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Catalysis of the hydrogen evolution reaction by hydrogen carbonate to decrease the voltage of microbial electrolysis cell fed with domestic wastewater

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A B S T R A C T

Microbial electrolysis applied to wastewater treatment allows hydrogen to be produced at low cost, provided that the cell voltage is as low as possible. Here, hydrogen production at low cell voltage was optimized through the use of a carbonate solution that acted as a homogeneous catalyst of hydrogen evolution on stainless steel cathodes at mild pH and allowed the conductivity to be increased near the cathode. Replacing wastewater by a 1 M carbonate solution as the catholyte allowed the cathode potential to be reduced by 380 mV at 10 A/m². Optimizing the pH in the range of 7–12 revealed that the key species in water reduction catalysis was HCO₃⁻ and that the reaction rate was highest at pH 8. Tests with various materials (stainless steels, nickel alloy and graphite) as cathodes showed that the catalytic effect of HCO₃⁻ ions was highest on stainless steels containing Ni, Mo and Mn, such as 316L or 254SMO.

1. Introduction

Hydrogen gas is predominantly produced from fossil fuels (96%) at present. The remaining 4% of the international production comes from water electrolysis [1,2]. Assuming that the electrical energy used for powering electrolyzers comes from renewable resources, the production of hydrogen by water electrolysis is a sustainable process with a small ecological footprint. Microbial electrolysis applied to wastewater treatment is an electrolysis technology that can produce low cost hydrogen [3,4], thus further restricting the ecological impact of hydrogen generation. Typically, a microbial electrolysis cell (MEC) generates hydrogen in the voltage range of 0.5 V–1.5 V, while a conventional alkaline electrolyser needs an operating voltage of 2.0–3.0 V. The electrolysis voltage required to generate hydrogen in an MEC is lowered thanks to the electroactive microbial biofilm developed on the anode surface, which catalyses the oxidation of the organic load contained in the wastewater [5,6].

While the aerobic wastewater treatment process based on activated sludge is energy intensive (1.2 kWh/kg COD (chemical

oxygen demand)), the dual function of an MEC (producing hydrogen while cleaning wastewater) is, in principle, a promising solution for wastewater treatment plants that run in close to energy neutral conditions. This consideration is only true if the electrical energy supplied to the MEC is less than the energy potentially contained in the hydrogen produced when it is converted into water vapour and heat by catalytic combustion, or directly into electricity in a fuel cell. The energy consumed by an MEC is proportional to the voltage applied to the cell (U_{cell}). For a given hydrogen production, the value of U_{cell} depends on many factors, as shown by equation (1):

$$U_{\text{Cell}} = \Delta E^{\circ} + \eta_a + \eta_c + \sum R \cdot I \quad (1)$$

where ΔE° is the standard potential of the reactions occurring in the cell (V), η_a and η_c are the anode and cathode overpotentials (V), respectively, and $\sum R \cdot I$ is the ohmic drop (V).

The use of domestic wastewater in an MEC is still a technological challenge as domestic wastewater induces limitations due to:

- (i) its low conductivity (0.5–2.5 mS/cm [4,7]), which limits the ion transport within the electrolysis cell [8] and creates a

large ohmic drop proportional to the inter electrode distance [9].

- (ii) its low soluble COD load (150–400 mg/L [10]), which limits the kinetics of the bioanode when no artificial carbon source, such as acetate, is added to the electrolyte [11,12].
- (iii) its pH, often close to neutrality (6.5–7.5 [7,13]), which is unfavourable for the electrochemical reduction of water into hydrogen. Commercial electrolysers operate more conventionally with concentrated alkaline electrolytes (alkaline electrolysis [14]) or strongly acidic pH (polymer electrolyte membrane fuel cell technologies [15,16]).
- (iv) the microbial production of gaseous by products (H₂S, CO₂, ammonia, CH₄), which are related to the microbial activity of the aerobic, anaerobic and fermenting consortia and degrade the purity of the hydrogen gas produced. Using a membrane to separate anodic and cathodic compartments limits gas mixing but also creates a barrier to the exchange of ions between compartments, increasing the ohmic drop and creating a pH gradient in the cell [17].

Many areas of improvement have been proposed to reduce the U_{cell} of MECs fed with domestic wastewater. The anode over potential can be reduced by using 3D electrodes or porous electrodes that promote biofilm development thanks to their huge specific surface area [18]. The cathode overpotential can be lowered by using metallic catalysts, e.g. Ni based catalysts [19,20], applied to the cathode surface or biological catalysts naturally forming from wastewater [21,22]. The ohmic drop in the MEC can be decreased by designing specific reactor geometries that minimize the distance between electrodes [23] or by using membrane electrode assemblies [24].

Homogeneous catalysis has, so far, been little exploited for reducing the cathode overpotential of MECs. Weak acids have been demonstrated to catalyse hydrogen evolution reaction on metallic materials [25,26]. The mechanism of water reduction catalysed by weak acids has been investigated in depth with phosphate species [27] and has been described as a four step process (HA and A⁻ are the non dissociated and dissociated forms, respectively):



The use of carbonate instead of phosphate as a homogeneous catalyst would have many environmental and economic advantages. Carbonate has less effect on the environment than phosphate, which causes problems of eutrophication and dystrophication in aquatic environments, and carbonate is nearly 50% cheaper than phosphate.

The purpose of this work was to assess the capacity of carbonate to catalyse H₂ evolution on metallic cathodes. The effect of the carbonate concentration on the kinetics of water reduction was studied. The kinetics of water reduction in carbonate solutions and in domestic wastewater were compared in order to estimate the cathode potential (E_c) gain due to the carbonate solution. Experiments were conducted at pH ranging from 7.0 to 12.0 so as to understand which carbonate species (CO₃²⁻, HCO₃⁻, H₂CO₃) were involved in the mechanism of water reduction catalysis. Finally, various grades of stainless steels and Ni alloys were compared to graphite as cathode material to determine which one would be the most suitable to enhance the catalytic effect of carbonate.

2. Materials and methods

2.1. Chemicals

The chemical products used in the experiments were: potassium hydrogen carbonate (KHCO₃, 99.5%; Sigma Aldrich), potassium carbonate (K₂CO₃, 99+%; Acros Organics), potassium chloride (KCl, 99+%; Acros Organics), potassium hydroxide (KOH, 85%; Acros Organics), and hydrochloric acid (HCl, 37%; Acros Organics).

