Synthesis of Graphite Porous Electrode Based on Coconut Shell as a Potential Cathode in Bioelectrosyntesis Cell

Aris Mukimin*, Rustiana Yuliasni, Nur Zen, Kukuh Aryo Wicaksono, Januar Arif Fatkhurahman, Hanny Vistanty, and Rizal Awaludin Malik**

Center of Industrial Prevention Technology, Jl. Ki Mangunsarkoro No. 6, PO Box. 829, Semarang 50136, Indonesia

Abstract: *Electrodes, as well as microorganisms, are key materials for the development of bioelectrosynthesis cell reactor. Materials used as electrodes should be inert, crystalline in structure with high surface area and porous morphology, enhancing their electroactive and adsorptive properties. Carbon material derived from coconut shell was modified by simultaneous sintering-activation methods, $FeCl_3$ and $ZnCl_2$ were supplemented at temperature 900 °C at the non-atmospheric condition. The modified carbon was then molded with polyvinyl alcohol as a binder and the temperature was maintained at 80 °C and 10 ton of pressure. Molded carbon was then installed in bioelectrosynthesis cell with a working volume of 200 mL, as a cathode. XRD, BET, and SEM measurements showed the transformation of carbon surface from amorphous into the crystalline, increased surface area (11 times higher) and higher porosity (up to 500 nm). This cathode modification was able to increase current density up to 4 times and reduce CO_2 into butyrate, 250 mg/L, in bioelectrosynthesis cell.*

Keywords: *coconut shell carbon; bioelectrosynthesis; sintering-activation; carbon dioxide; butyrate*

■ INTRODUCTION

Carbon dioxide can be reduced into ethanol and other organic compounds such as acetate [1] by applying electrical energy and facilitated by electroactive bacteria as a catalyst [2]. This technology is called microbial electrosynthesis cell (MES). In a reducing environment, acetogenic bacteria can utilize CO_2 as sole substrate and an electron acceptor, and further use it to sustain bacterial metabolism via *wood ljungdahl pathway* mechanism [3], transform CO_2 into organic compounds such as acetate [4-5], and ethanol [6-7]. Aside from organic acids, methane can also be obtained bioelectrochemically [8].

In a microbial electrosynthesis cell system, apart from a microorganism as the sole subject of carbon dioxide reduction, the role of the electrode is also important as a substrate for bacterial attachment and electron donor [9]. Liu [10] pointed out that materials with high absorptive capacity, heat stability, and surface area would give the highest electron storage capacity. The optimal cathode for MES should have high electronic conductivity, low charge-transfer resistance, the large surface area available for electron transfer to the microbial catalyst, exceptional mechanical strength, and biocompatibility [9]. Carbon-based cathodes which are relatively cheap have been employed in MES [11-12], besides graphite felt, carbon cloth, carbon nanotube, granular graphite carbon [13-16]. Surface modification by forming three-dimensional structures was developed to enhance the performance of MES cathode due to its significant effect in improving the surface area of electrode [17-18].

Porous carbon has a strong potential to be used as a cathode in MES due to its high electron density, good accessibility and vast surface area [19]. Porous nano-sheet graphite made of coconut shell by simultaneous sintering-activation synthesis method was employed in this study. Ferric chloride, 3 M, was used as a precursor of template formation through the co-diffusion process. At the same time, zinc chloride was added to facilitate

the metal ion activation. Heating at 80 °C and calcined at 900 °C and non-atmospheric condition had transformed the character of carbon to the crystal. This preparation method had successfully formed the cementite phase by Fe and when catalyst removed, nano-sheet carbon. Rampe et al. [21] succeeded in making carbon material with aromatic characteristic and semi-crystalline structure from coconut shell. Sintering at 1673 °K was able to change the carbon material into a turbostratic structure and uniformed particle size in spherical shape.

The aim of this research was to utilize coconut shell carbon as a basic electrode material. This natural material is modified by a sintering-activation method in order to upgrade the crystal structures, enhance the surface area and porosity. Modified material was then used as bio-cathode in MES system to reduce CO_2 into simple organic compounds.

