

# Natural Fiber Welded Electrode Yarns for Knittable Textile Supercapacitors

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Natural fiber welded (NFW) yarns embedded with porous carbon materials are described for applications as electrodes in textile electrochemical capacitors. With this fabrication technique, many kinds of carbons can be embedded into cellulose based yarns and subsequently knitted into full fabrics on industrial knitting machines. Yarns welded with carbon and stainless steel have device capacitances as high as  $37 \text{ mF cm}^{-1}$ , one of the highest reported values for carbon-based yarns. The versatility of this technique to weld any commercially available cellulose yarn with any micro- or nanocarbon means properties can be tuned for specific applications. Most importantly, it is found that despite having full flexibility, increased strength, and good electrochemical performance, not all of the electrode yarns are suitable for knitting. Therefore, it is recommended that all works reporting on fiber/yarn capacitors for wearables attempt processing into full fabrics.

electronic components into fabrics, including sensors,<sup>[4]</sup> energy harvesting systems,<sup>[3,5,6]</sup> communication devices,<sup>[7–9]</sup> and they may one day be combined into full garments as depicted in **Figure 1a–c**. Currently, electronic textiles (e-textiles) remain limited by the requirement of a significant power source such as a pouch lithium battery, coin cell, or hard “battery pack.” One solution to this problem is textile energy storage (**Figure 1d**). Research in this field has grown significantly, with more reported devices being highly flexible and wearable, which we call garment devices.<sup>[2,3,10,11]</sup> In particular, because of the versatility of linear strands, (i.e., thread for stitching and embroidery or yarn for woven or knit textile production), a series of recent reports have focused on devel-

oping carbon based yarn and fiber (monofilament) electrochemical capacitors (ECs).<sup>[10,12–16]</sup> These papers report fibers with double-layer capacitances from  $0.5\text{--}15 \text{ mF cm}^{-1}$ , and pseudocapacitance reaching up to  $150 \text{ mF cm}^{-1}$ .<sup>[10]</sup> Due to their negligible toxicity and long cycle life, carbon based supercapacitors have been of particular interest to the community because they are readily wearable without the need to be replaced during the lifetime of the garment.

Previous reviews on ECs<sup>[14,17]</sup> discuss tailoring electrode materials to suit a particular power application. For example, while highly conductive carbons with low equivalent series resistance (ESR) are better suited for high power applications, inexpensive activated carbons with high surface area per volume are better suited for higher energy applications (while maintaining sufficiently high power compared to batteries). Some proposed devices, fabricated with capacitive yarns have excellent performance, but may only be able to incorporate a single kind of carbon material, such as grown graphene<sup>[18]</sup> or carbon nanotube (CNT),<sup>[19,20]</sup> into the yarns. Very few energy textile studies report on the performance of activated carbon,<sup>[15,21–23]</sup> yet it is still the most widely used and least expensive electrode material for conventional supercapacitors.

Knitting was used to assemble energy storing fabrics because computerized machine knitting requires less yarn and set-up time than industrial weaving machines to complete a sample textile. Thus smaller batches of yarn could be NFW and subsequently tested for knitting without wasting large quantities of yarn. With the appropriate knitting machinery (i.e., Shima Seiki, 122SV-SSG), conductive yarns can also be designed

## 1. Introduction

Wearable electronics<sup>[1]</sup> are finding applications in sports-wear, military uniforms, and medical gowns/bandages.<sup>[2,3]</sup> Researchers are currently working to incorporate various

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**Figure 1.** Concept illustration of a garment device embedded with electronic components knitted into the fabric: a) sensing fabric to monitor vitals or the environment; b) communication/logic fabric for sending, receiving, and interpreting information, c) energy harvesting fabric, such as piezoelectric materials or triboelectrics that can harvest energy from breathing or movement; and d) energy storing fabric, with alternating anodic/cathodic stripes.

into various geometries while remaining insulated from other conductive yarns. Once knitting conditions are optimized for use with industrial knitting equipment, and a knit program is complete, it can be sent to a factory immediately for mass manufacturing.

Scalability of yarn production is also a consideration for any proposed yarn supercapacitor or battery system if it will be a viable solution for powering textile electronics. The natural fiber welding (NFW) coating process presented in this report can produce hundreds of feet of coated yarn at a time, delivering consistent mass loadings of capacitive material. This scalable yarn production process integrated with the industrial knitting process as demonstrated in this report presents strong potential for a completely scalable system.

Here, cellulose yarns were converted to ECs through NFW,<sup>[24]</sup> a process that uses controlled amounts of ionic liquids (ILs) and molecular co-solvents to selectively swell and mobilize biopolymers in fibrous materials for functional modification. NFW processes control and minimize the amount of dissolution (denaturation) of fibrous natural substrates, maintaining or often enhancing the inherent strength of the native biopolymer material. During the welding process, hydrogen bonding networks between biopolymers are reconfigured and extended by only mobilizing the outermost biopolymers of individual fibers. By regulating the ratio of solvent to substrate, solvent efficacy, time, temperature, pressure, location of solvent exposure, etc., fibrous materials are welded together to create complex composites while maintaining the structure of individual fibers in their native states in the core.<sup>[24,25]</sup> Through fiber welding, functional materials (i.e., nanocarbons, magnetic materials) as well as molecules (i.e., fluorescent dyes and pharmaceuticals) can be incorporated into natural fibers to generate composite systems with advanced functionalities.

In this study, activated carbon materials were introduced into swelled cellulose yarns (cotton, linen, bamboo, viscose) during the welding process. When the ionic liquid was removed,

carbon particles were embedded in the fiber surface, forming a conductive network between welded fibers. The electrode materials and electrochemical properties were investigated. The welded systems showing the most potential were assembled into two-electrode EC systems and evaluated for electrochemical performance. The NFW material entrapment method yields high carbon mass loadings per length of yarn ranging from 0.35 mg cm<sup>-1</sup> up to 0.62 mg cm<sup>-1</sup>, corresponding to high capacitance per length of 8 mF cm<sup>-1</sup> up to 37 mF cm<sup>-1</sup> at 2 mV s<sup>-1</sup>. When initial attempts to knit the NFW yarns were unsuccessful, the NFW process was tuned to deliver modified yarns capable of knitting. Though some yarns were successfully created, tested, and knitted, challenges remain in the textile fabrication portion of the project, and likely represent the biggest obstacle researchers will have in order to deliver a knittable supercapacitor.

