



## Optimizing operating conditions and electrochemical characterization of glucose–gluconate alkaline fuel cells

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### ABSTRACT

The direct oxidation of glucose to produce electrical energy has been widely investigated because of renewability, abundance, high energy density and easy handling of the carbohydrate. Most of the previous studies have been conducted in extreme conditions in order to achieve complete glucose oxidation to CO<sub>2</sub>, neglecting the carbohydrate chemical instability that generally leads to useless by-products mixtures. The partial oxidation to gluconate, originally studied for implantable fuel cells, has the advantage of generating a commercially valuable chemical.

In the present paper we optimized fuel composition and operating conditions in order to selectively oxidize glucose to gluconate, maximizing the power density output of a standard commercial platinum based anode material. A deep electrochemical characterization concerning reversible potential, cyclic voltammetry and overpotential measurements have been carried out at 25 °C in the D-(+)-glucose concentration range 1.0 × 10<sup>-2</sup> to 1.0 M. NMR and EIS investigation clarify the role of the buffer in enhancing the electrochemical performance.

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### 1. Introduction

At the beginning of the 80s, the substitution of hydrogen with different feeds was considered in fuel cell technology. The direct methanol or ethanol–air cells (DMFC) investigated with pioneering attempts about 20 years before attracted again the attention of the scientific community [1]. The approach was fascinating not only for the promising experimental results but also even for the availability of large renewable primary energy sources (i.e. sugar) in the case of ethanol. According to this strategy, the possibility to feed fuel cells with carbohydrate solutions was considered. Hydrogen or ethanol was directly produced in the cell by catalytic reformers or metabolic degradations (biological fuel cells) [2].

The presence of one or more intermediate steps between the fuel primary energy source and the electrochemical oxidized species lowers the energy efficiency with respect to the direct oxidation process of the carbohydrate molecules; therefore fuel cells operating with direct sugar oxidation should have higher efficiency. Furthermore, the carbohydrates are not only renewable and widely

available energy sources, but they also present other advantages with respect to hydrogen or ethanol (i.e. safe storage and easy delivery).

The investigation of direct carbohydrate oxidation fuel cells started in 1964 [3] and continued as a promising approach to autonomous energy supply for medical implants [4] until the coming of the lithium batteries, a dozen years later.

About 10 years ago, the studies concerning the direct glucose oxidation fuel cells recovered strength owing to the development of nanostructured electrodes [5,6] with high electrocatalytic performance for glucose oxidation in aqueous solution. The few results obtained using both alkaline [5–7] or proton conducting membrane [8] electrolytes are often unreliable and scattered as well as the related anode reaction is far from well defined. These shortcomings are probably due to the technological and engineering approaches used by the authors [9,10]; in fact the experimental work was mainly devoted to the evaluation of the electrical cells' performances (power densities) by short-circuiting experiments rather than investigation of the fundamental aspects of the electrochemical process. A more systematic study of the thermodynamics and kinetics of glucose electro-oxidation should provide useful data for better evaluating the energy performances, which will be absolutely necessary to guide the exploitation of the direct glucose oxidation or abiotically catalyzed [4] fuel cells. The present paper reports results concerning the electrochemical characterization of

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the anode material of a commercial fuel cell able to directly convert glucose selectively to gluconic acid generating electrical energy and the investigation on its energy performance, with the aim to also produce an actual benchmark for the evaluation of upcoming electrode materials.

## 2. Experimental

The electrochemical cell was purchased from Electro-Chem-Technic (UK). The cell is specifically designed for small-scale studies with liquid alkaline electrolytes and fuels. It is comprised of a 65 ml fuel and electrolyte compartment that also contains a carbon-supported platinum catalyst together with a PTFE (polytetrafluoroethylene) binder. The electrode is supported on a nickel mesh (catalyst area 17.64 cm<sup>2</sup>). The air cathode consists of manganese [as KMnO<sub>4</sub> at greater than or equal to 4% (wt of carbon)] on carbon with a PTFE binder and this is also supported on a nickel wire mesh (catalyst area 13.86 cm<sup>2</sup>). The surface of the cathode is coated with a gas-permeable layer of PTFE. The nickel mesh supports at both the anode and the cathode are connected to terminals on the cell [7].

The anode material of the cell was electrochemically characterized by equilibrium electrode potential ( $E_{rev}$ ), current–voltage ( $I$ – $V$ ), and electrochemical impedance spectroscopy (EIS) measurements as well as the energy performance of the cell investigated. All the experiments were executed at  $25.0 \pm 0.1$  °C.

