Electrochimica Acta 372 (2021) 137853

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Gas diffusion electrodes modified with binary doped polyaniline for enhanced CO_2 conversion during microbial electrosynthesis

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ARTICLE INFO

Article history:
Received 17 December 2020
Revised 15 January 2021
Accepted 23 January 2021
Available online 27 January 2021

Keywords:
Bioelectrochemical systems
Microbial electrosynthesis
Carbon dioxide
Gas diffusion electrode
Polyaniline

ABSTRACT

Microbial electrosynthesis (MES) is a promising technology to convert CO_2 into value-added chemicals. Enhancing the interactions between biofilms and electrodes is the key of bioelectrochemical systems (BES). In this work, we studied the conversion of CO_2 by MES in reactors equipped with novel gas diffusion electrodes (GDEs) modified with a polyaniline (PANI) polymer binary doped with H_2SO_4 and ammonium lauryl sulfate. The enhanced conductive and hydrophilic properties of the polymer increased the biocompatibility of the PANI-modified GDEs compared to the non-modified carbon GDEs. This increased biocompatibility resulted in faster start-up and higher bioproduction of volatile fatty acids (VFAs) such as acetate and butyrate. Up to 4400 ppm acetate was produced in PANI-modified reactors after 24 days of operation, compared to 408 ppm in reactors equipped with non-modified GDEs. A maximum acetate concentration of 7500 ppm (production rate of 554.8 ± 267.5 ppm day^{-1}) was reached in reactors equipped with PANI-GDEs. After 60 days, apart from acetate, 245 ppm butyrate was produced in reactors equipped with the electrodes modified with PANI, while less than 60 ppm was produced with non-modified GDEs. SEM analysis revealed the development of biofilms on both modified and non-modified electrodes, but the images also suggest differences in compositions.

1. Introduction

In light of the on-going climate crisis and more specifically of the accumulation of greenhouse gases (GHGs) such as CO_2 in the atmosphere, efforts have been undertaken globally towards developing technologies for carbon capture and storage (CCS) and carbon capture and utilisation (CCU) [18]. Despite being a major contributor to global warming, CO_2 is also a potential resource as a building block for more valuable organic molecules, especially when using microorganisms as catalysts [55]. In this context, technologies such as gas fermentation and microbial electrosynthesis (MES) are particularly attractive, with the required reducing power coming from a gaseous stream or in solution in the former case, or from renewable energies in the latter [15,55]. Since the first studies reported in 2010 [49], MES has attracted increasing attention, although ten years later the technology is far from being mature enough for industrialisation.

To date, acetate is the main product from CO_2 conversion by MES [28] and efforts have been put in increasing selectivity, titres and production rates [2,8,17,24,31,32]. Recently, an acetate production rates of 18.7 g L^{-1} day^{-1} was reached [39]. Most valuable compounds such as n-butyrate, propionate, ethanol, butanol, and isopropanol have also been targeted with more or less success in terms of productivity and selectivity [3,7,26,34,35,53,59]. The production of higher value compounds has indeed increased over the last few years, but major bottlenecks remain for the development of the technology. Amongst them, the slow development of CO_2-reducing biofilms leading to the slow start-up of the MES process has often been mentioned [27,29] and so has the solubility of CO_2 and its availability to the biocatalyst [7,48]. It was reported that the utilisation of gas diffusion electrodes (GDEs) could significantly improve the bioavailability of gaseous substrates in bioelectrochemical systems (BES). For instance, GDEs were successfully implemented as cathodes in BES for the reduction of O_2 [22,62]. It was also reported that

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https://doi.org/10.1016/j.electacta.2021.137853

GDEs could improve the bioavailability of CO_2 and thus increase its conversion rate and the production of the corresponding reduced compounds compared to conventional submerged systems [5,57].

Improving the interactions between the microorganisms and the electrode in terms of biofilm development and electron transfer is the key of every bioelectrochemical system. Electrode surface modification to improve these interactions has been widely studied for the development of bioanodes with the coating of organic and non-organic layers on carbon- or metallic-based materials [4,14,21,25,61,63,64]. Polyaniline (PANI) is a conductive polymer that has been widely employed in BES because of its low fabrication cost, excellent electrochemical activity and good biocompatibility [25,60]. A large number of studies reporting the utilisation of PANI in BES focus on the development of bioanodes [16,21,25,45,61,63,64]. It was indeed reported that the modification of conventional carbon-based material with PANI polymers greatly increases microorganisms adhesion onto the electrode surface, thus also increasing the current densities achieved [16]. The polymer has also been successfully associated with various metal-based catalysts such as iron phtalocyanine, $MnFe_2O_4$, Cu, MnO_2 or Fe_2O_4 to be used as inexpensive and effective air cathodes in microbial fuel cells (MFCs) [1,36,56,65]. However, to the best of the authors knowledge, only a few studies reported the of PANI polymer for aerobic biocathodes [40], and none for CO_2-reducing biocathodes for MES. As mentioned previously, the slow development of CO_2-reducing biofilms as well as the long start-up time associated with the bioproduction is currently limiting the development of MES. Therefore, in this study, enhancing the bioavailability of CO_2 *via* the utilisation of GDEs and increasing the biocompatibility and conductivity of the electrodes using PANI polymer is an interesting approach to overcome these limitations. In this work, we studied the impact of the utilisation of carbon-based GDEs modified with PANI doped with H_2SO_4 and ammonium lauryl sulfate on the CO_2 conversion by MES, especially in terms of start-up time and bio-production. Physico-chemical and electrochemical properties of the electrodes prior to and after the MES experiment were evaluated, and the concentrations of the main volatile fatty acids produced were followed.

