A high performance pseudocapacitive suspension electrode for the electrochemical flow capacitor

Kelsey B. Hatzell a, Majid Beidaghi a, Jonathan W. Campos a, Christopher R. Dennison a,b, Emin C. Kumbur b,c, Yury Gogotsi a,**

a 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 1 May 2013
Received in revised form 17 July 2013
Accepted 17 August 2013
Available online 30 August 2013

Keywords:
Electrochemical flow capacitor
Energy storage
P-phenylenediamine
Pseudocapacitor
Supercapacitor
Redox mediator

ABSTRACT

The electrochemical flow capacitor (EFC) is a new technology for grid energy storage that is based on the fundamental principles of supercapacitors. The EFC benefits from the advantages of both supercapacitors and flow batteries in that it is capable of rapid charging/discharging, has a long cycle lifetime, and enables energy storage and power to be decoupled and optimized for the desired application. The unique aspect of the EFC is that it utilizes a flowable carbon-electrolyte suspension (slurry) for capacitive energy storage. Similar to traditional supercapacitor electrodes, this aqueous slurry is limited in terms of energy density, when compared to batteries. To address this limitation, in this study a pseudocapacitive additive has been explored to increase capacitance. A carbon-electrolyte slurry prepared with p-phenylenediamine (PPD), a redox mediator, shows an increased capacitance on the order of 86% when compared with KOH electrolytes, and a 130% increase when compared to previously reported neutral electrolyte based slurries. The redox-mediated slurry also appears to benefit from a decrease in ohmic resistance with increasing concentrations of PPD, most likely a result of an increase in the ionic diffusion coefficient. Among the tested slurries, a concentration of 0.139 M of PPD in 2 M KOH electrolyte yields the largest capacitance and rate handling performance in both cyclic voltammetry and galvanostatic cycling experiments. The improved performance is attributed to the addition of quick faradaic reactions at the electrolyte-electrode interface as PPD undergoes a two-proton/two-electron reduction and oxidation reaction during cycling.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Currently, the primary technologies employed for grid-level energy storage are pumped hydroelectric and compressed air energy storage [1]. These technologies are geographically constrained and require large capital investments when compared with electrochemical energy systems (EES), such as batteries and supercapacitors [2–4]. Thus, EES systems have emerged as the most opportunistic type of technology for grid-scale applications [1,5]. In transportation or portable electronics applications, where energy density is the critical factor, batteries are favored [2]. However, in large-scale stationary storage applications, the scalability, low power density, and cost hinder the widespread implementation of battery systems [6,7]. The critical performance requirements for grid-level energy storage are cost, scalability, and lifetime [8]. Furthermore, the market for stationary energy storage is vast, requiring capacities that range from kW to GW systems which most likely cannot be achieved with a single technology [1,9]. Thus, similar to energy generation systems, there is a need for a portfolio approach of tailored energy storage systems designed for specific applications such as voltage and frequency regulation, load leveling, and bulk power management [1,9]. In order to address the scalability requirements and broader power/energy range, various flow-assisted electrochemical systems have been recently proposed. The architecture seen in the redox flow battery [10], semi-solid lithium battery [11], and electrochemical flow capacitor (EFC) [12,13] offers tremendous design flexibility for use in grid-level energy storage.

Recently, a new energy storage concept called the electrochemical flow capacitor (EFC) has been proposed by our group at Drexel University. The EFC is a rechargeable EES that utilizes a flow battery architecture and is based on the fundamental working principles of...
supercapacitors [3,12]. The primary difference between traditional flow cells and the EFC is that the EFC utilizes a flowable carbon-electrolyte electrode, similar to the ‘slurry electrode’ introduced by Kastening et al. [14], for capacitive energy storage (Fig. 1b). During operation the slurry is pumped from a storage reservoir through two polarized plates (charging process). Once fully charged, the slurry is pumped out of the cell and stored in external reservoirs until the process is reversed and the slurry is discharged (Fig. 1a). The charged slurry stores charge electrostatically at the carbon/electrolyte interface which allows for rapid charging and discharging (Fig. 1c). Traditional flow batteries suffer from slow response rates due to faradaic reactions at the electrode-electrolyte surface and have limited cycle lifetimes (<12,000 cycles) which is a critical factor for grid scale energy storage [8,15]. The EFC in comparison is capable of rapid charging/discharging, is based on cheap and abundant materials (e.g., carbon), and enables energy storage and power to be decoupled and optimized. Furthermore, since the charge storage mechanism is physical, the EFC has the potential to exhibit long cycle life, a characteristic commonly seen in supercapacitors. Power is directly related to stack size, and energy capacity can be scaled according to reservoir volume.