The solutions were prepared using pure deionized water (“Millipore Milli-Q System”) and D-(+)-glucose, KOH, and Na<sub>2</sub>HPO<sub>4</sub>, all from Sigma–Aldrich. Before each experiment the electrochemical cell was washed in sequence with mQ water, 2-propanol, H<sub>2</sub>O<sub>2</sub> (3.5%, v/v) and finally again with mQ water.

Electrochemical characterization was carried out using a Bio-Logic VMP3 potentiostat–galvanostat multichannel equipped with EIS board.

The  $I$ – $V$  and EIS experiments were performed by two compartments three electrodes cell with a standard calomel electrode (SCE) and platinum mesh as the reference and counter electrodes, respectively.

The chemical analyses were achieved by HPLC (High Performance Liquid Chromatography) using Shimazu LC-10 with a refractive index RID-10A detector and Varian MetaCarb 87H Plus 300 mm × 7.8 mm column; the operating conditions were: H<sub>3</sub>PO<sub>4</sub> 0.01 M as eluant, column temperature of 70 °C and flow rate of 0.6 ml min<sup>-1</sup>.

The NMR measurements were carried out by using a Varian Mercury 400 MHz spectrometer and working at 25 °C.

## 3. Results

### 3.1. Electrode reversible potential measurements

It is well known in the literature that glucose is unstable in aqueous alkaline solution and degrades into complex mixtures [11–13]. Nevertheless glucose electrochemical oxidation is favored at high pH values [6]. In order to establish the optimum operating pH at which the carbohydrate degradation takes place, the glucose concentration in aqueous solutions as a function of time was measured. From each solution some aliquots were sampled and analyzed by HPLC: no variation in composition was observed for pH values equal or less than 11. As a consequence, a buffered solution (0.5 M Na<sub>2</sub>HPO<sub>4</sub>, pH 10.5), purged by N<sub>2</sub> flux was used as an electrolyte in the anodic compartment. The role of the buffer will be discussed in detail later in the text.

In these buffered solutions the equilibrium electrode potential ( $E_{rev}$ ) of the anode was measured vs. the SCE. In such operating

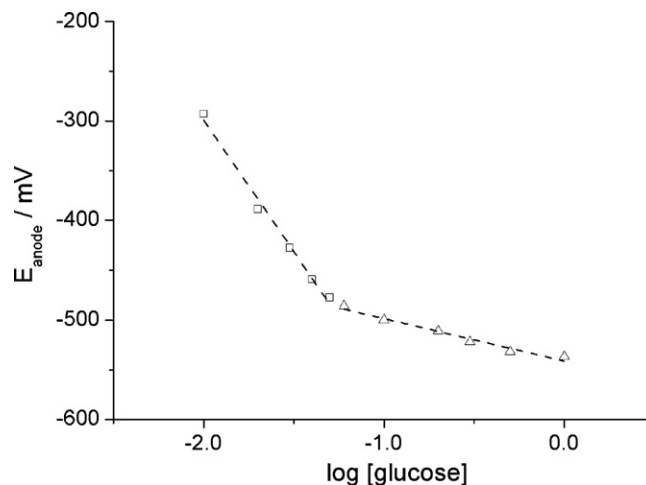
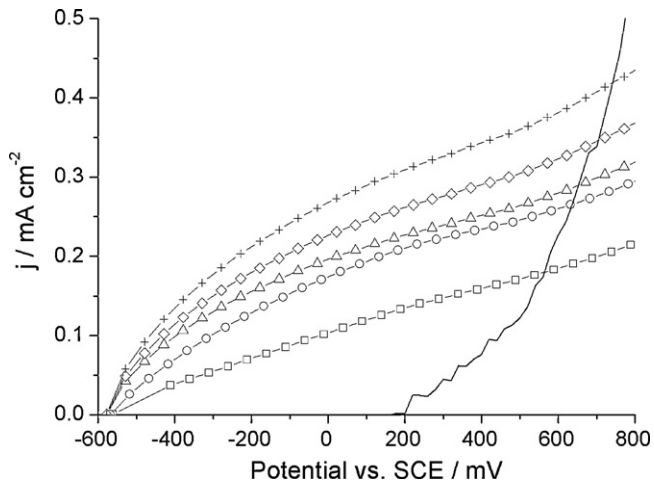


Fig. 1. Reversible anode potential as a function of the glucose concentration.

