Stack air-breathing membraneless glucose microfluidic biofuel cell

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Abstract. A novel stacked microfluidic fuel cell design comprising re-utilization of the anodic and cathodic solutions on the secondary cell is presented. This membraneless microfluidic fuel cell employs porous flow-through electrodes in a “V”-shape cell architecture. Enzymatic bioanodic arrays based on glucose oxidase were prepared by immobilizing the enzyme onto Toray carbon paper electrodes using tetrabutylammonium bromide, Nafion and glutaraldehyde. These electrodes were characterized through the scanning electrochemical microscope technique, evidencing a good electrochemical response due to the electronic transference observed with the presence of glucose over the entire of the electrode. Moreover, the evaluation of this microfluidic fuel cell with an air-breathing system in a double-cell mode showed a performance of 0.8951 mWcm⁻² in a series connection (2.2822mAcm⁻², 1.3607V), and 0.8427 mWcm⁻² in a parallel connection (3.5786mAcm⁻², 0.8164V).

1. Introduction

Microfluidic fuel cells that use enzymes as catalysts to convert the chemical energy of fuels into electrical energy are of special interest due to their operational conditions such as low-temperature (20–40 °C), activity near to neutral pH, selectivity and specificity [1-3]. Additionally, designing aspects have shown also an increase in the performance of these miniaturized devices. For instance, the incorporation of an air-breathing window intake increases the oxygen concentration, and due to its superior diffusivity in air than in aqueous solution avoids the transfer limitations of dissolved oxygen [4, 5]. Stacked membraneless microfluidic hybrid or biofuel cells have been tested in both, series or parallel electrical modes enhancing the overall fuel utilization by reusing the unreacted fuels from the first cell to the others [6, 7]. In this work, we present the scanning electrochemical microscope characterization of glucose oxidase immobilized on Toray carbon paper and its use as bioanode towards the evaluation of two air-breathing membraneless microfluidic fuel cells, one operated in a single mode, and the other in the stack mode in both series and parallel.
2. Experimental

2.1 Reagents

Glucose oxidase (EC 1.1.3.4 from *Aspergillus niger*), tetrabutylammonium bromide (TBAB), glutaraldehyde solution 5% (GA), potassium phosphate dibasic dihydrate (K$_2$HPO$_4$), potassium phosphate monobasic monohydrate (KH$_2$PO$_4$), Nafion® (5% diluted in water), and potassium hydroxide (88.7%) were purchased from Sigma-Aldrich.

2.2 Electrodes fabrication

The bioanode consisted on Toray carbon slides (EC-TP1-060T) of 1.25 mm width and 30 mm length dipped for 15min in a catalytic ink composed of the following components: 7 μL Nafion, 13 μL glutaraldehyde solution, 990μL of 0.1M phosphates buffer at pH 7, 20 mg Vulcan carbon (Vulcan XC-72 from E-ETEK) and 1 mg of TBAB for each mg of enzyme glucose oxidase. This ink was prepared by sonication during 20 min followed by a vortex for other 15 min. The bioanode was then dried at room temperature. On the other side, the air-breathing cathode was prepared on a piece of carbon nanofoam (2.5×30 mm, Marketech®) and covered with an ink containing 7 μL of Nafion® 5% (Sigma–Aldrich), 73 μL of isopropyl alcohol (J.T. Baker) and 1 mg of commercial Pt/C (30 wt. % on Vulcan XC-72 from E-TEK), which was deposited using an airbrush to assure homogeneous deposition with a final metal loading of 1 mgcm$^{-2}$ over the entire surface.

2.3 Construction and evaluation of microfluidic air-breathing membraneless fuel cells.

Schematic representations of the single and stack microfluidic fuel cells are illustrated in figure 1. The significant difference between them consists in the electrode array due to the stack microfluidic design allows re-utilization of the anodic and cathodic solutions in the second cell in order to increases the fuel and oxidant utilization.

