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Electrodeposition of nickel particles on a gas diffusion cathode for hydrogen production in a microbial electrolysis cell

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ABSTRACT

Gas diffusion cathodes with electrodeposited nickel (Ni) particles have been developed and tested for hydrogen production in a continuous flow microbial electrolysis cell (MEC). A high catalytic activity of electrodeposited Ni particles in such a MEC was obtained without a proton exchange membrane, i.e. under direct cathode exposure to anodic liquid. Co-electrodeposition of Pt and Ni particles did not improve any further hydrogen production. The maximum hydrogen production rate was 5.4 L/L_R/day, corresponding to Ni loads between 0.2 and 0.4 mg cm⁻². Continuous MEC operation demonstrated stable hydrogen production for over one month. Owing to the fast hydrogen transport through the cathodic gas diffusion layer, the loss of hydrogen production to methanogenic activity was minimal, generally with less than 5% methane in the off-gas. Overall, gas diffusion cathodes with electrodeposited Ni particles demonstrated excellent stability for hydrogen production compared to expensive Pt cathodes.

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1. Introduction

Meeting today's global energy demand in a green and sustainable way has become a challenge of paramount importance, prompting scientists towards research on production and utilization of renewable and carbon neutral fuels. Hydrogen utilization is sustainable if produced from renewable sources rather than fossil fuels. Although hydrogen can be produced in a bio-fermentation process, thermodynamic constraints limit the yield to below 25% of the theoretical value [1]. In a microbial electrolysis cell (MEC) a hydrogen yield of up to 70–90% can be achieved by overcoming endothermic limitation of end bio-products through a unique electrically driven process known as electrohdrogenesis [2,3]. MECs equipped with Pt-based cathodes [4–7] are not amenable for large scale applications as platinum or platinum group metals are scarce and expensive.

Inexpensive electrode materials with high electrocatalysis for hydrogen evolution can be realized by using stainless steel and nickel alloys [8] or electrodeposited NiW and NiMo [9]. Of particular interest is the enhanced performance of stainless steel and Ni alloy cathodes with an electrodeposited nickel oxide layer on the sheet metal surface [8,10]. Electrodeposition of Ni particles onto a porous material might be more efficient in membraneless MEC configuration, as the latter design reduces the transfer of hydrogen to the anodic liquid for producing methane by methanogenic microorganisms. Recently, we compared the performance of several Ni alloys for hydrogen production and concluded that a gas diffusion cathode prepared by chemical deposition of Ni alone can successfully be used for hydrogen production [11]. The study presented below focuses on the development of a low cost MEC cathode by Ni electrodeposition onto a porous carbon paper and demonstrates its applicability for prolonged hydrogen production.

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2. Materials and methods

2.1. Materials and analytical procedures

Nickel sulfate hydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, nickel chloride hydrate, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, boric acid, H_3BO_3 , cetyl trimethylammonium bromide (CTAB), hydrogen hexachloro-platinate, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, and sulfuric acid were obtained from Aldrich–Sigma (St. Louis, MO).

Acetic acid was analyzed by an Agilent 6890 gas chromatograph (Wilmington, DE, USA). Gas production in the MEC was measured by bubble counters, connected to glass U-tubes containing a dye. Gas composition was measured using a 6890 Series gas chromatograph (Hewlett Packard, Wilmington, DE, USA). More details can be found elsewhere [5].

2.2. Instrumentation for cathode surface characterization

SEM analysis was performed on a Hitachi S 2600N scanning electron microscope (Hitachi Scientific Instruments, Tokyo, Japan) coupled with a microanalysis detector for energy dispersive X-rays, EDX (Inca x-act, Oxford Analytical Instruments, Abington, UK). EDX spectra were collected under 30° angles, 20 kV of accelerating voltage and 20 mm working distance. EDX results were analyzed using incorporated Inca, Point & Analyze software.

Field emission scanning electron microscope (FESEM) micrographs were acquired using Low Voltage Electron Microscope by a Delong LVEM (Soquelec Ltd., Montreal, Canada) operating in high resolution SEM mode at 5.30 kV and a working distance of 2 mm. The square-shaped, 2×2 mm sample containing Ni particles on C paper was glued on a very small SEM stub using double-side conductive carbon tape.

