Regenerable Nickel-Functionalized Activated Carbon Cathodes Enhanced by Metal Adsorption to Improve Hydrogen Production in Microbial Electrolysis Cells

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Supporting Information

ABSTRACT: While nickel is a good alternative to platinum as a catalyst for the hydrogen evolution reaction, it is desirable to reduce the amount of nickel needed for cathodes in microbial electrolysis cells (MECs). Activated carbon (AC) was investigated as a cathode base structure for Ni as it is inexpensive and an excellent adsorbent for Ni, and it has a high specific surface area. AC nickel-functionalized electrodes (AC-Ni) were prepared by incorporating Ni salts into AC by adsorption, followed by cathode fabrication using a phase inversion process using a poly(vinylidene fluoride) (PVDF) binder. The AC-Ni cathodes had significantly higher (≈50%) hydrogen production rates than controls (plain AC) in smaller MECs (static flow conditions) over 30 days of operation, with no performance decrease over time. In larger MECs with catholyte recirculation, the AC-Ni cathode produced a slightly higher hydrogen production rate (1.1 ± 0.1 L-H2/Lreactor/day) than MECs with Ni foam (1.0 ± 0.1 L-H2/Lreactor/day). Ni dissolution tests showed that negligible amounts of Ni were lost into the electrolyte at pHs of 7 or 12, and the catalytic activity was restored by simple readsoption using a Ni salt solution when Ni was partially removed by an acid wash.

INTRODUCTION

A microbial electrolysis cell (MEC) can be used to electrochemically produce hydrogen gas from organic matter using microorganisms called exoelectrogens.1 Electrons obtained from oxidation of organic matter by exoelectrogens at the anode are transferred to the cathode for the hydrogen evolution reaction (HER) with addition of voltage to the circuit (>0.14 V).2 Various types of organic wastes such as domestic wastewater, swine wastewater, and fermentation effluent have been tested in MECs to produce hydrogen gas, but most of these tests have been conducted with cathodes containing a Pt catalyst.3−5 The use of a precious metal catalyst for the HER in MECs is not practical for such wastewater applications due to its high capital cost.6

Various alternative catalysts to Pt have been tested in MECs, including nickel, Pd, MoS2, and stainless steel,7−10 but most alternative catalysts that are used in MECs are inexpensive metals such as nickel or stainless steel due to their good electrical conductivity and reasonable catalytic activities for the oxygen reduction reaction.21 For example, single-chamber MECs with Ni alloy plates (Ni 625, projected surface area: 7 cm2) produced 0.79 ± 0.27 L-H2/L/d, which was comparable to results using Pt cathodes (0.68 ± 0.06 L-H2/L/d).9 The cost of these metals is still very high, and corrosion of the cathode can result in decreased activity over time that cannot be restored without cathode replacement.11,14−16 One of the highest H2 production rates was reported using Ni foam cathodes, but performance of the cathode declined over time.8 To reduce the amount of metal used, metal particles have been used instead of metal plates. For example, Ni particles were bound to graphite blocks using a polymer, to examine methane production in MECs.17 However, the current densities were much less than those obtained using a Pt catalyst. Other approaches to add Ni into have required high temperatures (200−900 °C)18,19 or electrodeposition.20 However, all these methods do not solve the problem of restoring catalytic activity after metal corrosion without completely replacing the cathode.

