An Amorphous Nanosized Tin-Zinc Composite Oxide as a High Capacity Anode Material for Lithium Ion Batteries

Zhengyong Yuan, Feng Huang, Jutang Sun,* and Yunhong Zhou
Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China

(Received December 10, 2001; CL-011248)

A new anode material for lithium ion batteries, $ZnSnO_3$, was prepared through the pyrolysis of $ZnSn(OH)_6$. The powder XRD analysis and TEM image demonstrated that the product is amorphous, the powder particles take the shape of square flake and the size is about 70 nm. Electrochemical measurements showed that the reversible capacity of the $ZnSnO_3$ electrode was more than 800 $mAh{\cdot}g^{-1}$.

Since the introduction of commercial lithium ion batteries with carbon as anode material in 1990 by Sony Energetics Inc., research has been undertaken to search for new anode materials in place of carbon (theoretical maximum capacity of 372 $mAh{\cdot}g^{-1}$) to improve energy density. Recently, the amorphous tin-based oxides have received considerable attention as promising new anode materials for lithium ion batteries due to their high volumetric and gravimetric capacity.[1–5]

Courtney and Dahn claimed that the reaction of tin oxides with lithium proceeds in two steps.[2] Initially, the tin oxides are reduced by lithium to form small clusters of tin metal, and dispersed in Li_2O framework. Further, lithium can be reversibly inserted into the metallic tin to form Li/Sn alloy. Lithium inserts into tin metal directly to cause a large volume expansion. The expansion and subsequent contraction on removal of lithium cause disintegration of the structure, and rapid loss of capacity and rechargeability.[3,6] Prior work has shown that both the size of the particles constituting the electrode and the size of the grains within these particles play critical roles in this decomposition process. Thus, electrodes composed of smaller particles and crystallites can increase the capacity and cycle life.[3,6]

In this paper, we report a new tin zinc composite oxide as an anode active material for lithium ion batteries. $ZnSnO_3$ was synthesized by means of the pyrolysis of precursor $ZnSn(OH)_6$ at 300 °C. X-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed that it was amorphous and nanosized material. The electrochemical properties were examined.

Stoichiometric Na_2SnO_3 (analytical grade) and $ZnSO_4{\cdot}2H_2O$ (analytical grade) were separately dissolved in distilled water and mixed with stirring, and precipitation occurred instantaneously. The white precipitate was washed with distilled water to remove Na^+ and SO_4^{2-} ions, finally was dried in an oven at 120 °C and the precursor $ZnSn(OH)_6$ powder was obtained. The prepared $ZnSn(OH)_6$ was heated at 300 °C for 6 h in air to form amorphous nanosized tin zinc composite oxide.

The electrochemical cell consisted of a $ZnSnO_3$ working electrode and a lithium foil counter-electrode. It was assembled in an Ar-filled glove box. The working electrode was prepared by pressing $ZnSnO_3$ powders, acetylene black and polytetrafluoroethylene (PTFE) binder (weight ratio of 80 : 15 : 5) onto a nickel gauze current collector. The electrolyte used was a 1 $mol{\cdot}L^{-1}$ solution of $LiPF_6$ dissolved in a 50 : 50 mixture by volume of ethylene carbonate (EC) and diethyl carbonate (DEC). The cell was discharged and charged between 2.0 and 0 V vs. Li^+/Li at a constant current density of 50 $mA{\cdot}g^{-1}$.

Figure 1 shows the XRD patterns of the precursor $ZnSn(OH)_6$ and the product $ZnSnO_3$. It confirms that the precursor is $ZnSn(OH)_6$ without any impurity phases. The XRD data correspond with the JCPDS card No. 20-1455 (Figure 1a). For the product, no diffraction peaks can be observed (Figure 1b). This indicates that the structure of $ZnSnO_3$ is amorphous or amorphous-like. The TG measurement reveals that the dehydration process of the precursor occurs at 150–280 °C and corresponds to a weight loss of 18.5% (theoretical weight loss of 18.89%). The TEM image of $ZnSnO_3$ is shown in Figure 2. The average size of the particles is 70 nm with the square flake shape.

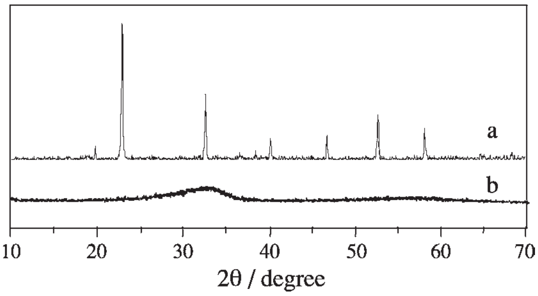

Figure 1. XRD patterns of precursor (a) and $ZnSnO_3$ (b).

