Supercapacitor Materials and Applications Review

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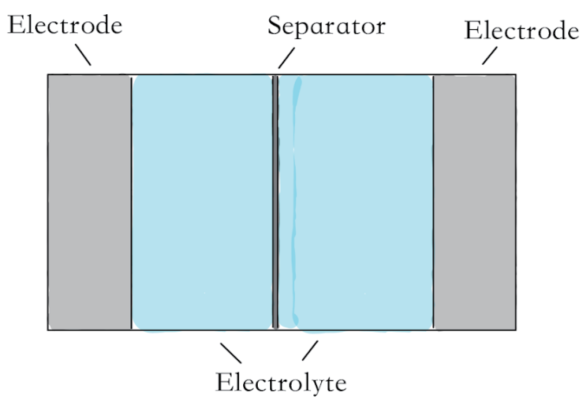
Abstract: Supercapacitor is becoming a promising new energy storage device with multiple advantages, such as high power density, fast charge-discharge rate, long lifespan, and good cyclability. There are three types of supercapacitor: electric double layer capacitor (EDLC), electrochemical pseudocapacitor, and a hybrid of EDLC and pseudocapacitor. The electrode is a key component that plays an important role in determining the performance of the supercapacitor. This review has discussed five popular electrode materials: carbon-based materials, manganese-oxide (MnOx) material, nickel disulfide (NiS2) hollow nanoprisms material, cellulose nanocrystal (CNC) aerogels material, and cobalt oxide (Co3O4) nanotube material. Also, three main applications of the supercapacitor have also been discussed: renewable energy generation, mobile devices, and electric vehicles. Although the limitations of the current materials are preventing the supercapacitor from achieving a comparable energy density to the battery, the advancing of the material technology will allow it to have a higher capacitance in the future. With higher capacitance, the application of the supercapacitor could be even broadened as well.

Keywords: supercapacitor, material, application, energy storage, energy systems

1. Introduction

Supercapacitor, also known as ultracapacitor, is a new type of capacitor. In short, the supercapacitor features high power density, fast charge-discharge rate, long lifespan, and good cyclability. There are three types of supercapacitor: one is electric double layer capacitor (EDLC), which stores electric energy physically through electrostatic attraction; the second is electrochemical pseudocapacitor, which stores electric energy electrochemically through redox reactions; the last one is the hybrid capacitor that combines both EDLC and pseudocapacitor. The electrostatic attraction allows EDLC to have super fast charge-discharge rate and very good cyclability, while the electrochemical storage gives pseudocapacitor significant high energy density. Currently, there are also another two common energy storage devices: capacitor and battery. The supercapacitor is superior to a capacitor in that the supercapacitor usually has 10-100 times more capacitance than a common capacitor. Normally, a capacitor consists of two conductive metal plates, usually made with aluminum, separated by dielectric insulating materials, such as ceramic. Differing from the capacitor, a supercapacitor's electrode is usually made from carbon-based materials instead of metals. This material features a larger surface area, allowing the supercapacitor to store more electrons than a common capacitor. In addition, the distance between electrodes in a supercapacitor is also shorter than that in a capacitor. According to the formulation of capacitance, $C = \varepsilon A/d$ (C is capacitance in farads; ε is permittivity of dielectric material; A is area of plate overlap in square meters; d is distance between plates in meters), the supercapacitor has a higher capacitance than a common capacitor. In comparison to a battery, the supercapacitor features a higher power density. Since the supercapacitor stores electric energy physically, it is able to withstand higher voltage than a battery. According to the formula of power, $P = IV$ (I is current; V is voltage), the increase in voltage made its power output higher than that of the battery. As the charges are deposited by electrostatic attraction, the supercapacitor has a rapid charge-discharge rate. It is known that there is a conversion between chemical and electrical energy in a battery. As time passes, the chemical in the battery will gradually degrade, resulting in reduced lifespan and storage capacity. Since there is no chemical and electrical energy conversion, the supercapacitor thus has a longer lifespan and better cyclability than a battery. Nowadays, vehicle is an essential part of our life. The internal combustion engine (ICE), which was invented by Nicolaus Otto in 1876, has long been playing an important role in functioning our vehicles. Meanwhile, it also brings severe pollution to our environment. Since supercapacitor could be a clean, efficient energy source for driving vehicles, it would be a promising alternative to ICE in the future. This review outlines the recent advancements on the electrode material of the supercapacitor, which is the essential component. The application of supercapacitors in vehicles has also been discussed in detail. In addition, some other potential applications of supercapacitor will be explored simultaneously.

