

## Preparation of pseudocapacitor electrodes via electrodeposition of polyaniline on nonwoven carbon fiber fabrics

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**ABSTRACT:** Aniline has been polymerized via electrodeposition onto various nonwoven carbon fiber fabric (CFF) substrates for use as a pseudocapacitive electrochemical capacitor. Four types of CFF were initially tested for double layer capacitance before polyaniline deposition, and again for specific capacitance after deposition. A binder-free CFF was selected for further analysis due to its high capacitance change following PANI deposition (three orders of magnitude). The aniline monomer concentration, deposition potential, and deposition time were varied and resulting materials were characterized using chrono-potentiometry, cyclic voltammetry, and scanning electron microscopy. The deposition potential range yielding highest capacitance was found to be between 0.744 and 0.777 V. A solution concentration of 0.5M aniline at a 20 min deposition time resulted in the highest specific capacitance (>80 F/g based on total electrode mass and >300 F/g based on PANI mass) within this study. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43315.

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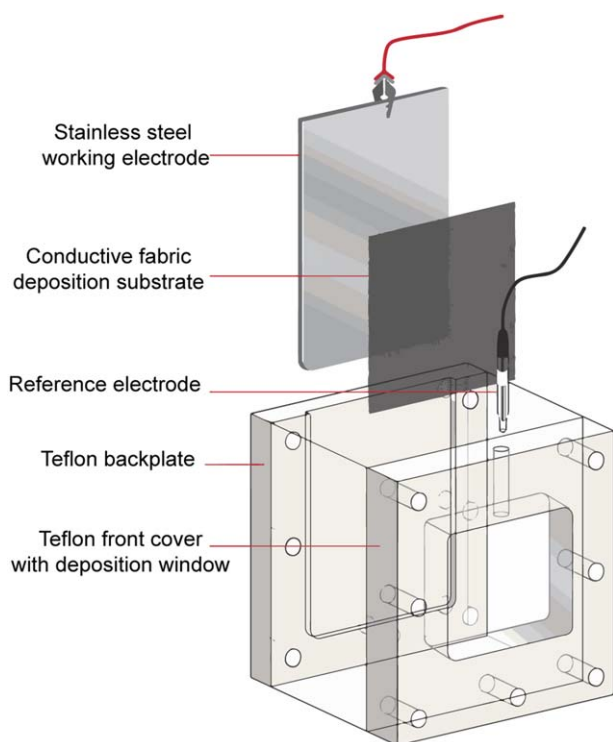
### INTRODUCTION

Since the synthesis of polyacetylene in 1974, intrinsically conductive polymers (ICPs) have been widely explored for various applications<sup>1,2</sup> thanks to their tunable conductivity and low material cost.<sup>3</sup> Polypyrrole (PPy), polythiophene (PT), polyethylenedioxythiophene (PEDOT), and polyaniline (PANI) are a few of the more commonly studied ICPs. With differences in their conductivity, stability, and processability, each is suitable for its own range of applications. Here, we focus on PANI for use as a redox material in pseudocapacitive supercapacitors, a class of energy storage devices which present superior power density compared with the majority of batteries and fuel cells. They are typically either constructed with porous activated carbon electrodes backed by current collectors, forming electric double-layer capacitors (EDLC), or with redox active materials coated onto current collectors, forming pseudocapacitors.

PANI is preferred to other ICPs for use as a pseudocapacitive material due to its stability, low cost and high theoretical specific capacitance (i.e., 750 F/g vs. 210 F/g for PEDOT).<sup>3–7</sup> The electrochemical charge storage mechanism of PANI in a symmetrical supercapacitor involves simultaneous oxidation and reduction reactions at two adjacent electrodes. A fully charged state is achieved when one electrode has reached maximum electron doping and the other electrode is completely de-doped. A discharged state is seen when there is an equal partial de-

doping on the two electrodes.<sup>6</sup> Thus, the true maximum specific capacitance that can be expected from a PANI supercapacitor is half of its full theoretical value, or 325 F/g, although experimental values have been reported to range from 160 F/g to over 1000 F/g.<sup>8,9</sup>

