Different Composite Materials for Supercapacitor Electrodes—A Review

Tian-hao WU*
North China Electric Power University, Baoding, China
*Corresponding author

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Abstract. The main aim of this paper is to introduce several composite materials that work as electrode materials of supercapacitors. For each kind of material, this paper analyses its internal physical structure and electrochemical properties. Meanwhile, the paper cites some precious reference and experiments to indicate the progress of some materials and the achievements that have been obtained in the field of supercapacitor materials. Conclusion shows that the graphene based carbon materials usually help to improve the specific capacitance of supercapacitor. As for metal oxide materials, although lack stability compared to carbon materials, they can sometimes provide longer cycling property especially. At present, there is a tendency to study double metal oxide for its excellent electrochemical properties and moderate price. In the end, tips on improving the capability of composite materials and future research directions are also presented in detail in order to provide reference for the research field.

Introduction

Due to excessive consumption of fossil fuels, serious energy crisis and environmental pollution, it’s urgent that there should be development of new energy technologies which are sustainable and environmentally friendly. Therefore, supercapacitor emerged as a new-type power storage device which is alternative for batteries, and has been used for practical application in various fields. The supercapacitor is often known and called electrochemical capacitor. As an energy storage-delivery device, supercapacitor to be of great technical potential in power systems due to its high-power characteristics with long cycle life and acceptable capacity [1].

According to the electric energy storage mechanism, supercapacitor can be divided into two categories: electric double layer capacitors (EDLCs) and Faradic pseudo capacitors.

As for EDLCs capacitance, it has its charge stored electrostatically at the electrode/electrolyte interface which depends significantly on the surface area of electrodes, which is in contact with electrolyte ions. On the other hand, the production of faradic pseudo capacitance is due to fast and reversible redox reaction at the surface of the active electrode material such as transition metal oxides and conducting polymers. The principle diagram of the super capacitor is shown in Figure 1. In fact, a variety of supercapacitors simultaneously contain a double layer capacitance and Faradaic pseudo capacitance of two components, only the proportion is different.

Since there are lots of advantages of supercapacitors, it becomes increasingly significant to figure out which factors will affect the performance of supercapacitor. According to previous researches, the performance of supercapacitor will be influenced by the internal structure, the electrolyte concentration and the type of electrode materials. Among them, the electrode materials usually occupy the biggest influential factor. Sometimes due to the poor chemical stability and intrinsic property of the electrode materials, the capacity and cycle life of the storage charge of the supercapacitor will be limited, so the high performance of the electrode materials has become a hot research topic in the field of energy storage.

Massachusetts Institute of Technology (MIT) has created double metal oxide material NiCo2O4, which increased the energy density of the supercapacitor to more than 1000F/g [2]. Also, China South Locomotive and Rolling Stock Industry Corporation Company of China (usually known as CSR) have created graphene based carbon composite electrode material and got a maximum capacitance of monomer 3000F/g [3]. However, to make the supercapacitor to be used in a wider context

325
range of areas such as large power grid, it should be equipped with higher power density and longer cycle life, so our already existing achievements are far from enough.

Figure 1. The principle diagram of the super capacitor.

This paper mainly starts from the classification of electrode materials, and then introduce some practical research cases of different types of electrode materials as well as their strength and weakness, which provides some guidance and reference for future generations to understand and study electrode materials of the supercapacitor.

**Graphene Mixed Material**

Graphene is a single layer of graphite that is made up of carbon atoms. It is the thinnest one of the electrode materials with very strong skeleton structure. It can transfer electrons at room temperature faster than any conductor at all. More importantly, compared with carbon nanotubes, graphene has more excellent characteristics, such as high conductivity, thermal conductivity, ideal carrier mobility, free electron moving space, high strength and stiffness, high theoretical specific surface area and so on. So graphene is a preferred choice of the new high performance super capacitor electrode material. When mixed with some other materials such as hydrogen or oxides, it usually shows a better and more stable performance [5].

At present, combining graphene with metal oxide is an ideal method to make use of advantages of the two materials [6]. By using graphene as a support framework, we can achieve higher specific capacitance without worrying about structure collapse of carbon materials, which can guarantee more efficient power transmission. Because that energy is stored in three-dimensional space, these supercapacitors have much higher specific capacitance and energy density [7]. The process for the preparation of graphene can be summarized below in Figure 2.

Figure 2. Illustration of the preparation process of graphene hollow spheres.

The CTAB modified Co(OH)$_2$-graphene composites were prepared via hydrothermal method by Ghosh [8]. Through the electrochemical test in 6M KOH solution, it showed that the charging current density for 5 A/g, composite of specific capacitance for 1244.2 F/g. And when the
charge-discharge current density increased to 20 A/g, the specific capacitance was still 971.3 F/g retained, which meant that this type of supercapacitor had better rate performance and cycle stability than simple graphene supercapacitor.

Lee used hydrothermal synthesis method on graphene loaded NiO-Co$_3$O$_4$-nano needle [9]. As a result, after 6000 charge-discharge cycles, the capacity retention rate was close to 95.8%. Through the comparison with simple graphene-Co$_3$O$_4$, they found that the specific capacitance of nanometer NiO-Co$_3$O$_4$ electrode material increased significantly, indicating that by making use of the electrical conductivity of graphene, it can reduce the internal resistance of the electrode material as well as reduce the influence of electrochemical polarization. Meanwhile, mixing graphene with materials with high surface area can also improve the rate of utilization of NiO-Co$_3$O$_4$, which helps to increase the specific capacitance of the supercapacitor. The electrochemical test curves are as follows in Figure 3 [10].

