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Supplementary Information

Mixing with herringbone-inspired microstructures: Overcoming the diffusion limit in co-

laminar microfluidic devices

Julian Marschewski^{a,b}, Stefan Jung^a, Patrick Ruch^b, Nishant Prasad^a, Sergio Mazzotti^a, Bruno Michel^b,

Dimos Poulikakos^{a,*}

^aLaboratory of Thermodynamics in Emerging Technologies, Department of Mechanical and Process

Engineering, ETH Zürich, 8092 Zürich, Switzerland

^bIBM Research Zurich, Säumerstrasse 4, 8803 Rüschlikon, Zürich, Switzerland

Physiochemical phenomena in membraneless redox flow cells

Two physiochemical phenomena are characteristic to membraneless redox flow cells (cf. Fig. S1): First, diffusive cross-over at the liquid-liquid interface leads to intermixing of the two co-laminar flows, i.e. catholyte and anolyte.¹ Second, as a result of the electrochemical reactions of both catholyte and anolyte at the respective electrodes, depletion boundary layers form at these locations.² The corresponding reactant concentration gradients, from high concentrations in the bulk liquid, to reduced concentrations directly at the electrode surfaces, have a negative effect on cell performance. The thickness of these depletion boundary layers, δ_{dpl} , is influenced by the flow characteristics within the microchannel.



Figure S1: Schematic of a membraneless redox flow cell. Catholyte and anolyte flow in a colaminar redox flow cell with evolving diffusion zone at the liquid-liquid interface and depletion boundary layer of thickness δ_{dpl} along the electrode (exemplified for cathode, not drawn to scale).

Surface contact simulations

For dimensioning of the grooves we studied the particle-surface interactions in a microchannel with a symmetric herringbone mixer following the framework recently developed by Forbes et al.³ For this purpose we solved the 3-dimensional steady state Navier Stokes equation for the velocity and pressure fields using the Laminar Flow Module of COMSOL Multiphysics[®] version 4.4. Working fluid was water at with a constant density of 1000 kg/m³ 25°C. The validity of the laminar flow assumption was conserved by fixing the Reynolds number to Re = 200. Figure S2a exemplifies the numerical result of the in-plane velocity at Re = 200. From comparison with experimentally measured data (see Fig. S2b), obtained by μ PIV, we deduced that the simulation and experiment match closely, validating the simulation.



Figure S2: Absolute in-plane fluid velocity in a microchannel with flow promoters. (a) numerical simulation and (b) µPIV experiment.

For surface contact evaluation the modeled channel geometry (400 μ m in width and 100 μ m in height) resembled the experimental device S2. It featured 10 symmetric grooves (cf. geometry S2 in Fig. 1c), each 100 μ m deep (cf. Fig. 1a). A parametric study comprised of the variation in groove pitch (350 μ m and 500 μ m) and width (200 - 340 μ m and 340 - 470 μ m, respectively). We evaluated the effectiveness of the geometry with respect to the mixing propensity using a particle tracing algorithm. This method was based on a transient simulation employing the Particle Tracing For Fluid Flow

module in COMSOL Multiphysics[®] (subsequent to solving for the velocity and pressure field). In total, 2000 massless particles, faithfully following the flow field, were inserted at the time t = 0 s and the following equation was solved for the particle trajectories (with a time step of $\Delta t < 10^{-4}$ s):^{4,5}

$$\frac{\Delta \vec{x}_{particle}}{\Delta t} = \vec{u}_{flowfield}, \tag{1}$$

where $\vec{x}_{particle}$ is the position of the particles at each time step and $\vec{u}_{flowfield}$ the previously calculated flow field at the respective position.

A representative image of the particles moving through the channel is given in Figure S3a. Surface interactions with flow boundaries were evaluated at the wall opposing the grooves (i.e. where the electrodes are located in the experiments). For post-processing purposes a MATLAB script was implemented, which flags particles as soon as they penetrate into a virtual critical geometric surface boundary layer of thickness $z_{crit} = 10 \ \mu m$ (i.e. the upper 10 % of the channel height, see Fig. S3a), defining particle-surface interaction.³ Surface contacts were eventually determined by building the ratio of flagged particles to the total number of particles at t = 0 s. Figure S3b plots the particle-surface contacts for two different groove pitches (350 μm and 500 μm). In both cases we observe an initial steep increase of surface contacts with increasing groove widths before surface contacts level off. In figure S3c we normalized the x-axis by dividing the groove width by the groove pitch to highlight the previous insight further.



Figure S3: Surface contact increase with respect to groove dimensions. (a) Image of massless particles following streamlines after reaching first grooves. The dimension z_{crit} defines the thickness of the critical geometric surface boundary layer (b) Surface contacts of particles as a function of groove width. (c) Surface contacts as a function of groove width over groove pitch.

Electrochemical testing by cyclic voltammetry

Figure S4 shows typical cyclic voltammograms obtained during electrochemical testing (here sample S1 with equimolar solution of FI-CN and FO-CN). This plot shows that with increasing Reynolds number the current response increases. To compare the different devices and flow conditions we extract from these cyclic voltammograms the current at $E_{we} = 0.4$ V vs. Pt quasi-reference electrode (see Fig. S4).



Figure S4: Oxidation of FO-CN in plain channel. Cyclic voltammograms for the electrochemical reaction of FO-CN in device S1, Re = 6 - 600 (equimolar experiments).

References

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