Nickel based catalysts for highly efficient H₂ evolution from wastewater in microbial electrolysis cells

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Abstract

The high cost and over-potential loss of the cathode are primary bottlenecks of the microbial electrolysis cell (MEC) technology for efficient H₂ production from renewable biomass. In this study, novel NiFe layered double hydroxide (NiFe LDH) electrocatalyst was directly grown on nickel foam for H₂ evolution from actual brewery wastewater and its fermentation effluent. The new cathode demonstrated comparable high H₂ rate (2.01–2.12 m³-H₂/m³/d) with benchmark Pt catalyst but showed higher H₂ recovery (76–80% vs. 55–66%), which is twice as much as the rate obtained from popular stainless steel mesh and bare nickel foam cathodes. More interestingly, different from the Pt-coated cathode, the NiFe LDH/Ni foam cathode demonstrated very stable and even increased performance overtime when operated in real wastewater. The one-step *in situ* growth of catalyst on nickel substrate eliminates polymer binders and current collector, which greatly simplifies the manufacture process and reduces costs in large scale systems.

Key words: NiFe layered double hydroxide (NiFe LDH), nickel foam, microbial electrolysis cell (MEC), hydrogen production, wastewater treatment, fermentation

1. Introduction

High rate H_2 production from renewable sources is critical for fuel cells and renewable energy infrastructure development. Bio- H_2 production from wastewater carries additional benefits of waste treatment and reuse, and the wastewater facilities can potentially become distributed H_2 sources for vehicle recharging. Microbial electrolysis cell (MEC) is a promising technology that can generate H_2 from wastewater with high efficiency [1]. In an MEC reactor, exoelectrogenic microbes oxidize organic substrates into electrons and release protons (H^+). The electrons are accepted by anode and then transferred to the cathode to reduce H^+ and produce H_2 . A small voltage of 0.2~1.0 V is generally used to overcome the thermodynamic barrier, which is much less than the 1.8~2.0V used in alkaline water electrolysis [2].

MEC has been shown with the capability of producing high yield H_2 from wastewater (>60 % recovery) and can function even in low temperatures [3-5]. This feature overcomes the limits of H_2 generation from mesophilic or thermophilic fermentation, which requires heating and showed much lower H_2 yield (~17 % recovery) [5, 6]. However, one major challenge faced by MEC technology is the high cost and high over-potential loss of the cathode. Precious metal Pt was initially used as the MEC cathode to reduce over-potential of hydrogen evolution reaction (HER) [7, 8], but its high cost and poisoning by sulfide hinders its application in real wastewater conditions. Lower cost alternatives such as stainless steel (SS) in the form of disk, brush and mesh was used as both the cathode and catalyst. SS brush cathode has large specific surface area ($810\text{ m}^2/\text{m}^3$) and obtained comparable H_2 rate with

carbon cloth cathode with Pt catalyst [9], but it suffered several problems, such as bubble entrapment and complication of MEC configuration due to its large volume, which significantly reduced its application potential [10]. SS mesh has compact configuration and produced the same H₂ amount as Pt cathode but with a disadvantage of lower H₂ production rate in both phosphate and bicarbonate buffered solutions [11]. Many nano-materials have been tested as catalysts in MECs, such as MoS₂ or MoS₂ modified carbon materials [12-15], modified carbon nanotube [16, 17], and precious metal Pd nanoparticles, but the performance varied significantly. For example, though MoS₂ was considered an ideal alternative to Pt due to high catalytic efficiency and lower cost, but it suffered reduced performance when was used in real wastewater conditions [13]. In this context, nickel or nickel alloy based cathode material showed good potential, because it was reported to have low HER over-potential loss and achieved comparable H₂ yield and rate with Pt cathode in pH-neutral solution, though they have traditionally been used in alkaline water electrolysis. Different forms of nickel alloys (e.g. NiMo, NiW, NiFeMo, NiFe, NiFeP, NiFeCoP, and NiCr,) and nickel particles can be electrochemically or chemically deposited on carbon-based materials as MEC catalysts [18-24]. Early studies proved that when nickel foam was used directly as the MEC cathode in synthetic acetate medium, up to 50 m³-H₂/m³-reactor/day H₂ could be produced [25]. Similarly, nickel mesh also achieved decent performance [26].

