Research Status and Application of Supercapacitors

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Abstract. Research and development of new green and sustainable energy storage technologies is urgent due to the severity of the energy crisis and environmental pollution, as well as the need for sustainable development. Supercapacitors are a new type of energy storage device that has a higher power density and a longer service life than other energy storage devices. Thanks to its superior characteristics with extended use and quick rate of charge and discharge, it has attracted widespread attention from researchers. This paper reviews the structure, classification, and working principle of supercapacitors. Besides, utilizing electrode materials is summarized in this article, such as materials with a carbon basis and conductive polymers in supercapacitors, and expounds the application status of supercapacitors in industries, power, transportation, and daily life. In addition, this paper also analyzes the shortcomings and challenges faced by current supercapacitors, and finally summarizes the new potential application fields (such as hydrogel electrolyte and flexible capacitor) and research directions of supercapacitors.

Keywords: Supercapacitor, Electrode Materials, Application.

1. Introduction

In the 21st century, energy storage is one of the greatest challenges for humanity. Developing low-cost, low-carbon and environmentally friendly energy conversion and storage systems is essential to satisfy modern society's environmental demands and address the increasingly prominent ecological issues. Fossil fuels are gradually being replaced by clean energy sources like geothermal, solar, wind, and tidal energy. The shortcomings of new energy sources such as randomness and unsustainability seriously hinder their widespread application. Therefore, developing efficient and stable devices for storing energy are crucial for fostering energy conversion and utilization.

Among them, lithium-ion batteries have become the most successful commercial secondary batteries because of their benefits, which include minimal self-discharge, high working voltage, and high energy density. However, the shortage of lithium sources and the increase in mining costs have limited their application. Supercapacitors' exceptional cycling stability, high power density, and rapid charging and discharging have made them one of the most promising electrochemical devices, as well as no harsh environmental temperature requirements, and green environmental protection.

Supercapacitors are a novel class of environmentally friendly energy storage technology that performs in a range between secondary batteries and conventional capacitors. Despite their rich benefits, their low energy density limits the application domains they can be used in. Due to the performance of the electrodes is significantly influenced by the type of electrode used. Therefore, supercapacitor electrode material research has garnered a lot of interest.

At present, in addition to electric energy storage, new energy vehicle power supply, public transportation, uninterruptible power supply, aerospace and other fields, Supercapacitors have drawn a lot of interest from the wearable and portable electronics industries as well. The performance requirements for supercapacitors vary in different application scenarios. Higher energy density supercapacitors are needed in the energy storage area in order to attain lower volumes; Supercapacitors must be able to deliver high power, high current instantaneous discharge, and rapid charging and discharging in the region of energy supply; Applied to wearable devices, supercapacitors in the field of sub equipment should have a certain degree of flexibility. For example, those supercapacitors based on smart fabrics have long-term durability and waterproof properties [1]. Thus, deep and comprehensive research on the electrode materials used in supercapacitors is crucial to enhancing their performance, which supports the creation and application of new energy sources and aids in the purposeful implementation of national carbon neutrality.

This article elucidates the structure of supercapacitors, provides a detailed introduction to the electrode materials of supercapacitors such as carbon-based compoundsls and metal oxides, and polymer electrolytes, and elaborates on the limitations of supercapacitors. Emphasis is placed on introducing the applications and effects of supercapacitors in different fields, in order to achieve resource utilization and performance optimization in applications. Finally, the future research directions of supercapacitors are summarized and prospected.

2. Energy Storage Principle of Supercapacitors

Supercapacitors—electric double-layer capacitors, hybrid supercapacitors, and pseudo capacitors—fall into three groups when it comes to the energy storage principle. Their fundamental distinction from one another is based on various energy storage principles. In Figure 1, various materials' energy storage concepts are compared.

