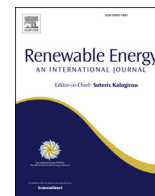




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Review

Considerations for application of granular activated carbon as capacitive bioanode in bioelectrochemical systems



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ABSTRACT

In the last decades, the research in Microbial Fuel Cells (MFCs) has expanded from electricity production and wastewater treatment to remediation technologies, chemicals production and low power applications. More recently, capacitors have been implemented to boost the power output of these systems when applied as wastewater treatment technology. Specifically, the use of granular capacitive materials (e.g. activated carbon granules) as bioanodes has opened up new opportunities for reactor designs and upscaling of the technology. One of the main features of these systems is that charge and discharge processes can be separated, which offers multiple advantages over more conventional reactor types. In this manuscript, we discuss several aspects to consider for the application of capacitive granules as bioanodes in MFCs and other bioelectrochemical systems, as well as the recent advances that have been made in applying these granules in various reactor systems. Similarly, we discuss the granule properties that are key to determine system operation and performance, and show that biofilm growth is highly dependent on the efficiency of discharge.

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1. Microbial Fuel Cells for wastewater treatment

The Microbial Fuel Cell (MFC) is a technology that extracts electricity from the degradation of organics present in wastewater. This extraction of electrons is catalysed by bacteria which are known as electrochemically active bacteria (EAB) or electrogens [1–4]. These bacteria are commonly grown on carbon electrode materials, such as activated carbon, carbon paper/felt/rod or carbon nanotubes (CNTs) [5]. The combination of EAB with an anode for current production is called a bioanode. Bioanodes are also applied in other Bioelectrochemical Systems (BESs), of which an MFC is a specific application, such as the production of hydrogen or specific chemicals, the removal of pollutants and the recovery of nutrients like e.g. ammonia [6–10].

An MFC is an anaerobic wastewater treatment technology and is, in that respect, most comparable with anaerobic digestion [11]. The power output reported for MFCs is highly variable and values that are quite comparable to those achieved with anaerobic digestion have been reported ($\sim 1 \text{ kW m}^{-3}$) [12]. Most of these high power densities, however, have been reached only at laboratory scale [13,14]. It is known that the type of substrate, choice of electrode material, mode of control, cell configuration and operational conditions, directly affect the power output of MFCs [15–20]. Furthermore, when scaling the system up, new challenges arise related to increased internal resistances, limited ionic conductivity of wastewaters and clogging issues [21].

Many of these issues can be solved through the application of capacitive materials as electrodes; the so-called capacitive bioanodes [23]. A clear advantage of such capacitive bioanodes is that, due to the ability of charge storage (known as capacitance), MFCs can be operated intermittently and deliver higher current densities during discharge [22]. In addition, when these capacitive bioanodes are in the form of granules (i.e. granular capacitive bioanodes), they offer the possibility of new reactor types that solve many of the issues related to the upscaling of MFCs. In this review, we provide an overview of important considerations to apply capacitive granules, and more specifically activated carbon granules, as bioanodes in BESs.

2. Capacitive bioanodes allow for charge storage in MFCs

Capacitive bioanodes are an integration of bioanodes with electrochemical capacitors (ECs) [23–26]. ECs, also known as supercapacitors, are widely used for short-term energy storage in electronic devices and have two different charge storage principles: i) electrostatic charge, where charge is stored by the formation of an electrical double layer (EDL) on the electrode/electrolyte interface; and ii) electrochemical charge or pseudocapacitance, where charge is stored by the adsorption/desorption of cations or/and intercalation/de-intercalation coupled with reversible redox reactions of metal ions at the electrode/electrolyte interface [27,28]. In the case of a capacitive bioanode based on porous carbon material, the charge is stored electrostatically but this is delivered by EAB through a faradaic process, i.e. the oxidation of organic matter. Fig. 1 shows an example of these two phenomena occurring in granular activated carbon (AC), a three-dimensional carbonaceous electrode material that is widely used in BESs because of its high specific surface, which is suitable for both biofilm and EDL formation.

For electricity storage purposes, the system must be operated intermittently, meaning that it should experience a charge and a discharge process. In the case of a capacitive material, an EDL is formed during charge and it is released during discharge. This electrostatic process produces a (non-faradaic) current known as capacitive current (I_{cap}). However, in the case of a capacitive

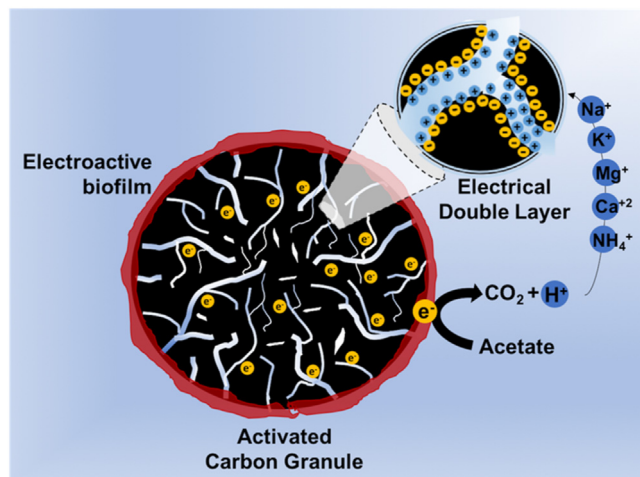


Fig. 1. Single activated carbon (AC) granule with electroactive biofilm (EAB) growing around it. The current that is produced by EAB (I_{far}) from the oxidation of substrate (i.e. acetate) is stored as charge (I_{cap}) in the electrical double layer (EDL).

bioanode, the EDL formation in the porous electrode during charge results from the chemical oxidation of substrate by EABs, which leads to a faradaic current (I_{far}). Therefore, a combination of faradaic (I_{far}) and capacitive (I_{cap}) currents will be released during the discharge of a capacitive bioanode. Fig. 2 illustrates the electron flow (current) during charge/discharge processes on a single AC granule

