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Review

Effect of COD and H_2O_2 concentration on DC-MFC

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ABSTRACT

The main challenges in constructing microbial fuel cells (MFCs) are the identification of materials and architectures that maximize power generation and efficiency, also minimizing the cost of fabrication. In some cases aqueous cathodes have been used to provide dissolved oxygen to the electrode. An attempt. has been made to use hydrogen peroxide (H_2O_2) in different concentrations as substitute for ferricyanide and permanganate as catholyte in DC-MFCs. It has been found that the power generation was not significantly affected by the 20%–60% and 100% concentrations while 80% concentration exhibited higher power generation. Power densities were virtually dependent on the chemical oxygen demands (CODs) as observed to be 24.56 W/m^2 for Balance substrate (7562 mg/L) against 80% H_2O_2. This confirms that H_2O_2 is a very powerful oxidizing agent between the concentrations of 70%–90%.

1. Introduction

Lagan et al. (2008) have shown that power densities can be increased by choosing high-energy catholytes such as ferricyanide or permanganate, but concluded that the use of these materials are not sustainable or cost effective. In most MFCs oxygen is used as the electron acceptor and as such all cathodic substrates are selected to achieve maximum acceptor level. The ideal performance of an MFC depends on the electrochemical reactions that occur between the organic substrate at a low potential such as glucose and the final electron acceptor with a high potential, such as oxygen [12]. However, the ideal cell voltage is uncertain because the electrons are transferred to the anode from the organic substrate through a complex respiratory chain that varies from microbe to microbe and even for the same microbe when growth conditions differ. Though the respiratory chain is still poorly understood, the key anodic reaction that determines the voltage is between the reduced redox potential of the mediator or the final cytochrome in the system for the electrophile/anodophile. For those bacterial species that are incapable of releasing electrons to the anode directly, a redox mediator is needed to transfer the electrons directly to the anode [2]. The search for anode substrate is still on-going, although species such as Geobacter sulfurreducens, is speculated to form an electrical conductive biofilm capable of electron transfer in the system, a replacement would be necessary. Diluted H_2O_2 in different concentrations at the cathode in two MFCs using wastewater of different COD was used.

Hydrogen peroxide, known in IUPAC cycles as dihydrogen dioxide, is a colourless liquid formed by the combination of a molecule of oxygen with a molecule of water. It is denser than water (1.45 g/cm^3) and has a boiling point of 150 °C. Pure hydrogen peroxide is a weak acid with a pH of 6.2. Hydrogen peroxide has been chosen as cathode material due to its strong oxidizing properties as well as its availability. One 200 mL bottle costs $0.50, that is, less than half a dollar [9].

Gil et al., in their paper used 50 mM phosphate buffer (pH 7.0) with 100 mM NaCl as the catholyte [6]. Also air was purged into the cathode compartment in order to supply oxygen needed for the electrochemical reaction. The highest current of between 1.2 A and 1.4 mA was generated from their experiment.

Lee et al. filled the cathode chamber with 100 mM ferricyanide and phosphate buffer at 100 mM in which the initial pH was adjusted at 7.57 with 0.1 M NaOH. The potassium ferricyanide was more than twice the number of electron equivalents available at the anode, which ensured that the terminal acceptor concentration did not limit the process. In addition, the sufficient ferricyanide kept the cathode potential constant during the experiments. The maximum current achieved was a little below 5 mA. They were, however, silent on the influence of the catholyte [10]. In another paper the catholyte chamber was filled with seawater and its pH adjusted in the range of 1.0–9.0 with concentrated HCl or NaOH [3]. Zhao et al. [16] gave one example in their paper as the oxygen reduction reaction where anions such as Cl^-, HSO_4^-, HPO_4^{2-}, and HS^-

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were well known to be species that poison Pt catalysts and seriously interfere with the electrode reactions on Pt catalytic surfaces. They concluded that the majority of MFC and related studies involve the presence of phosphate buffers, ionic strength adjusters such as NaCl and other nutrients.

