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RESEARCH ARTICLE

Towards the implementation of a more economical catalyst for hydrogen production in microbial electrolysis cells

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Abstract

Background

Microbial electrolysis cells (MECs) enable hydrogen production while simultaneously oxidizing the organic matter present in wastewater. However, the efficiency of this process is limited by the slow kinetics of the cathodic reaction, which require the use of a catalyst. Platinum (Pt) is frequently employed because of its high catalytic performance; however, its cost precludes large-scale applications. This study investigates alternative cost-effective catalysts (Cu_{100}, Ni_{100}, $Ni_{85}Mo_{15}$, $Ni_{64}Fe_{18}Mo_{18}$, and $Ni_{76}Fe_{16}Mo_{8}$) composed of non-noble metals.

Methods

The catalysts were electrodeposited on a carbon cloth and felt electrodes, and Cu_{100} and Ni_{100} were manually deposited to compare the electrochemical and physical deposition methods. Techniques such as Scanning Electron Microscopy, Linear Sweep Voltammetry, and Electrochemical Impedance Spectroscopy were used for the characterization.

Results

The results demonstrated that electrochemical deposition was a more efficient and cost-effective method than manual deposition, and was therefore excluded. Among the catalysts, $Ni_{64}Fe_{18}Mo_{18}$ demonstrated comparable performance to Pt in terms of the current density (1.2 $mA{\cdot}cm^{-2}$) and uniform deposition. The carbon felt electrodes

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demonstrated superior performance compared to carbon cloth, which can be attributed to their larger electroactive areas. Carbon felt electrodes outperformed carbon cloth, attributed to their larger electroactive area, achieving up to 9% higher current density with $Ni_{64}Fe_{18}Mo_{18}$.

Conclusions

This study suggests that a more economical alloy, such as $Ni_{64}Fe_{18}Mo_{18}$ on carbon felt electrodes is a promising alternative to Pt for enhancing H_2 production in MECs.

Keywords
Alloys catalysts, Nickel, Copper, Molybdenum, Iron, Carbon electrodes, Hydrogen production, Platinum substitutes



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1. Introduction

Hydrogen (H_2) is a good carrier of clean energy, with a high heat of combustion (122 $kJ \cdot g^{-1}$) when compared to other fuels.[1] Another advantage of H_2 is that it can be sustainably produced from the degradation of organic matter using a microbial electrolysis cell (MEC).[2] In MECs, electrons, CO_2, and H^+ are generated at the anode, while H^+ is reduced at the cathode to form H_2. However, the production of H_2 in an MEC also has some drawbacks: (i) it is not a spontaneous process; therefore, it requires the application of a voltage through an external power supply or a potentiostat, and (ii) the reduction reaction of H^+ to H_2 has very slow kinetics. Consequently, a catalyst is necessary to carry out the reaction, which significantly increases the cost of the cells[3].

According to the Nernst equation, a voltage of 0.14 V should be applied for the electrochemical reactions to take place under standard conditions (298 K and 1 bar). Still, in practice, a higher voltage, between 0.6 and 1.2 V is required to produce H_2, due to the overpotential of the cell. Consequently, a catalyst was used to decrease the activation overpotential of the H_2 production reaction, *i.e.* the overpotential of the cathodic reaction.[4] The excellent catalyst used in MECs is Platinum (Pt) because of its high performance in such reactions. However, its high cost has stimulated the search for alternative catalysts[5] such as non-noble transition metals. Thus, some studies have shown that catalysts based on other non-noble metals, such as Mo,[6] Fe,[7,8] or Ni, can[9–13] be used for H_2 production in MECs, in addition to cathodes based on alloys of these metals. Previous studies have shown that metal alloys perform well in H_2 production; however,[14–17] the performance of Pt as a catalyst has not been exceeded.

The challenge of this work was to evaluate alternative catalysts that are less expensive than Pt and to evaluate their effectiveness for H_2 production. Moreover, these catalysts must be deposited on carbon materials with good electrochemical properties to be used as cathodic electrodes in cells for H^+ reduction. For this reason, the materials selected were carbon cloth and carbon felt, two carbon-based supports with good properties for use as electrodes, in addition to being two of the most widely used cathode materials. Thus, different transition metals were used as catalysts, both individually and to create alloys with more than one metal; the catalysts tested were Cu_{100}, Ni_{100}, $Ni_{85}Mo_{15}$, $Ni_{64}Fe_{18}Mo_{18}$ and $Ni_{76}Fe_{16}Mo_8$. The subscript numbers correspond to the mole fractions of the individual metals. Likewise, two complementary strategies have been defined to deposit these metals on the electrode: electrodeposition and manual deposition,[18] as both are the two most widely used and least costly techniques.

After obtaining the catalysts and depositing them on the corresponding cathodes, the final objective was to evaluate the performance of the cells and determine the real efficiency of the alloy-based catalysts versus the use of Pt as a catalyst. The performance of MECs was evaluated using a bioanode under more realistic conditions. To evaluate and characterize the different catalyst materials, different analytical and electrochemical techniques, such as Electrochemical Impedance Spectroscopy (EIS) and Linear Sweep Voltammetry (LSV), and optical microscopy techniques, such as Scanning Electron Microscopy (SEM), were used. Although these alloys have been tested previously, for the first time, they will be deposited on carbon cloth and carbon felt, comparing both materials. In addition, for the first time, both types of electrodes will be tested in electrochemical cells to observe their behavior under realistic conditions.

2. Materials and methods

2.1 Microbial electrolysis cell construction

Call and Logan[19] first presented a cubic MEC (Figure S1). The MEC used in this work consisted of a 35 mL cubic cell consisting of a methacrylate body 4.4 cm long x 5 cm wide x 5 cm high height body and a glass cylinder (7.7 cm height × 2 cm diameter) placed hermetically at the top, where a gas collection bag was placed. The main body was assembled with two methacrylate side plates using O rings to prevent electrolyte leakage. These parts were held together using screws and wing nuts.[20]

The gas obtained was collected in a 100 mL gas bag containing a twist-type valve (Cali-5-Bond, Ritter) located at the end of the glass cylinder by piercing a septum placed at the end of the cylinder, which made the cell remain airtight.

A graphite fiber brush was used as the anode. On the other hand, the cathode was made of carbon felt or carbon cloth (*Carbon Felt 3.18 mm thick 99.0%,* ThermoScientific Chemicals and *Carbon Cloth Zoltek Fabrics* Carbonized, Woven Fabric, Plain Weave 237 $g \cdot m^{-2}$), slightly modified with a catalytic layer on the inner side of the cathode.

The electrodes were connected to a power supply (Valleman Energy, LABPS3005DN). In addition, 10 Ω R_{ext} was connected in series to monitor the cell current.

Cells were filled with 35 mL of fresh mineral medium and sodium acetate at a concentration of approximately 1.5 $g \cdot L^{-1}$. The mineral medium composition for all cells contained (per L of Milli-Q-water) 15.09 g $Na_2HPO_4 \cdot 2H_2O$, 2.06 g

KH_2PO_4, 0.2 g NH_4Cl, 4.0 mg $FeCl_2$, 6.0 mg Na_2S and 5 ml of nutrient solution, which contained per L: 1 g EDTA, 0.164 g $CoCl_2{\cdot}6H_2O$, 0.228 g $CaCl_2{\cdot}2H_2O$, 0.02 g H_3BO_3, 0.04 g $Na_2MoO_4{\cdot}2H_2O$, 0.002 g Na_2SeO_3, 0.02 g $Na_2WO_4{\cdot}2H_2O$, 0.04 g $NiCl_2{\cdot}6H_2O$, 2.32 g $MgCl_2$, 1.18 g $MgCl_2$, 1.18 g $MnCl_2{\cdot}4H_2O$, 0.1 g $ZnCl_2$, 0.02 g $CuSO_4{\cdot}5H_2O$, and 0.02 g AlK $(SO_4)_2$.[18] All reagents were of analytical grade and supplied by Scharlau SL (Spain). The initial pH and conductivity of the cells were approximately 7.5 and 13 $mS{\cdot}cm^{-1}$, respectively. In addition, the cells were bubbled with nitrogen for 10 min to remove the dissolved oxygen from the medium.