All solutions were prepared with deionized water (Elga Purelab Option R; 15 MΩ cm). The pH of the solutions was measured with a pH meter (Eutech Instruments) and, in some cases, adjusted using 3 M solutions of KOH or HCl. The conductivity of the solutions was measured with an EC meter (RadioMeter) and, in some cases, adjusted to a given value by adding KCl.

2.2. Domestic wastewater

Domestic wastewater was collected at the wastewater treatment plant of Castanet (France) and stored at 4 °C before use.

2.3. Materials

Working electrodes (cathodes) were rectangular plates (1.5 cm × 2 cm). Current densities were expressed with respect to the surface area of the two sides of the electrode, i.e. 6 cm². Seven materials were tested: stainless steels AISI 316L, 304, 310, 430 and 254SMO; nickel alloy (Ni 80%, Fe 20%), and graphite. The compositions of the materials were determined by energy dispersive X ray spectroscopy (EDX). Before each experiment, the electrodes were ground with abrasive discs (P800, P1200, P2400; Presi). No chemical treatment was applied to the electrodes. The current collectors were threaded titanium rods insulated along their length with heat shrinkable tube.

2.4. Voltammetric study

Electrochemical experiments were carried out in a 150 mL three electrode cell using a VSP2 potentiostat (Bio Logic SA, France) controlled by the EC Lab software. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a DSA plate 1.5 × 2 cm² purchased from Magneto (Netherlands).

The current/potential curves were recorded with the linear sweep voltammetry technique of EC Lab. E_c was ramped from the open circuit potential to 1.3 or 1.5 V vs. SCE at 10 mV/s. Each curve was recorded 3 times to ensure the reproducibility of the results. The curves were superimposable so only one was chosen to be displayed in the results.

Unless otherwise stated, carbonate solutions were deaerated by bubbling nitrogen gas at a rate of 10 mL/s for 15 min. The pH was measured after air removal so that its variation due to the N₂ bubbling could be taken into account. The pH of all carbonate solutions was pH 8.7 after deaeration. The nitrogen flux was maintained above the solution during the experiments.

3. Results

3.1. Preliminary calculations to determine the targeted MEC electrolysis voltage and the average current density

Wastewater treatment by MEC technology can be considered as energy neutral when the energy recovered from the hydrogen produced is equal to the energy supplied to the MEC to produce the hydrogen. The energy supplied (E_{sup}) depends on the cell voltage

(U_{cell}) according to Equation (6):

$$E_{\text{sup}} - U_{\text{cell}} = N_{e^-} F \quad (6)$$

where U_{cell} is the cell voltage, N_{e^-} is the quantity of electrons extracted by the bioanode and F is the Faraday constant (96500 C/mol).

Assuming that the faradaic yield of hydrogen evolution at the cathode is 100%, the energy recovered (E_r) from the combustion of hydrogen is:

$$E_r = \frac{N_{e^-}}{2} LCV_{\text{H}_2} \quad (7)$$

where LCV_{H_2} is the net calorific value of hydrogen (242.7 kJ/mol).

By combining Equations (6) and (7), the limit value of U_{cell} for $E_{\text{sup}} \leq E_r$ should not exceed 1.2 V and this voltage does not depend on the number of electrons extracted by the bioanode. Several studies conducted with domestic wastewater fed MECs have displayed an applied voltage lower than 1.2 V but the production rates of hydrogen reported were far below those of conventional industrial water electrolysis cells (Table 1).

Basically, bioanodes operate at potentials ranging from 0.4 V vs. SCE to +0.6 V vs. SCE [39]. In this range of anode potential, the best performances reported in the literature in terms of current density obtained with bioanodes fed with real wastewater were about 10 A/m², which corresponds to a hydrogen production of approximately 4 L/h/m²_{cathode} at 100% coulombic efficiency [26,40,41]. This highest value of current density obtained from the oxidation of real domestic wastewater will be used further in this study as a reference of current density for optimizing the cathode reaction.

3.2. Influence of the carbonate concentration on the water reduction kinetics

Current/potential reduction curves were recorded with a 254SMO stainless steel cathode immersed in potassium carbonate solutions (Fig. 1). In the first set of experiments, carbonate concentrations ranged from 0.01 to 0.2 M and the solutions contained 0.1 M of KCl as supporting electrolyte (Fig. 1. A&B). In the second set (Fig. 1. C&D), a wider range of carbonate concentrations was tested, up to the saturation concentration (2.8 M). To avoid any possible bias caused by a difference in conductivity, the conductivity of all the solutions was adjusted with KCl to the same constant value of 152 mS/cm. This value corresponds to the conductivity of a saturated carbonate solution (2.8 M at 20 °C). A current/potential curve was also recorded in domestic wastewater without any addition of KCl (conductivity 0.9 S/m) as is commonly done in the literature

on wastewater treatment by MEC.

In the concentration range of 0 M–2.8 M of carbonate, the water reduction kinetics improved when the carbonate concentration rose (Fig. 1A and 1C).

For carbonate concentrations ranging from 0.01 M to 0.2 M, the current density at 1.3 V vs. SCE was directly proportional to the carbonate concentration (correlation coefficient 0.989) (Fig. 1B). These results are consistent with those obtained by De Silva et al. with phosphate solutions having concentrations ranging between 0.01 M and 0.5 M on a 316L SS cathode at pH 8.0 [27].

In the concentration range 0.2–2.8 M, the relation between carbonate concentration and water reduction rate was no longer linear (Fig. 1D). The electro catalytic mechanism proposed by Da Silva et al. [25] involves the deprotonation of the weak acid and the adsorption of the H atom on the cathode surface (reaction (2)). The nonlinear behaviour observed in Fig. 1D may have been due to the saturation of H atom adsorption sites on the cathode surface or the fact that there were no longer any carbonate ion transport related limitations when the carbonate concentration was higher than 0.2 M.

At a current density of 10 A/m², E_c in 1 M and 2.8 M carbonate solutions was 1.04 V vs. SCE. This represents a 380 mV gain in E_c compared with that obtained at the same current density in domestic wastewater (1.42 V vs. SCE). Working with a 1 M carbonate solution as catholyte instead of domestic wastewater would reduce the value of U_{cell} by 32% compared to the 1.2 V MEC limit voltage calculated in 3.1. This reduction of E_c is due to both the increase of the electrolyte conductivity and the catalytic effect of the carbonate species.

