

Short communication

Synthesis and characterization of SnO₂–polypyrrole composite for lithium-ion battery

L. Yuan^a, J. Wang^{a,c,*}, S.Y. Chew^{a,c}, J. Chen^{b,c}, Z.P. Guo^{a,c},
L. Zhao^a, K. Konstantinov^{a,c}, H.K. Liu^{a,c}

^a Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia

^b Intelligent Polymer Research Institute, University of Wollongong, NSW 2522, Australia

^c ARC Centre of Excellence for Electromaterials Science, University of Wollongong, NSW 2522, Australia

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Abstract

A conducting SnO₂–polypyrrole composite material was prepared by a chemical polymerization method. Nanosize conducting polypyrrole particles were uniformly coated onto the surface of the SnO₂ powder. The composite demonstrated significantly improved capacity and cycle durability compared with the bare SnO₂ electrode.

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1. Introduction

Recently, tin oxide and tin-based composite oxide electrodes have been investigated as possible negative electrodes for next generation lithium-ion batteries [1–4] due to the desirable material properties of high capacity on both a gravimetric and a volumetric basis and the low potential of Li ion intercalation. However, there is a large volume expansion and contraction problem associated with Li⁺ insertion and removal reactions, respectively. Thus, mechanical stresses, related to the volume changes, induce a rapid decay in mechanical stability. The electrode suffers from cracking and crumbling (‘pulverization’) as well as from consequent loss of electrode interparticle contact [5–7], resulting in the loss of capacity.

Many efforts have been devoted to attempt to reduce the capacity fading. Courtney [8] used “spectator ions” (e.g. B₂O₃, P₂O₅) that do not undergo lithium alloying to create a dilution effect and keep the tin regions small. Several authors have combined tin or tin oxide with graphite and carbon in an attempt to reduce capacity fade [9,10]. The approach has been to prevent the tin from becoming electrically disconnected through

the use of a conductive matrix. Recently, conducting polymer polypyrrole has been studied as an additive to improve the performance of cathode and anode materials in lithium-ion batteries [11–13]. The polypyrrole can work as a conducting matrix for the electrode particles. However, using polypyrrole powder as an additive for a tin-based anode material in lithium-ion batteries has not been explored.

In this study, SnO₂–polypyrrole composite was synthesized using a chemical polymerization method. The possibility of using SnO₂–polypyrrole composite as an anode material for lithium-ion batteries has been examined.

2. Experimental

2.1. Preparation of SnO₂–polypyrrole composites

Nanostructured SnO₂ powder was synthesized using a spray pyrolysis technique. A 1.0 M SnCl₂ aqueous solution was used as the spray precursor. The SnO₂ powder was obtained using a vertical type of spray pyrolysis reactor at 700 °C. Then SnO₂–polypyrrole (SnO₂–PPy) composites were then prepared by a chemical polymerization method with sodium *p*-toluenesulfonate (PTSNa) as the dopant, and FeCl₃ as the oxidant. The molar ratio of monomer pyrrole to dopant was 3:1, and the molar ratio of monomer to oxidant was 1:3. Firstly, SnO₂ was dispersed into a solution of sodium *p*-toluenesulfonate and pyr-

* Corresponding author at: ARC Centre of Excellence for Electromaterials Science, University of Wollongong, NSW 2522, Australia.
Tel.: +61 2 4221 5722; fax: +61 2 4221 5731.

E-mail address: jjazhao@uow.edu.au (J. Wang).

role. The mixture was stirred while the oxidation agent, FeCl_3 solution, was slowly added to the previous aqueous solution. The gradual change of color from light black to deep black indicated the formation of PPy. The reaction mixtures were then kept under the same conditions for 20 h. The total black mass was centrifuged, and then the mass washed thoroughly with distilled water until free of FeCl_3 . Finally, the black mass was dried at 50°C for 4 h under vacuum. Adding appropriate weights of the monomer to 1 g of the SnO_2 powder varied the polypyrrole content in the composites. Before polymerization, the monomer was distilled and guarded against exposure to light to prevent residual polymerization.

2.2. Materials characterization

Powder X-ray diffraction (1730 X-ray diffractometer) using $\text{Cu K}\alpha$ radiation was used to identify the crystalline phase of the SnO_2 powder. The morphologies and energy dispersion spectrum (EDS) mapping of the samples were obtained with a JEOL JSM 6460A scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was performed via a SETARAM Thermogravimetric Analyzer (France) in air to determine the changes in sample weight with increasing temperature and to estimate the amount of polypyrrole in the sample.

