Cathodic hydrogen recovery and methane conversion using Pt coating 3D nickel foam instead of Pt-carbon cloth in microbial electrolysis cells

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Abstract
A cheap but efficient electrode material is required to explore and apply to microbial electrolysis cell (MEC) with high hydrogen evolution reaction (HER) efficiency and low overpotential loss. Pt coating carbon cloth (Pt/CC) was one of the most efficient catalyst for hydrogen production in current lab research, but it is difficult to be applied in practice because of expensive cost and week strength from the base material (carbon cloth). Thus a cheap and effective supporting base material is worth to evaluate on hydrogen recovery and loss to methane for the MEC future application. In this study, nickel foam (NF) was used as an alternative to expensive carbon cloth, and NF coated with Pt (Pt/NF) was applied and evaluated through catalytic performance, hydrogen production efficiency and economic assessment in comparison with Pt/CC. The Pt/NF showed a competitive HER performance to Pt/CC. The highest hydrogen yield was reached 0.71 ± 0.03 m3/m3$^3$ by Pt/NF under 0.8 V, which exceeded 6%, 10% over Pt/CC and NF, respectively. The energy efficiency relative to the electrical energy input was 127% for Pt/NF and 123%, 110% for Pt/CC and NF, respectively. For fifteen cycles, the methane content of Pt/NF got the lowest due to its higher hydrogen evolution activity. The economic analysis showed a 56% reduction when using Pt/NF as supporting base in place of carbon cloth to achieve similar performance. The linear sweep voltammetry (LSV) showed the possibility to further reduce input voltage in a long term operation.

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Introduction
Bioelectrochemical system (BES) is a novel emerging process that can realize the interconversion between chemical and electrical energy through the metabolic machinery of microorganisms [1,2]. For its excellent capacity of pollutants transformation and energy recovery, BES has become an innovative technology in the field of wastewater treatment and wastes
disposal for energy production, such as hydrogen, electricity or other biofuels [3]. Hydrogen can be generated through the electron transfer from a biotic anode to an abiotic/biotic cathode in microbial electrolysis cell (MEC) [4]. Compared with water electrolysis for hydrogen production, MEC requires lower energy input and can realize simultaneous removal of organic pollutants [5]. The cathode that determines the hydrogen evolution reaction (HER) becomes a decisive factor for hydrogen production rate [6].

In the past decade, many metal-catalyst electrode have been fabricated for MEC [4], like Pt, stainless steel (SS) [7], nickel alloys [8], tungsten carbide [9], MoS2 [10] and iron [11], because of their high electrical conductivity, biocompatibility, and HER potential [12–14]. Studies show that noble or alloy metal catalysts can efficiently reduce cathodic overpotential by lowering the activation energy compared with non-metals-based electrode [15]. Some metals like Pt, nickel, cobalt, Fe and palladium can realize HER as an individual catalyst. Pt covered on a carbon cloth (Pt/CC) is widely applied as cathode in MECs [4,16–19], due to its excellent catalytic capability and stability. However, Pt/CC cathode is costly and difficult to expand application because of low mechanical strength, which restricts the development of MEC [20]. Hence, the development of electrode materials is crucial for future MEC application. Moreover, it has been proved that hydrogen yield and loss are closely related to cathode property, such as materials [21], structures [22], and linked biofilm communities [23,24].

At present, the study of electrodes for MECs mainly focus on obtaining a good material with high HER performance and reducing the cost of materials for future application [26]. In practice, the HER of cathode is both determined by the catalytic material (coating catalyst) and cathodic surface area (supporting base). For example, the Pd–Au cathode supported by nickel foam (NF) achieved much higher cathodic current density than by SS in respect to the intrinsic catalytic activity [26]. Current density of 64 A/m² was achieved by a plat SS cathode with a specific surface area of 25 m²/m³, while 188 A/m³ was achieved by SS brush cathode with higher specific surface area (810 m²/m³). However, a much better hydrogen yield can be efficiently achieved by Pt/CC cathode compared with any of SS [27]. Meanwhile, carbon cloth is still much more expensive but lower strength than any SS. Recently, Ni-based alloys have shown a promising electrocatalytic activity in water electrolysis in alkaline condition [28]. Compared with SS, nickel-based material need lower reaction overpotential for HER [8], but 2D nickel mesh cathode has lower biocatalytic property than Pt catalyst. However, a better performance of two-dimensional (2D)-nickel mesh biocathode on COD removal and bioelectrochemical methane production was achieved compared with 2D-stainless steel or copper meshes [21]. Recently nickel-based material NF with three-dimensional (3D) network structure, has been developed as a base material for electrochemical capacitance [29,30] and achieved favorable results [31]. To be used as a base material to fabricate electrode in MECs, NF has a great property of supercapacitors [30,32] for its higher electrical conductivity and mechanical strength than carbon cloth.

