

Hydrogen Production from Acetate in a Sleeve Shape Microbial Electrolysis Cell with a Mipor Cathode

Yali Feng^{1,*}, Yulong Cheng¹, Yunlong Du^{1,2}, Qing Teng^{1,2}, Haoran Li^{2*}

¹ School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

² State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China)

*E-mail: Yalifeng126@126.com

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A sleeve-shape microbial electrolysis cell (MEC) was designed by making the anode surround the cathode. A mipor titanium tube coated with platinum was employed as the cathode, and seven pieces of graphite felts with exoelectrogens absorbing on surface piled up together served as the anode. Sodium acetate was used as a feed. Larger cathode surface area, shorter electrode spacing, greater system capacity and more reasonable structure design were contributed to enhance this system's performance. In 24 h batch tests, the hydrogen production rate increased from 0.14 to 2.36 L/L/d and the hydrogen recovery increased significantly from 40.15% to 86.13%, as the applied voltage increased from 0.2 to 1.0 V. And the chemical oxygen demand (COD) removal rate ranged from 0.23% (at 0.2 V) to 31.44% (at 1.0 V). The results demonstrated that high overall energy recovery and hydrogen production could be obtained by a relative higher applied voltage (>0.5 V).

Keywords: Microbial electrolysis cell; Hydrogen production; Energy recovery; Hydrogen recovery; Sleeve-shape

1. INTRODUCTION

Environmental pollution and energy shortage are two major international puzzles in the new century. The present energy comes mainly from burning of fossil fuels. With the growing concerns about the finite supply of fossil fuels and increasingly serious of environmental pollution, clean and effective energy source to replace fossil fuels has attracted more and more attentions in recent years. Hydrogen as a clean fuel is a promising alternative to fossil fuels [1]. At present, there are three general methods for hydrogen production: thermo-chemical process from fossil fuels [2], water electrolysis[3], and biological process from biomass [4]. Microbial electrolysis cell (MEC) is a new

approach for renewable biohydrogen production, based on microbial fuel cells (MFC) [5]. In an MEC, substrate is oxidized, which release electrons and protons to the anode. Electrons transport to cathode with the help of the voltage added to the circuit. At cathode, electrons combine with protons to form hydrogen.

Compared with water electrolysis, a typical voltage of 0.2 V or larger is required for hydrogen production, which is conspicuous less than the typical voltage of 1.8-2.0 V used in water electrolysis[6]. Substrate used by MEC is more comprehensive than traditional biological process from biomass. Almost all organics could be oxidized by microorganism that can be utilized to generate hydrogen via MECs [7]. Therefore, MECs can reclaim bioenergy from a cheap and alternative carbon source. MECs could be divided into membrane and membraneless MEC according to the presence of ion exchange membrane. In the early days, most MECs were designed with membranes to separate the cathode from the anode. However, the existence of membrane can increase the cost and give rise to the pH gradient between cathode and anode. Recently, more studies focus on single-chamber MECs without membrane, for membraneless reactor can lower the internal resistance and avoid the pH gradient. However, without membrane the concentration of hydrogen descends for the growth of methanogens on the cathode [8]. Hence, how to increase the hydrogen purity is a key technology for membraneless MECs. Furthermore, electrode spacing is another factor which can affect the performance of MECs. Reducing electrode spacing can increase hydrogen production rate to a certain degree [9]. Similarly, increasing the cathode superficial area can enhance the hydrogen production rate.

Therefore, based on above reports, we designed a new reactor named sleeve-shape MEC. The anode electrode was graphite felts which enclosed the cathode electrode with a plastic casing partition them. This design reduced the electrode spacing significantly. On the other hand, we conjectured that the use of graphite felts could minish the internal resistance of the system. In addition, mipor titanium bar coated with platinum served as cathode which increased the cathode superficial area conspicuously. According to these two observations, we emphasized that the new design could enhance the hydrogen production rate and energy recovery.

