

Catalysis of oxygen reduction in PEM fuel cell by seawater biofilm

Alain Bergel ^{a,*}, Damien Féron ^b, Alfonso Mollica ^c

^a *Laboratoire de Génie Chimique-CNRS, Basso Cambo, 5 rue Paulin Talabot, BP 1301, 31106 Toulouse, France*

^b *SCCME, CEA Saclay, Bat 458, 91191 Gif-sur-Yvette, France*

^c *Genova Section of ISMAR-CNR, via de Marini 6, 16149 Genova, Italy*

Abstract

The catalysis of oxygen reduction on metallic materials has been widely studied in the domain of aerobic corrosion. In this framework, it has been stated that seawater biofilms are able to catalyse efficiently oxygen reduction on stainless steels. This capacity was transferred here to the catalysis of the cathodic reaction of a proton exchange membrane fuel cell. A laboratory-scale fuel cell was designed with a stainless steel cathode, a platinum anode, and two separated liquid loops. The cathodic loop was air-saturated, while the anodic loop was hydrogen saturated. Seawater biofilm was previously grown on the stainless steel cathode, which was then set up into the fuel cell. The presence of the seawater biofilm on the stainless steel surface led to efficient catalysis of oxygen reduction. The biofilm-covered cathode was able to support current density up to 1.89 A/m². Power density of 0.32 W/m² was supplied with 1.34 A/m² current density.

Keywords: Biofilm; Microbial fuel cell; PEM fuel cell; Oxygen reduction; Stainless steel

1. Introduction

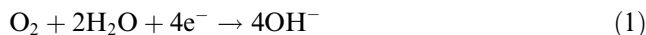
In the very first demonstration of fuel cell capabilities, platinum was already used as an electrode material [1]. Nowadays, the use of platinum-based catalysts still remains a drastic drawback to the large commercialisation of low cost efficient fuel cells [2]. Recently, several studies have demonstrated the capability of certain micro-organisms to connect directly to graphite anodes, and to transfer to the anode the electrons they extracted from different fuels contained in marine sediments or domestic wastes [3–5]. The occurrence of a direct electron transfer from the micro-organisms to the anode, without any soluble mediator, led to higher performances than never obtained before, with biofuel

cells using organic electrochemical mediators. This discovery draws an extremely exciting new scope for further practical developments [6], which could avoid the use of platinum as catalyst of the anode reaction. The number of articles devoted to so-called microbial fuel cells has been rapidly increasing for two years, particularly in biotechnology- and microbiology-oriented journals [7–9]. Nevertheless only very few papers deal with the cathode reaction and, to our knowledge, none has been devoted yet to the catalysis of oxygen reduction, which remains a drastic problem to design low cost fuel cells.

On the contrary, the catalysis of oxygen reduction has been widely studied for many years in the area of marine corrosion, because it constitutes a strong motor of aerobic microbial corrosion. When stainless steel coupons are immersed in aerobic seawater, micro-organisms form a biofilm on their surface, which increases the rate of oxygen reduction on the metal surface:

* Corresponding author. Tel.: +33 5 34 61 52 48; fax: +33 5 34 61 52 51/53.

E-mail address: Alain.Bergel@ensiacet.fr (A. Bergel).



The electrons required for this reduction are provided by the oxidation of the underlying alloy. As first effect of the extraction of the electrons from the metal, biofilm growth causes an increase of the free corrosion potential (phenomenon called potential ennoblement) [10,11], which may lead to the disruption of the oxide layer that naturally protects stainless steel surfaces. The biofilm-driven catalysis of oxygen reduction consequently increases the probability of corrosion onset, and may induce subsequent fast propagation of localised corrosions on stainless steels and similar active-passive alloys. Although the link between the corrosion enhancement of stainless steel (potential increase and propagation) beneath marine biofilms and the catalysis of oxygen reduction has been established for a long time [12], the mechanisms are still controversially discussed. Different assumptions have been suggested to explain it, such as production of hydrogen peroxide in the biofilm [13], modification in the nature of the oxide layers of stainless steel beneath the biofilm [14], involvement of extra-cellular compounds and enzymes [15–18].

