Direct observation of active material interactions in flowable electrodes using X-ray tomography†

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Understanding electrical percolation and charging mechanisms in electrochemically active biphasic flowable electrodes is critical for enabling scalable deionization (desalination) and energy storage. Flowable electrodes are dynamic material systems which store charge (remove ions) and have the ability to flow. This flow process can induce structural changes in the underlying material arrangement and result in transient and non-uniform material properties. Carbon-based suspensions are opaque, multi-phase, and three dimensional, and thus prior characterization of the structural properties has been limited to indirect methods (electrochemical and rheology). Herein, a range of mixed electronic and ionically conducting suspensions are evaluated to determine their static structure, function, and properties, utilizing synchrotron radiation X-ray tomographic microscopy (SRXTM). The high brilliance of the synchrotron light enables deconvolution of the liquid and solid phases. Reconstruction of the solid phase reveals agglomeration cluster volumes between 10 μm³ and 10³ μm³ (1 pL) for low loaded samples (5 wt% carbon). The largest agglomeration cluster in the low loaded sample (5 wt%) occupied only 3% of the reconstructed volume whereas samples loaded with 10 wt% activated carbon demonstrated electrically connected clusters that occupied 22% of the imaged region. The highly loaded samples (20 wt%) demonstrated clusters of the order of a microliter, which accounted for 63–85% of the imaged region. These results demonstrate a capability for discerning the structural properties of biphasic systems utilizing SRXTM techniques, and show that discontinuity in the carbon particle networks induces decreased material utilization in low-loaded flowable electrodes.
1. Introduction

Redox flow batteries (RFBs) are electrochemical energy storage systems currently being explored for large-scale grid energy storage.\(^1,2\) RFBs offer tremendous design flexibility at scale, because they utilize an architecture that enables scalable energy and power densities (Fig. 1a). The active material in a RFB is either a metal ion or an organic species dissolved in a solvent to form a redox-active electrolyte. Thus, in a typical RFB system the active material exists in a single liquid phase and reactions occur at a stationary electrode. Typically, these systems suffer in terms of energy density, because they are limited by the active material solubility. To overcome this challenge, Duduta et al. demonstrated the use of solid materials suspended in a liquid for flowable energy storage.\(^3\) In this scenario the active material is suspended rather than dissolved, in what is coined a semi-solid or flowable electrode. The use of energy dense and power dense solid materials enables a broader range of formulations that can be examined for flowable energy storage applications (Fig. 1a).\(^2\) Flowable electrodes that utilize intercalation compounds or faradaic electrochemistry are known as semi-solid flow batteries,\(^3,4,6\) while those that utilize electrostatic (electric double layer) charge storage are electrochemical flow capacitors.\(^2,7-9\) Moreover, carbon-based flowable electrodes have gained attention for water applications, such as flow-electrode capacitive deionization,\(^10,11\) capacitive mixing,\(^13,14\) and microbial fuel cells.\(^15\)

Semi-solid systems primarily differ from RFBs because they utilize a biphasic semi-solid or suspension flow-electrode for energy storage.\(^5\) A suspension electrode is typically composed of an ion-containing electrolyte (70–95 wt%) and a solid charge storage material (5–30 wt%) (Fig. 1a). Suspension electrodes with a high solid loading have higher energy capacities, but at the consequence of higher viscosities. The flow behavior of these electrode systems is important for minimizing pumping requirements and promoting energy efficient charge
storage and transfer mechanisms. Recently, it has been demonstrated that charging can occur outside of the electroactive region due to underlying electrical connections between particles inside and outside the cell during ‘continuous’ flow operation. This has negative effects such as thermal losses, and reduced coulombic and energetic efficiencies. To address these issues, computational studies have demonstrated that intermittent plug-flow or ‘static’ operational charging modes may yield greater charge storage capabilities.\textsuperscript{16–18} However, these studies were based on models that assume homogeneous distributions of the active material within a flowable electrode, when in reality these systems are highly heterogeneous and dynamic in nature. The simple act of flowing a suspension into a charging cell can break up material agglomerations. Over time these agglomerations or percolation networks can reform if left in a quiescent state. An understanding of equilibrium structural states is important for understanding how efficient electrical percolation can be achieved.