Control over PANI reaction steps, rates, and products can be achieved through variation of the monomer type,<sup>10</sup> deposition duration,<sup>11</sup> deposition potential,<sup>12</sup> and aniline concentration.<sup>1,13,14</sup> For instance, Genies *et al.* observed a change in current density during the potentiostatic electrodeposition of PANI depending on the deposition potential used.<sup>12</sup> In an aqueous sulfuric acid medium, a potential of 1.0 V (vs. SCE) resulted in the highest current density, while the lowest current density occurred at 1.4 V. A later study by Kanamura *et al.* found that current density during deposition impacted the morphology and discharge characteristics of the deposited species, implying that discharge behavior could also be impacted by tuning the deposition potential.<sup>15</sup> In addition to its morphology, the conductivity of PANI is crucial to its performance in an electrochemical capacitor. ICPs derive their electrical conductivity from their conjugated structure. While in a conductive state, they can be considered to be either positively charged (p-doped) or negatively charged (n-doped). Over-oxidation or reduction can establish an insulating “undoped” state.<sup>12,16</sup> In the case of PANI, interest is focused upon the emeraldine salt form, as this



**Figure 1.** Deposition cell setup including working electrode, deposition substrate, reference electrode, and Teflon frame. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

is considered its most electrically conducting state.<sup>3,17–20</sup> Control of oxidation state can be imparted during the synthesis process, which is achieved by chemical or electrochemical means. Although chemical polymerization exhibits increased bulk yields over electrochemical methods, the latter provides superior control over the resulting charge state of the polymer.<sup>5,21</sup> Electrochemical synthesis further provides the advantage of coating the polymerized material directly onto a conductive scaffold such as a three-dimensional carbon substrate, yielding a ready-made supercapacitor electrode with low equivalent series resistance (ESR).<sup>1</sup>

Carbon fiber fabric (CFF), also termed carbon cloth (CC) in the literature, is an ideal scaffold for PANI deposition due to its low electrical resistance and flow-through structure. Without being subjected to a micropore-developing activation procedure, CFF has a low specific surface area ( $\sim 1\text{--}10\text{ m}^2/\text{g}$ ) and thus

**Table I.** Specific Capacitance of Various Carbon Fiber Nonwoven Scaffolds, Based on CP Discharge at 0.5 mA, Before and after Deposition of PANI

Substrate	Initial specific capacitance (F/g)	Specific capacitance after PANI deposition (F/g)
VCFF	0.22	4.47
NPCFF	0.06	3.29
BFCFF-1	0.02	14.81
BFCFF-2	0.02	14.44

exhibits very little capacitance. Following deposition, the PANI-coated CFF can be directly used as a pseudocapacitive-type supercapacitor electrode. A significant increase in capacitance between a PANI deposited CFF electrode and a bare CFF electrode has already been reported.<sup>8</sup> However, the particular fabric structure of the CFF is important to consider. Prior research has generally explored polyaniline deposition onto woven fabrics.<sup>9</sup> Through visual analysis of PANI coating on an electrode, a positive correlation between uniform distribution of active material and capacitance levels has been noted.<sup>23</sup> Typical woven fabrics are composed of yarns, in which fibers are tightly twisted together, whereas in typical nonwoven fabrics, the fibers are individualized and uniformly distributed in a web. Thus, nonwovens can potentially provide ideal fiber arrangements upon which to deposit PANI. In this report, a variety of nonwoven CFF materials were compared as substrates for polyaniline electrodeposition. Through varying monomer concentration, deposition potential and deposition time, the effects of processing conditions were also examined.