2.3. Electrochemical measurements

The electrodes were prepared by mixing 80 wt.% SnO_2 or SnO_2 -PPy composite with 10 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder with *N*-methyl-2-pyrrolidinone (NMP) solvent to form a slurry. The slurries were spread on copper foil substrates. After drying under vacuum, the electrodes were cut into a $1\text{ cm} \times 1\text{ cm}$ size. CR2032 coin-type cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) using lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK KgaA, Germany). The cells were galvanostatically charged and discharged in the range of 0.01–2.00 V at a current density of 50 mA g^{-1} . Cyclic voltammetry (CV) measurements were performed using a potentiostat (model M362, EG&G Princeton Applied Research, USA) at a scanning rate of 0.1 mV s^{-1} .

3. Results and discussion

Fig. 1 presents the XRD pattern of SnO_2 powder synthesized by the spray pyrolysis method. All diffraction lines are indexed to a tetragonal ($P4_2/mnm$) structure. The X-ray diffraction peaks for SnO_2 powder is very broad, indicating the nanocrystalline nature, and the peaks position agree well with JCPDS 41-1445. The average crystal size of the SnO_2 powder was determined by using the Traces Program and the Scherrer formula. The average crystal size was about 5–15 nm. The scanning electron micrographs of bare SnO_2 powder and SnO_2 -PPy composite are shown in Fig. 2(a) and (b), respectively. The SnO_2 particles are spherical agglomerates, which are around 1–2 μm in size.

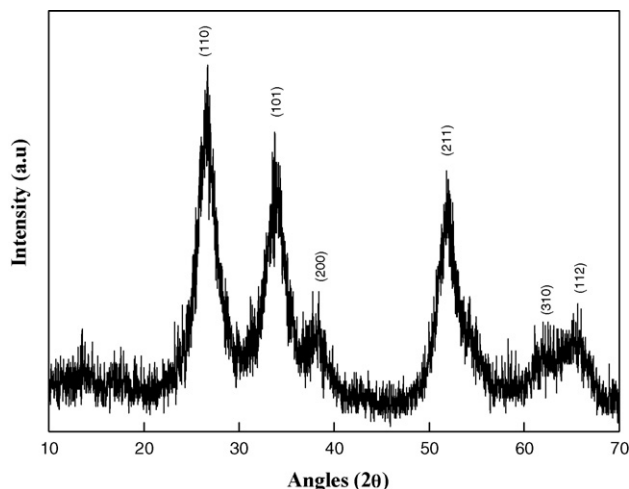


Fig. 1. XRD patterns of sprayed SnO_2 powder.

The SnO_2 -PPy composite shown in Fig. 2(b) indicates that the nanosize polypyrrole glues the SnO_2 particles together. To verify the formation of a composite of SnO_2 -PPy, EDS mapping analysis was used (see Fig. 2(b)–(e)). The bright spots correspond to the presence of the elements Sn, N and C, respectively, in which the N and C are the elements of polypyrrole. The results show that N and C are distributed uniformly throughout the whole area, which indicates that the polypyrrole particles had uniformly coated the surface of the SnO_2 powder.

For quantifying the amount of PPy in the SnO_2 -PPy composite materials, TGA analysis was carried out in air. Fig. 3 shows the TGA analysis of the SnO_2 -PPy composite samples along with those of bare SnO_2 and PPy powders. As can be seen from Fig. 3, bare PPy powder burns off at 700°C , while the bare SnO_2 powder remains stable in the temperature range used for this experiment. It can also be seen that the composites show weight loss over a temperature range of 300 – 700°C , which corresponds to the oxidation of PPy. There is no further weight change in the composites after the initial oxidation of PPy. Therefore, the change in weight before and after the oxidation of PPy directly translates into the amount of PPy in the SnO_2 -PPy composites. Using this method, it was found that the amounts of PPy in the composites were 9.12, 18.25 and 25.10 wt.% for the powders synthesized with various amounts of PPy, respectively.

The CV curves of pure SnO_2 powder and SnO_2 -PPy composite electrodes are shown in Fig. 4. The curves of the two samples are very similar. No additional peak was observed for the SnO_2 -PPy composite. This suggests that polypyrrole was just acting as a conducting additive, and not as an active material contributing to the charge–discharge process. The initial cycle charging and discharging curves are shown in Fig. 5. Note that the capacity is based on the weight of the active material. Although all the samples have shown some irreversible capacity losses, the amount of irreversible capacity loss of the SnO_2 -PPy composites is much lower than that of the pure SnO_2 .

