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Nickel powder blended activated carbon cathodes for hydrogen production in microbial electrolysis cells

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ABSTRACT

Although pure Ni catalysts can achieve a hydrogen production rate similar to Pt in microbial electrolysis cells (MECs), a reduction in the amount of Ni used is needed to reduce the cost. In this study, nickel powder (pNi) was blended with activated carbon (AC) to reduce the mass of Ni used, while improving catalytic activity for the hydrogen evolution reaction (HER) by increasing the active surface area. Ni powder blended AC cathodes (AC-pNi) were fabricated at different nickel powder loadings (4.8, 19, 46 mg/cm² with AC and 77 mg/cm² without AC as control). AC-pNi4.8 (Ni loading: 4.8 mg/cm²) produced higher hydrogen production rates (0.38 ± 0.04 L-H₂/L-d) than pNi77 (0.28 ± 0.02 L-H₂/L-d) with a 16 times less Ni loading. Cathodic hydrogen recovery of using the AC-pNi4.8 ($98 \pm 5\%$) was also higher than pNi77 ($82 \pm 4\%$), indicating catalytic activities were improved by AC blending. Nickel dissolution into the catholyte after completion of each cycle was negligible for AC-pNi4.8 (<0.2 mg/L), while Ni dissolution was detected for pNi77 (5–10 mg/L). These results indicate that AC blending with Ni powder can improve hydrogen production in MECs while minimizing the amount of Ni in the cathode.

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Introduction

A microbial electrolysis cell (MEC) can be used to electrochemically produce hydrogen from electrons derived from organic matter using microorganisms called exoelectrogens [1–5]. Electrons obtained from organics in wastewaters can be utilized for hydrogen production so that wastewater treatment can be coupled with hydrogen production [6–11]. While

hydrogen production through water electrolysis requires a high energy input (theoretically > 1.2 V), an MEC needs only a small additional voltage (>0.14 V) to drive the hydrogen evolution reactions (HER) at the cathode due to the thermodynamically favorable oxidation of organics at the anode [12]. A precious metal such as Pt has been widely used as a cathode catalyst in MECs due to its excellent catalytic activities for HER [2], but the use of precious metal catalyst is not practical in MECs due to its high capital cost [13]. Thus, developing

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alternative cathode catalysts to Pt is important to move MECs forward towards practical applications and scaled-up systems.

Nickel has been widely tested as an alternative catalyst to replace Pt in MECs due to its weak atomic hydrogen binding energy and low cost [14,15]. Ni has been tested in MECs in different forms, including a metal sheet [16], powder [17], metal foam [18–20], alloy [21,22], mesh [23], and metal salts adsorbed onto the activated carbon (AC) [24]. A Ni electrode with a 3-dimensional structure can have a greater active surface area, and thus produce higher hydrogen production rates than a flat metal electrode. For example, the MEC with a Ni powder (Ni210, particle size 0.5–0.1 μm) catalyst produced 1.2–1.3 L-H₂/L-d in a single chamber MEC, which was higher than that of the MEC with a nickel sheet (Ni625, 0.79 ± 0.27 L-H₂/L-d) in the same reactor configuration [16,17]. An MEC with a Ni foam produced 2.01–2.12 L-H₂/L-d with a NiFe layered double hydroxide [20], and 50 L-H₂/L-d was produced with a pure Ni foam with more optimized conditions (flow forced through the Ni foam cathode, and graphite felt anode), but performance decreased over time [19]. The MEC with Ni powder cathodes used 60 mg of Ni powder (8.6 mg-Ni/cm²) to achieve hydrogen production rates similar to Pt, but only 1 mg of Pt was used (0.1 mg-Pt/cm²). About 5 times more Ni is used in a Ni foam cathode (50 mg-Ni/cm², assuming the foam is 100% nickel) as a catalyst [17,24]. Although Ni electrodes can have hydrogen production rates comparable to Pt electrodes, the amount of Ni needs to be reduced in order to make the process more economically favorable. In a previous approach, Ni was added onto AC by a simple adsorption process, which slightly improved hydrogen production rates (1.1 ± 0.1 L-H₂/L-d) compared to Ni foam, even with the low mass loading of Ni (8.8 mg-Ni/cm² onto the AC, compared to 50 mg-Ni/cm² for Ni foam) [24]. In another study, Ni cathodes using a type Ni210 powder blended with electrically conductive carbon black (CB, 4.3 mg-CB/cm²), which is often added to Pt catalyst electrodes, showed no significant changes in hydrogen production compared to Ni cathodes with only Ni powder [17]. However, CB was only added at a single fixed loading, making it difficult to understand the relative impact of CB on hydrogen production using nickel powder cathodes.

