Li-Ion Battery And Fabrication Of An Anode For A Li-Ion Battery

FIELD OF INVENTION

The present invention relates broadly to a Li-ion battery and to fabrication of an anode for a Li-ion battery.

BACKGROUND

Tin oxide is an important wide band semiconductor and has numerous potential applications in the areas of resistors, gas sensors, dye sensitized solar cells, and transparent conducting coatings for glasses and electrodes. In particular, it has high theoretical capacity of 781 $mAhg^{-1}$, which is twice higher than that of a graphite anode ($372mAhg^{-1}$). However, a large specific volume change usually occurs in the host matrix during charge and discharge processes [1], which leads to the rapid pulverization of the electrode [2, 3] and decrease of electrical conductivity between active material particles. As a result, this material has not been applied in practical lithium-ion batteries (LIBs) until now.

At present, one proposed strategy to circumvent the problem of easy pulverization and poor cyclability of tin compounds is to search for a suitable matrix which is able to accommodate the volume change. Since carbonaceous materials have smaller expansion during charge and discharge processes and fair ductility, they are widely chosen as the matrices for tin-based anode materials to improve their cycle performances, for example, carbon nanotubes [4,5], expanded mesocarbon microbeads [6], graphite [7], graphene [8, 9] and so on. Among the carbon materials, hollow core-shell nanopartices are considered favourable, especially for thin carbon shells, they possess high electronic conductivity and good elasticity. They not only can prevent the aggregation of inner active materials and effectively accommodate the strain of volume change during Li-ions insertion/extraction processes, but also can preserve the electronic conductivity of the overall electrode. Therefore, the core-shell Sn/C and SnO_2/C composites, where Sn or SnO_2 nanoparticles were encapsulated into

amorphorous carbon spheres, have been fabricated by pyrolysis of Sn-containing organic precursors to improve their electrochemical performance [10,11].

Very recently, Wang and coworkers [12] synthesized a type of SnO_2-encapsulated/decorated crystalline carbon hollow spheres with the size of about 750 nm and found that tin/oxides both dispersing in carbon matrix and coating with carbon layer are effective to improve their electrochemical properties in lithium-ion batteries. However, the synthesis process of crystalline carbon hollow spheres in [15] is complicated including the preparation of silica spheres as template, pyrolysis of benzene vapor at a very high temperature and treatment with HF solution to remove the template spheres. Moverover, the big size of hollow carbon spheres is unfavorable for the homogeneous distribution and restriction of SnO_2 nanoparticles during battery cycle process.

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SUMMARY

According to a first aspect of the present invention there is provided a use of hollow carbon spheres formed by a template-free formation process in the fabrication of an anode of a Li-ion battery.

According to a second aspect of the present invention there is provided a Li-ion battery comprising an anode formed by the use defined in the first aspect.

According to a third aspect of the present invention there is provided a Li-ion battery comprising an anode incorporating hollow, Ti oxide doped carbon spheres having a size smaller than about 100nm.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will be better understood and readily apparent to one of ordinary skill in the art from the following written description, by way of example only, and in conjunction with the drawings, in which:

Fig. 1 shows a schematic drawing illustrating a Li-ion battery according to an example embodiment.

Figs. 2 (a, b) show SEM images of OC and SnO_2/OC-40; and (c, d) show TEM images of OC and SnO_2/OC-40 according to example embodiments;

Fig. 3 shows comparative X-ray diffraction patterns of OC and SnO_2/OC-40 composite;

Fig. 4 shows an HRTEM image of the SnO_2/OC-40 composite.

Figs. 5. (a) shows the cycle performances of pure SnO_2, SnO_2/OC-33, SnO_2/OC-40 and OC electrodes at the current density of 0.2mA/cm^{-2}; and (b) shows rate-capabilities of pure SnO_2, SnO_2/OC-33 and SnO_2/OC-40 at various current densities.

DETAILED DESCRIPTION

The example embodiments describe provide a Li-ion battery incorporating onion-like carbon hollow carbon spheres as buffer matrix for Li storage in a core-shell SnO_2/C composite.

