Effects of flow cell design on charge percolation and storage in the carbon slurry electrodes of electrochemical flow capacitors

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HIGHLIGHTS

• System and cell design parameters for electrochemical flow capacitors are studied.
• Increased salt concentration was shown to improve electronic conductivity.
• Interfacial resistance between current collector/slurry was significant.
• Channel depth and flow rate shown to affect slurry conductivity during operation.
• Slurry capacitance (utilization) was maximized at small channel depths.

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ABSTRACT

The electrochemical flow capacitor (EFC) is an electrical energy storage concept recently introduced for grid-scale energy storage applications. The EFC utilizes flowable carbon-based electrodes as the active material in a flow battery type architecture for capacitive storage and recovery of energy. Charged slurry can be stored in external reservoirs until it is needed, enabling scalable energy storage to satisfy a variety of large-scale applications. Here, the capacitance and conductivity of EFC slurry electrodes were measured as a function of flow rate (from 0 to 10 ml min⁻¹) and flow cell channel depth (electrode 'thickness', ranging from 0.5 to 3 mm). The effect of salt concentration in the electrolyte was also explored. The interfacial resistance associated with the current collector/slurry interface was found to constitute a large portion of the total cell resistance. Bulk slurry conductivity was found to vary significantly with changes in electrolyte concentration, flow rate and channel depth. Very respectable capacitance values of up to ~30 F ml⁻¹ (150 F g⁻¹) were obtained during intermittent flow operation. However, significant underutilization of the slurry due to increased ohmic losses at larger channel depths was observed, as evidenced by a rapid decay in capacitance with increasing channel depth.

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1. Introduction

The rapid and efficient storage and recovery of electrical energy is emerging as a key technological challenge hindering the widespread implementation of renewable energy sources, such as wind and solar. As these resources become more widely utilized, their intermittent and largely unpredictable output is expected to create grid stability issues, particularly for areas with little grid-inertia (e.g. micro grids) [1–4]. Electrical energy storage (EES) systems can help to mitigate these issues by acting as a buffer between generation sources and consumers, and time-shifting the energy to periods of greatest demand. EES systems can also be used to provide ancillary grid services such as frequency regulation, voltage support, overload protection, transmission-congestion relief, and black start capabilities [1–4].

With the increasing demand for grid-level EES, significant effort is being made to develop new technologies for these applications. Batteries, including Li-ion, NaS, and redox flow batteries are currently in the early demonstration and commercialization phases of development. However, these technologies currently have efficiency, cost, safety, and lifetime limitations which drive the community to seek alternative solutions [1–4]. Capacitive energy
storage can overcome many of these limitations, offering long cycle life, high power density, and low cost per unit of power [5–7]. However, current supercapacitor devices are too small to cost-effectively scale up for grid-level EES applications.

To bridge this gap, our group recently proposed a grid-scale energy storage concept called the electrochemical flow capacitor (EFC) [8–10]. The EFC combines the high power density, efficiency, and lifetime of supercapacitors with the scalable energy capacity and design flexibility of flow batteries. The system architecture closely resembles a redox flow battery; consisting of an electrochemical flow cell connected to a circulation system containing reservoirs to store charged and uncharged active material [11–14]. The flow cell utilized in the EFC consists of two half cells, each containing a current collector (CC) and a flow channel (electrode compartment) with inlets and outlets, separated by an ion-permeable membrane (Fig. 1).

Unlike flow batteries, which employ a redox electrolyte as an active material, the EFC utilizes a flowable slurry (suspension) of capacitive carbon particles in a liquid electrolyte. This slurry acts as a ‘flowable electrode’, both storing and transporting charge. Spherical activated carbon particles have primarily been utilized as the active material in this system, though other carbon materials have been explored as well [8,9]. As slurry is pumped through the flow cell, a conductive network is continually formed between these carbon particles, allowing them to be charged and discharged. Charge is stored through the formation of the electrical double layer at the interface between the porous capacitive particles and the surrounding electrolyte. Once the slurry is charged, it is pumped into ionically and electronically isolated external reservoirs, where the material is held until the stored energy is needed. Energy recovery occurs in the opposite manner; charged slurry is pumped back into a flow cell connected to a circulation system containing a current collector (CC) and a flow channel (electrode compartment) with inlets and outlets, separated by an ion-permeable membrane (Fig. 1).