Prasertsung et al. [1,5,8,14], have tested single-chambered MFCs that used cathodes exposed directly to the atmosphere. That is, oxygen (about 20% of atmospheric air) was taken from the ambient environment saving them from the thought of other chemical chamber. Air aeration in the cathodic area was also used to increase the oxygen concentration. Others authors experimented MFC construction with pressurized cathodic chamber to increase the solubility of oxygen [4,7]; An air pump was used to supply the required oxygen to the cathodic compartment. During the experiments, the air pump supplied air at about 1.5 atm of pressure to the chamber. However literature revealed that no experiment has considered H_2O_2 as catholyte for MFC, hence this paper considered the properties of H_2O_2, non-toxic nature and its availability.

2. Methodology

The double-chambered cell was the exact replica system used in the previous study [15]. The two. MFC chambers were designed and fabricated using Plastic containers bought from local market nearby at a cost of $1.50. The cell consisted of two equal volume (1.8 L) chambers for anode and cathode separated by proton exchange membrane (PEM-Nafion117). PEM was fixed between the Perspex slabs with bolts and nuts between 4 cm diameter hollow PVC pipes connected to the containers using adhesive made from Perspex chips and chloroform as shown Fig. 1.

This setup is a mediatorless anode chambers containing Domestic wastewater (COD – 1273 mg/L) for experiment 1 and wastewater (COD – 7562 mg/L) from Guinness Ghana Brewery limited (GGBL) for experiment 2 and Hydrogen Peroxide (H_2O_2) in the cathode side for both cells. Plain graphite rods (surface area of 86.7 cm^2) without any coating were used as electrodes for both anode and cathode. The electrodes were positioned at a distance of 9 cm on either side of the PEM, because of the container size. Copper wires were used as contact with electrodes to the datalogger. Open circuit voltages plotted as a function of time at varying concentration were run, in turn using the same cell, for 120 h each.

Voltage and current in the MFC were measured with a Digital Multimeter (Peak Tech®2010DMM) for each concentration.

Open circuit voltage, E was acquired and stored using a data acquisition system (Campbell Scientific Ltd. Datalogger – CR10X). As studies revealed; the surface area of the anode electrode does not always affect power production [11,13]. In systems that contain a membrane separating the two electrode chambers, it is possible to normalize power based on the membrane projected surface area;

$$\text{Current Density normalized by PEM area} = \frac{E}{R \times A_{\text{PEM}}}$$

$$\text{Power density as normalized with PEM area} = \frac{E^2}{R \times A_{\text{PEM}}}$$

$$\text{Power density as normalized with volume of anode chamber} = \frac{E^2}{R \times V_{\text{an}}}$$

where E is load voltage, R is load resistance, A_{PEM} is active PEM area and V_{an} is volume of anode chamber.

3. Results and discussion

The open circuit voltage as against concentration of H_2O_2 at the anode chamber is shown in Fig. 2. It was expected to follow a linear trend towards higher concentration of H_2O_2, but this was not so. That is, applying the basic combustion equation

$$2H_2 + O_2 \Leftrightarrow 2H_2O$$

The higher concentration of oxygen at the cathode side was expected to set up high potential to augment the lower potential at the anode electrode, thus creating a resultant trend of potential deference in accordance with the concentration. A 100% concentration of H_2O_2 (Contains 6% w/v of H_2O_2 with a stabilizer) is more reactive and may have high oxidation property, but it was observed that the oxidation is rather dependent on the rate at which useful protons were generated by microbial agents in the anode substrate. A 80% concentration on the other hand shot up to a higher OCV in the range above 400 mV. Dilution with 20% water might have increased the potential at the cathodic electrode. Lower concentrations namely 60%, 50%, 40% and 20% H_2O_2 concentration showed

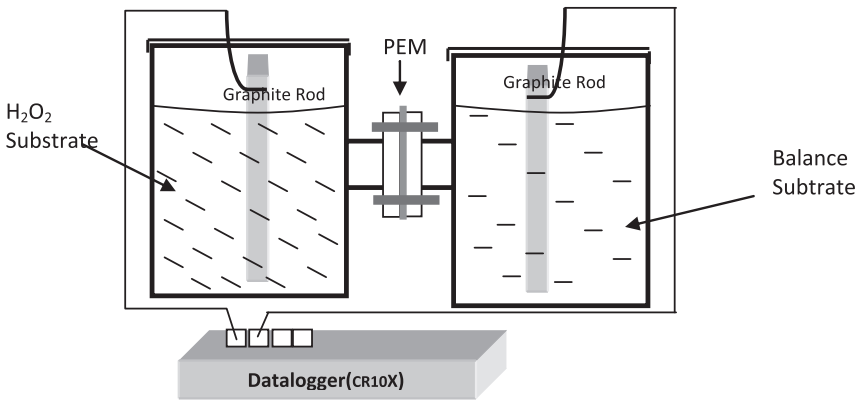

Fig. 1. Double-chamber MFC.