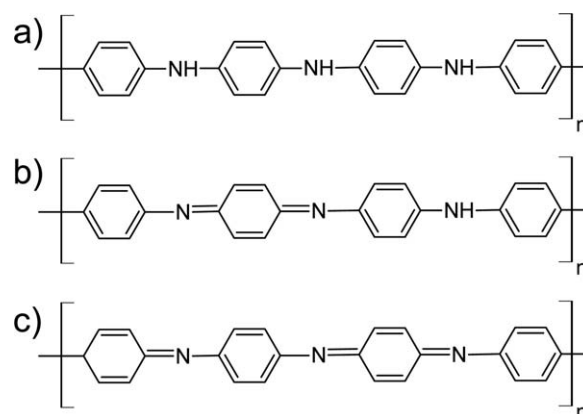
## EXPERIMENTAL

### Materials

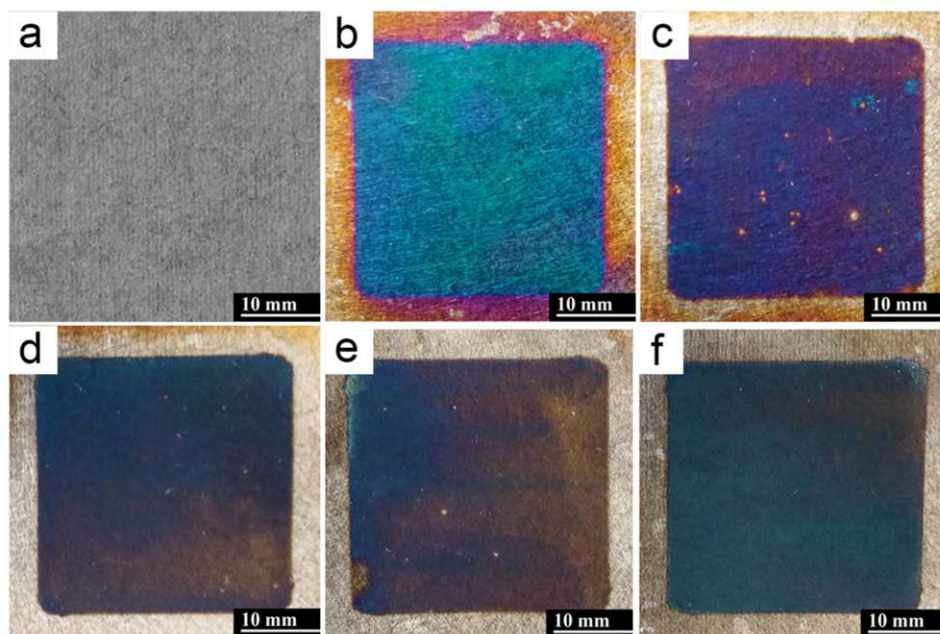
Four commercially available nonwoven CFFs were collected: thick binder-free CFF sample 1 (BFCFF-1) and thin binder-free CFF sample 2 (BFCFF-2) are both made from polyacrylonitrile webs prepared by carding and hydroentangling, and subsequently carbonized; nickel-plated CFF (NPCFF) is wet-laid carbon staple fiber bonded by polymer resin binder and plated with nickel; and carbon fiber veil fabric (VCFF) is tissue-like wet-laid carbon staple fiber bonded by a polymer resin binder. Aniline (certified ACS grade 99%), sulfuric acid (4N solution, certified pH 4.4), and sodium sulfate anhydrous (granular 10–60 mesh, certified ACS grade) were purchased from Fisher Scientific. Whatman grade 413 filter paper (VWR) was used as the separator material in the test cells.

### Deposition of PANI onto CFF

Samples of each of the four CFF types were coated with PANI under the same conditions. The CFF samples, measuring 4 cm  $\times$  4 cm were pressed against a stainless steel electrode in a custom made



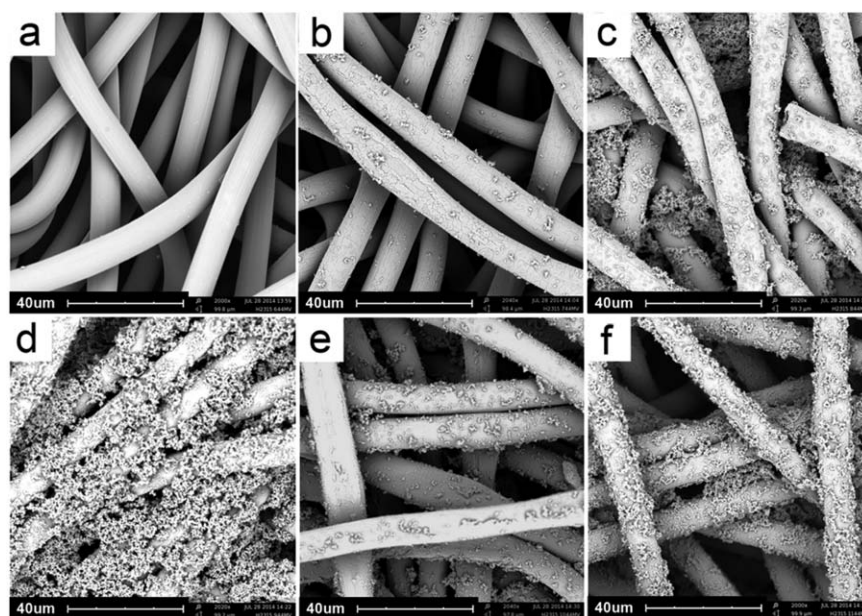
**Figure 2.** The three primary forms of PANI in their undoped structures, in order of increasing oxidation: (a) leuco-emeraldine, (b) emeraldine, and (c) pernigraniline.