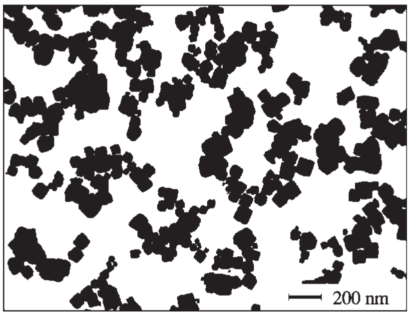

Figure 2. TEM image of $ZnSnO_3$.

In order to obtain a discharge-charge profile of $ZnSnO_3$, the cell was subjected to 10 cycles at constant current mode. The initial two discharge-charge curves are shown in Figure 3a. The difference between the first discharge curve and the rest discharge curves is indicative of the two different mechanisms in the lithium insertion process. In the first discharge curve, two plateaus at about 1.1 and 0.65 V can be observed. The voltage level of the first plateau matches with the potential of lithium inserted in the

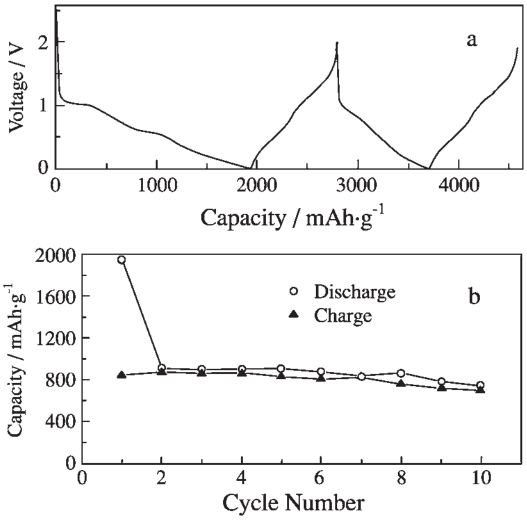

Figure 3. The first two cycle curves (a) and the variation in the discharge and charge capacity with the cycle number (b) of $ZnSnO_3$/Li test cell.

nanosized SnO_2,[7] and the voltage level of the second plateau matches with that in ZnO.[8] The discharge capacity reaches to 1951 $mAh{\cdot}g^{-1}$ and the charge capacity is 844 $mAh{\cdot}g^{-1}$ in the first cycle. A large irreversible capacity is associated with both the conversion of the Sn(IV) to Sn(0), Zn(II) to Zn(0) and the formation of the solid-electrolyte-interface (SEI)[9] region at the electrode/solution interface. If Li^+ ions reversibly insert into the metallic tin and zinc and form an $Li_{4.4}Sn$ alloy[2,5] and LiZn alloy,[8,10] the theoretical reversible capacity of $ZnSnO_3$ ought to be 623 $mAh{\cdot}g^{-1}$. In fact, the observed reversible capacity of $ZnSnO_3$ is more than 800 $mAh{\cdot}g^{-1}$, and it indicates that more lithium can be reversibly inserted into the anode except for the lithium of $Li_{4.4}Sn$[2,5] and LiZn[8,10] alloys. The lithium intercalation mechanism is studied at present in our laboratory for this material.

The cycling behavior within ten cycles is shown in Figure 3b. As mentioned above, the large irreversible capacity can be observed in the first cycle. The first-cycle irreversible loss was 57%. The ratio of discharge and charge is more than 90% in the subsequent cycles and an average fade in charge capacity of 1.8%/cycle. These results show that the amount of extracted lithium can be reversibly inserted.

An amorphous nanosized $ZnSnO_3$ demonstrates large capacity over the existing tin-based anode materials and a low insertion potential with respect to Li metal. Further work is needed to fully study the mechanism and to improve the cycle life and to make it a commercially available material.

This work was supported by The National Natural Science Foundation of China (No. 29971024).

References and Notes

1 Y. Idota, T. Kubata, A. Matsufuji, Y. Mackawa, and T. Miyaska, *Science*, **276**, 1395 (1997).
2 I. A. Courtney and J. R. Dahn, *J. Electrochem. Soc.*, **144**, 2045 (1997).
3 I. A. Courtney and J. R. Dahn, *J. Electrochem. Soc.*, **144**, 2943 (1997).
4 J. Y. Lee, Y. Xiao, and Z. Liu, *Solid State Ionics*, **133**, 25 (2000).
5 M. Mohamedi, S. Lee, D. Takahashi, M. Nishizawa, T. Itoh, and I. Uchida, *Electrochim. Acta*, **46**, 1161 (2001).
6 J. O. Besenhard, J. Yang, and M. Winter, *J. Power Sources*, **68**, 87 (1997).
7 N. Li and C. R. Martin, *J. Electrochem. Soc.*, **148**, A164 (2001).
8 F. Belliard and J. T. S. Irvine, *J. Power Sources*, **97–98**, 219 (2001).
9 E. Peled, *J. Electrochem. Soc.*, **126**, 2047 (1979).
10 F. Belliard, P. A. Connor, and J. T. S. Irvine, *Solid State Ionics*, **135**, 163 (2000).