Direct 3D observation and unravelling of electroconvection phenomena during concentration polarization at ion-exchange membranes

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Abstract

A decade ago, two-dimensional microscopic flow visualization proved the theoretically predicted existence of electroconvection roles as well as their decisive role in destabilizing the concentration polarization layer at ion-selective fluid/membrane interfaces. Electroconvection induces chaotic flow vortices injecting volume having bulk concentration into the ion-depleted diffusion layer at the interface. Experimental quantification of these important flow patterns have so far only been carried out in 2D. Numerical direct simulations suggest 3D features, yet experimental proof is lacking. 3D simulations are also limited in covering extended spacial and temporal scales.

This study presents a new comprehensive experimental method for the time-resolved recording of the 3D electroconvective velocity field near a cation-exchange membrane. For the first time, the spatio-temporal velocity field can be visualized in 3D at multiples of the overlimiting current density. In contrast to today's simulations, these experiments cover length and time scales typical for actual electrodialytic membrane processes.

We visualize coherent vortex structures and reveal the changes in the velocity field and its statistics during the transition from vortex rolls to vortex

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rings with increasing current density. The transition is characterized by changes in the rotation direction, mean square velocity, and temporal energy spectrum with only little influence on the spatial spectrum. These findings indicate a more significant impact of EC's structural change on the mean square velocities and temporal spectra than on the spatial spectra. This knowledge is a prerequisite for engineering ion-selective surfaces that will enable the operation of electrically driven processes beyond the diffusion-limited Nernst regime.

Keywords: Ion transport, Electroconvection, 3D PTV, Velocity field, Electrodialysis

1. Introduction

Ion-selective membranes are frequently used in industrial processes for water purification such as electrodialysis (ED) [1, 2] and flow-electrode capacitive deionization (FCDI) [3, 4, 5], or in systems for energy storage like redox-flow battery systems [6, 7]. In these processes, an electric potential between two electrodes acts as the driving force for ion transport through membranes in contact with an electrolyte. For small currents, the current density increases linearly with the applied potential. However, the transport stagnates at a limiting current density i_{lim} when concentration polarization (CP) leads to depletion of the Nernst diffusion layer close to the membrane, see Fig. 1 a) [8]. This limitation is visible as a plateau region in a current density over potential plot in Fig. 1 b).

When increasing the current density beyond i_{lim} , overlimiting currents emerge having their origin in a variety of superimposed phenomena, one of them being electroconvection (EC). Electroconvection can be observed as vortices, which convectively mix the boundary layer supplying the depleted layer with the ion-rich bulk solution, see Fig. 1 a). The increased ion concentration at the membrane allows for an overlimiting current beyond the diffusion limit, see Fig. 1 b) [9].

Until now, quantitative studies on the hydrodynamics of EC were limited to computationally demanding 2D and 3D direct numerical simulations (DNSs) which unfortunately only offer limited length and time scales [10, 11, 12, 13, 14]: experimental quantification of velocity profiles could only be done using 2D experiments [15, 16, 17]. In fact, understanding and controlling the hydrodynamics of EC is expected to facilitate mass transport

observed as overlimiting currents. Enabling higher current densities results in lower membrane area required to achieve a desired desalination degree: this results in a desired investment costs reduction. It is therefore obvious that understanding the details of the overlimiting transport, in particular EC, is a prerequisite for process optimization of an electrical-field driven membrane process. Also, understanding electroconvection’s intricate details comprehensively is important to tailor membrane surfaces such that overlimiting can be actually utilized in practice.

2. Background

In a milestone paper of Rubinstein [18], the authors predicted that the onset of electroconvection can be triggered at lower voltages if the surface of the membrane would be "wavy". This prediction has spurred research in understanding the phenomena itself, but also into the synthesis of new membrane surface topologies to avoid any potential drop in the plateau region prior to the overlimiting currents. With respect to experimental strategies to initiate early electroconvection, membrane modification methods developed by the Kuban research community have proven to be effective [19, 20, 21]. As early as 2007, Balster reported that line undulations on the membrane surface normal to the flow direction, having distances in the range of approximately 50-200 % of the boundary-layer thickness, lead to an earlier onset of the overlimiting current [22]. Also 2D micropatterns of nanometer-thick lateral polyelectrolyte patches induce electroconvection, i.e. macroscopic electroosmotic chaotic fluid instabilities [23]. Also Roghmans et al. described that inkjet printed microgel patterns induce electroconvection [24]. Yet the work hypothesizes that the surface charge of the patterns may even determine the direction of vortices rendering them either effective or less effective for destabilizing the diffusion boundary layer and reducing the length of the plateau. Clearly, more experimental visualization methods are highly desired to elucidate and quantify the spatio-temporal fluid velocities during electroconvection at the membrane/fluid interface.

Historically, our 2D work on proving the existence of electroconvection through visualization with a particle imaging technique [25] confirmed the predicted vortex-like features at the membrane/liquid interface with growing vortices at increasing current densities. Subsequently, De Valenca et al. quantified the 2D velocity field of EC in the cross-section of the CP layer [15, 16]. They correlated the vortex size and fluid flow velocity with the cur-

Figure 1: Stages of electroconvection. a) Concentration profiles of anions and cations in front of the membrane for three different regimes (I: $i < i_{\text{lim}}$, II: $i = i_{\text{lim}}$, and III: $i > i_{\text{lim}}$). b) Sketch of the current versus voltage curve for an electrically driven membrane process. The three regimes in a) appear as the Ohmic, plateau, and overlimiting regions. c) Sketches of the different vortex structures developing in the overlimiting regime. First, EC appears as vortex rolls that order in a 2D fashion. With increasing i/i_{lim} , the linear structure of vortex rolls breaks up into 3D vortex rings.

rent density through the system. This approach was recently advanced by Warren et al. [17] who correlated the effect of the applied potentials to the 2D velocity field of EC. However, their proposed electrochemical chip had an aspect ratio non-existent in common membrane modules. Other studies also analyzed EC by optically recording tracer substances in 2D but without quantification of velocities [25, 26, 27, 28, 29, 30, 31]. Recently, Kang et al. visualized the structural transition of EC in the overlimiting current region with and without flow parallel to a membrane surface with confocal microscopy in 3D [32]. This transition from 2D vortex rolls towards 3D vortex rings, see Fig. 1 c), was predicted by Demekhin et al. in the first 3D DNSs of EC [11]. Although qualitatively accurate, such confocal microscopy methods do not supply information on the 3D EC velocity field and its energy transfer.