As an emerging technology, there is not yet an extensive base of scientific literature regarding the EFC, though several studies are currently underway. The most similar energy storage technology is the recently introduced semi-solid flow cell (SSFC) proposed by Chiang and co-workers [15,16]. Like the EFC, the SSFC also utilizes a suspension of active material in a liquid electrolyte as a ‘flowable electrode’ within the flow battery system architecture. However, the SSFC utilizes alkali metal-based redox chemistry to store energy, rather than electrochemical double layer capacitance (EDLC). In their initial paper [15], Duduta et al. experimentally demonstrated the fundamental operation of the SSFC and provided preliminary performance data for the system. In a subsequent investigation [16], mathematical modeling was used to study the effect of electrode residence time (flow rate) and the capacity-voltage relationship of the chosen redox couple. It was concluded that system performance is significantly affected by spatial gradients of state-of-charge, and maximum efficiency and utilization are achieved when these gradients are minimized. Although the SSFC and EFC are governed by very different energy storage processes (redox reactions and EDLC, respectively), their mutual dependence on highly conductive slurry electrodes acts as a linking factor between the two technologies.

The concept of a ‘flowable electrode’ has also been applied outside of the field of energy storage. Kastening et al. utilized this concept to design a chemical reactor system for carrying out reduction and oxidation processes [17]. In this early work, the authors highlight the challenge of minimizing the resistance of the slurry and the contact resistance at the interface between the ‘feeder electrode’ (i.e. current collector) and the slurry. As a result of these challenges, the authors concluded that the design of the electrochemical cell for such applications is a “priority” [17].

Recently, Kim et al. utilized the concept of flowable electrodes in a novel approach for capacitive deionization (CDI) of seawater [18]. Essentially, the authors replaced the static electrodes of conventional CDI systems with a flowing suspension of carbon particles in a process they have termed ‘flow-electrode capacitive deionization’ (FCDI). The flow configuration of FCDI addresses one of the key challenges facing capacitive deionization technologies; electro sorption capacity. In theory, a flowable electrode can yield an infinite capacity. In their study, the authors demonstrated that there was no need to interrupt the deionization process to ‘regenerate’ (discharge) the electrodes [19], as this could be accomplished through a separate process. Moreover, whereas conventional CDI systems become less efficient as the electrodes become saturated with ions, the FCDI system maintained a constant ion removal efficiency due to the continuous supply of fresh electrode material. The introduction of flowable electrodes has the potential to overcome many of the limitations of conventional CDI systems, and may represent a significant advance in this field.

As flowable electrodes become more widely used for electrical energy storage and other applications, a better understanding of how charge percolates within the slurry, and how this relates to flow cell design, will be necessary. In order for charge to be stored on a carbon particle within the flow cell, the particle must be electrically connected to the external load via a conductive pathway. Unlike conventional supercapacitors, which utilize solid state film electrodes with well-defined fixed conduction paths [5,6], the EFC utilizes a ‘flowable electrode’ in which charge percolates through a dynamic network of conductive particles. The conductive pathways in this network of particles are continuously changing under the influence of flow, and it is hypothesized that the dynamics of the flow within the flow channel strongly affects charge transport and storage within the slurry. Specifically, it is believed that the effective bulk conductivity of the slurry is affected by localized variations in conductivity due to particle-particle interactions near the walls of the flow channel. The dominance of these localized effects is believed to be largely determined by the

Fig. 1. Schematic showing the general system layout of an electrochemical flow capacitor (EFC). The flow cell consists of two half cells, each with a current collector and a flow channel, separated by an ion permeable membrane. This flow cell is connected to a slurry circulation system, consisting of pumps (not pictured) and separate isolated reservoirs for both charged and uncharged slurry.
flow rate and the geometry of the flow channel. A thorough understanding of these variables is critical to guide system design and operation strategies.

