

Review Article on Supercapacitors: Emerging Electrodes and Materials

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ABSTRACT

Supercapacitors (SCs) are an essential energy storage device known for their high power density, fast charging/discharging rates, and long cycle life. Traditional SCs have been limited by energy density, making them less competitive than batteries for long-term energy storage. The development of new generation supercapacitors with innovative electrodes and materials has significantly enhanced their performance. This review highlights the latest advancements in electrode materials, including carbon-based, conducting polymers, transition metal oxides, hydrogel electrodes, and nanomaterials. We explore the synthesis methods, characterization techniques and performance metrics of these materials. Moreover, we examine their potential applications in fields such as electric vehicles, renewable energy systems, and portable electronics. This article provides a comprehensive overview of the future directions in SC technology and the critical role of next-generation electrodes in addressing existing challenges.

Keywords: Supercapacitor, Energy density, Cyclic voltammetry, Energy storage

INTRODUCTION

Supercapacitors (SCs), also known as ultracapacitors or electrochemical capacitors (ECs), are energy storage devices that provide high power density, rapid charge/discharge cycles, and exceptional durability compared to conventional batteries. Unlike batteries that store energy chemically, supercapacitors store energy electrostatically through the formation of an electric double layer at the electrode/electrolyte interface. This fundamental difference results in several advantages for supercapacitors, including fast charging, long cycle life, and high efficiency in power delivery [1]. However, supercapacitors generally offer lower energy density compared to batteries, which limits their use in applications requiring long-term energy storage. The performance of supercapacitors is typically quantified by their specific capacitance, energy density, and power density, which depend largely on the choice of electrode materials. Over the years, the development of supercapacitors has advanced through various types of materials, resulting in the evolution of three types of supercapacitors. First type of supercapacitors is relied on carbon-based materials such as activated carbon and graphene, which provided good electrical

conductivity and a large surface area for charge accumulation. These materials are widely used in the commercial production of electrochemical double-layer capacitors (EDLCs) [2]. Second type of supercapacitors introduced the concept of pseudocapacitance, where transition metal oxides (TMOs), such as MnO₂ and RuO₂, were used as electrodes. These materials store energy through faradaic reactions in addition to the electrostatic charge accumulation, which allows for higher energy density. However, the challenge with these materials has been their low conductivity and poor stability over extended cycles [3]. Third type of supercapacitors includes novel materials such as conducting polymers, 2D materials, and hybrid nanomaterials. These materials aim to combine the advantages of both EDLCs and pseudocapacitors to improve both energy density and power density. Notable materials in this category include graphene oxide, MXenes, polyaniline (PANI), and conducting polymer composites. The development of these materials is a key factor in overcoming the limitations of energy density, making supercapacitors more competitive for applications in energy storage [4]. While supercapacitors are widely used in applications

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requiring high power output (such as electric vehicles, uninterruptible power supplies (UPS), pulse power systems, and energy harvesting systems), their limited energy density compared to batteries has hindered their adoption for long-duration storage. This limitation has driven extensive research to discover and develop new electrode materials, as well as to explore innovative device architectures that enhance the overall performance of supercapacitors [5]. The focus of current research is to develop next-generation supercapacitors with improved energy density, charge/discharge rates, and long-term cycling stability. This involves exploring new electrode materials with high surface area, nanostructured architectures, enhanced electrochemical performance, and environmentally friendly synthesis methods. By utilizing advanced materials such as carbon nanotubes (CNTs), graphene oxide, transition metal hydroxides, and hydrogel-based composites, it is possible to engineer supercapacitors that meet the growing demand for more efficient, lightweight, and flexible energy storage solutions [6]. The pursuit of sustainable, cost-effective, and scalable electrode materials has also led to increased interest in green synthesis methods. Biomass-derived carbon, bio-based polymers, and hydrothermal/solvothermal methods are some of the eco-friendly approaches gaining traction for the large-scale production of supercapacitor electrodes [7]. These methods aim to reduce the environmental impact and production costs, making supercapacitors more attractive for widespread commercial and industrial applications.

2. Types of New Generation Electrodes

2.1. Carbon-Based Electrode Materials

Carbon materials such as activated carbon, graphene, and carbon nanotubes (CNTs) are commonly used in supercapacitor electrodes due to their excellent electrical conductivity, large surface area, and chemical stability. Graphene has emerged as a leading candidate for high-performance SC electrodes. With its high conductivity, large surface area (2675 m²/g), and mechanical strength, graphene offers significant improvements in the power density and cycle life of SCs [8]. Carbon Nanotubes (CNTs), with their high surface area and exceptional mechanical and electrical properties, have also shown considerable promise. Researchers have explored their functionalization and combination with other materials to improve SC performance [9]. Activated

Carbon (AC) remains one of the most widely used materials for EDLCs. Although it has a lower energy density compared to some newer materials, it offers low cost and high stability, making it a popular choice for commercial SCs.

