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CHAPTER 7

General Introduction of Nanocomposites Electrode Material for Supercapacitor Application

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Abstract: Nanocomposite electrode materials are gaining attention towards supercapacitors owing to their high surface area, high performance, superior conductivity, and electrochemical stability. Supercapacitors provide fast charge/discharge rates and extended cycle life but struggle to balance energy and power densities. To overcome these limitations, nanocomposites integrate oxides of transition metal (e.g., MnO_2, NiO) with conductive carbon materials (e.g., graphene, CNTs), leveraging synergistic effects to enhance charge storage. Doping and polymer incorporation further optimize conductivity and structural stability. This paper offers a summary of new progressions in nanocomposite electrode materials for supercapacitors, highlighting various production approaches, structural characterizations, and electrochemical performance evaluations. Special emphasis is placed on the role of nanostructured design, interfacial interactions, and material composition in optimizing electrochemical properties. The development of high-performance nanocomposite electrodes offers a pathway toward next-generation energy storage technologies, bridging the gap between conventional supercapacitors and high-energy-density batteries.

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1. Introduction

Supercapacitors (SCs) are lighter and smaller than traditional capacitors, which have a comparatively great energy density compared to lithium-ion batteries. For their simple structure, wild discharge, and charge rates, as well as commercial and environmental attraction, Supercapacitors are widely used across various fields, including the electronics industry, new energy vehicles, aerospace, defense technology, information technology, and more [1]. Figure 1 presents a schematic illustration of the electrochemical behavior of a typical supercapacitor and battery. Additionally, Figure 1.1 shows the Ragone plots for different types of energy storage systems. Therefore, supercapacitors are recognised as electrochemical capacitors. They have reliably fast charging and high power with an exceptionally long cycle life (>100000 cycles), and they can supplement or even replace batteries in particular applications [2]. Therefore, they have an increasing amount of interest in situations where excellent cycling stability, and quick charging, great power density, are necessary. Supercapacitors are increasingly used in diverse applications, such as heavy-duty vehicles, regenerative braking in electric vehicles, energy load-leveling for renewable sources, and hybrid systems for trucks, buses, and light rail transit.

1.1 Supercapacitors as renewable energy sources

Energy is essential to improving people's quality of life, which ultimately aids in the development of any nation. In both rural and urban areas, energy is essential for the use of new technologies in a numerous area, such as industry, agriculture, and social services. The global energy mandate is expected to nearly double over the next two periods [3, 4]. Therefore, there is a significant impact on our community and commercial development and our general class of life [5].

The convenience of energy sources empowers the modern economy. Remains fuels such as petrol, coal, and oil are conservative energy bases that are rapidly running out. This is being attended by the destruction of animals, the degradation of ecosystems, and habitats, and environmental pollution [6-10]. Therefore, the researchers have adopted justifiable and renewable energy tools then one of the main causes is not using fossil fuels which are not long-term sustainable. As a result, wind, solar, geothermal, and biofuels are being adopted as renewable energy sources. Additionally, extensive research has focused on supercapacitors and rechargeable batteries for electrochemical energy storage devices [11-13].

Since electrical engineers first experimented with supercapacitors in 1957, they have found marketable uses in the aerospace industry, portable transportation, and electronics [14, 15]. Advancements in materials and manufacturing techniques have enabled the integration of supercapacitors into these applications. Several components, including the electrolytes, anodes, separators, binders, and cathodes, have increased performance and decreased manufacturing costs [16-18]. One example of a supercapacitor is the storage of energy and delivery technology that can collect and release energy quickly, providing excessive current in a small amount of interval. Supercapacitors,

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which are also recognized as ultracapacitors, as a type of electrochemical storage device. The current capacity is very large and has a very quick rate of energy loading and delivery. They are used in memory backups in IT systems, electric vehicles, and uninterruptible power supplies (UPS). They also offer high specific power and an almost unlimited cycle life. They also offer superior low-temperature charge and discharge performance, outperforming batteries in harsh climates. The Ragone plot [19-21] (Figure 2) compares numerous storage energy systems in terms of energy density and power. While the graphic offers a comprehensive indication of storage energy performance, it does not address serious factors such as cost, cycle life, and safety. To gain a deeper understanding of a specific energy storage technology, these aspects must be evaluated separately.

