Optimal interval of periodic polarity reversal under automated control for maximizing hydrogen production in microbial electrolysis cells

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Abstract
Microbial electrolysis cells (MECs) are a promising approach for producing hydrogen gas from low-grade substrates with low energy consumption. However, pH increase in a cathode due to proton reduction and thus the need for buffering this pH increase remains a challenge for MEC operation. In this study, a previously reported operational strategy for pH buffer - periodic polarity reversal (PPR) was further studied by developing and applying an automatically control system. The effect of PPR interval on the hydrogen production was investigated and the optimal PPR interval was determined. With an optimal PPR interval of 40 min, the MEC had a significantly low pH increase rate of 0.0085 min⁻¹ in its cathodes, and this resulted in the highest current density of 1.58 ± 0.02 A m⁻², Coulombic efficiency of 130.3 ± 1.8%, hydrogen production rate of 1.65 ± 0.01 m³ H₂ m⁻³d⁻¹, overall hydrogen recovery of 75.9 ± 0.4%, and energy efficiency relative to the substrate input of 140.8 ± 1.4%. Further analysis suggested that this optimal value of PPR interval was affected by both reaction time and hydrogen supply. When the PPR interval increased from 10 min to 40 min, a longer reaction time helped produce more protons and thus generated a stronger buffer capacity. Beyond 40 min, the mass transfer of the dissolved hydrogen gas could become a limiting factor, leading to a weaker buffer capacity with a longer PPR interval. Those findings have provided an effective pH control strategy with a convenient control system for maximizing hydrogen production in MECs.

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Introduction
Hydrogen is a promising alternative fuel to fossil fuel because of its high energy density and clean combustion products [1]. Hydrogen production is performed mostly by thermo-chemical processes (e.g., steam reforming, water electrolysis and coal gasification), which are highly energy-intensive [2]. Biological processes for hydrogen production such as bio-
electrochemical cell, biophotolysis, and fermentation are attractive because of low energy consumption and producing hydrogen from low-grade substrates such as waste organics [3,4]. Especially, microbial electrolysis cells (MECs) can produce hydrogen from non-fermenting substrates by taking advantage of microbial respiration with an electrode [5,6]. A great benefit of MEC technology is its low energy requirement. To achieve hydrogen evolution reaction (HER), an MEC would need an external voltage of 0.11 V vs. SHE (standard hydrogen electrode) in theory, or > 0.20 V vs. SHE in practice, which is significantly lower than that of water electrolysis (1.23 V vs. SHE in theory, or > 1.80 V vs. SHE in practice) [7,8]. Thus, MECs can function as an energy-efficient process for simultaneous waste treatment and energy (hydrogen) production [4]. Given those potential advantages, MECs have been intensively studied in microbiology, substrates, reactor configuration, catalysts, electrochemistry, and operation [6,7,9]. Recent pilot tests of MECs have demonstrated the possibility of using winery/domestic wastewater as a substrate to produce hydrogen gas in real word [10–12].

One of the key factors that hinder the MEC operation is the pH imbalance between the anolyte and the catholyte, due to organic oxidation in the anode (pH decrease) and HER in the cathode (pH increase) [13–15]. Continuous operation of MECs will experience alkalization of the catholyte caused by consumption of protons and accumulation of hydroxyl whereas acidification of the anolyte occurs because of competitive membrane transport of nonspecific cations (e.g., sodium, potassium, ammonium, magnesium, and calcium) and accumulation of protons liberated from microbial oxidation of organic compounds [16]. Thus, a successful pH control, especially the catholyte pH, is of critical importance to ensure efficient hydrogen production in MECs. To minimize the pH imbalance between the anode and the cathode, various methods such as adding buffers, designing single-chamber MECs, or looping the anolyte over the cathode, have been investigated [17–20]. However, the existing methods have problems that can potentially impair the MEC operation. For example, the use of phosphate buffer saline (PBS), a common buffer, would not be economical and environmentally friendly, and can increase the operational expense and create the need for post-disposal [9,15]. Although the design of single-chamber MECs or looping the anolyte over the cathode may help buffer the electrolyte pH, such a design/operation introduces the hydrogenotrophic bacteria (in the presence of organic compounds) competing for protons and hydrogenotrophic methanogens into the cathode side, resulting in methane production and reduced hydrogen production [21].

