



Reactant recirculation in electrochemical co-laminar flow cells



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ABSTRACT

Co-laminar electrochemical cells utilize hydrodynamic engineering rather than a physical separator to prevent mixing of reactants. Commonly known as microfluidic fuel cells and batteries, these cells are based on stratified laminar flow of reactants in a microfluidic channel. The objective of the present work is to evaluate the feasibility and effectiveness of reactant recirculation in co-laminar flow cells with flow-through porous electrodes. Two representative device architectures are fabricated with separate outlets for reactant recirculation in Y-junction and dual-pass configurations. It is found that crossover at the electrodes reduces the open circuit potential of both cells and serves as a useful diagnostic method for assessing the degree of crossover at the outlets. Outlet concentration is monitored at a range of flow rates and indicates that asymmetric splitting of the co-laminar interface can lead to a constant 2% loss of state of charge, while the loss due to diffusion ranges from 0–40%. The dual-pass cell is shown to have greater diffusive loss due to deceleration at the splitting junction but also demonstrates better performance due to its higher convective velocity through the porous electrodes. These effects are observed during a series of discharge operations with recirculating reactants, in which the dual-pass cell results in greater reactant utilization despite its higher crossover rates. Overall, the present results demonstrate reactant recirculation as a useful strategy to combine high reactant utilization and high power density in membraneless co-laminar flow cells.

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1. Introduction

Among the possibilities for electrochemical energy conversion and storage, fuel cells and flow batteries are advantageous particularly for high power applications due to their ability to admit more reactants upon demand [1]. Traditionally these cells have required some form of physical barrier such as porous separators or ionically conductive membranes to separate the reactants and prevent a mixed potential [2]. Co-laminar flow cells on the other hand, are those which utilize hydrodynamic engineering and the properties of laminar flow to prevent the mixing of individual streams of liquid.

Fluid dynamics is characterized as laminar when the ratio of inertial to viscous forces, otherwise known as the Reynolds number, is sufficiently small [3]. In this flow regime, the absence of turbulence or perpendicular convection allows layered streams to flow side by side with cross-stream mixing occurring strictly through diffusion. This phenomenon has been used for applications ranging from patterning [4], T-sensors [5], subcellular drug delivery [6], and other lab-on-chip applications [7]; but was also proposed as a way

of keeping reactants separate in fuel cells and thereby eliminating the ion-conducting polymer membrane [8,9]. In a pioneering work, Ferrigno et al. introduced two parallel streams of vanadium redox reactants into a micro-channel containing wall deposited anode and cathode electrodes. Although this membraneless cell demonstrated a reasonable power output of $38 \text{ mW}\cdot\text{cm}^{-2}$, the boundary layer depletion at the planar electrodes required very high flow rates which translated into low fuel utilization of only around 0.1%. Since then, many studies have explored various reactant combinations or cell architectures to improve the performance of these microfluidic co-laminar flow fuel cells. Among these, the introduction of flow-through porous electrodes in particular, by Kjeang et al. in 2008, resulted in considerably greater power output and fuel utilization. It was shown that fuel utilization up to 100% was achievable albeit at much lower flow rates [10]. Other notable highlights in the field of co-laminar flow cells has been the development by Jayashree et al. of air-breathing cells for which an ion-conducting blank electrolyte maintains the co-laminar interface and prevents the anolyte from reaching the cathode [11]. Apart from the type of electrodes used, the most critical attribute for co-laminar flow cell design is the geometry of the cell. Even in the absence of convection perpendicular to the flow, reactant mixing and crossover still occurs due to diffusion of species. Cells must be designed so that the residence time for the reactant species at the co-laminar interface

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is shorter than their diffusion time towards the opposite electrode. A comprehensive review of these concepts and the early developments in microfluidic fuel cells was published in 2009 by Kjeang et al. [12]. Since then the field has expanded to include closely related rechargeable flow batteries [13,14], new electrode materials [15–17], and the reintroduction of porous separators among other developments [18,19].