This work will initially explore results from cotton yarns and subsequently present other cellulose-based yarns and carbons, and compare their electrochemical properties.

## 2. Results and Discussion

### 2.1. Carbon-Natural Fiber Welded Cotton Yarns

The IL solvent (1-ethyl-3-methylimidazolium acetate [EMI][Ac]) was used as received from Sigma Aldrich. Cellulose yarns (cotton, linen, bamboo, and viscose) and carbon materials (i.e., activated carbon, carbon black) were used as received. The 0.5% and 1.0% binder consisted of a 50:50 (w/w) blend of microcrystalline cellulose (MCC):cotton dissolved in the IL solution. The 1.5 wt% binder was only MCC. Controlled ratios of solvent, solute, and carbons were utilized with consideration to optimize mechanical integrity of coatings while allowing and facilitating acceptable mass transport. Solutions of 0.25 mole fraction [EMI][Ac] : [ACN], biopolymer binder and suspensions of carbon materials were prepared in a glove box to rigorously control water concentration. Previous research in NFW has shown that appreciable water content can inhibit the fiber welding process.<sup>[24,25]</sup> Binder and carbon materials were dispersed in IL-based solutions with sonication and a Flacktek Speed Mixer (Model DAC 150 SP) running at 3500 rpm for 2 min intervals prior to coating. These binder ratios and mass loadings are presented in **Table 1**.

Spooled yarns were directed through a syringe filled with desired IL solution into an appropriate gauge needle (**Table 1**) at a speed of 3.7 cm s<sup>-1</sup> (**Figure 2a–c**). The coated yarn was wrapped around a Teflon-coated drum and heat treated in a 60 °C oven for 30 min (**Figure 2d**). Immediately following heat treatment, the IL solution was removed with anti-solvent (water) in a deionized water reconstitution bath for 12 h (**Figure 2e**). The fiber-welded yarns were dried thoroughly prior to testing and/or incorporation into further electrode assemblies. These yarns are so-called activated carbon-natural fiber welded yarns (AC-NFW).

For lab scale purposes, a handheld yarn spinner (“Lacis” Power, 4-ply Cord Maker and Fringe Twister) was used to twist the AC-NFW yarns with a highly conductive stainless steel yarn (**Figure 2f,g**). Both yarns are spun individually in a Z twist<sup>[26]</sup>

**Table 1.** Material performance summary. Capacitance per length and ESR per length determined from CV and EIS.

Coating process	Yarn type	Binder <sup>a)</sup> mass [%]	Carbon mass <sup>b)</sup> [mg cm <sup>-1</sup> ]	Needle gauge	Reconstitution	Capacitance per length [mF cm <sup>-1</sup> ]				
						2 mV s <sup>-1</sup>	5 mV s <sup>-1</sup>	10 mV s <sup>-1</sup>	20 mV s <sup>-1</sup>	ESR at 1 kHz
AC-NFW	Cotton	1.0	0.35	1" heat shrink	60 °C, 30 min	7.6	6.4	5.2	4.1	2.3
	Cotton	1.0	0.37	2" 20G	in-line water	6.7	5.1	3.9	2.8	2.5
AC-St-NFW	Cotton/Steel	0.5	0.62	1" 16 G	in-line water	37.2	27.2	19.5	13.1	1.5
AC-NFW	Viscose Blend	0.5	0.44	2" 18 G	in-line water	2.6	2.0	1.5	1.1	1.5
	Linen	0.5	0.59	2" 18 G	in-line water	11.5	8.0	5.9	4.1	1.7
	Bamboo	0.5	0.54	2" 18 G	in-line water	13.0	9.8	7.6	5.6	–
Gr-NFW	Cotton	1.0	0.41	2" 18 G	in-line water	8.3	6.7	4.9	3.2	1.4

<sup>a)</sup>Binders were 50:50 MCC/cotton blend, except yarn C (100:0 MCC:cotton blend, and yarns F and G (0:100 MCC:cotton blend); <sup>b)</sup>All carbon ratios were =90:10 activated carbon YP50:other carbons (carbon black, graphene).

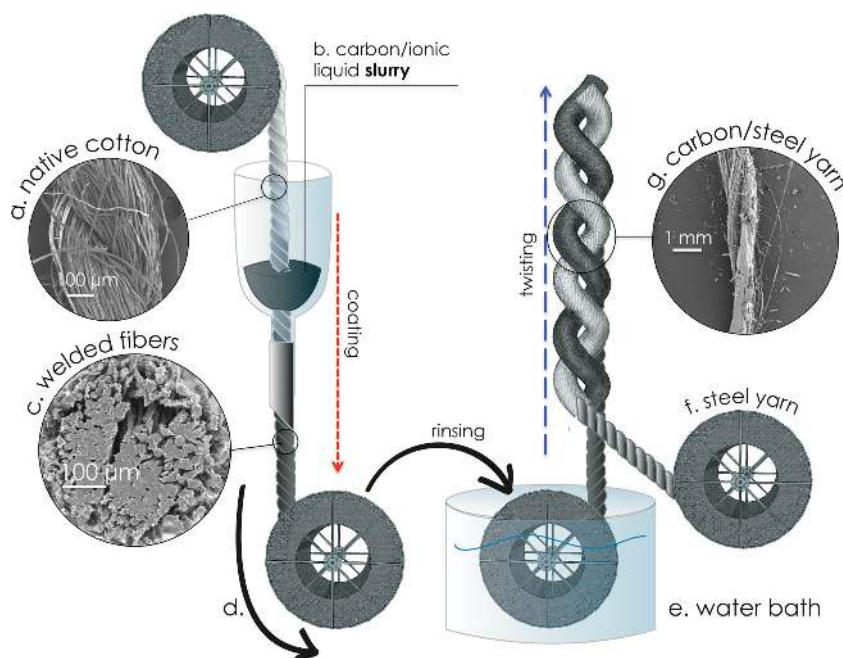
(turning right), until  $\approx 10$  turns per inch, then are plied together in an S twist (left turn), also  $\approx 10$  turns per inch. The combination of Z and S twisting locks the yarns together.