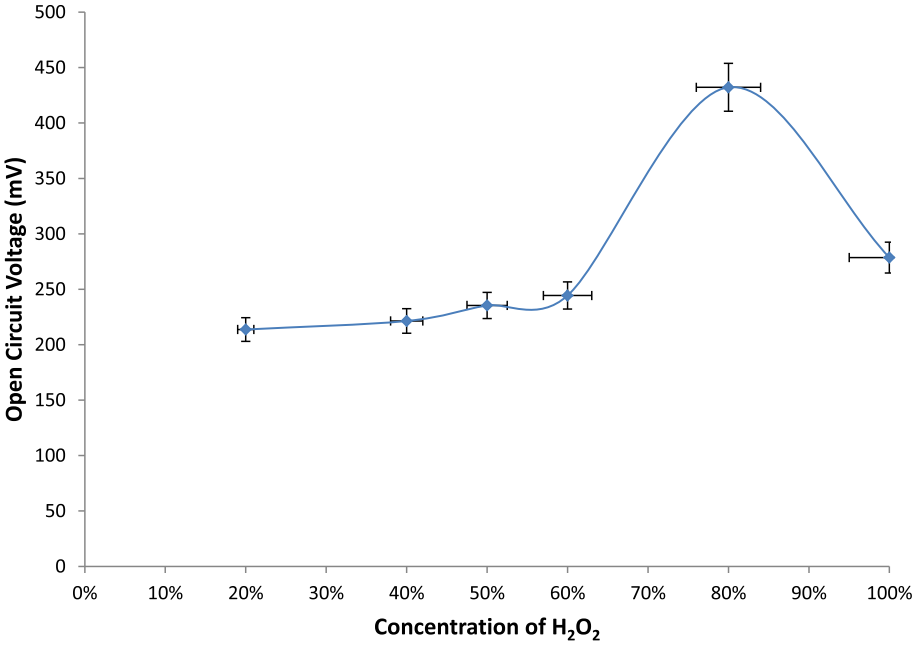

Fig. 2. OCV versus hydrogen peroxide concentration.

linear characteristic of OCV, but no significant variation in relation to the non-diluted H_2O_2.

The open circuit voltage in relation with time has been shown in Fig. 3. All the cells picked up after the first day and got to higher value. These values were maintained for the rest of the days. It was observed that the rate of oxidation in the cathode chamber solely depended on the rate of flow of ions from the anode chamber, in other words, the rate at which bacteria activity occurred. One would suggest that oxidation threshold may have been reached between 60% and 80%. The use of pure H_2O_2 (non-diluted) has other reactive property. In this experiment non-diluted H_2O_2 tends to wash clean the surface of the cathode electrode. Strong bonding of hydrogen and oxygen is also suspected.

The drops and the ramps were observed to occur in the nights where the temperature dropped from 28 °C to between 27 °C and 25 °C. This temperature effect may not be for the peroxide, but for the biological substrate. This type of H_2O_2 was bought from a nearby chemical store in 200 mL bottles (ECL'S, Solution of Hydrogen Peroxide B.P. 20 Volumes – Contains 6% w/v of H_2O_2 with a stabilizer, made in Ghana by Ernest Chemists Ltd.). Performance of 20%–60% H_2O_2 concentrations were almost the same showing that only dilution with distilled water of some sort was needed.