In this paper, the knowledge that has been gained in the domain of corrosion was adapted to take advantage of marine biofilms in designing new low cost cathodes for oxygen reduction in fuel cells. Tests were done in a laboratory-scale proton exchange membrane (PEM) fuel cell [19]. This approach may be very promising because marine biofilms resulted in an effective catalysis of oxygen reduction on an alloy that is quite cheap and under operating conditions that may protect them against corrosion. In the fuel cell, electrons for oxygen reduction were provided by hydrogen oxidation on the anode, so that stainless steel was polarised at slightly cathodic potential values: it has been shown that weak cathodic polarisation was sufficient to prevent stainless steels, even not highly alloyed, from localised corrosion onset [20].

2. Experimental

Cathodes were made of stainless steel UNS S31254, 1 mm thick and $10 \times 10 \text{ cm}^2$ surface area. Stainless steel coupons were cleaned before experiments with an ethanol/acetone 50–50% mixture to dissolve organic adsorbed species, and then a fluoridric/nitric acids 2–30% solution to dissolve the oxide layer. Platinum anodes were grids of 196 mesh/cm², made up with 0.5 mm diameter wires. Platinum grids were cleaned by red-hot heating in a flame.

During biofilm growth, the stainless steel electrodes were immersed in a tank filled with continuously renewed seawater from Genova harbour (Italy). The elec-

trodes were polarized for several days at constant potential value with respect to a saturated calomel reference electrode (SCE).

The laboratory-scale hydrogen/air fuel cell is schematised in Fig. 1. The filter-press cell was made up of two compartments separated by a Nafion[®] membrane, which allowed proton migration. The anode compartment was equipped with a platinum grid of 23.5 cm² geometric surface area. The active surface area of the cathode was determined by the size of the open windows in a rubber foil tightly applied against its surface. The anodic and cathodic compartments were connected to a closed loop composed of a pump and a storage tank. Pumps forced the circulation of the solution in each loop. A reference saturated calomel electrode was connected to the cathode compartment through a Luggin capillary. Both loops were generally filled with 0.1 L seawater but, when indicated seawater was replaced by a NaOH, pH 12.5, solution in the anodic loop. Air was continuously bubbled in the cathodic storage tank and hydrogen in the anodic storage tank. The electrodes were electrically connected through an electrical resistance R , which was varied in the range from 1 to $10^6 \Omega$. The ohmic drop ΔV across the resistance R and the potential of the cathode E_C with respect to reference electrode were measured through a Keithley 614 high impedance voltmeter. Measures were taken at least 10 min after connecting the electrodes through the resistance, i.e. when current and potential values were stabilised. For each value of R , the current and the power provided were derived from the ΔV measure.

Blank experiments were performed after removing the biofilm by mechanical cleaning. Electrodes were cleaned by thorough rubbing with paper wetted with ethanol, and then rinsed with seawater.

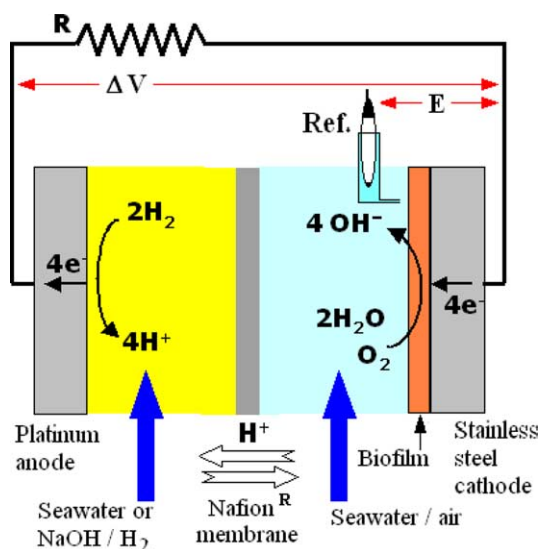


Fig. 1. Scheme of the hydrogen/air PEM fuel cell (see Section 2).

