Electrochemical Capacitors
Theory, Materials and Applications

Edited by
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Electrochemical capacitors are most important for the development of future energy storage systems and sustainable power sources. New superior hybrid supercapacitors are based on binary and ternary thin film nanocomposites involving carbon, metal oxides and polymeric materials. The synthesis of materials and fabrication of electrodes for supercapacitor applications is discussed in detail. The book also presents the fundamental theory and a thorough literature review of supercapacitors.

**Keywords:** Energy Storage, Electrochemical Capacitors, Nanocomposites, Hybrid Supercapacitors, Carbon/Metal Oxide Composites, Metal Oxides/Hydroxides Composites, Polymer Type Capacitors, Nanoscience, Hydrothermal Synthesis, Graphene-based Composites, Ultrasonic Assisted Synthesis
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Theory, Materials and Applications

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Preface

The book on Electrochemical Capacitors: Theory, Materials and Applications provides up-to-date knowledge related to the experimental background and state-of-the-art survey of composite thin films for electrochemical capacitors: the most important innovation for energy storage, which is imperative for future energy storage. The broad-spectrum coverage of this book will provide a premise for innovative work of electrochemical capacitors in the coming decades. This edition covers the theory, fundamental and literature review of supercapacitors. The synthesis of materials and fabrication of electrodes for supercapacitor applications are discussed in details. The reader will appreciate the contextual investigations extending from carbon, metal oxides and polymeric materials based binary and ternary composites energy storage systems for superior hybrid supercapacitors. This book is also covering the whole range of nanocomposite science and technology and innovation for sustainable power sources.

This book is the consequence of the precarious accountability of experts from various interdisciplinary science fields. It extensively explores the most plenteous, top to bottom, and innovative research and reviews. We are grateful to all the contributing authors and their co-author for their technically sound and in-depth contributions. We would also like to thank all distributors, authors, and other who conceded consent to utilize their figures, tables, and schemes.

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Chapter 1

Theory, Fundamentals and Application of Supercapacitors

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Abstract

Supercapacitors or electrochemical capacitors are electrochemical energy storage devices which have drawn huge attention from the scientific community in recent years due to their compactness and long cyclic stability. Great efforts have been paid to improve the energy density of supercapacitor electrodes. Recent research focuses on synthesis of advanced carbon metals, polymers, and metal oxide based composites which can be used as electrode materials for supercapacitor applications. In this chapter, we focus on the history, recent developments concerning supercapacitors electrode materials, electrolytes and separators that have been widely used in supercapacitor devices. The basic parameters and electrochemical properties of supercapacitors are also summarized. Finally, to achieve high specific capacitance in supercapacitors some perspectives and outlook are proposed.

Keywords

Supercapacitors, Energy Storage, Electrodes, Carbon Materials

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1. Introduction

In the past few decades, the fast advancements made in various areas such as
industrialization have resulted in increased demands for energy storage devices. At the
meantime, the global increase in population has also led to these growing energy
requirements. These factors have combined to cause a major problem on the existing
power infrastructure and pose serious troubles for the future of mankind [1]. Until now,
petroleum fuels have been largely exploited for the power needs of our society. However,
with limited resources of petroleum products, there is a requirement for an alternate
energy sources. In this context, notable efforts have been devoted to developing more
efficient energy storage devices and technologies. An example of such an efficient device
is the electrochemical capacitors, often called as a supercapacitor. Supercapacitor
technology has gained considerable research interest among the scientific community in
recent years due to its unique properties. They exhibit higher capacitances that are much
higher than traditional capacitors [2]. Supercapacitors can be used in various energy
storage devices, either stand-alone or in combination with batteries. Supercapacitors have significant advantages over conventional capacitors in terms of their large charging-discharging stability and high power capacity. However, the energy density of supercapacitors is much lower than that of rechargeable batteries. This necessitates coupling with batteries for applications requiring a surplus energy supply for longer periods of time. Therefore, there is a huge interest in increasing the energy density of supercapacitors [3]. This is one of the major obstacles for the development of advanced electrode materials in supercapacitor technology. This chapter describes the fundamentals, electrode materials and their properties, and electrode fabrication and analysis techniques for supercapacitors.