2. MATERIALS AND METHODS

2.1 Reactor construction

The sleeve-shape MEC reactor's main body was assembled by a glass sleeve (inner diameter 70 mm and height 150 mm) with a top cover (fig.1). The total empty volume of the reactor was 800 ml. A water outlet and an air outlet were installed at the top of the cover, and water inlet was assembled at the bottom of the glass sleeve. The cathode, a mipor titanium tube (inner diameter 20 mm, outer diameter 30 mm, height 50 mm, mipor diameter 10 μm) coated with platinum was placed at the center of the reactor. The anode, seven pieces of graphite felts (thickness 7 mm, inner diameter 20 mm, outer diameter 30 mm) (Sanye Carbon Co., Ltd., Beijing) were piled up together, surrounding the cathode. The two electrodes were separated by a plastic casing with many tiny pores. The distance between the anode and cathode was 9 mm. Titanium wire was used for the connection of the electrodes

to form a circuit. An external resistor of $10\ \Omega$ was connected in series on the circuit, for calculating the current. A data acquisition board (AD8201H, Ruibohua Co., Beijing, China) was connected in parallel with the resistor to monitor the voltage. The applied voltage was provided by a power supply (IT6322, ITECH, Nanjing, China).

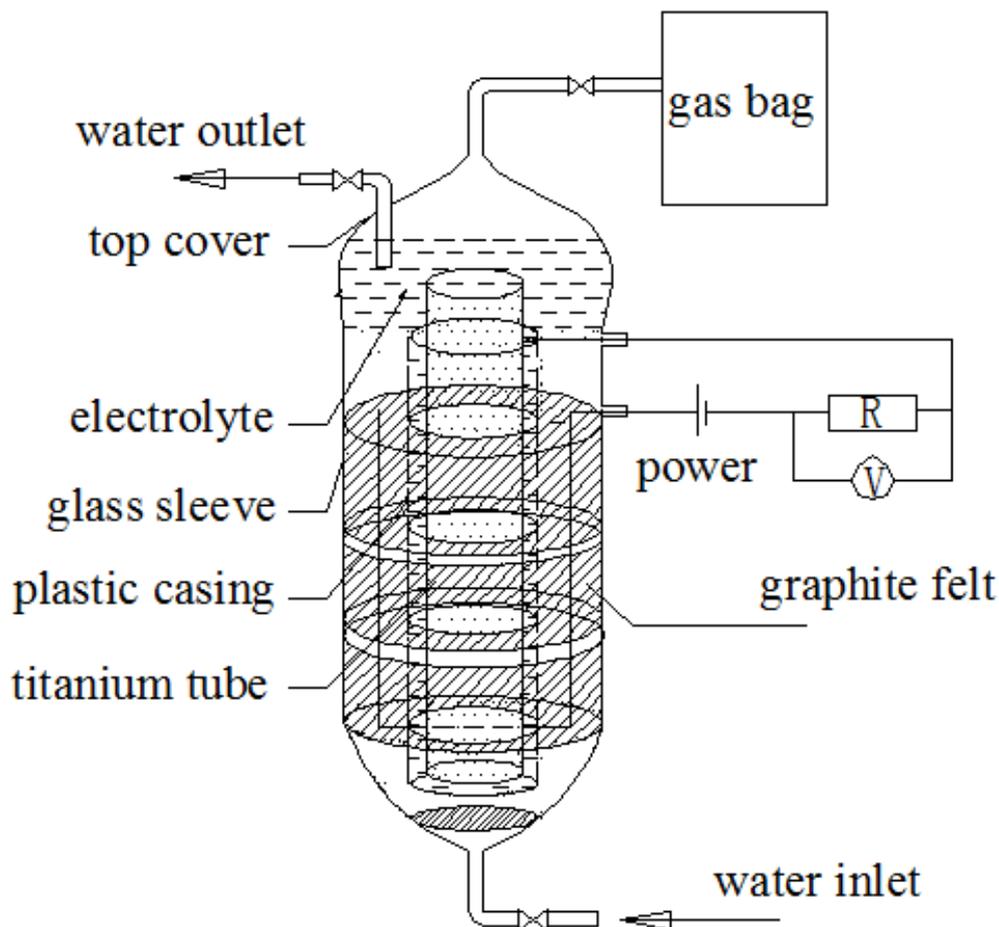


Figure 1. Schematic of the sleeve shape single-chamber MEC.

