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PG and Research Department of Chemistry, Presidency College (Autonomous), Chennai-600 005, India

Synthesis of SnO_2@C Nanoparticles with Enhanced Storage Capacity for Lithium Ion Battery anodes

E. Priyadharshini[1] & S. Srinivasan[1]*

[1,1*]Department of Physics, Presidency College, Chennai- 600 005, India.

Abstract: The SnO_2 @ carbon nanoparticles have been successfully synthesized using commercial filter paper as the carbon source and tin dichloride dehydrate ($SnCl_2$ $2H_2O$) as a precursor. The SnO_2@C nanoparticles were characterized by XRD, SEM&EDX, TGA, FT-Raman, techniques. The crystalline nature of the synthesized particle was examined by Powder X-ray diffraction (XRD) analysis. The SEM analysis is used to identify the surface morphology of prepared samples. The purity of SnO_2 compound was confirmed by energy dispersive X-ray diffraction study. Thermal stability of the SnO_2 @ carbon nanoparticles was studied using Thermo gravimetric (TG) and Differential thermal (DT) analyses. A qualitative study was done by FT-Raman spectral investigation and assigned the various vibrational modes to confirm its purity. When studied as anode materials for lithium ion batteries, such unique electrodes with the long ability and a high discharge capacity due to the existence of the carbon layer.

Keywords: Tin oxide, Carbon nanoparticle, Lithium-ion battery, Anode materials.

Introduction

Energy conversion and storage device in current society[1]. The carbonaceous materials are the most commonly used anode materials for Rechargeable Lithium ion batteries are the most promising candidates for electrochemical lithium ion battery due to their low cost and low electrochemical potentials with respect to lithium metal[2]. To meet the demands of future high power and high energy density lithium ion batteries, it is challenging to explore novel anode materials with high reversible capacity, long cycle life and high safety at low cost. In this respect, metal oxides such as Fe_2O_3, Fe_3O_4, Co_3O_4 and SnO_2 have attracted much attention as improved anode materials because of their high theoretical specific capacities[1].The different types of carbon including graphite[3] and coke[4] have been studied as anodes for the lithium ion battery. Out of these various carbon materials, graphite is favored because it possesses a high theoretical capacity of 372 mAh/g, has desirable potential profile for Li-ion intercalation and, is much cheaper and also provides good cycle life and safety[5]

It is well known that lithium ion battery get wider and wider application in today's information rich society and has become one of the most potential chemical power sources[6]. Tin oxides have been proposed as alternative anode materials with high energy densities and stable capacity retention in Lithium ion batteries[7]. It is a potential candidate primarily due to its high capacity (790 mAh g^{-1}). However the practical application of

SnO_2 is limited by its poor cycling performance due to the large volume change (up to 250%) to the reduced Sn form SnO_2 which causes mechanical failure and loss of electrical contact[8], A carbon coating is widely used for preventing the exfoliation of the inner active material as well as improving the electrical conductivity of electrode materials such as carbon decorated SnO_2 and iron oxides because the carbon coating tightly wraps the surface of the active materials, it somehow cannot effectively release the large strain caused by volume expansion and also increase the resistance for the lithium ion to reach the core of active materials[9].Up to now,various tin dioxide-based carbon composite anode materials, such as tin oxide-graphite[10], tin oxide-graphene[11], tin oxide-carbon nanotubes[12] etc., have been prepared, and their electrochemical performances have been investigated. However, the introduction procedure of carbon in composite material was usually complicated and costly [13-14]which limited their practical application. Here in, we report a simple one step process to fabricate large-scale SnO_2 @ carbon nanoparticle as anode materials for lithium ion battery. The key features of this method are easy preparation, low cost, mass production and non-toxic source materials. Moreover, the method provides an easy strategy for the controlled introduction of carbon to optimize the performance of lithium ion battery using SnO_2 @ carbon nanoparticle as anode materials.

Experimental section

Material synthesis

All the chemicals were analytical grade and used without further purification. In a typical procedure and synthesis of the SnO_2 @ carbon nanoparticle, 0.1 mol of tin dichloride dehydrate ($SnCl_2.2H_2O$) was dissolved in 100 mL of ethanol. The solution was then transferred into the conical flask, sealed, and stirred at 70°C for 4 h. Subsequently, the commercial filter papers as a carbon sources (quantitative ashless, Grade No.40, what men) were immersed in the solution for 24 h at room temperature, and dried at 80°C. The treated filter papers were finally sintered at 425 and 475°C in muffle furnace under atmosphere. The weight of a piece of filter paper is 0.46g .The weight of the treated filter paper without sintering is increased to 1.86 g.