In this study, inexpensive activated carbon (AC) was used as a base material for producing cathodes containing small but effective amounts of a Ni catalyst. AC has been used as a cathode material in microbial fuel cells (MFCs) due to its high specific surface area (~2500 m2/g) and good catalytic activity for the oxygen reduction reaction.21−23 However, AC is not a good catalyst for the HER. In one study using nitrogen-doped AC cathodes in MECs, the hydrogen production rate was very high temperatures (200−900 °C)
low (0.0030 ± 0.0004 L-H2/Lreactor/day) and similar to that of the unmodified AC control in a neutral pH solution. To add Ni to AC, we used a simple adsorption process as it is well-known that AC is an effective adsorbent of heavy metals. The Ni-adsorbed AC powder was then used to fabricate cathodes (AC-Ni) on a stainless steel current collector by a simple phase inversion technique with a poly(vinylidene fluoride) PVDF binder. This new AC-Ni method has two advantages compared to previous approaches (such as using a Ni foam): a very low amount of Ni needs to be used to make the cathode, and the electrode catalytic activity can be easily restored by additional adsorption of nickel salts. The latter point is especially important as a previous study with Ni foam showed a decline in cathode performance over time. The new AC-Ni cathodes with different Ni loadings were tested in smaller MECs (7 cm² cathode projected area) under static flow conditions under fed-batch conditions. Ni dissolution from the AC-Ni cathodes was investigated in these MECs at different solution pHs, and regeneration tests were conducted to see if Ni salts could be successfully added to fully fabricated AC-Ni cathodes in the event of loss of Ni from the cathodes. AC-Ni cathodes were then examined in larger scale MEC (40 cm² cathode) with catholyte recirculation, in continuous flow mode, and compared to a Ni foam cathode, as this has been shown to be one of the best alternative materials to Pt cathodes in MECs. While Ni loss from the cathode could reduce HER, we further demonstrate that catalyst activity can easily be restored by subsequent readsorption of Ni onto a cathode treated with an acid wash to reduce catalyst activity. To our knowledge, this is a first time that an AC material has been functionalized with Ni salts on the AC surface for HER.

### MATERIALS AND METHODS

**AC-Ni Cathode Preparation.** The AC powder (Norit SX plus, Norit Americas Inc., TX) loading onto the AC-Ni electrode was 26.5 mg/cm² based on a previous study.23 The amount of NiCl₂·6H₂O (J.T. Baker, 2768–04, U.S.A.) added to the AC powder was varied to produce AC-Ni electrodes with different Ni loadings of 2.2, 4.4, and 8.8 mg/cm², based on a previous study where metal catalysts were added for oxygen reduction on cathodes.26 The mixture of AC powder and Ni salts was stirred in deionized (DI) water for 30 min to induce adsorption of Ni onto the AC surface, then dried overnight (Figure S1 of the Supporting Information, SI). The Ni-adsorbed AC powder was used to fabricate AC-Ni electrodes using a phase inversion technique,32 poly(vinylidene fluoride) (PVDF) was dissolved (5% w/v) in N,N-dimethylacetamide (DMAC) with vigorous stirring and combined with the Ni-adsorbed AC powder (AC:PVDF = 5.8:1, mass ratio). For tests in the smaller MECs, the Ni-adsorbed AC powder and PVDF solution were mixed and directly spread onto a circular stainless steel mesh (7 cm², 50 × 50, type 304, McMaster-Carr, U.S.A.), submersed in DI water for 15 min to induce phase inversion, and then dried in the fume hood overnight. The mass of Ni in the AC electrodes was indicated based on the Ni loading as AC-Ni2.2, AC-Ni4.4, and AC-Ni8.8. A control cathode (plain AC) was fabricated using same procedures for the AC-Ni electrodes without the addition of Ni. For tests in the larger MEC, cathodes (40 cm²) were then examined with 8.8 mg/cm² of Ni (AC-Ni8.8).

Pt cathodes (Pt control) were prepared for the smaller MECs as previously described. Briefly, platinum and carbon powder (0.5 mg/cm² Pt loading, ETEK C1–10, 10% Pt and Vulcan XC-72), and a Nafion binder (5 wt % solution, Aldrich Nafion perfluorinated ion-exchange resin), were mixed and spread onto the stainless steel mesh that described above. For the larger MECs, nickel foam (Ni control; MTI Corporation, U.S.A.) cathodes were compared to the AC-Ni8.8 cathodes.

**Abiotic Electrochemical Tests.** Electrochemical tests were conducted using a two cubic chamber reactor with 7 cm² working-area electrodes (AC-Ni, plain AC, and Pt), with a platinum mesh counter electrode, and a Ag/AgCl (model RE-5B, BASI, IN) reference electrode. A plain phosphate buffer solution (PBS, 50 mM; Na₂HPO₄, 4.58 g/L; NaH₂PO₄, 2.13 g/L) was used as the electrolyte in both chambers. The electrolyte for the working electrode was deoxygenated by sparging with a high purity nitrogen gas for 5 min before tests. Chronopotentiometry (CP) tests were conducted using a potentiostat (VMP3 Workstation, BioLogic Science Instruments, U.S.A.), with current increased from 0 to 1, 2.5, 5, 7.5, 10, 12.5, and 15 mA with 20 min at each set current. For the larger cathodes (40 cm²), CP tests were conducted under abiotic conditions using the large scale MEC reactor description above, except the counter electrode was a single mixed metal oxide electrode (IrO₂ coated on Ti substrate, 4.5 × 7.5 cm²; Rio Grande #335422). Current was increased from 0 to 35 mA in 5 mA increments, and both electrolytes (50 mM PBS) were recirculated at a rate of 40 mL/min.

