Comparative Study of Supercapacitor, Battery and Supercapattery

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Abstract. Nowadays, the consumption of fossil fuels is increasing, which means there may be some serious environmental problems caused by greenhouse emissions. Solar and wind electricity, for instance, are examples of renewable energy sources that are important for the growth of human society. However, due to their unpredictability, these energy sources are susceptible to the effects of the environment, including the weather. In order to continue using renewable energy sources, energy storage technology development will be crucial. These devices would be able to store energy under favorable external conditions and release it when the environment was not ideal for converting the renewable energy to electrical energy. There have been two main types of energy storage devices, which are respectively supercapacitor and battery. Supercapacitor has an outstanding energy density with a long-life cycle while there are still some challenges with the power density. Battery has an impressive power density while there are still some problems with the energy density. Therefore, a new type of energy storage device is highly required. So, more attention has been devoted to supercapattery, which could have both high power and energy density. This essay will introduce the working principle of supercapacitor, battery with more details. Next, there will be a comparison between supercapacitor and battery. Finally, supercapattery will be proposed, and there will be a simple introduction of Lithium-ion hybrid capacitor based on silicon carbon material.

Keywords: Supercapattery, Supercapacitors, Batteries, Power density, Energy density.

1. Introduction

Energy is an inevitable component of the whole universe. In particular, electrical energy is crucial to the functioning and advancement of human civilization. Almost all the devices in real life need to be powered by electrical energy, from watches, phones and computers to cars, trains and planes. Electrical energy could be obtained in multiple ways, such as renewable (solar, wind, thermal, nuclear) sources or non-renewable (oils, coal) sources. Nowadays, the number of petrol vehicles is increasing, which means there will be some serious environmental problems. The largest proportion of air pollutants is the emissions from cars. As a result of the incomplete combustion of gasoline, the exhaust from moving automobiles comprises hydrocarbons as well as certain byproducts of their partial oxidation, such as carbon monoxide, nitrogen oxides, and sulfur dioxide. To be more precise, 93kg of hydrocarbons, 530kg of carbon dioxide, and 27kg of nitrogen oxides will have been discharged into the environment after an automobile with a gasoline or diesel engine has travelled around 15000km. More than that, some toxic substances could be emitted into the air, and the exhaust fumes could also be harmful to humans. Under these circumstances, the need for renewable energy is growing daily, and one of the most important solutions to these problems is the development of electrical energy. More research has focused on the widespread use of electrical vehicles. It can be driven by electrochemical energy. The electrical engine can achieve the conversion between electrical energy and mechanical energy, which could be environmentally friendly. Due to that, the living place of humans can be more sustainable by reducing air pollution and environmental disorders. However, there are still some challenges with electrical vehicles. The two most common forms of electrochemical energy storage systems, which are essential for electrical vehicles, are batteries and supercapacitors. The two primary subcategories of supercapacitors are electric double layer capacitors and pseudocapacitors. The ions in the electrolyte may be drawn by electrostatic force to the electrodes with opposing charges when electric double layer capacitors are used in the circuit with some current. Reduced space between electrodes and ions, which would increase capacitance, could result from ion rearrangement at the electrode-electrolyte interface. Pseudocapacitor, a different class of supercapacitor, uses a different method of energy storage. Energy can be stored by pseudocapacitors through reversible redox processes. Additionally, the electrode surface itself may be the site of these processes. Pseudocapacitors have a significant specific surface area, which may encourage reversible reactions and contribute to their excellent power density. Supercapacitors outperform batteries in terms of life cycle and power density ($10\ kW/kg$) [1, 2]. But in terms of energy density, batteries might be able to produce more than $300\ Wh/kg$ [3, 4], but supercapacitors might only be able to generate between 10 and $100\ Wh/kg$ [4]. There should consequently be increased focus on a novel sort of energy storage technology with a long lifespan, high level of safety, and high energy and power density. This could be the cause of the increased interest in asymmetric supercapacitors. This paper will introduce the supercapacitor's operating principle and provide further information on its energy and power density. Next, there will be an introduction to batteries with the same criteria. Finally, the concept of supercapattery will be introduced, and compared with supercapacitors and batteries.