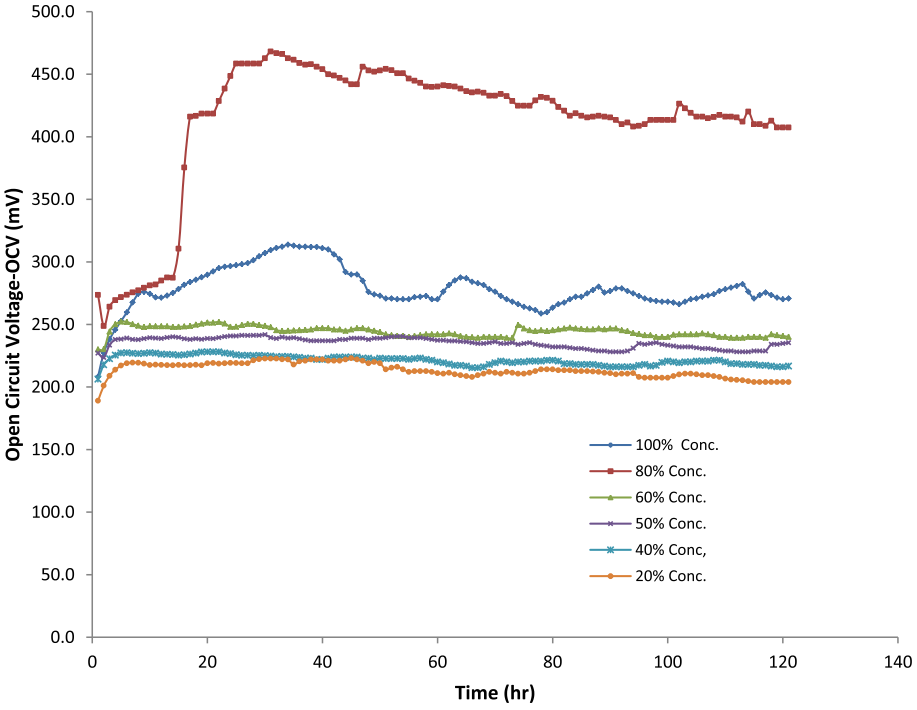

Fig. 3. Performance comparison in relation to Open circuit voltages plotted as a function of time for varying concentration.

Polarization curves were obtained by varying external resistances from 100 to 10,000 Ω.

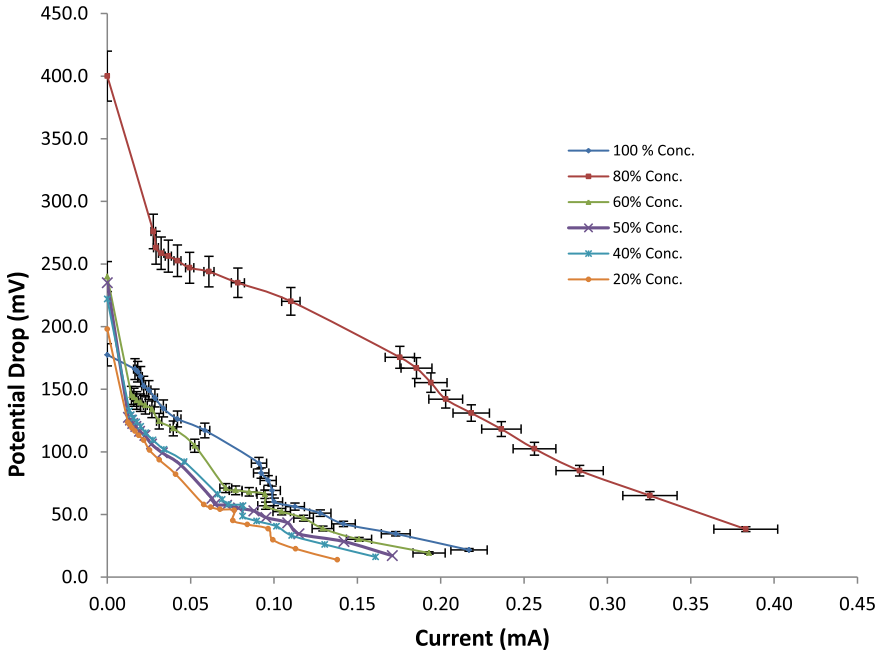

Fig. 4. Performance comparison in relation to peroxide concentration.

This reason accounted for the jump in the power production from 6.57 W/m^2 for100% to 24.4 W/m^2 for 80%. As stated earlier, other researchers used bubbled water to increase oxidation at the cathode; the diluted H_2O_2 may behave similarly. In other words, this type of H_2O_2 fragments into H and HO_2 molecules in the solution, but between 70% and <90% concentration it decomposes to two OHs and becomes more powerful oxidizing agent. Of course, 100% is more reactive.