Scanning electron microscopy (SEM) was used to examine the individual materials and the morphology of the yarns in their native state (Figure 3). The cotton fibers were  $\approx 15\text{--}20\ \mu\text{m}$  thick and made up a  $500\ \mu\text{m}$  diameter two-ply yarn (Figure 3a). The activated carbon (AC) particles range from  $2\ \mu\text{m}$  to  $10\ \mu\text{m}$  in size (Figure 3b). The stainless steel fibers were measured to be  $\approx 7\ \mu\text{m}$  thick (Figure 3c). Figure 3d,e show the AC-NFW yarn twisted together, and the surface morphology of the carbon embedded cotton. After coating with AC, the yarns did not appreciably change in thickness; for NFW yarns (biopolymer binder without carbon), the thickness decreased as fibers welded together and collapsed the internal porosity (Figure S1, Supporting Information). For AC-NFW yarns, the fibers appear less heavily welded at the core due to the interference of AC particles with binder (Figure 3g). A more porous electrode structure will allow effective incorporation of electrolyte. A cross-sectional image of the AC-St-NFW cotton yarn (Figure 3h) shows similar porosity to the AC-NFW, indicating it will also allow good incorporation of electrolyte.

The masses of each yarn were measured before and after welding to determine the mass loading of carbon. Due to some variability from yarn to yarn, the masses were averaged from  $\approx 100\ \text{cm}$  of native and AC-NFW yarns. The mass of AC, binder and carbon black (CB) in the AC-NFW yarns ranges from  $0.34\ \text{mg cm}^{-1}$  to  $0.37\ \text{mg cm}^{-1}$ , and AC-St-NFW yarns yield masses of  $0.62\ \text{mg cm}^{-1}$ . These average masses per length were used to determine gravimetric capacitance. As described in our previous work,<sup>[2,21,22]</sup> active material mass loading is a significant metric for the practical application of capacitive yarns. Though some works report very high gravimetric capacitances (e.g.,  $200\text{--}300\ \text{F g}^{-1}$ ), these often are testing

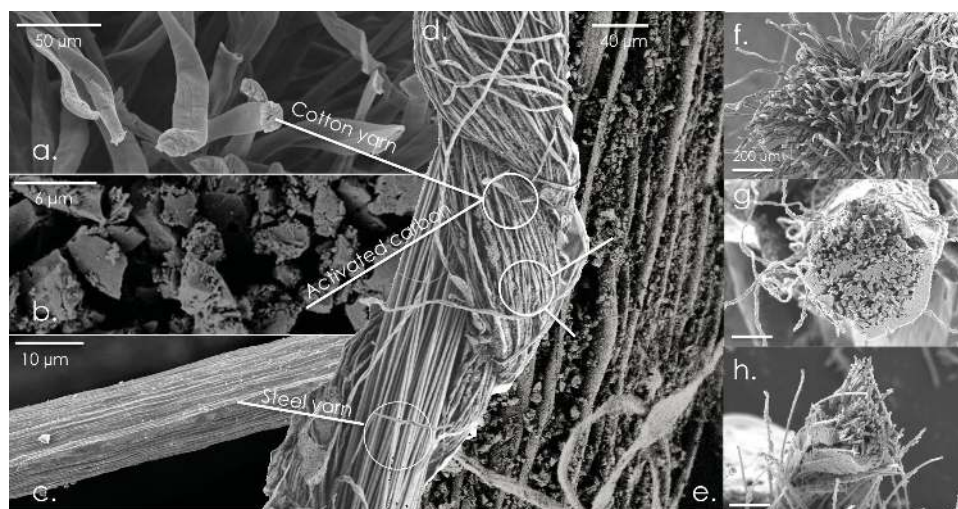
very small amounts of active material<sup>[20,27,28]</sup> ( $<10\ \text{mg}$  per electrode). The resultant devices have very low capacitance per area or length, on orders of  $7\ \text{mF cm}^{-2}$  or  $0.5\ \text{mF cm}^{-1}$ ,<sup>[12,27,29]</sup> which are less suitable for applications that have limited available surface area. The masses reported here are appreciably higher than masses reported in other supercapacitive yarns.<sup>[2,12,19]</sup>

Prior to knitting any yarn, electrochemical characterization was performed to determine which fabrication conditions yielded the highest capacitance and lowest resistance. Strands of yarn were assembled into two-electrode symmetric  $6\ \text{cm}$  long devices with two layers of Celgard separator (polypropylene nanofibers), and soaked in a PVA based polymer electrolyte, so called "SiWA".<sup>[30]</sup> A single strand of stainless steel yarn was



**Figure 2.** Yarn coating via NFW and stress-strain curves of various native and AC-NFW yarns. a) SEM image of native cotton yarn. b) Schematic of carbon/ionic liquid slurry in a vessel that cotton yarns travel through to be coated. c) SEM image of welded cotton fibers. d) Yarn being spooled onto a drum after welding. e) Welded yarns being reconstituted in a water bath, which also removes the ionic liquid. f) Steel yarn then twisted with the reconstituted AC-NFW yarns. g) SEM image of AC-NFW yarn twisted with stainless steel yarn.





