Hydrogen production in microbial electrolysis cells (MECs) is a promising approach for energy harvesting from wastewater. The kinetic barriers toward proton reduction necessitate the use of catalysts to drive hydrogen formation at appreciable rates and low applied potentials. Towards this end, cost effective alternatives to platinum catalysts are of paramount interest. In this study, Ni(OH)\textsubscript{2} films were synthesized by electrophoretic deposition from a Ni(II)cyclam precursor solution at varying concentrations (6 mM, 15 mM, and 23 mM). The films were characterized by scanning electron microscopy and X-ray photo-electron spectroscopy to confirm the deposition of Ni(OH)\textsubscript{2}. The Ni(OH)\textsubscript{2}-modified electrodes were then examined by both traditional electrochemical measurements and in an MEC for hydrogen production. Tafel analysis indicates an exchange current density of ~0.36 mA cm\textsuperscript{-2} with a Tafel slope of ~120 mV decade\textsuperscript{-1} consistent with a rate determining proton adsorption step. The hydrogen production rates increased with increasing Ni(II)cyclam concentration in the precursor solution, with the 23 mM-derived film exhibiting a rate comparable to that of a Pt-based catalyst in MEC tests.

In this study, a nano-Ni(OH)\textsubscript{2} modified cathode was developed by electrophodeposition from a nickel(II) cyclam (cyclam = 1, 4, 8, 11-tetraazacyclotetradecane) precursor. The synthetic method was based on a procedure of the deposition of Ni(OH)\textsubscript{2} using [Ni(en = ethylene diamine)cyclam]Cl\textsubscript{2} resulting in homogeneous, well adhered Ni(OH)\textsubscript{2} thin films. The [Ni(en)cyclam]Cl\textsubscript{2}-derived Ni(OH)\textsubscript{2} films were shown to exhibit significantly higher catalytic activity toward water oxidation than films derived from Ni(OH)\textsubscript{2} samples with similar conditions. The morphology and composition of the films generated here were investigated via scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The catalytic activity toward hydrogen production was examined through electrochemical techniques and in an MEC.

**Experimental**

**Materials.**—Reagents or analytical grade chemicals were sourced from commercial suppliers and used as received unless stated otherwise. Deionized water was used throughout the study.

**Synthesis procedure.**—Ni(II)cyclam was prepared by refluxing equimolar nickel(II) chloride hexahydrate (99.3%, Alfa Aesar) and 1,4,8,11-tetraazacyclotetradecane (>95%, Ark Pharm Inc) in dimethylformamide (DMF) (99.8% spectrophotometric grade, Spectrum) at 90 °C for 12 hours. The purple precipitate was filtered and washed with a copious amount of DMF to remove any excess Ni(II)Cl\textsubscript{2} \cdot 6H\textsubscript{2}O and then allowed to dry. This method differs slightly from typical synthetic approaches in which equimolar amounts of Ni(II)Cl\textsubscript{2} and the tetraazacyclotetradecane are dissolved in methanol at a sustained current density of 12 A m\textsuperscript{-2} (A per m\textsuperscript{2} cathode surface area). The rate of hydrogen production by the NiMo-modified carbon cloth was comparable to that of a Pt-modified carbon cloth (0.10 m\textsuperscript{3} m\textsuperscript{-2} d\textsuperscript{-1}). Commercially available nickel was also used as a catalyst coated on carbon cloth for MEC cathodes. Nickel oxide catalysts have also shown great promise as catalysts for hydrogen evolution in MECs. Electrodeposition of nickel oxide onto stainless steel and nickel alloy surfaces have been shown to improve the MEC hydrogen production from 0.0002 m\textsuperscript{3} m\textsuperscript{-2} d\textsuperscript{-1} (no Ni oxide) to 0.019 m\textsuperscript{3} m\textsuperscript{-2} d\textsuperscript{-1} at a current density of 3.25 A m\textsuperscript{-2} when a 0.9 V external voltage bias was applied.