3.3. Influence of the pH of the carbonate solution on water reduction catalysis

Linear sweep voltammeteries were performed on a 254SMO stainless steel electrode in aqueous 1 M carbonate solutions where the pH was adjusted in the range of 7–12 (Fig. 2). The highest water reduction rate was obtained at pH 8. The water reduction rates obtained at pH 7, pH 9 and pH 10 were lower than at pH 8 but still satisfactory. At pH 11 and pH 12, the water reduction rates were significantly lower than at more acidic pH.

According to the predominance diagram of carbonic acid (Fig. 3A), the HCO₃⁻ form is predominant in the pH range from 6.3 to 10.3 (85% at pH 7; 97% at pH 8; 90% at pH 9; 52% at pH 10). Fig. 3B plots the cathode potential at 10 A/m² versus pH (Fig. 3B, triangles) and the percentage of the HCO₃⁻ species at the same pH values (Fig. 3B, diamonds). The two curves are almost identical in shape, which implies that HCO₃⁻ is the key species involved in the water reduction catalysis.

Table 1

Applied voltages and operating conditions reported in the literature for domestic-wastewater-fed MECs and abiotic industrial electrolyzers for water electrolysis.

	Applied voltage	Current density	H ₂ production	COD removal	Reference
MECs	1 V	0.25 A/m ²	0.15 L/g-COD	45%	[28]
	0.41 V	0.47 A/m ²	0.045 L/d	87–100%	[29]
	1.1 V	0.27 A/m ²	0.088 L/d	Av 34%	[30]
	1 V	0.2 A/m ²	0.03 L/d	80%	[31]
	0.75 V	0.42 A/m ²		76%	[32]
	0.7 V	0.45 A/m ²		max 92%	[13]
	0.9 V	3.77 A/m ²	0.18 L/d	81–86%	[33]
	1 V	0.2 A/m ²		85%	[34]
	0.9 V	1.1 A/m ²		75%	[35]
	Industrial electrolyzers	2 V ^a		5 Nm ³ /h	N/A
2 V ^a			12 Nm ³ /h	N/A	S18 MP from McPhy [37]
2 V ^a			1100 Nm ³ /h	N/A	Electrolyser producing H ₂ for the Ariane V rocket [38]

^a Applied voltages calculated from energy consumption of industrial water electrolysis cells (kW/m³_{H₂}) and maximum H₂ production.

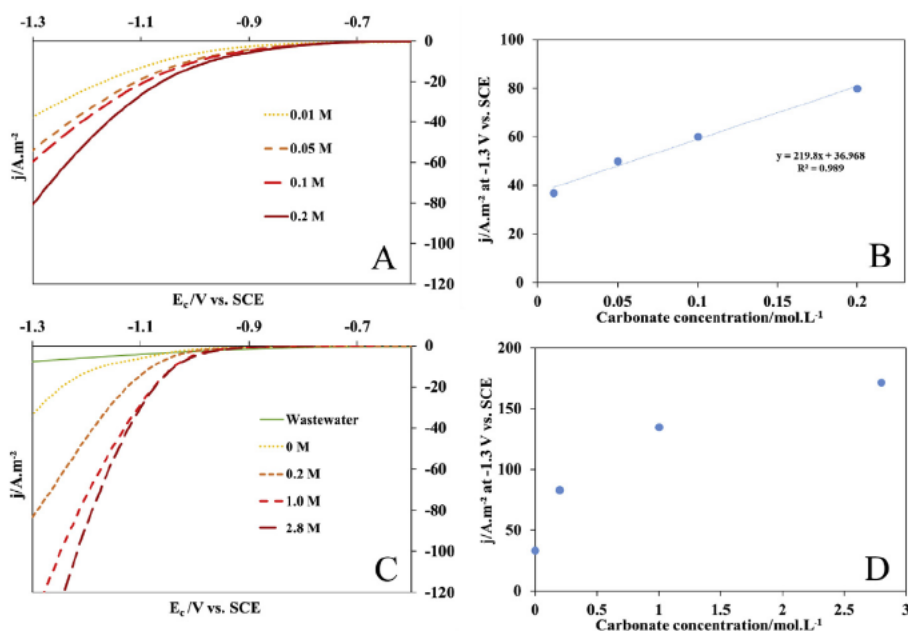


Fig. 1. Current/potential curves obtained for water reduction on stainless steel (254SMO) at pH 8.7 in potassium carbonate solutions for concentrations ranging from 0 M to 2.8 M. A: Solutions contained 0.1 M of KCl and C: Conductivity was adjusted to 152 mS/cm with KCl. In domestic wastewater, the conductivity is 0.9 mS/cm. Scan rate 10 mV/s. B and D: Current density at -1.3 V vs. SCE vs. carbonate concentration.

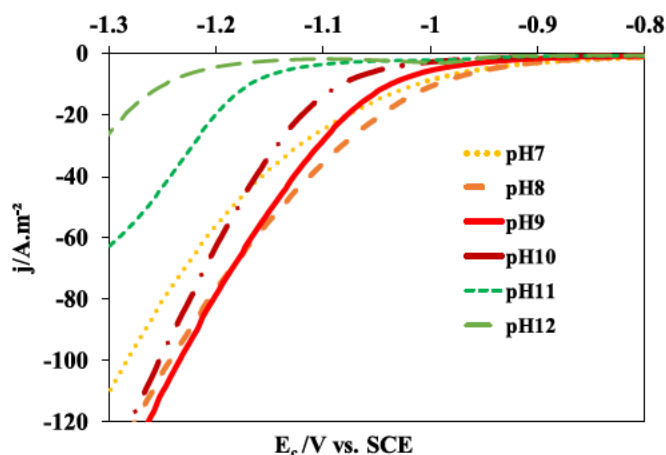
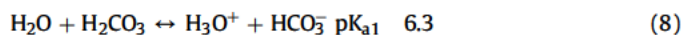


Fig. 2. Current/potential curves obtained for water reduction on stainless steel (254SMO) in 1 M potassium carbonate solutions with pH adjusted to values from 7 to 12. Scan rate 10 mV/s, not deaerated.