The chaotic 3D velocity field of EC is up to now only accessible via intensive simulations simultaneously solving the Navier-Stokes, Nernst-Planck, and Poisson-Boltzmann equations [9]. In such a simulation, Druzgalski et al. analyzed and compared the statistics of chaotic EC from 2D to 3D results in an attempt to derive energy spectra needed for the development of a

statistically averaged reduced-order model [10, 12]. Such a statistical averaged model would enable low-cost simulations in the overlimiting regime for process optimization [9]. Experimentally, a simple reduced-order parameter approach has been suggested based on fitting the overlimiting currents utilizing a Schmidt number [33]. However, this approach has not been further explored until today. Furthermore, Druzgalski et al. also found qualitative and quantitative differences in their 2D and 3D simulations, emphasizing the need for a new methodology quantifying the 3D hydrodynamics. The required fine resolution in space and time limited their simulations to small geometries and short time spans only. Therefore, the ability to extrapolate their conclusions to the length and time scales of practically relevant devices remains unclear until experimental results of the 3D velocity field are available.

To overcome this lack of experimental data, we developed and report an electrochemical cell allowing the optical recording of the 3D EC velocity field close to a cation-exchange membrane using micro particle tracking velocimetry (μ PTV). With this setup, one can now make the important step from 2D to 3D velocity field quantification: at practically relevant length and time scales over a range of overlimiting current densities. We use the velocity data to analyze the structural change of EC from vortex rolls to vortex rings in terms of vortex rotation direction. Additionally, we evaluate the velocity field statistics and the fluctuating velocity component. This proposed methodology allows to unravel details of EC hydrodynamics experimentally which in future can be compared to simulated velocity statistics when the reported length and time-scales will be accessible through high performance computing efforts.

3. Experimental Methods

3.1. Electrochemical cell

We designed the experimental cell shown in Fig. 2 which is suitable for electrochemical experiments with simultaneous recording of the evolving 3D velocity field using microparticle tracking velocimetry (μ PTV). The cell is based on the publication of Linz et al. [34] and consists of a Nafion N117 (Chemours, Wilmington, Delaware, USA) cation-exchange membrane sealed between two housing parts. The transparency of the membrane allows for imaging of buoyancy stable EC through the membrane [35, 36]. Two copper

Figure 2: Cell design for electrochemical experiments with simultaneous μ PTV recording. The electrochemical cell consists of two 3D printed housing parts which are sealed with O-rings against two copper electrodes and a Nafion N117 membrane. The cathode has a circular hole with a diameter of 9 mm to allow optical access. The hole is sealed with a microscope glass slide, which is not shown in the rendering, on top of the electrode.

plates ($25\text{ mm} \times 75\text{ mm} \times 0.5\text{ mm}$) seal the top and the bottom of the chip and act as electrodes in each half cell. The cathode has a circular hole ($d = 9\text{ mm}$) and is glued to a glass slide to enable optical access. This setup forms electrolyte chambers above and below the membrane, which are filled with 1 mM copper sulfate (CuSO_4) as the electrolyte. The bottom chamber has a height of 0.8 mm, matching the maximum focal depth, and a diameter of 8 mm, resulting in an aspect ratio of 10. Such a large aspect ratio is desired to prevent the confinement of the EC vortices [37, 38].

A cell comprising two copper electrodes, a cation-exchange membrane, and CuSO_4 in aqueous solution as electrolyte is a simple and well studied electrochemical system for evoking EC [15, 39]. In this system, CuSO_4 dissociates to Cu^{2+} and SO_4^{2-} and both electrodes favor copper deposition and dissolution as faradaic reactions [40].

During operation, copper is dissolved at the anode, transported through the membrane, and deposited on the cathode. Additionally, this reaction system limits gas evolution at the electrodes and the membrane to a minimum, which ensures stable reaction conditions and clear optical access without gas bubbles.

The copper ions moving towards the cathode result in an ion flux i per membrane area also describes as the current density. The limiting current density of the process, described in Fig. 1, can be calculated by [16]:

$$i_{\text{lim}} = \frac{c_B}{\delta} \cdot \frac{F \cdot z}{t_M - t_E} \quad (1)$$

According to de Valenca [16], the bulk concentration c_B is approximated with a linear gradient between electrode and membrane as twice the electrolyte starting concentration c_0 in the anode chamber. F is Faraday's constant and z the ionic valence. The transport numbers in the membrane and electrolyte t_M and t_E describing the ion velocity difference are 0.96 and 0.4, respectively. For a 1 mM CuSO_4 solution, current densities larger than $i_{\text{lim}} = 0.73 \text{ A m}^{-2}$ will result in the EC vortex formation close to the membrane of the anode chamber [15].

3.2. Micro particle image velocimetry

Figure 3: Schematic illustration of the setup for stereo micro particle image velocimetry. The setup for stereo micro particle image velocimetry consists of a laser that illuminates tracer particles in a sample volume through a stereo microscope which splits the laser beam in two separate beams. The fluorescence response returns through the microscope and is recorded by two slightly angled high-speed cameras. Returning laser light is blocked by a high-pass filter. This technique allows the recording of tracer particles in a 3D volume.

We use micro particle tracking velocimetry (μPTV), which is an optical technique for measuring fluid flow in millimeter-scale geometries [41] to record the velocity field of EC during our experiments. When using this

method, tracer particles are illuminated by a high-frequency 532 nm Nd:YAG laser (DM150, Photonics Industries International Inc.) and recorded by two high-speed cameras (Phantom VEO 710L, Vision Research Inc.) through a stereo microscope (SteREO Discovery.V20, Carl Zeiss Microscopy Deutschland GmbH, Germany) containing a $1\times$ objective (Plan-Aprochromat $1\times$, Carl Zeiss Microscopy Deutschland GmbH, Germany), see Fig 3. The cameras record the resulting particle images inside the microscope's focal depth from two different viewing angles. With our setup, the recorded volume at a magnification of $5.12\times$ and a halfway closed aperture has a size of $4.9\text{ mm}\times 3.1\text{ mm}\times 0.8\text{ mm}$ with $1280\text{ px}\times 800\text{ px}$ resolution in x- and y-direction. The depth of the recorded volume of 0.8 mm matches the depth of our electrochemical cell's anode chamber. Therefore, it is possible to reconstruct the full velocity field of EC between membrane and anode.