2.2 Analytical methods and instrumentation

To monitor the cells, the composition of the cell medium was analyzed using different instrumental techniques. For this purpose, a sample of the mineral medium was taken at the beginning and the end of each cycle without exceeding 10% of the complete volume of the reactor. The cells were then filled with fresh mineral medium.

Acetate was analyzed using a gas chromatograph (Agilent Technologies, 7820-A) employing a DB-FFAB column, flame ionization detector, and He as the carrier gas.[21]

Some materials were studied and morphologically characterized using SEM to observe the electrodeposition of different metals and alloys on the electrodes. SEM measurements were carried out using a Merlin Zeiss microscope operated at 5 kV with an EDX detector (SEM-EDX) analysis system and Jeol JSM 6010 (JEOL, Ltd, Tokyo, Japan).[22]

Both electrodes were linked to a power supply at a 1.0 V potential. The voltage across each resistance was measured using a 16-bit resolution data-acquisition card (Advantech PCI-1716). AddControl software, programmed in LabWindows/CVI2021, was used for process control and data storage.[23] H_2, CH_4, and CO_2 were measured using a gas chromatograph (Agilent Technologies, 7820-A).

2.3 Electrochemical techniques

The different electrochemical techniques described in this section were used to study the behavior of the different catalysts. These techniques were applied in a three-electrode configuration and in a single methacrylate cell in all cases, employing the same anode for all catalysts. A commercial Ag/AgCl electrode (BioLogic) with KCl 3 M internal solution was used as a reference electrode, and the different cathodes were studied as working electrodes (WE).

2.3.1 Electrochemical impedance spectroscopy

EIS is a non-destructive technique used to determine the internal resistances, both ohmic and charge transfer, of the cell under study, as well as the value of the electrolytic double layer. Consequently, the measurements are helpful for gathering the performance information of both electrodes.[24,25] Unlike other techniques, EIS allows measurements at equilibrium or steady state. A small sinusoidal alternating current (AC) of variable frequency was applied to measure the impedance of a circuit element or a complete cell, and the corresponding potential was measured as a function of frequency.

EIS analyses were performed in the frequency range of 100 kHz–10 mHz at the open-circuit potential. The amplitude was set to 1 mV to avoid detachment of the biofilm and to reduce disturbance to the steady-state conditions of the cell.[22] In addition, acetate was added to prevent it from being the limiting factor, and nitrogen was sparged for 30 min to simulate the real conditions in the cell. The circuit used for fitting the results was a simplified version of the Randles circuit, without the Warburg element.[26]

2.3.2 Linear sweep voltammetry

LSV is a technique that performs a linear potential sweep from the lower potential limit to the upper potential limit, *i.e.*, the technique consists of recording the intensity when a potential sweep is performed in a given direction at a constant speed of 10 $mV{\cdot}s^{-1}$.

The potential sweep applied to the cell was from −1.0 to −3.0 V, in 0.1 V intervals. A period of 1 min was used for current stabilization at each voltage. To analyze the different electrodes fabricated, LSV was performed under abiotic conditions to evaluate the catalytic efficiency of the cathode without the intervention of microorganisms. With this technique, it was possible to evaluate the performance of the catalyst because for the same applied potential, the intensity obtained by the abiotic electrode can be monitored. Thus, the electrode with the highest current intensity in absolute value, that is, that with the highest slope, showed the highest performance.

2.4 Manual deposition of different catalysts

To manufacture parts of the different cathodes used, different metals (Cu and Ni) were manually deposited on the two types of carbon-based materials, with a projected area of 7 cm^2.

2.4.1 Manual Cu_{100} deposition

A Cu_{100} catalyst was manually deposited using a knife or roller to spread the ink. To make the Cu ink, which was subsequently deposited, first, 6.6 ml of Milli-Q deionized water (Millipore, Billerica, MA, USA); 13.4 mL of ethanol and 0.2 mL of acetic acid were added in a beaker to obtain a total volume of 20.2 mL, and percentages of 33%, 66%, and 1%, respectively. This mixture can be stored in a dry place without light for one month so that it can be used to make different electrodes, because a small amount (≈ 8 mL) is used in one deposition.

Then, in a 5 mL beaker, 1 g of Cu nanoparticles (Sigma Aldrich, 25 nm nanoparticle size) was added to 2 mL of the above mixture. Thus, for each electrode, an ink batch was prepared with 4 g of Cu nanoparticles and 8 mL of the above mixture and homogenized. To this dispersion, 10 drops of the commercial solution Tween 20 (polysorbate 20) were added, and the mixture was sonicated in an ultrasonic bath for 30 min. The ink was homogeneously and continuously deposited on the surface of the entire electrode. The electrode was placed on a heating plate at a temperature of approximately 30–40 °C to accelerate the evaporation of the mixture during deposition.

At the end of the sonication, the ink was spread on the electrode with a roller or knife, and the entire electrode was covered. Finally, the electrode with the catalyst was left to dry overnight in a flask under nitrogen atmosphere at 100 °C to seal the deposition. The Cu_{100} electrode was ready for use the following day.

2.4.2 Manual deposition of Ni_{100}

One of the two depositions of the Ni_{100} catalyst was carried out manually on the carbon cloth electrode using a knife or roller to spread the ink. For this deposition, the same procedure as described in section 2.4.1 was followed, but Ni nanoparticles were used instead (Sigma Aldrich, average nanoparticle size <100 nm). The amounts of reagents used and the steps followed were identical to those used for the Cu deposition.

2.5 Electrochemical deposition of the different catalysts

Different metals (Cu and Ni) or alloys were electrochemically deposited on two types of carbon-based materials to fabricate different cathodes. A projected area of 7 cm^2 is used in this study. The proposed metals were Fe, Ni, and Mo, and different alloys of these three metals because they are highly conductive metals and abundant in nature, which makes them accessible and inexpensive to scale up, unlike Pt.

A Gamry Instruments Interface 1010 potentiostat/galvanostat (model 25065) was used to perform electrodeposition. In all deposition baths, together with the reagents mentioned in each corresponding section, 0.15 moles of $Na_3C_6H_5O_7$ and 0.5 moles of $NaHCO_3$ were added per liter. When the deposition bath was prepared, the electrode to be deposited, either the carbon cloth or carbon felt, was immersed in the bath and connected to the potentiostat acting as WE. A commercial graphite electrode was used as the counter electrode (CE) and $Ag/AgCl_{(sat)}$ was used as the reference electrode.

2.5.1 Electrodeposition of Ni_{100}

The electrode was immersed in a 1 L Ni deposition bath prepared by adding 0.250 mol of $NiCl_2$. The bath was left to stir for 15 min, and then the pH was adjusted to 10.5 with 1 M NaOH. Finally, the electrode is immersed and connected to a potentiostat.

Electrodeposition was performed by chronoamperometry at a current of 50 $A{\cdot}m^{-2}$ for 3 h. The electrode was then disconnected from the potentiostat and allowed to dry overnight in a flask under nitrogen atmosphere at 120 °C. After the drying step, the electrode was washed with Milli-Q deionized water to remove excess Ni and then ready for use as a cathode.

2.5.2 Electrodeposition of alloys

For $Ni_{85}Mo_{15}$ electrodeposition, a 1 L deposition bath containing Ni and Mo was prepared: 0.213 mol of $NiCl_2$ and 0.038 mol of Na_2MoO_4. The procedure described in section 2.5.1. followed, except that chronoamperometry for electrodeposition was performed at a current density of 100 $A{\cdot}m^{-2}$ for 6 h.

Similarly, the electrodeposition of $Ni_{64}Fe_{18}Mo_{18}$ was performed by preparing 1 L of the deposition bath with Ni, Fe, and Mo: 0.160 mol of $NiCl_2$. 0.045 mol $FeCl_3$, and 0.045 mol Na_2MoO_4. The same procedure as for the $Ni_{85}Mo_{15}$ electrodeposition was followed, except that chronoamperometry for electrodeposition was performed at a current density of 200 $A{\cdot}m^{-2}$ for 6 h. $Ni_{76}Fe_{16}Mo_8$ electrodeposition was performed by preparing a 1 L deposition bath containing Ni, Fe, and Mo: 0.190 mol of $NiCl_2$, 0.040 mol of $FeCl_3$, and 0.020 mol of Na_2MoO_4, followed by the same procedure as for $Ni_{64}Fe_{18}Mo_{18}$.