2. Energy needs and energy storage devices

The challenge associated with the production of renewable energy using the available natural resources is of serious concern for researchers throughout the world. Furthermore, the burning of fossil fuel produces large amounts of CO₂ emissions which lead to adverse effects such as global warming and ocean acidification.

There is no single solution to solve these challenges related to energy and environment problems. Furthermore, the growth of novel technologies and devices with a large interest in the protection of nature and environment is utmost importance. On the other hand, we cannot imagine our modern day life without electronic portable devices such as laptops, cell phones etc., also without the transportation vehicles like airplanes, buses, cars, and many other innovations made our life more sophisticated [1-2]. Though they provide a high degree of comfort, they are the major cause for environmental issues.

The last decade was a witness to more significant research efforts towards the development of various renewable energy systems like solar cells and fuel cells. However, these alternative energy sources still suffer on account of some limitations. Among the energy storage devices, batteries and supercapacitors (SCs) are viewed with greater attention due to their superior electrochemical properties. Batteries provide higher energy density but suffer from poor power density and cycle life. In contrast, the SCs can store and release a huge amount of power within a short time [3]. SCs are appealing as a modern energy storage system that possess most fascinating features such as high power density, long cycle life, environment safety [4]. SCs provide best solutions for electrical energy requirement in our day to day life. For instance, many electric vehicle companies are utilizing SCs for greater power delivery during acceleration. Apart from this, SCs are used in digital cameras, power back up systems and various electronic devices [5]. The cyclic performance of a supercapacitor is determined by the electrode, which can be designed through novel routes with nano or microstructures to improve the charge storage
capability. Selection of an appropriate electrolyte might also improve the energy density of a supercapacitor system [6,7].

3. Breakthrough in supercapacitor research

Howard Becker from General Electric company first reported electrical double-layer charge storage in 1957. After Becker’s initiatives, Robert A. Rightmire (1966) and Donald L. Boos (1970) from (SOHIO) fabricated a new capacitor with higher capacitance value which is now commonly available.

In 1978, Nippon Electric Company (NEC) commercialized supercapacitors under license from SOHIO. After commercialization, SCs have been produced with several designs. Initially, these capacitors were termed as a power back up systems for many consumer electronic devices. Nippon made great efforts towards the commercialization of various new series of supercapacitors [8]. More significantly supported by organic electrolytes; in 2001 they introduced spiral-wound, thin-format series capacitors. Further, they changed the product name as NEC-Tokin in the year 2002. Nippon ChemiCon of Japan started mass production of their supercapacitors with higher performance (3000F, 2.5 V) in 1998.

The gold cap double layer capacitors were marketed by Panasonic in the year of 1978. Use of non-aqueous electrolytes and non pasted electrodes is the major deviation from the Nippon design. Due to these differences, the Panasonic capacitors gained higher operating voltage [9,10].

Daewoo group of Korea developed supercapacitors named as Nesscap supercapacitor in 1998. Nesscap operated with the help of organic electrolyte with a spiral wound prismatic cell construction. NessCap presently supplies supercapacitors from a few farads to 5,000F at 2.7V [8]. In 1993, ESMA a Russian company developed supercapacitors of capacity ranging from 3,000F to 100,000F.

In recent years many research groups are working towards the fabrication of novel materials as an electrode for supercapacitors. Few of the inspiring works are discussed here. P.W. Ruch et al. investigated the characteristics of single-wall carbon nanotubes (SWCNTs) as supercapacitors [12]. For the first time, Ruch exploited the SWCNT for supercapacitor electrode applications. Graphene-based SCs were first reported by M. D. Stoller et al. [13]. This advanced electrode active material exhibited high surface area (2630 m\(^2\)g\(^{-1}\)) and with the maximum specific capacitance of 99 Fg\(^{-1}\) and 135 Fg\(^{-1}\) in organic and aqueous electrolytes respectively. Recently Liu et al. reported graphene-based SC energy density of (86 Whkg\(^{-1}\) at room temperature and 136Whkg\(^{-1}\)at 80˚C) [14]. El-Kady et al. reported a facile method of fabricating supercapacitor devices on
DVD discs [15]. Choudhary et al. core/shell nanowire supercapacitor using two-dimensional (2D) transition-metal chalcogenides which shows a superior charge retention of over 30,000 cycles. This work may be considered as a recent breakthrough in supercapacitor research.

