Characters of Different Materials as Supercapacitor Electrodes

Ziqing Song
Materials Science and Engineering, Ohio State University, Columbus 43201, the USA
Email: szq200072@163.com

Abstract. As a new type of energy storage device between traditional capacitors and batteries, supercapacitors have the properties of fast charging and discharging of capacitors, as well as the energy storage characteristics of batteries. With the deterioration of the global climate and the reduction of resources, supercapacitors have received widespread attention. Electrode materials take an important part of ultracapacitors, which affect the performance and production of ultracapacitors. This paper studies the effects of different preparation methods and different dopants on the performance of activated carbon electrodes. The purpose of this article is to summarize the methods and research directions for improving the performance of activated carbon electrodes. Through the summary, it can be found that the specific capacity, internal resistance and cycle life of the activated carbon electrode are greatly improved by forming the composite electrode material of the metal compound or polymer and activated carbon. But whether it can be put into mass production has also become one of the factors to be considered in future research.

1. Introduction
Supercapacitors can be divided into two types: double layer supercapacitors and pseudocapacitor. Among them, the double-layer capacitor mainly relies on the electric field between two electrode materials to store and convert energy. It has the characteristics of high power density, fast charge and discharge rate and long cycle life, etc. The electrode materials are mainly carbon based materials, such as carbon fiber and carbon nanotube. Pseudoparacters are capacitors that store charge in a fast Faraday charge transfer reaction between an electrode and an electrolyte. They have a higher capacitance and energy density, which is 100-1000 times the capacity of a double-layer capacitor and the electrode materials are mainly metal oxides and conductive polymers. But the power characteristic of the instantaneous amplification current discharge of the double layer capacitor is better than the pseudocapacitors [1]. At present, the electrode materials of supercapacitors are mainly carbon materials, metal oxides and their hydrate electrode materials, and conductive polymer electrode materials [1]. Among them, activated carbon serves as the earliest carbon material used in supercapacitors. The main research in this article is the double-layer supercapacitor, which is composed of activated carbon materials. As the earliest carbon-based material being used in supercapacitors, there are many and more detailed studies on activated carbon electrodes, including both basic performance research and some innovative studies. However, many research articles are rather messy. Through summary and comparison, the influence of different preparation methods and doping materials on the performance of activated carbon capacitors can be seen more clearly.

2. Activated carbon as electrode materials for supercapacitors
There are many different ways to prepare activated carbon as electrode material of supercapacitors. KOH activation method is a basic method to prepare activated carbon with high specific surface area. The process of high temperature activation of potassium vapor explosion extremely easily because KOH is a strong base. Many studies on activated carbon electrode have used this preparation method, but the preparation of raw materials and preparation temperature and time are different, so that the performance data of activated carbon electrode is also different.

Baolin Xing takes Indonesian lignite as raw material and adopts medium-low temperature KOH activation method (460-580°C). The results showed that with the increase of activation temperature, the specific surface area, pore diameter distribution, total pore volume and mesopore ratio of activated carbon were increased. When the temperature reached 580°C, the specific surface area of activated carbon was up to 1598m², the total pore volume was up to 0.828cm³, and the mesoporous ratio reached 41.4%, as the electrode material of supercapacitor, it has good charging and discharging performance in the 3mol/L KOH electrolyte, and the specific capacitance reaches 369F/g and 305F/g at the low current density of 50mA/g and the high density current density of 2500mA/g respectively. And after 1000 cycles, the specific permittivity keeps over 92%, which has a good cycle performance and life [2].

Shijie Li et al. Li used sargassum as raw material to prepare activated carbon for supercapacitors by KOH activation method. When the impregnation ratio is 4:1, the activation time is 120min, and the activation temperature is 800 °C, the super activated carbon has a huge surface area, rich pore structure and low cost. The data showed that prepared activated carbon has a specific surface area of 2,926 m²/g, a pore size of no more than 4 nm, and a uniform distribution. The pore volume is as high as 1.536 cm²/g. The specific capacitance of the supercapacitor prepared is up to 358.5F/g in the 6 mol/L KOH electrolyte with good electrochemical performance [3].

Ximiao Liu prepared activated carbon with high specific surface area by KOH activation process using bituminous coke as raw material. Petroleum coke powder and KOH solution were mixed in different proportions. After full immersion in the protection of N2 to devolve into 800 °C, in nickel activation, the specific capacitance of the super activated carbon in the inorganic electrolyte KOH and H2SO4 system was up to 257 F/g and 228 F/g at the highest [4].

3. Surface modification of activated carbon
In addition to different preparation methods, the later surface modification of activated carbon can also increase the activated carbon performance of the electrode material. Since carbon materials mainly form an electric double layer on the surface of the electrode to store energy, increasing the specific surface area of the carbon material is considered to increase the specific capacitance of the carbon electrode. However, studies have shown that the specific capacity and the specific surface of the electrode are not linearly related. The pore structure and surface chemistry of the material have an influence on its capacitance performance [5].