Flowable electrodes are examples of complex fluids that can display a reconfigurable microstructure or active material arrangement during flow. Deformation of the electrode material \textit{via} flow (into the charging cell) can cause a decrease in the material connectivity and electron percolation, and can limit the material utilization in a suspension electrode.\textsuperscript{19} Typically, indirect characterization methods are utilized to extract global information about the local structure of concentrated suspension systems. Rheology, electro rheology, and dielectric rheology—small angle neutron scattering are three such methods that have been utilized for extracting structural information from flowable electrodes.\textsuperscript{19–23} Dielectric rheology has been demonstrated as a powerful technique that can evaluate the evolution of the suspension microstructure under flow conditions and relate this understanding directly to electron percolation pathways.\textsuperscript{21} Each of these methods provides a rich understanding of the electrical percolation pathways and can be considered an indirect method for understanding the active material arrangement in a suspension electrode. There is still a need for the development of direct methods to observe the underlying microstructure of a flowable electrode to aid multi-physics modeling of these systems and estimation of the material system properties (pore size distribution, aggregation size, and connectivity) that are challenging to obtain experimentally.

This paper explores the relationship between the material loading, arrangement and utilization in an electrically conducting suspension. Here, we report the use of synchrotron radiation X-ray tomographic microscopy (SRXTM) to obtain 3D reconstructions of the electron percolation pathways in static biphasic suspension electrodes composed of a high surface area activated carbon suspended in a neutral aqueous electrolyte containing sodium sulfate. The static or equilibrium structures of various suspension electrodes with different activated carbon loadings are qualitatively and quantitatively characterized for pore size and chord length distributions. The results are intended to provide insight into unique material system properties that are challenging to measure utilizing currently available characterization techniques. In addition to introducing a direct method for observing the arrangement of the active material in a suspension electrode, we also include indirect (rheology and electrochemistry) characterization tools to relate the observed structure to the flow-electrode’s functional properties. Future work that utilizes synchrotron sources with sub-second XTM capabilities, may
enable a greater understanding of the dynamics of deformation in concentrated suspension electrodes during flow.

2. Experimental section

Suspension electrode preparation

YP-50 activated carbon (Kuraray Chemical Co., Japan) was added to an electrolyte (1 M Na$_2$SO$_4$) in order to achieve the desired loading or wt% (5, 10, 15, 20, 25, and 30 wt%). The suspensions were mildly heated and magnetically stirred for several hours until uniform suspensions were obtained. Mild heating was used to improve the carbon wettability, but the weight was recorded to avoid changes in the material loading.

Electrical and electrochemical characterization

The effective electrical conductivity was measured using a single channel set-up, where the flowable electrode was pumped into a channel and contained between two stainless steel current collectors. For DC measurements, a constant potential (0.1, 0.25, and 0.5 V) was applied across the sample for 20 minutes. After 20 minutes, the current was extracted and the electrical conductivity was measured using the following equation:

$$\sigma = \frac{\Delta I}{\Delta V} \times \frac{t}{SA},$$

where $t$ is the sample thickness and SA is the current collector surface area in contact with the suspension (liquid and solid regions). The same setup was used for AC measurements, except that the sample was probed from $10^{-2}$ to $10^6$ Hz with an oscillating voltage whose amplitude was 100 mV (ref. 19), and an equivalent circuit characterized by a RC element in parallel with an electronic resistor was used to estimate the electrical resistance of each electrode. For the electrochemical studies, the suspension electrodes were tested in a two-electrode symmetric configuration, similar to previously reported studies. The current collectors were made of stainless steel and the two electrodes were contained in channels designated by latex gaskets that were 610 μm thick and had an area of 1 cm$^2$. Each electrode was volumetrically similar and they were separated from each other using a polyvinylidene fluoride (PVDF) membrane (average mesh size 100 nm, Durapore®; Merck Millipore, Germany). The electrochemical performance of the flowable electrodes was studied using cyclic voltammetry with a VMP3 potentiostat (BioLogic, France).

Rheology

The rheology measurements were conducted with a Discovery Hybrid Rheometer-3 (DHR-3, TA Instruments), using the 8 mm parallel plate geometry. The samples were stirred on a hotplate at 25 °C prior to loading on the rheometer. Samples were loaded using a metal spatula. The top plate was then lowered to a gap height of 900–1000 μm. All measurements were conducted at room temperature. Amplitude sweeps were conducted in order to determine the linear viscoelastic regime for each sample. Frequency sweeps were conducted at appropriate
amplitudes from 0.1–100 rad s\(^{-1}\). Several amplitude and frequency experiments were performed to ensure reproducibility for all the samples reported.