2.1. Electrical Double-Layer Capacitor

The basic idea behind electrical double-layer capacitor energy storage is the electrostatic effect, which stores energy by adsorbing and desorbing ions in the electrolyte on the surface of the electrode materials. During charging, under the influence of an external electric field, the positive and negative ions in the electrolyte migrate toward the positive and negative electrodes, respectively, forming a double layer at the interface between the electrolyte and the electrode and producing an electric field. During the discharge process, the positive and negative electrodes' voltage differential steadily drops, causing double layer charge to detach and ions to return to the electrolyte. At the same time, the electrons generated during the discharge process flow to the external circuit to form a current (see Figure 1 (a)).

2.2. Pseudo Capacitor

Pseudo capacitors, as opposed to Electrical Double-Layer Capacitors (EDLCs), store energy on or near the surface of the electrode material via reversible Faraday processes. The energy storage idea is illustrated in Figure 1(b). As the electrolyte's ions move to the electrode/electrolyte contact and undergo electrochemical reactions brought on by the action of an external electric field, deeper active material phases penetrate the electrolyte ions during the charging process. The discharge process completes the conversion of stored energy during charging when ions return to the electrolyte from the active material phase and charges are discharged as current through the external circuit. The electrolyte ions participate in oxidation-reduction reactions with the surrounding atoms and electrons, producing charges that are then stored in the electrode.

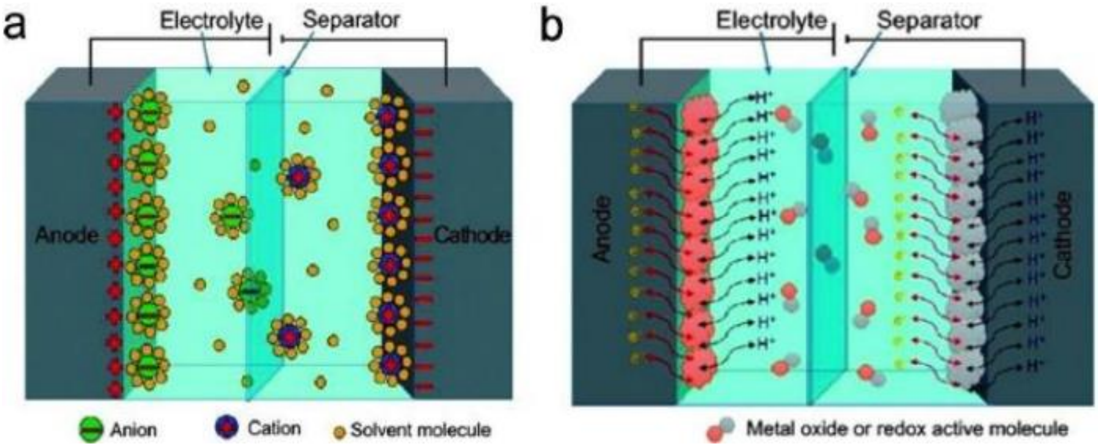

Fig. 1 (a) Diagrammatic representation of the energy storage system for both (a) double-layer and (b) pseudo capacitors [2]

2.3. Hybrid Supercapacitor

Hybrid supercapacitors are a novel kind of asymmetric energy storage technology with outstanding all-around performance. Usually, they are a hybrid system made up of electrodes in two layers and electrodes in the form of pseudo capacitors. The quick charging and discharging times of double layer capacitors and the high specific capacitance of pseudo capacitors are both exhibited by hybrid supercapacitors. Working potential window is wider, and the overall environmental adaptability of the device is stronger, which can meet people's demand for high-performance capacitors.