Although the EFC has high power density, its energy density needs to be improved in order to compete with alternative systems for grid-level energy storage applications. The energy released by a supercapacitor, $E$, is:

$$E = \frac{1}{2}CV^2$$  \hspace{1cm} (1)

where $C$ is the capacitance (in F), and $V$ is the operational voltage window (in V). Therefore, in order to increase the energy density, one can either increase the voltage window or the active material’s capacitance. For aqueous electrolytes, the voltage window is thermodynamically limited to approximately 1.0 V because water decomposition occurs above 1.23 V [16]. Nevertheless, it has been shown that the voltage window of supercapacitors based on neutral electrolytes may extend beyond 1.23 V because the di-hydrogen overpotential is higher for neutral electrolytes[16–20]. In a recent study on the EFC, flowable electrodes based on sodium sulfate demonstrated voltage stability up to $\sim$1.5 V[19]. While an increased voltage window will yield increased energy density, the current study seeks to examine methods to enhance the capacitance of the flowable electrode. Thus, this study restricts its focus to available methods to enhance the capacitance of the flowable electrode.

Fig. 1. (a) Operational schematic of the electrochemical flow capacitor. Uncharged slurry flows through polarized plates and charged. At the pore level, electrode neutrality is maintained at the interface between the electrolyte and active material. This slurry is then pumped into external reservoirs for storage. The process is reversed during discharge. (b) Schematic of a carbon/electrolyte interface between charged spherical particles and (c) SEM image of carbon beads.
One method for increasing capacitance is through the addition of quick redox reactions at the electrode-electrolyte interface (pseudocapacitive effects). The primary means for achieving pseudocapacitance is through the use of transition metal oxides [21–23], conducting polymers [21,24] or the addition of surface functionalities such as nitrogen or oxygen to the surface of carbon materials [25]. Recently a fourth strategy, the use of redox-mediated electrolytes, has emerged as a new method of achieving pseudocapacitive behavior [26]. The addition of redox mediators into electrolytes has been shown to increase ionic conductivity and provide an additional charge storage mechanism, and thus has been explored in supercapacitor applications as a way to enhance specific capacitance [27]. Furthermore, there is no need for surface modification because the redox species react at the carbon/electrolyte interface. Most redox-mediated electrolytes are based on proton-coupled electron transfer (PCET) mechanisms that are pH-dependent and prefer basic or acidic environments in order to facilitate proton transfer at the active material surface [28–30]. In supercapacitors, electrochemically active compounds such as indigo carmine [31] and hydroquinone [33], have shown significant capacitance increases in acidic mediums. In addition, it has been recently shown that aromatic diamines such as p-phenylenediamine (PPD) [21,34–37], and m-phenylenediamine [38] (MPD) are possible redox mediators in basic electrolyte systems. A MnO2-based supercapacitor [36] demonstrated a 6-fold increase in capacitance and an activated carbon supercapacitor [35] showed a 4-fold increase in capacitance after the addition of PPD into KOH electrolytes [36]. Thus, PPD as a redox mediator has been shown to dramatically enhance capacitance. Pseudocapacitance, where the source of the redox reaction is in the electrolyte, is favorable for systems such as the EFC because the major component in the slurry is the electrolyte. Thus, redox mediators integrated into a capacitive slurry offer opportunities for increased capacitance and enhanced electrochemical performance. However, in many cases pseudocapacitors suffer from poor rate capacities due to irreversible redox reactions and physicochemical changes that take place during charging and discharging [39].

The objective of this study is to develop a carbon-based pseudocapacitive flowable electrode for the EFC that utilizes the phenylenediamine/p-phenylenediamine (PPD/PP) redox couple for additional storage of energy. Herein, a redox-mediated slurry is prepared by the addition of PPD to 2 M KOH electrolyte and the performance of the slurry is characterized electrochemically. This study also examines the effectiveness of PPD in a suspension environment (flowable electrode) and assesses its performance (rate handling and capacitance) across a wide range of rates and concentrations.

