Supercapacitors and Common Electrode Materials for Sustainable Energy Storage

Bahreselam Sielu Abraha

Department of Chemical Engineering

Mainefhi, College of Engineering and Technology

Mainefhi, Eritrea

bahre.eri@gmail.com

Ramesh Babu Aremanda

Department of Chemical Engineering

Mainefhi, College of Engineering and Technology

Mainefhi, Eritrea

ramesh.nitrkl@gmail.com

ABSTRACT

Renewable energy will play a major role in the future. Owing to the intermittent nature of renewable energy sources, to meet the growing power supply demand of this era, a rapid development of high-performance and high-quality electrochemical energy storage system is instantly required. Research and development in the synthesis of electrode materials and study on the electrode energy storage mechanism are the foundation for building an electrochemical energy storage system to meet the demand. In particular, supercapacitors are being considered as next-generation energy storage devices for their high-power density, fast charge–discharge ability, safe operation, and long cycling life. Therefore, this book chapter provides a clear explanation on the basics of supercapacitors, their classification, and the commonly used electrode materials with the current research and development trends on finding a better electrode material. Finally, it also highlights the effect of electrolyte on the performance of supercapacitors.

Keywords—Energy storage, Supercapacitors, Electrode materails

# INTRODUCTION

In the latest decades, the dramatic global warming and the accessibility to fossil fuels on our planet require society to shift in the direction of renewable and sustainable resources. With the exponentially growing portion of the power generated from renewable assets (solar, wind, and tidal power) in whole electricity production throughout the globe, the task of enforcing environment-friendly energy storage technology is even more important to the future sustainable economy. However, one of the prime challenges with these renewable energy sources is that they are intermittent, therefore effectual and cost-effective storage technologies to handle the intermittent nature of these renewable energy technologies are required. Furthermore, the energy storage technology is in particular critical for undeveloped regions without reliable power grid infrastructure, and for ocean vehicles or space probes. For this reason, the storage and transmission of energy have become one of the most important research topics in the world today under a common theme: development of high capacity and stable electrode materials [1-4]. In this regard, electrochemical energy appliances such as batteries, fuel cells, and electrochemical supercapacitors are some of the most promising energy storage technologies that can help mitigate the intermittent nature of renewable sources. The most common feature of these three devices is that the energy-producing processes take place at the electrode/electrolyte interface. Among these technologies, supercapacitors, evolving as one of the most important energy storage and delivery devices for the 21st century, are in particular the most reliable and safe devices with a very high-power density, a low self-discharge, wide temperature tolerance [5] and good cycling stability in many applications including portable electronics, automobile vehicles, stationary power stations, backup power supplies, etc. [6]. Nevertheless, the energy density of supercapacitors is lower than batteries and fuel cells. This requires coupling with batteries or alternate power sources for applications requiring an energy supply for a longer period [7]. Therefore, there is an interest in increasing the energy density in supercapacitors to a level comparable to batteries. This is one of the major reasons for the recent significant interest in research and the development of numerous materials and synthesis methods in supercapacitor  
technology [8].

# SUPERCAPACITORS

## **Supercapacitor Basics**

Supercapacitors (SCs), also known as electrochemical capacitors, have received extensive attention in the design and manufacture of energy storage devices similar to batteries. Traditional capacitors consist of dielectric plates for electrostatic charge storage. The supercapacitor is composed of electrodes immersed in the electrolyte. The two electrodes are separated by a diaphragm to ensure the diffusion of electrolyte ions and prevent direct contact or short circuit of the electrodes, as shown in Figure 1.

The energy storage of supercapacitors is based on the charge-discharge process at the electrode-electrolyte interface. The principle of energy storage of supercapacitors is the same as that of traditional capacitors, but they are more suitable for fast storage and release of energy. Compared with traditional capacitors, supercapacitors use high specific surface area electrode materials and thin electrolytic media, which makes the capacitance 10,000 times higher than traditional capacitors. While conventional capacitors store capacities in the micro to millifarad range, supercapacitors store charge in the range of 100 to 1000 F per device while maintaining low equivalent series resistance and high-power density [9]. With proper design of supercapacitors, the energy and power of supercapacitors can vary by several orders of magnitude.

|  |
| --- |
|  |
| **Figure 1: Constituents of a supercapacitor.** |

## **Taxonomy of Supercapacitors**

According to the charge storage mechanism, supercapacitors can be divided into three categories, Electric Double-Layer Capacitors (EDLCs), Pseudocapacitors, and their combinations which are called Hybrid Supercapacitors.