Motivated by this, our objective in this study is to investigate the effects of flow channel depth and slurry flow rate on slurry conductivity and effective capacitance and provide insight on the fundamental processes governing charge percolation and storage, establishing preliminary guidance for the design and operation of EFC systems. The interfacial resistance associated with the CC|slurry interface is investigated to better understand the interactions at the interface. Electronic conductivity within the slurry is determined using electrochemical impedance spectroscopy (EIS), and correlated to practical system design parameters. Variations in these parameters changes are then correlated directly to system performance by measuring their impact on slurry utilization and capacitance. Finally, the effect of salt concentration in the electrolyte on electronic conductivity is investigated to understand how the connectivity of the flowable electrode is determined by electrostatic interactions between particles.

2. Method of approach

2.1. Slurry preparation and flow cell design

In this study, a slurry consisting of activated carbon suspended in an aqueous electrolyte was used. 14 wt% activated carbon (YP-50F, Kuraray Corp., Japan) was mixed with 2 wt% carbon black (conductive additive; 100% compressed, Alfa Aesar, USA) in a 1 M Na2SO4 (anhydrous, Alfa Aesar, USA) aqueous electrolyte solution. A known mass of excess deionized water was added to achieve complete wetting of the carbon particles, and the mixture was stirred for a minimum of 45 min to disperse the activated carbon and carbon black. The slurry was then gently heated until the additional mass of excess water had evaporated away. At this point, the composition of the slurry was assumed to have returned to the mass fractions specified during the initial mixing. The final slurry was quite flowable, with a consistency resembling motor oil (Fig. 2a). The viscosity of carbon slurries was analyzed in our previous study [9], and found to be shear-thinning with viscosities ranging from approximately 10 to 0.01 Pa s.

A flow cell consisting of polytetrafluoroethylene (PTFE) end plates, bi-layer stainless steel/graphite foil current collectors, and latex flow channel gaskets was used to conduct the measurements (Fig. 2b and c). A polyvinylidene fluoride (PVDF) separator (100 nm mesh width, Durapore, Merck Millipore, Germany) was used to separate the cell into two compartments during capacitance measurements (Fig. 3a). The flow channel was approximately 6 mm wide and 39 mm long. Flow channel gaskets of known thickness were stacked in order to achieve the desired channel depth for each experiment. The flow rate of slurry through the cell was controlled using a syringe pump (KD Scientific KDS220). All electrochemical measurements were performed using a VSP potentiostat/galvanostat (Biologic, France) in a two-electrode configuration.

2.2. Conductivity measurements

Conductivity measurements were conducted in a manner similar to [15]. The flow cell was assembled in a single-compartment configuration with slurry flowing between the adjacent current collectors (Fig. 3b). Volumetric flow rates ($V$) of 0, 1, 2, 5 and 10 ml min$^{-1}$ were tested in this configuration for channel depths ($d$) ranging from 1 to 3 mm, in 0.5 mm increments.

Potentiodynamic electrochemical impedance spectroscopy (PEIS) was used to assess the electronic conductivity of the slurry under flowing and static conditions. The overall resistance of the system was taken to be the real component of the impedance when the imaginary impedance equals zero. When the spectrum is plotted on a Nyquist diagram, this resistance value occurs where the high frequency spectrum intersects the real axis. This intersection occurred at ~300 kHz for the conditions presented. At this high frequency, the measured impedance is assumed to be dominated by the conduction of electrons through the solid phase of the slurry, rather than the migration of ions through the electrolyte which is thought to be a slower process. To ensure
sufficient sampling time and reduce the amount of slurry consumed during each test, the PEIS frequency range was limited from 1 MHz to 100 kHz. Five PEIS sweeps were performed for each flow condition in order to provide greater confidence in the measurements.

It is important to note that the values measured using this method include the resistive contribution of the current collectors (CCs) and the CC:slurry interfaces, as well as the slurry itself. In order to isolate the ohmic contribution of the slurry ($R_{\text{slurry}}$), the measured resistance ($R_{\text{measured}}$) was plotted as a function of channel depth and a linear fit was applied to the data. The resistance of the system at a channel depth of 0 mm (i.e. hypothetical channel interface). $R_{\text{slurry}}$ was then computed according to:

$$R_{\text{slurry}} = R_{\text{measured}} - R_{\text{fixed}}$$

All conductivity measurements presented in this study are based on this calculation of $R_{\text{slurry}}$, unless otherwise noted.

