Doctoral Thesis

Porous Carbon Nanomaterials for Energy Storage Application

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Abstract

With the advantages of the high specific surface area, conductivity and chemical stabilities in several conditions, the porous carbon materials have been used in varieties of fields especially in the energy storage field. Supercapacitor is one of the energy storage devices with high power density and extraordinary cyclability even at high current density. However, the low energy density of the supercapacitor device limited the application in practical applications. In this thesis based on the solution of that problem, we prepared a series of metal-organic framework (MOF) derived nanoporous carbon material for supercapacitor application, the results showed that the MOF derived porous carbon materials have great potential for supercapacitor electrode materials in energy storage field.

In chapter I, we first summarized the properties and preparation methods of carbon-based materials, then the energy storage mechanism of supercapacitor has been fully researched according to the electric double layer capacitor and pseudocapacitor models. Based on the investigations, MOF derived NPC materials were chosen for supercapacitor materials due to its unique physical and chemical properties.

Chapter II summarized the research techniques, basic experimental and calculation methods used in the research.

In chapter III, Al-based MOF material was prepared, then an interconnect-structured NPC material was derived from the direct carbonization of Al-MOF material at a certain temperature. The NPC materials without the interconnect structure were also prepared as the control. Symmetric supercapacitor device was used to evaluate the electrochemical performances of this material. Different electrolytes were used to investigate the effect of the interconnect structure and mesopore structure on supercapacitor application.

Chapter IV~V exhibited two types of nitrogen-doped NPC materials prepared via different heteroatom doping method. A high nitrogen content of >10% (atom ratio) in

the N-NPC material was achieved. Beneficial to the MOF precursors, the two N-NPC materials exhibit highly porous and interconnected structures. With the unique structures and high nitrogen content, both of the N-NPC materials present ultrahigh supercapacitive performance in several electrolytes. High energy densities of these materials are compatible with the Li-ion battery.

In chapter VI, graphene oxide - MOF (GO-MOF) complex was prepared via a simple *in situ* growth method. Then a graphene@NPC material is derived from the carbonization of GO-MOF. The adding of the graphene not only promote the aggregation of the NPC monomers but also increase the conductivity of the NPC materials. Furthermore, the loading of NPCs on graphene surface prevents the restacking of graphene so that the graphene layers can be fully accessed by the electrolyte and be used for energy storage. With the unique structure of this material, a high capacitance of 472 F g^{-1} was obtained in symmetric supercapacitor device, which is the highest capacitance value measured in pure carbon material.

In chapter VII, waste PET bottle was used as the raw material for MOF synthesis, and an NPC material was derived from the PET-based MOF. The improved synthesis method leads to an efficiency manufacture with high product yield, which is considered as a promising way to solve the plastic pollution problem. The NPC material was prepared via the carbonization of PET-MOF, and the NPC material exhibit good supercapacitor behavior in both acidic and organic electrolytes.

The research of the nanoporous carbon materials for supercapacitor application in this thesis will help the other researchers for their research on nanoporous carbon materials and supercapacitors, and provide new ideas for energy storage field.

Keywords:

Metal-organic framework (MOF), Supercapacitor, Nanoporous carbon (NPC), Heteroatom doping

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