

Hydrogen Production Using Electrodeposited Ni and Ni/Co on Carbon Paper as Cathode Catalyst in Microbial Electrolysis Cells

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Received: 29 June 2018 / Accepted: 9 September 2018 / Published: 1 October 2018

Microbial electrolysis cells (MECs) utilize microorganisms to decompose organic matter in wastewater and produce hydrogen at the cathode. Thus, a low-cost and highly active cathode material is of great important in such system. In this study, electrodeposited Ni, Co, and Ni/Co on carbon paper (CP) were prepared as cathode to replace platinum. At an applied voltage of 0.7 V, the Ni MEC cathode produced most gas of 11.40 mL at current density of 15.31 A m^{-2} , which was 73.24% higher than that of bare CP electrode (3.05 mL). Linear sweep voltammetry and Cyclic voltammetry measurements showed that the hydrogen evolution performance of the Ni cathode was significantly better than Co and Ni/Co cathodes. The tafel plots proved that the hydrogen evolution overpotential of Ni cathode ($59.89 \text{ mV decade}^{-1}$) was lower than that of bare CP electrode ($99.22 \text{ mV decade}^{-1}$). Owing to the improved current density, hydrogen recovery rate and low hydrogen evolution overpotential, the developed electrodeposited Ni on CP materials possessed much higher catalytic activity than bare CP. Thus, electrodeposited Ni on CP are promising electrocatalysts for hydrogen evolution reaction and low-cost cathode materials in MECs.

Keywords: Microbial electrolysis cells; electrodeposited Ni/Co; carbon paper; hydrogen evolution reaction.

1. INTRODUCTION

With economic development, environmental pollution is getting increasingly serious. Microbial electrolysis cells (MECs) [1-3] utilize microorganisms to decompose organic matter in wastewater and produce hydrogen at the cathode. MECs not only contribute to limiting environment pollution to a certain extent, but also provide a new direction for solving the energy problem. Hydrogen based energy is a high-calorie fuel and a zero-pollution resource. In MECs, the electrons and protons

generated by the decomposition of the organic substance by the anode microorganisms reach the cathode through the external circuit and the solution, respectively. Then, the electrons and the protons are combined with the cathode at the auxiliary voltage to generate hydrogen gas [4,5].

To improve the hydrogen evolution reaction (HER), one of the hot topics in MECs is the selection and optimization of cathode. The cathode is the most important part in MEC where H_2 is produced, and the price of the cathode accounts for approximately half of the total cost [6]. Platinum is the best cathode material because of its high surface area and low overpotential for HER [7,8]. However, it is expensive and prone to poisoning and thus cheap alternatives have been given particular attention. For example, SSM (stainless steel mesh) has a large active surface area of up to $78 \text{ m}^2 \text{ m}^{-3}$ [9,10]. Meanwhile, Ni mesh cathode is superior to Pt in producing rate and volumetric current density [11]. Ni foam cathode has high specific surface area ($128 \text{ m}^2 \text{ m}^{-2}$ projected area) that can achieve a high H_2 production rate [12,13]. MoS_2 has a large output current density ($8 - 10 \text{ A m}^{-2}$), a high hydrogen production rate ($0.19 \text{ m}^3 \text{ H}_2 \text{ m}^{-3} \text{ d}^{-1}$) and excellent cycling stability [14,15]. A suitable cathode should have the following properties: large active surface area, electrochemical stability, high specific surface area, high H_2 production rate, excellent cycling stability and low hydrogen overpotential. Given that Ni has a lower overpotential and higher current density, it is considered a very promising non-noble metal catalyst for MECs cathode [16].

In the past years, many Ni-catalyst electrodes have been fabricated for MEC. Electrodepositing NiMo and NiW on carbon cloth have been used as cathode in MEC [17], in which a hydrogen production rate of $2.0 \text{ m}^3 \text{ day}^{-1} \text{ m}^{-3}$ is achieved at current density of 270 A m^{-2} (12 A m^{-2}) and applied voltage of 0.6 V. The hydrogen production by NiMo is 33% higher than NiW MEC and only 13% lower than Pt catalyst ($2.3 \text{ m}^3 \text{ day}^{-1} \text{ m}^{-3}$).