**MEC Construction and Operation.** Smaller MECs (28 mL) were made from cubes of Lexan drilled to produce cylindrical chambers (4 cm long, 3 cm diameter), and those cubes were used as the anode and cathode chambers. For the cathode chamber, a glass tube (length, 7.5 cm; diameter, 1.5 cm) was attached on the top for gas collection, and sealed with a thick butyl rubber stopper as previously described.33 A gas collection bag (0.1 L, Calibrated Instruments, NY) was 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, and an anion exchange membrane (AEM, Selenium AMV, AGC Engineering Co. Ltd., JP) was placed between the anode and cathode chambers. Four MECs were used to test the AC-Ni cathodes (AC-Ni2.2, AC-Ni4.4, and AC-Ni8.8) and AC control. The cathodes were placed in the middle of the cathode chamber, and connected to the circuit using a titanium wire.

The synthetic fermentation effluent (anolyte, conductivity: 6.5 mS/cm) was prepared as previously described.28 The solution contained 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 PBS (Na₂HPO₄, 4.58 g; NaH₂PO₄, 2.13 g; NH₄Cl, 0.31 g; KCl, 0.13 g in 1 L of DI water with mineral and vitamin solutions). The total chemical oxygen demand (COD) of the solution was 1.2 g/L. The catholyte (conductivity: 5.5 mS/cm) was 50 mM PBS without nutrients.

Microbial anodes were acclimated using domestic wastewater from the Pennsylvania State University Wastewater Treatment Plant for over 6 months in a microbial fuel cell (MFC) with an air-cathode and PVDF membrane diffusion layer,29 and switched to MEC mode with synthetic fermentation wastewater as an anolyte for this study. Both anolyte and catholyte were completely replaced at the end of cycle (~24 h for one cycle), and 0.9 V was applied using a power supply (BK Precision, U.S.A.) over the cycle. Prior to each cycle, the catholyte was deoxygenated using high purity nitrogen gas for 5 min. Current generation was monitored using a multimeter (Model 2700, 7132 DOI: 10.1021/acs.est.7b06005 Environ. Sci. Technol. 2018, 52, 7131–7137
Keithley Instruments, Inc., OH) by measuring voltage across a 10 Ω resistor.

A larger two-chamber MEC (anode chamber, 100 mL; cathode chamber, 68 mL) was constructed as previously described, and used to examine the performance of a larger AC-Ni cathode relative to a Ni foam control with catholyte recirculation. Previous tests have shown that flow past the cathode can substantially improve cathode performance. The anode chamber contained 8 graphite fiber brushes (4.5 cm length, 0.8 cm diameter, Mill-Rose, Mentor, OH). A synthetic fermentation effluent was continuously fed to the anode chamber using a peristaltic pump (Model No. 7523-90, Masterflex, Vernon Hills, IL) at 0.5 mL/min (hydraulic retention time, HRT = 8 h). Catholyte (50 mM PBS) was recirculated through the cathode chamber using a peristaltic pump at the rate of 40 mL/min. The cathode was either an AC-Ni8.8 electrode or nickel foam (active surface area of 40 cm²). Nickel Dissolution Tests. Tests were conducted using the AC-Ni4.4 electrode to investigate possible Ni losses from the AC-Ni electrodes at different pHs. The electrodes were soaked in glass beakers with 50 mM PBS solutions (in duplicate) at pHs of 2, 7, and 12 using a strong acid or base, since metal adsorption can be greatly impacted by the solution pH. Solutions containing the electrodes or AC-Ni4.4 powder were shaken at 250 rpm (MAXQ 4000, ThermoScientific, U.S.A.), and periodically sampled for the concentration of Ni in solution using inductively coupled plasma atomic emission spectrometry (ICP-AES, PerkinElmer Optima 4300 UV, U.S.A.). All tests were conducted in room temperature (24 °C).

