# IMPROVING ENERGY DENSITY AND RESPONSE TIME OF SUPERCAPACITORS THROUGH ELECTROCHEMICAL TREATMENT AND DEFECT ENGINEERING

RUPESH M TAMGADGE


DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI

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# Improving Energy Density and Response Time of Supercapacitors Through Electrochemical Treatment and Defect Engineering

by

**Rupesh M Tamgadge**

**Department of Chemical Engineering**

Submitted

in fulfillment of the requirements of degree of Doctor of Philosophy

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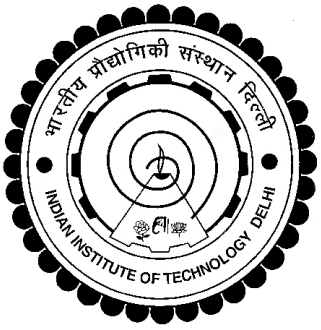



**Indian Institute of Technology Delhi**

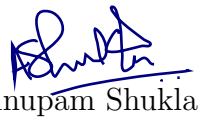
**June 2020**

*- I would like to dedicate my thesis to my beloved grandparents for teaching me the importance of education in life -*

# Certificate

This is to certify that the thesis entitled "**Improving Energy Density and Response Time of Supercapacitors Through Electrochemical Treatment and Defect Engineering** " submitted by **Mr. Rupesh M Tamgadge** 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. Mr. Rupesh M Tamgadge 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.



Anupam Shukla
Department of Chemical Engineering
Indian Institute of Technology, Delhi
India - 110016.

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Rupesh M Tamgadge

# Abstract

Supercapacitor is a class of electrochemical energy storage device that show a variation in the potential with the amount of charge stored. It is ideally suited to applications requiring pulse power, such as emergency opening of doors in jet planes, regenerative breaking in automobiles, etc. It bridges the gap between the conventional dielectric capacitor and a battery. It has higher energy density as compared to a dielectric capacitor and larger power density, cyclic life compared to a battery. However, commercial applications of supercapacitors is limited by very small energy density that is an order of magnitude smaller than a battery. Further, the requirement of higher energy and power density on the storage device is rising with the continuous improvement and increase in features modern portable and flexible electronic gadgets and other applications. Research to improve the energy density of supercapacitor is primarily focused on developing better electrode materials. The strategies depend on the type of supercapacitor. For an electric double layer capacitor, the effort is on developing electrodes with high specific surface area without compromising on the electronic conductivity. For a pseudocapacitor electrode, apart from the surface area improvement in electronic conductivity of the semi-conducting active material is also a prime focus. Another direction in the supercapacitor research is to improve the frequency response of the device. Most-

supercapacitor show capacitive behavior up to 5 Hz signal frequency and there's is a huge scope for fast frequency response supercapacitor for filtering applications at high frequency which are currently employ bulky electrolytic capacitor.

In this work, I aimed to improve the energy density (based on total weight of a device) and frequency response of supercapacitors through electrochemical treatment and defect engineering. In the first experimental study, a commercially available highly oriented pyrolytic graphite sheet was partially exfoliated in different sulfate ion based electrolytes to get vertically oriented graphene nanoflakes morphology on the surface. Different process parameters such as current density of exfoliation, time of exfoliation, pH and concentration of the electrolyte were optimized and the best electrode showed areal capacitance of 752 mF $cm^{-2}$ at current density of 2 mA $cm^{-2}$. The rate of partial exfoliation was found to be slow in low pH electrolyte solution and the obtained electrode has higher areal capacitance. It was observed that expansion of electrode play an equally important role as the open channel morphology of vertically oriented graphene nanoflakes in improving the capacitive performance.

