 200 g m⁻². This was determined in accordance with DIN EN ISO 536:2012-11 using an analytical balance with an accuracy of 1/1000 g (Sartorius). The paper matrix contained different wt% of graphite, < 3 wt% starch, 1.5 wt% latex as the main binder, < 1 wt% retention aid and the rest was long and short fiber pulp.

A laboratory calender (Jagenberg Paper Systems GmbH, Germany) with one hardened and polished steel roll with a diameter of 150 mm and a softened steel roll covered with polymer with a diameter of 200 mm was used for calendering the paper filled with graphite. The pressure is given as the line load applied perpendicular to the calendering direction. All samples were calendered with a line load of 90 kN/m at a temperature of 60 °C. Later samples produced with a paper machine were calendered perpendicular to the machine direction. The effect of the compression on the paper was tested by calendering graphite papers with different wt% of S-type graphite 2, 4 and 6 times.

For the paper evaluation, the resistivity \( \rho \) (Ω cm) of the composites was determined by measuring the resistance of at least five samples of known dimensions, while employing the 4-wire technique. This was done using a source measurement unit (SMU, Model 2701, Keithley, USA). An example of the 4-wire measurement is shown in Figure SI-2.

The tensile strength was determined in accordance with DIN EN ISO 1924–2:2009-05 using a universal testing machine (TIRAtest 2703, Tira, Germany) with a 2 kN load cell. The strain was monitored while the test specimens (cut from machine direction [MD] and cross-machine direction [CD] from machine produced graphite papers) were elongated with a constant rate of elongation. The elongation speed was 20 mm/min for a clamping length of 100 mm. The strip width was 15 mm. With the tensile test, the following values can be determined/calculated also using the area-related mass and thickness:

- Width-related breaking load
- Tearing length
- Bending stiffness, etc.

Materials with different basis weight are thus approximately comparable in terms of tensile strength.

Electrochemical Setup

All bioelectrochemical experiments were carried out in 250 mL three-neck glass reactors using a three-electrode arrangement. The tests were monitored using a multi-channel potentiostat (MPG2, BioLogic, France). The counter electrodes were made from stainless steel mesh (EN 1.4401, trade name: V4 A, Ohlendorf, Germany), with 1.5 mm nominal opening, 0.18 mm wire diameter. Two-layers were folded into an 11 × 7 cm rectangle and made as a surface area of ~34.1 cm² of the wires and connected to a stainless-steel wire. As the reference an Ag/AgCl electrode (sat. KCl, Sensortechnik Meinsberg GmbH, Germany) was employed with a potential of 0.197 V vs. standard hydrogen electrode. All potentials if not stated otherwise are given against this reference value. Initially, all anodes were operated under potentiostatic control at 0.2 V. Cyclic voltammetry (CV) was carried out at different stages of biofilm development, beginning with CV measurements during the turn-over state in the first batch cycles. For this analysis, the potential window was set from −0.5 V to 0.2 V with a scan rate of 1 mV s⁻¹. The potential applied to each electrode \( (E_{cell}) \) during chronoamperometry (CA) was adjusted based on the results of the turnover cyclic voltammograms.

Anode Assembly

The electrodes were framed using a laminating machine so that the total exposed area in the front- and backside was equal to 8 cm². A copper wire was used as current collector and was hooked through and into upper area of the graphite paper cutouts. To ensure an optimal contacting and conductivity between the collector and graphite paper, the linkages as well as the top part of the outer-frame surface were coated with conductive silver paint (Busch GmbH & Co. KG, Germany) followed by waterproof lacquer (AkzoNobel Farbe & Heimitex GmbH, Germany) to prevent silver coating and cable from corroding. A scheme is shown in Figure SI-3.

Biological Experimental Conditions

All bioelectrochemical experiments were carried out under anaerobic conditions by purging the synthetic media with nitrogen gas prior to operation for at least 20 minutes. All bioelectrochemical and control triplicates were incubated at a temperature of 35 °C. Secondary biofilms were obtained by using biomass of an acetate-fed bioelectrochemical reactor as inoculum. The biomass was obtained by scraping of biofilm from a bioanode. Sodium acetate in a concentration of 10 mM was selected as carbon and electron source. Phosphate buffer solution (PBS, pH 7) was employed as synthetic growth medium. Its composition and concentration are described in detail in. Additionally, all reactors were supplied with vitamins and minerals (12.5 ml per liter of growth media). Exact concentrations for the vitamin and mineral stock solutions can be found in. This is referred to as Art. WW 1.