Materials characterization

The crystal structure of the sample was determined by X-ray powder diffraction. (XRD) analysis was performed with a Rigaku D/ max -2500 V, using filtered Cu Kα radiation. The morphology of the synthesized nanoparticles was examined by scanning electron microscope (SEM, Hitachi Japan S-34100). The energy-dispersive x-ray (EDX) was done with the help of SEM equipped with EDX facility. Raman spectra were recorded using a confocal microprobe Raman system (LabRam-001, 632 nm as excitation source). Simultaneous Thermo gravimetric analysis (TGA) was performed with a Perkin- Elmer Diamond TGA apparatus from room temperature to 800°C in air at a heating rate of 10°C min^{-1}.

Electrochemical measurement

The electrochemical test was characterized in a CR2032-type coin cell. Metallic Li was used as the negative electrode. The working electrode was fabricated by compressing a mixture of the active materials (SnO_2), conductive material (acetylene black), and binder (polytetrafluoroethylene) at a weight ratio of 80: 10: 10 onto an aluminium grid at 10 Mpa. The electrode was dried at 80°C for 12 h before assembly. The well mixed slurry was coated onto a copper foil, and pressed after drying for better contact between the coated film and the current collector. The as prepared electrodes are abbreviated as SnO_2 –CS, SnO_2@Carbon –PVDF according to the used active material and binder. A pure lithium foil filled was used as the counter electrode, and celgard 2400 as the separator. The coin cells were galvanostatically discharged – charged at different densities between 0.01 and 2.5 V on a battery testing system. The electrolyte solution was 1 M LiPF6/ethylene carbonate (EC)/diethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1 : 1 : 1 by volume) Discharge–charge curves were recorded from 2.5 to 0.01 V using a Roofer Battery Tester. All electrochemical measurements were carried out at room temperature.

Results and discussion

XRD analysis

Fig.1. shows the XRD pattern of as prepared and heat treated samples at various temperatures (425 and 475°C). All the characteristic diffraction peaks can be assigned to the tetragonal structure (P42/ mnm No.136, JCPDS 41-1445) of SnO_2 with lattice parameters of a=b=4.7386 Å and c=3.1865 Å. The absence of carbon

peaks can be ascribed to the formation of amorphous carbon .The intensities of the peaks located at 26.8° increases significantly and their full width half maximum (FWHM) decreases with increasing the sintering temperature. This indicates that crystalline size increases as the sintering temperature increases. The crystallite size of SnO_2 can be estimated by the Debye Scherrer formulad = 0.9 λ/β cosθ. Where d is the grain size, β is the FWHM, θ is the Bragg angle, λ is the X-ray wavelength of Cu kα radiation, the average crystallite sizes of the sample calculated by the Scherer equation using the high intensity peak (110) was18.4 nm (425°C), and25.4nm (475°C)respectively. The average size becomes larger as the sintering temperature increases which was coincide with result of XRD

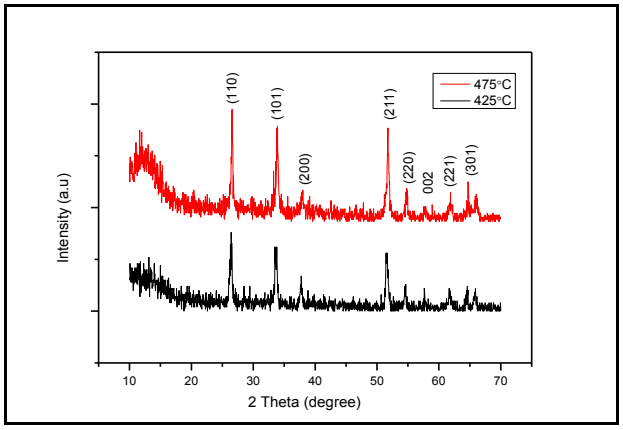
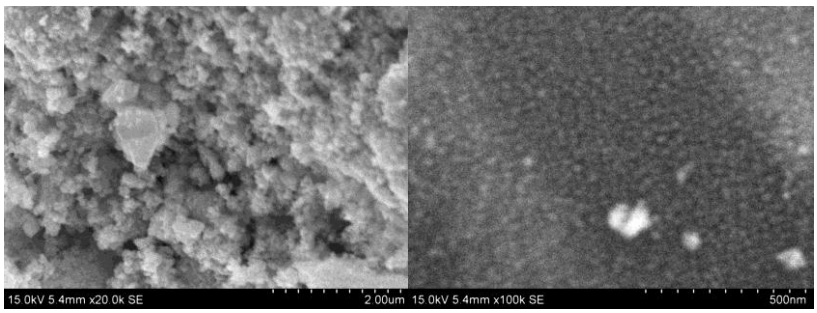