In this study, cathodes for MECs were made by blending Ni powder with AC (AC-pNi) to see if this high surface area electrode could provide a sufficiently high catalytic activity for HER while using less Ni than some other approaches. AC by itself is not a good catalyst for HER [25], but the AC has a large surface area (2500 m²/g) with a high electrical conductivity, which could provide a greater overall active surface area for a HER catalyst such as Ni [26]. Here, AC-pNi cathodes were fabricated at different nickel powder loadings (4.8, 18, 46 mg-Ni/cm²) with AC and 77 mg-Ni/cm² without AC (control), and tested in MECs over 15 cycles (total 22 days including acclimation). Abiotic electrochemical tests were conducted to evaluate catalytic activities of the fabricated electrodes, and hydrogen production and current densities were measured over the 24 h cycles. Catholyte samples were collected after each cycle to monitor if there was measurable Ni dissolution over the cycles. Electrochemical tests were conducted again on the Ni cathodes after the tests to see if there were changes in electrochemical performance following MEC tests.

Materials and methods

Fabrication of Ni powder blended AC cathodes

Ni210 powder (particle sizes 0.5–1 μm , Alfa-Aesar, MA) was chosen for tests here based on a previous study that identified Ni210 powder as having the highest catalytic activity for HER [17]. Different amounts of Ni powder were added to AC powder (4–30 μm , Norit SX plus, Norit America Inc., TX) to fabricate AC-pNi electrodes, with Ni powder loadings of 4.8, 19, 46 mg/cm². A Ni powder electrode (pNi, containing no AC) with Ni powder at a loading of 77 mg/cm² was also fabricated as a control (Table S1). The AC-pNi and pNi cathodes were fabricated using a phase inversion technique with a poly(vinylidene fluoride) (PVDF) binder [27]. PVDF powder was dissolved (5% w/v) in *N,N*-dimethylacetamide (DMAc), and 0.7 mL of this solution was added to the Ni and AC powder mixture (5.4 mg-PVDF/cm²). The mixture was spread onto a circular stainless steel mesh (6.5 cm², 50 × 50, type 304, McMaster-Carr, USA), and then submerged into deionized water for 15 min to induce phase inversion. Less AC (15.4 mg/cm²) was used for the AC-pNi46 electrode than that (28.6 mg/cm²) of AC-pNi4.8 and AC-pNi19 as Ni powder loading increased to 46 mg/cm² to fix the amount of PVDF binder for all tested electrodes.

Abiotic electrochemical tests

Chronopotentiometry (CP) tests were conducted using a potentiostat (VMP3 Workstation, BioLogic Science Instruments, USA), with an AC-pNi electrode as the working electrode and a platinum mesh counter electrode, and a Ag/AgCl (model RE-5B, BASi, IN) reference electrode. Current was set to 0, 1, 2.5, 5, 7.5, 10, 12.5 and 15 mA with 20 min at each current. A two-chamber cubic reactor (working electrode chamber: 28 mL, counter electrode chamber: 14 mL) separated by anion exchange membrane (AEM, Selemion AMV, AGC Engineering Co. Ltd., JP) was used to separate the chamber, with a plain phosphate buffer solution (50 mM, Na₂HPO₄: 4.58 g; NaH₂PO₄: 2.13 g) electrolyte in both chambers. The phosphate buffer solution for the working electrode chamber was sparged with a high purity nitrogen gas (99.998%) to remove dissolved oxygen before the tests.

MEC reactor construction and operation

Two polycarbonate cubes with cylindrical chambers (4 cm long, 3 cm diameter) were used as the anode and cathode chambers (28 mL each), with the AEM placed between the two chambers as previously described [28]. For the cathode chamber, a glass tube (length: 7.5 cm, diameter: 1.5 cm) sealed with a thick butyl rubber stopper was attached on the top, gas was collected using a gas collection bag (0.1 L, Calibrated Instruments, NY) attached through the rubber stopper using a needle. A graphite brush electrode (2.5 cm length, 2.5 cm diameter, Mill-Rose, Mentor, OH) was used as an anode, with the cathodes placed directly against the AEM and connected to the circuit using a titanium wire. Microbial anodes were acclimated for over 7 months in microbial fuel cells (MFCs) and other MEC tests prior to these studies [24]. Synthetic