Artificial wastewater 2.1 (Art. WW 2.1) containing a mixture of carbon sources was prepared as described previously. Tertiary or higher EAB biofilms were obtained by using biomass scraped off of bioanodes of a bioelectrochemical reactor that was continuously being fed Art WW 2.1, which was cultivated under the same conditions. This biomass was used as the inoculum for a number of batch cycles, in which the biofilms that formed on the graphite papers were fed Art WW 2.1.
Electrode Surface Analysis

After operation as bioanode, a number of 80 wt% graphite paper electrodes were examined using scanning electron microscopy (EVO LS-25 or LS-100, Zeiss, Germany) operated with an EHT of 15.00/20.00 kV under a residual atmosphere with a maximum pressure of 4 × 10⁻³ Pa. Each paper electrode was taken out of the cell, dried at room temperature and then examined without further preparation. Additionally, bare composite of the type S-40, E-40 and E-80 were randomly sampled – 2 × 2 cm squares – and directly examined without further conditioning. Exemplarily images hereof are shown in Figure S1-4.

2. Results and Discussion

2.1. Development of the Graphite Paper

Type S graphite papers were the first to be produced and were evaluated at different graphite as well as latex contents and calender repetitions. The aim was to develop graphite papers with a suitably low resistivity, and which could be produced, that is, having the necessary mechanical stability, on an industrial-scale paper machine. 60 wt%-graphite papers were made with between 0.5 and 3 wt%-latex contents and the resistivity was determined. The results are shown in Figure S1-5. 1.5 wt%-latex was selected to be used for all further produced graphite papers, because this content is the best compromise between mechanical stability as well as resistivity of the papers and residues on the drying cylinders of the paper machine due to an increased proportion of latex.

As shown in Figure 1 the resistivity of the graphite papers decreases with increasing graphite content. The decrease is almost linear between 40 and 80 wt% and compared to 100 wt% graphite (measured at a round pure graphite tab) the decrease tailors off. Furthermore, the percolation threshold of the dried composites is located at a graphite content of approx. 10 wt% graphite. Samples with 10 wt% were measured but the resistance could not be measured even with the measurement leads placed 1 mm apart. At greater conductor loads the composites exhibit resistivity (\(\rho\)) values close to that of 100 wt% graphite, this was attributed to the conduction network, where-as the conductivity (1/\(\rho\)) of composites with a low-loading will be mainly controlled by the electron tunneling across the insulator matrix. The graphite papers in this study with graphite contents between 40 to 80 wt% have resistivities on par or better than those produced with a combination of graphite powder and carbon fibers, best case 0.104 Ω cm⁻¹.[14] using a process similar to the “Rapid Köthen” procedure.

In cases were the particle load is low, the material compression may also optimize the composite conductivity as the gap width between conductor aggregates is reduced mechanically⁹¹⁰ resulting in lower resistivity. Thus, calendering the produced graphite papers has a positive effect on resistivity up to a point. As shown in figure 1, the effect of calandering decreases with increasing graphite content. At a graphite content of 70 wt% papers had average resistivities of 0.402 Ω cm uncalendered, 0.029 Ω cm after 2x, 0.023 Ω cm after 4x and 0.020 Ω cm after 6x calendered, respectively. To put this into perspective: If the resistance contribution of a bioanode is to be limited by design to a maximum of 20 Ω, then with the above resistivities, their respective thicknesses and with a width of 1 cm, bioanodes of 1.55 cm, 9.74 cm, 11.7 cm and 14.3 cm length, respectively, could be used.

The mechanical properties of the material are also important. To achieve a high system performance, a high electrode surface area to the reactor volume is required. This can be realized by means of specific geometric structures, e.g. by targeted folding of the material or other means of material processing. For material processing and producing of a highly filled paper at pilot paper machine scale, with continuous roll-off as opposed to lab scale single sheets, it is necessary that the mechanical stability of the paper reach a certain value.

