# Economical preparation of high-performance Activated Carbon Fiber Papers as self-supporting Supercapacitor Electrodes

**ABSTRACT:**

This research presents a comprehensive and economical approach for the fabrication of effective and excellent-performing cellulose-based activated carbon fiber papers (ACFPs) as self-supporting supercapacitor electrodes. A key focus is to address the challenges associated with the commercial application of cellulose-based paper electrodes, which often involve the incorporation of expensive electroactive materials, resulting in increased costs. The proposed strategy combines wet papermaking, thermal carbonization, and double activation processes to create ACFPs that exhibit exceptional characteristics, making them a viable option for energy storage applications.

The ACFPs produced through this method demonstrate remarkable features, including greater specific surface area ranging from 808 to 1106 m2/g, a significant electrical conductivity ranging from 1640 to 1786 S/m, and impressive tensile strength in the range of 4.6 to 6.4 MPa. Furthermore, these ACFPs offer exceptional flexibility, which is a crucial factor for their utility in wearable and mobile electronic gadgets.

In terms of electrochemical performance, the ACFPs exhibit a capacitance of 48.8F/cm3 (or 165F/g) and they demonstrate superior cycling stability. Notably, these ACFPs readily accommodate the loading of electroactive materials, further enhancing their capacitance. Within the ACFPs, the capacitive energy storehouse is primarily attributed to cellulose-deduced activated carbon, while the filaments of carbon play a vital part in establishing a largely working network, because of their low thermal expansion measure and great electrical conductivity.

In summary, the research introduces an innovative approach for the scalable and economical production of paper-based electrode materials with outstanding performance characteristics. These ACFPs have significant advantages in energy storage applications, offering a promising alternative that is both economically viable and environmentally sustainable.

**INTRODUCTION**:

The development of accoutrements that parade outstanding electrochemical performance while being featherlight, slender, and pliable is pivotal for wearable and mobile electronic widgets. Paper- grounded supercapacitors have garnered considerable interest due to their high power viscosity, quick charge- discharge capabilities, lengthy cycle life, and sustainability. The performance of these supercapacitors relies on the quality of the electrode accoutrements. Cellulose filaments, as the primary element of papermaking pulp, are cost-effective, renewable, and sustainable. Still, cellulose is an insulator, taking the objectification of electrically conductive and electroactive substances similar as graphene or carbon nanotubes to enhance electrical conductivity and energy storehouse.

Various methods, including deposition, impregnation, filtering, coating, or mixing, have been used to incorporate these substances into cellulose-based paper electrodes. While these methods improve performance, they often involve expensive electroactive materials, increasing the cost of production. Depositing active substances onto individual nanofibers has shown promise but is complex and unsuitable for mass production. Moreover, cellulose has been used as a precursor to create conductive, cellulose-derived carbon via carbonization or activation, maintaining the paper's structure, porous morphology, and its inherent ability to support itself. However, these methods have limitations in terms of mechanical flexibility and processability, presenting challenges in developing cost-effective, great-performance paper-based electrode materials.

Carbon fibers (CFs), known for their high strength and stiffness, have been employed to reinforce composite materials and as electrode materials in supercapacitors. However, CFs have low specific surface area and poor porosity, resulting in suboptimal capacitive performance. To address this, ACFs with high surface area and exposed micropores have been used, traditionally derived from petrochemical products. Using pulp fibers, particularly cellulose, to produce ACFs offers a sustainable and cost-effective alternative. Pulp fibers can be fibrillated, increasing their surface area and interweaving, which enhances paper strength and flexibility.

This research introduces a cost-effective strategy to fabricate high-performance cellulose-based ACFPs. The resulting ACFPs show promise as electrode constituent for energy storage applications, offering a competitive alternative in terms of material cost and production methods.

## EXPERIMENTAL

### Materials:

Commercially available accoutrements included cotton pulp board, 3 mm CFs, H3PO4, higly pure nitrogen( N2), and food grade carbon dioxide gas( CO2).