3.3. Combining electrochemical experiments and velocity recording

To conduct simultaneous electrochemical and μ PTV experiments, the electrolyte in the anode chamber is seeded with 0.001 wt% inert, fluorescent polystyrene microspheres (Thermo Scientific, Waltham, MA, USA). These tracer particles have a diameter of $3.2\text{ }\mu\text{m}$ and a Zeta potential of -14.9 mV measured with a Malvern Zetasizer Nano ZS (Malvern Panalytical Ltd), which are comparable to the study of De Valenca et al. [15]. Different to De Valenca et al., the microscope is focused below the membrane in the middle of the anode chamber enabling to record the particle tracks over the whole z-dimension of that chamber. The experiments are conducted without forced flow and electrolyte movement only results from EC.

The chronopotentiometric experiment are conducted at fixed multiples of the limiting current using a potentiostat (Interface 1010E, Gamry, Pennsylvania, USA). For each potential, the time until CP is fully built-up and EC starts to develop can be calculated with Sand's equation [42]:

$$\tau = \frac{\pi D}{4} \cdot \left(\frac{c_0 z F}{t_M - t_E} \right)^2 \frac{1}{i^2} \quad (2)$$

Here, c_0 is the electrolyte's initial concentration in the anode chamber. The diffusion coefficient of the electrolyte $D = 0.855 \times 10^{-9}\text{ m}^2\text{ s}^{-1}$ is calculated from both individual diffusion coefficients $D_{\text{Cu}^{2+}} = 0.714 \times 10^{-9}\text{ m}^2\text{ s}^{-1}$ and $D_{\text{SO}_4^{2-}} = 1.065 \times 10^{-9}\text{ m}^2\text{ s}^{-1}$ with the following equation [43]:

$$D = \frac{(z_+ + z_-)D_+D_-}{z_+D_+ + |z_-|D_-} \quad (3)$$

183 The + and - signs indicate the values for cation and anion, respectively.
 184 However, EC takes longer than the calculated transition time τ to reach a
 185 steady-state [24]. Therefore, we analyze the flow well after the transition
 186 time in the steady sections of the chronopotentiometry to ensure evaluation
 187 of the steady-state.

188
 189 At $4 \cdot i_{\text{lim}}$, the formation of the EC vortices takes longer than the elec-
 190 trostatic exclusion of tracer particles from the ESC, effectively preventing
 191 recording the EC vortex field. In this experiment, the current density is
 192 linearly decreased from $8.1 \cdot i_{\text{lim}}$ to the desired current density at a rate of
 193 $4 \times 10^{-3} \text{ A m}^{-2} \text{ s}^{-1}$. Afterward, a steady-state at $4 \cdot i_{\text{lim}}$ could be measured.
 194 This approach ensures the presence of particles close to the membrane due
 195 to previous EC mixing of the domain.

196
 197 When a steady-state in the experiment was reached, the recording of the
 198 particle images is started. The flow is recorded for a maximum of 126 s at
 199 a frequency of 20 Hz. The time-resolved recording of the velocity field also
 200 enabled the reconstruction of the velocity field during the build-up of EC.

202 3.4. Velocity processing

203 The recorded particle images are analyzed with the tools available in
 204 the software DaVis (version: 10.0.5.47779, LaVision GmbH, Göttingen, Ger-
 205 many). In a preprocessing step, static particle signals are removed by sub-
 206 tracting the time-averaged intensity for each pixel. For the reconstruction of
 207 the particle tracks, the Shake-the-Box algorithm is used [44, 45]. However,
 208 experiments at current densities below $2 \cdot i_{\text{lim}}$ cannot be processed. Here,
 209 the particles move too slow and the velocities are too small to be detected.

210 A fine-scale reconstruction is used for transforming the particle tracks
 211 to velocities (u_x, u_y, u_z) on a regular grid. The fine-scale reconstruction is
 212 performed with the VIC# method implemented in the DaVis Software [46,
 213 47]. For our experiments, we chose a grid size of ten voxels, which results
 214 in reasonable computing times. Therefore, the final resolution of the recon-
 215 structed velocity fields is $128 \text{ px} \times 80 \text{ px} \times 21 \text{ px}$ with a voxel size of $38.4 \mu\text{m}$.

216 To visualize the vortex structure of EC, DaVis offers plotting coherent
 217 vortex structures with the λ_2 -method [48]. This method computes vortex
 218 core lines by evaluating the eigenvalues of the squared and summed sym-
 219 metric and antisymmetric parts of the gradient velocity tensor. Coherent
 220 structures are visualized as isosurfaces at a specific eigenvalue λ_2 .

221

222 After exporting the velocity field data to MatLab (version: R2019b, The
 223 MathWorks Inc.), the mean square velocities is calculated as a spatial and
 224 temporal average in the steady-states of the experiments [10]:

$$\overline{u_i^2} = \frac{1}{N_t \cdot L_x \cdot L_y} \int u_i^2 \cdot dx \cdot dy \cdot dt \quad (4)$$

225 The equation includes the number of time steps N_t and the mesh points
 226 in x- and y-direction L_x and L_y .

227 The fluctuating velocity component is calculated by subtracting the tem-
 228 poral and spatial mean velocity from each velocity data point for evaluation
 229 of the temporal and spatial energy spectra. To this data, we apply a Han-
 230 ning window. The Hanning window or Hann function is a weighting function
 231 which is used to reduce the input signal from the middle of the x,y-domain
 232 towards its borders [49]:

$$w_i(n_i) = 0.5 \left(1 - \cos \left(2\pi \frac{n_i}{N_i} \right) \right) \quad (5)$$

233 Here, n_i and N_i are the array of data points and the number of data
 234 points in x- or y-direction, respectively. The 2D window is created with
 235 $w_{x,y}(n_x, n_y) = w_x(n_x) \cdot w_y(n_y)$.

236 For spectral analysis, a Fourier transformation of the fluctuating velocity
 237 components over time or space is performed. The velocities, that were 1D
 238 Fourier transformed over time $\tilde{u}_i$, are then converted to temporal spectral
 239 energies and averaged in the x,y-planes with [10]:

$$E(z, \omega) = \frac{1}{2 \cdot N_t \cdot N_x \cdot N_y} \int |\tilde{u}_x|^2 + |\tilde{u}_y|^2 + |\tilde{u}_z|^2 dx dy \quad (6)$$

240 Here, N_t , N_x , and N_y are the number of data points in time, the x-direction,
 241 and the y-direction.

242 For spatial spectral analysis, a 2D Fourier transformation of each fluc-
 243 tuating velocity component in each z-plane for each time step is performed.