![Figure 3. The electrochemical properties of graphene/Mn$_3$O$_4$ composite.](image)

In addition, people also do research in Zn-based carbon nanofibers, manganese dioxide based carbon nanofibers, and some other composite electrode materials. The key to the improvement of the properties of these composites lies in how to excavate the surface utilization ratio of carbon materials and improve the electrochemical properties of metal oxide materials. Because the excellent properties of graphene, more and more researchers have paid attention to it, hoping to mix graphene with some other materials such as hydroxide or metal oxide in order to increase the power density and specific capacitance of supercapacitor.

**Conductive Polymer Mixed Material**

For this type of material, the conductive polymer, its mechanical properties are not very good, and it is easy to aging and fall off. But if it be attached to a certain skeleton, its performance can change a lot and can play the advantages of its pseudo-capacitance characteristics. For carbon materials (such as activated carbon, carbon nanotubes, carbon gas gel, etc.), they are all good choices of skeleton. Carbon materials and conductive polymers are mainly divided into carbon materials and polyaniline (PANI), polypyrrole (PTY) and polythiophene (PTA) composite.

Keskinen [11] chose activated carbon as the framework material and then composited an electrode material with better recycling performance. After 3000 cycles, the loss was only 5% and its specific capacitance was 192F/g. Zhiromirshy [12] found that PPY deposited on carbon nanotubes was not easy to fall off, the formation of composite materials can get a higher specific capacitance. Shen deposited PANI on carbon nano spheres. Due to the larger electrical activity area and short diffusion path provided by the nanometer carbon sphere, the high efficiency of the pseudo
capacitance reaction in PANI was promoted. The detection results showed that the maximum specific capacitance of the composite electrode was 553 F/g, and the capacitance loss was only 6% after the 3500 cycle, which illustrated that the cyclic of some specific conductive polymer mixed materials were excellent.

All in all, the combination of carbon materials and conducting polymers is a hot topic in present researches. The challenge is to improve the stable distribution of conductive polymer in the skeleton material, so as to improve the specific capacitance and cycle performance. At the same time, looking for new conductive polymer materials and improving preparation technology is the future direction of carbon/conductive polymer composite electrodes.

**Double Oxides @ NF Material**

Since the performance of single metal oxides in electrode are not bad, researchers now try their best to find out excellent double oxides. When applied these double oxides such as NiCo$_2$O$_4$ or Mn$_x$Co$_{1-x}$O$_y$ on the nickel foam, the supercapacitor will show a greater improvement on cycle life and specific capacitance.

Nikynd [13] used NiCo$_2$O$_4$ dioxide as the axis of preparing coaxial NF nanowires, let NF evenly coated in the NiCo$_2$O$_4$ nanowire surface. The electrochemical tests were performed and results showed that compared to pure NiO$_2$ and CoO, the specific capacitance of NiCo$_2$O$_4$@NF was much higher, which can even reached 1266 F/g under the current density of 1 A/g. With the increase of charge-discharge current density, although the ratio of capacitance decreased, there was still 350 F/g retained at the current density of 20 A/g, which suggested that it had better rate performance than single NiO and CoO. In Gao’s [13] test, the Mn$_x$Co$_{1-x}$O$_y$@NF structure was created and a 1800 F/g specific capacitance was achieved under 1 A/g current density. Also, after 3000 cycles, its specific capacitance remained 92.5% than before, which was excellent result under electrochemical test.

From the current point of view, the double oxides @NF materials have ideal power density and long-cycle life, but it also has some weakness: during the charging-discharging process, the phase transformation, volume expansion and powder of the material can be induced by the Faraday reaction, which would greatly weaken the rate and cycle performance of the electrode materials, thus limiting the commercial application. So researchers are now constantly optimizing the structure of metal oxide and conducting polymer in order to make up the deficiency.

**Conclusion**

As emergence of the supercapacitor, the contradiction between power density and energy density in energy system is alleviated in some degree. Due to its superior advantages such as superior power density, long-cycle lifespan, fast charging-discharging, and sustainable nature, there must be wider application for this new-type device.

Different kind of materials, such as composite electrode materials and graphene-based materials, are all new types of electrode materials with ideal advantages such as low cost, high volume, faster charging-discharging time. With the discovery of new structures and improvement of the synthesis processes, these composite or skeleton-based electrode materials are bound to take the place of traditional materials.

While in recent years, the research directions of supercapacitor electrode materials mainly lie in the following two fields:

a) The nano double metal oxides and skeleton-based materials: these materials not only have a high specific surface area, but also can improve the diffusion path of electron and ion transport, which do favors to improve the performance of the electrode.

b) Material composite: the synergy between different materials, such as metallic oxide and graphene, can lead to excellent performance of electric pole material.

Therefore, it can be expected that these composite materials have a good prospect of application in electrochemical field.
At present, most of researches pay attention to composite electrode materials. The graphene-based materials, some nanotubes with metal oxides and multi metal oxides are future development directions of electrode materials. For these composite materials, the following main problems needed to be solved.

a) Some of single or double oxides, such as MnO$_2$ or NiCo$_2$O$_4$, their relatively low stability and poor cycle lifespan.

b) The problem of conductive polymer mixed materials with too little variety, and further development of new composite conductive polymer materials.

c) Methods to further enhance the specific capacitance and energy density of the mixed or composite electrode supercapacitor.

To make a long story short, what we want to achieve is the popularity of supercapacitors in the power grid and even in everyone’s lives ultimately. It has become an increasingly hot field to make the supercapacitor be alternative for conventional batteries and apply the supercapacitor into every coroner of our life.

References