■ EXPERIMENTAL SECTION

Device and Material

MES System: A two-chamber H-cell BES reactor with graphite porous electrode was made of coconut shell. Anode and cathode chamber was divided by cation exchange membrane Nafion 117. A potentiostat (Digi Ivy) with Ag/AgCl as a reference electrode was connected to the system and fed with a stream of N_2 and CO_2. Microbial Seed: microbial seed used in this study was derived from a mixed culture sludge from WWTP (wastewater treatment plant). Growth medium and nutrients were referred to DSMZ 311 growth medium. Coconut shell material activation: KOH 1 M (Merck), $ZnCl_2$ (Merck), $FeCl_3$ (Merck), HCl 2 M (Merck) and polyvinyl alcohol (Merck). Non-atmospheric Furnace Tube (Carbolite) was used to sinter and activate the carbon material. Analysis instrumentation: SEM-EDX (JEOL JSM-6360LA), XRD (Panalytical Xpert 3 powder) and BET (Quantachrome NovaWin).

Procedure

This research was performed in three stages: cathode graphite porous fabrication, growth and enrichment of microbial in the MES system and application of MES cell.

Cathode graphite porous fabrication

A 50 g coconut shell was ground and sieved with 100 mesh filter, then calcined at 600 °C for 3 h, soaked in KOH 1 M for 24 h, then rinsed with H_2O to achieve a neutral pH and then heated at 110 °C for 12 h. A 6 g of treated activated carbon was added to the mixture solution of $ZnCl_2$ and $FeCl_3$, by varying weight (g) 3:18, 3:20 and 3:22. Afterward, the solution was heated and mixed at 80 °C for 2 h to evaporate water. The mixture was then added into the non-atmospheric furnace tube while nitrogen gas was passed and the temperature was gradually raised at 5 °C/min to a final temperature of 900 °C and kept stable for 1 h. The graphite material was rinsed with HCl 2 M and heated at 60 °C for 12 h. 4 g graphite porous product was added in the mixture of 0.2 g PVA and 3.2 mL H_2O, heated at 80 °C and molded in tarno grocki at 10 ton of pressure. Graphite porous of 5 cm of length and 1 cm diameter was obtained.

Microbial growth and enrichment in the MES system

Growth medium was made referred to DSMZ 315 medium, spurged with N_2 and CO_2. pH was adjusted to 7.4 and the medium was sterilized afterward. A 100 g microbial seed was added, and the volume was adjusted to 500 mL with distilled water and heated at 90 °C for 1 h. Microbial inoculation was done by adding seed, media, and N_2 and CO_2 into an anaerobic jar at 37 °C.

Application of MES system

Graphite cathode was installed in H-cell MES reactor, and carbon cloth was used as the anode. Microbial inoculum and phosphate buffer solution were transferred to cathode and anode chamber, respectively. Cathode potential was set at -0.5 V to -1 V vs.. Ag/AgCl. Current response was recorded every 300 sec. CO_2 was spurged to the cathode chamber and samples were collected for organic compound analysis using HPLC. The bioelectrochemical scheme is shown in Fig. 1.

■ RESULTS AND DISCUSSION

Fabrication of Graphite Porous Cathode

Graphite porous cathode, as a material component in the MES system, was successfully molded. Cathode material exhibited a distinct crystal characteristic

compared to its precursor. Fig. 2 shows the change of crystal structures of modified coconut shell based on the formulation ratio of Fe:Zn.

XRD data shows the trend of coconut shell diffraction configuration as per formulation of Fe:Zn ratio. The undetected diffraction peak at range degree theta 2-theta 5° to 80° indicated an amorphous characteristic. The diffraction peak was changed after modification of simultaneous sintering-activation method was applied by adding a mixture of $FeCl_3$ 3 M and $ZnCl_2$ solution. For modification with the formulation of C(6)Fe(100-3)Zn(18), diffraction pinnacle was also distinctly measurable. Both diffraction pinnacles have wide diameters, indicating a high degree of crystallinity. These results showed that different formulation composition would affect the diffraction peak. Diffraction pattern became evident at modification formulation C(6)Fe(100-3)Zn(22) with angle 22, 26, 36, and 42°. Lim et.al [22] mentioned that diffraction peak at a 26° angle was suggesting the formation of carbon material with pristine graphite shaped. Meller index for diffraction angle was 002 for 26° and 100 for 42° [23].

The simultaneous sintering-activation method had also altered the surface image of a coconut shell. The image transformation is clearly evident in SEM analysis as shown in Fig. 4.