244 The energy is normalized, and averaged over time:

$$E(z, k) = \frac{1}{2 \cdot N_t} \cdot \frac{d^6}{(2 \cdot \pi)^3 \cdot L_x \cdot L_y \cdot L_z} \int |\tilde{u}_x|^2 + |\tilde{u}_y|^2 + |\tilde{u}_z|^2 dt \quad (7)$$

245 The result is integrated over annuli with a radius of $k = \sqrt{k_x^2 + k_y^2}$ and a
 246 thickness of one in the Fourier-space (see appendix Appendix A). Here, d
 247 is the mesh spacing, and L_x , L_y , and L_z are the domain sizes in the x-, y-,
 248 and z-directions, respectively. This procedure results in energy graphs over
 249 the wavenumber k which is the spatial frequency in x,y-direction. During
 250 the integration, the mesh is refined by a factor of ten in both directions to
 251 generate smoother graphs.

253 3.5. Comparability to simulations

254 To achieve comparability to the 3D DNSs of Druzgalski et al. [12]. We
 255 chose process parameters that best match their dimensionless numbers sum-
 256 marized in Tab. 1. The relevant dimensionless parameters concerning this
 257 comparison include: i) the applied voltage divided by the thermal volt-
 258 age $\frac{V}{V_T} = \frac{Vze}{k_B T}$, ii) the Schmidt number $Sc = \frac{\mu}{\rho D}$, iii) the electrohydrody-
 259 namic coupling constant $\kappa = \frac{\epsilon}{\mu D} \cdot (\frac{k_B T}{ze})^2$, iv) the dimensionless Debye length
 260 $\lambda_d = \sqrt{\frac{\epsilon k_B T}{2c_b(zeL_z)^2}}$, and v) the aspect ratio $a = \frac{d}{L_z}$. Here, k_B , T , z , and e
 261 are the Boltzmann's constant, temperature, ionic valence, and the electron
 262 charge, respectively. Furthermore, the electrolyte defines the permittivity
 263 ϵ , dynamic viscosity μ , diffusion coefficient D , and bulk concentration c_b .
 264 Lastly, d and L_z are the active membrane diameter and the distance between
 265 the membrane and electrode, respectively.

266 Out of these parameters, our main targets were a large channel aspect
 267 ratio, a large dimensionless Debye length, and the possibility to conduct
 268 experiments at large overlimiting currents, which is proportional to large ap-
 269 plied voltages. Advantageous to simulation, our setup allows for dimensions
 270 and a Debye length found in practically relevant applications. This difference
 271 in Debye length of about three orders of magnitude leads to a smaller ex-
 272 tended space charge region in the experiments and, thus, velocity generation
 273 closer to the membrane [9].

Table 1: Comparison of dimensionless numbers of this study and the reference DNSs [12].
 *The applied voltage in our experiments includes the voltage drop at the electrodes, in the membrane, and in the second electrolyte chamber.

Dimensionless number	DNS [12]	This study
Applied voltage	$120 \frac{V}{V_T}$	$64 - 362 \frac{V}{V_T}^*$
Schmidt number	1×10^3	1.17×10^3
Electrohydrodynamic coupling constant	0.5	0.14
Dimensionless Debye length	1×10^{-3}	6×10^{-6}
Aspect ratio	6.3	10
i/i_{lim}	10	1.4 - 10.8

274 4. Results and Discussion

275 Using the electrochemical chip, the movement of tracer particles between
 276 the membrane and anode can be followed. Particle tracking velocimetry re-
 277 veals the 3D velocity field as a consequence of electroconvection at increasing
 278 current densities.

279 4.1. Evolution of the velocity field with increasing current density

280 First, I-V experiments identify the different current regimes in a current
 281 density over potential graph at multiples of the theoretical limiting current
 282 density ranging from $0 \cdot i_{\text{lim}}$ to $10.8 \cdot i_{\text{lim}}$, see Fig. 4 a). The plateau is clearly
 283 visible between potentials of about 0.4 V to 0.64 V matching the calculated
 284 theoretical limiting current density of 0.73 A m^{-2} (Eq. 1). At larger poten-
 285 tials, the system enters the overlimiting current region where EC vortices
 286 appear. Graphs of the chronopotentiometric experiments are shown in the
 287 appendix Appendix B. The data points shown are time-averaged values
 288 of the fluctuating signals having their origin in the dynamic nature of the
 289 chaotic flow conditions close to the membrane surface.

290

Figure 4: Development of electroconvection in the overlimiting regime. **a)** The graph shows mean voltages of chronopotentiometry experiments at increasing multiples of the limiting current. The dotted line is drawn for visual guidance. **b) - e)** Top views on isosurfaces of coherent vortex structures during experiments at **b)** $4 \cdot i_{lim}$ (at 90 s), **c)** $6.1 \cdot i_{lim}$ (at 70 s), **d)** $8.1 \cdot i_{lim}$ (at 70 s), and **e)** $10.8 \cdot i_{lim}$ (at 81 s) in the steady-state. The velocity is colored in magnitude and direction according to the scale bar from blue to red.

291 We record the velocity fields with our setup during experiments at differ-
 292 ent magnitudes of the overlimiting current. Fig. 4 b)-e) show snap-shots of
 293 the top view on iso-surfaces of coherent vortex structures at $4 \cdot i_{lim}$, $6.1 \cdot i_{lim}$,
 294 $8.1 \cdot i_{lim}$, and $10.8 \cdot i_{lim}$, respectively. With increasing current density, the
 295 roll-like structure seen in Fig. 4 b) collapses and vortex rings of oval shape
 296 emerge, see Fig. 4 c). With even higher current densities, the vortex rings
 297 first become more regular, see Fig. 4 d), before chaotic changing of patterns
 298 emerges, see Fig. 4 e). While we show the quantification of such 3D veloc-
 299 ity field for the first time, this transition from vortex rolls to vortex rings
 300 matches the qualitative observations of Demekhin et al. [11] and Kang et
 301 al. [32].

302

303 Additionally to the vortex structure, the measurement of velocity vectors
 304 enables the evaluation of rotation directions. At $4 \cdot i_{lim}$, pairs of counter-
 305 rotating vortex rolls are the dominant structure. Fig. 4 b) shows that the
 306 rolls of a pair connect in the vicinity of other vortex rolls. The velocity be-
 307 tween two rolls of a pair is directed towards the membrane. Contrary, the
 308 velocity in the centers of vortex rings (Fig. 4 c)-e)) is directed away from

the membrane. This change in rotation direction indicates that vortex roll pairs do not simply split up in sections and recombine with themselves when transitioning to rings. Two other mechanisms seem more likely: First, vortex roll pairs could split up in sections and recombine but reverse their rotation direction. This change in direction could be induced by the emergence of a smaller vortex ring with a reversed rotation direction in the center of a recombined vortex roll. This smaller ring could increase in size and consume the recombined vortex ring resulting in a ring with a reversed rotation direction. Second, vortex roll pairs could split up at their contact points with other pairs and recombine at the contact point. This observation needs further investigation for a certain explanation.