2. Experimental

2.1. Synthesis of binary doped PANI polymer

The synthesis of the binary (sulphuric acid and ammonium lauryl sulfate) doped PANI was carried out as described elsewhere [13]. Brifely, 9.8 mmol of aniline were added to 0.62 mol of chloroform in a round bottom flask under constant stirring at room temperature following by the addition of 8 mmol of ammonium lauryl sulfate. After this, 1.2 mmol of H_2SO_4 and ammonium persulfate dissolved in 100 ml water, were dropwise added in the above mixture, respectively. The mixture turned green with time showing formation of PANI. After 24 h the reaction was stopped, the polymer was separated from this mixture through a separatory funnel and washed with distilled water and acetone. The obtained PANI powder was dried in vacuum.

2.2. Electrode surface modification

In order to increase the reproducibility of the modification procedure, higher surfaces of GDEs were modified at once before being cut into the desirable size. Typically, 30 mg of H_2SO_4-PANI were dissolved into 5 mL N-Methyl-2-pyrrolidone (NMP) and stirred until complete dissolution was obtained. A large GDE with a geometric surface area of 60 cm^2 was homogeneously painted with an air gun and let to dry. The GDE was painted layer by layer following this procedure until a 0.5 mg cm^{-2} loading was reached. GDEs with active surface area of 12.5 cm^2 were then cut out to be used as cathodes in the MES reactors.

2.3. Electrode characterisations

Electrochemical characterisations: Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis were performed using an Autolab PGSTAT204 potentiostat and controlled by a NOVA electrochemistry software (Metrohm, Switzerland). CVs were recorded in N_2-saturated medium at a scan rate of 2 mV s^{-1} with potential steps of 0.5 mV. Ag/AgCl reference electrodes (+0.197 V vs SHE) were used. Second voltammograms are shown in this study, unless stated otherwise. EIS was performed using a 3-electrode configuration and at an applied potential of −1.0 V vs Ag/AgCl to the cathode. The gas chamber was filled with CO_2. Frequencies from 10,000 to 0.1 Hz were applied with an amplitude of 10 mV.

Contact angle measurements: Contact angle measurements were carried out using a KSV Cam 101 system at ambient conditions. A drop of deionized water was dropped perpendicularly from a syringe onto the surface of the electrode. Images were captured once the droplet contacted the electrode surface and after 20 and 80 s, contact angles were then analysed with the tangent method of Sessile Drop Fitting.

Scanning Electron Microscopy (SEM): SEM images of the electrodes were recorded using a Tescan Vega 3LMU SEM. 1 cm × 1 cm electrode samples were prepared by fixing in 2% glutaraldehyde for 24 h, rinsed in the MES medium and dehydrated in a graded series of ethanol. Electrodes were dried using critical point drying and finally coated with gold in a SEM coating unit.

2.4. Organic compounds analysis

Volatile fatty acids (VFAs) analysis by ion chromatography using an Eco IC (Metrohm, Switzerland) equipped with a METROHM 6.1005.200 column. Alcohols were measured by gas chromatography (GC-2010, Shimadzu Tracera, Japan) equipped with a Barrier Ionization Discharge (BID) detector. A Zebron ZB-WAXplus capillary column (Phenomenex) was used for separation of acetone and alcohols. 1 mL samples were regularly taken from the anolytes and catholytes and filtered on 0.20 µm syringe filters.

2.5. Microbial electrosynthesis experiment

Each 3-chamber cells used for the MES experiment was made of Perspex and composed by anode and cathode chambers of 80 mL working volume each and by a gas chamber of 60 mL working volume. A home-made 70 mL glass reservoir was used as a gas collector at the top of the cathode chamber. The anode and cathode chambers were separated with a cation exchange membrane (FUMASEP-FKB-PK-130, Fumatech, Germany) while the cathode and gas chambers were separated with a carbon paper coated with a gas diffusion layer (GDL) purchased from Quintech (H2315 I2 C6, Göppingen, Germany) and which was used as a gas diffusion electrode. 3 × 4 cm stainless steel meshes were used as anodes (counter electrodes) with titanium wires as current collectors. The surface of the GDEs used as cathodes was 12.5 cm^2, and titanium sheets were used as current collectors. Ag/AgCl reference electrodes (RE-5B, BASi, USA) were placed 1 cm from the GDEs. All the potentials in this study are reported vs. Ag/AgCl. 20% of the cathodic compartment was inoculated with the effluent of a previously running MES reactor with a microbial community dominated by *Acetobacterium Pullulanibacillus* and *Rummeliibacillus,* with acetate as the main product. Considering that the inoculum was

