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Review

A Review: Exploring Carbon Electrode Structures and Electrochemical Parameters to Enhance Supercapacitor Performance

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Abstract- Supercapacitors, also known as electric double-layer capacitors, have gained substantial attention for their remarkable energy storage capabilities, making them vital for numerous applications, including portable electronics, electric vehicles, and renewable energy systems. This review delves into the intricate world of carbon electrodes in supercapacitors, highlighting the diverse carbon materials used, such as activated carbons, carbon blacks, zeolite-template carbons, and graphene meso-sponges, and their significant impact on supercapacitor performance. Some research explores the synthesis of carbon electrodes using zeolite templates, which provide precise control over structural properties for enhancing performance in high-rate applications. The review also provides a comprehensive understanding of the fundamental principles of electrochemical cells, emphasizing the critical factors affecting carbon electrode performance, including surface functional groups, electrolyte composition, voltage range and stability, cycle life, operating temperature, current density, and rate capability. Recognizing the interconnected nature of these factors is essential for optimizing supercapacitor technology. This knowledge forms the foundation for ongoing research and innovation needed to advance supercapacitors, providing sustainable and efficient solutions to pressing energy challenges.

Keywords- Capacitance; Electrochemical Cell; Electrolyte; Energy Storage; Functional Group

1. INTRODUCTION

Electric double-layer capacitors, commonly known as supercapacitors, have garnered significant attention in recent years due to their exceptional energy storage capabilities [1]. These devices are renowned for their high-power density and remarkable cycle life, which make them pivotal for a wide array of applications, ranging from portable electronics to electric vehicles and renewable energy systems [2,3].

As the global demand for clean and sustainable energy sources continues to surge, supercapacitors have emerged as promising candidates for bridging the gap between traditional batteries and capacitors [4]. Their unique ability to store and deliver energy efficiently, coupled with their impressive longevity, has prompted extensive research to realize their full potential. However, like any energy storage system, supercapacitors are not without their challenges, and understanding the intricacies of their operation and potential pitfalls is vital for further optimization and widespread adoption.

Carbon materials are integral components of supercapacitor electrodes, and their performance directly impacts the device’s energy storage and delivery characteristics [5], particularly in the negative potential range, where degradation can be notably significant. The ability to comprehend and mitigate these degradation mechanisms is pivotal, as it can lead to enhanced supercapacitor stability – a fundamental prerequisite for their deployment in demanding environments, such as high-temperature settings, high-voltage applications, and extended operational lifespans [6].

Supercapacitors operate on the principle of the electrochemical double-layer (EDL) effect, where electrical energy accumulates at the interface between a solid electrode and an electrolyte solution [7]. Unlike traditional batteries, where chemical reactions are the primary means of energy storage, supercapacitors rely on the rapid and reversible adsorption of ions at the electrode-electrolyte interface. This mechanism grants them their exceptional power density and cycle life. The development and optimization of supercapacitor materials and designs are active research areas aimed at achieving even higher performance standards [8].

The world of supercapacitor materials is vast and diverse. One of the most crucial aspects of a supercapacitor is its electrode materials, particularly those in the negative electrode (anode). Carbon materials have been the preferred choice for supercapacitor electrodes due to their exceptional electrical conductivity, high surface area, and chemical stability [9].

There are several types of carbon materials commonly employed in supercapacitors, such as activated carbon, carbon black, zeolite-template carbon, and graphene meso-sponge [10]. The selection of carbon materials significantly influences the overall performance and degradation behavior of supercapacitors, thus warranting a comprehensive investigation. Figure 1 displays various carbon materials commonly utilized in supercapacitors, including activated carbon, zeolite-template carbon, graphene meso-sponge, and carbon black. Activated carbon's porous structure, comprising micropores, mesopores, and macropores, offers a large surface area and high capacitance. Zeolite-template carbon boasts ordered pores, providing a specific surface area and low resistance. Graphene meso-sponge has interconnected graphene sheets, which can exhibit a high specific capacitance and excellent cycling performance. Carbon black features interconnected carbon particles, enhancing electrical conductivity and stability.