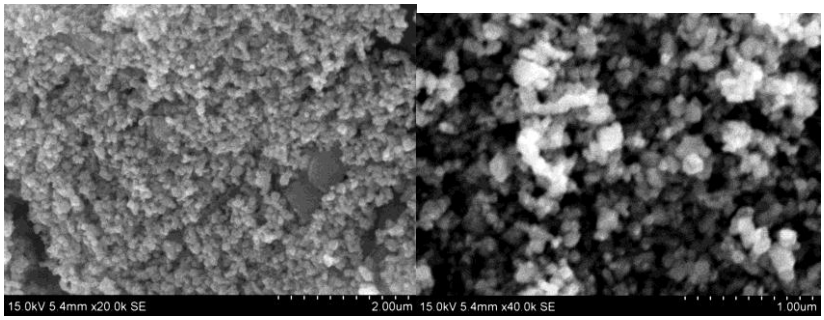
Fig.1. XRD patterns of the annealed a different temperature of SnO_2@C Nanoparticles

SEM analysis

SEM images representing surface morphology of the SnO_2 @C nanoparticles with different annealing temperatures 425, and 475 °C. The images low and high magnifications are shown in fig.2(a,b,c,d) The micrographs of high magnification SEM picture show uniform shape with different sizes. It is seen that the microstructure of these nanoparticles are quite similar except size. Moreover, the morphological characters of the original filter paper, a typical cellulosic structure, are faithfully inherited in the sintered samples. In the inset of the fig.2a is the clearly reveals that the nanoparticles in SnO_2@C NPs



(a) **(b)**

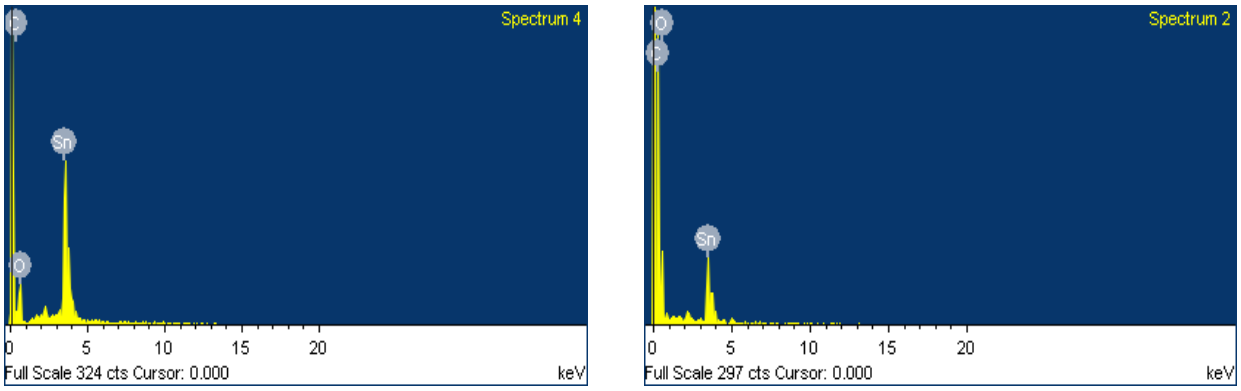


(c) **(d)**

Fig.2. Typical SEM images of SnO_2@C Nanoparticles at a two different temperatures 425 ° C (a), (b) and 475 ° C (c),(d)

Energy Dispersive Spectroscopy Analysis

The quantitative analysis of the nanoparticles was carried out by Energy Dispersive Spectroscopy and the spectrum obtained shown in the fig.3. From the spectrum it is clear that only Sn, C and O are present in the nanoparticle which confirms the purity of SnO_2 @ carbon nanoparticle. The EDS spectra of the samples prepared at different calcinations temperatures: (a) 425°C, (b) 475°C and as shown in the Fig.3 (a,b) respectively. In the entire sample the oxygen (atomic %) is observed to be almost twice that of tin, hence confirming the chemical composition of SnO_2@C nanoparticles.



(a) **(b)**

Fig.3. EDS spectra of the obtained SnO_2@C Nanoparticles prepared at (a) 425° C and (b) 475° C

Thermal analysis

Fig.4. shows the thermal stability of SnO_2@ C nanoparticle using thermo gravimetric (TG) analysis and differential thermal analysis (DTA) was carried out in air atmosphere. The samples were heated from 25°C to 800°C at a rate of 10°C min^{-1}. The TGA results of the SnO_2 @ carbon nanoparticle shows two weight loss regions. It clearly indicates that the two weight losses mainly take place at the temperature below 700°C. The first weight loss occurs in the temperature range of 30-120°C corresponding to the removal of water and the residual organic molecular absorbed on the samples, while the second weight loss in the temperature range of 200-600°C is ascribed to the oxidation of the carbon nanoparticles. The carbon is burn off at the temperature over 700°C for all samples.Therefore, according to the change in weight before and after the oxidation of carbon, the weight of carbon in samples can be calculated, which is 23.732% and 20.812%for the samples prepared at 425 and 475°C, respectively.

