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Design, fabrication and performance of a mixed-reactant membraneless micro direct methanol fuel cell stack

J.C. Abrego-Martínez[a], A. Moreno-Zuria[b], F.M. Cuevas-Muñiz[b], L.G. Arriaga[b], Shuhui Sun[a], Mohamed Mohamedi[a,*]

[a] *Énergie, Matériaux et Télécommunications (EMT), Institut National de La Recherche Scientifique (INRS), Université de Recherche, 1650 Boulevard Lionel Boulet, Varennes, Québec, J3X 1S2, Canada*

[b] *Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Parque Tecnológico Querétaro S/N, Pedro Escobedo, Querétaro, 76703, Mexico*

HIGHLIGHTS

- The fabrication and evaluation of a passive membraneless μDMFC stack is reported.
- The stack operates in mixed-reactant mode using 5 M MeOH in KOH.
- Mixed-reactant operation was achieved by using a highly methanol-tolerant cathode.
- The 2-cell stack design allowed to double the OCV with virtually no cost increase.
- The stack showed good stability throughout a 10 h test.

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ABSTRACT

In the present work, we report the design, fabrication and evaluation of a membraneless mixed-reactant and air-breathing microfluidic direct methanol fuel cell (ML-μDMFC) stack operated in passive mode. The operation under mixed-reactant conditions was achieved by using a highly methanol-tolerant Ag/Pt/CP cathode with ultra-low Pt loading in alkaline medium. Prior to the fabrication of the stack, a flow simulation was made in order to study the behavior of the reactants stream in the microchannel through the 2 cells. Subsequently, the device was tested in passive mode using a mixture of 5 M MeOH +0.5 M KOH. The results showed that by connecting the 2 cells in series, it is possible to effectively double the voltage of a single ML-μDMFC, as well as increasing the absolute power by 75% with practically no cost increase. The stack was capable of operate continuously for more than 2 h with a single charge of 40 μL, producing an OCV of 0.89 V and a maximum power density of 3.33 mW mg_{Pt}^{-1}. Additionally, the device exhibited good stability throughout a 10 h test.

1. Introduction

Fuel cells are electrochemical cells capable of converting chemical energy directly into electrical energy through electrochemical reactions. Depending on the amount of power generated, fuel cells are a potential alternative for replacing the ongoing power sources like fossil fuels used for transportation or batteries employed in a wide range of electronic equipment. In the case of portable devices, such as smartwatches, cell phones and laptops, the need for longer operating periods makes fuel cells an attractive alternative due to the possibility of being instantly recharged [1–6]. Direct methanol fuel cells (DMFC), which are low temperature devices, have been in the spotlight of many research groups during the last 2 decades [7], mostly due to the virtues of methanol as fuel, such as high energy density (4820 Wh L^{-1}) and ease of storage and transportation, compared to other fuels like hydrogen gas [8–10].

The occurring reactions in a DMFC in acidic media are [11]:

$$\text{Anode: } 2CH_3OH + 2H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \quad E^0 = 0.02\ V \tag{1}$$

$$\text{Cathode: } 12H^+ + 12e^- + 3O_2 \rightarrow 6H_2O \quad E^0 = 1.23\ V \tag{2}$$

And in alkaline media are [11]:

$$\text{Anode: } 2CH_3OH + 12OH^- \rightarrow 2CO_2 + 10H_2O + 12e^- \quad E^0 = -0.81\ V \tag{3}$$

$$\text{Cathode: } 3O_2 + 6H_2O + 12e^- + 3O_2 \rightarrow 12OH^- \quad E^0 = 0.40\ V \tag{4}$$

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[*] Corresponding author.
E-mail address: mohamedi@emt.inrs.ca (M. Mohamedi).

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With an overall reaction in acidic or alkaline:

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O \quad \Delta E = 1.21 \ V \tag{5}$$