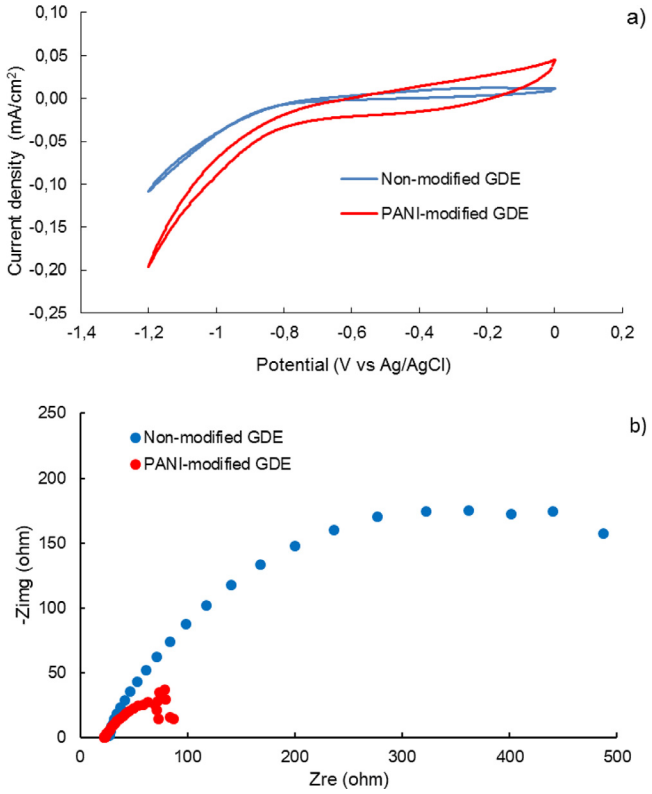

Fig. 1. a) Cyclic voltammograms of non-modified and PANI-modified GDEs recorded in N2-saturated medium at 2 mV s-1, b) Nyquist plots of the non-modified and PANI-modified GDEs recorded at −1.0 V vs Ag/AgCl with the gas chamber filled with CO_2.

from a running MES reactor, acetate (about 420 ppm) was present in the cells at the beginning of the experiment. Both the anodic and cathodic media consisted of K_2HPO_4 (0.35 g L^{-1}), KH_2PO_4 (0.25 g L^{-1}), NH_4Cl (0.25 g L^{-1}), KCl (0.5 g L^{-1}), $CaCl_2 \bullet 2H_2O$ (0.15 g L^{-1}), $MgCL_2 \bullet 6H_2O$ (0.6 g L-1), NaCl (1.2 g L-1), yeast extract (0.01 g L^{-1}), Trace metal solution (1 ml L^{-1}), Vitamin solution (2.5 ml L^{-1}), Tungstate-selenium solution (0.1 ml L^{-1}) as reported elsewhere [50]. 5 mM sodium 2-bromoethanesulfonate was added to the cathodic medium at the beginning of the experiment to act as a methanogen inhibitor. Experiments were carried out in duplicates: 2 cells equipped with non-modified GDEs and 2 cells equipped with PANI-modified GDEs were run in parallel, and averaged results are presented. CO_2 was constantly supplied in the gas chamber of each cell. The cathodes potential was set to −1.0 V vs Ag/AgCl and controlled with a Quad potentiostat (Whistonbrook Technologies, UK). Reactors were placed in a polystyrene box filled with aluminium foil and the temperature was maintained around 30 °C throughout the experiment.

3. Results and discussion

3.1. Electrochemical and contact angle characterisations of the non-modified and PANI-modified GDEs

Electrochemical characterisation of the non-modified and PANI-modified GDEs was carried out prior to the start of the BES experiment. Cyclic voltammograms as well as electrochemical impedance spectra (Nyquist plots) are presented in Fig. 1,a and b, respectively. As can be seen in Fig. 1,a, PANI-modified GDEs present a higher capacitive current which can be explained by a higher specific surface area of modified GDEs due to the presence of the polymer, compared to non-modified electrodes.

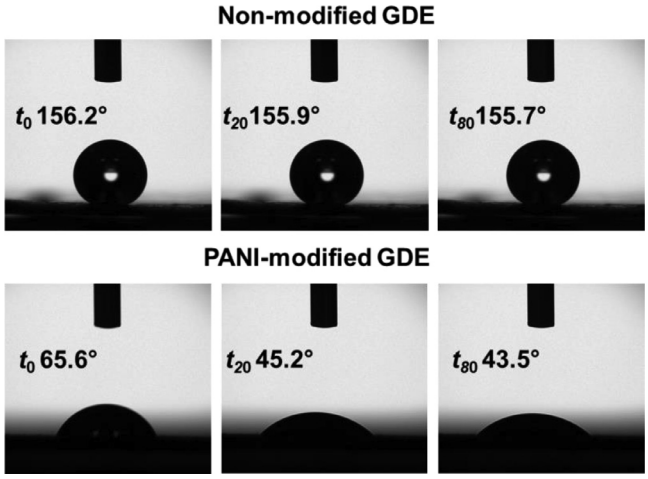

Fig. 2. Contact angle measurements for non-modified (top) and modified (bottom) GDEs at $t = 0$, 20 and 80 s.

In addition, the signal observed for the PANI-modified GDEs highlights a higher activity towards the hydrogen evolution reaction (HER). Considering that the CVs were recorded in N_2-saturdated medium (no contribution of the oxygen reduction reaction), the higher current density monitored on PANI-modified electrodes than on non-modified electrodes (−0.20 mA cm^{-2} at −1.2 V vs Ag/AgCl vs −0.10 mA cm^{-2}, respectively) can be attributed to a higher activity towards HER. According to recent studies, a higher activity towards HER is expected to be beneficial for MES as it was shown that H_2-mediated electron transfer (MET) is the most likely mechanism for CO_2 conversion in bioelectrochemical systems [23,47,58]. The Nyquist plot of the non-modified GDE (Fig. 1,b) is consisted of a semi-circle with high charge-transfer resistance that can be compared with a finite length Warburg element. The spectrum of the PANI-modified GDE also exhibits a clear semi-circle but with a much lower charge transfer resistance (which can be estimated with the intercept of the semi-circle with the x-axis). This observation suggests the positive impact of the polymer on the conductivity of the electrode material.