Recently, the new concept of supercapattery has been introduced to understand the hybrid systems in which the charge storage principles of supercapacitor and battery are integrated into a single device. In this device, one electrode acts as capacitor like characteristics and other one shows battery like properties. However, there is a possibility of higher influence of the battery electrode over the capacitor electrode and this hybrid device will behave as a battery. Such device is termed as a super battery. If the capacitor property is dominant in the hybrid device then it is termed as supercapattery [17].

4. Energy storage principles: EDLC Vs pseudocapacitance

Famous German physicist Helmholtz was the first person to demonstrate the idea of the electric double layer in the year of 1853 [18]. Generally an electrochemical capacitor has two electrodes with a separator. The electrodes are electrically connected by the aqueous electrolyte. The electrodes immersed in an electrolyte solution attract the counter ions by the application of an external potential. The voltage on this setup produces two layers of polarized ions. The first one is created on the surface of the electrode the second one from the opposite polarity is separated by a layer of solvated molecules. This plane separates the oppositely polarized ions and acts as a molecular dielectric.

In 1913, Gouy and Chapman proposed the “diffuse double layer” theory to explain the double layer capacitance [19-21]. In this theory, the solvated ions in the electrolyte are assumed as point charges contained within a single diffuse layer. Otto Stern in 1924 suggested a realistic proof to explain the physical situation at the electrode/ electrolyte interface [22]. He combined both Helmholtz and Gouy-Chapman theories. He used different electrolytes and the ionic radius of the associated ions to arrive at the capacity of the double layer capacitor. Stern model proposed that $q_{\text{solution}}$ (charge from solution side) to be a combination of $q_{\text{Helmholtz}}$ (Helmholtz charge) and $q_{\text{Gouy}}$ (charges from the diffuse layer).

\[
q_{\text{solution}} = q_{\text{Helmholtz}} + q_{\text{Gouy}}
\]

Then the total capacity at the interface “C” is denoted as,

\[
\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_G}
\]
In this equation, \( C_H \) is the capacity due to Helmholtz layer and \( C_G \) the capacity due to the diffuse layer. Graham from America proposed a model to further demonstrates the double layer [23]. According to Graham concept, some of the ionic species can penetrate the Stern layer and approach the solvated ion molecules. Bockris et al. proposed the BDM model which we are commonly using for double layer capacitance [24]. In this model solvent molecules have a fixed alignment with the electrode. Most specifically adsorbed ions could appear in this layer. The electrical energy is stored by means of Faradic (redox process) reactions on the surface of the electrode with an electric double layer. Basically, pseudocapacitance (redox process) arises from charge transfer between the electrode and electrolytes. Only the charge transfer (or) change in oxidation process takes place.

5. **Design of Supercapacitor**

In General, a supercapacitor consists of three main components namely electrode, electrolyte and separator. The electrochemical properties of SCs mainly depend on electrode and electrolyte. Nevertheless, the electrode is the primary component for storing energy and delivery. The following sections elaborate on the individual components of a supercapacitor system.

5.1 **Electrode materials**

During past few decades, the invention of novel electrode materials with excellent specific capacitance has enabled the rapid growth in the supercapacitor field. The electrode material is the most important component in determining the electrochemical property and stability. There are three different types of electrode materials which are usually used for supercapacitor devices. These include carbon-based materials and metal oxides and conducting polymers.

5.1.1 **Carbon and allied materials**

In practice, Carbon with large surface area is widely used for supercapacitor electrodes. Generally, carbon materials exhibit an advantageous combination of physical and chemical properties. The superior characteristics of low cost, high specific surface area, high conductivity, porous nature, corrosion resistance, processability and being eco-friendly make carbon-based materials an attractive candidate for supercapacitor electrode applications. Activated carbon (AC), carbon aerogels (CA), carbon nanofibers (CNF), carbon nanotubes (CNT) and graphene are the various forms of carbon which are exploited as electrode materials for SCs.

