Membraneless Vanadium Redox Fuel Cell Using Laminar Flow

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This communication describes a small redox fuel cell fabricated using a design that omits the membrane normally used to separate anodic and cathodic compartments. This design exploits the laminar flow[1] that occurs in liquids flowing at low Reynolds number (Re) to eliminate convective mixing of fuels. Two separate streams − one oxidizing and one reducing − flow parallel to one another through the channel, and no membrane is needed to separate these streams (only diffusive exchange occurs across the interface between them). We demonstrate this concept by operating a millimeter-scale redox fuel cell that uses the redox couples V(V)/V(IV) (cathodic compartment) and V(III)/V(II) (anodic compartment)[2−5] and that presents no *added* mechanical nor electrical resistance between the two aqueous solutions.

Previous work on fuel cells that do not require a membrane has used selective catalysts or enzymes to restrict reactions of oxidant and reductant present in a mixture to the appropriate electrode.[6−11] An example from Dyer[6] used a mixture of O_2 and H_2; another, by Willner et al.,[9,10] was a biofuel cell with enzymes as catalysts.

Figure 1 shows a schematic representation of a single cell. We used soft lithography to fabricate a channel with two inlets and one outlet either in poly(dimethylsiloxane) (PDMS) using soft lithography (for thick channels: $h \approx 200\ \mu m$) or in SU-8 photoresist using conventional lithography (for thin channels: $h \approx 50\ \mu m$);[12,13] details of fabrication are given in the Supporting Information. We used graphite rather than metals as the electrodes to reduce electrolysis of water during the operation of the cell.[14]

The vanadium system has two redox couples with a large difference in formal potentials, ~ 1.0 V/NHE for V(V)/V(IV) (as VO_2^+/VO^{2+}) and -0.25 V/NHE for V(III)/V(II).[15] We prepared these two redox species by electrolyzing an ~ 1 M solution of $VOSO_4$ in 25% H_2SO_4 in two half-cells separated by a Nafion membrane. (The concentrations used in the fluidic fuel cell were ~ 1 M for both V(V) and V(II), and 10^{-3} M for V(III) and V(IV)). When the V(V) and V(II) solutions were flowing at 25 $\mu L\ s^{-1}$ in the channel, the cell generated a maximum open-circuit voltage (i.e., the potential when no net current was flowing) of 1.52 V in a 200-μm thick membraneless structure; it generated 1.59 V in a 50-μm thick system at a flow rate of 0.07 $\mu L\ s^{-1}$.[16] These voltages are approximately 90% of the experimental value (1.67 V) obtained using two platinum wires separated by a membrane in a two-electrode configuration. The permeation of O_2 through the PDMS slab is sufficiently slow, as compared to the residence time of the solution in the channel, that it does not affect the open-circuit potential.

As the two half-cells of the fuel cell are not physically separated by a membrane, they are defined only by the laminar flow of the two streams of fuel. For two fluids with the same viscosity (the
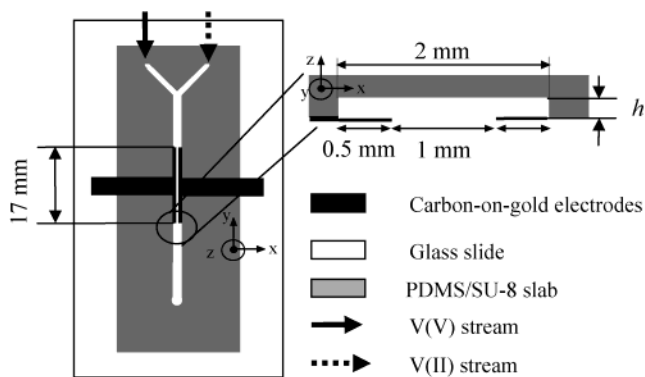
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Figure 1. Schematic design of a single cell.[12]

case for our two solutions) and flow rate, the interface between the two miscible aqueous liquids is located midway between the two electrodes (Figure 1). At this interface, some redox species are inevitably lost by diffusive mixing and reaction. A good approximation of the ratio between the wasted species at the boundary and the used species at the electrodes is given by the ratio between the height of the channel and the width of the electrodes. When the channel is 50 μm thick and the electrodes are 500 μm wide, this ratio is 1/10; that is, one molecule is wasted for 10 molecules used. The diffusively mixed region has an hourglass shape that is broader near the top and bottom walls than in the center of the channel.[17] We predict[17−19] that near the top and bottom walls, the width of the intermixed region between the two streams, Δx, will grow as the cube root of the residence time in the channel. At the highest flow speeds used (25 $\mu L\ s^{-1}$ or $U = 12.5$ cm s^{-1}), $\Delta x \approx 32\ \mu m$ at a distance $y = 2$ cm; at the lowest flow speeds used (0.07 $\mu L\ s^{-1}$ or $U = 1.4$ mm s^{-1}), $\Delta x \approx 89\ \mu m$. The diffusively mixed region does not overlap with the electrodes, which are separated by 1 mm.

