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## On the mass transfer performance enhancement of membraneless redox flow cells with mixing promoters

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## ABSTRACT

Membraneless flow cells for electrochemical energy conversion exploit the laminarity of microscale flows to avoid undesirable mixing of reactants. To increase the performance of microfluidic redox flow cells we employ herringbone-inspired flow promoters, thereby increasing convection of each individual species to the electrodes, while minimizing reactant mixing. Polarization curves from electrochemical discharge measurements with a dilute anthraquinone/iron redox system reveal that the presence of flow promoters substantially boosts device performance. Mass transfer enhancement for devices with flow promoters is demonstrated through both higher limiting currents and increased power density; the former is more than double compared to a plain reference microchannel for Reynolds numbers of  $Re > 155$ . The chaotic mixing effect induced by the flow promoters also becomes apparent in the scaling regimes, the limiting currents are proportional to  $Re^{0.58}$  instead of  $Re^{1/3}$  (as for purely laminar flow). Further, we quantify the area specific resistance (ASR) of the electrolyte in our membraneless devices finding a reduction of more than one order of magnitude compared to the ASR of conventional membranes employed in redox flow cells. Overcoming mass transfer limitations, this work highlights the necessity of passive mixers in significantly raising the performance of microfluidic flow cells.

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### 1. Introduction

Commercially available macroscale redox flow batteries [1] use pairs of redox couples (e.g.  $Cr^{3+}/Cr^{2+}$  and  $Fe^{3+}/Fe^{2+}$  [2,3],  $V^{3+}/V^{2+}$  and  $VO_2^+/VO^{2+}$  [4]) in liquid electrolytes with the favorable characteristic that the storage capacity and the power scale independently [5]. The storage capacity depends on the quantity and the composition of the electrolyte stored in tanks external to the electrochemical cell, whereas the available electrode surface and cell design dictates the power. Current research tackles the challenge of increasing energy and power density from many sides with the ambition of reducing the total cost associated with energy storage in redox flow batteries [6–8]. In addition, in combination with performance enhancements, downscaling opens pathways to new applications for redox flow cells, such as power generation for stationary micro devices [9,10].

Microfluidic approaches striving to increase performance are especially appealing because in microfluidic channels the ratio of

wall surface area available for electrochemical reactions to fluid volume involved is high. The length scales encountered in microfluidics, however, typically lead to laminar flow. This laminarity can be exploited to operate a redox flow cell in a membraneless configuration as the two reactants stably flow side-by-side and mix only by diffusion [9]. The exclusion of a membrane is a typical design characteristic of microfluidic redox flow cells in comparison to their macroscale counterparts. The great challenge of such microscale devices is that mass transfer to the electrodes is hindered in a purely laminar flow regime due to the build-up of a depletion boundary layer above the electrodes [11,12]. For this reason research in microfluidic membraneless redox flow cells has evolved from early proof-of-concept demonstrations to studies in which mass transfer is specifically augmented in order to increase power density [13,14].

Ferrigno et al. [15] demonstrated a co-laminar redox flow cell using the vanadium redox system on carbon coated gold electrodes. In this laminar cell the two electrolytes mixed only by diffusion due to a purely laminar flow regime at low Reynolds numbers. The authors reported a power density of  $38 \text{ mW}\cdot\text{cm}^{-2}$  in a  $200 \mu\text{m}$  high microchannel.

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Further work by Choban et al. [16,17] with methanol as fuel and dissolved oxygen in sulfuric acid as the oxidant reported a power density of  $2.8 \text{ mW}\cdot\text{cm}^{-2}$ , and their work already clearly showed that co-laminar microfluidic cells suffer from mass transfer limitations. They concluded this by observing that the performance of their cell was a function of the flow rate.

Both the devices presented by Ferrigno et al. and Choban et al. employed a flow-over electrode configuration, for which a depletion boundary builds up above the planar electrode and thus limits mass transport. Later, Kjeang et al. [18] used porous carbon electrodes in a flow-over configuration and reached  $70 \text{ mW}\cdot\text{cm}^{-2}$  with an all-vanadium redox chemistry due to the increased electrode surface. A different electrode configuration, the so-called flow-through configuration, was pioneered by Kjeang et al. [19] for use in microfluidic redox flow cells. In such a flow-through configuration the electrolytes are forced to pass through the porous electrode, thereby enhancing mass transfer. Again with the vanadium system Kjeang et al. reported power densities up to  $131 \text{ mW}\cdot\text{cm}^{-2}$  [19]. Later, Kjeang and co-workers studied different kinds of porous carbon electrodes in order to increase the surface area and enhance reaction kinetics [20]. Continuous work of Kjeang's group has included studies on mass transport related issues [21] and recently led to a microfluidic co-laminar flow cell with a dual-pass architecture and a maximum reported power density of  $750 \text{ mW}\cdot\text{cm}^{-2}$  with respect to the projected area normal to the flow through the electrodes [22]. In general, a major challenge in using porous electrodes in a flow-through configuration is the increased pressure drop and the ohmic resistance of these electrodes [23].