The carbon-based materials derived from natural resources like wood and other biomasses like plants contain impurities like ash, cause a reduction in the supercapacitor
performance. Further, the pore sizes also vary from source to source. Therefore the method of improving the surface area as well as the porosity of carbons by thermal or chemical process is called as “activation” which converts carbon into activated carbon (AC). The ACs has a porous structure composed of micro, meso and macro pores [25-28]. Generally, the presence of a large number of mesopores (2-50nm) in the AC electrode materials provides maximum capacitance values. The ACs possesses higher surface area but the limited availability of mesopores limits the specific capacitance values due to lower ion accessibility [29]. The carbon aerogels are other forms of carbon with excellent conductivity, high surface area, and tunable porous structure. These attractive properties of carbon aerogels are well suited for electrode materials for SCs with long cyclic stability [30-37]. Since 1990’s major research interest has been renowned to carbon nanotubes (CNTs) as a superior electrode material for supercapacitor applications. It holds many profitable properties such as narrow pore size distribution, higher surface area, and high structural stability [38]. These profitable features of CNTs have made them an alternative material for supercapacitor [39-43]. However, due to high cost, CNTs are not viable for large-scale production. But at the same time, they are widely used as conductivity booster and replace activated carbons in supercapacitor electrodes.

Recently Graphene, the King of carbons with 2D lattices are considered as alternative electrode materials for SCs due to their high intrinsic surface area and excellent electrical conductivity. In addition, graphene possesses outstanding intrinsic strength, good chemical stability, and excellent thermal conductivity. Owing to these unique features, graphene provides a better platform for storage of ions and electrons. Graphene has been extensively studied for supercapacitor electrode applications by many researchers [44-47].

5.1.2 Conducting polymers

The conducting polymers are a new class of electrode materials for supercapacitors owing to their three-dimensional (3D) porous structure, high capacitance value, scalable synthesis and lightweight. The most commonly applicable conducting polymers for SCs include polypyrrole, polyaniline, polythiophene, and poly[3,4-ethylenedioxythiophene] (PEDOT) and their derivatives. [48-51]. However, some of the key issues like poor cyclic stability, bulging of the electrolyte and oxidative degradation of active material limits the usage of conducting polymers in supercapacitor electrodes [52].
5.1.3 Metal oxides

Owing to its high redox chemistry, the metal oxides (TMOs) are exploited as smart candidates for supercapacitor electrodes. More specifically, nanostructured ruthenium oxide (RuO₂), manganese oxide (MnO₂), nickel oxide (NiO), cobalt oxide (CO₃O₄) and bismuth oxide (Bi₂O₃) and some metal oxides have been examined as supercapacitor electrodes. In addition, mixed metal oxides, metal oxides with carbon and conducting polymers also have been examined towards enhancing the electrochemical performance of the supercapacitor.

The RuO₂ is a suitable material for supercapacitor due to its various oxidation states. It showed maximum capacitance of 1450 Fg⁻¹ with low electrical resistivity. This attractive material has been studied extensively towards supercapacitor electrode applications [53-55]. Nevertheless, the higher cost and environmental issues restrict its usage in commercialization. Worldwide many research groups devoted their research work towards an alternative material for RuO₂ in energy storage applications. The MnO₂ is considered as a better alternate material for RuO₂ in supercapacitor electrodes. MnO₂ with the peculiar properties like large specific capacitance, cost effectiveness, environmental friendliness have gained huge attention in constructing supercapacitors. Many researchers have reported the use of MnO₂ as an alternative electrode material for SCs [56-61]. However poor specific surface area and dissolution of manganese ions in aqueous media restrict its commercial usage.

Co₃O₄ nanostructures are also emerging in supercapacitor electrodes due to their higher specific capacitance and cost-effective nature. Thus, Co₃O₄ shows good structural stability against charge-discharge process [62-67].