2. Materials and methods

2.1. Chemicals

All the reagents used in this study were of analytical grade. PPD anti-fade reagent supplied by Sigma–Aldrich was employed as a redox mediator, and 2 M potassium hydroxide (KOH) supplied from Alfa Aesar, was used as the supporting electrolyte. A baseline experiment was performed in 1 M sodium sulfate supplied by Sigma-Aldrich for comparison with KOH electrolyte experiments. Six different concentrations of the redox mediators were examined: 0.046 M, 0.092 M, 0.139 M, 0.185 M, and 0.277 M PPD in the supporting electrolyte solution (2 M KOH). Different concentration solutions were explored in order to identify the optimal conditions for improved system performance (capacitance and rate handling). Previously, it has been shown high concentrations of redox mediators can lead to aggregation of free ions and thus diminish the performance [38]. Thus, this study intends to demonstrate the optimal concentration for a flowable electrode system. The molar concentrations correspond to increments of 5 mg/ml solutions. The PPD was sonicated in 2 M KOH electrolyte until completely dissolved. All solutions were prepared immediately prior to the testing.

2.2. Electrode active materials

Carbon beads derived from phenolic resins were obtained from MAST Carbon (United Kingdom) and used as the active capacitive material in the slurry electrodes (Fig. 1d). In our previous work we characterized the active material, MAST carbon beads, extensively in terms of the physical attributes and electrochemical performance [12,19]. Three different sizes (diameter) of MAST beads were examined ranging from 9 μm to 500 μm, and it was determined that the mid-size beads (particle size: 125–250 μm) produced the best electrochemical and rheological performance [19], and thus was selected as the active material in this study.

N2 gas sorption was carried out in a Quadsorb gas sorption instrument (Quantachrome, USA) and the average, volume-weighted pore size was derived from the cumulative pore volume assuming slit-shaped pores and using the quenched-solid density function theory (QSDFT) algorithm. The pore size distributions of the carbon beads (average particle size: 161 ± 35 μm) had an average volume-weighted pore size of 4.7 nm. The Brunauer–Emmett–Teller (BET) method was used to calculate a specific surface area (SSA) of 1576 m²/g. This value is in agreement with the SSA value calculated from QSDFT with a maximum of 10% deviation. Carbon black (100% compressed; Alfa Aesar, USA) was employed as the conductive additive between carbon beads. For calculation purposes, the active mass was considered to be the total mass of the carbon black and activated carbon in the slurry. A Zeiss Supra 50VP scanning electron microscope (Carl Zeiss AG, Germany) operating at 3 kV was used for observing any surface changes to the carbon beads as a result of the redox- mediator.

2.3. Preparation of slurry electrodes

The slurry electrodes were prepared by mixing carbon beads with carbon black (100% compressed; Alfa Aesar, USA) to achieve a 9:1 weight ratio, as this ratio is defined as the baseline condition in our previous study. The carbon black served as a conductive additive. The aqueous electrolyte (2 M KOH) was then added to achieve 23 wt% (solid-to-liquid ratio), as it was shown previously to exhibit favorable capacitive and rheological properties [12,19]. In order to achieve a wetted carbon surface to adsorb the carbon black, an incremental amount of deionized water (~5 wt% of slurry) was weighed and added to the slurry mixture. The mixture (with the excess deionized water) was mildly heated and stirred until a homogenous slurry was obtained, and the excess deionized water evaporated.

2.4. Electrochemical performance

The slurry performance was studied in a symmetric static cell configuration, with equal masses in both electrode suspensions. The static cell is comprised of two stainless steel current collectors, onto which the slurry was uniformly loaded into a channel region defined by latex gaskets. The channel region (active area) was 1 cm². The latex gaskets were 610 μm thick when completely compressed prior to testing. 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. All electrodes tested had a carbon content of 32 mg per electrode and a solid fraction of 23 wt%.
All electrochemical measurements were performed at room temperature with a VMP3 or VSP potentiostat/galvanostat (BioLogic, France). Cyclic voltammetry (CV) was carried out at 2, 5, 10, 20, 50, and 100 mV s\(^{-1}\) sweep rates. From CV, the specific gravimetric capacitance (\(C_{sp}\)) was derived using the following equation:

\[
C_{sp} = \frac{2}{\Delta E} \times \int \frac{idV}{vm}
\]

(2)

where \(\Delta E\) is the width of the voltage window, \(i\) is the discharge current, \(V\) is the voltage, \(v\) is the sweep rate, and \(m\) is the mass of carbon in one electrode. The factor of two accounts for the two electrode setup, assuming that the charge is evenly distributed between two capacitors in series [40]. Three flowable electrodes were tested for each case (concentration), and an average value is reported in the figures. Error bars are plotted for each average value and represent the standard deviation from the average capacitance.