Cyclic voltammetry was performed using an electrochemical analyzer CHI 601A (CH Instruments, Austin, TX). A Pt wire (Aldrich, 99.9% purity, 1 mm diameter) and an Ag/AgCl, 3 M NaCl (BAS, West Lafayette, IN, USA) electrode were used as counter and reference electrodes, respectively. Bare and Ni-modified electrodes were cut into stripes, glued on double-side conductive carbon tape, and insulated exposing 0.25 cm^2 of the geometric surface to a 6 M NaOH.

2.3. Preparation and characterization of nickel deposits

The electrodeposition was performed using a BK Precision, model 1670A power supply (B&K Precision Corp, Yorba Linda, CA, USA) in a square-shaped 1 dm^3 cell with a porous Ni sheet as the anode and a carbon paper as a cathode in an 1:1 geometric surface area ratio. Electrodes were glued on double-side carbon tape and mounted on the sample holder. Unwanted deposition of Ni on the other side of the electrode was prevented by carefully inserting the electrode and clamping it against the wall of the bath. The electrode separation was 11 cm, and a constant DC voltage of 2.20 V during 3–30 min at 55°C was applied.

The Ni bath contained 150 mM $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 25 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 500 mM H_3BO_3 , and 1 mM CTAB (at pH 4.5). For the improvement of the Ni adhesion on such porous electrodes,

CTAB was used as a wetting agent. Also, air purging was used during the deposition process in order to provide a more uniform distribution of Ni particles. Sigracet GDL 25BC carbon paper (SGL Group, Germany) was used for the electrodeposition of Ni particles. Prepared Ni-C cathodes were rinsed several times in deionized water and sonicated for 30 s to remove Ni salts and unbound Ni residues. The presence of deposited Ni particles was confirmed by SEM/EDX analysis and cyclic voltammetry.

Ni loading was determined by the weight difference ($\pm 0.1 \text{ mg}$) before and after electrodeposition. The electrodes were cleaned, rinsed and dried under vacuum at 60°C for 1 h before and after electrodeposition. The reproducibility of the electrodeposition technique was verified by measuring the Ni loadings of 5 different electrodes prepared under the same conditions. The results showed a variation within 2%.

Platinum/nickel co-deposits were obtained by exposing the electrode with electrodeposited Ni (0.22 mg cm^{-2}) to a platinum solution containing 2 mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 0.5 mM H_2SO_4 . The application of 1.50 V during 10 min (current typically increased from 4.5 to 7.8 mA), resulted in a platinum load of 0.24 mg cm^{-2} . SEM/EDX and cyclic voltammetry confirmed Pt deposition on Ni and on the free carbon interspace (results not shown). In addition to the electrodes prepared by Ni and Pt electrodeposition, an E-TEK ELAT[®] GDE LT120EW carbon cloth gas diffusion electrode with a Pt load of 0.5 mg cm^{-2} (E-TEK Division, PEMEAS Fuel Cell Technologies, Somerset, NJ, USA) was used in the tests.

2.4. MEC construction and operation

A continuous flow membraneless MEC was constructed with a series of polycarbonate plates, forming a 50 mL anodic chamber and a hydrogen collection chamber of the same volume. The hydrogen collection chamber had a gas exit line and a liquid drainage line (at the chamber bottom). More details on MEC design can be found elsewhere [5,12]. The liquid filled (anodic) chamber contained a 5-mm thick carbon felt measuring $10 \times 5 \text{ cm}$ (Speer Canada, Kitchener, ON, Canada). A 0.7 mm thick piece of J-cloth as described by Fan et al. [13] was sandwiched between the two electrodes. All cathodes investigated are described in Table 1.

MEC was operated at 30°C . A stock solution of carbon source and nutrients was continuously fed using an infusion pump (model PHD 2000, Harvard Apparatus, Canada) at 5.0 or 7.5 mL d^{-1} . This stock solution contained (in g L^{-1}): sodium

Table 1 – A description of cathodes tested.