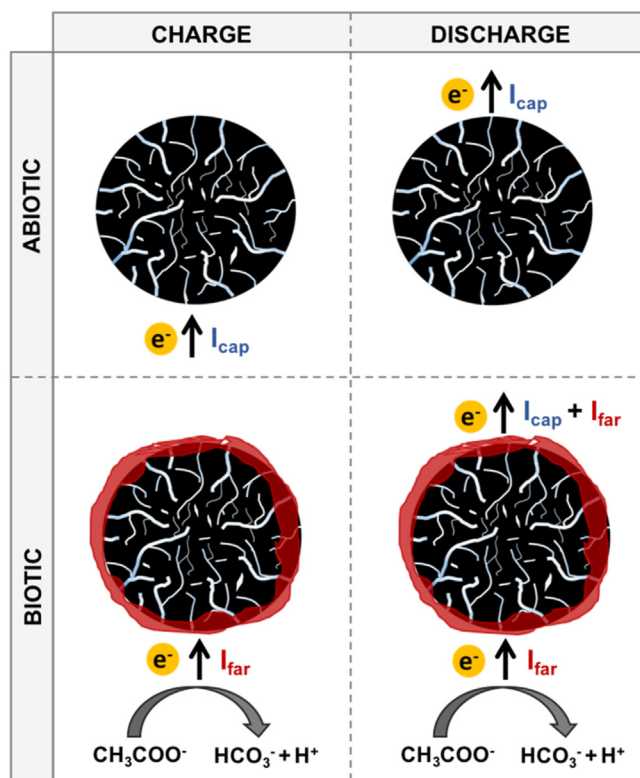


Fig. 2. Charge (left) and discharge (right) processes for a single AC granule without (abiotic, up) and with (biotic, down) biofilm growth. Under abiotic conditions, the granule behaves as an electrochemical capacitor where I_{cap} is responsible for both charge and discharge processes. Under biotic conditions, the I_{far} produced by bacteria is responsible for the charge, while both I_{far} and I_{cap} are combined during the discharge of the granule.

without (abiotic) and with (biotic) biofilm.

In the literature, capacitive bioanodes have been reported to increase charge production (53%) over non-capacitive bioanodes [29], in this case by casting a capacitive layer on top of an electrode. The increase in charge production was not only related to the increase in charge storage (I_{cap}) (35%), but also to the enhanced current production (18%) by the EAB (I_{far}). In line with this, another study [30] showed that intermittent polarization of flat electrodes (glassy carbon) led to an increased current density due to the presence of (3.6 times) more charge carriers within the biofilm. These charge carriers increased the charge storage capacity of the biofilm (pseudocapacitance) and allowed for a faster electron discharge from the biofilm to the electrode. In summary, these studies showed how the use of capacitive materials and intermittent operation mode can enhance current production by EABs in MFCs. In the next section, we will further explain the differences between capacitive and non-capacitive carbon granules in terms of their current and potential responses, emphasizing on the intermittent operation mode with charge and discharge cycles.

3. Intermittent operation mode of capacitive bioanodes increases power generation

Due to the charge storage capacity of capacitive bioanodes, these can be operated in intermittent mode. Generally and as pointed out in the previous section, an intermittent operation mode of capacitive electrodes will produce more current compared to non-capacitive electrodes. For example, Deeke et al. (2012) [31] reported a charge recovery of 0.9 for a non-capacitive electrode while a charge recovery of 1.6 for a capacitive electrode. The reason for this lies in the difference of current and potential responses during charge/discharge cycles between capacitive and non-capacitive electrodes (Fig. 3). During charge, the cell is in open circuit (no current) while EAB continue to oxidize the substrate and thus charge the electrode (with I_{far}). This reduces the electrode potential to the open circuit value (~ -0.300 V vs NHE in the case of acetate),

as shown in Fig. 3A. However, the potential drop for a non-capacitive electrode (blue line) is much faster within the same time period compared to a capacitive material (red line), where the potential changes more gradually. Fig. 3B illustrates this phenomenon; non-capacitive (e.g. graphite) granules have a relatively small surface area and so have a small storage capacity, leading to a large decrease in potential. On the contrary, capacitive (activated) granules have a large surface area that facilitates the distribution of charges and allows for large storage capacity, leading to a lower potential drop than non-capacitive granules. The amount of charge stored over a potential difference is known as capacitance (expressed in Farads) [23], and so it is larger in the case of activated carbon granules (see also section 7.1).

During discharge, the potential difference between the charged electrode and the applied anode potential gives the driving force needed for the stored charge to be released. The current peak is thus related to I_{cap} , which is much smaller for non-capacitive electrodes (blue line) than for capacitive electrodes (red line). After this first peak, current gradually decreases until reaching a steady-state current, which is the I_{far} produced by the EAB at that specific potential. By subtracting the faradaic current to the total produced current, the capacitive current can be determined, which directly relates to the capacitance of the electrode [43] (see also section 6). It should be pointed out that the higher steady-state current with AC granules might be due to the residual stored charge or an enhancement of EAB growth and activity (see section 5).

Now, if we compare the intermittent mode with a continuous mode, the former one can release an increased amount of overall charge, as this is released at a higher rate compared to a continuous energy harvest [22,32]. However, the intermittent operation mode needs open circuit periods where there is no current production, so its overall performance should be compared to that under continuous operation mode (with no “off” period), known by the term of charge recovery (η_{rec}).