Recently, Mitov et al. [18] used a novel NiMo and NiW electrodeposited on Ni-foam as cathode in MEC. In a single-chamber MEC reactor, the hydrogen recoveries of NiW and NiMo cathodes are 79% and 89%, respectively, at applied voltage of 0.6 V. The intrinsic electrocatalytic activity of NiW is six times higher than that of NiMo. The cathodic hydrogen recovery and energy efficiency achieved by the developed electrocatalyst are twice that of the unmodified Ni-foam. Li et al. reported that the hydrogen production rate using the Ni-P cathode is 7.5% higher than that by using Ni foam and 110% higher than that by SS; the hydrogen production rate of Ni-P reached $2.29 \pm 0.11 \text{ L H}_2 \text{ L}^{-1} \text{ d}^{-1}$ [19]. Mitov et al. studied that electrodeposited NiFe, NiFeP and NiFeCoP nanostructures onto carbon felt and achieved higher catalytic activity than bare carbon felt [20]. The NiFeCoP/carbon felt electrodes exhibited a high current production rate of $1.7 \pm 0.1 \text{ m}^3 \text{ H}_2 \text{ day}^{-1} \text{ m}^{-2}$.

The development of non-noble metal cathode catalysts is highly significant in MECs. In this study, Ni, Co, and Ni/Co were used as cathodes in MECs by electrodeposition on carbon paper (CP). Their HER performance was evaluated relative to that of bare CP catalysts.

2. MATERIALS AND METHODS

2.1. Cathode electrode preparation

CP electrode of 4 cm^2 (2×2) were prepared. The electrodes were washed by the distilled water and then treated with $1 \text{ mol L}^{-1} \text{ HCl}$ and $1 \text{ mol L}^{-1} \text{ NaOH}$ for 5h each to make the electrode surface more electrophilic, followed by washing with distilled water until $\text{PH} = 7$, Finally, the electrodes were dried in an oven at 120°C for 12 h. Co, Ni, and Ni/Co electrodeposited on CP by a three electrode system; Ag/AgCl reference electrode, a platinum counter electrode ($2 \text{ cm} \times 2 \text{ cm}$), and CP with working electrode in an electrochemical station (CHI660D, Chenhua, China). Then, the prepared electrodes were naturally dried in the air. The electrolyte composition is $0.12 \text{ mol L}^{-1} \text{ Co}$, $0.12 \text{ mol L}^{-1} \text{ Ni}$, and $0.06 \text{ mol L}^{-1} \text{ Co} + 0.06 \text{ mol L}^{-1} \text{ Ni}$.

2.2. MEC set up

The single-chamber MEC was constructed using Plexiglas (i.e., cylinder with a total volume of 100 mL). The solution consisted of 20 mL of activated sludge which came from a local coking wastewater treatment plant (Taiyuan, China), and 80mL of phosphate buffer solution ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 5.618 g L^{-1} ; $\text{NaH}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 6.155 g L^{-1} , 1 g/L glucose, 0.026 g L^{-1} of KCl, 0.062 g of NH_4Cl , and 12.5 mL of trace metal solution). The anode was carbon felt ($2 \times 5 \times 1 \text{ cm}^3$) initially inoculated in the steadily running double-chamber MFCs [21]. A power source (HB 17301 SL; Hossoni, Inc., China) was used to apply 0.7 V to the reactors. The prepared processes are shown in Fig. 1.

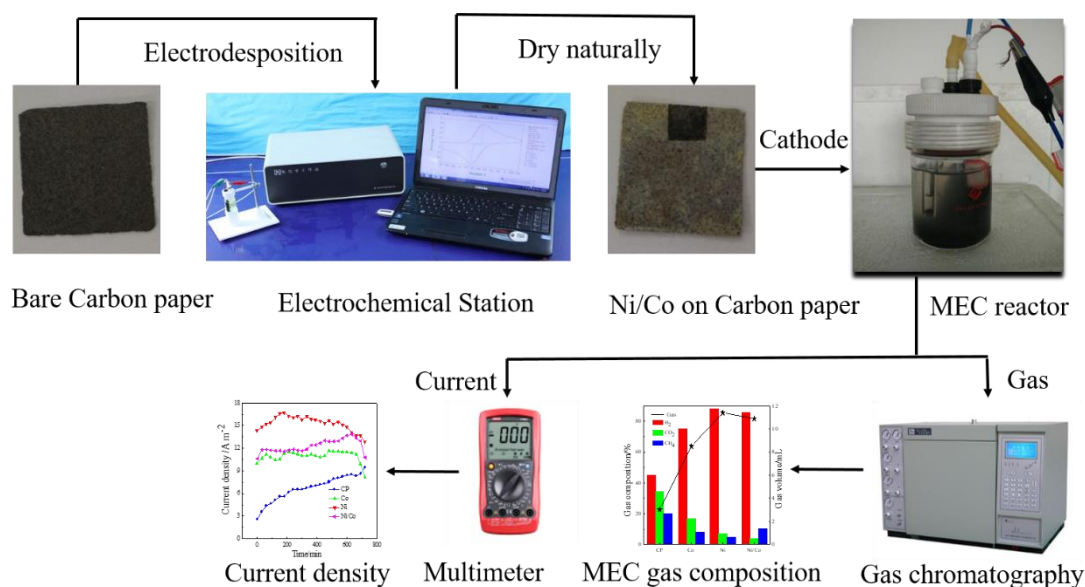


Figure 1. Schematic illustration for preparation processes of MECs.

