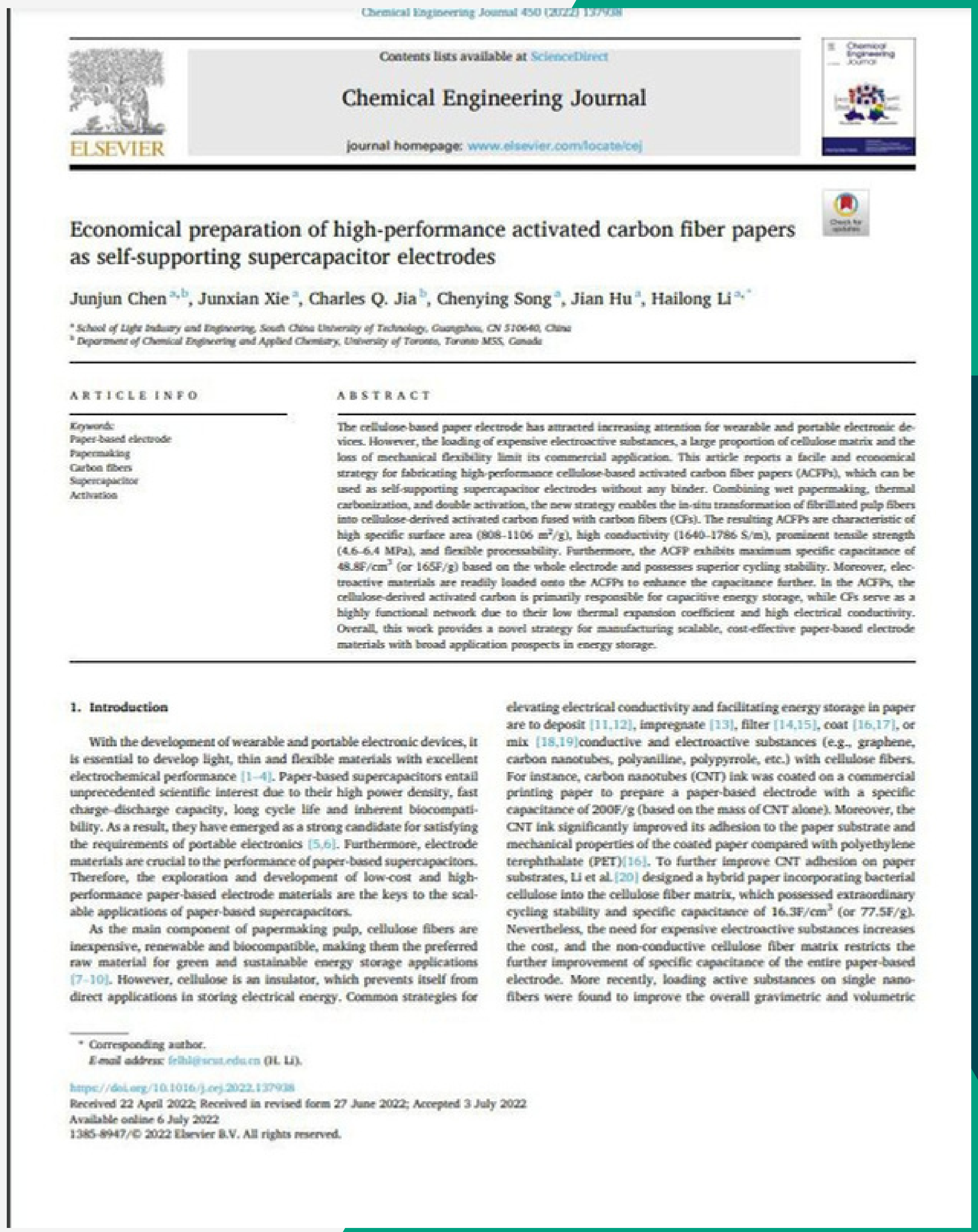
TECHNICAL WRITING AND PRESENTATION

Economical preparation of high-performance activated carbon fiber papers as self-supporting supercapacitor electrodes