2. Materials



Different from an ordinary capacitor, the supercapacitor usually structures in the following way: two electrodes coated with porous material, such as activated-carbon, positioning on each side; a separator, typically made with graphene, placing in the middle; and electrolyte filling in the space between the electrodes and the separator. Among the different parts, the electrode is responsible for storing the electron, which is directly determining a supercapacitor's capacitance. Apparently, the supercapacitor's performance depends heavily on its electrode. Therefore, to select the electrode materials is crucial in improving the supercapacitor. The following part will discuss five recently developed popular electrode materials for the supercapacitor.

2.1 Carbon-Based Materials

According to the article of Bose et al. [1], Carbon-based materials, such as graphene, can provide large surface area to increase the rate of ion diffusion and improve the cyclability of supercapacitors. Indeed, graphene-based hydrogel is a high-performance material for making supercapacitor electrodes. However, using a large ratio of graphene sheets can affect the kinetic of electrode processing. To solve this problem, researchers have tried to mix it with nickel hydroxide to create a hybrid-material electrode [2]. Besides the improvement in performance, using carbon-based materials could also reduce the cost and simplify the process in manufacturing the supercapacitors. In addition to the nickel-hydroxide graphene hybrid material, Liu *et al*. [3] introduced another hybrid electrode material: carboxyl-functionalized graphene oxide–polyaniline (CFGO–PANI). With charge-discharge configuration, this hybrid material shows excellent electrochemical capacitance performance with aqueous H2SO4 electrolytes. Moreover, Carbon fabrics that are activated by mixing with KOH could also be used as electrode material in supercapacitors. The capacitance is determined by activated carbon fibers' porous texture, elemental composition, and surface functionality. Normally, the KOH activated carbon fabrics have the capacitance range from 270 to 340 F/g, depending on the medium used [4].

2.2 Manganese-Oxide (MnOx) Material

Manganese-Oxide (MnOx) is an inorganic, naturally born material. It is a very popular material for energy storage because theoretically it could achieve high capacitance and be extremely redox-active. In fact, MnOx has a very low electrical conductivity in its raw state. Therefore, it is necessary to engineer the raw MnOx into suitable supercapacitor electrode material. While it's quite challenging to achieve the goal, the researchers have proposed many solutions to overcome this challenge. Among those solutions, to grow nanosized MnOx nanosheets to a thickness of 2-4 nm could allow the MnOx to have a significant amount of redox-active sites, high electrical conductivity, and high capacitance. The improvement on electrochemical performance of MnOx made it become an appealing supercapacitor electrode material, specifically for pseudocapacitors. Indeed, the cyclic voltammetric characterization indicates that the supercapacitor electrodes made by MnOx have higher electrical conductivity than those made by other materials. Experiments also show that this new material has a very fast charge–discharge rate [5].

2.3 Nickel disulfide (NiS2) hollow nanoprisms Material

With ample amounts of valence states and redox sites, high conductivity and high capacitance, transition metal sulfides (TMSs) are promising electrode materials for supercapacitors. Nickel disulfide (NiS2) is one of the TMSs. Compared to other TMS, NiS2 has been attracting more attention in recent years because of its facile production process, which makes the mass production of supercapacitors become cost-efficient. Researchers are constantly dedicating themselves to finding the best way to utilize NiS2 as an electrode material. For example, Pang *et al*. [6] synthesized the NiS2 nanocubes through a microwave-assisted method, displaying a high capacitance as 695 F/g. However, due to its structural advantage, to make the NiS2 into shape-tailorable hollow nanoprisms is a better option. This derivation of NiS2 could be easily produced from low-cost nickel complex templates. With the unique structure, this new supercapacitor material features high capacitance and amazing cycling stability (i.e., after 10000 charge-discharge cycles, its capacitance still retains 1680 F/g) [7]. Because of higher surface area, the NiS2 supercapacitor exceeds the carbon based double-layer supercapacitor on capacitance under equivalent weight.

2.4 Cellulose Nanocrystal (CNC) Aerogels Material

Chemically cross-linked cellulose nanocrystal aerogel (CNC aerogel) is another promising material for supercapacitor electrodes. It possesses ultra-lightweight (i.e., 5.6 mg/m^3) and high porosity (e.g., as high as 99.6%) [8]. As a result, it is able to store a large amount of electrons, significantly increasing the supercapacitor's capacitance. Moreover, compared to the most commonly used aerogel (silica aerogel), CNC aerogel is less fragile, so it is a more stable material for making supercapacitor electrodes. The fact that it is chemically cross-linked also indicates its high stability. However, CNC aerogel is not easy to produce. Similar to other aerogels, it retains water from the formation process with solutions. Due to their porous nature, it is very difficult for scientists to fully dry out water inside these pores. In fact, if the drying method is improper, the porous structure inside the aerogel will collapse. As a result, the aerogel will transform into xerogel, a much less useful material. Currently, most of the CNC aerogel is produced by critical point drying or freeze-drying techniques, which effectively clear out the water and prevent its porous structure from collapsing [9]. Furthermore, to incorporate polypyrrole nanofibers, polypyrrole-coated carbon nanotubes, and manganese dioxide nanoparticles will further increase the CNC aerogels' performance. The incorporation of these nanoparticles could bring CNC aerogel better conductivity, higher capacitance, and faster charge-discharge rates, allowing it to become a very suitable material for making supercapacitor electrodes [10].