2. Supercapacitor

2.1. Electric Double Layer Capacitor

The energy storage mode of an electric double layer capacitor is similar to that of a traditional electrostatic capacitor. An electrostatic capacitor is composed of two conductive flat plates separated by dielectric materials. When voltage is applied between two stages, charges with opposite signs can be stored and quickly released in nanosecond pulse mode. However, its capacitance is very small, which is only at the level of pico or nanofarad per cm^2 [5]. It is a kind of physical capacitor. Its capacitance (C) is:

$$C = \frac{Q}{V} = \varepsilon \frac{A}{d} \tag{1}$$

In the equation of (1), C refers to the capacitance, Q refers to the quantity of charge, V refers to the voltage applied to the capacitor, d refers to the dielectric thickness of the capacitor, A refers to the electrode plate area, and ε is the medium permittivity. Due to the Coulomb force or other chemical and physical reasons, when the metal electrode comes into contact with the electrolyte solution, the free charges or dipoles from the bulk phases of the two substances must be rearranged at the electrode/electrolyte interface. In 1853, German scientist Helmholtz put forward the first model on the distribution of interface charges [1, 5]. On the solution side of the interface, according to his theory, single-layer ions are present, and on the electrode side, electrons. The electric double layer's construction was similar to that of the flat plate capacitor. The thickness d of the electric double layer was equal to the radius of the electrolyte ions. The excess charge density on the electrode side is equal to the excess charge density on the solution side [5], and charge density is proportional to the interface potential difference created by the electric double layer.

$$q = \frac{\varepsilon}{4\pi d} V \tag{2}$$

The capacitance per unit area (C_d) is:

$$C_d = \frac{\delta q}{\delta V} = \frac{\varepsilon}{4\pi d} \tag{3}$$

C_d is not a constant. It changes with the potential and electrolyte concentration. This formula only considers the electrostatic attraction and ignores the influence of ion thermal motion. Knowing this, the inner tight layer and the outer dispersed layer should make up the electric double layer [6], which could be shown in this equation:

$$\frac{1}{C_{double}} = \frac{1}{C_H} + \frac{1}{C_G} \tag{4}$$

Where Stern layer capacitance is denoted by C_H, and diffuse layer capacitance is denoted by C_G (Fig. 1). But in a concentrated electrolyte solution, C_G is huge, which means C_{double} could be considered as equal to C_H. This results in a very tiny magnitude of d [6] and a very large capacitance for the electric double layer. Electrical double layer capacitors also offer a remarkable power density. The rapid adsorption and desorption of electrolyte ions at the electrode/electrolyte contact during charging or discharging of the device could result in the formation of an electric double layer [1]. Therefore, more attention is paid to the renewable materials of electrodes, which could keep an outstanding power density and be significant for environmental concerns. Carbon materials have become the first choice of electrode materials for electric double layer capacitors due to their abundant resources, low price, simple preparation method and impressive electrical conductivity. By using carbon materials, the power density of EDLC could reach an impressive $10.336\,kW/kg$ [6]. Additionally, research has shown that using hardwood kraft lignin can significantly increase conductivity due to its high carbon concentration. Spraying conductive carbon black onto the fibre mat while electrospinning allowed the power density to even approach $76.2\,kW/kg$ [7]. Electric double layer capacitors' energy density, however, may provide certain difficulties. Due to their high specific surface area, carbon materials can have their energy density increased by capacitance, although this still leaves them with a lower energy density than secondary batteries. Therefore, the primary research focus has been on how to significantly improve the energy density of EDLCs.

