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Investigating the coupled influence of flow fields and porous electrodes on redox flow battery performance

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HIGHLIGHTS

• Coupled influence of electrodes and flow field geometries on reactor performance.
• Woven electrodes perform best with flow through geometries.
• Non-woven electrodes perform best with interdigitated designs.
• Flow fields and electrodes must be designed in tandem.

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ABSTRACT

At the core of redox flow reactors, the design of the flow field geometry—which distributes the liquid electrolyte through the porous electrodes—and the porous electrode microstructure—which provides surfaces for electrochemical reactions—determines the performance of the system. To date, these two components have been engineered in isolation and their interdependence, although critical, is largely overlooked. Here, we systematically investigate the interaction between state-of-the-art electrode microstructures (a paper and a cloth) and prevailing flow field geometries (flow through, serpentine and four variations of interdigitated). We employ a suite of microscopic, fluid dynamics, and electrochemical diagnostics to elucidate structure-property-performance relationships. We find that interdigitated flow fields in combination with paper electrodes—which features a uniform microstructure with unimodal pore size distribution—and flow-through configurations combined with cloth electrodes—which have a hierarchical microstructure with bimodal pore size distribution—provide the most favorable trade-off between hydraulic and electrochemical performance. Our analysis evidences the importance of carrying out the co-design of flow fields and electrode microstructures in tandem.

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1. Introduction

In the ongoing transition to a sustainable energy economy, electrochemical energy storage is poised to play a pivotal role in the integration of the growing supply of intermittent renewable energy into the electric power system [1]. Redox flow batteries (RFBs) are a promising technological option for multi-hour and large-scale energy storage that can potentially satisfy cost requirements [2,3]. RFBs are rechargeable batteries consisting of the electrochemical stack (determining the power output) and the electrolyte tanks (determining the energy capacity). The electrolyte solutions, containing dissolved or suspended redox active couples in the anolyte and catholyte, are pumped through the electrochemical stack where the chemical energy and electrical energy are interconverted, charging and discharging the battery system [4–7]. The unique architecture of RFBs provides a set of advantages, the most notable being the ability to decouple power and energy, providing opportunities for economic upscaling, intrinsic safety, and high roundtrip efficiency. Despite of their promise, RFBs still confront barriers in market penetration and widespread implementation [8].

To increase cost competitiveness, research efforts have targeted the design of new electrolytes [8,9], high performance materials [10–13], and alternative electrochemical reactor concepts [14–17]. One effective strategy to lower costs is to increase the overall efficiency of the electrochemical cell, which can be achieved by enhancing the electrochemical performance and reducing the pumping power required to sustain the flow of electrolyte through the system. Increasing the power density of the electrochemical cell reduces the capital costs (i.e. more compact stacks for a given power output) and the overall leveled costs for low to medium discharge durations. At the core of the electrochemical cell, the flow field geometry, typically imprinted into the bipolar plate, determines the electrolyte distribution, electrode utilization, and pressure drop. From the flow field channels, the electrolyte enters the porous electrode which provides the surface area for electrochemical reactions, governing the overall cell performance through kinetic and mass transfer overpotentials. Furthermore, the physical interaction between the flow field geometry and the porous electrode is critical to the cell performance, as it determines the electronic contact resistance, compression distribution, electrolyte permeation, and pressure drop. Popular strategies to enhance cell performance include the development of high performing electrode materials [18], engineering of flow field designs, and regulating the operating conditions (i.e., flow rate, state of charge and temperature) [19]. Additionally, pressure loss through the cells can be reduced by optimizing the electrode microstructure, flow distributors, and manifolds [16,20–22]. Taken together, the flow field and porous electrode microstructure determine the electrochemical and hydraulic performance, but their interdependence has not been clearly elucidated to date. A deeper level of fundamental understanding and systematic analysis is needed to enable the bottom-up design of advanced electrochemical reactors.

Drawing inspiration from low temperature fuel cells, current flow battery constructs leverage flow-through, interdigitated and serpentine flow field designs [23]. However, while functional, these designs have not been tailored for the specific requirements of RFBs (e.g. pumping viscous electrolytes, single-phase flows). Latha et al. [24], Milstein et al. [25] and Messaggi et al. [26] among other groups, performed experimental and numerical studies on various flow field designs such as parallel, interdigitated and serpentine geometries. In general, there is consensus that flow by (parallel) flow field provides the lowest cell performance due to its limited convective contribution. However, disparate findings are reported for interdigitated and serpentine flow designs, and it remains unclear which flow field geometries are best suited for redox flow cells. Other groups have also demonstrated outstanding electrochemical performance when combining woven electrodes with flow-through flow fields [27]. Additional efforts have targeted the optimization of the geometric dimensions of the basic flow fields described above. Ali et al. [28] and Wei et al. [29] leveraged serpentine patterns with varying number of flow channels as a strategy to increase cell performance. They found that these modified flow field designs provide a more uniform distribution of electrolyte and that the electrolyte disturbance and flow resistance can be reduced when the number of flow channels increases. Additionally, Latha et al. [24] and Gerhardt et al. [30] studied the influence of the channel and rib dimensions in serpentine and interdigitated flow fields. They demonstrated the beneficial impact on the performance of the under-the-rib convection that takes place in geometrical patterns with wide ribs, while having a detrimental impact on the pressure drop. Recently, Sun et al. [31] investigated the influence of rib dimensions in serpentine flow fields on the convective transport under-the-rib. They showed that these modifications can enhance the uniformity in electrolyte penetration and enable higher limiting currents and energy efficiencies. Moreover, Zeng et al. [32] demonstrated the versatility of hierarchical designs to minimize pumping losses and increase the overall voltage efficiency. They proposed a two-level interdigitated flow field that enhances mass transport in the electrode and decreases the hydraulic resistance under the ribs. Despite all these meaningful advances, in all the previous studies the flow fields were not tested using a common electrode material (e.g. carbon felt, paper or cloth), leading to disparity in the scientific literature, which challenges quantitative comparisons.

Next to the impact of the flow field geometry, the properties of the porous electrode, namely its surface chemistry and microstructure, govern the flow battery performance [33]. While the surface properties of the electrode determine the reaction kinetics and activation overpotentials [34], the three-dimensional structure of the electrode (here referred to as electrode microstructure) is responsible for distributing the electrolyte at low pressure drop, providing the surfaces for electrochemical reactions, delivering mass to and from the electrode surface, and conducting electrons and heat through the solid network. Thus, the electrode microstructure –defined by the pore size distribution, porosity, pore morphology, anisotropy ratio and fiber alignment- plays a major role in determining the flow cell performance [23,35–39]. For example, we and others revealed the role of the electrode microstructures on the electrochemical performance and resulting pressure drop, by studying several carbon papers, cloth and felt electrodes [27,40,41]. It was found that woven electrodes with bimodal pore size distributions provide a favorable balance of electrochemical performance and pressure drop [27]. Tenny et al. [42] and Wong et al. [43] compared physical and electrochemical properties of various woven electrodes with different weave patterns. The understanding of structure-performance relationships of existing commercial fibrous electrodes has motivated the exploration of alternative synthetic approaches to manufacture electrode microstructures with bimodal pore size distributions and controlled pore diameters and shapes. For example, non-solvent induced phase separation has been recently introduced to manufacture electrodes with tunable microstructures, resulting in improved electrochemical performance [11,44]. While others, like, Sun et al. [37], have explored the bottom-up design of a novel electrode based on microscale-aligned fibers interwoven with porous carbon nanofibers. In this context, emerging computational approaches such as pore network modeling [45,46] and topology optimization [47] can aid and accelerate the design of optimized porous electrodes. Despite the major progress has been made on understanding and engineering electrode microstructures, most of these studies have been conducted using a specific flow field configuration (e.g. flow through), which limits their scope to only one type of flow field geometry and might not be representative of more realistic designs for industrial applications.