A massive surface characteristic of natural carbon, as shown in Fig. 3, was turned into hollow pillars. This gradual surface image indicated sheets formation, with micrometer diameter. A transformation of surface characteristic was caused by $FeCl_3$ catalyst and $ZnCl_2$, in which Fe formed carburation phase [20]. The modification has also transformed carbon material, as shown in Fig. 3(b)., with a dimension around 500 nm.

The sintering-activation process had changed the material surface area. Table 1 shows the change of the carbon surface area after the sintering-activation process.

Sintering and activation process by Fe and Zn had greatly improved surface area, from 83 to 907.7 m^2/g, or almost 11-fold higher. This result was higher than previous research [24] where the surface area obtained was just 402 m^2/g; it is possibly due to the single process employed in previous research, i.e. sintering. Data analysis
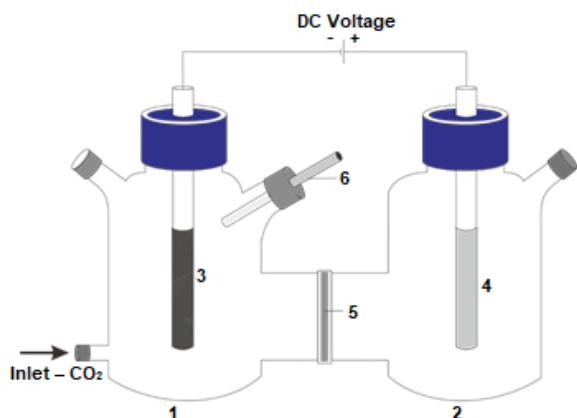
Fig 1. Scheme of BES reactor consists of (1) cathode chamber, (2) anode chamber, (3) biocathode, (4) an anode, (5) nafion membrane and (6) pH electrode
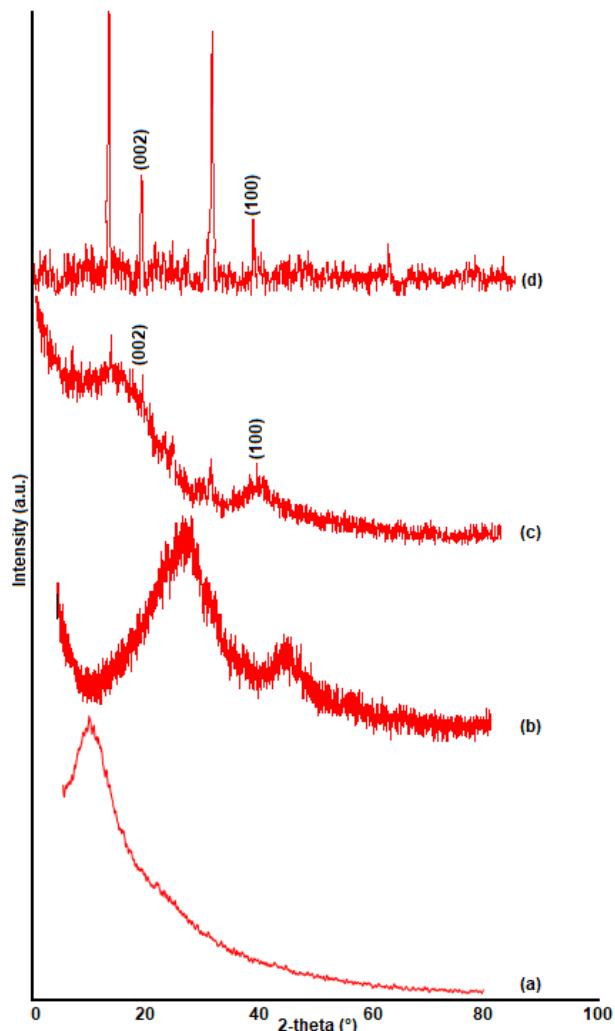
Fig 2. Carbon XRD patterns before (a) modification, synthesized sheet nanoporous by (b) $C_6Fe_3Zn_{18}$, (c) $C_6Fe_3Zn_{20}$ and (d) $C_6Fe_3Zn_{22}$
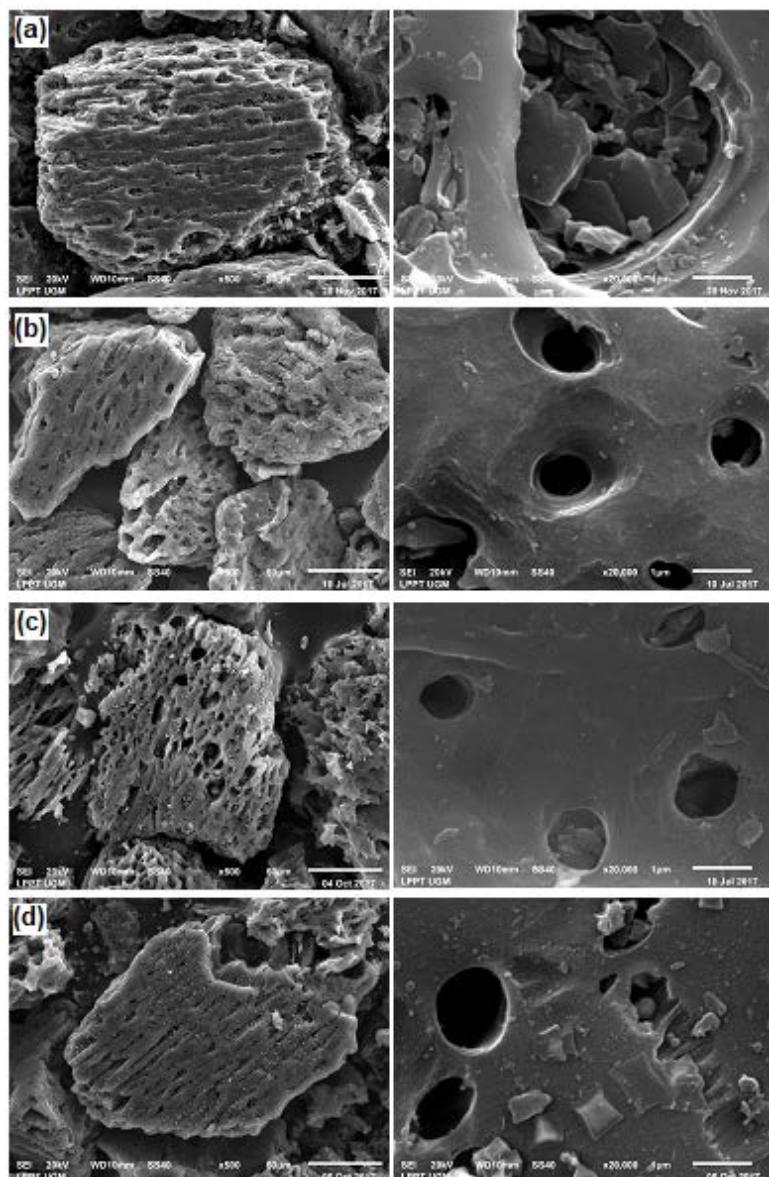
Fig 3. Carbon surface image (a) prior to activation, activation with formula (b) $C_6F_3Zn_{18}$, (c) $C_6Fe_3Zn_{20}$ and (d) $C_6Fe_3Zn_{22}$