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or ethanol and the product separated by addition of ether. Our approach affords a precipitated product in nearly quantitative yields.

The Ni(OH)₃ films were electrodeposited onto carbon cloth (PANEX 30PW03, Zoltek Corporation, St. Louis, MO, USA) with an area of 4 cm² (2 cm × 2 cm) by dissolving the Ni(II)cyclam precursor in a solution of 0.1 M NaOH. The potential was then cycled between 0 V and 1.3 V (vs Ag/AgCl) for 150 cycles. A three electrode arrangement was employed using the carbon cloth as the working electrode, a platinum mesh counter electrode, and an Ag/AgCl (sat. KCl) half-cell as the reference electrode. The electrodeposition was carried out in a one-compartment electrochemical cell under aerobic conditions at room temperature. The procedure employed was similar to that used by Singh, et al. for the deposition of Ni(OH)ₓ films onto glassy carbon electrodes and fluorine doped tin oxide electrodes from Ni(NH₃)₆, Ni(OH)₂, Ni(en)₃ (en = 1,2-diaminoethane), and other Ni(II) amine molecular precursors. The nomenclature of nano-scaled Ni(OH)₃ represents the nickel hydroxide prepared with X mM Ni(II) cyclam as the precursor where X could be 6, 15, and 23.

Characterization.—LEO (Zeiss) 1550 field emission scanning electron microscope (FESEM) operating at an acceleration voltage of 300 kV was employed to study the morphology and structural properties of the nanoparticulate films. FEI Quanta 600 FEG environmental scanning electron microscope (ESEM) with Bruker energy-dispersive X-ray spectroscopy (EDS) was used to analyze the elemental composition of the catalyst. XPS was conducted using a PHI 5300 spectrometer with a Perkin-Elmer Dual Anode X-ray source operating with monochromatic Mg Kα radiation (hv 1253.6 eV) at 13 kV and 250 W and a pass energy of 17.9 eV. A step size of 0.1 eV was used and 256 sweeps were averaged for all measurements. The photoelectrons emitted were detected by a hemispherical analyzer. Operating pressure in the sampling chamber was below 1 × 10⁻¹⁰ Torr. The spectral range for Ni 2p was 894–844 eV, N 1s was 410–390 eV, and O 1s 545–525 eV. The spectra were calibrated according to the C 1s peak at 284.6 eV.

Electrochemical analysis.—The synthesized catalysts were coated onto a piece of rectangular carbon cloth (PANEX 30PW03, Zoltek Corporation, St. Louis, MO, USA) with an area of 4 cm² (2 cm × 2 cm), which was used as a cathode electrode. A cathode coated with 0.5 mg cm⁻² Pt/C (10% wt Platinum on Carbon Vulcan, Fuel Cell Earth LLC, Wakefield, MA, USA) was prepared and served as a control. Tafel plots (scan rate 1 mV s⁻¹) were prepared with chronopotentiometric data obtained on a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA). Electrochemical experiments were conducted using a three-electrode arrangement in a PBS (1 M, 120 mL) electrolyte solution. The modified cathode electrodes served as a working electrode, a platinum wire served as the counter electrode, and an Ag/AgCl electrode (CH Instruments, Inc., Austin, TX, USA) was used as a reference electrode. The electrochemical cell was sparged with nitrogen gas for 15 min prior to each test.

