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Conducting Polymers Based Composite Electrode Materials in Supercapacitor Application

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Abstract. Recently, as a new type of energy storage material, conducting polymer has attracted much attention due to its excellent electrochemical properties. We summarize research on polymer based composite electrode materials and supercapacitors. The conducting mechanism, advantages and disadvantages in supercapacitor electrodes were reasoned through extensive based on the extensive analysis of the literatures., and new trends based on conducting polymers material and capacitor development are reviewed.

1. Introduction

There is an increasing and urgent need for the development of renewable, clean and sustainable alternative energy sources (wind tidal, and solar), as well as low-cost, advanced and environmentally friendly energy conversion and storage equipment to meet the needs of modern societies and emerging ecological problems. Supercapacitors and Lithium-ion batteries are at the forefront of various energy conversion and storage devices, as shown in the Ragone diagram.

Supercapacitor is an important energy storage devices with excellent electrochemical performance [1-3]. Supercapacitors currently fill the energy gap between batteries and conventional solid-state and electrolytic capacitors, producing higher bursts of energy than batteries and producing high energy than capacitors.

According to the energy storage process, faradaic capacitor is more popular than electrical double layer capacitor. So it has been a common strategy to improve the capacitance of supercapacitors by using pseudomaterials, which have redox reactions with electrolytes during the process of charging and discharging [4, 5]. Through redox processes, conductive polymer can store and release charge, when oxidation occurs, ions are transferred to the polymer backbone. When reduction occurs, the ions are released back into the solution. As a result, the charge in the conductive polymer film occurs in the entire volume of the film, rather than only on the surface, such as carbon. This provides an opportunity to achieve a high capacitance ratio.

In order to achieve the goal of high-performance, we studied numerous hybrid or composite materials including pseudo-materials like conducting polymers have been proposed. Conducting polymers include polythiophene, polyaniline, polypyrrole, poly [3,4-ethylenedioxythiophene] had been highly studied because of its low cost, environmental stability and high electrical conductivity.



Comparison with other electrode materials, conductive polymer was attracted much attention owing to its easy processing and relatively good flexible, and the conductive polymer film thickness and composition could be obtained with good control [6, 7]. In addition, with the implantation and release of charged ions in the charging system and discharging system, the expansion and contraction of conducting polymer will be under the action of ions and charges. This process often leads to the degradation of the cycle stability performance of the electrode material [8-10].

Taking the above problems into the consideration, the components design of composites between polymers and other materials has been regarded as a feasible solution. The cycle stability of conductive polymer composite electrode materials can be enhanced by improving the molecule chain segment structure, mechanical firmness, electroconductibility and machinability to alleviate the problem of mechanical stress [11-13].

2. Polymer Based Composite Electrode Materials

During the cycle, the insertion/insertion of antiions will cause the volume change of the electroconductive polymer composites, and the electrode will gradually degrade due to expansion, fracture and contraction, which is the root of the loss of conductivity. So, The carbon materials, such as carbon fiber, carbon black, carbon nanotubes (CNTs) or graphene were appropriate used[14-16].

2.1. Polymer/carbon material composite electrode

Nanotubes have been widely studied as a component of electronic conductive polymer composites. In general, because of the mesopores, carbon nanotubes are extremely profitable, good conductive networks, and high elasticity. Obviously, the application of graphene with mesoporous and flexible properties has the same practical effect [17, 18].

2.1.1. Conductive polymer/carbon nanotube composites. Carbon nanotubes (CNTs) often were used as an electrochemical supercapacitors (ECs) double layer electrode material owing to its well electrical properties, good mechanical strength, high surface area and good spatial structure. We compared the electrochemical performance of conductive polymer composite electrode in Table1. CNTs is very difficult to disperse and easy agglomerate in the solution without any modification on the surface [19]. The composites of carbon nanotubes and polymers are bound to the polymers, relying only on physical adsorption. It is easy to cause the sliding between the interface of them, which plays a key effect on the composite mechanical properties and electrical properties. Many researchers have successfully prepared the composites between conductive polymer and CNTs with modification like sulfonation and carboxylation [20-24].

Therefore, not only the capacitance but also the recycle stability of the composite after the modification has an improvement.