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Economical preparation of high-performance activated carbon fiber papers as self-supporting supercapacitor electrodes

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ABSTRACT

The cellulose-based paper electrode has attracted increasing attention for wearable and portable electronic devices. However, the loading of expensive electroactive substances, a large proportion of cellulose matrix and the loss of mechanical flexibility limit its commercial application. This article reports a facile and economical strategy for fabricating high-performance cellulose-based activated carbon fiber papers (ACFPs), which can be used as self-supporting supercapacitor electrodes without any binder. Combining wet papermaking, thermal carbonization, and double activation, the new strategy enables the in-situ transformation of fibrillated pulp fibers into cellulose-derived activated carbon fused with carbon fibers (CFs). The resulting ACFPs are characteristic of high specific surface area (808–1106 m^2/g), high conductivity (1640–1786 S/m), prominent tensile strength (4.6–6.4 MPa), and flexible processability. Furthermore, the ACFP exhibits maximum specific capacitance of 48.8F/cm^2 (or 165F/g) based on the whole electrode and possesses superior cycling stability. Moreover, electroactive materials are readily loaded onto the ACFPs to enhance the capacitance further. In the ACFPs, the cellulose-derived activated carbon is primarily responsible for capacitive energy storage, while CFs serve as a highly functional network due to their low thermal expansion coefficient and high electrical conductivity. Overall, this work provides a novel strategy for manufacturing scalable, cost-effective paper-based electrode materials with broad application prospects in energy storage.

1. Introduction

With the development of wearable and portable electronic devices, it is essential to develop light, thin and flexible materials with excellent electrochemical performance [1–4]. Paper-based supercapacitors entail unprecedented scientific interest due to their high power density, fast charge-dischage capacity, long cycle life and inherent biocompatibility. As a result, they have emerged as a strong candidate for satisfying the requirements of portable electronics [5,6]. Furthermore, electrode materials are crucial to the performance of paper-based supercapacitors. Therefore, the exploration and development of low-cost and high-performance paper-based electrode materials are the keys to the scalable applications of paper-based supercapacitors.

As the main component of papermaking pulp, cellulose fibers are inexpensive, renewable and biocompatible, making them the preferred raw material for green and sustainable energy storage applications [7–10]. However, cellulose is an insulator, which prevents itself from direct applications in storing electrical energy. Common strategies for elevating electrical conductivity and facilitating energy storage in paper are to deposit [11,12], impregnate [13], filter [14,15], coat [16,17], or mix [18,19]conductive and electroactive substances (e.g., graphene, carbon nanotubes, polyaniline, polypyrrole, etc.) with cellulose fibers. For instance, carbon nanotubes (CNT) ink was coated on a commercial printing paper to prepare a paper-based electrode with a specific capacitance of 200F/g (based on the mass of CNT alone). Moreover, the CNT ink significantly improved its adhesion to the paper substrate and mechanical properties of the coated paper compared with polyethylene terephthalate (PET)[16]. To further improve CNT adhesion on paper substrates, Li et al. [20] designed a hybrid paper incorporating bacterial cellulose into the cellulose fiber matrix, which possessed extraordinary cycling stability and specific capacitance of 16.3F/cm^3 (or 77.5F/g). Nevertheless, the need for expensive electroactive substances increases the cost, and the non-conductive cellulose fiber matrix restricts the further improvement of specific capacitance of the entire paper-based electrode. More recently, loading active substances on single nanofibers were found to improve the overall gravimetric and volumetric

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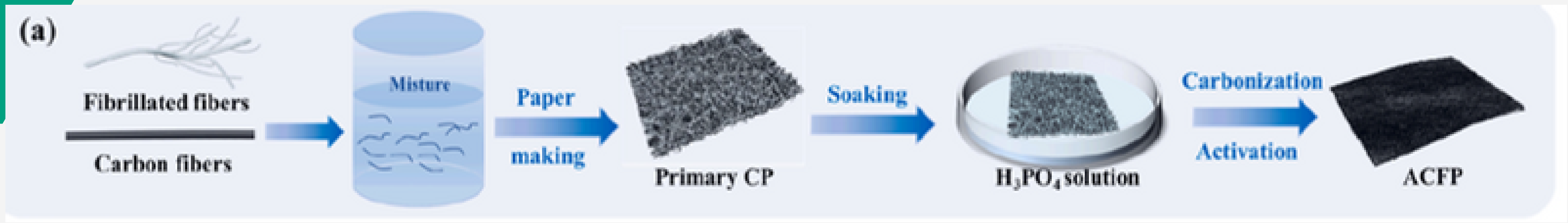
CONTENT