MEC setup and operation.—A two-chamber MEC (Figure 1) was built by connecting two glass bottles with a cation exchange membrane (CEM) as separator (UltexCMI7000, Membranes International, Inc., GlenRock, NJ, USA), according to a previous study. The liquid volume of the anodic chamber and the cathodic chamber was 130 and 140 mL, respectively. The anode electrode was a carbon brush (Gordon Brush Mfg. Co., Inc., Commerce, CA, USA) which had been coated with a microbial fuel cell mode for three months. The anolyte contained (per liter of DI water): sodium acetate (1 g), NaCl (1 g), MgSO₄ (0.015 g), CaCl₂ (0.02 g), KH₂PO₄ (0.53 g), K₂HPO₄ (1.07 g), NaHCO₃ (1 g), and trace element (1 mL). PBS (0.1 M, K₂HPO₄ (5.3 g/L), KH₂PO₄ (10.7 g/L)) solution was used as a catholyte. An external voltage of 0.8 V was applied to the circuit by a power supply (CSIS3644A, Circuit Specialists, Inc., Mesa, AZ, USA) according to a previous study. The MEC was operated under a batch mode with an HRT of 30 h. In each cycle, part of the anolyte (60 mL) and the whole catholyte (140 mL) were replaced.

The voltage across resistor was recorded with a digital multimeter (2700, Keithley Instruments, Inc., Cleveland, OH, USA) with a time interval of 5 min. Current was calculated by Ohm’s law. Hydrogen production in the MEC was collected by water displacement and measured with a syringe. Chemical oxygen demand (COD) was measured with a DR890 colorimeter (HACH Co., Ltd., USA) according to the manufacturer’s instructions. The content of H₂ was analyzed using a Shimadzu GC-14A gas chromatograph equipped with a thermal conductivity detector (TCD).

Calculation.—Coulombic efficiency, cathodic hydrogen recovery, overall hydrogen recovery and hydrogen production rates were used to evaluate reactor performance. The total charge (C_total, C) generated by each batch cycle can be calculated based on the measured current:

\[
C_{\text{total}} = \int I \, dt \tag{1}
\]

where \(I\) is the current (A) calculated from the voltage across the resistor (10 Ω) and \(dt\) is the time interval (300 s) for data collection. The Coulombic recovery (\(C_R\)) is the ratio of electrons recovered from substrate consumption relative to the total possible electrons available due to substrate consumption, calculated as

\[
C_R = \frac{C_{\text{total}}}{nF\Delta \text{COD}} \tag{2}
\]

where \(n\) is the number of electrons released from each oxygen (4), \(F\) is the Faraday constant (96,485 C mol⁻¹ e⁻), and \(\Delta \text{COD}\) is total mole of consumed bacterial feedstock within time \(t\).

The cathodic hydrogen recovery (\(R_{\text{H₂}}\)) is the fraction of electrons that are recovered as hydrogen gas from the total generated electrons:

\[
R_{\text{H₂}} = \frac{2n_{\text{H₂}} \cdot F}{C_{\text{total}}} \tag{3}
\]

where \(n_{\text{H₂}}\) is the actual number of hydrogen moles produced.

The overall hydrogen recovery (\(R_{\text{H₂}}\)) is the ratio of generated hydrogen gas compared to the theoretical hydrogen generation based on substrate degradation:

\[
R_{\text{H₂}} = \frac{C_R \cdot R_{\text{cat}}}{} \tag{4}
\]

The hydrogen production rate (\(Q_{\text{H₂}}, \text{m}³\ H₂ \text{m}⁻² \text{d}⁻¹\)) is calculated based on the generated hydrogen gas (\(m³\)) per m² cathode electrode per day.
Results and Discussion

Ni(II) catalyst electrodeposition and electrode preparation.—
Cyclic voltammograms (CVs) of a carbon felt electrode (CFE) in the presence of 23 mM Ni(II)cyclam in a solution of 0.1 M NaOH are shown in Figure 2a. The CVs display an anodic peak at 410 mV (vs. Ag/AgCl) whose current density increases with increasing potential sweeps. The increase in current density is accompanied by a shift in the anodic peak to more negative potential up to 285 mV. The observed current increase with respect to sweep number is attributed to the deposition of nanoparticulate Ni(OH)2 species. This is consistent with literature reports of Ni(OH)2 deposition from soluble molecular Ni(II) coordination complexes as pre-catalysts on glassy carbon (GCE) as well as fluorine-doped tin oxide (FTO) electrodes in basic borate buffers and NaOH solutions.15 The Ni(OH)2 has been proposed to form by a Ni—N de-ligation mechanism in the presence of strongly coordinating basic groups.15