*(i) Electric double layer capacitor (EDLC)*

Electric double layer capacitors (EDLCs) store energy by forming an electric double layer of electron, ion, or dipole arrangement at the electrode/electrolyte interface, as shown in Figure 2, and the energy storage process is a physical process [10]. In contrast, batteries store energy through faradaic reactions, where the active material diffuses across the active sites for the reaction to occur. The energy storage of EDLCs is only based on the adsorption of ions without any Faradaic reaction, so compared with other energy storage devices such as batteries or fuel cells, EDLCs have higher power density and longer cycle life. At the same time, the distance between the positive and negative charges of an electric double layer capacitor is extremely short, resulting in a much larger capacitance than ordinary capacitors.

|  |
| --- |
|  |
| **Figure 2: The energy storage mechanism of double-layer supercapacitors.** |

Currently, a wide variety of EDLCs materials exist, each with unique properties that have a significant impact on the performance of the device. The electrode material is the key to determine the electrochemical performance. Since electric double layer capacitive charge storage is a surface process, the surface properties of electrode materials have a significant impact on capacitance. At present, the electrode materials of electric double layer capacitors are mostly carbon materials (carbon nanotubes, graphene, carbon black, carbon fibers, activated carbon, etc.), due to its low cost and practicality, different forms of carbon materials and their derivatives have been in-depth research in the field of supercapacitors [11]. As electrodes for EDLCs, carbon materials should have three characteristics: high specific surface area; high porosity; and good electrical conductivity. In addition, studies have shown that the matching degree of pores and electrolyte ions is also an important factor affecting the electrochemical performance [12]. It should be pointed out that the ion mobility in pores is completely different from that in most electrolytes. The appropriate electrolyte solution should be selected according to the pore size of the electrode material, and the pore size distribution should be optimized according to the ion size of the electrolyte solution. If the pore size is too large, the electrolyte ions may not be adsorbed; if the pore size is too small, the electrolyte ions are not easy to migrate to the electrode surface.

*(ii) Pseudocapacitor*

The charge storage mechanism of pseudocapacitors is different from conventional capacitors and EDLCs, which is a fast-reversible redox reaction between the electrode surface and the electrolyte takes place, as shown in Figure 3. The two capacitive behaviors of pseudocapacitance and electric double layer capacitance together form a supercapacitor. The size of the pseudocapacitance largely depends on the chemical affinity of the electrode material to the ions adsorbed on the electrode surface as well as the pore structure and size of the electrode. Electrochemically active materials with redox properties, such as transition metal oxides, including nickel oxide (NiO), iridium oxide (IrO2), manganese oxide (MnO2), and ruthenium oxide (RuO2), as well as sulfides of certain noble metals (such as titanium sulfide (TiS2) can be used as electrode materials for pseudocapacitors. These transition metal oxides have high specific capacitance, pseudocapacitive behavior in multiple oxidation states, good reversibility, and long cycle life. Conductive polymers such as polypyrrole, polyacetylene, polythiophene, polyaniline, and polystyrene can also be used as pseudocapacitive electrode materials. Conductive polymers have low conductive resistance, high conductivity, and large specific capacitance, but their mechanical properties are poor, and the cycle life of conductive polymers is not as long as that of transition metal oxides because of their slow faradaic charge transfer and low reversibility.

|  |
| --- |
|  |
| **Figure 3: Schematic diagram of a pseudocapacitor.** |

In general, three types of Faradaic processes occur on pseudocapacitive electrodes: (1) reversible electrolyte ion adsorption on the electrode surface; (2) reversible doping and dedoping on the electrode surface of conducting polymers; and (3) reversible redox reactions between the transition metal oxide electrode surface and electrolyte ions. Studies have shown that these Faradaic electrochemical reactions can broaden the voltage operating range while increasing the specific capacity of supercapacitors. The specific capacity and energy density of pseudocapacitors are generally higher than EDLCs, but the power density is generally lower than that of EDLCs, because the Faraday process is slower [53]. In addition, pseudocapacitors are often not stable during cycling due to the redox reactions occurring at the electrodes, similar to batteries.

*(iii) Hybrid supercapacitor*

Higher voltages are required if supercapacitors are to be used as power sources in electronic circuits and other practical applications. Higher voltages can be obtained by connecting capacitors in series, but if there are more than 3 or 4 capacitors in series, there will be overvoltage problems, which need to be avoided by proper voltage balancing. In addition, general supercapacitors have energy densities ranging from 1 to 10 Wh kg−1. In order to obtain a higher energy density of 20 to 30 Wh kg−1 and a higher operating voltage, a new type of capacitor, a hybrid supercapacitor, has emerged (Figure 4). The formation of hybrid supercapacitors is obtained by combining different redox and EDLCs materials (such as graphene, metal oxides, conductive polymers, and activated carbon), and the combination of the two energy storage mechanisms constitutes the energy storage mechanism of hybrid supercapacitors. Hybrid supercapacitors can be based on the combination of two different electrodes, the same electrode with different mass loading, or two electrodes with different charge storage behavior to realize asymmetric or symmetric supercapacitors. Such a combination results in a supercapacitor with a higher operating voltage and a capacity two to three times higher than conventional capacitors, EDLCs, and pseudocapacitors.