2.5 Cobalt Oxide (Co_3O_4) nanotube Material

Cobalt oxide (Co_3O_4) is a low-cost, safe material with comparable electrochemical performance in energy storage to other expensive and harmful materials, such as RuO_2. However, in order to become a supercapacitor electrode, modifications to Co_3O_4 are essential. Indeed, researchers have tried different methods to best utilize the Co_3O_4 as electrode material throughout the time. Wang *et al*. [11] has introduced the Mesoporous Co_3O_4 microspheres, which have a considerable capacitance of 102 F/g. Xie et al. [12] layered Co_3O_4 through the hydrothermal method, displaying a high capacitance of 263 F/g. With its intrinsic structural advantage, the Co_3O_4 nanotube often has more surface area than the Co_3O_4 microsphere and the layered Co_3O_4. Xu *et al.* [13] presented a way to prepare the Co_3O_4 nanotubes: anodic aluminum oxide (AAO) template. Traditionally, nanotubes are often produced by a method called chemical vapor deposition. One example produced with this method is the carbon nanotubes. Though, to deliver the best material performance, the production of Co_3O_4 nanotubes requires more precise control of their diameter, length, wall thickness, and electronic structure. The AAO template has been proven to be a facile and cost-efficient method to meet the above precision requirements [14]. Co_3O_4 nanotube is a highly conductive material. Because each cobalt atom in Co_3O_4 nanotubes is only bonded to 3 other cobalt atoms, there would be a free valence electron available for electrical conduction, making it an efficient conductor. With the cyclic voltammetry, galvanostatic charge–discharge studies and electrochemical impedance spectroscopy, the Co_3O_4 nanotube displays strong electrochemical capacitance (574 F/g). Moreover, it can retain 95% of energy after 1000 continuous charge–discharge cycles. Thus, the Co_3O_4 nanotube is a promising supercapacitor material.

Clearly, it is crucial to improve the performance of the supercapacitor by utilizing a prominent material for the electrode. Currently, among the materials mentioned above, Nickel disulfide (NiS_2) is indeed shown to be a more promising electrode material. With a specific capacitance of 1680 F/g, its energy storing ability outperforms many other current electrode materials. In addition, NiS_2 cost relatively less in the production process. With these characteristics, NiS_2-based supercapacitors would be able to mass-produce, benefiting the development of energy storage systems on a large scale.

3. Applications

With advancement in the electrode materials, the supercapacitor with significantly improved performance has been playing important roles in many industries. In applications demanding fast charge-discharge rate rather than high energy storage ability, supercapacitor perform much better than the battery and the capacitor. This review lists three most popular application areas of the supercapacitor, including renewable energy generation, mobile devices, and electric vehicles.

3.1 Renewable Energy Generation

In renewable energy generation, there has been an issue that the electric power may frequently fluctuate because the energy flows out of unpredictable sources, such as wind turbines and solar power plants [15, 16]. A group of researchers has proposed applying a supercapacitor as a supplement to stabilize the fluctuation in the renewable energy generation [17]. Specifically, when the demand of power is high while the renewable energy production is dipping momentarily, the supercapacitor with fast discharge rate is responsible for instantly supplying large amounts of energy to meet the demand. Conversely, when the energy demand is low but the renewable energy production is high, the excess energy could quickly recharge the supercapacitor because of its fast charging feature. Moreover, the supercapacitor could also be used to improve the performance of the home photovoltaic system. Combining battery and supercapacitor is critical for home photovoltaic systems because it could not only use the battery to meet the energy storage demand, but also utilize the supercapacitor to enhance the power output. This combination of battery and supercapacitor could maximize the lifespan and overall performance of the renewable power generator [18].