also shows that the SAG (sintering-activation graphite) method plays important role in developing carbon material with vast surface area, as SAG parameter controls the porosity of graphite micro sheet [20].

Microbial Growth and Enrichment in a Serum Bottle

Before applying in the MES system, initial inoculation was carried out in the serum bottle with fructose 0.1 M as a substrate, and microbial seed is grown in DSMZ 135 media. The seed was incubated at 37 °C for 72 h. Microbial growth was investigated by plotting optical density (OD) analysis versus time. The OD analysis was conducted by measuring absorbance value of the sample at 600 nm wavelength as microbial growth corresponds with absorbance. The highest growth achieved at the highest absorbance. Fig. 4. shows microbial growth trend on DSMZ 135 media with fructose 0.1 M addition.

A 72 h incubation of microbial inoculum resulted in optical density range between 0.378–1.46, with

maximum growth achieved at 24 h with an absorbance value of 1.9. Absorbance value then gradually decreased after 24 h incubation, suggesting that the death rate surpassed growth rate due to the substrate limitation.

After initial inoculation and enrichment in serum bottle, seed culture was supplemented to the BES reactor after DSMZ 135 media and fructose. Microbial growth, pH and absorbance were then observed for 5 days, as displayed in Fig. 5. Correlation between microbial growth and pH was plotted and shown in Fig. 5.