A plot of the anodic peak current as a function of the sweep number displays a monotonic increase in the concentration current density with a plateau at approximately 420 mA cm\(^{-2}\) M\(^{-1}\). Varying the starting solution concentration of Ni(II)cyclam had little effect on the behavior of the concentration-normalized current densities and value of the observed plateau, between 400 mA cm\(^{-2}\) M\(^{-1}\) and 470 mA cm\(^{-2}\) M\(^{-1}\) (Figure 3). The steepness of the inflections differ significantly in going from 6 mM Ni(II)cyclam to higher concentrations of Ni(II)cyclam, possibly suggesting a concentration dependent mechanism of film formation.

For comparison, the electrodeposition of Ni(OH)2 films onto CFE from a Ni(II)Cl2 · 6H2O solution was also carried out (Figure 2). The CV of Ni(II)Cl2 · 6H2O in 0.1 M NaOH displays cathodic and anodic peaks at 520 mV and 440 mV, respectively. Upon continued sweeps the anodic peak potential was observed to shift to slightly more positive potentials reaching a value of 460 mV after 30 sweeps. Much like the electrodeposition from Ni(II)cyclam, nickel hydroxide formation from Ni(II)Cl2 on the surface of the CFE (as evidenced by increasing the anodic peak current density) is monotonic as a function of increasing number of potential sweeps. Due to the poor solubility of Ni(II)Cl2 · 6H2O in 0.1 M NaOH the effect of Ni(II)Cl2 · 6H2O concentration on Ni(OH)2 formation and deposition could not be probed.
Cyclic voltammetry was performed on the Ni(OH)2 films on CFE and compared to Ni(II)cyclam in anaerobic 0.1 M TBAPF6 solutions in CH3CN. At a scan rate of 25 mV s−1 the CV of the Ni(OH)2 film displays cathodic features at −0.785 V and −1.03 V with an anodic feature at −0.555 V (Figure 4). Similar cathodic features at −0.95 V and −1.22 V with a cathodic feature at −0.68 V were observed in the CV of Ni(II)cyclam at 25 mV s−1. The origin of these features are, as of yet, uncertain. They are, however, consistent with results observed for Ni(OH)2 films deposited from other Ni(II)-amine coordination complexes.15 Their presence in the Ni(OH)2 films leads us to believe that they may be related to redox activity of Ni(OH)2 adsorbed on the electrode surface that may have formed during polarization.20 It is important to note that the reversible redox features observed with Ni(II)cyclam with E1/2 = 0.398 V and −1.61 V (vs Ag/AgCl) corresponding to the Ni3+2+/ and Ni2+/+ redox couples, respectively, are not observed in the Ni(OH)2 film.21–24

**Figure 4.** Cyclic voltammograms of a Ni(OH)2 film deposited on CFE (black – left y-axis), carbon cloth (black dash – left y-axis), and Ni(II)cyclam in solution (red – right y-axis, working electrode: glassy carbon) in anaerobic 0.1 M TBAPF6-CH3CN solutions (scan rate 25 mV/s).

**Figure 5.** SEM images of carbon cloth (a and b) and Ni(OH)2-modified carbon cloth that results from electrodeposition from a Ni(II)cyclam precursor solution at concentration of 23 mM (c and d), 15 mM (e) and 6 mM (f).