2.2 Start-up and operation

Two methods of enriching exoelectrogens onto the anode electrode were reported [10]. One way was to enrich exoelectrogens via MFC. The other way was starting up by MEC, which supply applied voltage directly after inoculating. In this study, the first mean was used. Construct a MFC system using the graphite felts which were meeting the requirements of our MEC. Mixed bacteria that screened from marine surface sediments was employed as exoelectrogenic microbes. The culture medium for both MFC and MEC contained sufficient inorganic supplements was composed of (in $\text{g}\cdot\text{L}^{-1}$): KCl 0.1, NH_4Cl 0.2, NaH_2PO_4 0.6, NaCl 2.9, NaHCO_3 2.5, and trace vitamins and minerals [11]. When a recyclable maximum power output was achieved, the anode graphite felts were taken out and placed into MEC.

The anode feeding solution of MEC was identical to the MFC. Experiments were conducted in fed-batch mode. Each batch was running cycle (three times) for 24 h at 25 ± 2 °C room temperature. When the MEC was running, the system had a liquid volume of 250 ml. In order to eliminate the possibility of less substrate affecting the experimental results, 2 g acetate sodium was added in each fed-batch. A series of applied voltages varying from 0.2 to 1.0 V by step of 0.1V were added in each runs. Expose the two electrodes to air for 30 min during interval between each runs, in order to suppress methanogen growth [12]. Before medium was added to reactor, it was flushed with nitrogen gas for 10 min to remove oxygen.

2.3 Analyses and calculation

Chemical oxygen demand (COD), gas production, gas composition, and current were measured along every batch cycle. COD was measured at the end of every cycle following standard methods [13]. Prior to measure, solution should be centrifuged at 6000 g. And the acetate concentration was calculated as $c = \text{COD} \times 82.4/64$, where c was acetate concentration in mg/l. Gas sample bags were employed to collect produced gas, and gas production was measured by water replacement. Gas composition (H_2 , CH_4 , CO_2) was analyzed by using a gas chromatography (GC4000, Dongxi, Beijing).

The COD removal (K) was calculated as $K = \frac{\text{COD}_{\text{in}} - \text{COD}_{\text{out}}}{\text{COD}_{\text{in}}} \times 100\%$, where COD_{in} was the initial COD concentration of the electrolyte; COD_{out} was the COD concentration of the effluent after each batch cycle.

The gas production rate, Q in L/L/d was calculated as $Q = V_x / (V \cdot t)$, where V_x was the volume of one gas produced during each batch cycle, $V = 250$ ml was the volume of the electrolyte in the reactor, $t = 24$ h was the time of one batch cycle.

The hydrogen recovery, r_{H_2} (%) was a significant index for MEC performance, which was defined as the ratio of the hydrogen recovered (n_{H_2}) and the maximum theoretical hydrogen produced based on substrate utilization (n_{th}). And the hydrogen recovery was related to coulombic efficiency (r_{CE}) and cathodic hydrogen recovery (r_{cat}). The r_{cat} was calculated as $r_{\text{cat}} = n_{\text{H}_2} / n_{\text{CE}}$, where n_{H_2} was the moles of hydrogen recovered, n_{CE} was the moles of hydrogen produced calculated by the current, and $n_{\text{CE}} = \frac{\int_{t=0}^t I dt}{2F}$, where $F = 96485$ C/mol was Faraday's constant, I was the current of the circuit. The r_{CE} was calculated according the reference [14]. Based on the above equations, the r_{H_2} could be worked out.

Electrical energy recovery (η_{E}) and overall energy recovery ($\eta_{\text{E+S}}$) were considered. The electrical energy recovery, η_{E} (%) was energy recovery that only consider electrical input, and it was calculated as $\eta_{\text{E}} = n_{\text{H}_2} \cdot \Delta H_{\text{H}_2} / \int_{t=0}^t (IE - I^2R) dt$, where $\Delta H_{\text{H}_2} = 285.83$ kJ/mol was the higher heating value of hydrogen, E was the applied voltage added to the circuit, $R = 10\Omega$ was the external resistor. Accordingly, the overall energy recovery, $\eta_{\text{E+S}}$ (%) was the energy recovery consider all the energy input including electrical energy and energy obtained from substrate. It was calculated as $\eta_{\text{E+S}} = n_{\text{H}_2} \cdot \Delta H_{\text{H}_2} / [\int_{t=0}^t (IE - I^2R) dt + n_s \cdot \Delta H_s]$, where n_s was the moles of the substrate consumed in one cycle and $\Delta H_s = 870.28$ kJ/mol was the higher heating value of the substrate [15].