**Figure 3.** SEM images of yarn and carbon materials: a) uncoated cotton yarn, b) activated carbon particles, c) a single stainless steel fiber, d) twisted AC-NFW and steel yarns, e) close-up of the yarn surface after AC-NFW on cotton, f) native cotton yarn cross-sectional view, g) AC-NFW cotton yarn, and h) AC-St-NFW cotton yarn.

used as the current collector in each electrode, and was directly connected to the potentiostat with alligator clips. For the AC-NFW cotton yarns, the active material had a low gravimetric capacitance of  $36 \text{ F g}^{-1}$  per electrode when tested at  $2 \text{ mV s}^{-1}$ . YP-50 AC is rated for  $88 \text{ F g}^{-1}$  by the manufacturer, and previous studies also confirmed a higher capacitance with the same polymer electrolyte.<sup>[22]</sup> In an effort to increase electrochemical performance, we modified the NFW process, coating the steel and cotton yarns after they had been pre-twisted together (AC-St-NFW). This modification increased contact between current collector and the electrode yarns, greatly improving mass loading, gravimetric capacitance, and capacitance per length. **Figure 4a** shows cyclic voltammograms at  $5 \text{ mV s}^{-1}$  of the AC-NFW and AC-St-NFW yarns. The AC-St-NFW yarn results in higher AC mass loadings of  $0.66 \text{ mg cm}^{-1}$ , compared to  $0.34 \text{ mg cm}^{-1}$ , and increases the gravimetric capacitance from  $36 \text{ F g}^{-1}$  to  $120 \text{ F g}^{-1}$  (at  $2 \text{ mV s}^{-1}$ ). In AC-St-NFW yarns, the carbon is also intermixed with the steel fibers, improving the contact between the current collector and the various carbon particles embedded in the cotton yarn and yields  $37 \text{ mF cm}^{-1}$  vice  $6\text{--}8 \text{ mF cm}^{-1}$ . Electrochemical impedance spectroscopy (EIS) was performed using a  $10 \text{ mV}$  amplitude fluctuation centered at  $0.0 \text{ mV}$  vs OCV, and scanned between  $200 \text{ kHz}$  and  $10 \text{ mHz}$  oscillation frequencies. **Figure 4b** shows that the AC-NFW yarns are less resistive than the AC-St-NFW,  $0.5 \text{ } \Omega/\text{cm}$  vs  $1.5 \text{ } \Omega \text{ cm}^{-1}$ , which can also be attributed to having lower carbon mass. A semicircle characteristic of charge transfer resistance is present for both materials at high frequencies, which can be attributed to the diffusion of ionic species through the polymer electrolyte into small activated carbon pores.<sup>[31,32]</sup> This feature would be less prominent in non-porous systems, as this polymer electrolyte has been thoroughly tested at scan rates up to  $20 \text{ V s}^{-1}$  in previous work.<sup>[30]</sup>

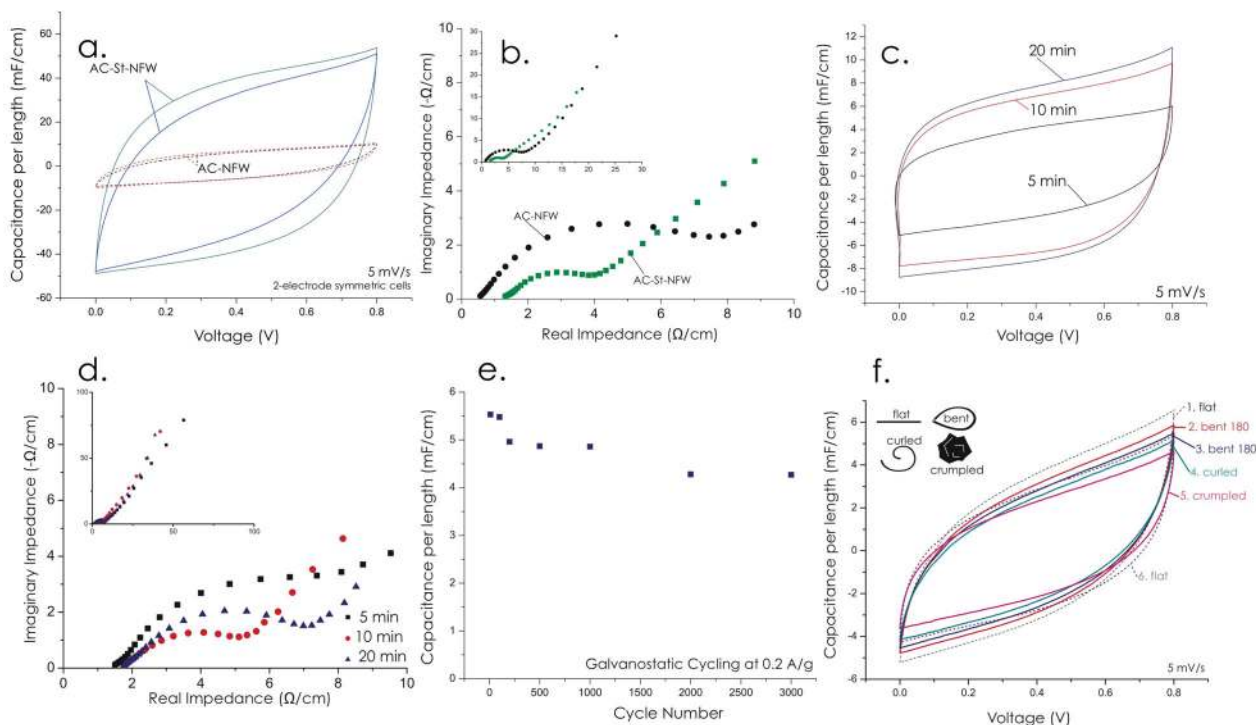
Evident from the poor rate handling at fast scan rates, this particular material system has power limitations due in part to the low conductivity of the activated carbon combined with a slower ion transport in gel electrolyte. To ensure that this material was

safe for integration into wearable fabrics and frequent skin contact, we chose to use activated carbon as the electrode material. However, the power can be improved by using more conductive carbons such as CNTs, carbon onions, or graphene flakes, as demonstrated in other works,<sup>[12,18,33]</sup> and will be discussed later.