4.1.1. Particle tracks of vortex rolls

Figure 5: Snapshot of particle tracks for $4 \cdot i_{lim}$ at 90 s. Top view of the particle tracks in the reconstructed 3D volume and a cross-section (A-A) with a track length of 49 time steps (2.45 s). A-A shows a 2D cross-section of the 3D particle field between the electrode and membrane. The velocity is colored in magnitude and direction according to the scale bar from blue to red. The axes are scaled by the channel height $L_z = 800 \mu m$. Black domains indicate regions where no tracer particles are present due to space charge exclusion as proven by [38]

Fig. 5 shows the 3D reconstructed particle tracks at $4 \cdot i_{lim}$ which is in the region of vortex rolls. The vortex roll pairs, described in the previous section, are visible in the top view as pairs of particle tracks with opposing rotation directions. De Valenca et al. and Davidson et al. already reported that the slight Zeta potential of the tracer particles leads to their exclusion

327 from locations with high anion concentration [15, 38]. These locations appear
 328 as black areas which are void of particles. Another distinct observation is
 329 particles moving on separate orbits along each vortex roll, forming hollow
 330 cylindrical structures (Fig. 5). The cross-section A-A shows that the particles
 331 are moving on exclusive trajectories. A possible explanation could be the
 332 formation of secondary vortices between these separate circles comparable
 333 to Taylor flow [50]. These vortices could exclude the particles from the rest
 334 of the roll. Another explanation could be the formation of regions of high
 335 ion concentration inside the vortex rolls. Such regions would also exclude
 336 tracer particles. To identify the validity of these hypotheses, quantitative
 337 information on the concentration field would be necessary.

338 4.1.2. Velocity field of chaotic vortex rings

Figure 6: Snapshot of particle tracks and the corresponding velocity correlation for $10.8 \cdot i_{\text{lim}}$ at 81 s. a) Top view of the particle tracks in the reconstructed 3D volume with a track length of 1 s. A-A shows a 2D cross-section of the 3D particle field between the electrode and membrane. b) Top view of the isosurface of coherent vortex structures in the reconstructed 3D volume showing a chaotic pattern of vortex rings at 81 s. c) Velocity maps of the cross-section B-B, C-C, and D-D. The white symbols mark the positions of the highest positive (plus) and negative (cross) velocities in each cross-section. The cross-sections A-A and D-D show velocity fields calculated from the particle tracks. Videos of the time-resolved particle tracks and vortex structure can be found as supplementary material. The velocity is colored in magnitude and direction according to the scale bar from blue to red.

339 Fig. 6 shows a snapshot of the steady-state of EC in the regime of chaotic
 340 vortex rings at $10.8 \cdot i_{\text{lim}}$. The top view of reconstructed particle tracks
 341 in Fig. 6 a) reveals the appearance of vortex rings with varying diameters.
 342 In the cross-section A-A, the particle tracks show circular movement at the

343 borders of vortex rolls, for example, at $x/L_z = 4.5$. These circular tracks
 344 strongly resemble structures recorded in the 2D experiments of Valenca et
 345 al. [15].

346
 347 For further investigation, the particle tracks are converted to a 3D veloc-
 348 ity field. From this velocity field, coherent vortex structures are extracted
 349 and displayed as isosurfaces as shown in Fig. 6 **b**). The top view of the
 350 vortex field structure shows coherent vortex rings as reported by Demekhin
 351 et al. [11]. The largest displayed velocities seem to appear in the centers of
 352 small vortex rings and at contact points of multiple rings. To confirm this
 353 observation, cross-sections of the vortex field through such structures are dis-
 354 played in Fig. 6 **c**) B-B, C-C, and D-D. The analysis of the cross-sections
 355 prove that the largest absolute velocities in the respective planes appear close
 356 to the membrane and between coherent vortex rings. These velocities are up
 357 to 4.8 times larger than the average absolute velocities in their respective
 358 plane. This velocity distribution can be explained by continuity. The area
 359 with velocities towards the electrode is proportionally larger than the area
 360 with velocities towards the membrane (Fig. 6 **b**)) which results in higher
 361 velocities for the latter.

362
 363 These local velocity hot spots might be connected to local current den-
 364 sity hot spots at the membrane. At the positions of high velocities towards
 365 the membrane, a larger quantity of high-concentrated electrolyte solution is
 366 transported from the bulk to the cation-depleted membrane surface. The re-
 367 sulting local jump in cation concentration will, in turn, lead to a local jump
 368 in ionic current through the membrane. Thus, the numerically-predicted for-
 369 mation of current density hot spots [12] could be connected to the velocity
 370 hot-spot and verified by our experiments.

371 372 *4.2. Velocity statistics of electroconvection*

373 The spatio-temporal 3D velocity information allows to quantify the ve-
 374 locity statistics with increasing current density. This enables to compare
 375 the experimental statistics for chaotic vortex rolls to the velocity statistics
 376 simulated by Druzgalski et al. from 3D DNSs [12].

Figure 7: Comparison of mean square velocity, temporal- and spatial energy spectra between 3D μ PTV (upper row) and 3D DNSs (lower row) [12]. The graphs present a direct comparison of our 3D μ PTV results at $10.8 \cdot i_{\text{lim}}$ (1000 time steps, 74.5 s to 124.5 s) a) - c) to the 3D DNSs results of Druzgalski et al. d) - f) redrawn from [12] with permission from *Physical Review Letters*. a) and d) show the mean square of one in-plane and the out-of-plane velocity components over the dimensionless distance to the membrane z/L_z with $L_z = 0.8 \text{ mm}$. b) and e) show temporal energy spectra of the fluctuating velocity components. c) and f) show spatial energy spectra of the fluctuating velocity components. The spectra of 3D μ PTV results b) and c) are plotted for dimensionless distance to the membrane of 0.05, 0.10, 0.25, and 0.80. The linear zoom of the spatial spectrum emphasises the maxima at low wavenumbers. e) and f) are plotted for the normalized distances to the membrane of 0.037, 0.104, 0.250, and 0.820.