The leading DMFC technology involves a proton exchange membrane (PEM), usually Nafion® to separate the anodic and cathodic reactions [12–14]. However, methanol crossover from the anode to the cathode through the membrane is a recurrent issue that impacts negatively on the overall performance of PEM-DMFCs. The presence of methanol at the cathode causes depolarization losses due to simultaneous oxygen reduction and methanol oxidation processes [15,16]. Moreover, in a real DMFC, the cell voltage is always lower than the thermodynamic value due to different losses, such as anodic and cathodic activation overpotential, anodic and cathodic crossover effect, ohmic overpotential and mass transport losses [17,18]. Depending on the pH, the catalysts employed, cell configuration and tests conditions, a DMFC can generate an open-circuit voltage (OCV) between 0.4 and 0.8 V [8,11,19,20]. Therefore, for a practical application it is necessary to design and fabricate stacks to increase the voltage and current of DMFCs. It is at this point where the development and commercialization of PEM-DMFCs meets a setback. Due to the number of components in a stack (catalysts, membrane, gas diffusion layers, bipolar plates, clamping plates, current collectors, gaskets, hardware etc.), the fabrication cost escalates rapidly. As recently shown by Sgroi et al. in their cost analysis of PEM-DMFC stacks, the fabrication expenses of a lab-made 10-cell stack prototype can reach almost €3000, of which only 12% is due to the catalysts, 20% to the membrane-electrode assembly (MEA) and 60% is related to bipolar plates, clamping plates and current collectors [21]. In this sense, a more viable path in the quest of alternative power sources, particularly for portable devices, could be the membraneless (ML)-μDMFC. As the name itself suggests, this technology doesn't require any membrane to separate the two half-reactions. Instead, ML-μDMFCs rely on the co-laminar flow of fuel and oxidant in a microfluidic channel to operate [6,22,23]. By eliminating the MEA and the bipolar plates, the cost of a ML-μDMFC is dramatically lowered. However, in most of ML-μDMFC stacks, the reactants that come together at the outlet of a cell must be re-separated into fuel and oxidant streams before entering the next cell [24,25]. Additionally, these systems depend on an external pump to keep the reactants flowing and prevent the two streams from mixing [26]. A potential alternative to sort out this situation is to apply the concept of mixed-reactant fuel cells (MRFC) to facilitate the design and operation of ML-μDMFC stacks. Essentially, in a MRFC, the fuel and oxidant are mixed in a single stream before feeding the fuel cell and the use of selective electrocatalysts is necessary to minimize mixed-potential at the electrodes [27,28]. In a DMFC, this means an anode active to the methanol oxidation reaction (MOR), and a cathode active to only oxygen reduction reaction (ORR). There are a number of advantages associated to the use of MRFCs compared with other DMFCs, e.g., no need for laminar flow and external pumps as in ML-μDMFCs, no need for solid polymer membrane as in PEM-DMFCs, reduced weight and volume, simplified manifolding, reduced sealing requirements and, overall they have simpler designs. By having smaller volume, a mixed-reactant ML-μDMFC stack can lead to higher volumetric power density [17,27–30]. From an engineering point of view, this translates into cheaper fabrication and easier operation than conventional fuel cells. Calabrese-Barton and his group have developed some MEAs-based MRFCs [27,31,32], and more recently a borohydride-oxygen Swiss-roll MRFC was reported [30,33,34]. Nevertheless, not many works on methanol MRFCs are found in the literature, due mainly to the requirement of selective electrodes and their low mass specific activity, compared with Pt [27]. Though the MOR is hardly affected by the presence of oxygen, the ORR is suppressed by the presence of MeOH [35]. In recent years, many research groups have developed methanol-tolerant cathodes for reducing the methanol crossover effect in DMFCs [36–38]. We recently reported a highly methanol-tolerant Ag/Pt bilayer catalyst with ultra-low Pt loading and high mass specific activity, synthesized by PLD on carbon paper (CP) [39]. That work has shown that Pt acts as the catalyst for the ORR, while Ag acts as a protective coating for the Pt layer. Since Ag is not active to the MOR, it effectively prevents the methanol molecules from reaching the Pt surface, while O_2, being a much smaller molecule can permeate trough the porous of the Ag layer and reacts on the Pt surface [39]. This material has demonstrated its capability to reduce the methanol crossover effect in a typical 2-stream ML-μDMFC in presence of concentration of MeOH as high as 5 M [40]. We propose that these kind of materials could be also useful in the case of MRFCs and at the same time, facilitate the development of simpler stacks to increase the voltage and power density of these devices. To prove this hypothesis, in the present work we have tested the bilayer Ag/Pt/CP cathode in a newly fabricated mixed-reactant ML-μDMFC stack operated in passive mode, whose design was made with basis on the behavior of the single ML-μDMFC operated under mixed-reactant conditions.

2. Experimental

2.1. Synthesis of the Ag/Pt/CP cathode and Pt/CP anode

The cathode catalyst consisted in a Pt film coated with an Ag film, both synthesized by pulsed laser deposition (PLD) technique on a carbon paper (CP) substrate, using the optimum deposition conditions previously reported by our group [39]. Briefly, the Pt layer was deposited with 20,000 laser pulses on CP and the Ag layer was deposited with 20,000 laser pulses on the Pt layer.

The anode consisted in a Pt film synthesized by PLD on a CP substrate, which was deposited using the same conditions than the Pt layer in the Ag/Pt/CP cathode.

2.2. Physicochemical characterization of the electrodes

The physicochemical characterization of the PLD-synthesized catalysts by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS) was already reported [39]. Briefly recalling the results, the analyses revealed porous Pt and Ag layers with thickness of approximately 25 nm each, in a layer onto layer architecture, where both Pt and Ag are in metallic state and they do not interact each other as confirmed by XPS analysis [39]. Pt and Ag loadings, measured by neutron activation analysis were 0.04 mg cm^{-2} each.

2.3. Design of the mixed-reactant ML-μDMFC 2-cell stack and flow simulation

The microfluidic membraneless stack arrangement consists in 2 mixed-reactant fuel cells (cell A and cell B) in a serial path, resembling an hourglass, i.e. the inlet of the cell B is located at the outlet of the cell A. The microchannel scheme and its dimensions are shown in Fig. 1. The design of the individual fuel cells is a variation of the air-breathing ML-μDMFC with flow-through electrodes reported by our group [40]. In

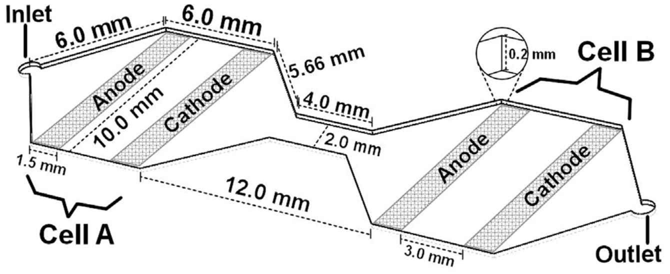

Fig. 1. Scheme of the microfluidic 2-cell microchannel used in the mixed-reactant μDMFC stack.