Investigation of carbon materials for use as a flowable electrode in electrochemical flow capacitors

Jonathan W. Campos, Majid Beidaghi, Kelsey B. Hatzell, Christopher R. Dennison, Benjamin Musci, Volker Presser, Emin C. Kumbur, Yuri Gogotsi

A. J. Drexel Nanotechnology Institute, Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA
b. Electrochemical Energy Systems Laboratory, Department of Mechanical Engineering and Mechanics, Drexel University, Philadelphia, PA 19104, USA

ARTICLE INFO

Article history:
Received 5 December 2012
Received in revised form 6 March 2013
Accepted 7 March 2013
Available online 15 March 2013

Keywords:
Carbon slurry
Electrochemical flow capacitor
Flow battery
Supercapacitor

ABSTRACT

A recently introduced, novel electrical energy storage concept, the electrochemical flow capacitor (EFC), holds much promise for grid-scale energy storage applications. The EFC combines the principles behind the operation of flow batteries and supercapacitors, and enables rapid charging/discharging and decoupled energy/power ratings. Electrical charge is stored in a flowable carbon slurry composed of low-cost and abundantly available carbon particles in pH-neutral, aqueous electrolyte. Charge storage and transfer is analogous to solid carbon electrodes in conventional supercapacitors. Here, the effects of carbon particle solid fraction, shape, and size on the electrochemical and rheological properties of slurry electrodes are investigated. A static cell configuration is utilized for studying the electrochemical properties of the flowable electrodes. The electrochemical properties of the slurry electrodes tested in a static cell are found to be similar to that of solid electrodes in conventional supercapacitors for both, large spherical and anisometric activated carbons. Flow properties of the slurry electrodes are obtained for shear rates corresponding to pumping shear rates by rheometry. Results indicate that electrochemical and rheological properties of slurries depend on their concentration, shape and size of the carbon particles used in the slurries. For a range of concentrations, slurries based on spherical carbon particles show lower viscosities compared to anisometric activated carbon based slurries while performing similar electrochemically.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Electrochemical energy storage (EES) has emerged as a key technology to address the increasing problem of grid instability imposed by the large scale implementation of renewable energy sources (such as wind or solar) on the grid. Current technological solutions for power management, peak shaving, and load leveling range from mechanical systems such as pumped-storage hydroelectricity, compressed air, and fly wheels to superconducting magnetic energy storage, to name a few. However, these technologies are often less scalable and more geographically constrained than modular EES systems. In past decades, there has been significant progress in the development of EES technologies which has had an immense impact on the consumer and microelectronics industries. Most of the progress has been achieved in regards to batteries [1–3] and electrochemical double-layer capacitors (also known as supercapacitors) [4–6]. With the emerging issues of grid stability resulting from the need for large-scale implementation of renewable energy sources, finding a viable EES solution to meet the complex challenges of grid scale energy storage and power management has only recently started to attract significant attention.

One of the main barriers to grid-scale energy storage is the ability to scale a system’s energy- and cost-efficiently from ≈100 kW to several MW power requirements while simultaneously showing longevity, safety, stability, and reliability. Today, there are several large EES facilities in the megawatt range around the world which employ liquid based electrochemical systems such as redox flow batteries (RFBs) [7] or molten salt batteries (primarily Na/S) [8]. The recently reported semisolid liquid flow cell (SSFC) [9,10] reflects the tremendous interest in scalable technological solutions for grid energy storage and is characterized by a high energy density compared to Na/S and RFB systems. Unlike static batteries, the unique aspect of flow-assisted systems is the decoupling of energy and power ratings and, thus, the system energy storage capacity. Flow-assisted system energy is determined by the choice of electrolyte and size of electrolyte reservoirs while the power handling ability is...
dependent on the size and quantity of electrochemical cell stacks. This enables independent and flexible scaling of the energy and power ratings in flow batteries to meet the specific requirements of a local energy grid, a wind farm, a factory complex, or a community block. However, the current flow technologies are based on relatively slow redox reactions or ion intercalation (solid state diffusion). Such processes are limited in regards to the maximum charge and discharge rates (on the order of hours) and cycle lifetimes (<20,000 cycles), hindering their widespread usage especially for advanced power management applications [11].