AC-Ni Electrode Regeneration Tests. To determine if Ni loss from the cathode could be restored, Ni was removed from the cathode by an acid washing procedure. An AC-Ni4.4 electrode was soaked in 50% ethanol solution for at least 30 min to wet the hydrophobic PVDF layer of the electrode, rinsed with deionized water, and then submerged in 1 M hydrochloric acid (HCl) solution for at least 4 h. The acid-washed electrode was first soaked in 50% ethanol solution for 30 min, rinsed, and then soaked in a 1 M NiCl₂ solution to readsorb Ni onto the AC. Abiotic electrochemical tests were conducted, as described above, after acid washing and readsorption treatment, to determine the impact on cathode performance. Successive acid washing and readsorption tests were conducted to determine the impact of multiple treatments on performance.

Analytical Methods and Calculations. Electrode surfaces were imaged using scanning electron microscopy (SEM, Nano NanoSEM 630, FEI Company, U.S.A.), and energy dispersive X-ray spectroscopy (EDS, Silicon Drift Detector-X Max³, Oxford Instruments, U.K.). Gas collected from the gas bag was analyzed for hydrogen using a gas chromatograph (Model 8610B, SRI Instruments Inc., U.S.A.), and the hydrogen production rate (L-H₂/Lreactor/d) was calculated based on the energy of the hydrogen recovered compared to the electrical energy input, were calculated as previously described.33

Results and Discussion

SEM and EDS Analyses. Both nickel and chloride ions were observed on the AC-Ni electrode surface based on analysis using EDS (Figure 1). On the plain AC electrode, carbon (deep blue color) was predominantly observed, and as more Ni was added the dark blue color faded as the colors for nickel (green) and chloride (yellow) became more predominant at increasing concentrations of Ni in the AC powder. SEM images demonstrated that Ni can be successfully added to the surface of the AC electrodes.

Chronopotentiometry Tests. AC-Ni electrodes produced lower potentials than the plain AC electrode at all applied current densities (Figure 2). For example, the plain AC cathode produced −0.94 V at 3.5 A/m² while AC-Ni cathodes produced less negative potentials at the same current density: AC-Ni2.2, −0.88 V; AC-Ni4.4, −0.83 V; and AC-Ni8.8, −0.83 V. These results clearly showed that the adsorbed Ni could improve catalytic activity of the AC-based electrode for HER. The changes in the current densities with Ni adsorption varied depending on the current range. Increasing the proportion of Ni in the AC electrodes produced lower potentials at the lower current densities (<4 A/m²), but a different trend with the amount of adsorbed Ni was observed for higher current densities (Figure 2). At current densities <4 A/m², for example, the AC-Ni8.8 showed the lowest potential among other AC-Ni electrodes. However, AC-Ni18.8 and AC-Ni4.4 produced higher potentials than AC-Ni2.2 at current densities >4 A/m². Also, AC-Ni electrodes produced similar potentials (within a standard deviation range) to Pt electrodes (−0.75 V) at current densities of 3.5 A/m², although significantly lower potentials were produced with a Pt electrode.
The highest hydrogen production production rates in MECs increased with the proportion of Ni (24 h) was 0.30 more negative cathode potential. Hydroxide ions on the porous AC electrode, could result in a at the higher current densities due to higher production rates of hydroxide ions on the porous AC electrode, could result in a more negative cathode potential.

**MEC Performance with AC-Ni Cathodes.** Hydrogen production rates in MECs increased with the proportion of Ni in the cathodes (Figure 3A). The highest hydrogen production for the AC-Ni cathodes, normalized to the complete batch cycle (24 h) was 0.30 ± 0.02 L-H2/L/d (AC-Ni8.8 cathode), with significantly lower rates (student t-test: p < 0.05) obtained for the other two cathodes (0.28 ± 0.02 L-H2/L/d, AC-Ni4.4; and 0.27 ± 0.03 L-H2/L/d, AC-Ni2.2 (n ≥ 15 cycles). The hydrogen production rate with the AC-Ni8.8 was 58% higher than that of the plain AC cathode (0.19 ± 0.03 L-H2/L/d). The performance of the different catalysts is more clearly based on the maximum current density at the start of the cycle (averaged over the first 5 h) rather than the hydrogen production (which was averaged over the whole 24 h cycle). The three AC-Ni catalysts all produced higher maximum current densities compared to the plain AC, with the Pt having the highest current density (Figure 3A).