All values for the capacitance were normalized by the weight of the carbon material in one electrode, not the total slurry mass, to enable a direct comparison with conventional supercapacitor electrodes (which are also normalized to the content of active material in a single electrode). \(C_{sp}\) was also calculated from galvanostatic cycling (GC) using Eq. (3):

\[
C_{sp} = \frac{2i}{m \times dV/dt}
\]

(3)

where \(dV/dt\) is the slope of the entire discharge curve starting from the bottom of the IR drop and ending at the time when the voltage is equal to zero. The whole slope was taken to best account for the redox behavior exhibited in the galvanostatic charge/discharge results. The equivalent series resistance (ESR) of the cell was determined by dividing the total change in voltage of the IR drop in a galvanostatic cycle with the total change in current (between charge and discharge) using Eq. (4):

\[
ESR = \frac{\Delta V}{\Delta I} = \frac{\Delta V}{|i_{charge}| + |i_{discharge}|} = \frac{\Delta V}{2I}
\]

(4)

Potentiodynamic electrochemical impedance spectroscopy (PEIS) was used to assess the change in ohmic resistance due to changes in concentrations of PPD in the slurries. The ohmic resistance of the static cell, \(R_{Ohm}\), was determined from the impedance spectrum intersection with the real axis. This value is representative of the total resistances associated with the current collectors, active material, electrolyte, and separator [41]. With all characteristic held constant (except PPD concentration), the ohmic resistance highlights the kinetic changes in the slurry due to the addition of PPD. Furthermore, PEIS was used to evaluate the changes in ion diffusion at the surface of the electrode. In order to characterize changes in the diffusion coefficient, a Randles circuit was employed to analyze the impedance responses. All spectra were run in the frequency range of 200 kHz to 10 mHz at a sine wave signal amplitude of 10 mV.

3. Results and discussion

The morphology of the carbon beads with and without PPD was analyzed by a scanning electron microscope (SEM) as seen in Fig. 2.

---

![Fig. 2](image-url)

**Fig. 2.** SEM image of activated carbon beads. (a) As-received beads with pristine surface, (b) Carbon beads from slurry after being cycled 1000 times in 2 M KOH and 0.139 M PPD. Insets show magnified images of the bead surfaces.
PPD, as a monomer, has been reported to polymerize under electrochemical oxidative conditions [42]. Polymerization can result in electrode “poisoning”, or the coating of a polymeric film on the carbon surface [43]. This can cause a blocking effect on the carbon surface that can result in limited ion mobility and poor electronic conductivity. These limitations can be observed electrochemically by a rapid decrease in the peak current of a CV plot during successive cycles. In order to examine whether polymerization occurred during cycling, a SEM micrograph of pristine carbon beads, Fig. 2a, was compared with a SEM micrograph of cycled slurry (0.139 M PPD in 2 M KOH electrolyte) after undergoing 1000 cycles at 20 mV s⁻¹ between 0 V and 1 V. From the SEM micrographs in Fig. 2b, it is observed that the cycled slurry shows little evidence of polymer films on the carbon surface. The noticeable particles around the carbon beads in Fig. 2b are aggregates of carbon black, which is added to the slurry as a conductive additive. Furthermore, it should be noted that no drastic declines in the peak current were observed during the first 20 CV cycles typically when polymerization is expected to occur. A gas sorption analysis was taken on a sample of the cycled slurry with a concentration of 0.139 M PPD. The surface area of the cycled slurry (carbon beads, carbon black, PPD, and 2 M KOH) exhibited a BET surface area of ~1210 m²/g. Carbon black is approximately 10 wt% of the slurry, and explains this decrease in surface area when compared to dry carbon beads (~1576 m²/g). Thus, the fact that a large decrease in surface area was not observed supports the notion that the PPD is not polymerizing. This is advantageous for our system because polymerization during oxidation and reduction cycles forms polymer chains which could contribute to irreversible reactions and deterioration of PPD over the cycle life. We assessed only the flowable electrode concentration with the greatest overall performance in order to ascertain whether polymerization occurred. It is expected that below 0.139 M, there is no polymerization. In later sections we assess the effect of the concentration of PPD on the electrochemical performance of the flowable electrode.