Supercapacitors show great promise to address load-leveling, peak-shaving and grid stabilization issues because of their ability to charge and discharge on the order of seconds. The energy storage mechanism is based on physical energy storage via ion electrosorption in the electric double layer (EDL) at the interface between the electrolyte and a solid electrode. Without electrochemical reactions, supercapacitors provide ≈10× higher power-density, ≈100× faster charge/discharge rates, and ≈1000× longer lifetimes compared to current lithium ion batteries [12]. Although conventional supercapacitors are already considered for use in wind farms and solar farms in conjunction with batteries, their high costs and moderate energy density hinders their widespread grid-scale implementation.

Recently, we have reported a novel technology, the electrochemical flow capacitor (EFC), that can potentially overcome some of the major limitations of supercapacitors [13]. The EFC combines the scalable energy capacity of flow batteries with the high power ratings of supercapacitors and provides decoupled power/energy handling. At the core of the EFC is the utilization of a flowable, capacitive slurry of porous carbon particles suspended in an electrolyte. During operation, the slurry is charged through an electrochemical flow cell and positively and negatively polarized slurry is stored in separate reservoirs. From these reservoirs, the slurry can be pumped back into the electrochemical cell, where the material can be fully discharged for energy recovery (Fig. 1). Our earlier work has shown that the slurry maintains its capacitive energy storage during pumping. The first prototype system was capable of storing energy with a coulombic efficiency of more than 98% [13]. While promising, the results obtained in our proof-of-concept study indicate the potential for significant performance improvements by slurry optimization, which forms the basis of this study. Motivated by the previous findings, in this study, several flowable capacitive slurry compositions are evaluated using electrochemical characterization in a static configuration to establish a baseline for EFC operation. The effects of the solid fraction of the slurry, the particle size, and the shape on the electrochemical and rheological properties of the slurries are studied to explore strategies for identification of an optimized slurry for EFCs.

2. Experimental

Phenolic resin derived spherical porous carbon particles (activated carbon beads, MAST Carbon, UK) and YP-50F activated carbon (Kuraray Chemical Company, Japan) were used as the active capacitive material in the slurry electrodes. Carbon beads (referred to as CB) with three different particle size distributions were tested, namely; MAST micro beads (CB1; average particle size: 9 ± 4 μm), MAST 125/250 (CB2; average particle size: 161 ± 35 μm) and MAST 250/500 (CB3; average particle size: 385 ± 53 μm). YP-50F activated carbon (AC) with anisometric particles (size: 5–20 μm) was used to enable comparison of the tested slurries with a commonly used, inexpensive material for conventional supercapacitors. Carbon black (100% compressed; Alfa Aesar, USA) was employed as the conductive additive.

to prepare the slurries, the selected porous carbon particles were first mixed with carbon black at a ratio of 9:1. The aqueous electrolyte (1 M Na2SO4) was then added to achieve the desired liquid-to-solid ratio. The mixture was mildly heated and stirred to achieve homogenous slurries with solid fractions varying from 16 to 27 wt%. To remove dissolved oxygen, all slurries were bubbled with argon gas for 2 h before electrochemical testing. During all preparation steps, the solid fraction of the slurry was kept constant by addition of deionized (DI) water as needed.

Gas sorption at a relative pressure range from 0.05 to 0.30 P/P0 was carried out in a Quadrasorb gas sorption instrument (Quantachrome, USA) with N2 at −196°C to determine the specific surface area (SSA) and pore size distribution. The average, volume-weighted pore size was derived from the cumulative pore volume by assuming slit-shaped pores and employing quenched-solid density functional theory (QSDFT) deconvolution of N2-sorption isotherms [14]. A Zeiss Supra 50VP scanning electron microscope (Carl Zeiss AG, Germany) operating at 3 kV was used for size measurement and morphological inspection of the carbon materials.

