Separation of acetate produced from C1 gas fermentation using an electrodialysis-based bioelectrochemical system.

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Abstract: The conversion of C1 gas feedstock, such as carbon monoxide (CO), into useful platform chemicals has attracted considerable interest in industrial biotechnology. One conversion method is electrode-based electron transfer to microorganisms using bioelectrochemical systems (BESs). In this BES system, acetate is the predominant component of various volatile fatty acids (VFAs). To appropriately separate and concentrate the produced acetate, a BES type electrodialysis cell with an anion exchange membrane was constructed and evaluated under various operational conditions, such as the applied external current. The higher acetate flux of 23.9 mmol/m^2·hr was observed under -15 mA current in an electrodialysis-based bioelectrochemical system. In addition, the initial acetate concentration affects the separation efficiency and transportation rate. The maximum flux appeared at 48.6 mmol/m^2·hr when the acetate concentration was 100mM, whereas the effect of the initial pH of the anolyte was negligible. The acetate flux was 14.9 mmol/m^2·hr when actual fermentation broth from BES based CO fermentation, was used as a catholyte. A comparison of the synthetic medium with the actual fermentation medium suggests that unknown substances and metabolites in the actual medium interfere with electrodialysis in the BES. These results provide information on the separation and optimal concentration for VFAs produced by C1 gas fermentation through electrodialysis, and a combination of a BES and electrodialysis.

Keywords: Electrodialysis; Bioelectrochemical system; Microbial fuel cell; C1 gas; Carbon monoxide; Acetate

1. Introduction

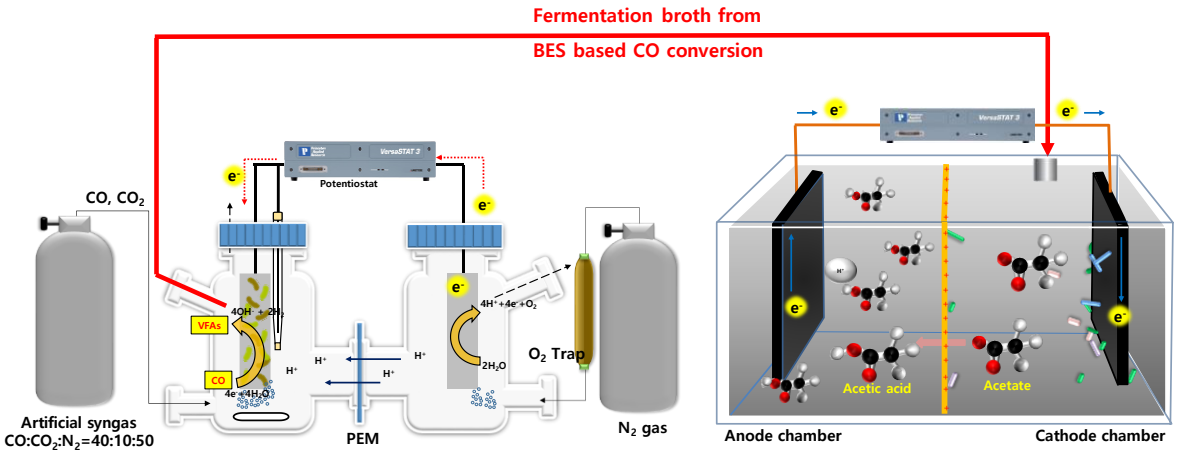

Figure 1. Separation and concentration concept for acetate produced from C1 gas by a BES. Acetate separated by an anion exchange membrane.

The biological conversion of industrial waste gases containing carbon dioxide and carbon monoxide are being highlighted to reduce the emissions of greenhouse gases, and simultaneously produce the building blocks of fuel and more useful commodity chemicals [1, 2]. Among them, CO, which is toxic and recalcitrant to the environment, accounts for 50 to 70% of the effluent gas from steel factories. Hence, appropriate treatment technology is anticipated. Recently, Im et al. (2018) reported that the bioelectrochemical system (BES) could compensate for the limitation of natural biological CO conversion, and enhance the production of volatile fatty acids [3]. The applied potential to the BES supplies reducing power for autotrophic microorganisms and improves the yield of C1 gas conversion and cell growth [4-8].

The metabolites produced from BES-based C1 fermentation may contain not only acetate, but also various volatile fatty acids (VFAs) and alcohols. Therefore, additional separation processes are needed to isolate and/or concentrate acetate. In a conventional study, the separation of ionic metabolites was carried out using methods, such as acidification, ion-exchange, crystallization, and adsorption. On the other hand, these studies may need to be moderated with the recent trends of environmentally and economically sustainable research and development [9, 10]. For example, in the case of acidification or ion exchange, considerable amounts of acid and alkali are consumed during the operation, which is problematic. Regarding crystallization or adsorption, additional purification and chemical waste discharge have been a concern.