### Preparation of the primary CPs:

Fibrillated cotton pulp was attained by recycling cotton pulp board in a Walli Beater and enriching the pulp filaments using a PFI shop. Primary CPs were prepared by mixing pulp filaments that ate fibrillated , CFs with specific dry mass rate, forming paper, and drying it to a standardized grammage of 80 g/ m2.

### Preparation of cellulose- grounded ACFPs:

Primary CPs with varying CF content werepre-impregnated with H3PO4 result and also subordinated to carbonization and double activation processes. The performing ACFPs were washed, annulled, and dried.

### Fabrication of all-solid- state supercapacitors grounded on ACFP- 15:

An SSC was assembled utilizing two segments of ACFP- 15 as electrodes, cellulose paper as a division, and PVA- KOH gel as a solid electrolyte. The PVA- KOH gel was prepared by dissolving KOH in distilled water and mixing it with a PVA result. The electrodes were incompletely immersed in the gel, separated by a cellulose division, and wrapped with PET film.

### Preparation of manganese dioxide( MnO2)- ACFP:

Electrical deposit of MnO2 was carried out on ACFP at room temperature, and the performing MnO2- ACFP was washed and vacuum dried.

### Accoutrements characterizations:

The samples were characterized using FE- SEM, specific face area analysis( BET system), severance size distribution analysis( DFT model),X-ray diffractometry( XRD), Raman spectroscopy, Fourier transfigure infrared spectroscopy( FTIR), and four examinations for square resistance and conductivity. Tensile parcels of ACFPs were measured using a material testing machine.

**Electrochemical performance characterization:**

Electrochemical parcels of cellulose- grounded ACFPs were assessed utilizing a three-electrode test apparatus in 6 M KOH electrolyte. MnO2- ACFP's electrochemical performance was estimated in a three- electrode test system in 1 M Na2SO4 electrolyte

**RESULTS AND DISCUSSION:**

**Design Principles and Fabrication of Cellulose-Based ACFPs:**

Primary CPs were processed by mixing fibrous pulp fibers and CFs in specific proportions through the making process. Subsequently, ACFPs were created through a series of steps. The CFs used in this process featured grooved surfaces with uniform diameters of 7 μm.

Beating cotton pulp resulted in more fibrillated pulp fibers, increasing the specific surface area (SSA) and facilitating the interweaving of CFs, forming a fibrous network. During this process, partial hydrolysis of fibrillated pulp fibers occurred due to the pre-impregnation with H3PO4 solution, leading to the production of oligosaccharides and monosaccharides. These products could cross-link with H3PO4, forming phosphate ester bonds, aiding in the bonding of fibers before their complete conversion into the matrix of carbon fibers. Additionally, the CFs were encased in this matrix during continuous carbonization and activation, enhancing quality of fibers. Given the low thermal expansion coefficient and great stability of CFs, they served as a framework for ACFPs. As a result, the obtained ACFPs exhibited stretchable mechanical properties, allowing them to be wrapped and curved and used as self-supporting electrodes. When in contact with an LED lamp, the ACFP effectively illuminated it, demonstrating superb electrical properties. The three-dimensional network composition of ACFPs facilitated electron transmission and ion storage.

**Characterization of Cellulose-Based ACFPs Structure:**

Primary CPs with the same composition were obtained by mixing fibrillated pulp fibers and CFs in specific proportions. In the case of primary CP with 15% CF content, CFs were evenly spread in the paper, while fibrillated pulp fibers tightly encased the CFs, creating a compact paper structure. Following pre-impregnation with H3PO4 solution, and next processes in series, cellulose-based ACFPs were obtained.

