Activated carbon-Fe catalyst modification on stainless steel cathode affects hydrogen production in microbial electrolysis cell

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Abstract. Microbial Electrolysis Cell (MEC) can be used to produce hydrogen gas from organic matter contained in wastewater. However, at the cathode of MECs, hydrogen production may be limited by methanogenesis wherein CO\textsubscript{2} and hydrogen protons react to form methane and water. In this study, activated carbon (AC)-Fe was used as a catalyst coated onto SS mesh 304 cathode. AC-Fe/SS was chosen for its high surface area, good activity, and stability. The combination of AC-Fe on SS was expected to increase hydrogen production in MECs. Adsorption and phase inversion were chosen to coat AC-Fe mixture on SS. The research was carried out in a 100 mL MEC reactor with an operating time of 258 h. The produced hydrogen was analyzed for its purity by GC-TCD. Voltage measurements were carried out using a digital multimeter. Additionally, bacterial growth was analyzed by spectrophotometer. The highest fraction of hydrogen gas production was 60% without catalyst (uncoated) over only 0.08% with AC-Fe/SS. The highest value of optical density for bacterial growth was 0.611 for AC-Fe/SS, higher than 0.427 without catalyst. The highest current density was 99.11 mA/m\textsuperscript{2} for AC-Fe/SS and 59.52 mA/m\textsuperscript{2} without catalyst. The results suggested AC-Fe/SS coating allows for increased bacterial growth and voltage generation at the cost of an adverse effect on hydrogen gas production.

1. Introduction

MEC or Microbial Electrolysis Cell is a technology that can convert biomass waste into hydrogen with small electrical energy requirements. MEC has the potential to convert organic waste into an energy source in the form of hydrogen by applying external electric current. Microorganisms will attach to the surface of the anode and convert organic compounds into electrons, protons, and CO\textsubscript{2}. Then, electrons flow to the cathode to produce hydrogen. However, hydrogen production in MECs may be limited due to methanogenesis in which CO\textsubscript{2} and hydrogen protons react to form methane and water. The largest production of hydrogen was reported at 3.6 m\textsuperscript{3}-H\textsubscript{2}.m\textsuperscript{-3}.d\textsuperscript{-1} using platinum cathode with a voltage of 0.6 Volt [1], but methanogens were present in this study, leading to limited hydrogen production. Therefore, efforts are needed to increase hydrogen production considering the negative effects of methanogenesis in MECs.

Various types of catalysts such as MoS\textsubscript{2} and nickel catalysts were studied in MECs with the aim to replace expensive platinum catalysts. Coating cathodes with Ni/W catalysts yield a hydrogen production rate of 1.5 m\textsuperscript{3}H\textsubscript{2}.m\textsuperscript{-3}.d\textsuperscript{-1} [2]. Nickel catalysts and their alloys have the advantages of having low overpotential, inexpensive, and are relatively stable in electrolytes. However, nickel catalysts were naturally associated with low catalytic property, requiring further development to increase hydrogen production [3].
Activated carbon (AC) was also widely used as a catalyst in MFC cathodes. AC was known for its characteristic high surface area. The rate of hydrogen production using AC doped nitrogen at the MEC cathode was still very small at $0.0030 \pm 0.0004 \text{L-H}_2.\text{L}^{-1}\text{-reactor} \text{d}^{-1} [4]$.

According to Kyoung-Yeol Kim [5], AC-Ni coated SS mesh cathodes can be operated for 30 days without a decrease in performance over time. Ni catalysts could also be regenerated by immersing the cathode in a Ni salt solution. However, the rate of hydrogen production was still low at $1.1 \pm 0.1 \text{L-H}_2.\text{L}^{-1}\text{-reactor} \text{d}^{-1}$.

Besides nickel, Fe-electrodepositied alloy was a promising electrode for the hydrogen evolution reaction. Fe presented good catalytic activity and stability [6]. In this study, AC-Fe catalyst was coated on stainless steel (SS) mesh using a sequential adsorption and phase inversion method. Adsorption was used to combine Fe with activated carbon. Phase inversion was achieved using PVDF Poly(vinylidene Fluoride) for AC-Fe coating on SS mesh. Phase inversion method presents an interesting approach since it allows for preparation at room temperature and is able to bind the catalyst with a current collector [7]. The use of AC-Fe on SS mesh with this method was expected to increase hydrogen production at the cathode of MECs.