Carbonic acid (H_2CO_3) can dissociate twice in water:



According to Da Silva et al. [25], the catalytic effect of weak acids on water reduction is due to their ability to deprotonate easily. Less energy is required to break the bond that links a hydrogen atom to the weak acid molecule than to break a water molecule. Fig. 4 describes the hydrogen production electrocatalytic mechanism applied to carbonate species in aqueous solutions. Theoretically, both HCO_3^- and H_2CO_3 species are able to catalyse the water reduction reaction since they can both deprotonate.

The $\text{p}K_a$ of the $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ pair is 6.3 and that of the $\text{HCO}_3^-/\text{CO}_3^{2-}$ pair is 10.3. The ease of deprotonation of a weak acid is linked to the strength of the bond between the proton and the weak acid molecule. The deprotonation of H_2CO_3 requires less energy than the deprotonation of HCO_3^- since H_2CO_3 is a stronger acid than HCO_3^- . In other words, H_2CO_3 is a better catalyst for the water reduction

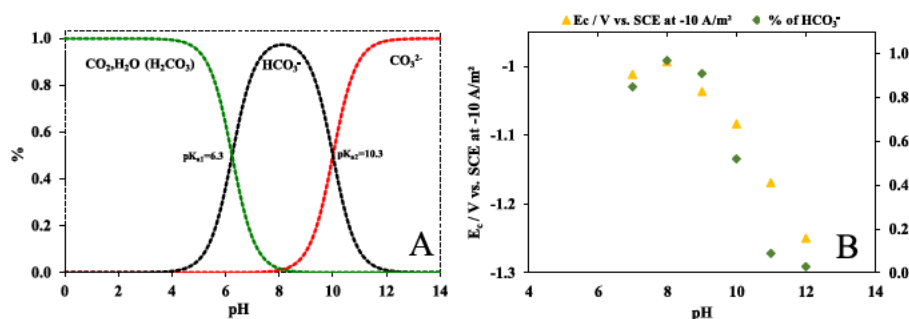


Fig. 3. A: Carbonic acid predominance diagram and B: Comparison of cathode potentials at -10 A/m^2 obtained in 1 M carbonate solutions and HCO_3^- percentage at pH ranging from 7 to 12.

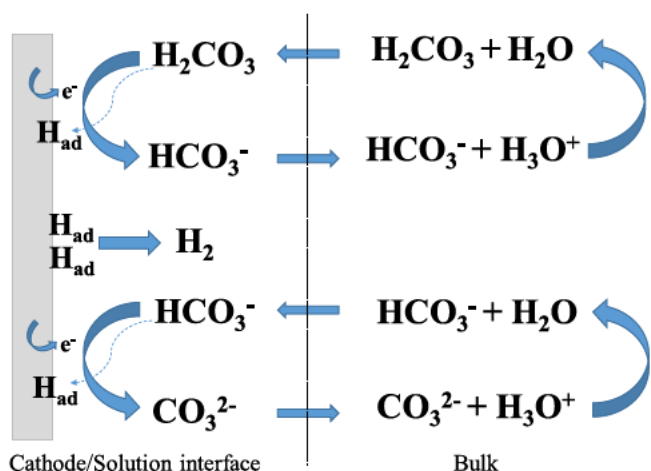


Fig. 4. Hydrogen production electrocatalytic mechanism applied to carbonate species in aqueous solutions.

reaction than HCO_3^- . Consequently, the water reduction kinetics in a carbonate solution should be best at pH 7, since the solution contains both H_2CO_3 (15%) and HCO_3^- (85%). In comparison, at pH 8, a carbonate solution contains only 3% of H_2CO_3 and 97% of HCO_3^- and, at pH 9, there is 90% of HCO_3^- and 10% of CO_3^{2-} (which does not catalyse the water reduction reaction since it is not a weak acid).

Actually, H_2CO_3 is an unstable molecule and dissolved carbon dioxide is predominantly in the form of $\text{CO}_2, \text{H}_2\text{O}$. Only 0.3% is in the form H_2CO_3 [42]. The $\text{CO}_2, \text{H}_2\text{O}$ cannot deprotonate and does not participate in the catalysis of the water reduction reaction. In a 1 M carbonate solution at pH 7, only 0.045% of the total amount of carbonate is in the form H_2CO_3 , which represents a concentration of 4.5×10^{-4} M. This very low H_2CO_3 concentration coupled with a lower proportion of HCO_3^- ions at pH 7 than at pH 8 and 9 explains why the water reduction rate was lower at pH 7 than at pH 8 and 9 (Fig. 2).

3.4. Influence of cathode material on water reduction catalysis

Five grades of stainless steel (SS) containing various proportions of Fe, Cr, Ni, Mo and Mn, and also a nickel alloy containing 80% of Ni and 20% of Fe were compared. The compositions of SS surfaces determined by EDX are given in Table 2. A graphite plate was also tested as a cathode since graphite is a usual material for MEC cathodes.

Each material was tested with increasing carbonate concentrations adjusted to the same conductivity (152 mS/cm) by KCl addition. Fig. 5 presents the current density obtained at 1.3 V vs. SCE for water reduction at each concentration for all the materials tested.

For each stainless steel grade, the current density at 1.3 V vs. SCE rose when the carbonate concentration increased from 0 M to 2.8 M. This was not the case with Ni80/Fe20 and graphite since the

Table 2
Composition (wt%) of the stainless steel grades used in this study (determined by EDX).