377 4.2.1. Comparison of velocity statistics to simulation

378 Fig. 7 shows the velocity statistics calculated from our experiment with
 379 the statistics extracted from the simulations by Druzgalski et al. [12] for 3D
 380 DNSs. The statistical analysis quantifies (a) the mean square velocity and
 381 (b) the energy distribution across frequencies.

382 The mean square velocity for the 3D μ PTV measurements and 3D sim-
 383 ulation [12] are plotted over the normalized distance to the membrane z/L_z
 384 in Fig. 7 **a)** and **b)**. The mean squares of the in-plane and out-of-plane
 385 velocity components show local maxima at about the same distances to the
 386 membrane of $z/L_z = 0, 0.25$, and 0.75 in the experiment and the simula-
 387 tion. A deviation is identified at the $z/L_z = 0$ and 1 positions that can be
 388 attributed to the ideal boundary conditions of the simulations compared to
 389 the experiments. The maxima positions originate from the vortex generation
 390 close to the membrane leading to the first maximum. The second maximum
 391 in the out-of-plane component marks half the vortex height with mostly ve-
 392 locity towards or away from the membrane. The last local maximum in the
 393 in-plane velocity is located at the average vortex height where the fluid turns
 394 its direction. However, the ratio between the amplitudes of both components
 395 differs between our measurements and the DNS.

396 An explanation for the differences between our measurements and the
 397 DNSs of Druzgalski et al. can be the discrepancy in the electric double layer
 398 thickness by three orders of magnitude, see Tab. 1. The consequence of this
 399 difference is a decreased ESC region and, thus, the appearance of the maxi-
 400 mum in-plane velocities closer to the membrane in the experiments [12]. The
 401 velocities in z -direction are averaged in segments of $38.4 \mu\text{m}$ ($\sim 0.05 \cdot z/L_z$)
 402 length. This averaging always results in values above zero in the planes
 403 next to the membrane and electrode. Compared to DNSs, our experiments
 404 also include electrodes, the membrane, and a second electrolyte chamber,
 405 which influences the electrochemical cell's resistance and chemistry. This
 406 comparison proves that the velocity fields and its statistical mean features
 407 originating in the EC can be successfully extracted at practically relevant
 408 length and time scales.

409 The μ PTV velocity field data is used to calculate the temporal spectra
 410 in planes parallel to the membrane shown in Fig. 7 **b)**. The energy graphs
 411 show similar trends in energy levels compared to the numerical results of
 412 Druzgalski et al. [12] in Fig 7 **e)**.

413 Close to the membrane ($z/L_z = 0.05$ and 0.10), the graphs' slope con-

414 tinuously decreases from small to large frequencies. At $z/L_z = 0.25$, a sim-
 415 ilar energy level is reached in the beginning but shows a more prominent
 416 decrease in slope afterwards. The temporal spectrum closest to the elec-
 417 trode notably start at similar energy levels. Different to the DNSs refer-
 418 ence, the energy follows a linear decrease that can be fitted by a power-law
 419 of $E_{x+y+z, \text{ temporal}} \sim \omega^{-1.44}$ between angular frequencies of $\omega = 2.8 \cdot 10^2$ and
 420 $\omega = 1.3 \cdot 10^4$. Between frequencies of $\omega = 1.3 \cdot 10^4$ and $\omega = 2.1 \cdot 10^4$, fluctuations
 421 appear followed by a decrease in energy. All graphs show a change in slope
 422 above an angular frequency of $\omega = 3.5 \cdot 10^4$.

423 The fluctuations and changes in slope most probably originate from small-
 424 scale noise in the experiments and the measurement error of PTV at small
 425 scales [51].

426 The spectra for planes close to the membrane indicate the dissipation of
 427 kinetic energy across all frequencies without power-law dependencies, as also
 428 reported by Druzgalski et al. for all x,y-planes (Fig. 7 e)) [12].

429 The power-law relation close to the electrode can be explained by the
 430 forces that evoke EC. The body force that generates EC vortices is located
 431 close to the membrane [9]. Therefore, vortices will propagate from the mem-
 432 brane towards the electrode. The shape of the spectra also indicates the
 433 generation of fluctuations of all time scales at the membrane. The fluctu-
 434 ations with small frequencies, e.g. large vortices, could propagate towards
 435 the electrode and dissipate their energy, whereas fluctuations with larger fre-
 436 quencies might not reach the regions close to the electrode.

437
 438 The spatial energy spectra calculated from our experiment's velocity fields
 439 are displayed in Fig 7 c). All graphs follow the same trend at different energy
 440 levels. They show a local maximum at a wavenumber of $k \sim 4.40$. The slope
 441 of the graphs decreases at $k = 22$ with two local maxima above $k = 44$.
 442 These local maxima at high frequencies in the spatial μ PTV energy spectra
 443 can also be linked to small-scale noise and the measurement error of μ PTV
 444 for small scales [51]. The spatial energy spectra reported by Druzgalski et
 445 al. [12] are reproduced in Fig 7 f). Comparable to our experiment, all graphs
 446 show an increase in energy with a maximum at a wavenumber of $k \sim 4$ [12].

447 The peak at a wavenumber $k \sim 4.40$ in the experiment (Fig. 7 c)) cor-
 448 responds to a length of 1.43 times the electrode-to-membrane distance (L_z)
 449 carrying the largest energy. This length of $1.43 \cdot L_z$ matches well with liter-
 450 ature and the diameter of the vortex rings in Fig. 6 b).

451 Due to the time-resolved recording of the velocity field, the evolution of

the EC statistics over the whole experimental time are additionally analyzed in the appendix Appendix C.

4.3. Development of velocity statistics with increasing current density

Figure 8: Development of the mean square velocity, temporal and spatial energy spectra in the overlimiting regime for $4 \cdot i_{lim}$, $6.1 \cdot i_{lim}$, $8.1 \cdot i_{lim}$, and $10.8 \cdot i_{lim}$. The graphs represent an average over 1000 time steps (74.5 s to 124.5 s). The first row shows the development of the mean square of one in-plane and the out-of-plane velocity components over the plane-to-membrane distance from 3D experiments. The second and third row show the development of the temporal and spatial energy spectra, respectively. Note the changing axes for the graphs showing the mean square velocities and the linear zoom on the maxima of the spatial energy spectra.

Fig. 8 shows the mean square velocity, temporal and spatial energy spectra for the experiments at $4 \cdot i_{lim}$, $6.1 \cdot i_{lim}$, $8.1 \cdot i_{lim}$, and $10.8 \cdot i_{lim}$. All graphs have shapes typical for EC as also seen in Fig. 7.