Electrodialysis (ED) is a technology to separate and enrich the target substances by transferring the ionic forms through a selectively transmissible ion exchange membrane under an electrochemically induced oxidation/reduction reaction [9]. The separation of fermentation metabolites by electrodialysis was proposed to prevent the inhibition of lactic acid [11]. H^+ / OH^- can be supplied continuously by electrochemical control in electrodialysis, and it can separate various metabolites from the fermentation broth without the need for additional chemical reagents, such as salts. Moreover, it is capable of separating and concentrating high purity substances efficiently compared to other methods, enabling applications in a wide range of industrial processes, including food and biofuels productions [12, 13]. In particular, there are many applications of electrodialysis in bioelectrochemical systems [14-16]. For example, ethyl acetate was produced through biphasic

esterification; acetic acid was separated from the fermentation broth by electrodialysis [17]. In addition, acetic acid was produced from carbon dioxide in a three-chamber MFC system. As a result, 13.5g L^{-1} of acetate was separated by electrodialysis over a 43 day period [18]. In this C1 gas fermentation, the external electrical energy provided the reducing power to convert the CO_2 to acetate.

The system configuration of BES and electrodialysis have some similarity in terms of using an ion exchange membrane (or separator) and electrical input (or output) to (or from) the reactor. Thus, electrodialysis allows direct production and isolation of the target metabolites from C1 gas fermentation. On the other hand, the most important and problematic issue of separation by electrodialysis has been indicated as membrane fouling [19]. In the sludge, wastewater or fermentation broth, there are not only secondary metabolic products, but also unused growth media components and large number of cells [20]. These undesirable substances or microbial cells attach to the surface of the membrane and/or block the functional group of the ion exchange membrane during the electrodialysis process, eventually resulting in a decrease in separation efficiency [21]. To solve these problems, pretreating the fermentation broth before introduction to electrodialysis or various modification methods of the ion exchange membrane have been suggested [20, 22, 23].

This study examined the operational parameters in electrodialysis to separate acetate, which is applicable to C1 gas fermentation (Figure 1). The optimal conditions in the model solution were investigated and applied to the fermentation broth. The efficiency and flux of acetate separation were compared in both the actual fermentation broth and synthetic media. The aim of this study was to examine the potential of combination of electrodialysis with BES-based C1 gas fermentation.

2. Materials and Methods

2-1. Electrodialysis reactor configuration

The reactor used in this experiment consisted of an acrylic anode and cathode chamber; each chamber had a working volume of 73.5 ml ($7 \times 7 \times 1.5$ cm^3) (See Figure S1). Both electrodes were carbon paper (surface area of 42.25 cm^2, 120 - TGP-H-120, Toray, Japan) and a carbon fiber (20 cm) connecting the carbon paper to the electrode. An anion exchange membrane (49 cm^2, FKB-PK-130, Fumasep, Germany) was used as the ion exchange membrane for the cell, and it was rinsed with a 0.5 M NaCl solution for 24 hours prior to use. A potentiostat (WMPG1000, WonA Tech, Korea) in galvanostatic mode was used to apply a current to the reactor.

2-2. Composition of electrolyte

Two types of catholytes were used to examine acetate transportation across the ion exchange membrane: synthetic medium and fermentation broth. The synthetic broth contained CO/CO_2 fermentation medium, which was composed of the following (g L^{-1}): 1.5g KH_2PO_4, 2.9g K_2HPO_4, 2.0g $NaHCO_3$, 0.5g NH_4Cl, 0.09g $MgCl{\cdot}6H_2O$, 0.0225g $CaCl_2{\cdot}2H_2O$, and 0.5g yeast extract. Sodium acetate (20mM to 100mM for each reaction condition) was added to the catholyte to examine transportation through the membrane. The fermentation broth consisted of the same substances with the synthetic medium but additionally added 2.11g of sodium-2 bromoethanesulfonate, 2ml of Pfennig's trace element solution, and 5ml of a vitamin solution [3]. The pH was adjusted to 6.0 with 1M H_2SO_4 and 1M NaOH. In some experiments, centrifugation was conducted at 7500 RPM and 15 min to remove the cell and precipitates produced from former fermentation. To prevent acetate consumption due to contamination, streptomycin (20ug/ml) was added as an antibiotic. The anode electrolyte consisted of the following ingredients (g L^{-1}); 0.8g K_2HPO_4, 1.0g NH_4Cl, 2.0g KCl, 0.15g $CaCl_2{\cdot}2H_2O$, 2.4g $MgCl{\cdot}6H_2O$, 4.8g NaCl, 10.08g $NaHCO_3$[18].

2-3. Reactor operation

The cathode and anode electrodes were set as the working and counter electrodes, respectively. The current applied to the cathode ranged from 0 to -15mA using a galvanostatic method. The electrodialysis cells were located in the incubator at 25 ± 1℃ and gently shaken at 30 rpm.