In this study, NF was used as alternative to expensive carbon cloth. Pt coating NF was evaluated through catalytic performance, hydrogen production efficiency and economic assessment in comparison with Pt coating carbon cloth for a long time operation.

Material and methods

**MEC reactor structure and operation**

Single chamber MEC reactors with the effective volume of 28 mL and 10 mL gas tube headspace were built of carbon fiber brush anode (2.5 cm diameter × 2.5 cm length; 0.22 m² surface area) [4,33,34] The anodes were pretreated at high temperature (450 °C, 30 min) before inoculation. Nine reactors were set up as replicates and divided into three groups in the test. The cathodes of each group were constituted by three different kinds of materials Pt/CC, NF and Pt/NF, respectively. The gas was finally collected in a 50 mL gas bag (Calibrated Instrument Inc.).

The functional bacteria were inoculated by the mixture of activated sludge from local municipal wastewater treatment plant (Harbin, China) [35,36]. All the tests were conducted in a phosphate buffer solution (PBS, 50 mM, pH = 7) containing 1 g/L acetate as carbon source [4]. The external voltage maintained at 0.8 V [37]. The current was automatically monitored by a data recorder (Acquisition system; Keithley Instrument) through a 10 Ω resister.

**Cathode material preparation**

The 3D NF (Ni ≥ 99.9%) was 5 mm thickness and 3 cm diameter with 95% porosity and 0.9 m²/g specific surface area. The Pt/CC electrode was prepared by mixing 31.4 mg carbon powder (containing 20% Pt, Geshi New Energy. Co. Ltd) and 26 µL dilute water, 105 µL isopropanol and 210 µL Nafion solution [38]. The mixture evenly smeared on carbon cloth with a soft brush and dried in room temperature for 24 h. The Pt/NF electrode was made as the same method as Pt/CC electrode. Finally, the Pt/CC and Pt/NF were the same Pt content of 0.5 mg/cm² Pt.

**Analysis items and methods**

The components and volume of gas were measured by a gas chromatography (Fuli, GC9790; Zhengjiang Instrument Inc., China) and a glass syringe, respectively. The energy and coulombic efficiency were analyzed and calculated to evaluate the performance of MEC reactors [4]. Columbic efficiency (CE) was defined by the percentage of effective electrons available to form hydrogen which could be calculated by the equation η = Q/QET × 100%, Q was the electronic equivalent of generated hydrogen and QET = 244.7, calculated by consuming the 1 g/L acetate was total electrons generated by substrates oxidation respectively. Energy efficiency (ηE) was the ratio of input energy and output energy which was defined as ηE = (nH2 × QH2)/(Q × 0.8), and nH2 was the moles of hydrogen in the standard condition; QH2 was the calorific value of hydrogen. Performance of the cathodes was evaluated by linear sweep voltammetry (LSV) using an electrochemical workstation (model CHD660, China Instruments, Chenhua. Co. Ltd, China). A pure Pt foil (2 × 5 mm) served as counter-electrode; an Ag/AgCl reference electrode served as reference electrode and the
test cathodes were used as working electrodes. Each LSV scans from −0.2 to −1.2 V was repeated three times, at a scan rate of 5 mV s⁻¹. All the experimental tests were carried out at room temperature. If there was no special explanation, all the potential was relative to the saturated calomel electrode.

Results and discussion

Performance of catalytic activity for hydrogen evolution

Three electrodes were fabricated and their HER performances were tested before application to an MEC. The scheme of the MEC configuration was shown in Fig. 1. EIS analysis showed that all electrodes had good electrical conductivity with low internal resistance. The Pt/NF got the lowest ohm inner resistance (0.2 ± 0.1 Ω), and the inner resistances of Pt/CC was 2.5 ± 0.4 Ω owing to good conductivity of NF in comparison with carbon cloth.

The HER performance of different materials was tested by LSV with the voltage range from −0.2 to −1.2 V. All the tests were repeated three times and the final test result was shown in Fig. 2. The initial voltage for hydrogen production and the slope of the voltammogram were two factors to evaluate the performance of catalysts when current was produced [39]. The initial voltage was the detected potential of hydrogen production, which was different to theoretical hydrogen evolution potential or the overpotential [7,8,40]. The cathode potential should be up to or lower than the initial reaction voltage for continuous hydrogen overflow. The slope of the voltammogram indicated the hydrogen evolution rate. In the same condition, the cathode with low overpotential and higher hydrogen evolution rate was more easily and fast to get hydrogen [39,41]. The LSV showed that the Pt/NF cathode required a potential of ~0.6 V for hydrogen generation that was the lowest potential for hydrogen production, while the Pt/CC and NF were slightly be low ~0.6 V, indicating a better catalytic performance of NF coating Pt for HER. Hence, the Pt/NF cathode theoretically required a reduced external voltage for hydrogen production due to its lowest overpotential. The NF required the highest initial voltage (~0.7 V) for hydrogen production, indicating the highest overpotential of NF itself for HER. A Pt coating modification increased electrochemical property of NF based cathode. The slope of Pt/NF was 17.15 A cm⁻² V⁻¹ (R² = 0.99) which was 8% higher than Pt/CC.