- Introduction
- Materials and Methodology
- Results and Discussion
- Summary and Conclusion
- References

INTRODUCTION

- **Introducing a novel approach for developing cellulose-based supercapacitor electrodes with exceptional electrochemical performance and mechanical flexibility.**
- **Addressing the need for cost-effective and sustainable electrode materials by utilizing cellulose fibers, a renewable and abundant resource, to create high-performance activated carbon fiber papers (ACFPs).**
- **Combining wet papermaking, thermal carbonization, and double activation, the new strategy enables the in-situ transformation of fibrillated pulp fibers into cellulose-derived activated carbon fused with carbon fibers (CFs).**
- **Demonstrating a scalable and economical manufacturing strategy for paper-based flexible electrode materials with broad applications in wearable and portable electronic devices, offering a sustainable alternative to traditional petroleum-based resources.**



LITERATURE GAPS

Cost-Effective Cellulose-Based Electrodes: While prior work has concentrated on enhancing electrode performance, there exists a need for economically viable cellulose-based electrode materials that can rival conventional petroleum-derived alternatives.

Mechanical Flexibility and Processability Challenges: Numerous cellulose-derived carbon materials face limitations concerning their mechanical flexibility and ease of processing.

Scalability and Mass Production: Developing scalable manufacturing processes for these novel electrode materials is essential for their widespread adoption in energy storage applications.

Integration of Cellulose and Carbon Fibers: The integration of fibrillated pulp fibers and carbon fibers into a cohesive structure with enhanced properties represents a promising avenue for achieving high-performance and flexible paper electrodes.

LITERATURE COMPARISON

Graphene/Carbon Nanotube-Based Papers

Integration of graphene or carbon nanotubes into cellulose-based papers to enhance conductivity and electrochemical performance.

Carbon Fiber-Based Electrodes

Some research has utilized carbon fibers as electrode materials due to their strength and electrical conductivity but they have limited specific surface areas.

Carbonization of Cellulose

Another avenue of research involves the carbonization of cellulose to create carbon materials with improved electrochemical properties. However, these studies often resulted in materials with reduced mechanical flexibility and limited processability.

LITERATURE COMPARISON OF CARBON BASED MATERIALS

MATERIALS	CAPACITANCE (F/cm3)	CAPACITANCE (F/g)	CYCLE STABILITY	CONDUCTIVITY (S/m)	REFERENCE
Bacterial Cellulose	--	74	99.5%	--	S. Li, D. Huang, B. Zhang, X. Xu, M. Wang, G. Yang, Y. Shen et. al. (2014)
Cellulose Fiber	16.3	77.5	98.4%	590	X. Wu, M. Zhang, T. Song, H. Mou, Z. Xiang, H. Qi, et. al (2020)
Cellulose(RGO)	2.4	212	94%	17.2	J. Bi, H. Wu, L. Wang, X. Pang, Y. Li, Q. Meng, L. Wang, et. al.(2021)
Graphene Cellulose	--	120	99.1%	16.6	Z. Weng, Y. Su, D.-W. Wang, F. Li, J. Du, H.-M. Cheng, et. al. (2011)
PANI Nanoribbon	40.5	--	79%	--	D. Ge, L. Yang, L. Fan, C. Zhang, X. Xiao, Y. Gogotsi, S. Yang et. al. (2015)
RGO/CNT Aerogel	--	110	80%	--	O. Okhay, A. Tkach, M.J.H. Gallo, G. Otero-Irurueta, S. Mikhalev, P. Staiti, F. Lufranoet. al. (2020)
ACFP-10	37.8-41.8	134.1	--	1786	THIS WORK
ACFP-15	22.0-24.1	80.0	100%	1640	THIS WORK

GOALS and OBJECTIVES

Develop High-Performance Cellulose-Based Supercapacitor Electrodes

- Fabricate cellulose-based activated carbon fiber papers (ACFPs) with superior electrochemical performance, including high specific surface area and conductivity
- Enhance the mechanical flexibility and processability of ACFPs, making them suitable for flexible and wearable electronic devices.