Among the best-performing microfluidic RFBs with a flow-over architecture is a cell presented by Da Mota et al. [24]. They used sodium borohydride as fuel and cerium ammonium nitrate as oxidant and reported power densities as high as  $270 \text{ mW}\cdot\text{cm}^{-2}$  in a flow-over configuration on thin film Pt electrodes. It is noteworthy that such high power densities were only reached by addressing mass transfer limitations through integration of a staggered herringbone mixer to induce chaotic flow [25]. Without such flow promoters the power density was only about half as high at the same flow rate. In this way, Da Mota et al. proved that addressing depletion boundary layers by integration of flow promoters is crucial for enhanced performance of microfluidic RFBs.

Despite some progress, the effect of flow behavior on device performance needs further systematic research. Ha and Ahn [26] presented an experimental study on a microfluidic cell with grooved electrodes confirming the positive effect of flow promoters on maximum power density. Later, the same group studied differently shaped grooved electrode surfaces in order to find an optimum design [27]. Also, Alessandro and Fodor [28] numerically studied membraneless fuel cells and optimized angled grooves for maximum fuel utilization.

Surprisingly, although above research indicates that flow mixing effectively mitigates mass transfer limitations, only little data is available on the scaling behavior of current density and power density in such microfluidic redox flow cells with integrated flow promoters. Da Mota et al. [24] state that the limiting current density is roughly proportional to the flow rate by  $\dot{V}^{2/3}$ . In earlier work [29] we investigated in detail the scaling behavior by monitoring the electrolysis current of a model redox system based on the ferro-/ferricyanide redox couple at constant voltage and found that the diffusion-limited current scales with  $\dot{V}^{0.58}$  when flow promoters are present. This scaling is much steeper than in a purely laminar flow, in which the limiting current follows the theoretically predicted  $\dot{V}^{1/3}$  regime. In addition, we showed that the benefits of flow promoters in terms of improved heat transfer outperform the penalty of higher pressure losses [30]. Due to the analogy

between heat and mass transfer we expect this finding to hold true for the enhancement of performance of microfluidic redox flow cells in the presence of flow promoters.

Here we investigate the effect of flow mixing in the actual discharge operation of a membraneless flow cell. Due to the absence of a membrane, the challenge is to achieve advective enhancement within the respective individual species streams while avoiding negative mixing effects between the two streams. We experimentally quantify the performance benefits of such a redox flow cell microsystem with integrated flow promoters. The employed dilute redox system consists of dissolved anthraquinone (AQ2SH) on the negative side and an inorganic iron salt on the positive side. We first show the experimentally obtained polarization curves and the derived plots of power density. A comparison of the limiting current and the maximum power density in devices with and without flow promoters already proves the substantial performance increase obtained through the utilization of passive mixers. Subsequently, we analyze the scaling behavior of both the limiting current and the maximum power density as a function of flow rate and further substantiate the beneficial effects of flow mixing. The limiting current scales consistently with our earlier work based on constant-voltage electrolysis [29], but the maximum power density scales less steeply with flow rate than the limiting current. These scaling regimes are confirmed by simulations. In our efforts to increase device performance, this observation of the different scaling of limiting current and power density triggers the question what aspect of the device design restricts taking full benefit of the enhanced mass transfer. The last section we therefore dedicate to resistance measurements in order to shed light on the resistance within our cell and identify the mechanisms limiting device performance.

## 2. Experimental

### 2.1. Microfluidic device fabrication and dimensions

Microfluidic test devices (Fig. 1) consisting of dry etched microchannels with or without flow promoting structures were fabricated in silicon by a series of microelectromechanical systems (MEMS) and integrated circuit (IC) standard fabrication processes in a class 100/1000 cleanroom. For chemical inertness and electrical insulation, 300 nm  $\text{SiO}_2$  was deposited on both sides of the Si wafer. Thin-film electrodes (10 nm Cr and 150 nm Pt) were structured on a glass wafer. The channels were then enclosed with this glass cover by wafer-level anodic bonding after alignment of the structures on both wafers. The details of the fabrication process are described in earlier work [29,30].

In all devices the microfluidic channel was  $400 \mu\text{m}$  wide. In design S1 the microchannel was  $100 \mu\text{m}$  deep, while in designs S2–S4 the channels had a maximum depth of  $200 \mu\text{m}$ . In the devices with flow promoters (i.e. S2–S4), the flow promoters had a pitch of  $350 \mu\text{m}$ , a nominal wall thickness of the ridges of  $50 \mu\text{m}$  (i.e. the individual grooves extended over  $300 \mu\text{m}$  downstream) and a height of  $100 \mu\text{m}$  (i.e. the herringbone ridges extended halfway into the microchannel). Designs S3 and S4 had an additional solid/vacant  $100 \mu\text{m}$  wide centerline zone. The flow promoters protruded with an angle of  $45^\circ$  into the main microfluidic channel. In fact, design S4, with the vacant zone at the centerline, resembles a geometry also studied previously in Refs. [26,28], albeit at a different dimensional range. The electrodes were in total  $5.2 \text{ mm}$  long and  $175 \mu\text{m}$  wide, thus anode and cathode were separated by  $50 \mu\text{m}$ . Fluidic-to-chip interfaces were implemented using NanoPorts (Upchurch Scientific). Electrically, the chip was accessed with a conductive elastomeric connector in between the chip and a custom-made printed-circuit board (c.f. Fig. 1d).

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