Yafei Liu et al. used nitric acid, hydrogen peroxide, and ammonia to modify the surface of the activated carbon electrode. Tests in the electrolyte KOH solution showed that the modified activated carbon has a reduced specific surface area and average pore diameter. After introducing oxygen-containing or nitrogen-containing functional groups on the surface, the resistance of the electrode material is reduced, the wettability is enhanced, and the electrochemical performance is significantly improved. Among them, the electrode material modified with 65% nitric acid has a specific capacity of up to 250F/g, which is 72.4% higher than the original activated carbon electrode material [5].

4. Activated carbon and transition metal oxide composite as a supercapacitor electrode materials
Transition metal oxides and their hydrate electrode materials, such as RuO2, MnOx, NiOx and CoOx, have high pseudo capacitance. The Faraday quasi capacitance generated by the reaction at the interface of the electrode solution is much higher than that of the two-layer capacitance of carbon materials, so they are expected to be used as electrode materials for supercapacitors [6]. In order to improve the capacitance of the super capacitor performance, chemical processing on the surface of
4.1. Activated carbon and ruthenium oxide compounds

Expensive metal RuO2 and activated carbon composite experiments are common, and the composite electrode material obtained has a specific capacitance significantly higher than that of activated carbon. Xiaofeng Wang dehydrated RuCl3 and KOH reaction solutions at different temperatures to prepare RuO2/AC composite materials, and made them into electrodes. It was found that when discharging at a current density of 20 mA•cm2, the specific capacitance of activated carbon is 172 F•g-1, and the specific capacitance of RuO2/activated carbon composite electrode is 359 F•g-1. According to the CV analysis results shown in figure 1, the two symmetrical triangular curves show that it has the basic performance of capacitor charging and discharging, and the RuO2/AC composite electrode material has a significant increase in capacitance compared to the pure AC electrode material [7].

![Figure 1. Charge and discharge curve for the supercapacitor at 20 mA•cm² [7](A curve is AC electrode, B curve is RuO2/AC composite electrode)](image)

At the same time, the content of Ru and activated carbon also has an important impact on the electrical properties of this composite electrode material. According to the study of Yue Feng et al., the sol-gel method was used to synthesize hydrated ruthenium oxide on the surface of activated carbon, and the ruthenium content was found that the specific capacitance of 30w/% composite electrode material at low current density is about 333F/g. With the increase of Ru content, when its content exceeds 10w/%, the specific capacitance is about 440F/g [8]. Xiang Li and et al. used the colloidal method to prepare activated carbon/ruthenium oxide composite electrode materials with different contents. The results showed that when the mass fraction of carbon in the composite electrode increased from 13.6% to 36.18%, the specific capacitance decreased from 664F/g to 526F/g, the energy density decreases from 103.27 Wh/kg to 75.18 Wh/kg, the power density increases from 0.48 kW/kg to 0.64 kW/kg, and the impedance decreases [9]. However, because RuO2 material are relatively expensive, not friendly to the environment, and are not in a wide range of production, there are many other different transition metal oxides which are considered and researched in recent years.

4.2. Activated carbon and manganese oxide compound

Cai Min et al. used Mn(NO3)2 and mesosphere carbon microsphere-based spherical activated carbon as raw materials (MSAC) to prepare MNO2/MSAC composite electrode material by thermal decomposition. After testing, the material and the working voltage of the composite material can be up to 3.0V. At a current density of 0.002A/cm2, the first cycle specific capacity of the composite material and the pure MSAC electrode material are 186F/g and 167F/g, respectively. In addition, the charging efficiency of the electrode material basically remained above 95% after 200 cycles [10].
Li Sheng-juan et al. used mechanical vibration grinding for the first time to prepare nano-activated carbon electrode materials at room temperature, and synthesized nano-manganese dioxide doped with bismuth oxide by sol-gel method, and 10% nano-manganese dioxide and nano-activated carbon composite. The electrode material has the best electrochemical performance, and the specific capacitance can reach 308F/g when doped with bismuth oxide [11].

5. Activated carbon and conductive polymer composite electrode material
The advantages of conductive polymers are high specific capacitance, relatively low price, and the overall performance of the capacitor can be improved by designing the structure of the polymer and optimizing the matching of the polymer. The composite electrode of activated carbon and conductive polymer also has the characteristics of electric double layer capacitance and pseudocapacitance. The specific capacitance will be much larger than that of ordinary activated carbon electrode materials. All of the excellent performance makes activated carbon and conductive polymer a research focus [12].

5.1. Activated carbon and polyaniline composite electrode material
Polyaniline (PANI) PANI has a high degree of importance due to its high conductivity, good stability, simple preparation method and easy control of conditions [13].