The NiO is one among the most extensively studied metal oxide for supercapacitor electrode applications. This material also exhibits high theoretical specific capacitance in a wide potential range of 0.5 V, low cost, high chemical stability. Owing to these unparalleled characteristics NiO is used for supercapacitor electrodes nowadays [68-70].

Due to less toxicity, magnetic separation, and natural abundance, Fe₂O₃ has attracted the attention of many researchers. Apart from that Fe₂O₃ is incombustible and eco-friendly. Recently many researchers reported performance of Fe₂O₃ nanostructures for supercapacitor electrode applications [71-74]. Apart from NiO and Co₃O₄ nanostructures Ni(OH)₂ and Co(OH)₂ nanostructures are also extensively studied for supercapacitor applications [75-78].
5.1.4 Hybrid electrode
The use of Transition metal oxide as a supercapacitor electrode material is emerging recently due to its better ion transportation kinetics and high electrical conductivity. Furthermore, the conductivity of transition metal oxide could be improved by incorporating carbon-based materials like activated carbon; carbon nanotubes (CNTs) and graphene. Over the past decade variety of hybrid nanostructures have been synthesized and examined for supercapacitor electrode applications [79-83].

5.1.5 Mixed metal oxide electrodes
Recently mixed metal oxide composites are considered as most popular in terms of achieving high electrochemical performance in SCs. The blending of two different transition metal oxides to form a heterostructure greatly reduces the inactive sites present in the material and it is possible to take full advantage of both kinds of active materials. This kind of synergetic architectures exhibits better results in SCs [84-88].

5.2 Electrolyte
Electrolytes play a major role in SC devices, which connect two electrodes and establish the charge transfer. In General, there are three different categories of electrolytes used, aqueous electrolytes, organic electrolytes, and ionic liquids. All these electrolytes are associated with their own advantages and disadvantages. For instance, SCs utilizing aqueous electrolytes show higher conductivity and specific capacitance. But its working voltage is restricted to only (1.2V). In contrast, organic electrolytes operate at a still higher voltage but suffer from poor ionic conductivity. Though the best operating voltage is obtained in room temperature ionic liquids, the prohibitive cost makes them unsuitable. For supercapacitors the selection of electrolytes mainly depends upon the stability of electrolyte at an applied potential window and its ionic conductivity.

5.2.1 Aqueous electrolytes
Aqueous electrolytes have been used extensively for studying the supercapacitor performance. For example, nearly 90% of published work in 2014 descripted the use of aqueous electrolytes [89]. Further; cost-effectiveness and easy handling of aqueous electrolytes simplify the device fabrication process. Neutral aqueous electrolytes for SCs show high ionic conductivity and low cost. The aqueous electrolytes possess smaller sized solvated ions and high dielectric constants values. Both of these features significantly enhance the specific capacitance of a supercapacitor [90,91]. However, the low value of the operating window (~1.2V) limits its usage. Increase in the electrolyte voltage window improves the energy density of supercapacitor.
5.2.2 Organic electrolytes

Nowadays organic electrolyte based commercial SC devices influencing market due to improved voltage performance. The increased cell voltage increases the electrochemical properties like specific capacitance and energy density. In addition, the organic electrolytes permit the use of inexpensive materials as electrodes and packaging. There are many efforts focused to design stable organic electrolytes with higher conductivity and wide potential window. However, the high cost, lower ionic conductivity, flammability, and toxicity are the important issues to be seriously considered before employing as an electrolyte for SC applications.

5.2.3 Ionic liquid electrolytes

The ionic liquids are termed as solvent-free electrolytes are another class of electrolytes for SCs. Use of ionic liquids as electrolytes pushes the potential window to over 3V [92]. Fluoromethane sulphonyl imide is mainly employed as the ionic liquid electrolyte for supercapacitor. However, the ionic conductivity of these ionic liquids is very low at room temperature. But the energy storage systems are used in the temperature range from –30°C to +60°C. The ionic liquids still need improvements to increase their stability and conductivity at room temperature. Though the ionic liquids are effective, their use is restricted by the high cost of these materials.