3. Results and discussion

3.1 Abiotic electrochemical characterization

Before inoculating the corresponding cells, an abiotic study was conducted to determine the efficiency of the different cathodes and evaluate their performance in H_2 production. For this purpose, LSVs of the carbon cloth electrodes with the different catalyst depositions were performed through a potential sweep from −1.0 V to −3.0 V (Figure 1). The $Ni_{64}Fe_{18}Mo_{18}$ alloy exhibited the best performance, as it exhibited the highest current intensity in absolute value for the same applied potential. Following the same reasoning, the $Ni_{76}Fe_{16}Mo_8$, $Ni_{85}Mo_{15}$ electrodeposited, and Cu catalysts with manual deposition exhibited similar behavior. Conversely, the catalysts with the worst performance was Ni_{100} with manual deposition, followed by Ni_{100} electrodeposited. Consequently, Ni_{100} manual deposition was discarded from this study, not only because of its low performance, but also because of the high time required to perform each manual deposition of the catalyst.

In addition, the effect of using carbon cloth and carbon felt as base materials for the manufacture of electrodes was studied. The catalysts studied were Ni alloys and metallic Ni electrodeposited on carbon cloth and carbon felt electrodes.

The internal resistance of each cell was studied using two different WE support materials by performing abiotic EIS. The EIS results (Figure 2) and the parameters extracted from the Randles circuit adjustment (Table 1) show that all carbon felt and carbon cloth cathodes modified with all catalyst electrodepositions presented a similar R_Ω, which is related to the fact that the electrolyte and the cell design are the same in all cases. In contrast, R_{ct}, which is related to the ease of electron flow, *i.e.*, the ease with which the WE carried out the electrode reaction, was very variable from one electrode to another. In general, all carbon felt electrodes showed lower R_{ct} values than the carbon cloth electrodes for a given catalyst. Therefore, carbon felt electrodes offer fewer limitations on electron transfer (small R_{ct}) and consequently provide a higher electron transfer rate. Thus, carbon felt WEs performed better than carbon cloth WEs if they were modified with the same catalyst.

Table 1 shows that the carbon felt electrode with the $Ni_{64}Fe_{18}Mo_{18}$ catalyst had the lowest R_{ct} followed by the carbon cloth electrode with the same catalyst. The results were in concordance with those obtained by LSV, where $Ni_{64}Fe_{18}Mo_{18}$ was the catalyst with the highest current intensity in absolute value obtained (Figure 1). Moreover, comparing the R_{ct} of all the WE, it was found that the electrodes modified with the $Ni_{64}Fe_{18}Mo_{18}$ catalyst, both using cloth and felt, showed a much lower R_{ct} compared to all other catalysts (Table 1), followed by the WE with the $Ni_{76}Fe_{16}Mo_8$ catalyst. This may be due to the fact that this alloy has a higher electrical conductivity than the others or at least makes it easier to transfer electrons from one electrode to another. The results also show that the carbon felt provided always had a lower charge

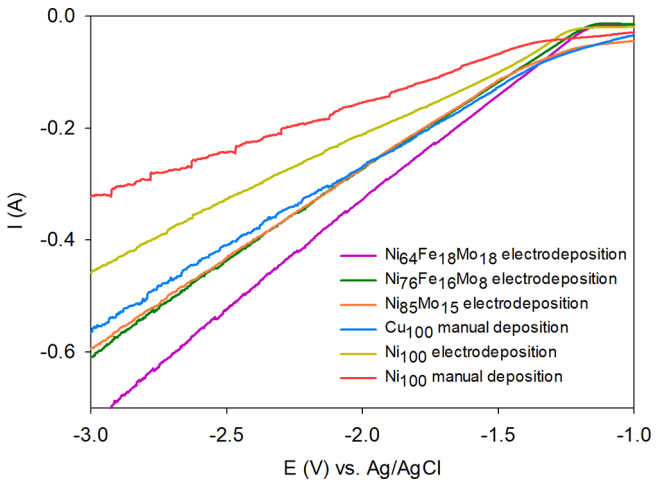

Figure 1. LSV of different catalyst depositions on carbon cloth. Scan rate 10 $mV{\cdot}s^{-1}$.

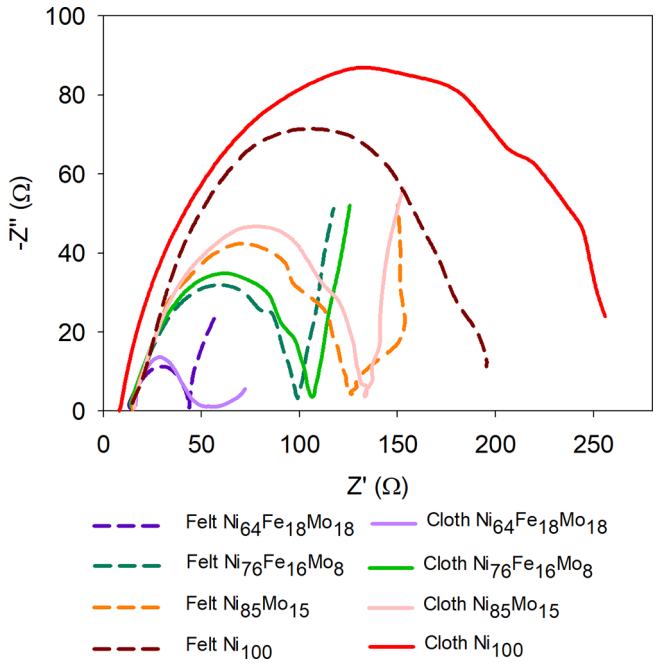

Figure 2. Abiotic EIS using the different types of WE: carbon cloth electrode and carbon felt with the different Rext catalysts subsequently fitted to Randles' simplified circuit: $R_{\Omega}\cdot(R_{ct}\cdot C_{dl})$. Frequency ranges from 100 kHz to 10 mHz.

Table 1. Resistances R_{Ω} and R_{ct} obtained from Randles' equivalent circuit ($R_{\Omega}\cdot(R_{ct}\cdot C_{dl})$) in cells with felt and carbon cloth cathodes with the various electrodeposited catalysts. Frequency ranges from 100 kHz to 10 mHz.

Material	Internal resistance R_{Ω} (Ω)	Charge transfer resistance R_{ct} (Ω)
Carbon felt $Ni_{64}Fe_{18}Mo_{18}$	13.6	45.6
Carbon cloth $Ni_{64}Fe_{18}Mo_{18}$	16.4	60.2
Carbon felt $Ni_{76}Fe_{16}Mo_{8}$	14.9	98.9
Carbon cloth $Ni_{76}Fe_{16}Mo_{8}$	14.4	107.3
Carbon felt $Ni_{85}Mo_{15}$	15.0	126.7
Carbon cloth $Ni_{85}Mo_{15}$	15.9	134.2
Carbon felt Ni_{100}	14.7	195.3
Carbon cloth Ni_{100}	8.7	255.9

transfer resistance than the carbon cloth for all the deposited materials tested.[27] This is due to the fact that the carbon felt has a larger surface area than the carbon cloth, due to its thickness. The electrode with the highest R_{ct} corresponds to the carbon cloth WE modified with Ni_{100}, which presents an R_{ct} almost six times higher than that obtained with the $Ni_{64}Fe_{18}Mo_{18}$ catalyst on the carbon felt WE. It should be noted that a higher difference in charge transfer resistance was obtained for the carbon cloth with respect to the carbon felt covered with both the Ni_{100} catalysts (31%) and the $Ni_{64}Fe_{18}Mo_{18}$ catalyst (32%). The trend observed in the behavior of the catalysts is consistent with the results obtained using the LSV technique for WE carbon cloth modified with the same catalysts. It can be concluded that carbon felt was the best support material for WE, while $Ni_{64}Fe_{18}Mo_{18}$ was the most efficient catalyst, according to the LSV and EIS results.