A study was performed to determine the ideal soaking time for these materials to optimize capacitance and ensure all of the material is accessible to the electrolyte. Samples were soaked for 5, 10, and 20 min in SiWA before heat treating at  $90 \text{ }^\circ\text{C}$  for 20 min. All devices were made from the same length of AC-NFW yarns and tested in a symmetric set-up with electrodes  $6 \text{ cm}$  in length. **Figure 4c** shows the resulting CVs at  $5 \text{ mV s}^{-1}$ . Soaking for at least 20 min results in almost twice the capacitance compared to the 5-min soaked samples. EIS (**Figure 4d**) shows that the ESR remains  $\approx 1.6 \text{ } \Omega \text{ cm}^{-1}$  at  $1 \text{ kHz}$  for each system tested, indicating the observed capacitance increase is due solely to the electrolyte accessing more carbon material.

Long term cycling was conducted on an AC-NFW sample that was soaked for 20 min in SiWA (**Figure 4e**). Galvanostatic cycling was conducted at  $0.2 \text{ A g}^{-1}$  ( $0.408 \text{ mA}$  for  $\approx 2.04 \text{ mg}$  of active material), for 3000 cycles in a  $0.8 \text{ V}$  window over the course of 3 days. **Figure 4e** depicts the capacitance per length at cycles 10, 100, 200, 500, 1000, 2000, and 3000. From cycle 10 to 3000, there is an appreciable decay of  $\approx 23\%$ , decreasing from  $5.5$  to  $4.3 \text{ mF cm}^{-1}$ . It is possible that over the course of testing, some of the activated carbon particles delaminated from the cotton surface and from each other, reducing the overall conductivity of the sample. Regardless, future studies are needed to identify the cause of this capacitive decay.

Flexibility testing of these materials compared to their electrochemical performance is crucial for wearable and other flexible applications. We tested a cotton AC-NFW yarn while initially flat, bent  $180^\circ$ , curled, and crumpled into a ball. **Figure 4f** shows the resulting CVs from these stress tests at  $10 \text{ mV s}^{-1}$ . The device was precycled at  $20 \text{ mV s}^{-1}$  for 100 cycles prior to bending. There was some capacitive decay upon bending and deforming the yarns, but even when severely crumpled, the



**Figure 4.** Electrochemical results for all carbon welded yarns. a) CVs taken at  $5 \text{ mV s}^{-1}$  for cotton yarns that underwent AC-NFW and AC-St-NFW normalized to capacitance per length. b) EIS plots taken from 200 kHz to 10 mHz for the cotton devices from a, the larger plot is the close-up of the high frequency region, and the inset depicts the entire curve down to 10 mHz. c) CVs of AC-NFW samples soaked at 5, 10, and 20 min in SiWA and are normalized to capacitance per length ( $\text{mF cm}^{-1}$ ) vs voltage. d) EIS results taken from 200 kHz to 10 mHz, large plot: close up of high frequency region, inset: full plot from high to low frequencies. e) Long term cycling at  $0.2 \text{ A g}^{-1}$  over 3000 galvanostatic cycles. f) Flexibility testing of AC-NFW cotton yarns at  $10 \text{ mV s}^{-1}$ . The device was tested while 1) flat, 2) bent  $180^\circ$ , 3) bent again at  $180^\circ$ , 4) curled twice upon itself, 5) crumpled into a ball without crossing the anode and cathode leads, and 6) finally flat again.

device remained operational and recovered some capacitance when flattened again.

In separate experiments, graphene nanoplatelets were fiber welded into cotton yarns and investigated as an alternative or supplement to activated carbon (Figure 5a). Mechanical and electrochemical testing of these electrode systems were both performed for comparison. As assembled, these graphene cotton NFW yarns yielded  $\approx 8 \text{ mF cm}^{-1}$ , the same as the AC-NFW cotton yarns. Of note, these experiments were performed prior to the NFW optimization involving AC-St-NFW yarns and the soaking studies, both of which greatly enhanced electrode electrochemical performance. From these results, we demonstrate our presented methods' capability to incorporate other micro/nanocapacitive materials for the discussed application. Further studies with graphene need to be pursued to optimize the material.

Initial knitting of the cotton welded yarns revealed that they were all too brittle to withstand being processed though the machine. Even at slow speeds, the knitting needles typically cut through the material instead of forming knit loops. Therefore, other cellulose based materials needed to be explored.

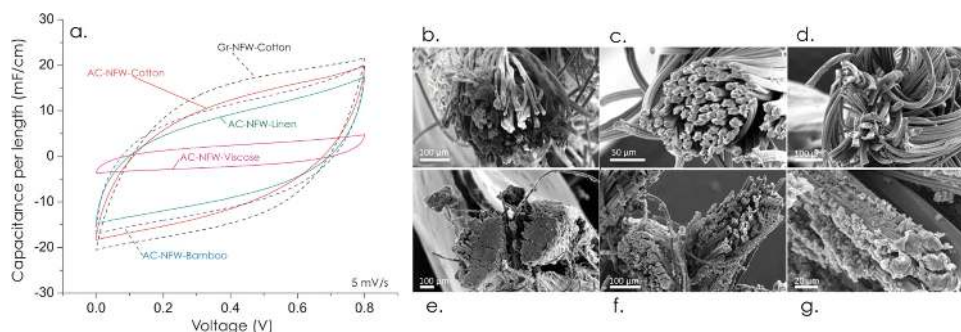
## 2.2. AC-NFW on Other Cellulose Based Yarns

Because AC-NFW-cotton yarns yielded good electrochemical results, and the AC-NFW process can be used for any cellulose

based yarn, we conducted AC-NFW on linen, bamboo and viscose yarns (Figure 5).

Cotton yarns have average solid mass loadings of  $0.34 \text{ mg/cm}$ . The bamboo, linen and viscose yarns delivered higher initial mass loadings ranging from  $0.44\text{--}0.59 \text{ mg cm}^{-1}$  (Table 1). SEM images of the native and AC-NFW yarns can be seen in Figure 5b–g. Similarly to the cotton welded yarns, the linen, bamboo, and viscose retain more porosity with the incorporation of AC into the welding process.