2-4. Analyses

A liquid sample (< 300 µl) was taken from each chamber periodically. The liquid samples were filtered through a 0.2µm syringe filter, acidified by HCl to prevent acetate volatilization, and stored in a freezer at -80 ℃. The samples were analyzed by gas chromatography (GC, 7890B, Agilent Technologies, USA) and high performance liquid chromatography (HPLC, HP 1100 series, Agilent Technologies, USA). The initial and final pH were measured using a pH meter (Orion 420A+, Thermo Orion, USA). The current efficiency (η_A)was estimated using the following equation:

$$\eta_A = \frac{\Delta N_A}{iA\Delta t/F} \quad (1)$$

where ΔN_A is the change in the molarity of acetate; i is the current density; A is the membrane area; F is the faraday constant (96485 C mol^{-1} = 26.8 Ah mol^{-1}); and Δt is the interval of time [24].

The flux (J_A) of acetate from the cathode to anode chamber was calculated using the following equation:

$$J_A = \frac{\Delta mA}{A\Delta t} \quad (2)$$

where Δm_A is the amount of acetate transported from the cathode to the anode chamber; A is the membrane area; and Δt is the interval of time.

3. Results and Discussion

3.1 Different applied current on acetate transportation in BES

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Acetate transport across the ion exchange membrane is affected by the applied potential and current in microbial fuel cells [9, 18, 25, 26]. Therefore, the changes in acetate concentration in both the anode and cathode chambers were examined while various currents (-5 to -15 mA) were applied to the cell (Figure 2). In the absence of an applied current, the final acetate concentration of 9.17mM was transported to the anode chamber during 16 hours of operation, indicating that acetate diffused to the anode by the concentration gradient. On the other hand, acetate transport was increased to 12.55 mM when a current was applied across the electrodes (-5 mA). Under -15 mA application, 24.98 mM of acetate was transported to the anode chamber. An externally applied current can move acetate anions against the concentration gradient between the anode and cathode chambers (Figure 2 B, C & D) over 16 hours, whereas the acetate only diffuses naturally in the absence of an applied current (Figure 2 A).

The amount of acetate transportation increased with increasing current in BES. On the other hand, the estimated current efficiency on the applied potential decreased at a higher current (Figure 6A). The current efficiency estimated by equation (1) was higher (54.4 ± 0.2%) under a lower applied current (-5mA), and it decreased at a higher current (36.1 ± 1.2% at -15 mA). (Table 1, Figure 6A). On the other hand the acetate flux across the membrane was 23.9 ± 0.8 mmol/m²·hr at -15mA, whereas it decreased at a lower applied current (8.8 ± 0.4 mmol/m²·hr at -5 mA) (Table 1). The driving force for acetate anion transportation by electrodialysis is lost under a higher current in electrodialysis. These results are consistent with the previous observation that the selectivity for ions at a low current density was higher than that at a high current density [27]. At a high current density, the current efficiency is reduced because the driving force is dispersed by the movement of other ions in addition to the target acetate.

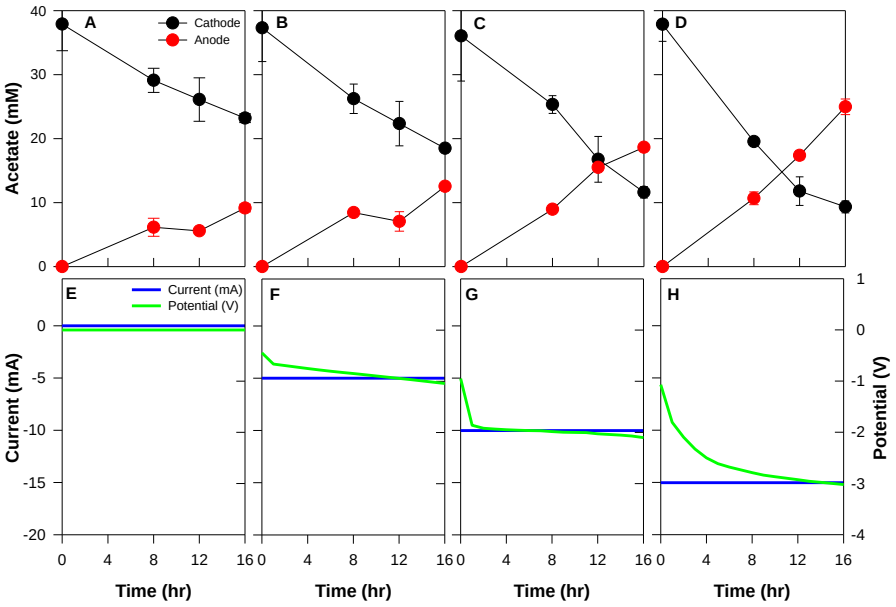

Figure 2. Acetate transfer from the cathode to the anode chamber under different current conditions. Without current application (A,E); -5mA (B,F); -10mA (C,D); -15mA (D,H) which operated for 16hr.