SS grade	Fe	Cr	Ni	Mo	Si	Mn
430	79.0 ± 0.2	16.8 ± 0.2			0.5 ± 0.1	
304	70.4 ± 0.2	17.7 ± 0.1	8.2 ± 0.1		0.7 ± 0.1	1.4 ± 0.1
316L	62.7 ± 0.3	16.4 ± 0.2	9.7 ± 0.1	2.3 ± 0.1	0.5 ± 0.1	1.7 ± 0.1
254SMO	50.1 ± 0.3	19.3 ± 0.1	16.6 ± 0.3	6.3 ± 0.2	0.5 ± 0.1	
310	51.6 ± 0.2	24.5 ± 0.2	18.6 ± 0.2		0.5 ± 0.1	1.8 ± 0.1

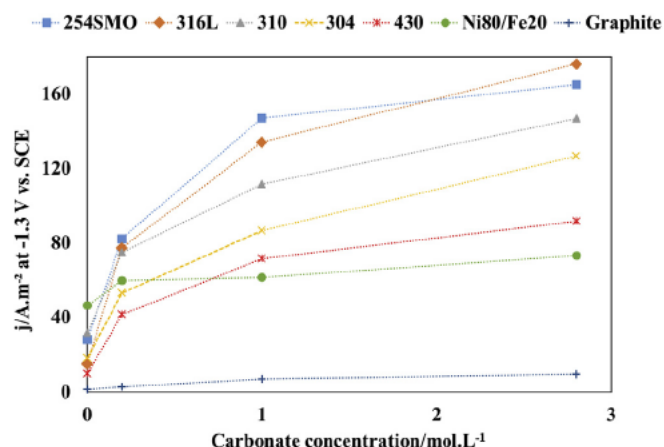


Fig. 5. Current density at -1.3 V vs. SCE according to carbonate concentration for each cathode material tested; taken from current-potential curves recorded in carbonate solutions of various concentrations in which conductivities were adjusted to 152 mS/cm with KCl, pH 8.7 (curves not shown).

current densities at 1.3 V vs. SCE had almost constant values whatever the carbonate concentration. Carbonates catalysed the water reduction reaction on stainless steel, whatever the grade, but this catalytic effect was weaker with Ni80/20 and almost absent with graphite.

Unlike all the other materials tested, graphite does not contain any metallic elements. Metallic elements on the electrode surface are favoured adsorption sites for H atoms during the deprotonation reaction and their absence in graphite explains the weak current densities obtained with this material compared to SS and Ni80/Fe20.

The Ni80/Fe20 alloy contained by far the highest amount of Ni of all the materials tested (almost 4 times more than any SS grade). The current densities obtained with this Ni alloy were lower than those obtained with stainless steels. The steel containing no Ni (AISI 430) showed the lowest current densities. The steel the most loaded in Ni (AISI 310) gave lower current density than 316L and 254SMO. The catalytic effect of carbonate was consequently not directly related to the amount of Ni in the cathode material.

The main difference between Ni80/Fe20 and SS is that the Ni alloy did not contain chromium. The presence of chromium may consequently be a key parameter for a material to be efficiently associated with water reduction reaction catalysis by carbonate.

Stainless steels 316L and 304 have relatively close compositions except that 316L contains Mo and 304 does not. The presence of Mo had a strong impact on the current density (current density at 1.3 V vs. SCE in a 1 M carbonate solution was 35% higher for 316L than for 304). A comparison of the current density at 1.3 V vs. SCE vs. carbonate concentration curves obtained with 310 and 254SMO led to the same conclusion. The highest current densities were obtained with 316L and 254SMO. These are the only materials tested in this study that contain Mo, which indicates that Mo may be another key element in water reduction reaction catalysis by carbonates.

316L and 254SMO offered similar performance in terms of current density at 1.3 V vs. SCE. Both materials contain Ni and Mo but 316L has 63% less Mo and 41% less Ni. The presence of Mn in 316L SS might compensate for the moderate Mo and Ni contents and be the reason why its performance was close to that of 254SMO and even better in a 2.8 M carbonate solution.

In conclusion, the key elements of cathode material that enhance homogeneous catalysis of the hydrogen evolution reaction by carbonate are Cr, Ni, Mo and probably Mn. These results are

consistent with many studies in the literature in which different associations of Cr, Ni, Mo and Mn are used as alloy elements to catalyse the hydrogen evolution reaction in alkaline media. Nickel alloy seems to catalyse hydrogen production even more efficiently than pure nickel. Bachvarov et al. [43] tested a nickel alloy electrode, containing iron, cobalt and phosphorus, as a catalyst for hydrogen production through alkaline water electrolysis. The presence of iron, cobalt and phosphorus in nickel alloys significantly decreased the overpotential of the hydrogen evolution reaction compared to pure nickel. Gonzales Buch et al. [44] also studied alkaline water electrolysis with 3D macroporous Ni and NiMo cathodes. NiMo electrodes had higher catalytic activity than Ni for the hydrogen evolution reaction. Tang et al. studied a nanosheet of Co Mn carbonate hydroxide deposited on nickel foam as a cathode material for the hydrogen evolution reaction and observed a reduced cathode overpotential in comparison with any other metal carbonate hydroxide [45]. All these results were obtained in highly concentrated alkaline solutions. This suggests that there is a parallel between water deprotonation and weak acid deprotonation since the same elements (Cr, Ni, Mo and Mn) seem to intensify the reaction rate in both cases. These elements could intervene in a key adsorption step, probably limiting, of the catalytic mechanism.

4. Discussion

4.1. Reducing the cathode potential by optimizing the catalytic effect of carbonate on stainless steel

4.1.1. Concentration of the carbonate solution

The maximum hydrogen evolution on 254SMO SS was obtained with a highly concentrated carbonate solution (1 M and 2.8 M). At 10 A/m^2 , working with a 1 M carbonate solution as the catholyte instead of domestic wastewater reduced E_c by 380 mV, which represents a gain of 32% over the 1.2 V MEC limit voltage calculated in III.1.

In addition, using a highly concentrated carbonate solution instead of domestic wastewater as catholyte in an MEC also increases the ionic conductivity in the cathode compartment very significantly (by a factor of 10). High conductivity facilitates ion transport in the solution and reduces the internal resistance of the MEC [8].

4.1.2. Cathode material

Platinum is known to be a great heterogeneous electrocatalyst for hydrogen evolution but its high price discourages its use in industrial scale electrolysis cells. Nickel is also known to be an efficient catalyst for water reduction reaction and nickel based materials are viewed as a cheaper alternative to platinized cathodes [19,20,46–49]. For example, Raney nickel is a Ni Al based powder used as a catalyst in many industrial processes and especially in water electrolysis [38]. Also, De Silva et al. have demonstrated that SS AISI 316L is a more stable cathode material than platinum when associated with the homogeneous catalysis of water reduction by phosphate [27].