fermentation effluent (anolyte) was prepared as previously described [29]: the solution contains sodium acetate (0.27 g), glucose (0.15 g), ethanol (0.11 g), lactic acid (0.07 g), and bovine serum albumin (BSA, 0.32 g) per liter of 50 mM phosphate buffer solution (PBS, Na_2HPO_4 : 4.58 g; NaH_2PO_4 : 2.13 g; NH_4Cl : 0.31 g; KCl: 0.13 g in 1 L of DI water with mineral and vitamin solutions). A plain PBS (50 mM) solution (without nutrients) was used as a catholyte, and it was deoxygenated by sparging using high purity nitrogen gas prior to tests. Both the anolyte and catholyte were completely replaced at the end of cycle (~24 h for a cycle). Voltage (0.9 V) was applied to MEC circuit using a power supply (BK Precision, USA), with the current monitored using a multimeter (Model 2700, Keithley Instruments, Inc., OH) by measuring the voltage across a 10 Ω resistor in the circuit.

Analytical methods and calculations

Gas in the gas bag and tube was analyzed for hydrogen using a gas chromatograph (Model 8610B, SRI Instruments Inc., USA), and the hydrogen production rate ($\text{L-H}_2/\text{L-d}$) calculated based on the volume of hydrogen gas produced during the cycle divided by reactor working volume (0.056 L) and the cycle time (24 h). Dissolved Ni concentration in the catholyte after each cycle was analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES, PerkinElmer Optima 4300 UV, USA). An average current density (i_{avg} , A/m^2) was calculated as current produced over the period time that 90% of the total charge transferred over the 24 h cycle as previously described [30]. Cathodic hydrogen recovery (r_{cat} , %) and energy yield (η_E , %) based on the energy of the hydrogen ($-237.1 \text{ kJ/mol-H}_2$ based on Gibbs Free energy) recovered compared to the electrical energy input, were calculated as previously described [31].

Results and discussion

Abiotic electrochemical tests before use in MECs

The different amounts of AC and Ni powder loadings produced slight differences in electrode potentials at current densities $<10 \text{ A/m}^2$. For example, AC-pNi19 (-0.91 V), AC-pNi46 (-0.90 V) and pNi77 (-0.92 V) produced slightly more positive potentials than AC-pNi4.8 (-0.97 V) at 7.7 A/m^2 (Fig. 1). At current densities greater than 10 A/m^2 , AC-pNi4.8 produced more negative potentials (-1.04 V at 12 A/m^2) than the other electrodes (AC-pNi19, -0.95 V ; AC-pNi46, -0.94 V ; and pNi77, -0.95 V). Ni powder loadings greater than 4.8 mg/cm^2 produced similar electrode potentials at the current densities $>10 \text{ A/m}^2$, but not observable correlations between Ni powder loadings and electrode potentials were found at current densities $<10 \text{ A/m}^2$.

Hydrogen production and current generation

AC-pNi electrodes with lower Ni powder loadings (higher AC loadings) produced higher hydrogen production rates than those with a greater mass of Ni powder (Fig. 2A). For example, AC-pNi4.8 ($0.38 \pm 0.04 \text{ L-H}_2/\text{L-d}$) and AC-pNi19 ($0.37 \pm 0.03 \text{ L-H}_2/\text{L-d}$) cathodes had higher hydrogen production rates than AC-

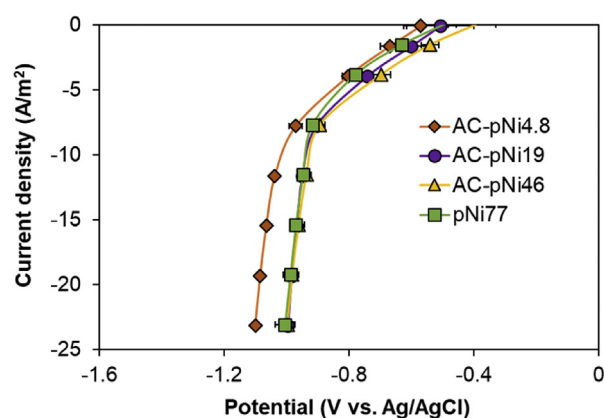


Fig. 1 – Current-voltage curves of Ni powder blended AC electrodes (AC-pNi) and a nickel powder electrode (pNi77) obtained by chronopotentiometry (CP) test. Error bars indicate mean \pm standard deviation ($n = 3$).