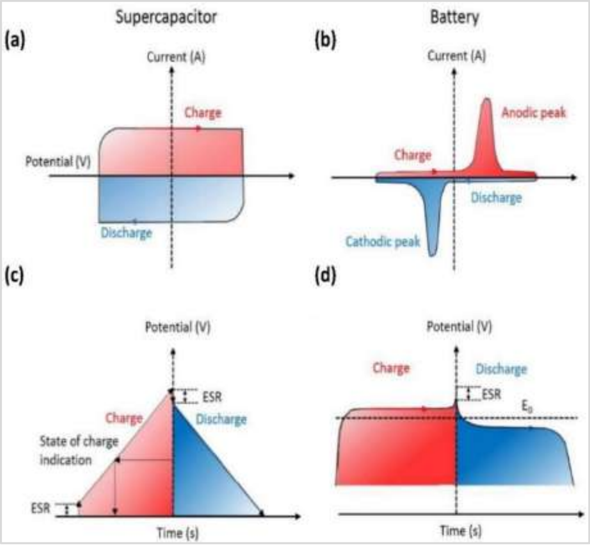

Fig. 1: The electrochemical behavior of supercapacitor (a, to b) typical battery: cyclic voltammograms curvatures and (c and d) galvanostatic charge-discharge curves [22].

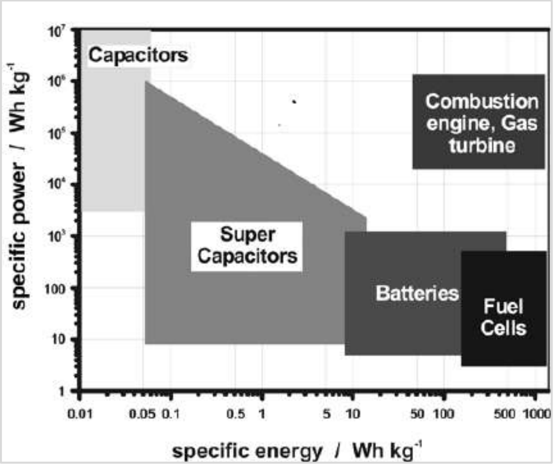

Fig. 2: Various energy storage devices of Ragone plot [23].

The exceptionally long cycling life of supercapacitors is attributed to their charge storage mechanism. Reports indicate that their cycle life exceeds 500,000 cycles, significantly surpassing that of other storage technologies [24-26]. This is so because, in contrast to conventional technologies like batteries, which rely mostly on chemical reactions, on the surface of electrodes supercapacitors store reversible electrostatic charges.

There are two systems in the electrical distribution application. They are for the energy backup power and transportation Batteries, flywheels, supercapacitors, etc. which are used in transportation applications. Examples of energy backup power applications include batteries, flywheels, hybrid energy storage systems, and thermal storage energy systems. However, batteries, supercapacitors, and electrostatic capacitors can also be used to store electrical energy in both small and large-scale applications. The supercapacitors are located in the space between the battery and the traditional capacitor. The power and energy density of the supercapacitor are moderate [27]. As a result, the supercapacitor is filling in the space between batteries and traditional capacitors. In addition, the subsequent sections provide a detailed examination of the various kinds of energy storage systems.