Cyclic voltammetry (CV) was utilized for characterizing the capacitance of the slurries in a static cell configuration. Fig. 3a shows that for the cases without the redox mediator (i.e., 2 M KOH and 1 M Na₂SO₄ electrolyte), the slurries demonstrate a typical quasi-rectangular shape without redox peaks, implying an ideal electric double layer capacitor [44]. KOH electrolyte based slurries exhibit a higher capacitance (118 F g⁻¹ at 2 mV s⁻¹) when compared to sodium sulfate solution (94 F g⁻¹ at 2 mV s⁻¹). This may be attributed to the fact that protons as mobile species may exhibit faster ionic diffusion inside the pores and access a larger pore surface causing a greater capacitance [45]. Furthermore, the conductivity of 1 M Na₂SO₄ electrolyte is observed to be about 60 mS cm⁻¹ whereas 2 M KOH electrolyte has a conductivity of approximately 170 mS cm⁻¹, facilitating transport throughout the slurry medium. The KOH based flowable electrode exhibits higher capacitance, but also exhibits signs of faradaic reactions as the voltage approaches 1 V in Fig. 3a. The sudden increase in current at 1 V is a sign that electrolysis of water occurs which evolves hydrogen and oxygen as byproducts [46]. In contrast, neutral electrolytes have a stability window that reaches around 1.6 V because of a high over-potential for di-hydrogen evolution, whereas KOH electrolytes are limited to about 1 V [17]. Fig. 3b shows the rate performance for the slurries without a redox-mediated slurry. Across all rates tested, the 2 M KOH slurry outperformed the sodium sulfate based slurries as a working electrolyte for the flowable electrode (Fig. 3b). Above 20 mV s⁻¹ both slurries exhibit a decline in rate performance (capacitance decay). At 100 mV s⁻¹ the Na₂SO₄ based slurry saw a 66% decrease from its initial capacitance taken at 2 mV s⁻¹, which is comparable to the 2 M KOH electrolyte which exhibited 65% capacitance decay. The observed capacitance decay at high sweep rates for both slurries is a result of ion transport limitations, which is typically seen in porous activated carbon [47]. Diffusion limitations in slurry arise as a result of the slurry’s thickness and as a result of the network of particle-particle contacts. In traditional supercapacitors with film electrodes, it has been shown that increased thickness yields increased barriers to ion diffusion within the inner region of the electrode [47]. This results in longer diffusion paths, higher electrode resistivity, and poor power performance at high rates. This explanation can be transferred to slurry electrodes which are on average three to five times thicker than film electrodes, and can explain the decreased power performance at high rates. In addition to diffusion length challenges, while loading the cell during charging, some losses can arise when beads are not in direct contact, and transport paths are broken. Nevertheless, the desired rate handling of the slurry for a grid scale applications will most likely lie below 20 mV s⁻¹, which is very well in the range of acceptable performance for the EFC.

Fig. 4 shows the effect on capacitance and rate handling with increasing concentrations of the redox mediator (PPD) in the slurry. In contrast to the slurries without redox mediators, the redox-active slurries demonstrate an increased capacitance. The area under CV curve is proportional to the capacitance, thus in Fig. 4a the increase in capacitance can be observed qualitatively by the expansion of the CV curve with changing concentration of PPD. The anodic and cathodic peaks centered around 0.4 V can be attributed to a pseudocapacitive behavior produced by the redox couple p-phenylenediamine and p-phenylenediamine (PPD/PPI), resulting in a two-electron two-proton transfer reaction [29]. Following the redox peak, the CVs of each redox-active slurry (across all concentrations of PPD) exhibits a relatively flat region with a current density of about 0.175 A/g. The similar voltammetric current
densities implies that for each concentration studied, the slurries appear to experience similar double layer storage [48]. The CV curves show that the capacitance increases as a function of concentration of PPD. This behavior can be attributed to increases in pseudocapacitive charge storage by the fully reversible PPD/PPI redox couple, rather than changes in double layer charge storage. This can be observed by the varying redox peak heights on the voltammogram shown in Fig. 4a. The effect of PPD on the charge storage mechanisms will be discussed in detail later.

As shown in Fig. 4b, between the sweep rates of 2–20 mV s$^{-1}$, capacitances remain relatively stable for the redox-mediated slurries. The PPD concentrated slurries (0.046–0.277 M) demonstrate a typical decreasing capacitance with increasing sweep rates. Above 20 mV s$^{-1}$, all slurries are observed to demonstrate a more rapid drop in capacitance (Fig. 4b). This capacitance drop is more pronounced in the redox-mediated electrolyte with 0.277 M PPD concentration which exhibits a 69% capacitance decay between 2 and 100 mV s$^{-1}$. Table 1 shows a comparison of the observed capacitance decay between 2 and 100 mV s$^{-1}$ for each redox-active slurry studied. The slurry with 0.139 M PPD shows a 57% capacitance decay, and the slurry without PPD has a 65% capacitance decay, indicating that rate handling can be improved by the addition of PPD into the slurry. However, the deepest capacitance decay was observed in the highest concentration PPD slurry which underscores the concentration limitations of PPD.