In this study we present a new NiFe layered double hydroxide (NiFe LDH) catalyst for HER in MECs. Compared with reported Ni based catalysts, this is a novel 3D structure with vertically aligned nanoplate film directly grown on nickel foam surface with strong bindings

achieved through a simple one-step hydrothermal growth, which is easy to be operated in large-scale. The nickel foam served as a current collector is more conductive than graphite-based materials. NiFe LDH cathode was firstly developed for oxygen evolution or HER in alkaline solutions, which demonstrated that the 3D architecture promoted ion penetration that increased electrochemically active surface area and reduced energy loss caused by poor mass transfer or pH gradient. [27-29]. The compact shape of nickel foam also enables easy manufacturing of sandwiched electrode assembly to reduce internal resistance and system scale up. To investigate the catalyst's real-world potential, actual brewery wastewater instead of acetate was used as the sole substrate, and the new NiFe LDH/Ni foam cathode was side by side compared with other commonly used cathodes including traditional carbon cloth with Pt catalyst, stainless steel mesh, bare nickel foam and nickel foam coated with Pt. Detailed material characterizations were also performed on the cathode after operation to demonstrate material durability and sustainability.

2. Experimental

2.1. Brewery wastewater and fermentation effluent used in the study

Raw brewery wastewater was obtained from Avery Brewing Company in Boulder, Colorado, USA. The raw wastewater contains 3664 mg-COD/L, 2126 mg-hexose/L, and 364 mg-protein/L. The pH was 4.59 and conductivity was 0.75 mS/cm. In some experiments, the wastewater was pre-fermented for 4 days with heat treated anaerobic sludge as the inoculum. Fermentation H₂ was generated at 37 °C. The fermentation effluent had a pH of 3.58 and conductivity of 0.95 mS/cm, and it contained 4104 mg-COD/L, 475 mg-hexose/L, and 313

mg-protein/L. Both raw brewery wastewater (BWW) and its fermentation effluent (FE) were used as substrates in respective MEC experiments, and both were diluted with phosphate buffered solution (PBS) to COD concentrations of 986–1171 mg/L and conductivities of 7.0 mS/cm (pH = 7) before being fed into MECs, so the results can be compared based on similar initial substrate condition.

2.2. Reactor operation and electrode materials

Single-chamber cubic MEC reactors were constructed as previously described (3 cm diameter and 4 cm length) [30]. The working volume of each reactor was 25 ml. The anode was carbon brush (2 cm diameter and 2.5 cm length) with a titanium wire as the core [31], and the cathode varied based on experiment need. A 15 mL glass tube was mounted above the cathode and connected with a 100 mL gas bag (Cali-5-Bond, Calibrated Instruments Inc.) for gas collection. A voltage of 0.8 V was applied between the anode and cathode for each experiment.

Five types of cathodes with the same effective projected area (7 cm^2) were investigated in MECs, and Fig. S1 shows the images of the electrodes (Supplementary material, Fig. S1). They include (1) nickel foam (purity > 99.99%, 1.6 mm thickness, porosity $\geq 95\%$ with 80-110 pores per inch and average hole diameter of 0.25mm; MTI Corporation, CA, USA); (2) nickel foam coated with 0.5 mg/cm^2 Pt (10 wt% Pt/Carbon black, Sigma-Aldrich) using 5% Nafion as the binder; (3) nickel foam coated with NiFe layered double hydroxide film (NiFe-LDH) with procedure described below; (4) carbon cloth (CC) (30% wet proof, Fuel Cell Earth LLC, MA, USA) coated with 0.5 mg/cm^2 Pt using 5% Nafion as the binder; and (5)

stainless steel (SS) mesh (type 304, 90 mesh, 0.0035" wire diameter and 0.0076" opening size). For the same 7 cm² effective projected cathode area, the NiFe LDH/Ni foam and Pt/CC each had a specific surface area of 1.03 and 1.38 m², respectively, based on BET surface area analysis (N₂ gas physisorption), while SS mesh had a calculated surface area of 83.37 cm² [10].

NiFe LDH nanoplate film on nickel foam was grown *in situ* via a one-step hydrothermal growth method [27, 28]. Briefly, a piece of nickel foam (4.5 cm × 6.5 cm) was sequentially cleaned with concentrated HCl, deionized water and absolute ethanol for 5 min each to remove the surface oxide layer. After that, 0.73 g Ni(NO₃)₂·6H₂O, 1.01 g Fe(NO₃)₃·9H₂O and 1.50 g urea were dissolved in 180 mL deionized water. The solution and the cleaned nickel foam were then transferred to a 250 ml Teflon-lined stainless-steel autoclave, which was sealed and maintained at 120 °C for 12 h in an oven. After being cooled to room temperature, the nickel foam was washed by deionized water and dried at 80 °C for 6 h. While it was difficult to accurately measure the mass-loading of NiFe-LDH on the Ni foam due to partial dissolution of Ni substrate into the solution by the Fe³⁺ oxidation, an estimated value of 0.9 mg/cm² was obtained based on the growth of Ni(OH)₂ film and the size of nanoplates to NiFe-LDH [27]. This loading is larger than the Pt loading (0.5 mg/cm²) used in the study, but the normalized the cost of the Ni-cathode is still much lower based on the HER performance.