Table 1 presents the irreversible capacity loss in the composites and the bare SnO_2 for various loading of PPy on SnO_2 . From the table, it can be seen that the initial irreversible capacity loss associated with bare SnO_2 is 69.2%, and

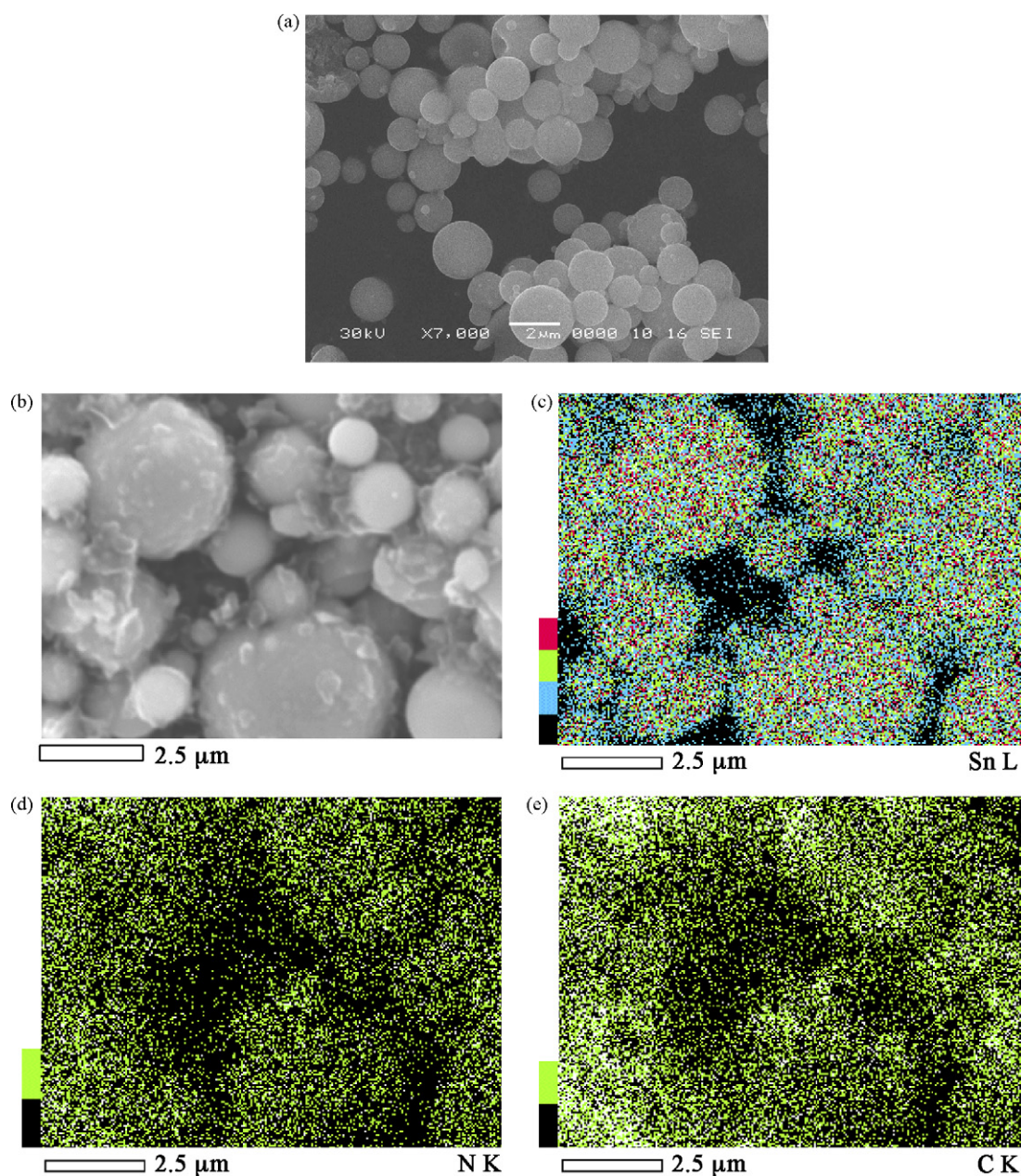


Fig. 2. SEM images for (a) bare SnO_2 powder, (b) SnO_2 -PPy (9.12 wt.%) composite, and corresponding EDS mapping for image (b) as follows: (c) Sn mapping, (d) N mapping, and (e) C mapping.

that the amount of irreversible capacity loss decreases with increasing polypyrrole content. The reason for this is that addition of conducting polypyrrole results in a conducting matrix, which provides a conducting backbone for the particles, thereby improving the conductivity of the electrode by reducing the

particle-to-particle contact resistance [13]. The PPy loading of 18.25% represents the optimum concentration, since further increases in polypyrrole would only add to the dead weight of the electrode, and consequently, to reduction in specific capacity.