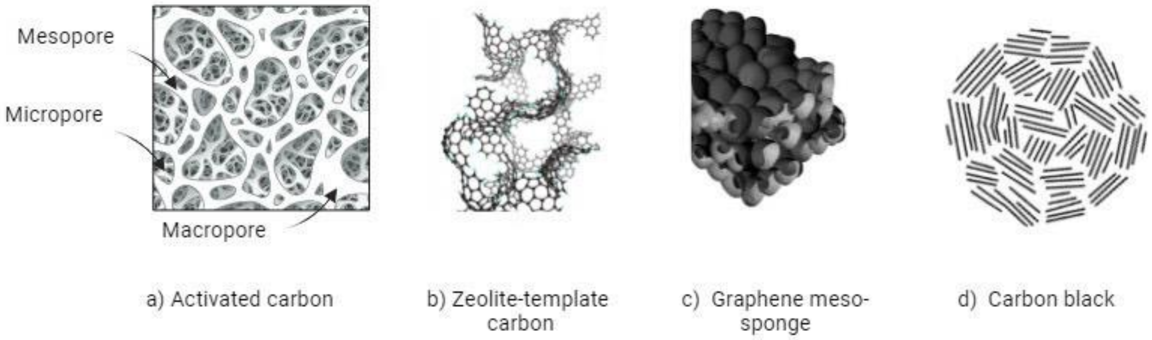

Figure 1, Different carbon materials for supercapacitors

In recent years, there has been a growing interest in applying supercapacitors in various industries. For instance, in the automotive sector, supercapacitors are integrated into hybrid and electric vehicles to manage peak power demands and enhance energy recovery during braking [11]. Similarly, in renewable energy systems, supercapacitors play a critical role in buffering and stabilizing power fluctuations from intermittent sources such as solar and wind [12]. These diverse applications underscore the importance of achieving robust and long-lasting supercapacitor performance, even in challenging environments and operating conditions.

Focus on the negative potential range is significant, as it is here that the mechanisms leading to degradation become particularly pronounced [13]. Exploring the interplay between various carbon materials and surface structures can help reveal their roles in influencing degradation behaviour. Understanding these mechanisms is a multi-faceted endeavour, encompassing electrochemical, structural, and molecular aspects, and demands an interdisciplinary approach [14].

In the complex realm of supercapacitors and their carbon electrodes, it is crucial to recognize the central role of research and innovation in advancing these energy storage systems. These insights are poised to contribute to the ongoing efforts to improve supercapacitor performance, strengthen their stability, and facilitate their integration into even more challenging applications [15]. The potential impact of the research in supercapacitors extends to energy storage, transportation, and beyond, offering sustainable and efficient solutions to some of the world's most pressing energy challenges.

2. CARBON ELECTRODE STRUCTURE IN SUPERCAPACITOR

Carbon electrodes are a cornerstone of supercapacitor technology, serving as the critical interface where electrical energy accumulates through the electrochemical double-layers (EDL) mechanism [1]. understanding the intricate structure of carbon electrodes is pivotal as it profoundly influences the performance and behaviour of supercapacitors.

2.1. Carbon electrode in supercapacitor

Carbon electrodes are central to the functioning of supercapacitors due to their unique combination of properties. These properties include high electrical conductivity, extensive surface area, and excellent chemical stability, making them an ideal choice for supercapacitor electrodes [4]. Carbon materials provide an interface for charge accumulation via the electrochemical double-layer (EDL) mechanism, forming the foundation of supercapacitor energy storage [2].

