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Nanofluidic fuel cell

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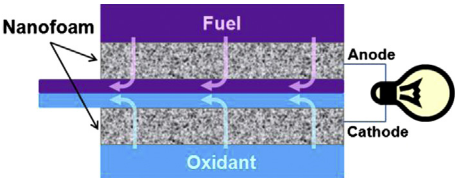
HIGHLIGHTS

- For the first time, the concept of nanofluidics is utilized in a fuel cell.
- The proposed nanofluidic fuel cell is membraneless and catalyst-free.
- The nanoporous electrodes show superior electrochemical kinetics.
- The fuel cell performance is enhanced in the high cell voltage regime.

GRAPHICAL ABSTRACT



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ABSTRACT

Fuel cells are gaining momentum as a critical component in the renewable energy mix for stationary, transportation, and portable power applications. State-of-the-art fuel cell technology benefits greatly from nanotechnology applied to nanostructured membranes, catalysts, and electrodes. However, the potential of utilizing nanofluidics for fuel cells has not yet been explored, despite the significant opportunity of harnessing rapid nanoscale reactant transport in close proximity to the reactive sites. In the present article, a nanofluidic fuel cell that utilizes fluid flow through nanoporous media is conceptualized and demonstrated for the first time. This transformative concept captures the advantages of recently developed membraneless and catalyst-free fuel cell architectures paired with the enhanced interfacial contact area enabled by nanofluidics. When compared to previously reported microfluidic fuel cells, the prototype nanofluidic fuel cell demonstrates increased surface area, reduced activation overpotential, superior kinetic characteristics, and moderately enhanced fuel cell performance in the high cell voltage regime with up to 14% higher power density. However, the expected mass transport benefits in the high current density regime were constrained by high ohmic cell resistance, which could likely be resolved through future optimization studies.

1. Introduction

Laminar flow based fuel cells (LFFCs) [1], also known as membraneless or microfluidic fuel cells [2], is a recently developed fuel cell technology that operates using microscale co-laminar parallel streaming of fuel and oxidant electrolytes in place of an ion-conducting membrane in the space between the two electrodes (anode and cathode). In contrast to conventional hydrogen and methanol fuel cells comprising a membrane electrode assembly design in a layered sandwich configuration, membraneless fuel cells can be fabricated in a unibody design that benefits from compatibility with standard micromachining and MEMS fabrication methods [3]. Moreover, the cost and durability issues associated with ion-conducting membranes are eliminated [4]. A variety of microfluidic fuel cell devices operating on liquid and gaseous fuels and oxidants have been demonstrated to date [4,5]with typical microchannel cross-sectional dimensions between 10 μm and 1 mm. In terms of dimensions, the upper bound is not only formally restricted by the definition of 'microfluidics' but also fundamentally by the hydrodynamics that ultimately transitions into turbulent flow at high Reynolds numbers and disrupts the co-laminar streaming. The lower bound, in contrast, has no fundamental limit

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other than the constraints imposed by fabrication. It is well-established, however, that the surface-area-to-volume ratio of microchannels scale as the inverse of the length scale [2], and thereby increases proportionally with decreasing size. Fuel cells, having surface-based electrochemical reactions, would consequently stand to benefit from further miniaturization.

Nanomaterials as electrodes and electrolytes in energy conversion and storage devices such as lithium ion batteries, fuel cells, and supercapacitors were investigated by various researchers [6]. For fuel cell applications, a promising concept based on an array of nanochannels as proton conductive membrane was investigated by Liu et al. [7]. Due to the electric double layer overlap enabled by the nanochannels, the proton conductivity was enhanced by orders of magnitude with improved fuel cell performance. Moghaddam et al. [8] demonstrated a silicon-based inorganic–organic membrane with 5–7 nm pores for a similar purpose. A scalable nanostructured membrane for solid oxide fuel cells was reported by Tsuchiya et al. [9]: nanoscale yttria-stabilized zirconia membranes were combined with a nanostructured dense oxide cathode in a thin-film architecture to increase the performance of these cells. On the contrary, no published studies have explored the opportunity of utilizing nanomaterials for membraneless fuel cells, nor has the concept of nanofluidics been previously applied to fuel cells. The practical use of nanoscale channels or pores in membraneless fuel cells is however dependent on the timescale for interdiffusive mixing between the two co-laminar streams. The mixing timescale is proportional to the channel width and governed by the Péclet number for mass diffusion, given by $Pe = LU/D$, where L is the characteristic length for diffusion, U the mean velocity, and D the mass diffusion coefficient. The mixing timescale in nanochannels is therefore three orders of magnitude faster than in previously employed microchannels [10], and must be taken into account for practical design of nanofluidic fuel cells.