2. Materials and Methods

2.1 Electrode Preparation

Graphite plate and SS mesh 304 were cut to an average size of 2.7 cm x 3.7 cm to act as anode and cathode, respectively. Electrodes were prepared following the protocol of logan by sequential sonating, rough sanding, immersion in 1 N HCl overnight for anode, and rinsing with milli-Q water before use [8]. Ti and SS wires were sanded and rinsed with milli-Q water before use.

Activated carbon was impregnated with Fe(NO$_3$)$_3$.9H$_2$O using a 5%(w/v) Fe solution. Fe(NO$_3$)$_3$.9H$_2$O solution was mixed into 300 mg activated carbon. Fe was adsorbed onto the pore of activated carbon for 1 hour prior to drying at 110°C for 6 h. Poly(vinylidene fluoride) was dissolved in (5% w/v) N,N dimethylacetamide (DMAc) with stirring. Dried AC-Fe powder was introduced to the solution following a mass ratio for AC:PVDF at 5.8:1. The mixture of activated carbon and PVDF was coated on SS mesh 304 using a spatula. Impurities were removed by soaking cathodes in milli-Q water for 15 minutes [5]. Finally, SS mesh 304 were dried under a fume hood for 8 h.

2.2 Microbiology

Microbiological media used in this research were modified based on consisting of organics, inorganics, trace element solution which can be seen in Table 1.

Microbial consortium used in this research consisted of 4 species obtained from local environmental isolates Pseudomonas plecoglossicida (P1-503), Pseudomonas taiwanensis (P1-406), Pseudomonas monteilii (C1-405), Pseudomonas nitritireducens (C1-412) [11], and 1 commercial strain of Geobacillus stearothermophilus ATCC 7953.

2.3 Methods

Microbial electrolysis cell (MEC) is a bioelectrochemical system (BES) that applies voltage to cells to encourage bioelectrochemical reactions. In MECs, active bacteria use organic chemicals and produce CO$_2$, electrons, and protons. The bacteria will transfer electrons to the anode and release protons into the solution. The electrons flow in the outer circuit to the cathode and join free protons in the solution.

Anode: $\text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^-$

Cathode: $8\text{H}^+ + 8\text{e}^- \rightarrow 4\text{H}_2$

Overall: $\text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{H}^+ + 4\text{H}_2$

Ti wire was connected to the positive voltage source and the SS Wire was connected to the negative voltage source. The reactor was flushed with UHP-grade nitrogen gas to create anaerobic conditions in the reactor by removing dissolved oxygen from the solution. Headspace gases including the produced hydrogen were analyzed for its purity using a GC- TCD (Shimadzu, Japan). Voltage
measurement was carried out using a multimeter (APPA 109N, Taiwan) and bacterial growth was analyzed using a spectrophotometer UV-VIS (Bel Engineering, Italia). Catalyst was characterized using BET analyzer (Quantachrome QuadraWin ©2000-16, Quantachrome Instruments).

| Table 1. Composition of Microbiological Media |
| --- |
| **Solution** | **Composition** | **Concentration** | **Reference** |
| Organics | Yeast extract | 0.02 g/L | [9] |
| | CH₃COONa | 1.641 g/L | |
| Inorganics | NaNO₃ | 0.85 g/L | |
| | NaCl | 1.0 g/L | |
| | NH₄Cl | 1.345 g/L | |
| | CaCl₂·2H₂O | 0.0795 g/L | |
| | K₂HPO₄ | 2.7 g/L | [9] |
| | KH₂PO₄ | 1.3 g/L | |
| | MgCl₂·6H₂O | 0.235 g/L | |
| | EtOH | 40 µL | |
| Trace Element | FeCl₃·6H₂O | 1.35 g/L | |
| | MnCl₂·4H₂O | 0.1 g/L | |
| | CaCl₂·2H₂O | 0.1 g/L | |
| | ZnCl₂ | 0.1 g/L | [10] |
| | H₂BO₃ | 0.01 g/L | |
| | Na₂MoO₄·2H₂O | 0.024 g/L | |
| | NaCl | 1.0 g/L | |
| Reducing solution | Cysteine-HCl | 12.5 g/L | [10] |
| | Na₂S·9H₂O | 12.5 g/L | |
| Resazurin solution | | 0.004 g/L | [10] |
| MEM Vitamin solution | | 10 mL | Sigma Aldrich, USA |