The filler (graphite) does not contribute to the mechanical strength of the sheet, which is generated by the fiber-fiber bond and depends on the pulp content as well as processing thereof. As shown in Figure 2A, the mechanical strength indicated by the tear length decreases with increasing proportion of graphite in the material. The tear length of a 20 wt% graphite paper is 3850 m. The tear length decreases by 48% to 2000 m at 40 wt% and by 81% to 730 m at 80 wt% graphite. These values must be taken into account, when going to the pilot scale paper machine production, since too low strengths can lead to paper web tearing during the manufacturing process. However, there is no general limit, each paper machine requires a specific value, which depends on the configuration (e.g. the gap between forming section and first pressing or drying section) as well as run speed.

An equally important parameter for further material processing is the bending stiffness, which in particular for future work indicates how well for example the graphite papers can be folded into complex geometries. Figure 2B shows that the bending stiffness of the S-type graphite papers does not decay as extremely as the tear length with increasing graphite content. The average bending stinesses at 40 wt% and, 80 wt% graphite are 1243 Nm and, 890 Nm, respectively. Compared to the 1258 Nm at 20 wt%, this is only a loss of 2%
and 29%, respectively. These promising results prompted the testing of the folding of a number of sample graphite papers, which were folded by 90° and 180°. The determined resistivities are shown in Figure SI-6 and show that folding the samples did not cause a significant increase to the resistance of the samples.

Please note that there is a significant difference between lab-scale sheets produced with the “Rapid Köthen” process and those, which would be produced with a paper machine. The pulp fibers in the lab sheets have an anisotropic orientation, visible in Figure SI-4, whereas in the rolls produced by a paper machine they are isotropic i.e. orientated parallel to the direction of roll-off or in machine direction. Which means that structurally paper from a paper machine is mechanical stronger in machine direction and weaker perpendicular to machine direction.

Two different graphite types were considered as fillers and their composites containing 40 and 80% graphite were evaluated by there resistivities. The papers containing expanded graphite flakes i.e. E-type, presented the lowest resistivity values and were also used for the biotic experiments in addition to the S-type papers. Both E- and S-types were chosen because of the difficulty in creating a stable E-type graphite-pulp fiber suspensions, required for paper machine production. i.e. if S-type papers allowed similar bioelectrochemical performances, then it would be selected for further development, because of the easier handling. Table 1 shows the resistivity as well as the average resistances of the assembled-electrodes for each composite type.

The suitability of these materials for their application as an electrode is still given at loading ratios as low as 40% graphite, with an average p of 0.114 ± 0.032 Ω cm in contrast to 0.014 ± 0.001 Ω cm of an 80% graphite paper. Although the values of the low graphite-loaded electrodes are clearly larger than the high-loaded, the materials can be still functional since there are other materials that have been successfully tested as bioanodes e.g. indium tin-oxide (ITO) and which had a reported sheet resistance of up to 20 Ω.[23] Although S- and E-40 composites have the same graphite contents, expanded graphite has been found to have higher conductivity than natural graphite, when used as composite filler,[24] and this effect seems to be more pronounced at lower graphite loadings.

In all cases, because these novel electrode materials are still “paper”-like, they can absorb water which will change their electrical and mechanical properties. Mechanically, neither after these nor any of the following tests did the graphite papers show any an instability after prolonged exposure to the liquid mediums. This characteristic is a prerequisite for production with a paper machine, see section below on “Can the graphite paper be produced en masse?”

The average Ohmic resistance values in Table 1 were determined for the same batch cycles as the average maximum current densities (\(j_{\text{Max}}\)), listed in Table 3. Determining the contributions of individual components to the total Ohmic resistance of a MET is very complex and beyond the scope of

| Graphite type | Resistivity [Ω cm] | Blank electrode resistance [Ω] | Ohmic resistance[a] [Ω] | @\(j_{\text{Max}}\) listed in Table 3 |
|---------------|-------------------|-------------------------------|--------------------------|
| S-80          | 0.013 ± 0.001     | 1.30 ± 0.120                 | 36.9 ± 5.07              |
| S-40          | 0.154 ± 0.026     | 14.0 ± 3.23                  | 41.3 ± 12.4              |
| E-80          | 0.007 ± 0.0004    | 0.890 ± 0.060                | 35.6 ± 7.17              |
| E-40          | 0.064 ± 0.004     | 6.15 ± 0.568                 | 25.6 ± 4.70              |