These hydrogen production rates using the AC-Ni cathodes were comparable to those obtained using the Pt cathode (0.27 ± 0.03 L-H2/L/d). H2 production rates using these two-chamber MECs (0.5−0.7 L-H2/L/d)27,35 were lower than those reported using single-chamber MECs (1.3−1.7 L-H2/L/d)12,14 due to the lower internal resistances of single-chamber MECs. However, a two-chamber MEC design was chosen for this study to avoid loss of the hydrogen by biological conversion to methane.36 Also, a high concentration of protein (BSA) was used in a complex synthetic fermentation solution here to mimic that produced during fermentation of cellulose, which would result in lower H2 production rates than other two-chamber MEC studies using only acetate in the medium.4

Cathodic hydrogen recoveries and energy yields showed similar trends with hydrogen production rates relative to the Ni content of the electrodes (Figure 3B). The AC-Ni8.8 had the highest energy recovery of rcat = 88 ± 2%, and energy yield of ηE = 120 ± 4%. The plain AC cathodes had the lowest hydrogen energy recovery of rcat = 54 ± 12%, even though the average current density (2.7 ± 0.2 A/m2) was similar to that of the other AC-Ni cathodes (for example, 2.6 ± 0.2 A/m2 for AC-Ni8.8). Cathodic hydrogen recovery of the plain AC cathode was much lower than that of the AC-Ni cathodes, likely due to the lack of catalyst for HER. Cathodic hydrogen recoveries below 100% obtained by AC-Ni cathodes were likely due to hydrogen gas losses through reactor fittings and diffusion into the anode chamber. The much lower hydrogen recoveries for the plain AC cathode suggest current generation in the absence of hydrogen gas evolution, possibly through parasitic reactions due to the lack of adequate formation of hydrogen gas. The results given in Figure 3 were based on at least 15 cycles of operation for each cathode. The performance of the AC-Ni cathodes was maintained for over 30 d of operation (Figure S4).

**Nickel Dissolution Tests.** Ni dissolution test was conducted at different pHs since catholyte pH in MECs varies from neutral to basic due to proton consumption, and different form of Ni-adsorbed AC (e.g., AC powder and AC-Ni electrode) were tested to see if the PVDF binder impacts on Ni dissolution. As a result, less Ni dissolution was observed as the solution pH increased (Figure 4). At pH 12, for example, no dissolved Ni was detected in the solution (detection limit: 0.005 mg/L) over 50 h regardless of the form of AC. At neutral pH (pH 7), less than 100 mg/L of Ni was detected in the solution after 24 h but no further dissolution was observed since then. Catholyte pH of MECs generally starts at neutral (pH 7) but the pH increases as protons are consumed (or hydroxide ions are produced) for hydrogen production.7 Thus, the pH range of catholyte during MEC operation would not be an issue for Ni dissolution from the AC-Ni cathode which supports the result of longevity test that showed maintained performances over 30 days of operation (Figure S4).

At pH 2, however, Ni concentration in the solution reached up to ~400 mg/L with AC powder form within 10 h. Ni dissolution
increased as solution pH became acidic since carbonyl groups on the AC surface (−CO\(^{-}\)) are protonated under acidic condition.

With a PVDF binder, much less amount of Ni was dissolved into the solution even with acidic condition. At pH 7, 41% less Ni was dissolved into the solution with a PVDF binder, and 52% less Ni was dissolved at pH 2 (Figure 4). This result is likely due to the PVDF layer which was induced by a phase inversion technique. In a previous MFC study, the PVDF layer induced by the phase inversion greatly improved water pressure resistance of the porous AC cathode.\(^2\) The PVDF concentration used in this study was lower than the previous study, but we conclude that the hydrophobic PVDF layer might be able to prevent Ni dissolution from AC surface.