The slurry viscosity was measured at shear rates ranging from 1 to 200 s−1 using an AR 2000 rheometer (TA Instruments, USA). A vane rotor in cup geometry was used to decrease the effect of settling on viscosity and was kept at room temperature with ±28.6 mL of slurry. Each of the porous carbon particles (CB1, CB2, CB3, and AC) were used with carbon black and sodium sulfate electrolyte to make slurries with solid fractions of 20 and 23 wt%.

The electrochemical performance of the slurry electrode was studied using a symmetric two-electrode electrochemical cell with stainless steel current collectors. The slurries were loaded into channels of the cell defined by a latex or a polytetrafluorethylene (PTFE) gasket. Latex gaskets offered better sealing and had a channel depth of 610 μm after compression, while the PTFE gasket had a channel depth of 800 μm (used only for 23 and 27 wt% CB3 slurries). A polyvinylidene fluoride (PVDF) membrane separator with a mesh width of 100 nm (Durapore®; Merck Millipore, Germany) was used as the separator between the two slurry electrodes. The carbon content in the cells varied between 24 and 41 mg per electrode for solid fractions of 16–27 wt% due to density differences between slurries with different carbon loadings. However, the carbon content was adjusted to be the same for all the different porous carbon particles at each solid fraction.

All electrochemical measurements were performed at room temperature with a VMP3 or VSP potentiotstat galvanostat (BioLogic, France). Cyclic voltammetry was carried out at 2, 5, 10, 20, and 50, and 100 mV s−1 scan rates. From cyclic voltammetry, the specific gravimetric capacitance (Csp) was derived using Eq. (1):

\[
C_{sp} = \frac{2}{\Delta V} \int \frac{i \, dV}{v \cdot m}
\]

where \(\Delta V\) is the width of the voltage window, \(i\) is the discharge current, \(V\) is the voltage, \(v\) is the scan rate, and \(m\) is the mass of carbon in one electrode. The factor of 2 accounts for the two electrode setup, assuming that the charge is evenly distributed between two capacitors in series [15].

All values for the capacitance were normalized by the weight of the carbon material, not the total slurry mass, to enable a direct comparison with conventional supercapacitor electrodes (which are also normalized to the content of active material).

\[
C_{sp} = \frac{2}{m} \cdot \frac{i}{(dV/dt)}
\]

where \(dV/dt\) is the slope of the discharge curve starting from the bottom of the IR drop to half of the high potential, \(V_{max} [15]\). The equivalent series resistance (ESR) of the cell is determined by
dividing the total change in voltage of the IR drop in a galvanostatic cycle with the total change in current. The specific gravimetric energy density $E_{sp}$ is calculated using Eq. (3):

$$E_{sp} = C_p \cdot (V_{max}^2 - V_0^2)$$

where $V_0$ is the minimum potential.

3. Results and discussion

3.1. Physical properties of porous carbon materials

Scanning Electron Microscopy (SEM) images of the four carbon materials used in this study are shown in Fig. 2a. SEM images show CB1, CB2, and CB3 have spherical shapes while AC particles are anisometric. As shown by gas sorption measurements, the pore size distribution is similar for all CB carbon particles with a dominance of micropores and only a very limited amount of mesopores (Fig. 2b). CB2 shows a slightly higher peak for small diameters than CB1 and CB3.

The Brunauer– Emmett–Teller (BET) method was used to derive the specific surface area (SSA) [16]. The average pore size was calculated as the volume-weighted average, that is, 50% of the total pore volume is associated with pores either smaller or larger than this value. CB1 has a BET SSA of 1127 m² g⁻¹ (Table 1) and an average volume-weighted pore size of 7.8 nm. CB2 has a slightly larger BET SSA of 1576 m² g⁻¹ and an average volume-weighted pore size of 4.7 nm. CB3 has a slightly lower BET SSA than CB2, 1219 m² g⁻¹ and an average volume-weighted pore size of 6.5 nm. AC had a BET surface area of 1472 m² g⁻¹, average volume-weighted pore size of 1.3 nm. These values are in agreement with the SSA values calculated from QSDFT with a maximum of 10% deviation.