The hydrophilicity of the non-modified and modified electrodes was also evaluated by contact angle measurement (Fig. 2). Non-modified GDEs exhibit clear hydrophobic properties with a high contact angle only decreasing from 156.2° to 155.7° in 80 s. The lower contact angle of 65.6° decreasing to 43.5° after 80 s measured for PANI-modified GDEs shows a much higher hydrophilicity of the electrode surface after modification. Hydrophilic surfaces are expected to favour the attachment and development of electroactive microbes and are more conductive for the formation of electroactive biofilms [19,54]. Therefore, the higher activity towards HER of the PANI-modified GDEs as well as their higher hydrophilicity should be beneficial to MES.

3.2. Acetate and butyrate production from CO_2 during MES

Fig. 3 presents the current density (a), pH evolution (b) and acetate and butyrate production (c-f) in the microbial electrolysis cells during the 60-day experiment. The noise monitored at the beginning of the experiment (days 0–10) especially for non-modified cells was due to interferences from the reference electrode. The cyclic fluctuations observed for the four cells throughout the experiment correspond to day and night cycles, most likely related to small variations of temperature in the laboratory especially at night-time. The general trend shows that the current density increased as the bio-production (mainly acetate) increased, although

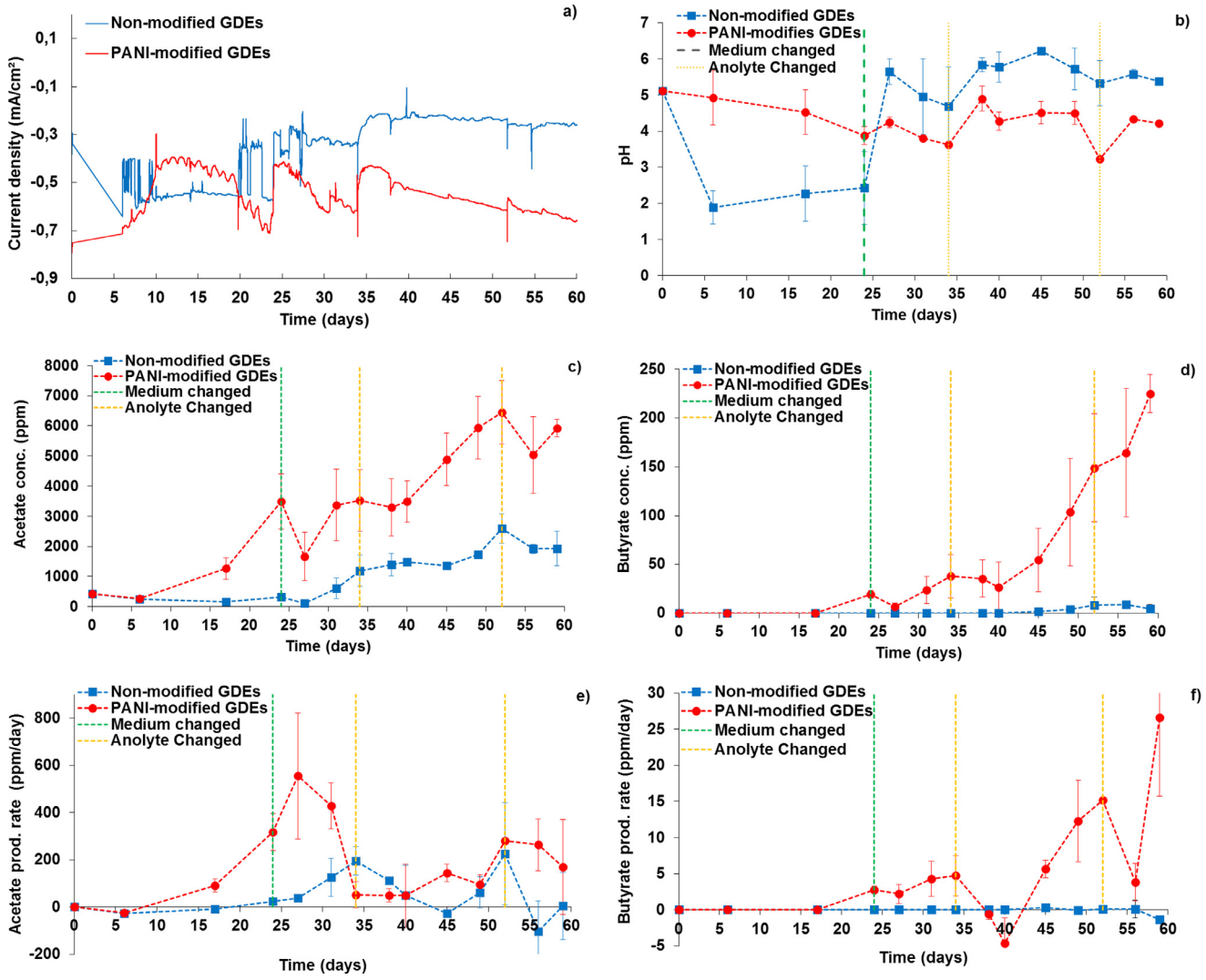

Fig. 3. a) Current densities measured during the MES experiment, b) Evolution of the pH of catholytes during the MES experiment, c) Concentration of acetate produced during the 60-day experiment, d) Concentration of butyrate produced during the 60-day experiment, e) Acetate production rate during the 60-day experiment, f) Butyrate production rate during the 60-day experiment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

this was more significant for PANI-modified cells than for non-modified cells.