At present, three methods are mainly used to fabricate supercapacitors with hybrid or asymmetric structure to replace the symmetrical structure of traditional EDLCs/pseudocapacitor supercapacitors. The first type of hybrid supercapacitor is composed of an electrode material that is a pseudocapacitive material such as a polymer or a metal oxide, and another electrode material that is an electric double layer capacitive material (i.e. carbon material). The energy density of such hybrid supercapacitors is significantly higher than that of pure pseudocapacitors or EDLCs [13]. Evans Hybrid capacitors (Evans Hybrid capacitors) is the second method, on which RuO2 is used as a cathode, Ta2O5 as an anode and liquid electrolyte capacitors with high energy density. The Evans hybrid capacitor not only maintains the characteristics of high voltage and high ratio capacitance, but also has the characteristics of high energy density of pseudocapacitor electrodes. The third and most effective and well-studied hybrid supercapacitors are those that mix rechargeable faradaic battery electrodes (such as Ni(OH)2-NiOOH or Pb/PbO2) with rechargeable non-faradaic supercapacitor electrodes [14]. The electrode-electrolyte interface of the battery ensures high specific capacity, while the capacitive interface ensures high power density.

|  |
| --- |
|  |
| **Figure 4: Schematic diagram of a Hybride supercapacitr.** |

# ELECTRODE MATERIALS FOR SUPERCAPACITORS

The most important component in a supercapacitor is the electrode material, so the quality of the electrode material seriously affects all aspects of its performance. Commonly used electrode materials mainly include carbon material, a metal oxide material, and conductive polymer material, of these three categories, carbon material became the most popular electrode material because of its unique advantages.

## **Carbon-based materials**

Carbon-based materials are a class of versatile materials owing to their tunability, surface chemistry, microstructure, and morphology. Due to its versatility as well as its chemical and thermal stability, carbon is a typical choice of active material in EDLCs. Carbon electrodes can be fabricated into various one-dimensional to three-dimensional structures, such as foams, fibers, and nanotubes.

Activated carbons (ACs) are currently the most commonly used active material in research and industry because of their low cost and high specific surface area (>2000 m2 g−1). For the EDLCs industry, activated carbon is currently the most suitable choice in terms of economic benefits [15, 16]. The high specific surface area of activated carbon is due to the complex porous structure inside the material, and there are interconnected channels between the pores. Its production involves two steps. First, the precursor needs to be charred, and then, the charred material needs to be activated. Natural or synthetic materials such as coconut shells, wood pitch, coal or polymers can be used as precursors, respectively. Activation is accomplished in two different ways: physical activation and chemical activation. Physical activation first uses inert gas for carbonization (700 to 1100 °C), and then uses gas activators such as water vapor and carbon dioxide to perform weak oxidation of carbon. Chemical activation uses the activators potassium hydroxide, sulfuric acid, phosphoric acid, or zinc chloride to lower the required temperature (400 to 700 °C), requiring post-synthesis washing steps to remove remaining reactants and inorganic residues. The size of the pores can vary from macropores (L > 50 nm), mesopores (2 nm < L < 50 nm) to micropores (L < 2 nm).

Activated carbon electrodes are currently mainly researched on the pore size distribution. Smaller pores result in a greater total surface area, while larger pores provide less resistance to electrolyte ions entering and exiting the electrode surface, especially at high currents. Therefore, in order to achieve high energy and high-power densities in final devices, the pore size distribution of activated carbon should be reasonably designed.

Carbide-derived carbons (CDCs) are obtained by etching metal from carbides using: high-temperature halogen-selective etching. CDCs can be applied to industrial production if production costs can be reduced. The pore size distribution of CDCs is relatively narrow, so it is easier to choose a suitable electrolyte to match the electrode, and a better match between the size of the electrolyte ion and the electrode can increase the capacitance [17]. For example, if the volume of the micropores is adjusted to optimally match the electrolyte ions, the specific capacitance can reach 160 F g−1 in nonaqueous electrolyte solutions [18]. In addition, there are no heteroatoms in CDCs, and CDCs also have higher conductivity values (up to 120 S cm−1) compared with activated carbons with similar porosity. This reduces the need to add carbon black during electrode preparation, thereby reducing production costs [19]. Recent studies have shown that the electrochemical performance of CDCs can also be further improved by external activation. TiC-derived carbon after steam treatment can increase the microporosity by 50% [18].

Graphene is a special type of graphite that consists of a single layer of carbon atoms. It has a specific surface area of 1500 m2 g−1 and a conductivity of 2000 S cm−1, and has been widely studied as an electrode material for energy storage devices [20]. Another reason for its popularity is that the surface of graphene is easy to modify, and graphene with different functional groups can be obtained, which have advantages in electrochemical and mechanical properties. At the same time, graphene with different structural sizes can be prepared as zero-dimensional, one-dimensional, two-dimensional and three-dimensional, including graphene quantum dots, yarn-like graphene, graphene flakes, graphene foams and carbon aerogels. Graphene can also be composited with many nanomaterials to form graphene conductive polymers, graphene metal oxides and graphene hydroxides. These nanocomposites have a variety of properties, including higher specific surface area, higher power density, tunable pore size and electrical conductivity, and etc. There are several synthesis methods of graphene, namely reduction graphene oxide method, bottom-up synthesis method, chemical vapor deposition method and so on. Each method has its own advantages and disadvantages in terms of yield, quality, cost, purity, and scalability. However, graphene is prone to restacking during electrode processing or cycling, so it is unlikely to be widely used in industry [21].