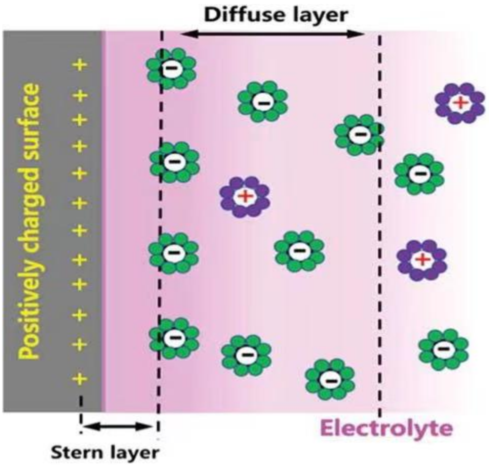

Figure 1. The structure of electric double layer capacitor [2]

2.2. Pseudocapacitor

The quick and reversible redox reaction on or near the electrode surface, which is frequently accompanied by charge transfer, is the foundation of Faraday pseudocapacitance. In addition, the Faraday pseudocapacitance process is also different from the ideal Nernst process of battery type materials. The latter is a constant potential process, whereas the former is a dynamic potential process called the Faraday pseudocapacitance process. According to Conway, there are three different forms of pseudocapacitors: intercalation system, surface redox system, and underpotential deposition (UPD) (2D) (quasi-2D). Underpotential deposition refers to the phenomenon of adsorption monolayer deposition on dissimilar metal matrix when metal ions are above their oxidation-reduction equilibrium potential. The pseudocapacitance created by Faraday charge transfer when active ions are electrochemically adsorbed on the surface or near the surface of electrode materials is known as redox pseudocapacitance, which is a substantial component of Faraday pseudocapacitance. Transition metal oxides (e.g., RuO2 and MnO2) and conductive polymers are common materials for electrochemical energy storage using redox pseudocapacitors (e.g., polyaniline). Intercalation system pseudocapacitance refers to the pseudocapacitance generated when Faraday charge transfer occurs when ions are embedded into the internal structural channels and layered structures of electroactive materials without crystal phase transition. Materials suitable for intercalation system pseudocapacitance generally have 2D or quasi 2D structures. In electrochemical reactions, the embedding process is different from the embedding process with phase transition that occurs in the charge transfer process of battery type materials. Li+, H, and an alloy of Pd and Ag are often incorporated into TiS2, MoS2, and V6O13 as part of the process of embedding pseudocapacitance. These three pseudocapacitive energy storage systems share comparable electrochemical properties based on thermodynamics:

$$E = E^0 + \frac{RT}{ZF}\ln\frac{X}{1-X} \tag{5}$$

Where Z is the number of electrons involved in the redox reaction (mole), E is the electrode potential (V), X is the occupation ratio of the surface or lattice layer, R is the ideal gas constant, F is the Faraday constant, and T is the temperature (K). In addition, the actual energy storage capacity of the pseudo capacitive materials depends on their dynamic properties in the electrochemical process. The electrochemical reaction mainly occurs on the surface or near the surface, so it is not controlled by the solid-state diffusion dynamics, so it could show an outstanding power density. Due to some charge or discharge test results, the power density can be calculated as:

$$P = \frac{\triangle V^2}{4\ x ESR\ x M_{ac}} \tag{6}$$

Where M_{ac} is the total mass of active electrode materials used in asymmetric pseudocapacitors, V is the applied voltage, ESR is the internal resistance, and C is the measured capacitance of the complete asymmetric pseudocapacitor. The greatest magnitude of the power density may reach a remarkable $242.1\ kW/kg$ [8], according to a set of statistics from trials shown in Fig. 3. The statistics also show that the power density and energy density could interact with one another. Furthermore, compared to electric double layer capacitors, pseudocapacitors may have a higher energy density. It could have an energy density of up to $304.1\ Wh/kg$, according to Fig. 3. However, it is still far below battery, and due to the redox reaction, it has some challenges with the cycle life, which is much shorter than electric double layer capacitors [8]. To fulfill the future energy demand, greater focus should be placed on the energy density of supercapacitors.

