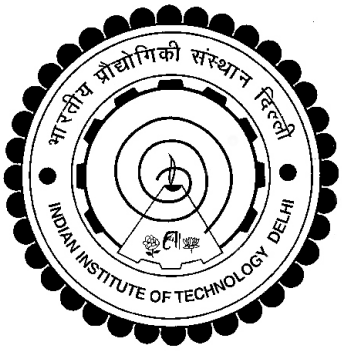
CARBON FIBER PAPER ELECTRODE OF HIGH CAPACITANCE FOR SUPERCAPACITOR

PEPARTHI MYTHILI



DEPARTMENT OF CHEMICAL ENGINEERING
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Carbon fiber paper electrode of high capacitance for supercapacitor

by

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Department of Chemical Engineering

Submitted

in fulfillment of the requirements of degree of Doctor of Philosophy

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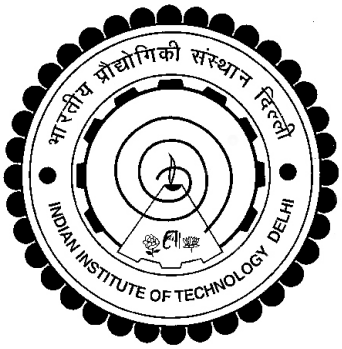

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- I dedicate this thesis to my beloved parents and Lord Venkateswara. My parents have been my first teachers, instilling in me the importance of education, integrity, and perseverance. Their unwavering support and constant encouragement have been my greatest strength throughout this journey. I also offer my deepest gratitude to Lord Venkateswara, whose divine blessings gave me hope and courage during the most challenging moments. This work is a humble offering of my faith, love, and gratitude-

Certificate

This is to certify that the thesis entitled "**Carbon fiber paper electrode of high capacitance for supercapacitor**" submitted by **Peparthi Mythili** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Chemical Engineering, is a record of bonafide research work carried out by him. Peparthi Mythili has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted in part or in full to any other university or institute for the award of any degree or diploma.

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Peparthi Mythili

Abstract

Electric double-layer capacitors (EDLCs), or supercapacitors, have garnered considerable interest in the pursuit of improved energy storage technologies owing to their elevated power density, extended cycle life, and fast charge-discharge capabilities. Nonetheless, a significant constraint that persists in hindering their extensive adoption particularly in portable devices, electric cars, and grid-scale storage is their very low energy density relative to batteries. Confronting this difficulty is essential for closing the performance disparity between batteries and capacitors. Carbon-based materials have been extensively investigated among diverse electrode materials owing to their elevated surface area, electrical conductivity, chemical stability, and economic viability. Carbon fiber paper (CFP) is particularly notable as a viable option due to its high conductivity, mechanical strength, and dual function as both the current collector and active electrode material. Notwithstanding these benefits, clean CFP exhibits low inherent capacitance, hence constraining its efficacy in high-energy-density applications. Consequently, formulating techniques to improve the capacitance and energy density of CFP-based supercapacitors is both urgent and crucial for realizing their full potential in next-generation energy storage systems.

This thesis aims to improve the energy density of carbon fiber paper (CFP)-

based supercapacitors using straightforward and efficient modification techniques. In the initial investigation, CFP underwent anodization in nitric acid, leading to a significant enhancement in specific capacitance by almost three orders of magnitude attributable to the incorporation of oxygen-containing functional groups. In the second study , the anodized CFP was deposited on nickel foam, and mass loading was optimized. This further augmented the electrochemical performance by enhancing conductivity and optimizing active material use. The high-capacitance electrode created in the second investigation was ultimately combined with a water-in-salt $NaClO_4$ electrolyte. This arrangement markedly enhanced the energy density by expanding the electrochemical stability window.

In the initial study, a self-standing carbon fiber paper (CFP) electrode of high capacitance (3.96 F cm^{-2}/ 198 F g^{-1}) was obtained by increasing the specific capacitance of pristine CFP by three orders of magnitude via a simple, one-step anodization in nitric acid. The FESEM images showed little change in the morphology, but XRD and Raman spectroscopy revealed a substantial increase in structural defects on anodization of the carbon fiber. The different oxygen functionalities introduced on the CFP surface during anodization were determined from the XPS analysis. Electrochemical characterizations, including CV and GCD, were used to measure the capacitance and rate capability of the CFP subjected to different anodization conditions and to determine the contributions of the double layer and pseudocapacitance. As a demonstration, a symmetric supercapacitor fabricated from the electrode displayed excellent specific energy of 14.7 Wh kg^{-1}.