2.2. Conducting Polymers

Conducting polymers such as polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT) are another class of materials used to enhance the performance of SCs. These materials combine the advantages of electrochemical capacitance from pseudocapacitance and electrical conductivity, leading to improved energy storage capabilities. Polyaniline (PANI) has shown significant promise due to its high pseudocapacitance, stability, and ease of synthesis. Modifying PANI with materials like graphene or carbon nanotubes has further enhanced the rate performance and cycling stability of supercapacitors [10]. Polypyrrole (PPy) and PEDOT are also attractive candidates due to their high capacitance and flexibility. These conducting polymers allow for enhanced charge storage via redox reactions, which boosts the energy density of SCs [11].

2.3. Transition Metal Oxides (TMOs)

Transition metal oxides, including MnO₂, Co₃O₄, RuO₂, and NiO, have gained significant attention for pseudocapacitive behavior, which allows for higher energy densities compared to traditional carbon materials. These materials store charge through faradaic redox reactions, improving energy density while maintaining relatively high power density.

Manganese dioxide (MnO₂) is one of the most widely studied TMOs for supercapacitor applications due to its low cost, high theoretical capacitance, and environmental friendliness. However, its poor electrical conductivity can limit performance, which has been addressed through composite formation with conductive materials like graphene or CNTs [12]. Ruthenium oxide (RuO₂), though one of the best materials for pseudocapacitance with high energy density, is costly and scarce. Ongoing research aims to enhance its electrochemical stability and cost-effectiveness by developing composite materials or alloyed forms [13].

2.4. Hydrogel Electrode Materials

Hydrogel-based materials are an emerging class of electrode materials for supercapacitors, particularly for flexible and stretchable devices. These materials

are attractive because of their biocompatibility, high ionic conductivity, and large electrochemical stability window. Polymeric hydrogels (such as polyvinyl alcohol (PVA)) are widely used due to their ease of synthesis, low cost, and mechanical flexibility. When combined with conducting agents like carbon nanotubes or graphene, the overall performance of these electrodes is significantly enhanced [14].

2.5. 2D Materials (Graphene Oxide, MXenes)

Two-dimensional (2D) materials like graphene oxide and MXenes are attracting attention for their high surface area, excellent conductivity, and fast ion diffusion properties, which are crucial for high-performance SCs. MXenes, a class of layered transition metal carbides/nitrides, offer high ionic conductivity and large surface area. They have been shown to offer high energy and power density while maintaining cycling stability [15]. Graphene oxide (GO) is a promising material for supercapacitor electrodes. Its tunable surface chemistry, high surface area, and excellent conductivity make it ideal for enhancing the overall electrochemical performance when combined with other materials like conducting polymers or TMOs [16].

3. Synthesis Methods

The performance of supercapacitors is directly influenced by the synthesis methods used for the electrodes. In this review we have reports various synthesis techniques, highlighting their advantages and limitations, to provide a comprehensive understanding for researchers aiming to enhance SC performance.

3.1 Hydrothermal Synthesis

Hydrothermal synthesis involves crystallizing materials from aqueous solutions at elevated temperatures and pressures within a sealed vessel. This method facilitates the growth of nanostructured materials with controlled morphologies.

Advantages:

Enables precise control over particle size and morphology, facilitates the formation of crystalline structures at relatively low temperatures and allows for the incorporation of various dopants to enhance material properties.

Limitations:

This method requires specialized equipment to withstand high pressures. Extended reaction times may be necessary to achieve desired crystallinity. For instance, hydrothermal synthesis has been effectively

utilized to produce metal oxide nanostructures for SC electrodes, resulting in materials with high specific capacitance and stability.

3.2 Sol-Gel Method

The sol-gel process involves transitioning a system from a liquid "sol" into a solid "gel" phase. This technique is advantageous for synthesizing homogeneous and pure materials.

Advantages:

It offers molecular-level mixing of precursors, leading to uniform compositions, operates at relatively low processing temperatures and enables the coating of substrates with thin films.