316L and 254SMO SS proved to be the most appropriate to implement in the carbonate catalysis of water reduction. The choice of the MEC cathode material must be relevant in terms of performance and also in terms of cost, availability and durability. 254SMO is a high quality SS, often used in media containing chlorides, e.g. marine environments [50] and HCl solutions [51], where the other grades of stainless steel are corroded. It is 30% more expensive, on average, than 316L, which is more commonly used in industry. The use of 316L as cathode material is thus a reasonable choice since it showed some of the best performance levels in terms of current

density at 1.3 V vs. SCE, is relatively cheap and is easily available. Additional studies will be needed to validate its long term durability in MEC operating conditions.

4.2. Impact of using a concentrated carbonate solution as catholyte on the MEC design

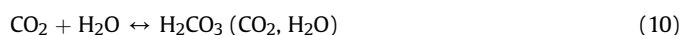
4.2.1. Presence of a membrane

In an MEC in which the anode compartment contains domestic wastewater and the catholyte is a carbonate solution, a membrane is necessary to avoid mixing the two solutions. Since domestic wastewater has a relatively low ion concentration [10], the use of a concentrated carbonate solution could create overpressure or overflow due to water osmosis from the wastewater to the carbonate solution. This issue may be easily solved by accepting some slight overpressure in the catholyte compartment. The best compromise should be found between improving the performance and minimizing technical constraints due to water osmosis.

4.2.2. pH balance within the cell

The water reduction reaction produces OH^- ions and so the pH increases near the cathode during electrolysis. In the case of a single chamber separator less MEC operating in batch mode, the global pH is balanced because H^+ ions are produced at the anode. In a dual chamber MEC, the separator limits the movement of ions within the cell. If a solution containing predominantly HCO_3^- ions is used as the catholyte, a cation exchange membrane should be used to prevent loss of these anions to the anolyte via diffusion and migration. In this case, electricity transport through the cell is mainly ensured by the motion of cations through the membrane, which do not contribute to the pH balance and result an enhanced pH increase in the cathode compartment [8]. At 10 A/m^2 , the water reduction potential is significantly more negative at pH 11 and pH 12 than at pH between 7 and 10 (Fig. 2). To ensure stable and fast water reduction, the pH of the cathode compartment should be regulated to stay between 7 and 10.

A sustainable way to buffer the pH in the cathode compartment is to pass CO_2 gas into the catholyte. Bubbling gaseous CO_2 into an aqueous solution:



shifts the pH towards lower values, according to the acid/base equilibrium (Equation (8)). Bubbling CO_2 into an MEC catholyte will lead to saturation of the carbonate solution. The precipitated carbonate salts can be recovered and reused [52]. This is a way to store CO_2 in solid form, which may be less hazardous for the environment than gaseous storage in deep geological formations, with risk of CO_2 leakage [53].

5. Conclusion

The catalytic effect of HCO_3^- for hydrogen evolution on stainless steel has been demonstrated and optimized. Using a 1 M potassium carbonate solution instead of domestic wastewater as the catholyte enabled the cell voltage to be reduced by 32%, at 10 A/m^2 , in relation to the calculated objective of 1.2 V. The water reduction reaction reached its highest rate at pH 8 but the kinetics remained satisfactory in the pH range from 7 to 10. Testing various materials as cathodes highlighted that the electro catalytic effect of HCO_3^- was enhanced on 316L and 254SMO SS. These results are a first step towards the design of an energy neutral MEC for wastewater treatment. The next challenge is to associate a carbonate catalysed cathode with a microbial anode to evaluate and fix the possible issues connected with osmosis and pH drift.

Declaration of conflict of interest

None.