Starting from day 25, the current density recorded for PANI-modified cells was noticeably higher than for non-modified cells, which is in good correlation with the production of acetate. From day 0 to day 6, the acetate concentration was similar in PANI-modified and non-modified cells, decreasing from 421 ppm to ca. 254 ppm (Fig. 3,c). The presence of acetate from the beginning of the experiment can be explained with the inoculum coming from a previously running MES and already containing acetate (about 420 ppm), which was almost totally consumed by day 6 in all cells. The quick consumption of acetate observed in all reactors can be explained by the presence of heterotrophic microorganisms in the inoculum used [23]. As depicted in Fig. 3,c-f, the presence of PANI polymer at the surface of GDE had a significant impact on the bio-production in terms of both start-up time and productivity: after day 6 acetate concentration significantly increased in PANI-modified cells to reach 1268 ± 363 ppm in PANI-modified cells on day 17 compared to 161 ± 16 ppm in non-modified cells. On day 24, acetate concentration reached 3485 ± 913 ppm in PANI-modified cells, about 10 fold the concentrations measured in non-modified cells. Changing media on day 24 logically led to a decrease in acetate total concentration, followed by an increase in production rate as high as 555 ± 268 ppm day^{-1} on day 27 in PANI-modified cells (Fig. 3,e). The acetate production rate then drastically dropped between days 34 and 37 (Fig. 3,e) which can be explained by a drop of pH as depicted in Fig. 3,b, which can be due to the accumulation of organic acids such as acetate in the catholyte. The pH dropped to about 3.5 in the PANI-modified reactors and in one of the non-modified reactor, which is much lower than the optimal pH of 5–6 for the growth of acetogens [9,37]. Although the accumulation of acetate could lead to a decrease in pH, the drop was mainly associated with the very low pH of 2 measured in the anolyte compartments during the experiment and leading to a slow equilibrium of pH through the membranes. The pH drop in the anolyte is most likely due to the oxygen evolution reaction (OER), leading to the accumulation of protons in the medium. Therefore, to limit the shift of pH in the cathodic compartments, anolytes only were completely replaced on days 34 and 52 (initial pH of the anolyte circa. 7.0). The highest acetate concentrations reached during this 60-day experiment were 7499 ppm in one duplicate of PANI-modified reactors compared to 3088 ppm in the non-modified reactors. The highest acetate production rate reached in PANI-modified reactors was 554.8 ± 267.5 ppm day^{-1}

on day 27, compared with 224.6 ± 216.5 ppm day^{-1} on day 52 in non-modified reactors, showing again the impact of PANI-modified GDEs on the bio-production. As shown in Fig. 3,d, traces of butyrate were detected on day 24 in PANI-modified reactors with 19.4 ± 3.6 ppm. Butyrate concentration increased gradually in these two reactors to reach the highest concentrations of 225.1 ± 19.6 ppm on day 59. In reactors equipped with non-modified GDEs, however, only traces of butyrate could be detected with a maximum concentration of 8.6 ± 3.4 ppm. It should be noticed that the acetate and butyrate production rates in PANI-modified reactors were inversely correlated: when the highest acetate production rate was reached (554.8 ± 267.5 ppm day^{-1} on day 27), the butyrate production rate was low (2.2 ± 1.3 ppm day^{-1}). However, from day 34 and until the end of the experiment, the acetate production rate significantly slowed down to remain fairly constant as the butyrate production rate increased (Fig. 3,d and f). Remarkably, no other compound than acetate and butyrate was detected consistently and in significant concentration during the time of experiment. Low concentrations of formate (≤ 20 ppm) were detected in all reactors whereas low concentrations of ethanol (≤ 10 ppm) were only detected in reactors equipped with PANI-modified electrodes. The low and inconsistent concentration of ethanol detected in PANI-modified reactors and not in non-modified reactors is however consistent with the presence of butyrate detected in these reactors. Indeed, these results strongly suggest that butyrate was produced from chain elongation of acetate with ethanol acting as electron donor as it was reported in other studies [2,7,24]. Therefore, as ethanol was constantly consumed by microorganisms for the chain elongation of acetate, its concentration remained low during this 60-day experiment. The trend of butyrate production in PANI-modified reactors (Fig. 3d and f) is very promising. As the results suggest, a longer experiment would lead to an accumulation of butyrate and potentially to the production of C6 VFAs or alcohols. Indeed, the low pH of 4.2 measured at the end of the experiment in PANI-modified reactors provides ideal conditions to trigger the production of alcohols by solventogenesis [3].

It should be noted that the main purpose of this experiment was to show the impact of PANI-modified GDEs on the start-up time of bio-production and productivity from CO_2 reduction compared to non-modified GDEs. However, in order to increase the productivity and selectivity of the system studied, a continuous feeding mode would be more beneficial than a fed-batch mode. It was reported that a continuous mode for both compartments could help limit the drop of pH as well as increase the productivity by continuously extracting the organics produced from the catholyte [2]. In addition, a longer experiment would be needed in order to allow the organics concentration to build-up and to steer the production towards butyrate and C6 compounds.

3.3. Electrochemical and SEM characterisations of the non-modified and PANI-modified GDEs after MES

The electrodes covered with biofilms implemented in BES were characterised after the 60-day experiment. The cyclic voltammograms and the electrochemical impedance spectra recorded after changing the medium are presented in Fig. 4.