A carbon electrode possesses a complex structure characterized by numerous micropores and various functional groups. These attributes are instrumental in its energy storage capabilities within supercapacitors. However, the prevalence of micropores can impede ion diffusion, potentially reducing electrode efficiency [16]. Nevertheless, carbon electrodes exhibit favorable performance in supercapacitors. Enhancing electrode efficiency entails optimizing pore size distribution to facilitate improved ion transport. This optimization is crucial for enhancing energy storage and delivery in supercapacitors.

2.2. Activated carbons: porous structures for high surface area

Activated carbons are frequently employed in supercapacitor electrodes, distinguished by their highly porous structures. The activation process involves creating a vast network of pores and channels, thereby providing a large surface area for charge accumulation. These pores are essential for the efficient adsorption of ions from the electrolyte onto the carbon surface, enabling high capacitance and rapid charge/discharge cycles [5,17].

The specific surface area (SSA) of activated carbons can vary significantly depending on the activation method and precursor materials. This tunability enables the design of carbons with tailored properties for specific supercapacitor applications [18]. Additionally, activated carbons often feature a combination of micropores, mesopores, and macropores, offering a diverse range of sites for ion adsorption. This diversity in pore sizes enhances the accessibility of electrolyte ions to the carbon surface, contributing to the supercapacitor's performance [19]. For instance, adding Zinc Oxide (ZnO) nanorods and nanoparticles to activated carbon (ACC) alters its pore structure, significantly enhancing its performance as a supercapacitor electrode. While this modification reduces the specific surface area and total pore volume due to ZnO particles covering the pores, ACC with ZnO nanorods forms new, larger surface pores that facilitate ion storage and improve ion movement into smaller internal pores. These changes enhance the electrochemical performance by improving ion diffusion and storage, making the modified activated carbon more effective for supercapacitor applications [20].

The structural properties of activated carbons have a direct impact on their electrochemical behaviour, influencing parameters such as capacitance, energy density, and power density [21]. The extensive surface area and pore structure promote high capacitance values, making activated carbons a preferred choice for supercapacitor applications [22].

2.3. Carbon blacks: spherical nanoparticles

Carbon electrodes are central to the functioning of supercapacitors due to their unique combination of properties. These properties include high electrical conductivity, extensive surface area, and excellent chemical stability, making them an ideal choice for supercapacitor electrodes [4]. Carbon materials provide an interface for charge accumulation via the electrochemical double-layer (EDL) mechanism, forming the foundation of supercapacitor energy storage [2]. Carbon blacks, commonly used in supercapacitors, are distinguished by their spherical nanoparticles with a primary particle size typically in the nanometre range. The high surface area, along with the existence of sp2-hybridized carbon structures, facilitates rapid charge storage and release [23].

The small particle size and the absence of macropores contribute to the low ionic diffusion resistance within the carbon black particles, leading to fast charge/discharge rates. Additionally, carbon black particles can be combined with other carbon materials to create composite electrodes with enhanced electrochemical properties [24].

The specific properties of carbon blacks, such as their surface chemistry and pore distribution, can be tailored through various manufacturing processes. The flexibility in customizing carbon black characteristics allows researchers to optimize supercapacitor performance for specific applications [11].

2.4. Zeolite-template carbon: ordered mesoporous structures

Zeolite-template carbons offer a unique structure with ordered mesopores. These materials are synthesized by templating the carbon structure within the porous framework of zeolites. The resulting carbon possesses a well-defined and interconnected mesopore network that can enhance ion transport and accessibility [12].

The regularity of the mesopore structure in zeolite-template carbons can lead to improved capacitance retention at high discharge rates. This property makes them suitable for applications where rapid energy delivery is crucial, such as regenerative braking in electric vehicles [13].

Additionally, the ordered mesoporous structure of zeolite-template carbons provides greater control over ion adsorption and desorption kinetics, leading to enhanced supercapacitor performance [14].

2.5. Graphene meso-sponge: two-dimensional architecture

Graphene, a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice, has attracted significant attention in supercapacitors. Graphene meso-sponge, a three-dimensional network of interconnected graphene sheets, offers a unique combination of properties [15].

