**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 becomes also 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.

Keywords

Microfluidic flow cell; Redox flow battery; Herringbone flow promoters; Mass transfer; Performance enhancement; Membraneless

1. Introduction

Commercially available macroscale redox flow batteries [1] use pairs of redox couples (e.g. $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ [2,3], $\text{V}^{3+}/\text{V}^{2+}$ and $\text{VO}_2^+/\text{VO}^{2+}$ [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 enhancement, 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 microfluidic membraneless redox flow cells research 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 a Reynolds number $Re = 25$. The authors reported a power density of $38 \text{ mW} \cdot \text{cm}^{-2}$ in a $200 \text{ } \mu\text{m}$ high microchannel.

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 borohydrate 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 $Q^{2/3}$. 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 $Q^{0.58}$ 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 $Q^{1/3}$ 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 consistent 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 SiO₂ 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 μm wide. In design S1 the microchannel was 100 μm deep, while in designs S2-S4 the channels had a maximum depth of 200 μm . In the devices with flow promoters (i.e. S2 – S4), the flow promoters had a pitch of 350 μm , a nominal wall thickness of the ridges of 50 μm (i.e. the individual grooves extended over 300 μm downstream) and a height of 100 μm (i.e. the herringbone ridges extended halfway into the microchannel). Designs S3 and S4 had an additional solid / vacant 100 μm wide centerline zone. The flow promoters protruded with an angle of 45° into the main microfluidic channel. In fact, design S4, with the vacant zone at the centerline, resembles a geometry also studied previously in Ref. [26,28], albeit at a different dimensional range. The electrodes were in total 5.2 mm long and 175 μm wide, thus anode and cathode were separated by 50 μm . 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).

2.2 Chemicals

Experiments were performed with 18 MΩ·cm water and VLSI grade sulfuric acid (H₂SO₄). Active redox couples were chosen so as to enable full-cell operation with flow-over platinum electrodes while avoiding hydrogen evolution and platinum oxidation at the negative and positive electrode, respectively. Mixed test solutions for electrochemical discharge experiments were prepared by adding 10 mM iron(II) sulfate heptahydrate (Sigma-Aldrich, purity > 99%) and 5 mM of hydrogenated anthraquinone (AQ2SH, derived by ion-exchange from sodium anthraquinone-2-sulfonate monohydrate, Tokyo Chemical Industry, purity >98%) to a stock solution of 1 M sulfuric acid. The molarity of iron was twice the one of the AQ2SH to account for the two-electron half-cell reaction of the latter [31,32]:

thus resulting in a balanced overall reaction:

The solutions were charged in a custom-made flow-through electrolyzer with carbon felt electrodes (c.f. Fig. 1d). The electrolyte was charged at a potential of 1 V until the charging current stabilized at a minimum value. Visually, the electrolyte changed color during charging, from light yellow to dark green on the negative side. To avoid degradation by oxidation of the charged solutions in air, the electrolytes were constantly bubbled with humidified nitrogen and experiments in the microfluidic test devices were carried out immediately after charging.

Test solutions with a sulfuric acid concentration ranging from 0.1 to 3 M for electrochemical impedance spectroscopy (EIS) were prepared by dilution. For concentrations of 0.1 to 1 M, the conductivity of these solutions were measured with a conductivity meter (inoLab Multi

Level 3 equipped with a WTW TetraCon 325 cell) and correlated well with experimental data reported by Darling [33]. Above 2 M our conductivity meter was out of measurement range. For this reason we used data provided by Darling [33] in these cases.

2.3 Electrochemical testing

Electrochemical tests were performed on a potentiostat (BioLogic SP-300) and the volume flow of the electrolytes was controlled with a syringe pump (cetoni neMESYS) equipped with two glass syringes (SGE Analytical Science, 25 mL). **Figure 1d shows photographs of the experimental set-up.**

Polarization curves during discharge experiments were obtained by flowing the charged electrolyte through the microfluidic device and sweeping the cell voltage from the open-circuit voltage (OCV) to a lower limit of 0.01 V at a scan-rate of $25 \text{ mV}\cdot\text{s}^{-1}$. Overlapping forward and reverse scans indicated that we probed the discharge within the device close to steady-state conditions. Prior to flow experiments, the electrodes were carefully activated by electrochemical cycling using redundant electrodes on the device as counter and pseudo-reference electrodes [29].