Carbon nanotubes have electrochemical properties such as high specific capacitance, stability under high current loads, allows internal resistance, and is an excellent polarized electrode material. They are made by the catalytic decomposition of hydrocarbons, and for electrochemical applications it is important to remove the catalyst or amorphous carbon after synthesis to avoid the influence of these residues on the electrochemical performance. Depending on the synthesis, single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) can be prepared. Recent research progress provides an opportunity to further explore the application of carbon nanotubes as electrode materials in EDLCs. The performance of carbon nanotubes is strongly influenced by two factors, micropores and internal resistance, both of which will make the actual specific capacitance value lower than the theoretical estimate. Therefore, researchers are now trying to develop flexible carbon fiber hybrid electrodes to exploit their synergistic effects.

## **Metal Oxide materials**

In supercapacitors, metal oxides exhibit higher storage capacity than conventional carbon materials. Various metal oxides including RuO2, MnO2, NiO, SnO2, In2O3, IrO2, MoOX, Co2O3, V2O5, Fe2O3, Bi2O3, BiFeO3, etc., have been studied as electrode materials for supercapacitors. These materials rely on surface redox reactions to store charge in the working potential window.

Ruthenium oxide (RuO2) belongs to the group of platinum on the periodic table of elements. Platinum grouped metals are high in value and expensive, the high cost of this type of material limits its wide application [22]. In addition to its excellent thermal and chemical stability, RuO2 also has metal-like electrical conductivity [23-25]. Although the pseudocapacitive capacity is extremely dependent on the properties of the electrolyte, both amorphous and crystalline RuO2 exhibit high capacities. The measured capacitance value of amorphous RuO2 material in H2SO4 electrolyte is 720 F g−1[26]. After calcination at 200 °C, crystalline RuO2 can be obtained, with a capacity of 710 F g−1 in KOH electrolyte [27]. Although the capacity values are very close in these two electrolytes, their storage mechanisms are different. In acidic electrolytes, RuO2 stores charges through a reversible redox reaction, where the oxidation state of Ru changes from Ru(IV) to Ru(II), as follows [28]:

(1)

In alkaline electrolytes, the redox reaction is much more complex, where RuO2 is oxidized to RuO42−, RuO4− or RuO4. Most of the current research on RuO2-based supercapacitor materials uses acidic electrolytes, so the mechanism is more deeply understood [29]. The key factors for the high electrochemical performance of RuO2-based supercapacitors are the surface morphology, particle size, and crystallinity. Current research on RuO2 electrodes mainly focuses on doping porous carbon materials (ACs, CFs, CNTs, etc.) or transition metal oxides (TiO2, SnO2, MnO2, Co3O4, etc.) or conductive polymers such as polyaniline (PANI). [30, 31].

After ruthenium oxide, manganese oxide has become the most concerned electrode material due to its low cost, low toxicity, environmental safety, and high theoretical capacity (1100 to 1300 F g−1). Synthesis methods include sol-gel method, dipping method, drop coating method and electrochemical deposition method, with this manganese dioxide thin film can be prepared. In addition, MnO2 can also be prepared into one-dimensional nanostructures, including nanowires, nanorods, nanoribbons, and nanoneedles. During charge and discharge spontaneous redox reactions of Mn(III) and Mn(IV) occur. It is reported that the mass capacity of MnO2 is 600 to 700 F g−1 in 1 M Na2SO4, 195 to 275 F g−1 in 2 M KCl, 310 F g−1 in 2 M (NH4)2SO4, and 720 F g−1 in LiClO4 aqueous electrolyte [32-34].

In addition, nickel oxide (NiO) has attracted extensive attention in recent years because of its unique optical, acoustic, electrical, magnetic, thermal, and catalytic properties. It has two or more oxidation states, which are conducive to fast oxidation reactions and thus store charges. Cobalt tetroxide (Co3O4) has a large theoretical capacity (3560 F g−1), is environmentally friendly, and exhibits excellent electrochemical performance [35]. However, fabricating Co3O4-based supercapacitors with high capacitance remains a challenge because in many cases, the tested capacitance values are much lower than the theoretical ones. The conductivity of Co3O4 is low and the capacity will suffer. Therefore, many studies have focused on the combination of Co3O4 with conductive carbon nanomaterials.

At present, supercapacitor technology based on metal oxides is still in its infancy. In order to further increase the energy density of supercapacitors, it is necessary to further study the combination of nanostructured electrode material and their surface charge storage properties.

## **Conductive polymer materials**

Conductive polymers (CPs) are derived from intrinsically conductive polymers (ICPs), which were discovered in 1960. Conducting polymers have high electrical conductivity (104 S cm−1), their typical cyclic voltammetry curves are not rectangular, and show current peaks at the redox potential of the polymer. Conductive polymers store and release charges through a redox process known as doping/dedoping. When an oxidation reaction occurs, ions are doped onto the polymer backbone. When the reduction reaction occurs, the ions are dedoped back into solution. As a result, the charging process occurs throughout the conductive polymer, not just at the surface as in carbon materials. This also allows conductive polymers to achieve higher capacitance. Among several common conductive polymers such as polypyrrole, polythiophene, polyphenylene vinylene, and polyaniline, polyaniline (PANI) and polypyrrole (PPy) are the most widely studied because of its simple synthesis, low monomer cost, high theoretical capacity, and wider operating voltage window.