A new operating method, named periodic polarity reversal (PPR), has been developed to temper the accumulation of protons or hydroxyl ions in bioelectrochemical systems [14,22,23]. PPR switches the direction of the applied voltage between the anode and the cathode and has been demonstrated as an effective method for pH control in the MEC cathode for enhancing hydrogen production. The prior study of PPR was conducted in a two-chamber MEC reactor and switched between two biotic electrodes [14]. Although such a switch could improve hydrogen production by 5.3 times, compared to that the control without PPR mode [14], the presence of microorganisms and organic compounds in the cathode would result in production of methane and competition for electron acceptors between the cathode electrode and other electron donors. Therefore, abiotic cathodes will be necessary to ensure the purity of the produced hydrogen gas and to eliminate the competition for electron acceptors. We have previously developed a dual-cathode MEC for self-buffering pH with PPR and achieved 1.7–3.6 times hydrogen production compared to the MEC without PPR [24]. In this MEC, PPR was conducted between two abiotic cathodes, instead of anode-cathode, and the reversed cathode was directly connected to the anode by an electric circuit (short circuit connection). Our research found that the in situ oxidation of residue hydrogen gas in the reversed cathode helped to buffer the pH and thus improved hydrogen production in the subsequent operation as a working cathode.

Despite the promising results of enhancing hydrogen production via PPR in this three-chamber MEC, there are still challenges to address. For example, the PPR was performed manually and such a method would not be feasible for actual operation of an MEC system that could consist of multiple MEC modules. In addition, the interval of PPR in our previous study was fixed at 20 min, and the effects of the PPR interval on MEC performance must be further understood towards the determination of an optimal interval for maximal hydrogen production. In this study, an automated control system was designed and applied to control the PPR in the dual-cathode MEC. The influence of the PPR interval was systematically investigated for hydrogen production, current density, and electrolyte pH. The possible reason/mechanism for optimal PPR interval was analyzed.

Material and methods

MEC setup

A flat plate MEC was used in this study and consisted of an anode chamber and two cathode chambers (Fig. 1), physically separated by two pieces of cation exchange membrane (CEM) that had the same cross-sectional area of 166.4 cm² (26 cm × 6.4 cm, Membrane International Inc., Ringwood, NJ, USA). The liquid volume of the anode chamber was 90 mL, and each of the cathode chambers contained 150 mL of catholyte. The anode electrode was a piece of non-wet-proof carbon brush, which was pretreated by being immersed in acetone overnight and then heated at 450 °C for 0.5 h [25], while the wet-proof carbon cloth (26 cm × 6 cm, Zoltek Corporation, St. Louis, MO, USA) was used as the material for the cathode electrodes coated with 0.5 mg cm⁻² Pt/C powder (Thermo Fisher Scientific, Bridgewater, NJ, USA) as a catalyst for HER.

MEC operation

The MEC was operated in a continuous mode at room temperature (21 ± 1 °C). An external power supply of 0.80 V (3644 A, Circuit Specialists, Inc., Mesa, AZ, USA) was applied to the circuit, according to a previous study [24]. The anode chamber was inoculated with 20 mL of anaerobic sludge from Peppers Ferry Wastewater Treatment Plant (Radford, VA, USA). The anode feeding solution was prepared containing 1170 ± 26 mg
sodium acetate \( \text{L}^{-1}, 70 \pm 5 \text{ mg L}^{-1} \), \( \text{NH}_4^- - \text{N}, 15 \pm 3 \text{ mg L}^{-1} \), \( \text{MgSO}_4, 20 \pm 2 \text{ mg L}^{-1} \), \( \text{CaCl}_2, 500 \pm 10 \text{ mg L}^{-1} \), \( \text{NaCl, } 100 \pm 8 \text{ mg L}^{-1} \), \( \text{NaHCO}_3, 2.6 \pm 0.2 \text{ mg L}^{-1} \), \( \text{K}_2\text{HPO}_4, 2.6 \pm 0.6 \text{ mg L}^{-1} \), and 1 mL trace elements. The relatively high concentration of acetate was to ensure a sufficient supply of organic compounds to the anode, so that the anodic activity would not be a limit factor; this is important to the study of the cathode performance. The anode hydraulic retention time (HRT) was set at 10 h throughout the entire experiment. The catholyte was 50-mM NaCl solution and was completely replaced when the pH of the catholyte rose over 12.00. The use of NaCl solution instead of a buffer solution as the catholyte was to exclude the external buffer effect when studying the PPR buffer effect, while still maintaining certain conductivity. The PPR operation was examined following this procedure (Fig. 1): one of two cathodes was connected to an external resistor (1 \( \Omega \)), then to the negative lead of the power supply, acting as a working cathode for hydrogen production, and the positive lead was connected to the anode electrode, while the other cathode was directly connected to the anode (as a reversed cathode for hydrogen oxidation). A small external resistor of 0.1 \( \Omega \) was connected between the anode and the positive lead of the power supply for studying the contribution of the anode and the reversed cathode to current generation; this small external resistor did not significantly affect the overall internal resistance of the MEC.