3. Results and Discussion

The reactors were operated for 24 h as an MFC and then shifted to MEC operation mode until 258 h. Headspace gas, bacterial growth and current density measurements were carried out, aiming to determine the effect of AC-Fe coating on the cathode.

3.1 Headspace Gas Analysis

The results showed the reactor with AC-Fe catalyst on SS mesh cathode performed worse compared with uncoated SS cathode in terms of hydrogen production. Positive hydrogen gas production was observed in the uncoated reactor at 40 h of culture time (see Figure 1(a)). Hydrogen gas in the uncoated reactor continued to increase until the end of the culture period.

Gas headspace composition consisted of N₂O, CO₂, N₂ in air and H₂. N₂ in air made up the majority of headspace gas in the MEC reactor. The term N₂ in air originated from the technical limitation of the GC-TCD instrument used to detect N₂ and O₂ as separate components of air. Nonetheless, the use of oxygen indicator, resazurin, confirmed the anoxic operation of each MECs. Nitrogen gas originated from the MEC reactor flushing stage. N₂O gas at the cathode without catalyst was formed, amounting to 2.19% at 119 h of culture time. N₂O gas was formed due to denitrification process, in which inorganic Nitrogen compound (NaNO₃ in the medium) was converted to nitrogen in the gas phase. The denitrification process took place in stages from the reduction of nitrate to nitrite (NO₂⁻) to nitrogen monoxide (NO) and to nitrous oxide (N₂O). This denitrification process occurred almost entirely by denitrifying bacteria [12]. The bacteria used in this study are denitrifying bacteria obtained from a previous research [11]. In the reactor with AC-Fe / SS cathode, the headspace gas was dominated by air (Figure 1(b)). At 1.25 h of cultivation, CO₂ gas was formed and N₂O gas was formed at 41 h of culture period. CO₂ and N₂O gases were formed at earlier culture periods compared to the reactor without a catalyst (uncoated).
If the hydrogen gas was specifically considered for example in Figure 2, the fraction of hydrogen gas produced in the reactor with uncoated cathodes (a) may reach up to 60%. The highest hydrogen fraction of headspace gas was largely consistent with a previous study on biohydrogen production using this consortium [13]. Meanwhile, the maximum hydrogen gas fraction in the reactor with AC-Fe / SS catalyst can only reach 0.08%. It can also be said that no hydrogen was produced in this setup, if the value is compared to existing literature working on this same consortium. The lack of hydrogen produced for the MECs with coated cathodes bring a question towards the possible underlying hydrogen production inhibition mechanisms. AC-Fe catalyst coating was not suitable for biohydrogen production using stainless steel cathode. The presence of Fe$^{3+}$ caused the corrosion potential of SS 304 to shift positively. The potential for corrosion in SS 304 make it difficult for hydrogen evolution reaction to occur [14].

3.2 Electrical Analysis

Current density analysis was done by measuring the voltage produced, then processing it to obtain current produced per anodic surface area. Voltage had a relationship that was directly proportional to the current density. The higher the voltage produced, the higher the current density produced. The results showed the voltage generated from the MEC reactor using AC-Fe / SS was higher than the MEC reactor with uncoated cathodes. Current density on the AC-Fe coated cathodes could reach 99,11
mA/m² at 189.83 h of culture period (see Figure 3(b)). Whereas the current density for MECs with uncoated cathodes could only reach 59.52 mA/m² at 220 h of culture period (see Figure 3(a)).