3. RESULTS AND DISCUSSION

3.1 Hydrogen production

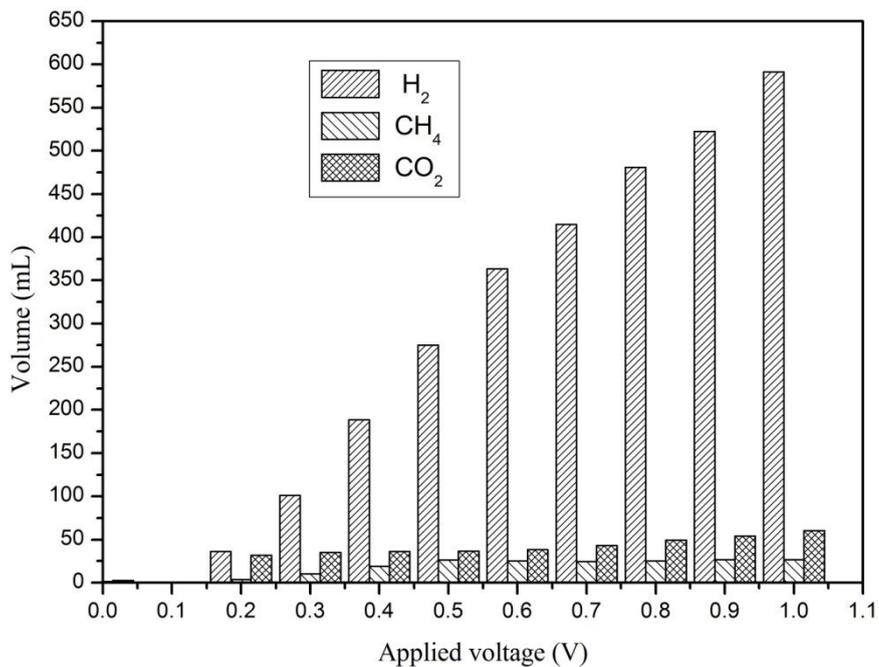


Figure 2. Gas production variation as different applied voltage.