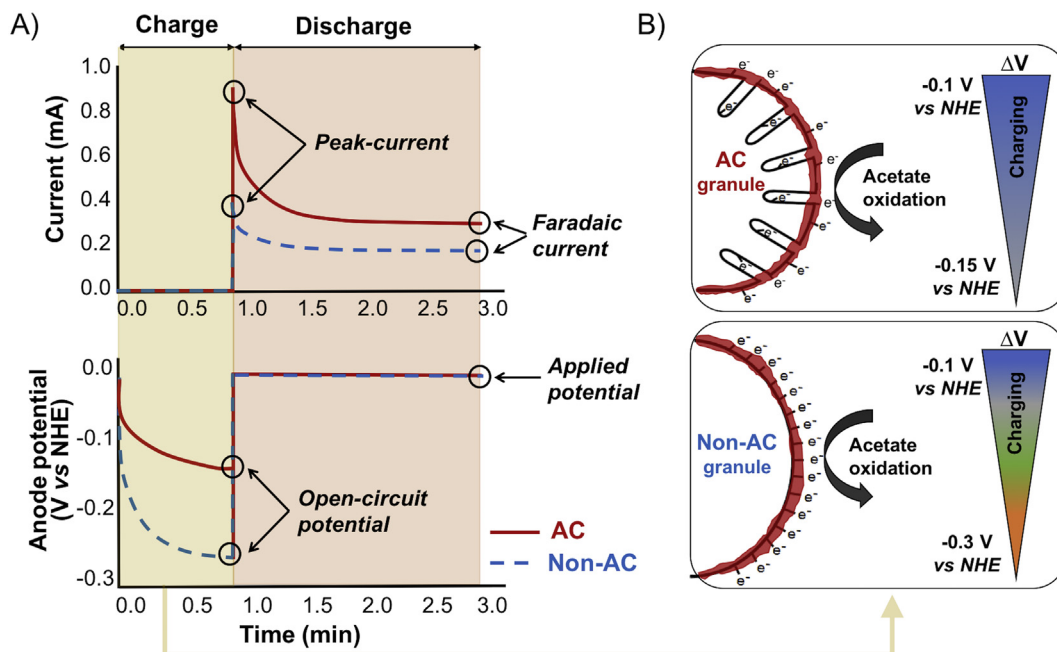


Fig. 3. Left: Example of current (up) and potential (down) responses of activated carbon (AC, in red) and non-activated carbon (non-AC, in blue) during a charge/discharge cycle. Right: Schematic representation of the surface area in capacitive (AC, in red) and non-capacitive granules (non-AC, in blue) and the respective electron distribution. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$$\eta_{rec} = \frac{\sum Q_{int}}{n Q_{cont}} \quad (1)$$

This charge recovery is the charge produced by a capacitive electrode under intermittent operation mode (Q_{int}), with n charge/discharge cycles, normalized to the charge produced by a non-capacitive electrode under continuous conditions operation mode (Q_{cont}). When $\eta_{rec} > 1$, the intermittent mode performs better, while when $\eta_{rec} < 1$, the continuous mode is preferable. Borsje et al., in a study using single granules, showed that AC granules accumulated 20–100% more charge under intermittent conditions than non-AC granules under continuous conditions ($\eta_{rec} = 1.2\text{--}2.0$), while no differences were observed for non-AC granules between intermittent and continuous conditions [33]. This suggests that, the lack of current production during open circuit conditions, is compensated with the high-peak current production during discharge in the case of capacitive granules, but not in the case of non-capacitive graphite granules (even though intermittent operation mode was reported to increase bacterial activity in flat electrodes [30], see section 2). Sections 5 and 7 delve deeper into biofilm growth regarding intermittent conditions and granule properties, respectively.

4. New reactor designs are possible with granular capacitive bioanodes

Due to the charge storage capacity and the intermittent operation possibilities, granular capacitive bioanodes offer new possibilities for reactor design. In fact, capacitive properties of the material allow for separated charge and discharge steps, as the oxidation of organics occurs at open circuit while the capacitive material gets charged and the discharge occurs at closed circuit when the capacitive material contacts the current collector. Similarly, this discontinuity allows for physically separated charge/discharge processes, i.e. in different parts of the same reactor. AC granules in particular, due to their shape and light mass, can be suspended through the wastewater thus avoiding clogging issues and allowing the treatment of larger volumes of wastewater in comparison to flat MFC configurations. Additionally, the formation of EDL in granular AC bioanodes is favorable for the treatment of low conductivity wastewaters, as upon discharge the counter ions stored in the electrode/electrolyte interface are released at once and they locally increase the ionic conductivity [32]. Fig. 4 gives an overview of the different reactor types described in the literature that use carbon granules: a) fixed or packed bed reactor, where (graphite) granules are immobilized and filling up the whole anode compartment [34,35]; b) a cell where AC granules are mobilized by stirring and intermittently contacting the current collector [36]; c) a fluidized bed reactor where AC granules are being fluidized with gas and intermittently contacting the current collector [37–41]; d) a fluidized bed reactor with AC granules that are recirculated to a smaller cell where they get in contact with the anode electrode [32] and e) a moving bed reactor in which AC granules form a bed in the discharge cell [42].

Table 1 gives an overview of the main properties of these reactor systems. In the case of fixed beds, the contact with the current collector is constant and the operation mode can be chosen to be continuous or intermittent, unlike in the other reactor types where the contact between AC granules and the current collector is always intermittent. While the contact resistances between granules might be the main cause of energy losses in fixed bed reactors, when granules are in movement the most challenging is to ensure low contact resistance between granules and the current collector. In the case of recirculating and moving bed reactors, where the

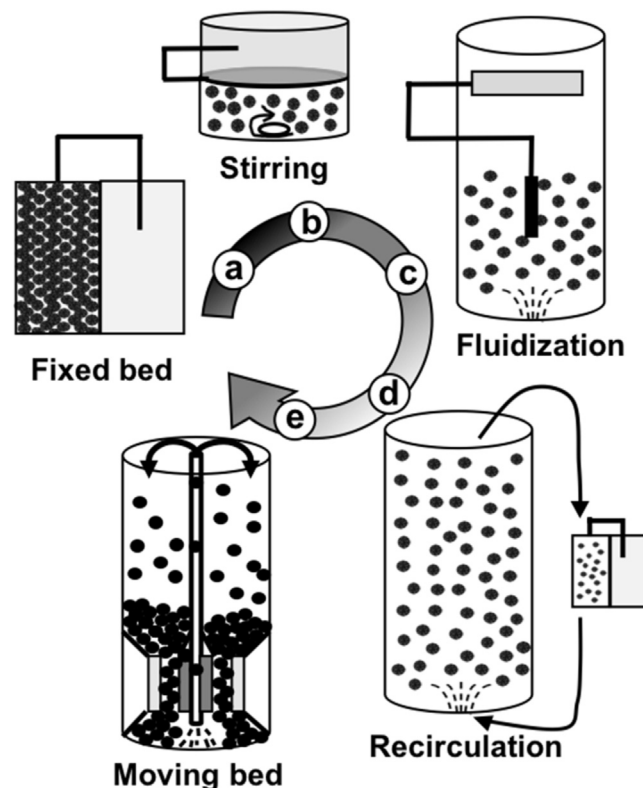


Fig. 4. Different set-up configurations of reactors using carbon granules as bioanodes: a) Fixed or static reactors [34,35]; b) Stirring reactors [36]; c) Fluidized reactors without recirculation [37–41]; d) Fluidized reactors with recirculation [31]; and e) Moving bed reactors [42].

charge/discharge cycle times can be set (see section 5), granule retention times in the discharging cell can be increased and thus lower contact resistances. This will similarly increase the energy that can be possibly harvested and thus decrease the energy investment on granule fluidization. Other parameters such as granule mass should be also considered in these reactor systems [32,36,37]. In general, a high volumetric current output leads to the requirement of less electrode material, as the volumetric activity for organics removal of the reactor is high, and hence, a more economically feasible reactor will be achieved.