A 2D graphite sheet can expand only along the thickness of electrode, whereas fiber paper has advantage of possible expansion of the fibers in three dimensions. Therefore, in our second study, I have used carbon fiber paper as an electrode material. The Electrochemical anodization of the carbon fiber paper was carried out in sulfuric acid solutions of different concentrations, ranging from 1 M−14 M. The characterization done show that it causes structural adjustments that expose a greater number of electrochemically active graphene edges to the surface, increases surface roughness, increases defects in graphitic structure and introduces oxygen functionality on the surface. These changes result in two orders of magnitude

increase of the surface area, and several order of magnitude increased in areal capacitance compared to pristine electrode. The areal capacitance of the anodized carbon fiber paper at the optimal conditions, 2.47 F $cm^{-2}$ at 2 mA $cm^{-2}$, is 50% more than the best literature value for a carbon-based or a pseudocapacitive material-loaded carbon electrode.

The third study was on improving the capacitive performance of anatase, a pseudocapacitive material of low cost, electrochemical stability, and high theoretical capacitance, but poor electrical conductivity. A simultaneous improvement in electrical conductivity and nanostructuring was undertaken. A two step hydrothermal route was employed to dope anatase with fluorine element. Fluorine doping leads to the creation of oxygen vacancies as well as the $Ti^{3+}$ states. Electrochemical characterizations show that these defects increase electronic charge carrier density and local conductivity of the doped anatase by an order of magnitude compared to the pristine anatase. In addition, the hydrothermal treatment lead to nanostructuring of anatase that increased the surface area by order of magnitude. As a result of the two improvements, doped anatase showed three times (236 F $g^{-1}$) higher specific capacitance than the pristine one and its rate capability is also better.

In the last study, the focus was to improve the frequency responsne of a pseudocapacitor for kilohertz frequency applications. I have fabricated a pseudocapacitor electrode with a thin anatase layer of open pore morphology by anodization of a titanium sheet in $NH_4F$ solution. Electrochemical reduction was performed to improve the electrical conductivity of the anatase electrode. The electrode synthesis parameters such as anodization potential, reduction potential, and time of reduction were optimized to get a kilohertz response pseudocapacitor. The kHz

pseudocapacitor displayed ability to retain capacitive behavior at high frequencies (190 $\mu$F cm$^{-2}$ at self resonance frequency (SRF) of 60 kHz) that is far superior to the kHz EDLCs (20 $\mu$F cm$^{-2}$ at 80 kHz SRF or 67 $\mu$F cm$^{-2}$ at 20 kHz SRF). The pseudocapacitor could filter a 50 kHz sinusoidal signal to a smooth line with a variance of less than $4\times10^{-4}$.

**Keywords**: Supercapacitors, electrochemical treatment, defect engineering, electrochemical energy storage, vertically oriented graphene nanoflakes, carbon fiber paper, anatase, kilohertz capacitor.