3.2. Electrochemical performance

Cyclic voltammetry (CV) was employed to examine the electrochemical performance of the cells with different carbon particle compositions. Fig. 3a shows the specific capacitance of slurry electrodes from the different carbon particles and for different weight fractions of carbon. For CB, the specific capacitance of the electrodes increases with increasing weight fraction of carbon with a maximum at 23 wt%. At these compositions, slurries with all three sizes of spherical carbon beads show comparable specific capacitances (between 83 and 92 F g⁻¹) with CB2 slurries showing the highest average specific capacitance of 92 ± 10 F g⁻¹. The specific capacitances of AC slurry electrodes are also shown in Fig. 3a for comparison. Slurries based on carbon beads show a similar specific capacitance to AC, a common electrode material for commercial supercapacitors. Within the statistical scatter of the recorded values, there is a minor change in the capacitance trend for the entire studied range of solid fractions. Typical CV curves of cells with slurry electrodes of different carbon particles at 23 wt% are shown in Fig. 3b–d. At the low scan rate of 5 mV s⁻¹, CV curves of slurries consisting of all four types of carbon particles show near-rectangular shapes, indicating highly capacitive behavior. The best performance is achieved for the cell with CB2 slurry electrodes, which shows capacitive behavior with minimal resistive contributions. At a higher scan rate of 10 mV s⁻¹ (Fig. 3c), similar behavior.

Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>BET SSA (m² g⁻¹)</th>
<th>DFT SSA (m² g⁻¹)</th>
<th>$\varnothing_{pore} (\mu$m)</th>
<th>$\varnothing_{particle} (\text{nm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB1</td>
<td>1127</td>
<td>1122</td>
<td>7.8</td>
<td>9 ± 4</td>
</tr>
<tr>
<td>CB2</td>
<td>1576</td>
<td>1542</td>
<td>4.7</td>
<td>161 ± 35</td>
</tr>
<tr>
<td>CB3</td>
<td>1219</td>
<td>1195</td>
<td>6.5</td>
<td>385 ± 53</td>
</tr>
<tr>
<td>AC</td>
<td>1472</td>
<td>1323</td>
<td>1.3</td>
<td>5–20</td>
</tr>
</tbody>
</table>
is observed for the slurries with larger carbon beads (CB1 and CB2). At this scan rate, slurries consisting of CB3 and AC carbon particles show decay in capacitive behavior and a more pronounced resistive contribution. At a higher scan rate of 20 mV s\(^{-1}\) (Fig. 3d), CB2 and CB3 slurries still show moderate capacitive behavior.

The variations of the specific capacitances of the slurry electrodes with CV scan rate (rate handling) are shown in Fig. 4a–d. For CB1 slurries, the most pronounced rate dependency was observed for the electrodes with solid fraction of 16 wt%. Slurries with solid fraction of 20, 23, and 27 wt% show a similar rate handling ability.
The CB1 slurry with 23 wt% solid fraction shows a higher capacitance at all scan rates compared to all other solid fractions of CB1 slurry. This slurry shows a peak capacitance of \( \approx 99 \text{F g}^{-1} \) at 2 mV s\(^{-1}\) which drops to 76 \( \pm \) 6 F g\(^{-1}\) at 20 mV s\(^{-1}\) and 32 \( \pm \) 2 F g\(^{-1}\) at 100 mV s\(^{-1}\), yielding a \( \approx 30 \) and \( \approx 70\% \) loss in capacitance, respectively. This is a much faster decay compared to conventional activated carbon, solid electrodes [17]. This may be explained by a lesser degree of contacts between particles in slurry electrodes. The slurries consisting of CB2 particles also show similar rate dependency for solid fractions of 20, 23, and 27 wt\% (Fig. 4b). For these slurries, the highest specific capacitances at all scan rates are achieved for a solid fraction of 23 wt\%. At a scan rate of 2 mV s\(^{-1}\), the 23 wt\%, CB2 slurry shows a specific capacitance of 95 \( \pm \) 9 F g\(^{-1}\) which drops to 81 \( \pm \) 7 F g\(^{-1}\) and 33 \( \pm \) 1 F g\(^{-1}\) at scan rates of 20 and 100 mV s\(^{-1}\), a less than 29 and 69\% loss, respectively. However, the capacitance remains stable until \( \approx 20 \) mV s\(^{-1}\), which should be a sufficient rate for large, stationary EES systems. The rate dependencies of CB3 slurries are similar to those of CB1 and CB2 slurries at the three higher solid fractions. However, unlike the other two types of carbon beads, lowering the solid fraction of CB3 slurries to 16 wt\% does not result in a decrease rate handling ability. This can be attributed to the larger size of CB3 particles relative to the depth of the channel, which leads to a much better particle versus current collector contact. The highest specific capacitance for CB3, 92 \( \pm \) 4 F g\(^{-1}\) is obtained for 23 wt\% solid charged at 2 mV s\(^{-1}\). The best rate performance for slurries consisting of AC particles is achieved for a 20 wt\% solid fraction, which shows a \( \approx \) 81\% loss in specific capacitance by increasing the scan rate from 2 to 100 mV s\(^{-1}\).