Figure 2 shows the curves of potential versus current density obtained with two channels: one had a thickness of 50 μm and a flow rate of 0.07 $\mu L\ s^{-1}$, and the other had a thickness of 200 μm and a flow rate of 25 $\mu L\ s^{-1}$. Impedance measurements gave an internal resistance of 3 Ω for a 25% H_2SO_4 electrolyte for the 200-μm thick channel; this measurement is close to the theoretical value (2.6 Ω) calculated using the expression derived for a coplanar and interdigitated electrode geometry.[20] The fuel cell having a thicker channel delivered 35 mA cm^{-2} at 1.1 V (i.e., 38 mW cm^{-2} at a flow rate of 25 $\mu L\ s^{-1}$), or ~ 3 mA for the cell with the dimensions shown in Figure 1. These values compare well with those obtained using a macroscopic fuel cell (geometrical dimension of the electrodes ≈ 9 cm^2) reported by Kummer et al.[2] (35 mA cm^{-2} at 800 mV). The thinner system ($h \approx 50\ \mu m$) delivered 3 mA cm^{-2} at the same potential; we attribute this lower current density to the
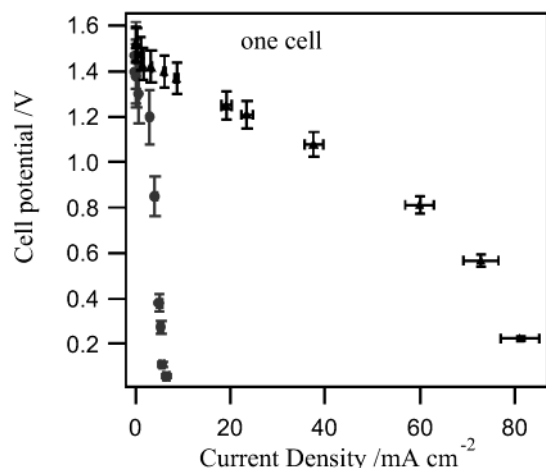
Figure 2. Polarization curve of two vanadium membraneless fuel cells. (▲) $h = 200$ μm (the flow rate was 25 μL s^{-1}, Re = 25), (●) $h = 50$ μm (the flow rate was 0.07 μL s^{-1}, Re = 0.07). h is defined as the height of the channel; its width is 2 mm. The potential is measured between two Au/graphite electrodes positioned with their proximate edges separated by a distance of 1 mm. ∼1 M solutions of V(V) and V(II) in 25% H$_2$SO$_4$ electrolyte are used in the channel.

lower flow rate used. With three cells ($h \approx 200$ μm) in the series, the system reached an open-circuit voltage of 4.35 V (i.e., 1.46 V per cell). Three cells in series delivered 80 mA cm^{-2} at 2.4 V (i.e., 192 mW cm^{-2}); using this level of power, we were able to light a LED.

The polarization curves in Figure 2 demonstrate that a redox fuel cell can be operated in the absence of a separation membrane by taking advantage of laminar flow. A drawback of the present version of the system is its poor utilization of fuel. The fuel utilization (the ratio of the amount of fuel consumed at the electrodes and converted to current to the total amount of fuel delivered to the cell) was ∼0.1% when $h = 200$ μm (as compared to 0.5% in the cell described by Kummer et al.[2]); it rose to ∼10% when $h = 50$ μm.[21] This efficiency is limited, we believe, by mass transport. The kinetics of electron transfer in this system is sufficiently rapid that the concentration of fuel species near the surfaces of the electrodes is depleted. We expect that by optimizing the contact of the fuel with the electrodes, and by using new methods for mixing,[22,23] this efficiency will improve.

This low efficiency notwithstanding, the device demonstrates a design that is interesting for a number of reasons: (i) It demonstrates a design for a miniaturized cell, the fabrication of which is simpler than that required if a membrane were included. (ii) It eliminates ohmic losses due to the membrane, and problems due to its fouling or damage. (iii) It uses the same species (vanadium) as oxidant and reductant, both of which can be regenerated from a mixture of the products without separation.[3-5] (iv) It allows the active electrochemical region to have a small cross section (∼0.1 mm^2). (v) It is compatible with microfluidic systems used for other purposes. (vi) It is a general format for electrochemistry in microsystems. (vii) It is comparable in its performance to a macrosystem in terms of current density and electrochemical potential, although lower in the efficiency with which it utilizes fuel.[2] (viii) It can be configured in either series or parallel configurations for high-voltage or high-current power supplies.

The cell can be miniaturized further, but with associated inefficiencies. For example, reducing the size of the channel will increase the viscous losses in pressure pumping. Making the width of the channel smaller will increase losses in fuel by diffusive mixing in the interfacial region, and decrease the open-circuit potential.

This work demonstrates some of the advantages and disadvantages of a fuel-cell design that substitutes laminar flow for a membrane in separating anodic and cathodic half-cells. We believe that this concept can be generalized to other electrochemical systems (e.g., electrolysis reactors, electroanalytical systems).

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The solutions in the channels were either pumped by syringe pump or injected by gravity. In the experiments we describe, the cell was operated in a mode in which the solutions of redox components were discarded after use; we have not demonstrated coupled regeneration of the fuels [Bergens, S. H.; Gorman, C. B.; Palmore, G. T. R.; Whitesides, G. M. *Science* **1994**, *265*, 1418].

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(19) $\Delta x \approx (Dhy/U)^{1/3} \approx (Dh\tau_r)^{1/3}$. Here, D is the diffusivity of the electroactive species ($D \approx 10^{-5}$ cm^2/s), h is the height of the channel, y is the distance traveled down the channel, U is the average speed of the flow, and τ_r is the residence time.

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