3.2 Cathode surface morphology characterization

SEM optical microscopy was used to study the distribution of metals on the cathode surface for the electrodeposition of different alloys on the two types of bare electrodes, both on carbon cloth and carbon felt. Figure 3 shows SEM images of the carbon cloth electrodes at 20 × magnification covered with $Ni_{64}Fe_{18}Mo_{18}$ (Figure 3a), $Ni_{76}Fe_{16}Mo_{8}$ (Figure 3b), $Ni_{85}Mo_{15}$ (Figure 3c), and Ni_{100} (Figure 3d).

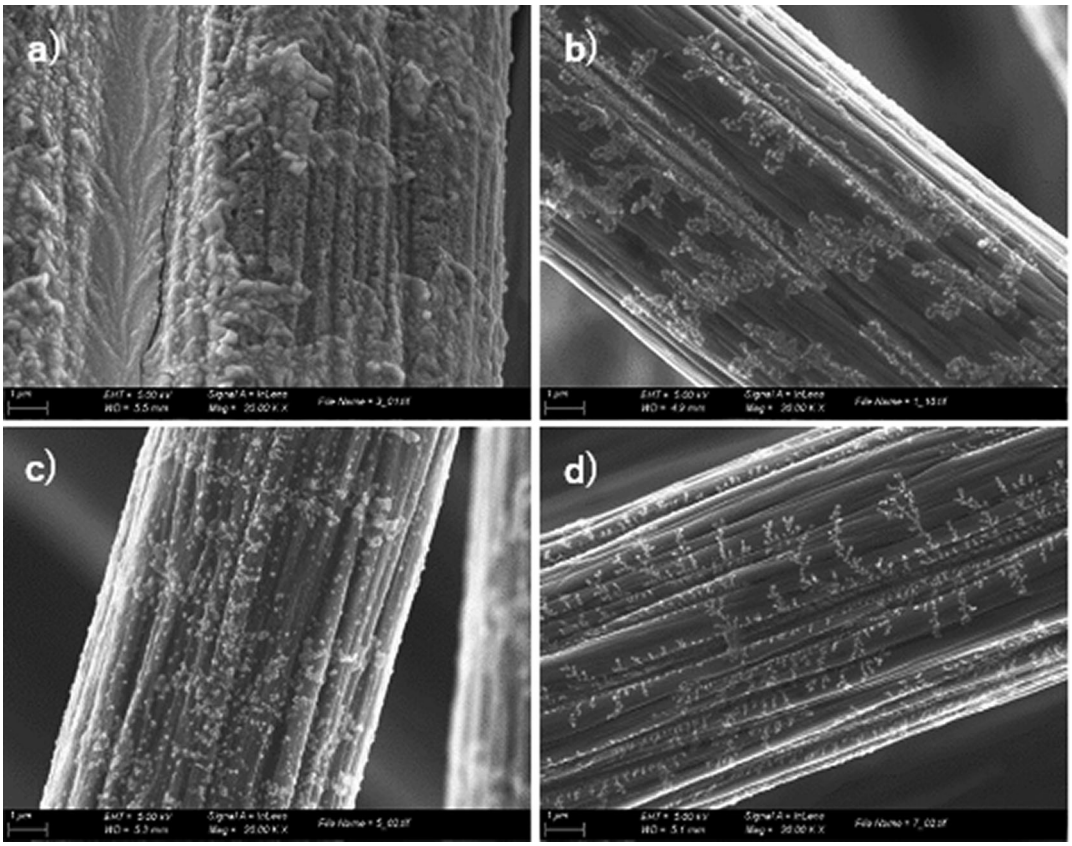

Figure 3. SEM images at 20 k magnification of carbon cloth WE covered with a) $Ni_{64}Fe_{18}Mo_{18}$ catalyst, b) $Ni_{76}Fe_{16}Mo_8$ catalyst, c) $Ni_{85}Mo_{15}$ catalyst, and d) Ni_{100}.

When comparing the surface of the carbon cloth with the different catalysts, it is observed that there is a part of the electrode that is not covered with the catalyst in all cases, *i.e.* there are parts of the electrode where the catalyst has not been electrodeposited. The electrode with the most covered surface was the electrode with the $Ni_{64}Fe_{18}Mo_{18}$ catalyst (Figure 3a), followed by the electrode with the $Ni_{76}Fe_{16}Mo_8$ catalyst (Figure 3b). On the other hand, Figure 4 shows the SEM images of the carbon felt electrodes at 20 k x magnification covered with $Ni_{64}Fe_{18}Mo_{18}$ (Figure 4a), $Ni_{76}Fe_{16}Mo_8$ (Figure 4b), $Ni_{85}Mo_{15}$ (Figure 4c) and Ni_{100} (Figure 4d). In the case of carbon felt, all the catalysts were homogeneously electrodeposited on the entire electrode surface.

In addition, Figure 3 shows that the electrodeposition on the carbon cloth WEs creates branching on the electrode fibers and, conversely, with the carbon felt, the catalyst deposition is more granular (Figure 4), causing the electroactive area of the electrode to increase because of its 3D structure as a catalyst. In addition, Figure S2 and S3 show the SEM images of the carbon cloth and carbon felt, respectively, at 1 k x magnification for the same catalysts shown in Figures 3 and 4. Figure S2c shows that the $Ni_{85}Mo_{15}$ catalyst did not completely coat the fibers. A similar behavior was observed for the Ni_{100} catalyst (Figure S2d), where a branching coating was observed, and a less homogeneous deposition was observed compared to the $Ni_{64}Fe_{18}Mo_{18}$ and $Ni_{76}Fe_{16}Mo_8$ catalysts. Figure S3 shows that in contrast to Figure S2, the least homogeneous depositions with carbon felt were $Ni_{76}Fe_{16}Mo_8$ and Ni_{100}. Interestingly, the catalyst deposition of Ni_{100} on both carbon materials was neither continuous nor homogeneous. The difference between the Ni_{100} coatings could be because they were made at a lower current density and for half the time of the alloys studied. A branching electrodeposition was produced without completely coating the carbon fibers of both materials, which is in line with the Ni metal catalyst, which exhibited the worst performance in catalysis for H_2 generation (Figure 1).

The results from the SEM images were in accordance with the LSV and EIS results. In terms of electrochemical efficiency, the deposition of the catalyst on the carbon felt electrode offered better results than the deposition on the carbon cloth. SEM images showed that the deposition of alloy catalysts on carbon felt was more granular, the coating was more homogeneous, and the electrode fibers were completely covered, thus increasing the catalytic surface area where the electrochemical reaction takes place. The carbon felt electrode has a more geometric surface and more fibers than the