Cathode no	Ni load (mg cm^{-2})	Pt load (mg cm^{-2})
C-1	0	0
C-2	0	0.5 ^a
C-3	0.22	0.24
Ni-1	0.058	0
Ni-2	0.22	0
Ni-3	0.38	0
Ni-4	0.98	0
^a ELAT [®] GDE LT120EW carbon cloth gas diffusion cathode.		

acetate (90.7), yeast extract (6.7), NH_4Cl (18.7), KCl (148.1), K_2HPO_4 (64.0), and KH_2PO_4 (40.7), corresponding to an acetate load of 4 or 5.8 $\text{g/L}_R/\text{day}$. A dilute solution of trace metals was prepared according to Tartakovsky et al. [5] and fed at 200 mL d^{-1} (HRT = 6 h) using a peristaltic pump (Cole–Parmer, Chicago, IL, USA). The acetate and dilution streams were combined before entering the anodic chamber. The resulting influent stream had a conductivity of 12–14 mS cm^{-1} . The MEC was inoculated with 5 mL of a homogenized anaerobic mesophilic sludge obtained from a local food processing industry (A. Lassonde Inc., Rougemont, Quebec, Canada).

The applied voltage was controlled using an adjustable power source (2400 Source Meter, Keithley, Cleveland, OH, USA). For all tested cathodes, a minimum period of 72 h was maintained to insure steady state operation. MEC was considered to be in steady state when the hydrogen production rate and the current generation were stable (i.e. no trends were observable within a period of 48 h) with variations not exceeding 20% of the average values. More details on the MEC design can be found elsewhere [5].

2.5. MEC characterization

Voltage scans were performed by changing the applied voltage between +0.4 and +1.2 V and measuring the resulting current and electrode potentials against a reference electrode (Ag/AgCl, 222 mV vs NHE). A 10 min interval was allowed after each voltage change [11,12]. Total internal resistance (R_{int}) was calculated as the slope of the linear portion of the voltage vs current curve. Similarly, total internal resistance (ohmic and solution resistance) of the anode (R_{an}) or the cathode (R_{ca}) was estimated using electrode potential measurements against the reference electrode. The open circuit electrode potential (OCP) of the anode and the cathode were also evaluated by linear extrapolation of the corresponding polarization curves [14].

The MEC performance was characterized in terms of volumetric hydrogen production rate, expressed per liter of the reactor volume (L_R). Coulombic efficiency was calculated as the ratio of electrons relative to the total electrons available from acetate consumption. Cathodic efficiency was calculated as the ratio of electrons recovered as hydrogen gas to the total number of electrons that reach the cathode; and as power consumption per liter of hydrogen recovered in the off-gas. Detailed explanation can be found elsewhere [8,15]. Electrochemical characteristics were also acquired using voltage scans performed at the end of each cathode testing period.

3. Results and discussion

3.1. Nickel electrodeposition and electrode characterization

First attempts to deposit 30–50 nm Ni particles on the Sigracet GDL 25BC carbon paper by using 20 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 10 mM KCl and 10 mM H_3BO_3 at $V = 2.70$ V and pH 3.2, resulted in good initial activity when tested in MEC, but the catalyst was not stable resulting in a decrease in current and hydrogen production within the first 48 h of testing (results not shown).

A greenish-grey color on the electrodes was observed indicating the formation of mixed nickel oxides (up to 50% oxygen by EDX analysis) rather than metallic Ni. Consequently, the Ni bath was optimized to contain 150 mM $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 25 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 500 mM H_3BO_3 , and 1 mM CTAB at pH 4.5.

The resulting current during the electrodeposition was very reproducible, increasing from 85 to 120 mA, depending on the deposition time. The current increase indicated the enhanced conductivity and the surface area due to the increasing amount of nickel particles. Due to the highly porous nature of the carbon substrate, the Ni distribution was not uniform. Fig. 1A,B shows the FESEM images of the electrode surface upon optimized Ni electrodeposition. Ni nuclei of 200 nm (Fig. 1A) were densely distributed throughout the electrode and coalesced into nodular Ni structures of over 10 μm in diameter with inter-nodular distances varying from 20 to 50 μm (Fig. 1B). Electrode examination after 45 days of MEC operation demonstrated unchanged Ni characteristics (Fig. 1C). Thus, we attributed the observed nodular Ni structures to enhanced electrode stability since the electrode after 45 days of use in MEC was still demonstrating a similar cyclic voltammetry profile (Fig. 1D, curve c) with well-pronounced Ni redox peaks. The minimal increase in the capacitive current in CV scan could be attributed to the presence of a biofilm on the electrode surface.