From the CV experiments (Fig. 4), at low sweep rates below 5 mV s$^{-1}$, the capacitance increases for all concentrations studied (0.046–0.277 M). Fig. 6 shows the effects of varying PPD concentration on the both rate handling and capacitance of the slurry. At sweep rates greater than 5 mV s$^{-1}$, the optimal concentration for rate handling and capacitance is 0.139 M PPD in 2 M KOH solutions. It appears that at high sweep rates, transport properties become an issue for highly concentrated solutions. In slurries with high concentrations of the PPD, the PPD may obstruct ion mobility at the pore level, and thus might contribute to the deep capacitance decay with sweep rate. Thus, in order to optimize for both rate performance and capacitance, 0.139 M of PPD (2 M KOH) yields the best results for the rates that an EFC is expected to operate (<20 mV s$^{-1}$).

At a concentration of 0.139 M, for our two-electrode set-up, it is estimated that the increased capacitance only amounts to utilizing ~3.26% of the available PPD molecules in the suspension. This number suggests that with further optimization of the electrode, we can achieve an even higher capacitance in the flowable electrode using PPD as a redox-mediator.

Utilizing a partition method, commonly applied in examining the electrochemically active sites at the outer and inner regions of a metal oxides electrode [48–50], it is possible to distinguish between pseudocapacitive and double layer charge storage mechanisms for the various redox-mediated slurries (0.046–0.277 M). In metal oxides, the inner region is characterized by slower diffusion dynamics, due to extended diffusion lengths in comparison to the surface accessibility. Thus, in this analysis the slower diffusion dynamics (i.e. inner region) is analogous to pseudocapacitive effects that occur at slower timescales than electric double layer charge storage mechanisms. As demonstrated in Fig. 4b, the capacitance (charge storage) decreases as the sweep rate ($\nu$) increases. Thus, if we assume semi-infinite linear diffusion, the charge storage mechanism is expected to be linearly related to $\nu^{-1/2}$ [49].

The results from the partition method are shown in Fig. 7. The total voltammetric charge can be extrapolated from the plot of $q\nu$ vs. $\nu^{1/2}$ as $\nu \to 0$ (Fig. 7b), and the double-layer charge, $q_d$ can be estimated from the plot of $q$ vs. $\nu^{1/2}$ as $\nu \to \infty$ (Fig. 7a) [48]. In this analysis, a linear fit is used for the data at low sweep rates (2, 5, 10, and 20 mV s$^{-1}$), which demonstrated the linear dependence between $q$ and $\nu^{-1/2}$ and $1/q$ vs. $\nu^{1/2}$. At higher rates polarization can occur, and thus are not included in the in the linear fit [51]. The fitted regions are represented by the shaded regions on Fig. 7a and b. The total and double layer charge storage values ($q$) were obtained from the cathodic portion of the CV curve:

$$q = \int \nu dt$$

Intuitively, as the sweep rate goes to infinity, the total charge will be stored electrostatically in the double layer, because faradaic reactions are too slow to occur. Furthermore, as the sweep rate approaches to zero, or a very slow rate, one can estimate the total charge storage possible because both faradaic and double layer charge storage mechanism can occur concurrently. Thus, these approximations are valid assumptions for deciphering the different storage mechanisms. Finally, the difference between the total charge and the double-layer charge is assumed to equal the pseudocapacitive charge storage contributions. In Fig. 7c, the pseudocapacitive contributions increase with concentration, while double layer storage appears to remain relatively stable across all concentrations studied. The stable double layer charge storage

---

Table 1: Observed decreases in capacitances for different PPD concentrations redox-active slurries after increasing the sweep rate from 2 mV s$^{-1}$ to 100 mV s$^{-1}$.