Table 1. Entire migration amount of acetate in the cathode chamber, total applied current, current efficiency and acetate flux.

	Conditions	Acetate migration from the cathode (mM)	Total applied current (C)	Current efficiency (%)	Acetate flux (mmol/m²·hr)
Applied current	0mA	14.7±4.9	-	-	8.8±0.4
	-5mA	18.8±5.2	288.0	54.4±0.2	12.0±0.0

	-10mA	24.4±7.9	576.0	40.4±0.6	17.8±0.3
	-15mA	28.5±3.6	864.0	36.1±1.2	23.9±0.8
Acetate concentration	20mM	16.3±2.1	864.0	23.8±0.6	15.8±0.4
	40mM	30.1±4.5		40.2±1.2	26.6±0.8
	80mM	44.2±9.3		63.1±2.6	41.8±1.7
	100mM	55.9±11.3		73.4±4.6	48.6±3.0
pH test	2.0	31.2±3.1	864.0	43.4±2.8	28.2±1.8
	4.0	30.6±6.3		42.8±3.4	28.4±2.2
	6.0	28.9±3.9		40.1±4.1	26.6±2.7
Catholyte composition	synthetic	25.3±0.9	864.0	34.5±1.2	22.9±0.8
	fermented w/ centrifuge	11.4±1.2		22.5±1.5	14.9±1.0
	fermented w/o centrifuge	11.1±0.3		18.6±0.7	12.3±0.4

3.2 Effect of different acetate concentration

The effects of the acetate concentration on electrodialysis were investigated at an applied current of -15 mA (Figure 3). The initial acetate concentration was varied from 20 to 100 mM. The acetate flux was estimated to be 48.6 ± 3.0 mmol/m^2·hr at an initial acetate concentration of 100mM, whereas it proportionally decreased to 15.8 ± 0.4 mmol/m^2·hr with an initial acetate concentration of 20 mM (Figure 3 and Table 1). At the highest acetate concentration (100 mM), the current efficiency (73.4%) was much higher than that of the lower concentration (20 mM vs. 23.8%) (Figure 6). These results suggest that higher efficiency of acetate separation can be obtained at a higher acetate concentration. When no current was applied to the cell, separation was carried out by diffusion depending on the acetate concentration. This indicates that diffusion plays an important role in the transport of acetate as well as the applied current [25]. Accordingly, the maximum acetate concentration is required for the optimal process efficiency, even though the performance of electrodialysis is related to the reactor configuration as well. Im et al. examined the fermentation of acetate production from CO by electrosynthesis, and revealed the productivity of acetate at a maximum of 8.4 g L^{-1} in a BES [3]. Therefore, electrodialysis-driven acetate separation around the maximum was examined in the electrodialysis cell. The separation of acetate at this point is expected to increase both the growth of microorganisms and the acetate productivity from CO conversion.

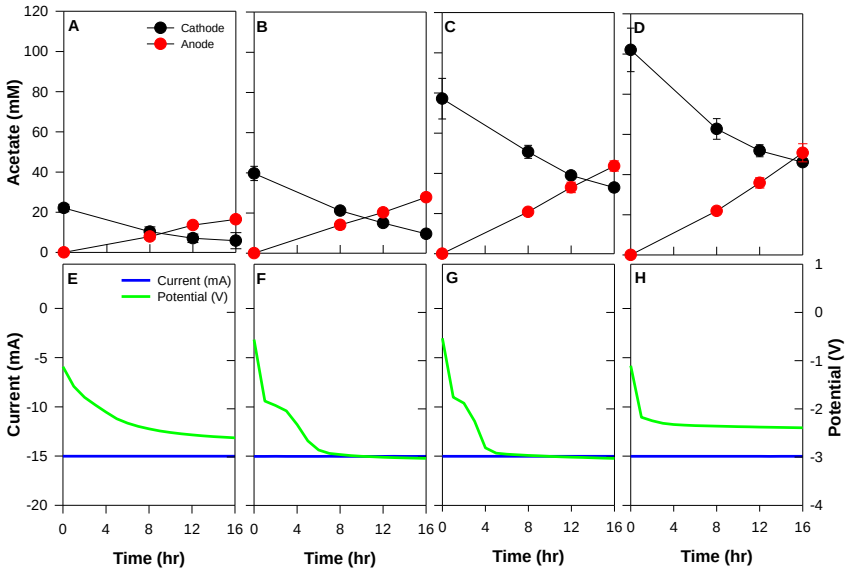

Figure 3. Acetate concentration changes by electrodialysis when the initial acetate concentrations in the cathode chamber were varied from 20 mM (A,E), 40mM (B,F), 80mM (C,G), 100 mM (D,H).