The two-dimensional nature of graphene provides an exceptionally high surface area, while the three-dimensional meso-sponge structure enables efficient electrolyte access and ion diffusion. This combination results in excellent capacitance and rapid charge transfer, making graphene meso-sponge a promising material for supercapacitors [25]. The interconnected graphene sheets also contribute to the structural stability of the electrode, reducing the risk of structural degradation during charge/discharge cycles.

2.6. Carbon Structure for Supercapacitors

The choice of carbon material and its structural characteristics directly impacts the electrochemical performance of supercapacitors. This selection can tailor carbon electrode structures to meet specific application requirements, whether high power density, high energy density, or long cycle life is needed. Furthermore, advances in material synthesis techniques, such as chemical activation, templating, and chemical vapor deposition, offer opportunities to design carbon materials with precise structural control, opening new avenues for supercapacitor development [26].

It is worth noting that the development of carbon materials for supercapacitors is an active area of research. Researchers continuously seek to strike a balance between various structural parameters to achieve the optimal performance for a given application [27].

3. SYNTHESIS OF CARBON ELECTRODES WITH ZEOLITE TEMPLATES FOR SUPERCAPACITOR

In the quest to optimize the performance of supercapacitors, a key area of focus is the synthesis of carbon electrodes. These carbon electrodes are pivotal in enabling high-energy storage and rapid charge/discharge capabilities in supercapacitors. Among the various approaches for carbon electrode production, one intriguing avenue is the application of zeolite templates.

3.1. Diverse Carbon Materials in Supercapacitors

Improving the performance of supercapacitors necessitates exploring a range of carbon materials. It encompasses several diverse carbon materials, such as activated carbons, carbon blacks, zeolite-template carbon (ZTC), and graphene meso-sponge (GMS). Each of these materials possesses unique structural properties that have a substantial impact on the resulting supercapacitor performance [2].

The diversity of carbon materials in this study allows for a comprehensive investigation into their structural characteristics and their potential as supercapacitor electrodes. By comparing these materials, it gains valuable insights into the structural factors that influence supercapacitor performance.

3.2. Unique Structural Properties of Carbon Materials

Carbon materials exhibit diverse structural properties, including specific surface area and edge sites, which are instrumental in supercapacitor applications. The specific surface area (SSA) directly influences the amount of charge storable on the carbon surface, rendering it a critical parameter for supercapacitor performance [17].

The presence of edge sites on carbon materials is another significant factor. Edge sites, also known as defects, provide active sites for charge adsorption and desorption. The type and density of edge sites can influence the electrochemical behaviour of carbon materials in supercapacitors [28].

3.3. Characterization techniques: nitrogen physisorption

Understanding the structural properties of carbon materials involves sophisticated characterization techniques. Nitrogen physisorption is one such technique that plays a crucial role in evaluating the specific surface area of these materials. By subjecting the carbon materials to nitrogen gas at low temperatures, it is possible to measure the adsorption and desorption of nitrogen molecules, enabling the calculation of the specific surface area [1].

This method provides valuable information about the porous nature of carbon materials, as well as their ability to adsorb and store ions at the electrode-electrolyte interface. For supercapacitors, a higher specific surface area generally correlates with increased capacitance and improved energy storage capabilities [26].

3.4. High-sensitivity temperature-programmed desorption

High-sensitivity temperature-programmed desorption (TPD) is another vital technique in the study of carbon materials for supercapacitors. TPD involves heating the carbon sample while monitoring the desorption of gases, providing insights into the surface chemistry and reactivity of the material.

In the context of supercapacitors, TPD is especially valuable for investigating the presence of functional groups and defects on the carbon surface. The desorption of specific gases at characteristic temperatures can reveal information about the nature of the edge sites and their potential involvement in charge storage mechanisms [26]

3.5. Zeolite-templates for controlled structure

Zeolite-template carbon (ZTC) is a unique class of carbon materials synthesized using zeolites as templates. Zeolites are crystalline materials with ordered nanometres-scale pores. By infiltrating the carbon precursor into the zeolite framework and subsequently removing the zeolite template, a carbon material with an ordered mesoporous structure is obtained [25].