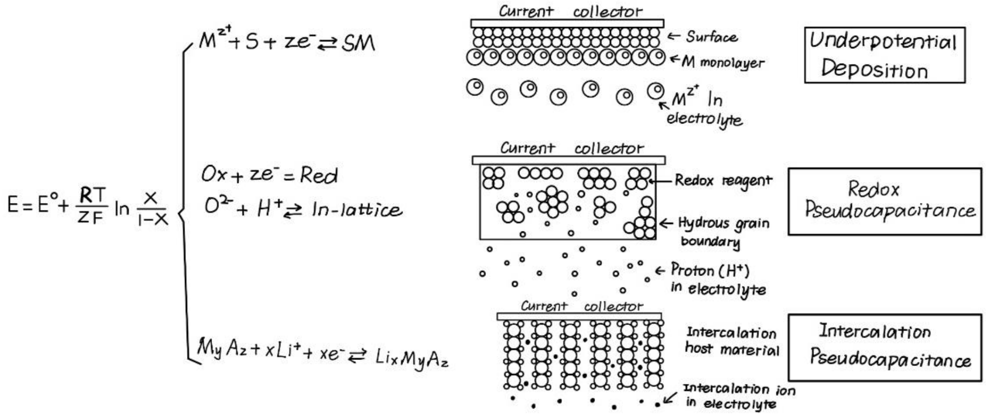

Figure 2. Three types of pseudocapacitor

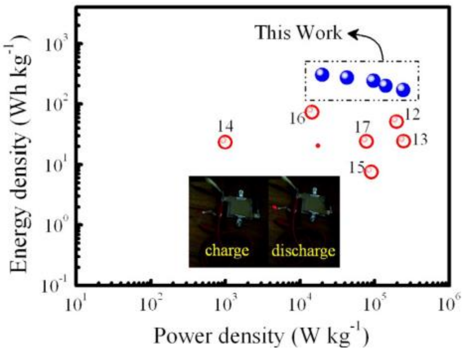

Figure 3. Experimental results of energy density and power density [8]

3. Battery

The lithium-ion battery is one of the most promising types of batteries. Lithium-ion batteries have received a lot of attention among secondary battery systems since they have the highest energy density. After more than 50 years of iterative improvement, it has become the most widely used new rechargeable battery in the market and is widely used in various industries, such as mobile communication, portable equipment, electric vehicles, and energy storage. The four main elements—the positive electrode, separator, negative electrode, and electrolyte—contribute to or guarantee the normal charge and discharge of lithium-ion batteries. Some lithium salts with low cost, high platform potential and high safety, such as lithium manganate and lithium iron phosphate, are usually used as cathode materials. The negative electrode materials are chosen because they have strong cycle stability and lithium storage performance, such as metal oxide, silicon, and carbon-based materials. During the electrode preparation process, the positive and negative electrode components must be mixed with binder, conductive carbon black, and organic solvent in the correct ratios to produce a homogenous slurry before being applied to the current collector. The positive and negative electrodes are made from aluminium and copper foil, respectively. The most popular separator material for lithium-ion batteries right now is polyolefin. Dry and wet filmmaking are the two main types of conventional filmmaking. Lithium ions may move quickly through the separator, which serves as a physical barrier separating the positive and negative electrodes, and the battery system can be adequately shielded from electrons. In order to guarantee the safety of the entire battery under adverse circumstances, the separator must also have excellent mechanical performance, exceptional thermal stability, and good wettability to electrolyte. Making electrolyte involves dissolving electrolyte salt in an organic solvent, which typically has high ion conductivity and thermodynamic stability, provides ions for the battery's normal operation, and ensures the cycle's chemical reactions are safe and reversible. Currently, the commonly used electrolyte salts are vinyl carbonate and propylene carbonate. Lithium ions are transferred from the positive electrode's lithium content to the negative electrode via a separator and the electrolyte as a transmission medium when the battery is charged, as shown in Fig. 4. The external circuit's electron transmission, which travels in a direction completely different from that of lithium ions, eventually completes the conversion of electric to chemical energy and changes the negative electrode from a lithium-poor to a lithium-rich condition. Because of the difference in lithium-ion concentration between the positive and negative electrodes, the process of turning ions into electrons during discharge is entirely different from that during charging.