3.3 Effect of different initial anodic pH

The pH of the anode chamber can also be an important factor for the efficient separation of acetate. The pK_a of acetate is 4.76. Hence, acetate exists mainly as an ionized form in the catholyte in the cathode chamber (~ pH 6.0), which is provided from the former CO fermentation reactor. To examine the effects of the anodic pH in electrodialysis, the anodic pH was adjusted from 2.0 to 6.0 while the cathodic pH was fixed to 6.0 because the pH from the effluent from the former C1 gas fermentation is approximately 6.0. As shown in Figure 4, the pH effect on acetate separation was negligible, and the current efficiencies were estimated to be approximately 40-43% under these pH conditions (Table 1). In electrodialysis cells, the following oxidation and reduction reactions take place in the anode (3) and cathode chamber (4);

$$H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^- \quad (3)$$

$$2e^- + 2H_2O \rightarrow 2OH^- + H_2 \quad (4)$$

The H^+ produced by reaction (3) lowers the pH in the anode chamber continuously, which eventually approaches pH 2.0, even if the initial pH of the anode chamber started from a higher than pH 2.0. The final pH of the anode chamber in the tested reactors was pH 1.9 to 2.0, which were converted from a varied initial pH 2.0 to 6.0. These results suggest that proton transport from the anode to the cathode in the reverse direction of acetate anion species separation, is limited by the ion exchange membrane [28].

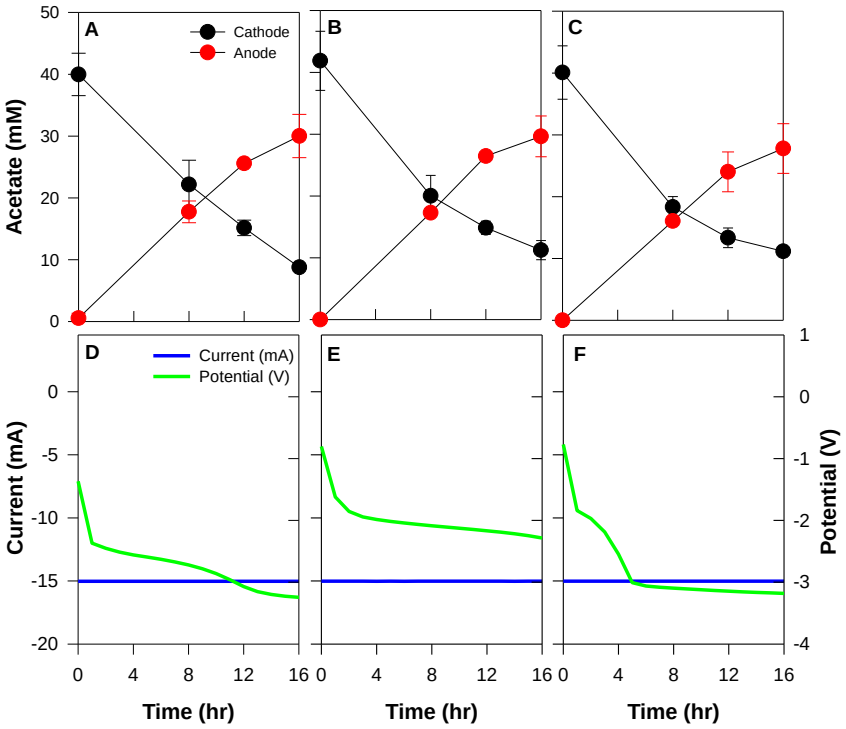

Figure 4. Changes in the acetate concentration by electrodialysis when the initial pH of the anode was varied. Initial anode pH 2.0 (A, D); pH 4.0 (B, E); pH 6.0(C, F).

3.4 Acetate separation from the actual fermentation broth

The combination of acetate fermentation followed by electrodialysis-based acetate separation, has been highlighted for biological C1 gas conversion. Based on the results of the above experiments, synthetic media and fermentation broth containing acetate were compared for the separation of acetate in an electrodialysis cell. First, the cell and precipitate in the former fermentation broth were removed by centrifugation to exclude the effects of particulates in the broth. The final acetate concentrations with the fermentation and synthetic broth were 15.6 mM and 23.9 mM, respectively (Figure 5). The results show that approximately 20 % less acetate in the fermentation broth (i.e. effluent from the former electrosynthesis process) is transported to the anode chamber than the synthetic solution, even when the particulates were removed by centrifugation (Figure 5B). Similar but slightly lower acetate separation was obtained using a non-centrifuged fermentation broth (13.30 mM) during the 16 hours of operation (Figure 5C). The other metabolites from C1 gas fermentation in BES, such as butyrate, propionate and iso-butyrate [3], hinders acetate separation significantly. As observed in the GC analysis results, unlike the synthetic medium, the fermentation broth contains various volatile fatty acids as well as acetate (Figure S2 C & D). Among these metabolites, the longer chain VFA, such as propionate, may pass through the membrane competitively with acetate, which might reduce the rate and efficiency of acetate separation. The GC results also clearly show that propionate has passed through the anion exchange membrane used in this study (Figure S2 A & B). The competitive flux of these other anions are considered to be the cause of the relatively low current efficiency for acetate separation [17]. Because the former C1 gas fermentation process was usually inoculated with inoculum, including sludge and isolated microorganisms, it contains a variety of particulates, colloidal and dissolved fractions, all of which may act as inhibitors and potential foulants. Microorganisms and soluble substances potentially cause membrane fouling, which decreases the electrodialysis performance [21, 29, 30]. Ghasemi et al. reported that the microorganisms attached to the membrane surface and the biofilm formation are major factors to reduce the separation efficiency in the electrodialysis cell [19]. After the operation of the