Current redox flow cell architectures integrate flow field geometries and electrodes which have selected and engineered in isolation; however, the interdependence between these two components, although critical for the cell performance, remains largely overlooked. The coupled influence between flow fields and electrode has multiple effects in battery performance metrics, affecting the wetted area of the electrode (which determines the accessible surface area), the velocity
distribution of the electrolyte, the electronic contact resistance, the pressure drop, and the mass transfer rates. The lack of knowledge in the electrode-flow field interplay hamper engineering advances in electrochemical reactors due to: (1) the disparity of electrode materials used previously in literature to compare flow field geometries and (2) limitations in performance improvements driven by the engineering of one of the elements in isolation. Furthermore, the lack of standardized testing protocols in flow batteries (e.g. different groups use different electrode materials for comparison) and the use of volumetric flow rate comparisons that do not account for variations in the flow field geometric area challenges our understanding of the coupled influence of flow field geometries and porous electrodes in the battery performance. Pursuant to this need, we are poised to answer the following question: What are the best performing combinations of flow fields and electrode microstructures in redox flow batteries?

In this work, we systematically evaluate the interaction between prevailing flow field geometries – a flow-through, four types of interdigitated and a serpentine (Table 1 and Fig. 1) – and porous electrode microstructures – a Freudenberg carbon paper and an ELAT carbon cloth. Despite graphite felts have historically been the preferred electrode material, in this work, we choose to study thin electrode materials such as carbon paper and cloth, motivated by the recent advances in electrode material and functional groups, measurement technique, supporting electrolyte and concentration of active species, can make their kinetics difficult to compare, encountering similar reaction rate constant as that of vanadium redox couples in some cases [48-53]. For reference, kinetic rate constants in the range of 1.84 × 10⁻⁵ – 1.0 × 10⁻³ cm s⁻¹ have been obtained for Fe³⁺/Fe²⁺ in acidic electrolytes on glassy carbon and pyrolytic graphite [48,51] and within 1.0 × 10⁻⁶ – 1.1 × 10⁻³ cm s⁻¹ for V²⁺/V³⁺ and VO²⁺/VO³⁺ in acidic electrolyte on glassy carbon, carbon felt and carbon paper [51,52,54]. Driven by the enhanced kinetic rates (in the order of 10⁻³ cm s⁻¹) reported in literature [48,55], in this work we elect to use an electrolyte based on Fe²⁺/Fe³⁺ in hydrochloric acid (HCl) and thermally treated electrodes [56]. The choice of this electrolyte enables the deconvolution of kinetics and mass transfer resistances, which is well suited for assessing the effect of flow field geometries on the accessible electrode area and mass transfer overpotentials. A suite of electrochemical impedance

<table>
<thead>
<tr>
<th>FF name</th>
<th>N</th>
<th>Channel width [mm]</th>
<th>Rib width [mm]</th>
<th>Channel contact area [mm²]</th>
<th>Exchange perimeter [mm]</th>
<th>Electrolyte velocity (vₑ) calculation</th>
<th>Required flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow-through</td>
<td>1</td>
<td>1</td>
<td>14</td>
<td>–</td>
<td>–</td>
<td>Q</td>
<td>Q</td>
</tr>
<tr>
<td>Serpentine</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>116</td>
<td>–</td>
<td>Q</td>
<td>0.096 Q</td>
</tr>
<tr>
<td>Light ID</td>
<td>5</td>
<td>1.5</td>
<td>1.5</td>
<td>112.5</td>
<td>69</td>
<td>Q</td>
<td>4.9 Q</td>
</tr>
<tr>
<td>ID</td>
<td>7</td>
<td>1</td>
<td>1</td>
<td>105</td>
<td>90</td>
<td>(\frac{Q}{N-1}tₑ)</td>
<td>7.4 Q</td>
</tr>
<tr>
<td>Dense ID</td>
<td>13</td>
<td>0.5</td>
<td>0.5</td>
<td>97.5</td>
<td>189</td>
<td>(\frac{Q}{N-1}tₑ)</td>
<td>14.8 Q</td>
</tr>
<tr>
<td>Wide-rib ID</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>75</td>
<td>66</td>
<td>(\frac{Q}{N-1}tₑ)</td>
<td>4.9 Q</td>
</tr>
</tbody>
</table>

Fig. 1. Geometrical designs of the different flow fields used in this study. (a) flow-through; (b) serpentine; and four versions of interdigitated (ID): (c) light interdigitated; (d) basic interdigitated; (e) dense interdigitated; (f) wide-rib interdigitated. Their geometrical parameters are listed in Table 1.
spectroscopy (EIS) and polarization measurements was used to quantify their electrochemical performance and resulting overpotentials. Finally, by coupling the pressure drop and the electrochemical results, we compare the pumping power required for different electrochemical performances and provide recommendations for electrode-flow field configurations. While this study focuses on aqueous electrolytes, the provided guidelines can be applied to other RFB chemistries and evidences the importance of co-designing flow fields and electrodes in electrochemical flow reactors.

2. Experimental

2.1. Electrode materials

Two different commercial electrodes were investigated: Freudenberg H23 carbon paper (Fuel Cell Store) and ELAT carbon cloth (Fuel Cell Store), hereafter referred to as paper and cloth, respectively. Their uncompressed thickness is listed in Table 2. The electrodes were pre-treated by thermal oxidation at 450 °C for 12 h to increase the hydrophilicity of the electrode and ensure electrolyte infiltration into the pores [56].

2.2. Flow field designs

The six studied flow fields, i.e. Flow-through, Serpentine, light interdigitated (Light ID), basic interdigitated (ID), dense interdigitated (Dense ID), and wide-rb interdigitated (Wide-rb ID), were designed in Autodesk Inventor and milled in graphite (G347B Plate, MWI). In Fig. 1 the top view of all flow fields are presented, with the electrolyte inlets and outlets located at the bottom and top, respectively. In Table 1, their specific dimensions are listed, such as channel length, channel contact area and exchange perimeter. All channels have a depth of 0.5 mm. In this study we elect to focus on the impact of flow field geometry and kept all channel depth as a fixed parameter. Although the channel depth might have an influence on performance at high current densities [54], previous studies have shown that the impact of the channel depth on the flow cell performance is minimal due to its negligible effects on the electrolyte distribution and velocity in the electrode [55,56]. However, channel depth optimization is a good strategy to minimize pressure drop through the cell [30], but this investigation is beyond the scope of this work. The comparison among flow fields was elected to be done at same electrolyte velocity in the electrode, aiming to isolate the impact of flow field geometry. While for interdigitated and flow-through flow fields, the electrolyte velocity in the electrode can be calculated directly from the geometrical properties, for the Serpentine design the electrolyte velocity was determined in accordance with Messaggi et al. [26] to be 4% of the inlet velocity in the channel.