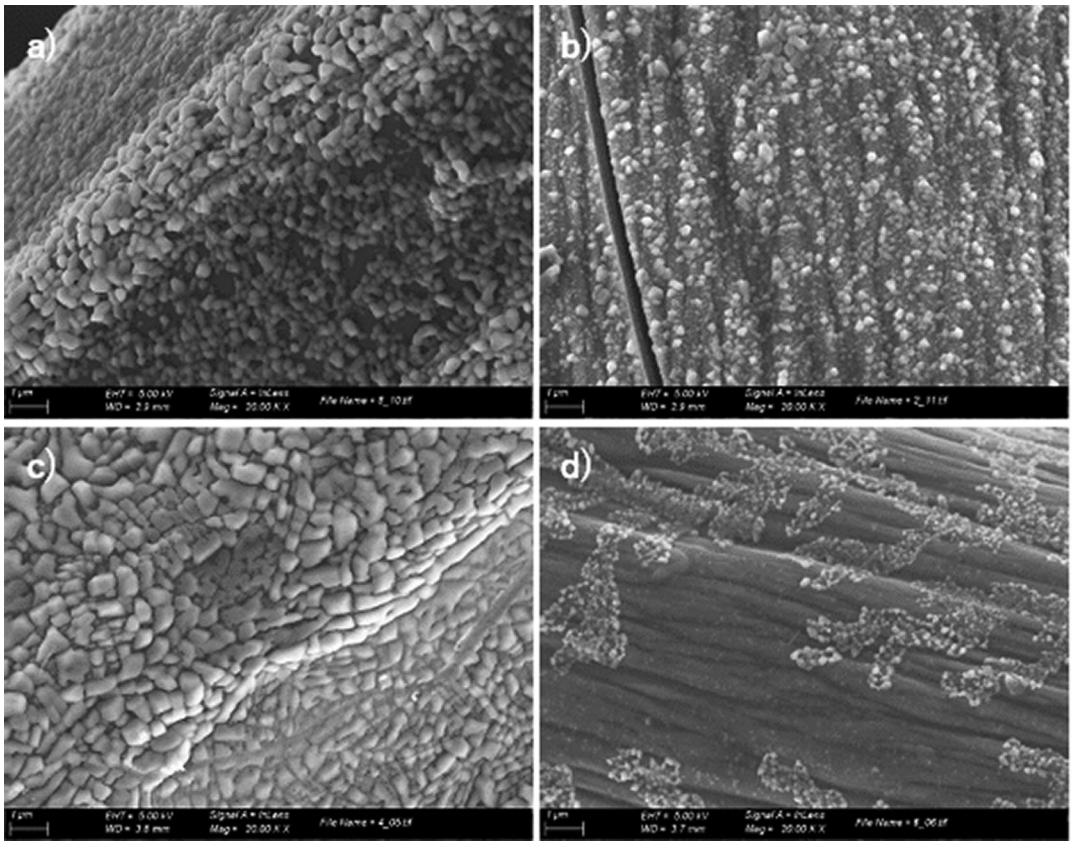

Figure 4. SEM images at 20 k magnification of carbon felt WE covered with a) $Ni_{64}Fe_{18}Mo_{18}$ catalyst, b) $Ni_{76}Fe_{16}Mo_8$ catalyst, c) $Ni_{85}Mo_{15}$ catalyst, and d) Ni_{100}.

carbon cloth electrode, where the alloy can be electrodeposited. In addition, carbon felt is a carbonaceous material with a larger surface area and is also a good and inexpensive conductive material, making it suitable for use as a cathode electrode. Therefore, the increase in the catalyst performance observed from the LSV and EIS results when a carbon-felt WE was used can be attributed to the increase in the geometric area, which facilitates a higher degree of metal electrodeposition. Overall, electrodeposition on carbon felt led to a higher yield of H_2 production.

Comparing all the catalysts used in this study, it can be concluded that the catalyst with the best performance corresponded to the carbon felt electrode with the $Ni_{64}Fe_{18}Mo_{18}$ catalyst. This performance can be related to several factors, such as the homogeneous electrodeposition of the catalyst on the WE (Figure 4) and the composition and ratio of metals in the alloy, which increases the efficiency of the catalyst, making it possible to favor the production of H_2 and increase the efficiency of the WE modified with the $Ni_{64}Fe_{18}Mo_{18}$ catalyst.

3.3 Evaluation of cell performance

The biotic evaluation of the catalysts on the MECs was performed during the three weeks of operation. Six electrodes were tested: three carbon felt and three carbon cloth (CC) electrodes electrodeposited with $Ni_{85}Mo_{15}$, $Ni_{64}Fe_{18}Mo_{18}$ and $Ni_{76}Fe_{16}Mo_8$. The Ni_{100} electrode was discarded based on the results of abiotic electrochemical characterization.

Figure 5 shows the current densities obtained during the three weeks of operation. The $Ni_{64}Fe_{18}Mo_{18}$ cathode exhibits the best performance. The highest current density was obtained for the carbon felt electrode, with a maximum of 1.1 $mA{\cdot}cm^{-2}$, followed by the carbon cloth electrode with the same catalyst (1.0 $mA{\cdot}cm^{-2}$). Both cells generated a similar amount of gas, 1.2 $m^3m^{-3}d^{-1}$ for the cell with the carbon felt electrode and 1.1 $m^3m^{-3}d^{-1}$ for the carbon cloth electrode. As an alternative to the $Ni_{64}Fe_{18}Mo_{18}$ catalyst, the WE covered with the $Ni_{76}Fe_{16}Mo_8$ catalyst followed the former in terms of performance. In this case, a similar current density was obtained for both the carbon felt electrode and the carbon cloth electrode with the $Ni_{76}Fe_{16}Mo_8$ catalyst (Figure 5); however, in the last cycle, the electrode with carbon felt provided the highest current density. This result is consistent with that obtained in abiotic experiments (see Section 3.1). This could be attributed to the slightly larger geometric area of the carbon felt. These cells generated 0.9 ± 0.2 $m^3m^{-3}d^{-1}$ of gas for the carbon cloth electrode cell and 1.1 ± 0.1 $m^3m^{-3}d^{-1}$ for carbon felt electrode cell.

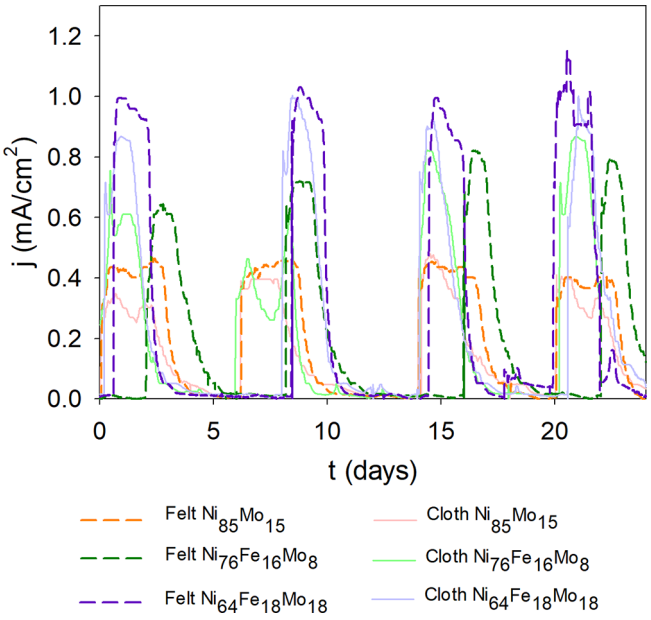

Figure 5. Current density of the cells with the six cathodes studied and the different catalysts.

Finally, the catalyst exhibited the worst biotic performance was the $Ni_{85}Mo_{15}$ catalyst. In this case, similar performance was also observed for the carbon felt and carbon cloth catalysts, even though the carbon felt electrode produced a higher current density (maximum 0.5 mA·cm^{-2}) compared to the carbon cloth electrode (maximum of 0.4 mA·cm^{-2}). The H_2 production was 0.8 $m^3m^{-3}d^{-1}$ with the carbon felt electrode and 0.5 $m^3m^{-3}d^{-1}$ with the carbon cloth electrode. The amount of gas produced in each cell was much lower than would be expected when the cells were operating at 100%. It is likely that the cells suffered from gas leaks and possible gas recirculation, which reduced the amount of H_2 that was produced.

To properly evaluate the behavior of the H_2 catalysts in MECs, their performance was compared with that of other electrodeposited catalysts studied in the literature, other than Pt, because the main objective of this work was to find an alternative catalyst to replace Pt in the H_2 production electrode produced by the H^+ reduction reaction. A current density of 0.9 mA·cm^{-2} was reported in MECs with electrochemically deposited NiW catalyst, which is 25% lower than in the case of the $Ni_{64}Fe_{18}Mo_{18}$ catalyst in carbon felt WE.[14] Other studies have used Ni foam as a catalyst instead of a Ni alloy. In this case, although the cell dimensions were smaller, the $Ni_{64}Fe_{18}Mo_{18}$ catalyst electrodes studied here achieved up to 20% higher current density.[28] A maximum volumetric H_2 production of 0.76 m^3m^{-3} day^{-1} was reported using nickel 625 as the cathode, which was significantly lower than that of our best catalyst, which had a maximum volumetric H_2 production rate of 1.2 m^3m^{-3} day^{-1}. Finally, Lee et. al[29] reported the use of a carbon felt electrode without any metal for H_2 production, obtaining a current density of 0.33 mA·cm^{-2}, 73% lower than the maximum current density obtained with the carbon felt WE and $Ni_{64}Fe_{18}Mo_{18}$.

It can be concluded that the $Ni_{64}Fe_{18}Mo_{18}$ catalyst with carbon felt WE could be used in MECs because of its higher performance compared to other catalysts used for H_2 production. It should be emphasized that the study of these catalysts needs to be extended to a longer operation time to stabilize the maximum current density and to more precisely define the advantages and limitations of using these metallic alloys as catalysts.