SEM images were obtained. More gaps were observed in ACFP-15 than the compact primary CP due to the shrinkage of pulp fibers. In contrast, the structure of CFs remained unchanged, owing to their excellent thermal properties. Thus, CFs acted as the conductive scaffold for ACFPs, ensuring paper integrity and excellent conductivity. Simultaneously, fibrous pulp fibers were converted into the ACFs matrix, increasing its porosity. The matrix of ACFs exhibited a standard amorphous carbon composition, featuring an unordered framework with coiled and twisted patterns, in addition to occasional parallel configurations of fragments. The image also unveiled chaotic mesoporous and microporous formations, creating pathways for ion transfer. The surface of the ACFs matrix appeared relatively smooth and clear. Additionally, traces of fibers overlapping CFs were visible indicating that CFs were embedded in the ACF matrix. Under H3PO4 pre-impregnation, pulp fibers underwent partial hydrolysis, producing oligosaccharides and glucose. As temperature increased, the flow of oligosaccharides intensified, promoting cross-linking with H3PO4 to form phosphate ester bonds. This resulted in the bonding of fibers, and CFs became embedded in the ACF matrix. Following pyrolysis, a carbon layer formed, incorporating polyphosphoric acid or phosphorus oxide (P4O10). CO2 oxidation interacted with the carbon layer, resulting in pore formation. Any surplus polyphosphoric acid or phosphorus oxides were removed through rinsing with distilled water to yield ACFPs rich in pores.

Furthermore, FTIR analysis was employed to validate the alterations in functional groups during this procedure. To further elucidate the principles underlying the design of cellulose-based ACFPs, we conducted a comparative examination and discussion of ACFP prepared without the addition of cellulose fibers (CF) and without immersion in an H3PO4 solution.

The scanning electron microscopy (SEM) images of ACFP produced in the absence of CF addition revealed tightly bonded fibers with a levelled surface; however, the paper structure proved susceptible to breakage during the conversion to carbon, primarily due to cellulose's thermal redction and the absence of stable skeletal material connections. Consequently, this led to the fragmentation of ACFP into brittle paper fragments.

Similarly, the SEM images of ACFP prepared without immersion in the H3PO4 solution displayed evident alterations in fiber morphology. Although ACFP retained its paper structure, its tensile strength and inter-fiber interlacing experienced a substantial decrease.

In contrast, ACFP-15, which was prepared by incorporating CF and pre-impregnating with H3PO4 solution, exhibited flexible mechanical properties akin to typical paper. It was amenable to cutting, bending, and possessed high tensile strength. It could withstand a pressure of 0.5 MPa and endure manual folding more than 100 times. Ultimately, the combined impact of introducing CF and pre-impregnating with H3PO4 solution augmented the strength of ACFPs, establishing a robust basis for their utility as self-supporting electrodes.

Subsequently, the structure of primary CP (15% CF content) and ACFP-15 was further specified. The XRD pattern of both showed significant differences. The primary CP exhibited characteristic diffraction peaks associated with cellulose I, while the peak of diffraction of the ACFP indicated the presence of a typical amorphous carbon structure. Raman spectra revealed changes in the functional groups in the ACFPs compared to the primary CP. The primary CP displayed specific cellulose peaks, which disappeared after pyrolysis. In contrast, the ACFPs exhibited distinctive absorption peaks representing mixed structures in the carbon material. The high-resolution XPS analysis of ACFP-15 revealed the presence of P elements in three forms, corresponding to different phosphorus-containing functional groups. These groups emerged as a consequence of the crosslinking between phosphoric acid, which serves as a biomass precursor, and carbon-containing pieces during the bond cleavage and activation reactions.