[a] After deduction of the catalytic or polarization potentials at the anode, i.e., the applied potential and the cathode. Cathodic hydrogen evolution potential calculated from data obtained for the same stainless-steel mesh determined in a previous study.[26]
this study, but the reader is referred to Madjorov et al.\textsuperscript{(25)} for a recent example. As expected, the S-80 and E-80 had a lower resistance than the S-40. This is likely due to the difference in graphite content. Graphite is hydrophobic, so less water with a lower conductivity is absorbed into the graphite papers. Why the E-40 displayed such a relatively low Ohmic resistance is unknown and could be the focus of future research, based on this study.

2.2. Graphite Paper Stability in a Biologically Active Matrix

In addition to the requirement of being mechanically stable for mass production in a paper machine, the graphite papers have to be biologically stable. Pulp fibers and graphite make up the majority of the mass of the papers, with approx. 18.4 and 58.4 wt% pulp fibers in the graphite papers tested in the bioelectrochemical cells. Pulp fibers are mainly composed of cellulose and hemicellulose, both of which can be degraded in bioelectrochemical systems.\textsuperscript{(27,28)} As such, the stability or likelihood of degradation of the electrodes was tested under different conditions. Figure 3 shows SEM micrographs of an E-80 electrode after operation with Art. WW 1. In Figure 3A a top-down view of the graphite paper and biofilm are shown, wherein the dried biofilm layer is visible, lighter color due to the loss of conductivity, and the graphite paper is visible the darker forms. Figure 3B shows a cross section of the same electrode revealing a clear delimitation between the electrode and biofilm. An invasive degradation of the graphite paper by the EAB is, therefore, unlikely to occur during operation in a MET.

In addition to SEM inspection, triplicates of the paper electrodes were exposed to artificial with real wastewater as an inoculum and real wastewater prior to and post operation, i.e. without and with an EAB biofilm covering the electrode surface. This represents a disconnection from the electrical circuit, which could occur in different states of operation. The observations of these control experiments are listed in Table 2. With samples of the type S-80 and in the presence of acetate as well as inoculum a planktonic growth was observed, which is indicated by a noticeable increasing turbidity of the media during the experiment.

The suspended solids formed a film on the paper surfaces, of the composites that were immersed in wastewater, which was perceivable from the first until the last day of the experiment. However, all samples remained structurally intact. Furthermore, the electrodes could be easily physically handled at the end of the control experiments without falling apart, which also demonstrates structural stability. While this evidence does not completely preclude the possibility of biological degradation of the graphite papers in all extreme scenarios, it does provide reasonable grounds for the assumption, that during any normal operation with wastewater the electrodes will remain stable for long periods of time.

2.3. Bioelectrochemical Characterization of the Different Graphite Papers

In practice MET need to achieve high substrate turnovers and current densities at the lowest possible (over-)potentials, because the combination of these parameters determines their viability.\textsuperscript{(29)} Initially, all electrodes were studied using acetate as the only substrate, which led to the development of typical red-colored biofilms, see Figure SI-2. Furthermore, a solid EAB development was observed at all bioanodes. As shown for the example E-40-I replicate in figure 4, in the first batch cycle there is a significant lag phase followed by an exponential increase in the current density. Thereafter in the consecutive batch cycles the activity i.e. current production after exchanging the media is almost immediate in the plateau phase i.e. there is no longer resistance than the S-40.

![Figure 3. SEM image of an E-80 electrodes after operation in a bioelectrochemical cell. The dried, decomposed biofilm is found adhered on the electrodes surface. Parts of the same electrode are shown A) looking perpendicular to the surface and B) into a cross section of the electrode. The bars indicate a distance of 10 μm. The magnification is 500x.](image)

| Composite type | Aqueous media | Observation time [d] | Visible degradation |
|---------------|---------------|----------------------|-------------------|
| Without biofilm | PBS, acetate, inoculum | 25 | no |
| Effluent from the primary sedimentation tank | 31 | no |
| With biofilm | PBS, acetate, inoculum | 25 | no |
| Effluent from the primary sedimentation tank | 21 | no |
a lag phase. This example trend was observed for all the anodes, regardless of the differences in maximum current densities.