Exploit the Synergy between Cellulose and Carbon Fibers

- Investigate how cellulose-derived activated carbon fibers (ACFs) and carbon fibers (CFs) work in synergy to improve the capacitive energy storage capabilities of the ACFPs.

Establish Scalable and Economical Manufacturing Processes

- Develop a manufacturing strategy that is scalable for mass production, ensuring the potential for widespread adoption in energy storage applications.

Materials and Methodology

Materials Required

- Cotton pulp board
- Carbon fibers (3 mm CFs)
- Phosphoric acid (H_3PO_4)
- High-purity nitrogen (N_2)
- Food-grade carbon dioxide gas (CO_2)

Instruments Used

- Field Emission Scanning Electron Microscope (FE-SEM)
- Specific Surface Area Analyzer (ASAP 2460, Micromeritics)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Material Testing Machine (INSTRON 3300, USA)
- X-ray Diffractometer (XRD) and Raman Microscope (Raman)
- Three-Electrode Test System
- All-Solid-State Symmetric Supercapacitor Setup

METHODOLOGY

Preparation of Primary Composite Papers (CPs): Fibrillated cotton pulp is prepared by beating it in a Walli Beater. Fibrillated pulp fibers and CFs are mixed with water to form primary composite papers (CPs).

Preparation of Cellulose-Based ACFPs: Primary CPs are pre-impregnated with H3PO4 solution which are then carbonized and activated at 450°C in N2 atmosphere and then under C02 atmosphere at 850°C.

Fabrication of Supercapacitors: All-solid-state symmetric supercapacitors (SSCs) are fabricated using two pieces of ACFP-15 as electrodes, cellulose paper as a separator, and PVA-KOH gel as a solid electrolyte.

Preparation of MnO2-ACFP: MnO2 electrodeposition is performed on ACFP (1x1 cm2) in a manganese sulfate solution at room temperature using reference and counter electrodes.

Materials Characterizations and . Electrochemical Performance Characterization

Results and Discussion

RESULTS

Unique ACFP Structure

- ACFPs exhibited a three-dimensional structure with a fibrous network, providing excellent electrical conductivity.
- CFs served as a conductive framework, while ACFs matrix contributed to ion storage.

Fabrication of Cellulose-based ACFPs

- ACFPs had a large specific surface area (808-1106 m^2/g) and high electrical conductivity (1640-1786 S/m).

Mechanical Properties

- ACFPs showed flexible mechanical properties, High tensile strength (up to 6.4 MPa) and Young's modulus (up to 1185 MPa)