5. Charge/discharge cycles in relation to biofilm growth

An important aspect to consider in reactors running intermittently is the duration of charge/discharge cycles. The total cumulative charge (result of 15 cycles) for different charging (5–60 min) and discharging (10–120 min) times were compared in a previous study [31]. The results showed that the discharging process was more limiting than the charging process, as longer discharging times increased the cumulative charge produced while longer charging times did not. These results are similar to those found in Caizán-Juanarena et al. (2019) for shorter charge/discharge times; the cumulative charge (result of 15 cycles) for 5–15 min increased 1.8-folds compared to that for 5–10 min [43]. This increase in cumulative charge was not attributed to a limited release of the stored charge, but to a larger contribution of the faradaic current (I_{far}) instead. In fact, the contribution of stored charge (I_{cap}) to the total produced charge showed to only be beneficial for short discharge times (2 min), which is expected due to sharp and short current peak at the beginning of the discharge and a decreased contribution

Table 1
Advantages and disadvantages of several reactor types with carbon granules as bioanodes.

| Reactor type | Operation mode | Contact resistance granules-current collector | Density of particles | Clogging risk | Set charge/discharge cycle time | Energy requirement for reactor operation |
|-------------------------|---|---|----------------------|---------------|---------------------------------|--|
| Fixed/packed bed | Continuous contact (intermittent polarization possible) | Low | High | High | Yes | Low |
| Stirring | Intermittent contact | High | Low | Low | No | High |
| Fluidization | Intermittent contact | High | Low | Low | No | High |
| Recirculation | Intermittent contact | Medium | Low | Low | Yes | Low |
| Moving bed | Intermittent contact | Low | High | Low | Yes | Low |

of the I_{far} .

These results suggest that I_{far} has a larger effect on the overall performance of capacitive bioanodes compared to I_{cap} as it accounted for 70% of the total produced charge. Hence, the final performance of AC granules is not only determined by its capacitive properties but also by the amount and activity of the EAB on its surface. Bacterial growth is a very important aspect to consider when optimizing the current production and Coulombic efficiency of the system. In fact, the growth of EAB is directly linked to the oxidation of substrate (i.e. removal of organics) and the production of I_{far} both during charge and discharge. But, more importantly, proper bacterial growth during charge (at OCP) will only take place if granules are sufficiently discharged, i.e. if there is a sufficient potential difference (driving force) to do so. We can say that the charge released during discharging is the one refilled during charging, hence the importance of an optimum contact between granules and the current collector in reactor systems [31,33].

Fig. 5 is meant to give a schematic overview of the different currents during charging and discharging and the consequent changes in granule potential. During charging, the EAB grow on the surface of the granules and use the granule as an electron acceptor for the oxidation of acetate. The oxidation of substrate leads to a I_{far} that is stored in the EDL of the granule (Fig. 5A). The electrons stored in the granule during charging are, more or less, at the energy level of acetate oxidation and therefore, as the amount of stored charge increases, the potential of the granule decreases

towards the equilibrium potential of acetate oxidation. When the equilibrium potential is reached, acetate oxidation and consequent charging of the granule stops. During discharging (Fig. 5B), the stored charge is released. The released charge, driven by this potential difference results in I_{cap} . As charge moves out of the granule, the potential of the granule increases. At the same time, the electrons from the oxidation of acetate by the EAB can directly be released, which results in a simultaneous I_{far} . Therefore, it is of great importance that granules have a correct charging and discharging process to ensure an optimum bacterial growth.

Besides the ratio of capacitive and faradaic currents, which is reflected in the duration of charge/discharge cycles, the biofilm growth is also affected by parameters like fluid dynamics, shear stresses and other physio-chemical parameters. As example, Caizán-Juanarena et al. (2019) reported that the shortest charge and discharge times (2 min), and thus faster granule flow rates, should be used to achieve the maximum potential of charge storage in AC granules [43]. In this study, biofilm growth was under static conditions and SEM images showed that the whole carbon surface was covered with microorganisms. On the contrary, this was not the case in granules from a moving bed reactor, where biofilm growth was limited to inner macropores as consequence of shear stress [42]. This shows how reactor conditions can also affect biofilm growth, which similarly will affect the specific current production and Coulombic efficiency, as well as the charge/discharge rates of capacitive bioanodes. In fact, an optimum charging and consequent discharging process will only occur if there is sufficient bacterial activity to charge the granules. For this reason, in the future up-scaled reactors should incorporate regular check-ups on the performance of capacitive bioanodes, such as the measurements of granule potential or biomass activity, as already done in some studies [42,44].

6. Capacitance of porous electrodes in combination with biofilm

Current and potential responses in AC granules are different during charge/discharge cycles when biofilm is present compared to bare granules. Fig. 6 shows an overview of the charge/discharge cycles of abiotic and biotic (days 6, 18 and 35 after bacteria inoculation) single AC granules at a controlled current (galvanostatic), potential (potentiostatic) and cyclic voltammetry test.