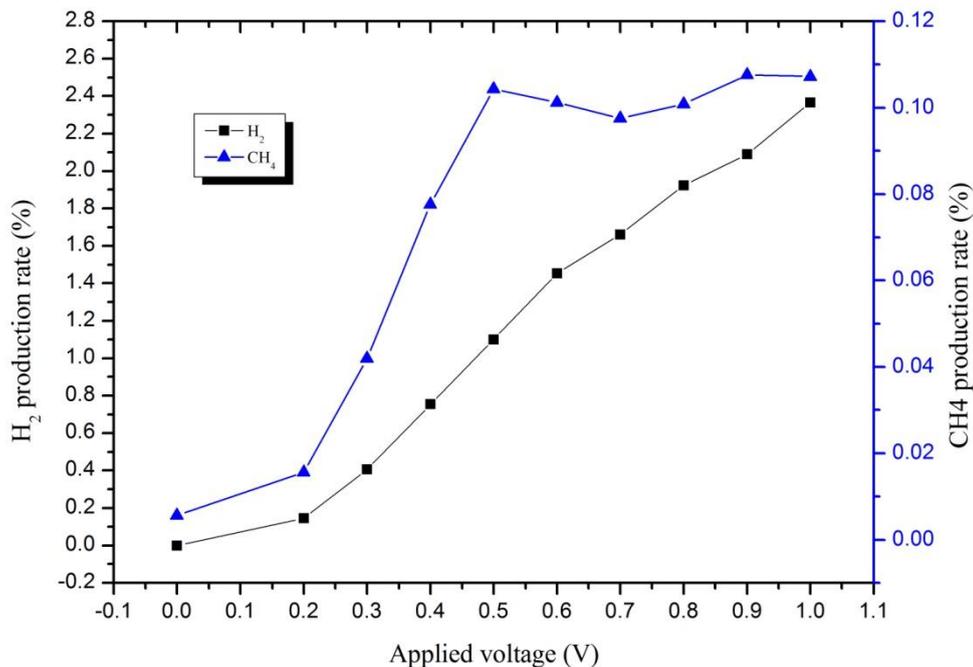


Figure 3. Hydrogen production rate as a function of applied voltage

Fig.2 showed the yield of hydrogen and methane at range of applied voltage from 0.2-1.0 V. One batch test without applied voltage was operated as a negative control group. When the applied voltage was greater than 0.2 V, hydrogen bubble began to generate at cathode. And as was shown in Fig.3 hydrogen production rate increased substantially from 0.14 L/L/d to 2.36 L/L/d as the applied voltage increased from 0.2 V to 1.0 V. The highest hydrogen production rate of 2.36 L/L/d was obtained at voltage of 1.0V. Hydrogen production was accompanied by production of methane and carbon dioxide. Methane production rate substantially increased from 0.017 L/L/d (at 0.2 V) to 0.104 L/L/d (at 0.5 V). However, further increase in the applied voltage did not vary methane production rate significantly, it fluctuated slightly around a value (about 0.10 L/L/d). In addition, variation of carbon dioxide production was negligible as the change of applied voltage.

An applied voltage of 0.14 V is required to generate hydrogen gas for MEC in theory [16]. Applied voltage of at least 0.2 V is needed because of energy losses due to electrode overpotentials and solution resistance. Compared with other designs rationally, hydrogen production rate here could reach 2.36 L/L/d at 1.0 V which was higher than majority. Analyzing the reasons, two factors were considered. Firstly, the anode graphite felt enclosed the cathode titanium tube lowered resistance of the system and beneficial to the proton transfer. It also decreased the electrode spacing significantly. Then, the usage of mipor titanium bar could increase the cathode superficial area conspicuously. Both of the two factors could improve the hydrogen production rate to a certain degree. However, hydrogenotrophic methanogens would propagate easily at cathode because of the membrane-less. Hence, though this design enhanced the hydrogen production rate, it also increased the hydrogen loss rate.

3.2 COD removal

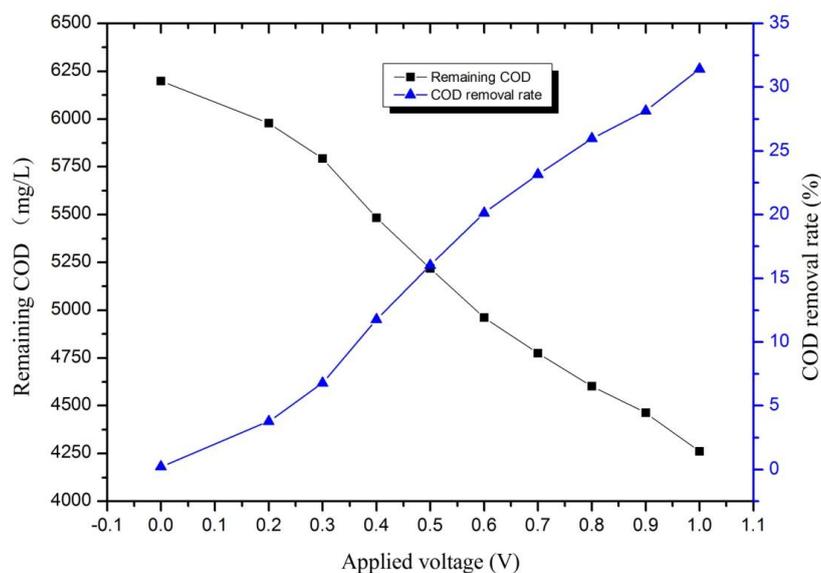


Figure 4. Effluent COD and COD removal as a function of applied voltage

The remaining COD concentration and COD removal variation with applied voltage were shown in Fig.4. The initial COD concentration was 6240 mg/L. Remaining COD decreased from 6200 mg/L (at 0 V) to 4260 mg/L (at 1.0 V). Correspondingly, the COD removal increased from 0.23% to 31.44% as the applied voltage increased from 0 V to 1.0 V.

Low COD removal was mainly due to short running time and high initial COD concentration.