**Synchrotron X-ray tomography**

X-ray tomographic microscopy data was collected using the TOMCAT beamline\(^{25,26}\) of the Swiss Light Source (SLS) using monochromatic X-rays at 20 keV (Ru/C multilayer monochromator, \(\Delta E/E \sim 0.02\)). slurries with 5, 10 and 20 wt% YP-50 in 1 M Na\(_2\)SO\(_4\) were placed in pipette tips that were sealed with wax at the bottom and parafilm at the top. The pipettes were placed about 5 cm from the scintillator screen (20 \(\mu\)m LAG:Ce) of the X-ray microscope that had a 20× magnification lens and a pco.edge scientific CMOS camera (2560 × 1200 pixel readout, 6.5 \(\mu\)m pixel pitch) resulting in a voxel size of 0.325 \(\mu\)m at scan times of 1 to 3 minutes. The local tomography absorption contrast scans were reconstructed using GridRec-Software of the beamline. Subvolumes of 800\(^3\) voxels ((260 \(\mu\)m)\(^3\)) were extracted from the cylindrical raw data. The noise in the raw XTM data was reduced using an edge preserving regularized inverse scale space filter\(^{27}\) implemented within the software KipTool.\(^{27,28}\) The filtered XTM data was binarized using a maximum entropy autothreshold routine\(^{29}\) implemented in Fiji/ImageJ.\(^{30}\) Individual clusters of solid particles were identified using the bwlabeln function of Matlab (Mathworks Inc., USA), considering connectivity to all 26 neighboring voxels of a voxel. The PoroDict module of GeoDict (Version 2014, Math2Market GmbH, Germany) was used to calculate the continuous phase distribution (cPSD\(^{31}\)), the chord length distribution (CLD) and the percolation paths of the electrolyte domain of the binarized datasets. The cPSD and CLD were scaled by the total amount of electrolyte voxels or total number of chords, respectively, into a probable density representation.

The conductivity of the largest cluster of each slurry sample was determined through conductivity simulations using GeoDict and by assuming a bulk conductivity of 100 mS cm\(^{-1}\) for YP-50. The applied GeoDict version considers only connection of the six voxels that share a face with face-to-face voxel connectivity. In order to enable full 26-neighbor connectivity analysis of the percolation path and conductivity simulations using GeoDict, additional voxels were assigned to the solid phase, where solid phase voxels were in contact only at edges or vertices after the initial binarization. This processing step had only a minor influence on the overall volume fraction of the different samples, as it increased the number of solid voxels by no more than 3% for all the samples. The constriction factor \(\beta\) represents the ratio of the cross-sections of the throats (contact points of the particles) and widenings (particles) of the conducting solid network. It was calculated as defined by Holzer et al.\(^{32}\)

\[
\beta = \frac{A_{\text{min}}}{A_{\text{max}}} = \left(\frac{D_{50,\text{dPSD}}}{D_{50,\text{cPSD}}}\right)^2,
\]

where \(A_{\text{min}}\) is the throat cross-section, \(A_{\text{max}}\) is the cross-section at the pore entrance, and \(D_{50}\) is the average diameter acquired from the cPSD or the discrete phase size distribution (dPSD or virtual intrusion porosimetry). The electrical conductivity, percolation paths, dPSD and constriction factor were calculated as direction dependent for all three Cartesian coordinates and the average values are
presented. The CLD is given for one horizontal direction and the cPSD was calculated in 3D.