The electrochemical performance of static slurry electrode cells was further studied by galvanostatic charge/discharge cycling (Fig. 5). Galvanostatic cycles show symmetric, triangular shapes and linear charge and discharge curves for the carbon beads at 200 mA g\(^{-1}\). The absence of Faradaic reactions is observed for all types of carbon particles used here. Average specific capacitances for CB1, CB2, and CB3 slurries at solid fractions between 16 and 27 wt\% range from 70 to 106 F g\(^{-1}\) at a current density of 200 mA g\(^{-1}\) (Fig. 5c). This corresponds to a specific energy density of 5.6–8.2 Wh kg\(^{-1}\). CB2 slurries with 23 wt\% carbon show the most capacitive behavior, similar to CV results, with a coulombic efficiency of 95\% (Fig. 5a) and \( C_{ip} \) of 93 \( \pm \) 13 F g\(^{-1}\) (Fig. 5c). The device capacitance of the 23 wt\% CB2 slurry shown in Fig. 5a is 1.58 F which corresponds to an energy density of 1 Wh L\(^{-1}\) at a power density of 476 W L\(^{-1}\). CB1 slurries have similar specific capacitances across the solid fractions tested with maxima of 85 \( \pm \) 5 F g\(^{-1}\) at 16 wt\% and 82 \( \pm \) 9 F g\(^{-1}\) at 23 wt\%. CB3 slurries have similar specific capacitances of 77 \( \pm \) 2, 79 \( \pm \) 4, and 78 \( \pm \) 4 F g\(^{-1}\) at 16, 23, and 27 wt\%, respectively.

The ESR is shown for each solid fraction of carbon particles in Fig. 5d. Slurries consisting of 23 wt\% AC show a somewhat higher resistance than slurries consisting of CB1 and CB2 which have resistances ranging from 0.75 to 2.50 \( \Omega \) cm\(^2\). The ESR for CB3 is the lowest at 16 and 27 wt\%. The CB2 ESR is similar for solid fractions of 20–27 wt\% with 16 wt\% having a large standard deviation. The CB1 ESR is minimized at 23 wt\% solid having a value of 0.8 \( \pm \) 0.3 \( \Omega \) cm\(^2\). Overall, differences in the electrochemical properties are fairly small over the entire range from 20 to 27 wt\%.

The energy density of a supercapacitor is proportional to the capacitance and the square of the used potential window (Eq. [3]). Recently, Fic et al. demonstrated extension of the supercapacitor potential window with sulfate electrolytes beyond the hydrolysis potential of 1.23 V [18]. It is believed that the potential window can be extended due to the strong solvation shell bond energy.
Fig. 5. (a and b) Fifth galvanostatic cycle (200 mA g\(^{-1}\)) after pre-cycling shows low resistance and symmetry of bead and AC slurries. (c) Dependency of the average specific capacitance and (d) ESR on solid fraction of porous carbon calculated from GC.

which must be overcome for electrolysis [18]. Potential window extension is also possible with the porous carbons tested here in aqueous sodium sulfate electrolyte (Fig. 6). The solid fraction and slurry consisting of the carbon particles with the highest \(C_{sp}\), 23 wt% CB2 slurry, shows rectangular shape and a small onset of faradaic reactions. The coulombic efficiencies for potential windows of 0.9, 1.1, 1.2, 1.3, 1.4, and 1.5 V were 99.2, 99.0, 98.8, 98.8, 98.7, and 98.5%, respectively. For a potential window of 1.5 V, a \(C_{sp}\) of 121 F g\(^{-1}\) is obtained. With this potential window extension and capacitance, the energy density is increased about four times.

