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2 **Enhanced hydrogen production in microbial electrolysis cell with 3D**
3 **self-assembly nickel foam-graphene cathode**

4 **Weiwei Cai^a, Wenzong Liu^{b*}, Jinglong Han^b and Aijie Wang^{a, b*}**

5 a State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of
6 Technology (SKLUWRE, HIT), Harbin 150090, P.R.China

7 b Key Laboratory of Environmental Biotechnology, Research Center for Eco-Environmental
8 Sciences, Chinese Academy of Sciences, Beijing, 100085, China

9 *Corresponding author. E-mail address: waj0578@hit.edu.cn, wzliu@rcees.ac.cn

10 ***Corresponding authors:**

11 **Dr. Aijie Wang**

12 1 State Key Laboratory of Urban Water Resource and Environment
13 Harbin Institute of Technology

14 Harbin, 150090, China

15 2 Key Laboratory of Environmental Biotechnology
16 Research Center for Eco-Environmental Sciences
17 Chinese Academy of Sciences

18 Beijing, 100085, China

19 E-mail: waj0578@hit.edu.cn

20 **Dr. Wenzong Liu**

21 Key Laboratory of Environmental Biotechnology

22 Research Center for Eco-Environmental Sciences

23 Chinese Academy of Sciences

24 Beijing, 100085, China

25 E-mail: wzliu@rcees.ac.cn

26

Abstract

In comparison to precious metal catalyst especially Platinum (Pt), nickel foam (NF) owned cheap cost and unique three-dimensional (3D) structure, however, it was scarcely applied as cathode material in microbial electrolysis cell (MEC) as the intrinsic laggard electrochemical activity for hydrogen recovery. In this study, a self-assembly 3D nickel foam-graphene (NF-G) cathode was fabricated by facile hydrothermal approach for hydrogen evolution in MECs. Electrochemical analysis (linear scan voltammetry and electrochemical impedance spectroscopy) revealed the improved electrochemical activity and effective mass diffusion after coating with graphene. NF-G as cathode in MEC showed a significant enhancement in hydrogen production rate compared with nickel foam at a variety of biases. Noticeably, NF-G showed a comparable averaged hydrogen production rate ($1.31 \pm 0.07 \text{ mL H}_2 \text{ mL}^{-1} \text{ reactor d}^{-1}$) to Platinum/carbon (Pt/C) ($1.32 \pm 0.07 \text{ mL H}_2 \text{ mL}^{-1} \text{ reactor d}^{-1}$) at 0.8 V. Profitable energy recovery could be achieved by NF-G cathode at higher applied voltage, which performed the best hydrogen yield of $3.27 \pm 0.16 \text{ mol H}_2 \text{ mol}^{-1} \text{ acetate}$ at 0.8 V and highest energy efficiency of $185.92\% \pm 6.48\%$ at 0.6 V.

Keywords: Nickel foam, Graphene, Cathode, Hydrogen recovery

1. Introduction

Recently, microbial electrolysis cell (MEC) has been developed to use widely organics in wastewater to produce hydrogen by employing electrode respiring bacteria (Liu et al. 2005; Liu et al. 2010). Cathode material played an important role on efficient hydrogen recovery for application in terms of its cost, electrochemical property, specific surface area (Brown et al. 2014; Logan 2010). Almost half of the cost were associated with cathode in laboratory scale, while the number should be decrease to 10% before large scale application (Rozendal et al. 2008). Although commercially available carbon materials (e.g. carbon cloth (Hu et al. 2008; Hu et al. 2009), or carbon paper (Logan et al. 2008)) could be employed as electrode material in bioelectrochemical system, however, the noble metal catalysts are necessary to be coated to the cathode surface to reduce energy barrier of proton reduction. So far, Platinum (Pt) base materials have been the most effective cathode catalysts for MEC, which also accounted for most capital cost (Call and Logan 2008). Many non-precious metals such as steel mesh, nickel (Ni) and Ni alloy (Call et al. 2009; Hu et al. 2009; Selembo et al. 2009; Zhang et al. 2010b) and carbon base materials were developed as cost-effective alternative cathode in MEC (Hou et al. 2014b; Wang et al. 2012b), but low catalytic property of these cathodes have to be modified to achieve higher hydrogen production rate (Hou et al. 2014b).