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References

- [1] I. Dincer, C. Acar, Review and evaluation of hydrogen production methods for better sustainability, *Int. J. Hydrogen Energy* 40 (2014) 11094–11111, <https://doi.org/10.1016/j.ijhydene.2014.12.035>.
- [2] C.-J. Winter, Into the hydrogen energy economy - milestones, *Int. J. Hydrogen Energy* 30 (2005) 681–685, <https://doi.org/10.1016/j.ijhydene.2004.12.011>.
- [3] H. Liu, S. Grot, B.E. Logan, Electrochemically assisted microbial production of hydrogen from acetate, *Environ. Sci. Technol.* 39 (2005) 4317–4320, <https://doi.org/10.1021/es050244p>.
- [4] D. Call, B.E. Logan, Hydrogen production in a single chamber microbial electrolysis cell lacking a membrane, *Environ. Sci. Technol.* 42 (2008) 3401–3406, <https://doi.org/10.1021/es800182z>.
- [5] B.E. Logan, D. Call, S. Cheng, H.V.M. Hamelers, T.H.J.A. Sleutels, A.W. Jeremiasse, R.A. Rozendal, Microbial electrolysis cells for high yield hydrogen gas production from organic matter, *Environ. Sci. Technol.* 42 (2008) 8630–8640, <https://doi.org/10.1021/es801553z>.
- [6] I. Ivanov, L. Ren, M. Siegert, B.E. Logan, A quantitative method to evaluate microbial electrolysis cell effectiveness for energy recovery and wastewater treatment, *Int. J. Hydrogen Energy* 38 (2013) 13135–13142, <https://doi.org/10.1016/j.ijhydene.2013.07.123>.
- [7] Y. Dong, Y. Qu, W. He, Y. Du, J. Liu, X. Han, Y. Feng, A 90-liter stackable baffled microbial fuel cell for brewery wastewater treatment based on energy self-sufficient mode, *Bioresour. Technol.* 195 (2015) 66–72, <https://doi.org/10.1016/j.biortech.2015.06.026>.
- [8] M. Oliot, S. Galier, H. Roux de Balmain, A. Bergel, Ion transport in microbial fuel cells: key roles, theory and critical review, *Appl. Energy* 183 (2016) 1682–1704, <https://doi.org/10.1016/j.apenergy.2016.09.043>.
- [9] R.A. Rozendal, H.V.M. Hamelers, K. Rabaey, J. Keller, C.J.N. Buisman, Towards practical implementation of bioelectrochemical wastewater treatment, *Trends Biotechnol.* 26 (2008) 450–459, <https://doi.org/10.1016/j.tibtech.2008.04.008>.
- [10] M. Verbanck, J. Vanderborght, R. Wollast, Major ion content of urban wastewater: assessment of per capita loading, *Res. J. Water Pollut. Contr. Fed.* 61 (1989) 1722–1728.
- [11] S. Peng, D.W. Liang, P. Diao, Y. Liu, F. Lan, Y. Yang, S. Lu, Y. Xiang, Nernst-ping-pong model for evaluating the effects of the substrate concentration and anode potential on the kinetic characteristics of bioanode, *Bioresour. Technol.* 136 (2013) 610–616, <https://doi.org/10.1016/j.biortech.2013.03.073>.
- [12] E. Blanchet, E. Desmond, B. Erable, A. Bridier, T. Bouchez, A. Bergel, Comparison of synthetic medium and wastewater used as dilution medium to design scalable microbial anodes: application to food waste treatment, *Bioresour. Technol.* 185 (2015) 106–115, <https://doi.org/10.1016/j.biortech.2015.02.097>.
- [13] A. Escapa, M.I. San-Martín, R. Mateos, A. Morán, Scaling-up of membraneless microbial electrolysis cells (MECs) for domestic wastewater treatment: bottlenecks and limitations, *Bioresour. Technol.* 180 (2015) 72–78, <https://doi.org/10.1016/j.biortech.2014.12.096>.
- [14] K. Zeng, D. Zhang, Recent progress in alkaline water electrolysis for hydrogen production and applications, *Prog. Energy Combust. Sci.* 36 (2009) 307–326, <https://doi.org/10.1016/j.pecs.2009.11.002>.
- [15] L.J. Nuttall, A.P. Fickett, W.A. Titterton, General Electric's Solid Polymer Electrolyte Water Electrolysis, *Direct Energy Convers. Programs*, 1976.
- [16] M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, A comprehensive review on PEM water electrolysis, *Int. J. Hydrogen Energy* 38 (2013) 4901–4934, <https://doi.org/10.1016/j.ijhydene.2013.01.151>.
- [17] M. Zeppilli, A. Lai, M. Villano, M. Majone, Anion vs cation exchange membrane strongly affect mechanisms and yield of CO₂ fixation in a microbial electrolysis cell, *Chem. Eng. J.* 304 (2016) 10–19, <https://doi.org/10.1016/j.cej.2016.06.020>.
- [18] X. Xie, C. Criddle, Y. Cui, Design and fabrication of bioelectrodes for microbial bioelectrochemical systems, *Energy Environ. Sci.* 8 (2015) 3418–3441, <https://doi.org/10.1039/C5EE01862E>.
- [19] M. Mitov, E. Chorbazhiyska, L. Nalbandian, Y. Hubenova, Nickel-based electrodeposits as potential cathode catalysts for hydrogen production by microbial electrolysis, *J. Power Sources* 356 (2017) 467–472, <https://doi.org/10.1016/j.jpowsour.2017.02.066>.
- [20] P.A. Selembo, M.D. Merrill, B.E. Logan, Hydrogen production with nickel powder cathode catalysts in microbial electrolysis cells, *Int. J. Hydrogen Energy* 35 (2010) 428–437, <https://doi.org/10.1016/j.ijhydene.2009.11.014>.
- [21] A. Bergel, D. Féron, A. Mollica, Catalysis of oxygen reduction in PEM fuel cell by seawater biofilm, *Electrochem. Commun.* 7 (2005) 900–904, <https://doi.org/10.1016/j.elecom.2005.06.006>.
- [22] Z. He, L.T. Angenent, Application of bacterial biocathodes in microbial fuel cells, *Electroanalysis* 18 (2006) 2009–2015, <https://doi.org/10.1002/elan.200603628>.
- [23] Y. Hou, R. Zhang, H. Luo, G. Liu, Y. Kim, S. Yu, J. Zeng, Microbial electrolysis cell with spiral wound electrode for wastewater treatment and methane production, *Process Biochem.* 50 (2015) 1103–1109, <https://doi.org/10.1016/j.procbio.2015.04.001>.
- [24] F. Zhang, Y. Ahn, B.E. Logan, Treating refinery wastewaters in microbial fuel cells using separator electrode assembly or spaced electrode configurations, *Bioresour. Technol.* 152 (2014) 46–52, <https://doi.org/10.1016/j.biortech.2013.10.103>.
- [25] S. Da Silva, R. Basséguy, A. Bergel, Electrochemical deprotonation of phosphate on stainless steel, *Electrochim. Acta* 49 (2004) 4553–4561, <https://doi.org/10.1016/j.electacta.2004.04.039>.
- [26] L. De Silva Munoz, B. Erable, L. Etcheverry, J. Riess, R. Basséguy, A. Bergel, Combining phosphate species and stainless steel cathode to enhance hydrogen evolution in microbial electrolysis cell (MEC), *Electrochem. Commun.* 12 (2010) 183–186, <https://doi.org/10.1016/j.elecom.2009.11.017>.
- [27] L. De Silva Munoz, A. Bergel, D. Féron, R. Basséguy, Hydrogen production by electrolysis of a phosphate solution on a stainless steel cathode, *Int. J. Hydrogen Energy* 35 (2010) 8561–8568, <https://doi.org/10.1016/j.ijhydene.2010.05.101>.
- [28] R. Moreno, M.I. San-Martín, A. Escapa, A. Morán, Domestic wastewater treatment in parallel with methane production in a microbial electrolysis cell, *Renew. Energy* 93 (2016) 442–448, <https://doi.org/10.1016/j.renene.2016.02.083>.
- [29] J. Ditzig, H. Liu, B.E. Logan, Production of hydrogen from domestic wastewater using a bioelectrochemically assisted microbial reactor (BEAMR), *Int. J. Hydrogen Energy* 32 (2007) 2296–2304, <https://doi.org/10.1016/j.ijhydene.2007.02.035>.
- [30] E.S. Heidrich, J. Dolfing, K. Scott, S.R. Edwards, C. Jones, T.P. Curtis, Production of hydrogen from domestic wastewater in a pilot-scale microbial electrolysis cell, *Appl. Microbiol. Biotechnol.* 97 (2013) 6979–6989, <https://doi.org/10.1007/s00253-012-4456-7>.
- [31] L. Gil-Carrera, A. Escapa, B. Carracedo, A. Morán, X. Gómez, Performance of a semi-pilot tubular microbial electrolysis cell (MEC) under several hydraulic retention times and applied voltages, *Bioresour. Technol.* 146 (2013) 63–69, <https://doi.org/10.1016/j.biortech.2013.07.020>.
- [32] A. Escapa, L. Gil-Carrera, V. García, A. Morán, Performance of a continuous flow microbial electrolysis cell (MEC) fed with domestic wastewater, *Bioresour. Technol.* 117 (2012) 55–62, <https://doi.org/10.1016/j.biortech.2012.04.060>.
- [33] M.L. Ullery, B.E. Logan, Anode acclimation methods and their impact on microbial electrolysis cells treating fermentation effluent, *Int. J. Hydrogen Energy* 40 (2015) 6782–6791, <https://doi.org/10.1016/j.ijhydene.2015.03.101>.
- [34] L. Gil-Carrera, A. Escapa, R. Moreno, A. Morán, Reduced energy consumption during low strength domestic wastewater treatment in a semi-pilot tubular microbial electrolysis cell, *J. Environ. Manag.* 122 (2013) 1–7, <https://doi.org/10.1016/j.jenvman.2013.03.001>.
- [35] M.L. Ullery, B.E. Logan, Comparison of complex effluent treatability in different bench scale microbial electrolysis cells, *Bioresour. Technol.* 170 (2014) 530–573, <https://doi.org/10.1016/j.biortech.2014.08.028>.
- [36] Products - Sagim, (n.d.). <http://sagim-gip.com/en/products/> (accessed September 26, 2017).
- [37] Small and medium capacity | McPhy, (n.d.). <http://mcphy.com/en/our-products-and-solutions/electrolyzers/small-and-medium-capacity/> (accessed September 26, 2017).
- [38] A. Damien, *Hydrogène par électrolyse de l'eau*, Tech. l'Ingenieur, 1992.
- [39] M. Rimboud, D. Pocaznoi, B. Erable, A. Bergel, Electroanalysis of microbial anodes for bioelectrochemical systems: basics, progress and perspectives, *Phys. Chem. Chem. Phys.* 16 (2014) 16349–16366, <https://doi.org/10.1039/C4CP01698J>.
- [40] T.C. Pannell, R.K. Goud, D.J. Schell, A.P. Borole, Effect of fed-batch vs. continuous mode of operation on microbial fuel cell performance treating bio-refinery wastewater, *Biochem. Eng. J.* 116 (2016) 85–94, <https://doi.org/10.1016/j.bej.2016.04.029>.
- [41] J. Yu, Y. Park, B. Kim, T. Lee, Power densities and microbial communities of brewery wastewater-fed microbial fuel cells according to the initial substrates, *Bioproc. Biosyst. Eng.* 38 (2015) 85–92, <https://doi.org/10.1007/s00449-014-1246-x>.
- [42] C.B. Andersen, Understanding carbonate equilibria by measuring alkalinity in experimental and natural systems, *J. Geosci. Educ.* 50 (2002) 389–403, <https://doi.org/10.5408/1089-9995-50.4.389>.
- [43] V. Bachvarov, E. Lefterova, R. Rashkov, Electrodeposited NiFeCo and NiFeCoP alloy cathodes for hydrogen evolution reaction in alkaline medium, *Int. J. Hydrogen Energy* 41 (2016) 12762–12771, <https://doi.org/10.1016/j.ijhydene.2016.05.164>.
- [44] C. González-Buch, I. Herraiz-Cardona, E. Ortega, J. García-Antón, V. Pérez-Herranz, Study of the catalytic activity of 3D macroporous Ni and NiMo cathodes for hydrogen production by alkaline water electrolysis, *J. Appl. Electrochem.* 46 (2016) 791–803, <https://doi.org/10.1007/s10800-016-0970-0>.
- [45] T. Tang, W.J. Jiang, S. Niu, N. Liu, H. Luo, Y.Y. Chen, S.F. Jin, F. Gao, L.J. Wan, J.S. Hu, Electronic and morphological dual modulation of cobalt carbonate hydroxides by Mn doping toward highly efficient and stable bifunctional electrocatalysts for overall water splitting, *J. Am. Chem. Soc.* 139 (2017) 8320–8328, <https://doi.org/10.1021/jacs.7b03507>.