**Automated PPR control system**

To better control the polarity reversal operation for the MEC, an electromechanical control system was designed and applied to switch the polarity automatically. This control system included one microcontroller board (Arduino Uno), one motor driver (L293D, Texas Instruments) and one low pass RC filter (Fig. 2A). The microcontroller board was in charge of controlling the polarity reversal interval and gathering data; the motor driver was applied to switch the polarity and provide voltage for the bioanode and abiotic cathodes; and the low pass filter was used to cut off high frequency voltage noise to provide smooth and constant voltage. The microcontroller output electrical signal was sent to motor driver periodically (Fig. 2B). State machine was used in the microcontroller to control different polarity periods. The motor driver received signal and behaved as a double-pole double-throw (DPDT) switch, changing the current direction in the MEC circuits. The low pass RC filter that was attached at the end of this control system could smooth the electric current and provide stable voltage to the MEC.

**Measurement and analysis**

The MEC voltage across the resistor was monitored and recorded by a digital multimeter (2700, Keithley Instruments, Inc., Cleveland, OH, USA) every 2 min. The concentration of chemical oxygen demand (COD) was measured by using a DR/890 colorimeter (Hach Company, Loveland, CO, USA). The electrolyte pH was measured by using a bench-top pH meter (Oakton Instruments Co., Ltd., USA). The production of hydrogen gas was measured by water replacement and analyzed by using a gas chromatograph (GC) (Focus GC, Thermo Scientific, USA).

The key parameters were calculated according to previous studies [19,24]. Current density (A m\(^{-2}\)) was calculated based on the liquid volume of the anode chamber. Coulombic efficiency (CE) is defined as the total produced Coulombs over all the available Coulombs from the removed acetate:

\[
CE = \frac{Q}{nFCa}
\]

where \(Q\) is integration of current over time, \(n\) is the number of electrons released from each molecule of acetate, \(F\) is the Faradic constant (96,485 C mol\(^{-1}\) e\(^{-}\)), and \(Ca\) is the mole of the removed acetate. The hydrogen production rate (\(Q\_H\_2\)) is the hydrogen production per anode unit working volume per time:

\[
Q\_H\_2 = \frac{V_{H\_2}}{Va \times t}
\]

where \(V_{H\_2}\) is the hydrogen volume (m\(^3\)), \(Va\) is the anode working volume (m\(^3\)), and \(t\) is the time period of one cycle (d). Cathodic hydrogen recovery (\(R_{cat}\)) is the ratio...
between the electrons contained in the produced hydrogen gas and the electrons produced as current: 
\[ R_{\text{cat}} = \frac{2n_{H_2}}{Q_{F}} \]
where \( n_{H_2} \) is the mole of the produced hydrogen gas. The overall hydrogen recovery \( (R_{H_2}) \) represents the substrate used for hydrogen production: 
\[ R_{H_2} = \frac{R_{\text{cat}}}{C_{E}} \]

The energy efficiency relative to the electrical input \( (h_E) \) is the ratio of the energy content of the produced hydrogen to the input electrical energy required: 
\[ h_E = \frac{n_{H_2}D_{HH_2}W_E}{W_E} \]
where \( D_{HH_2} \) is the energy content of hydrogen based on the heat of combustion (285.8 kJ mol\(^{-1}\)), \( W_E \) is the electricity input determined by 
\[ W_E = \int (l E_{ap} - F r) \, dt \]
with \( E_{ap} \) being the applied voltage, and \( r \) being the external resistance. The energy efficiency relative to the substrate input \( (h_s) \) is the ratio of the energy content of the produced hydrogen to the input substrate energy required: 
\[ h_s = \frac{n_sD_{Hs}}{D_{Hs}} \]
where \( n_s \) is the mole of the substrate input, and \( D_{Hs} \) is the substrate energy based on the heat of combustion (872.9 kJ mol\(^{-1}\)).