![Figure 3](image)

**Figure 3.** Current density for (a) Stainless steel mesh cathode without catalyst (b) Stainless steel mesh cathode with AC-Fe catalyst

3.3 *Bacterial Growth Analysis*

Analysis of bacterial growth showed that bacteria grew better in the MEC reactor with AC-Fe than the MEC reactor without a catalyst. The highest bacterial growth was obtained when the culture time was 93 h, when the optical density value was 0.611 in the reactor with AC-Fe / SS catalyst and 0.427 in the reactor with uncoated cathodes. *Pseudomonas* showed increase in growth with increase FeCl₃ concentration [15]. In this study, it was shown that Fe derived from AC-Fe / SS catalyst may have contributed to the increased bacterial growth in MECs with coated cathodes compared to MECs with just SS serving as cathode (uncoated).

![Figure 4](image)

**Figure 4.** Medium turbidity (bacterial growth) over time

3.4 *Catalyst Characterization*

Catalyst characterization with a BET analyzer was needed to determine the surface area and pore size of the catalyst. The results of characterization could be seen in Table 2. The surface area showed a decrease when compared to pure activated carbon. When measuring the surface area of the catalyst with a BET analyzer, N₂ gas was ran gradually to the sample. As the relative pressure
increases, the adsorbed gas would form a multilayer. The amount of adsorbed gas was plotted against the relative pressure so that the surface area can be calculated. The lesser the amount of $\text{N}_2$ gas that was adsorbed indicates that the texture of the activated carbon, although it may be changed, was not necessarily due to the addition of metal [16]. Changes in the texture of activated carbon with the addition of metal could cause a decrease in porosity which will impact the surface area. In this study, besides the addition of Fe, PVDF solution was used as a binder between activated carbon and SS mesh. This solution caused a decrease in the porosity of the activated carbon so that the amount of $\text{N}_2$ gas that is adsorbed was small, resulting in a decrease in the surface area of AC-Fe / SS.

Small surface area can reduce hydrogen production. Meanwhile, SS mesh was designed with a large surface area to increase the formation of hydrogen gas [3]. The small surface area could result in low hydrogen production which was the case for the coated cathodes.

| Table 2. Catalyst Characterization with BET Analyzer |
|---|---|---|
| Surface Area | 714.966 m$^2$/g | 512.194 m$^2$/g | 377.661 m$^2$/g |
| Pore Size | 1.43545e+01 Å | 1.39221e+01 Å | 1.39109e+01 Å |

Performance evaluation at the AC-Fe preparation stage with the phase inversion method was also of particular concern. Activated carbon had low mechanical strength. This caused the activated carbon coating on SS to be relatively weak when it was introduced into the solution in the reactor. At the time of immersion of AC-Fe / SS in milli-Q water for 15 minutes, the cathode should be turned and pressed to provide mechanical assistance to the activated carbon so that it could stick more firmly to SS [7]. In addition, to make it easier to apply pressure on the AC-Fe / SS coating, SS should be perforated after the coating process was completed and SS wire could be installed afterwards.

4. Conclusions

Cathode modification using AC-Fe catalyst on SS cathode in the MEC reactor did not produce the desired hydrogen gas. MEC reactors without catalysts at the cathode (uncoated SS cathode) produced higher hydrogen gas compared to using AC-Fe/SS. The highest hydrogen gas production was 60% without catalyst and 0.08 % using AC-Fe/SS catalyst. On the other hand, MEC reactor using AC-Fe/SS displayed a higher bacterial growth and higher electrical generation. The highest optical density value was 0.611 using an AC-Fe/SS catalyst at a culture period of 93 h compared to 0.427 for uncoated cathodes at the given culture period. The highest current density was 99.11 mA/m$^2$ at 189.83 h using AC-Fe/SS catalyst and 59.52 mA/m$^2$ at 220 h without using a catalyst (uncoated). Small hydrogen gas production obtained in the former setup was due to the positive shifting of corrosion potential of the cathode as well as the small cathode surface area. Further research could do well with selecting the right coating on the cathode/anode to increase hydrogen production and studying the performance of the consortium on wastewater with other substrate compositions.

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