Electrochemical impedance spectroscopy (EIS) was performed in stagnant solutions of 0.1 – 3 M sulfuric acid. A sinusoidal voltage with an amplitude of 20 mV was applied in the frequency range between 100 Hz and 49 kHz.

3. Results and discussion

3.1 Concentration profiles

Figure 2 illustrates the challenges associated with flow mixing in membraneless microfluidic redox flow cells. In this figure we plot the concentration of the anolyte, i.e. species AQ2SH, in the x-y-planes as derived from our numerical modeling (3-D model implemented in COMSOL Multiphysics®, c.f. [Appendix A](#)). In the 3-D view of Fig. 2a the position of this x-y-plane at the center of the main channel is apparent (i.e. 50 μm above the ridges of the flow promoters). Fig. 2b allows to directly compare the four different designs. In design S1, which is a plain channel, anolyte and catholyte remain well separated and only a small amount of the anolyte diffuses across the membraneless interface. However, in this colaminar configuration mass transfer to the electrodes (in the z-direction of Fig. 2) is also only occurring due to diffusion, which limits device performance. Therefore, our aim is to introduce passive mixers in order to increase mass transfer to the electrode surfaces. At the same time, it is essential that passive mixing retains this clear separation of reactants, otherwise the cell discharges in-situ by mixing without generating useful work. At the given bulk inlet velocity of 1 m/s designs S2 and S4 indeed partially fail in this respect as the anolyte is quickly diluted, i.e. cross-over is not only occurring diffusively but also convectively. Of the devices including flow promoters only design S3 with the additional solid zone along the centerline can cope with the restriction of convectively mixing the respective reactants in themselves without additional mixing between reactants. From this observation we conclude that design S3 is able to sustain the co-laminarity, however design S3 also mixes less vigorously compared to the other tested flow promoter devices due to the additional stratification zone in the center. We therefore devote the following sections to the question which device performs best with respect to the mass transfer limited current and the maximum power density.

3.2 Polarization curves and power density

Polarization curves (i.e. voltage E vs. current density i) constitute a graphic tool to characterize the performance of flow cells and reveal the origins of performance limitations[34]. Figure 3 shows the polarization curves scanned at 25 mV/s (dashed lines) and the power density p ($p = i \cdot E$, solid lines) for our four different devices as a function of the tested flow rates. Both the current density i and the power density p are based on the single electrode area (of $175 \mu\text{m} \cdot 5.2 \text{ mm} = 9.1 \cdot 10^{-3} \text{ cm}^2$). The axes are scaled to fit the data. For all devices we observe a negligible hysteresis between the forward and backward scan at 25 mV/s, which validates our assumption of measuring at quasi-stationary conditions.

Device S1 (c.f. Fig. 3a) is a plain channel and thus the flow regime is purely laminar. For low flow rates the open-circuit potential OCV (i.e. E at $0 \text{ mA} \cdot \text{cm}^{-2}$) reaches 0.6 V and we observe only a small activation overpotential in the polarization curves. Instead the E - i -curves quickly transition to a pronounced ohmic regime. At low flow rates the polarization curves show a mass transfer limitation, manifested by a sharp downward deflection at higher currents. In agreement with studies on macroscale redox flow batteries this drop due to concentration polarization is delayed to larger current densities for increasing flow rates [35]. Only at higher flow rates the devices are no longer diffusion limited, however the measured i - E -curves start to oscillate. These oscillations are at a first glance unexpected because device S1 features no flow promoters and thus the flow profile is expected to be purely laminar without fluctuations in the examined range of Reynolds numbers of $\text{Re} < 500$. Similar oscillations, however, in the polarizations curves were also observed in previous work on microfluidic redox flow cells [22]. We believe that the oscillations are caused by slight flow instabilities induced by manufacturing imperfections (such as misalignment errors and surface defects) and the unsynchronized pulsation of the two syringe pumps. To this end, arising free shear layers possibly have a profound effect on the sensitive development of depletion boundary

layers and the membraneless interface. This instability at higher flow rates is further accompanied by lower open-circuit voltages.