2.3. X-ray tomography

The paper and cloth electrode microstructures were obtained with X-ray tomographic microscopy (XTM) in a GE Nanotom scanner (GE Inspection Technologies) with a voxel edge length of 1.8 μm. The electrode compression was set to 20%, using a cylindrical sample holder of polyether ether ketone (PEEK) with a fine pitch thread [57]. The samples were scanned using a peak voltage of 60 kV and a current of 240 μA. Each scan took a total time of 1.6 h with a 500 ms exposure averaged over 5 frames per projection angle, for a total of 1900 projections. The X-ray tomography dataset presented here was obtained with the same parameters as in our previous publication [58].

The XTMs were post-processed with the image processing software Fiji ImageJ [59]. To prevent boundary effects and obtain a homogeneious image, a sub volume (1.53 mm × 1.53 mm width and depth) was selected from the center of the processed images. Finally, the first and last few slices in the through plane dimension were removed from the image stack to exclude segmentation artefacts caused by the compression setup to artificially reduce the porosity at the electrode interfaces. 2D cross sections of each electrode in the XY, XZ and YZ planes were extracted from the center of the samples. The pore size distribution (PSD) was obtained using the PSD plugin in Fiji ImageJ [60] for the entire 3D stack of images with a bigger sample size (2.7 mm × 2.7 mm). 3D visualization of the microstructure was done using the visualization software ParaView.

2.4. Pressure drop measurements

The pressure drop through the different combinations of flow field geometries and electrodes was measured in a custom flow cell setup (see Fig. S1). To obtain representative data under realistic operating conditions, the pressure drop cell is composed of the same elements as the electrochemical flow cell, except that the membrane is replaced by a dense aluminum plate to ensure that the electrolyte flows only through the flow field and porous electrode. To determine the specific electrode—flow field pressure drop, the fluid was pumped through the cell at different flow rates calculated according to the desired electrolyte velocity in the electrode (0.5–8 cm s⁻¹), and the pressure was measured at the inlet and outlet of the cell. Digital pressure gauges were used for the inlet and outlet pressure measurement (Stauff® SPG-DIGI-USB). For simplicity, experiments were performed using water as both fluids feature similar viscosities and surface tensions and therefore wetting properties due to the low electrolyte concentration [63]. The pressure drop per unit length of electrode was correlated to the electrolyte velocity using the Darcy-Forchheimer equation [62], which allows to fit the permeability accounting for inertial effects

$$\frac{\Delta P}{L} = \frac{\mu}{k} + \beta \rho v^2$$

(1)

where the ratio $\mu/k$ represents the hydraulic resistance ($R_h$, kg m⁻³ s⁻¹), $k$ is the apparent permeability (m²) and $\beta$ the apparent Forchheimer coefficient (m⁻³). The quasi-1D advection implied by this law can be a limitation for interdigitated flow fields and may not be reliable for getting hydraulic information about the electrode in an isolated form. However, since we assumed the electrode—flow field as a single pack, the relationship can be applied to estimate the pressure loss and fluid velocity relationship for each specific system.

To deconvolute the individual contributions of the flow field and the electrode to the overall pressure drop, we also measured the pressure drop of an empty cell with the different flow field configurations, where we used an incompressible Teflon gasket of 160 and 315 μm, for paper and cloth electrode, respectively, to approximate for the equivalent volume that would be occupied by the electrode material. To estimate the electrode contribution, we subtracted the empty cell pressure drop from the measurement including both the electrodes and the flow fields. All experiments were performed in duplo.

2.5. Flow cell experiments

Electrochemical experiments were performed in a single electrolyte flow cell configuration (Fig. 2a) to isolate the influence of the electrode-
flow field interactions [63,64]. This diagnostic platform enables operation under constant state of charge and secondary effects such as membrane crossover do not convolute the results as the electrolyte of both compartments is mixed in the tank. Thus, this configuration is well suited to study the effects of cell components (e.g. electrodes, flow fields) in a systematic fashion. The flow cell is composed of two half-cells separated by a Nafion 212 membrane (Fuel Cell Store, thickness ~50.8 μm). Each compartment contains one porous electrode (geometric area: 2.55 cm², 1.7 cm × 1.5 cm) and one flow field which also acts as current collector. The membrane was pre-treated by immersion in 2 M HCl for 3 days. Each porous electrode is sandwiched in their half-cell between the flow field and the membrane using incompressible Teflon gaskets to ensure leak-free operation, reduce contact resistance between electrically connected components, and define the cross-sectional area for fluid flow. The thickness of the Teflon gaskets was chosen to set the electrode compression to 20%. To control the compression, the four bolts of the cell were tightened with a torque-controlled screwdriver to 2 N m. The kinetically facile redox couple Fe²⁺/Fe³⁺ was used as electrolyte (at 50% state of charge) with a composition of 0.1 M ferrous chloride hydrate (FeCl₂ · 4H₂O, 98%, Sigma-Aldrich) and 0.1 M ferric chloride hydrate (FeCl₃ · 6H₂O, 97%, Sigma-Aldrich) in 2.0 M hydrochloric acid (37% w/w HCl diluted in deionized water) at ambient temperature.

A Biologic VMP3 potentiostat was used for the electrochemical diagnostics. For all electrode—flow field configurations the same procedure was followed. First, the pump was calibrated with the 2 M HCl supporting electrolyte at 5 cm s⁻¹. The capacitance measurements were carried out while halting the electrolyte flow by performing cyclic voltammetry at different scan rates (see Section S4). After the capacitance measurement, the electrolyte was pumped out of the system and the actual iron electrolyte was filled into it. Before data collection, the electrochemical cell was preconditioned by pumping electrolyte for 30 min at a velocity of 5 cm s⁻¹ while applying voltage steps of 25 mV up to 0.2 V. The voltage sweep was repeated three times after which stable conditions for the electrochemical response were reached. Once the system was stabilized, the flow rate was set according to the desired electrolyte velocity (Table 2) and the polarization and electrochemical impedance spectroscopy protocol were performed.

Polarization measurements were carried out by potentiostatic holds of 1 min at constant voltage steps of 20 mV during which the steady-state current was measured at a rate of one point per second. For further analysis only the average over the last 20 s was used. Since the cell is operated with a single-electrolyte configuration, the same electrode reaction occurs in both half-cells but in opposite directions. As a result, the open circuit voltage is zero, and the applied potential corresponds to the overpotential of the cell (representing the ohmic, kinetic and transport resistances). The polarization curves (Fig. 2b) are represented based on the iR-corrected potential which refers to the potential applied to the cell subtracting the ohmic overpotential losses [27]. Thus, the iR-corrected potential shown in the polarization plots represent the summation of charge and mass transfer overpotential losses. The polarization and impedance sequences were recorded at five different superficial velocities (0.5, 1.5, 3.5, 5, 7.5 and 10 cm s⁻¹) starting from the lowest, as observed in Fig. 2b and c. As can be seen, no measurements were performed below 10 cm s⁻¹, since no appreciable performance differences were observable at this point. All experiments were repeated twice and the current values were averaged. The reproducibility of the measurements setup was verified as shown in Fig. S2.