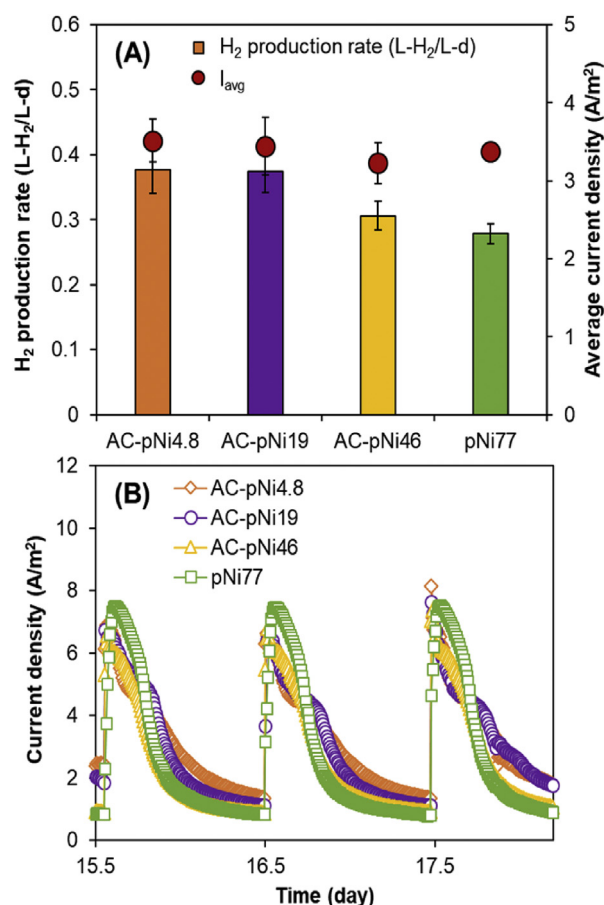


Fig. 2 – (A) Hydrogen production rates ($\text{L-H}_2/\text{L-d}$) and average current densities (A/m^2) and (B) consecutive current generation of MECs with AC-pNi and nickel powder only electrodes. Error bars indicate mean \pm standard deviation ($n > 11$).

pNi46 (0.31 ± 0.02 L-H₂/L-d) and pNi77 (0.28 ± 0.02 L-H₂/L-d). The highest hydrogen production rates were obtained with the AC blended cathodes with the lowest Ni power loadings (4.8 and 19 mg/cm²), indicating the hydrogen production can be improved with AC blending despite the lower amount of Ni catalyst. The greatest mass of Ni powder was used for the pNi77 cathode, however, the lowest hydrogen production rate was obtained for this cathode that did not contain AC.

Hydrogen production rates in this study (0.38 ± 0.04 L-H₂/L-d by AC-pNi4.8) are lower than those reported in a previous study that also used Ni powder in the cathodes ($1.2\text{--}1.3$ L-H₂/L-d). The lower hydrogen production rates are likely due to the different reactor configuration and the type of substrate [17]. A complex synthetic fermentation effluent, which contains a high concentration of protein, was used here as the fuel for the MEC. MECs fueled by a complex substrate have been shown lower rates of hydrogen production than MECs fueled by a simple substrate such as acetate that can be used directly by exoelectrogens [7,32,33].

There are several reasons why the use of AC may have improved performance. AC is electrically conductive, so it could help improve electrical connections in the cathode in the presence of the binder, and its presence could also alter the permeability of the cathode relative to both ion transport and gas evolution [34–36]. The porosity and three-dimensional structure of the cathode is very important for overall performance. The larger AC particles (4–30 μm) could provide a greater surface area for exposing Ni powder particles (0.5–1 μm) to the solution, thus impacting the way the binder interacts with the catalysts for the HER. While AC has a much greater specific surface area than that of a cathode made only of Ni powder (6.64×10^5 m²/m² for AC, 860 m²/m² for Ni powder) [17,26], it is unlikely that the Ni power could access the inner surface of the AC.