electrodialysis cell with a non-centrifuged fermentation broth, contamination by unknown substances was observed on the cathodic electrode, which was different from the synthetic medium and centrifuged fermentation broth (Figure S3 D-F). These contaminant on the electrode and membrane may lower the current efficiency of acetate separation from the non-centrifuged fermentation broth in the electrodialysis cell.

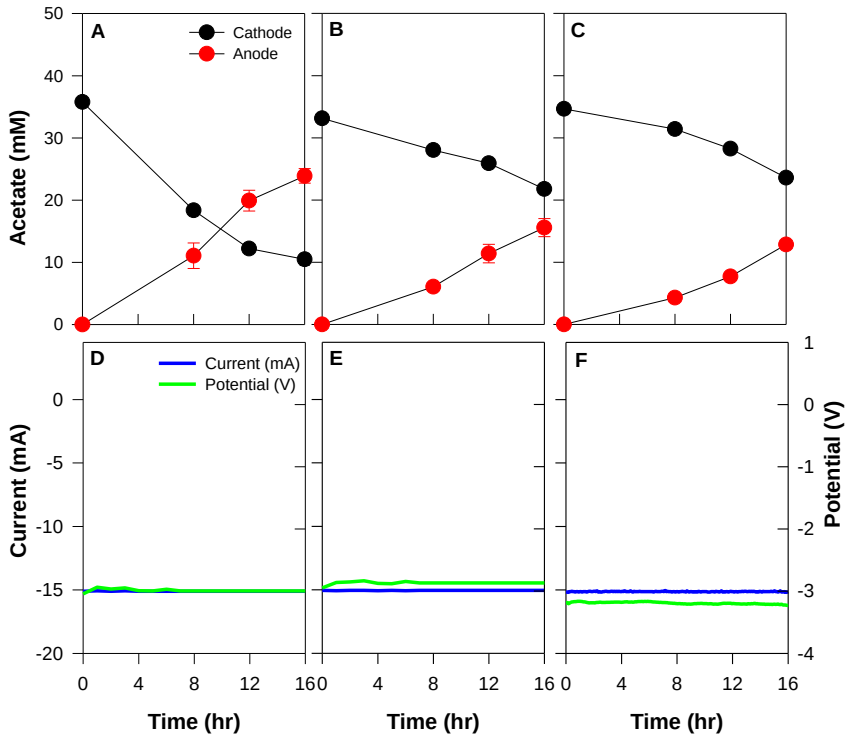

Figure 5. Comparison of acetate transportation in an electrodialysis cell with synthetic media containing acetate (A, D), and centrifuged C1 gas fermentation broth (B, E) and non-centrifuged C1 gas fermentation broth (C, F).

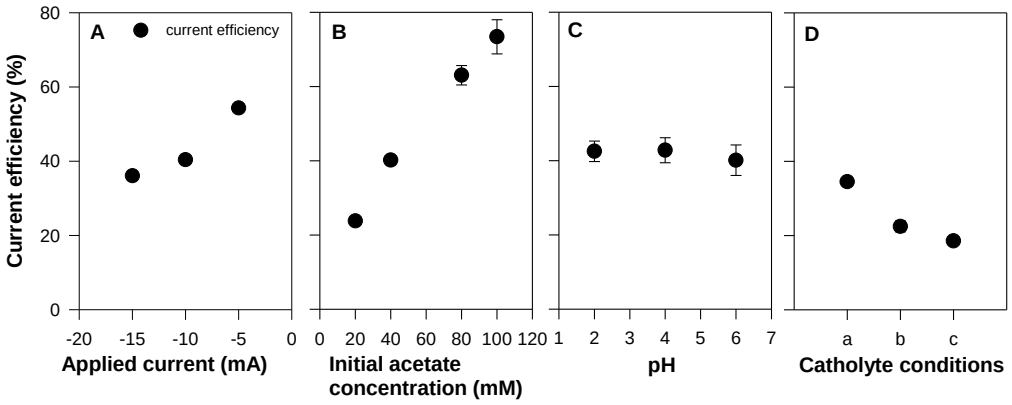

Figure 6. Estimated current efficiency on different parameters tested. (A) Current efficiency of different currents from -5 mA to -20 mA, (B) Effect of the initial acetate concentration, (C) Effect of different initial anodic pH, (D) Effect of different catholytes with synthetic media (a), centrifuged fermentation broth (b) and non-centrifuged fermentation broth (c).