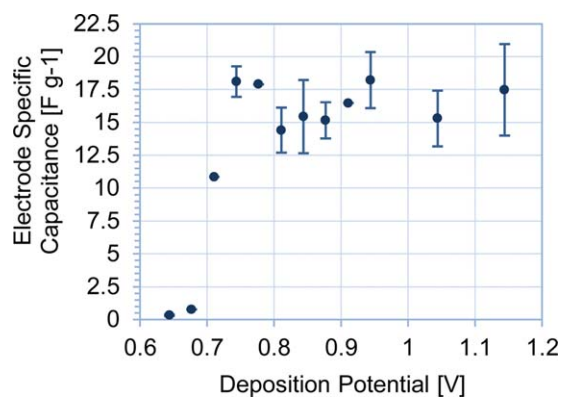
**Figure 3.** Carbon fiber binder free material (BFCF-2) deposited with PANI at various deposition potentials: (a) 0.644 V, (b) 0.744 V, (c) 0.844 V, (d) 0.944 V, (e) 1.044 V, and (f) 1.144 V, all versus Ag/AgCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

deposition cell (Figure 1) fitted with an Ag/AgCl (saturated NaCl) reference electrode (+0.196 V vs. NHE,  $-0.044$  V vs. SCE). The cell was then immersed in an aqueous solution containing 0.1M aniline and 0.5M  $\text{Na}_2\text{SO}_4$ . A stainless steel counter electrode was employed. A potential of 0.894 V versus Ag/AgCl (0.850 V vs. SCE) was applied for 10 min, causing the oxidative polymerization of aniline on the nonwoven CFF surface. Following deposition, each sample was rinsed under running DI  $\text{H}_2\text{O}$  for 20 sec on each side and dried at  $70^\circ\text{C}$  under air.

The coated CFF samples were then tested for specific capacitance, and among the four types, one which exhibited a large capacitance increase was subjected to further experimentation with deposition settings. For the subsequent deposition studies, the applied voltage was set to between 0.644 and 1.144 V (vs. Ag/AgCl) in 0.1 V increments (0.644, 0.744, 0.844, 0.944, 1.044, and 1.144 V). Within a limited range of 0.744–0.944 V, the potential was varied in 0.033 V increments (0.744, 0.777, 0.811, 0.844, 0.877, 0.911, and 0.944 V). Next, in order to study the



**Figure 4.** SEM images showing PANI deposited at (a) 0.644 V, (b) 0.744 V, (c) 0.844 V, (d) 0.944 V, (e) 1.044 V, and (f) 1.144 V.



**Figure 5.** Specific capacitance as a function of the potential used during deposition, from 0.644 to 1.144 V. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

effect of deposition time, the duration was set to 1, 5, 10, and 20 min, under a fixed potential. The effect of aniline concentration was also studied by preparing aniline solutions with concentrations of 10 mM, 100 mM, and 500 mM, and carrying out deposition under set potential. All experimentation was carried out using a VMP-3 potentiostat/galvanostat (Bio-Logic Science Instruments, Claix, France).

### Characterization

Electrochemical testing was carried out using a symmetrical two-electrode cell, with both electrodes taken from the same sample. Aqueous 0.5M Na<sub>2</sub>SO<sub>4</sub> was used as the electrolyte and standard cellulose filter paper was used as the separator. Cyclic voltammetry (CV) was conducted at sweep rates of 10, 50, and 100 mV/s to track the redox reactions of the deposited PANI, and chrono-potentiometry (CP) was carried out at 0.5, 1, and 2 mA to measure the capacitance of the deposited PANI.

CP was repeated for 10 cycles to ensure stability, and the charge value used in calculations was taken from the last cycle, using a current of 0.5 mA. Equation (1), based on the series capacitor circuit model of a two-electrode cell,<sup>24</sup> was then used to obtain the gravimetric specific capacitance  $C_S$  (in units of F/g, where F = Coulomb/V).  $Q$  is charge (in Coulombs), calculated as the product of the discharge current and the discharge time.  $\Delta V$  is the

voltage window. Throughout this study, the voltage window was fixed at 0.8 V (starting at 0.0 V and ending at 0.8 V vs. Ag/AgCl). The two electrode masses, represented by  $m_1$  and  $m_2$  (in grams) were measured using a Mettler–Toledo model MS105 balance (readability = 0.01 mg).

$$C_S = \frac{Q}{\Delta V} \left( \frac{m_1 + m_2}{m_1 * m_2} \right) \quad (1)$$