Average current densities (calculated based on the portion of the cycle with 90% coulomb accumulation) produced by AC-pNi4.8 (3.6 ± 0.2 A/m²) and pNi77 (3.4 ± 0.1 A/m²) were not significantly different ($p > 0.05$, student t-test) despite their different hydrogen production rates normalized to the total 24 h cycle (Fig. 2A). However, in the first 5 h of each cycle, pNi77 produced higher current densities than other tested electrodes (Fig. 2B and S3). Current generation of AC-pNi4.8 and AC-pNi19 was then maintained at higher densities than that of pNi77 over the rest of the cycle, resulting in similar average current densities over the 24 h cycle. The different trends in current generation over time were likely due to the different catalytic activities of tested electrodes as shown in the abiotic electrochemical tests (Fig. 1). Hydrogen production rates could therefore be different in the first 5 h and those obtained in the remainder of the cycle, resulting in different overall hydrogen production rates.

Cathodic hydrogen recovery and energy yield

Cathodic hydrogen recoveries (CR of using the AC-pNi4.8 ($98 \pm 5\%$) and AC-pNi19 ($97 \pm 6\%$) electrodes were significantly higher ($p < 0.05$) than those obtained with the AC-pNi46 ($91 \pm 5\%$) and pNi77 ($82 \pm 4\%$) cathodes (Fig. 3). The CRs decreased as AC loading decreased, indicating that AC blending was crucial for improving catalytic activities for HER.

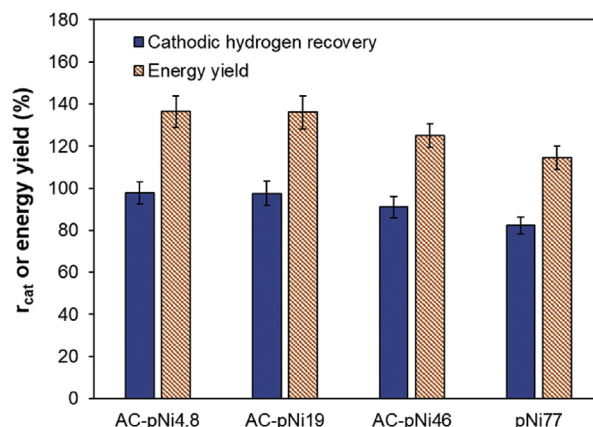


Fig. 3 – Cathodic hydrogen recoveries and energy yields of MECs with AC-pNi and nickel powder only electrodes. Error bars indicate mean \pm standard deviation ($n > 11$).

The lower CRs of AC-pNi46 and pNi77 resulted in lower hydrogen production rates despite comparable average current densities (Fig. 2A and B). The CR produced using AC-pNi4.8 here was higher than that in the previous study ($88 \pm 2\%$) where tested AC based cathodes were examined with adsorbed Ni salts as a catalyst, using the same synthetic fermentation solution [24]. The higher CR with a Ni powder catalyst than adsorbed Ni salts might be due to the different loading capacity of AC for the Ni powder and Ni salts. The amount of Ni catalyst functionalized by adsorption could be limited by adsorption capacity of the AC.

Energy yields (η_E , %) were greater than 100% in all tests which indicates that the amount of energy obtained by the hydrogen produced was greater than electrical energy input. AC-pNi4.8 ($136 \pm 8\%$) and AC-pNi19 ($136 \pm 8\%$) cathodes produced higher electrical energy yields than AC-pNi46 ($125 \pm 6\%$) and pNi77 ($114 \pm 6\%$) cathodes due to greater hydrogen production over the 24 h cycles.

Ni dissolution

Ni dissolution was negligible at the two lowest nickel loadings, 0.2 ± 0.2 mg/L with AC-pNi4.8 and 0.7 ± 0.6 mg/L with

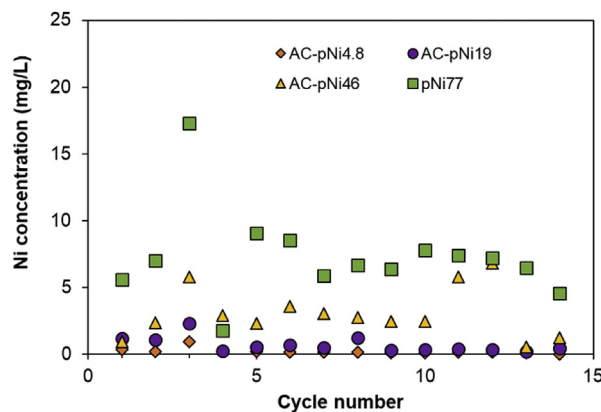


Fig. 4 – Dissolved Ni concentration in the catholyte after completion of each cycle.