5. Conclusions

Many research groups have attempted to separate acetate from a range of wastewater or microbial fermentation broth [31, 32]. Recently, C1 gas fermentation has been studied extensively due to the requirement of greenhouse gas abatement and the search for cost-effective feedstock for refinery. Acetate is one of the main metabolites from C1 gas fermentation and is a useful intermediate chemical for further biosynthesis. The electrosynthesis of C1 gas using a bioelectrochemical system has been highlighted to facilitate microbial C1 gas conversion [3, 4, 33-36]. In this respect, the combination of a bioelectrochemical system and electrodialysis can provide an appropriate platform for the in-situ processing and separation of acetate. Through these experiments, it was confirmed that a maximum acetate flux of 48.6 ± 3.0 mmol/m²·hr can be achieved using the model solution. When the C1 fermentation broth was applied, the flux was 14.9 ± 1.0 mmol/m²·hr, which was approximately half that of the model solution (22.9 ± 0.8 mmol/m²·hr) under the same conditions, probably due to the various substances and other longer chain VFAs in the fermentation broth. Therefore, there are still challenges that need to be overcome before this system can be applied to an actual industrial environment; several studies are underway to solve these problems. To solve the fouling of an ion-exchange membrane, some research groups have focused on modifying the membrane by a treatment with polymer compounds, such as poly(sodium 4-styrene sulfonate) (PSS)/poly(diallyldimethylammonium chloride) (PDADMAC)[30]. An ultra-low voltage customized DC-DC booster circuit [37] and a maximum power point tracking (MPPT) [38], may provide an affordable voltage and current for self-sustained electrodialysis applications . Although further studies will be needed in the future, these results may provide a basis for techniques to isolate acetate from actual fermentation products based on bioelectrochemical systems.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1,

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Conflicts of Interest: The authors declare no conflict of interest for personal circumstances and financial support.

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Supplementary Materials

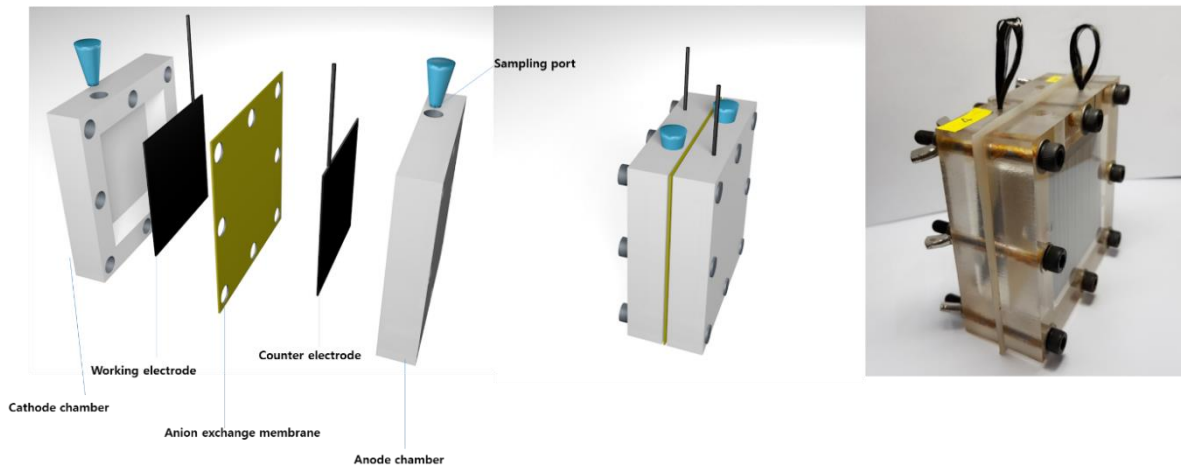

Figure S1. Schematic diagram of the electrodialysis reactor used in this study and a photograph.