460 The overall mean square velocities increase with an increasing current
461 density, as expected due to the higher energy input. The biggest difference
462 appears between $8.1 \cdot i_{\text{lim}}$ and $10.8 \cdot i_{\text{lim}}$. Here, the sharp maximum in the
463 out-of-plane velocity and the local maximum in the in-plane velocity seen
464 at $8.1 \cdot i_{\text{lim}}$ broaden at $10.8 \cdot i_{\text{lim}}$. Additionally, the local maximum in the
465 in-plane velocity shifts its position from $\sim 0.5 L_z$ to $\sim 0.75 L_z$. This behavior
466 can be explained by the change from the distinct vortex ring pattern into a
467 more chaotic pattern, described in Fig. 4, with vortices that span the whole
468 distance between membrane and electrode as seen in Fig. 6.

469
470 The energy spectra in Fig. 8 also reflect the overall higher velocities with
471 increased energies for temporal and spatial fluctuations with increasing cur-
472 rent densities. Again, the quality of the results at high frequencies in the
473 temporal as well as the spatial energy spectra suffer from small-scale noise
474 and the measurement error of PTV at small scales [51].

475 All temporal energy spectra in Fig. 8 can be partly fitted by a power-
476 law relation which was also seen in Fig. 7 c). The slope of the fitting first
477 increases from $\omega^{-0.68}$ at $4 \cdot i_{\text{lim}}$ to $\omega^{-0.36}$ at $8.1 \cdot i_{\text{lim}}$ and then decreases to
478 $\omega^{-1.39}$ at $10.8 \cdot i_{\text{lim}}$.

479 The graphs at $4 \cdot i_{\text{lim}}$ additionally show a region of constant energy be-
480 tween $\omega = 1 \times 10^3$ and $\omega = 1 \times 10^4$ which is less visible at higher current
481 densities. The reason for this steady section could be the absence of informa-
482 tion on velocities between the vortex rolls, as seen in Fig. 5. The velocities
483 in these regions potentially fluctuate in small length scales and at high fre-
484 quencies.

485 The difference in the temporal energy graphs between $4 \cdot i_{\text{lim}}$ and $6.1 \cdot i_{\text{lim}}$
486 coincides with the structural transition from vortex rolls to vortex rings al-
487 ready seen in Fig. 4. Moreover, the changes between the graphs at $8.1 \cdot i_{\text{lim}}$
488 and $10.8 \cdot i_{\text{lim}}$ match the transition from regular vortex rings to chaotic vor-
489 tex rings shown in Fig. 4.

490
491 In contrast, the shapes of the spatial spectra do not change significantly
492 between current densities. However, the overall energy increases and the
493 maxima emphasised in the linearly scaled inserts change positions from 5.02 k
494 and 4.48 k to 8.95 k and finally to 4.40 k. These maxima positions reflect the
495 changes in structure that were seen in Fig. 4. The correlated diameter of the
496 vortex structures first reduces from $6.1 \cdot i_{\text{lim}}$ to $8.1 \cdot i_{\text{lim}}$ and then increases
497 again at $10.8 \cdot i_{\text{lim}}$. The linearly scaled insert at $10.8 \cdot i_{\text{lim}}$ shows a broader

energy distribution over multiple wavenumbers compared to the graphs at lower current densities. The absence of a sharp maximum indicates that no single dominant length scale exists but a composition of different length scales. This composition is caused by the chaotic change in vortex structure at this large overlimiting current density with the fluctuating size of vortex rings.

Overall, our experiments confirm that large vortices are the dominant actors during EC [12]. The results additionally indicate that an increasing current density seems to have a more considerable impact on the mean square velocities and temporal spectra than on the spatial spectra.

5. Conclusion

We established the first experimental setup for the time-resolved recording of the 3D velocity field during electroconvection (EC) close to a cation-exchange membrane. With this setup, the EC velocity field was recorded in the steady-state at multiples of the overlimiting current density covering length and time scales found in industrial applications inaccessible by current 3D direct numerical simulations (DNSs).

We visualized coherent vortex structures and revealed the change in vortex structure from vortex rolls to vortex rings along the iV -graph. This change in structure is coherent with the findings reported by Demekhin et al. and Kang et al. [11, 32]. Additionally, our method enables evaluating the rotation direction of vortex structures. We found reversed rotation directions between vortex roll pairs and vortex rings, raising the question of the fluid mechanics during the transition from rolls to rings.

The particle tracks in the regime of vortex rings showed the movement of particles on separate orbits. However, possible explanations for this behavior need further physical evidence.

The velocity measurement in the regime of chaotic vortex rings revealed local velocity hot spots between the vortex rings directed towards the membrane. These possibly enable the transport of the cation-rich solution at the electrode towards the membrane. This phenomenon could explain the predicted current density hot spots by 3D DNSs [12].

Further statistical analysis of the velocity field disclosed the nature of energy transfer with a partial power-law behavior in the temporal spectrum. The spatial energy spectrum showed that the length scale carrying the largest

energy is $1.43 \cdot L_z$. These findings showed good agreement of general trends with the reported statistics of Druzgalski et al. for 3D DNSs [12]. Differences were found especially for high frequencies.

Lastly, the evolution of the vortex statistics for increasing limiting current densities was analyzed. The results reveal changes in the mean square velocities and the temporal energy spectra during the transition of EC from vortex rolls over vortex rings to chaotic behavior. The spatial energy spectra showed similar trends for all analyzed current densities. These findings indicated a more significant impact of EC's structural change on the temporal spectra than the spatial spectra.

All in all, the presented results provide a first insight of the fundamental physics of EC at practically relevant length and time scales. The experimental technique also builds a foundation to solve the remaining challenges in future detailed 3D studies. Especially the combination of experimental studies, that cover larger scales, and simulations, that more precisely resolve small scales, could lead to significant progress. Furthermore, the methodology permits studying the impact of membrane surface modifications on the hydrodynamics of EC. These modifications aim to manipulate the 3D vortex build-up and reduce the limiting current plateau with increasing success [52, 38, 53, 54]. Additionally, knowledge of the velocity statistics enables the development of a RANS-like statistically averaged reduced-order model. Such a model will allow for feasibility analysis and optimization of electrically driven membrane processes in the overlimiting regime at a low computational cost. Full comprehension of EC will push the feasibility of desalination processes beyond the limiting current.