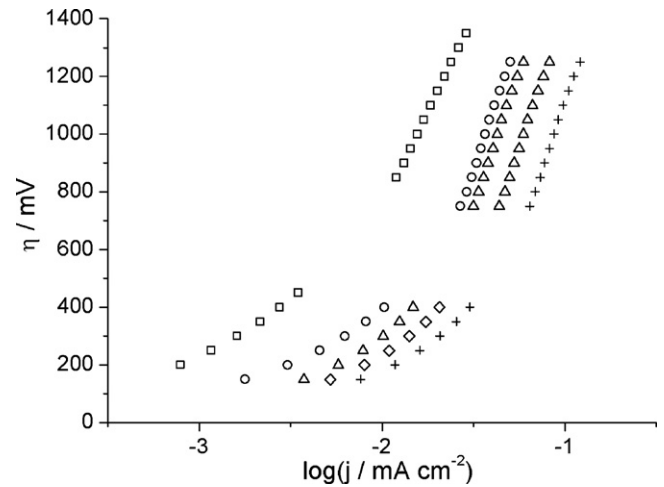
conditions the electrode potentials, after 2 h of equilibration time, were very reproducible ( $\pm 1$  mV) and stable; constant values for 70 h or more were observed. As the glucose concentration rises, the electrode potential becomes more and more negative, their values vs. the logarithm of glucose concentration show a straight line correlation with a change in the slope taking place at about  $5.5 \times 10^{-2}$  M (see Fig. 1). The number of electrons consumed per molecule of glucose,  $n$ , obtained from the two slopes are equal to 0.22 ( $[\text{glucose}] < 5.5 \times 10^{-2}$  M) and 1.4 ( $[\text{glucose}] > 5.5 \times 10^{-2}$  M). The extremely low value of  $n$  obtained for a low glucose concentration may be explained by the simultaneous occurrence of two reactions at the anode: glucose oxidation and oxygen reduction. In fact, even if the solution is purged with nitrogen some traces of oxygen still remain. In such conditions the measured potential is a mixed potential (partially due to the kinetics of both the reactions). Naturally, when the concentration of glucose is sufficiently high, the oxygen reduction rate is negligible with respect to the exchange current of glucose oxidation. The value of  $n$  at high concentration, 1.4, is probably the result of a partial oxidative adsorption of glucose ( $n = 1$ ) and partial oxidation of glucose to gluconate ( $n = 2$ ), following the mechanism of electro-oxidation of glucose on a platinum electrode proposed by Beden et al. [14]. Another possible explanation for the slope change at different glucose concentrations may be the variation in the elemental redox reaction, as previously reported [15]. Nevertheless, the low value of  $n$  for low concentrations makes this hypothesis unrealistic. By fitting the curve in Fig. 1 at high glucose concentration, a value for the standard redox potential,  $E_0$ , of glucose electro-oxidation at pH 10.5 equal to  $-0.5412$  (vs. SCE) is obtained.

### 3.2. Current–voltage characterization

The measurements were performed without and with a buffer in the solution. In the former case before the electrolyte decomposition potential, the anode voltage (V) vs. current density ( $j$ ) shows (see Fig. 2) typical behavior associated to the charge transfer overpotential ( $\eta$ ). In fact,  $\eta$  vs.  $j$  has a linear relationship at the lowest applied voltages, while the Tafel equation describes the electrode behavior at higher values. Two Tafel can be identified (Fig. 3), which are associated to the two main steps of the electro-oxidation of glucose [14]. After the initial oxidative adsorption of glucose to the platinum surface (step 1, Fig. 4), the adsorbed intermediate is further oxidized to  $\delta$ -gluconolactone (step 2, Fig. 4). In step 3  $\delta$ -gluconolactone is desorbed and then hydrolyzed to gluconate. From the shape of the  $I$ – $V$  curve, it appears that the limiting steps



**Fig. 2.** *I*-*V* characterization of the anode material at pH 10.5 and different D-glucose concentration: (□) = 100 mM, (○) = 200 mM, (△) = 300 mM, (◇) = 400 mM, (+) = 500 mM and (---) = KOH solution at pH 10.5.