Utilizing zeolite templates imparts a high degree of structural control to the resulting carbon material. Choosing the appropriate zeolite template allows for customization of mesopore size and regularity. This level of control is advantageous in optimizing the structural properties of carbon materials for supercapacitor applications [11].

3.6. Advantages of zeolite-template carbon

Zeolite-template carbon offers several advantages that make it a promising candidate for supercapacitor electrodes. First and foremost, the ordered mesoporous structure enhances ion transport and accessibility to the carbon surface. These modifications yield superior electrochemical performance, especially at high discharge rates, where rapid energy delivery is essential [22].

Utilizing zeolite templates also enables precise control of the specific surface area, pore size, and pore distribution in the resulting carbon material. These parameters match the requirements of supercapacitor applications, whether for high energy density, high power density, or long cycle life [14].

3.7. Applications of zeolite-template carbon in supercapacitor

Zeolite-template carbon finds application in various supercapacitor systems, including those designed for high-power energy storage in hybrid and electric vehicles. Its ordered mesoporous structure, coupled with high surface area, enhances rapid charge and discharge capabilities, which are ideal for capturing and releasing energy during regenerative braking and high-demand acceleration [24]. Moreover, the controlled structure of zeolite-template carbon contributes to long-term stability, reducing the risk of electrode degradation over extended cycles. Such characteristics make it an attractive choice for applications where durability and longevity are essential, such as in renewable energy systems and grid storage.

For instance, Graphene Meso-sponge (GMS) significantly outperforms activated carbon YP-50F when used as an electrode material in electric double-layer capacitors (EDLCs) with an organic electrolyte. Specifically, GMS exhibits higher specific capacitance, energy, and power density. Additionally, GMS has an extended voltage range and demonstrates superior stability compared to activated carbon. These attributes underscore the potential of GMS as a high-performance electrode material for EDLCs. The ordered mesoporous structure of GMS, derived from a zeolite template, facilitates the rapid diffusion of ions and electrons, resulting in high capacitance and low resistance, which explains its exceptional performance [24].

4. FACTOR AFFECTING THE ELECTROCHEMICAL PERFORMANCE OF CARBON ELECTRODE IN SUPERCAPACITOR

Numerous factors govern the electrochemical performance of carbon electrodes in supercapacitors. These factors can significantly influence the stability and efficiency of these energy storage devices, especially in the context of degradation reactions at negative potential ranges. This section delves into the intricate interplay of these factors and their impact on supercapacitor performance. Figureble 2 illustrates the initial degradation reactions that occur in supercapacitors. The reaction sites are the H-edge, phenol, ether and carbonyl groups on the positive electrode and the basal plane on the negative electrode. These reactions can significantly impact the performance of the supercapacitor by reducing the specific capacitance, increasing the equivalent series resistance, and altering the charge transfer kinetics.

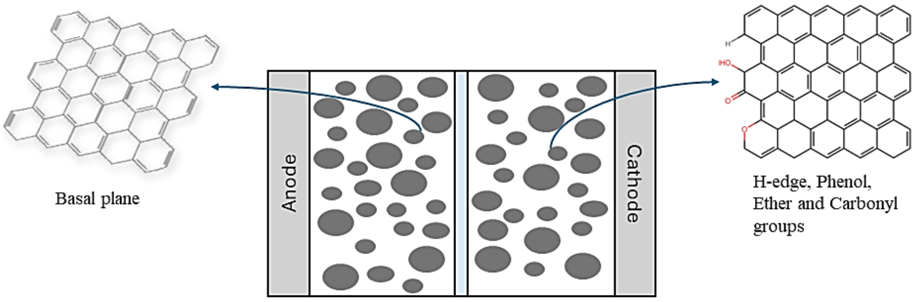

Figure 2. Initial degradation reactions of carbon electrodes in supercapacitors

4.1. Carbon Material Properties

The choice of carbon material is a fundamental factor influencing supercapacitor performance. Different types of carbon, such as activated carbons, carbon blacks, zeolite-template carbons, and graphene meso-sponges, possess varying structural and surface properties. The specific surface area, pore size distribution, and surface functional groups of these carbon materials play a crucial role in determining their electrochemical behaviour [25].

