Air-breathing microfluidic fuel cells with a cylinder anode operating in acidic and alkaline media

Biao Zhang [a,b], Ding-Ding Ye [a,b,*], Jun Li [a,b], Xun Zhu [a,b], Qiang Liao [a,b]

[a] Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400044, China
[b] Institute of Engineering Thermophysics, Chongqing University, Chongqing 400044, China

ABSTRACT

An air-breathing microfluidic fuel cell with a cylinder anode is fabricated and characterized in the acidic and alkaline media. The dynamic behavior of CO_2 bubbles is visualized in the acidic media, and its impact on current production is discussed. The effects of electrolyte concentration, reactant flow rate and channel length on the cell performance are also evaluated in the alkaline media. The results show that most of the CO_2 bubbles are trapped between the anode and spacer in the acidic media, and the corresponding chronoamperometry curve is well correlated with the bubble movement. Further analysis indicates that the gas bubble improves the internal ohmic resistance by reducing proton conduction. In the alkaline media, the fuel cell yields a much higher performance than the acidic case, and fuel transfer limitation and cathode potential reversal occur at combined low flow rate and high current density. The cell performance is found to be predominated by ohmic resistance at flow rates over $200\,\mu L\,min^{-1}$.

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1. Introduction

Having been developed for more than a decade, membraneless microfluidic fuel cells (MMFCs) have been regarded as one of the most promising miniaturized power sources [1,2]. The potential application area involves portable electronic devices (e.g., smart phones and tablets) and micro sensors. MMFCs exploit the co-laminar flow of multistream at microscale to segregate the fuel and oxidant. In a microfluidic channel, the fuel and oxidant solution flow in parallel laminarly without convective mixing. The ion transport between the anode and cathode is also facilitated by the supporting electrolyte containing abundant highly mobile protons or hydroxide ions. Hence, the physical proton exchange membrane can be removed, benefitting both the cell fabrication and miniaturization. In particular, air-breathing microfluidic fuel cells (AMFCs) show superiority over conversional MMFCs in eliminating the liquid oxidant (e.g., dissolved oxygen) transfer limitation by integrating a gas diffusion electrode to utilize the atmospheric oxygen [3,4]. Moreover, the fuel-oxidant interdiffusion is also removed, and the waste solution can be used for potential reactant recycle.

For most AMFC architectures, a planar anode is deposited on the channel wall opposite to the cathode [5,6]. Although the

architecture and fabrication are quite simple, the planar anode induces several fuel transfer challenges that restrict the cell performance and efficiency. One of the main challenges is the continuous formation of fuel concentration boundary layer (FCBL). Due to the ineffectively diffusive mass transport and the consumption of anode reaction, the fuel concentration in the vicinity of the planar anode is decreased downstream [7]. As a result, the anode current density distribution is non-uniform and is biased towards the inlet [8]. The other challenge is the low fuel utilization rate, especially at high flow rates. As hindered by the FCBL, a large fraction of the fuel stream passes through the channel without contributing to the anode reaction, leading to low fuel conversion efficiency. To manipulate the FCBL and enhance fuel transport, several strategies have been reported. The continuous formation of the FCBL can be interrupted by separated electrode pairs [9,10], but at the expense of declined total output at fixed channel length. A multi-inlet/outlet configuration was demonstrated by Yoon et al. [11] to actively control the FCBL by adding fresh fuel or removing depleted solution. A spiraling flow in the fuel stream can be caused by the micro-ribs on the channel wall to convectively compensate the FCBL [11–14]. The fuel stream can also be pressed to a thin layer over the anode to improve concentration gradient by hydrodynamic focusing [5,15,16]. However, these strategies would increase the system complexity and fabrication cost. Besides, although the flow-through porous anode shows great promise in enhancing fuel transport and reducing fuel crossover [8,17], the short hydraulic retention time of

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the fuel within the thin catalyst layer inherently limits the fuel conversion efficiency.

Compared with the planar anode, the advantage of non-planar electrode has been demonstrated [18–20]. In particular, the cylinder anode provides spatially distributed circumferential catalytic surface area to increase the available reactive surface in a fixed volume. The FCBL can be partly compensated by the crossflow around the cylinder anode to enhance local fuel transport. Moreover, although the acidic media is widely adopted and well-studied, it may not be very promising since the cell performance can be limited by the sluggish reaction kinetics and detrimental effects of trapped CO_2 gas bubbles [21,22]. In contrast, it has been proved that the alkaline media can promote the electro-oxidation of small molecule biofuel by providing substantial hydroxide ions for oxidizing intermediate products (e.g., CO_{ads}), and can inherently eliminate the two-phase flow effect [13,22]. Consequently, it is expected that operating in an alkaline environment is promising for practical application.

In this study, an AMFC with a cylinder anode was fabricated and tested in the acidic and alkaline media. The dynamic behavior of CO_2 gas bubbles in the acidic solution was studied by visualization. The effect of electrolyte concentration, flow rate and channel length on the cell performance was characterized in the alkaline media.