Recently, nickel foam (NF) attracted more attentions in the field that using it as cathode in MEC for hydrogen production due to its unique three-dimensional (3D) scaffold structure and low cost (Chen et al. 2010; Chen et al. 2011). However, the

intrinsic lower electrochemical activity limits the overall reactor performance. Attractively, it has been extensively considered using the nickel foam as the template to fabricate 3D foam-like graphene macrostructures with entire sp^2 -hybridized carbon atoms for energy conversion and storage (Chen et al. 2012; Xiao et al. 2012; Yan et al. 2015). Importantly, this combination between NF and two-dimensional (2D) graphene could effectively improve electrochemical activity because of the presence of the highly electrically conductive graphene as “skeleton” (Chen et al. 2011; Meng et al. 2013; Wang et al. 2012a). NF-Graphene (NF-G) not only provides a uniform macro-porous scaffold for effective mass diffusion of the culture medium, but also large specific surface area due to the presence of wrinkle in the surface of graphene (Wang and Shi 2015). Thus, modified NF-G cathode has been suggested as a promising potential catalyst for bioelectrochemistry application as its improved surface area and electrochemical properties that could reduce overpotential and boost electron transfer for hydrogen evolution reaction (HER) (Filip and Tkac 2014; Kumar et al. 2012; Su et al. 2015).

Considering these advantages of NF-G mentioned in the context, herein, we economically fabricated this composite as cathode material to enhance hydrogen production in MEC at various external voltages. Benefiting from the higher surface area and improved electrochemical activity of this hybrid, enhanced hydrogen production rate in MEC has been achieved using NF-G.

2. Method and materials

2.1 Preparation and assembly of 3D nickel foam-graphene cathode

We prepared graphene oxide (GO) with graphite powder using Hummers' method (Hummers Jr and Offeman 1958). Before mixing with nickel foam, the stacked GO solution was ultrasonic treated for 1 hour. In order to deposit graphene on the surface of NF, NF was transferred into a sealed cylindrical reactor tank and immersed into aqueous GO suspension (1 g/L). The reactor tank was heated for 4 h at 120 °C. Then the tank was allowed to expose to the air to cool down at room temperature (35 °C). The color of nickel foam turned into black from the original silver after reaction. After cooling, the composite was exposed to the air for drying.

2.2 Characterization

The specific surface area was determined by Brunauer–Emmett–Teller (BET) (ASAP 2020 HD88, Micromeritics Instrument, US). The Scanning Electron Microscope (SEM) image and Energy Dispersive X-Ray Spectroscopy (EDX) was collected by a field-emission SEM (FE-SEM) (SU8020, Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) analysis was carried out on the photoelectron spectrograph (ESCALab220i-XL, VG Scientific, US), using aluminum (Al) source gun type with a passive energy 50 eV. The pressure of the analyzer chamber was maintained at lower than that of 5×10^{-8} Pa during the process, meanwhile, the C 1s photoelectron peak at 284.6 eV was used to calibrate the binding energy. The Raman spectroscopy was conducted on the samples using a confocal Raman microscope (inVia-Reflex, Renishaw, UK).

2.3 Electrochemical measurements

The electrochemical property of NF and NF-G was characterized using a

electrochemical station (CHI 660e, TX, US). The electrolyte used for Linear Scan Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) was 50 mM phosphate buffer solution (PBS) excluded oxygen. LSV was determined under whole cell conditions with Pt wire as reference electrode, ranging from 0 V to -1.0 V. The scan rate was 100 mV/S. EIS was carried out to analyze the effective of mass diffusion of individual cathode electrode (He and Mansfeld 2009). A sine sigmoidal wave ranged from 100000 kHz to 10 mHz was employed to apply on the cell at the open-circuit potential. ZSimp software was employed to analyze the data and simulated the EIS spectra.