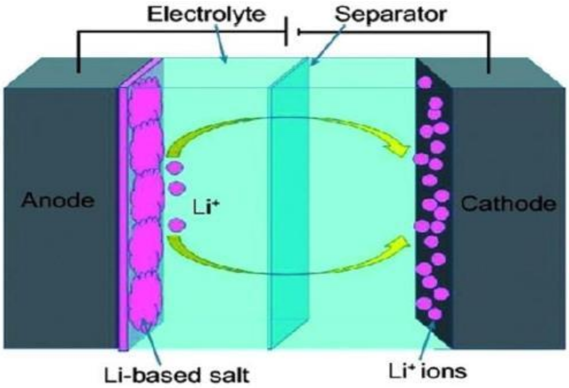

Fig. 2 Energy storage mechanism schematic diagram of hybrid capacitors [2]

3. Materials for Supercapacitor Electrodes

3.1. Carbon-Based Material

A new avenue for the study of carbon materials for supercapacitors has been made possible in recent years by the advancement of nanotechnology. Carbon materials have garnered significant interest as electrode or substrate materials for supercapacitors because of their many benefits, including their low cost, excellent conductivity, huge specific surface area, and good chemical stability. Carbon-based substances can be pre-treated to increase their specific surface area and high pore accessibility, which will improve their conductivity and stability during cycling, thus exhibiting large and stable double-layer capacitors. Moreover, the vast majority of biomass materials themselves have natural porous or layered structures that can promote ion diffusion [3].

Ma et al. from Qilu University of Technology prepared porous carbon microspheres (PPCM) using Phoenix Tree Leaves (PTLs) as raw materials and decorated them with tiny gold nanoparticles, resulting in the synthesis of three-dimensional honeycomb shaped gold nanoions modified porous carbon microspheres (Au PPCM) [4]. The Au PPCM electrode demonstrates good stability and an exceptional specific capacitance of up to 440 F/g at a current density of 0.5 A/g.

Using maize straw as the raw material, Yu Xinghai et al. from the Basic Research Institute of Flexible Composite Materials Application at Hexi University created three-dimensional graded porous carbon materials [5]. The raw material was heated to a high temperature and then activated under N2 protection. Sulfuric acid/PVA is utilized as the electrolyte when utilized as an electrode material to create a flexible, all-solid-state supercapacitor. The specific capacity is 125 F/g with a current density of 1 A/g. In bending tests, flexible supercapacitors also exhibit good mechanical flexibility and electrochemical stability.

Ghosh et al. from Verol University of Technology in India synthesized four different types of hard carbon using biomass as raw materials [6]. Supercapacitor electrodes for studies were made of KOH-activated banana stem derived carbon (KHC), phosphoric acid-treated banana stem derived carbon (PHC), corn cob derived carbon (CHC), and potato starch derived carbon (SHC). According to the findings, 479 was the capacitance value of KOH activated carbon made from banana stems. Under the same 81 F circumstances, the hard carbon produced from corn cob similarly yielded a maximum capacitance value of 309 at 23 F/g.

3.2. Metal Oxide

Since transition metal oxides have a high energy density, they have been extensively explored. Common transition metal oxides include NiO, Co_3O_4, etc. However, due to insufficient intrinsic conductivity, their internal resistance is relatively high, and their actual specific capacitance is much lower than expected.

Zhang et al. in-situ grew ultra-thin $NiCo_2O_4$ nanosheet arrays on the surface of foam nickel. By using this technique, adhesives can be used less frequently, which lowers the materials' internal resistance. Simultaneously, the resulting ultra-thin nanosheet structure can offer $NiCo_2O_4$ a rich electron transport channel and a large specific surface area. At a current density of 1 A/g, the mass specific capacitance of $NiCo_2O_4$ is 2017.8 F/g, and at a current density of 30 A/g, its rate performance can reach 93.2%. After 5000 cycles, it can still hold onto its initial capacity at 90.9%.

4. Polymer Electrolytes

Polymer electrolytes are a type of electrolyte based on polymers that can undergo ion migration. Polymer electrolytes can not only act as separators, but also provide transportable ions like liquid electrolytes, greatly reducing the amount of liquid electrolytes used [7].