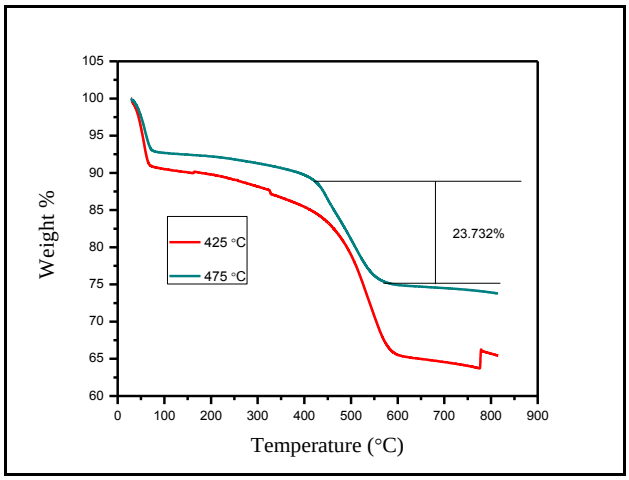


Fig.4. Thermo gravimetric analysis of SnO_2@ C Nanoparticles Synthesized at Different temperature

FT-Raman spectroscopy

The FT-Raman spectra of the SnO_2 @C nanoparticle at different temperatures were shown in Fig.5. The peaks at 1596 and 1698 cm^{-1} correspond to the D band and the G band, respectively, which are characteristic

Raman peaks for carbon materials. Since G band with E_{2g} symmetry, ascribed to ordered sp^2 carbon at 1596 cm^{-1} and a D band with A_{1g} symmetry at 1698 cm^{-1}, ascribed to disordered carbon, edge defects, and other defects oriented sp^3 bonded carbons such as, dangling bonds, vacancies, and topological defects. The symmetry breaking is a likely reason, because impregnated SnO_2 nanoparticles made the graphene layers more wavy or curly in SnO_2 due to stronger interaction, which further reduced the sp^2 domain size of graphenelayers.

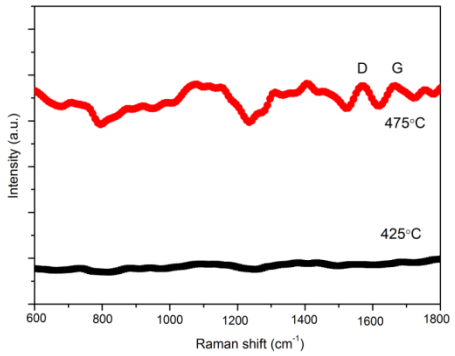


Fig.5. Raman spectra of the SnO_2@C Nanoparticles annealed at different Calcinations temperatures (a)425 °C and (b) 475 °C.

Charge – discharge

The first charge and discharge voltage profile of SnO_2 @ carbon nanoparticle annealed at 500 °C was shown in fig.7. The charge –discharge studies was carried out at a constant current rate of 0.1C in the range of 0-0.9V. The first discharge step, where the irreversible reaction is $SnO_2 + 4\ Li \rightarrow Sn + 2\ Li_2O$ takes place. The first irreversible specific capacity was determined and it is in the region of about712 mAh/g, showing a good agreement with the theoretical value. This means at least for the first reversible cycle that all the deposited material is accessible for the Li-ions, i.e. contributes to the storage capacity. With increasing cycle number the capacity drops. This capacity loss is attributed to internal stress caused by the large volume change during the alloying process resulting in cracks and loss of active material. Though not yet sufficiently stable for technical applications, the observed cycle stability is in the range of typical tin-based materials but without the need of any binder and secondary treatment.

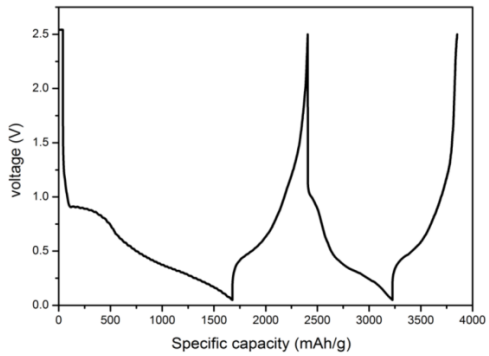


Fig.6. First Charge - discharge voltage profile of SnO_2 @C Nanoparticles

Conclusion

In summary SnO_2@C Nanoparticles have been synthesized by annealing approach using the commercial filter paper as carbonresource. When used as the anode materials of rechargeable LIBs, SnO_2@C could exhibit a high specific capacity, to improve the cycling performance of lithium ion battery. The method introduced of carbon to optimize the performance of LIBs using SnO_2 @C Nanoparticles as anode materials. Investigation shows that the sample with optimal content of carbon is sintered at 425ºCwith best specific capacity at a current density of 100 mAg^{-1}

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