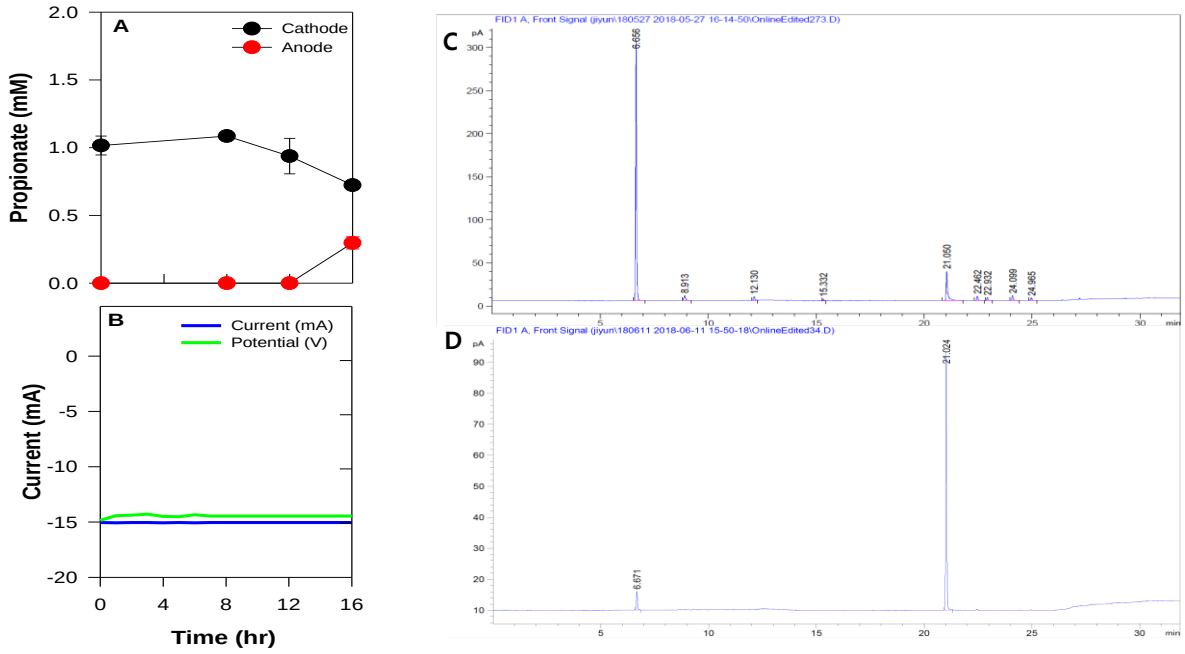

Figure S2. Comparison of propionate transfer through an anion exchange membrane. (A) Amount of propionate transferred to the anodic chamber, (B) applied current in the reactor for 16hr, (C) GC analysis results of fermentation broth, (D) GC analysis results of synthetic medium.

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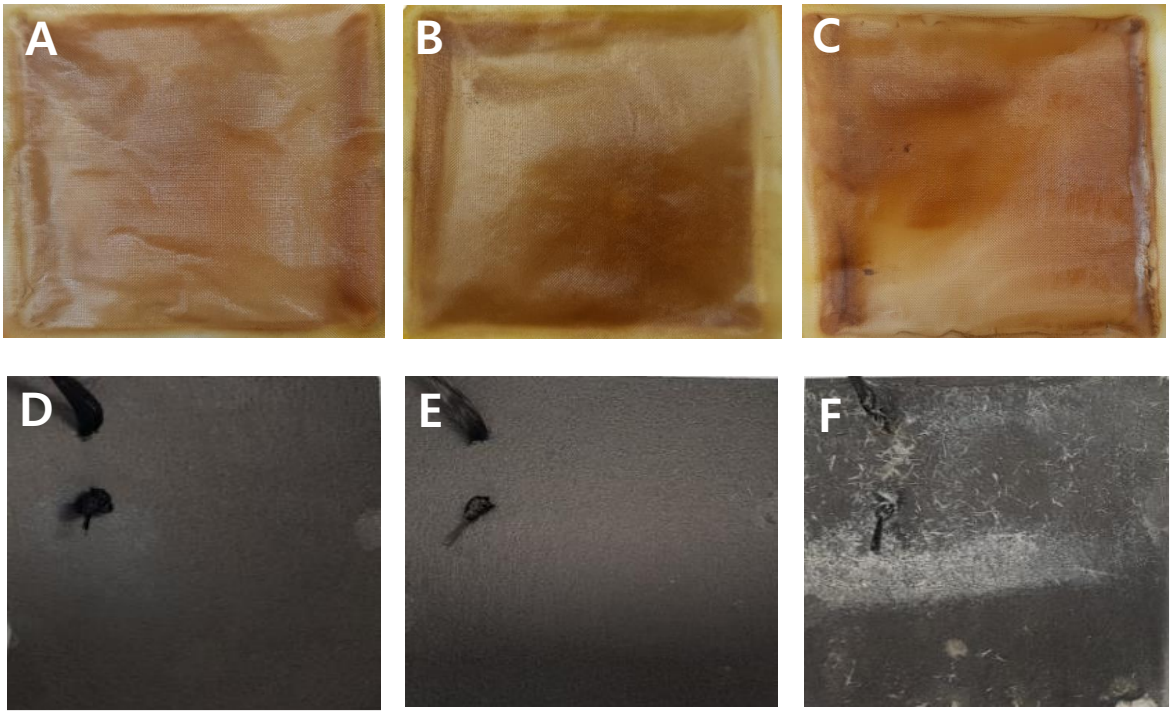

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Figure S3. Membrane and cathodic electrode surface after the completion of electrodialysis for acetate separation. membrane (A) and cathodic electrode (D) from the cell using synthetic broth meida, respectively. (B) and (E) from centrifuged fermentation broth, (C) and (F) from non-centrifuged fermentation broth.

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