2.3. Analysis and calculations

Scanning electron microscopy (SEM) was used to analyse the surface morphology of its electrodes and the micrographs of various compositions at 10000 magnification (JSM-7001F, JEOL, Japan). Electrochemical measurements were performed by an electrochemical working station

(CHI660D, Chenhua, China), in which the electrolyte was 100 mM phosphate buffer solution (PBS) (pH7). The Ag/AgCl electrode was used as the reference electrode and platinum wire as the counter electrode as well as the prepared cathode as the working electrode in the three-electrode system. Cyclic voltammetry (CV) was conducted by sweeping the potential from -0.8 V to 1.0 V (V vs. Ag/AgCl) at a scan rate of 10 mV/s. Linear sweep voltammetry (LSV) tests were conducted by sweeping the potential from 2 V to -2 V with a scan rate of 10 mV s⁻¹, Polarization curves were obtained by sweeping the potential from -1.0 V to -0.2 V at a scan rate of 1 mV s⁻¹. Current was recorded every half an hour by a multimeter (UNI-T 803, Uni-Trend Electronics Co., Ltd., Shanghai, China). After one cycle the gas was collected in a gas bag.

The collected gas was analysed by gas chromatography (Thermo Fisher Scientific, Waltham, MA, USA). Cathode H₂ recover efficiency (r_{cat}) and Energy yield efficiency (h_w) were calculated to illustrate the performance of MEC reactors. r_{cat} could be calculated by the equation $r_{cat} = n_{H_2}/n_{CE} \times 100\%$, where $n_{H_2} = V_{H_2} \times P/RT$, V_{H_2} is the volume of hydrogen (L), P is pressure (atm), R is the gas constant (0.08 L·atm/mol·k), T is thermodynamic temperature (298.15 K), the $n_{CE} = \int_0^t I dt / 2F$, I is current (A) and F is Faraday's constant (96485 C/mol e⁻); 2 mol of electrons are generated per mole of hydrogen. The h_w could be calculated by the equation $h_w = \Delta H_{H_2} \times r_{cat} / 193 E_{ps}$, where ΔH_{H_2} is hydrogen combustion heat (285.83 kJ mol⁻¹) and E_{ps} is input voltage (0.7 V). The current density could be calculated by the equation $I_m = I/S$, where I is the measured current (A) and S is the surface area (m²) of the prepare cathode.