Fig. 6A shows that a higher current regime due to I_{far} in granules with biofilm causes charge and discharge cycles to shorten up compared to abiotic granules (day 0). Fig. 6B shows that, with biofilm growth, the current did not decrease to zero during discharge as in abiotic conditions, but instead reached a certain steady-state that is equal to I_{far} . The current peak, belonging to I_{cap} , decreased with an increased growth of biofilm. This is an indication of a lower charge storage capacity of the granular bioanode when a biofilm is present. Fig. 6C shows that at the same potential range and scan rate (0.3 mV s^{-1}), biotic AC granules did not have a symmetric current response as in abiotic conditions (typical of

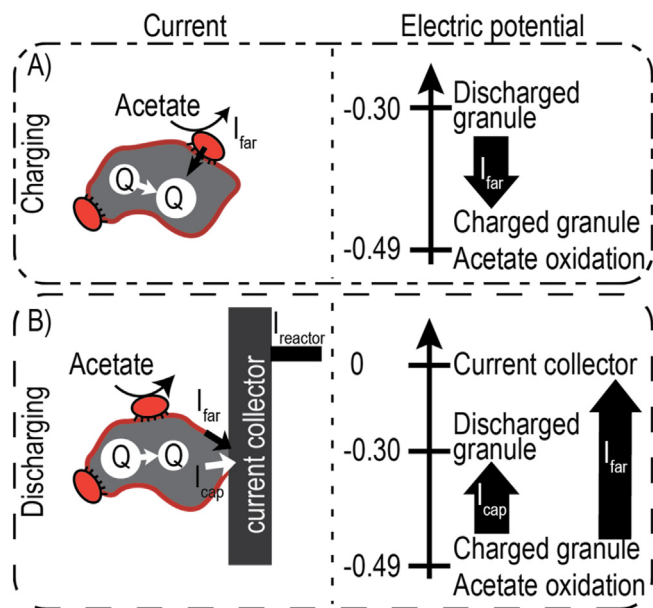


Fig. 5. Charging and discharging of granules in a reactor system. Schematic overview of currents and the resulting changes in the electric potential. (A) for charging and (B) for discharging. The charge stored is shown as Q , with the relative amount indicated by the size of the Q .

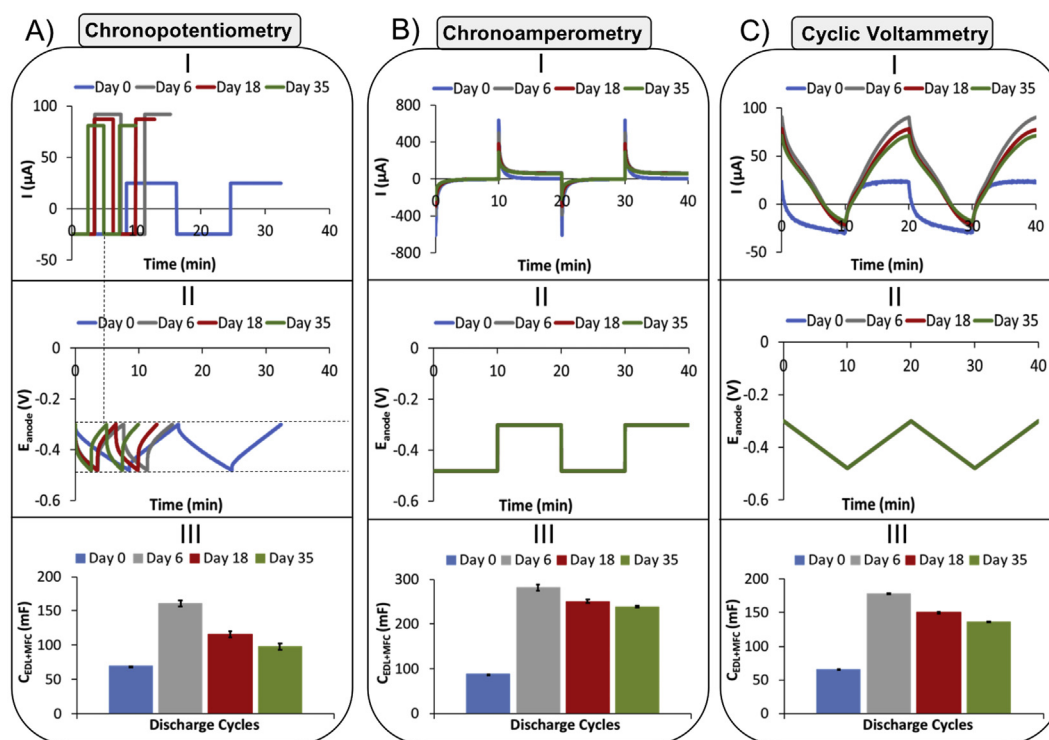


Fig. 6. Current (I) and potential (II) responses of a capacitive anode (single AC granule) with biofilm during 2 charge/discharge cycles with different electrochemical techniques: A) Chronopotentiometry; B) Chronoamperometry and C) Cyclic Voltammetry. The horizontal dotted lines mark the potential range at which the measurements were set, while the vertical dotted line points the end of a charge/discharge cycle in both current and potential graphs. The average apparent capacitance (III) of 3 discharge cycles was also calculated.

capacitive materials) but instead a quasi linear response (typical of pseudocapacitive materials), reaching negative values only close to the open cell potential (OCP).

As consequence of these responses, the apparent capacitance (Fig. 6, III) increases for capacitive bioanodes compared to abiotic AC granules, although over time and along with biofilm growth there is a decrease due to a lower I_{far} (measured as 67, 62 and 53 μA on days 6, 18 and 35, respectively) and/or I_{cap} (with a consecutive decrease of 139, 117 and 88 μA on days 6, 18 and 35, respectively). I_{cap} showed the largest decrease already at day 6, indicating that bacterial colonization of the carbon surface rather than an increase of biofilm thickness influences it. Two possible reasons are that i) bacterial growth blocks the pores of the granule, thus decreasing the available surface area for EDL formation and ii) the surface for EDL formation is the same but the rate at which it is formed is limited by an increased ion transport resistance, even though these effects seem to be more important in a mature biofilms rather than in thin biofilms [45,46]. Nuclear magnetic resonance has been used to calculate effective diffusion coefficients in EABs [47,48], which could be useful to do during *in situ* charge/discharge experiments. Also monitoring 3-dimensional biofilm growth in time around AC granules can give information of the distribution, thickness and volume of such biofilm [49].

