Preparation of mesoporous SnO$_2$–SiO$_2$ composite as electrodes for lithium batteries

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Mesoporous SnO$_2$–SiO$_2$ composite stable up to 600 °C with a BET surface area of 350 m$^2$ g$^{-1}$ and an average pore size of 3.4 nm is successfully prepared, which exhibits promising cycling properties as anodes for lithium batteries.

Following the discovery of the M41S family of mesoporous silicates using supramolecular templating approach, mesoporous materials have attracted considerable attention because of their tunable pore size, narrow pore size distribution, and remarkably large surface areas, which make them ideal candidates for catalysts, molecular sieves, and electrodes for solid-state ionic devices. 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 cations or anions. To date, a wide range of mesoporous materials have been prepared using the structure-directing functions of electrostatic, hydrogen-bonding, covalent bonding and van der Waals interactions associated with amphiphilic surfactant molecules.

Tin-based composite oxides are promising candidates for anodes in lithium batteries because of their much larger reversible capacity compared to carbonaceous materials. In this study, mesoporous SnO$_2$ stable up to 600 °C has been prepared using Brij 56 as a structure-directing agent and TEOS as precursor in an aqueous solution. Further, a tin compound is introduced into porous SiO$_2$ using a sol-gel technique to form SnO$_2$–SiO$_2$ composite. The objective of our study is to create a nano-structured SnO$_2$–SiO$_2$ electrodes for lithium batteries. The structural stability of the tin-based materials during cycling is a major barrier to the successful application of this material as anodes in Li-batteries. Our approach to improving the structural stability is to incorporate a tin compound into a mesoporous SiO$_2$ matrix, which is structurally stable and hence offers structural stability to the nanocomposite electrode. The mesoporous SnO$_2$–SiO$_2$ structure will facilitate the penetration of the liquid electrolyte into the electrodes and hence increase the rate of charge and discharge.

Shown in Fig. 1 are XRD patterns of mesoporous SiO$_2$ powder samples before and after calcination at 600 °C for 2 h prepared using Brij 56 as surfactant. The XRD pattern of the as-synthesized powders indicates that the surfactant molecules were organized into a hexagonal structure when aged at room temperature for 2 d. The peak at about 1.2° corresponds to the (100) reflection, which has a $d$-spacings of 6.8 nm. Thermogravimetric analysis shows that Brij 56 surfactant is completely removed upon calcination in air at 400 °C for 1 h. The appearance of a low-angle diffraction peak of the SiO$_2$ powder calcined at 600 °C for 2 h indicates that mesoscopic order is preserved upon removal of the surfactant by calcination, although the structure contracted slightly as evidenced from a slight shift of the XRD peak to a higher angle. The corresponding $d$-spacings is reduced to about 6.3 nm. The increased intensity of the XRD peak of the calcined SiO$_2$ indicates that the ordering of the mesostructure is improved during calcination. Shown in Fig. 1(c) is the XRD pattern of a SnO$_2$–SiO$_2$ composite. The peak is broader than that of pure SiO$_2$, suggesting that either the degree of ordering was reduced or the size distribution of the mesopores was broadened. However, the position of the peak did not change, implying that the $d$-spacings remained the same upon incorporating tin species into the pores of the mesoporous SiO$_2$. Further, the wide-angle XRD pattern shown in the inset of Fig. 1 indicates that the SnO$_2$ incorporated into the mesoporous SiO$_2$ is crystalline, rather than amorphous.