**Result and discussion**

**Electricity generation**

Current generation was obviously affected by the PPR interval and the highest current density was obtained with the PPR interval of 40 min \( (p < 0.05, \text{one-tailed two-sample } t\text{-test with unequal variance at } \alpha = 0.05 \text{ for all the following statistical tests}) \) (Fig. 3). Current density increased from 1.42 ± 0.02 A m\(^{-2}\) to 1.58 ± 0.02 A m\(^{-2}\) with increasing the PPR interval from 10 min to 40 min; a larger PPR interval than 40 min decreased current density, for example to 1.27 ± 0.03 A m\(^{-2}\) (120 min). The COD removal efficiency in the MEC with different PPR intervals were not statistically different \( (p > 0.05) \), and the MEC achieved the removal efficiency >80% under all the conditions (Fig. 3). The conversion of COD to electricity was represented by CE as shown in Fig. 3. Because of the similar COD removal with different PPR intervals, CE followed the trend of current generation, and all of them exceeded 100%. The highest CE of 130.3 ± 1.8% was obtained with the PPR interval of 40 min \( (p < 0.05) \). This confirmed our previous finding that in addition to organic compounds in the anode, there were other electron donors in this MEC system such as residue hydrogen gas in the reversed cathode [24]. Further analysis revealed that with the PPR interval of 40 min, the anode contributed 110.7 ± 2.9% to current generation, and the rest (19.5 ± 0.4%) could be from the reversed cathode.

**Hydrogen production**

The hydrogen production performance was described by four parameters, including hydrogen production rate, cathodic hydrogen recovery \( (R_{\text{cat}}) \), overall hydrogen recovery \( (R_{H_2}) \) and...
energy efficiency (Fig. 4). Because hydrogen production is driven by electricity generation in an MEC, it was expected that the MEC with the PPR interval of 40 min would have the highest hydrogen production rate. The hydrogen production rate increased from $1.26 \pm 0.01 \text{ m}^3 \text{H}_2 \text{ m}^{-3} \text{d}^{-1}$ to $1.65 \pm 0.01 \text{ m}^3 \text{H}_2 \text{ m}^{-3} \text{d}^{-1}$ with increasing the PPR interval from 10 min to 40 min, and then decreased to $1.32 \pm 0.01 \text{ m}^3 \text{H}_2 \text{ m}^{-3} \text{d}^{-1}$ with a PPR interval of 120 min (Fig. 4A). Cathodic hydrogen recovery ($R_{\text{cat}}$) was less affected by the PPR interval when it was higher than 40 min ($p > 0.05$). When the PPR interval was lower, $R_{\text{cat}}$ increased from $47.6 \pm 0.4\%$ to $56.1 \pm 0.4\%$ with increasing the PPR interval from 10 min to 40 min, and then became relatively stable when the PPR interval was higher than 40 min ($56.4 \pm 0.4\%, 55.7 \pm 0.3\%, \text{ and } 56.1 \pm 0.3\% \text{ with the PPR interval of } 60 \text{ min, } 90 \text{ min, and } 120 \text{ min, respectively} \) (Fig. 4B). Because of the similar $R_{\text{cat}}$ of the MEC, overall hydrogen recovery ($R_{\text{H}_2}$) followed the trend of the hydrogen production rate and thus, the MEC with the PPR interval of 40 min had the highest $R_{\text{H}_2}$ of $75.9 \pm 0.4\%$ (Fig. 4C). The energy efficiency was evaluated relative to both electrical energy input ($\eta_E$) and the substrate (acetate) input ($\eta_S$). $\eta_E$ increased from $102.2 \pm 1.2\%$ to $124.8 \pm 1.2\%$ with increasing the PPR interval from 10 min to 90 min, and then decreased to $118.5 \pm 1.2\%$ with the PPR interval of 120 min ($p < 0.05$). $\eta_E$ followed the trend of $Q_{\text{H}_2}$, and the highest $\eta_E$ of $140.8 \pm 1.4\%$ was achieved with the PPR interval of 40 min (Fig. 4D). The results of energy efficiency were within the range of those reported in the MEC studies [7,26–28].