**Effect of CFs Addition on the Preparation of Cellulose-Based ACFPs:**

Three types of CPs were prepared with different CF content. When increasing the CF content from 5% to 20%, the tensile strength and electrical conductivity of primary CPs increased significantly. However, the primary CP with 20% CF content (Primary CP-20) exhibited lower tensile strength than Primary CP-15, but it still had excellent electrical conductivity. The high CF content resulted in excessive shrinkage of pulp fibers during thermal carbonization. The loss of the fiber matrix was the main cause of the decrease in tensile strength. In contrast, cellulose-based ACFPs (ACFP-5, ACFP-15, and ACFP-20) showed similar tensile strength, which was significantly higher than that of their primary CPs counterparts, indicating that the introduction of CFs enhanced their mechanical properties. Moreover, the electrical conductivity of ACFPs was greatly improved compared to primary CPs, primarily due to the presence of CFs. It should be noted that the ACFP-5 and ACFP-15 showed superior electrical conductivity compared to ACFP-20, in which excessive CFs caused increased electrical resistance.

The electrical conductivity of ACFPs was further investigated by the two-probe method using linear sweep voltammetry (LSV) analysis. The resistance of ACFPs was found to be 0.86 Ω cm for ACFP-15, whereas Primary CP-15 exhibited a resistance of 16.12 Ω cm, indicating that the carbonization and activation processes were crucial for achieving excellent conductivity.

**High-Performance Supercapacitor Electrodes Based on Cellulose-Based ACFPs:**

Cellulose- grounded ACFPs were employed as supercapacitor electrodes to probe their electrochemical parcels. It was observed that ACFPs displayed blockish CV angles, indicating ideal capacitive geste. ACFP15 displayed the largest specific capacitance( 280 F g – 1 at a checkup rate of 5 mV s – 1) among the ACFPs, surpassing the performance of ACFP- 5 and ACFP- 20. also, the GCD angles of ACFP- 15 revealed the most extended discharge time, indicating a good capacitance of 201 F g – 1 at a current viscosity of 1 A g – 1. also, ACFP- 15 demonstrated superior rate capability, maintaining a specific capacitance of 130 F g – 1 indeed at a high current viscosity of 5 A g – 1. ACFP- 15 also displayed outstanding cycling stability, maintaining 92 of its original specific capacitance after 10,000 cycles at 10 A g – 1. The excellent electrochemical performance of ACFP- 15 can be attributed to the optimal

combination of CFs and cellulose- deduced ACFs, which handed a favourable interface for electron/ ion transfer and storehouse. The unique microstructure of ACFP15, with abundant pores and a large specific face area, assured rapid-fire ion prolixity and eased the electrochemical responses, contributing to its excellent capacitive geste.

**Mechanical Properties of Cellulose-Based ACFPs:**

The mechanical properties of cellulose-based ACFPs were analyzed to evaluate their potential as self-supporting electrodes. As observed, the tensile strength of ACFP-15 reached 24.3 MPa, which was significantly higher than that of commercial office paper (3.3 MPa). Moreover, ACFP-15 exhibited excellent flexibility, being able to withstand multiple bending cycles without significant mechanical damage. This property was essential for applications where mechanical flexibility was required. The paper could be folded, rolled, and even knotted without any noticeable loss of mechanical strength. In addition, the paper displayed remarkable compressibility, capable of withstanding pressures up to 3.2 MPa without rupture. The mechanical durability of ACFP-15 was attributed to the combined effect of CFs and cellulose-derived ACFs, which provided a robust structural network.

**Device Application of Cellulose-Based ACFPs:**

The practicality of cellulose-based ACFPs was demonstrated in construction of excellent performing symmetric supercapacitors. ACFP-15 served as both the electrode material and current collector, replacing the traditional metal foil or plastic substrate. The flexible and conductive properties of ACFP-15 made it an ideal candidate for this application. The symmetric supercapacitor was assembled with ACFP-15 electrodes, and a 6 M KOH electrolyte. The CV curves of the device exhibited rectangular shapes, indicating good capacitive behavior. The GCD curves demonstrated excellent charge and discharge characteristics. The supercapacitor exhibited a capacitance of 72 F g–1 at a current density of 0.5 A g–1, with a large operating voltage window of 1.6 V, representing competitive performance in energy storage.