3. RESULTS AND DISCUSSION

3.1. Morphology characterization

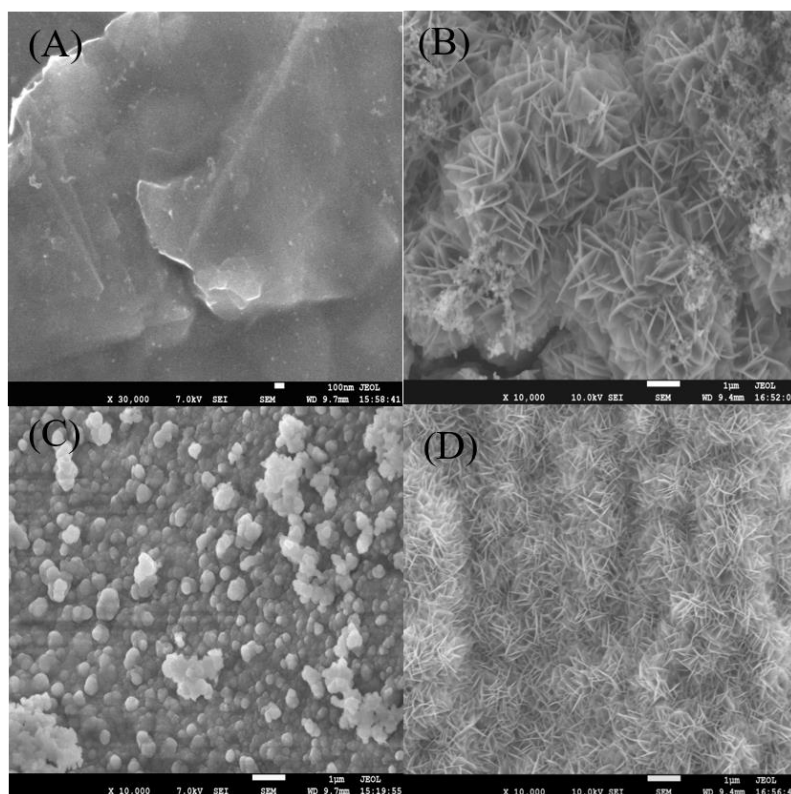


Figure 2. SEM micrographs of bare CP (A), Co (B), Ni (C), and Ni/Co on CP (D).

The morphologies of Co, Ni, and Ni/Co electrodeposited on CP cathode in MEC operation were characterized by SEM and compared with bare CP cathode (Fig.2). In Fig. 2A, CP displayed a flat structure without any impurity and additive. Fig. 2B shows that the pure Co had a high uniformity of vertically-standing sheets, which is consistent with previous studies [22,23]. The morphology of electrodeposited Ni showed spherical particles of different sizes that were uniformly distributed in the coating (Fig. 2C). The surface was rough and thus the specific surface area of the electrode was increased. Therefore, to a certain extent, the catalytic hydrogen evolution activity of the electrode was improved. Uniformly small vertically-standing sheets were formed on the CP surface (Fig.2 D). Thus, the addition of Co changed its surface morphology. The hierarchical structure afforded the small Ni/Co pores and large specific area, which contributed to the improvement of the catalyst. Moreover, the density of Ni/Co on CP increased compared with the lone Co deposition. However, the coating is relatively dense, thereby reducing its specific surface area compared to the Ni electrode.

3.2. Electrochemical properties of cathode

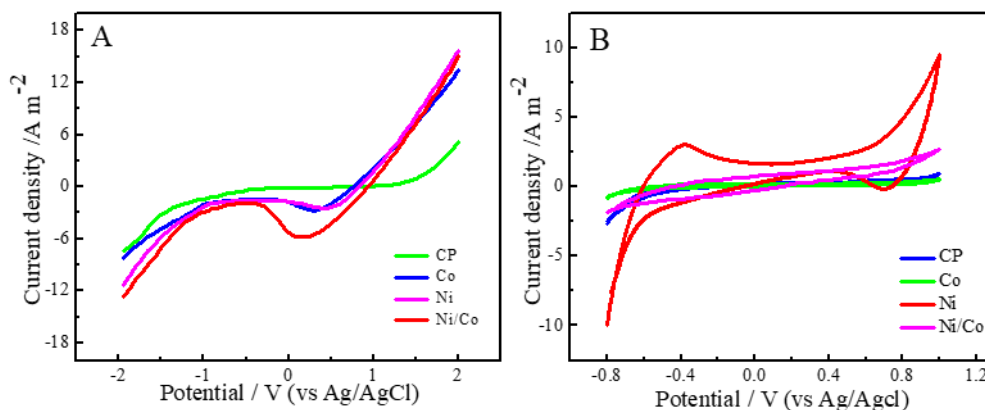


Figure 3. LSV (A) tests were conducted by sweeping the potential from 2 V to -2 V with a scan rate of 10 mV s^{-1} and CV (B) was conducted by sweeping the potential from -0.8 V to 1.0 V (V vs. Ag/AgCl) at a scan rate of 10 mV/s for all investigated materials in PBS (PH=7).

LSV was used to characterize the HER performance of different materials and all the tests were repeated three times and the final test result was shown in Fig. 3(A) Ni exhibited the highest current density, whereas the bare CP showed lowest. The LSV results suggested that Ni, Ni/Co, Co and bare CP showed a current density of 12.65 , 11.40 , 8.17 , and 7.40 A m^{-2} , respectively, at the potential of -2.0 V. The Ni electrode showed about 1.71 times higher current density than the bare electrode and roughly 1.11 or 1.55 times of Ni/Co and Co [25,26].

Steeper slopes of the voltammogram indicated more effective production of H_2 by allowing a greater current at the same cathodic potential [29]. In other words, at the lower overvoltage, the hydrogen can be obtained easily and quickly under the higher hydrogen evolution rate of cathode, which is in the same conditions as described above. The slope of Ni is better than the other cathodes, and thus the hydrogen evolution rate of Ni cathode was superior to that of the other cathodes. Although CP itself has the catalytic activity, it is weaker than Co, Ni, and Ni/Co. Both the current density and steeper slope showed that deposition Ni on CP was beneficial to improve electrochemical properties.