Device S2 on the other hand shows no such oscillations as the mass transfer limiting boundary layers are less sensitive due to chaotic flow patterns induced by the passive mixers [36]. Both the diffusion limited currents as well as the maximum power density are much higher than in device S1 for the same flow rate, thus demonstrating the beneficial effect of flow mixing. For all flow rates the OCV is slightly lower in device S2 than in S1 which hints toward advective cross-over of electrolyte at the centerline of the device. This cross-over, however, is low as the OCV remains high for flow rates up to $2.4 \text{ ml} \cdot \text{min}^{-1}$. It is remarkable that at a flow rate of $V = 3.6 \text{ ml} \cdot \text{min}^{-1}$ the OCV drops steeply. This can be understood as a flow condition in which the cross-over starts to dominate and we can expect strong mixing of anolyte and catholyte [29].

In comparison to device S2, devices S3 and S4 feature an additional solid or vacant zone, respectively, along the centerline. This zone is intended to mitigate advective cross-over, and only take advantage of passive mixing of the reactants on their respective side of the membraneless interface. In device S3 the additional solid zone clearly helps keeping the two charged electrolytes separated. The OCV is close to 0.6 V for all flow rates and qualitatively mass transfer limitations are less visible in the polarization curves (i.e. at high currents the voltage drops more gradually) for device S3 than for device S2. In fact, the limiting current as $E \rightarrow 0 \text{ V}$ is the highest for the design S3 compared to all other designs at all flow rates. This observation confirms the effectiveness of the additional separation zone in design S3. This points toward a high level of mixing within the individual reactants combined with low mixing of the two reactants. However, the maximum power densities of devices S2 and S3 are similar.

Device S4 performs worst of all devices with integrated flow promoting microstructures. First, we notice again oscillations of the polarization curves which imply a certain unsteadiness in

the flow profile. Interestingly, such rather strong oscillations are only observed for devices S1 and S4, but not for devices S2 and S3. This hints towards a higher fragility of the depletion boundary layers in devices S1 and S4 as no flow promoters are included (in device S1) or the flow promoters work inefficiently in thinning the depletion boundary layers and enhancing mass transport (as in device S4). This results for device S4 in slightly lower limiting currents than in devices S2 and S3, however the attained maximum power densities remain much lower than in devices S2 and S3.

3.3 Comparison at selected flow rates

Figure 4 compares the four different devices in terms of polarization curves and power density at two selected flow rates, thereby highlighting certain aspects discussed above. Both in Fig. 4a and b it is evident that flow mixing significantly increases the maximum power density compared to the base case of a plain channel as in design S1 (black lines), with the exception of device S4 at a flow rate of $0.48 \text{ ml} \cdot \text{min}^{-1}$, which is attributed to pronounced mixing of reactants already at low flow rates in this configuration. At a flow rate of $0.48 \text{ ml} \cdot \text{min}^{-1}$ design S2 achieves similar power densities (solid lines) as device S3 although the latter features a distinctly higher limiting current. This means on the one hand that the additional solid zone in device S3 is helpful to keep the two reactants separated as seen from the higher limiting current. On the other hand the similar maximum power densities in devices S2 and S3 already point toward limitations other than purely mass-transfer related, which we will investigate below in detail.

The same argumentation holds true for the faster flow rate of $2.40 \text{ ml} \cdot \text{min}^{-1}$ (c.f. Fig. 4b). Again the limiting current in device S3 is the highest, but still devices S2 and S3 achieve similar levels of power density. However, device S3 displays a higher stability of the membraneless interface, which translates to retaining a higher local concentration of

reactants and thus the mass transport limited region is shifted by about $2 \text{ mA} \cdot \text{cm}^{-2}$ further to the right (which corresponds to an increase greater 10 %) compared to device S2.

3.4 Performance enhancement

The integration of flow promoter structures enhances the performance of the microfluidic flow cell significantly, as illustrated in Fig. 5, where we normalized the limiting current (c.f. Fig. 5a) and the maximum power density (c.f. Fig. 5b) with respect to the plain reference channel of design S1. The devices including flow promoter structures (S2 - S4) show a significant enhancement of performance compared to the S1 normalization.

The limiting current (i.e. $i_{lim} = \max(i)$) in our best performing device S3 outperforms the plain channel device S1 by 2.05 times already at $Re = 155$. The improvements in mass transfer due to mixing continue and the limiting current rises steeply with increasing flow rate. Only above $Re = 250$ the slope seems to decrease due to a partial collapse of the co-laminar regime, however the enhancement of the limiting current in device S3 increases monotonically to a factor of 2.85 until the end of our measurement range at $Re = 470$. The improvement of the limiting current of the other two devices including flow promoters (S2 and S4) shows a similar overall trend, but the values remain below the ones of device S3 with the additional separation zone in the center. For S2, the limiting current even begins to decrease for the maximum Re value of 470, which is attributed to the onset of strong mixing of the two electrolyte streams in agreement with the pronounced drop in OCV for this device (c.f. Fig 4b).