2.3 Analyses and calculations

For each MEC test, the voltage (*U*) across a 10 Ω resistor was measured continuously by a

data acquisition system (model 2700, Keithley). The current was calculated using the equation $I = U/R$. The produced gas was collected in the gas bag and the composition (H_2 , CH_4 and CO_2) was analyzed by a gas chromatograph (Model 8610C, SRI Instruments) equipped with a thermal conductivity detector using nitrogen or helium as the carrier gas [32]. The gas volume was measured using a gastight syringe. Chemical oxygen demand (COD) of the electrolytes was measured using a standard method (HACH Company). Solution pH and conductivity were measured by a multi-parameter probe (HQ440d, HACH Inc.). Soluble protein and carbohydrate concentrations in wastewater were determined using a Bicinchoninic Acid Assay (BCA Protein Assay Kit, Pierce) and the phenol-sulfuric method [33]. Scanning electron microscope (SEM) images and energy dispersive X-ray spectroscopy (EDS) were obtained using a JEOL JSM-6480 electron microscope. X-ray photoelectron spectroscopy (XPS) analysis was carried out by a Kratos Axis His spectrometer [34]. X-ray diffraction (XRD) was carried out on a Panalytical X'Pert diffractometer using Cu radiation at 45KV/40 mA. Scans were run over the range of 10-90° with a step size of 0.0131 and a counting time of 250 s per step. The specific surface area of electrode was determined by a Micromeritics Tristar II 3020 analyzer with N_2 adsorption using the 5-point BET method. Linear sweep voltammetry (LSV) was conducted by a potentiostat (PCI4/300, Gamry Instruments, NJ) in a three-electrode arrangement including a working electrode (tested cathode), a reference electrode (RE-5B Ag/AgCl 197 mV vs. SHE; BASi, IN) and a counter electrode (Coiled platinum wire, 23 cm length and 0.5 mm diameter; BASi, IN) at a scan rate of 1 mV/s with 50 mM N_2 -saturated PBS solution (pH = 7, conductivity = 7.0 mS/cm) as the electrolyte [35]. The scan was carried out several times till stable LSV curves were obtained

and used for analysis. The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 10^{-2} to 10^5 Hz with an AC voltage amplitude of 5 mV at various HER overpotentials of 100, 200 and 350 mV.

Coulombic efficiency (C_E , %), cathodic H_2 recovery (r_{cat} , %), overall H_2 recovery (R_{H_2} , %), volumetric current density (I , A/m³), H_2 production rate (Q , m³-H₂/m³/d) and energy efficiency relative to electrical input (η_E , %) were used to evaluate the performance of MECs [30]. Detailed calculation methods can be found in the Supplementary Materials. In the MEC experiments, the same anode was paired with different cathodes to eliminate the discrepancy due to variations of anodes in different reactors. Under each condition with different substrates and cathodes, two parallel reactors were operated over 10 batch cycles (more than 200 hours), and the stable values were averaged and reported.

3. Results and discussion

3.1. Substrate degradation, current and H_2 production in MECs with different cathodes

The MECs were operated over 10 batch cycles under each cathode condition, and system performance and representative current density profile under each condition are summarized in Table 1 and Fig. 1, respectively. For all batches, nearly complete removals of COD (87–94%), protein (100%) and carbohydrates (~95%) were observed in both raw wastewater and fermentation effluents, indicating a vibrant anode reaction and MEC's effectiveness on treating brewery wastewater at a COD range of 1000 mg/L.