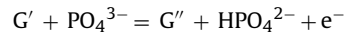
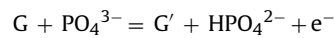


**Fig. 3.** Overpotential as a function of the current density at pH 10.5 and different glucose concentration: (□) = 100 mM, (○) = 200 mM, (△) = 300 mM, (◇) = 400 mM and (+) = 500 mM.

are the two electrochemical reactions, while the desorption of the gluconolactone is relatively fast. This observation can be deduced by the fact that no peak is observed in the *I*-*V* curve. If the electrochemical steps were limiting, the adsorbed products would slow down the reaction rate at higher surface coverage, and therefore one or more peaks should appear in the *I*-*V* curve.

In the presence of the buffer (Fig. 5) the reaction rates of the electrochemical steps change. In fact, two maxima appear which are indicative of two faster electrochemical steps and a slow desorption of the gluconolactone (see the previous explanation). Moreover, it is observed that the peak maxima positions in the potential scale do not vary with the concentration of glucose while the peak current densities do. The maxima locations in the potential scale depend on the buffer concentration as shown in Fig. 6, in particular the higher is the concentration of the buffer the more cathodic is the potential, and simultaneously the intensity of the peak increases. The cathodic shift of the maxima is quite exclusively due to the shift of

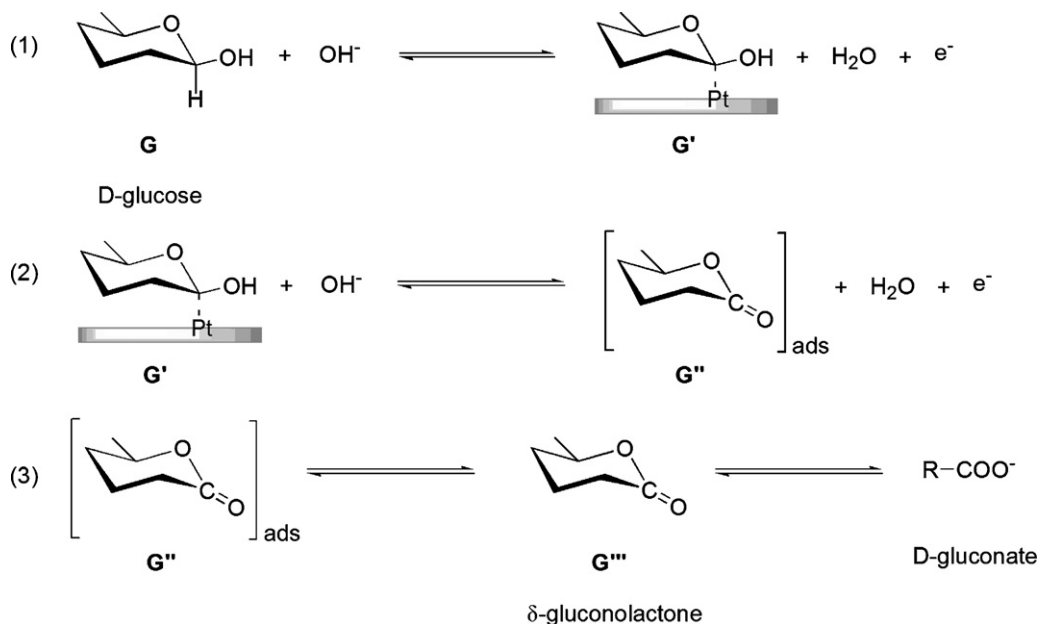
the reversible reaction potential, thus indicating that the reaction now is changed and that the buffer is a reactant. We presume that the following electrochemical steps are now happening:



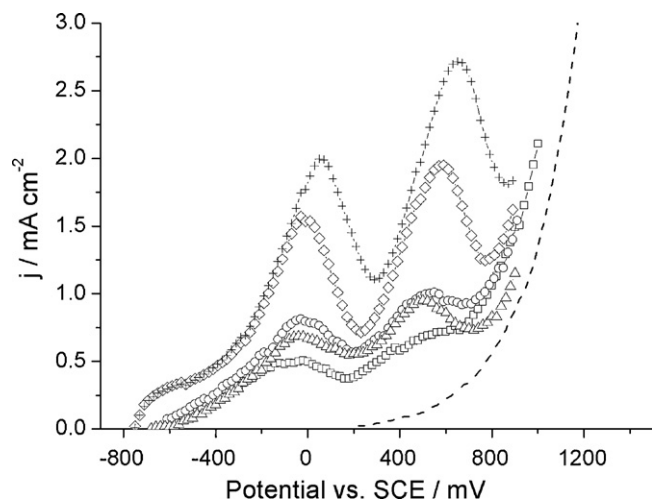
As a consequence the OCV is dependent on the concentration of  $\text{PO}_4^{3-}$ . At pH 10.5, the amount of  $\text{PO}_4^{3-}$  in the solution is around 1% of the total amount of  $\text{Na}_2\text{HPO}_4$ . Thus, in the case of the buffered solution, the limiting reactant is the phosphate ion.