Table 1
Initial irreversible capacity loss of the composites as a function of the polypyrrole content

Amount of PPy loading (wt.%)	Initial lithiation capacity (mAh g^{-1})	Initial de-lithiation capacity (mAh g^{-1})	Total irreversible capacity loss ^a (%)
0	1851.6	570.0	69.2
9.12	1456.3	562.2	61.4
18.25	1191.7	562.0	54.0
25.10	1085.4	521.0	51.9

^a Total irreversible capacity loss = [(initial lithiation capacity – initial de-lithiation capacity)/initial lithiation capacity] × 100.

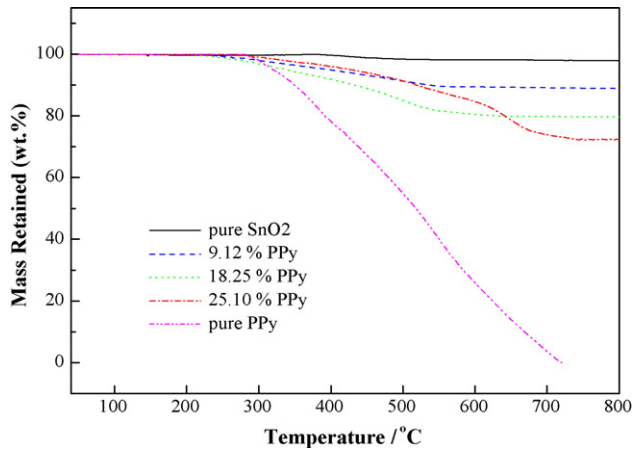


Fig. 3. TGA curves of SnO₂-PPy composite, bare SnO₂ powder and bare PPy powder.

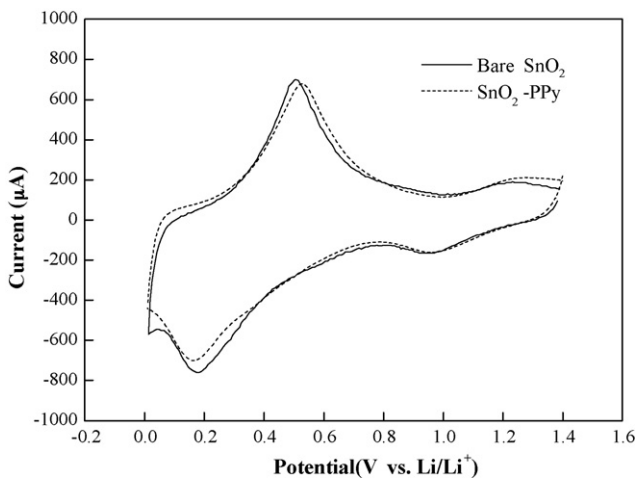


Fig. 4. Cyclic voltammograms of the electrodes composed of bare SnO₂ powder and SnO₂-PPy composite.

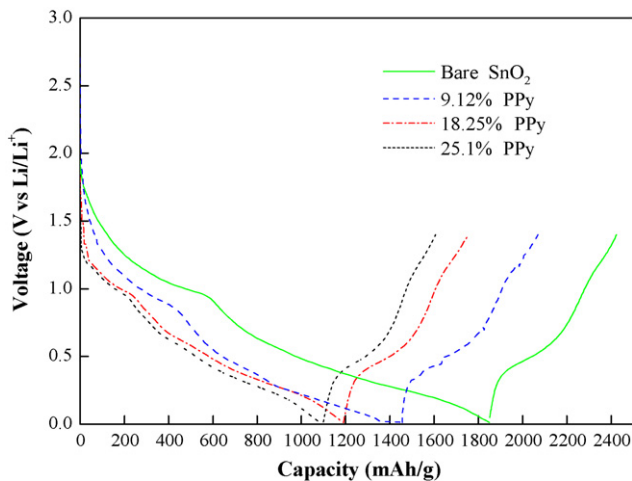


Fig. 5. The charge-discharge profiles of the electrodes of bare SnO₂ powder and SnO₂-PPy composite.

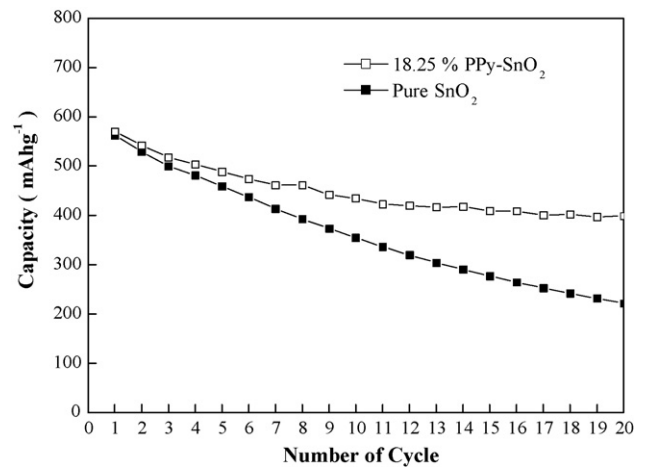


Fig. 6. Discharge capacities vs. cycle number for the electrodes of bare SnO₂ powder and SnO₂-PPy composite electrodes.