3. Results and discussion

Mixed ionic and electronic conducting suspension electrodes composed of varied solid loadings were evaluated for their structure, function, and properties. For all the suspension electrodes studied, microporous activated carbon with an average pore size of \( \sim 1 \) nm was utilized as the solid material (Fig. S1†). The activated carbon is anisometric in nature and can be described as containing fused particles between 1 and 10 microns in diameter and having a high specific surface area (1600 m\(^2\) g\(^{-1}\)). The active material was dispersed at different ratios in an ionic solution (electrolyte) to form strongly aggregated structures with defined electron-percolation pathways (Fig. 1a). The ions serve two primary roles: (1) intercalating or electroadsorption elements that enable charge storage and (2) particle stabilization. The high ion concentration (>1 M) and small particle size mitigates sedimentation in the flowable electrodes. Depending on the loading, the suspension can exhibit a more solid-like (gel) or liquid-like behavior. Fig. 1b and c show the effect of the material loading on the rheology for the electrostatically screened activated carbon materials. All three examples clearly show that the electrodes have formed an interconnected network of particles, i.e. a colloidal gel, where the elastic modulus, \( G' \), is significantly larger than the viscous modulus, \( G'' \).\(^{33}\) The strength of the gels, indicated by the magnitude of \( G' \), is increasing with increased carbon loading. The observed overlap of \( G' \) and \( G'' \) at low frequency for 30 wt% carbon is suggestive of a thermoreversible colloidal network.\(^{34}\) However, a different temperature and larger frequency sweep are required to confirm the thermoreversibility of the system. Two unexpected results are the upswing in \( G' \) and constant \( G'' \) at high frequency for the 10 wt% solution, and the gel-like response observed in the absence of salt. The former has no explanation at this time. The latter is an observation made from Fig. S2,\(^{†} \) whereby no salt was added to the solution but yet colloidal gel-like behavior was observed. This suggests that the activated carbon was near its isoelectric point of pH 6, effectively screening any electrostatic interactions.\(^{35}\) It is of note that the moduli of the 20 wt% colloidal gel are very similar with and without salt, while the moduli for 30 wt% carbon are significantly reduced (2 orders of magnitude) without salt. However, both these loadings in the absence of salt show a high frequency upswing similar to the 10 wt% carbon sample with salt.

The electrical percolation pathways were imaged directly using synchrotron X-ray tomographic microscopy. A schematic and a photograph of the experimental configuration are shown in Fig. 2a and S3,\(^†\) During experimentation, a pipette tip was filled with a suspension, capped, and mounted on a stage perpendicular to the direction of the beam. All the samples were exposed to monochromatic synchrotron radiation at 20 keV, and the transmitted beam was converted into visible light by a scintillator (20 μm LAG:Ce). A full reconstruction of the flowable electrode’s ‘microstructure’ at sub-micron resolutions (Fig. 2b and 4a) can be obtained by rotating the sample and taking consecutive images. After binarization the solid and electrolyte region can be observed more distinctly (Fig. 2c) and the particle free electrolyte domains can be quantified (Fig. 2d). Thus, to minimize the noise in the raw XTM data we used an edge preserving regularized inverse
scale space filter\textsuperscript{27} implemented using the software KipTool\textsuperscript{27,28} and the filtered XTM data was binarized using a maximum entropy autothreshold routine\textsuperscript{29} implemented within Fiji/ImageJ\textsuperscript{30} before reconstruction of the percolating clusters.

Suspension electrodes composed of 5, 10 and 20 wt\% carbon were investigated using SRXTM. Samples without a salt (purely electronically conducting) could not be imaged because of rapid sedimentation and observed Brownian motion between the particles, which led to blurred images. To avoid these artifacts sub-second scans are necessary. Fig. 3a and b show the raw XTM slices obtained from the low-loaded samples (5 and 10 wt\%). The water and particle domains can be individually identified despite the fact that water and carbon have similar attenuation coefficients. For reference, these suspensions will be referred to as SE5 and SE10 for the remainder of this work. Table 1 summarizes the experimental wt%/vol\% and the XTM extracted wt%/vol\% values. For the low wt\% samples (SE5/SE10), there is an agreement between the XTM extracted data and the experimentally measured values within 10\%. At 20 wt\%, there is less agreement between the measured and computed values (Table 1). Thus, two different samples of the 20 wt\% suspension were analyzed as shown in Fig. 3c and d (SE20r1 and SE20r2). Sample 1 (SE20r1) appears less densely packed than sample 2 (SE20r2), which is reflected in the extracted XTM vol\% and wt\% values (Table 1). This deviation is probably a result of the pipetting procedure or imperfect mixing of the small slurry volumes, but is also potentially relevant to the variability in these systems induced by shear forces (flow). Three-dimensional reconstructions of each sample could be achieved through a binarization and labeling procedure, and individual percolating clusters can thus be identified. A non-homogeneous distribution of the active material within a flowable electrode is contrary to previous assumptions.\textsuperscript{36} It is well documented that fluidized bed electrodes, characterized by larger particles (>100 \textmu m), display wide mass distributions due to gravitational effects. Nevertheless, this property has not been
discussed for powder-based systems and is assumed to be amplified during operation (continuous and intermittent flow).