### 2.3. Capacitance measurements

The same approach described in [8] was used in this study to measure the intrinsic capacitance of the system as a function of channel depth. The flow cell was assembled in a conventional two-compartment configuration (Fig. 3a), with channel depths ranging from 0.5 to 3 mm. Cyclic voltammetry (CV) was used to provide baseline data for the cell and slurry under static conditions. However, conventional techniques for measuring capacitance, such as CV, are not appropriate for characterizing the capacitance of the EFC under flowing conditions because these techniques do not account for the flux of slurry through the cell during the experiment. Rather, to measure capacitance under flowing conditions an intermittent flow regime was adopted and the technique of chronoamperometry was applied to charge and discharge the slurry (Fig. 4). In this approach, a slug of uncharged slurry was pumped into to the cell and charged potentiostatically at 1 V for 1 h. During this potentiostatic period, the majority of the charging occurs in the first few minutes. The charged slug was pumped out of the cell into an insulated polymer tubing, and then returned to the cell where it was discharged potentiostatically at 0 V for 1 h. Again, the majority of the stored charge is recovered during the first few minutes of discharge. The gravimetric capacitance, $C_{\text{gr}}$, was extracted from discharge curves according to:

$$C_{\text{gr}} = \frac{2 \Delta E}{m} \int \frac{\text{d}t}{i}$$

where $\Delta E$ is the discharge voltage window, and $m$ is the mass of carbon in one electrode. The volumetric capacitance, $C_{\text{vol}}$, was calculated as:

$$C_{\text{vol}} = C_{\text{gr}} \cdot \rho_{\text{carbon}}$$

where $\rho_{\text{carbon}}$ is the carbon density of the slurry. For the slurry used in this study, $\rho_{\text{carbon}} \approx 0.2$ g ml$^{-1}$.

### 3. Results and discussion

#### 3.1. Preliminary slurry characterization

The slurry utilized in this study was initially characterized using conventional static cell techniques to provide a reference to compare subsequent measurements against. Fig. 5a shows CV data for scan rates of 1, 2, 5, and 10 mV s$^{-1}$ at a channel depth of 0.5 mm. Fig. 5b shows the EIS spectrum at the same channel depth. At 2 mV s$^{-1}$, the slurry exhibits a volumetric capacitance of 11.9 F ml$^{-1}$ (63.8 F g$^{-1}$). This value is slightly lower than what was obtained in our previous study for an equivalent slurry (~14 F ml$^{-1}$, 75 F g$^{-1}$) [9], due to differences in the cell design and assembly procedure.

As seen from the low frequency behavior of the system shown in Fig. 5b, the slurry electrode exhibits a relatively shallow slope, which is attributed to limitations of the migration of ions in solution. Additionally, the effect of significant interfacial resistance can be seen in the high frequency data. This interfacial resistance is explored in greater detail in the following section.

#### 3.2. Effects of flow rate on interfacial resistance

Fig. 6 shows the variation of $R_{\text{fixed}}$ with flow rate. Under static conditions, $R_{\text{fixed}}$ was found to have a value of 173 m$. At intermediate

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flow rates (2 to 5 ml min\(^{-1}\)), \(R_{\text{fixed}}\) nearly doubles in value from 173 mΩ to 308 mΩ, indicating much less facile conduction across the interface under these flow conditions. However, at the highest flow rate tested, \(R_{\text{fixed}}\) was observed to again decrease to 172 mΩ, slightly less than observed under static conditions.

It was initially believed that the contribution of \(R_{\text{fixed}}\) would be negligible compared to the resistance of the flowable slurry electrode, because charge percolation within the slurry is limited by dynamic particle-particle interactions rather than established solid-state conduction pathways. However, it was found that the contribution of \(R_{\text{fixed}}\) is quite significant, and varies considerably with changes in flow rate. In some cases nearly 40% of the total measured resistance was due to the ohmic contributions of the fixed cell components, namely: solid-state conduction within the CCs and interfacial resistance across the CC|slurry interfaces \([5,20]\).