The electrocatalytic activity of different cathode catalysts was investigated by CV [24]. As shown in Fig.3(B), a strong reduction peak at a potential of 0.7 V and a current density of -0.015 A m^{-2} was observed for the Ni cathode. which was demonstrated the importance of Ni cathode on the potentials of the reduction peaks. Nevertheless, no obvious oxidation/reduction peaks were observed for the bare CP, Co, and Ni/Co catalysts, higher redox currents were observed at Ni/Co catalysts. Therefore, Ni/Co shows faster electron transfer properties than CP and Ni. This significant change in electrochemical properties can help improve the performance of MEC [27]. This phenomenon confirmed that electrodes with CP supported Ni have high evolution hydrogen activity [28]. The results of CV followed the same trend as that of the LSV curves.

3.3. MEC tests

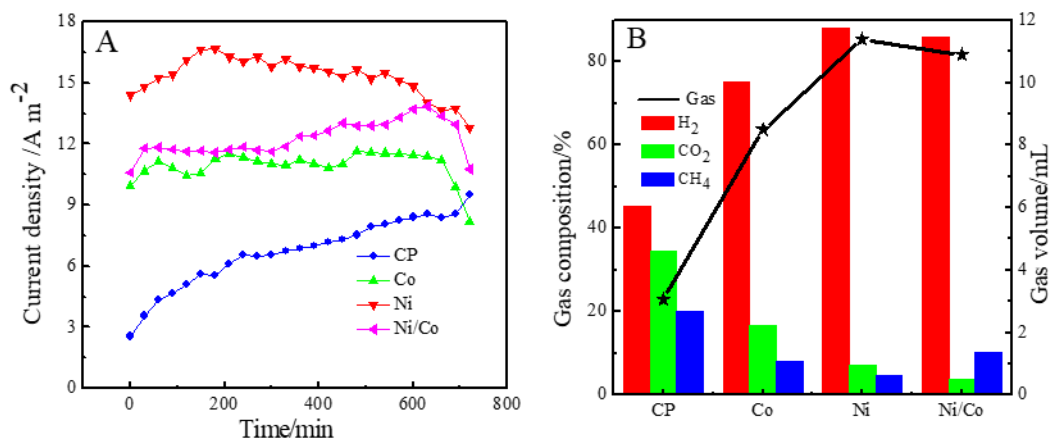


Figure 4. The current density variation in MEC during one cycle (A). MEC gas composition per cycle (bar, left axis) and gas volume (blank dots, right axis) (B).

First, stability of the MECs with platinum net cathodes was examined by running the reactors for 3 months. The Pt mesh was replaced with the prepared cathode, and three measurements were conducted per cathode cycle. Data were recorded once every half hour for 12 hours per cycle. The average current density for the cathodes in the MECs was 15.31 A m⁻² for Ni cathode, 12.26 A m⁻² for Ni/Co cathode, 10.93 A m⁻² for Co cathode, and 6.70 A m⁻² for bare CP. The current density of Ni cathode was 24.87% higher than that of the Ni/Co cathode, 40.07% higher than that of the Co cathode and 56.23% higher than that of bare electrode cathode. Moreover, the MEC with Ni cathode exhibited a higher current density (Fig. 4A). The large current density indicated more electrons could be transferred to cathode for hydrogen generation. Thus, the electrodeposition of Ni catalyst on CP increased the catalytic activity toward the HER compared to bare electrode.

As shown in Fig. 4B. During the experiment, the gas products were collected and analyzed to evaluate the hydrogen production performance and showed the stability of several cycles operation. Average gas per cycle produced gas volume of Ni was 11.40 ± 0.8 mL. This value far exceeded that for CP cathode (3.05 ± 0.5 mL). The amount of produced gas from Ni/Co was close to Ni, gas volume of 10.90 mL. The produced gas volume of Co under Ni was 8.50 mL. The Ni cathode produced gas higher than CP by 273.77%. The composition of the gas produced by the Ni cathode MEC included H₂ (86.03 ± 0.7%), CH₄ (3.67 ± 0.4%), and CO₂ (10.27 ± 0.3%). while other cathode produced a much higher methane production, up to around 34.52 ± 0.5% of CP, 16.78 ± 0.8% of Co, and 7.28 ± 0.6% of Ni/Co. Thus, the Ni cathode has a slowest rate of methane production, leading to a stable and effective rate of hydrogen production all the time. In past studies, the production of methane can reduce the purity of hydrogen. [30,31] Both the material itself and the growth of methanogenic bacteria can lead to the formation of methane in MEC. The release of hydrogen or methane from the cathode is determined by the bond energy of the H atom of the metal. Higher bond energies can lead to the formation of methane instead of hydrogen. [32] Due to the lowest bond energy, Ni cathode has the best her-performance compared with other materials, so the methane content is the lowest. It proved that the electrodeposited Ni on CP is better than bare CP. [33]