![Figure 1. Schematic representations of single and stack air-breathing membraneless and electrode array.](image)

The single microfluidic air-breathing device was previously reported [8]. The second section consisted of a home-made silicone elastomer film (Silastic®, Dow Corning, prepared using an Elcometer® Film Applicator with a final thickness of 200 μm). On the other hand, the stack air-breathing membraneless microfluidic fuel cell employs porous flow-through electrodes, but in a “V”-shape architecture. The microfluidic fuel cells were evaluated by injecting 5mM glucose N$_2$-saturated (4 U. P. D. Praxair) as the fuel and oxygen from the air as the oxidant within two aqueous streams consisting in 0.1M phosphate buffer (pH 7) and 0.3 M KOH injected on the anodic and the cathodic side, respectively, with a flow rate of 30 μL min$^{-1}$ for both streams.

3. Results and discussion

3.1 Topography and localized enzymatic activity.

Scanning electrochemical microscopy (SECM) has been used widely to monitor the distribution and the enzymatic activity on surfaces [9], therefore the study of glucose oxidase on Toray paper was
achieved using a BioLogic scanning system instrument model ac-SECM/SECM470. SECM measurements were performed in a four electrode cell consisting of a graphite rod and Ag/AgCl|3M KCl served as auxiliary and reference electrodes, respectively, a Platinum ultramicroelectrode (UME) of 25 µm, using 5mM of glucose in 2mM K₃[Fe(CN)₆] in 0.1M phosphate buffer pH 7.0 as working solution. Activity evaluated by H₂O₂ production due to an applied potential of 0.7V, thus ensuring diffusion-controled oxidation of H₂O₂ [10]. The SECM images were obtained using software MIRA.

Figure 2. SECM images of catalytic ink of GOx in absence (a) and presence of 5mM glucose (b) at Eᵣ = +0.7 V vs Ag/AgCl in pH 7.0 (0.1 M) phosphate buffer solution.

Figure 2 shows SECM images obtained following the H₂O₂ generated by influence of both, the enzyme and the applied potential. In the absence of glucose (figure 2a), currents in the order of nano-Amps are observed associated mostly to non-Faradic processes. Meanwhile, with the addition of glucose (figure 2b), yellow and red zones related to higher current are observed and related to the Faradic process involving the electron transference from the glucose oxidation to form gluconolactone and hydrogen peroxide, indicating that the enzyme is on the electrode.

3.2 Evaluation of the single and stack microfluidic fuel cells.

The single microfluidic fuel cell produced a power density of 0.4522 mW/cm² (figure 3a). Meanwhile, the stack cells increased at least twice the power density compared with the single cell regardless the electrical configuration (figure 3b). As expected, the highest current density was obtained in the parallel mode, with a value of 3.5786 mA/cm². However, the maximum cell performance (0.89 mW cm⁻²) was obtained in series mode due to the reduction of both, the polarization and ohmic losses.

Figure 3. Polarisation and power density curves using 5Mm glucose in 0.1M buffer phosphates pH 7.0 at10 mV s⁻¹ as fuel and 0.3M KOH as oxidant of a) single and b) stack microfluidic fuel cell connected in series and parallel.
According with table 1, the best results were obtained using the stack cell in a series mode, where the re-utilization of fuel and oxidant from the first to the second cell increased the open circuit potential and, in a lower manner the current density compared with the single cell, demonstrating the excellent energetic capability and versatility of this device.

4. Conclusions

Evaluation of two different designs of microfluidic fuel cells was performed varying the number of cells that composed them. The first design corresponds to a previously reported single membraneless microfluidic fuel cell and, in the second case, a stack cell composed of two cell in which the oxidant and fuel are re-utilized in the second cell promoting the fuel consumption. In addition, the stack cell was tested in both modes, series and parallel, increasing the current density or the voltage. The enzymatic activity was tested by cyclic voltammetry and scanning electrochemical microscope evidencing the electron transference from the glucose oxidation through the entire electrode related to a good enzymatic immobilization. Consequently, the stack membraneless microfluidic fuel cell operated in a series configuration showed the highest cell performance herein found (0.8951 mW cm\(^{-2}\)) due to the decreasing of the polarization losses associated mainly to the electrode kinetics and reduction of ohmic losses.

5. References

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