Mesoporous, Nanocrystalline SnO_2 Anodes for Excellent Lithium Ion Storage

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INTRODUCTION

Lithium ions batteries are promising candidates for electrochemical energy storage due to their high energy density, enhanced rate capabilities and safety features.[1-3] They also find wide range of applications in portable electronic devices, implantable medical devices, electric vehicles etc. Use of graphite as anode (specific capacity of 372 mAh/g) is one of the main reasons responsible for the low specific capacity of Li-ion batteries, which is critical for many commercial applications including long range driving. Consequently, intensive research has been devoted to the development of high capacity anode materials. Due to superior theoretical capacity (781 mAh/g) than the conventional graphite anode, SnO_2 anode materials have attracted significant interest since the first report by Idota[4] et al. However, the critical factor that hinders the use of SnO_2 anodes is their poor cycling stability due to the huge volume change during the lithiation-delithiation (charge-discharge) process. A number of methods have been proposed to improve the cycling performance of SnO_2 anodes by minimizing the effects of drastic volume change. For instance, Li *et al.* reported that SnO_2 nanofibers effectively accommodated the volume change.[5] SnO_2 nanofibers anodes retained a good cycling stability at a high charge rate. Thin-films and nanosheets of SnO_2 were also studied for the same purpose.[6, 7] However, most of these electrode materials utilized complex and expensive synthesis methods. Introduction of solid alkoxide precursors into boiling water is a general very productive approach to prepare uniform mesoporous oxide materials, achieved through diffusion-controlled nucleation.[8] Here, we report synthesis and superior electrochemical performance of mesoporous SnO_2 nanoparticles through hydrolysis and heat treatment of tin tetraisopropoxide. This study also proved the requirement of higher order of mesoporosity for improving the cycling stability of nanocrystalline SnO_2 anodes with modified electrolytes.

MATERIALS AND METHODS

The preparation of ultrafine mesoporous SnO_2 was carried out by quick introduction of one gram of tin tetraisopropoxide (Multivalent Co UK) into 50 ml of boiling Milli-Q water with subsequent refluxing of the obtained milky dispersion for 30 min. The mixture was then left for precipitation overnight, the supernatant was removed by decantation and the solid residue was dried at 110^o C in air for 3 hours, and calcined at 400 °C for 1 h; heating and cooling rates were 10 °C/min. X-ray diffraction (XRD) patterns of the samples ($2\theta = 10–70°$) were collected using a Bruker D8 advance diffractometer equipped with a Lynx-Eye detector and parallel beam optics using Cu-Kα radiation ($\lambda = 0.154184$ nm). TGA investigations were made with Perkin-Elmer Pyris 1 instrument (heating rate 5 ^{o}C/min, temperature range 22°C – 600°C). TEM investigations were made using CM12 transmission electron microscope (Philips, Holland) with an accelerating voltage of 100 kV. SEM-EDS studies were carried out with a Hitachi TM-1000-μ-DeX tabletop scanning electron microscope. Textural characteristics (specific surface area, mean pore size, porous volume) were measured using nitrogen sorption at 77 K on a Quantachrome Autosorb 1 apparatus.

Electrodes for Li-ion batteries were prepared by mixing 80 % active material, 10 % carbon black and 10 % PVDF, and coated on a copper foil. These electrodes were assembled into coin-type using a Celgard 2500 polypropylene separator, and Li-foil as the counter electrode. The electrolyte consists of 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) and 3 volume % vinylene carbonate (VC). The electrochemical cells were assembled in a glovebox filled with high-purity argon (99.99%). Galvanostatic electrochemical measurements were performed using a Neware battery tester in the voltage range 10mV to 1.5 V.

RESULTS AND DISCUSSION

X-ray diffraction patterns (Fig. 1a) confirmed the phase purity of the as-prepared nanocrystalline cassiterite phase SnO_2. Particle size calculation using Scherrer equation and TEM images (Fig. 1b) confirmed the particle growth upon heat treatment. Calculated particle size of the as prepared and 400 °C heat-treated SnO_2 samples are 5 and 15 nm, respectively. N_2 adsorption-desorption isotherms of heat-treated SnO_2 sample demonstrated type IV with H1 type hysteresis,[9] and the as-prepared sample displayed no such hysteresis (Fig. 1c).