3.4. Hydrogen recovery and energy efficiency

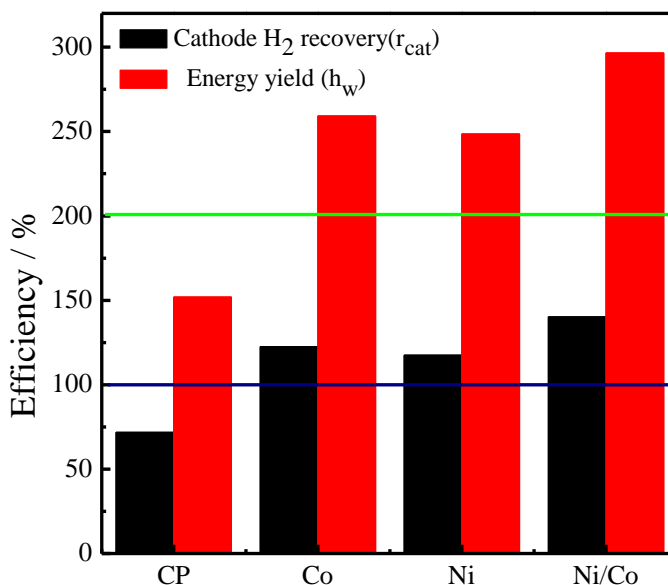


Figure 5. Cathode H₂ recover efficiency (r_{cat}) and energy yield efficiency (h_w) with different types of cathode.

The key factors affecting hydrogen yield include current density and cathode hydrogen recovery efficiency. [34]. Fig.5 show the r_{cat} values obtained in MEC tests CP electrode 71.8%, Co 122.5%, Ni 117.5%, and Ni/Co 140.2%. At an applied voltage 0.7 V, relative to that needed to split water (1.23 V), a lower applied voltage may increase energy yield efficiency, but may lower cathode H₂ recover efficiency. The energy yield efficiency of Co, Ni, Ni/Co electrode was higher by 200%, which was due to the high hydrogen gas recovery efficiencies. CP showed the lower value (152%) compared to Co (259.2%), Ni (248.5%), and Ni/Co (296.5%). Compared with others electrodes, the Ni/Co cathode achieved higher r_{act} and h_w. These results could be attributed to the hydrogen rate and yield were both determined by the coating metal activity and the base material property. The selection of cathode catalysts should take into account both hydrogen consumption and energy economics, not simply the higher the better. Because it will provide reference for the decision of running parameters in industrialized MECs.

3.5. Kinetics Activity

Table 1. Exchange current density calculated from the Tafel plots.

electrode	bare electrode	Co	Ni	Ni/Co
i ₀ (A m ⁻²)	0.18	0.93	2.80	0.84

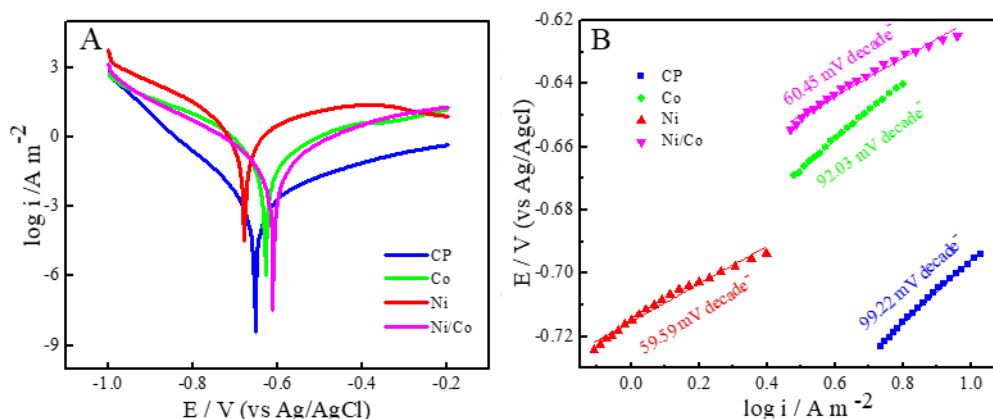


Figure 6. (A) Polarization curves were obtained by sweeping the potential from -1.0 V to -0.2 V at a scan rate of 1 mV s⁻¹. (B) The linear fit for the Tafel plots.