<table>
<thead>
<tr>
<th>Concentration of PPD (ML$^{-1}$)</th>
<th>0</th>
<th>0.046</th>
<th>0.092</th>
<th>0.139</th>
<th>0.184</th>
<th>0.277</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity decay (%)</td>
<td>64</td>
<td>53</td>
<td>52</td>
<td>57</td>
<td>60</td>
<td>69</td>
</tr>
</tbody>
</table>
phenylenediamine (total, Fig. 7. (a) Double layer charge storage contribution for each concentration of p-phenylenediamine (v = sweep rate), (b) the total charge storage mechanism, derived as the sweep rate approaches very 0 mV s⁻¹, (c) partitioned charge storage quantities (total, double layer, and pseudocapacitive contributions).

mechanism can also be observed in Fig. 4a as the current density after the redox peak for each concentration is approximately equal. Furthermore, this is expected because for all slurries studied, the same active material with the similar surface areas were used. Overall, double layer charge storage appears to contribute a greater proportion of the charge storage over all concentrations of PPD tested, except at 0.277 M of PPD, where double layer and pseudocapacitive charge storage mechanisms are approximately equal. This analysis demonstrates that the highest charge storage was observed in the slurry that had 0.277 M of PPD. This observation is qualitatively confirmed, by the CV plot shown in Fig. 4a as 0.277 M demonstrates the greatest area at 2 mV s⁻¹. However, at increased rates it is expected that the charge storage at 0.277 M would be sub-optimal to 0.139 M because it is performance degrades above 2 mV s⁻¹ (Fig. 6).

Fig. 8 shows typical galvanostatic cycling for the redox mediated slurries at a charge rate of 200 mA g⁻¹. Each curve shows a similar charge and discharge time which indicates good coulombic efficiency across all redox slurries examined. Typical supercapacitors demonstrate triangular shape galvanostatic curves. However, for these pseudocapacitive slurries, we see reduction and oxidation bumps in the middle region, which indicates that redox reactions occur. The fact that charge and discharge curves are symmetric emphasizes the reversibility of the redox-couple in KOH electrolytes. Furthermore, the slurry with 0.139 M of PPD charges in ~600 s (~6 C), which demonstrates its ability charge and discharge quickly, a characteristic that is desired in grid energy storage applications. The equivalent series resistance which reduces the power output of supercapacitors is found to be low, around 1.5 Ω cm² (Fig. 8a). Moreover, Fig. 8b shows that the capacitance appears to be optimized at 0.139 M of PPD in 2 M KOH. In the CV experiments it was shown that for rates above 2 mV s⁻¹, 0.139 M of PPD surpasses 0.277 M PPD in terms of capacitance. This trend is confirmed with the galvanostatic results shown in Fig. 8.

Fig. 9 shows the Nyquist plot for all redox-mediated slurries. The Nyquist plots exhibit a small semi-circle in the high frequency region, and a linear region at low frequency. The imaginary impedance is linearly related to the real impedance at low frequency which indicates a diffusion controlled system. With increasing concentrations of PPD, we see a decrease in the ohmic resistance ($R_Ω$) from 0.8 to 0.2 Ω cm². The maximum specific power for a supercapacitor can be found from:

$$P_{\text{max}} = \frac{V^2_{\text{max}}}{4R_Ωm}$$

(6)

where $V$ is the voltage window, and $m$ is the mass of the active material in both electrodes. When all the parameters are held constant, except for concentration, the only parameter that changes is the ohmic resistance. Thus, we see with increasing concentrations of PPD, $R_Ω$ decreases and thus the maximum specific power increases.

A typical Randles circuit was employed to distinguish the effects of PPD concentration on the faradaic impedance (Fig. 9b inset). A Randles circuit is comprised of a resistor (which represents ohmic or solution resistance) in series with a parallel RC circuit. The parallel RC circuit is characterized by a branch with a capacitor which represents pure capacitance, and another branch that captures the faradaic impedance. The faradaic impedance is comprised of charge transfer resistance and a Warburg impedance which represents mass transfer losses [52]. For the pseudocapacitive slurry, we are interested in examining the changes in Warburg impedance with concentration of PPD. The Warburg impedance, for the equivalent circuit described above can be calculate from [39,52]:

$$Z_ω = [\sigmaω^{-1/2} - j(σω^{-1/2})] = ω^{-1/2}τ[1 - j]$$

(7)
where \( j \) is the imaginary number, \( \omega \) is the angular frequency, and \( \sigma \) is Warburg coefficient. Thus the slope of a plot of \( \omega^{-1/2} \) versus either the real or imaginary part of the impedance spectra provides the Warburg coefficient (Randles plot, Fig. 9b). The Warburg coefficient is defined as [52]:

\[
\sigma = \frac{RT}{nF^2A\sqrt{2}} \left( \frac{1}{D_0^{1/2}C_0} \right) \tag{8}
\]

where \( R \) is the ideal gas constant, \( T \) is the temperature, \( n \) is the charge transfer number, \( A \) is the area of the electrode surface, \( F \) is faraday’s constant, \( D_0 \) is the diffusion coefficient, and \( C_0 \) is the bulk concentration. The effects on the diffusion coefficient with concentration of PPD can be determined qualitatively by examining how the magnitude of the Warburg coefficient changes with concentration of PPD because the diffusion coefficient is inversely related to the Warburg coefficient.