Electrochemical impedance spectroscopy was carried out at open circuit voltage (OCV), with an amplitude of 10 mV over a frequency range from 10 kHz to 30 mHz with 6 points per decade, 3 measurements per frequency, and a waiting time of 0.1 period before each frequency. In Fig. 2c, Nyquist plots are presented and used for the analysis of the ohmic, kinetic and mass transfer resistances. The ohmic resistance of each cell was obtained from the high-frequency intercept with the real axis, which accounts for the contact, membrane, electrolyte and solid phase electronic resistances. Since the charge and mass transfer resistances are complex to deconvolute, an equivalent circuit model [65, 66] was used to fit the averaged values of two repetitions of each experiment. The model consists of an inductor (L) to account for the lead inductance, in series with an ohmic resistor (R₀), as well as a constant-phase element (CPE), which accounts for the non-ideal capacitive effects of porous electrodes [67], in parallel with a charge transfer resistor (RₚT), in series with a second constant-phase element (CPE) in parallel with a mass transfer resistor (RₘT) to account for the diffusive effects of species.

Fig. 2. Methodology for the electrochemical characterization used in this work. (a) Diagram of the single electrolyte flow cell setup. Example of impedance and cell polarization experiments at different superficial velocities in the electrode for the combination of ID flow field and Freudenberg paper: (b) polarization measurements and (c) Nyquist plots together with the equivalent circuit used for the fittings.
3. Results and discussion

3.1. Electrode microstructures and surface area

The spatial arrangement of the carbon fibers determines the electrode microstructure, which dictates important performance metrics such as pressure drop, available surface area, and mass transfer resistance in the electrochemical cell. Thus, we first perform X-ray tomographic microscopy of paper and cloth electrodes to analyze their microstructure in detail. In the manufacturing process of the Freudenberg paper the fibers are arranged together by a hydroentangling process driven by water jets, enabling a binder-free and mechanically robust mat [27]. In the cloth material, the carbon fibers are grouped into threads that conform a periodic structure in two spatial dimensions (in-plane following a weave pattern) and a third spatial dimension (through-plane) [42, 68, 69]. In this work, we elect to name through-plane to the direction perpendicular to the membrane plane (XY cross sectional views) and in-plane to the direction parallel to the membrane plane (XZ and YZ cross sectional views). The 3D renderings of both electrode microstructures obtained from X-ray tomographies (Fig. 3a) are shown together with the cross sections taken from the center of the sample along the different planes (Fig. 3b). In order to complement the visual analysis, we computed the pore size distributions and the cumulative pore volume (Fig. 3c). All three XY, XZ and YZ planes for the paper electrode reveal a unimodal PSD with similar fiber distributions along all spatial directions, with pore sizes below 30 μm, and a dominant peak at 5 μm obtained from the PSD calculations. Although the paper electrode is known as a non-woven material, the use of water jets during the hydroentangling process results in preferential alignment as observed in the XY-plane radiograph (Fig. 3b). The cloth electrode, unlike those of the paper, shows a broader distribution of pore sizes, in the range of 0–90 μm. The cross-sectional views reveal pore sizes on two different scales in a hierarchically ordered microstructure with larger voids (~60–80 μm) corresponding to the intersection between fiber bundles and smaller pores (~5 μm) corresponding to the inner space among individual fiber threads. The PSDs of both paper and cloth show comparatively smaller pore sizes in comparison with previous studies [27, 45, 63], which we attribute to the 20% electrode compression applied in our experiments in comparison to the non-compressed electrodes previously analyzed. Despite the bimodal pore size distribution of the cloth in the in-plane cross sections at x2 and y2 (threads intersection), previously demonstrated in experimental PSD measurements using mercury intrusion porosimetry [27, 42], the PSD calculations reveals a broad range of pore sizes. The discrepancies in the experimentally determined and computed PSDs, also noted in previous studies [63], can be explained by the fundamental differences between the physical

Fig. 3. Microstructural characteristics of paper (left) and cloth (right): (a) 3D rendering of X-ray tomography images, (b) cross-sectional views XY, YZ and XZ taken from the center of the sample (x1 and y1) and additional sections for cloth in the bundles intersection (x2 and y2), (c) PSDs calculated with ImageJ – PSD continuous. The normalized volume on the left axis is defined as the ratio between the volume occupied for a certain pore size and the total volume occupied by all pores. The cumulative volume on the right axis is also normalized within the total volume occupied by all pores. Same geometrical volume is taken for both 3D representations. The XY plane corresponds to through-plane views (perpendicular to the membrane), while the YZ and XZ planes to in-plane views (parallel to the membrane).
assumptions made with both methods. For example, the algorithm used to process the tomographic data estimates pore size distributions by maximizing the volume of spheres to fill the pore volume. On the contrary, mercury intrusion used in experimental measurements uses liquid mercury and extracts pore size from penetration pressures and the assumption of perfect cylinders. In Section S3, additional in-plane and through-plane visualizations of the cloth electrode are shown (Figs. S3 and S4). Another notable structural difference between the paper and cloth electrodes is the pore morphology, which for the carbon cloth is observed to be more ellipsoidal, similar to other studies that have reported this pattern for hierarchical porous materials [70].

As reported in Table 1, the different microstructural characteristics lead to diverse intra-electrode properties which will interact differently with the velocity field induced by every flow field geometry. In particular, electrode microstructures with hierarchical and bimodal pore size distributions (i.e., cloth) might benefit from a better electrolyte distribution if the flow configuration induced by the flow field enables the electrolyte to access large pores by convection and smaller pores by diffusion. The paper electrode features lower porosity (67.7%) than the cloth electrode (76.6%), which is calculated from the XTM. Determination of available surface area is unreliable from tomographic data given the limited spatial resolution (3.3 μm/voxel). To quantify the electrochemically active surface area (ECSA), we perform electrochemical double layer capacitance (EDLC) measurements in a flow cell setup. We find that the specific surface area of the cloth electrode (6.24 ± 0.05 × 10³ m² m⁻³) is significantly lower than that of the paper (12.3 ± 0.7 × 10³ m² m⁻³), which aligns well with previous studies in the literature at similar compression rates [27, 42]. We anticipate that the lower porosity and overall narrower pore size of the carbon paper will increase the flow penetration resistance into the electrode. Besides, the lower surface area of the cloth might have an impact on kinetic over-potentials as will be discussed in a following section. Future work should focus on increasing the available surface area in woven electrodes by functionalization techniques [48, 71, 72], however, this is beyond the scope of this work.