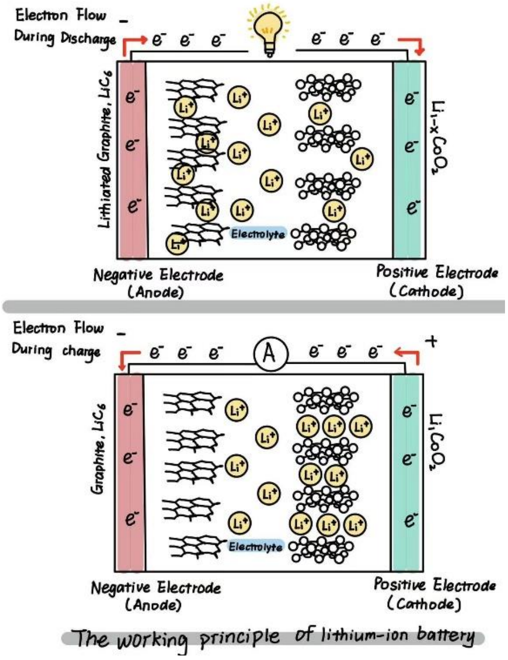

Figure 4. The working principle of lithium-ion battery

4. The comparison between supercapacitor and battery

In electrical double layer capacitors, the electrode/electrolyte interface experiences cracking adsorption and desorption of ions in the electrolyte. This might be the cause of the impressive power density of EDLC. During the charging or discharging of the device, the electrolyte ions rapidly adsorb and desorb at the electrode/electrolyte interface, which could lead to the creation of an electric double layer [1]. Therefore, more attention is paid to the renewable materials of electrodes, which could keep an outstanding power density and be significant for environmental concerns. Carbon materials have become the first choice of electrode materials for electric double layer capacitors due to their abundant resources, low price, simple preparation method and impressive electrical conductivity. By using carbon materials, the power density of EDLC could reach an impressive $10.336\, kW/kg$ [6]. More than that, a study found that the high carbon content of hardwood kraft lignin might be used to significantly increase conductivity. By electrospinning conductive carbon black onto the fibre mat, the power density could even be raised to $76.2\, kW/kg$ [7]. Electric double layer capacitors have a high energy density, which could provide certain challenges. Even though carbon materials' high specific surface area may boost capacitance and improve energy density, it is still lower than that of secondary batteries. Therefore, the primary research focus has been on how to significantly improve the energy density of EDLCs. Pseudocapacitor is another type of supercapacior, according to a series of statistics in Fig. 3 from experiments, the power density and energy density could interact on each other, and the maximum magnitude of the power density could reach an outstanding 242.1 kW kg-1 [8]. Furthermore, compared to electric double layer capacitors, pseudocapacitors may have a higher energy density. According to Fig. 3, it might reach an energy density of up to $304.1\, Wh/kg$. Due to the redox process, its cycle life is less than half that of electric double layer capacitors [8], and it still falls far short of a battery. A bigger emphasis should be put on the energy density of supercapacitors to meet the future energy demand. These days, lithium-ion batteries—a new generation of secondary battery systems—are extensively used and have valuable qualities including high specific energy and high specific power. The most promising aspect of batteries is their extraordinary energy density. The amazing energy density of $779\, Wh/kg$, which is much greater than supercapacitors, was achieved by a unique rechargeable lithium/air battery using a fuel-cell-like air-diffusion cathode, acetic acid-water electrolyte, and a water-stable multilayer Li-metal anode [9]. Due to their high theoretical energy density of $1084\, Wh/kg$ [10], which is even higher than lithium batteries, zinc air batteries have recently gained growing interest. Although supercapacitors (about $10\, kW/kg$) and lithium batteries (about $1\, kW/kg$) have different power densities, zinc batteries' power density is significantly lower than that of lithium batteries [1, 2]. In the view of safety, because of that supercapacitor could storage the energy by a series of physical reaction, it could be safe although there is a large current. However, battery storages energy though chemical reversible reactions, under the low power density, if the current is huge, there may be some dangerous, which hinder the application of battery. Therefore, there is a critical need for a novel energy storage system that combines the advantages of a supercapacitor and a battery. The summary of comparison between supercapacitor and battery with the average statistics is presented in Table 1.