Comparing the maximum power density (i.e. $p_{max} = \max(i \cdot E)$) of the devices with flow promoters against the plain reference channel (c.f. Fig. 5b), we observe that device S4 yields little improvement and peaks at an improvement of only 1.60 times due to the unfavorable fluid patterns that cause early mixing of the reactants (c.f. Fig. 2b) [29]. On the

other hand, devices S2 and S3 markedly exceed the plain reference channel in terms of power density, showing an almost equally high improvement in performance. In both devices power density increases more than two-fold above $Re = 250$. The maximum for device S2 is reached at an enhancement of 2.35 times at $Re = 310$ before cross-over effects start to dominate. In device S3 the improvement of power density continues to rise to a factor of 2.45 at $Re = 470$. Fig. 5b thus demonstrates the profound effect of flow promoters on the device performance. Above $Re = 250$ the power density is easily doubled simply by engineering the fluid flow within the microchannels, inducing chaotic flow patterns which thin the depletion boundary layers and thus increase the mass transfer rates.

3.5 Scaling regimes: **experimental**

In the previous sections we discussed the polarization curves and the device performance. We stated that both the limiting current and the power density generally increased with higher flow rates due to a thinning of the depletion boundary layer at the electrodes and thus device performance is greatly enhanced. In this section we analyze in detail the scaling dependence of both the limiting current (Fig. 6a) and the maximum power density (Fig. 6b) on the Reynolds number.

In the plain channel device S1 the limiting current i_{lim} approaches a scaling of $Re^{1/3}$ as expected from laminar flow theory [37–39], in analogy to the classical Lvque problem in heat transfer[40]. In all devices with flow promoters (S2 – S4) the scaling of the limiting current differs distinctly from that of the plain channel. As illustrated in Fig. 6a, the scaling approaches $Re^{0.58}$, which is much steeper than in the laminar case. This scaling with an exponent of 0.58 is due to a transition from a purely laminar flow to a flow condition which shows certain characteristics of the onset of turbulence (c.f. correlations for the Sherwood number compiled by Newman [37]: laminar $Sh \sim Re^{1/3}$, mass transfer entry region in turbulent flow $Sh \sim Re^{0.58}$). However, the turbulence created in the flow while passing over

the flow promoters is quickly dissipated again by the dominating effects of viscosity as typical for microfluidic flows. Therefore, the limiting current scales with $Re^{0.58}$ as in the entry region to turbulence [37]. These results on the limiting current confirm our earlier measurements on the effect of flow promoters on mass transfer [29].

The scaling of the maximum power density p_{max} yields striking differences compared to the scaling behavior of the limiting current. Again we start our analysis with the plain channel of device S1. For the lower flow rates studied in this work the maximum power density scales again with $Re^{1/3}$. However, above $Re = 100$ the maximum power density starts to saturate and thus does not follow the $Re^{1/3}$ scaling any longer. Comparing with the polarization curves and power density plots of Fig. 3a, we observe that with increasing flow velocity the cell is no longer limited by mass transfer as the species are replenished faster than being consumed at the electrode surface. Instead, the peaks of the power density plots are successively shifted into the linear region of the polarization curves with increasing flow rate. Therefore, the maximum power density in device S1 saturates above $Re = 100$, which is a highly undesirable behavior as it restricts the operational regime to rather low flow rates and prevents exploitation of the full potential of the device.

In devices S2 and S3, which feature flow promoters, the maximum power density is distinctly enhanced in comparison to the plain channel device S1. But the maximum power density in these devices S2 and S3 scales over the range of all tested flow rates similar to $Re^{1/3}$ and not as $Re^{0.58}$ as is the case for the mass transfer limited current in these devices. As argued above, for increasing flow rates the point of maximum power density is not solely controlled by mass transfer limitations but also by other loss mechanisms, which can explain the slower scaling. We notice that device S3 follows one scaling regime for the entire tested range of flow rates, while in device S2 the maximum power density suddenly drops. This sudden drop we attribute to a flow situation in which the co-laminarity within the cell breaks down, thus the two reactants are mixing and therefore the electrochemical energy is lost for power generation. Similarly we observe for device S4 that the maximum power density saturates at

higher flow rates, which we also attribute to loss mechanisms within the cell, such as crossover due to the induced flow fluctuations triggered by flow mixing.