Microbial activity in anaerobically reducing fructose to organic acid was detected in the MES system, proven by a gradual decrease of pH and the escalation of absorbance value and the formation of VFA (volatile fatty acid) (Fig. 5 and 6). At day 0 pH was 7.2 (neutral) and gradually decreased to 6.75 at day 5, coupled with VFA formation. At day 0 VFA concentration was 139.65 mg/L at absorbance 0.398 then at day 5, VFA concentration reached 1046.442 mg/L; this increase was in accordance with the rise of absorbance value of 0.435. However, in this phase, VFA formation was merely derived from anaerobic fructose degradation.

Coconut Shell-Based Cathode for Application in MES System

Electric current is a representation of electrons transport from the anode to the bio-cathode. It also indirectly indicating the electroactivity property of an electrode. The MES reactor equipped with coconut shell-based graphite porous as a cathode has a higher electroactivity property than commercial carbon cloth, as observed by its current density in Fig. 7. Crystallinity,

Table 1. The analysis result of carbon surface area prior to and after modification

No	Sample	Surface area (m^2/g)
1	Coconut Shell	83.0
2	Modification $C_6Fe_3Zn_{18}$	610.9
3	Modification $C_6Fe_3Zn_{20}$	907.7
4	Modification $C_6Fe_3Zn_{22}$	611.3
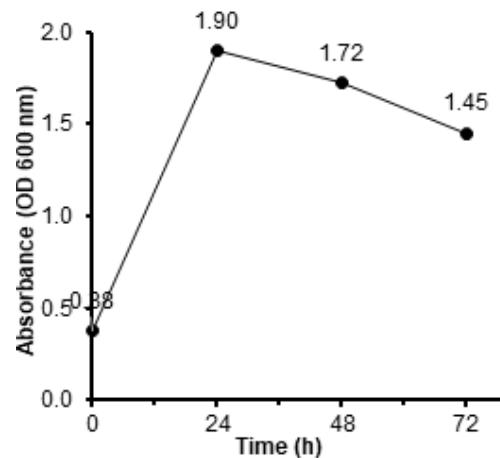
Fig 4. Absorbance (OD) of microbial seed at various times
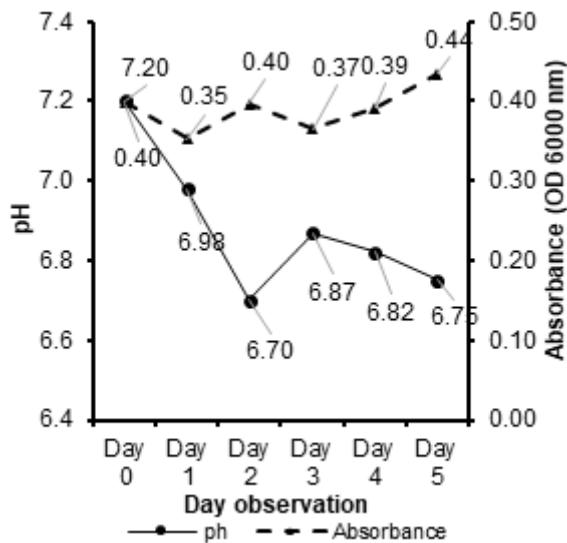
Fig 5. Absorbance and pH in BES reactor
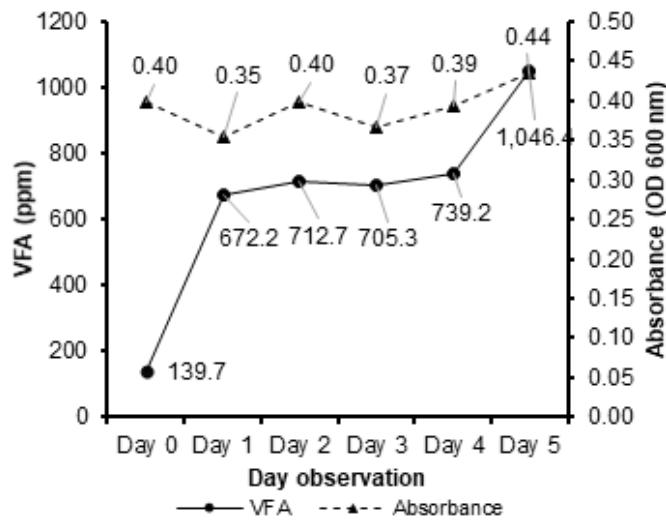
Fig 6. VFA concentration and absorbance at various times
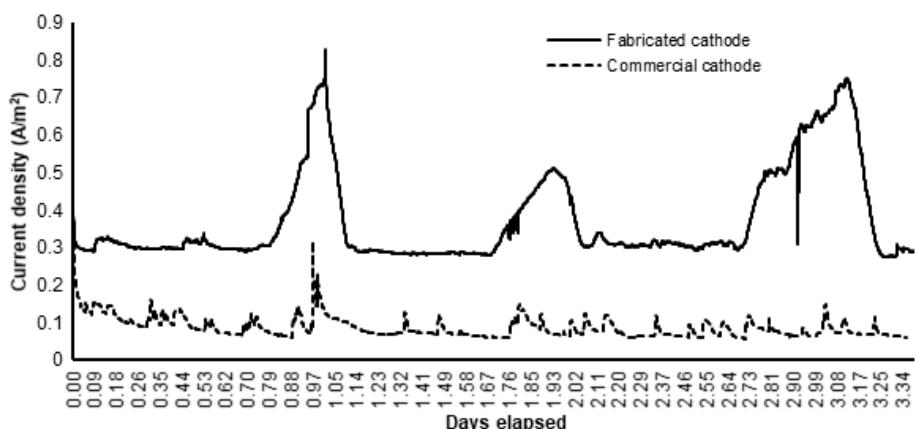
Fig 7. Current density performance of coconut shell-based and commercial cathodes
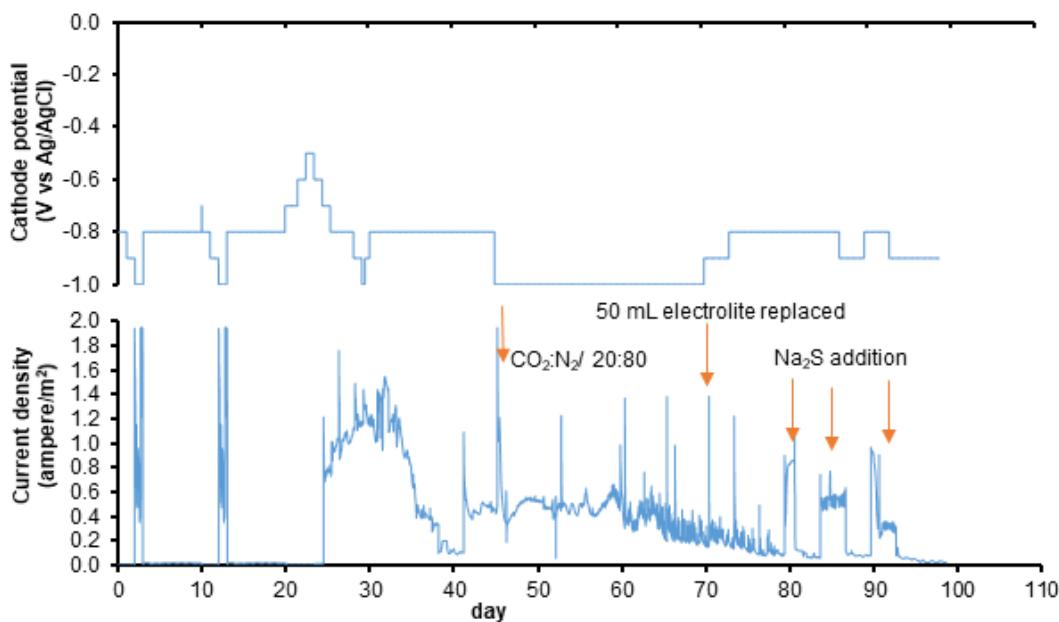
Fig 8. Current response in line with cathode potential setting in MES

porosity, and surface area of the synthesized cathode are important determining factors of electroactivity. A 2 to 4-fold higher electroactivity was observed in Fig. 7.

MES reactor was applied at varying voltage using a potentiostat. At the initial stage, -0.8 V vs. Ag/AgCl was given to the MES system, the voltage was gradually increased to -0.9 V vs. Ag/AgCl and -1 V vs. Ag/AgCl. At day 20–27, the voltage was decreased from -0.8 V vs. Ag/AgCl to -0.5 V vs. Ag/AgCl for every day and then started to rise gradually from -0.8 to -1 volt. Fig. 9 depicts electric current response during MES application.