**Characterization of the nickel oxide films.**—X-ray photoelectron spectroscopy was performed for the films deposited on CFE from 6 mM, 15 mM, and 23 mM Ni(II)cyclam solutions in an attempt to elucidate the nature of the films. The spectra corresponding to the Ni 2p2/3, N 1s, and O 1s electron binding energies are shown in Figure S1. The Ni 2p2/3 and O 1s spectra were decomposed by non-linear least squares fitting using Gaussians where the peak positions and FWHM were allowed to vary. The Ni 2p2/3 and satellite signals for the 23 mM samples display similar results with Ni 2p2/3 and satellite signals at 858.0 eV (863.9 eV) and 856.2 eV (862.2 eV), as well as O 1s signals at 532.9 eV (867.5 eV) and 534.4 eV (869.6 eV), respectively, whereas the observed O 1s signal was found to be comprised of two underlying Gaussians where the peak positions and FWHM were varied to allow for the Ni 2p2/3, N 1s, and O 1s electron binding energies. The Ni 2p2/3 and satellite signals for the 23 mM sample film were adequately fit to a single Gaussian each centered at 858.5 eV and 864.3 eV, respectively, whereas the observed O 1s signal was found to be comprised of two underlying Gaussians centered at 532.8 eV and 534.4 eV. The 6 mM and 15 mM samples display similar results with Ni 2p2/3 (satellite) signals at 858.0 eV (863.9 eV) and 856.2 eV (862.2 eV), as well as O 1s signals at 532.9 eV (with second component at 534.4 eV) and 531.4 eV, respectively.

Based on the data above it is proposed that the films are Ni(OH)2 in nature.15 XPS signals for Ni(OH)2 are typically 855 eV - 858 eV for the Ni 2p2/3 and 531 eV for the O 1s binding energies, which are in agreement with the results found here (vide supra).25–27 The cause of the O 1s shift to near 533 eV is uncertain, but may be due to interactions between the Ni(OH)2 nanoparticles and oxygen functional groups on the CFE that may form during the oxidative electrodeposition process under basic conditions. These oxygen functional groups (i.e. carbonyls) on the surface of the CFE may also explain the presence of the second band at 534 eV in the 6 mM and 23 mM preparations.

SEM (with EDS) was also employed to characterize the structure of Ni(OH)2 on carbon cloth. Figure 5 shows the FESEM images of Ni(OH)2-coated carbon cloth substrates (Figures 5c–5f). For comparison, FESEM images of the unmodified cloth are also shown (Figures 5a and 5b). The carbon cloth is composed of large interwoven bunches of microfibers with a diameter of ~15 μm. The figure shows that the surface of unmodified carbon cloth is relatively rough over the size of samples (not all shown here). The SEM images (Figures 5d–5f) indicate the morphology of the Ni(OH)2 nanostructures is comprised of a network of intergrown plates. The irregularity of the orientations of the nano-plates suggest that the films may have large surface areas for reactivity. This could open up new opportunities and applications for catalytic Ni(OH)2-based materials. The Ni(OH)2 film prepared with 23 mM Ni(II)cyclam appeared denser when compared to the films prepared with lower amounts of the precursor material, suggesting the potential of an increased number of catalytic sites when making films with higher amounts of Ni(II)cyclam. This could open up new opportunities and applications for catalytic Ni(OH)2-based materials. The Ni(OH)2 film prepared with 23 mM Ni(II)cyclam appeared denser when compared to the films prepared with lower amounts of the precursor material, suggesting the potential of an increased number of catalytic sites when making films with higher amounts of Ni(II)cyclam. Figure S2 presents the ESEM images and EDS spectra of the unmodified carbon cloth and Ni(OH)2 generated from nickel(II) cyclam. All samples displayed EDS peaks corresponding to carbon, resulting from the carbon cloth base. Nickel and oxygen peaks were also present at both sites materials prepared by electrodeposition from nickel(II) cyclam solutions, indicating successful coating of the microfibers. Small amounts of iron were observed in the Ni(OH)2 modified carbon cloth likely due to the contamination during the electrode preparation.
Figure 6. a. Tafel slope for carbon cloth (green), Ni(OH)\textsubscript{2} -6 mM precursor (navy), Ni(OH)\textsubscript{2} -15 mM precursor (red) and Ni(OH)\textsubscript{2} -23 mM precursor (black) with a scan rate of 1 mV s\textsuperscript{-1} measured in PBS buffer (1 M). b-d. CV in the region of 0.1–0.2 V vs. RHE plotted against scan rate and linear regression for the $C_{dl}$ estimation with 23mM, 15 mM and 6 mM Ni(II)cyclam. Scan rate: 130 mV/s (orange), 100 mV/s (blue), 80 mV/s (navy), 50 mV/s (green), 30 mV/s (black), and 10 mV/s (red).