The viscose yarn had the lowest capacitance per length though it has carbon loading on the same order as all of the other yarns (Figure 5a). Since it is a blend (viscose/nylon 80/20), we believe that the nylon fibers, which do not weld with the carbon or cellulose, block the steel yarn current collector from making electrical contact with some of the carbon particles, thus lowering the overall capacitance of the yarn to  $1.79 \text{ mF cm}^{-1}$ , still three times higher than other reported devices.<sup>[12,18,19,34,35]</sup> Comparatively, bamboo and linen had capacitances of  $13.0$  and  $11.45 \text{ mF cm}^{-1}$ , respectively, compared to  $8.5 \text{ mF cm}^{-1}$  for heat treated cotton, and  $7.0 \text{ mF cm}^{-1}$  for non-heat treated from CVs at  $2 \text{ mV s}^{-1}$  (Figure 5a). Similarly to the AC-NFW cotton, the gravimetric capacitance was surprisingly low,  $48$  and  $38 \text{ F g}^{-1}$  for bamboo and linen respectively, compared to  $36 \text{ F g}^{-1}$  for non-heat treated AC-NFW cotton. Each of the viscose, bamboo, and linen AC-NFW yarns were successfully machine knitted.



**Figure 5.** a) Cyclic voltammety at  $5 \text{ mV s}^{-1}$  of AC-NFW linen, bamboo and viscose yarns as compared to AC-NFW for cotton, and graphene embedded cotton (Gr-NFW). SEM images b) native linen yarn, c) native bamboo yarn, d) native viscose-nylon yarn, e) AC-NFW linen, f) AC-NFW bamboo, and g) AC-NFW viscose-nylon.

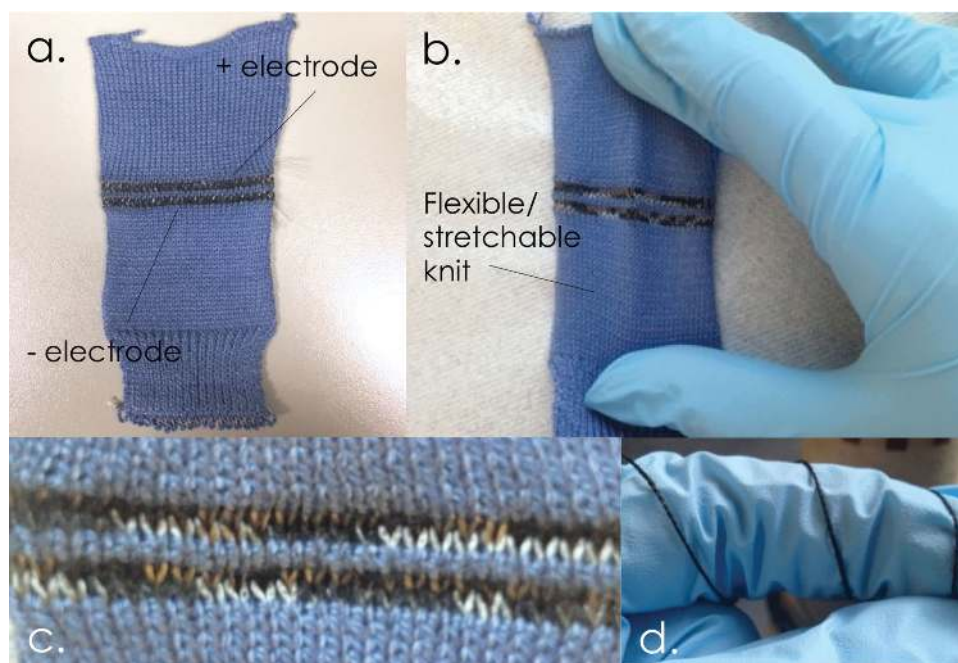
Given the better performance of AC-NFW bamboo, AC-St-NFW was prepared for bamboo yarns and tested after being soaked for 20 min. Flaking on these yarns was unexpectedly severe and resulted in electrical shorting of every assembled device. For future work, the polymer electrolyte will be coated and dried onto the yarns prior to handling to avoid additional flaking. Additionally, this yarn was processed through the knitting machine to determine if the mechanical properties were ideal, and it failed to knit.

### 2.3. Knitted Devices

Knitting of the yarns was carried out on a Shima Seiki SSG 122SV V-bed knitting machine. Small swatches of fabric were programmed on the Apex-3 knit paint software (Figure 6). Each electrode is two knitted rows, composed of  $\approx 48 \text{ cm}$  of yarn

per electrode. Two rows of non-conductive yarn are knitted in the middle of each electrode to act as a physical separator, and the SiWA electrolyte is coated onto the fabric after assembly.

We began by attempting to knit the AC-NFW and AC-St-NFW cotton yarns. It was found that all of the cotton yarns were too brittle to withstand being contorted through the knitting machine, and subsequently the knit structure, and broke into many small pieces. After the failure of the cotton yarns, we proceeded to successfully knit the linen, bamboo and viscose AC-NFW yarns depicted in Figure 6. We believe that because the fibers in linen (2–4 feet), bamboo (2–3 inch), and viscose (continuous filament) are all longer than the cotton yarn fibers (0.5–1.5 inch), they were less likely to pull apart from each other while under tension in the knitting machine, and the strength of the cellulose polymer could actually contribute its support while knitting. Future work will elaborate on the electrochemical performance of the knitted devices.



**Figure 6.** Photographs of knitted samples: a) photograph of a flat knitted supercapacitor, b) photograph of knitted supercapacitor while stretched, c) close-up photograph of knitted electrode stripes, and d) yarn prior to knitting wrapped around a finger demonstrating its flexibility.