Li et al. of Tongji University prepared a kind of poly composite gel crosslinked by synthetic graphene clay and graphene oxide (GO) through in-situ copolymerization [8]. Under infrared light treatment, the ion conductivity is equivalent to that of traditional polyvinyl alcohol (PVA) electrolytes, and the ductility and self-healing properties are the same. Using this new nano composite hydrogel as electrolyte, the all solid state supercapacitor not only shows good flexibility and ductility (up to 1000%), but also has self-healing properties.

Cevik et al. from Imam Abdulrahman University used new redox polymer electrolytes, including PAMPS (Pathogen-associated molecular pattern) and ammonium molybdate, to construct flexible supercapacitors [9]. Polymer electrolytes of different compositions, PAMPS/Mox (x as a mass fraction), were prepared. Using PAMPS/Mo3 as the electrolyte and activated carbon (AC) as the electrode, the system's maximum specific capacitance of 530 F/g was 30% more than that of molybdenum-free supercapacitors. This gadget has a power density of 580 W/kg and an energy density of 73 Wh/kg. After 2500 cycles of charging and discharging, the capacitance retention rate of this flexible supercapacitor is approximately 92%.

Chen et al. not only used polymers in electrolytes, but also prepared a hierarchical honeycomb like hydrogel electrode by doping polypyrrole nanoparticles in the GCP [gold nanoparticles/CNT/polyacrylamide (PAM)] framework [10]. In electrochemical testing, the elongation rate of the electrode can reach 2.380%, and the self-healing rate is 94%. The area capacitance of this supercapacitor is 885 mF/cm2. The energy density is 123 Wh/kg. The capacitance retention rate of the device remains stable at 89 About 5%.

By using in-situ oxidative polymerization of aniline monomers, Hu et al. from Xiangtan University successfully constructed the NiCoFeO particle surface covered in a conductive coating of polyaniline (PANI) and utilized the NiCoFeO/PANI composite material as an electrode for supercapacitors [11]. According to the findings, the composite material's capacitance loss was 29.54 percent following 5000 cycles of charge and discharge. Furthermore, the NiCoFeO/PANI composite material supercapacitor exhibits a specific capacitance of 843 F/g and a current density of 2 A/g, whereas NiCoFeO only shows 478 F/g.

5. Application of Supercapacitors

5.1. Transportation

Supercapacitors are a viable power source for hybrid automobiles in the new energy passenger vehicle market. Supercapacitors conserve fuel and enable rapid acceleration of the vehicle. Supercapacitors are not only used in passenger cars, but also widely used in neutral tractors, forklifts, and excavators. The application of supercapacitors in rail transit and urban buses is an important application scenario in the transportation field. The driving routes and stopping points of urban buses are fixed, and they will frequently start and stop during the driving process. The frequent braking of traditional fuel vehicles will cause energy waste, not only reducing the overall economy of the vehicle, but also generating more harmful gases. The use of supercapacitor modules in the energy storage and power system of buses can solve these problems. Heavy urban transportation vehicles such as subways, trains, and trams have high requirements for rapid energy release and recovery. Supercapacitors have natural fast charging and discharging characteristics, making them very suitable for rail transit. At present, supercapacitor energy storage trams have been operating in cities such as Zhuhai, Shenzhen, Dongguan, Wuhan, and Guangzhou.

In recent years, the number of private and public transportation electric vehicles has significantly increased around the world, resulting in a high power demand for the power grid, which requires fast and ultra fast charging performance. Supercapacitors, due to their own characteristics, can be applied to fast charging infrastructure and then act on energy storage systems on electric buses.

5.2. Aviation sector

High tech equipment and instruments have been continuously developed and applied with the modernization of aviation, but the equipment or instruments used often operate in more demanding working environments, resulting in higher requirements for energy storage power sources, such as wider working temperatures, longer service life, and higher working power. Supercapacitors have instantaneous high current discharge characteristics and can provide instantaneous high power for certain portable electronic devices. Additionally, this gadget is incredibly lightweight and appropriate for use on flights.