As chronoamperometry has a fixed potential (-0.3 V) during discharge, it allows for the determination of I_{far} (Fig. 6B), which can be subtracted from the total current and thus be used to determine the I_{cap} [43]. Nevertheless, these calculations may be subject to errors; on the one hand, I_{far} is difficult to determine as it depends on the anode potential and, even at a constant potential discharge, it could fluctuate. Therefore, reporting the apparent capacitance as in Fig. 6 (III) could be a safer option than calculating the electrode capacitance under biotic conditions. On the other hand, the exact

values of electrode potential differences between charge and discharge cycles, which are needed to determine the capacitance, cannot always be correctly taken (e.g. in some cases the OCP cannot be recorded). Therefore, charge storage instead of capacitance is often reported, which describes the actual charge release by the capacitive bioanodes at a certain potential [43]. Of course, the OCP will vary largely according to bacterial activity, and so it is important to keep bacterial growth similar between different capacitive bioanodes in order to make more reasonable comparisons. In fact, a lower charge storage was found for the same type and size of granules that had lower current production during discharge, although not specific differences could be found on the discharge rate or curve [43].

7. Properties of granular activated carbon and their significance as capacitive bioanodes

Common precursors of activated carbon are biomass (e.g. wood, nut cells), coals, petroleum coke or selected polymers (e.g. polyvinylidene chloride). These precursors usually have relatively low porosity and blocked pore entrances. Therefore, the activation process, which is mainly physical or chemical, opens these existing pores but also creates new ones, so the total pore volume of the material is higher after activation. Depending on the carbon precursor and activation conditions (mostly temperature, time and gaseous environment), the resulting properties of the activated carbon will vary and can be controlled to some extent [50]. But generally, AC granules have a very complex and heterogeneous structure that makes the charge storage process difficult to understand. Additionally, when microorganisms are also involved in the charge process, operational conditions of MFCs such as the availability of substrate, electrolyte composition, internal

resistances or cell design, among others, will also determine the performance of granular capacitive bioanodes. Here, we discuss the key properties and factors to consider when choosing granular AC as electrode material in capacitive bioanodes, with focus on the correct evaluation of its performance and its interaction with bio-film growth.

7.1. Capacitance

Capacitance is the measure of charge storage per voltage unit and is expressed in Farads [23]. Capacitance of carbon electrodes will largely depend on the surface area of the material, which allows for EDL formation and thus charge storage. BET (Brunauer-Emmett-Teller) surface area, determined by N_2 adsorption, is traditionally used to define the sorption capacity of electrode materials [51]. However, this area is often overestimated as the N_2 gas is less susceptible than the electrolyte to carbon properties and so its accessible area is less restricted [52].

Theoretically, an approximated capacitance value of 100 F g^{-1} is expected for a carbon surface area of $1000 \text{ m}^2 \text{ g}^{-1}$ [53]. Nevertheless, it was proven that a strong activation process, leading to an increased surface area of the carbon (usually above $1200\text{--}1500 \text{ m}^2 \text{ g}^{-1}$), does not necessarily come along with an increase in capacitance [50]. This can relate to the pore size distribution of activated carbons; while micropores ($< 2 \text{ nm}$) are the ones contributing most to the surface area (due to their high surface area-to-volume ratio), they generally lead to restricted electrolyte diffusion into and outside the pores and, ultimately, to a restricted EDL formation or capacitance. In aqueous electrolytes (H_2SO_4), the optimum micropore range was found to be $0.8\text{--}2 \text{ nm}$ [50]; in fact, it was calculated that pores bigger than 1.1 nm could be accessed by the electrolyte in less than 0.1 s , while pores of about 0.6 nm could only be accessed after 5 s [52]. As for mesopores ($2\text{--}50 \text{ nm}$) and macropores ($> 50 \text{ nm}$), even though contributing less to the carbon surface area, they are known to improve the accessibility of ions and act as transport channels to smaller pores [50]. Therefore, pore size distribution and network connection between large and small pores are of great importance to increase capacitance of carbon materials and lead to high energy delivery rates [52]. Additionally, there are other factors that can influence the value of capacitance [50] and explain its non-linearity with the carbon SSA, such as carbon morphology (e.g. size, shape) [43], surface chemistry (e.g. oxygen functional groups) (see section 7.4), electrical conductivity of the carbon (see section 7.4) or the electrochemical techniques used to calculate capacitance (see section 6).

Capacitance, despite all above explained complexity, it is the main criteria upon material selection and system design both in EDLCs and capacitive MFCs [24]. Table 2 shows some values of

capacitance and BET surface area for carbon materials used in MFC studies, together with some others from the field of EDLCs and capacitive deionization (CDI). These capacitance values were obtained under static conditions, i.e. with constant contact to the current collector, without the presence of biofilm and with aqueous electrolytes. The reported capacitance values are several orders of magnitude different among each other, even though the BET areas are similar. This shows the large variability found in the literature, which could relate to the already mentioned factors adding complexity to capacitance determination. It is worth highlighting that, in the field of MFCs, capacitance can also be reported as apparent capacitance (see section 6) [54] and in many cases is not reported at all [31,40,55].

7.2. Volume

AC granules are very porous and have a rough and heterogeneous surface with a three-dimensional structure. This makes the precise characterization of granule volume and surface area challenging. Characterization of the pore size distribution of activated carbon can be done by different techniques. Mercury and helium displacements are usually used to determine the total pore volume ($\text{cm}^3 \text{ g}^{-1}$), while the adsorption with CO_2 or N_2 gases are respectively used to determine the volume of narrow micropores ($< 0.7 \text{ nm}$) and wider pores. The cumulative pore volume of both mesopores and macropores can also be obtained by mercury porosimetry [61].

Depending on the measured granule volume, different kind of densities can be reported (Fig. 7) [62]. Bulk volume, accounting for the bulk density, refers to a group of particles, in which case an additional space is included: the inter-particle volume. This volume

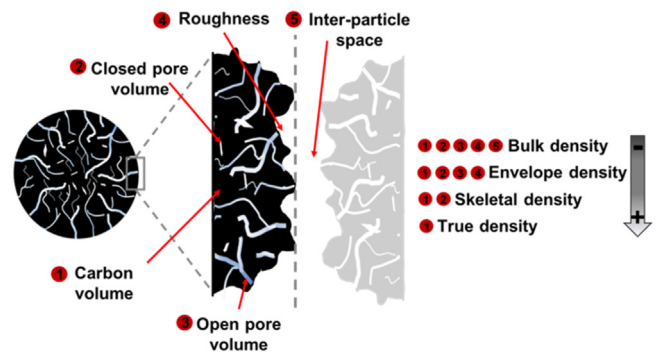


Fig. 7. Illustration of the complex structure of AC granule(s) and the possible volumes to consider (1–5) in order to calculate their density. The smaller the volume considered, the higher the density value. Modified from Ref. [62].