# सार

सुपरकैपेसिटर विद्युत ऊर्जा भंडारण उपकरण का एक वर्ग है जो ए दिखाता है की संचित चार्ज की मात्रा के साथ क्षमता में भिन्नता होती है. यह आदर्श रूप से अनुकूल है अनुप्रयोगों में जहा पल्स पावर की आवश्यकता होती है, जैसे कि जेट विमानों में दरवाजे के आपातकालीन उद्घाटन, ऑटोमोबाइल में पुनर्योजी ब्रेकिंग, आदि. सुपरकैपेसिटर, कन्वेंशनल कैपेसिटर और बैटरीज के गैप को मिटाता है. डिएलेक्ट्रिक कपैसिटर के तुलना इसमें ज्यादा ऊर्जा घनत्व होता है और बैटरीज के तुलना ज्यादा पावर घनत्व और साइकिल क्षमता होती है. हालांकि छोटे ऊर्जा घनत्व के वजह से इसके प्रैक्टिकल ऍप्लिकेशन्स कम है. भविष्य के मॉडल पोर्टेबल और फ्लेक्सिबल उपकरणों के विकास के वजह से ऊर्जा स्टोरेज उपकरणों की डिमांड कन्टिन्यूसली बढ़ती जा रही है. सुपरकैपेसिटर ऊर्जा स्टोरेज में सुधार के लिए शोध मुख्य रूप से बेहतर इलेक्ट्रोड सामग्री विकसित करने पर केंद्रित है. रणनीतियों सुपरकैपेसिटर के प्रकार पर निर्भर करती हैं. इलेक्ट्रिक डबल लेयर कपैसिटर में शोध मैटेरियल्स का सरफेस एरिया और इलेक्ट्रिकल कंडक्टिविटी बढ़ाने पर केंद्रित है. वही सुडोकपैसिटर में सरफेस एरिया बढ़ाने के साथ सेमीकंडक्टर मटेरियल की कंडक्टिविटी बढ़ाना एक मुख्य उद्देश है. सुपरकैपेसिटर रिसेर्च में उसका फ्रीक्वेंसी रिस्पांस बढ़ाना भी एक अहम् कार्य है. अधिकांश सुपरकैपेसिटर 5 हर्ट्ज तक ही फ्रीक्वेंसी तक ही कपैसिटिव बेहिवियर दिखाते है. एसी फिल्टर एप्लीकेशन के लिए एक सुपरकैपेसिटर की फ्रीकंसी प्रतिक्रिया में सुधार की बहुत बड़ी गुंजाइश है.

इस काम में, एलेक्ट्रोकेमिकल ट्रीटमेंट और डिफेक्ट इंजीनियरिंग से सुपरकैपेसिटर ऊर्जा घनत्व (कुल वजन के आधार पर) और फ्रीक्वेंसी रिस्पांस में सुधार करने का लक्ष्य रखा है. पहले प्रायोगिक अध्ययन में, एक व्यावसायिक रूप से उपलब्ध हाइली ओरिएंटेड पैरोलीटिक ग्रेफाइट शीट को विभिन्न सल्फेट आयन आधारित इलेक्ट्रोलाइट्स में आंशिक रूप से एक्सफ़ोलीएट किया गया था ताकि वर्टीकल ओरिएंटेड ग्राफीन, ग्रेफाइट सरफेस पर प्राप्त किया जा सके. प्रोसेस पैरामीटर्स जैसे की एक्सफोलिएशन का समय, करंट घनता , इलेक्ट्रोलाइट पीएच आदि को ऑप्टिमाइज़ किया. कम पीएच इलेक्ट्रोलाइट में एक्सफोलिएशन का रेट कम पाया गया और चार्ज स्टोर करने की क्षमता ज्यादा पायी गयी. यह पाया गया की इलेक्ट्रोड का एक्सपांशन, एनर्जी डेंसिटी बढ़ाने में एक महत्वपुर्ण रोल अदा करता है.

दो आयामी कार्बन में एक्सपांशन केवल एक ही दिशा में सिमित है , जब की कार्बन फाइबर इलेक्ट्रोड में तीन दिशा में एक्सपांशन की क्षमता है. इसलिए, मैंने अपने दूसरे अध्ययन में, इलेक्ट्रोड के रूप में कार्बन फाइबर पेपर का उपयोग किया है. कार्बन फाइबर का एलेक्ट्रोकेमिकल ट्रीटमेंट विभिन्न कॉन्सेंट्रेशन (1-14 मोलर)के सल्फुरिक एसिड में किया गया. किए गए कैरेक्टराइजेशन से पता चलता है कि सक्रिय ग्राफीन किनारों की संख्या बढ़ जाती है. साथ ही सरफेस में खुदरापन, क्रिस्टल स्ट्रक्चर में डिफेक्ट और ऑक्सीजन वेकन्सी को बढ़ाता है. यह बदलाव, प्रिस्टिन कार्बन फाइबर के मुकाबले ट्रीट किये हुए कार्बन फाइबर का सरफेस एरिया और एनर्जी स्टोरेज क्षमता को परिमानक्रम बढ़ाता है. ऑप्टिमम कंडीशन में बढ़ा हुआ कैपासिटंस २.४७ फैरड पर सेंटीमीटर, २ मिलीएम्पियर पर सेंटीमीटर स्केअर करंट घनता पर पाया गया , जो की रिपोर्टेड संख्या से ५० गुना ज्यादा है.