As shown in Fig. 4,a and b, the voltammograms recorded on non-modified and modified electrodes after 60 days of experiment are quite similar, despite the evident impact of PANI on bio-production start-up and performance. In both cases, a significant shift of the onset potential of the HER of about +100 mV can be observed. In addition, voltammograms display an oxidation feature at −0.4 V vs Ag/AgCl most likely associated with the shift of onset potential of the HER. Indeed, when the cathodic potential was limited to −0.8 V instead of −1.2 V vs Ag/AgCl, this re-

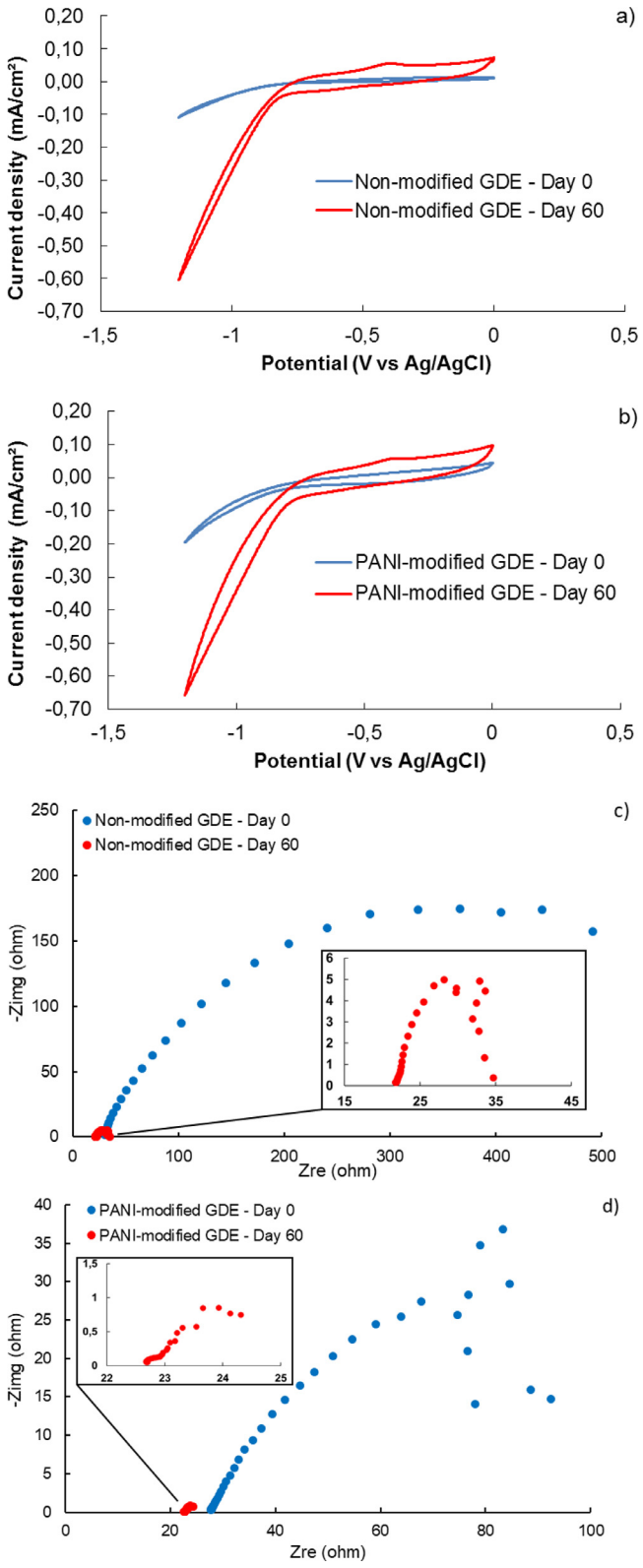

Fig. 4. a) Cyclic voltammograms of non-modified GDEs before and after the 60-day experiment N_2-saturated medium at 2 mV s-1, b) Cyclic voltammograms of PANI-modified GDEs before and after the 60-day experiment in N_2-saturated medium at 2 mV s-1, c) Nyquist plots of the non-modified GDEs before and after the 60-day experiment recorded at −1.0 V vs Ag/AgCl with the gas chamber filled with CO_2, d) Nyquist plots of the PANI-modified before and after the 60-day experiment recorded at −1.0 V vs Ag/AgCl with the gas chamber filled with CO_2.