Tafel curves were recorded to analyse activation loss and rate of oxygen reduction catalyzed in MEC. The Tafel plot of four cathodes are shown in Fig. 6. The catalytic activity of the cathode electrode was mainly evaluated by the exchange current density (i_0), which is a promising parameter to prove the electron transfer rate between electrolyte and electrode. The exchange current densities results are listed in Table 1. The MEC with Ni cathode exhibited the maximum exchange current densities of 2.8 A m⁻², which was 1455.55%, 201.07%, and 233.33% higher than those of bare CP (0.18 A m⁻²), Co (0.93 A m⁻²), and Ni/Co (0.84 A m⁻²), respectively. The higher values of exchange current density signified that the kinetics activity and electrochemical performance were obviously improved. Moreover, a higher i_0 represents faster reaction rate and more effective utilization of the electrons [35, 36].

The Tafel slope is also an inherent property of electrocatalysts. A smaller Tafel slope of the catalyst indicates a faster HER rate [37]. According to the hydrogen evolution kinetic model, the reaction speed control steps are Tafel, Heyrovsky, and Volmer steps under acidic conditions with the Tafel slope of 30, 40, and 120 mV dec⁻¹, respectively. Under neutral conditions, the Tafel slope is slower than that of acidic conditions [38]. Fig. 6 (B) shows that the Tafel slopes of Ni electrodes were much lower than that of the bare CP electrode (99.22 mV dec⁻¹), indicating that the hydrogen evolution catalytic activity of the two was much higher than that of bare CP. The Tafel slope of Ni was 59.59 mV dec⁻¹ (i.e., >40.00 mV dec⁻¹). This finding confirms that the kinetics of HER under neutral condition is slower than that under acidic condition. The Tafel slopes of Ni, Co, and Ni/Co were 59.89, 92.03, and 60.45 mV dec⁻¹, respectively. Which were lower than that of bare CP.

4. CONCLUSION

The Ni cathode exhibited a higher electrochemical performance, higher current density, and lower hydrogen evolution overpotential than the Co, Ni/Co, and CP catalysts. The spherical particle morphology also greatly increased the hydrogen production. Thus, Ni electrodeposited on CP offers a low-cost material that can be easily manufactured with the same durability as platinum but not as

prone to poisoning. The Ni cathode has great potential as the cathode for MECs to produce hydrogen. It is also believed that the Ni is a high efficient cathode to replace Pt catalytic cathode, and make the MEC to be commercialized.

ACKNOWLEDGEMENTS

This work was funded by the Provincial Natural Science Foundation of Shanxi Province, China (2014011014-6, 201701D121028). The authors also acknowledged the Institute of Coal Chemistry, Chinese Academy of Sciences for technical assistance.