Table 2

Capacitance values of different carbon-based materials with certain Brunauer–Emmett–Teller (BET) surface area with aqueous electrolytes.

| Electrode material | Capacitance ($\mu\text{F cm}^{-2}$) | BET surface area ($\text{m}^2 \text{ g}^{-1}$) | Aqueous Electrolyte | Application field | Source |
|--------------------------|---------------------------------------|--|----------------------------------|-------------------|--------|
| Activated carbon granule | 9.2 | 764 | 50 mM PBS | MFC | [43] |
| Plain activated carbon | 1.6 e^6 | 542 | 50 mM PBS | MFC | [56] |
| Carbon black | 0.5 e^6 | 213 | 50 mM PBS | MFC | [56] |
| Carbon brush | 46 e^{3a} | – | 50% buffer solution ^c | MFC | [57] |
| Graphite plate | 1 e^{3a} | – | 20 mM PBS | MFC | [58] |
| 3D-graphene nanosheets | 13 e^{-3} | 300–400 | Buffer solution ^c | MFC | [59] |
| Activated carbon | 12.6 | 1072 | 1 M H_2SO_4 | EDLC | [60] |
| Graphite cloth | 10.7 | 630 | 10% NaCl | EDLC | [50] |
| Activated carbon cloth | 12.2 | 778 | 0.1 M ^b | CDI | [51] |

PBS= Phosphate Buffered Saline.

^a Electrode projected surface area.

^b Mixture of stock solutions (0.1 M) of LiCl, NaCl, KCl, NaBr and $NaNO_3$.

^c 0.1 M Potassium phosphate buffer and 0.1 M KCl.

will largely depend on the size and shape of the individual particles and how well they are packed. When regarding a single particle, bulk volume refers to the dimensional measurements of such particle (i.e. length x width x depth), also known as geometric volume. The roughness of a particle refers to the space in between the open pores (penetrating in the interior of the particle) and the bulk solution, while the open pores cover three different sizes: macropores (> 50 nm), mesopores (2–50 nm) and micropores (< 2 nm) [63]. Together with the carbon structure, these volumes account for the envelope density. When only the volume of the carbon structure and closed pores is considered, the skeletal density is defined, while if only the carbon volume is considered, the true density of the material is determined. The true density is therefore the highest density, while the bulk density is the lowest one. When reporting current densities in terms of volume, whether in a single granule study or a reactor system, it should be clear which volume of the carbon particle is referred to.

7.3. Surface area

Besides the volume, considering which surface area is relevant for assessing the performance of AC granules is also important. The surface area will determine both the formation of EDL, which relates to charge storage, and the current production, which relates to microbial activity. Since bacteria can only colonize the carbon surface (roughness) and pores bigger than their own size (0.5–1 μm), the question arises which surface area is the most relevant one.

The outer surface area (SA) can be calculated from the bulk volume by assuming the granules are spherical. Even though a spherical shape seldom corresponds to the real shape of AC granules, a linear relation ($R^2 = 0.9$) between the outer SA and the amount of quantified biomass (as total nitrogen) has been found [43]. Therefore, as larger surface area benefits bacterial growth, AC granules with high surface-area-to-volume (SA:V) ratio can be beneficial from an application point of view. In this sense, small granules would be preferable as they have a larger SA:V ratio (Fig. 8) and showed higher volumetric current densities. While current production relates mostly to the outer SA of granules, charge storage relates to their specific surface area (SSA), as it represents the available internal area for ion adsorption and hence the support for EDL formation (see sections 3 and 7.1 for more information).

7.4. Other material properties and possible electrode modifications

The research direction of carbon-based electrochemical

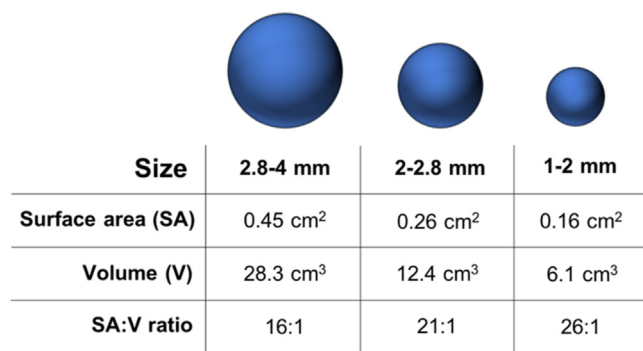


Fig. 8. Examples of the size range of AC granules (PK), with their approximated outer surface area, volume, and surface-area-to-volume ratio values. The smallest the (spherical) granule, the higher the SA:V ratio.

capacitors focuses on materials with high SSA and a rational pore distribution, but also materials with smaller internal resistances and surface modification [64]. Regarding internal resistances, using highly electrically conductive (S m^{-1}) carbon materials is crucial to achieve high power output supercapacitors [50]. The electrical conductivity will depend on the chemical and structural morphology of the carbon, i.e. the degree of crystallographic orientation. In general, carbon precursors have very high resistivity ($> 10^{12} \Omega \text{ cm}$) and hence low electrical conductivity, but when they are heat treated (up to 600–700 $^{\circ}\text{C}$) this resistivity decreases as electrons delocalize and become available as charge carriers. Active carbon has an approximate electrical resistivity of $\sim 0.2 \Omega \text{ cm}$ (calculated at a compaction pressure of 2000 kgf cm^{-2}) while graphite has a resistivity of $1.3 \cdot 10^{-3} \Omega \text{ cm}$ and titanium of $42 \cdot 10^{-6} \Omega \text{ cm}$ [50,65]. As suggested in the previous section, a thin capacitive layer could be coated on a (spherical) carrier, which could actually be a more conductive material than AC such as graphite or a metallic particle. In this way, the combined effect of a capacitive material (in the outer layer) and a conductive material (in the inner layer) could be investigated, which might benefit both a high charge storage and roughness but also a high electron transfer rate. It is important to realize that, during electrode formation with AC powder, for example, a binder (often polytetrafluoroethylene) is also needed, which will add extra electrical resistivity and might also block some pores of the carbon [66]. While resistivity is an intrinsic material property, electrical resistance is linearly related to the path length of electron flow. Therefore, special attention should be paid to the electrode configuration in order to minimize travel distances and so decrease electrode ohmic losses [65]. This can be the case on a granular bed reactor consisting of several layers of carbon particles, where the resistivity might not be dependent of the carbon properties itself but instead be related to the contact between particles or between the particles and the current collector [50].