Fig. 3e–h depict the ten largest percolating clusters for each reconstructed XTM sample. As the solid loading increases, the average percolating cluster or network size increases. SE5 displays a unique and discrete clustering behavior that spans over at least one direction of the analyzed sample volume (Fig. 3e). The

<table>
<thead>
<tr>
<th>Sample</th>
<th>YP-50 wt%</th>
<th>Expected XTM vol%</th>
<th>XTM vol%</th>
<th>XTM wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE5</td>
<td>5</td>
<td>7.3</td>
<td>6.8</td>
<td>4.7</td>
</tr>
<tr>
<td>SE10</td>
<td>10</td>
<td>14.4</td>
<td>11.8</td>
<td>8.0</td>
</tr>
<tr>
<td>SE20r1</td>
<td>20</td>
<td>31.1</td>
<td>21.1</td>
<td>14.0</td>
</tr>
<tr>
<td>SE20r2</td>
<td>20</td>
<td>31.1</td>
<td>34.7</td>
<td>22.1</td>
</tr>
</tbody>
</table>

Fig. 3 Synchrotron X-ray tomography horizontal cross-sections acquired for flow-electrodes composed of 5 wt% (a), 10 wt% (b) and 20 wt% (c and d) carbon, and a three-dimensional reconstruction of the 10 largest particle agglomerations in each electrode (e–h). The measured and simulated electrical conductivities (i), and the cluster volume distributions for the agglomerations (j).
small size and disperse nature of the SE5 percolating clusters made obtaining rheological measurements challenging. These results support previous findings which indicate that electrical percolation is negligible in flowable electrodes composed of less than 5 wt% active material.\textsuperscript{36} As the loading increases, the average size of the percolating clusters subsequently increases, which results in higher electronic conductivities. Fig. 3i demonstrates the AC and DC measured electronic conductivities for the suspension electrodes with loadings between 5 and 30 wt%. A positive correlation between the electronic conductivity and the active material loading was detected. The alternating current measurements provided higher electronic conductivities than the direct current measurements. This difference is consistent with a mixed ion- and electron-conduction mechanism. The AC measurements capture both transport mechanisms for a higher total conductivity, while the lack of charge-transfer reactions at the current collector means that the DC measurement can consider only electron conduction. In order to corroborate these values, we estimated the conductivity of the largest cluster in each XTM reconstruction. The simulated conductivities (see Fig. 2i) matched better with the DC measured conductivities.

Fig. 3j displays the cluster volume distribution for each reconstructed volume. All the samples display an inflection point between 10–30 $\mu$m\textsuperscript{3}. This inflection point, in part, occurs because the resolution of the imaging method is about 1 $\mu$m, but also is a sign that the typical particle aggregation size exceeds 10 $\mu$m.\textsuperscript{3} This is unsurprising given the high salt concentration ($\sim$1 M) and particle morphology (anisometric). SE5 is characterized by cluster volumes between $10^1$ and $10^3$ $\mu$m\textsuperscript{3}. Moreover, the size distribution for SE5 is linear and continuous, which indicates a large variation in cluster size. The other samples (SE10, SE20r1, and SE20r2) display a characteristic s-curve distribution of cluster sizes, which all seem to plateau at a picoliter cluster volume. At a picoliter volume, the curve becomes discontinuous and jumps to an aggregation size close to or exceeding one microliter. The observed discontinuity between picoliter and microliter percolation cluster sizes suggests that there may be a critical cluster size, which induces gelation and the generation of uniform percolation networks. The largest percolating clusters occupy 3% (SE5), 22% (SE10), 63% (SE20r1), and 85% (SE20r2) of the imaged volume for each sample. For both the SE20r1 and SE20r2

![Fig. 4](image-url)

**Fig. 4** Pore size distribution of solid active material used in the flow electrodes (a) and the electrolyte void space distribution within flow electrodes of varied wt% (b), and the chord length distribution for the distances between particles in a flow electrode (c). The legend in (b) is the same as (c) and both unitless y-axes.
samples, the majority of their percolating clusters are greater 1 microliter, which supports the order of magnitude increase in the electronic conductivity observed between the SE10 and SE20 samples.