Limitations:

The material has Potential for cracking during drying due to shrinkage, challenges in controlling pore size and distribution. The sol-gel method has been employed to synthesize metal oxide aerogels with high surface areas and enhancing the energy storage capabilities of SCs.

3.3 Electrochemical Deposition

The electrochemical deposition method entails the reduction of metal ions from a solution onto a conductive substrate under an applied electric field. This method is widely used for fabricating thin films and nanostructures.

Advantages:

This method allows for precise control over film thickness and morphology, operates under ambient conditions without the need for high temperatures or pressures and facilitates the direct deposition onto complex substrate geometries.

Limitations:

Uniform deposition can be challenging on non-conductive substrates, requires meticulous control of deposition parameters to prevent defects. Electrochemical deposition has been successfully applied to fabricate conducting polymer films, such as polyaniline and polypyrrole, which exhibit high pseudocapacitance in SC applications.

3.4 Microwave-Assisted Synthesis

This technique utilizes microwave radiation to heat reactants, leading to rapid and uniform nucleation and growth of nanomaterials.

Advantages:

This methods significantly reduces reaction times compared to conventional heating methods, promotes uniform heating, resulting in homogeneous materials

and energy-efficient due to direct interaction of microwaves with the material.

Limitations:

Requires materials to be microwave-responsive, limiting the choice of precursors. Scale-up for industrial applications can be challenging. Microwave-assisted synthesis has been employed to produce metal oxide nanoparticles with enhanced electrochemical properties for SC electrodes.

3.5 Chemical Vapor Deposition (CVD)

CVD methods involve the deposition of a solid material from a vapor by a chemical reaction occurring on or near a substrate surface. It is commonly used for producing high-purity and high-performance thin films.

Advantages:

This method produces uniform and conformal coatings over large areas, capable of depositing a wide range of materials, including metals, semiconductors, and insulators. Scalable for industrial production.

Limitations:

High operational temperatures may limit substrate compatibility, involves complex equipment and higher operational costs. CVD has been utilized to synthesize carbon-based materials, such as graphene and carbon nanotubes, which serve as effective electrode materials in SCs due to their high surface area and conductivity.

3.6 Co-Precipitation Method

This method involves the simultaneous precipitation of multiple components from a solution, leading to the formation of homogeneous composite materials.

Advantages:

This method is simple and cost-effective with straightforward procedures, enables uniform distribution of different components at the molecular level and suitable for large-scale production.

Limitations:

It requires precise control over pH and temperature to achieve desired stoichiometry. Post-synthesis treatments, such as calcinations, may be necessary to achieve the desired phase. Co-precipitation has been used to synthesize metal hydroxide/carbon composites, enhancing the pseudocapacitive performance of SC electrodes.

Selecting an appropriate synthesis method is crucial for optimizing the performance of supercapacitor electrodes. Each technique offers distinct advantages and presents specific challenges. A thorough

understanding of these methods enables researchers to tailor

4. Electrolytes:

Electrolytes are crucial in determining the performance metrics of supercapacitors, including their capacitance, operating voltage, energy density, and thermal stability. The selection of an appropriate electrolyte is crucial for optimizing these parameters. In this review we have to focus the primary electrolytes used in supercapacitors, highlighting their respective advantages and limitations.

4.1 Aqueous Electrolytes

Aqueous electrolytes, such as sulfuric acid (H₂SO₄), potassium hydroxide (KOH), and various salt solutions, are commonly employed due to their high ionic conductivity.

Advantages:

The aqueous electrolyte has high ionic conductivity, leading to low internal resistance and high power density. Cost-effective and environmentally benign.

Limitations:

Limited electrochemical stability window, restricting the operating voltage to approximately 1.23 V, which can limit energy density. Potential for corrosion of electrode materials in certain pH conditions [17]

4.2. Organic Electrolytes

Organic electrolytes, typically comprising organic solvents like acetonitrile or propylene carbonate with dissolved salts (e.g., tetraethylammonium tetrafluoroborate), offer a broader electrochemical stability window.

Advantages:

It has higher operating voltage, often up to 2.7 V, enabling increased energy density. Wider operational temperature range.

Limitations:

The organic electrolytes have lower ionic conductivity compared to aqueous electrolytes, potentially resulting in higher internal resistance. Also, it has higher costs and environmental concerns due to the use of organic solvents [18].

4.3 Ionic Liquid Electrolytes

Ionic liquids are salts in a liquid state at room temperature, known for their negligible vapor pressure and high thermal stability.