### 3.2. Hydraulic resistance

The hydraulic resistance of the system determines the pressure drop and, consequently, the pumping power required to sustain a given electrolyte flow rate. To maximize the overall system efficiency, the pressure loss can be reduced by engineering the electrolyte, electrode and flow field configuration. To assess the hydraulic resistance, we systematically determine the pressure drop for all electrode-flow field combinations as a function of the electrolyte velocity, as shown in Fig. 4a and b. In general, we find stark differences between the pressure drop relationships for both electrodes, as anticipated from their distinct microstructural features.

When using the paper electrode, we find that interdigitated flow field designs result in lower overall pressure loss in comparison with flow-through flow fields. In contrast, the cloth electrode in combination with flow field patterns with higher contribution of in-plane electrolyte flow, such as Flow-through, present lower pressure drops (~2 MPa m⁻¹ at vₑ ≈ 8 cm s⁻¹) than with paper (~13.5 MPa m⁻¹ at vₑ ≈ 8 cm s⁻¹). We hypothesize that the unimodal microstructure and isotropic properties of the paper electrode, featuring similar in-plane and through-plane permeabilities [73], can explain that interdigitated flow fields reduce the pressure loss, as the electrolyte flows through shorter distances.

![Fig. 4. Pressure drop measurements normalized by the total electrode length (17 mm) as a function of the electrolyte velocity in the electrode for (a) paper and (b) cloth together with Darcy-Forchheimer fittings. Apparent permeability and Forchheimer coefficients for every flow field in combination with (c) paper and (d) cloth obtained from the fittings of the pressure drop measurements to Darcy-Forchheimer equation.](image-url)
within the electrode structure. On the contrary, the cloth electrodes feature a unique multiscale microstructure with large through-plane voids (i.e. intersection of threads) and smaller pores within individual threads. We posit that the use of flow-through flow fields facilitates electrolyte flow in the direction of the aligned fiber threads, which feature lower tortuosity. For this reason, interdigitated flow field designs in combination with woven electrodes forces the fluid to flow across the fiber threads, where average pore diameters are smaller than in the paper (see Fig. 3), resulting in a lower permeability in the through-plane direction. Therefore, the higher the density of channels, the more the electrolyte is forced to flow in the through-plane direction, and the higher is the resulting pressure loss. This hypothesis is further supported by the Light ID and Wide-rib ID results. In the first case, Light ID has wider channels which intersect with both small and large pores in the XY plane of cloth, leading to preferential paths across the large pores with low tortuosity and pressure drop. In the latter case, Wide-rib ID, the small number of channels, and wider ribs, induces a higher in-plane flow (similar to a flow-through design), reducing the pressure drop across the cloth. Moreover, in comparison with the paper, interdigitated flow fields feature a higher pressure drop not only because of the small pore size between the fibers in the bundles, but also because the larger thickness of the cloth requires a higher flow rate to sustain the same electrolyte velocity in the electrode (i.e. for \( v_1 \approx 5 \text{ cm s}^{-1} \)), the cloth requires 46 mL min\(^{-1} \) while paper 91 mL min\(^{-1} \) with the ID flow field).

Among the different interdigitated flow fields, designs with high channel densities result in increased hydraulic resistance in combination with both types of electrodes. Moreover, these pressure losses are found to be significantly influenced by the pressure drop in the channels and not only in the electrode (see Fig. S7). To further investigate this, in Fig. 4c and d, the apparent permeability obtained from Darcy-Forchheimer fittings is presented together with the Forchheimer coefficient. With this analysis, these parameters represent a macroscopic, averaged property instead of capturing specific elements of a permeability tensor. With both electrodes, the ID and Dense ID flow fields feature the highest hydraulic resistance, mainly due to the large contribution of flow channels to the overall pressure drop. When using the cloth electrode, this effect is exacerbated with the additional drawback of the lower permeability in the through-plane direction, where the flow is forced to cross the fiber bundles. For all flow field geometries except the Dense ID, combinations with the cloth electrode result in higher apparent permeabilities than with paper electrodes as expected due to the larger pore sizes. Using the Flow-through flow field, we can assume that the electrode primarily determines the apparent permeability. This analysis shows that the paper electrodes feature an order of magnitude lower permeability than the cloth electrode, and these values are comparable to those reported in the literature [43, 73].

More specifically, the apparent permeability obtained in this work for the Flow through - paper combination is \( \approx 0.7 \times 10^{-11} \text{ m}^2 \), while for the Flow through - cloth combination is \( \approx 7 \times 10^{-11} \text{ m}^2 \). This again supports our hypothesis of the presence of preferential paths through the largest pores evading the small spaces between fibres in the bundles. In the case of the paper, there are no dominant preferential paths due to the more homogeneous microstructure, resulting in almost six times lower permeabilities than with the cloth.

The analysis of apparent Forchheimer coefficients is valuable to quantify the non-linear effects (e.g. inertial effects) in porous media flow that can appear in the flow field configurations and electrode domains with different degrees of heterogeneity [74]. In general, interdigitated flow fields present the highest apparent Forchheimer coefficient; in particular, the Dense ID induces more flow perpendicularly to the electrode layer, resulting in \( \beta \approx 0.8 \times 10^{-6} \text{ m}^{-1} \) for the paper electrode and \( \beta \approx 3.2 \times 10^{-6} \text{ m}^{-1} \) for the cloth electrode. The Forchheimer coefficient depends on the properties of the porous medium such as porosity, tortuosity and permeability (i.e., heterogeneity parameters) [75]. This explains why the inertial effects for the cloth are, in general, four times higher than for the paper.

3.3. Electrochemical performance of the paper electrode with different flow fields

After assessing the morphological properties of each electrode and the resulting hydraulic resistances, we then characterize the electrochemical performance and resistive losses of all electrode-flow field combinations. First, we analyze the performance of the paper electrode in combination with the six different flow fields using the single electrolyte flow cell configuration. Electrochemical impedance spectroscopy and polarization results were obtained under steady-state conditions at constant 50% SOC for five different superficial velocities (Fig. 5 and Fig. S8). The crucial role of the electrolyte flow rate on the performance has been shown before in several previous reports [25, 63, 76, 77]. Here we elect to compare two characteristic electrolyte velocities, i.e. 0.5 and 3.5 cm s\(^{-1}\), to assess two distinct operation intervals. Extended data at multiple electrolyte velocities can be found in Fig. S8. At the lower velocity, reactant depletion induces operation under mass transfer limited conditions. At higher velocities, faster electrolyte replenishment and advective mass transport favors operation in the charge transfer limited regime.