Polarization curves were obtained by varying external resistances from 100 to 10,000 Ω.

As may be seen in Fig. 4, the 80% concentration at the cathode exhibited a significantly high polarization than expected. It should also be observed that the addition of 20% water showed about 80% increase in voltage over the pure peroxide (100%). The fact that the other concentrations in the cathode chamber performed so poorly in comparison to the 80% concentration is evidence that potential

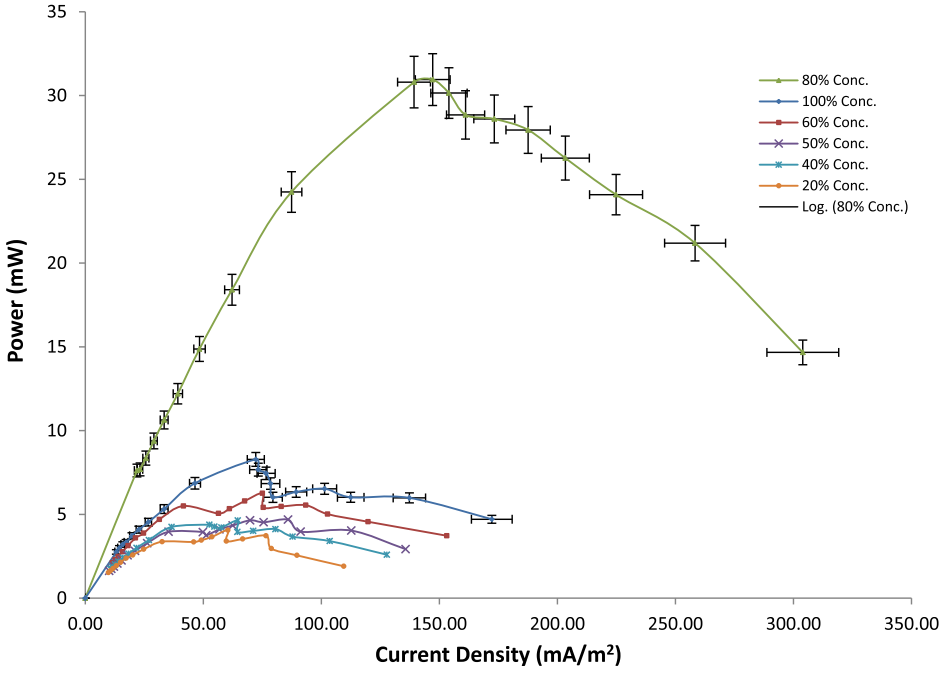

Fig. 5. Variation of power with current density for various concentrations of H_2O_2.

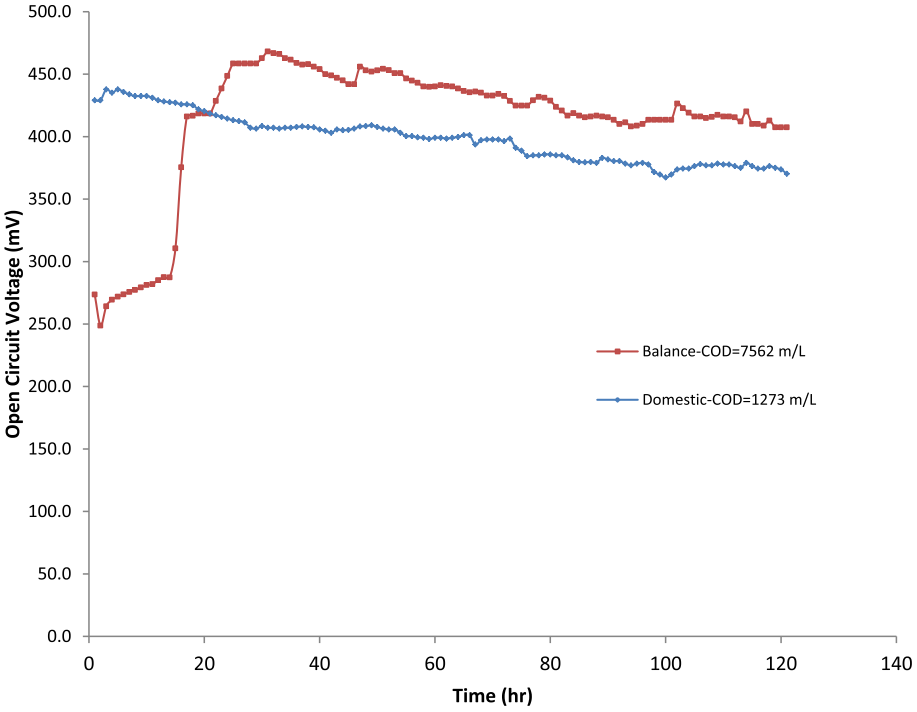

Fig. 6. Comparative state of the two similar MFCs.