We can conclude that the buffer has multiple roles in the final performances of the anode:

- it changes the reaction rates and steps;
- it increases the amount of  $\beta$  form of glucose (see Section 3.3);
- it increases the conductivity of the solution (see Section 3.4);



**Fig. 4.** Proposed mechanism at platinum electrodes. G = D-glucose ( $\beta$ -D-glucopyranose formed predominantly in water), G' = dehydrogenated glucose (intermediate generated by anomeric carbon dehydrogenation), G'' =  $\delta$ -gluconolactone, G''' = D-gluconate. Adapted from [16].



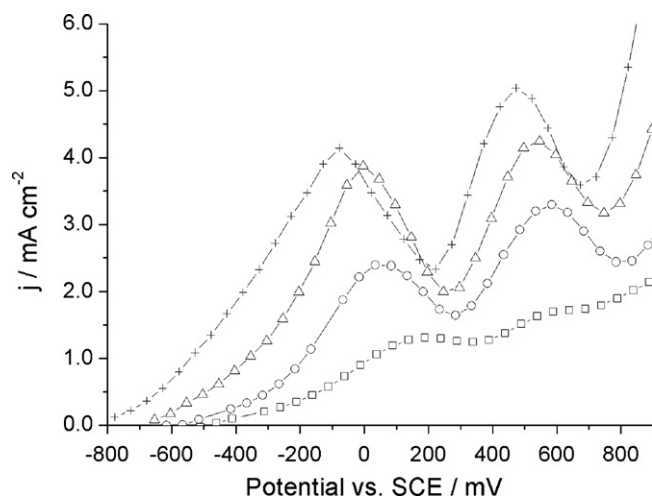
**Fig. 5.** *I*-*V* characterization of the anode material in buffered solution at different D-glucose concentrations: (□)=100 mM, (○)=200 mM, (△)=300 mM, (◇)=400 mM and (+)=500 mM and (---)=buffered electrolyte.

- it may adsorb at the surface of platinum and subtract active sites for the electro-oxidation of glucose as already highlighted at gold electrodes [16].

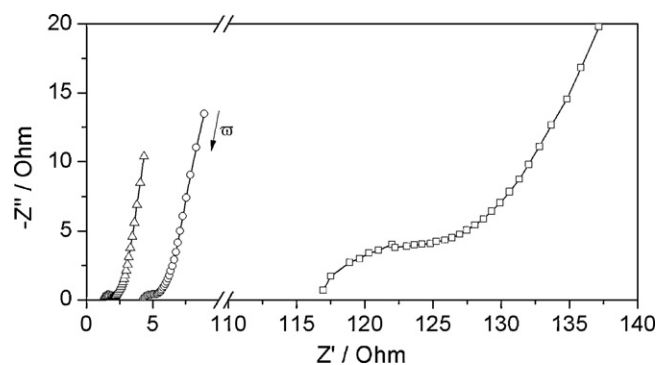
### 3.3. NMR measurements

NMR measurements were performed to study the possible interaction between D-glucose and Na<sub>2</sub>HPO<sub>4</sub>. To do this, two solutions were prepared and let equilibrate for 1 h before the experiment: solution A containing D-glucose 0.5 M in d-H<sub>2</sub>O, solution B with D-glucose 0.5 M and Na<sub>2</sub>HPO<sub>4</sub> 0.5 M in d-H<sub>2</sub>O, pH 10.5 (pH adjusted with d-NaOH). The [β]/[α] ratio was calculated in the two samples by the ratio of the integrations of corresponding H-1 (anomeric) signals in the proton spectra.

H-1(α) is a doublet (*J*=3.7 Hz) at 5.02 ppm, and H-1(β) is a doublet (*J*=8.0 Hz) at 4.44 ppm. In solution A (containing only glucose) [β]/[α] is 0.46, while in solution B (containing the phosphate) [β]/[α] is 1.87. The <sup>1</sup>H and <sup>13</sup>C spectra of solutions A and B did not display any difference in the signal chemical shifts or in the coupling constant values, thus indicating that neither covalent bonds nor tight sugar-phosphate complexes are formed in these conditions.