The slope of the Randles plot is \( \sigma \), the Warburg coefficient. From the Randles plot (Fig. 9b) it can be seen that increasing the concentration of PPD decreases the ohmic resistance, and increases the diffusion coefficient (Fig. 9b). The diffusion coefficient reflects the mobility of the ionic species across the supercapacitor. Increasing the diffusion coefficient is advantageous for obtaining fast reactions. Thus, the addition of PPD increases the performance of the supercapacitor initially by both decreasing the ohmic resistance and increasing the diffusion coefficient of the ionic species.

Fig. 10b shows the specific discharge capacitances for a slurry containing 0.139 M PPD in 2 M KOH during successive cycling. Over 1000 CV cycles (20 mV s\(^{-1}\)), an 11% decrease in capacitance was observed. In typical pseudocapacitor systems cycle life is often an issue because volume changes during the redox reaction (metal oxides and conducting polymers) leads to losses of active material [53]. This loss is typically alleviated by integrating pseudocapacitive material into a carbon support. In our carbon-based redox-mediated slurries the redox peaks appears to compress toward the inside of the CV curve with cycling, which represents a decrease in capacity (Fig. 10a). It can be assumed from this transition that the system is losing faradaic charge storage over the cycle lifetime as a result of possible loss of active PPD. This is evident because the flat region beyond the redox bump remains relatively stable, indicating that we are not losing double layer charge storage with cycling. The loss of faradaic charge storage could be due to degradation of the redox-active PPD during cycling. Furthermore, deterioration might be related to \( \text{pH} \)-related changes of the electrolyte which would stifle redox reactions. This test was done in a static cell, which does not fully mimic the conditions that would be encountered during flow cell operations. In an actual flow system, a simple feedback control system could be implemented in
the storage tanks to ensure that pH remained constant, and the active material weight percentage remains constant, which may contribute to better electrolyte stability.

4. Conclusions

The high power, low cost, and long lifetime characteristics of the capacitive flowable carbon-based electrodes in the electrochemical flow capacitor (EFC) offer the opportunity to address a diverse range of applications on the grid level. The limited energy density, common in carbon-based electrodes that use physical adsorption of ions as their charge storage mechanism, can be enhanced through the addition of pseudocapacitance. This study introduced a redox-mediated slurry as a facile method for increasing the energy density of the flowable electrodes for the EFC. A pseudocapacitive slurry utilizing a PPD/PPI redox-couple in 2 M KOH electrolyte demonstrated high capacitance for the EFC. The alkaline redox-mediated slurry shows increases in capacitance on the order of 86% when compared alkaline solutions without redox mediators, and a 130% increase compared to previously reported neutral slurries [12]. Furthermore, the rate handling performance of the redox-mediated slurry increased from approximately 64% capacitance decay to about 57% between rates of 2–100 mV s⁻¹. The redox-mediated slurry is found to decrease the ohmic resistance, with increasing concentrations of PPD, which can be described by the increase in the ionic diffusion coefficient. Among tested slurries, a concentration of 0.139 M of PPD in 2 M KOH yielded the highest capacitances in both CV and GC experiments over a wide range of charging rates. The high performance is attributed to the addition of quick redox reactions at the electrolyte/electrode interface as PPD undergoes a two-proton/two-electron reduction and oxidation during cycling.

Acknowledgements

Y.G. and M.B. would like to acknowledge support from the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy. Partial support from the Ben Franklin Technology Partners of Southeastern Pennsylvania group (Grant# 001389-002) and the National Science Foundation (NSF) (Grant# 1242519) is also appreciated. K.B.H. was supported by the NSF Graduate Research Fellowship (Grant# 1002809). J.C. was supported by the NSF Bridge to the Doctorate Fellowship (Grant# 1026641). C.R.D. was supported by the NSF IGERT program (Grant# 0654313). The authors would also like B. Dyatkin for assistance with gas adsorptions data and helpful conversations.

SEM was carried out using instruments in the Centralized Research Facility (CRF) of the College of Engineering at Drexel University.

References


