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

E. Roubaud [a], [*], R. Lacroix [b], S. Da Silva [b], A. Bergel [a], R. Basséguy [a], B. Erable [a]

[a] Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France
[b] 6T-MIC Ingénieries, 9 rue du développement — ZI de Vic, 31320 Castanet-Tolosan, France

ABSTRACT

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/m^2. Optimizing the pH in the range of 7—12 revealed that the key species in water reduction catalysis was HCO_3^- 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 HCO_3^- ions was highest on stainless steels containing Ni, Mo and Mn, such as 316L or 254SMO.

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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 electrolysers 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):

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

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 $\sum R.I$ 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

* Corresponding author.
 E-mail address: emma.roubaud@ensiacet.fr (E. Roubaud).

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 (H_2S, CO_2, ammonia, CH_4), 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 overpotential 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):

$$HA + e^- \leftrightarrow H_{ad} + A^- \qquad (2)$$

$$H_{ad} + HA + e^- \leftrightarrow H_2 + A^- \qquad (3)$$

$$2H_{ad} \leftrightarrow H_2 \qquad (4)$$

$$A^- + H_2O \leftrightarrow HA + OH^- \qquad (5)$$

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 H_2 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 (CO_3^{2-}, HCO_3^-, H_2CO_3) 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 ($KHCO_3$, 99.5%; Sigma Aldrich), potassium carbonate (K_2CO_3, 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 N_2 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