2.4 MEC construction and operation

Nine single chamber microbial electrolysis cells (MECs) were constructed according to previous description, with effective volume of 28 mL (Liu et al. 2012), to evaluate the performance of different assembled cathodes (3 cm diameter, plate). Graphite brushes (3 cm diameter x 4 cm, 0.22 m² surface area), after pretreating in acetone for 24 h and heated at 450 °C for 1 h in a muffle oven (Wang et al. 2009b), were used as anodes in all reactors. The NF, NF-G and Platinum/carbon (Pt/C) (0.5 mg Pt/cm²) were used as cathode electrode in three replicate reactors, respectively. All reactors were inoculated by activated sludge taken from Gaobeidian municipal wastewater treatment plant in Beijing. The inoculum sludge was mixed with 50 mM PBS with acetate (up to 1500 mg/L) as carbon source. All reactors were applied 0.8 V external bias for startup, and operated for at least 10 cycles to maintain stable hydrogen production at room temperature (30±2 °C).

2.5 Analysis and calculation methods

Gas production (hydrogen, methane) was detected by gas chromatography (GC) (4000A, EWAI, China). Current was automatically monitored with a data logger (2700 Keithley, US). The gas was collected in the multi-layer foil sampling Bag (200 mL, Dalian Delin, China). All calculation methods in this study were referenced from previous description (Liu et al. 2015). Coulombic efficiency (CE) is calculated as the ratio of coulombs recovery ($Q=\int i \cdot \Delta t$) to the total coulombs of acetate. Electron recovery efficiency (ERE) was the ratio of coulombs in hydrogen to the coulombs in current. We calculated the energy efficiency (η) based on the equation that $\eta=W_{H_2}/W_E=(n \cdot \Delta H)/(E_{app} \cdot \int i \cdot \Delta t)$.

3. Result and discussion

3.1 Porous structure and XPS analysis

SEM images illustrated the micrographs of microcellular NF and NF-G, showing a foldable structure with the mean diameter of macropore being around at 200 μm (Fig. 1). Graphene successfully wrinkled on the surface of NF, which extended the specific surface area of NF (Fig. S1). The main elements in this hybrid material were C, Ni, O and the C content increased significantly comparing with original NF by EDX analysis. The content of C, Ni, O were 43.56%, 8.15%, 48.13% respectively. This result further confirmed that graphene had been coated on the surface of NF. Figure 1 (a) Schematic process of the composite fabrication; (b) High magnification SEM image of NF; (c) High magnification SEM image of NF-G; (d) EDX of NF-G. Importantly, the intensity of the signals related with C-O and C=O dropped significantly after the thermal treatment, revealing surface oxygen had been reduced

and the electrical conductivity should be improved (Fig. S2). The $I(D)/I(G)$ value (Fig. S3) of GO was 1.28, while a clear decrease of NF-G (decrease to 0.97) further suggested low degree of exfoliation/disorder in graphene (Dreyer et al. 2010). Higher quality graphene is also desirable for better electrical conductivity (Jung et al. 2008; Wu et al. 2009).

The electrode surface area was closely related to the loading of graphene. According to the result of BET, there was a significant improvement on surface area from 1.0137 m^2/g of NF to 3.1068 m^2/g after coating with graphene. The wrinkle of graphene observed with FE-SEM could contribute to this increase, and lower average pore diameter was achieved in the composite accordingly. The higher specific surface area would increase accessible reaction regions for electrochemical reaction in MECs, which could boost the HER (Call et al. 2009).