difference may be dependent on the number of ions exchanged between anode and cathode chambers. Non-diluted hydrogen peroxide (100%) in the experiment washed the surface of the cathode clean. This may be due to the high reactivity of H_2O_2 (Fig. 5).

Similar characteristics were observed for power versus current density relationship. Maximum Power density as normalized with PEM area is 24,564 mW/m^2, which is equivalent to 17.2 mW/L as normalized by substrate volume.

3.1. *Effect of CODs and H_2O_2 concentration on power density*

As H_2O_2 concentration is crucial in this experiment as the CODs of the substrates, though the percentage dilution has significant impact on the performance of the two systems. Moderately, the earlier result indicated that the power density actually depends on the chemical oxygen demand (COD) of the anodic substrate. As shown in Fig. 6 the OCVs were not far apart and thus compare favourably, but this could not be said about their power densities.

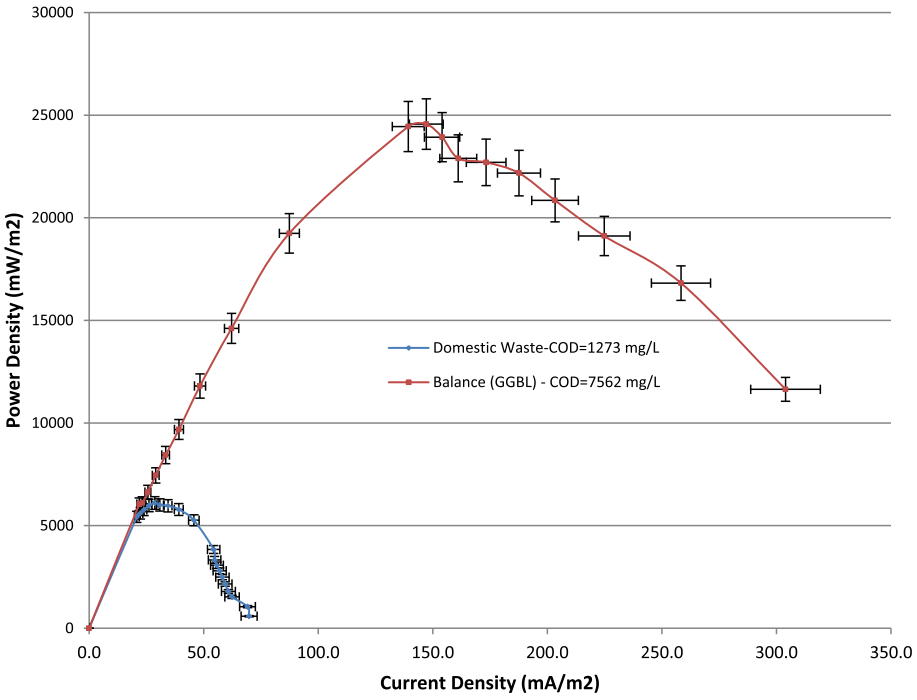

Fig. 7. Comparative power densities versus current densities of the two MFCs.

From 20 h on more ions may have been released as bio-activity increases. The peaks of their power densities were far apart and would have been dependent on the CODs of the two systems as exhibited in Fig. 7.

The OCV may be similar, but as current strictly depends on the number of useful electric charges present in the system are responsible of bio-electrochemical reaction; the reason would be probable.

4. Conclusion

The results of this study indicate that the efficiency in DC-MFCs can effectively be increased by varying the concentration of H_2O_2 as cathodic substance. Specifically, the investigation shows that this paper supports the earlier result by Tamakloe et al. of the use of hydrogen peroxide as cathode substrate. Upon investigation of different catholyte concentrations, dilution of H_2O_2 at a certain level must be necessary to achieve high efficiency and power generation.

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