3. Results and discussion

3.1. Biofilm formation

Stainless steel coupons of 100 cm² surface area were immersed in continuously renewed seawater under constant polarization. Current variations during polarisation at values in the range -0.10 V to -0.40 V/SCE and at different seasons are reported in Fig. 2. The current was close to zero during the first days, because oxygen reduction is very slow on clean stainless steel at these potential values. An exponential current increase then started between the third and the eighth day depending on the season and the applied potential value. Studies devoted to microbial corrosion have demonstrated that this phenomena corresponded to the catalysis of oxygen reduction that is induced by the formation of the biofilm [21,22]. The fuel cell experiments were performed in November with a seawater temperature around 20 °C. During polarisation at -0.30 V/SCE, the current increased after ten days up to 0.46 A/m², i.e. the same maximal current value that was obtained in summer at around 28 °C. Only the kinetics of the current increase seemed dependent on the temperature, but not the maximal current.

3.2. PEM fuel cell

When the current reached the maximum values, the biofilm-covered stainless steel electrode was set up in the filter-press fuel cell. Fig. 3 shows the power densities that were supplied by the fuel cell as a function of the current densities for three different experiments A, B and C. These experiments were performed with three different stainless steel cathodes covered by the biofilm, and then after cleaning. Each point represents the results obtained for a given value of the resistance R . Experiments A, B and C corresponded to the three different experimental conditions reported in Table 1. The varia-

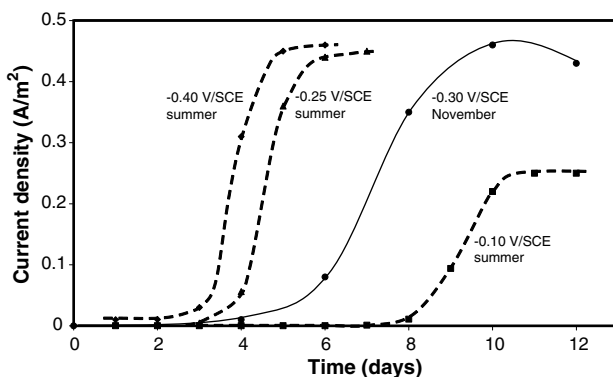


Fig. 2. Current density recorded during constant potential polarisations. Stainless steel coupons (100 cm² geometric surface area) were immersed in continuously renewed seawater at constant potential.

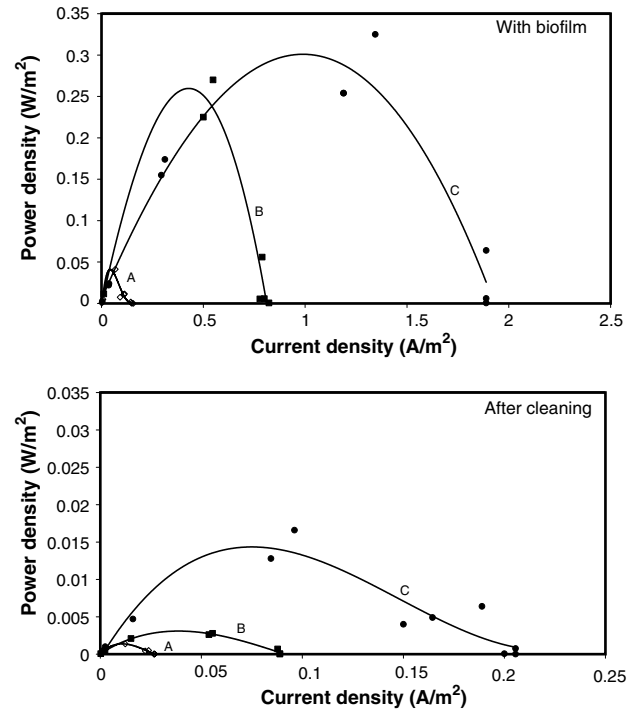


Fig. 3. Power density as a function of current density with biofilm-covered stainless steel cathodes and after cleaning. Seawater was flowing in the anodic loop for experiment A, it was replaced by a sodium hydroxide solution for experiments B and C. In experiments A and B the surface area of the cathode was 9 cm², and 1.8 cm² in experiment C. Both X and Y scales of the second figure (after cleaning) were divided by a factor of 10 to facilitate direct comparison of the results.

tions affected either the pH of the anode compartment, or the surface area of the cathode, always with the view to reach experimental conditions where the cathode process may be rate-limiting.