Activated carbons, recognized for their high specific surface area and porous structure, are favoured for their capacity to accommodate numerous ions through physisorption, contributing to high capacitance [1]. Carbon blacks, with their fine nanoparticles, facilitate rapid charge/discharge cycles due to low ionic diffusion resistance.

Zeolite-template carbons, with their ordered mesoporous structures, offer advantages in high-rate applications by enhancing ion transport and accessibility. Graphene meso-sponges, owing to their interconnected three-dimensional graphene networks, combine a high surface area with structural stability, reducing the risk of degradation.

Each type of carbon material undergoes customization for specific supercapacitor applications, depending on its distinctive properties. It aims to balance surface area, pore structure, and electrical conductivity to optimize supercapacitor performance.

4.2. Surface Functional Groups

The presence of surface functional groups on carbon materials significantly influences their electrochemical properties. These functional groups can include oxygen-containing moieties like hydroxyl, carbonyl, and carboxyl groups. The type and abundance of these functional groups impact the wettability, hydrophilicity, and electrochemical behaviour of carbon electrodes. Figure 3 shows the types of oxygen-containing functional groups on carbon materials. Various carbon and oxygen bonds exhibit distinct characteristics attributed to variations in atomic hybridization degrees. Oxygen atoms with sp2 hybridization function as electron absorbers, whereas those with sp3 hybridization function as electron donors. Moreover, the arrangement of diverse oxygen-containing functional groups within the graphite sheets of carbon materials varies.

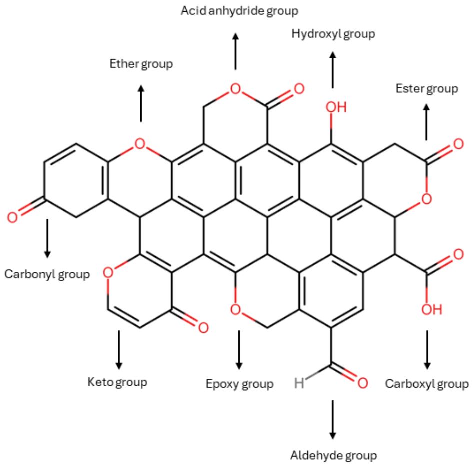

Figure 3. Types of oxygen-containing functional groups on carbon materials

Functional groups are associated with pseudo-capacitance, which involves faradaic reactions at the electrode-electrolyte interface. Pseudo-capacitance is particularly relevant in cases where specific functional groups facilitate redox reactions, contributing to enhanced charge storage.

Understanding the role of surface functional groups is essential for tailoring carbon materials to specific supercapacitor applications. By controlling the type and density of functional groups, researchers can fine-tune the electrochemical performance of carbon electrodes.

4.3. Electrolyte composition

The composition of the electrolyte solution in supercapacitors is a critical factor that influences the device's electrochemical behaviour. The choice of electrolyte can impact both the electrochemical stability and the capacitance of the supercapacitor [29]. Common electrolytes include aqueous solutions, organic solvents, and ionic liquids, each with distinct advantages and limitations.

Many choose aqueous electrolytes because of their environmental friendliness and high ionic conductivity. They find frequent use in low-temperature applications. Organic electrolytes provide a wider voltage window, enabling higher energy density, although they may exhibit lower ionic conductivity. Ionic liquids offer excellent stability and low volatility but can be costlier [30].