Plotting the limiting current and the maximum power density as a function of the Reynolds number (c.f. Fig. 6) gives important insight into the mode of functioning of flow promoters. Although the limiting current scales like $Re^{0.58}$ for the flow promoting devices, which is much steeper than in a purely laminar scaling regime of $Re^{1/3}$, the maximum power density approaches a scaling of $Re^{1/3}$, irrespective of the presence of herringbone-inspired microstructures. In this regard, we speculate that the scaling of the maximum power density is restricted by loss mechanisms other than mass transfer related, namely kinetic or ohmic losses. This hypothesis will be further discussed in the next sections, in which we confirm the experimental results on the scaling regimes by simulations and report the cell resistances in order to investigate whether ohmic losses are responsible for limiting the power density of the devices.

3.6 Scaling regimes: simulation

In addition to our experimentally derived results on the scaling behavior, we performed simulations in COMSOL Multiphysics® resembling the experimental conditions (c.f. Appendix A for details). These simulations were intended to independently validate the scaling regimes we found during the experimental study. Figure 7 shows that the limiting current in device S1 scales over the simulated range of flow rates with $Re^{1/3}$. For the flow promoting devices S2 and S3 the scaling regime changes at higher Re . At the low end of the range of Reynolds numbers the limiting current follows laminar scaling and approaches only later a scaling of $Re^{0.58}$. These results thus confirm on an extended range of Re numbers our experimental findings on the scaling behavior presented in previous section. The numerical values of the limiting currents in the experiment and simulation match well, although in direct comparison the limiting currents in the simulation are lower than in the experiments. This slight mismatch

could be alleviated by parameter fitting, but as the trends are correctly reflected we refrained from iterative parameter fitting of the simulation and instead employed experimentally determined parameters adapted from earlier work (c.f. table A1). Noteworthy is that the simulations correctly resemble the different performance of the four different designs. Design S1 shows the lowest limiting current. Of the devices with integrated flow promoters design S3 with the separation zone along the centerline performs best in terms of limiting current, which is in line with our experiments and also our earlier work [29].

The numerical values of the maximum power density in Fig. 7 fall below the experimental measurements for the aforementioned reason. More importantly, it is worth considering the entire scaling regime: The simulation validates the trends observed in our experiments in the sense that the scaling regimes are similar, i.e. despite the presence of flow promoting elements in devices S2 – S4 the scaling behavior of the maximum power density does not differ from the behavior found in the purely laminar case of device S1. Hence, the results of the simulations strengthen the hypothesis that other loss mechanisms besides mass transfer limitations, namely kinetic or ohmic losses, are present in the cell and require investigation.

3.7 Resistance measurements

To measure the resistance within our test devices we performed electrochemical impedance spectroscopy (EIS) measurements with H_2SO_4 at different molarities from 0.1 to 3 M, thereby spanning a solution resistivity ρ_{sol} from 22.9 to 1.32 $\Omega \cdot \text{cm}$. Figure 8a presents the measured impedance Z at no flow in device S1 in a Nyquist plot, in which the real and imaginary part of the impedance are plotted:

$$Z = Z' + j \cdot Z'' \quad . \quad (\text{Eq. 4})$$

The inset shows the measurements at high frequencies up to 49 kHz. We obtain the series resistance by linearization within the shown high frequency range and extrapolation to the axis intercept $Z'' = 0$ [19]. In Fig. 8b this series resistance is plotted against the resistivity of the test solution. The correlation is clearly linear ($R^2 = 0.9999$) and we are now able to distinguish between the series resistance, which stems from the electrolyte solution itself and the resistance due to the electrodes and leads:

$$R_{series} = R_{sol} + R_{leads} \quad . \quad (\text{Eq. 5})$$

The axis intercept of the fit in Fig. 8b at zero solution resistivity is the cumulative resistance of the electrodes and leads, $R_{leads} = 25.8 \, \Omega$. The total series resistance at a concentration of 1 M, i.e. the concentration employed in the discharge experiments above, accounts for $R_{series \, 1M} = 33.5 \, \Omega$, i.e. the difference between these two values is the solution resistance $R_{sol \, 1M} = 7.7 \, \Omega$ (note that the low concentration of active species, 5 mM AQ2SH and 10 mM Fe in total, contributes negligibly to the overall electrolyte conductivity of 1 M H_2SO_4). This measured solution resistance is about half as high as the theoretical value derived for coplanar electrodes in an infinite volume of electrolyte [41]. The discrepancy is attributed to the imposed confinement due to the small height of the channel in comparison to the electrode width, see also [Appendix B](#).

