Cu_6Sn_5-SnO_2/carbon nanocomposite as high performance anode for lithium ion batteries

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Lithium ion batteries have been widely used as power sources for portable electronic devices and expanded to use in electric vehicles and energy storage system due to their high energy/power density, long lifespan, and so on. However, in the recent decade, many studies have been focusing on replacing the commercially used graphite anodes with Sn-based materials due to that Sn has a high theoretical capacity of $994mAhg^{-1}$, which is much higher than that of the graphite ($372mAhg^{-1}$). However, their extensively applications have not been realized because they suffer from serious capacity degradation due to the huge volume change (about 260% for $Li_{4.4}Sn$ formation) upon Li insertion and extraction [1].

In order to enhance the cycle performance of the Sn –based anode, dispersing the active Sn phase inside a matrix was employed, in which the host matrix component was expected to buffer the large volume change of the Sn particles during the Li insertion/extraction processes. Accordingly, various inactive/active metal elements (M), or high elasticity amorphous carbon materials, or non-crystalline oxide compounds were combined with Sn to form intermetallic Sn_xM_y phases, such as Cu_6Sn_5[2], or kinds of Sn-(M)-C nano-composites[3], such as Sn-C, Sn-Cu-C, acting as the LIB anodes. The large volume change of Sn upon Li insertion actually can be accomodated to some extent by the Cu/carbon buffer matrices and thus resulted in much enhanced cycle performance in these Sn-based anodes. Nonetheless, the preparation methods for most the reported Sn-M-C anodes are very complicated and time-consuming [4].

In this presentation, we will report a new simple way, ball milling of a composite with SnO_2, C, Cu and Sn under H_2 atmosphere, to prepare a nanostructure composite as anode for lithium ion batteries, in which nanosized Cu_6Sn_5 and SnO_2 phases were homogenously dispersed in the amorphous carbon matrix (see Fig.1). As the Cu_6Sn_5-SnO_2/carbon nanocomposite electrode were tested in a half cell using lithium foil as counter electrode, it showed quite good cycle performance. The electrode delivered a reversible capacity of 575mAh/g at the first cycle, which was gradually decreased to a value of 320mAh/g after 100 cycles (see Fig.2). A full coin-type cell, with $LiNi_{0.5}Mn_{1.5}O_4$ as cathode and the Cu_6Sn_5-SnO_2/carbon nanocomposite as anode were fabricated to further investigate the electrochemical performance of the as-prepared materials. The battery was tested by galvanostatic charge–discharge cycles and Fig. 3 shows the results in terms of voltage profiles of the 2nd, 3rd, and 4th cycle. The voltage profiles, which shows that the practical working voltage of the battery ranges between 3.8 V and 4.4 V, match those expected by the combination of the Sn–C and Li-$[Ni_{0.45}Co_{0.1}Mn_{1.45}]O_4$ voltage evolutions[5].

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References

[1]. J. L. Tirado, *Mater. Sci. Eng. R* 2003, 40, 103.
[2]. R. Z. Hu, M.Q.Zeng, M. Zhu, *Electrochim. Acta*, 2009, 54, 2843,
[3]. R.Z.Hu, H. Liu, M. Q. Zeng, H.Wang, M. Zhu, *J. Mater. Chem.* 2011, 21, 462.
[4]. A. R. Kamali, D. J. Fray, *Rev.Adv.Mater.Sci.* 2011,27,14,
[5] J. Hassoun, K. S. Lee, Y. K. Sun, B. Scrosati, *J. Am. Chem. Soc.* 2011, 133, 3139.

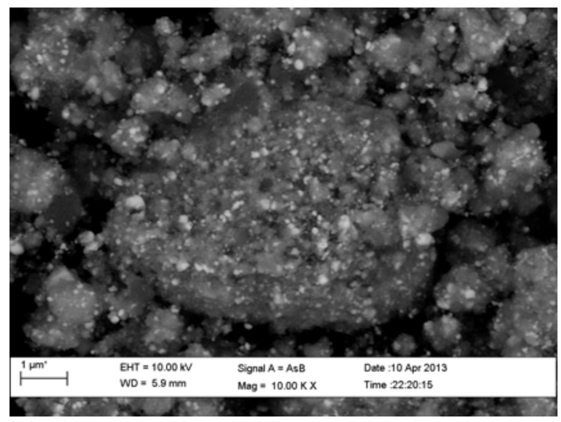

Fig.1 SEM image of the Cu_6Sn_5-SnO_2/carbon nanocomposite prepared by ball milling under H_2 atmosphere.

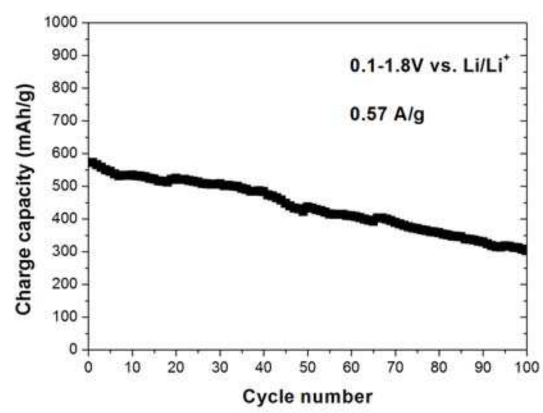

Fig.2 Charge capacity vs. cycle number of the half cell of $Li/LiPF_6/Cu_6Sn_5$-SnO_2/carbon.

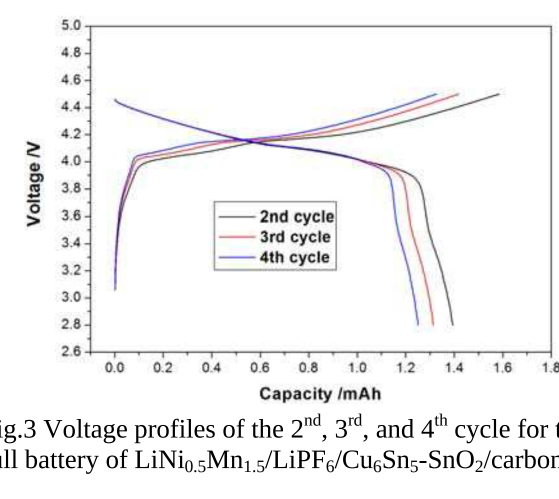

Fig.3 Voltage profiles of the 2nd, 3rd, and 4th cycle for the full battery of $LiNi_{0.5}Mn_{1.5}/LiPF_6/Cu_6Sn_5$-$SnO_2$/carbon .