**Fig. 6.** *I*-*V* characterization of the anode material in 500 mM D-glucose solution at different buffer concentrations: (□)=50 mM, (○)=250 mM, (△)=500 mM and (+)=saturated solution.



**Fig. 7.** Nyquist plot obtained at pH 10.5 with constant glucose amount (50 mM) and different buffer concentrations: (□)=0 mM; (○)=50 mM; (△)=500 mM. Spectra were collected at OCV using a perturbation potential of 10 mV in the frequency range 20,000–0.10 Hz.

However, only a consistent increase in the β-anomeric form was observed by adding phosphate. A solution containing a lower glucose concentration (0.01 M) and the same buffer amount (0.5 M) presents higher value of anomers concentration ratio ([β]/[α]=2.2).

Proton spectra of a series of solutions with glucose 0.5 M and increasing concentrations of bibasic phosphate, covering a range from 0.05 M to 1 M, showed that the [β]/[α] ratio is almost independent of phosphate concentrations (an average value of 1.92 was found in all experiments); 24 h later the same solutions gave similar results.

It has been already reported that the β form of glucose exhibits a higher electrochemical reactivity toward electrooxidation at gold electrodes compared to the α form [17]. Nevertheless we want to stress that the increase in [β]/[α] with the phosphate buffer cannot alone take into account the electrochemical results.

Moreover, both NMR and HPLC of solutions after polarization showed the presence of the only gluconate and no other by-products.

### 3.4. Electrochemical impedance spectroscopy (EIS)

EIS measurements were used to understand the role of the phosphate buffer on the conductivity of the solution and the mechanism of the reaction. The conductivity of the solution also influences the amount of usable electrode. In fact, a higher conductivity of the solution permits an easier transport of the current inside the electrode and consequently a higher portion of the electrode to be active. The measurement can be used to optimize the thickness of the electrode as a function of the working conditions.

EIS measurements were performed in solutions having different buffer concentrations and constant glucose amounts. For each solution the experimental results (reported in Fig. 7 in a Nyquist plot) show, at high frequency, an arc whose origin lies on the real axis (uncompensated ohmic resistance) followed by a capacitive distorted semicircle. Fitting of the impedance spectra was performed by using the equivalent circuit in Fig. 8 and the theory of porous electrode reported in Ref. [18]. In Table 1 the parameters of the fitting and the standard deviations are reported.

By increasing the buffer concentration, we observed that both the resistance of the electrolyte in the bulk and in the pores decreases, and also the resistances of adsorption and charge transfer decrease; the double layer capacitance remains quite constant, as expected, and the same is valid for the capacitance of adsorption. The latter is proportional to the number of active sites in the platinum particles, and therefore it is expected to not be dependent on the concentration of the buffer. The higher conductivity of the buffered electrolytes permits a better use of the active material

**Table 1**

Fitting parameters and standard deviations of the impedance spectra in Fig. 7, performed by using the equivalent circuit in Fig. 8.

[Na <sub>2</sub> HPO <sub>4</sub> ] mM	R <sub>ei</sub> (Ω cm <sup>2</sup> )	R <sub>p</sub> (Ω cm <sup>2</sup> )	C <sub>dl</sub> (F cm <sup>-2</sup> )	R <sub>ad</sub> (Ω cm <sup>2</sup> )	C <sub>ad</sub> (F cm <sup>-2</sup> )	W (S s <sup>0.5</sup> cm <sup>-2</sup> )	R <sub>ct</sub> (Ω cm <sup>2</sup> )	χ <sup>2</sup>
0	115	31.9	0.00325	2.83	0.168	0.0732	16,000	0.00010
50	4.17	3.54	0.00398	0.280	0.139	0.313	348	0.00021
500	1.14	3.02	0.00153	0.224	0.177	0.525	300	0.00015

inside the pores of the electrode. The charge transfer resistance is in good agreement with the value of exchange current densities observed from the *I*–*V* curves.

### 3.5. Cycling performance

To roughly evaluate the energy performance of the FC01 Mini Fuel Cell, some connection–disconnection cycles were carried out. After reaching the OCV the two electrodes were connected to an electrical resistance (*R*) and afterwards disconnected when the electrical potential reached steady-state conditions. Such procedure was repeated consecutively for several times.