Solid-state conduction within the CCs is determined by material properties and assumed to be constant for all cases. Thus, the significant variation observed in Fig. 6 can be attributed to flow-induced changes in the interfacial resistance across the CC|slurry interface.

The relatively low resistance measured under static flow conditions (0 ml min\(^{-1}\)) is believed to be caused by the presence of quasi-static conduction sites (contact points) at the interface. These conduction sites are relatively constant due to the absence of flow, and provide a consistent conduction path across the interface, resulting in a relatively low interfacial resistance. As flow is applied, conduction across the interface becomes a stochastic process dependent on the frequency and duration of particle collisions. At low flow rates, these particle collisions are expected to be relatively infrequent, leading to the observed increase in interfacial resistance. Beyond a certain point (~ 5 ml min\(^{-1}\)), however, flow conditions near the surface cause very frequent, albeit brief, collisions resulting in the rapid decrease in interfacial resistance observed at higher flow rates.

It is clear that the resistance across this interface can be quite significant, and is affected by the flow conditions within the cell. In practice, an EFC operating in an intermittent flow regime (i.e. 0 ml min\(^{-1}\) flow rate during charging/discharging) should exhibit relatively low interfacial resistance. However, for continuous flow operation higher flow rates are desirable in order to minimize resistive losses across the interface. The magnitude of these losses is also expected to be affected by other factors, such as the surface roughness of the current collectors, inertial effects near the inlet/outlet of the channel, and the development of flow along the length of the channel, although these are outside the scope of the present study. Further study of these effects is necessary to better understand charge conduction across this key interface.

### 3.3. Effect of salt concentration on electronic conductivity

The conductivity of aqueous slurries containing different concentrations of sodium sulfate salt was measured at varying channel depths under static (no flow) conditions, and found to vary greatly according to the concentration of salt in the electrolyte. Fig. 7 shows the effect of salt concentration on bulk electronic resistance, as well as electronic conductivity.

It is observed that lower salt concentrations result in a greater dependence of electronic resistance on channel depth (Fig. 7a), indicating a decrease in electronic conductivity. Fig. 7b supports this observation, indicating that the conductivity for the 1.0 M and 1.25 M solutions are approximately constant at all channel depths tested. At 0.5 M, a decrease in conductivity with increasing channel depth is observed. The cause of this decreasing trend is not clear. In general, however, increased salt concentration is correlated with increased average conductivity. A 10% increase in electronic conductivity is observed between 0.5 M and 1.0 M, while an even larger improvement is noted at 1.25 M (~25%). It is interesting that the electronic conductivity in the solid phase of the slurry is dependent on the concentration of salt in the liquid phase. It is believed that this dependence is caused by changes in the electrostatic interactions between particles, leading to a better connected particle network at higher salt concentrations. At higher salt concentrations, the electrical field associated with the electrical double layer is increasingly screened by the mobile ions in the electrolyte.
values are observed under static conditions (0 ml min \(^{-1}\)) as well to maintain the suspension of particles in slurries with very low conductivity. However, mechanical agitation may be incorporated allowing higher salt concentrations to be used to achieve improved conductivity. The lowest conductivity, nel depth for all variations requires further investigation into the dynamics of the slurry, and the development of flow along the length of the flow channel. Shear-thinning slurries will produce very different velocity profiles than strictly Newtonian fluids \([26,27]\), and the geometry of the channel will determine the dominance of inertial effects near the inlet/outlet, potentially leading to large spatial conductivity gradients along the length of the channel \([25]\). As previously noted, the approach proposed here can only resolve volume averaged properties. Computational studies are necessary to gain a full understanding of the coupling between these effects and their impact on conductivity.