Tafel plots (log (current density) vs overpotential) for unmodified carbon cloth and Ni(OH)\textsubscript{2}-coated electrodes generated from nickel(II) cyclam were constructed to identify the rate limiting step of hydrogen production (\textit{vida infra}) and are shown in Figure 6. The unmodified electrode exhibits a Tafel slope of 211 mV decade\textsuperscript{-1} and an exchange current of 0.23 mA cm\textsuperscript{-2}. The Ni(OH)\textsubscript{2}-coated electrodes generated from Ni(II)Cl\textsubscript{2} \cdot 6H\textsubscript{2}O showed a Tafel slope of 201 mV decade\textsuperscript{-1}. Comparatively, the Tafel analysis of Ni(OH)\textsubscript{2}-modified electrodes generated from nickel(II) cyclam precursor solutions exhibited Tafel slopes of 105, 123, 129 mV decade\textsuperscript{-1} when the nickel(II) cyclam concentration in the deposition solution were 23, 15, and 6 mM, respectively. The exchange current was 0.34, 0.36, and 0.36 mA cm\textsuperscript{-2}, respectively.

The hydrogen evolution reaction (HER) involves three steps: the Volmer (Eq. 5), Heyrovsky (Eq. 6), and Tafel (Eq. 7) reactions, which involve adsorption of a reduced proton on a surface and chemical recombination to produce H\textsubscript{2} as outlined in Equations 5 to 7.

$$H_3O^+ + e^- \rightarrow H_{ads} + H_2O \quad [5]$$

$$H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O \quad [6]$$

$$2H_{ads} \rightarrow H_2 \quad [7]$$

The expected Tafel slopes for a Volmer, Hyrovsky, or Tafel rate-determining reaction are 120 mV dec\textsuperscript{-1}, 40 mV dec\textsuperscript{-1}, and 30 mV dec\textsuperscript{-1} respectively. Considering the observed Tafel slope of 120 mV decade\textsuperscript{-1}, the rate-determining HER step for the Ni(OH)\textsubscript{2} films prepared here is most likely the adsorption related reaction (Volmer).

The active catalytic area was estimated through determination of the electrochemical surface area (ECSA) (Figures 6b–6d). The double layer capacitance ($C_{dl}$), which is expected to be linearly proportional to the effective active surface area, can be determined through investigation of the current response of the Ni(OH)\textsubscript{2}-modified electrodes in a potential region where no faradaic processes occur. For the Ni(OH)\textsubscript{2}-modified electrodes, the region of 0.1–0.2 V vs. RHE was used. By plotting the non-faradaic (charging) current vs. scan rate the $C_{dl}$ was quantified. The $C_{dl}$s for the Ni(OH)\textsubscript{2}-modified electrodes were determined to be 2.77 ± 0.32 mF cm\textsuperscript{-2}, 2.45 ± 0.25 mF cm\textsuperscript{-2} and 1.70 ± 0.14 mF cm\textsuperscript{-2} for electrodes prepared in 23 mM, 15 mM and 6 mM Ni(II)cyclam precursor solutions, respectively. The ECSA increased as the starting concentration of Ni(II)cyclam in the electrodeposition reaction is increased. Assuming that the $C_{dl}$ is directly proportional to the active surface area, these results strongly suggest that a higher concentration of Ni(II)cyclam precursor results in an increased density of catalytically active sites for hydrogen evolution.