3.4 Economic study of the different catalysts

To properly evaluate the different catalysts and check their potential for full-scale implementation of MECs, a cost study of each type of alloy was carried out. This study presents a preliminary assessment of the total costs estimated from the cost of the materials needed at the laboratory scale. Obviously, a proper marketability analysis that is beyond the scope of this work is warranted to scale up these results.

The analysis was performed using two types of bare electrodes used in this study. In the case of the carbon felt, *Carbon Felt 3.18 mm thick 99.0%* (ThermoScientific Chemicals) was used (99.36 €·m^{-2}) whereas *Zoltek Fabrics* (Carbonized Woven Fabric, Plain Weave 237 g·m^{-2}) was used in the case of the carbon cloth (38.09 €·m^{-2}). As for the preparation of

the technique, 13.4 mL of ethanol, 0.6 ml of Milli-Q water, and 0.2 mL of acetic acid, were used in all cases, leading to an equivalent cost for all of electrodes manufactured.

On the other hand, some reagents change for each catalyst used: to perform the manual Cu deposition, for one electrode it is necessary to use 4 g of Cu (Cu nanoparticles (Sigma Aldrich), 25 nm nanoparticle size) and 10 drops of the commercial solution Tween 20. A total of 0.5 mL of Tween 20 is needed, assuming that one drop is 0.05 mL. For the manual deposition of Ni_{100}, the procedure and reactants were exactly the same as those for the manual deposition of Cu_{100}, except that Cu was substituted for Ni.

For the electrodeposited catalysts, all solutions required the use of 0.16 mol $Na_3C_6H_5O_7$ and 0.5 mol $NaHCO_3$, added per 1 L. Specifically, for the electrodeposition of Ni_{100}, 0.250 mol of $NiCl_2$ was needed. For the $Ni_{85}Mo_{15}$ electrodeposition, 0.213 mol of $NiCl_2$ and 0.038 mol of Na_2MoO_4 were used. For the $Ni_{64}Fe_{18}Mo_{18}$ electrodeposition, 0.045 mol $FeCl_3$, 0.160 mol $NiCl_2$, and 0.045 mol Na_2MoO_4 were required. Finally, 0.040 mol of $FeCl_3$, 0.190 mol of $NiCl_2$ and 0.020 mol of Na_2MoO_4 were used for the $Ni_{76}Fe_{16}Mo_8$ electrodeposition.

The electrical cost for electrodeposition was also considered, considering the unit cost of electricity (Table 2), a potentiostat power requirement of 2 kWh, and the time required for the electrodeposition of Ni (3 h) or the rest of the catalyst electrodeposition (6 h).

The unit cost of these materials is shown in Table 2, where Milli-Q water has a negligible cost.

Table 3 shows the cost of the materials for the construction of electrodes for each technique based on the quantity and cost of each material used. It should be noted that the carbon felt electrode is more expensive than the carbon cloth electrode, but it provides better results and is more homogeneous. In fact, the costs normalized by the H_2 production in Table 3 show that carbon felt leads to lower costs and is therefore more cost-effective for use in electrochemical cells. Besides, it can be seen that manual depositions are more expensive than electrodeposits, as well as showing worse results. Among the electrodeposits, the most economical is $Ni_{76}Fe_{16}Mo_8$ followed by $Ni_{64}Fe_{18}Mo_{18}$, Ni_{100} and $Ni_{85}Mo_{15}$. When normalized by H_2 production, these prices were the most economical is $Ni_{64}Fe_{18}Mo_{18}$, followed by $Ni_{76}Fe_{16}Mo_8$ and $Ni_{85}Mo_{15}$.

Considering the quantities of each material used, the cost of the materials for the construction of electrodes for each technique would be 61.5 € per cathode for manual Cu deposition and 58.4 € for manual Ni deposition, whereas for electrodeposition techniques it would be 43.4 € for Ni_{100}, 44.8 € for $Ni_{85}Mo_{15}$, 42.5 € for $Ni_{64}Fe_{18}Mo_{18}$ and 42.0 € for $Ni_{76}Fe_{16}Mo_8$ per cathode manufactured. It is worth mentioning that the absolute costs of materials are unrealistic from an

Table 2. Unit costs of different materials used for different catalysts ink.

Material	Unit costs
Carbon cloth	38.09 €·m^{-2}
Carbon felt	99.36 €·m^{-2}
Ethanol	41 €·L^{-1}
Milli-Q water	Negligible
Acetic acid	133 €·2.5 L^{-1}
Cu nanoparticles	76 €·5 g^{-1}
Tween 20	36.90 €·100 mL^{-1}
Ni nanoparticles	73 €·5 g^{-1}
$Na_3C_6H_5O_7$	64.80 €·1 kg^{-1}
$NaHCO_3$	47.80 €·500 g^{-1}
$NiCl_2$	279 €·250 g^{-1}
Na_2MoO_4	78.90 €·100 g^{-1}
$FeCl_3$	46.0 €·100 g^{-1}
Electricity	0.090 €·kWh^{-1}*

*Data acquired on 16.07.2024 from the Sigma Aldrich website. The average electricity price was that of Spain on the date 16.07.2024.

Table 3. Construction costs of cathodes and normalized costs based on the H_2 production of the different depositions.

	Deposition	Cathode cost (€)	H_2 production ($m^3m^{-3}d^{-1}$)	Normalized cost ($€(m^3m^{-3}d^{-1})^{-1}$)
Carbon felt	Cu Manual	61.8	-	-
	Ni Manual	58.7	-	-
	Ni_{100} electrodep.	43.7	-	-
	$Ni_{85}Mo_{15}$ electrodep.	45.1	0.8	56.4
	$Ni_{76}Fe_{16}Mo_8$ electrodep.	42.3	1.1	38.5
	$Ni_{64}Fe_{18}Mo_{18}$ electrodep.	42.8	1.2	35.7
Carbon cloth	Cu Manual	61.5	-	-
	Ni Manual	58.4	-	-
	Ni_{100} electrodep.	43.4	-	-
	$Ni_{85}Mo_{15}$ electrodep.	44.8	0.5	89.6
	$Ni_{76}Fe_{16}Mo_8$ electrodep.	42.0	0.9	46.7
	$Ni_{64}Fe_{18}Mo_{18}$ electrodep.	42.5	1.1	38.6

industrial production scale, as well as biased by market fluctuations and the variability of materials. However, benchmarking at the lab scale can shed light on the relative viability of each technique.

In general, manual deposition is more expensive and less efficient than electrodeposition. Therefore, manual deposition could be discarded in the future. Electrodeposition, in addition to being more economical, offers better current density results and more homogeneous electrode modification. In addition, all electrodepositions have similar costs per electrode, with $Ni_{76}Fe_{16}Mo_8$ and $Ni_{64}Fe_{18}Mo_{18}$ being the cheapest and best-performing catalysts, respectively. Thus, considering the economic and performance factors, electrodeposition of $Ni_{64}Fe_{18}Mo_{18}$ is the most profitable.

Under these considerations, $Ni_{64}Fe_{18}Mo_{18}$ electrodeposition using carbon felt was found to be the most economical alternative, considering its cost and performance.

The economic comparison with electrodes with Pt ink, which is the most common, would be complicated, as the conditions must be the same. Commercial Pt ink has previously been used by the research group,[30] but because the deposition conditions of the catalytic ink and the cell are different, a direct comparison of the associated costs could not be made.

4. Conclusions

In this study, the use of different catalysts for H_2 production in MECs, namely Cu_{100}, Ni_{100}, $Ni_{85}Mo_{15}$, $Ni_{64}Fe_{18}Mo_{18}$ and $Ni_{76}Fe_{16}Mo_8$, was evaluated. The WEs were modified using two complementary strategies, manual deposition and electrodeposition, and two carbon materials, carbon cloth and carbon felt, were used.

All the catalysts were biotically characterized, and it was observed that the catalysts with manual deposition had worse performance than those with electrodeposition. EIS and LSV results during the characterization of the cells operating in abiotic mode showed that the electrode with electrodeposited Ni_{100} had worse performance than the other catalysts.