SRXTM of the suspension electrodes can provide rich insight into the underlying interactions between the active materials. Typically, the material characterization of flowable electrodes is limited to ex situ characterization of the dry material with standard techniques such as scanning and transmission electron microscopy. SRXTM enables three-dimensional analyses across multiple length scales to be conducted directly. Information obtained at these length scales becomes important for capturing some of the more dynamic aspects of flowable electrodes. Fig. 4 demonstrates a standard gas sorption profile for the solid activated carbon material used in all the suspension electrodes studied in this paper. The material is microporous in nature, has an average pore diameter of 1 nm and is characterized by a narrow pore size distribution between ~0.5 and 2 nm. A similar analysis can be conducted for the reconstructed suspension electrodes in order to estimate micro-scale phenomena such as the void space between the active materials. The particle free electrolyte domain was quantified, shown in Fig. 4b, using a continuous phase size distribution method. This method involves fitting the void space or micro-pores with discrete spheres to approximate the pore size distribution. The high loading samples demonstrated a narrow distribution of interparticle voids, with peaks at 3 and 5 μm. The samples with limited percolation were characterized by a broad distribution of interparticle voids between 5 and 15 μm (SE10) and 5 and 30 μm (SE5). The chord length data shows a similar trend (Fig. 4c).

Aside from the continuous void space (porosity), tortuosity is a key property that can elucidate how the flowable electrode’s microstructure affects performance properties such as the capacitance, the rate performance, and self-discharge processes. Using an effective medium approach we derived tortuosity values τ for the largest percolating clusters of each sample (Table 2). The simplest effective media approach can be defined as:

\[
\frac{\sigma_{\text{eff}}}{\sigma} = \frac{\varphi_{\text{BB}}}{\tau^2},
\]

where \(\sigma_{\text{eff}}\) is the effective electrical conductivity, \(\sigma\) is the actual electrical conductivity, \(\tau\) is the tortuosity, and \(\varphi_{\text{BB}}\) is the solid fraction within the bounding box of the largest percolating cluster. The tortuosity values obtained using this method are shown in Table 2 and are unrealistically high. If the actual solid

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\varphi_{\text{BB}})</th>
<th>(\varphi_{\text{CL}})</th>
<th>Constriction factor (\beta)</th>
<th>(\frac{\sigma_{\text{eff}}}{\sigma} = \frac{\varphi_{\text{BB}}}{\tau^2})</th>
<th>(\frac{\sigma_{\text{eff}}}{\sigma} = \frac{\varphi_{\text{CL}}}{\tau^2})</th>
<th>(\frac{\sigma_{\text{eff}}}{\sigma} = \frac{\varphi_{\text{CL}} \beta}{\tau^2})</th>
<th>(\tau_p = \frac{L_{\text{perc}}}{L})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE5</td>
<td>6.8</td>
<td>2.9</td>
<td>0.03</td>
<td>27.4</td>
<td>16.1</td>
<td>2.8</td>
<td>2.1</td>
</tr>
<tr>
<td>SE10</td>
<td>11.8</td>
<td>3.4</td>
<td>0.02</td>
<td>34.2</td>
<td>16.8</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>SE20r1</td>
<td>21.1</td>
<td>12.9</td>
<td>0.04</td>
<td>12.9</td>
<td>10.1</td>
<td>1.9</td>
<td>1.6</td>
</tr>
<tr>
<td>SE20r2</td>
<td>34.7</td>
<td>25.7</td>
<td>0.08</td>
<td>8.0</td>
<td>7.3</td>
<td>2.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>
fraction is restricted to the effective solid fraction of the largest cluster, \( \varphi_{\text{CL}} \), the tortuosity values decrease but remain still very high compared to the tortuosity of the shortest percolation path within the largest cluster, \( \tau_{\text{p}} \). In this formulation, the influence of throats (contact points of the particles) and widenings (particles) of the percolation network is mapped into the value for the tortuosity. In order to isolate the tortuosity from the constriction effects, a constriction factor \( \beta^{32,38} \) was introduced into the analysis and this resulted in tortuosity values that are close to the lower limit of the geometric analysis of the shortest percolation paths, \( \tau_{\text{p}} \). A decrease in the tortuosity, from \( \sim 3 \) to 2, was observed by increasing the active material loading from 5 to 20 wt%. The decrease in tortuosity corresponds with the observed decrease in the interparticle distances, but it contributes only to a small extent to the increase in conductivity. The increase in conductivity appears to be dominated by an increase in the number of particle-to-particle contacts in the percolation network at higher material loadings.