The selection of the appropriate electrolyte depends on the specific requirements of the supercapacitor application. Some factors, including voltage range, operating temperature, and compatibility with electrode materials, play a crucial role in optimizing supercapacitor performance [4].

4.4. Voltage range and stability

The voltage range over which a supercapacitor operates is crucial for its electrochemical performance. Exceeding the specified voltage window can lead to undesirable side reactions, which can degrade the carbon electrodes and the electrolyte. The voltage stability of supercapacitors is a critical parameter that defines their operational limits.

Understanding the voltage range and maintaining stability is essential in high-voltage applications, where the risk of heightened electrode and electrolyte degradation exists. Research efforts focus on developing carbon materials and electrolytes that can withstand higher voltages while maintaining long-term stability [3].

4.5. Cycle life and degradation mechanisms

The cycle life of a supercapacitor, referring to the number of charge and discharge cycles it can endure while maintaining performance, is a critical factor. Carbon electrodes can undergo degradation during cycling due to various mechanisms.

These degradation mechanisms can include structural changes, such as the collapse of pore structures and the reduction of surface area, leading to a decrease in the electrode's capacitance.

Additionally, electrolyte decomposition and side reactions can contribute to irreversible capacity loss.

Understanding the underlying degradation mechanisms is crucial for extending the cycle life of supercapacitors. Some endeavours seek to mitigate degradation effects by creating more robust electrode materials and improved electrolytes.

4.6. Operating temperature

The operating temperature of a supercapacitor can significantly affect its electrochemical performance. Temperature impacts both the ionic conductivity of the electrolyte and the kinetics of charge transfer at the electrode-electrolyte interface [31]. High-temperature environments can accelerate degradation mechanisms, reducing the cycle life of the supercapacitor. On the contrary, low-temperature conditions can result in reduced ionic conductivity and slower charge/discharge rates.

Developed supercapacitors are optimized for effective operation over a broad temperature range, providing versatility for diverse applications.

4.7. Current density and rate capability

The current density at which a supercapacitor operates, and its rate capability are critical factors. High current densities are essential for applications that require rapid charge/discharge rates, such as regenerative braking in electric vehicles.

Carbon electrodes with high electrical conductivity are well-suited for high-rate applications, ensuring efficient charge transfer. Enhancing the rate capability of supercapacitors to improve the electrochemical behaviour of carbon materials.

4.8. Interactions between factors

The choice of carbon material is a fundamental factor influencing supercapacitor performance. Different types of carbon, such as activated carbons, carbon blacks, zeolite-template carbons, and graphene meso-sponges, possess varying structural and surface properties. The specific surface area, pore size distribution, and surface functional groups of these carbon materials play a crucial role in determining their electrochemical behaviour [25]. It is essential to recognize that these factors do not operate in isolation. They interact in complex ways, and optimizing one parameter may affect others. For example, enhancing the capacitance of a carbon electrode by increasing its specific surface area may also impact its voltage stability.

Taking a holistic approach that considers the interplay of these factors is crucial to achieving the desired electrochemical performance for specific supercapacitor applications.

Comprehensive understanding and control of these factors are essential for the continued advancement of supercapacitor technology.

5. CONCLUSION

The multifaceted realm of carbon electrodes in supercapacitors is elucidated, highlighting the diverse range of carbon materials utilized and their profound influence on device performance. From activated carbons to graphene meso-sponges, each material offers unique structural properties crucial for optimizing energy storage and delivery. Synthesis techniques like chemical activation and templating enable precise control over carbon electrode structures, underscoring the importance of customization for specific application requirements. Moreover, the interplay of electrochemical factors, including electrolyte composition, voltage stability, cycle life, and operating temperature, necessitates a holistic approach to supercapacitor design and optimization. Continued research and collaboration are imperative for addressing remaining challenges and realizing the full potential of supercapacitors as sustainable and efficient energy storage solutions, thus propelling the transition towards a more sustainable energy future.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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