559

560 **Appendix A. Integration and refinement**

Fig. A.9 displays a graphical representation of the integration and refinement scheme for the spatial spectra also described by Druzgalski et al. [12]. On the left side (Fig. A.9 **a**), the two yellow circles with a difference in radius of one form the annuli for integration. The wavenumber k increases from the center of the k -space in steps of one. The grey highlighted data points show the selection for the non-refined integration. In Fig. A.9 **b**), a integration scheme with a refinement factor of ten in both directions is displayed. The refined integration results in a smoother graph especially for small wavenumbers by distributing the information in one cell between two

Figure A.9: Graphical representation of the spatial spectra integration and refinement scheme. **a)** Example of the integration for $k = 1$. **b)** Example of the refined integration for $k = 1$. The detail on the right shows the selected fraction of the data point in one original pixel

570 adjacent annuli. The detail on the right shows the selected fraction of the
571 data point.

572 Appendix B. Chronopotentiometry Graphs

Figure B.10: Chronopotentiometry graphs of the experiments at a) $4 \cdot i_{lim}$, b) $6.1 \cdot i_{lim}$, c) $8.1 \cdot i_{lim}$, and d) $10.8 \cdot i_{lim}$. The red area displays the recorded sections.

573 Fig. B.10 shows the chronopotentiometry graphs during the experiments
574 at $4 \cdot i_{lim}$, $6.1 \cdot i_{lim}$, $8.1 \cdot i_{lim}$, and $10.8 \cdot i_{lim}$. The graph in Fig. B.10 a)
575 directly starts at the steady state potential due to the linearly decreased

576 current density prior to the experiment as described in the main document's
577 method section.

578 At current densities of $6.1 \cdot i_{\text{lim}}$ and $8.1 \cdot i_{\text{lim}}$, the graphs (Fig. B.10 b)
579 and d)) show a similar trend. After the calculated transition times of 3.94 s
580 and 2.24 s, the systems resistance increases until EC reaches a steady state.

581 In the experiment at the highest current density of $10.8 \cdot i_{\text{lim}}$ (Fig. B.10 d)),
582 the potential increases over the course of the measurement. This behavior
583 indicates increasing resistance of the system due to chemical changes or gas
584 bubble formation. Both phenomena could originate from possible water dis-
585 sociation at the membrane and the electrodes at this large potentials. The
586 resulting OH^- ions possibly form solid CuO or $\text{Cu}(\text{OH})_2$ scaling at or in-
587 side the membrane [55]. In our experiments, we did not observe any visual
588 changes of neither the membrane nor the electrodes. Excess H^+ and OH^-
589 would form H_2 and O_2 gas bubbles at the electrodes. However, gas bubble
590 formation was only observed for experimental times larger than 500 s.

591 Appendix C. Temporal Development of Chaotic Electroconvec- 592 tion

593 Our set up also allows to analyze the development of the EC velocities,
594 vortex structure, and statistics over time. Fig. C.11 and C.12 show this
595 development for the case of $10.8 \cdot i_{\text{lim}}$ in steps of 20 seconds for the first 120 s
596 of the experiment.

597 The development of the coherent vortex structures is depicted in Fig. C.11.
598 The first coherent structures already build up at 20 s of the experiment ap-
599 pearing as mostly regular vortex rings. The structures grow in diameter over
600 the course of 80 s while loosing their regular size and shape. Up to this stage,
601 the velocity in most centers of coherent structures is directed towards the
602 electrode. The velocity field becomes more chaotic between 100 s and 120 s.
603 In this stage, coherent structures appear in a wide range of shapes and sizes
604 with velocities directed both ways.

605 Fig. C.12 shows the change in one in-plane and the out-of-plane mean
606 square velocities. The distinct velocity profile of EC is not completely build
607 up in the first 20 s. Similar to later stages of EC, the maxima of both velocity
608 components are close to the membrane. However, the out-of-plane velocity
609 is higher than the in-plane component. Both velocity maxima first increase
610 between 20 s to 40 s and decrease to a steady state value thereafter. At this
611 point, the profiles are fully developed.

Figure C.11: Temporal development of the EC vortex structure for $10.8 \cdot i_{lim}$. The top views of the structure of coherent vortices is depicted at **a)** 20 s, **b)** 40 s, **c)** 60 s, **d)** 80 s, **e)** 100 s, and **f)** 120 s of the experiment.

Figure C.12: Temporal development of the mean square velocity, temporal and spatial energy spectra for $10.8 \cdot i_{lim}$. The first row shows the development of the mean square of one in-plane and the out-of-plane velocity components over the plane-to-membrane distance from 3D experiments between 0 s and 120 s. The second and third row show the development of the temporal and spatial energy spectra between 0 s and 120 s, respectively. Note the changing axes for the graphs showing the linear zoom on the maxima of the spatial spectra.

612 The above perceptions reflect in the development of the temporal and
 613 spatial spectra (Fig. C.12). As explained in the previous section, the local
 614 maxima at high frequencies in both the temporal as well as the spatial energy
 615 spectra and the following change in slope originate from small-scale noise and
 616 the measurement error of PTV for small scales [51]. Only slight changes are
 617 visible in the overall shapes of the spectra for both temporal and spatial
 618 analysis. However, some distinct observations can be made. First, the slope
 619 of the temporal spectrum for the plane closest to the electrode ($0.8 \cdot L_z$)
 620 changes between 0 s and 40 s from $\omega^{-0.79}$ to $\omega^{-1.35}$ indicating that the energy
 621 reaching the region closer to the electrode dissipates faster when EC is fully
 622 developed. Second, the energy levels in both spectra increase from 0 s to 20 s
 623 and decrease again after 40 s as already seen in the mean square velocities.
 624 Third, the position of the maxima of the 2D spatial spectra change to smaller
 625 wavenumbers for all planes over time. The maxima positions shift from
 626 $11.6 k$ to $5.8 k$ between 0 s and 100 s as can be seen in the linear zoom of each
 627 spectrum. The shift of the maxima correlates to increasing contributions to
 628 the energy of vortex structures with larger length scales in the respective
 629 planes. The structures with the highest energy share grow from $0.61 \cdot L_z$ to
 630 $1.43 \cdot L_z$ over the course of 80 s. The negligible changes in all graphs confirm
 631 that the experiment was in a statistical steady state after about 40 s.

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649 administration. Michael Schatz: Formal analysis, Investigation, Visualiza-
650 tion. Malte Habermann: Formal analysis, Investigation, Visualization. John
651 Linkhorst: Writing - Review & Editing, Project administration, Supervi-
652 sion. Ali Mani: Interpretation of the data; Writing - Review & Editing .
653 Matthias Wessling: Conceptualization, Resources, Project administration,
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655 **Competing interests**

656 The authors declare that there are no competing interests.

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