Open circuit voltage decay in supercapacitors is a problematic issue caused by ion redistribution and charge transfer across separators and cell channels. Impurities such as carbon functional groups and inorganic matter from synthesis can undergo redox reactions with the electrolyte and the electrolyte itself can decompose at high potential [12,19]. Open circuit voltage measurements, after galvanostatic cycling and 20 min of charging at a constant potential of 0.75 V, show a voltage decay of about 25% for slurries.

Fig. 6. Cyclic voltammograms of 23 wt% CB2 slurry charging to 0.9–1.5 V at 10 mV s\(^{-1}\). Coulombic efficiency drops slightly from 99.2 to 98.5% for the extended voltage window.

Fig. 7. Open circuit voltage decay of 20 wt% porous carbon slurries after cycling and 20 min of constant 0.75 V potential.
consisting of CB2 after 3 h (Fig. 7). The voltage decay rate may be increased by the drying out of the slurry electrode in the non-optimized cell from inspection after cycling for several days. Our previous studies of slurry electrodes show that using organic electrolytes will decrease the time-dependent loss of open circuit voltage in agreement with conventional device performance [13]. It should be noted that the open circuit potential was measured in the static cells where the two oppositely charged slurries were kept in the cell after constant potential charging. This facilitates the charge transfer across the separator and insulating gaskets and results in faster self-discharge. In an actual flow capacitor setup, storage of oppositely charged slurries in separate containers is expected to decrease the self-discharge [13].

3.3. Viscosity of the slurry electrode

Macroscopic flow with shear-thinning characteristics is observed for all slurries (Fig. 8). The rheological behavior follows the Ostwald–de Waele power law model of shear thinning (pseudoplastic) fluids with Eq. (4):

\[ \eta = k \cdot \gamma^{n-1} \]

where \( \eta \) is effective viscosity, \( k \) is the consistency index, \( \gamma \) is the shear rate, and \( n \) is the shear thinning index (see fitting parameters in Table 2) [20]. The slurry viscosity increases with increasing the fraction of suspended solid particles. All slurries with a 23 wt\% solid fraction are observed to be more viscous than 20 wt\% slurries with the same carbon particle type. AC slurries appear to have a greater viscosity for the same solid fraction of CB slurries. This observation is likely due to the irregular shape of AC particles with corners and edges catching on neighboring particles causing higher resistance to flow, and the irregular particle shape causing more frequent particle-particle interactions than spherical CB particles. Microparticulate coal–water slurries, nearly analogous to the EFC slurry in terms particle size and carbon content, exhibit gravitational effects due to the large particle size [21]. These gravitational effects yield settling within the slurry and can affect the viscosity of the slurry but a comprehensive study of these effects and their bearing on EFC performance are outside the scope of this study. The rheological analysis shows that for various particle sizes, concentrations, and shapes, similar results have been achieved by other reported studies on spherical particles in literature [22]. From prior work, slurries with larger particles have shown lower viscosities than smaller particles with the same solid fraction. In addition, slurries with more uniform size distributions and greater sphericity have shown lower viscosities than those with wide size distributions and anisometric particles which agrees with our findings [21]. Our results show that CB2 has the lowest viscosities. We ascribe this to its larger particle size than CB1 and more uniform size distribution than CB3.