The performance of biotic MECs showed that the catalyst that provided the highest performance was $Ni_{64}Fe_{18}Mo_{18}$ on carbon felt WE, obtaining a current density of 1.2 $mA{\cdot}cm^{-2}$, similar to the electrode with the same catalyst but deposited in carbon cloth (1.1 $mA{\cdot}cm^{-2}$). These catalysts achieve over 50% of the current density of $Ni_{85}Mo_{15}$ (0.4 $mA{\cdot}cm^{-2}$ with carbon cloth and 0.5 $mA{\cdot}cm^{-2}$ with carbon felt). $Ni_{76}Fe_{16}Mo_8$ shows 1.1 ± 0.1 $mA{\cdot}cm^{-2}$ with carbon felt and 0.9 ± 0.2 $mA{\cdot}cm^{-2}$ with carbon cloth.

Although the results obtained in terms of the current intensity are similar to those found in the literature, the volume of H_2 obtained is much lower than expected. Therefore, it can be concluded that the cells probably had gas leaks because the operation time was too short for the H_2-competing microorganisms to grow.

However, taking into account the cost of manufacturing the electrodes with different depositions of $Ni_{76}Fe_{16}Mo_8$ electrodeposition in carbon cloth provided the lowest cost for their construction, whereas $Ni_{64}Fe_{18}Mo_{18}$ electrodeposited in carbon felt showed the lowest cost of the materials with respect to hydrogen production.

Ethics and consent

Ethical approval and consent were not required.

Data availability

CORA.RDR. "Towards the implementation of a more economical catalyst for hydrogen production in microbial electrolysis cells". The data are publicly available at https://doi.org/10.34810/data2866.[31]

This project contains the following underlying data:

- DATA:

  Current density_Alloys.ods

  EIS_Catalysts_Electrodes.ods

  LSV_Catalysts_CarbonCloth.ods

- IMATGES:

  Photographs C-MEC.jpeg

  SEM_Carbon Cloth_1K.tif

  SEM_Carbon Cloth_20K.tif

  SEM_Carbon Felt_1K.tif

  SEM_Carbon Felt_20K.tifNote: Figure S1 corresponds to Photographs C-MEC.jpeg, Figure S2 corresponds to SEM_Carbon Cloth_1K.tif and Figure S3 corresponds to SEM_Carbon Felt_1K.tif.

Data are available under the terms of the Creative Commons Attribution 4.0 International license (CC-BY 4.0).

Acknowledgments

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References

1. Sewsynker Y, Kana EBG, Lateef A: **Modelling of Biohydrogen Generation in Microbial Electrolysis Cells (MECs) Using a Committee of Artificial Neural Networks (ANNs).** *Biotechnol. Biotechnol. Equip.* 2015; **29**: 1208–1215.
Publisher Full Text

2. Jeremiasse AW, Bergsma J, Kleijn JM, *et al.*: **Performance of Metal Alloys as Hydrogen Evolution Reaction Catalysts in a Microbial Electrolysis Cell.** *Int. J. Hydrog. Energy.* 2011; **36**: 10482–10489.
Publisher Full Text

3. Logan BE, Call D, Cheng S, *et al.*: **Microbial Electrolysis Cells for High Yield Hydrogen Gas Production from Organic Matter.** *Environ. Sci. Technol.* 2008; **42**: 8630–8640.
Publisher Full Text

4. Kundu A, Sahu JN, Redzwan G, *et al.*: **An Overview of Cathode Material and Catalysts Suitable for Generating Hydrogen in Microbial Electrolysis Cell.** *Int. J. Hydrog. Energy.* 2013; **38**: 1745–1757.
Publisher Full Text

5. Sánchez-Peña P, Rodriguez J, Gabriel D, *et al.*: **Graphene Functionalization with Metallic Pt Nanoparticles: A Path to Cost-Efficient H2 Production in Microbial Electrolysis Cells.** *Int. J. Hydrog. Energy.* 2022; **47**: 15397–15409.
Publisher Full Text

6. Ribot-Llobet E, Nam JY, Tokash JC, *et al.*: **Assessment of Four Different Cathode Materials at Different Initial PHs Using Unbuffered Catholytes in Microbial Electrolysis Cells.** *Int. J. Hydrog. Energy.* 2013; **38**: 2951–2956.
Publisher Full Text

7. Selembo PA, Merrill MD, Logan BE: **The Use of Stainless Steel and Nickel Alloys as Low-Cost Cathodes in Microbial Electrolysis Cells.** *J. Power Sources.* 2009; **190**: 271–278.
Publisher Full Text

8. Call DF, Merrill MD, Logan BE: **High Surface Area Stainless Steel Brushes as Cathodes in Microbial Electrolysis Cells.** *Environ. Sci. Technol.* 2009; **43**: 2179–2183.
Publisher Full Text

9. Selembo PA, Merrill MD, Logan BE: **Hydrogen Production with Nickel Powder Cathode Catalysts in Microbial Electrolysis Cells.** *Int. J. Hydrog. Energy.* 2010; **35**: 428–437.
Publisher Full Text

10. Hrapovic S, Manuel MF, Luong JHT, *et al.*: **Electrodeposition of Nickel Particles on a Gas Diffusion Cathode for Hydrogen Production in a Microbial Electrolysis Cell.** *Int. J. Hydrog. Energy.* 2010; **35**: 7313–7320.
Publisher Full Text

11. Manuel MF, Neburchilov V, Wang H, *et al.*: **Hydrogen Production in a Microbial Electrolysis Cell with Nickel-Based Gas Diffusion Cathodes.** *J. Power Sources.* 2010; **195**: 5514–5519.
Publisher Full Text

12. Jeremiasse AW, Hamelers HVM, Saakes M, *et al.*: **Ni Foam Cathode Enables High Volumetric H2 Production in a Microbial Electrolysis Cell.** *Int. J. Hydrog. Energy.* 2010; **35**: 12716–12723.
Publisher Full Text

13. Selvarani V, Kiruthika S, Jayaprakash P, *et al.*: **Enhanced Ethylene Glycol Oxidation in Membraneless Fuel Cells: Comparative Analysis of Nickel Alloy Nanocatalysts.** *Int. J. Hydrog. Energy.* 2024; **77**: 441–449.
Publisher Full Text

14. Hu H, Fan Y, Liu H: **Hydrogen Production in Single-Chamber Tubular Microbial Electrolysis Cells Using Non-Precious-Metal Catalysts.** *Int. J. Hydrog. Energy.* 2009; **34**: 8535–8542.
Publisher Full Text

15. Hu H, Fan Y, Liu H: **Optimization of NiMo Catalyst for Hydrogen Production in Microbial Electrolysis Cells.** *Int. J. Hydrog. Energy.* 2010; **35**: 3227–3233.
Publisher Full Text

16. Wang L, Chen Y, Ye Y, *et al.*: **Evaluation of Low-Cost Cathode Catalysts for High Yield Biohydrogen Production in Microbial Electrolysis Cell.** *Water Sci. Technol.* 2011; **63**: 440–448.
PubMed Abstract | Publisher Full Text

17. Harnisch F, Sievers G, Schröder U: **Tungsten Carbide as Electrocatalyst for the Hydrogen Evolution Reaction in pH Neutral Electrolyte Solutions.** *Appl. Catal. B.* 2009; **89**: 455–458.
Publisher Full Text

18. Sánchez-Peña P, Rodriguez J, Baeza JA, *et al.*: **A Critical Evaluation of Platinum Deposition Techniques for Hydrogen Production in Microbial Electrolysis Cells.** *Int. J. Hydrog. Energy.* 2024; **90**: 1012–1022.
Publisher Full Text

19. Call D, Logan BE: **Hydrogen Production in a Single Chamber Microbial Electrolysis Cell Lacking a Membrane.** *Environ. Sci. Technol.* 2008; **42**: 3401–3406.
Publisher Full Text

20. Liu H, Logan BE: **Electricity Generation Using an Air-Cathode Single Chamber Microbial Fuel Cell in the Presence and Absence of a Proton Exchange Membrane.** *Environ. Sci. Technol.* 2004; **38**: 4040–4046.
Publisher Full Text

21. Sánchez-Peña P, Rodriguez J, Montes R, *et al.*: **Less Is More: A Comprehensive Study on the Effects of the Number of Gas Diffusion Layers on Air–Cathode Microbial Fuel Cells.** *ChemElectroChem.* 2021; **8**: 3416–3426.
Publisher Full Text

22. Borole AP, Aaron D, Hamilton CY, *et al.*: **Understanding Long-Term Changes in Microbial Fuel Cell Performance Using Electrochemical Impedance Spectroscopy.** *Environ. Sci. Technol.* 2010; **44**: 2740–2745.
PubMed Abstract | Publisher Full Text

23. Baeza JA: **Advanced Direct Digital Control (AddControl): Lessons Learned from 20 Years of Adding Control to Lab and Pilot Scale Treatment Systems.** *Proceedings of the 13th IWA Conference on Instrumentation, Control and Automation. ICA 2022.* Beijing (China): Tsinghua University; 2022; pp. 13–15.