The electrochemical performance of CFP based supercapacitor obtained in the previous study was further improved by synthesizing an electrode from a anodized

carbon fiber paper (CFP) that exhibits a high areal capacitance of 4.42 F cm^{-2} and a specific capacitance of 228 F g^{-1} at a current density of 20 mA cm^{-2} (1 A g^{-1}). The electrode is made by a two-step process that involves the anodization of CFP in nitric acid followed by its deposition onto nickel foam. The impact of mass loading of the anodized CFP on nickel foam has been studied and optimized. A symmetric supercapacitor fabricated with the electrode exhibited an impressive specific energy of 15.6 Wh kg^{-1}.

In the final study, a high energy density aqueous supercapacitor was developed using a high capacitance carbon fiber paper(CFP) based electrode(NiCFP20) and $NaClO_4$ water-in-salt electrolyte with high electrochemical stable potential window(2.3V).The voltage window of the NiCFP20 electrode in various concentrations of $NaClO_4$ was evaluated using cyclic voltammetry and further validated through chronoamperometry and electrochemical impedance spectroscopy measurements.The cyclic voltammograms, GCD curves, and EIS spectra reveal the robust electrochemical kinetics of the NiCFP20 electrode in a highly concentrated $NaClO_4$ water-in-salt electrolyte. The NiCF20 electrode exhibited a high areal capacitance of 3.43 F cm^{-2} (178 F g^{-1}) at 20 mA cm^{-2}(1 A g^{-1}).Further, a symmetric supercapacitor made from electrodes demonstrated exceptional specific energy of 34.75 Wh kg^{-1} at 359.4 W kg^{-1}, and maintained a specific energy of 16 Wh kg^{-1} at 2.6 kW kg^{-1}.

Keywords: Carbon fiber paper, supercapacitor, anodization, nickel foam, water-in-salt electrolyte, energy density, EDLC

Abstract in Hindi

विद्युत द्वि-परत संधारित्रों (ईडीएलसी), या सुपरकैपेसिटर, ने अपने उच्च ऊर्जा घनत्व, विस्तारित चक्र जीवन और तीव्र आवेश-निर्वहन क्षमताओं के कारण, बेहतर ऊर्जा भंडारण तकनीकों की खोज में काफ़ी रुचि अर्जित की है। फिर भी, विशेष रूप से पोर्टेबल उपकरणों, इलेक्ट्रिक कारों और ग्रिड-स्केल भंडारण में, इनके व्यापक रूप से अपनाए जाने में एक महत्वपूर्ण बाधा बैटरियों की तुलना में इनका बहुत कम ऊर्जा घनत्व है। बैटरियों और संधारित्रों के बीच प्रदर्शन असमानता को कम करने के लिए इस कठिनाई का समाधान आवश्यक है। कार्बन-आधारित पदार्थों का उनके उच्च पृष्ठीय क्षेत्रफल, विद्युत चालकता, रासायनिक स्थिरता और आर्थिक व्यवहार्यता के कारण विभिन्न इलेक्ट्रोड पदार्थों में व्यापक रूप से अध्ययन किया गया है। कार्बन फाइबर पेपर (सीएफपी) अपनी उच्च चालकता, यांत्रिक शक्ति और धारा संग्राहक तथा सक्रिय इलेक्ट्रोड पदार्थ, दोनों के रूप में दोहरे कार्य के कारण एक व्यवहार्य विकल्प के रूप में विशेष रूप से उल्लेखनीय है। इन लाभों के बावजूद, स्वच्छ सीएफपी में कम अंतर्निहित धारिता होती है, जिससे उच्च-ऊर्जा-घनत्व वाले अनुप्रयोगों में इसकी प्रभावशीलता सीमित हो जाती है। परिणामस्वरूप, अगली पीढ़ी की ऊर्जा भंडारण प्रणालियों में उनकी पूर्ण क्षमता को साकार करने के लिए सीएफपी-आधारित ईडीएलसी की धारिता और ऊर्जा घनत्व में सुधार करने के लिए तकनीकों का निर्माण करना अत्यावश्यक और महत्वपूर्ण दोनों है।

इस शोध प्रबंध का उद्देश्य सरल और कुशल संशोधन तकनीकों का उपयोग करके कार्बन फाइबर पेपर (सीएफपी)-आधारित सुपरकैपेसिटर के ऊर्जा घनत्व में सुधार करना है। प्रारंभिक अध्ययन में, सीएफपी को नाइट्रिक अम्ल में एनोडाइज़ किया गया, जिससे ऑक्सीजन युक्त क्रियात्मक समूहों के समावेश के कारण विशिष्ट धारिता में लगभग तीन क्रम परिमाण की उल्लेखनीय वृद्धि हुई। दूसरे अध्ययन में, एनोडाइज़्ड सीएफपी को निकल फोम पर निक्षेपित किया गया और द्रव्यमान भार को अनुकूलित किया गया। इससे चालकता में वृद्धि और सक्रिय पदार्थ के उपयोग को अनुकूलित करके विद्युत-रासायनिक प्रदर्शन में और वृद्धि हुई। दूसरे अध्ययन में निर्मित

