Conducting Polymers in Supercapacitor Application

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Abstract. Two important future research directions: polymer/carbon material/metal oxide ternary composite electrode and asymmetric capacitors were indicated and summarized. With its excellent mechanical strength, high electrical conductivity, high specific surface area and good flexibility, graphene is considered as an ideal candidate material for electrochemical double-layer capacitor. These studies show that there is a significant synergistic effect between graphene and polyaniline. For these composites, due to the mechanical rigidity of graphene, the expansion of polyaniline and volume shrinkage during charging and discharging are limited.

1. Introduction
In recent years, electrochemical capacitors have attracted extensive consideration because of their better energy density. Supercapacitor, called electrochemical capacitor, is an important new type of energy storage devices with the excellent electrochemical performance. In addition, these also provide better power density and longer cycle life than secondary batteries. Therefore, ultracapacitors are used in portable electronic devices, automobiles, and other applications [1,2]. Supercapacitors can be divided into two classifications according to the charging and discharging mechanism. Firstly, electric double layer-stage capacitors is based primarily on high-surface area carbon materials, which use electrodes/electrolytes to separate charges to produce capacitors. Secondly type is pseudo-capacitance, which is mainly composed of transition metal oxide and conductive polymer, and is generated by rapid reversible REDOX reaction on the surface of electrode [3–6].

Because these two conductive polymers show great potential in the construction of various devices, the combination of the two can show superior application potential of devices. Our previous studies have also shown that the introduction of sulfonated polyaniline/graphene composites can improve the performance of its supercapacitors [7–10]. In recent years, the research work mainly focuses on the preparation of mixed electrode for mixed capacitor. In particular, graphene-based ternary composites have attracted much attention due to their excellent electrochemical properties.

2. Polymer Based Capacitors
2.1. Asymmetric capacitors
There are limited studies on the measurement of complete cells constructed with conductive polymer as the electrode and most of these studies focus on the single electrode.
Not all water-based electrochemical devices operate at a voltage limit of 1.2V. Lead-acid batteries can operate more than 2V in concentrated sulphuric acid. Combined with the advantages of long period, fast reversible ac negative electrode and high conductivity ionic water electrolyte of large capacity Faraday electrode, it can meet the requirements of high energy and high power density devices [11-16].

As for asymmetric devices, the positive polymer electrode was successfully constructed; however, the negative electrode was an activated carbon. The main purpose of using Faraday electrodes with capacitive properties is to increase operating voltage of a battery more than the symmetrical battery.

Chang and colleagues [17] studied MnO$_2$/graphene and MoO$_3$/graphene asymmetric supercapacitors. Conductive polymer/AC configuration was improved by Beguin and his colleagues [18]. The hybrid nanostructure asymmetric capacitors (MnO$_2$//PPY; MnO$_2$//PANI; MnO$_2$//PEDOT) can work stably on 1.0 V with the specific capacitance of 307 F g$^{-1}$, when the power density of 276 W kg$^{-1}$ at an energy density of 42.6 Wh kg$^{-1}$. Also, such asymmetric capacitors (ASCs) also improved cycling stability more than 1000 cycles with metal oxides wrapped by graphene. Compared with pure metal oxide ASCs (MnO$_2$//MoO$_3$), the power density and energy density of hybrid nanostructured ASCs are significantly improved [19,20]. The hybrid nanostructured electrode materials and battery structure of ASC have important effects on improving the energy density of universal supercapacitors and high-power density solid-state flexible supercapacitors[21, 22].

2.2. Conductive polymers supercapacitor

Conductive polymers can be used as a super capacitor electrode material in different ways due to the different doping forms of conducting polymers and the different kinds of doped conducting polymers capacitor. There are three main types of conductive polymer capacitors as showing in Fig 1. The first type one is composed of a completely identical p type doped conductive polymer [23]. The charge quantity released by this kind of capacitor discharge is only 1/2, and the difference of the potential difference between the two poles is small. The second type capacitors are composed of different kinds of conducting polymers, and both of them can be doped with p type. Due to the different conductive polymer electrode materials, the potential range of doping is different so that the capacitor can have a higher voltage difference in the fully charged state [24, 25]. This kind of the super capacitor is not enough good to distinguish between the positive and negative, and the capacitor cannot be reverse charge which limits the application of capacitors and has an impact on the cycle life of capacitors. The last type one is composed of an n type doped electrode and a doped p type. In the fully charged state, the cathode of the capacitor is in completely n doped state while the positive electrode is in a fully p doped state, increasing the voltage difference between the two electrodes. The main advantage of such a capacitor structure is the capacitor voltage is higher, charge release completely; charging two electrodes were incorporated, charge storage capacity. In addition electrode materials own high conductivity, small internal resistance of the capacitor and output power of large due to the two electrodes simultaneous doping.

Emel [26] et al. synthesized n-alkyl-dihydro-1, 4-oxazine ring fused thiophene monomer. The monomers were electrochemically polymerized and stainless steel electrodes coated with these polymers were used as negative electrode materials to counter the coated polyethylene dioxythiophene (PEDOT) in asymmetric pseudocapacitor batteries. The capacitance characteristic ratio of the n/p pseudo-capacitor is 285.6 F g$^{-1}$ and 325.1 F g$^{-1}$, respectively. The calculation range was 64.26 ~ 86.74 Wh kg$^{-1}$.

The big problem was unstable especially when it used as a negative electrode, or positive and negative electrodes were also conductive polymers, which is prone to degradation of polythiophene derivatives.
Figure 1. Different type of conductive polymers supercapacitor.

It should be noted that the original AC/conductive polymer hybrid ECs were based on organic electrolytes. This concept is proposed to solve the instability problem of negative conducting polymer electrodes.

3. Summary

Therefore, a lot of research work has been done to improve the energy density of supercapacitors without sacrificing their high power capacity, making them close to or even exceed the energy density of batteries, and at the same time reduce the manufacturing cost around the world in recent years.

Considering that conductive polymers can only be reversible at a very small potential range, their best applications require asymmetric configurations, such as types on different select of conductive polymers as negative and positive electrodes, or combined with another electrode material.

This concept expands the voltage of the capacitor to achieve higher energy and power densities. For the development of low cost and environmental protection system, this is undoubtedly a research direction that needs extensive research in the future.

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