3.2. Hydrogen production

At startup, the MEC was equipped with a Pt-based gas diffusion cathode C-2 (Table 1) and operated at 1 V. Progressive increase in both current and hydrogen production was observed with stable performance achieved one week after MEC startup. At steady state, a current density of $3.8 \pm 0.3 \text{ A m}^{-2}$ corresponded to a volumetric hydrogen production rate of $2.9 \pm 0.3 \text{ L d}^{-1} L_R^{-1}$. The hydrogen production rate observed for the Pt (C-2) cathode was somewhat lower than the rate obtained in our previous experiments [12]. This difference could be attributed to the difference in hydraulic retention times used in the two experiments (6.4 h in this work vs 10 h in the previous work). Following the startup, MEC was operated for more than 240 days where several gas diffusion cathodes were tested against the same anode. A summary of observed current densities, hydrogen production rates, and other MEC parameters is given in Table 2.

Initial cathode tests were carried out with an acetate load of 4 $\text{g d}^{-1} L_R^{-1}$, corresponding to an influent acetate concentration of 1000 mg L^{-1} . Analysis of anodic chamber liquid showed that at this load acetate concentration was below 100 mg L^{-1} in most tests. This acetate level was considered as rate-limiting and therefore cathode performance was re-tested at an increased acetate load of 5.8 $\text{g d}^{-1} L_R^{-1}$. The increased acetate load resulted in 300–500 mg L^{-1} acetate in the effluent, which was considered sufficient for the growth and metabolism of anodophilic bacteria.

For all Ni-based cathodes tested, a comparison of hydrogen production rates was obtained at low and high acetate loads. With cathode Ni-1 containing the least amount of Ni, only minor differences in current density and hydrogen production as a function of the acetate load were observed (Table 2). These differences were within the margin of error for current

Fig. 1 – (A–B) SEM micrographs of optimized Ni deposits on C 25BC. Ni nuclei of 200 nm (A) agglomerated into nodular Ni structures (B) of over 10 μm . (C) The same electrode upon 45 days of use in MEC. (D) Cyclic voltammetry profiles in 6 M NaOH at a scan rate of 100 mV^{-1} of C 25-BC prior (curve a) and after Ni electrodeposition (curve b). The electrode kept Ni electrochemical characteristics after 45 days of use in MEC (curve c).

and gas measurements. However, when MEC was operated with cathodes Ni-2, Ni-3 and Ni-4, containing more Ni catalyst, significantly more hydrogen was produced at the higher acetate load, suggesting that in the Ni-1 test catalyst load was rate-limiting, while in tests where cathodes contained more catalyst acetate was rate-limiting, at least at an acetate concentration below 100 mg L^{-1} . While an increase in acetate supply resolved carbon source limitation, for Ni cathodes

containing more than 0.22 mg cm^{-2} (e.g. Ni-3 and Ni-4) electron transfer limitation at the anode cannot be excluded.

Ni-based cathodes showed hydrogen production rates between 3.5 and $5.4 \text{ L d}^{-1} \text{ L}_R^{-1}$, outperforming the Pt cathode C-2 (Table 2). Apparently, at pH 7 catalytic activity of Pt was negatively affected by salts and metals present in the MEC medium [16]. At a lower acetate load ($4 \text{ g d}^{-1} \text{ L}_R^{-1}$), the highest hydrogen production was observed for Ni-1 (Fig. 2A), but the

Table 2 – MEC performance during cathode tests at an applied voltage of 1 V.