तीसरा अध्ययन एनाटेस के कैपेसिटिव प्रदर्शन में सुधार पर था, यह एक कम लागत, विद्युत रासायनिक स्थिरता और उच्च सैद्धांतिक कैपासिटंस वाला सुडोकपैसिटिव मटेरियल है. इलेक्ट्रिकल कंडक्टिविटी में सुधार और नैनोस्ट्रक्टरिंग एक साथ किया गया. एक दो कदम हाइड्रोथर्मल मार्ग को फ्लोरीन तत्व के साथ एनटेज को डोप करने के लिए नियोजित किया गया था. इलेक्ट्रोकेमिकल कैरेक्टराइजेशन यह बताते है की निर्माण किये गए डिफेक्ट्स इलेक्ट्रॉनिक चार्ज करियर घनता और इलेक्ट्रिकल कंडक्टिविटी को परिमाणक्रम बढ़ाते है. यह ट्रीटमेंट सरफेस एरिया को भी अधिक बढ़ाता है. यह दो सुधार के वजह से प्रिस्टिन मटेरियल के मुकाबले कैपासिटंस को ३ से ४ गुना बढ़ता है.

मेरे अंतिम अध्ययन में, मेरा उद्देश्य एक किलोहर्ट्ज फ्रीक्वेंसी रिस्पांस सुडोकपैसिटर निर्माण करना था. एक पतली, ओपन पोर स्ट्रक्चर की एनटेज लेयर ग्रो करने के लिए मैंने टाइटेनियम शीट को $NH_4F$ इलेक्ट्रोलाइट में ऑक्सीडाइज किया. इलेक्ट्रिकल कंडक्टिविटी बढ़ाने के हेतु इलेक्ट्रोड को रिदुस किया. इलेक्ट्रोड सिंथेसिस के पैरामीटर्स जैसे की ऑक्सीडेशन वोल्टेज, ऑक्सीडेशन समय, रिडक्शन पोटेंशियल और टाइम  को अनुकूलन किया. हमारे ऑप्टिमम सुडोकपैसिटर की किलोहर्ट्ज फ्रीक्वेंसी पर कैपेसिटिव व्यवहार को बनाए रखने की क्षमता बहुत बढ़ गयी.

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# Nomenclature and list of abbreviations

| Symbol | Definition |
|---|---|
| $A$ | Area of electrode ($cm^{-2}$) |
| $C$ | Capacitance (F) |
| $C_{dl}$ | Specific double layer capacitance (F $g^{-1}$) |
| $C_{ps}$ | Specific pseudocapacitance (F $g^{-1}$) |
| $C_A$ | Areal capacitance (mF $cm^{-2}$ or F $cm^{-2}$) |
| $C_{Fe}$ | Concentration of the ferricyanide ion (mM) |
| $C_i$ | Specific capacitance due to less-accessible inner surface (F $g^{-1}$) |
| $C_o$ | Specific capacitance due to easily accessible outer surface (F $g^{-1}$) |
| $C_{sp}$ | Specific capacitance (F $g^{-1}$) |
| $C_V$ | Volumetric capacitance (F $cm^{-3}$) |
| $C'$ | Real component of complex capacitance (F) |
| $C''$ | Imaginary component of complex capacitance (F) |
| $D$ | Diffusion coefficient of ferricyanide ($m^2$ $s^{-1}$) |
| $E$ | Applied bias potential, Electrode potential (V) |
| $E_i$ | Initial potential of the discharge curve (V) |
| $E_f$ | Final potential of the discharge curve (V) |
| $e$ | Electron charge (C) |
| ESR | Equivalent series resistance ($\Omega$) |
| $\Delta E$ | Voltage window (V) |
| $\frac{\Delta E}{\Delta t}$ | Slope of discharge curve (mV $s^{-1}$) |
| $f_0$ | Frequency at maximum $C''$ (Hz) |