**AC-Ni Electrode Regeneration tests.** To examine the potential for regeneration of the cathode by adsorbing additional Ni, a new cathode was first acid washed (using a 1 M HCl) to remove Ni prior to regeneration by Ni adsorption. While acid washing reduced performance as demonstrated by a more negative potential at the same current densities (7.1 A/m\(^2\)) of the original and acid-washed AC-Ni electrodes produced more positive potentials than plain AC likely due to some Ni salts that were strongly embedded into the AC pores or bound between AC with PVDF binder.

To demonstrate the Ni regeneration process, the cathode (acid treated to remove Ni) was immersed in a 1 M NiCl\(_2\) solution, and then chronopotentiometry tests were conducted. The regenerated cathode showed an improved catalytic rate even compared to the original cathode. For example, the regenerated AC-Ni produced potential of −0.87 V at 7.1 A/m\(^2\) while the original and acid-washed AC-Ni electrodes produced a more negative potential (−1.07 V) (Figure 5). A second acid treatment, produced results similar to that of the AC following the first acid wash, and a second regeneration step using the 1 M NiCl\(_2\) also restored the AC-Ni cathode to that obtained after the first regeneration step (Figure S6). These results indicate that AC particles in the AC-Ni electrode still can adsorb Ni salts in the solution even after electrode fabrication, which makes it possible to use the AC-Ni electrodes for a long time without full replacement of the cathode. This type of regeneration process Ni addition would not be possible for other types of cathodes that might undergo a reduction in performance, such as SS cathodes or Ni foam. This ability to regenerate, and even further improve the cathode performance, is a good advantage of the AC-Ni cathodes compared to other types of cathodes in MECs.

**Larger MECs with Catholyte Recirculation.** The AC-Ni8.8 was further investigated in a larger scale (40 cm\(^2\) cathode area) with catholyte recirculation, to minimize mass transport limitations on the electrode surface, and compared to a Ni foam cathode. The MEC with AC-Ni8.8 produced hydrogen production rate of 1.1 ± 0.1 L-H\(_2\)/L/d and current density of 3.9 ± 0.3 A/m\(^2\) during continuous flow operation for 7 days (Figures 6 and S8). When the Ni foam cathode was tested in

![Figure 4](image1.png)

**Figure 4.** Concentration of Ni dissolved into the PBS from the Ni-adsorbed AC powder (AC-Ni powder) and AC-Ni electrode (AC-Ni-PVDF) at different pHs (2, 7, and 12). Dissolution tests were conducted in duplicate. Error bars indicate range of duplicate results.

![Figure 5](image2.png)

**Figure 5.** AC-Ni electrode tests using all new cathodes. The green diamonds show the impact of the acid washing on a new AC-Ni, which has decreased performance due to Ni removal. The purple squares show results after the acid washed cathode underwent regeneration by additional Ni adsorption. Error bars indicate standard deviation (n ≥ 2).

![Figure 6](image3.png)

**Figure 6.** Comparison of MEC performances (hydrogen production rate, current density, cathodic hydrogen recovery, and energy yield) with AC-Ni8.8 and Ni foam cathodes in a continuous flow mode larger-scale MEC (total volume: 168 mL) with catholyte recirculation. Error bars indicate mean ± standard deviation (n ≥ 5).

same MEC under the same operational condition, the MEC with the Ni foam produced a slightly lower average hydrogen production rate (1.0 ± 0.1 L-H\(_2\)/L/d) and current density (3.4 ± 0.3 A/m\(^2\)). The better performance of AC-Ni8.8 in the MEC was primarily due to the slightly larger cathodic H\(_2\) recovery of the AC-Ni8.8 cathode (r\(_{cat} = 106 ± 3\%\)) than Ni foam (r\(_{cat} = 101 ± 9\%\)) (Figure 6). Cathodic H\(_2\) recovery rates should not
be greater than 100%, and thus these results are likely just indicating that cathodic recoveries were ~100% for both cathodes.