उच्च-धारिता वाले इलेक्ट्रोड को अंततः जल-में-नमक $NaClO_4$ इलेक्ट्रोलाइट के साथ संयोजित किया गया। इस व्यवस्था ने विद्युत-रासायनिक स्थिरता खिड़की का विस्तार करके ऊर्जा घनत्व को उल्लेखनीय रूप से बढ़ाया।

प्रारंभिक अध्ययन में, नाइट्रिक एसिड में एक सरल, एक-चरण एनोडाइजेशन के माध्यम से तीन क्रम के परिमाण द्वारा प्राचीन सीएफपी की विशिष्ट धारिता को बढ़ाकर उच्च धारिता ($3.96\ F\ cm^{-2}$/ $198\ F\ g^{-1}$) वाला एक स्व-स्थायी कार्बन फाइबर पेपर (CFP) इलेक्ट्रोड प्राप्त किया गया था। FESEM छवियों ने आकृति विज्ञान में थोड़ा परिवर्तन दिखाया, लेकिन XRD और रमन स्पेक्ट्रोस्कोपी ने कार्बन फाइबर के एनोडाइजेशन पर संरचनात्मक दोषों में पर्याप्त वृद्धि का खुलासा किया। एनोडाइजेशन के दौरान CFP सतह पर पेश की गई विभिन्न ऑक्सीजन कार्यात्मकताओं को XPS विश्लेषण से निर्धारित किया गया था। CV और GCD सहित विद्युत रासायनिक लक्षण वर्णन का उपयोग विभिन्न एनोडाइजेशन स्थितियों के अधीन CFP की धारिता और दर क्षमता को मापने और दोहरी परत और छद्म धारिता के योगदान को निर्धारित करने के लिए किया गया था।

पिछले अध्ययन में प्राप्त सीएफपी आधारित सुपरकैपेसिटर के विद्युत-रासायनिक प्रदर्शन को एनोडाइज्ड कार्बन फाइबर पेपर (सीएफपी) से एक इलेक्ट्रोड के संश्लेषण द्वारा और बेहतर बनाया गया था, जो $20\ mA\ cm^{-2}$ ($1\ A\ g^{-1}$) के धारा घनत्व पर $4.42\ F\ cm^{-2}$ की उच्च क्षेत्रीय धारिता और $228\ F\ g^{-1}$ की विशिष्ट धारिता प्रदर्शित करता है। यह इलेक्ट्रोड दो-चरणीय प्रक्रिया द्वारा निर्मित होता है जिसमें नाइट्रिक अम्ल में सीएफपी का एनोडाइजेशन और उसके बाद निकल फोम पर उसका निक्षेपण शामिल है। एनोडाइज्ड सीएफपी के द्रव्यमान भार का निकल फोम पर प्रभाव का अध्ययन और अनुकूलन किया गया है। इस इलेक्ट्रोड से निर्मित एक सममित सुपरकैपेसिटर ने $15.6\ Wh\ kg^{-1}$ की प्रभावशाली विशिष्ट ऊर्जा प्रदर्शित की।

अंतिम अध्ययन में, एक उच्च ऊर्जा घनत्व वाला जलीय सुपरकैपेसिटर विकसित किया गया, जिसमें उच्च धारिता वाले कार्बन फाइबर पेपर (CFP) आधारित इलेक्ट्रोड (NiCFP20) और $NaClO_4$ जल-में-लवण

इलेक्ट्रोलाइट का उपयोग किया गया, जिसमें उच्च विद्युत-रासायनिक स्थिर विभव विंडो (2.3V) थी। NaClO4 की विभिन्न सांद्रताओं में NiCFP20 इलेक्ट्रोड की वोल्टेज विंडो का मूल्यांकन चक्रीय वोल्टमेट्री का उपयोग करके किया गया और क्रोनोएम्परोमेट्री तथा विद्युत-रासायनिक प्रतिबाधा स्पेक्ट्रोस्कोपी मापों के माध्यम से आगे इसकी पुष्टि की गई। चक्रीय वोल्टमैमोग्राम, GCD वक्र और EIS स्पेक्ट्रा, अत्यधिक सांद्रित NaClO4 जल-में-लवण इलेक्ट्रोलाइट में NiCFP20 इलेक्ट्रोड की सुदृढ़ विद्युत-रासायनिक गतिकी को प्रकट करते हैं। NiCF20 इलेक्ट्रोड ने 20 mA cm−2(1 A g−1) पर 3.43 F cm−2 (178 F g−1) की उच्च क्षेत्रीय धारिता प्रदर्शित की। इसके अलावा, इलेक्ट्रोड से बने एक सममित सुपरकैपेसिटर ने 359.4 W kg−1 पर 34.75 Wh kg−1 की असाधारण विशिष्ट ऊर्जा का प्रदर्शन किया, और 2.6 kW kg−1 पर 16 Wh kg−1 की विशिष्ट ऊर्जा बनाए रखी।