Henry Letheby proposed polyaniline in the middle of the 19th century. He studied the electrochemical and chemical oxidation products of aniline in acidic medium. Polyaniline is one of the most widely used materials in the field of energy storage due to its large theoretical capacitance, low cost, and redox properties. Especially in the field of supercapacitors, polyaniline can be used not only as a conductive agent, but also directly as an electrochemically active material. The morphology of polyaniline is very important in all-solid-state supercapacitors. In all-solid-state supercapacitors, the electrochemically active materials are not soaked in the electrolyte. It is necessary to increase the electrode/electrolyte interface. By forming porous polyaniline to increase the electrochemically accessible surface area, the performance of the supercapacitor can also be significantly improved. PANI can be synthesized by chemical or electrochemical polymerization of monomer aniline. Different forms of PANI can be obtained by different synthesis methods. Chemical polymerization usually produces nanotubes, nanofibers, nanospheres, nanorods, nanosheets and even nanoflowers, depending on the reaction conditions and the type of oxidant. Electrochemical polymerization can only produce nanofibers and films, and unlike chemical polymerization, the morphology of PANI produced by electrochemical polymerization mainly depends on the properties of the substrate.

Polyaniline with multiple redox states has excellent pseudocapacitive properties, so PANI has been studied in the field of supercapacitors since its discovery. Kaner et al. were the first to study PANI as an electrochemically active material for supercapacitors. Rudge [36] studied the effect of PANI doping on its supercapacitor performance. Arbizzani et al. [37] did a comparative study of conductive polymers and found that the charge-discharge curve in the supercapacitor test can be a straight line, instead of a charge-discharge platform appearing on the curve like the battery test. Chen et al. [38] prepared PANI films with different morphologies (particles, flakes and nanofibers) by galvanostatic pulse method (PGM) and galvanostatic method (GM) to study the electrochemical performance of supercapacitors. Nanofibrous PANI exhibits better capacitive properties due to its larger specific surface area and better electronic or ionic conductivity. Bian and Yu [39] found that the specific capacitance of PANI after dedoping was 29% higher than that of doped PANI. Sharma and his colleagues [40] synthesized nanoporous polyaniline with a specific surface area of 1059 m2 g−1 and a mass capacitance of 410 F g−1. Florence Fusalba et al. [41] evaluated the stability of PANI-PANI supercapacitors by galvanostatic charge-discharge and lost about 60% of the initial charge after 1000 cycles. Sivakkmar and co-workers [42] prepared PANI nanofibers by interfacial polymerization and studied their performance as supercapacitor electrodes. It is shown that the initial specific capacity (554 F g−1) drops rapidly during cycling and drops to 57 F g−1 after 1000 cycles. Furthermore, they also found that only a small fraction (31%) of the theoretical capacity of the PANI nanofibers was utilized.

PANI is unstable and has limited capacity contribution, so in order to prepare supercapacitor electrodes with better performance, polyaniline can be combined with other materials. The PANI/SWCNT supercapacitor has a capacity of 485 F g−1 and good cycle stability [43]. The flexible sheet made of graphene nanofibers loaded with PANI has a capacity of 976 F g−1 at 0.4 A g−1 [44]. Vertical ordered growth of PANI on graphene nanoflakes can achieve a high capacity of 1665 F g−1 [45]. Recently, Zhang et al. [46] used a facile and economical method to obtain polyaniline/activated carbon (PANI/C-ACs) composites. Using filter paper as a precursor, they prepared the C-ACs framework by the "selective surface dissolution" (SSD) method, and PANI nanorods were uniformly grown on the prepared C-ACs framework. Figure 5 shows the synthesis process of PANI/C-ACs. When it is used as a supercapacitor electrode, it exhibits good specific capacitance (765 F g−1 at 1 A g−1) and good cycle stability (91% capacity retention after 5000 cycles), which is much better than that of pure PANI. The KCa2Nb3O10 perovskite/polyaniline supercapacitor has a capacity of 250 F g−1 after 5000 cycles [47], and the graphene/Fe2O3/polyaniline nanocomposite has a capacity of 638 F g−1 after 5000 cycles, with a capacity retention rate of 92% [48].

|  |
| --- |
|  |
| **Figure 5: Schematic of PANI/C-ACs synthesis process.** |

# ELECTROLITES

The electrolyte is another key component of supercapacitors for ion transfer. Important parameters in choosing an electrolyte are the size and type of ions, electrode material, concentration, and ion-solvent interactions. The electrolyte affects capacity, cycle life, energy density, and power density [49]. Important properties of the electrolyte are temperature coefficient and conductivity, which affect the equivalent series resistance (ESR) of the supercapacitor. Thermodynamic stability is also important, and the thermodynamic stability of non-aqueous electrolytes is higher than that of aqueous electrolytes [54]. In some cases, the freezing point and viscosity of the electrolyte can also affect the thermal stability of supercapacitors [50, 51]. Although aqueous electrolytes can provide high capacitance and high conductivity, the operating voltage window is narrow due to the influence of decomposition voltage. Inorganic liquids and organic electrolytes can work at high voltages, but their ionic conductivity is poor [49]. It is important that the size of the ions of the electrolyte be equal to or smaller than the pore size of the electrode material. For example, if the material used is carbon and the electrolyte is sodium hydroxide, then the pore size of the carbon should be larger than the size of the ions in the electrolyte, which will lead to higher capacity and higher power density of the supercapacitor. But it is impossible for a single electrolyte to meet all requirements. For example, aqueous electrolytes can guarantee high capacity and excellent ionic conductivity, but their breakdown voltage is low and the operating voltage of the electrolyte is low. Moreover, the electrochemical stability window of aqueous electrolytes is small, which can be as low as about 1.2 V, which is much lower than that of organic electrolytes [55]. Organic and ionic liquid electrolytes can provide a wide range of operating voltages but suffer from large internal resistances. The electrolytes used in supercapacitors are mainly divided into three types: aqueous electrolytes, organic electrolytes, and ionic liquids.