3.2 Mobile Devices

As the development of supercapacitors progresses, many novel supercapacitors emerge as promising energy sources in mobile devices. For example, the flexible supercapacitor is a recent-developed supercapacitor to be used in consumer electronics. With the advantages of lightweight, low-cost, and environmentally friendly, this type of supercapacitor displays great potential as an energy source for wearable devices, such as watchband and smart clothing. Moreover, when coupling with a battery, the supercapacitor could help the cell phones achieve a faster charging speed and maximize energy efficiency [19]. Also, this hybrid system could slow down the overall battery aging and increase the run-time of the cell phones by 4 - 12%. Currently, there are three approaches to build up the hybrid system: (i). A direct connection between the battery and the supercapacitor; (ii). battery-inductor-supercapacitor connection; (iii). to connect the battery and the supercapacitor through a DC convertor. The results of multiple experiments proved that the third option to connect the battery and the supercapacitor through a DC convertor is the most cost-efficient solution. It requires the least amount of supercapacitors but still able to maintain a considerable performance [20]. Furthermore, the supercapacitor could also be of assistance in powering the uninterruptible power supplies (UPS). The UPS system is designated to continuously provide energy to the crucial appliances at home during energy outages [21]. This system is usually powered by batteries, which have low power density. This characteristic might result in serious problems. Sometimes, many home appliances might require more power occasionally. For example, the air compressor of an air conditioner (AC) often requires twice the starting power as its running power. If the UPS fails to meet that increase in power demand, it might result in the failure of starting the appliance. The worst scenario is that it might even cause the energy source to overheat and set the house on fire. Luckily, incorporating the supercapacitor into the UPS could solve this problem. With the fast charge-discharge ability and high power density feature, the supercapacitor would be able to instantly deliver large amounts of energy to meet the abrupt increase in demand, improving the performance and reliability of the UPS system.

3.3 Electric Vehicles

Although battery technology is advancing, it doesn't quite meet the energy consumption demand of electrical vehicles (EV). The capacity of the battery will noticeably reduce over time. Fortunately, coupling the battery with supercapacitors could address this problem by virtue of its better cyclability. Zhu *et al.* [22] proposed an optimal sized hybrid system consisting of battery and supercapacitor, which could extend the battery lifetime by up to 37%. Meanwhile, it could reduce the overall cost by 39%. Additionally, supercapacitors could also generate the required energy that batteries occasionally fail to provide to the EV. Ultimately, the goal is to create a hybrid system with both battery and supercapacitor in powering the future electric vehicle [23]. In addition, there is another suggested hybrid system for the EV which consists of three main components: the battery, the supercapacitor, and the DC bus. Basically, the system works in the following way: the battery charges the supercapacitor first, and the supercapacitor powers the DC bus, then the DC bus drives the vehicle. As a result, the power output could be increased, therefore the system features a better dynamic performance. This system is a promising solution for EV because it incorporates both energy and power density strength [24]. However, due to its high power output, supercapacitors could sometimes generate significant amounts of heat. The field experiments have demonstrated the profound effect of overheating on the performance of the EV. Thus, designing an efficient cooling system for the supercapacitor in EV is vital [25]. Zhang *et al*. [26] proposed a system to regenerate energy in EV, which could be achieved through using supercapacitors to collect the friction and heat energy lost by the vehicle's shock absorber. This system works in the following way: first, when driving through an uneven surface, the shock absorber will collect energy and send it to a transmission that translates the bidirectional vibration into a unidirectional rotation; then, the rotation will drive the power generator, provide energy to the supercapacitor, and extend the cruise range of the EV. The supercapacitor plays an important role in this system because it is able to obtain energy significantly faster than battery.

Evidently, the supercapacitor is also boosting energy system technology. Today, many electric systems have included supercapacitors to improve their performance, and the above only discussed three typical applications and how supercapacitors have dramatically improved their performance. These are all evidence of supercapacitors playing an important role in our daily lives. Further, with the advancement of material science, the supercapacitor would have more potential in the future, further broadening its application fields and benefiting human society

4. Conclusion and Future Perspectives

Due to its unique characteristics, the supercapacitor has received much attention as a new energy source in recent years. With the desired characteristics of high power density, fast charge-discharge rate, long lifespan, and good cyclability, it's becoming a trending alternative to batteries in the energy systems. This review has discussed the importance of electrodes on the performance of the supercapacitor, and it is critical to develop the optimal material for electrodes manufacturing. Although the current supercapacitors can provide a high power density, the energy density is low compared to the battery due to the limitation of material used for the electrodes. Eventually, with the advancement in materials science, it is promising that the supercapacitor will reach higher energy density. Besides, reducing production-cost of manufacturing supercapacitors should also be a focus of researchers. Many current high-capacitance materials are usually very expensive, preventing it from broader applications. As discussed above, the current most popular way is to combine the supercapacitor with the battery to compensate for its low energy density. This combination has been used in energy storage systems, such as home photovoltaic (PV) system, uninterruptible power supplies (UPS) system, and energy regenerate system in electrical vehicles. Although the combination has solved the problem of low energy density, it has one major disadvantage that the chemical inside the battery could be a source of pollution to the environment. Ultimately, the supercapacitor with both high energy density and high power density may be able to completely replace the battery in the future, making energy storage clean and efficient.

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