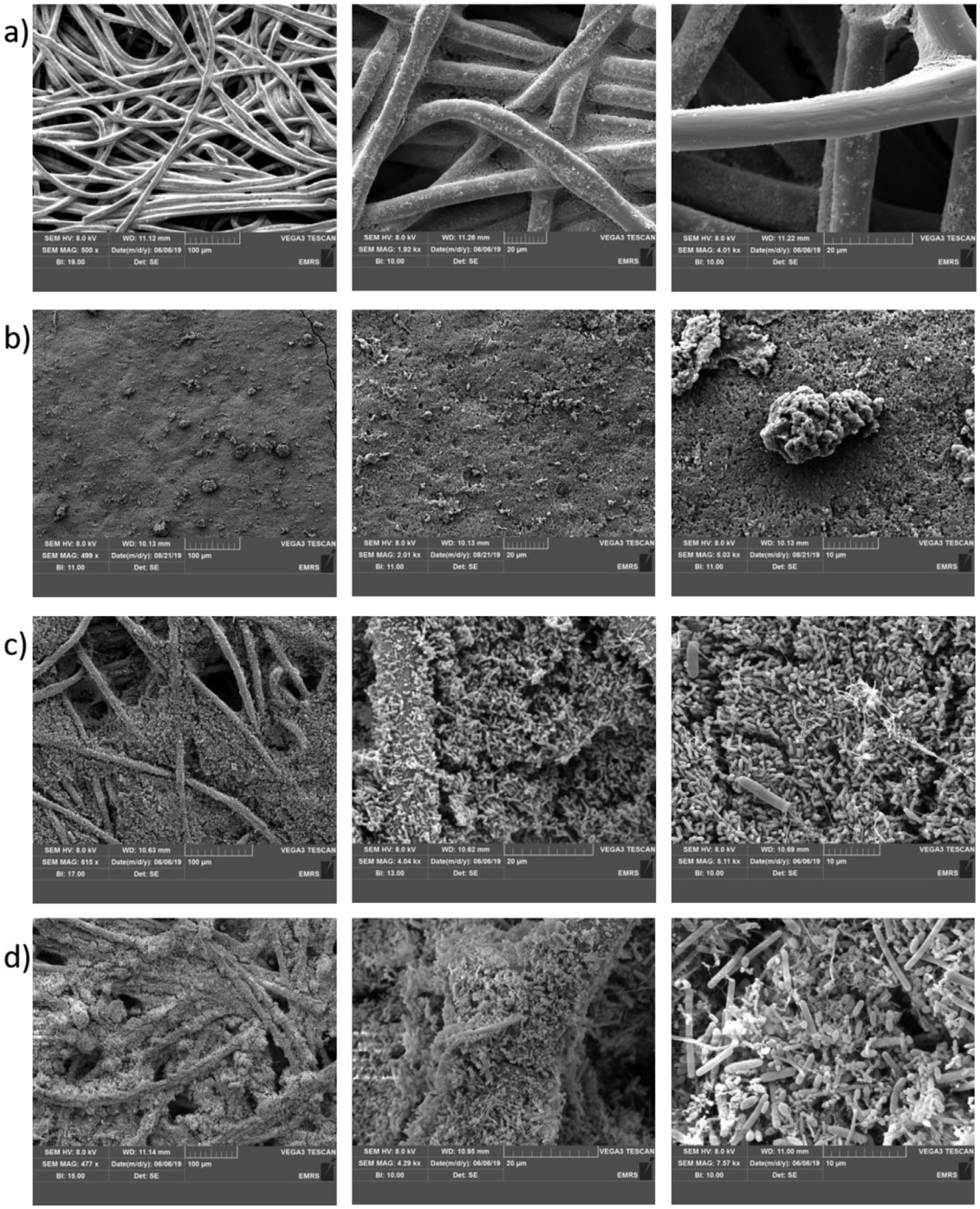

Fig. 5. Scanning Electron Microscopy images of the a) non-modified GDEs before the experiment, b) PANI-modified GDEs before the experiment, c) non-modified GDEs after the 60-day experiment, d) PANI-modified GDEs after the 60-day experiment. From left to right: 100 µm, 20 µm and 10 µm.

dox feature could not been observed anymore. These redox features were reported in a previous study and attributed to the catalytic activity of hydrogenase present in the biofilm [41]. Therefore, the cyclic voltammograms recorded on non-modified and PANI-modified electrodes at day 60 reflect the presence of the biofilms developed and their catalytic activity towards the HER. The increase of the capacitive current compared to CVs recorded on day 0 is also in agreement with this hypothesis, with the biofilms being an additional "layer" onto the electrodes' surface. Similarly, the electrochemical impedance spectra recorded on day 60 on modified and non-modified electrodes showed a strong evidence of the presence of conductive biofilms (Fig. 2,c and d). The Nyquist plot of non-modified electrode after 60 days displays a semi-circle with a much lower charge transfer resistance than on day 0 (Fig. 2, c). It was reported that the presence of a conductive biofilm at the surface of the electrode results in the Nyquist plot in an additional semi-circle (corresponding to a charge transfer resistance of smaller value), as can be observed here [20]. Similarly, the Nyquist plot of PANI-modified GDEs shows a much lower charge transfer resistance than on day 0. In the case of PANI-modified GDEs, two successive semi-circles can almost be discerned, which could be explained with the presence of several layers (biofilm and polymer) at the surface of the electrodes. GDEs were also analysed by SEM, and images are presented in Fig. 5. A significant difference

was observed between non-modified GDEs (Fig. 5,a) and PANI-modified GDEs (Fig. 5,b) at the beginning of the experiment, as the individual carbon fibres were clearly discernible in the non-modified GDEs whereas they were fully covered by the polymer on modified electrodes. These results are in agreement with the characterisation presented in Fig. 1 which also suggested the presence of a layer at the surface of the carbon GDEs.

SEM images of the non-modified electrodes after 60 days (Fig. 5,c) display the presence of a biofilm colonising the fibres but mostly limited to the surface of the electrode as voids could be observed in-between the fibres and in depth of the electrode. Interestingly, after 60 days, carbon fibres could also be observed on PANI-modified electrodes (Fig. 5,d) which could suggest the partial degradation of the polymer during the experiment. In addition to the short time of experiment, the absence of C6 compounds and high concentrations of C4 compounds can be correlated to the relatively low density of the biofilms observed. In all reactors and disregarding the nature of the GDE, carbon fibres were still visible after 60 days of experiment. However it was reported in other studies that the density of the biofilm is positively correlated with the current densities recorded and in turn with the bioproduction measured [34]. This work clearly highlights the positive impact of PANI-modified GDEs for MES. GDEs enhance the bioavailability of CO_2, but their low porosity especially compared to that of carbon felts used in most studies might be a limitation to the development of dense biofilms. It was recently reported that electrode materials with pore size ranging from 500 to 2000 µm are actually more beneficial for the development of dense and high performing anodic biofilms [10,11]. Similar results could thus be expected for cathodic biofilms.