Hydrogen generation in an MEC.—Hydrogen generation catalyzed by the developed nano-scale Ni(OH)\textsubscript{2} films was investigated in an MEC applying a 0.8 V external voltage. The typical batch-profile current density is shown in Figure 7. In general, the decrease in current density observed with operation time is related to substrate consumption. The results are summarized in Table I. Some salient points arise from the analysis of the MEC experiments. First, it is not surprising that the total charge and Coulombic recovery observed for both the Ni(OH)\textsubscript{2} film electrodes (regardless of the method of preparation) and the Pt electrode are within statistical error of each other considering these are dependent on the degree of feedstock consumption by the bacterial anodes.

It is noteworthy, then, that the hydrogen recovery efficiencies, $R_{cat}$, and overall hydrogen recovery rates, $Q_{H2}$, for Pt (78.3 ± 1.9% and 0.013 ± 0.001 m\textsuperscript{3} H\textsubscript{2} m\textsuperscript{-2} d\textsuperscript{-1}, respectively) and the Ni(OH)\textsubscript{2} film...
The latter results are consistent with a previous study.\textsuperscript{11} Finally, there appears to be a linear relationship between the Ni(II)cyclam precursor concentration and the $R_{\text{cat}}$ and $Q_{\text{H}_2}$, which is likely related to an increase in the number of catalytic sites available with films prepared at higher precursor concentration, as supported by the determination of ESCA.

In summary, a method of preparing Ni(OH)$\text{\textsubscript{2}}$ films has been demonstrated here by electrophoretic deposition from Ni(II)cyclam precursor solutions. The films prepared in this manner displayed excellent performance for catalyzing HER for hydrogen production in MECs comparable to Pt. In addition, the MECs employing the Ni(OH)$\text{\textsubscript{2}}$ catalyst exhibited stable hydrogen production for one month, therefore, making these Ni-based materials stable electrodes in MECs.

### Table I. Hydrogen production and efficiencies of the MECs with modified carbon cloth with Ni(OH)$\text{\textsubscript{2}}$ and unmodified carbon cloth at an applied voltage of 0.8 V.

| Cloth       | $C_{\text{total}}$ | $C_{\text{H}_2}$ | $R_{\text{cat}}$ | $R_{\text{H}_2}$ | $Q_{\text{H}_2}$ |
|-------------|-------------------|------------------|------------------|------------------|-----------------|
| Ni(II)cyclam| 23 mM             | 71.6 ± 2.1       | 25.0 ± 3.4       | 84.3 ± 3.3       | 20.7 ± 1.1      | 0.014 ± 0.002   |
| Ni(II)cyclam| 15 mM             | 75.5 ± 2.9       | 27.6 ± 4.7       | 69.6 ± 4.0       | 19.2 ± 1.9      | 0.012 ± 0.003   |
| Ni(II)cyclam| 6 mM              | 75.4 ± 2.1       | 26.4 ± 3.1       | 59.2 ± 2.1       | 15.7 ± 1.3      | 0.010 ± 0.001   |
| Ni(II)Cl$_2$·6H$_2$O | 71.1 ± 0.8 | 22.3 ± 4.0       | 48.4 ± 4.2       | 10.8 ± 2.1       | 0.008 ± 0.002   |
| Pt          | 71.4 ± 1.2        | 26.2 ± 2.4       | 78.3 ± 1.9       | 19.1 ± 0.9       | 0.013 ± 0.001   |
| Carbon cloth| 40.1 ± 1.0        | 10.2 ± 1.9       | 21.1 ± 3.8       | 2.1 ± 1.4        | 0.002 ± 0.001   |

\textsuperscript{a}Total coulombs passed – reports on the complete consumption of the electron source (organics – acetate) in the anode chamber and is expected to be similar for all catalytic cathodes.

\textsuperscript{b}Coulombic recovery.

\textsuperscript{c}Cathodic hydrogen recovery.

\textsuperscript{d}Overall hydrogen recovery.

\textsuperscript{e}Hydrogen production rate. All were calculated according to the equation in experimental part.

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