References

1. M. Z. Khan, A. S. Nizami, M. Rehan, O. K. M. Ouda, S. Sultana, I. M. Ismail, K. Shahzad, *Appl. Energ.*, 185 (2017) 410.
2. R. K. Brown, U. C. Schmidt, F. Harnisch, U. Schroder, *J. Power Sources*, 356 (2017) 473.
3. A. Kundu, J. N. Sahu, G. Redzwan, M. A. Hashim, *Int. J. Hydrogen Energy*, 38 (2013) 1745.
4. H. Liu, S. Grot, B. E. Logan, *Environ. Sci. Technol.*, 39 (2005) 4317.
5. P. A. Selembo, M. D. Merrill, B. E. Logan, *J. Power Sources*, 190 (2009) 271.
6. A. Tenca, R. D. Cusick, A. Schievano, R. Oberti, B. E. Logan, *Int. J. Hydrogen Energy*, 38 (2013) 1859-1865.
7. A. W. Jeremiasse, H. V. M. Hamelers, C. J. N. Buisman, *Bioelectrochemistry*, 78 (2010) 39.
8. M. Su, L. Wei, Z. Qiu, G. Wang, J. Q. Shen, *J. Power Sources*, 301(2016) 29.
9. Y. Zhang, M. D. Merrill, B. E. Logan, *Int. J. Hydrogen Energy*, 35 (2010) 12020.
10. J. R. Ambler, B. E. Logan, *Int. J. Hydrogen Energy*, 36 (2011) 160.
11. A. Kadier, Y. Simayi, K. Chandrasekhar, M. Ismail, M. S. Kalil, *Int. J. Hydrogen Energy*, 40 (2015) 14095.
12. A. W. Jeremiasse, H. V. M. Hamelers, M. Saakes, C. J. N. Buisman, *Int. J. Hydrogen Energy*, 35 (2010) 12716.
13. L. Lu, D. Hou, Y. Fang, Y. P. Huang, Z. Y. J. Ren, *Electrochim. Acta.*, 206 (2016) 381.
14. J. C. Tokash, B. E. Logan, *Int. J. Hydrogen Energy*, 36 (2011) 9439.
15. Y. Hou, B. Zhang, Z. H. Wen, S. M. Cui, X. R. Guo, Z. He, J. H. Chen, *J. Mater. Chem. A*, 2 (2014) 13795.
16. P. A. Selembo, M. D. Merrill, B. E. Logan, *Int. J. Hydrogen Energy*, 35 (2010) 428.
17. H. Hu, Y. Fan, H. Liu, *Int. J. Hydrogen Energy*, 34 (2009) 8535.
18. M. Mitov, E. Chorbazhiyska, L. Nalbandian, Y. Hubenova, *J. Power Sources*, 356 (2017) 467.
19. F. J. Li, W. F. Liu, Y. Sun, W. J. Ding, S. A. Cheng, *Int. J. Hydrogen Energy*, 42 (2017) 3641.
20. M. Mitov, E. Chorbazhiyska, R. Rashkov, Y. Hubenova, *Int. J. Hydrogen Energy*, 37 (2012) 16522.
21. Z. S Dong, Y. Zhao, L. Fan, Y. X. Wang, J. W. Wang, K. Zhang, *Int. J. Electrochem. Sci.*, 12 (2017) 10553.
22. X. Q. Wang, X. M. Li, X. Du, X. L. Ma, X. G. Hao, C. F. Xue, H. Y. Zhu, S. S. Li, *Electroanal.*, 29 (2017) 1286.
23. J. C. Chen, C. T. Hsu, C. C. Hu, *J. Power Sources*, 253 (2014) 205.
24. R. Kumar, L. Singh, A. W. Zularisam, *J. Taiwan Inst. T. Chem. E.*, 78 (2017) 329.
25. F. J. Li, W. F. Liu, Y. Sun, W. J. Ding, S. A. Cheng, *Int. J. Hydrogen Energy*, 42 (2017) 3641.
26. R. Kumar, L. Singh, A. W. Zularisam, F. L. Hai, *Bioresource Technol.*, 220 (2016) 537.
27. M. H. Zhou, M. L. Chi, H. Y. Wang, T. Jin, *Biochem. Eng. J.*, 60 (2012) 151.
28. T. S. Song, D. B. Wang, H. Q. Wang, X. X. Li, Y. Y. Liang, J. J. Xie, *Int. J. Hydrogen Energy*, 40 (2015) 3868.

29. L. Wang, W. Z. Liu, Z. W. He, Z. H. Guo, A. J. Zhou, A. J. Wang, *Int. J. Hydrogen Energy*, 42 (2017) 19604.
30. S. A. Cheng, D. F. Xing, D. F. Call, B. E. Logan, *Environ. Sci. Technol.*, 43 (2009) 3953.
31. A. Wang, W. Liu, S. Cheng, D. Xing, J. Zhou, B. E. Logan, *Int. J. Hydrogen Energy*, 34 (2009) 3653.
32. S. Trasatti, *J. Electroanal. Chem. Interfac.*, 39 (1972) 163.
33. H. Y. Dai, H. M. Yang, X. Liu, X. Jian, Z. H. Liang, *Fuel*, 174 (2016) 251.
34. K. Guo, X. H. Tang, Z. W. Du, H. R. Li, *Biochem. Eng. J.*, 51 (2010) 48.
35. B. Ge, K. X. Li, Z. Fu, L. T. Pu, X. Zhang, Z. Q. Liu, K. Huang, *J. Power Sources*, 303 (2016) 325.
36. T. T. Yang, Z. Wang, K. X. Li, Y. Liu, D. Liu, J. J. Wang, *J. Power Sources*, 363 (2017) 87.
37. D. Merki, X. Hu, *Energy Environ. Sci.*, 4 (2011) 3878.
38. L. Lu, D. X. Hou, Y. F. Fang, Y. P. Huang, Z. Y. JasonRen, *Electrochim. Acta*, 206 (2016) 381.

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