1.2 History and Current Position of Supercapacitors

The General Electric Company initially announced the applied use of double-layer capacitors for electrolytic capacitors in 1957 by expanding porous carbon electrodes. That was the beginning of the history of supercapacitors [28]. At that time the method of charge storage of supercapacitors was unknown this capacitor had an unexpectedly large capacitance, and it was also evident that energy was stored within the carbon pores. The oversupply of flooded batteries, and unworkable design it is essential to submerge both electrodes in an electrolyte vessel, this gadget was never marketed. In 1966, the Standard Oil Company of Ohio (SOHIO) advanced energy storage technology by leveraging the extensive surface area of carbon compounds in tetra-alkyl ammonium electrolytes [29]. However, SOHIO was unable to commercialize their concept, and in 1978, Nippon Electric Company (NEC) sold all the results of supercapacitors to maintain the memory of computers and other consumer goods as backup power under SOHIO's license. In 1975 B. E. Conway developed a novel theory of charge storage processes. It was predicated on disproportionation reactions that occur quickly and reversibly nearby to the electrode material's surface. The first pseudocapacitor, which is often referred to as a supercapacitor, was created using sheets of ruthenium oxide (RuO_2) as the electrode [30, 31]. Currently, highly redox-active RuO_2 and high-surface-area carbon (activated carbon) are both present in capacitors in the market [32]. In the 1980s, a portion of businesses explored the manufacture of electrochemical capacitors. The "gold capacitor" was created by Panasonic (formerly called as Matsushita Electric Industrial Co.) [33].

The electrolyte was the primary distinction between NEC and Panasonic devices, the former utilised a non-aqueous electrolyte, while the latter used an aqueous one. Under the brand name "Dyna capacitor," ELNA started manufacturing double-layer capacitors in 1987 [29]. The first metal-oxide electrode high-power double-layer capacitors were created in 1982 by "PRI Ultracapacitors" [34]. High-performance supercapacitor devices became the primary focus of the supercapacitor research community in 1990. Maxwell Laboratories produce ultracapacitors was initiated in 1992 after the US Department of

Energy (DoE) began investigating the possibility of using these devices in hybrid electric vehicles following the discovery of supercapacitor devices [35]. Up to 1998, the marketing of supercapacitors was represented by four companies, NEC Tokin, Panasonic, Maxwell Technologies, and Elena Capacitors. Furthermore, from 1999 to 2013, in response to global demand, which far exceeded the market growth value, several vendors began supplying supercapacitors. In 2013, 40 businesses were competing in the global market for carbon dielectric supercapacitors (per Paomanok's analytical data, the use of EDLC supercapacitors has increased by 27% globally, while the number of suppliers serving in the market has increased by 1000%) [36].

From Russia, the whole supercapacitor market is dominated by goods, the US, and Japan. Supercapacitor products come with features and advantages specific to each country, such as power, capacity, pricing, and so on. As per the study report by Bosch (2007–2022) regarding the investment potential and current status of China’s supercapacitor market, the global supercapacitor market was valued at $16 × 109 USD in 2015. It is anticipated by analysts that the market will surpass $92.3 × 109 USD by 2020. At the moment, the vast popularity of symmetric supercapacitors on the market uses activated carbon as their electrode material [37-39]. To compete with the current generation of asymmetric nickel-carbon-based supercapacitors, lithium-ion hybrids, IOXUS and Soft-ESMA are currently working to commercialize asymmetric hybrid capacitors [40].