In experiment A the maximum power supplied by the PEM fuel cell (41 mW/m²) in the presence of biofilm on the cathode is higher by a factor of about 30 in comparison to the maximum power supplied by the same cathode after cleaning (1.4 mW/m²). In the second experiment (B), in which the pH of the anode compartment was increased up to 12.5, the highest power value (270 mW/m²) was obtained in the presence of biofilm, while a maximum power less than 2.8 mW/m² was obtained with the cleaned cathode. The intensification induced by biofilm was close to 100 in this case. In experiment C, performed with a smaller cathode surface area in comparison to test B (1.8 cm² instead of 9 cm²), the maximum power density supplied by the PEM fuel cell in the presence of biofilm was still increased: 325 mW/m² were supplied with 1.34 A/m² current density, and 64 mW/m² were supplied with 1.89 A/m².

Fig. 4 reports polarisation curves with the biofilm-covered cathode and the cleaned cathode for experiment B. The current–potential curves demonstrated the high effect of the biofilm on the cathodic behaviour of

Table 1
Experimental conditions for fuel cell testing

Test	Cathode compartment	Anode compartment
A	9 cm ² SS/aerated seawater, pH 8.2	23.5 cm ² Pt grid/H ₂ saturated seawater
B	9 cm ² SS/aerated seawater, pH 8.2	23.5 cm ² Pt grid/H ₂ saturated NaOH solution, pH 12.5
C	1.8 cm ² SS/aerated seawater, pH 8.2	23.5 cm ² Pt grid/H ₂ saturated NaOH solution, pH 12.5

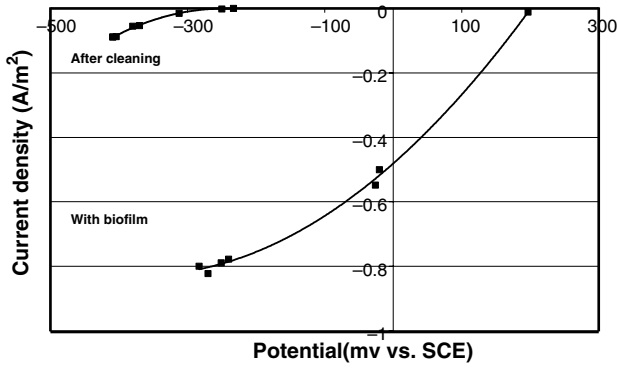


Fig. 4. Current as a function of the potential of the cathode vs. SCE for experiment B.

stainless steel. The clean electrodes showed an open circuit potential around -0.23 V/SCE, and then a very slow kinetics of oxygen reduction, as expected on this material. On the contrary, the biofilm-covered cathode exhibited an open circuit potential about $+0.20$ V/SCE, and the cathodic current rapidly increased when the potential became more negative (i.e. when the external resistance R was increased) to reach rapidly current up to 0.8 A/m² in this experiment.

3.3. Discussion

Biofilms were first grown under constant polarisation (Fig. 2). In this case, the diffusion-limited current density i_L of oxygen reduction is linked to the mass transfer coefficient k_D as:

$$i_L = 4Fk_D[\text{O}_2], \quad (2)$$

where F is the Faraday constant (96,500 C) and $[\text{O}_2]$ is the concentration of dissolved oxygen approximately equal to 0.24×10^{-3} M. The current density of 0.46 A/m² measured once the biofilm was formed on the stainless steel surface, would correspond to a k_D value around 5×10^{-6} m/s. This value was consistent with mass transfer in an almost quiescent solution, corresponding to the actual experimental conditions. It can consequently be concluded that the biofilm was efficient enough in catalysing the reduction of oxygen to reach the diffusion-limited current. This explains why the maximum current value was independent of the temperature and the potential in the range 0.25 – 0.40 V/SCE.