Table1. Comparison of the electrochemical performance of the conductive polymer composites

Composites	Rate capability (F g ⁻¹)	S _{BET} (m ² g ⁻¹)	Capacitance(F g ⁻¹)	Ref.
PANI/CNFs	92 at 800A/g	422	177 at 0.5 A/g	[17]
PANI/cellulose	221 at 200 mV/s	1326	296 at 2 mV/s	[18]
PPy/MWCNTs	71 at 200 mV/s	1902	105 at 2 mV/s	[19]
PANI/CNFs	158 at 200 mV/s	341	210 at 5 mV/s	[20]
PANI nanotubes	13 at 1A/g	46.4	163 at 0.1 A/g	[21]
PANI nanowires	186 at 5A/g	516	327 at 0.1 A/g	[22]
PPy/CNFs	165 at 30A/g	563	202 at 1 A/g	[23]
PANI@PANI nanofibers	175 at 32A/g	410	355 at 0.5 A/g	[24]

2.1.2. Conductive polymer/graphene (GS) composites. In recent studies, researchers have carried out the doping of GS and applied it to the supercapacitor, and found that the composite materials prepared by doping GS showed better capacitance performance. Graphite oxide (GO) was used as the precursor of GS, the surface of the film and its edge with a lot of hydroxyl, carboxyl and alkyl oxygen functional groups. So after ultrasonic treatment, it can be stably dispersed in aqueous solution. And GO lamellar surface of these negatively charged containing oxygen functional groups can be polymerized in the process of reaction center and promote the polymerization reaction for the preparation of polymer/GO composites.

Lai [25] reported that they have prepared the composites of nitrogen doped-GS, ammonia doped-GS, PANI/N-GS, PANI/NH₂-GS by high temperature treatment. The electrochemical test consequence show that the NH₂-GS/PANI composites have good specific capacitance. The high capacitance is attributed to the composites not only provides a double layer capacitance, but also provides Faraday quasi capacitance. At the latest finding, researchers have tried to construct a three-dimensional conductive polymer based ECs electrode material. The GS and CNTs are combined to construct a three-dimensional framework, and then the conducting polymer is covered on the skeleton to form a three-dimensional ECs electrode material. Biswas et al [26] prepared graphene nanosheets and polypyrrole nanowire multilayer nanostructures for high-performance ultracapacitor electrodes.

Combining GS with conductive polymer is beneficial of the improvement capacitance as high specific and well conductivity. Meanwhile, Faraday capacitance of conductive polymer and double layer capacitance of GS are contributed to the electrochemical performance.

2.2. Polymer/metal oxides (sulfides) composite electrode

Usually, metal oxide (sulfides) as electrode materials for ECS can add a better cycle stability and more energy density than carbon materials. Conductive polymers are very important in the composites. Metal oxide particle agglomeration can be prevented by steric and electrostatic interactions by polymers. Uniformly dispersed metal oxide particles are placed into polymer array. In addition, conductive polymers increase the contact area of metal oxide and electrolyte, and enhance adsorption between metal oxide and collector. Huang et al [27] prepared the RuO₂/poly(3,4- ethylene two thiophene) composite, specific capacitance of which is more than 1217 F/g, and the power density and energy density were 20 kW/kg, 28 Wh/kg.

2.3. Co-polymer electrode materials

Recently by adjusting their didymous construction, improving the process ability and combining the sole properties of different homopolymers to achieve higher supercapacitance, amounts of researches have been enforced to fabricate co-pyrrole by reasonable approaches and their related performance were also further investigated. Objective to prepare polyaniline-co-pyrrole copolymer with high conductivity by simple process. The aim of this design is to prepolymerize the monomer and to control the prepolymerization time properly before copolymerization. In this process, the high conductivity of pyrrole copolymer without prepolymerization can be controlled by the content of aniline. This means that the copolymer forms many short aniline chains in the later reaction. When the content of conductive aniline chain reaches a certain level, the conductivity of copolymer to homopolymer can reach the same order of magnitude. Wang and co-workers[23] have innovatively enveloped Poly(3, 4-ethylenedioxythiophene)/polypyrrole composite electrode.

3. Summary

Conductive polymers with low cost, high environmental stability, high conductivity, high charge storage capacity, excellent reversibility and so on, will become an important direction of the development of ECs electrode materials. The main disadvantages of current conducting polymers are as follows: the cycle stability is poor than carbon materials; compared with the metal oxide, the energy density, specific capacitance and the power density is relatively low. Construction of three-dimensional conductive polymer based composite materials to improve the spatial order of materials,

reduce the ion transport distance and reduce the electrochemical impedance. Various types of electrode materials like conductive polymer, carbon materials and metal oxide are made full use to build a multi electrode composite material, and the preparation process of the material is further optimized.

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