## **Aqueous electrolyte**

Aqueous electrolytes have the advantages of high conductivity, small ionic radius, and high ion concentration, so supercapacitors using aqueous electrolytes usually have larger capacities [54]. The high conductivity of the aqueous electrolyte also reduces the equivalent series resistance (ESR), resulting in a supercapacitor with high power density. At the same time, the use of water-based electrolytes does not require strict controlling conditions, but the working voltage window of water-based electrolytes is lower than that of organic electrolytes. The most commonly used aqueous electrolytes are KOH, sulfuric acid, and phosphoric acid.

Aqueous electrolytes are divided into three categories: acidic, alkaline, and neutral electrolytes. Sulfuric acid is the most common type of acidic electrolyte used in supercapacitors. The conductivity of ions depends on the concentration. Due to the low operating voltage window of the electrolyte and the low energy density of the supercapacitor, a hybrid supercapacitor can be used to increase the energy density of the supercapacitor in the electrolyte. The combination of two different electrodes at different working potentials can increase the supercapacitor working voltage window. However, acidic electrolytes are not suitable for all metal materials, so alkaline electrolytes are becoming more and more important alternatives. The most common alkaline electrolyte is potassium hydroxide (KOH), which has high ionic conductivity. In KOH electrolyte, the energy density of EDLCs is close to that reported for sulfuric acid electrolyte. The most important feature of neutral electrolyte is large voltage window and low corrosion. Neutral electrolytes such as LiCl, Na2SO4, NaCl, KCl, and K2SO4 have been used in supercapacitor research. Sodium sulfate is the most commonly used neutral electrolyte in electrochemical reactions, and MnO2, as the most commonly used pseudocapacitive material, has been extensively studied in neutral electrolytes. Neutral electrolytes can also be used in asymmetric supercapacitors, which can achieve high energy densities. In addition to solving the corrosion problem of supercapacitors, the neutral electrolyte also has the advantages of low cost, environmental friendliness, and high energy density.

## **Organic electrolyte**

Two solvents commonly used in organic electrolytes are acetonitrile (ACN) and propylene carbonate (PC). Acetonitrile dissolves more salts than other solvents, but has environmental and toxicity concerns [52]. Propylene carbonate is environmentally friendly, has a wide voltage window, a wide temperature range, and good conductivity. It is important to note that the water content of the organic electrolyte must be kept below 3.5 ppm. Otherwise, the voltage of the supercapacitor will drop significantly. Compared with aqueous electrolytes, organic electrolytes have a larger voltage window, but their resistance is large and their cost is high, and the use of organic electrolytes needs to be operated in a vacuum environment to prevent the influence of impurities such as O2 and water [55].

## **Ionic liquid**

Low-temperature ionic liquids (ILs) are pure organic salts, free of solvents, with melting points below 100 °C. If they remain liquid at room temperature, they are called room temperature ionic liquids (RTILs). RTILs have been widely used in the field of supercapacitors due to their unique properties and structures. RTILs are non-volatile, non-flammable, stable electrochemical performance, and good thermal stability. However, its high viscosity, low ionic conductivity and high cost limit its practical application [54].

##### REFERENCES

[1] X. Li and B. Wei. Supercapacitors based on nanostructured carbon [J]. Nano Energy*,* 2013, 2(2): 159-173.

[2] Kyriakopoulos, G. L., Arabatzis*, et al.* Electrical energy storage systems in electricity generation: Energy policies, innovative technologies, and regulatory regimes [J]. Renewable and Sustainable Energy Reviews, 2016, 56(2016): 1044-1067.

[3] K. Kubota and S. Komaba. Review—Practical Issues and Future Perspective for Na-Ion Batteries [J]. Journal of The Electrochemical Society, 2015, 162(14): A2538-A2550.

[4] J. B. Goodenough and K. S. Park. The Li-ion rechargeable battery: a perspective [J]. J Am Chem Soc, 2013, 135(4): 1167-1176.

[5] S. Ravuri and G. A. Nirmala. Synthesis, properties and performance evaluation of vanadium carbide MXene as supercapacitor electrodes [J]. Ceramics International*,* 2020, 46(4): 5323-5330.

[6] A. Yu, Z. Chen, R. Maric*, et al.* Electrochemical supercapacitors for energy storage and delivery: Advanced materials, technologies and applications [J]. Applied Energy, 2015, 153(2015): 1-2.