These values for the resistance of the leads and the solution demonstrate two important aspects of membraneless cells: First, a reduction of the lead resistance is crucial, however it is also difficult to implement in microfluidic RFBs, which commonly rely on lithographically patterned thin metal films as electrodes [15] or current collectors [23]. Second, the solution resistance is indeed small due to the absence of a membrane. To exemplify this statement we convert the solution resistance to an area specific resistance (ASR):

$$ASR_{sol} = 7.7 \, \Omega \cdot 5.2 \, \text{mm} \cdot 100 \, \mu\text{m} = 0.04 \, \Omega \cdot \text{cm}^2, \quad (\text{Eq. 6})$$

where we have taken the electrode length and the channel height as representative length scales. This result is more than an order of magnitude lower than typical values of commonly employed ion-exchange membranes (c.f. Nafion 117: $1.06 \Omega \cdot \text{cm}^2$ [42,43], Nafion 212: $0.6 \Omega \cdot \text{cm}^2$ [44]). Even if we calculate the ASR with the total series resistance, resulting in $ASR_{series}=0.17 \Omega \cdot \text{cm}^2$, we obtain an ASR below the best performing membranes, showing the benefit of lower resistances when excluding a membrane in a co-laminar configuration.

A thought experiment in which we assume the device to be solely ohmically controlled, i.e. without the effects of activation and polarization overpotentials, confirms that the resistance is indeed not the sole factor limiting device performance. In this case we calculate a hypothetical limiting current density of $i_{lim}=OCV/(R_{series} \cdot A_{electrodes})=163 \text{ mA} \cdot \text{cm}^{-2}$, i.e. a voltage drop of $OCV=0.6 \text{ V}$ occurs across a resistance of $R_{series}=33.5 \Omega$ from above (c.f. Fig. 8b). Again, we normalized the limiting current to the single electrode area. The maximum hypothetical power density would equal to $p_{max}=\max V \cdot i=24.4 \text{ mW} \cdot \text{cm}^{-2}$ with both V and i varying linearly (from OCV to 0 V and from 0 to i_{lim} , respectively). These two hypothetical values of i_{lim} and p_{max} are more than an order of magnitude higher than the experimental values in the plain microchannel device S1 (c.f. Fig. 6). Flow mixing can ideally substantially raise both the limiting current and the maximum power density (c.f. devices S2 – S4 in Fig. 6), but our experimental results still lag far behind these idealized values assuming ohmic limitations only. Instead, we showed that the performance of the experimental device suffers significantly from other sources of overpotentials than those due to ohmic and polarization effects alone, namely kinetic effects. Such a kinetic limitation arises from the choice of using a dilute redox system due to the dependence of the exchange-current density on the bulk concentration of the electrochemically active species [45].

4. Conclusions

We studied the performance of membraneless microfluidic redox flow cells with integrated flow promoters. Use of such flow devices results in significant performance enhancement as manifested by higher limiting currents and power densities compared to without flow mixing. We show further that such micro-structured mixing elements need to be carefully designed to enhance mixing and also retain the co-laminarity at the same time. In this manner, we demonstrate a more than two-fold performance enhancement: In a device which combines herringbones with a stratification zone at the centerline (design S3) the limiting current is raised by 2.85 times at $Re = 470$ in comparison to a plain reference channel at the same Re number.

Furthermore, this study elucidates the scaling regimes of limiting current with Re number for microfluidic redox flow cells employing herringbone-type flow promoter structures. Compared to strictly laminar flow in a plain channel, the scaling of limiting current is enhanced from $i_{lim} \propto Re^{1/3}$ to $i_{lim} \propto Re^{0.58}$ employing such flow promoters (c.f. also our earlier work [29]).