Catholyte pH

The above results have demonstrated that the PPR interval can affect the MEC performance. Such an effect could have been through affecting the catholyte pH with different PPR intervals. The catholyte pH would increase as a result of accumulation of hydroxyl ions due to proton reduction to hydrogen gas, and subsequently hydrogen production would be thermodynamically less favorable by the increased pH. Thus, slowing down the pH increase could benefit hydrogen production and reduce buffer consumption (and thus decrease operating expense). Fig. 5 shows the increase of the catholyte pH under the conditions of six PPR intervals operated for 360 min. All the catholyte pH exhibited an “up and down” pattern: the working cathode showed increased pH while the reversed cathode (non working cathode) exhibited decreased pH, and when the electrode connection was reversed, the pH variation trend also reversed. This was the same as that in our pervious study [24], but the scale of the pH variation was different with different PPR intervals. A short PPR interval such as 10 min or 20 min resulted in a small difference in the catholyte pH between the left (as working cathode first) and the right cathode (as the reversed cathode first). For example, at the end of the testing period, the pH increase rate of both catholytes reached a similar value, for example $0.0087 \text{ min}^{-1}$ of the left catholyte and $0.0085 \text{ min}^{-1}$ of the right catholyte with the PPR interval of 10 min. Increasing the PPR interval also increased the difference in pH between

![Fig. 4](https://example.com/fig4.png)

**Fig. 4** – Hydrogen production in the MEC with different PPR interval: (A) hydrogen production rate; (B) cathodic hydrogen recovery; (C) overall hydrogen recovery; and (D) energy efficiency relative to the electricity ($\eta_E$) and substrate input ($\eta_S$). Error bars ± SD is based on the average measured under stable operating conditions.
the two catholytes. With the PPR interval of 120 min, the pH increase rate of the left catholyte was 0.0138 min\(^{-1}\) during each PPR cycle, while that of the right catholyte was only 0.0034 min\(^{-1}\) (Fig. S1). Such pH unbalance between two cathodes has affected hydrogen production from each cathode, which would be discussed in the following sections.

**Effect of initial PPR connection**

One can observe from Fig. 5 that the left cathode, which firstly acted as a working cathode for hydrogen production, always had a higher catholyte pH than that of the right cathode that functioned as a reversed cathode firstly. To better understand this phenomenon, we examined the effect of initial PPR connection, and conducted the experiment with the right cathode as the initial working cathode and the left cathode as the initial reversed cathode. The hydrogen production rates under two initial PPR connection conditions with six PPR intervals are shown in Fig. 6. Fig. 6A shows the results with the left cathode initially connected as a working cathode and the right cathode as a reversed cathode; while Fig. 6B shows the other initial PPR connection. In general, two figures present the same pattern that from the PPR interval 10 min\(\rightarrow\)40 min, the two cathodes had similar hydrogen rates, both of which increased, and when the PPR interval was higher than 40 min, the initial working cathode had decreasing hydrogen production while the initial reversed cathode had relatively stable hydrogen production. For example, according to Fig. 6A, the hydrogen production rate of the left cathode increased from \(1.27 \pm 0.01\) m\(^3\) H\(_2\) m\(^{-3}\) d\(^{-1}\) to \(1.65 \pm 0.01\) m\(^3\) H\(_2\) m\(^{-3}\) d\(^{-1}\) with

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**Fig. 5** - The pH variation under different PPR intervals: (A) 10 min, (B) 20 min, (C) 40 min, (D) 60 min, (E) 90 min, and (F) 120 min. Note: left cathode firstly worked as a working cathode (for hydrogen production), and right cathode was the reversed cathode first.
increasing the PPR interval from 10 min to 40 min, but decreased eventually to 1.16 ± 0.01 m$^3$ H$_2$ m$^{-3}$ d$^{-1}$ when the PPR interval was 120 min ($p < 0.05$). Under the same condition (Fig. 6A), the hydrogen production rate of the right cathode increased from 1.27 ± 0.01 m$^3$ H$_2$ m$^{-3}$ d$^{-1}$ to 1.65 ± 0.01 m$^3$ H$_2$ m$^{-3}$ d$^{-1}$ with increasing the PPR interval from 10 min to 40 min, and this increase became much slower when the PPR interval was higher than 40 min, reaching 1.68 ± 0.01 m$^3$ H$_2$ m$^{-3}$ d$^{-1}$ (PPR of 120 min).

Fig. 6 – The hydrogen production in the two cathodes within 6 h. Left cathode firstly worked as hydrogen production cathode (A), and right cathode firstly worked as hydrogen production cathode (B). The calculation of hydrogen production in the two cathodes was based on working time.