Unless designated otherwise, electrode mass includes CFF + PANI mass. It is worth noting that this approach differs from the more common practice of considering solely PANI mass and excluding contributions from CFF mass, which yields values that appear much higher.<sup>9</sup> Including all electrode materials (CFF + PANI) results in a lower value but a more relevant measure in terms of application standpoint. It is also a more reliable determination, since obtaining a measurement of PANI mass on the electrode is complicated by the fact that the initial mass of each bare carbon electrode ( $m_{\text{carbon}}$  in grams) can only be estimated based on the average areal density of the CFF ( $\rho_c$  in units of g/cm<sup>2</sup>) and the area of the electrode ( $A_{\text{electrode}}$  in units of cm<sup>2</sup>):

$$m_{\text{carbon}} = A_{\text{electrode}} * \rho_c \quad (2)$$

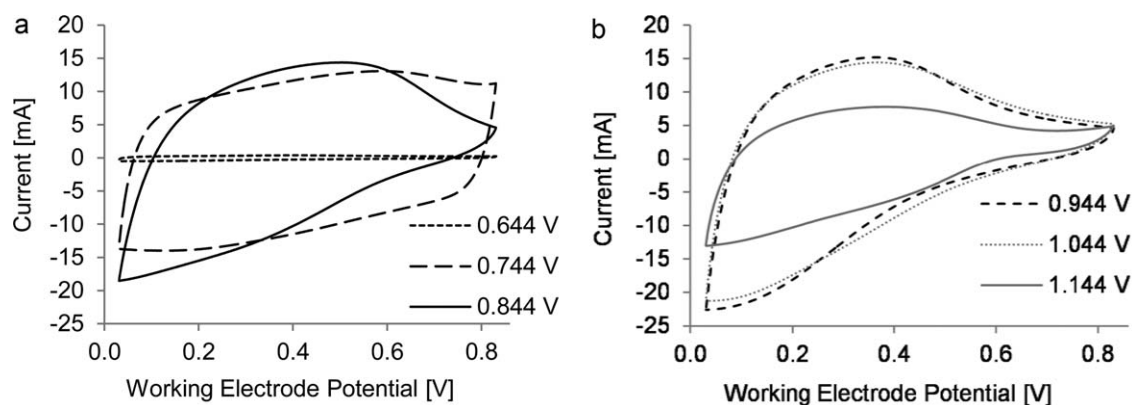
Following deposition, the total electrode mass ( $m_t$  in grams) is obtained by weighing, and the PANI mass on the electrode ( $m_{\text{pani}}$  in grams) is then assumed to be:

$$m_{\text{pani}} = m_t - m_{\text{carbon}} \quad (3)$$

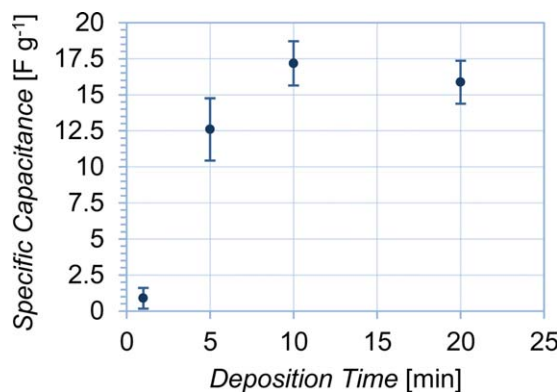
Cycle life was tested by measuring capacitance change over the course of 4000 charge–discharge cycles. The morphology of PANI depositions was examined using scanning electron microscopy (SEM) (Phenom Pro, Eindhoven NL), and color changes were documented by digital camera (Olympus STYLUS SZ-16).

## RESULTS AND DISCUSSION

For the initial screening, various nonwoven CFF materials were deposited with PANI from a solution of 0.1M aniline monomer in dilute H<sub>2</sub>SO<sub>4</sub> for 10 min. Capacitance of the samples was tested before and after deposition (Table I). Before deposition, all four samples—BFCFF-1, BFCFF-2, NPCFF, and VCFF—showed small capacitance values well below 1 F/g, arising due the electric double layer, which produces an electrostatic charge separation on the electrode surface and is surface area dependent. The



**Figure 6.** Cyclic voltammograms at a sweep rate of 10 mV/s for samples deposited at various potentials: (a) 0.644, 0.744, and 0.844 V. (b) 0.944, 1.044, and 1.144 V (all vs. Ag/AgCl reference).