### 3. Conclusions

In conclusion, we have demonstrated the potential of carbon-loaded cellulose fibers for capacitive energy storage. Activated carbon was embedded into the fiber surface in quantities up to  $\approx 0.6 \text{ mg cm}^{-1}$ . Cotton AC-St-NFW yarns yielded capacitances up to  $37 \text{ mF cm}^{-1}$ , with low ESR of  $1.5 \Omega \text{ cm}^{-1}$ , and AC-NFW had capacitance up to  $8 \text{ mF cm}^{-1}$ . Other types of cellulose based yarns and carbons were successfully fabricated using the welding process to make electrode yarns. Only the AC-NFW linen, bamboo and viscose yarns were knitted into symmetric fabric devices. Therefore, based on our observations, we suggest future work on capacitive and battery yarns also try to knit or weave their materials before determining whether they are viable for textile applications.

### 4. Experimental Section

**Materials:** 1) YP50F Activated Carbon (AC): 80% pores 1.0–1.2 nm, particles range from 2–10  $\mu\text{m}$ ,  $\approx 1500 \text{ m}^2 \text{ g}^{-1}$ , Kuraray, Japan (Figure 3b). 2) Carbon black (CB): 50 nm particles, SSA:  $\approx 100 \text{ m}^2 \text{ g}^{-1}$ , Sigma Aldrich. 3) Cotton yarn:  $\approx 15\text{--}20 \mu\text{m}$  thick fibers, 500  $\mu\text{m}$  thick yarn, Mercerized cotton (Camilla Valley Farmer's Weave Supply) (Figure 3a,f). 4) Linen yarn:  $\approx 27 \mu\text{m}$  thick fibers, 375  $\mu\text{m}$  thick yarn, (Silk City Fibers, NJ, USA) (Figure 5b). 5) Bamboo yarn: 14.5  $\mu\text{m}$  thick fibers,  $\approx 725 \mu\text{m}$  thick yarn, (Silk City Fibers, NJ, USA) (Figure 5c). 6) Viscose-nylon yarn:  $\approx 10 \mu\text{m}$  thick viscose fibers and 30  $\mu\text{m}$  thick nylon fibers,  $\approx 500 \mu\text{m}$  thick yarn, (Silk City Fibers, NJ, USA) (Figure 5d). 7) Stainless steel yarn (SS): 7  $\mu\text{m}$  thick fibers, 90  $\mu\text{m}$  thick yarn, (Bekaert, Germany)  $\approx 0.3 \Omega \text{ cm}^{-1}$  (Figure 3c). 8) Polymer gel electrolyte (SiWA):<sup>[30]</sup> 5.16 g Silicotungstic acid, 1.4g polyvinyl alcohol, 0.5 ml phosphoric acid, 20 mL water. 9) Cellulose binder: Microcrystalline cellulose ( $\approx 20 \mu\text{m}$ , Sigma Aldrich) or a few fibers from native yarn dissolved in ionic liquid. Specified per sample. 10) Celgard (separating membrane): 25  $\mu\text{m}$  thick. 10) IL: 1-ethyl-3-methylimidazolium acetate (BASF  $\geq 90\%$ ), Sigma Aldrich.

**Scanning Electron Microscopy:** Images were acquired using a JEOL JSM-6360LV SEM operating at 15–20 kV. Cross section samples were soaked in deionized water and frozen in liquid  $\text{N}_2$  before cross-sectioning (modified cryotome), to optimize the cut and obtain the clearest SEM images of the entire cross section. Each yarn was gold sputter-coated for five minutes prior to analysis.

**Electrochemical Testing:** Samples were cycled using a Biologic VMP3 or MPG potentiostat/galvanostat, and underwent cyclic voltammetry (CV), galvanostatic cycling (GC), and electrochemical impedance spectroscopy (EIS) to determine capacitance and equivalent series resistance (ESR). All devices underwent CV at  $20 \text{ mV s}^{-1}$  for 100 cycles to "pre-cycle" the device, then capacitance measurements were taken from CVs at 1, 2, 5, 10, 20, and  $50 \text{ mV s}^{-1}$ , followed by GV at 0.1, 0.2, 0.5 and  $1.0 \text{ A g}^{-1}$  of active material. All devices were tested in a 0.0–0.8 V window in a symmetric two-electrode cell. All devices were tested in SiWA electrolyte.

**Reported Metrics in this Work:** For all devices, the device capacitance could be determined from CV or GC according to Equation (1), (2) respectively. To determine the capacitance from CV, one must integrate the area under the discharge curve with respect to the voltage window (Equation (1)). To determine the capacitance from GV, one must take the slope (dV/dt) of the discharge curve and then divide that by the applied current (i). In both Equation (1), (2), i is the current, V is the voltage,  $\Delta E$  is the voltage window, and t is time. It can be converted to capacitance per gram ( $C_{F/g}$ ) by dividing the device capacitance ( $C_D$ ) by the mass of carbon on a single electrode (m). The device capacitance per length ( $C_{cm}$ ) of yarn was determined by dividing the device capacitance by the length (L) of the device (Equation 4).