Regarding surface properties, these can modify the electrochemical interfacial state of carbon and its double-layer properties, such as wettability, point of zero charge, adsorption of ions (capacitance) and self-discharge characteristics. Carbon-oxygen complexes are by far the most important surface groups on carbon. If the functional groups are electrochemically inert, they can enhance surface wettability and lead to larger specific capacitance of the carbon due to the improved pore accessibility. However, when they react, they can contribute to self-discharge of the capacitive carbon, as it is the case for oxygen functional groups that serve as active sites. Therefore, the removal of oxygen from the carbon (e.g. by high temperature treatment) generally improves the stability of capacitive electrodes [50]. A lot of research has been done on electrode surface modifications not only to increase MFC power output but also to explore on the effect of functional groups on capacitance and on biofilm colonization of the electrode surface [52]. Regarding the interface between biofilms and electrodes, recent research has focused on the treatment or modification of carbon-based materials to increase MFC performance in terms of current density and power output [65,67]. For example, it was found that negatively charged groups at the surface (carboxylate) decreased MFC power output while the introduction of positively charged groups (e.g. aryl-amine groups) doubled the power output due to an enhanced biofilm growth [68]. Biofilm attachment and hence MFC current density and power output were also found to increase by adding surface functionalities like boronic acids that have high affinity to compounds (lipopolysaccharides) present in the external membrane of known EAB [69].

Alternatively to carbon materials, pseudocapacitive materials (e.g. conductive polymers, metal oxides) are also widely used in electrochemical supercapacitors [70]. These can be used to create

carbon composites by modifying carbon materials with conductive polymers (e.g. aniline, pyrrole) or inserting electroactive particles of transition metal oxides (e.g. RuO₂, TiO₂, MnO₂), among others [52,64,71]. As they undergo fast and reversible faradaic reactions that occur both on the electrode surface and in the bulk near the surface, they are able to increase capacitance values and energy density of electrochemical supercapacitors [83]. Such pseudocapacitive effect can be similarly achieved by the presence of oxygen and nitrogen heteroatoms in the carbon network that undergo faradaic reactions [72].

8. Outlook

The use of AC granules as three-dimensional electrode material in BESs successfully increases the overall power output, it allows for the treatment of low conductivity wastewaters and reduces the risk of clogging. However, one of the key aspects that needs further study and development is the discharge of these granules, which is crucial to reach the full potential of such granules. In most proposed reactor systems, granules are charged in such way that they only have a limited contribution to the treatment of wastewater. Better discharging properties (e.g. better granule-current collector contact, larger retention times) would therefore allow for more overall charge storage and thus also wastewater treatment. Furthermore, better discharge processes could allow for a more defined charge/discharge cycling periods, which similarly would lead to better reactor designs as the desired contact time with the current collector would be known.

The final performance of activated carbon granules is very related to its physico-chemical properties, mostly to the specific surface area but not limited to it. In fact, we have seen how charge storage/capacitance will depend on many other factors (e.g. pore size distribution, surface chemistry, charge/discharge times, reactor conditions) that often make difficult to have comparable carbon materials and to optimize them according to the specific need. It is important to keep in mind that capacitive MFCs should not be directly compared to commercially available electric double layer capacitors (EDLCs) as, for example, these latter have capacitances in the order of Farads (50–7000 F [73]) that would require recharging times (i.e. open circuit periods) in the order of several minutes to hours at the low current regimes of MFCs (order of μA). Moreover, MFCs have an added factor that will determine their performance and that is the activity of EAB growing on the surface. Bacterial growth is a very important aspect to consider when optimizing the current production and Coulombic efficiency of the system. Therefore, studying biofilm formation, determining capacitive electrode properties and most importantly understanding the biofilm-electrode interaction is of utmost importance to achieve high MFC performance. To this end, the study of single AC granules [33,44] have shown to provide valuable information for their further implementation in larger scale systems such as packed [34] or fluidized bed reactors [32]. NMR has been used to make a 3D visualization of the biofilm on AC granules [49], however, more details on EAB growth as a function of material properties and experimental conditions are needed. Competition with methanogens becomes an important question here as well, and strategies need to be found to give a competitive advantage to EAB rather than to methanogens [74,75].

The use of AC granules is not only interesting for bioanodes, but has also been demonstrated for cathodes in methane-producing BESs (Liu et al., 2018), where the AC granule properties were shown to result in lower cathode overpotentials compared to non-capacitive granules. In addition to the use of AC granules as electrode material in anodes or cathodes, many studies have investigated the effect of adding conductive materials like such granules

on methanogenesis [76–80]. These conductive materials are thought to act as substitute for biological connections, such as membrane proteins (cytochromes) or nanowires, that allow direct interspecies electron transfer in anaerobic granules and consequently improve methanogenic rates and the overall performance of anaerobic digester. Another interesting property of AC is its ability to absorb different types of ions. Combined absorption and conversion may be beneficial in certain types of applications where specific ions need to be removed or are present in very low concentrations. In that respect, the use of AC as electrode material may offer opportunities for e.g. biodegradation of micropollutants [81,82]. With the insights reported in this work, we believe AC granules as electrode material offer many opportunities for further development of BESs towards application.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Catalogue

| | |
|------|---------------------------------|
| AC | Activated carbon |
| BES | Bioelectrochemical system |
| BET | Brunauer-Emmett-Teller |
| EAB | Electroactive bacteria |
| EC | Electrochemical capacitor |
| EDL | Electric double layer |
| EDLC | Electric double layer capacitor |
| MFC | Microbial fuel cell |
| OCV | Open cell potential |
| SA | Surface area |
| SSA | Specific surface area |

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