However, the maximum power that can be drawn from microfluidic redox flow cells is in general determined by a combination of the kinetic, ohmic and concentration overpotentials, of which only the last is flow-rate dependent. Therefore, deviations from the $Re^{0.58}$ scaling behavior in microfluidic devices with flow enhancement of the type studied herein indicates that the maximum power is not limited by the concentration overpotential.

Measuring the electrolyte resistance within our devices, we find that this resistance is already relatively low due to the absence of a membrane. Removing mass transfer limitations with passive mixers we argue that our devices are solely limited by kinetic overpotentials due to the dilute concentration employed in this study, focusing on the fundamentals of mass transfer enhancement in redox flow cells. Novel opportunities in microfluidic flow cells combining both flow promoters to increase mass transport and micropatternable flow-over electrodes compatible to the harsh environment and potential

window of common redox systems (such as carbon-based electrodes for the V^{3+}/V^{2+} and VO_2^+/VO^{2+} system [46]) are envisaged and merit future investigation.

Appendix A. Computational model

We implemented a 3-D model in COMSOL Multiphysics® 5.1 based on the governing equations as described in this section. All simulations were performed in steady state, i.e. without time dependency.

The fluid was assumed incompressible and the hydrodynamics followed the continuity equation:

$$\nabla \cdot \mathbf{u} = 0 \quad (\text{Eq. 7})$$

and the Navier-Stokes equation:

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} \quad (\text{Eq. 8})$$

here $\mathbf{u}$ is the velocity vector, p the pressure, ρ the fluid density and μ the viscosity. At the walls the no slip boundary condition was applied. At the outlet the pressure was set to zero, whereas at the inlet a hydro-dynamically fully developed laminar flow profile with a specified bulk velocity was applied.

The transport of species followed the diffusion-convection equation:

$$\frac{\partial c_j}{\partial t} + \mathbf{u} \cdot \nabla c_j = \nabla \cdot (D_j \nabla c_j) + R_j \quad (\text{Eq. 9})$$

in which c_j is the concentration of the species j , D_j the diffusion coefficient, and R_j the reaction rate. In total, the system comprised four species, AQ2SH and Fe in their respective

oxidized and reduced forms. Boundary conditions were set at the inlet assuming a fully charged state of the respective anolyte and catholyte. At the outlet species were transported convectively out of the system. At the electrode-electrolyte interface the diffusion-convection equation (Eq. 9) was coupled to the electrode reaction with the reaction rate term:

$$, \quad (\text{Eq. 10})$$

where ν_j is the stoichiometric coefficient, z the number of transferred electrons, F the Faraday constant, and i the local current density.

The Butler-Volmer equation relates the current density i to the overpotential η :

$$, \quad (\text{Eq. 11})$$

in which the anodic and cathodic terms of the current density terms are dependent on the local concentration of reduced and oxidized species (c_{red} and c_{ox}) normalized to the inlet concentration c_0 . The additional ratio of local concentration to overall reference concentration accounted for the dependency of reaction rates on reactant concentration. In this way, the modified Butler-Volmer equation included also mass transfer limitations [47]. The remaining variables in Eq. 11 are the exchange current density i_0 , the transfer coefficient α , and the overpotential η by which the electrode potential E deviates from the equilibrium potential E_{eq} :

$$. \quad (\text{Eq. 12})$$

The Nernst equation describes the concentration dependency of the equilibrium potential:

$$, \quad (\text{Eq. 13})$$

where E° is the standard potential. The exchange current density i_0 was modelled using the Tafel approximation:

$$, \quad (\text{Eq. 14})$$

here k_0 is the reaction rate constant and α the transfer coefficient.

All parameters were adapted from earlier work on rotating disk electrode experiments [48,49] and are reproduced for a temperature of 25°C in table A1.

The computational meshes were generated using COMSOL's physics-controlled meshing sequence. In the vicinity of the microchannel's walls, e.g. between fluid and electrodes, the grid was further refined with layers of successively increasing thickness. A grid independence study was conducted on three different meshes (M1: 406'973, M2: 1'148'634, and M3: 2'416'003 computational elements) for design S3. At 0.2 m/s bulk inlet velocity and 0.26 V electrode potential (close to maximum power density) mesh M2 proved to be sufficient as the difference in current density compared to mesh M3 was less than 0.8 %.

In order to save computational time we did not resolve the entire polarization curve in our simulations. Instead, we solved for the limiting current at $E = 0.01$ V and around the point of maximum power density we swept in discrete steps of $\Delta E = 0.02$ V. The maximum of the i - p -curve we finally found by fitting a polynomial of second degree to our discrete data points [50].