iR\(_{\text{e}}\)-corrected polarization measurements are compared at 0.5 cm s\(^{-1}\) electrolyte velocity to study the effects of mass transfer losses on the electrode-flow field selection (Fig. 5a). Due to the similar ohmic resistance of configurations with paper and cloth materials (Tables S4a–e and Tables S5a–e), the ohmic losses are subtracted for better understanding of the mass and charge transfer overpotential losses represented by the iR\(_{\text{e}}\)-corrected polarization curves. When comparing at low velocity, special attention must be paid since the required inlet flow rate is different depending on the flow field geometry (Table 1) and not all configurations will reach mass transfer limitations. At high current density, reactant depletion takes place, and the limiting current density is reached in some cases. In microstructures with near unimodal pore size distribution, as that of the Freudenberg carbon paper, the similar permeability in the in-plane and through-plane directions might have a more nuanced impact on the interaction with the geometrical flow pattern, while the characteristics of the geometrical pattern (e.g., exchange perimeter, channel-contact area and rib width) might have more notable effects on system performance. Flow cells with Flow-through and Serpentine flow fields feature the highest overpotentials in the series. As a consequence of their single inlet and outlet and the low flow rate required in these designs (Table 1), when operating at low velocities, the reactant is depleted before reaching the outlet, limiting the electrochemical reaction in the downstream region of the cell. The Light ID and the Wide-rib ID have five interdigitated channels (3 inlets and 2 outlets), which provides a better distribution and replenishment of the species at the electrode surface, leading to lower mass transfer resistances. An additional reason that causes the Light ID flow field to underperform in comparison with the Wide-rib ID flow field is that the former has wider channels and thinner ribs, which provides less under-the-rib convection and therefore less utilization of electrode reaction volume. Like the other interdigitated patterns, ID (7 channels) and Dense ID (13 channels) are more effective in distributing the electrolyte with 4 and 7 inlets, respectively, leading to enhanced species mass transfer. When comparing at the same electrolyte velocity, the geometry of the specific flow field under consideration directly affects the residence time of the fluid in the porous media. In this sense, we hypothesize that design patterns that force the electrolyte to reside longer within the porous medium without replenishment will lead to stronger reactant depletion and therefore lower limiting mass transfer rates.

At higher superficial velocities, i.e. 3.5 cm s\(^{-1}\) (Fig. 5b), the flow advection is enhanced and the performance of all paper-flow field systems is improved. A surprising behavior is observed for the Wide-rib ID flow field, which outperforms the regular ID flow fields and comes close to the Dense ID (~346 mA cm\(^{-2}\) for Wide-rib ID and ~374 mA cm\(^{-2}\) for Dense ID at 40 mV of iR\(_{\text{e}}\)-corrected potential and \( v_1 \approx 3.5 \text{ cm s}^{-1} \)). The Wide-rib ID has less channels (3 inlets and 2 outlets) than the Dense ID.
and ID, and a lower channel width compared to the Light ID, which altogether leads to more electrolyte flow forced into the electrode and utilization of the electrode volume under the channels (i.e. higher electrode accessibility), while providing enough reactant even at low velocities. Lastly, as expected, the performance of the Serpentine flow field (~142 mA cm$^{-2}$ at 40 mV of $iR$-corrected potential and $v_e \approx 3.5$ cm s$^{-1}$) falls between that of the Flow-through and the ID due to the hybrid in-plane and through-plane transport [24,26,78].

To gain insight into the overpotential losses, in Fig. 5 c we analyze the resistive contributions of the paper electrode with each of the flow fields at 3.5 cm s$^{-1}$ by electrochemical impedance spectroscopy [79]. In most cases the charge transfer resistance ($R_{\text{CT}}$) remains within comparable values (see values in Tables S4a–e), although for Flow-through and Serpentine flow fields higher resistances are observed. This can be due to preferential electrolyte paths across the electrode that cause worse electrolyte distribution, impacting the accessible surface area (see EDCL measurements in Table S1). As expected, the mass transfer resistances ($R_{\text{MT}}$) are linked to the trends observed in the polarization results. Flow-through, Serpentine and Light-ID feature the highest $R_{\text{MT}}$, while ID, Dense ID and Wide-rib ID improve the mass transfer in the system leading to lower resistances. The equivalent circuit fittings provide estimations of the different resistances. The fitted parameters for all electrode—flow field configurations at 0.5, 1.5, 3.5, 5 and 7.5 cm s$^{-1}$ are listed in the Supplementary Information (Tables S4a–S4e). As anticipated by the polarization results, the mass transfer overpotential contributes with a greater resistance than the charge-transfer overpotential at low velocities. Meanwhile, as the velocity is increased, mass transfer losses are reduced, until charge transfer starts dominating the system, which is further explained in the following sections.

The electrochemical performance metrics suggest that the paper electrode performs better in combination with interdigitated flow fields, where the flow is forced to flow into both the in-plane and through-plane transport. Due to its homogeneous microstructure and small pore sizes (i.e. low permeability), the combination with flow-through flow fields results in lower performance and higher pressure drop. On the contrary, flow patterns that promote electrolyte transport in the through-plane direction help to replenish the species at intermediate points in the electrode and to reduce the residence time of species within the porous electrode. Among all types of interdigitated patterns, the Dense ID is found to be the best performing design in combination with paper electrodes. This design presents a larger number of narrow channels while keeping an equal rib to channel width ratio, which provides a higher electrolyte exchange perimeter [30,32].

### 3.4. Electrochemical performance of cloth electrode with different flow fields

Next, we perform a similar systematic analysis of the electrochemical performance of cloth electrodes with different flow fields similar to the one performed for paper electrodes. The results are shown in Fig. 6 for iR-corrected cell potentials versus current density at velocities of 0.5 and 3.5 cm s$^{-1}$.

Fig. 5. Electrochemical performance of paper electrode with the six different flow fields: iR$_{\Omega}$-corrected cell potentials versus current density for the electrolytes velocities of (a) 0.5 cm s$^{-1}$ and (b) 3.5 cm s$^{-1}$; (c) electrochemical impedance spectroscopy at 3.5 cm s$^{-1}$.
performance and resistive losses for all cloth electrode – flow field combinations. In this case, the analysis is more nuanced due to the multiscale microstructure of the carbon cloth, featuring a bimodal pore size distribution. At low electrolyte velocities, i.e. 0.5 cm s \(^{-1}\) (Fig. 6a), qualitatively similar trends as those of the paper electrodes are observed among the different flow fields in combination with the cloth electrode, except for the Wide-rib ID, which outperforms the rest of interdigitated designs. Flow-through and Serpentine are the ones presenting the larger mass transfer resistances under reactant starvation conditions. We hypothesize that the residence time of the species within the porous electrode and the spatial distribution of channels that supply the electrolyte into the electrode are the limiting factors that make a difference among the different flow fields.

At high electrolyte velocities, i.e. 3.5 cm s \(^{-1}\) (Fig. 6b), the system works under fully developed electrolyte flow. The best performance is found for those designs where in-plane flow is forced, such as the Flow-through and the Wide-rib ID. Particularly, the Wide-rib ID flow field provides the largest current density output (~250 mA cm \(^{-2}\) at 100 mV of \(iR_\Omega\)-corrected potential for the \(v_e \approx 3.5\) cm s \(^{-1}\) case). We hypothesize that this is due to two factors: i) a beneficial electrolyte supply into the electrode by three inlet channels distributed along the entire electrode width and ii) the presence of wide ribs that forces the electrolyte to flow longer distances within the electrode in the in-plane direction, improving the transport of species and consequently the performance.

Next to the Wide-rib ID, the Flow-through flow field features one of the lowest overpotentials (~200 mA cm \(^{-2}\) at 100 mV of \(iR_\Omega\)-corrected for the \(v_e \approx 3.5\) cm s \(^{-1}\)). This configuration enables the electrolyte to flow similarly into the in-plane direction, however the resulting performance is slightly worse than that of the Wide-rib ID due to the longer residence time within the electrode. In general, in-plane flow improves the fluid dynamics of the electrolyte flowing in the aligned thread direction. Additionally, the perpendicular threads of the woven material can act as mixing elements improving the mass transport of species [40].