| | |
|---|---|
| $I$ | Constant discharge current (mA) |
| $i_p$ | Peak current (mA) |
| $iR_{drop}$ | Difference between final charge voltage and first point in discharge curve |
| $m$ | Mass of an electrode (mg) |
| $N_d$ | Charge carrier density ( $cm^{-3}$) |
| $P$ | Power density of the device (W $kg^{-1}$) |
| $q_T$ | Total charge stored (C) |
| $q_i$ | Charge stored by the less accessible surface (C) |
| $q_o$ | Charge stored by the easily accessible outer surface (C) |
| $R_{ESR}$ | Equivalent series resistance ($\Omega$) |
| $t$ | discharge time (s) |
| $U$ | Energy density of the device (Wh $kg^{-1}$) |
| $V$ | Volume of the device ($cm^{-3}$) |
| $v$ | Scan rate (mV $s^{-1}$) |
| $Z'$ | Real part of impedance ($\Omega$) |
| $Z''$ | Imaginary pat of impedance ($\Omega$) |
| $\epsilon_0$ | Permittivity of vacuum (F m−1 |
| $\epsilon_r$ | Relative permittivity |
| $\tau_{RC}$ | Resistance time constant (ms) |

| **Abbreviation** | **Description** |
|---|---|
| AcC | Activated carbon |
| AEC | Aluminum electrolytic capacitor |
| ASC | Asymmetric supercapacitor |
| BDM | Bockris, Devanathan, and Muller |
| BET | Brunauer-Emmett-Teller |
| C-AFM | Conductive atomic force microscopy |
| CDC | Carbide derived carbon |
| CFP | Carbon fiber paper |
| CNT | carbon nanotube |
| CV | Cyclic voltammetry or cyclic voltammogram |
| CVD | Chemical vapor deposition |
| EA | Electrochemically anodized electrode |
| EAR | Electrochemically anodized and then reduced electrode |

| | |
|---|---|
| ECSA | Electrochemical surface area |
| EDL | Electric double layer |
| EDX | Energy-dispersive X-ray spectroscopy |
| EDLC | Electric double layer capacitor |
| EED | Enegy conversion and storage devices |
| EES | Electrochemical energy conversion and storage devices |
| EIS | Electrochemical impedance spectroscopy |
| EPR | Electron paramagnetic resonance spectroscopy |
| ESR | Equivalent series resistance |
| EV | Electric vehicle |
| ExGrNH-1 | Electrode exfoliated in $(NH_4)_2SO_4$ by route 1 |
| ExGrNH-2 | Electrode exfoliated in $(NH_4)_2SO_4$ by route 2 |
| FESEM | Field emission scanning electron microscopy |
| EXFG | Exfoliated graphite sheet |
| FLG | Few layer graphene |
| FNP | Fluorine doped nanoparticles |
| GCD | Galvanostatic charge-discharge |
| GO | Graphene oxide |
| HOPG | Highly oriented pyrolytic graphite |
| HRTEM | High resolution transmission electron microscopy |
| IHP | Inner Helmholtz plane |
| iOT | Internet of things |
| MO | Metal oxides |
| OHP | Outer Helmholtz plane |
| PECVD | Plasma enhanced chemical vapor deposition |
| PEDOT | Poly(3,4-ethylenedioxythiophene |
| RGO | Reduced graphene oxide |
| SAED | Selected area electron diffraction |
| SHE | Standard hydrogen electrode |
| SSC | Symmetric supercapacitor |
| TNT | Titania nanotube |
| VOG | Vertically oriented graphene |
| XPS | X-ray photoelectron spectroscopy |
| XRD | X-ray diffraction |