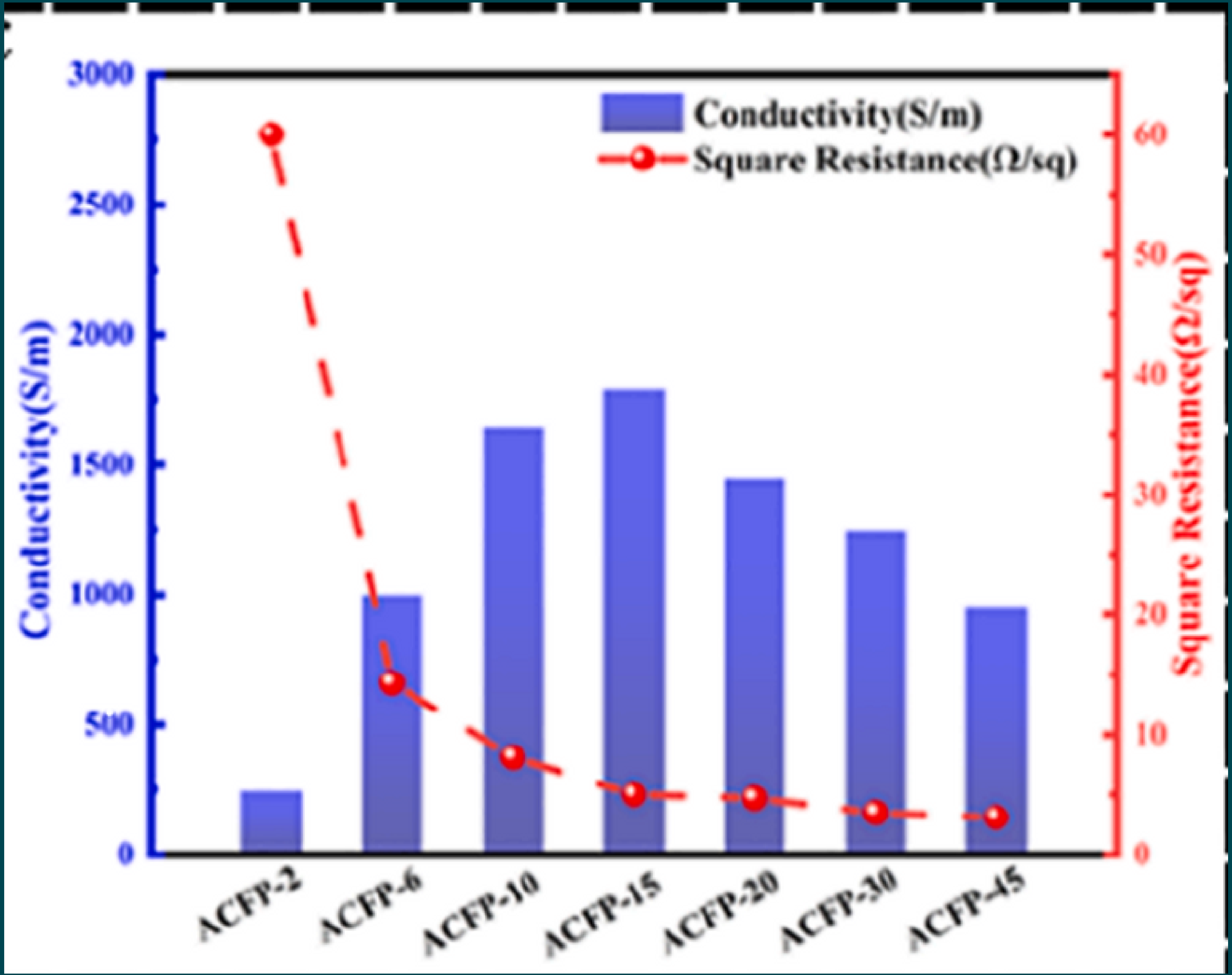
Pseudocapacitive Loading

Wettability and Durability

Electrochemical Performance

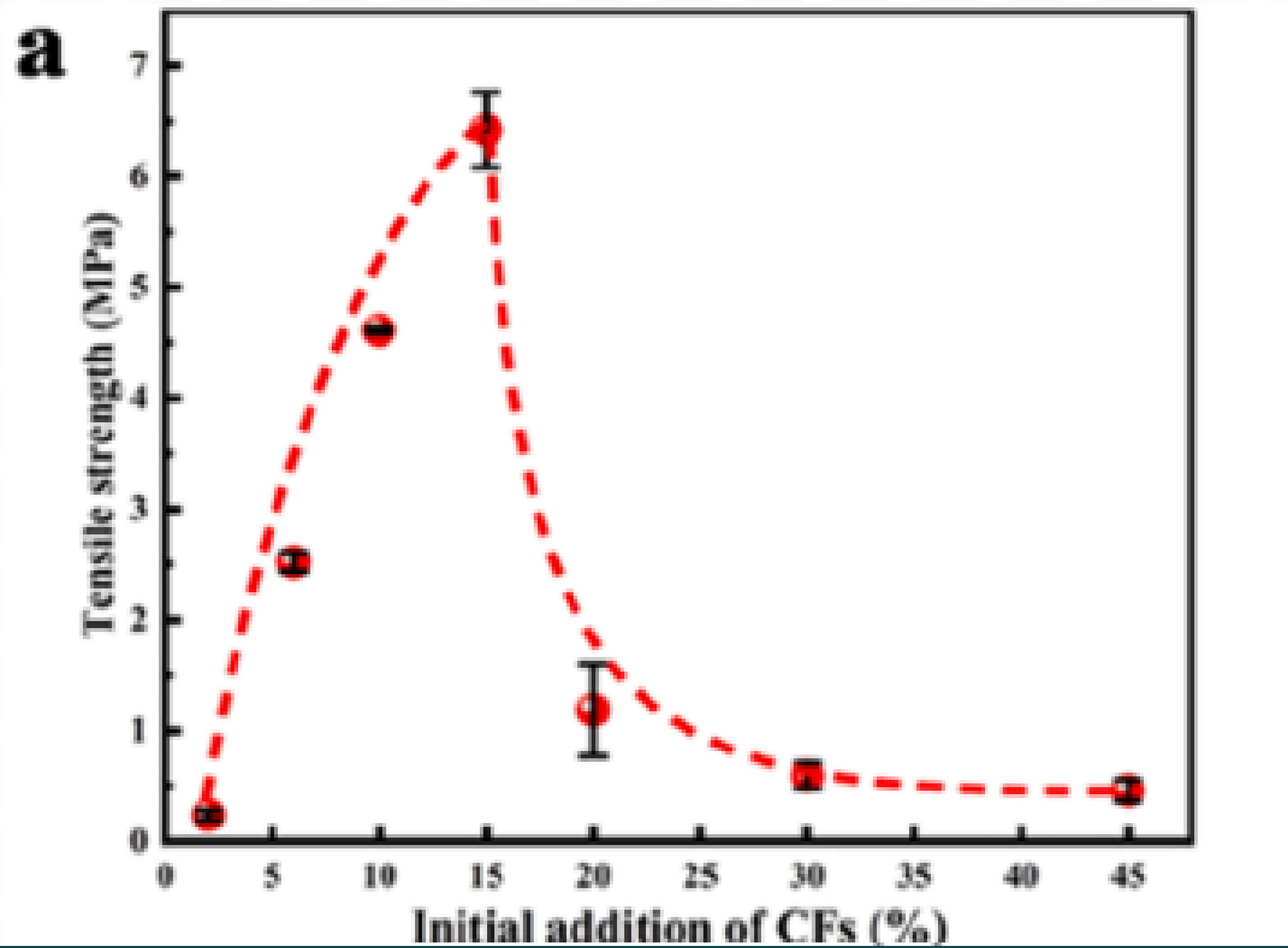
- ACFPs exhibited excellent electrochemical performance in a three-electrode system with a high specific capacitance.
- Good cycle stability (98.58% coulombic efficiency after 10,000 cycles) and energy density (6.01 Wh/kg) were achieved.

