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RAPID COMMUNICATION

Homogenous incorporation of SnO$_2$ nanoparticles in carbon cryogels via the thermal decomposition of stannous sulfate and their enhanced lithium-ion intercalation properties

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Abstract
An impregnation-calcination method based on the thermal decomposition of stannous sulfate is developed to prepare carbon cryogel-tin oxide nanocomposites with less impurity for anode materials of lithium-ion batteries. Structural characterization reveals that the tin oxide nanoparticles, arising from the decomposition of stannous sulfate, are homogeneously distributed inside the pores of carbon cryogels. The detail results demonstrate that carbon cryogels with large specific surface area, large porosity, and small mesopores are beneficial to the deposition of tin oxide nanoparticles. As a result, carbon cryogel-tin oxide nanocomposites with optimized structures show a discharge capacity of 590 mA h/g after 50 cycles, much higher than that of either carbon cryogels, pure tin oxides or their mechanical mixture. The superior electrochemical properties of carbon cryogel-tin oxide nanocomposites could be attributed to their novel microstructures and the synergistic effects between carbon cryogels and tin oxide.
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Introduction

Owing to their excellent properties and abundant resources, carbon materials are used in a variety of fields, such as

supercapacitors [1-6], fuel cells [7], lithium-ion batteries (LIBs) [8-14], catalyst carriers [15], and conductive materials [16]. Especially in energy fields, carbon materials have been widely used and drawn much attention for further development in recent years [17,18]. For example, carbon nanotubes and graphene have been investigated by many researchers for various energy-related applications [8,19-24]. Highly porous carbon, commonly known as carbon aerogels (CAs) and carbon cryogels (CCs) has been widely investigated [25-28] since 1989 when they were firstly synthesized by Pekala [25]. The CAs and CCs were prepared based on supercritical drying and freeze drying, respectively. Similar to CAs [29], CCs offer a number of advantages or benefits over the activated carbon derived from natural biomass, for example, adjustable porous structure including pore diameter, porosity, specific surface area, good electron conduction pathway, and superior mechanical stability [28]. In addition, CCs offer the ability to control the impurity and adjust the bulk surface chemistry [30]. Up to now, most published research on CCs focused on the aspects of their synthesis methods, structural and property characterizations, as well as their application in energy-storage, such as supercapacitors [27,31-34] and LIBs [35-37].

It is well known that carbon is a typical anode material for LIBs consisting of mesocarbon microbeads and $LiCoO_2$. However, the theoretical specific capacity of carbon is only about 372 mA h/g, which lags behind the demand of rapidly advanced electronics that require batteries with high energy density. Although graphene sheets can potentially host more Li^+ with a specific capacity reaching as high as 744 mA h/g by forming a compound of LiC_6 on both sides [38], the synthesis of graphene sheets is time-consuming and costly, making it difficult for wide-spread industrial applications [39,40]. Conversely, CCs could be prepared efficiently at large-scale with relatively low-cost. Generally, CCs are highly porous with large specific surface area. These characteristics are helpful to the transfer of both electron and Li^+, resulting in a high rate capacity. However, the volumetric capacities and energy density of CCs decrease appreciably because of their relative low density. Therefore, improving the specific capacities of CCs-based materials for LIBs is of great significance.

Efforts have been made to enhance the Li^+ insertion properties of CCs-based materials. For example, CCs-Si composites were prepared by simply adding Si nanoparticles to the water phase during the inverse emulsion polymerization of resorcinol with formaldehyde [37]. Another example is the modification of CCs with SiO powders via a high energy mechanical ball-milling route that could deliver a discharge capacity of 539 mA h/g after 30 cycles [36]. In those work, particles (Si or SiO) were not present in the pores of the CCs, resulting in the volumetric increase of the composites and capitalizing on little synergistic effects of intimate mixing of carbon with Si or SiO or other materials. Therefore, more efforts should be made to improve the properties of CCs-based materials, including the design and the synthesis of tin-carbon composites because of their high theoretical capacity.

The solution impregnation has been used to prepare carbon-tin oxide (or tin) composites [41-44]. For example, organometallic tin source tributylphenyltin solution was impregnated into porous carbon to synthesize carbon-tin composites [41,42]. $SnCl_4$ and $Sn(CH_3COO)_2$ also were employed to prepare carbon-tin (or tin oxide) composites [43,44]. However, those reagents are either expensive or easy to introduce the impurity of chlorine. In this study, CCs were modified by SnO_2 nanoparticles via a simple solution impregnation-calcination method using $SnSO_4$ as the tin sources. The experimental results demonstrated that SnO_2 particles with average diameter of 15 nm, were homogeneously dispersed throughout the CCs to form CCs-SnO_2 nanocomposites (CTs). The SnO_2 nanoparticles are homogenously dispersed in the pores of the CCs, and there is no volume change due to the addition of SnO_2 nanoparticles. The effects of the surface area, pore volume, and pore diameter of the CCs on the electrochemical properties of the CTs were investigated in detail. As anode materials for LIBs, the nanocomposites showed higher discharge capacity, enhanced cyclic stability and improved rate capacity as compared with those of both CCs and pure SnO_2. The synergistic effects between the two components in the CTs may be credited for the superior properties. It is believed that this efficient method will be of great benefit to the synthesis of other metal oxide-CCs composites for a range of applications.

Experimental

Preparation of CCs

CCs were prepared by using resorcinol, furaldehyde, hexamine and tert-butanol as raw materials. The procedure for the synthesis of CCs from resorcinol-furaldehyde gels was similar to previous papers [31]. Three kinds of CCs with different pore sizes, specific surface area, and pore volume were prepared to investigate their effect on the microstructure and properties of the composites. A typical procedure is briefly described as follow. Firstly, the resorcinol and furaldehyde were mixed together at a constant molar ration of 1:2. Then, a proper amount of solvent (tert-butanol) was added in the above mixture, followed by the addition of hexamine as the catalyst. A small amount of deionized water can also be added if necessary. Thirdly, the mixture was sealed and cured in an oven at 353 K for 7 days to complete the gelation process. After that, the gels were dried under vacuum at 223 K in a Labconco FreeZone 1 L freeze dryer. Finally, the dried samples were pyrolyzed in N_2 at 1173 K for 6 h to remove unwanted organic matter and achieve CCs. Sample preparation of the CCs with different microstructures and surface area is summarized in Table 1.

Synthesis of CTs

The solution impregnation-calcination method for the modification of CCs is described as follow. Firstly, CCs were impregnated with saturated solution of $SnSO_4$ in ethanol at 293 K. Secondly, the samples were dried in a freeze dryer for 12 h. Finally, the dried samples were calcined in N_2 at 723 K for 1 h. To improve the mass ratio of SnO_2 in the composites, the impregnation-calcination cycle was repeated for two or three times. After three cycles, the pore volume of the composites was very small. It was not easy to hold the solution of $SnSO_4$ and improve the mass ratio of SnO_2 in composites. Pure SnO_2 powders were prepared by calcining the CTs of C-2 in air at 773 K for 1 h.