3.2 Electrochemical analysis of new cathode resistance

LSV showed a lower onset potential of NF-G than NF (Fig. 2a). A clear increase in current density occurred around at -650 mV using NF-G composite as working electrode (all electrochemical potentials herein were reported *v.s* Ag/AgCl reference electrode, saturated KCl). In contrast, the corresponding onset potential for NF was -850 mV. The HER onset potential positively shifted about 200 mV for NF-G comparing to NF alone, indicating the electrocatalytic property had been improved through coating graphene on the surface of nickel foam. Additionally, current density at -800 mV of NF-G was 1.10 mA cm^{-2} that was significant higher than the value of NF alone (0.35 mA cm^{-2}). It was obvious that graphene was of significance to enhance

the electrochemical activity for HER.

Figure 2 (a) LSV of NF and NF-G; (b) EIS of NF and NF-G

It was obvious that NF-G exhibited lower ohmic resistance in EIS (Fig. 2b), which could be caused by the graphene coating. The ionic migrating through electrolyte film on the electrode/electrolyte interface and inner active sites was induced by the diameter of first semicircle (Wang et al. 2015a). The charge transfer was induced by the second semicircle, which was affected by the kinetic of electrode reaction. Resistance simulated by the equivalent circuit (Fig. S4) were significantly lower in NF-G. A small total resistance was obtained with NF-G could be ascribed to the higher specific surface area brought from the introduction of graphene on the surface of NF (Fan et al. 2008; Oh and Logan 2006). The reduced charge transfer resistance implied fast HER kinetics with NF-G hybrid (Hou et al. 2014a; Hou et al. 2014b).

3.3 Hydrogen production with 3D nickel foam-graphene cathode

Current differed distinctly with different cathodes when applied 0.8 V to all reactors (Fig. S5a and S6). Highest current value of Pt/C was 5.44 mA, while 4.28 mA and 3.80 mA were obtained with NF-G and NF respectively. It was noticeable that the current dropped sharply after 12 h in Pt/C cathode reactor when acetate was almost consumed. But a little prolonged reaction time was presented by NF-G and NF, which would not depress final conversion to products. NF-G showed a comparable average hydrogen production rate ($1.31 \pm 0.07 \text{ mL H}_2 \text{ mL}^{-1} \text{ reactor d}^{-1}$) to Pt/C ($1.32 \text{ mL} \pm 0.07 \text{ H}_2 \text{ mL}^{-1} \text{ reactor d}^{-1}$), while the lowest rate was obtained by NF ($1.21 \pm 0.01 \text{ mL H}_2 \text{ mL}^{-1} \text{ reactor d}^{-1}$) (Fig. 3a). The highest hydrogen production rate of Pt/C was 2.0 ± 0.19

mL H₂ mL⁻¹ reactor d⁻¹ in the initial 8 hours (Fig. 3b). While NF-G exhibited the highest of 2.2±0.31 mL H₂ mL⁻¹ reactor d⁻¹ in the next 8 hours.

Figure 3 (a) Hydrogen production rate of different cathodes; (b) Hydrogen production rate at 0.8V in individual time section

The hydrogen production rate decreased when lower voltages were applied on NF-G and NF cathode (Fig. 3a). Under 0.6 V condition, only 0.48±0.13 mL H₂ mL⁻¹ reactor d⁻¹ was obtained using NF as cathode. A higher rate of 0.69±0.04 mL H₂ mL⁻¹ reactor d⁻¹ was achieved with NF-G, which was close to hydrogen production on Pt/C (0.89±0.08 mL H₂ mL⁻¹ reactor d⁻¹). The hydrogen production rate of all cathode materials decreased subsequently at 0.4 V. The hydrogen production rate of Pt/C cathode dropped to 0.05±0.01 mL H₂ mL⁻¹ reactor d⁻¹, but that of NF-G was further lower to 0.02±0.01 mL H₂ mL⁻¹ reactor d⁻¹. NF exhibited the lowest hydrogen production rate. The results showed that NF-G performed improved electrochemical activities than NF at low external voltages. As a result, methane production rate of NF-G was also higher than that of NF (Fig. 3a), suggesting hydrogenotrophic microorganisms could utilize more recovery hydrogen on biocathode than original NF (Siegert et al. 2015). The increase of methane at lower external voltage condition was accordant with our previous study close to the relationship between methane production and external voltage variation (Wang et al. 2009a).