No	Acetate load ($\text{g/L}_R/\text{day}$)	Current density (A/m^2)	H_2 flow ($\text{L/L}_R/\text{day}$)	Power consumption (Wh/L)	Efficiency (%)		H_2 yield (mol/mol)
					anodic	cathodic	
C-1	4.0	3.6 ± 0.7	0	12.2	81.7	17.7	0
C-2	4.0	3.8 ± 0.3	2.94 ± 0.29	3.1	64.8	69.6	1.80
C-3	4.0	3.8	4.12 ± 0.38	2.2	74.4	97.5	2.90
C-3	5.8	4.8 ± 0.7	4.20 ± 0.46	2.7	90.6	78.7	2.85
Ni-1	4.0	4.6 ± 0.3	5.22 ± 0.40	2.1	82.4	102.0	3.36
Ni-1	5.8	4.4	5.02 ± 0.81	2.1	61.0	102.4	2.50
Ni-2	4.0	4.0	4.08 ± 0.52	2.0	81.6	91.6	2.99
Ni-2	5.8	4.6	5.4 ± 0.53	2.0	77.3	105.8	3.3
Ni-3	4.0	4.5 ± 0.4	4.45 ± 0.42	2.4	77.4	88.9	2.75
Ni-3	5.8	5.7 ± 0.4	5.16 ± 0.32	2.6	96.2	81.5	3.14
Ni-4	4.0	4.3 ± 0.1	3.49 ± 0.81	3.0	86.28	72.6	2.50
Ni-4	5.8	5.4 ± 0.3	4.68 ± 0.64	2.8	81.8	78.4	2.57

hydrogen production with cathodes Ni-2 and Ni-3 was not significantly different. Nevertheless, the trend of hydrogen production in Fig. 2A suggests a decrease in the production rate, at least at the highest Ni load. It could be due to the reduction of microbial activity by high Ni levels in proximity to the anode or a reduced electrode surface area due to excessive deposition of Ni, which in turn resulted in a decrease in hydrogen production.

For the operation of MEC at acetate non-limiting conditions, the effect of the Ni catalyst on hydrogen production was more pronounced (Fig. 2B). The maximal performance was observed with the Ni-2 cathode containing 0.22 mg cm^{-2} of Ni, while the hydrogen production and current density were decreased for cathode Ni-4 with the highest Ni content. These results agreed with hydrogen production rates in a range of $2\text{--}3 \text{ L d}^{-1} \text{ L}_R^{-1}$ reported for metal sheet Ni alloy cathodes with a high Ni content [8]. All cathodes demonstrated excellent stability with no observable decrease in hydrogen production over a 7–14 day operation. Furthermore, prolonged cathode stability was demonstrated when a MEC was operated for 45 days using the Ni-3 cathode; here stable current density and hydrogen production were observed as shown in Fig. 3. Throughout the tests, methane content varied between 2 and 6% with the exception of C-2 (15%) and Ni-2 (11%). In these tests the seed sludge containing a significant amount of

methanogenic microorganisms was added to the anodic chamber. It was reasoned that high porosity of the gas diffusion cathodes facilitated hydrogen transport to the collection chamber. Consequently, less hydrogen was available for hydrogenophilic methanogenic microorganisms thus limiting methane production from hydrogen.

In the absence of a Me catalyst (cathode C-1), hydrogen production did not proceed although current density was comparable to that observed with the C-2 (Pt) cathode (Table 2). Although MEC operation with a biocathode has been reported [17,18], the development of electrochemically active microorganisms at the cathode is slow. Apparently, the duration of the cathode tests was insufficient for the development of this microbial population and hydrogen evolution reaction (HER) in all tests might be attributed to the presence of Ni. The catalytic activity of Ni and Pt was compared by co-electrodeposition of Pt and Ni particles (cathode C-3). Co-electrodeposition of these catalytic species did not improve hydrogen production (Table 2 and Fig. 2), which was higher than that observed with C-2, but comparable to all other Ni-containing cathodes.

Overall, the observed dependence of hydrogen production on the Ni load agreed with our previous results where Ni was chemically deposited on carbon powder, and the resulting catalyst ink was sprayed on GDL 25BC carbon paper [11]. When Ni was chemically deposited, hydrogen production was maximal at a Ni load of 0.6 mg cm^{-2} with no further improvement in hydrogen production at higher Ni loads. Notice that the electrodeposition procedure resulted in a higher volumetric rate of hydrogen production at a lower Ni load of 0.22 mg cm^{-2} . Apparently, spraying of the Ni-C catalyst ink on the carbon paper reduced availability of active catalytic sites for HER.