Table 1. Comparison between supercapacitor and battery

	Supercapacitor	battery
Power density	About $10\, kW/kg$ [1, 2]	$< 1\, kW/kg$ [1, 2]
Energy density	Between 10 and $100\, Wh/kg$ [4]	＞$300\, Wh/kg$ [3, 4]
Life cycle	21000 cycles (the capacitance could still reach 85.3%) [11]	667 cycles under a special condition [12]
Safety	Strong	May be dangerous

5. Supercapattery

Examples of green energy storage methods include supercapacitors and lithium batteries, which now predominate in debate and study. There is an urgent need for energy storage devices with high energy density, high power density, and long life in the aerospace, national defence, and military industry, as well as electric vehicles, electronic information, and instruments, despite the fact that it is difficult for lithium-ion batteries or supercapacitors to meet these demands alone. Lithium-ion batteries offer the advantages of high energy density and low self-discharge, but the rate performance is not optimal, and the power density is poor, whereas supercapacitors have the advantages of high power density and long cycle life, but the energy density is relatively lower. To combine the advantages of the capacitor and the battery and discard the defects of the two, scientists used the external combination method to combine the battery and the capacitor. However, the device used in this combination is not only bulky, but also requires additional power management system. Therefore, a new type of energy storage device that has both a high power density and a high energy density from the inside and combines the benefits of supercapacitors and lithium-ion batteries is becoming more and more necessary. Supercapatteries are the prototypical representative of this new energy storage device. The significant improvement of supercapattery could solved the problem that the current supercapacitor and secondary battery cannot be solved separately and can be widely implemented in the society. Supercapapttery has the following advantages: (1) higher power density ($5.1\,kW/kg$ at $10.95\,Wh/kg$ at the cost of $3.0\,A/g$ current density) [13] and energy density ($23.2\,Wh/kg$ in the potential range of 0 to $2V$) [14], (2) the charge and discharge cycle time is short, which is far less than the time required for the battery charge and discharge cycle, (3) It can be used for a long time without frequent maintenance, (4) Wider working temperature range, which can work normally in the temperature range between $-45℃$ and $85℃$ [15]. It has a very wide application prospect in many aspects. To sum up, this new power supply system has excellent charge and discharge cycle performance and uses dual function composite technology to overcome the defects of traditional batteries and capacitors. This technology enables rapid transportation of electric energy at low cost. Its rated capacity, specific energy and specific power are better than those of traditional electrochemical capacitors and current batteries. By utilising innovative materials and cutting-edge technology, it combines the capacitor's powerful, quick energy storage capability with the battery's high energy output capacity. In terms of high power, it is comparable to the best commercial capacitor, and the energy provided is comparable to the lithium-ion secondary battery. So, the development of supercapattery is significant for the future to meet the demand of electrical energy.