The example embodiments described use a template-free, low cost and environmental-friendly approach to synthesis onion-like hollow carbon spheres (hereinafter "OC").Carbonization of phenolic resin , e.g. phenolic-formaldehyde resin at about 1000 °C, with the aid of a metal catalyst, e.g. ferric nitrate (FN), is used. This process can produce carbon hollow spheres of much smaller size (preferably less than 100nm preferably in a range from about 30nm to 50 nm, and more preferably around 40 nm) than existing techniques. In addition, defects in the carbon shell in example embodiments, can not only restrain the large volume change but also preferably provide channels during the Li-ion insertion and desertion processes. SnO_2 nanoparticles doped OC (SnO_2/OC) are prepared by an impregnating and oxidating method in example embodiments.

Figure 1 shows a schematic drawing illustrating a Li-ion battery 100 according to an example embodiment. In the battery 100, the anode 102 comprises SnO_2 doped OCs ,e.g. 104, for enhanced Li-ion storage during a charge cycle of the battery 100.

The inventors have found that the small particles size of the SnO_2/OC e.g. 104 advantageously decreases electron diffusion parameters, resulting in better charge storage properties.

Furthermore, it was found that the high surface area of the $Sn0_2$/OC e.g. 104 can allow the active material to exhibit a high absorption capacity for the Li-ions. The SnO_2/OC in example embodiments were found to show only a small volume expansion (< about 10%). Batteries according to example embodiments therefore advantageously offer long life, safety, and lower environmental impact.

The SnO_2 /OC composites are synthesized by impregnating $SnCl_2$/ethanol solution and oxidation of the carbon onion structure, in example embodiments. It was found that the SnO_2/OC composite can deliver a high reversible capacity of about 469 $mAhg^{-1}$ after 30 cycles, which was two times higher than that of un-doped OC (192 $mAhg^{-1}$). In addition, the SnO_2/OC composite showed desirable cycling stability and high-rate cyclability.

Preparation of OC nanoparticles in one example embodiment

Ferric nitrate (FN) and phenolic resin (PR) were firstly mixed in atomic ratio of about 1: 16 of Fe to C, then hexamethylenetetramine as crosslinking reagent was added into the mixture in the weight ratio of about 0.14:1 of hexamethylenetetramine to PR. A slurry mixture was obtained by adding a certain amount of ethanol with ultrasonic stirring for about 30 min. The slurry mixture was heated at about 150 °C for about 2 h, afterwards was carbonized at about 600 °C for about 6 h under the protection of flowing pure nitrogen, resulting in carbon encapsulated metal nanoparticles. The as-prepared product was dipped into mixed acid solution (HCl and HNO_3,) with magnetic stirring in order to get rid of the catalyst substantially completely, and finally onion-like carbon materials were prepared.

Preparation of SnO_2/OC composite in one example embodiment

About 0.1 g of the OC powder obtained above was added to an Tin containing alcohol solution, in this example about 25 ml, 2mol/L $SnCl_2$/ethanol solution and sonicated for about 30 min and then maintained at room temperature for about three days. Afterward, the suspension was washed three times with ethanol in order to eliminate the tin compounds adsorbed on the surface of OC. The collected powder was heated at about 350 °C for about 1 h to change $SnCl_2$ into SnO_2. Thus, the SnO_2-doped OC composite was obtained. Thermogravimetric analysis (TGA) indicates that the content of SnO_2 is about 40 %, so the sample was denoted as SnO_2/OC-40. In order to remove the coated SnO_2 nanoparticles completely, about 0.2 g SnO_2/OC-40 was rinsed in about 4 ml, 2mol/L hydrochloric acid for 10 h, then washed with distilled water repeatedly until the pH value of the solution was close to neutral. The TGA showed that the SnO_2 content in this sample are about 33 %, which was denoted as SnO_2/OC-33. For comparison, pure SnO_2 was prepared by heating the composite at about 800 °C for about 20 min in air to completely remove the carbon.