A comparison of current measurement obtained for each Ni cathode including the Ni/Pt cathode (C-3) showed that the current density for all Ni cathodes was proportional to the hydrogen production (Table 2). The power consumption was between 2.1 and 2.0 Wh/L-H_2 for Ni-1 and Ni-2, respectively, but increased to 2.6–3.0 for Ni-3 and Ni-4 cathodes. The power consumption of C-3 was higher than that observed for other Ni-containing cathodes, particularly Ni-2 with a similar Ni load. Furthermore, the Pt cathode C-2 showed an even higher

Fig. 2 – Volumetric hydrogen production rates observed at an acetate load of (A) $4 \text{ g/L}_R/\text{day}$ and (B) $5.8 \text{ g/L}_R/\text{day}$ (acetate non-limiting conditions).

Fig. 3 – Volumetric hydrogen production and observed current in a long-term stability test performed at 1 V. Maintenance procedures resulted in fluctuations in hydrogen production and current density.

power consumption, suggesting that part of the electrons harvested at the anode were lost at the cathode to electrochemical reactions other than the HER. Although Pt is known for its high catalytic activity; its excellent catalytic properties might lead to several concomitant electrochemical reactions [16]. Electron losses to reactions other than HER might be even more significant when MEC is operated on wastewater, which typically has a very complex composition. A high catalytic activity of Pt might also lead to inhibition of the Pt-based catalyst.

3.3. Acetate conversion efficiency

The overall efficiency of acetate conversion to hydrogen was estimated by computing hydrogen yields for each test. The results presented in Table 2 show that for all Ni cathodes tested the yield varied between 2.5–3.4 mol/mol and 63%–85%, in agreement with previously reported results [3,7–10]. More detailed analysis was performed by estimating anodic (i. e. Coulombic) and cathodic efficiencies (Fig. 2B). Regardless of the acetate load, the anodic efficiency of all cathodes remained above 75% with the exception of C-2 (65%) and Ni-1 (61%). Notice that C-2 test proceeded immediately after MEC inoculation with anaerobic sludge, which contained a significant amount of acetoclastic methanogens. Acetate consumption by these methanogenic microorganisms might

explain a lower anodic efficiency in this test. MEC handling during the cathode replacement resulted in anodic compartment exposure to air thus decreasing population of strictly anaerobic methanogens and improving the anodic efficiency. Periodic exposure of the anodic compartment to air has been previously used to decrease methane production in MECs [4,19]. Also, the anodic efficiency estimation of Ni-1 (61%) was based on a single measurement of acetate concentration in the anodic chamber, as opposed to an average of 2–4 measurements in other tests. An acetate concentration of 230 mg L⁻¹ was measured, significantly lower than the average (400–500 mg L⁻¹) in all other tests at the same acetate load. Apparently, the steady state acetate concentration was not reached in the Ni-1 test, which might result in a large error in anodic efficiency estimation.

Cathodic efficiencies for all Ni-based cathodes tested were close to 100%, compared to the standard platinum cathode C-2, with an efficiency of 70%. Such results confirmed electron losses to reactions other than the HER of the Pt cathode. Notice that with the Pt/Ni cathode (C-3), the cathodic efficiency improved, illustrating the advantages of using Ni for the HER.

3.4. Cathode characterization

Electrochemical characteristics of cathodes were compared by performing voltage scans at the end of each test (Fig. 4). At the

Fig. 4 – (A) Voltage scans (current vs applied voltage) and (B) corresponding cathode potentials at an acetate load of 4 g/L_R/day (acetate-limiting conditions).

Table 3 – Estimated internal resistances and open circuit electrode potentials (vs Ag/AgCl reference electrode).