$$C_D = \frac{\int idV}{\Delta E}$$

$$C_D = (dV/dt)/i$$

$$C_{F/g} = 2C_D/m$$

$$C_{cm} = C_D/L$$

**Yarn Cell Assembly for Electrochemical Testing:** Individual yarns were tested for their viability as electrode materials in fabric supercapacitors. All tested devices were two-electrode symmetric cells, composed of two yarn electrodes, two layers of Celgard separator, and SiWA electrolyte, encased in plastic for testing.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] S. Seymour, *The Intersection of Design, Fashion, Science, and Technology*, SpringerWien, New York 2008.
- [2] K. Jost, G. Dion, Y. Gogotsi, *J. Mater. Chem. A* **2014**, 2, 10776.
- [3] Z. L. Wang, W. Z. Wu, *Angew. Chem. Int. Ed.* **2012**, 51, 11700.
- [4] S. Choi, Z. Jiang, *Sens. Actuators A* **2006**, 128, 317.
- [5] F.-R. Fan, Z.-Q. Tian, Z. Lin Wang, *Nano Energy* **2012**, 1, 328.
- [6] M. Peckerar, Z. Dilli, M. Dornajafi, N. Goldsman, Y. Ngu, R. B. Proctor, B. J. Krupshaw, D. A. Lowy, *Energy Environ. Sci.* **2011**, 4, 1807.
- [7] C. Hertleer, H. Rogier, L. Vallozzi, L. Van Langenhove, *IEEE Trans. Antennas Propagation* **2009**, 57, 919.
- [8] N. Vacirca, J. K. McDonough, K. Jost, Y. Gogotsi, T. Kurzweg, *Appl. Phys. Lett.* **2013**, 108, 073301.
- [9] P. Salonen, Y. Rahmat-Samii, *Aerospace Electron. Sys. Mag.*, IEEE, **2007**, 22, 10.
- [10] N. Liu, W. Ma, J. Tao, X. Zhang, J. Su, L. Li, C. Yang, Y. Gao, D. Golberg, Y. Bando, *Adv. Mater.* **2013**, 25, 4925.
- [11] G. Dion, in Proceedings of the 8<sup>th</sup> International Conference on Body Area Networks, Institute for Computer Sciences, *Social-Informatics and Telecommunications Engineering*, Boston, MA **2013**, 97.
- [12] Y. Fu, X. Cai, H. Wu, Z. Lv, S. Hou, M. Peng, X. Yu, D. Zou, *Adv. Mater.* **2012**, 24, 5713.
- [13] Y. Fu, H. Wu, S. Ye, X. Cai, X. Yu, S. Hou, H. Kafafy, D. Zou, *Energy Environ. Sci.* **2013**, 6, 805.
- [14] P. Simon, Y. Gogotsi, *Nat. Mater.* **2008**, 7, 845.
- [15] V. Presser, L. Zhang, J. J. Niu, J. McDonough, C. R. Perez, H. Fong, Y. Gogotsi, *Adv. Energy Mater.* **2011**, 1, 423.
- [16] V. T. Le, H. Kim, A. Ghosh, J. Kim, J. Chang, Q. A. Vu, D. T. Pham, J.-H. Lee, S.-W. Kim, Y. H. Lee, *ACS Nano* **2013**, 7, 5940.

- [17] V. Presser, M. Heon, Y. Gogotsi, *Adv. Funct. Mater.* **2011**, *21*, 810.
- [18] Y. Meng, Y. Zhao, C. Hu, H. Cheng, Y. Hu, Z. Zhang, G. Shi, L. Qu, *Adv. Mater.* **2013**, 2326.
- [19] J. A. Lee, M. K. Shin, S. H. Kim, H. U. Cho, G. M. Spinks, G. G. Wallace, M. D. Lima, X. Lepro, M. E. Kozlov, R. H. Baughman, S. J. Kim, *Nat. Commun.* **2013**, *4*, 1970.
- [20] J. Carretero-González, E. Castillo-Martínez, M. Dias-Lima, M. Acik, D. M. Rogers, J. Sovich, C. S. Haines, X. Lepró, M. Kozlov, A. Zhakidov, Y. Chabal, R. H. Baughman, *Adv. Mater.* **2012**, *24*, 5695.
- [21] K. Jost, C. R. Perez, J. K. McDonough, V. Presser, M. Heon, G. Dion, Y. Gogotsi, *Energy Environ. Sci.* **2011**, *4*, 5060.
- [22] K. Jost, D. Stenger, C. R. Perez, J. K. McDonough, K. Lian, Y. Gogotsi, G. Dion, *Energy Environ. Sci.* **2013**, *6*, 2698.
- [23] L. Bao, X. Li, *Adv. Mater.* **2012**, *24*, 3246.
- [24] L. M. Haverhals, W. M. Reichert, H. C. De Long, P. C. Trulove, *Macromol. Mater. Eng.* **2010**, *295*, 425.
- [25] L. M. Haverhals, H. M. Sulpizio, Z. A. Fayos, M. A. Trulove, W. M. Reichert, M. P. Foley, H. C. De Long, P. C. Trulove, *Cellulose* **2012**, *19*, 13.
- [26] M. Humphries, *Fabric Reference*, Prentice Hall, Upper Saddle River, NJ **2000**.
- [27] L. B. Hu, M. Pasta, F. La Mantia, L. F. Cui, S. Jeong, H. D. Deshazer, J. W. Choi, S. M. Han, Y. Cui, *Nano Lett.* **2010**, *10*, 708.
- [28] S. H. Aboutalebi, R. Jalili, D. Esrafilzadeh, M. Salari, Z. Gholamvand, S. A. Yamini, K. Konstantinov, R. L. Shepherd, J. Chen, S. E. Moulton, P. C. Innis, A. I. Minett, J. M. Razal, G. G. Wallace, *ACS Nano* **2014**, *8*, 2456.
- [29] M. Pasta, F. L. Mantia, L. Hu, H. D. Deshazer, Y. Cui, *Nano Res.* **2010**, *3*, 452.
- [30] H. Gao, K. Lian, *J. Power Sources* **2011**, *196*, 8855.
- [31] P. L. Taberna, P. Simon, J. F. Fauvarque, *J. Electrochem. Soc.* **2003**, *150*, A292.
- [32] J. Segalini, B. Daffos, P. L. Taberna, Y. Gogotsi, P. Simon, *Electrochim. Acta* **2010**, *55*, 7489.
- [33] K. Wang, Q. Meng, Y. Zhang, Z. Wei, M. Miao, *Adv. Mater.* **2013**, *25*, 1494.
- [34] J. Bae, M. K. Song, Y. J. Park, J. M. Kim, M. L. Liu, Z. L. Wang, *Angew. Chem. Int. Ed.* **2011**, *50*, 1683.
- [35] X. Xiao, T. Li, P. Yang, Y. Gao, H. Jin, W. Ni, W. Zhan, X. Zhang, Y. Cao, J. Zhong, *ACS Nano* **2012**, *6*, 9200.