Lei Xu et al. used cyclic voltammetry (CV) to electropolymerize polyaniline (PANI) on the surface of the activated carbon electrode to prepare a PANI/activated carbon composite electrode. Through the test, the PANI/activated carbon composite electrode was at -1.0~1.5V potential (reference electrode Ag/AgCl) and has good electrochemical performance. The specific capacity is as high as 276F/g, when the specific capacity of activated carbon electrode is 92F/g. And the composite electrode resistance is only 2.4 Ω, when the activated carbon electrode resistance is 4.9 Ω. According to the CV curve in figure 2, it can be clearly found that figure b has two obvious redox peaks, showing the characteristics of pseudocapacitance; and figure b has a faster current response, smaller potential difference between the two peaks, and the area formed by the curve is much larger than figure a. It shows that the internal resistance of the composite electrode material is smaller, the reversibility is good, and the specific capacity is greatly improved [13].

![Figure 2. Cyclic voltammograms of the AC electrode(a) and PANI/AC composite electrode (b) at sweep rate of 5 mV•s⁻¹ [13]](image)

Mao Ding-wen et al. synthesized lithium-doped polyaniline/activated carbon electrode materials by in situ polymerization of aniline on the surface of modified activated carbon. The results showed that in the 6mol/L KOH solution, the specific capacities of the pure activated carbon electrode, polyaniline/activated carbon composite electrode and lithium-doped composite electrode were 239F/g, 372F/g and 466F/g, respectively, and the cycle performance was also significantly improved [14].

5.2. Activated carbon and polypyrrole composite electrode material
Polypyrrole is also a kind of conductive polymer materials with a wide range of uses. Due to its high conductivity, good environmental adaptability, good oxidizing regenerability and easy preparation in a variety of organic solutions and aqueous solutions, polypyrrole has become one of the focuses in the research of electrode materials for supercapacitors [15].
Xu Ke et al. used chemical oxidative polymerization to prepare the polypyrrole/active carbon (PPy/AC) composite electrode and find the best mass ratio of pyrrole and AC in order to improve the capacitive deionizing performance of composite electrode [15].

5.3. Activated carbon and polythiophene composite electrode material
Polythiophene (PTh) is an important structural conductive polymer material and a potentially important supercapacitor electrode material. It has been extensively studied due to its excellent conductivity and stability, but it is used as a supercapacitor electrode material. The research is not widespread [16].

Gao Fengge used in-situ polymerization to initiate thiophene polymerization on the surface of activated carbon, and studied the effect of different polythiophene/activated carbon ratios on the performance of electrode materials. The results show that when the molar ratio of activated carbon to polythiophene is 10:1, the composite material has relatively porous holes and is connected by fluffy mesh fibers. The specific capacity can reach up to 401.7 F/g, which improves the high current charge and discharge of the electrode material performance [16].

6. Discussion
Through the above summary of the research articles on activated carbon electrode materials, it can be found that the main purpose and result of improving the performance of activated carbon electrodes is to improve the specific capacity, internal resistance and cycle life of activated carbon electrodes, so that they have certain pseudocapacitance characteristics. In order to achieve this goal, it means that the raw materials for preparing the electrode and the modification of the surface of the electrode cannot be achieved well. Therefore, the current research on the performance of activated carbon is mainly doped with different elements or substances to achieve improved performance. In this article, the typical metal compound and polymer doping are introduced in detail. It can be found that they can significantly improve the specific capacity, internal resistance and cycle life of activated carbon electrodes, but the electrolytes and conditions used in different studies are not consistent. So it is not easy to compare them horizontally. However, it is necessary to consider the cost, pollution and ease of preparation of different doping materials, such as the metal compound RuO2. Although it can greatly improve the performance of activated carbon electrodes, RuO2 is too expensive to be mass-produced. Therefore, future research direction for activated carbon electrodes should not only focus on the improvement of activated carbon electrode performance, but also find methods or materials that are cost-effective and can be produced and used on a large scale.

7. Conclusion
Because of their wide application and huge market prospect, supercapacitors have attracted much attention from researchers at home and abroad and become one of the research hotspots in the field of new energy all over the world. Electrode material is an important component of supercapacitors and a key factor to affect the performance and production cost of supercapacitors. Activated carbon (AC), as the foundational electrode material of supercapacitor, is cheap and easy to obtain, which is conducive to the realization of large-scale industrial production. However, the low specific surface area utilization rate and the poor power characteristics of activated carbon material have become the obstacles to the development of activated carbon electrode. Chemical activation can significantly improve its available specific surface area and increase the specific capacitance. And activated carbon with other capacitor materials, such as metal oxide or conductive polymer composites, can improve the specific capacity and electrical properties of electrode materials. In the future, improving active carbon electrode specific storage conditions, composite material of low cost, mass production will be the main focus of the research and development. With the improvement of the performance of activated carbon electrode in a series of experiments, AC based composite electrode materials are expected to be industrialized in the near future. The research in this article only summarizes some typical dopant materials and the selected research articles are not cutting-edge, with only roughly summary of the basic research and results of activated carbon supercapacitors and providing a general
direction. In the future, more research and directions for improving the performance of activated carbon electrodes might be conducted.

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