In sum, hydrogen production rate was enhanced after coating graphene on the surface of NF at variety of external voltages. The high ERE indicated that cathode modification primarily influenced the enhancement of hydrogen production rate. With

the decreasing of external voltage, hydrogen production rate obviously declined in all reactors, while a significant improvement of hydrogen production rate and ERE was obtained in the presence of graphene (Table S1), suggesting graphene could facilitate the hydrogen production at cathode. On one hand, the increased specific surface area caused by graphene could facilitate the mass transport, which was supported by the lower resistance from EIS analysis. **On the other hand**, the improved onset potential testified by the LSV test could lead to lower overpotential for HER, it was intensively favorable for electrons transferred from electrode into hydrogen on graphene coating NF (Li et al. 2011; Zhang et al. 2010a).

Most reports have been focused on using graphene to decorate the electrode to boost oxygen reduction reaction (ORR), and it has been mainly concerning on producing more power density in MFC (Awan et al. 2014; Feng et al. 2011; Qu et al. 2010), but few was tested on bioproduct generation on cathode. An improvement of hydrogen recovery from $0.06 \text{ mL H}_2 \text{ mL}^{-1} \text{ reactor d}^{-1}$ to $0.19 \text{ mL H}_2 \text{ mL}^{-1} \text{ reactor d}^{-1}$ was reported when coating graphene on MoS_2 nanosheets as MEC cathode (Hou et al. 2014b), which was much lower than our study because the two-chamber reactor configuration limited its performance. A low hydrogen production rate was $0.55 \text{ mL H}_2 \text{ mL}^{-1} \text{ reactor d}^{-1}$ when coating graphene on NF for Co(II) reduction simultaneously after 15th cycle in MEC (Wang et al. 2015b). In our study, the maximum hydrogen production rate of NF-G could reach to $1.31 \pm 0.07 \text{ mL H}_2 \text{ mL}^{-1} \text{ reactor d}^{-1}$ that was significantly higher than that of NF, and it was comparable to the result of Pt at higher applied voltage. Apparently, the hybrid suggested the great potential of decorating

non-precious metals with graphene to replace the Pt catalyst in MEC.

With respect to the price of NF was only 13.76% (68.8 €/m^2 according to Alibaba Co. Limited) of the Pt/C cathode (500 €/m^2) (Rozendal et al. 2008), as well as the thermal approach to fabricate graphene, which could cost approximately two orders of magnitude lower than a Pt catalyst (Feng et al. 2011). Hence, the hybrid showed the potential to move cathode design for large-scale reactor without the use of expensive precious metals.

More work involving the fabrication, and chemical active sites should be further investigated in future. For example, mass loading of graphene on the NF and electrochemical activity should be controlled during the fabrication period in our coming study (Wang et al. 2013). The synergic between graphene and NF need more elucidations, which might further improve the electrochemical activity of NF-G.

4. Conclusion

A 3D composites of NF coated with graphene was fabricated and used as cathode for hydrogen production in MECs. The electrochemical activity of the composite cathode was successfully improved after coating graphene on various external bias. The NF-G cathode performed a similar hydrogen production rate to Pt/C at **0.8V**, indicating graphene coating was feasible to make up the weakness of non-precious metal in electrochemical activity. However, graphene coating surface did not substantially inhibit the interaction between electrode and microorganisms, such as methanogens to consume hydrogen, especially on low external bias. Therefore, graphene coating NF would be a substitute to precious metal catalyst for biocathode at a suitable external

266 bias in future applications.

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Figure 1 (a) Schematic process of the composite fabrication; (b) High magnification SEM image of NF;
(c) High magnification SEM image of NF-G; (d) EDX of NF-G

Figure 2 (a) LSV of NF and NF-G; (b) EIS of NF and NF-G

Figure 3 (a) Hydrogen production rate of different cathodes;
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Graphic abstract