With exception of the S-40 electrodes, all anodes performed similarly as they reached their maximum current densities within the first two cycles. After which a gradual decrease was observed (Figure 4) over the course of the remaining 4 batch cycles, except for the S-40 electrodes that plateau from cycle 3 onwards. Maturation and growth into more dense biofilms has been suggested as the main cause, since it hinders the substrate transport into the inner layers nearer to the electrode-biofilm interface.\[^{[30]}\] Moreover, a steady electrode performance, i.e. maximum current densities are expected to stabilize over the long-term from batch to batch.\[^{[31]}\]

Regarding the retention aids, these could have impacted the surface charge of the graphite paper and therefore had an effect on the initial adhesion of the EAB. Polyacrylamides (PAM) were used in both retention aids in different amounts. These could be modified to be more or less positively or negatively charged as well as designed to have a determined size and mass.\[^{[32]}\] However, based on the results shown in Figure 4, it would seem that these have no effect on the short to midterm bioanode performance.

In order to state the suitability of the composites as bioanodes, the average maximum current densities ($j_{\text{Max}}$) – calculated from the last three batch cycles of each triplicate – may be compared to those of the other graphite-based or carbonaceous electrodes in similar conditions. All four graphite paper electrodes achieved average maximum current densities between 0.7 and 0.8 mA cm$^{-2}$. Their performance is comparable to graphite rod and carbon cloth anodes operated under comparable conditions, as listed in Table 3.

When evaluating the anode performance, cyclic voltammetry may be a useful technique for a qualitative analysis of the EAB. Typically, a well-developed biofilm will present sigmoidal shaped voltammograms in substrate turnover conditions. These allow the estimation of the potential range in which the current production will be limited by biochemical turnover and resulting in a plateau in the typically $j$-$E$-curves.\[^{[33]}\] Less steep curves have been correlated to a less efficient electrochemical reaction compared to the biochemical reaction\[^{[34]}\], i.e. the electron transfer towards the electrode is limited by a biochemical reaction step.

All the types of bioanodes were, therefore, studied using cyclic voltammetry in substrate turnover conditions. During the first batch cycle, once the current density had passed a maximum for most of the reactors indicating a stable turn over state, the bioanodes were analyzed using cyclic voltammetry. The set potential of the CA procedure was adjusted based on the sigmoidal shape of the CV, i.e. a new more negative potential was selected, if a plateau or local maximum was found. These adjustments were done, when required, throughout the course of the experiments. The average of the potentials applied to each of the graphite paper anodes during CA in the last three batch cycles are listed in Table 3.

S-80 as well as E-80 reached a plateau, as shown in Figure 5A, whereas the biofilms that were grown on the composites with 40% graphite did not. These voltammograms are from the 5\(^{\text{th}}\) and, 6\(^{\text{th}}\) batch cycles for S-/E-40 and, S-/E-80, respectively. The differences between the EAB biofilms on the different graphite papers were already found in the first cycle and did not change significantly over the course of the experiments.

\begin{table}[h!]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
Electrode type & Average $E_{\text{ox}}$ [V vs. Ag/AgCl] & $j_{\text{Max}}$ [mA cm$^{-2}$] & Temperature [°C] & Reference \\
\hline
S-40 & 0.2 & 0.699 ± 0.039 & 35 & this study \\
S-80 & −0.089 ± 0.081 & 0.765 ± 0.130 & & \\
E-40 & 0.2 & 0.803 ± 0.065 & & \\
E-80 & 0.112 ± 0.149 & 0.752 ± 0.100 & & \\
Polycrystalline graphite rod & 0.2 & 0.496 ± 0.015 & 30 & \[35\] \\
Carbon fiber veil & 0.291 ± 0.023 & 40 & & \\
Carbon paper & 0.705 ± 0.021 & 30 & & \\
Carbon paper\[^{[a]}\] & 1.358 ± 0.035 & 40 & & \\
Polycrystalline graphite & 0.043 & >1.000 ± n. a. & 30 & \[36\] \\
Graphite block\[^{[b]}\] & 0.043 & 1.000 ± n. a. & 30 & \[37\] \\
\hline
\end{tabular}
\caption{Comparison of the composite-anode performance to several graphite-based electrodes using acetate as sole substrate source in similar experimental conditions. The average values from these experiments were calculated considering the last three cycles for a real application overview.}
\end{table}

\[^{[a]}\] Geobacter sulfurreducens pure culture used as the inoculum.
experiments. S-80, E-80 and E-40 electrodes achieved similar current density values at 0.2 V vs. Ag/AgCl during CV, however the current increment with increasing overpotential is lower for E-40. S-40 did not on average reach a plateau in the selected potential range.