1.3 Recent Trends in Supercapacitor Research

A supercapacitor is surrounded by the newest and greatest promising energy storage gadgets. Therefore, it will become an energy system in the future. The primary characteristic of supercapacitors is significant energy storage capacity, which helps many manufacturers [41]. Supercapacitors are gaining greater popularity worldwide because of ongoing advancements in research. Examples of new developments in developing areas like grid energy storage in railway and car segments. Government regulations on carbon emissions have created a demand for hybrid automobiles, driving market expansion for supercapacitors [42]. Modern consumer electronics, such as smartphones and sensors, have varying power requirements due to their diverse functions. Batteries, however, respond slowly because of the chemical reactions involved. During the past few decades, carbon-based materials utilized in commercial supercapacitors [43]. Because of their low specific capacitance, carbon-based materials are not as useful for commercial applications. According to recent studies, pseudocapacitive transition metal oxides have greater promise as supercapacitor electrode materials due to their affordability, reduced resistance, and eco-friendliness [44]. The supercapacitors were significantly increased by the quick and reversible surface redox reactions of the energy storage capacity of pseudocapacitive materials. Solid-state supercapacitors offer several advantages over aqueous-based capacitors, such as easier handling, enhanced flexibility, and the prevention of electrolyte leakage [45]. Also, the current study has concentrated on employing different ionic liquid electrolytes to enhance supercapacitors. Because these electrolytes are non-toxic and thermally stable they are more advantageous. These ionic liquid electrolytes can raise the voltage range to 4–6 V [46]. In addition to the electrolyte, electrode material, separator, and current collector all affect a supercapacitor's electrochemical performance. A supercapacitor's energy density and specific capacitance can be increased by selecting the right electrode material, which should be inexpensive and non-toxic, along with the appropriate electrolytes [47].

1.4 In-work Standard of Supercapacitor

The electrolyte and dielectric separating media differ between an electrochemical and conventional capacitor, although both have the same charge-storing mechanisms. In conventional capacitors, two plates of metal serve as the device's terminals, and electrical energy stored in the dielectric separator material. Similarly, the electrode-electrolyte contact forms in electrochemical capacitors an electric double layer, which stores energy. The electric double layer, determined by the choice of electrolyte, is separated by a distance on the order of a few angstroms. Figure 3 illustrates a graphic diagram of the energy storage mechanism in an electrochemical capacitor. In electroactive materials, two electrodes coated and spaced apart by the electrolyte make up an electrochemical capacitor.

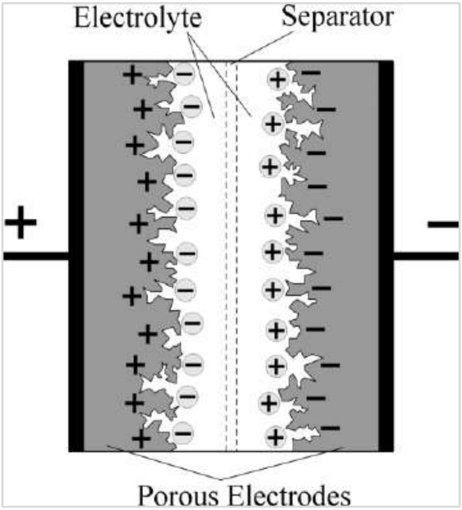

Fig. 3: Schematic diagram of electrochemical capacitor.

The fundamental concept of supercapacitors also referred to as electrochemical capacitors, is comparable to that used by conventional capacitors. These electrodes, which have greater surface areas (A) and an electric double layer and its effective thickness (d), produce higher energy densities and improved capacitance.

1.5 Types of Supercapacitors

The fundamental working principle of a supercapacitor is based on the movement of ions from the electrolyte to the electrode surface for energy storage. As shown in Figure 4, supercapacitors are classified into three types according to their energy storage mechanisms: electrochemical double-layer capacitors, pseudocapacitors, and hybrid supercapacitors.