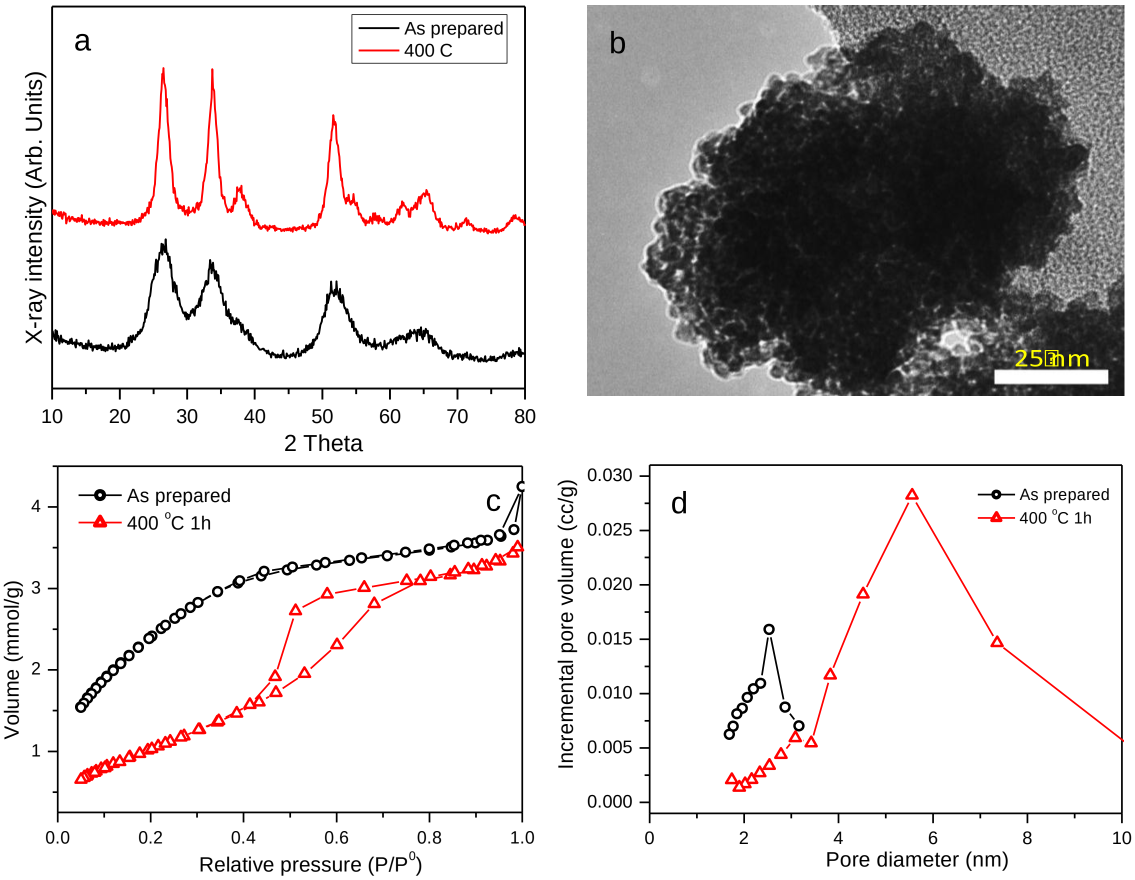

Fig. 1 (a) XRD patterns of as-prepared and heat-treated SnO_2 (400 °C in an air atmosphere); (b) TEM image of as-prepared SnO_2 sample; (c, d) N_2 adsorption-desorption isotherms and pore size distribution of as-prepared and heat-treated SnO_2 sample.