- [46] F. Safizadeh, E. Ghali, G. Houlachi, Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions - a review, *Int. J. Hydrogen Energy* 40 (2015) 256–274, <https://doi.org/10.1016/j.ijhydene.2014.10.109>.
- [47] I. Flis-Kabulska, J. Flis, Electroactivity of Ni/Fe cathodes in alkaline water electrolysis and effect of corrosion, *Corrosion Sci.* 112 (2016) 255–263, <https://doi.org/10.1016/j.corsci.2016.07.017>.
- [48] P.A. Selembo, M.D. Merrill, B.E. Logan, The use of stainless steel and nickel alloys as low-cost cathodes in microbial electrolysis cells, *J. Power Sources* 190 (2009) 271–278, <https://doi.org/10.1016/j.jpowsour.2008.12.144>.
- [49] A. Kundu, J.N. Sahu, G. Redzwan, M.A. Hashim, An overview of cathode material and catalysts suitable for generating hydrogen in microbial electrolysis cell, *Int. J. Hydrogen Energy* 38 (2013) 1745–1757, <https://doi.org/10.1016/j.ijhydene.2012.11.031>.
- [50] P. Rajala, M. Bomberg, E. Huttunen-Saarivirta, O. Priha, M. Tausa, L. Carpen, Influence of chlorination and choice of materials on fouling in cooling water system under brackish seawater conditions, *Materials* 9 (2016), <https://doi.org/10.3390/ma9060475>.
- [51] L. de Micheli, C.A. Barbosa, A.H.P. Andrade, S.M.L. Agostinho, Electrochemical behaviour of 254SMO stainless steel in comparison with 316L stainless steel and Hastelloy C276 in HCl media, *Br. Corrosion J.* 35 (2000) 297–300, <https://doi.org/10.1179/000705900101501371>.
- [52] R. Chang, S. Kim, S. Lee, S. Choi, M. Kim, Y. Park, Calcium carbonate precipitation for CO₂ storage and utilization: a review of the carbonate crystallization and polymorphism, *Front. Energy Res.* 5 (2017), <https://doi.org/10.3389/fenrg.2017.00017>.
- [53] W. Liu, A. Ramirez, State of the art review of the environmental assessment and risks of underground geo-energy resources exploitation, *Renew. Sustain. Energy Rev.* 76 (2017) 628–644, <https://doi.org/10.1016/j.rser.2017.03.087>.