Although the CVs presented in Fig. 4 strongly suggest the production of biologically-induced hydrogen, further investigations would be needed to conclude on the exact role of the biofilms observed here. For example, a continuous feeding mode with low HRT would show if a wash-out of the planktonic community would lead to a drop of the bioproduction, in which case the MES process would not be only limited to the biofilm [33]. Despite biofilms colonising both non-modified and modified GDEs in a rather similar manner, a noticeable difference can be observed in terms of shape and size of microorganisms composing these biofilms. As can be seen in Fig. 5c and d, non-modified electrodes were rather homogeneously colonised by rod-shaped microorganisms of 1–2 µm size, whereas it was more diverse on PANI-modified electrodes with longer rod-shaped microorganisms reaching 10–20 µm. This wider variety in terms of bacterial community can most likely be associated with the presence of butyrate in PANI-modified reactors, whereas only acetate was detected in reactors equipped with non-modified GDEs. All reactors were inoculated with the effluent from a previously running MEC with *Acetobacterium* as the most abundant bacteria in the biofilm of the corresponding reactor, and *Pullulanibacillus* and *Rummeliibacillus* as the most abundant bacteria in the bulk electrolyte. The rod-shaped microorganisms of 1–2 µm size observed in high abundance in both biofilms could suggest the presence of *Acetobacterium* [6]. *Acetobacterium* is known for dominating bacterial communities of most acetate-producing MES systems inoculated with environmental samples, which is in agreement with the results presented here [2,38,39,43,44,46]. In addition, despite *Acetobacterium* not being considered as an electroactive bacterium, it was showed that it can be involved in the extra- and intracellular production of H_2 *via* hydrogenases or nitrogenases enzymes, respectively [12,23,51,52], as the voltammograms presented in Fig. 3 suggested. To date, most MES studies focussing on acetate and H_2 production and discussing the composition of cathodic biofilms in MES reported fairly homogeneous size distribution of 1–2 µm [30,32]. Rods of 50 µm length and more were observed in a biofilm producing compounds up to C6 [34]. Although the exact role of these longer microorganisms has not been confirmed, their presence was associated with the production of a wider range of compounds than acetate. Therefore it cannot be excluded that the microorganisms of 10 – 20 µm length observed in the biofilms of the PANI-modified electrodes are related to the production of butyrate, either directly or indirectly for example *via* a synergistic mechanism with the other microorganisms observed. The presence of *Pullulanibacillus* and/or *Rummeliibacillus* in the biofilms of PANI-modified GDEs is also a possibility, which could explain the wider variety of microorganisms observed and most importantly the higher production of butyrate in these reactors. Indeed, it should be noted that *Pullulanibacillus* and *Rummeliibacillus* and were also detected in bioelectrochemical reactors running at pH $\leq$ 5 and were correlated to butyrate production [2,66]. Finally, the thin filaments of nm diameter observed in both biofilms might either be extracellular polymeric substances taking part in the structure of the biofilm, or conductive nanowires involved in the electron transfer mechanism, as reported in other studies [34,42]. The utilisation of binary doped PANI polymer significantly enhanced the MES process. The contact angle measurements presented in Fig. 2 showed that the polymer increased the hydrophilicity of the electrode surface, thus improving the bacterial adhesion, decreasing the start-up time of bioproduction and increasing its productivity. The production of butyrate along with the wider variety of microorganisms observed suggest that the polymer may have enhanced the adhesion and development of bacteria able to steer the production towards C4 compounds compared to the non-modified carbon GDEs. Nevertheless, further investigations such as community analysis and metagenomics would be needed to conclude on the exact composition of the biofilms observed and on the role of bacteria involved in the MES process.

Conclusions

In this work, we showed the potential of PANI-modified GDEs for the conversion of CO_2 by MES. The modification of carbon-based GDEs with H_2SO_4- and ammonium lauryl sulfate-doped polyaniline increased the hydrophilicity of carbon-based GDEs, thus increasing their biocompatibility and enhancing bacterial adhesion. The modification of GDEs with PANI led to a faster start-up of CO_2 conversion (6 days vs. 17 days) and a higher production of acetate and butyrate. Maximum concentrations of 7499 ppm of acetate and 245 ppm of butyrate were reached with PANI-modified electrodes compared to 3080 ppm and 52 ppm with non-modified electrodes, respectively. Acetate production rate was also much higher in reactors equipped with PANI-modified GDEs (554.8 ± 267.5 ppm day^{-1}) than with non-modified electrodes (224.6 ± 216.5). Imagining analysis of the GDEs after MES showed obvious differences in terms of composition in presence or absence of PANI, suggesting the impact of the polymer on the growth of the biofilm and its composition. This short 60-day experiment highlights the potential of PANI-modified GDEs to develop an efficient and rapid start-up MES by enhancing the biofilm formation and providing constant CO_2, however further optimisations and longer experiments are needed to understand the exact interaction between the polymer and the microbial community to eventually improve the selectivity of production towards longer chain organic compounds than acetate and butyrate including C6 VFAs and alcohols.

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.

Credit authorship contribution statement

Jean-Marie Fontmorin: Conceptualization, Methodology, Validation, Investigation, Visualization, Writing - original draft, Writing - review & editing, Supervision. **Paniz Izadi:** Investigation, Writing - review & editing. **Da Li:** Investigation. **Swee Su Lim:** Resources, Writing - review & editing. **Shehna Farooq:** Resources. **Sal Salma Bilal:** Resources. **Shaoan Cheng:** Funding acquisition. **Eileen Hao Yu:** Writing - review & editing, Funding acquisition, Supervision, Project administration.

Acknowledgements

The authors thank EPSRC LifesCO2R project (EP/N009746/1), EPSRC NECEM (EP/R021503/1), NBIC 002POC19034 and NERC MeteoRR (NE/L014246/1). P. Izadi thanks to the SAgE DTA PhD studentship provided by Newcastle University. The project was also supported by the Open Fund Project for State Key Laboratory of Clean Energy Utilization with Zhejiang University, project number ZJUCEU2019004. Data supporting this publication is openly available under an 'Open Data Commons Open Database License'. Additional metadata are available at https//:10.17028/rd.lboro.13655648.

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