The morphologies and structures were measured by scanning electron microscope (SEM, ZEIZZ SUPRA55), transmission electron microscope (TEM, Hitachi H-800), high resolution TEM (HRTEM, NEC JEM-3010) and X-ray diffraction (XRD). XRD measurement was conducted on a Rigaku D/max-2500B2+/PCX system with Cu Ka radiation (λ= 1.5406 A). The content of SnO_2 in the composites was calculated by residual mass of thermogravimetric analysis (TGA, Netzsch STA 449C), the samples were heated with a rate of about 10 °C min^{-1} to about 1000 °C in open air atmosphere.

The electrochemical performance was measured in a two-electrode system described previously in [6], the contents of which are incapacitated by cross-reference. Lithium foil was used as counter electrode, and composite electrode comprising active mass (about 80wt. %), carbonaceous additive (in one example acetylene black, 10wt. %) and poly (in one example vinylidene difluoride, PVDF, about 10wt. %) binder was used as working electrode.

One molar LiPF6 solution in a about 1:1 (volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte. The model cells were galvanostatically discharged (Li insertion) and charged (Li extraction) in the voltage range from about 0.01 to 2.50 V versus Li/Li^+ at various current densities from about 0.2 to 5 $mAcm^{-2}$ (corresponding the charge/discharge rate of about 0.5 to 10 mAg^{-1}) by LAND CT2001A battery test system.

As shown in Fig.2 (a,c), the nanosized and hollow structured carbon spheres can be clearly observed in SEM images. The diameter of OC is around 30~50 nm and the thickness of the carbon shell is estimated to be about 5 nm. From Fig.2 (b,d), it can be observed that all OC have been homogeneously covered by SnO_2 nanoparticles and aggregated particles were generated. The formation of SnO_2 particles should be attributed to the reaction of precursor $SnCl_2 \cdot H_2O$ with oxygen in the reaction chamber as :

$$2SnCl_2 \cdot H_2O + O_2 \rightarrow 2\ SnO_2 + 4HCl.$$

The structures of OC and SnO_2/OC composite were investigated by XRD measurements. As shown in Fig.3, in the case of OC, a relatively sharp peak of (0 0 2) diffraction of carbon at about 26.3° is observed, suggesting that semi-graphitized carbon shells have been formed during the carbonization process (about 600 °C). The other small quantity of noise peaks are attributed to residual impurities Fe_3C, but its content is less than about 5 % from TGA. After doping SnO_2 nanopaticles onto/into OC, additional diffraction peaks at about 2θ = 26.3°, 33.5°, 51.6° and 65.2° are clearly seen, which can be assigned to the diffraction peaks of (1 1 0), (1 0 1), (2 1 1), and (3 0 1) planes of SnO_2, respectively, according to the JCPDS standard card (no.72-1147). The very broad peaks in XRD patterns of SnO_2/OC-40 composite reveal that the doping SnO_2 particles have a small size or amorphous phase. It is worthy to note here that no other peaks corresponding to $SnCl_2$, Sn, or other impurities appear in the SnO_2/OC patterns, implying the substantially complete conversion of $SnCl_2$ to SnO_2.

To further investigate the distribution of SnO_2 grain in OC, HRTEM observation was performed. The HRTEM image of SnO_2/OC composites shown in Fig.4 indicates that besides coating on the surface of OC, SnO_2 nanoparticles are also present inside of OC. The average crystal size of SnO_2 grain can be observed to be around 5 nm.

Cycle performances of SnO_2, OC, SnO_2/OC-33 and SnO_2/OC-40 composites are compared in Fig. 5(a). It can be seen that the cycle properties of OC, SnO_2/OC-33 and SnO_2/OC-40 tend to be parallel each other during the 30 cycles, suggesting that both of SnO_2/OC composites exhibit good cycle performance similar to that of OC. In contrast, the reversible capacity of a pure SnO_2 electrode rapidly drops from 891 to 276 $mAhg^{-1}$ under the same testing conditions. After 30 cycles, the reversible capacities of SnO_2/OC-33 and SnO_2/OC-40 electrodes still remain 424 and 469 $mAhg^{-1}$ with 78.4% and 78.6% retention of the first reversible capacity (526 and 541 $mAhg^{-1}$, respectively), respectively, which is more than twice higher than that of OC (192 $mAhg^{-1}$) after the same cycles. Large irreversible loss should result from the irreversible reduction of SnO_2 to Sn and other possible irreversible processes, such as the formation of SEI film on the surface of electrode.