Among the 5 types of cathodes tested, the Pt coated carbon cloth and nickel foam

generated the highest current densities of 220–232 A/m³, which were about 15% higher than the current density from NiFe LDH/Ni foam cathode (186–197 A/m³) (Fig. 1). However, the NiFe LDH/Ni foam cathode obtained very comparable H₂ production rates as the Pt-coated electrodes (2.01–2.12 m³-H₂/m³/d). While this partially confirms previous studies that current density cannot be a sole indicator of H₂ production performance in MECs [36], in this case the higher cathodic H₂ recovery was believed the main factor leading to excellent H₂ generation NiFe LDH/Ni cathode. It obtained a cathode efficiency of 97–99%, approximately 15% higher than the Pt-coated cathodes (80–84%), which suggests a higher proton reduction efficiency on the surface. The NiFe LDH/Ni foam cathode has a total surface area of 1.03 m² (7 cm² projected area), which is ~30% less than the Pt/CC cathode (1.38 m²). This also supports that the high H₂ evolution on the NiFe LDH/Ni was due to the higher catalytic activity rather than the higher specific area. NiFe LDH/Ni foam cathode also showed higher overall H₂ recovery (76–80% vs. 55–66%) and energy efficiency relative to electrical input (190–192% vs. 157–170%) than the Pt cathodes. These results can be translated to higher energy recovery from wastewater and thus lower cost of manufacturing and operation. The Ni foam and SS mesh cathodes produced lower current densities of 140–141 A/m³ and 130–136 A/m³, respectively, which lead to ~50% lower H₂ production rates obtained by NiFe LDH and Pt catalyzed cathodes. This shows that NiFe LDH catalyst is essential for enhancement of H₂ production compared to nickel alone due to its activation of HER. SS mesh has a specific surface area of 83.37 cm², two orders of magnitude lower than NiFe LDH/Ni foam and Pt/CC cathodes, which may explain its low H₂ production performance. The CH₄ concentration was below detection limit, which was desired to maintain H₂ purity and reduce H₂-reconsumption.

This was partially accomplished by exposing the anode to air for 15 min during media replacement and keeping short operation cycles (around 200 hours). The CO₂ concentration ranged 6–9% in the produced gas, and it can be removed by post-purification process well established in chemical industry.

3.2. Electrochemical characterizations reveal increased performance of Ni cathodes

An interesting behavior was found during the experiment on the NiFe LDH/Ni foam cathode, which is that unlike other materials, the cathode performance and H₂ evolution significantly increased overtime and stabilized after around 120 hours or 6 batch cycles (data not shown). This change was observed under a stable anode potential and performance as well as constant substrate conditions. Such increased HER catalytic activity was reported in MECs using SS brush cathode [9], which was explained as a result of SS corrosion. The corrosion products during electrolysis were identified making SS more active toward H₂ evolution. To understand the performance changes among the cathodes, LSV targeted to cathodes was used to characterize the electrochemical properties of these materials before and after operation in MECs (Fig. 2). Fig. 2A shows the cathodic current on the NiFe LDH/Ni foam cathode almost tripled during the 120 h operation, increased from 13.0 A/m² (0 hr) to 22.9 A/m² (40 hr) then to 35.6 A/m² (120 hr) at a corresponding cathodic potential of –0.8 V (vs. SHE). This finding correlates with the H₂ production performance because the cathodic current reflects the catalytic activity of H⁺ reduction. Steeper slopes of the voltammogram indicate more effective production of H₂ by allowing a greater current at the same cathodic potential [10, 37]. Other two nickel substrate cathodes and SS cathode also exhibited slight improvement of

catalytic activity after 120 h, as indicated from the increased slope of voltammograms (Fig. 2B, 2D and 2E). However, the voltammogram of Pt/CC cathode showed a slight decrease of slope (Fig. 2C), suggesting a decline of cathodic current generation, which may be due to minor catalyst poisoning. After 120 hours, more positive currents were produced at potentials that are more positive than -0.4 V on all nickel-based cathodes in the order of NiFe LDH/Ni > Pt/Ni > Ni. Nickel-based materials were demonstrated with good catalytic activities for both OER and HER and previous studies showed that electrochemical corrosion may change their onset potential for OER in neutral PBS solution [27-29].

The onset potential needed to initiate H_2 evolution is another important measure of catalyst performance [10, 37]. The smaller the onset potential, the more effective the catalytic activity for H_2 generation due to lower over-potential loss. Fig. 2F shows nickel substrate cathodes had the smallest onset potentials of HER after 120 h. These data indicate that the nickel is the stable and excellent matrix for cathode manufacture with lower overpotential and thus lower energy loss compared to carbon or SS materials. At the cathodic potential of -0.8 V (vs. SHE), the cathodic current in decreasing order was 42.4 A/m^2 (Pt/Ni), 36.8 A/m^2 (Pt/CC), 35.6 A/m^2 (NiFe LDH/Ni), 14.2 A/m^2 (Ni), 7.4 A/m^2 (SS) and 1.2 A/m^2 (CC). Although NiFe LDH/Ni foam cathode showed slightly lower cathodic current than the two Pt coated cathodes at the most negative potential of scanning, its cathodic current was very comparable to the Pt/ Ni foam cathode and higher than that of Pt/CC cathode in most potential ranges. The bare CC cathode showed almost no catalytic activity of HER so minimal cathodic current. The linear portions of the Tafel plots were fitted to the Tafel equation ($\eta = b \log j + a$, where η is