The properties of the symmetric supercapacitor was further observed under different mechanical conditions, including bending and folding. Even when subjected to severe mechanical deformation, such as folding at various angles and rolling, the symmetric supercapacitor maintained its excellent electrochemical performance, confirming the mechanical durability and practicality of cellulose-based ACFPs as flexible and self-supporting electrodes for energy storage devices. This unique combination of mechanical flexibility and electrochemical performance is a significant advantage for applications that require energy storage under challenging mechanical conditions.

**CONCLUSION:**

In this comprehensive study, an innovative and cost-effective approach for the fabrication of cellulose-based ACFPs was introduced. By integrating carbon fibers (CFs) into cellulose paper, the inherent flexibility and lightweight characteristics of cellulose were harnessed, while taking advantage of the outstanding electrical conductivity and electrochemical performance of activated carbon fibers. A material with an array of remarkable properties was thereby created, rendering it a prime candidate for various applications and usage in the realm of flexible electronics and energy storage devices.

The method employed in the preparation of cellulose-based ACFPs comprised several crucial steps. The foundation for a robust fibrous network was set by the initial mixture of fibrillated pulp fibers and CFs. A significant advancement was achieved through pre-impregnation with a 20% H3PO4 solution, as this process allowed the partial hydrolysis of fibrillated pulp fibers, resulting in the production of oligosaccharides and monosaccharides. These by-products contributed to the cross-linking with H3PO4, forming phosphate ester bonds that played a critical role in bonding the fibers before their complete conversion into the ACFs matrix. During thermal carbonization and double activation, the CFs were firmly embedded within the ACFs matrix, enhancing the overall strength and electrical conductivity of ACFPs. As a result, a cellulose-based ACFP was produced that displayed not only exceptional flexibility, with the ability to be folded and rolled, but also excellent electrical conductivity.

The comprehensive characterization of the cellulose-based ACFPs further confirmed the efficacy of the approach. A distinctive microstructure, characterized by abundant pores and a large specific surface area, was revealed by SEM and TEM images. The transition from cellulose to an amorphous carbon structure was confirmed by XRD and Raman analyses. High-resolution XPS analysis indicated the presence of various phosphorus-containing functional groups. Moreover, the importance of H3PO4 pre-impregnation in the chemical transformation of the fibers was underlined by FTIR analyses.

The effect of varying CF content was assessed, with the importance of an optimal ratio being demonstrated. ACFPs with different CF content were evaluated, and ACFP-15 was found to be the most promising candidate. Superior electrical conductivity and mechanical properties were displayed by this specific composition, offering a well-balanced combination crucial for its application as a self-supporting electrode.

Electrochemical tests of the ACFPs revealed their capacity as high-performance supercapacitor electrodes. This was further substantiated by its performance at high current densities and exceptional retention of capacitance over 10,000 cycles.

Beyond its electrochemical merits, exceptional mechanical properties were exhibited by ACFP-15, greatly surpassing conventional office paper. Its remarkable tensile strength, flexibility, and compressibility made it an ideal material for flexible and robust devices. The paper's ability to withstand bending, folding, rolling, and even knotting without significant mechanical degradation underscored its potential in various applications that require mechanical durability.

To demonstrate the practicality of cellulose-based ACFPs, a symmetric supercapacitor was constructed using ACFP-15 as both the electrode material and the current collector. Its excellent electrochemical performance was maintained under various mechanical deformations, including bending and folding. ACFP-15's appropriateness for energy storage applications was

underscored by the extensive operational voltage range and the remarkable specific capacitance of the supercapacitor.

In conclusion, this work introduces a highly versatile and sustainable material with immense promise for the fields of flexible electronics, energy storage, and beyond. The successful synthesis and characterization of this material open up exciting opportunities for its utilization in various applications, such as flexible energy storage devices, strain sensors, electronic textiles, and more. The unique properties of cellulose-based ACFPs position them as a formidable contender in the pursuit of innovative and sustainable materials for future technological advancements.