The set applied potential of each CA procedure for each bioelectrochemical cell was adjusted immediately after the conclusion of the turn-over CV and in particular the current density of the S-80 electrodes started to rise to a second maximum, which yields an $J_{\text{Max}}$ of $1.06 \pm 0.32 \text{ mA cm}^{-2}$ as well as an $J_{\text{Max}}$ of $1.29 \pm 0.09 \text{ mA cm}^{-2}$ during the second cycle. These values were the highest among all anodes (S-40, E-80 and E-40 that were operated at 0.2 V vs Ag/AgCl).

By determining the first derivatives (Figure 5B) of the CV-curves (Figure 5A) of the biofilms during substrate turnover, formal potentials of $-0.35/-0.36 \text{ V}$ and $-0.31/-0.32 \text{ V}$ were found for the electrodes with 80 percent graphite content S-type and E-type, respectively. Formal potentials of $-0.37 \text{ V}$ and $-0.28 \text{ V}$ were found for the electrodes with 40 percent graphite content S-type and E type, respectively.

Although the formal potential values could be determined from the local maximum of the derivatives, the curves of the 40 wt% papers are clearly flatter, especially of S-40, and broader. Moreover, the enrichment of biofilms from wastewater using acetate as the only carbon and electron source has been proven to be mostly composed by *Geobacter sulfurreducens*. A formal potential of $-0.347 \text{ V}$ vs. Ag/AgCl ($-0.15 \text{ V}$ vs. SHE) has been obtained for Geobacter sulfurreducens during substrate turnover,[36] which is a similar value to those found for the S-80 and E-80 electrodes.

2.4. Graphite Paper Evaluation as Bioanode Using Art. WW 2.1.

The last step in the assessment of the composites for its applicability in bioelectrochemical systems at larger scales is the study of their structural and operational robustness when using complex substrates. Recently, a mixture of five organic carbon sources, representative of the soluble organics in domestic wastewater, was developed and tested in bioelectrochemical reactors. The development and performance of the new biofilm was successfully found to be suitable for subsequent treatment of wastewater coming from the primary settlement tank of an existing sewage plant.[17]

Due to this new substrate media being representative for the composition of domestic wastewater, it was selected for the testing of the graphite paper in more complex conditions. S-80 graphite papers were chosen for this experiment, because of the good combination of maximum current density and low applied potential in the previous experiments. The main evaluation parameters, $J_{\text{Max}}$, COD removal and Coulomb efficiency are displayed in Table 4. The S-80 composite was evaluated in triplicate. All electrodes developed a thick red-brown-looking biofilm and no degradation of the electrode material was perceivable during or after the MEC operation. On average, the EAB biofilms on the S-80 achieved comparable
average maximum current densities, but they have lower average removal and Coulomb efficiencies.

Overall, while the results obtained with the lab scale graphite papers are not the “best”, they are good enough to warrant further future investigation with machine produced graphite paper electrodes in MET fed real wastewaters.

### 2.5. Can the Graphite Paper be Produced En Masse?

In preparation for future studies e.g. with larger scale reactors, rolls of graphite papers were produced with a pilot scale paper machine: designated VPM 1, 2, 3, 3 A and 4. Based on the results of the tests with the lab scale sheets, SC 20 OS was selected as the graphite type to be used. These papers have area densities of 183, 186, 226, 302 and 180 g m\(^{-2}\) with respective graphite contents of 81, 81, 81, 71 and 80%. As with the lab scale paper sheets, they contained the same wt% of starch, latex and retention aid. Paper pulp contains fibers of different lengths: short and long. The longer the fibers, the more they orient themselves parallel to the machine direction, i.e. a more isotropic sheet will be created. Figure 7A shows that by adjusting the amount of unprocessed short fibers, unprocessed long fibers and ground long fibers the mechanical properties can be modified. Increasing the processed long fiber content in the pulp component increases mechanical stability of the graphite papers, increasing the ground long fiber amount from 50 to 100% almost doubles the tear length. However, the same increase in stability could also be achieved by decreasing the amount of graphite from 80 to 70 wt%, VPM 3 to 3 A. The production speed of the paper machine was 1.8 to 2 m min\(^{-1}\) and it is likely that at least the VPM 3 A and 4 graphite papers could be produced at even higher speeds. As shown in Table 4.