**Figure 7.** Specific capacitance as a function of deposition time used during deposition, from 1 to 20 min, at a deposition potential of 0.777 V (vs. Ag/AgCl). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

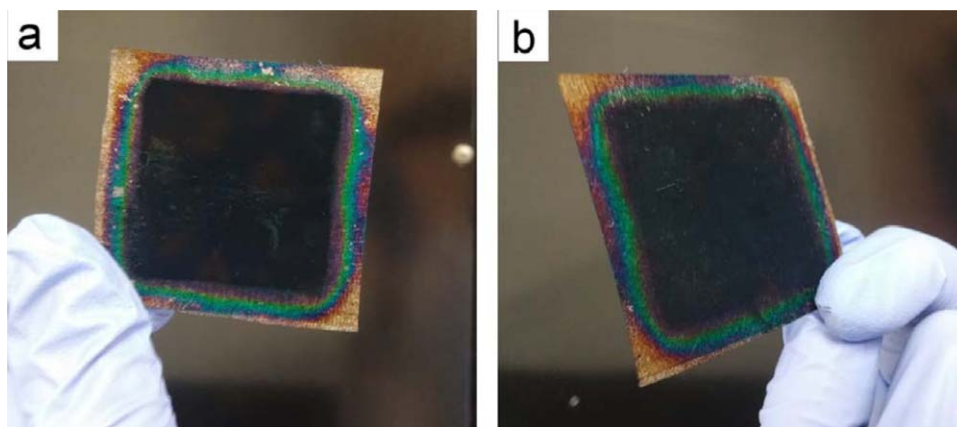
highest double layer capacitance was measured for VCFF, which was the veil-like material. This may be attributed to higher specific surface area due to lower fiber diameter. The typically low specific surface area (SSA) of CFF dictates that they are poor double layer capacitors unless the fiber surface is treated by physical or chemical activation to open up scores of micropores along the surface and increase SSA up to 2000 m<sup>2</sup>/g. Activation treatment is not the focus of the current study, rather the focus is on improving capacitance by adding a pseudocapacitive layer. Thus, while the capacitance values of the untreated samples indicated that they are poor electric double layer capacitors, they are useful as a starting material for a study which is focused on the impact of deposited PANI.

Specific capacitance values following deposition reflect the contribution of pseudocapacitive PANI. Although untreated VCFF had the highest initial specific capacitance, it only showed an increase of one order of magnitude, while NPCFF increased by two orders of magnitude upon PANI treatment. The two binder-free materials—BFCFF-1 and BFCFF-2—which had the lowest specific capacitance initially, showed the highest final specific capacitance values. These represented increases of three orders of magnitude.

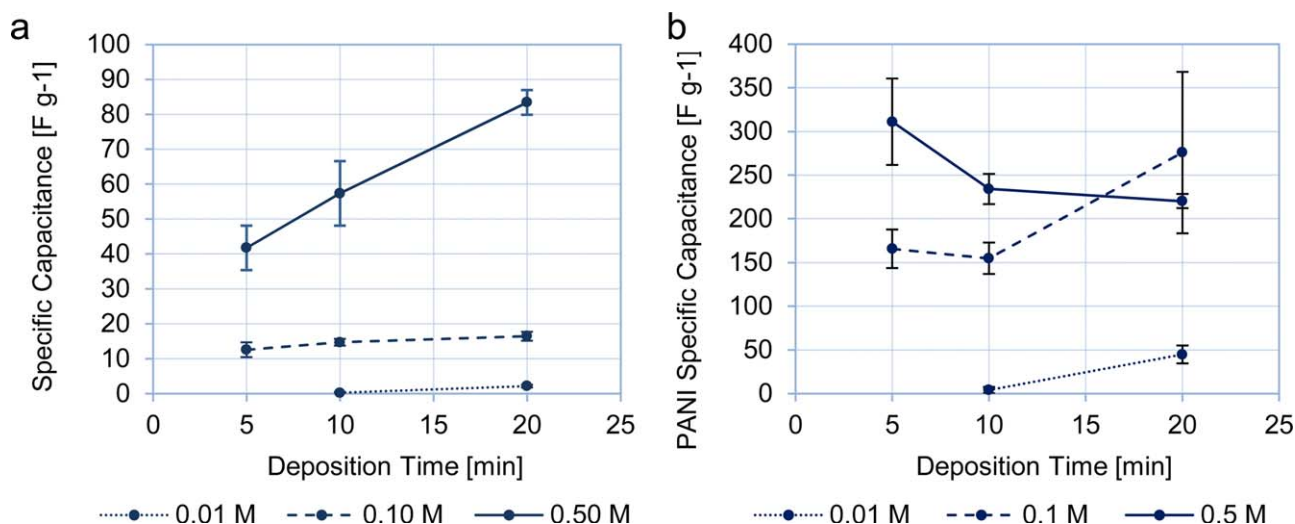
Compared with BFCFF-1, BFCFF-2 is thinner, which allows for better penetration of PANI. Therefore, BFCFF-2 was selected for further experiments with deposition conditions on the basis of the increase in capacitance that was exhibited in the initial screening. Six deposition potentials, between 0.644 and 1.144 V vs. Ag/AgCl, were applied. This range was chosen to coincide with the range of potentials typically used in potentiostatic polymerization of aniline.<sup>1</sup> PANI is a polymorph, with its particular form depending on oxidation state. Since the PANI produced here was synthesized across a range of potentials, it is possible that a variety of the well-known forms would be exhibited among the different samples. Figure 2 illustrates the chemical structures of three of the primary forms: leucoemeraldine, emeraldine, and pernigraniline.<sup>3</sup>