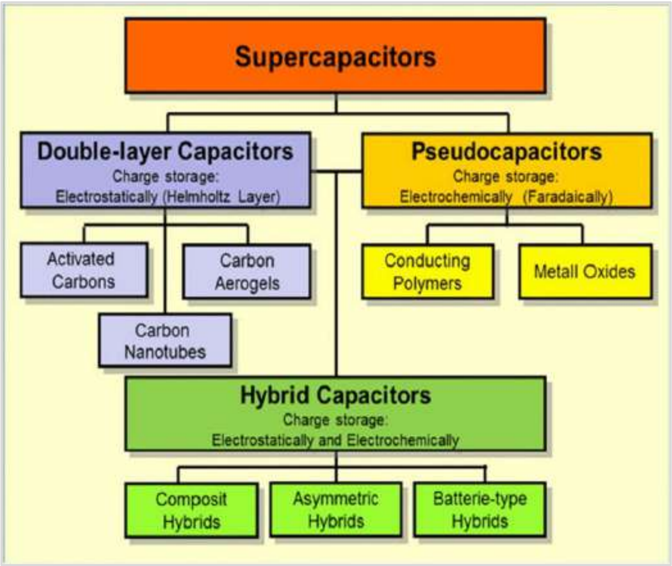

Fig. 4: Classification of supercapacitors

The charge storage mechanism consists of faradic, non-faradic, and a combination of both processes. In the faradic process, charge transfer enhances redox reactions at the electrode-electrolyte interface. Conversely, the non-faradic process involves charge accumulation on the electrode surface through a physical mechanism without forming or breaking chemical bonds. Therefore, no chemical reactions occur. Using a nonfaradic process, carbon-based materials form a Helmholtz double layer, their charges are electrostatically stored in EDLC-based electrodes [48-50]. Pseudocapacitors utilize a faradaic process that profits near the surface and is prevalent in most existing materials to store charges [51]. Pseudocapacitors are typically composed of conducting polymers, sulfides, phosphates, and metal oxides or hydroxides [52-54].

1.5.1 (EDLCs) Electric Double Layer Capacitors

In the construction of electrochemical double-layer capacitors (EDLCs), carbon-based materials are commonly used for electrodes, electrolytes, and separators. EDLCs store charge through two distinct mechanisms: a non-faradic process, where no charge transfer occurs between the electrolyte and the electrode, and an electrostatic process, which enables charge storage [55, 56]. The energy storage mechanism of electric double-layer capacitors (EDLCs) relies on the formation of an electrochemical double layer. When a voltage is applied, ions from the electrolyte migrate through the separator and into the pores of the oppositely charged electrode, driven by electrostatic attraction due to the potential difference. This results in charge accumulation on the electrode surfaces. To prevent recombination, a second layer of charge forms at the electrode interface. This secondary charge layer, combined with a high specific surface area and optimal electrode spacing, enables EDLCs to achieve higher energy density [57, 58].

1.5.2 Pseudocapacitors

EDLCs store charge electrostatically without involving charge transfer between the electrolyte and the electrode. In contrast, pseudocapacitors utilize a faradic process, where a charge is stored through redox reactions at the electrode-electrolyte interface [59]. When a voltage is applied to a pseudocapacitor, a faradic current flows through the supercapacitor cell due to redox reactions occurring at the electrode-electrolyte interface across the double layer. Because of this faradic process, pseudocapacitors achieve higher energy densities and specific capacitance compared to EDLCs. Common materials used in pseudocapacitors include metal oxides and conducting polymers. While these materials are of great interest due to their high capacitance, their faradaic nature, which involves redox reactions similar to those in batteries, results in lower power density and reduced stability during cycling [60-62].

Pseudocapacitors achieve approximately ten times greater capacitance and higher energy density than EDLCs due to the superior charge storage capability of their electrode materials. Several factors influence their performance, including electrode surface area, material conductivity, porosity, and particle size. However, pseudocapacitors typically have a shorter lifespan than EDLCs due to the delamination of active material caused by repeated electrochemical redox reactions. Despite this limitation, their high specific capacitance, enhanced energy density, and fast, reversible redox processes make them highly attractive for energy storage applications [63, 64].