5.3. Daily Life

At present, supercapacitors have been applied in various aspects of daily life, such as supercapacitors with integrated lighting and storage, supercapacitors based on intelligent fabrics, with long-term durability and waterproof performance. In addition, they are also widely used in power failure warning, real-time counters, and so on. In terms of communication applications, supercapacitors have certain feasibility as energy storage devices in wireless communication portable devices, chips, and other high-power pulse application scenarios.

6. Limitations of Supercapacitors

6.1. Cyclic stability Issues

Many factors affect the cyclic stability of supercapacitors. First off, distinct energy storage processes are directly determined by the type of electrode material. For instance, conductive polymers and metal compounds with battery or pseudo capacitance behavior show poor cycle stability, whereas carbon materials with EDLC activity show great cycling stability. Second, the performance and composition of the electrode materials also help to increase the supercapacitors' cycle stability. The development of sophisticated electrode materials can enhance the cycle stability of supercapacitors. Thirdly, high attention should be paid to the experimental parameters of cyclic stability testing, and other performance indicators should be considered, including mass load, current density, potential window, test temperature, scanning rate, electrolyte composition, etc.

6.2. Self Discharge Problem

The self discharge rate refers to the rate at which an electrochemical battery loses energy due to unnecessary chemical activity within the battery, which depends on the chemical properties and temperature of the cell. As a typical surface reaction energy storage mechanism, supercapacitors face serious self discharge problems, which also limit their practical applications in various fields. Smith et al. compared commercial supercapacitors (2000F), lithium-ion capacitors (2200F), and lithium-ion batteries (2.4 Ah). The self discharge behavior of the three in the charged state. Within a 72 hour open circuit storage time, the energy loss of supercapacitors is as high as 22%, far higher than the energy loss of only 3% in lithium-ion batteries.

6.3. Energy Density Issues

One of the important reasons for the low energy density of supercapacitors is the low rated voltage (<2.7 V). The main and most difficult problem in the field of supercapacitors is still how to increase their energy density because there is currently a discrepancy between their energy density and the real needs of batteries. Table 1 illustrates the disparity in energy density between batteries and supercapacitors.

Table 1. Energy density performance comparison of supercapacitors, power lithium batteries, and lithium titanate batteries [12]

	Supercapacitor	Power type lithium batteries	Low temperature power lithium battery	Lithium titanate battery
energy density(Wh/kg)	6	130~150	110	80~90

7. Conclusion

Supercapacitors, a novel kind of environmentally friendly and effective energy storage technology that blends conventional batteries with dielectric capacitors, are currently intimately associated with the growth of the new energy sector and have demonstrated immense promise across a wide range of sectors and domains. It is now certain that in the future, new energy sources will take the place of conventional energy sources in order to supply energy. This new breed of apparatus has good temperature characteristics, lengthy service life and quick charging, green environmental protection, and energy conservation, and has received widespread attention from countries around the world. China has been implementing pertinent policies to encourage the growth of the supercapacitor industry in recent years. In the future, supercapacitors will become an inevitable trend to replace traditional batteries for power generation and energy storage. However, supercapacitors still have problems such as poor cycling stability, low energy density, and severe self discharge, which have led to them being shrouded in the shadow and influence of batteries (mainly nickel hydrogen batteries and lithium batteries), and their practical applications are still in the early stages.

Despite a series of problems, supercapacitors have unparalleled advantages such as extended service life and excellent charging and discharging effectiveness, both of which will undoubtedly offer enormous future development possibilities.

It can be foreseen that in the next decade, supercapacitors will have huge application prospects in various fields such as new energy vehicles, electric energy storage, smart grids, wind power generation, solar energy, rail transit, military equipment, etc. In the future, supercapacitors will replace traditional battery power generation and energy storage as an inevitable trend.

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