2. Experimental

Fig. 1 schematically depicts the cell architecture and detailed components. The experimental prototype was fabricated by Polymethyl methacrylate (PMMA). The cell comprised a rectangular main flow channel with the dimension of $1.5 \times 3.0 \times 42.0$ mm, and two inlet channels with the cross section of 1.5×0.5 mm. Opposite to the inlets, a slot outlet was fabricated on the sidewall at the end of the main flow channel. The cylinder anode and spacer were based on commercial pencil leads (1.0 mm in diameter, Rotring), and were fitted into the main flow channel with the centerline spacing of 1.5 mm. The spacer was used without further treatment, while the anode was prepared by electrodeposition [23] with the Pd and Nafion loading around 5.0 and 0.3 mg cm^{-2},


Fig. 1. Schematic illustration of (a) the AMFC with a cylinder anode and (b) the detailed components.

respectively. The anode surface area was 1.32 cm^2. An air-breathing cathode was positioned on the main flow channel with the surface area about 0.63 cm^2. It was prepared as Li et al. [24] with the Pt black (HiSPEC 1000, Alfa Aesar) and Nafion loading about 3.0 and 1.0 mg cm^{-2}, respectively. A titanium foil (0.03 mm in thickness) was pressed onto the air-breathing cathode as the current collector.

In this study, the fuel cell was placed horizontally with the cathode on the top. For operation in the acidic media, formic acid was used as the fuel and sulfuric acid as the electrolyte. In contrast, sodium formate was employed as the fuel and potassium hydroxide as the electrolyte in the alkaline media. The respective electrode reactions are as follows.
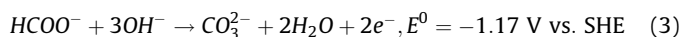
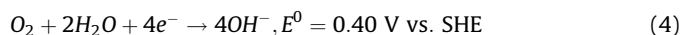In the acidic media, formic acid electro-oxidation occurs at the anode [25]:

$$HCOOH \rightarrow CO_2 \uparrow + 2H^+ + 2e^-, E^0 = -0.198V \text{ vs. SHE} \tag{1}$$
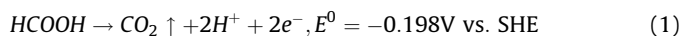
And oxygen reduction reaction takes place at the cathode [8]:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O, E^0 = 1.229 \text{ V vs. SHE} \tag{2}$$
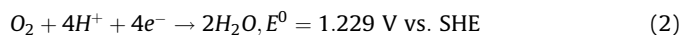
In the alkaline environment, formate is electro-oxidized at the anode [26]:

$$HCOO^- + 3OH^- \rightarrow CO_3^{2-} + 2H_2O + 2e^-, E^0 = -1.17 \text{ V vs. SHE} \tag{3}$$

And oxygen is reduced at the cathode [27]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, E^0 = 0.40 \text{ V vs. SHE} \tag{4}$$

In order to facilitate ion transport and reduce internal ohmic resistance, sulfuric acid and potassium hydroxide were added into the fuel solution as the supporting electrolyte, respectively [4,22,26]. The fuel and electrolyte were driven by a dual channel syringe pump (LSP02-1B, Longer) at identical volumetric flow rates.

The dynamic behavior of CO_2 bubbles was visualized by a digital camera (D7000, Nikon) equipped with a macro lens. The cell performance was evaluated by an electrochemical workstation (PMC-1000, Princeton Applied Research) at room temperature. The polarization curve was obtained by chronoamperometry with stepwise potentiostatic control from open circuit voltage (OCV) to 0.0 V at −0.1 V per step. The corresponding current output was recorded for 3 min and was time-averaged in the acidic media [20,28], while the steady state value was recorded for the alkaline operation. In this study, the reported current density and power density were normalized to the main flow channel volume (0.189 cm^3, including the anode and spacer). An Ag/AgCl reference electrode (0.198 V vs. SHE) was positioned near the outlet to separate electrode potentials. Moreover, the internal ohmic resistance of the fuel cell was determined by electrochemical impedance spectroscopy (EIS) with cathode as the working electrode. Nyquist plots were recorded at OCV with the perturbation amplitude of 10 mV and the frequency range from 50 kHz to 0.5 Hz. To obtain reliable and reproducible results, the measurement was repeated at least 3 times on two distinct fuel cells.

3. Results and discussions

3.1. Dynamic behavior of CO_2 bubbles

For conventional MMFCs with rectangular flow channel, it has been demonstrated that the released gas bubbles can perturb the co-laminar interface and even occupy the whole channel [28–31]. In this study, the dynamic behavior of CO_2 bubbles, and its impact on current production were investigated in the acidic media. Fig. 2 shows the time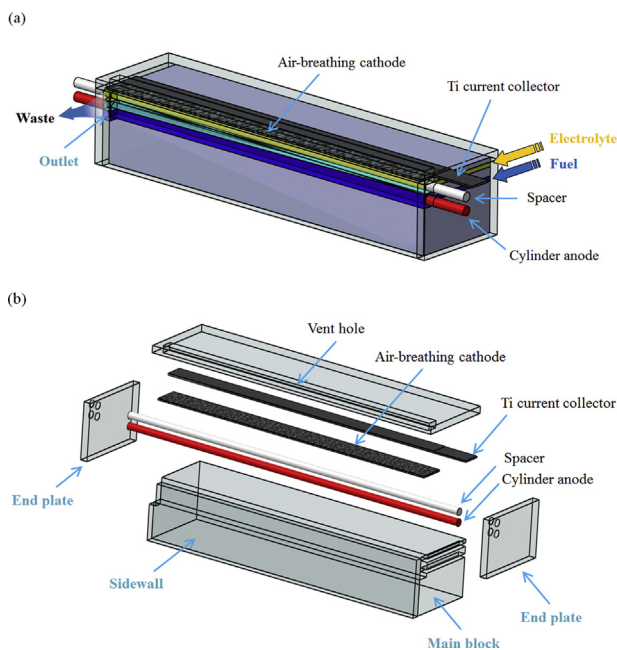 evolution images of CO_2 bubbles. The upper side of