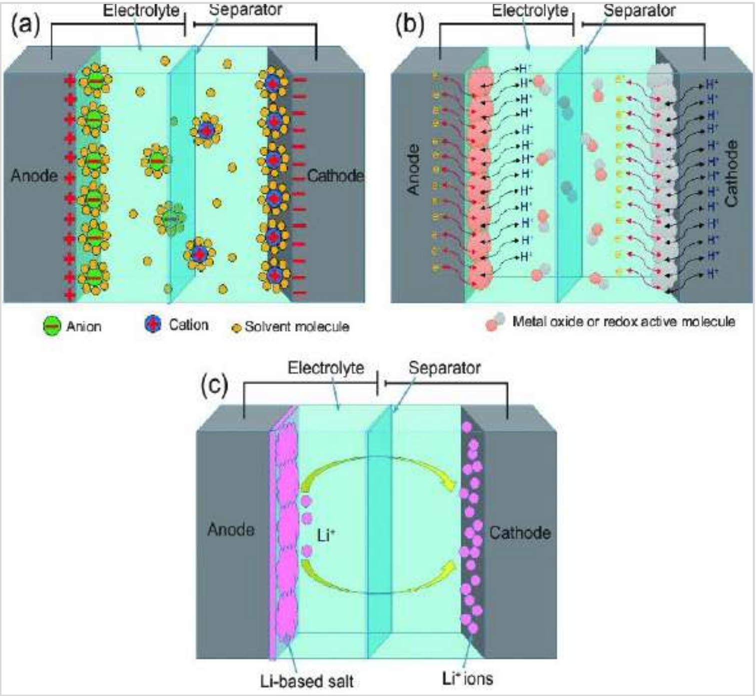

Fig. 5: Diagram illustrating the diverse mechanisms of electrical charge storage: (a) electric double-layer capacitor (EDLC), (b) pseudocapacitor, and (c) hybrid supercapacitor (HSC) [65].

1.5.3 Hybrid Capacitors

Earlier studies suggest that EDLCs offer high power output and excellent cyclic stability, whereas pseudocapacitors provide higher specific capacitance. A hybrid system can be achieved by combining the capacitor-like electrode, which functions as a power source, with the battery-like electrode, which serves as an energy source within a single cell [66, 67]. The primary drawback of hybrid devices compared to electric double-layer capacitors (EDLCs) is that faradaic electrodes, while increasing energy density, often compromise cyclic stability. Therefore, it is crucial to prevent the transformation of a high-performance supercapacitor into a conventional battery [68]. Therefore, studies have concentrated on the three distinct kinds of hybrid supercapacitors, asymmetric, composite, and battery-type, and they are identified by their electrode topologies.

1.5.3 A. Composite

Composite electrodes integrate conducting polymers or metal oxides with carbon-based materials to create a single electrode capable of storing charge through both physical and chemical mechanisms. The carbon-based materials contribute to charge storage by forming a capacitive double layer and providing a large specific surface area, which improves contact between the pseudocapacitive material and the electrolyte. Meanwhile, the pseudocapacitive component enhances overall capacitance through Faradaic redox reactions [69]. Currently, composite electrodes are categorized into two types: binary and ternary. Binary composites are made from two different electrode materials, while ternary composites incorporate three distinct materials into a single electrode. These composite electrodes can include conducting polymers, such as polypyrrole, and carbon nanotubes. Studies have shown that composite electrodes can achieve superior capacitance compared to electrodes made from pure carbon nanotubes or pure polypyrrole, as demonstrated in several investigations [70-72]. The uniform coating of polypyrrole and the three-dimensional charge distribution are attributed to the accessibility provided by the entangled mat structure. It has been confirmed that the mechanical stress caused by ion insertion and removal in the deposited polypyrrole affects the structural integrity of the entangled mat. Additionally, these composites have shown cycling stability similar to that of EDLCs, which contrasts with the stability of pure conducting polymers [73, 74].

1.5.3 B. Asymmetric

EDLC with a pseudocapacitor electrode couples asymmetric hybrids to integrate non-faradic and faradic processes. They are arranged in such a way that the conducting polymer or metal oxide serves as the positive electrode while the carbon substance serves as the negative electrode [69]. Conducting polymer electrodes gives lower resistances and lower maximum voltages than activated carbon electrodes, on the other hand, they also take greater capacitances and less cycling stability. Therefore, coupling these two electrodes, an asymmetric hybrid whose capacitors lessen the magnitude of this trade-off and suppress similar EDLCs in terms of energy and power densities. As well as, its cycling stability is superior to that of similar pseudocapacitors [75-77].