In order to clarify the influence of the hybridization on the electrochemical performance of SnO_2 nanopaticles, the theoretical capacity was calculated as follows:

$C_{theoretical}=C_{SnO2}$ *$\%_{mass\ of\ SnO2}$ + $C_{Graphite}$ * $\%_{mass\ of\ Graphite}$.

The theoretical specific capacity of tin dioxide and carbon is 781 and 372 $mAhg^{-1}$, respectively. Thus SnO_2/OC-33 and SnO_2/OC-40 composites should have a theoretical capacity of 507 and 536 $mAhg^{-1}$, respectively. More than 84% of this capacity could be retained after 30 cycles. These results demonstrate that the cycle performance of SnO_2 nanoparticles has been significantly improved by using OC as buffer matrix in the SnO_2/OC composites according to example embodiments. The great capacity retention ability is believed to be related to the nanostructure of SnO_2/OC composites. The SnO_2 nanoparticles are advantageously homogeneously distributed both inside and outside of OC. The OC in the composite act as buffer matrix and advantageously provide enough void space for SnO_2 nanoparticles located on both internal and external OC surfaces to accommodate the volume expansion upon lithium insertion. Furthermore, the OC is also able to keep SnO_2 nanoparticles against agglomeration and advantageously enhance the electronic conductivity of the composite.

Data from rate-capability tests (current density varied from about 1 to 5 $mAcm^{-2}$, corresponding to mass current density about 178 to 890 mA/g) of SnO_2 and composite electrodes are given in Fig. 5(b). At about 2 mA/cm^2 , the capacity of SnO_2 electrode gradually falls nearly to zero, whereas the composite electrodes still maintained around 270 mAh/g after 60 cycles. When the current density is increased to about 5 $mAcm^{-2}$, the composite capacity was still kept around 100 mAh/g without any fading, suggesting an excellent cyclability and high rate performance of SnO_2-doped OC electrode.

In example embodiments a nanostructured onion-like hollow carbon material has been synthesized by pyrolysis of the mixture of phenolic resin and iron compound in N_2 atmosphere. The SnO_2 nanocrytals OC composites were obtained by impregnating $SnCl_2$ and further oxidationfor incorporation into Li-ion batteries. Owing to the crystalline hollow nanostructure of OC as buffering matrix in the example embodiments, batteries incapacitating the SnO_2/OC composites exhibited high specific capacity, excellent cycle stability and rate capability when using as anode materials for Li-ion battery, and alleviated the volume change of SnO_2 nanoparticles during the charge/discharge processes.

It will be appreciated by a person skilled in the art that numerous variations and/or modifications may be made to the present invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects to be illustrative and not restrictive.

CLAIMS

1. The use of hollow carbon spheres formed by a template-free formation process in the fabrication of an anode of a Li-ion battery.

2. The use according to claim 1, comprising doping the carbon spheres with Tin oxide nanoparticles.

3. The use according to claim 2, wherein the idoping is performed such that the Tin oxide nanoparticles are present on the carbon spheres and inside the carbon spheres.

4. The use according to any one of claims 1 to 3, wherein the carbon spheres have a size of less than 100nm.

5. The use of according to claim 4, wherein the carbon spheres have a size in a range from about 30 to 50nm.

6. The use according to any one of the preceding claims, wherein the template free fabrication process comprises carbonisation of phenolic-formaldehyde resin with the aid of a metallic catalyst.

7. The use according to claim 6, further comprising applying an acid solution to remove the metallic resin.

8. The use according to claims 2 or 3, wherein the impregnating comprises applying a Tin containing alcohol solution and oxidation of the carbon spheres.

9. A Li-ion battery comprising an anode formed by the use according to any one of the preceding claims.

10. The battery according to claim 9, wherein the carbon spheres are attached at the anode by way of a carbonaceous additive and a poly binder.

11. A Li-ion battery comprising an anode incorporating hollow, Ti oxide doped carbon spheres having a size smaller than about 100nm.

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