### Table 4. Anode performance using a complex mixture of organic carbon sources (Art. WW 2.0/2.1) with an initial COD of 800 mg COD L\(^{-1}\). The values for the S-80 electrodes with at least secondary biofilms are based on the operation during the fourth and fifth batch cycles. For comparison, the performance of the secondary biofilms using graphite rods as anodes\(^{1(1)}\) are also listed. Both systems were operated at \(E_{\text{EM}} = 0.2\) V vs Ag/AgCl.

| Anode material | S-80 | Graphite rod |
|----------------|------|--------------|
| COD\(_{\text{r}}\) removal efficiency [%]  | 59.3 ± 11.7 | 78.0 ± 0.954 |
| \(J_{\text{max.}}\) [mA cm\(^{-2}\)]  | 0.489 ± 0.148 | 0.390 ± 0.082 |
| Coulomb efficiency [%]  | 39.5 ± 22.0 | 73.3 ± 4.23 |

Figure 6. Average (solid lines) and standard deviations (dashed lines) of A) voltammograms of the EAB biofilms at the graphite paper electrodes in turnover state shown as current density \(j\) vs. the applied potential \(E_{\text{EM}}\) as well as B) the first derivatives of (A). Data is from the 5th batch cycle for S-/E-40 batch and 6th batch cycle for the S-/E-80 triplicates.

Figure 7. A) Tear length of samples of graphite paper rolls produced on a pilot scale paper machine (VPM) without calendering and B) resistivities of samples from the same rolls of graphite paper. X % unprocessed short fibers/Y % unprocessed Long fibers/Z % ground long fibers. K: same calender as lab sheets – 4x @60 °C, 90 kN/m, G: calendered 2x @20 °C, 30 kN/m within the paper machine.
Figure 7B, the resistivity of the VPM 3A graphite paper is neither the best nor the worst. It has an average (parallel and perpendicular to machine direction) resistivity of 0.018 ± 0.002 Ω cm. It does however have the best combination of good mechanical stability and low resistivity of the produced graphite papers. The material costs of the graphite and pulp used to make the VPM papers are approx. 5.5 € m⁻² [39] (not incl. VAT), ~ 0.04 € m⁻² for the pulp and other substances other than graphite, which is a good step towards meeting previously suggested anode costs [5] and therefore reaching a state in which MET can become economically viable. Please note the above costs are estimates by the project partners, readers can estimate the prices via the resource costs per kg with wt% of graphite and pulp, etc.

3. Conclusions

This work shows an in-depth development and characterization of graphite papers as electrically conductive materials for oxidative wastewater treatment in microbial electrochemical technologies. The development of the graphite papers yielded mechanically stable and flexible materials with resistivities approaching that of 100 wt% natural graphite or within an order of magnitude. Graphite papers filled with 40 and 80 wt% graphite of two different types were successfully tested in bioelectrochemical experiments and proved to be resilient to biological degradation. The combination of these materials and secondary EAB biofilms yielded very satisfactory maximum current densities, in particular in the range of other acetate fed systems with carboxaceous anodes. Recent removal and Coulomb efficiencies were obtained when experiments were carried out with a more complex artificial wastewater. These results prompted the development of graphite papers for production at pilot scale paper machines rates. The paper machine produced, VPM 3 A K papers, will be used in future research. Specifically, because the mechanical properties are sufficient to allow folding to 3D configurations with over 100 m² m⁻³ surface area.

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ARTICLES

Paperchase: Microbial electrochemical technologies are complex systems requiring strong interdisciplinary approaches for developing bioelectrode materials. These need to be electrically conducting, mechanically and biologically stable as well as supportive of the biocatalysis of electrochemically active bacteria. This study shows the development of graphite papers with low resistivities and good bioelectrochemical performance.

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Developing Cheap and Mass-Producible Graphite-Filled Paper as an Anode Material for Microbial Electrochemical Technologies