Digital images and corresponding SEM results of the PANI-coated carbon fiber show various colors associated with each potential (Figures 3 and 4). At 0.644 V, digital images indicate that the surface is free of PANI [Figure 3(a)]. At 0.744 V and beyond, PANI is deposited on the carbon fiber nonwoven. A distinct color shift from 0.744 V (teal) to 0.944 V (navy blue) can be seen, beyond which the color is stable [Figure 3(d–f)]. This phenomenon, known as electrochromism, is in agreement with the reported observations.<sup>25</sup> PANI is well known for its visible response to changes in pH—a feature which is utilized in applications such as gas sensors.<sup>23</sup>

In terms of the morphology, SEM of the 0.744 V sample [Figure 4(b)] shows a slightly cracked film-like coating on the fibers, along with randomly dispersed particle-like clusters. Carlin *et al.* employed ellipsometry to track changes in coating thickness through the duration of deposition and found that in early stages, PANI formed as a film, as the aniline monomer initially came into contact with the electrode surface.<sup>11</sup> After a buildup of film approximately 150 nm thick, they found that the morphology changed to form fiber-like structures. Similarly, distinct morphologies are observed on the samples under SEM in the present study. It should also be noted that unusually dense growth is seen at 0.944 V [Figure 3(d)], which can be explained by the non-homogeneity seen in the digital image—some regions have dense clusters, while others are sparse.



**Figure 8.** PANI deposited onto BFCF-2 for 20 min at 0.777 V (vs. Ag/AgCl). (a) Front face of sample. (b) Back of sample. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9.** Specific capacitance for samples treated with 0.01M, 0.10M, and 0.50M concentrations of aniline for various durations. (a) Values calculated on the basis of total electrode mass. (b) Values calculated based on PANI mass only. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Following CP tests, specific capacitance was calculated on the basis of total electrode mass (CFF + PANI). As was indicated with SEM and digital imaging, the sample with PANI deposited at 0.644 V showed no redox behavior. Onset of capacitance appeared at 0.711 V and continued to rise until 0.744 V, after which it hovered around a value of approximately 18 F/g for the remainder of samples (Figure 5). A correlation between the color of the polymer and specific capacitance was not evident from the CP results.

CV curves (Figure 6) showed more of a correlation with the color shift trend. The most symmetrical reduction and oxidation curves are seen for the samples treated at 0.744 and 0.777 V [Figure 6(a)], following which the curve became highly asymmetrical [Figure 6(b)]. Although the reactions appear to be reversible (no change was observed over the course of 10 cycles) the ideal CV shape for a supercapacitor is rectangular—thus, deposition potentials at 0.844 V and above should be avoided. Furthermore, it was observed that PANI only deposited on the face of the fabric for these samples prepared, whereas at 0.777 V and below, PANI could be seen on both the face and back of the sample.

Following the deposition of PANI at various potentials, 0.777 V was chosen for further experiments and deposition time was examined (Figure 7). Specific capacitance reached a maximum of around 17.5 F/g at 10 min of deposition.

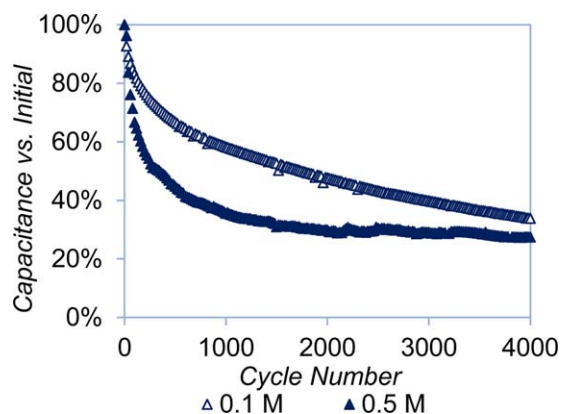
Aniline concentration was varied between 0.01M and 0.5M, and deposition time was also varied from 5 to 20 min. Surprisingly, the color resulting from the highly concentrated (0.50M) solution was distinctly different from the bright light green that had been seen at lower concentrations. Figure 8 shows the deep black color of the PANI on these samples—more similar to the color seen on samples deposited at high potentials. However, unlike the high potential samples, PANI was coated throughout the thickness of the material, appearing on both the face [Figure 8(a)] and the back [Figure 8(b)] of the samples. The color change between 0.10M and 0.50M remains unexplained.