Linking this result (Fig. 6) to the pH variation (Fig. 5) may suggest that the superior performance of hydrogen production with the initial reversed cathode may have benefited from its lower catholyte pH. The initial connection as a reversed cathode avoided rapid pH increase during the testing period. However, in a long-term operation without replacing the catholyte or replenishing the buffer capacity, the pH of both catholytes could become similar. It must be noted that the PPR operation will not eliminate the use of a buffer, which is a common approach for controlling pH in wastewater treatment (e.g., anaerobic digestion that requires input of alkalinity); instead, it will reduce the frequency of buffer addition and thus decrease the use of buffer.

Proposed mechanism

To further understand how the PPR interval affected the catholyte pH (and thus hydrogen production) and why the interval of 40 min was optimal, we conducted more analyses and proposed a potential mechanism. As stated before, current generation was a key factor that influenced the catholyte pH and there could be two sources of electrons for current generation, including the anode (organic oxidation) and the reversed cathode (hydrogen oxidation). The current density of the anode only was very stable among the six tested PPR intervals (Fig. S2). Thus, the reversed cathode that was affected by the PPR intervals should be the actual reason for different behavior of pH variation, resulting in different hydrogen production rates. As a result of proton reduction for producing hydrogen gas, the pH of the catholyte increased, while the PPR operation slowed down such an increase. As shown in Fig. 7A, the lowest pH increase rate of 0.0085 min$^{-1}$ (average of two catholyte pH increase rates of the MEC) occurred with the PPR interval of 40 min. The “buffer capacity” of a reversed cathode was from in situ oxidation of the residue hydrogen gas that was not collected. Because of hydrogen oxidation on the surface of the reversed cathode, there would be a concentration gradient from the liquid/gas interface (more hydrogen because of resupply from the gas phase) to the cathode surface (less hydrogen due to oxidation reaction) (Fig. 7B). As a result, hydrogen reaction rate/time and supply would affect the production of protons for pH buffer. We assumed that at the beginning of the reverse, the dissolved hydrogen was the same among different PPR conditions, because of similar hydrogen concentration in the gas phase (after collection). From the PPR 10 min–40 min, the reaction time could be a key factor, and the longer the PPR period was, more hydrogen gas was oxidized and thus resulted in a better pH buffer effect (a lower final pH); from PPR 40 min–120 min, the supply of hydrogen to the surface of the reversed cathode became a limiting factor, and there was not enough hydrogen for oxidation to buffer the increased pH (Fig. 7B). In addition, a longer PPR also caused more pH increase, which worsened the situation of pH buffer.

The above mechanism would need further verification with more experimental evidence and possible mathematical simulation to examine a broader range of the intervals. However, it indicates that the multiple processes were involved in the hydrogen oxidation by the reversed cathode and exhibited the opposite trends, leading to an optimal PPR interval. The buffer capacity of the PPR operation comes from the oxidation of residue hydrogen gas that is not effectively collected. Thus, to enhance the PPR buffer ability, it will be important to improve the use of the residue hydrogen gas, probably by increasing mass transfer efficiency via additional mixing or other methods. As was stated earlier, PPR can slow down the pH increase, but cannot eliminate the use of buffer. Seeking low cost buffer, or introducing the protons produced by the anode into the cathode (without bringing in microorganisms or
As stated above, the choice of buffer can exert obvious effects. In addition, the anolyte characteristics such as organic concentration and ionic strength may also influence the selection. The configuration of the MEC system used here, although containing three chambers, is actually a natural extension of traditional two-chamber (plate-type) MECs. One can see that, in a two-chamber MEC, the anode or the cathode chamber has one side (ion exchange membrane) used for ion transport and the other side not in use. Having three or more chambers would enhance the efficiency of MEC reactors. Although the initial cost of more-chamber MECs will become higher, there should be a tradeoff for better performance and this warrants further investigation.

Conclusions

In this study, an automated control system was designed and applied for the first time to manage the periodic polarity reversal in a dual-cathode MEC. It has been demonstrated that the optimal PPR interval of 40 min had the lowest pH increase rate of 0.0085 min⁻¹, resulting in the highest hydrogen production rate of 1.65 ± 0.01 m³ H₂ m⁻³ d⁻¹. The slow pH increase benefited from in situ oxidation of residue hydrogen gas, which was affected by both the reaction time and the supply of hydrogen to the surface of the reversed cathode. Those two factors functioned together leading to the best performance with the PPR interval of 40 min. The results and explanation of this study would encourage further development of the PPR-based MEC for hydrogen production from wastewater.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2017.06.028.

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