24. He Z, Mansfeld F: **Exploring the Use of Electrochemical Impedance Spectroscopy (EIS) in Microbial Fuel Cell Studies.** *Energy Environ. Sci.* 2009; **2**: 215–219.
Publisher Full Text

25. Manohar AK, Bretschger O, Nealson KH, *et al.*: **The Polarization Behavior of the Anode in a Microbial Fuel Cell.** *Electrochim. Acta.* 2008; **53**: 3508–3513.
Publisher Full Text

26. Muñoz J, Montes R, Baeza M: **Trends in Electrochemical Impedance Spectroscopy Involving Nanocomposite Transducers: Characterization, Architecture Surface and Bio-Sensing.** *TrAC - Trends in Analytical Chemistry.* 2017; **97**: 201–215.
Publisher Full Text

27. Al-Badani M, Chong PL, Lim HS: **A Mini Review of the Effect of Modified Carbon Paper, Carbon Felt, and Carbon Cloth Electrodes on the Performance of Microbial Fuel Cell.** *Int. J. Green Energy.* 2024; **21**: 170–186.
Publisher Full Text

28. Li F, Liu W, Sun Y, *et al.*: **Enhancing Hydrogen Production with Ni–P Coated Nickel Foam as Cathode Catalyst in Single Chamber Microbial Electrolysis Cells.** *Int. J. Hydrog. Energy.* 2017; **42**: 3641–3646.
Publisher Full Text

29. Lee H-S, Torres CI, Parameswaran P, *et al.*: **Fate of H2 in an Upflow Single-Chamber Microbial Electrolysis Cell Using a Metal-Catalyst-Free Cathode.** *Environ. Sci. Technol.* 2009; **43**: 7971–7976.
Publisher Full Text

30. Ul Z, Sánchez-Peña P, Baeza M, *et al.*: **Systematic Screening of Carbon-Based Anode Materials for Bioelectrochemical Systems.** *J. Chem. Technol. Biotechnol.* 2023; **98**: 1402–1415.
Publisher Full Text

31. Sánchez-Peña P, Ottone C, Aroca G, *et al.*: **Replication data for "Towards the implementation of a more economical catalyst for hydrogen production in microbial electrolysis cells".** *CORA. Repositori de Dades de Recerca.* 2026; **V1**.
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Reviewer Report 15 June 2026

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Omprakash Sarkar
Luleå University of Technology, Luleå, Sweden

Towards the implementation of a more economical catalyst for hydrogen production in microbial electrolysis cells

This study investigates cost-effective alternatives to platinum catalysts in microbial electrolysis cells (MECs) to improve hydrogen production from wastewater.
Need to provide some details on wastewater used and its chemical composition.

The authors may include a discussion of how the economic advantages of electrodeposition techniques, particularly Ni64Fe18Mo18, hold up against traditional methods like Pt ink, especially when factoring in the variability of conditions? Could the findings suggest a paradigm shift in electrode manufacturing preferences?

Comments

1. Authors may discuss how the choice of working electrodes-WE support material influence the internal resistance and electron transfer rates in electrochemical cells, particularly when comparing carbon felt and carbon cloth electrodes with identical catalyst modifications?
2. in Table 1, does the findings suggest that the superior performance of the carbon felt electrode with the Ni64Fe18Mo18 catalyst, evidenced by the lowest charge transfer resistance (Rct), is due to its enhanced electrical conductivity and larger surface area compared to carbon cloth?
3. 2.1 Microbial electrolysis cell construction--- need to provide some details on microbial culture and conditions
4. While carbon cloth promotes branching on fibers, carbon felt results in a more granular deposition. What is the observation of Authors regarding how does the electrodeposition process on carbon cloth and carbon felt influence the morphology and electroactive area of catalysts?
5. Could the Ni85Mo15 catalyst's poor biotic performance indicate a fundamental issue with its design or composition? While the carbon felt and cloth electrodes showed varying current densities, could the observed gas leaks and recirculation significantly affect the H2

production results?
6. The study highlighted the need for a comprehensive market analysis beyond preliminary cost evaluations at the lab scale. Can provide some more discussion on how the economic viability of various catalysts for MECs be effectively assessed?
7. While manual Cu and Ni deposition are notably more expensive, is it reasonable to consider these methods obsolete given their inefficiency? How can one justify the apparent cost discrepancies between manual and electrodeposition techniques for electrode construction?

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
Not applicable

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Microbial metabolites, Microbial fuel cells, fermentation, Bioelectrochemical system

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 15 June 2026

https://doi.org/10.21956/openreseurope.24093.r74996

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Ruggero Rossi

Johns Hopkins University, Baltimore, Maryland, USA

In this manuscript, the authors studied the optimal composition and deposition technique for catalyst preparation for MECs. Two different electrode supports were selected. The authors demonstrated that catalysts with specific molar fractions were more active toward HER than others and demonstrated higher performance in biotic MEC tests. The results reported here are in part novel. The presentation of the results is not clear in some points, and the discussion could be strengthened by including additional results.
Abstract / Results: "manually deposited" does not allow to grasp what the authors mean. Specifying that the catalyst was in an ink that was spread over the current collector surface could help clarifying this.
Abstract / Results: "and was therefore excluded" is not clear.
Abstract / Results: "demonstrated comparable performance to Pt in terms of the current density". The tests with Pt were not reported, a fair comparison is not possible.
Introduction: at neutral pH, the concentration of H+ is only 10^-7 M, compared to 55 M for H2O. It is more likely (and some papers in the literature support that) that H2O is being reduced rather than H+. This differentiation is important in that it explains mass transfer in the MEC and the development of pH gradients across the electrodes (H+ is produced at the anode but not transported or removed at the cathode.)
Introduction: "the reduction reaction of H^+ to H_2 has very slow kinetics" this is true only at high pH.
Introduction: It would be appropriate to report the rationale used to select the molar fraction of the different catalyst. It is not clear now why those specific molar fractions were selected.
Materials: "The amplitude was set to 1 mV to avoid detachment of the biofilm" it is not clear how a larger amplitude would facilitate the detachment of the biofilm. Also, running EIS at OCV, while common for corrosion studies, in which no current is typically applied, provide little information on electrochemical cells, which rarely operate at OCV.
Results: In the Introduction, the authors mentioned that some of the alloys and metals reported in this study are being used to replace Pt. Including the abiotic tests of Pt in Fig 1 would be helpful to understand the difference in performance of the new catalysts compared to the traditional Pt.
Results: "makes it easier to transfer electrons from one electrode to another" the sentence is not clear.
Results: "This is due to the fact that the carbon felt has a larger surface area than the carbon cloth, due to its thickness." The authors could include the electrochemically active surface area measurements to support this statement.
Results: SEM figures. It would be helpful to include EDS data to demonstrate that the reported molar ratio of the catalysts is retained on the electrode. With the currently available information, it is not possible to ensure that the molar ratio used to prepare the ink or in solution is matched with the molar ratio on the electrode itself.
Results: Ensure consistency in reporting units: the abiotic tests results are reported in A, while the biotic tests are reported in mA/cm2.
Results: there is no statistical analysis of the biotic tests.
Results: Using the whole cell results to demonstrate the activity of the different cathode catalysts could be problematic in that only a portion, and it is not clear how big or small, of the whole cell performance is due to the cathode, with anode and ohmic contributing to the other portion. Using the cathode potentials, if recorded, could solve this issue.
Results: The authors could look into more recent literature on the use of Ni based alloys in MECs. High current density and hydrogen production rates were demonstrated.

Conclusions: Only a portion of catalysts were biotically characterized, not all of them.

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Partly

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Partly

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?
Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Bioelectrochemistry

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.