In situ synthesis of encapsulated tin/tin oxides particles in porous carbon nano fibers with residual spaces around the particles and its electrochemical performance

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Tin, of which the theoretical capacity is 993 mAh g^{-1}, has been considered as one of the most promising anode materials in the coming decades. However, the pure tin suffers from large volumetric expansion during the charge-discharge cycles, which causes rapid fading of capacity. Recently, electrospinning has been used to fabricate anode material consisting of nano carbon fibers and nano metal/metal oxides particles showing good cycle performance. In this work, we report Sn/SnO_x/C electrospun fibers used as anode electrode directly, within specially designed porous structure and good cycle performance.

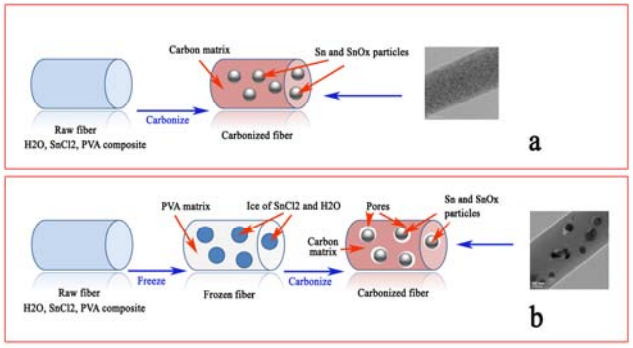

Figure 1. a) Preparation of Sn/C non woven fibers in our previous work [20]; b) In situ synthesis of encapsulated tin/tin oxides particles in porous carbon nano fibers with residual spaces around the particles

In our previous work [1], the raw fibers were carbonized directly after the electrospinning (Figure 1a). The final product consisted of nano sized tin/tin oxides particles and pyrolysis carbon fiber network. The tin/tin oxides particles were with very small size, around several nanometers. Such nano particles were well dispersed in the carbon fibers. In this work, novel encapsulated tin/tin oxides particles in porous carbon nano fibers with residual spaces around the particles (TEPC) were prepared by freezing and carbonization after electrospinning process (Figure 1b). After electrospinning, raw fibers were kept in icebox for several days firstly. The water transformed to ice during the freezing process, thus the raw fibers were separated into two phases. One was the PVA substrate, the other was the ice of $SnCl_2$ and H_2O mixture. The ice particles could also be homogeneously dispersed in the PVA substrate, because the precursor was homogeneous solution. After that, frozen fibers were carbonized under Ar/H_2 atmosphere. The PVA substrate was then transformed into pyrolysis carbon. The ice of water was evaporated and pores were formed in the pyrolysis carbon substrate. Meanwhile, the $SnCl_2$ was decomposed and reduced to tin and then grew up to particles encapsulated in the pores. Such tin particles were easily oxidized to tin oxides when the sample was kept in air. Then unique microstructure was formed, that was encapsulated tin/tin oxides in porous nano carbon fibers network. Tin/tin oxides particles were encapsulated in the pores. The size of the tin/tin oxides particles was smaller than the diameter of pores, therefore some spaces around the particles were remained.

The first attractive advantage of our study is the in situ formation of encapsulated tin/tin oxides particles in porous carbon nano fibers. The microstructure is unique. There is almost one particle in each pore (Fig. 2a and 2b). The pores are well dispersed in the pyrolysis carbon nano fibers. Furthermore, the size of the particles is smaller than the pores, thus there remain some spaces around the particles. Such residual spaces could act as the buffer of the large volumetric expansion of tin/tin oxides during cycles. This feature could greatly enhance the cycle performance of tin/tin oxides. Moreover, porous structure could also increase the capacity remarkably according to the micro-pore storage mechanism.

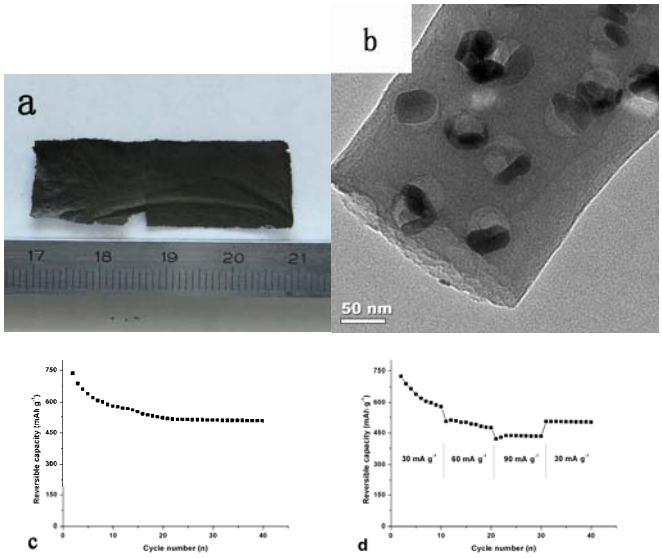

Figure 2. a) Photo of TEPC film; b) TEM of TEPC fiber; c) Cycle performance of TEPC; d) Rate performance of TEPC

As shown in Fig.2a, TEPC is a film with mechanism strength, which could be used as electrode directly without any binder or conductive additives. The BET surface area of TEPC is 352 m^2/g. In Fig. 2b, we can see the pores and tin/tin oxides particles encapsulated in the pores. There is almost one particle in each pore. The size of the particles is around 20 – 40 nm. We can also see some smaller particles in fibers from Fig. 2b. Actually, the size of the particles and pores could be controlled by adjusting the process. Fig.2c indicates the cycle performance of TEPC electrode. The reversible capacity fades quickly in the first 20 cycles and then becomes stable, that is 510 mAh g^{-1} after 40 cycles. TEPC also shows good high rate performance (Fig.3d). .

In summary, a novel encapsulated tin/tin oxides in porous carbon nano fibers with residual spaces around the particles has been prepared. Special nano porous structure of the TEPC electrode results in good cycle performance, which shows 735 and 510 mAh g^{-1} at 1st and 40th cycle, respectively. The basic idea of this method is to use phase separation to prepare porous structure. By controlling the solubility of the metal salt, in other word, the phase separation, the reduced metal particles could be in pores or combined in the pyrolysis carbon substrate. this method could not only be used to fabricate encapsulated tin/tin oxides in porous carbon nano fiber network, but also can be used to synthesize a series metal/metal oxide and carbon fiber composite, such as Co_3O_4/C, Fe_3O_4/C and so on. The authors believe that it may be more useful for Si/C composite, because the volumetric expansion of Si in cycles is more than 300%, which is larger than that of tin.

Reference:

[1] L.Zou, L.Gan, F.Y.Kang,et al. J.Power Sources. 2010, 195: 1216-1220

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