Fundamentally, the tortuosity of the flowable electrode is inversely related to macroscale ion diffusivity and plays a critical role in terms of the power density (or rate performance). In order to understand the effect of tortuosity on the rate performance and material utilization directly, cyclic voltammetry experiments were conducted on samples loaded with activated carbon (15–30 wt%) at 2 and 20 mV s\(^{-1}\). At 2 mV s\(^{-1}\), the CV curves resemble polarizable systems with a rectangular shape and a current density that is independent of the voltage. Moreover, a proportional rise in the current with increased loading was observed, which is indicative of a higher capacitance (Fig. 5a). As the scan rate was increased, the CV curves became distorted and the current showed a strong dependence on the voltage. The distortion of the CV curves suggests that there is a large but finite resistance for electrons travelling across the cell, as expected for a percolating network of conductive carbon (Fig. 5b). Fig. 5c shows the capacitance vs. loading and the inverse of the leakage resistance. The leakage resistance is inversely related to the leakage current and is a marker for measuring losses in the electrode system. These losses can be associated with charge redistribution, unwanted faradaic side reactions, fibril conduction through the separator, and shunt resistances.\(^{39,40}\) While the fundamental loss mechanisms for flow-capacitors and flow-electrode systems are not fully understood, an ideally performing supercapacitor would have an infinitely large leakage resistance, or an

![Fig. 5](image)  
**Fig. 5** Electrochemical characterization of the flowable electrodes. Cyclic voltammograms of the flow electrodes with varied active material loadings at 2 mV s\(^{-1}\) (a) and 20 mV s\(^{-1}\) (b), demonstrating a polarizable (electric double layer) behavior. The capacitance increases with loading while the inverse leakage resistance remains similar (c).
inverse leakage resistance of zero. The inverse leakage resistance increases with the rate but appears to be independent of the mass loading, while the mass normalized charge storage capacity shows a decline with mass loading. Previously, the inverse leakage resistance has been shown to be positively correlated with pseudocapacitive reactions,

41 which suggests that flowable electrodes are more prone to side reactions such as hydrogen generation,

42 or carbon oxidation

43 as the rate is increased. These reactions contribute to increased self-discharge processes and material degradation. Further studies are needed to better understand these side reactions as well as their implication within high-surface area material systems such as flowable electrodes. The results suggest that the material in the low-loaded flowable electrodes is fundamentally underutilized because of the limited electrical percolation and high tortuosity.

4. Conclusion

In this work, SRXTM was utilized to image the underlying material arrangements in flowable electrode systems that are opaque, three-dimensional, and biphasic. The physical loss mechanism occurring in flowable electrodes is currently not well understood. With a multitude of competing processes in a flowable system, it is challenging to identify a single mechanism. Regardless, the fundamental interactions between particles within a solution media induce a potential for triboelectric charging and non-uniform electron transfer processes. Herein, we have reported for the first time the ability to directly image particle interactions at sub-micron resolutions within concentrated suspension systems. Deconvolution of the solid and liquid phases revealed discontinuous percolation networks for cluster volumes between one picoliter and one microliter, depending on the solid content loading. Reconstructions of the suspension electrodes demonstrated that the largest percolating cluster occupied greater than 3% (SE5), 22% (SE10), 63% (SE20r1), and 85% (SE20r2) of each sample volume imaged. Furthermore, material utilization decreased with active material loading, which suggests that smaller cluster volumes are not being accessed. SRXTM reconstructions were utilized to assess the liquid region in terms of void space or the interparticle void size distribution. As the solid loading was increased to 20 wt%, a uniform interparticle void size of ~5 µm was observed, while the low-loaded samples (5 and 10 wt%) demonstrated wide and non-uniform micro- and macropore size distributions. Two different samples for the 20 wt% suspension electrode were analyzed and different material properties (pore size distribution and cluster size) were observed. Previous reports have suggested that slurry electrodes not dominated by gravitational forces display a uniform material arrangement, but this work presents a contrary findings

36 which are expected to be amplified during flow operation. Future flow experiments could potentially elucidate the dynamic nature of the structural rearrangement during flow and aid in the development of advanced flow regimes which promote efficient electron transfer and material utilization.

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