Mesoporous Sn–TiO₂ composite electrodes for lithium batteries

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Mesoporous TiO₂ is prepared stable up to 500 °C with BET surface area of 603 m² g⁻¹ and pore size 6.9 nm, and Sn–TiO₂ composites based on the mesoporous TiO₂ show good potential as an electrode for lithium batteries with large capacity and structural integrity.

Since mesoporous materials (e.g. MCM-41) were first prepared in 1992, surfactant-templated synthesis procedures have been widely used for the preparation of highly-ordered mesoporous or nanostructured materials which would be difficult to prepare otherwise. The ordering in these materials is a consequence of a self-assembly process in an aqueous solution containing organic surfactants (anionic, cationic or neutral) and inorganic (oligo-) cations or anions. A wide range of mesoporous materials have been prepared using the structure-directing functions of electrostatic, hydrogen-bonding, and van der Waals interactions associated with amphiphilic molecules. Mesoporous TiO₂ was first prepared using a phosphate surfactant through a modified sol–gel process. Since a significant amount of phosphorus still remained in these materials, they are not pure titanium oxides. Recently, mesoporous TiO₂ has been prepared using amphiphilic poly(alkylene oxide) block copolymers as structure-directing agents and titanium inorganic salts as precursors in a non-aqueous solution. The mesoporous structure was stable up to 400 °C with BET (Brunauer–Emmett–Teller) surface area of about 200 m² g⁻¹. The use of amine surfactants resulted in mesoporous TiO₂ with BET surface area about 700 m² g⁻¹ (for as-synthesized powders) while heat treatment of the obtained materials in dry air at 300 °C led to loss of surface area and disappearance of the low angle diffraction peak in X-ray diffraction (XRD) patterns. In this study, mesoporous TiO₂ stable up to 500 °C has been successfully prepared using tri-block copolymers, (EO)ₓ–(PO)ᵧ–(EO)ₓ, as directing agents and titanium butoxide as precursor in an aqueous solution. Further, tin oxide was introduced into the mesoporous TiO₂ using a sol–gel process and then reduced in an atmosphere containing hydrogen to form a Sn–TiO₂ composite electrode for lithium ion batteries. The objective of our study is to create a nano-structured Sn–TiO₂ electrode for lithium ion batteries because tin-based compounds may offer much larger capacity than a lithiated carbon electrode. The structural stability of the tin-based materials during cycling is a major concern. Our approach to improve the structural stability was to incorporate tin compound into a mesoporous TiO₂ matrix, which is structurally stable and hence offers structural stability to the nanocomposite electrode.

Shown in Fig. 1 are small-angle XRD patterns of TiO₂ powder samples prepared using a tri-block polymer surfactant (Pluronic 103). The XRD pattern of the as-synthesized sample, Fig. 1(a), implies that the surfactant molecules were organized into a hexagonal superstructure after being aged at 50 °C for one week. In addition to the major peak at about 1° due to the (100) reflection, which corresponds to a d-spacing of 8.4 nm, small peaks due to the (110) and (200) reflections are also observable. The XRD pattern of the as-synthesized sample, Fig. 1(b), indicates that the mesoporous structure was retained during the removal of the surfactant by calcination at 500 °C in air for 1 h, although the superstructure had contracted slightly as evidenced by a slight shift of the XRD peaks toward larger angle.

The XRD pattern of the as-calcined sample, Fig. 1(c), indicates that the mesoporous structure was retained during the removal of the surfactant by calcination at 500 °C in air for 1 h, although the superstructure had contracted slightly as evidenced by a slight shift of the XRD peaks toward larger angle.
The as-calcined TiO\(_2\) sample calculated from the BET curve; (b) nitrogen isotherm plots of a Sn–TiO\(_2\) composite sample (the insert curve is the pore size distribution for the as-calcined TiO\(_2\) sample calculated from the BET curve).

Fig. 3 (a) Nitrogen isotherm plots of as-synthesized (aged at 50 °C for 1 week) and as-calcined (at 500 °C in air for 1 h) TiO\(_2\) samples prepared using Pluronic 103 as surfactant (the insert curve is the pore size distribution for the as-calcined TiO\(_2\) sample calculated from the BET curve); (b) nitrogen isotherm plots of a Sn–TiO\(_2\) composite sample (the insert curve is the pore size distribution for the composite calculated from the BET curve).

Fig. 4 Cyclic voltammograms of a mesoporous Sn–TiO\(_2\) composite as studied using a powder microelectrode: (a) the cycle 1; (b) the 2 to 10 cycles. The potential sweep rate was 0.5 mV s\(^{-1}\).

There was little change from 5th to 10th cycle, implying that the composite electrode may have good cycleability. Long-term cycling behavior of the composite electrode is still under investigation using constant current charge–discharge cycling test and will be reported in the near future.

In a typical preparation, 10 g titanium butoxide was dissolved in 20 ml absolute ethanol and 2.92 ml acetylatedone at room temperature before 10 ml distilled water was added, followed by stirring for another 2–3 h. In a separate beaker, 5 g Pluronic 103 was dissolved in 20 ml ethanol and 100 ml 2 M HCl solution. This surfactant solution was then slowly added to the titanium butoxide solution. The resulting solution was subsequently kept at 50 °C with continuous stirring for one week. The obtained solid product was washed and centrifuged three times using distilled water and then dried at 60 °C for 24 h and 120 °C for 5 d. The dried powder was fired at 500 °C for 1 h in air using an alumina boat to remove the surfactant.

To incorporate Sn into the pores of the mesoporous TiO\(_2\), SnCl\(_4\) was dissolved in water, to which NH\(_4\)(aq) was added to ensure all Sn\(^{4+}\) was hydrolyzed and precipitated. The solid product was washed and centrifuged three times using distilled water and was then dissolved in nitric acid to obtain a solution containing Sn\(^{4+}\). The mesoporous TiO\(_2\) powder was then immersed in the solution containing Sn\(^{4+}\) for a few days. The resulting powder was obtained after drying at 80 °C for one day and at 120 °C for another day, followed by reduction at 300 °C for 24 h in a hydrogen atmosphere.

The electrochemical properties of the mesoporous Sn–SiO\(_2\) electrode were studied in 1 M LiN(SO\(_2\)CF\(_3\))\(_2\)/EC+DMC electrolyte solution using a powder microelectrode technique.

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Notes and references