The through-plane flow induced by interdigitated flow fields is observed to have a detrimental impact on the cloth performance. In fact, as the number of interdigitated channels is increased, the more forced is the electrolyte to flow in the through-plane direction, and the worse is the electrochemical performance, resulting in the Dense ID as the worst performing flow field of this series. An exceptional case is the Light ID, which despite its interdigitated-based pattern, provides a similar electrochemical performance to that of the Flow-through. We hypothesize that its wider channels enable the fluid to follow a pathway of lower resistance through the largest aligned pores of the cloth, thus improving the fluid dynamics. Notably, the Serpentine flow field provides slightly higher performance than the ID. Its hybrid induced flow allows the in-plane contribution to impact favorably the mass transport of species, while the through-plane contribution remains limiting the performance.

The resistive contribution of the cloth electrode is also analyzed in Fig. 6. Electrochemical performance of cloth electrode with the six different flow fields: \(iR_\Omega\)-corrected cell potentials versus current density for the electrolytes velocities of (a) 0.5 cm s \(^{-1}\) and (b) 3.5 cm s \(^{-1}\); (c) electrochemical impedance spectroscopy at 3.5 cm s \(^{-1}\).
combination with the different flow fields at higher velocities, 3.5 cm s\(^{-1}\) (Fig. 6c). In this case, the charge-transfer resistance has a larger contribution to the total overpotential losses than the mass-transfer resistance, which can be explained by the significantly lower ECSA in comparison with the paper electrode (see Table 2). While the mass transfer resistance is comparable for all flow field-electrode configurations, the charge transfer resistance differs significantly (e.g. \( \approx 0.95 \ \Omega \ cm^2 \) between ID and Wide-rib ID). We find that the use of the Wide-rib ID results in lower mass transfer and charge transfer resistances, which can be explained by the improved fluid dynamics and accessible electrode reaction volume. It should be noted that since ECSA values for all the flow field combinations are similar and deconvolution of charge transfer and mass transfer resistances from EIS data is challenging, future work should further investigate the origin of the differences in R\(_{CT}\) values.

### 3.5. Area-specific and mass transfer resistances

A deeper analysis on the area-specific resistance (ASR) and mass-transfer resistance is necessary to understand how the charge and mass transfer overpotential losses can be minimized when selecting different electrode-flow field configurations. ASR values are calculated from the slope of the iR\(_{corr}\)-corrected curves (potential values from 0 to 30 mV), and provide information about the accessible ECSA and reactant starvation.

We assess the ASR for both the paper and the cloth electrodes with the six different flow fields as a function of the electrolyte velocity (Fig. 7a and b). The Serpentine and the Flow-through flow fields in combination with the paper electrode show a strong dependence with electrolyte velocity. Their ASR values decrease significantly at higher velocity (\( 2 \ \Omega \ cm^2 \) from 0.5 to 7.5 cm s\(^{-1}\)), however the ASR remains higher than for all interdigitated designs. For the rest of electrode-flow field combinations the impact of electrolyte velocity is not as significant. For instance, for the paper electrode, the ASR can be reduced 0.25 \( \Omega \ cm^2 \) by increasing the electrolyte velocity from 0.5 to 7.5 cm s\(^{-1}\). In the case of the cloth, as expected based on the impedance results, noticeable ASR differences are measured among the six different flow fields. In general, for all flow field designs the system experiences a noticeable decrease in the ASR of at least \( \approx 0.5 \ \Omega \ cm^2 \) when increasing the electrolyte velocity from 0.5 to 7.5 cm s\(^{-1}\). Specifically, Serpentine, Flow-through and Light ID are the flow fields with higher ASR sensitivity to the electrolyte velocity, explaining the improved electrochemical performances at high velocity.

The increase of electrolyte velocity is an effective strategy to minimize the mass transfer resistance in the electrode [27], but the increase in pumping requirements should be considered, as analyzed in the following section. Studying the mass transfer resistance (with respect to charge transfer ratio (R\(_{MT}\) ratio) helps quantify the contribution of mass transfer relative to kinetics. This enables the identification of relevant system variables that can be optimized to increase the electrochemical performance of the system. In Fig. 7c and 7d the ratio between the mass transfer resistance and the total charge and mass transfer resistance is analyzed as function of the required pumping power. Calculating the
corresponding pumping power required is a practical way of studying the feasibility of the increasing electrolyte velocity strategy and the subsequent impact on the overall efficiency. In the graph, the pumping power is calculated by multiplying the system volumetric flow rate and the total pressure drop. Each data point represents a different electrolyte velocity for which the pumping power has been calculated. The results reveal similar minimization trends for all the electrode-flow field configurations. As can be observed from the combination with the paper electrode (in Fig. 7c), the mass resistance of all interdigitated patterns and Serpentine design can be satisfactorily decreased under similar pumping power. For example, in the ID case, a decrease from 0.8 to 0.3 \( R_{MT} \) ratio is achieved by increasing the pumping power in a range from 0.3 to 104 mW. Flow-through deviates from this trend and its mass transfer resistance can only be slightly decreased with a more modest required pumping power.

For the cloth electrode case (Fig. 7d), as the relative mass transfer contribution is lower compared to the paper (due to higher charge transfer resistances), further reducing the mass transfer resistance when using interdigitated flow fields requires a larger increase in pumping power. In addition, the resistance decrease in Interdigitated and Serpentine flow fields is not as remarkable as in combination the Flow-through flow field. For example, to reach the same \( R_{MT} \) ratio, the ID design requires 70 mW larger pumping power than the Flow-through. The Flow-through shows a higher sensitivity in the \( R_{MT} \) minimization, and the pumping power required is much lower in comparison with the other flow fields. The lowest value of \( R_{MT} \) is achieved when combining cloth with Flow-through, requiring only 8 mW to reach a 0.24 \( R_{MT} \) ratio. Overall, we conclude that paper electrodes feature a higher sensitivity to electrolyte velocity and cloth electrodes show a lower relative contribution of mass transfer resistances. We attribute this to the hierarchical microstructure and the lower surface area [35]. Future work should aim to produce high surface area cloth electrodes to review these performance relationships.

3.6. Performance trade-offs

Balancing the competing effects of electrochemical performance and pressure losses can guide end users to select adequate electrode-flow field combinations ensuring an efficient system operation.