4. Discussion

The experimental results indicate that solid fraction, particle shape, and particle size influence the electrochemical and rheological properties of the EFC slurry electrode. Our previous studies of the electrochemical properties of carbon slurries show that electron transport in these electrodes is achieved by the formation of a three dimensional network of interconnected particles [13]. CB slurry electrodes show some increase in specific capacitance with increasing the solid fraction from 16 to 23 wt\%, in part due to the increased interconnectivity of carbon particles at higher solid fractions. Slurries with 23 wt\% solid fraction also show higher volumetric capacitance and energy density compared to slurries with lower solid fraction due to the higher loading of the active material in the cell.

We speculate the difference in the correlation between solid fraction and capacitance between AC and CB is due to the anisometric shape of the AC particles which may result in the formation of the interconnected network of particles at a lower concentration of the slurry. However, the different particle compaction ability of anisometric particles may explain the resulting scatter of the performance of AC slurries. Accordingly, particle shape also strongly affects the viscosity of carbon slurries which, in turn, affects the performance of the EFC; slurries consisting of spherical carbon particles are shown to exhibit a lower viscosity compared to slurries consisting of AC particles. Similarly, within the scatter of the experimental results, the ESR values of all CB samples are comparable. More noticeable, even the largest particles may yield a very low ESR and high value for \( C_p \) for a low solid fraction while CB yields, in general, higher capacitance and significantly lower series resistance compared to AC. It must also be noted that the differences in SSA must be factored in when comparing the different materials. The size of the carbon particles should also affect the diffusion length of ions in the carbon particles and accessibility of the whole particle volume to the electrolyte ions, thus, playing a key role in determining the electrochemical performance and the rate handling ability of slurries [23].

![Figure 8. Rheograms of slurry electrodes, 20 and 23 wt\% solid, in 1 M Na2SO4 with fits to raw data. Shear rates for a flow rate of 1–10 mL min\(^{-1}\) in the current lab scale EFC range from 40 to 400 s\(^{-1}\).](image-url)
5. Conclusions

The performance of the EFC slurry electrodes composed of carbon particles with different shapes, sizes, and concentrations was assessed electrochemically and rheologically. Electrochemical characterization of the various carbons shows that CB2 slurries containing intermediate-sized spherical particles (CB2) exhibit the highest capacitances and rate capabilities, and longest self-discharge time for EFC operations. This can be attributed to improved percolation through the particle network, increased surface area and more favorable diffusion of ions through the pore-structure of the particles. Rheological measurements show that slurries with spherical particles have, in general, lower viscosities than suspensions with anisometric particles. This indicates that spherical particles seem to be a better option for an EFC; the pumping power is minimized while energy density is increased. After assessment of three spherical particles at varying diameters, CB2 (161 ± 35 μm) was observed to be the least viscous. Furthermore, weight percentages of each carbon particle were varied to determine the viscosity and gravimetric capacitance of each composition since design parameters such as total slurry capacitance (volumetric) and viscosity are important for EFC design. In the end, a balance of low viscosity (best for low solid fractions) and charge transfer efficiency should be identified.

The present work provides a first baseline for the performance of slurry electrodes for EFC systems based on carbon spheres and conventional activated carbon as well as guidance for future slurry optimization studies. However, a more detailed understanding of the effects of carbon particle type, shape, and size on the performance of slurries needs further experimental and theoretical studies.

Acknowledgements

This work was supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences under award no. ERKKCG61. The authors would also like to acknowledge the partial support from the Ben Franklin Technology Partners of Southeastern Pennsylvania (Grant# 001389-002) and the National Science Foundation (NSF) (Grant# 1242519). J.W.C. was supported by the NSF Bridge to the Doctorate Fellowship (Grant# 1026641). K.B.H. was supported by the NSF Graduate Research Fellowship (Grant# 1002809). C.R.D. was supported by the NSF IGERT program (Grant# 0654313). B.M. was supported by the Drexel NSF REU program (Grant# 1005090). The authors would also like to thank C. R. Perez for thoughtful discussions and electrochemical measurements and B. Dyatkin for assistance with gas sorption (both at Drexel University). SEM images from M. Lukatskaya and M. Heon (both at Drexel University), which were obtained using instruments in the Centralized Research Facility (CRF) of Drexel University are appreciated.

References