Table A1: Summary of parameters used in numerical model adapted from earlier work [48,49]

Parameter		Value
Diffusion coefficient, D	Iron	
	AQ2SH	
Reaction rate constant, k_0	Iron	
	AQ2SH	

Standard potential, E^0 vs. Hg/HgSO ₄ (sat. K ₂ SO ₄)	Iron	
	AQ2SH	
Transfer coefficient, α	Iron	
	AQ2SH	

Appendix B. Ohmic losses in microchannel

The solution resistance between two electrode bands is assumed to be only dependent on the movement of ionic species. In this case, a theoretical solution is readily available [41]. The lines of flux are ellipses as shown in Fig. A1, where x and y are dimensionless variables: and . Here X_1 represents the electrode offset from the centerline, i.e. the electrodes start at and span to in our devices.

However, the derivation of Belmont and Girault assumes that the movement of ionic species takes place in an infinite volume [41], whereas in our configuration the height of the microchannel restricts the movement of species (the microchannel spans from to y), see Fig. A1. Therefore, the solution resistance in the microchannel will be higher than the theoretically derived resistance assuming no confinement.

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Acknowledgments

We gratefully acknowledge Swiss National Science Foundation for financially supporting this work within the REPCOOL project (grant 147661). JM is also grateful for support from the German National Academic Foundation. Device fabrication and portions of the characterization were performed in the Binnig and Rohrer Nanotechnology Center. We especially thank Ute Drechsler for her advice while establishing the fabrication processes, Sarmenio Saliba for technical support regarding the anthraquinone redox species, and Kleber Marques Lisboa for fruitful discussions about microfluidics.

Figure Captions

Figure 1: Illustration of experimental set-up and device (not to scale). (a) A microfluidic redox flow cell with Y-shaped in- and outlets fed by syringe pumps. The enlarged area indicates the position of the flow promoters (dark blue) opposite the two electrodes (orange). (b) Illustration of the dimensions of the two electrodes. In total, the electrodes cover about 15 herringbone elements. (c) Illustration of the four different designs tested in this work. S1 is a plain channel, S2 includes symmetric herringbones, S3 adds a solid zone along the centerline, and S4 features a vacant zone along the centerline. (d) Photograph of the experimental set-up including the electrolyzer, the microfluidic test rig, and the syringe pump. Enlarged is the microfluidic flow cell shown.

Figure 2: Concentration of anolyte (COMSOL simulations) in x-y-plane at half-height of the main channel at 1 m/s bulk inlet velocity ($Re = 155$) and mass transfer limit ($E = 0.01$ V) (a) 3D illustration for device S3, (b) top view comparing designs S1 - S4.

Figure 3: Polarization curves (left axis, dashed lines) and power density (right axis, solid lines) for the different flow rates tested. The negligible hysteresis between forward and backward scan at 25 mV/s indicates quasi-stationary conditions. (a) S1, (b) S2, (c) S3, (d) S4.

Figure 4: Comparison of the four different devices at two selected flow rates. Left axis: polarization curves (dashed lines), right axis: power density (solid lines). (a) $0.48 \text{ ml} \cdot \text{min}^{-1}$ ($0.40 \text{ m} \cdot \text{s}^{-1}$) (b) $2.40 \text{ ml} \cdot \text{min}^{-1}$ ($2.0 \text{ m} \cdot \text{s}^{-1}$)

Figure 5: Performance enhancement of devices including flow promoters *versus* plain reference channel of design S1 (a) limiting current (b) power density.

Figure 6: Scaling of (a) limiting current and (b) maximum power density (experimental data). The dashed lines are given for visual guidance in the double-logarithmic plots.

Figure 7: Scaling of (a) limiting current and (b) maximum power density (COMSOL simulation). The dashed lines are given for visual guidance in the double-logarithmic plots.

Figure 8: Measurements of resistance in cell (a) Impedance measurements at varying concentrations of H_2SO_4 . The insert magnifies the high frequency region of the impedance measurements. (b) Series resistance as a function of test solution resistivity. The axis-intercept of the extrapolation gives the resistance at infinite electrolyte conductivity.

Figure A1: Illustration of theoretical flux lines and microchannel geometry (crosssection).

Figure 1a

a **Figure 2**

b

Figure 3

Figure 8