The objective of the present work is to develop and demonstrate a membraneless nanofluidic fuel cell architecture that captures the combined advantages of reactant flow on the nanoscale and high surface area electrodes. The proposed fuel cell features flow through nanoscale conduits in an electrochemically active and conductive nanoporous media. The mixing constraint described above is mitigated in this case by utilizing a central microchannel with sufficiently large dimensions intended to delay the mixing of fuel and oxidant, as previously demonstrated by our group [11]. The proposed fuel cell is thereby capable of exploiting high nanoscale transport rates *inside* the electrodes without compromising the stability of the co-laminar flow in the space *between* the electrodes.

2. Methodology

2.1. Fuel cell design

In the proposed nanofluidic fuel cell, a conductive nanoporous electrode material is incorporated with a membraneless, miniaturized fuel cell architecture, as shown in Fig. 1. The overall device layout features a flow through porous electrode design [12]. Fuel and oxidant are supplied by a syringe pump via separate inlet ports and forced to flow through the internal nanoscale pores of the nanoporous electrodes on the anode and cathode sides, respectively. In the microfluidic channel at the center of the device, the two opposite streams exiting the nanoporous media are forced to make a 90° turn and flow in a co-laminar format on the microscale toward an orthogonally situated outlet. The ‘nanofluidic fuel cell’ terminology used in this work refers to the *nanofluidic* flow inside the nanoporous electrodes, where the electrochemical reactions take place, while the flow in the center channel is *microfluidic* due to the microscale dimensions of the channel. The present device is generally categorized as a microfluidic electrochemical cell but described here as a *fuel cell* [1–5], provided its main function of electrochemical power generation from continuously supplied fuel and oxidant. Notably, the device also meets the definition of a primary redox flow battery for discharge operation. However, the present single-outlet design is not suitable for regenerative operation; certain device-level modifications are required to facilitate operation as a rechargeable, secondary redox flow battery, as described elsewhere [13].

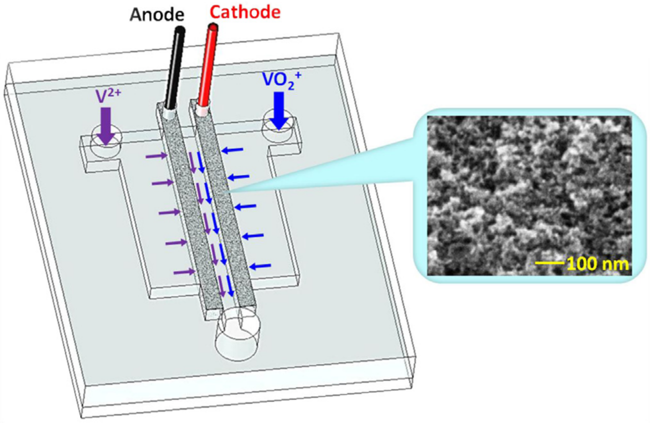

Fig. 1. Schematic of the nanofluidic fuel cell employing carbon nanofoam electrodes in a membraneless, catalyst-free configuration. The liquid fuel (V^{2+}) and oxidant (VO_2^+) flow orthogonally through the nanoporous electrodes and exit into the central channel, where a parallel, co-laminar flow is established toward the downstream outlet.

Vanadium redox electrolyte, which has become the industry standard for grid-scale vanadium redox batteries [14], is employed as fuel (V^{2+}, denoted as V(II)) and oxidant (VO_2^+, denoted as V(V)) in the present study to benchmark the performance of the nanofluidic fuel cell in relation to existing microfluidic fuel cell devices with carbon paper electrodes [12,15]. The cell operation is based on the following anodic and cathodic reactions at room temperature [16]:

$$V^{3+} + e^- \rightleftarrows V^{2+} \qquad E^\circ = -0.496 \text{ V vs. SCE} \tag{1}$$

$$VO_2^+ + 2H^+ + e^- \rightleftarrows VO^{2+} + H_2O \qquad E^\circ = 0.750 \text{ V vs. SCE} \tag{2}$$

The theoretical standard cell potential is 1.246 V but this can, however, be increased up to 1.5 V depending on the concentration ratio of the vanadium species. Provided that the vanadium redox reactions are rapid on carbon, the present fuel cell device is not only membraneless but also catalyst-free. As previously reported [12], 2 M vanadium redox electrolyte solutions in 4 M sulfuric acid are prepared from stock electrolyte. The active species concentrations (V(V) and V(II)) used in this work are 92% (equivalent to 1.84 M) or higher and all measurements are recorded at room temperature.

2.2. Electrode material

A conductive nanoporous material based on carbon aerogels is investigated and employed as the main electrode material. Developed at Lawrence Livermore National Laboratory [17], carbon aerogels are synthesized by the sol–gel polycondensation of resorcinol and formaldehyde, followed by supercritical drying and pyrolysis in an inert atmosphere. This innovative fabrication process yields unique carbon foams that are characterized by high porosity, high surface area, and ultrafine pore sizes (less than 50 nm) [18,19]. The key advantage of carbon nanofoam as potential electrodes of electrochemical devices over conventional carbon papers is its high