RESULTS



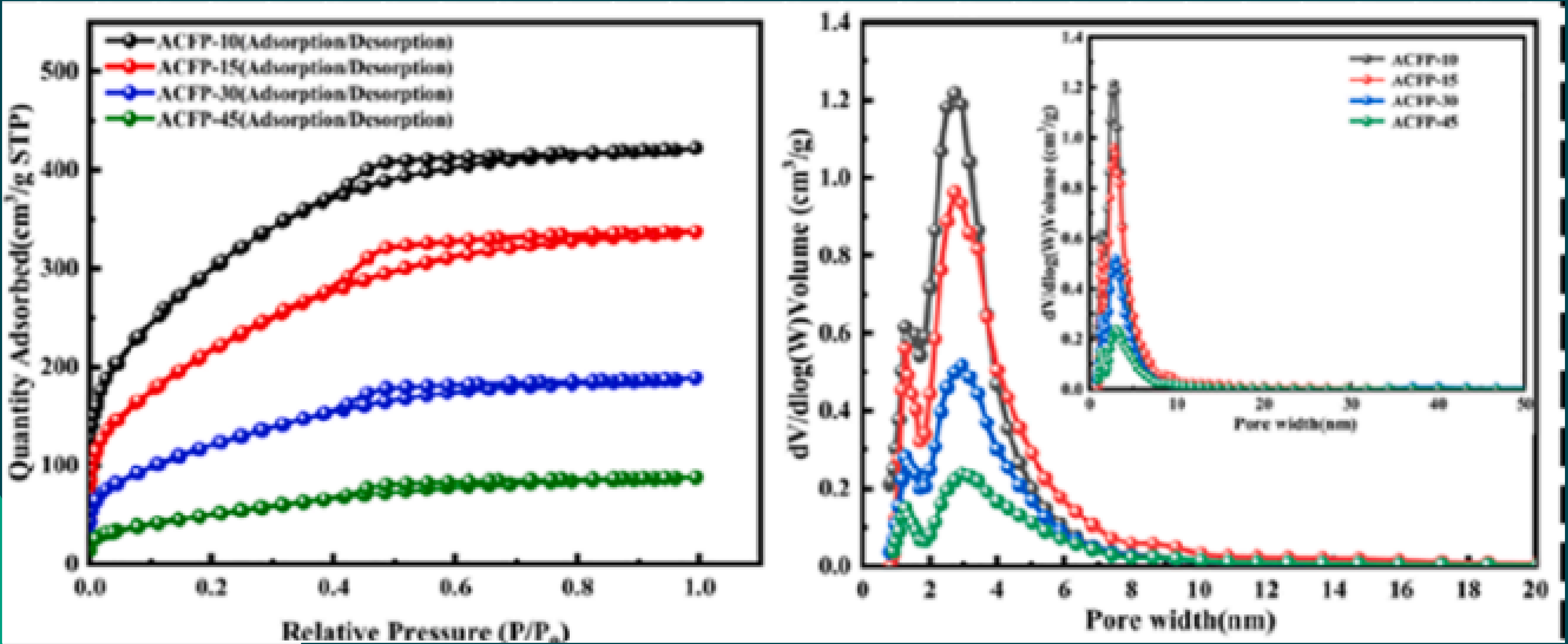
Square resistance and electrical conductivity of cellulose-based ACFPs with different CFs content.