[7] Meryl D. Stoller, Sungjin Park, Yanwu Zhu*, et al.* Graphene based ultracapacitors [J]. Nano Letters, 2008, 8(10): 3498-3502.

[8] U. S. Sani and I. H. Shanono. A review on supercapaciotors [J]. Akgec International Jornal of Technology, 2015, 6(2): 1-7.

[9] Muzaffar A, Ahamed M B, Deshmukh K, et al. A review on recent advances in hybrid supercapacitors: Design, fabrication and applications [J]. Renewable and Sustainable Energy Reviews, 2019, 101: 123-145.

[10] Li T, Ma R, Lin J, et al. The synthesis and performance analysis of various biomass-based carbon materials for electric double-layer capacitors: A review [J]. International Journal of Energy Research, 2019, 44(4): 2426-2454.

[11] Shukla A K, Sampath S, Vijayamohanan K. Electrochemical supercapacitors: Energy storage beyond batteries [J]. Current Science, 2000, 79(12): 1656-1661.

[12] Zhang L L, Zhao X S. Carbon-based materials as supercapacitor electrodes [J]. Chemical Society Reviews, 2009, 38(9): 2520-2531.

[13] Laforgue A, Simon P, Sarrazin C, et al. Polythiophene-based supercapacitors [J]. Journal of Power Sources, 1999, 80(1-2): 142-148.

[14] Pell W G, Conway B E. Peculiarities and requirements of asymmetric capacitor devices based on combination of capacitor and battery-type electrodes [J]. Journal of Power Sources, 2004, 136(2): 334-345.

[15] Simon P, Gogotsi Y. Materials for electrochemical capacitors [J]. Nature Materials, 2008, 7(11): 845-854.

[16] Hall P J, Mirzaeian M, Fletcher S I, et al. Energy storage in electrochemical capacitors: designing functional materials to improve performance [J]. Energy & Environmental Science, 2010, 3(9): 1238-1251.

[17] Beguin F, Presser V, Balducci A, et al. Carbons and Electrolytes for Advanced Supercapacitors [J]. Advanced Materials, 2014, 26(14): 2219-2251.

[18] Kaarik M, Arulepp M, Kook M, et al. Characterisation of steam-treated nanoporous carbide-derived carbon of TiC origin: structure and enhanced electrochemical performance [J]. Journal of Porous Materials, 2018, 25(4): 1057-1070.

[19] Chmiola J, Yushin G, Gogotsi Y, et al. Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer [J]. Science, 2006, 313(5794): 1760-1763.

[20] Raccichini R, Varzi A, Passerini S, et al. The role of graphene for electrochemical energy storage [J]. Nature Materials, 2015, 14(3): 271-279.

[21] Pandolfo A G, Hollenkamp A F. Carbon properties and their role in supercapacitors [J]. Journal of Power Sources, 2006, 157(1): 11-27.

[22] Augustyn V, Simon P, Dunn B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage [J]. Energy & Environmental Science, 2014, 7(5): 1597–1614.

[23] Hu C-C, Chen W-C. Effects of substrates on the capacitive performance of RuOx·nH2O and activated carbon–RuOx electrodes for supercapacitors [J]. Electrochimica Acta, 2004, 49(21): 3469-3477.

[24] K. Sakiyama, S. Onishi, K. Ishihara, et al. Deposition and properties of reactively sputtered ruthenium dioxide films [J]. Journal of The Electrochemical Society, 1993, 140(3): 834–839.

[25] Lee H, Cho M S, Kim I H, et al. RuOx/polypyrrole nanocomposite electrode for electrochemical capacitors [J]. Synthetic Metals, 2010, 160(9-10): 1055-1059.

[26] Majumdar D, Maiyalagan T, Jiang Z Q. Recent Progress in Ruthenium Oxide-Based Composites for Supercapacitor Applications [J]. ChemElectroChem, 2019, 6(17): 4343-4372.

[27] Wu N L, Kuo S L, Lee M H. Preparation and optimization of RuO2-impregnated SnO2 xerogel supercapacitor [J]. Journal of Power Sources, 2002, 104(1): 62-65.

[28] Han Z J, Pineda S, Murdock A T, et al. RuO2-coated vertical graphene hybrid electrodes for high-performance solid-state supercapacitors [J]. Journal of Materials Chemistry A, 2017, 5(33): 17293-17301.

[29] Li Q, Zheng S, Xu Y, et al. Ruthenium based materials as electrode materials for supercapacitors [J]. Chemical Engineering Journal, 2018, 333: 505-518.

[30] Ates M, Fernandez C. Ruthenium oxide-carbon-based nanofiller-reinforced conducting polymer nanocomposites and their supercapacitor applications [J]. Polymer Bulletin, 2019, 76(5): 2601-2619.

[31] Chou J C, Chen Y L, Yang M H, et al. RuO2/MnO2 core-shell nanorods for supercapacitors [J]. Journal of Materials Chemistry A, 2013, 1(31): 8753-8758.

[32] Broughton J N, Brett M J. Investigation of thin sputtered Mn films for electrochemical capacitors [J]. Electrochimica Acta, 2004, 49(25): 4439-4446.