AC-pNi19 in the catholyte after completion of each batch cycle (Fig. 4). The measured concentrations increased with Ni loading, with 3.0 ± 1.9 mg/L using AC-pNi46 and 7.2 ± 3.4 mg/L with pNi77 electrodes. A previous study using Ni powder cathodes also reported a similar level of dissolved nickel in the catholyte (4–6 mg/L) at the end of cycle [17]. A hydroxylated form of nickel (e.g. $\text{Ni}(\text{OH})_2$) can be formed when the cathode comes into contact with air, which can occur when switching the catholyte here, even in solutions with a neutral or alkaline pH. Nickel dissolution could be minimized by maintaining the cathode under strict anaerobic condition to avoid contact with the air. The lower Ni concentrations in the catholyte with AC-pNi4.8 and AC-pNi19 are likely due to the less chances of contacting air by AC blending or the adsorption of dissolved Ni onto the AC surface.

Abiotic electrochemical tests after 15 cycles in the MECs

CP tests for the tested electrodes were conducted after 15 cycles in the MEC reactors (22 days including acclimation) to see if there were changes in catalytic activities after use. All tested cathodes produced more negative potentials than before use, although relatively smaller changes were found for the lower Ni loadings (AC-pNi4.8, 0.01 V; and pNi77, 0.04 V) at 7.7 A/m^2 , compared to the cathodes with more Ni (AC-pNi19, 0.07 V; and AC-pNi46, 0.09 V) (Fig. 5). Noticeable differences in electrode potentials were found at the current densities $>10 \text{ A/m}^2$. For example, pNi77 produced -1.03 V , which was more positive than that produced by AC-pNi4.8 (-1.11 V). Although pNi77 produced more positive potentials at the current densities $>10 \text{ A/m}^2$, the more positive potentials did not affect the performance of MECs since the highest current density of tested electrodes was lower than 8 A/m^2 (Fig. 2B). The catalytic activity of pNi77 was not significantly decreased compared to other electrodes even with a greater loss of Ni over 15 cycles (Fig. 4). This result indicates that the amount of nickel that was lost was not sufficient to impact the overall catalytic activity likely due to the larger nickel powder loading (77 mg/

cm^2). However, AC blended Ni powder cathodes would be better to use than Ni powder only cathodes for a longer MEC operation to avoid large Ni losses to the environment.

Conclusions

Nickel is a non-precious metal and relatively inexpensive compared to other metal catalysts. However, it is still desirable to reduce the amount of nickel used in MECs to reduce total capital costs. In this study, nickel powder was selected as an alternative catalyst and blended with AC to try to reduce the mass loading of the nickel catalyst. The AC-pNi4.8 cathode had higher hydrogen production rates than the cathode containing only nickel powder (pNi77, 77 mg-Ni/cm^2), with a $98 \pm 5\%$ of cathodic hydrogen recovery. Over 15 cycles in the MECs, there was negligible Ni loss based on Ni concentrations at the end of a test in the catholyte ($<0.7 \text{ mg/L}$) for the AC-pNi4.8 and AC-pNi19 cathodes, while $5\text{--}10 \text{ mg/L}$ of nickel was detected in the catholyte with the pNi77 cathode after each cycle. These results indicate that AC blending with nickel powder could be useful to catalyze HER and use less nickel compared to that with a pure metal sheet or foam cathode.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2019.04.041>.

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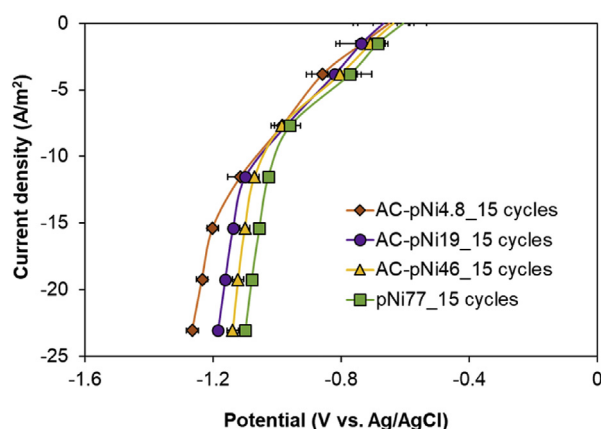


Fig. 5 – Current-voltage curves of Ni powder blended AC electrodes (AC-pNi) and a nickel powder electrode (pNi77) obtained by chronopotentiometry (CP) test after 15 cycles in MECs. Error bars indicate mean \pm standard deviation ($n = 3$).

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