In Fig. 8a, we compare the electrochemical performance represented by the current density and the pumping power calculated by multiplying the pressure loss and the volumetric flow rate. The paper and cloth electrodes are compared in combination with the three representative flow fields, namely Flow-through, ID and Wide-rib ID. In general, we find that the high ECSA of the paper electrode results in higher electrochemical performance than the cloth electrodes [36,73], which features a significantly lower ECSA (Table 2). As anticipated by the electrochemical and hydraulic analysis previously discussed, performance trade-offs reveal that the best balance for the paper is achieved when using interdigitated flow fields. On the contrary, the cloth electrode provides the best trade-off in combination with the Flow-through flow field, followed by the Wide-rib ID flow field. It is noted that the overall efficiency of the cloth in combination with interdigitated designs cannot be improved significantly even if the pumping rate is increased, which indicates internal mass transfer limitations (i.e. velocity independent) and/or kinetic overpotentials. On the contrary, when the paper electrode is used in combination with interdigitated flow field designs, we find a higher sensitivity to increasing the electrolyte velocity, leading to high electrochemical performance under moderate pumping power. For the same required pumping power (ca. 38 mW), the use of Wide-rib ID and ID flow fields results in \( \sim 300 \) and \( \sim 200 \) mA cm\(^{-2} \), respectively, which are 3x and 2x times higher than in combination with the Flow-through flow field. We envision future strategies on increasing channel depth as a pathway to mitigate pressure losses in the system improving the overall efficiency of the battery [30,80]. Furthermore, the different channel-rib patterns in the flow fields might lead to a non-uniform compression in the porous electrode due to electrode intrusion in the flow channels [20]. This could lead to gradients in porosity and pore size distributions affecting diverse physicochemical phenomena and local properties in the cell such as flow permeability, mass transport of species, ohmic resistance and overall performance [52,73]. A previous study has shown that well-engineered gradients in compression might help mitigate pressure losses and improve electrochemical performance [81].

Analysis of the Nyquist plots (Fig. 8b) shows large mass and charge transfer resistance for cloth electrodes in combination with the ID flow field and significantly lower for flow-through configurations. As anticipated, the large in-plane flow contribution together with the greater utilization of the reaction volume that the cloth experiences combined with Flow-through or Wide-rib ID results in the lowest mass and charge transfer resistances. The paper electrode presents the opposite behavior, resulting in the interdigitated flow fields providing the lowest
overpotential. The similar trade-off presented by the Flow-through flow field with the paper and cloth is mainly driven by a similar sum of charge and mass transfer resistances, which results in comparable current densities. However, when taking a detailed look at the Nyquist plot, opposite trends are observed for charge and mass transfer resistances. For the combination with the paper the charge resistance is 0.3 Ω cm² lower than with cloth, which evinces the larger ECSA of the paper. In contrast, its mass transfer resistance is 0.25 Ω cm² larger than with cloth, which reveal the beneficial impact of the cloth microstructure on the species transport when an in-plane flow is induced.

Increasing the available surface area is an effective strategy to enhance the electrochemical performance by reducing the charge transfer overpotential. Furthermore, we demonstrate that the selection of an appropriate electrode microstructure and flow field geometry can enhance species transport through a better electrolyte distribution, and as a result achieve higher electrochemical performance. Thus, to maximize the overall output, the optimization of flow field designs and electrode microstructure must be performed in tandem [47,82,83].

4. Conclusions

In this work, the coupled influence of the flow field geometry and the porous electrode microstructure in redox flow batteries has been investigated for the first time. To investigate the interaction of flow fields and electrodes on the battery performance, a series of microscopic, electrochemical and fluid dynamic techniques were employed. We studied six different flow fields—a flow-through, a serpentine and four variations of interdigitated patterns—in combination with two common electrode materials—carbon paper and cloth. Using X-ray tomographic microscopy, we analyzed the electrode microstructure and pore size distributions of the paper and cloth electrodes. The imaging analysis reveals a unimodal and smaller pore size distribution for the paper electrode, whereas the microstructure of the cloth features a bimodal pore size distribution (~5 and ~60-80 μm pores). Pressure drop measurements revealed the enhanced fluid dynamics of the woven electrodes in the in-plane direction (parallel to the membrane) attributed to the interconnected pathways between the larger pores. Thus, flow-through configurations provide the lowest pressure loss in combination with the cloth, while interdigitated flow field results in higher pumping requirements as the electrolyte is forced to cross the smaller pores within fiber threads in the through-plane direction. On the contrary, the paper electrode, which features a unimodal pore size distribution with average diameters around 5 μm, provides lower pressure drop in combination with interdigitated flow fields.

Using cell polarization and electrochemical impedance spectroscopy, we characterized the electrochemical performance in a single-electrolyte cell configuration with a kinetically facile redox couple (Fe³⁺/Fe²⁺) as electrolyte. Despite the higher available surface area of the paper, the mass transfer overpotential limits the electrochemical performance when using flow field designs that force in-plane fluid flow (e.g. flow-through). We find that the Dense ID is the best suited flow field selection in combination with the paper electrode due to the higher electrolyte exchange perimeter, which enables a more homogeneous distribution of species throughout the electrode reaction volume. While Dense ID reaches 374 mA cm⁻² at 38 mV IR-corrected cell potential, the use of Flow-through results in 83 mA cm⁻² under high electrolyte velocities (vθ ~ 3.5 m s⁻¹). Nevertheless, when balancing the obtained electrochemical performance with the pumping power requirements, we find that the Dense ID is not the optimal choice because of the high pumping power required to sustain a constant velocity in the electrode and the high contribution by the flow channels. Conversely, the Wide-rib ID flow field excellently accomplishes this trade-off due to the lower number of channels and wider ribs. In the case of carbon cloth, which features a hierarchical multiscale structure, the performance is best with flow field designs where in-plane flow is dominant, such as Flow-through, Wide-rib ID and Serpentine. Thus, when using cloth, flow-through and interdigitated flow fields with wide ribs and low number of channels are recommended since they enable higher current densities without a notable increase on the pumping power. While Flow-through reaches 74 mA cm⁻² at 38 mV IR-corrected cell potential, the use of ID results in 47 mA cm⁻² at high electrolyte velocities (vθ ~ 3.5 m s⁻¹). The lower reaction surface area of the cloth negatively impacts the achievable current density compared to that of the paper for most of the flow fields. However, the higher required pumping power by the paper electrodes has as a detrimental impact on the overall energy efficiency. These results motivate the development of functionalization techniques to produce cloth electrodes with high surface area.

Overall, these findings provide future directions to achieve high power density and minimize pumping power by combining paper electrodes with interdigitated flow fields and cloth electrodes with flow-through flow fields. Moreover, the bottom-up fabrication of novel, multiscale electrodes microstructures might promote facile mass transport of species in both in-plane and through-plane directions. In addition, we recommend the use of wide-rib interdigitated flow fields as versatile geometries for both paper and cloth electrodes due to their ability to simultaneously induce in-plane and through-plane flows providing outstanding performance. Since all experiments were performed on laboratory scale flow cells, scaling effects need to be evaluated for upscaling to industrial applications. Last, we envision that future efforts should aim to co-design flow fields and electrodes and leverage advanced manufacturing techniques (e.g. 3D printing, phase separation) to integrate both components for the engineering of next-generation electrochemical flow cells.

CRediT authorship contribution statement

Vanessa Muñoz-Perales: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration. Pablo Ángel García-Salaberri: Conceptualization, Writing – review & editing, Funding acquisition. Adrian Mularczyk: X-ray tomography, Writing – review & editing. Santiago Enrique Ibáñez: Writing – review & editing. Marcos Vera: Writing – review & editing. Antonio Forner-Cuenca: Conceptualization, Methodology, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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