5.3 Separator

The separator is also an important component of a supercapacitor system. The separators are ion-permeable and prevent the electrical and physical contact between two electrodes and allow the ionic charge transfer from electrolytes. To achieve high performance in SC’s the separators must possess higher ionic conductivity and smaller thickness. Generally, nonwoven paper and polymer separators are utilized with aqueous electrolytes for SCs.

5.4 Different analytical techniques used for the analysis of supercapacitors

Cyclic voltammetry, galvanostatic charge-discharge, and impedance techniques are important characterization techniques usually employed to analyze the properties of supercapacitors.

5.4.1 Cyclic voltammetry (CV)

The CV analysis was recorded using three electrode systems consisting of working, counter and reference electrode with suitable electrolyte at various scan rates. An aqueous electrolyte is usually added to the sample to increase its conductivity. The
commonly used materials for the working electrode are glassy carbon, platinum, and gold. The specific capacitance performance in appropriate electrolytes was carried out in their corresponding potential range and recorded at various scan rates (mVs⁻¹). In general scan rate increases, the specific capacitance value usually decreases. The following equation has been used to calculate the specific capacitance value by using cyclic voltammetry method

\[ SC = \frac{1}{V \times m (V_a - V_c)} \int_{V_a}^{V_c} IV. dV \]

The SC values were calculated by integrating the area and then dividing by the sweep rate (mVs⁻¹), the mass of the active material (m), and the potential window (Va to Vc).

### 5.4.2 Chronopotentiometry

The galvanostatic charge/discharge behavior of the supercapacitor electrode was evaluated using chronopotentiometry. From the charge/discharge method, it was observed that the charging curve was almost similar to the discharging curve, but slightly differs from the initial charging time. The specific capacitance at a particular current density of the electrode materials can be evaluated from the following Equation

\[ SC = \frac{I \times \Delta t}{\Delta V \times m} F g^{-1} \]

Where I is the discharge current, \( \Delta t \) is the discharging time, \( \Delta V \) is the discharging voltage, and m is the mass of the electroactive material. When compare to cyclic voltammetry the specific capacitance values calculated from the charge-discharge technique was almost reliable. This technique also has been employed to evaluate the stability of electrode materials. From charging and discharging curves, the SC values were calculated.

### 5.4.3 Power density (P) and energy density (E)

The energy density and power densities are two important parameters for the investigation of the electrochemical performance of supercapacitors. The charge-discharge method is the most suitable technique to evaluate the power density and energy density values of the supercapacitor. The energy density of supercapacitor decreases with increase in power density. Energy density (E) and power density (P) were calculated from the following Equations
\[ E = \frac{1}{2} C (\Delta V)^2 \]

\[ P = \frac{E}{t} \]

Where \( C \) is specific capacitance (\( F \ g^{-1} \)), \( \Delta V \) is a potential window (V), \( t \) is discharge time (s), \( E \) is energy density (\( Wh \ kg^{-1} \)) and \( P \) is power density (\( KW \ kg^{-1} \)).

**Conclusions**

With the invention of the supercapacitors, an alternative energy storage device emerged to offer high power density and good stability. As it was reported supercapacitors have the great quality that makes them suited for various applications including batteries, hybrid power systems, and emergency power supplies. As it can be seen from the review presented here, there is room for improvement in the fabrication of supercapacitor electrodes to be used in more applications needing high energy density.

**References**


https://doi.org/10.1016/j.micromeso.2010.01.007


Electrochemical Capacitors


Chapter 2

Metal Oxides/Hydroxides Composite Electrodes for Supercapacitors

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Abstract

Supercapacitors (Electrochemical capacitors) are promising energy storage devices and have attracted significant attention as ‘bridges’ for the energy/power gap between traditional capacitors and batteries. The performance of supercapacitors is essentially determined by its electrode material. Among various supercapacitor electrodes, transition metal oxides/hydroxides usually exhibit high specific capacitance and energy densities. This chapter discusses the advantages and disadvantages of the supercapacitor and the supercapacitor performance of various metal oxide/hydroxides. Also, this review focus on the development and challenges of metal oxide/hydroxide based electrode materials.

Keywords

Specific Capacitance, Metal Oxides/Hydroxides, Current Density, Ruthenium Oxide

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