Shown in Fig. 2 are representative TEM images of SiO$_2$ and SnO$_2$–SiO$_2$ samples after calcination at 600 °C for 2 h. Mesostructures with short-range hexagonal order can be seen and the corresponding $d$-spacings are 6.3 nm for both SiO$_2$ and SnO$_2$–SiO$_2$ composite, which are close to those determined from the XRD patterns. The nitrogen adsorption isotherms of the SiO$_2$ and SnO$_2$–SiO$_2$ samples after calcination at 600 °C for 2 h are shown in Fig. 3 and the calculated Brunauer–Emmett–Teller (BET) surface areas are 1100 m$^2$ g$^{-1}$ for SiO$_2$ and 350 m$^2$ g$^{-1}$ for SnO$_2$–SiO$_2$ composite, respectively. The gas-accessible surface area of the mesoporous SnO$_2$–SiO$_2$ composite was greatly reduced due to partial occupation of the pores by

Fig. 1 Representative small-angle X-ray powder diffraction patterns of (a) as-synthesized SiO$_2$, (b) SiO$_2$ calcined at 600 °C for 2 h, and (c) SnO$_2$–SiO$_2$ composite calcined at 600 °C for 2 h. The wide-angle X-ray diffraction pattern of SnO$_2$–SiO$_2$ composite is shown in the inset.

Fig. 2 TEM micrographs of (a) 600 °C calcined mesoporous SiO$_2$ and (b) mesoporous SnO$_2$–SiO$_2$ composite.
the tin species incorporated into the mesoporous SiO₂. Both nitrogen isotherm curves have a well-defined step in the relative pressure $P/P₀$ ranging from 0.4 to 0.8, a characteristic of the filling of the framework-confined mesopores, suggesting that both SiO₂ and SnO₂–SiO₂ samples are mesoporous after calcination at 600 °C for 2 h. As shown in the inset in Fig. 3, the average pore size in the SiO₂ structure is 4.0 nm while that in the SnO₂–SiO₂ composite is 3.4 nm, implying that a thin SnO₂ layer has been incorporated into the channel surface of the mesoporous SiO₂.

The electrochemical behavior of the obtained SnO₂–SiO₂ composite oxide is further studied using cyclic voltammetry. Shown in Fig. 4 are the cyclic voltammograms (CVs) of a mesoporous SnO₂–SiO₂ composite, as studied using a powder microelectrode in the potential range between 2.0 and 0 V (vs. Li⁺/Li) with a scan rate of 0.2 mV s⁻¹. The potential was swept from 2.0 V in the cathodic direction down to the set limit (0 V) and then in the anodic direction. Two very small irreversible reduction peaks appeared near 0.6 and 0.9 V, respectively, in the CV of the first cycle. This is quite different from the CVs of mesoporous SnO₂ in a vacuum under vacuum. Mesoporous SnO₂–SiO₂ composite was obtained by calcining the dried tin nitrate–SiO₂ powder at 600 °C for 2 h in air. A powder microelectrode was used to study the electrochemical performance of mesoporous SnO₂–SiO₂ composite in 1 M LiN(SO₂CF₃)₂/EC+DMC electrolyte solution.

Notes and references
1 In a typical preparation using Brij 56 as the structure-directing agent, 1.093 g Brij 56 was dissolved in 80 ml H₂O by stirring at room temperature. 2.667 g tetraethyl orthosilicate (TEOS) was added to the Brij 56 solution and the solution was stirred at room temperature for 2 h. Subsequently, 1.333 ml 0.2 M NaF was added to the above solution and the solution was stirred at room temperature for 2 h while a milky sol was obtained. The milky sol was placed at room temperature for 2 d and a white precipitate formed progressively. The precipitate was finally filtered off, washed 5 times using distilled H₂O, dried at 60 °C in a vacuum oven and finally calcined in air at 600 °C for 2 h to remove the surfactant. Incorporation of tin compound into the pores of SiO₂ was achieved by immersing mesoporous SiO₂ powder into tin nitrate solution and then drying at 40 °C under vacuum. Mesoporous SnO₂–SiO₂ composite was obtained by calcining the dried tin nitrate–SiO₂ powder at 600 °C for 2 h in air. A powder microelectrode was used to study the electrochemical performance of mesoporous SnO₂–SiO₂ composite in 1 M LiN(SO₂CF₃)₂/EC+DMC electrolyte solution.