As-prepared SnO_2 sample has a high BET surface area of 204 m^2/g and average pore size of 2.2 nm. Whereas the surface area reduced to 87 m^2/g and pore size increased to 4.5 nm after 1 h heat-treatment at 400 °C (Fig. 1d). These results verified the particle growth during heat-treatment and generation of mesopores either in between the particles or on the individual SnO_2 nanoparticles.

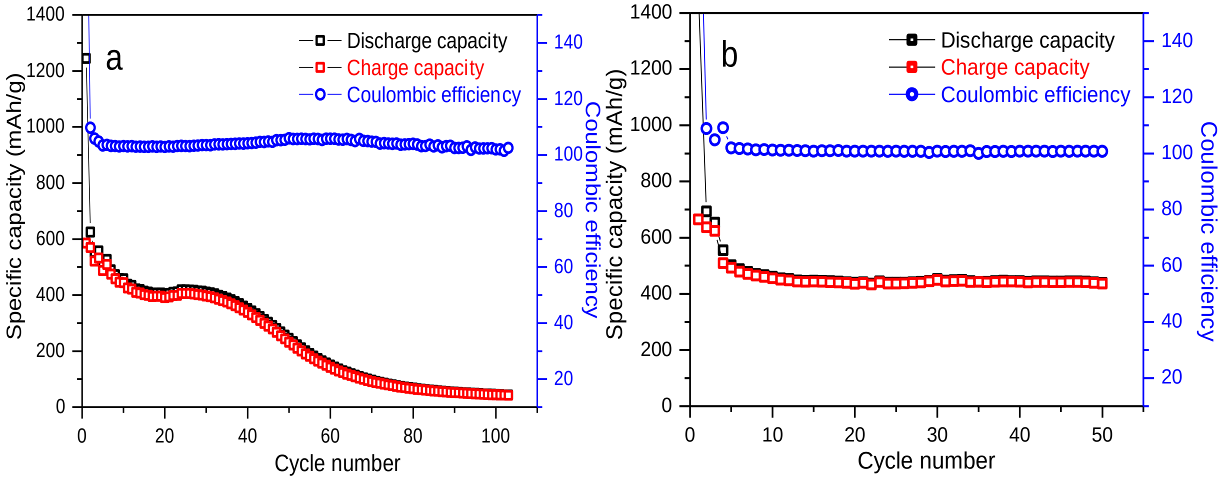

Fig. 2 Electrochemical performance of (a) as- prepared and (b) heat-treated SnO_2 nanoparticles

Despite of their small particle size and high surface area compared to the heat-treated SnO_2, as prepared samples displayed significant capacity fading upon prolonged cycling (Fig. 2a). On the other hand, low surface area SnO_2 heat-treated at 400 °C exhibited excellent capacity retention and coulombic efficiency on prolonged charge-discharge cycles (Fig. 2b). After 50 cycles at a charge-discharge rate of 2C (current density of 1560mA/g), mesoporous SnO_2 retained a specific capacity of 450 mAh/g, whereas the as-prepared showed a much lower capacity of 200 mAh/g. Electrochemical performance reported herein is superior to the previous reports on nanostructured SnO_2.[7,10] Vinylene carbonate used in this case also help to improve the cycling stability by forming polymeric surface films.[11] The excellent electrochemical performance of nanocrystalline SnO_2 heat-treated at 400 °C can be attributed to the high order mesoporosity, which facilitate superior electrode-electrolyte contact and strain relaxation during the lithiation-delithiation of Sn. Long term cycling performance and rate capabilities of the mesoporous nanocrystalline SnO_2 will be investigated.

CONCLUSIONS

In summary, mesoporous SnO_2 nanoparticles were successfully synthesized through the hydrolysis of tin tetraisopropoxide followed by heat treatment in air atmosphere. These nanoparticles demonstrated excellent Li-ion specific capacities and cycling stability. Electrolyte additive, vinylene carbonate was found to have a positive effect on the electrochemical cycling of current SnO_2 anode material. This study proved that high order of mesoporosity is highly beneficial for the electrochemical performance of inorganic SnO_2 nanoparticles.

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