Research on internal cross-construction of lithium-ion hybrid capacitors using electric double-layer capacitors and lithium-ion batteries has steadily increased in recent years. The hybrid capacitor, which is based on lithium-ion batteries, substitutes lithium-rich positive electrode materials with slow deintercalation rates with electric double-layer capacitor materials with quick adsorption and desorption rates. As a result, it possesses both high energy density from lithium-ion batteries and high power density from electric double-layer capacitors. It offers substantial competitive advantages in energy storage systems with high power and energy density, and in recent years, it has emerged as a research hotspot. However, there is still room for improvement in the performance of lithium-ion hybrid capacitors due to limitations imposed by the design and development of anode and cathode materials. It has become a research hotspot in recent years and offers significant competitive advantages in energy storage devices with high power and energy density. However, the mechanism of action between the doping elements and the electrochemical performance of the materials, especially the microscopic mechanism of action between the nitrogen-containing functional groups (N5, N6, N-Q, N-X) in the nitrogen-rich activated carbon and the organic lithium salt electrolyte, is still unclear [16]. In order to increase the specific capacity of nitrogen rich activated carbon and the energy density of lithium-ion hybrid capacitors, it will be important to study the structure-activity relationship between the microphysical structure and surface chemical state of nitrogen rich activated carbon and the electrochemical performance of materials. The power characteristics, operating voltage window, and specific capacity of the lithium-ion hybrid capacitor are mostly affected by the negative electrode material. Lithium ions are inserted and removed from the negative electrode material's bulk phase to primarily store energy there. The addition and removal of lithium ions from the material bulk phase has an impact on the process. The power characteristics, operating voltage window, and specific capacity of the lithium-ion hybrid capacitor are mostly affected by the negative electrode material. Lithium ions are inserted and removed from the negative electrode material's bulk phase to primarily store energy there. The addition and removal of lithium ions from the material bulk phase has an impact on the process. The operating voltage of the device reflects the second impact of the negative electrode material on the lithium-ion hybrid capacitor. Using lithium titanate and commercial graphite as examples, the deintercalation potential of lithium titanate is high (1.55 V vs Li+/Li), resulting in a lower than 3V operating voltage for lithium-ion hybrid capacitors [17], while the deintercalation potential of hard carbon and commercial graphite is low (0.2–0.5 V vs Li+/Li), allowing for a working voltage of 4V or even 4.5V for lithium-ion hybrid. The mass ratio of positive and negative electrodes reflects the impact of the specific capacity of negative electrode materials on the functionality of lithium-ion hybrid capacitors. According to the principle of charge balance between positive and negative electrodes, the higher the specific capacity of the negative electrode material below the lithium insertion platform point, the less it is used. Accordingly, the higher the specific capacity and energy density of the lithium-ion hybrid capacitor device. In conclusion, the negative electrode components used in lithium-ion hybrid capacitors must to exhibit the following qualities: (1) Fast deintercalation rate and good conductivity to narrow the difference between positive and negative power characteristics. (2) Lower deintercalation platform voltage to obtain higher device operating voltage. (3) Higher specific capacity to obtain higher device specific capacity and energy density. However, the current anode materials, either with low specific capacity or high deintercalation platform, cannot meet the above three common characteristics at the same time. A new generation of anode materials for lithium-ion hybrid capacitors with high specific capacity, low deintercalation platform, and good deintercalation kinetics should therefore receive more attention in research and development. Exploring and preparing high-performance electrode materials with a particular chemical composition and structure for the construction of high-performance lithium-ion hybrid capacitor devices is of great practical significance in order to enable the large-scale application of electrochemical energy storage devices.

6. Conclusion

Supercapattery has been cited as one of the important answers to the use of energy storage devices. In an electric double layer capacitor, when the electrode is charged to the ideal polarisation electrode state, the net charge on the metal surface will draw ions with different charges from the electrolyte solution, resulting in charge layers with equal and opposite charges on both sides of the electrode and the electrolyte solution. This is why the electric double layer is so named. Pseudocapacitor is based on the quick and reversible redox process that frequently involves charge transfer and occurs on or near the electrode surface. While having a low energy density, supercapacitors have an exceptional power density. The positive and negative electrodes of the lithium-ion battery, in particular, have relatively stable spaces and positions, which improves the reversibility of the battery charge and discharge reaction and ensures the battery's long cycle life and operational safety. The battery also relies on a reversible redox reaction to charge and discharge. However, because of the poor power density, batteries face significant difficulties. A supercapattery is a battery and a supercapacitor combined. It has a remarkable cycle life and excellent power and energy densities. The development of supercapattery, which might improve this technology as fast as feasible, should therefore receive more focus in order for it to become more pervasive in daily life and benefit society.

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