The values of current densities obtained in the fuel cell were higher than 0.46 A/m², because biofilm growth was performed under quiescent conditions, while the circulation of seawater was forced by a pump in the fuel cell. The k_D values were consequently higher in the fuel cell due to the hydrodynamic conditions.

At the end of biofilm growth (Fig. 2) a slight current decrease was observed at -0.30 V/SCE on the 12th day, which became more important when polarisation was kept several days after the maximum current was reached. This current decrease was certainly due to the local pH increase in the diffusion layer induced by oxygen reduction (Reaction (1)). pH increasing over a value around 8.7 resulted in calcium carbonate precipitation on the electrode surface, as was observed on some electrodes. Seawater contains around 1249 mg/kg magnesium ions and 413 mg/kg calcium ions [23], which precipitate at high pH values. It was consequently important to use the biofilm-covered stainless steel not too late after the maximum current value was reached as was done here. The duration of the biofilm formation step, before setting the electrode in the fuel cell, may consequently induce variations in the active surface area of the electrodes, because of different ratios of surface coverage by calcium precipitates.

Changing the anodic solution from seawater pH around 8.2 (Fig. 3, experiment A) to a NaOH solution, pH 12.5, (Fig. 3, experiments B and C) increased the efficiency of hydrogen oxidation, which took place on the anode:



Actually, this change certainly modified the global behaviour of the cell, because of the concentration difference between both compartments. The main interest of these experiments was to find conditions that put in light the remarkable effect of marine biofilms as catalyst of oxygen reduction, with around two order of magnitude of power enhancement. Moreover, reducing the surface area of the cathode (Fig. 3, experiment C) resulted in a supplementary increase of the power density up to 325 mW/m². This evolution meant that the cathode process was not fully rate-limiting. Either the anode reaction contributed to rate limitation, or ion migration was not fast enough. On the one hand, seawater contains high concentration of chloride, which may interact with the platinum surface and decrease its kinetic properties. On the other hand, when the anodic loop was

filled with NaOH solution, pH 12.5, while the cathodic loop contained seawater, a stiff pH gradient was created between both sides of the Nafion membrane that separated the compartments. This pH gradient may induce the precipitation of magnesium hydroxide $Mg(OH)_2$ on the membrane surface, which would significantly reduce its ionic conductivity. It was for instance easy to observe bulk precipitation of magnesium hydroxide in seawater when its pH was shifted above 10 by addition of sodium hydroxide.

The purpose of this work was to suggest a new track to design stainless steel bio-cathodes for oxygen reduction that may be easy to produce, cheap, and corrosion resistant. It must be noted that the promising behaviour of the biofilm-covered electrodes observed in this preliminary work may be easily improved. Results were obtained here with fully flat surfaces, the current density should be increased by implementing rough surface cathodes. Technical improvements of the cell should also be achieved to reach a better control of the hydrodynamic conditions. The most ambitious goal would be to reproduce this system in pure culture, out of the sea environment. It could thus be possible to avoid the problems of calcium and magnesium precipitations, which were identified here has possible causes of important disturbance.

4. Conclusion

Seawater biofilms give to stainless steel electrodes remarkably efficient catalytic properties for oxygen reduction. High efficiency of the biofilm covered cathodes was demonstrated here with a laboratory-scale pilot, but it was guessed that the yield may be significantly improved by optimising the operating conditions. Biofilm-driven catalysis may be a promising track to design new low-cost cathodes for PEM fuel cells. Work is now in progress to decipher the fine mechanisms and to identify the biofilm-forming micro-organisms that are responsible of the catalysis of oxygen reduction.

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