3.3. Hydrogen recoveries

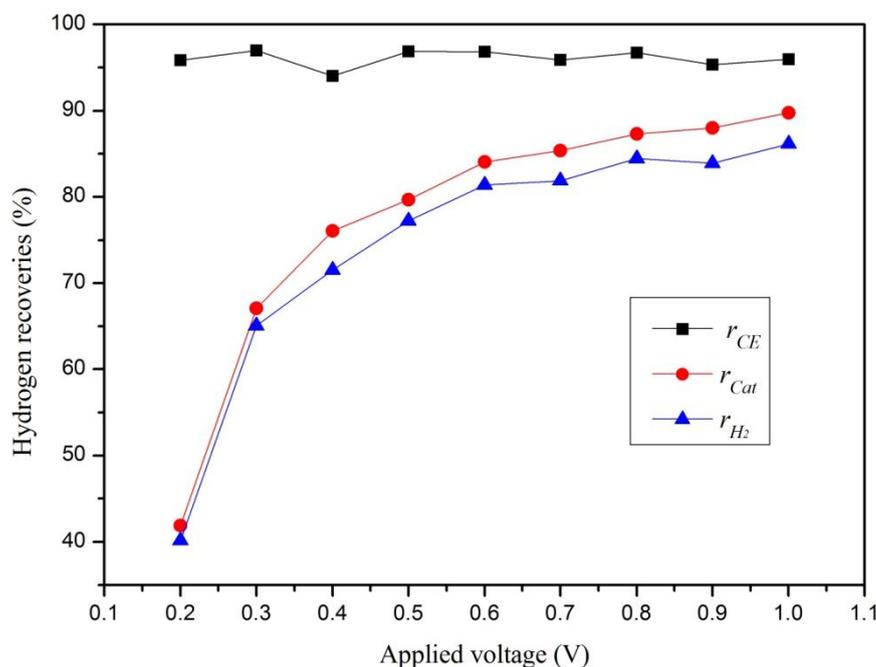


Figure 5. Hydrogen recoveries at different applied voltage

The hydrogen recovery (r_{H_2}), coulombic efficiency (r_{CE}) and cathodic hydrogen recovery (r_{cat}) variation with the difference of applied voltage were shown in Fig.5. The coulombic efficiency showed little change with the variation of applied voltage from 0.2 V to 1.0 V, and it fluctuated slightly around 95%. The results showed that the effect of substrate transfer to electric energy by exoelectrogens was influenced little with the variation of applied voltage, and the percent conversion was always kept a high level. Nevertheless, the cathodic hydrogen recovery increased significantly from 41.90% to 89.74% as the applied voltage increased from 0.2 V to 1.0 V. Accordingly, the variation tendency of hydrogen recovery was consistent with the cathodic hydrogen recovery. The hydrogen recovery also increased sharply from 40.15% (at 0.2V) to 86.13% (at 1.0 V).

The major reason for low cathodic hydrogen recovery was that hydrogen produced at cathode easily diffused to anode in this design and utilized by hydrogenotrophic methanogens. This point could be proved by the high methane production rate on cathode. Hydrogen could be cycled and reutilized by the exoelectrogens on anode [17]. Although it could increase the coulombic efficiency apparently, it also lost much of the efficiency of electrical power. In this MEC system, high coulombic efficiency and low electric energy efficiency accounted for part of hydrogen production may be consumed by

hydrogenotrophic methanogens on anode. Therefore, it is the key to ameliorate the cathodic structure to further increase the hydrogen recovery of this system.