No	Acetate load (g/L _R /day)	MEC R _{int} (Ω)	R _{an} (Ω)	R _{ca} (Ω)	OCP _{cell} (mV)	OCP _{an} (mV)	OCP _{ca} (mV)
C-1	0	4689.8	3325.5	1336.6	178	–265	93
C-1	4.0	22.6	8.7	11.6	569.1	–444	1025
C-2	4.0	30.8	15.7	13.6	247.6	–462	711
C-3	4.0	30.3	14.8	16.3	327.4	–529	840
C-3	5.8	26.7	13.8	12.4	379.1	–479	866
Ni-1	5.8	19.5	6.8	9.8	533.5	–413	941
Ni-2	4.0	23.7	13.4	11.0	520.3	–465	973
Ni-2	5.8	18.2	11.0	7.6	563.6	–473	1012
Ni-3	4.0	26.3	9.4	10.5	431.6	–443	918
Ni-3	5.8	16.0	7.7	7.4	599.7	–422	1000
Ni-4	4.0	26.3	12.0	10.9	432	–441	900
Ni-4	5.8	18.6	12.3	9.2	621	–489	999

end of the C-1 test MEC was operated without acetate in the influent stream while all other salts were retained. This test lasted 3 days with a voltage scan at the end of the test. The results of all voltage scans were used to estimate total MEC internal resistances, electrode resistances, and electrode OCPs. A summary of all calculated values is presented in Table 3. As expected, current was close to zero and anode internal resistance was sharply increased when the carbon source was absent. This was indicative of the activity of anodophilic microorganisms, which can transfer electrons by several mechanisms including direct electron transfer or production of extracellular mediators or both [20–24].

Voltage scans confirmed better performance of Ni cathodes as compared to the Pt-based cathode. Both total anodic and cathodic resistances were on average higher when the MEC was operated with less efficient cathodes (e.g. C-2, C-3, Ni-4). Total cathodic resistances were clearly related to the observed H₂ production rates. In particular, the cathodic resistance for Ni cathodes was lower than that estimated for the Pt-containing cathodes (C-2, C-3) and the resistance was also lower when the MEC was operated under acetate non-limiting conditions (Table 3). Voltage scans confirmed an optimal Ni load of 0.2–0.4 mg cm^{–2} since beyond this level, microbial activity appears to be limited, whereas at lower loads HER is limited.

Of interest was a comparison of estimated electrode resistances and OCPs, which might suggest a link between anode and cathode performances. Whenever cathode performance was higher than average, a gradual improvement of the anode performance was manifested in consistently lower estimations of R_{an} and more negative values of estimated anode OCP (Table 3). Therefore, it was reasoned that if the cathode reaction was rate-limiting (at least for cathodes showing lower H₂ production rates such as C-2 and N-1 at high acetate load), the growth of anodophilic microorganisms at the anode would be restricted. When the cathode reaction was not rate-limiting, the biofilm density of anodophilic microorganisms and metabolic activity increased and provided acetate non-limiting conditions.

4. Conclusion

Gas diffusion cathodes with electrodeposited Ni particles were successfully developed and used for hydrogen

production from acetate in a flow-through MEC. Hydrogen production as high as 5.4 L d^{–1} L_R^{–1} with a corresponding current density of 5.7 A m^{–2} was achieved at a Ni load of 0.2–0.4 mg cm^{–2} under acetate non-limiting conditions. This level of hydrogen production was higher than volumetric rates of 2.0–2.3 L d^{–1} L_R^{–1} reported for a batch-operated MEC equipped with similar anodes and Ni alloy or NiW cathodes [9]. The improved rate of H₂ production can be attributed to an optimized Ni load and to high porosity of the gas diffusion cathodes, which provided a higher surface area for Ni electrodeposition, compared to solid metal sheets used by Selembo et al. [8]. Also, high cathode porosity facilitated transport of hydrogen to the hydrogen collection chamber thus minimizing microbial conversion of hydrogen to methane. Co-electrodeposition of Pt and Ni particles did not enhance hydrogen production. These tests clearly demonstrated that under typical MEC conditions (i.e. near neutral pH and direct exposure of the cathode catalyst to the anodic liquid) Ni is a better catalyst compared to Pt. Cathodes prepared by Ni electrodeposition exhibited a similar or higher rate of hydrogen production as compared to the chemical deposition of Ni [11]. The electrodeposition procedure was highly reproducible for the fabrication of electrodes with well-defined surface areas, i.e. it could be effectively used to manufacture large size cathodes suitable for pilot and industrial scale applications. The size and density of Ni particles could be easily controlled by electrodeposition time and/or the concentration of Ni salt.

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