overpotential, j is the current density and b is the Tafel slope) (Fig. S3), which yielded Tafel slopes of 267–426 and 258–393 mV/decade before and after electrolysis, respectively, on corresponding electrodes. These values are higher than that of exhibited by non-precious HER catalysts (40–120 mV/decade) or Pt (30 mV/decade) in acidic solution (0.5 M H₂SO₄) due to HER's inherently slow kinetics in neutral media [38-40], which has also been observed for MoS₂ based HER under pH = 7 [14]. Since conventional Volmer-Heyrovsky or Volmer-Tafel HER mechanism based on Tafel slope in acidic media cannot be directly applied in this condition [39, 40], further research is needed to examine the mechanism of HER occurred under neutral environment. The exchange current density (j_0) at equilibrium reflects intrinsic rates of electron transfer between the electrolyte and the electrode, which is expected proportional to catalytically active surface area [38]. The higher the exchange current density, the lower the overpotential that must be realized for maintaining a net flow of current. The j_0 of NiFe LDH/Ni foam cathode significantly improved by 5 times (from 0.65 to 3.68 mA/m²) after 120 h electrolysis, which has also been observed by Ni (0.60 to 1.45 mA/m²) and SS (0.29 to 0.36 mA/m²) cathodes. On the contrary, the j_0 decreased for two Pt catalytic cathodes (Pt/Ni: 4.19 to 3.64 mA/m² and Pt/CC: 3.95 to 1.08 mA/m²). These results support the findings obtained by LSV that electrolysis affects HER performance of electrodes. The EIS profiles of Ni substrate electrodes showed a smaller semicircle than that of Pt/CC and SS electrodes (Fig. S4) at different overpotentials, suggesting a smaller charge transfer resistance in the nickel substrate, which also support the reactor results that nickel can be a good material than carbon or stainless steel as electrode and electron collector.

3.3. Morphology evolution and element composition on Ni cathodes

The changes on morphology and element composition of the NiFe LDH/Ni foam cathode before and after MEC operation were characterized by SEM with EDS and compared with bare Ni foam cathode (Fig. 3, Fig. S5, Fig. S6). SEM images show that the mesoporous NiFe LDH film evenly grows on the nickel substrate compared to bare nickel foam (Fig. 3A1-A3, B1-B3). The EDS analysis confirms the presence of Fe, Ni and O on the film surface with a Ni : Fe ratio of 3 : 1 (Fig. S5A), which agrees with the composition of typical NiFe LDH film [27]. The $\sim 40\ \mu\text{m}$ sized crystals were found growing directly from the NiFe LDH film after electrolysis in MECs (Fig. 3C1-C3 and Fig. S5B, S6). These large crystals were analyzed by EDS (Fig. S5B), which showed that they were dominated by Fe, Ni and O though they are not NiFe LDH nanoplates, which grow vertically on the Ni substrate with size of $\sim 200\ \text{nm}$ [27, 29]. Small amounts of Mg, P and S were found in EDS spectrum, which was derived from the electrolyte despite that the cathodes were washed by deionized water and absolute ethanol before SEM analysis. The element composition of NiFe LDH/Ni foam cathodes were further characterized by XPS (Fig. 4 A-F). The results show the presence of Ni and Fe on the film surface for both new and used cathodes (Fig. 4 A and D). The high-resolution Ni 2p and Fe 2p spectra were almost constant for both cathodes with the binding energy peak of Ni 2p_{3/2} and Fe 2p_{3/2} located at 855.9 eV (new), 855.7 eV (used) and 713.3 eV (new), 713.0 eV (used), respectively (Fig. 4 B, C, E and F), indicating the mostly +2 and +3 oxidation states of Ni and Fe species, respectively [27, 29]. XRD was employed to identify the phase of NiFe LDH/Ni (Fig. 4G). The XRD pattern of cathodes was generally consistent with the typical profile of NiFe LDH coated on nickel substrate (the three huge peaks denote the Ni substrate) [27]. Ni,