3.4 Energy recoveries

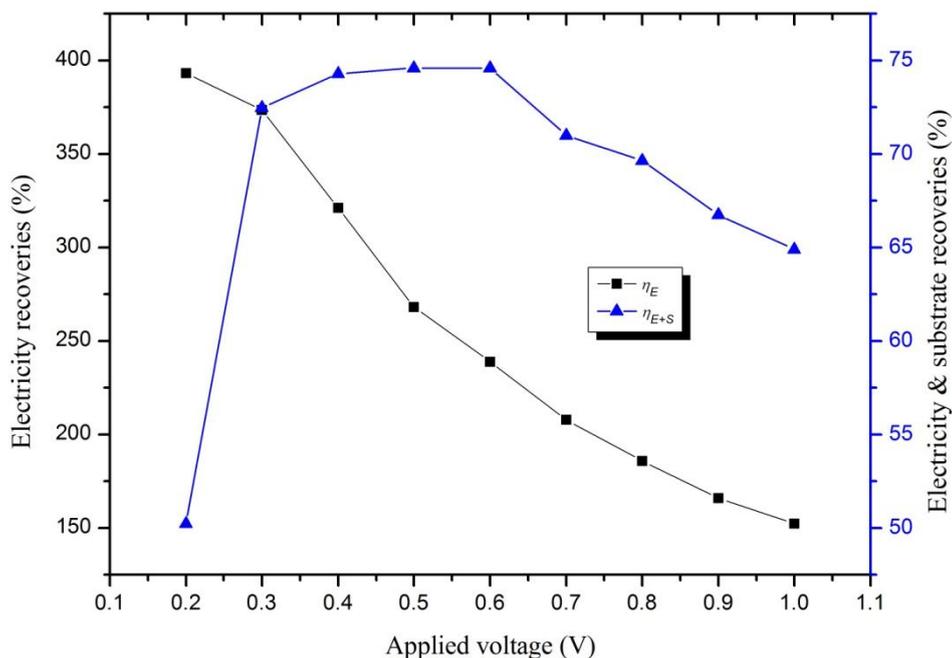


Figure 6. Energy recoveries at different applied voltage

Electrical energy recovery (η_E) and overall energy recovery (η_{E+S}) variation with the difference of applied voltage were shown in Fig.6. Electrical energy recovery (η_E) decreased with the increase of applied voltage. When the applied voltage was 0.2 V, the maximum value of electrical energy recovery was 393%; and the electrical energy recovery attained a minimum of 152%, when the applied voltage was 1.0V. On the other hand, overall energy recovery increased firstly and then decreased as the applied voltage variation from 0.2 V to 1.0 V. Its value increased from 50% (at 0.2 V) to maximum of 75% (at 0.5 V), and then gradually decreased to 64% (at 1.0 V). It was tempting to conclude that 0.5 V was the optimal applied voltage for a high energy recovery from the above analyses.

The reason why electrical energy recovery was more than 100% was that energy product from substrate had not been calculated. Compared with previous design, electrical energy recovery and overall energy recovery of this system were lower (Table 1). It is mainly because that hydrogen generated from cathode was consumed by hydrogenotrophic methanogens and exoelectrogens on anode. Although the product of hydrogenotrophic methanogens is methane which is also combustible gas, 4 mol hydrogen generate 1 mol CH_4 which wastes a part of energy. Moreover, hydrogen cycled and reutilized by the exoelectrogens on anode is a complete waste of electrical energy investment. Therefore, it should be avoided in the application and enlargement of MECs.

As is shown in Table 1, compared with single-chamber MECs published previous, hydrogen production of this design is higher. In addition, it has high hydrogen recovery, which is the best one among the larger MEC reactors published previous. These results demonstrated that the design in this paper has get the better effect.

Table 1. Performance of the single-chamber MECs reported in the literatures versus the reactor in this study

Substrate	V (ml)	Eap(V)	r _{H2} (%)	η_E (%)	η_{E+S} (%)	Q (L/L/d)	Ref
Buffered effluent	26	0.8	68	170	55	1.52	[18]
Swine wastewater	28	0.5	17	190	-	0.90	[19]
Sodium acetate	28	0.8	93	194	75	3.12	[12]
Sodium acetate	150	1.0	88	198	76	1.58	[14]
		1.0	86	152	64	2.36	This study
Sodium acetate	250	0.8	84	186	70	1.92	
		0.5	77	239	76	1.10	

4. CONCLUSIONS

A sleeve-shape microbial electrolysis cell was designed in this study. This new MEC device provides the possibility of the MECs enlargement. And its performance in all of the hydrogen production, hydrogen recoveries and energy recoveries in 24 h batch experiments were investigated.

Hydrogen began to appear on cathode when the applied voltage was >0.2 V. And hydrogen production rate increased substantially from 0.14 L/L/d to 2.36 L/L/d as the applied voltage increased from 0.2 V to 1.0 V. Meanwhile, hydrogen production was accompanied by production of methane, and the main methane producer in this MEC was hydrogenotrophic methanogens. One method to restrain methane production was to improve applied external voltage in 24 h batch tests.

The hydrogen recovery also increased signally from 40.15% to 86.13% as the applied voltage variation from 0.2 V to 1.0 V. And the major reason for restraining hydrogen recovery was low cathodic hydrogen recovery. Therefore, further study should focus on improving cathodic hydrogen recovery in order to increase hydrogen recovery.

The overall energy recovery increased firstly and then decreased as the applied voltage variation from 0.2 V to 1.0 V. Its value increased from 50% (at 0.2 V) to maximum of 75% (at 0.5 V), and then gradually decreased to 64% (at 1.0 V). Low overall energy recovery is mainly because that hydrogen generated from cathode was consumed by hydrogenotrophic methanogens and exoelectrogens on anode. Hence, how to inhibit the growth of hydrogenotrophic methanogens becomes the key for further improving energy recovery.

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