For practical power output, most conventional fuel cells typically operate at high flow rates and recirculate the unused reactants until depletion. In addition, individual cells are often stacked in series or parallel to reach higher power outputs. Although stacking traditionally involves fabricating cells which can be placed back-to-back to minimize space requirements and ohmic losses [14,20,21], planar multiplexing of monolithic cells [22,23] may also prove useful for lab-on-chip applications. Without any type of membrane or porous separator, fuel cells based on co-laminar flow would be expected to be more prone to reactant crossover than their conventional counterparts, thereby limiting the potential for efficient fuel recirculation. The vast majority of studies in this field have explored only single pass discharge operation and therefore little quantitative data is available in the literature for understanding the breadth of these limitations. The first study to attempt recirculation of depleted reactants was performed by Saloum et al. in 2011, in which a second co-laminar flow fuel cell was placed downstream from the first one [22]. Splitting of the reactant streams without crossover was achieved through the use of a third stream of blank electrolyte. Although this fuel cell pair was able to produce nearly twice the power output at high flow rates when both cells were connected in parallel, the change in concentration of the reactants was not measured and therefore it is unknown to what extent the reactants were diluted by the use of a blank electrolyte. A recent study published by our group proposed a symmetric dual-pass design with flow-through electrodes for reversible charging and discharging of vanadium reactants [13]. In discharge mode the cell performance was equivalent to other flow-through fuel cell designs with the same reactants [10,24], but the cell possessed the added functionality of cyclic operation as a secondary flow battery, and demonstrated for the first time that redox flow batteries can be designed and operated without a membrane. The cell achieved 20% full cycle energy efficiency and was named the microfluidic redox battery (MRB) due to its similarities with conventional vanadium redox flow batteries. Another more recent study by Braff et al. explored the idea of fuel regeneration with a co-laminar hydrogen-bromine flow battery with a gaseous anode. The cell demonstrated the highest power density of any co-laminar cell published to date in both charging and discharging operation with a purported cycle efficiency of up to 91% [14]. It is however not clear whether the cell was actually operated in a full cycle, or whether the voltage efficiencies were merely inferred from independent charge and discharge curves. More comprehensive experimentation would be required to assess whether cyclic operation is feasible for this device. As a liquid-gaseous system, any analysis of fuel recirculation and regeneration would be considerably different from a liquid-liquid system such as the all-vanadium battery.

In either case, reactant recirculation is likely to be essential for the practical application of co-laminar flow cell technology for electrochemical energy conversion and storage. Unless very high single pass fuel utilization becomes possible with simultaneously high power output, it will become necessary for co-laminar flow cells to minimize the waste of unused reactants through recirculation in order to maximize overall energy efficiency. The objective of the present work is therefore to assess the capability and functionality of co-laminar flow cell operation in recirculation mode, and provide guidelines for future developments of practical cell design and operational strategies.

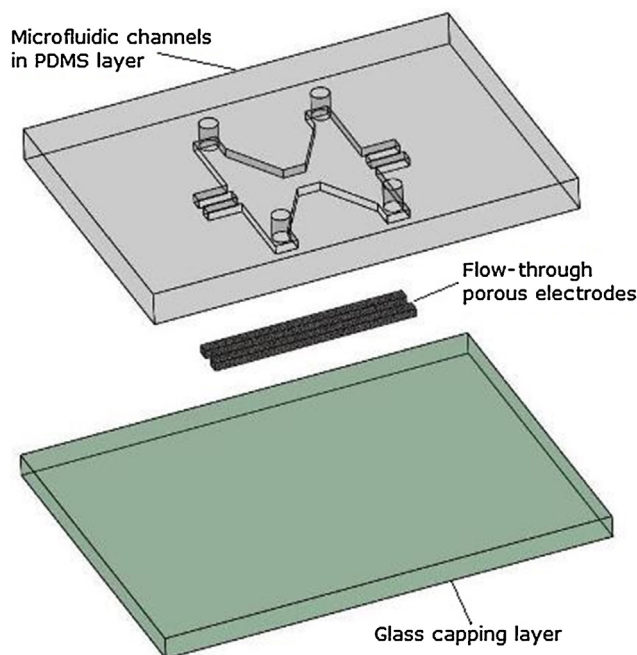


Fig. 1. Co-laminar flow cell assembly and materials.

2. Experimental

2.1. Device fabrication

The microfluidic channels for the co-laminar flow cells used in this study are fabricated by soft lithography of polydimethylsiloxane (PDMS) from a photoresist template. An illustrative example of the cell configuration is provided in Fig. 1 with more detail on the fabrication procedure to be found in earlier literature published by our group [10,25,26]. Unlike previous microfluidic fuel cell designs however, the present cells are designed to have two inlets and two separate outlets for collecting unused reactants. The electrodes are cut from carbon nanofoam (Type I, MarkeTech) and placed into PDMS channels of the same width. This layer is then permanently bonded to a glass substrate via plasma treatment of both surfaces (BD-20AC, Electro-Technic Products). The thickness of the electrodes exceeds the channel height by about 20 μm in order to facilitate slight electrode compression during cell bonding, thereby preventing unwanted bypass of reactants. Holes are punched and tubing inserted to provide access to the inlets and outlets. Electrical contact between the wires and electrodes is achieved through the use of silver conductive epoxy (MG Chemicals). In both co-laminar flow cell architectures presented in this study the active electrode dimensions are 10 mm long, 1 mm wide, and 0.18 mm thick. The channel width between electrodes is 1 mm, whereas the height is slightly lower than the electrode height at 0.16 mm in order to lightly compress the electrodes and prevent bypass of reactants. As such the active volume of each electrode is considered to be 1.6 mm^3 with the total volume of the essential electrochemical chamber, including both electrodes and the center channel, to be 4.8 mm^3 . With three-dimensional flow-through electrodes, there is some debate as to whether the projected electrode area or the area cross-sectional to the reactant flow should be used for normalization. For these cells, the projected active area of one electrode is therefore 10 mm^2 , whereas the cross-sectional area of the electrode is 1.8 mm^2 . Due to the ambiguity, the measured current values are reported without normalization.

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