Advantages:

Wide electrochemical stability window, allowing operating voltages up to 3.5 V. Non-flammable and thermally stable, enhancing safety.

Limitations:

Ionic electrolyte has higher viscosity leading to lower ionic conductivity, which can affect power performance. High cost and complex synthesis processes [19]. Polymer electrolytes, including gel polymer electrolytes, consist of a polymer matrix that hosts the ionic conductive species.

Advantages:

Flexible and can form thin films, suitable for various device configurations. Reduced leakage risk compared to liquid electrolytes.

Limitations:

Generally lower ionic conductivity than liquid electrolytes, which may impact performance. Potential stability issues over extended cycling [20].

4.4 Redox-Active Electrolytes

Redox-active electrolytes incorporate redox-active species to enhance capacitance through faradaic reactions.

Advantages:

It has increased energy density due to additional redox capacitance. Potential for tailoring electrochemical properties by selecting appropriate redox couples.

Limitations:

It has possible stability issues due to the reversible nature of redox reactions. Complexity in optimizing the concentration and compatibility of redox species with electrode materials.

The choice of electrolyte in supercapacitors is a critical determinant of their overall performance, influencing factors such as energy density, power density, operational voltage, and thermal stability. A nuanced understanding of the properties, advantages, and limitations of various electrolytes enables the strategic design and optimization of supercapacitors tailored for specific applications.

5. Characterization Techniques:

Characterization techniques are essential for evaluating and understanding the performance, efficiency, and mechanisms of supercapacitors. These methods provide insights into the electrochemical behavior, structural properties, and overall functionality of supercapacitor components. In this review we have to discuss the key characterization techniques commonly employed in supercapacitor research, along with their advantages and limitations.

5.1 Cyclic Voltammetry (CV)

Cyclic Voltammetry involves sweeping the potential of the working electrode linearly with time between

set limits and recording the resulting current. This technique is instrumental in assessing the electrochemical properties of supercapacitors.

Advantages:

This technique provides information on redox processes, electrochemical stability, and capacitance behavior. Also helps in identifying the type of capacitance (electric double-layer or pseudocapacitance).

Limitations

Interpretation can be complex due to overlapping redox peaks. May not accurately represent real-world operating conditions due to the controlled environment [21].

5.2 Galvanostatic Charge-Discharge (GCD)

GCD, also known as chronopotentiometry, involves charging and discharging the supercapacitor at a constant current and recording the voltage response over time.

Advantages:

GCD techniques enable calculation of specific capacitance, energy density, and power density. Provides insights into the charge-discharge efficiency and internal resistance.

Limitations:

These techniques may not reveal detailed information about the charge storage mechanisms. Long-term cycling can be time-consuming for stability assessments [22].

5.3 Electrochemical Impedance Spectroscopy (EIS)

EIS measures the impedance of the supercapacitor over a range of frequencies, providing information on resistive and capacitive behavior.

Advantages:

Offers insights into internal resistance, capacitance, and diffusion processes. Helps in understanding the frequency response and dynamic behavior.

Limitations:

Data interpretation requires complex equivalent circuit modeling. Sensitive to measurement conditions and requires careful calibration [23].

5.4 In Situ/Operando Characterization Techniques

These techniques involve monitoring the supercapacitor during operation to observe real-time changes in structure and composition.

Advantages:

Provides direct observation of charge storage mechanisms. Helps in correlating structural changes with electrochemical performance.

Limitations:

Requires sophisticated instrumentation and experimental setups. Data interpretation can be challenging due to the complexity of simultaneous measurements [24].

6. Applications of Supercapacitors

Supercapacitors have significant applications in several fields such as Electric Vehicles (EVs) to provide quick bursts of energy for acceleration and braking, complementing batteries to improve efficiency and range [25]. Supercapacitors are used in energy harvesting systems to store power generated from renewable sources like solar and wind. SCs can be integrated into devices like smartphones, wearables, and drones, offering fast charging and long cycle life [26]. SCs are used for load leveling and frequency regulation in power grids due to their ability to store and release energy quickly.

CONCLUSION

The development of new generation supercapacitors with advanced electrodes has significantly enhanced their performance. Materials such as graphene, conducting polymers, transition metal oxides, and 2D materials have shown promise in increasing the energy density, power density, and stability of SCs. Future research will likely focus on combining multiple materials to achieve a balance between high energy and power densities, as well as improving the scalability and cost-effectiveness of production methods. The continuing advancement of electrode materials and synthesis techniques holds the key to the widespread commercialization and application of supercapacitors

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