Even at low deposition times, the 0.5M solution produced dramatically higher specific capacitance than previous results [Figure 9(a)]. While the highest specific capacitance obtained from 0.10M solution had been approximately 18 F/g (10 min), the 0.50M solution resulted in approximately 42 F/g after just 5 min. At 10 min, it was nearly 60 F/g. While a threshold appeared after 10 min for lower concentrations, specific capacitance continued to increase and reached over 80 F/g at 20 min for 0.5M concentration.

For the sake of comparison with results from the literature, the specific capacitance is also calculated solely on the basis of PANI mass and is presented in Figure 9(b). Considering that the theoretical maximum specific capacitance of PANI is 325 F/g, the

**Table II.** Specific Capacitance Values, Shown Both on the Basis of Total Electrode Mass as well as PANI Mass only, for Various Aniline Solution Concentrations and Deposition Times

Aniline concentration	Deposition time (min)	Average specific capacitance (F/g)	
		Based on measured total electrode mass	Based on estimated PANI mass only
0.01M	10	0.3	4.2
	20	2.2	44.6
0.10M	1	0.9	19.8
	5	12.6	165.6
	10	17.2	154.8
	20	15.9	275.8
0.50M	5	41.8	311.1
	10	57.4	234.2
	20	83.4	220.3



**Figure 10.** Change in capacitance with cycle number for electrode formed from aniline concentrations of 0.1M and 0.5M at 0.777 V versus Ag/AgCl for a duration of 20 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

values shown here are very promising. For the lower concentrations, 0.01M and 0.1M, PANI specific capacitance rises with deposition time, reaching approximately 275 F/g (Table II). This trend reverses somewhat for the 0.5M concentration, where increased deposition time leads to lower PANI specific capacitance. This can be explained by the higher PANI loading seen at 20 min (33 wt %) as compared with 5 min (12 wt %). All else being equal, if a given total capacitance is attributed to a higher mass, specific capacitance will be lower. Another example of this effect is observed at 20 min deposition times for the 0.1M and 0.5M aniline solutions. The former results in an average PANI specific capacitance were of 275 F/g, while the latter was around 220 F/g despite having a higher average total specific capacitance (~83 F/g compared with ~16 F/g). Again, the elevated PANI specific capacitance is due to a relatively low PANI mass loading (4 wt %).

Observed flaking of the PANI deposited from 0.5M solutions hinted that gains in specific capacitance could be accompanied by loss of cycle life. Electrodes prepared by 20 min depositions from 0.1M and 0.5M aniline solutions were charged and discharged galvanostatically at 2.0 and 2.4 mA, respectively, for 4000 cycles between 0.0 and 0.8 V (Figure 10). During the first 500 cycles, the 0.5M sample showed a much steeper capacitance loss, but the 0.1M sample performance continued to decline steadily for the remainder of the tests so that by 4000 cycles, the percentage loss was comparable. Still, the final specific capacitance was around 24 F/g for the 0.5M sample, as opposed to around 6 F/g for the 0.1M sample, leading to the conclusion that high concentration is preferred despite early degradation.

## CONCLUSIONS

Among nonwoven CFFs tested, the binder free materials (BFCFF-1 and BFCFF-2) showed the largest increase in capacitance following PANI deposition. Below 0.710 V versus Ag/AgCl, PANI polymerization did not occur at significant rates. Between 0.744 and 1.144 V, specific capacitance as a function of deposition potential was relatively stable. However, only samples below 0.777 showed reversible reactions based on analysis of the CV. Addi-

tionally, the mass of deposited PANI was concentrated at the face of the carbon fiber nonwoven for depositions carried out above 0.777 V which may have led to caking at higher aniline concentrations or deposition times. Therefore, deposition from 0.744 to 0.777 V is recommended for the potentiostatic method.

The biggest impact on performance was caused by varying the aniline concentration. The highest total specific capacitance in this study (80 F/g) was obtained from a solution of 0.5M aniline at a 20 min deposition time. High PANI specific capacitance values (350 F/g) were also recorded. It is yet to be determined whether further improvement could be seen at higher concentrations and longer deposition times. Increasing deposition time had a positive effect on capacitor performance, but reached a threshold for the 0.1M samples beyond which very limited improvement, or even decrease, could be seen. This was likely due to inaccessible PANI following maximum coverage of the substrate fibers. Future work will focus on determining the threshold deposition time for 0.5M aniline solutions.

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