The discharge capacity versus cycle number for the composite and bare SnO₂ electrodes are shown in Fig. 6. After 20 cycles, the SnO₂-PPy (18.25%) composite and bare SnO₂ electrodes remained at 70% and 40% of their initial capacity, respectively. The SnO₂-PPy composite shows a significantly improved cycle-life performance compared with the pure SnO₂. The improvement in cyclic durability of the cell with SnO₂-PPy composite electrode may be due to the following reasons.

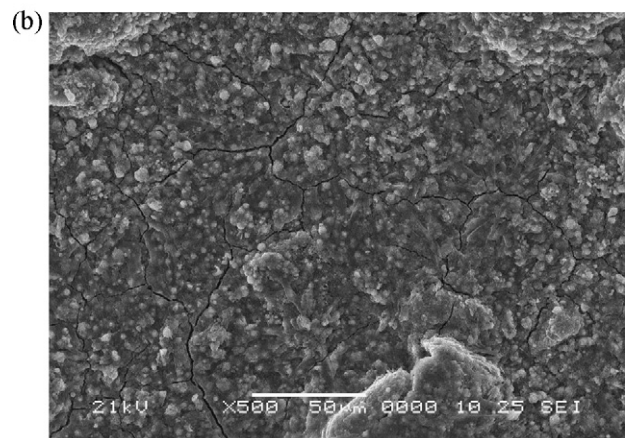
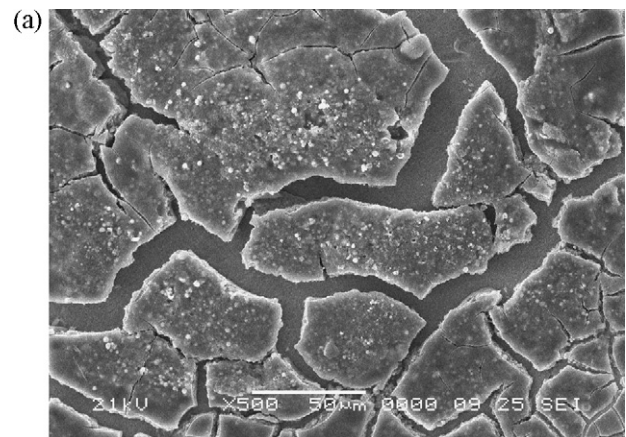
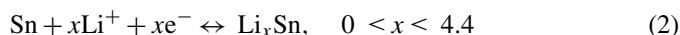
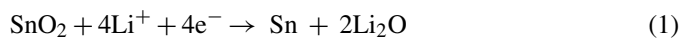


Fig. 7. SEM images of electrode: (a) bare SnO₂ electrode after 20 cycles and (b) SnO₂-PPy composite electrode after 20 cycles.

Tin dioxide reacts with lithium in a two-step process as follows [2]:



The first step in the irreversible reduction of SnO_2 results in the formation of tin regions dispersed within a Li_2O matrix. The second step is a lithium-alloying step that provides the reversible lithium storage capacity of these materials. The lithium-alloying step causes a large volume change in the Sn regions. As this material is cycled, the tin regions aggregate into larger regions. Even if the Li_2O matrix prevents these tin regions from cracking, when the tin regions become too large, they cannot withstand the volume change and cracking occurs, resulting in a loss of capacity. In this work, the conducting polypyrrole polymer serves not only for dilution, to prevent tin regions from aggregating [10], but also as an efficient matrix to prevent these tin regions from causing creaking and pulverization of the tin electrode [11]. This has been confirmed by SEM studies. Morphological study of the electrode after cycling shows that the cracks in the bare SnO_2 electrode are much larger than in the SnO_2 -PPy composite electrode (Fig. 7).

4. Conclusions

A novel SnO_2 -PPy composite, suitable for lithium-ion battery anodes, was prepared by chemical polymerization. The conductive polypyrrole serves as a conducting matrix to buffer the active material in the composite and thus reduce the volume

change associated with Li_xSn alloying and de-alloying reactions. The cyclability was improved compared to bare SnO_2 anodes.

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