Actually, a steeper slope can bring better catalytic performance with a higher current density given by a fixed applied voltage.

Although NF itself has the catalytic activity, it is weaker than Pt [15]. Both the steeper slope and lower overpotential showed that coating fabrication to NF was beneficial to improve electrochemical properties. Pt/CC and Pt/NF had a good Tafel slope, indicating an improved activity of hydrogen evolution by Pt catalyst. However, the differences of catalytic performance were determined by the structure of base material in the current study. Porous morphology of NF offered better catalytic condition than planar morphology of CC for Pt catalysis which offered more possibility for cathode reaction in solution.

In theory, Pt/NF will produce high current density than Pt/CC or NF itself at the same external voltage. Or higher current density can be reached by Pt/NF cathode but required a lower voltage compared with Pt/CC or NF itself. For example, platinum need lower applied voltage (0.4 V) than NiW (0.6 V) to achieve the same current density due to the higher catalytic activity [20]. In the comprehensive evaluation, the catalytic performance of Pt/NF was competitive to Pt/CC. Under 0.8 V external voltage applied in this study, the cathode potential should achieve around ~1.15 – ~1.20 V with a well-run anode potential of ~350 mV ~ ~400 mV (vs Ag/AgCl). From LSV scan results, the order of current density, directly related to catalytic performance for HER, was Pt/NF > Pt/CC > NF.

Hydrogen production rate and efficiency using Pt/NF cathode

The current was maintained at a stable value after several cycles, shown in Fig. 3. The highest peak current was got by Pt/CC, which reached 5.5 mA. The peak current of Pt/NF and NF achieved 5.0 mA and 3.5 mA, respectively. The larger area surrounded by current curve indicated more electrons could be transferred to cathode for hydrogen generation. As shown in Fig. 3, the peak current of Pt/NF was quite close to Pt/CC, but the duration was longer than Pt/CC, resulting in a higher coulombic transport by integration of current and time. It showed that Pt/NF cathode could offer stable electron transfer to ensure the hydrogen production compared with Pt/CC.

Fig. 1 – Scheme of the MEC configuration using three kinds of material.

Fig. 2 – LSV for all investigated materials in PBS (pH = 7).
The highest hydrogen production rate was achieved by Pt/NF cathode of $0.71 \pm 0.03 \text{ m}^3/\text{m}^3 \cdot \text{d}$, which exceeded Pt/CC of $0.67 \pm 0.02 \text{ m}^3/\text{m}^3 \cdot \text{d}$ (Fig. 4). At the same organic loading, organic removal was taken over 20 h by NF due to the lowest current value, while the degradation time by Pt/CC and Pt/NF was reduced to 12 h and 16 h, respectively. It indicated that a coating layer on NF could substantially increase cathode reaction. The coulomb efficiency of three kinds of reactors were between 90%–100%. While the coulomb efficiency of Pt/CC was the lowest (86%) compared to Pt/NF (95%) and NF (99%), which indicated the lowest electronic utilization rate of Pt/CC. It turned out that the Pt/NF got the considerable current value and utilization rate of electron. Furthermore, the recovery efficiency of Pt/NF was the highest (126%). Thus, the Pt/NF cathode got the alternative performance for hydrogen production in comprehensive assessment, taking advantage of its high HER performance.

Compared with other studies (Table 1), Pt/NF cathode achieved higher hydrogen yield than Pt/CC or NF. It indicated that the hydrogen rate and yield were both determined by the coating metal activity and the base material property. The Pt/NF got similar hydrogen yield with Ni mesh but required lower voltage than SS 304 [7]. More active sites for hydrogen evolution were formed on NF based cathode than SS. Hence, the Pt/NF cathode could be further amplified to get better performance.