Electrical current at day 27 to 30 rose significantly when the potential was set to -0.9 and -1 V vs. Ag/AgCl.

When the potential was decreased to -0.8 V vs. Ag/AgCl at day 30 to day 40, the current density slowly declined. At day 45–70 CO_2 gas flowed to the system and potential was dropped into negative -1 V vs. Ag/AgCl, and organic acid started to form (Fig. 8). The system was proven to be able to use CO_2 as a substrate, as shown by the decrease of CO_2 concentration in the headspace. Out of 20% CO_2 feed, only 13% was detected in the headspace and no methane gas detected. The utilization of CO_2 as substrate and the abundant formation of gas H_2 via hydrogen evolution reaction at – 1 V led into organic acid production in an MES system. Although the exact concentration of H_2 in the headspace gas was not measured,
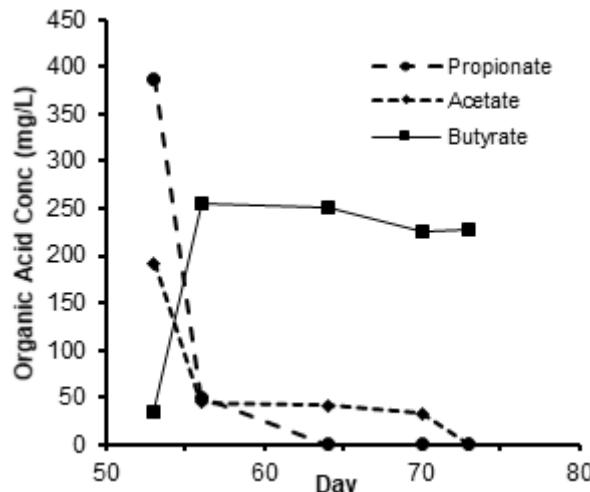
Fig. 9. The concentration of organic acid at various times

according to Wang et al. [25] and Zhen et al. [26] carbon cloth has a high capacity of H_2 evolution, which certainly occurred in the system. In this study, butyrate was the main product. As also stated by Batle et al. [27] and Gobner et al. [28], under acidic condition and abundant reducing power, acetogen prefers to produce butyrate over acetate due to slightly higher pKa (4.82 vs. 4.76).

VFA analysis shows that propionate and acetate were initially produced, 387 and 192 mg/L, respectively. At day 56, the production shifted into butyrate. Butyrate concentration increased from 35 to 250 mg/L. On the contrary, propionate production declined from 387 to 0 mg/L, as well as acetate from 192 to 33.48 mg/L.

At day 71 to 72, the potential was set to -0.9 V vs. Ag/AgCl and at day 70 catholyte was replaced by 50 mL buffer PBS (phosphate buffered saline) and current response was slightly declined. However, after catholyte replacement, there was still an indication of organic acid production due to the increase of COD concentration from 1345 to 1833 mg/L at day 73. During the last phase of the experiment, day 74 to 80, when cathode potential was set to -0.8 V, the current density was declined, and so did the concentration of total VFA. At day 80, VFA measured was only 15 mg/L. However, after 1 mL Na_2S 46 mM was added. Na_2S addition at day 80, 85 and 90 increased current density coupled with VFA formation from 15 to 83 mg/L. Na_2S addition might trigger the growth of sulfate-reducing bacteria (SRB). As confirmed by Xiang et.al [29] that sulfate-reducing bacteria (SRB)

can also facilitate electron transfer from electrode thus also triggered hydrogen formation via either direct or indirect mechanisms. The decline of current response after day 80 also could have been an indication of the carbon material robustness itself, especially for long-term operation. MES process is affected by multiple factors, not only the applied cathodic potential [30], but also cathode material [31], configurations/structure [32] and biofilm communities [33].

■ **CONCLUSION**

Carbon-based coconut shell material can be utilized as biocathode in MES system. The simultaneous sintering-Fe/Zn activation method can transform coconut shell carbon into porous graphite with large surface area, approximately 11-fold larger than the material precursor. Anaerobic mixed culture can be potentially used as acetogen seed source in the development of biocathode. MES system, with coconut shell based carbon material as bio-cathode, was able to produce butyrate 250 mg/L from CO_2 as sole substrate.

■ **ACKNOWLEDGMENTS**

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420

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