Cost and Performance Analysis. The cost of the AC-Ni cathodes was estimated to be $18/m² based on the cost of materials used to make them (Table S1). This materials cost is slightly less than the price of Ni foam ($20/m²), but this is not a direct comparison due to the differences in the basis of the estimates. It is difficult to estimate the AC surface area covered by Ni salts, but the highly porous structure of AC-Ni can potentially provide more surface area for the Ni relative to flat-plate type electrodes, for example flat sheets of different types of SS and Ni that have been previously investigated for use in MECs.† The specific surface area of the activated carbon was very high (2500 m²/g or 664286 m²/m²-projected area as reported by others[21]) and thus it could potentially provide a much higher surface area for the Ni catalyst than the Ni foam (0.047 m²/g or 128 m²/m²-projected area, as reported by Jeremiass et al. using a nitrogen adsorption test†). The mass of nickel needed per area of electrode is also reduced using the AC-Ni cathodes compared to Ni foam cathodes. For example, the amount of nickel in the Ni foam cathode (as tested in this study) was 50 mg-Ni/cm² (assuming the foam is 100% nickel). However, only 8.8 mg-Ni/cm² was needed to fabricate the AC-Ni8.8 electrode, which had a hydrogen production rate here similar to that of the Ni foam. The use of less Ni to fabricate a cathode would be helpful in reducing the environmental burden of using this metal for the environment. In addition, catalyst performance could easily be restored by a simple adsorption process if the cathode performance declined over time. In terms of fabrication methods, the manufacturing of the AC-Ni electrodes requires only a relatively simple phase inversion process, and addition of the Ni salts in water. This would be economically feasible to use this approach to make cathodes regeneration ability of the AC-Ni cathode, it should be estimated to be $18/m² based on the cost of materials used to make them (Table S1). This materials cost is slightly less than the price of Ni foam ($20/m²), but this is not a direct comparison due to the differences in the basis of the estimates. It is difficult to estimate the AC surface area covered by Ni salts, but the highly porous structure of AC-Ni can potentially provide more surface area for the Ni relative to flat-plate type electrodes, for example flat sheets of different types of SS and Ni that have been previously investigated for use in MECs.† The specific surface area of the activated carbon was very high (2500 m²/g or 664286 m²/m²-projected area as reported by others[21]) and thus it could potentially provide a much higher surface area for the Ni catalyst than the Ni foam (0.047 m²/g or 128 m²/m²-projected area, as reported by Jeremiass et al. using a nitrogen adsorption test†). The mass of nickel needed per area of electrode is also reduced using the AC-Ni cathodes compared to Ni foam cathodes. For example, the amount of nickel in the Ni foam cathode (as tested in this study) was 50 mg-Ni/cm² (assuming the foam is 100% nickel). However, only 8.8 mg-Ni/cm² was needed to fabricate the AC-Ni8.8 electrode, which had a hydrogen production rate here similar to that of the Ni foam. The use of less Ni to fabricate a cathode would be helpful in reducing the environmental burden of using this metal for the environment. In addition, catalyst performance could easily be restored by a simple adsorption process if the cathode performance declined over time. In terms of fabrication methods, the manufacturing of the AC-Ni electrodes requires only a relatively simple phase inversion process, and addition of the Ni salts in water. This would be relatively simple compared to other methods that use Ni materials that require high temperatures or electrodeposition. Since further Ni adsorption is possible even after electrode fabrication, the functioning of Ni catalyst for HER can be consistently maintained or regenerated during long-term operation of MECs. It is likely that MECs would be constructed from a series of anode modules and cathode modules, as described for MFCs. Thus, it should be a simple procedure to remove a cathode module and soil it in a nickel salt solution for catalyst regeneration. Due to the low cost of materials and regeneration ability of the AC-Ni cathode, it should be economically feasible to use this approach to make cathodes and minimize the total capital costs of large-scale MECs in the future.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b06005.

Illustration of preparation procedures for AC-Ni electrodes, SEM images and EDS spectra of AC-Ni electrodes, a longevity test result of AC-Ni electrodes, CP test for plain AC and acid-washed plain AC electrode, CP test and continuous MEC operation results for a larger-scale AC-Ni and Ni foam, result of cyclic voltammetry test for AC-Ni and Ni foam electrode, and price comparison of electrodes (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by funds provided by the US Department of Energy (DOE) Energy Efficiency and Renewable Energy (EERE) Fuel Cell Technologies Office, through a contract from the National Renewable Energy Laboratory (NREL), Project #21263.

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