### Duration test and hydrogen loss to methane production over several cycles operation

The gas proportion variation was tested to evaluate the stability of hydrogen production performance after several cycles operation (>15 cycles) shown in Fig. 5. In single chamber MEC system, the Pt/NF cathode produced the lowest methane production rate, and the methane content in produced gas increased from 0.1% to 0.3%; while NF cathode produced a much higher methane production, up to around 1.0%. The Pt/CC cathode reached the highest methane content of 1.4% after several cycles. The results indicated that Pt coating increased

### Table 1 – The performance of cathode materials in MECs.

<table>
<thead>
<tr>
<th>Cathodes</th>
<th>Applied voltage(V)</th>
<th>Hydrogen production rate ($\text{m}^3/\text{m}^3 \cdot \text{d}$)</th>
<th>Substrates/Reactor working volume</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS 304</td>
<td>0.9</td>
<td>0.59 ± 0.01</td>
<td>1 g/L acetate/28 mL</td>
<td>[8]</td>
</tr>
<tr>
<td>SS brush</td>
<td>0.6</td>
<td>1.7 ± 0.1</td>
<td>1 g/L acetate/28 mL</td>
<td>[27]</td>
</tr>
<tr>
<td>Ni mesh 625</td>
<td>0.9</td>
<td>0.79 ± 0.27</td>
<td>1 g/L acetate/28 mL</td>
<td>[6]</td>
</tr>
<tr>
<td>NiMo/CC</td>
<td>0.6</td>
<td>2.1</td>
<td>5 g/L sodium acetate trihydrate/</td>
<td>[42]</td>
</tr>
<tr>
<td>NF</td>
<td>1.1</td>
<td>4.18 ± 1</td>
<td>1 g/L acetate/100 mL</td>
<td>[43]</td>
</tr>
<tr>
<td>Pt/CC</td>
<td>0.8</td>
<td>0.67 ± 0.02</td>
<td>1 g/L acetate/28 mL</td>
<td></td>
</tr>
<tr>
<td>Pt/NF</td>
<td>0.8</td>
<td>0.71 ± 0.03</td>
<td>1 g/L acetate/28 mL</td>
<td></td>
</tr>
<tr>
<td>NF</td>
<td>0.8</td>
<td>0.64 ± 0.05</td>
<td>1 g/L acetate/28 mL</td>
<td></td>
</tr>
</tbody>
</table>
hydrogen production rate and retarded methanogenesis over a period of batch operation. Pt/NF cathode had a slow methane increasing rate, leading to a stable and efficient hydrogen yield over time.

Compared to other studies shown in Table 2, under similar operation time, the Pt/NF got the lowest methane content than other materials. The hydrogen purity can be decreased due to methane production [42,43]. Without considering price and cost, Pt coating, whether on CC or metals in Table 2, showed an improved hydrogen purity compared to CC or metal cathodes, hinting a retarded hydrogen conversion in the biofilm of Pt coating NF when using acetate as substrate. Both the material itself and methanogens growth can cause the methane formation in an MEC [43]. Hydrogen or methane evolution from cathode is determined by the bond energy of H atom of metal. Higher bond energy can lead to the methane formation instead of hydrogen [44]. The Pt/NF got the best HER performance compared to other materials due to the lowest bond energy, thus got the lowest methane content. Furthermore, the slow methane formation rate after several cycles indicated a slow growth of methanogens using with Pt/NF cathode. Thus, a slow growth of hydrogenotrophic methanogenesis on the Pt/NF cathode but high hydrogen production rate can make a limited part of hydrogen loss in the BES when hydrogen release rate competes hydrogenotrophic methanogenesis [43]. As a result, Pt/NF maintained a good hydrogen purity (94%) in biogas with the lowest methane content over 1.5 month. It proved that coating treatment with a high current and hydrogen production rate would prevent hydrogen utilization in the small single chamber MEC reactor.

Cost evaluation of NF-based cathode for hydrogen production

The economy and stability was tested to evaluate the feasibility for further application. As shown in Table 3, all the prices were calculated by the purchase price in this study. In order to achieve a competitive hydrogen production rate, the Pt coating is the same cost. The most expensive part is from the carbon cloth, which is 2842 $/m², much higher than 75 $/m² of NF. The price of Pt/CC was the highest compared with other materials, which was 2.27 times than Pt/NF. The economic analysis showed a 56% reduction using Pt/NF in place of Pt/carbon cloth. The NF could replace the expensive carbon cloth to reduce cost, and at the same time gain better performance which had discussed above. Furthermore, NF was a kind of plastic material with enough mechanical strength for future application which enlarging potential advantages.

Conclusion

The NF successfully replaced the expensive carbon cloth as base material and achieved a high efficiency Pt/NF cathode with good hydrogen performance in microbial electrolysis cells. The LSV test indicated the order of catalytic performance for HER was Pt/NF > Pt/CC > NF. The Pt/NF cathode got a competitive hydrogen yield of 0.71 ± 0.03 m³/m³·d to Pt/CC of 0.67 ± 0.02 m³/m³·d. The energy efficiency was 127% for Pt/NF under 0.8 V but the cost was only 44% of Pt/CC. Porous morphology as NF offered better catalytic condition for hydrogen production rate than planar morphology like CC for Pt catalysis. On the other side, the slow methane forming rate of Pt/NF cathode maintained a stable hydrogen yield and purity for a long time operation. The final choice of the catalyst was a compromise between costs, efficiencies and feasibility.

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