RESULTS



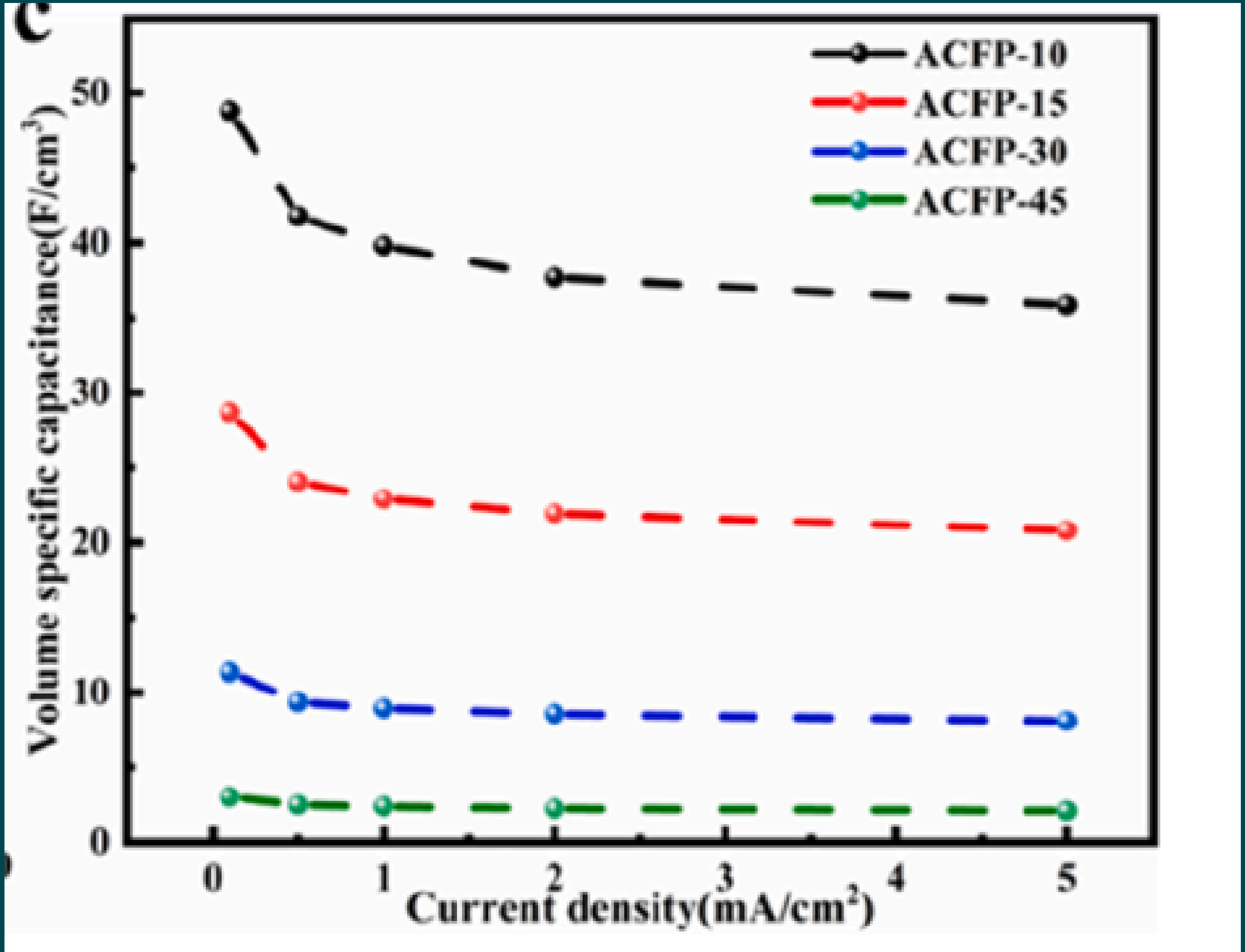
Tensile strength of cellulose-based ACFPs with different CFs content

RESULTS



N2 adsorption isotherms and pore size distributions of ACFPs with different CFs content.

RESULTS



Volume specific capacitance of ACFPs at different current densities

SUMMARY

Back to Agenda Page

Successful fabrication of cellulose-based Activated Carbon Fiber Papers (ACFPs) using a cost-effective process.

ACFPs have a unique three-dimensional structure with a fibrous network, providing excellent electrical conductivity.

Impressive mechanical properties, including high tensile strength and Young's modulus, make ACFPs flexible and self-supporting.

They demonstrate excellent electrochemical performance, with a high specific capacitance and good cycle stability.

In summary, cellulose-based ACFPs represent a promising material for energy storage applications due to their unique structure, mechanical strength, and electrochemical performance.

CONCLUSION

Subjective Conclusion

The research findings demonstrate that cellulose-based Activated Carbon Fiber Papers (ACFPs) hold immense promise as versatile materials for energy storage applications. These ACFPs offer an impressive combination of structural integrity, electrical conductivity, and electrochemical performance, making them a compelling choice for supercapacitors and other energy storage devices.

Objective Conclusion

The ACFPs exhibit exceptional mechanical properties, including high tensile strength and Young's modulus, confirming their structural integrity.ACFPs display a large specific surface area, high electrical conductivity, and excellent electrochemical performance, with a specific capacitance well-suited for supercapacitor applications The ACFPs maintain good structural stability and cycle stability over extended use, highlighting their potential for long-term energy storage applications.

FUTURE WORK

- Explore the scalability and commercial viability of producing ACFPs on a larger scale for practical applications.
- Investigate the use of different pseudocapacitive materials to optimize energy storage performance.
- Examine the potential for ACFPs in applications beyond supercapacitors, such as in flexible electronics or energy storage for renewable energy systems.
- Conduct in-depth environmental and economic assessments to assess the sustainability and cost-effectiveness of ACFP production.

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THANKYOU!

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