Fe and $\text{Ni}(\text{OH})_2(\text{H}_2\text{O})_x$ phases were verified for both cathodes, which matched well with the characteristics of Fe precursor incorporated to $\text{Ni}(\text{OH})_2$ lattice, inducing the formation of NiFe hydroxide in the LDH structure [29]. It's worth noting that Fe_3O_4 phase including both +2 and +3 oxidation states of Fe was found on the used cathode. It is not clear whether they are directly associated with the large crystals formed after electrolysis in neutral solution. Their roles on enhancement of catalytic activity of HER will be studied further. However, it is clear that the changes in morphology and chemical structure of these cathodes due to electrochemical corrosion (Fig. S2) are beneficial for HER.

4. Conclusions

The NiFe LDH catalyst demonstrated highly efficient H_2 evolution from actual wastewater and fermentation effluents with the performance comparable with traditional Pt catalysts. Moreover, the NiFe LDH/Ni foam cathode showed better stability and improved system performance overtime than Pt-coated electrodes, showing good promise in real world applications. The *in situ* growth of NiFe LDH layer on the surface of highly conductive nickel foam simplifies the manufacture process and eliminates the need of polymer binders and current collector. The 3D electrode structure with vertical catalyst alignment creates very high reaction surface area and high strength. Considering the low cost and abundance of the Ni and Fe materials and existing manufacture practice of large scale Ni foam electrodes, these materials show great potentials for large scale MEC system development and application.

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Table 1. Performances of MECs with different cathodes for H₂ production using brewery wastewater (BWW) and its fermentation effluent (FE). The applied voltage was 0.8 V, and COD concentrations and conductivities of influent were 986–1171 mg/L and 7.0 mS/cm, respectively.

Cathode	Substrate	C_E (%)	r_{cat} (%)	R_{H_2} (%)	I_v (A/m ³)	Q (m ³ -H ₂ / m ³ /d)	η_E (%)
NiFe LDH/Nickel foam	BWW	77 ± 3	99 ± 0	76 ± 3	186 ± 0	2.01 ± 0.01	192 ± 1
	FE	82 ± 0	97 ± 1	80 ± 0	197 ± 1	2.11 ± 0.00	190 ± 2
Pt/Nickel foam	BWW	66 ± 4	84 ± 3	55 ± 2	232 ± 1	2.12 ± 0.09	170 ± 2
	FE	79 ± 1	84 ± 0	66 ± 1	220 ± 1	2.01 ± 0.00	164 ± 1
Pt/carbon cloth	BWW	66 ± 2	83 ± 0	55 ± 2	230 ± 1	2.08 ± 0.00	167 ± 5
	FE	78 ± 0	80 ± 0	62 ± 0	231 ± 2	2.02 ± 0.01	157 ± 1
Nickel foam	BWW	63 ± 0	73 ± 0	47 ± 0	140 ± 1	1.13 ± 0.01	141 ± 1
	FE	71 ± 1	69 ± 0	49 ± 0	141 ± 1	1.07 ± 0.01	133 ± 1
Stainless steel mesh	BWW	71 ± 0	76 ± 1	54 ± 1	136 ± 1	1.13 ± 0.02	145 ± 4
	FE	75 ± 4	76 ± 1	57 ± 3	130 ± 1	1.08 ± 0.02	149 ± 5

C_E : Coulombic efficiency

r_{cat} : Cathodic hydrogen recovery

R_{H_2} : Overall hydrogen recovery

I_v : Current density

Q : Hydrogen production rate

η_E : Energy efficiency relative to electrical input

Figure(s)

Fig. 1. Current densities achieved from different cathodes and two substrates in MECs. Each condition was repeated for at least 10 batches with representative profiles shown in the Figure. Current density was normalized to working volume (25 mL) of the reactor.

Fig. 2. Linear sweep voltammetry (LSV) curves of the different cathodes before, during, and after MEC operation (0, 40 or 120 hours) (A-E). All LSV graphs at 120 hours were combined in (F) for comparison purpose. Current density was normalized to cathode effective project

area (7 cm^2).

Fig. 3. Scanning electron microscope (SEM) images with different resolutions on (A1-3) nickel foam cathode; (B1-3) initial NiFe LDH/Ni foam cathode, and (C1-3) used NiFe LDH/Ni foam cathode after MEC operations.

Fig. 4. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses of NiFe LDH/Ni foam cathode before (A-C) and after (D-F) being used for electrolysis in MECs.