1.5.3 C. Battery Type

In a battery-type hybrid, two distinct electrodes are combined, resembling asymmetric hybrids; however, one electrode consists of a battery while the other is a supercapacitor. This configuration aims to merge the rewards of together batteries and supercapacitors within a single cell [69]. Battery-type hybrids connect two distinct electrodes, similar to asymmetric hybrids, but with the key difference that they pair a supercapacitor electrode with a battery electrode. This unique configuration combines the energy characteristics of batteries with the power, cycle life, and recharge capabilities of supercapacitors, addressing the need for higher-energy supercapacitors and higher-power batteries. Common research has focused on using activated carbon for the other electrode, with materials like nickel hydroxide, lead dioxide, and LTO ($Li_4 Ti_5 O_{12}$) as the primary battery electrode materials [78-82]. Battery-type hybrids have less experimental data associated with extra forms of supercapacitors, but they have the potential to bond the break between supercapacitors and batteries. Despite promising results, experts agree that further research is needed to fully explore the capabilities of battery-type hybrids [83, 84].

1.6 Electrode Materials

The choice and fabrication of materials of electrode are essential for improving the capacitive performance of supercapacitors. To ensure effective performance, supercapacitor electrodes should demonstrate corrosion resistance, chemical stability, thermal stability, a high surface area, high electrical conductivity, and suitable surface wettability, all while being economical and naturally friendly [85, 86], the ability of electrode materials to transfer faradic charge is essential for improving capacitance performance. Capacitance and charge storage characteristics are heavily subjective by the nature of electrode materials employed in supercapacitors [87, 88, 89]. Manipulating the morphology of electrodes, including, pore shape, pore diameters, and pore size distributions and their accessibility to the electrolyte, significantly impacts specific capacitance [89-91]. Therefore, choosing electrode materials with great surface area and fine-tuning pore size and shape, such as circles, vertical rectangles, horizontal rectangles, squares, cylindrical, spherical, and slit structures, is essential for designing effective supercapacitor devices [92]. The transit of electrolyte ions through the electrode material, enhances electrochemically active sites and overall device performance [89].

1.7 Perspective and concluding remarks

Energy storage is just as important as energy production. Our current culture needs flexible, inexpensive, lightweight, and naturally approachable energy storage systems to address global challenges. Supercapacitors and batteries are the primary energy storage devices. However, short life cycles, the slow charge-discharge rate, and high weight of batteries limit their applications in portable and wearable devices.

Current supercapacitor research sheds light on advanced vitality storage devices crucial for applications in portable electronics, hybrid electric vehicles, laptops, power backups, and more. As a result, supercapacitors are increasingly viewed as a widespread alternative to conventional batteries.

They provide several benefits, such as increased energy and power densities, longer lifespans, and quicker charge-discharge rates. Furthermore, a rapid response is crucial for supercapacitors to deliver pulse power, which requires a reduction in equivalent series resistance (ESR). Consequently, the design and development of active electrode materials that meet these requirements have become a primary focus for many electrochemists. The recent development of various electrode materials, along with investigations into supercapacitor operation and charge storage mechanisms, have opened up new possibilities for utilizing advanced electrode materials in asymmetric flexible hybrid supercapacitors (ASFHSCs). The configuration of a hybrid-asymmetric supercapacitor offers the advantage of a broad operating potential window, stemming from the unique potential range of both cathodes and anodes.

Much of the recent research has concentrated on synthesizing various morphologies of nanostructured materials for supercapacitor applications. The morphology of these nanostructured materials can be easily adjusted by incorporating organic surfactants. Current studies have demonstrated that using organic extracts or surfactants in aqueous solutions can effectively tune the product's shape. As such, supercapacitors could become a realistic and widely available power solution for an expanding range of applications. It is anticipated that continued research and development will further drive advancements in this field and serve as a foundation for future applications.

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