### 3.4. Bulk slurry conductivity

The bulk electronic resistance of the carbon slurry is plotted as a function of channel depth in Fig. 8a. The resistance of the slurry was observed to increase approximately linearly with increasing channel depth for all flow conditions tested. Some variation is seen in the conductivity of the slurry (Fig. 8b). The lowest conductivity values are observed under static conditions (0 ml min \(^{-1}\)), while the highest conductivity values occurred at intermediate flow rates (2 and 5 ml min \(^{-1}\)). The bulk slurry conductivity was generally greater than strictly Newtonian fluids \([26,27]\), and the geometry of the channel will determine the dominance of inertial effects near the inlet/outlet, potentially leading to large spatial conductivity gradients along the length of the channel \([25]\). As previously noted, the approach proposed here can only resolve volume averaged properties. Computational studies are necessary to gain a full understanding of the coupling between these effects and their impact on conductivity.

### 3.5. Effect of channel depth on capacitance

In order to understand the coupling between the observed variations in conductivity and overall system performance, the intrinsic capacitance of the system was measured as a function of channel depth and shown in Fig. 9. The intrinsic capacitance was observed to decrease as the channel depth is increased, from over 30 F ml \(^{-1}\) (~150 F g \(^{-1}\)) at a channel depth of 0.5 mm to less than 5 F ml \(^{-1}\) (~23 F g \(^{-1}\)) at 3 mm.

It is important to recall that the capacitance values measured represent the intrinsic capacitance of the slurry, and are not significantly affected by charging rate or other operating parameters. The intrinsic capacitance measured at 0.5 mm channel depth is more than 2x higher than the value measured using cyclic voltammetry at 2 mV s \(^{-1}\) in Section 3.1. This indicates a significant rate-limitation associated with the cell/slurry system used in this study, and further underscores the importance of minimizing resistive losses in these systems. Furthermore, Fig. 9 demonstrates that maximum utilization of the slurry is achieved at low channel depths. This same trend has been observed in conventional film electrodes based on both activated carbon, as well as carbon nanotubes \([28]\). The underutilization observed in thicker electrodes likely occurs because ohmic
losses result in a significant potential gradient through the thickness of the electrode. As a result, material which is further away from the current collector will be charged to a lower potential, limiting the materials capacity to adsorb ions. The same potential drop is expected to have a further impact on the rate performance of the slurry under transient conditions, further reducing material utilization. As a consequence, from an engineering perspective it is advantageous to utilize very shallow channel depths to ensure maximum material utilization and power-handling. However, it is important to note that the hydraulic cross-section of the flow channel is reduced at shallow channel depths. Thus, for the same flow rate a larger pressure drop is expected occur across the cell, which will require additional pumping power. However, due to the shear-thinning behavior of the slurry, the increase in pressure drop will likely be lower than expected for a similar Newtonian fluid. Accordingly, the channel depth in an optimized system will have to be carefully selected in order to balance the improved utilization of the slurry with increased pumping losses.

4. Conclusion

The performance of EFC slurry electrodes was measured as a function of flow rate and channel depth. System performance was characterized in terms of slurry conductivity and capacitance for channel depths from 0.5 to 3 mm, and flow rates ranging from 0 to 10 ml min⁻¹. The interfacial resistance associated with the current collector|slurry interface was found to be minimized for both static flow conditions (0 ml min⁻¹) and high flow conditions (10 ml min⁻¹). Conversely, the electronic conductivity of the slurry was maximized at intermediate flow rates (2 to 5 ml min⁻¹). Channel depth had a similar influence on conductivity, displaying local minima at 2 mm for all cases. Very respectable capacitance values of up to ~30 F ml⁻¹ (150 F g⁻¹) were obtained during intermittent flow operation at a channel depth of 0.5 mm. However, rapid decay in capacitance was observed as channel depth was increased, indicating significant underutilization of the slurry at larger channel depths due to Ohmic losses in the system. Finally, the concentration of ions was found to have a strong effect on conductivity, likely due to changes in electrostatic forces between particles.
The present work provides the first insight into the design and operation of EFC systems, and highlights areas for further optimization. Based on the initial trends identified in this study, it appears that future optimization efforts should attempt to better understand the coupling between cell geometry, slurry composition, and operating conditions in order to effectively balance the competing effects of slurry utilization, interfacial and bulk slurry resistance, and hydraulic losses associated with pumping. This study indicates the existence of synergies between many of these parameters which may be used to maximize the performance of the system.

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