[33] Hu C C, Tsou T W. Ideal capacitive behavior of hydrous manganese oxide prepared by anodic deposition [J]. Electrochemistry Communications, 2002, 4(2): 105-109.

[34] Chin S F, Pang S C, Anderson M A. Material and electrochemical characterization of tetrapropylammonium manganese oxide thin films as novel electrode materials for electrochemical capacitors [J]. Journal of The Electrochemical Society, 2002, 149(4): A379-A384.

[35] Uke S J, Akhare V P, Bambole D R, et al. Recent Advancements in the Cobalt Oxides, Manganese Oxides, and Their Composite As an electrode Material for Supercapacitor: A Review [J]. Frontiers in Materials, 2017, 4: 6.

[36] A. Rudge, I. Raistrick, S. Gottesfeld, et al. A study of the electrochemical properties of conducting polymers for application in electrochemical capacitors [J]. Electrochim. Acta, 1994,39 (2): 273–287.

[37] C. Arbizzani, M. Mastragostino, L. Meneghello, Polymer-based redox supercapacitors: a comparative study [J]. Electrochim. Acta, 1996, 41 (1): 21–26.

[38] Chen H, Chen J S, Zhou H H, et al. The application of nano-fibrous polyaniline in electrochemical capacitor [J]. Acta Physico-Chimica Sinica, 2004, 20(6): 593-597.

[39] Bian C Q, Yu A S. De-doped polyaniline nanofibres with micropores for high-rate aqueous electrochemical capacitor [J]. Synthetic Metals, 2010, 160(13-14): 1579-1583.

[40] Sharma V, Sahoo A, Sharma Y, et al. Synthesis of nanoporous hypercrosslinked polyaniline (HCPANI) for gas sorption and electrochemical supercapacitor applications [J]. Rsc Advances, 2015, 5(57): 45749-45754.

[41] Fusalba F, Gouerec P, Villers D, et al. Electrochemical characterization of polyaniline in nonaqueous electrolyte and its evaluation as electrode material for electrochemical supercapacitors [J]. Journal of The Electrochemical Society, 2001, 148(1): A1-A6.

[42] Sivakkumar S R, Kim W J, Choi J A, et al. Electrochemical performance of polyaniline nanofibres and polyaniline/multi-walled carbon nanotube composite as an electrode material for aqueous redox supercapacitors [J]. Journal of Power Sources, 2007, 171(2): 1062-1068.

[43] Gupta V, Miura N. Polyaniline/single-wall carbon nanotube (PANI/SWCNT) composites for high performance supercapacitors [J]. Electrochimica Acta, 2006, 52(4): 1721-1726.

[44] He S, Hu X, Chen S, et al. Needle-like polyaniline nanowires on graphite nanofibers: hierarchical micro/nano-architecture for high performance supercapacitors [J]. Journal of Materials Chemistry, 2012, 22(11): 5114-5120.

[45] Li Y N, Huang F, Liu X L, et al. Allium sativum-derived allitridin inhibits treg amplification in cytomegalovirus infection [J]. Journal of Medical Virology, 2013, 85(3): 493-500.

[46] Zhang J M, Hua Q S, Li J, et al. Cellulose-Derived Highly Porous Three-Dimensional Activated Carbons for Supercapacitors [J]. Acs Omega, 2018, 3(11): 14933-14941.

[47] Simon S M, Chandran A, George G, et al. Development of Thick Superhydrophilic TiO2-ZrO2 Transparent Coatings Realized through the Inclusion of Poly(methyl methacrylate) and Pluronic-F127 [J]. Acs Omega, 2018, 3(11): 14924-14932.

[48] Xia X F, Hao Q L, Lei W, et al. Nanostructured ternary composites of graphene/Fe2O3/polyaniline for high-performance supercapacitors [J]. Journal of Materials Chemistry, 2012, 22(33): 16844-16850.

[49] Raza W, Ali F Z, Raza N, et al. Recent advancements in supercapacitor technology [J]. Nano Energy, 2018, 52: 441-473.

[50] Girard G M A, Hilder M, Zhu H, et al. Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content [J]. Physical Chemistry Chemical Physics, 2015, 17(14): 8706-8713.

[51] Zheng H H, Zhang H C, Fu Y B, et al. Temperature effects on the electrochemical behavior of spinel LiMn2O4 in quaternary ammonium-based ionic liquid electrolyte [J]. Journal of Physical Chemistry B, 2005, 109(28): 13676-13684.

[52] Pell W G, Conway B E. Voltammetry at a de Levie brush electrode as a model for electrochemical supercapacitor behaviour [J]. Journal of Electroanalytical Chemistry, 2001, 500(1-2): 121-133.

[53] Wang Y G, Song Y F, Xia Y Y. Electrochemical capacitors: mechanism, materials, systems, characterization and applications [J]. Chemical Society Reviews, 2016, 45(21): 5925-5950.

[54] González A, Goikolea E, Barrena J A, et al. Review on supercapacitors: Technologies and materials [J]. Renewable and Sustainable Energy Reviews, 2016, 58: 1189-1206.

[55] Wang G, Zhang L, Zhang J. A review of electrode materials for electrochemical supercapacitors [J]. Chem Soc Rev, 2012, 41(2): 797-828.