In each connection–disconnection step, the voltage (see Fig. 9) showed a sudden drop immediately after the connection of the cell to the resistance, followed by a slow fall until it reached a nearly constant value. Opening the circuit, the potential after a fast increase went slowly back to the initial OCV values which were achieved only in the buffered solutions. The same behavior was observed with different electrical resistance and their values of course influenced the short-circuit potentials. It was also observed that the presence of the buffer not only supports the recovery of

the OCV to early values but it increases the potentials in the short-circuit conditions, enhancing the energy performances. The power density was evaluated to be about 50 μW cm<sup>-2</sup>.

## 4. Discussion and conclusions

In the present study the operating conditions for achieving reproducible and constant OCV values have been found. In particular, the proper pH and the presence of the buffer not only stabilize the reversible anode potential, but also promote higher cell voltages during the energy supply.

The buffer has multiple roles in the final performances of the anode: it changes the reaction rates and steps; it increases the amount of β form of glucose (see Section 3.3); it increases the conductivity of the solution (see Section 3.4); it may adsorb at the surface of platinum and subtract active sites for the electro-oxidation of glucose as already highlighted at gold electrodes. NMR measurements highlight relatively larger β-anomeric percentages only at the lowest sugar concentrations as well as the chemical analyses by HPLC of solutions after their electrolysis showed the presence of the only gluconic acid, the decrease of the glucose amount and no other by-products. The anode potential, stabilized by the buffer presence, depends on the glucose chemical potential which has to be fixed either constantly replenishing with fresh reactant (flooded flow cell) the cell or having saturated glucose solutions.

Moreover the presence of the Na<sub>2</sub>HPO<sub>4</sub> not only stabilizes the potential, but also improves the electrochemical performances of the anode in terms of exchange current density. Such behavior is not ascribable to the chemical interaction with glucose, as shown by NMR measurements, but to the interaction with the anode material as indicated by the decrease of all the resistive components in the EIS measurement.

The results obtained with the tested commercially available anode (50 μW cm<sup>-2</sup>) are far from satisfactory even by comparison to the literature and represents a benchmark for the evaluation of upcoming electrode materials.

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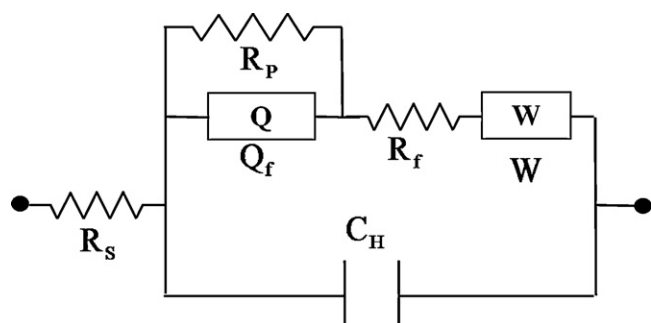


Fig. 8. Equivalent circuit of the platinum/electrolyte interface in presence of glucose.

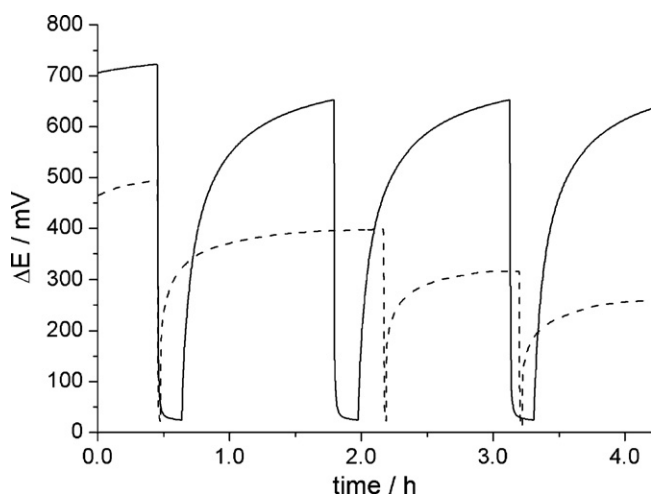


Fig. 9. Typical behavior of the fuel cell voltage as a function of time during consecutive connection–disconnection cycles. Glucose solution concentration 500 mM, pH 10.5, with (—) and without (---) buffer and *R* = 10 Ω.

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