मुख्य शब्द: कार्बन फाइबर पेपर, सुपरकैपेसिटर, एनोडाइजेशन, निकेल फोम, जल-इन-सॉल्ट इलेक्ट्रोलाइट, ऊर्जा घनत्व, ईडीएलसी

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Nomenclature and list of abbreviations

Symbol	Definition
q	charge stored on the plates
d	distance between charged plates
ε_o	Permittivity of free space (F m^{-1})
ε	Relative permittivity of dielectric (F m^{-1})
C	Capacitance
E	Energy density
P	Power density
t	time of discharge
R_{ESR}	Equivalent series resistance
C_{DL}	Total double layer capacitance
C_{Stern}	Capacitance of stern layer
$C_{Diffuse}$	Capacitance of diffuse layer
C_A	areal capacitance
C_m	specific capacitance
λ	Wavelength (nm)
θ	Angle of diffraction (°)
R	Universal gas constant (J mol^{-1} K^{-1})
K	Rate constant
v/v	Volume/volume
Z_{im}	imaginary component of impedance (Ω or Ω cm^2)
T	Temperature (°C or K)
f	Applied frequency (Hz)

j	Current density (A cm^{-2})
$\|Z\|$	Absolute value of impedance
(Ω or Ω cm^2)	
V	Voltage (V)
F	Farday constant (C mol^{-1})
I	Current (A)
Z_{re}	real component of impedance (Ω or Ω cm^2)
A	Area of electrode (cm^2)
ν	Scan rate (V/s)
ΔV	Voltage window (V)
R_{CT}	Charge transfer resistance (Ω cm^2)
D	diffusion coefficient
C	surface concentration
R_S	Solution resistance (Ω cm^2)
Z_W	Warburg impedance ($s^{0.5}\,\Omega^{-1}\,cm^{-2}$)
ω	angular frequency (rad/s)
I_D	Intensity of D peak
I_G	Intensity of G peak
$I_{D'}$	Intensity of D peak
C_{1s}	Carbon 1s orbital

Abbreviation	**Description**
Na	Sodium
N_2	Nitrogen
Pt	Platinum
Ni	Nickel
Ag	Silver
Hg	Mercury
CFP	Carbon fiber paper
NMP	N-Methyl-2-pyrrolidone
IHP	Inner Helmholtz plane
OHP	Outer Helmholtz plane
CB	carbon black
CNT	Carbon nanotubes
CDC	Carbon derived carbon

ESPW	electrochemical stable potential window EDLC
Electric double layer capacitor	
PC	Pseudocapacitance
SC	Supercapacitor
EC	Electrochemical capacitor
HNO_3	Nitric acid
H_2SO_4	Sulfuric acid
$NaNO_3$	Sodium nitrate
KOAc	Potassium acetate
AgCl	Silver chloride
HgO	mercuric oxide
CH_3COOK	potassium acetate
PVDF	Polyvinylidene Floride
$TEABF_4$	Tetraethylammonium tetrafluoroborate
$NaClO_4$	Sodium perchlorate
WiSE	Water-in-salt electrolyte
XRD	X-ray diffraction
SAED	Selected area electron diffraction
FESEM	Field emission scanning electron microscopy
TEM	Transmission electron microscope
EDX	Energy dispersive X-ray
XPS	X-ray photoelectron spectroscopy
SSC	symmetric supercapacitors
AQSSC	Aqueous symmetric supercapacitor
ORSSC	Organic symmetric supercapacitor
CV	Cyclic voltammetry or cyclic voltammogram
BET	Brunauer-Emmett-Teller
3D	Three-dimensional
DC	Direct current
EIS	Electrochemical impedance spectroscopy
CPE	Constant phase element
AC	Alternating current
PCFP	Pristine CFP
CFP4M	CFP electrodes anodized in 4M HNO_3
CFP7M	CFP electrodes anodized in 7M HNO_3
CFP10M	CFP electrodes anodized in 10M HNO_3
CFP15.7M	CFP electrodes anodized in 15.7M HNO_3

FWHM	full width at half maximum
LED	Light emitting diode
NiCFP10	CFP10M(10 mg cm^{-2}) loaded on Nickel foam
NiCFP15	CFP10M(15 mg cm^{-2}) loaded on Nickel foam
NiCFP20	CFP10M(20 mg cm^{-2}) loaded on Nickel foam
NiCFP25	CFP10M(25 mg cm^{-2}) loaded on Nickel foam