HRTEM Study on Tin-based Oxides as an Anode Material for Lithium Secondary Batteries

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The Li-alloy anode system for lithium secondary batteries have been studied extensively as an alternative to the current commercial carbon-based anode materials due to its high energy density and specific capacity. This study was performed for the purpose of cycle enhancement of tin-based oxide anodes through the synthesis of nano-sized materials by chemical methods. We investigated the electrochemical characteristics of newly synthesized materials.

We have already presented that new materials ($Sn_3O_2(OH)_2$) based on tin oxides have been synthesized by pH adjustment in aqueous solution and organic solution[1]. To investigate the microstructural change of the material synthesized and cycled electrode, high resolution transmission electron microscopy (HRTEM) was employed.

Fig. 1 shows the HRTEM image of HRTEM and selected area diffraction pattern (SADP) of pristine $Sn_3O_2(OH)_2$ powders. It reveals randomly oriented nanocrystallites of a size ranges from 5 nm to 10 nm within amorphous phase. The mixed phases of nanocrystalline and amorphous are demonstrated by SADP. Fig. 2 show the HRTEM image and SADP of $Sn_3O_2(OH)_2$ electrode after 20 cycles. Tin crystallites were observed and their size ranges from 20 nm to 30 nm. It confirms the existence of Sn metal clusters by SADP. The HRTEM image and SADP of $Sn_3O_2(OH)_2$ electrode after 40 cycles is presented in Fig. 3. In this case, the size of tin crystallites is in about 30 nm - 70 nm. Courtney and Dahn have already suggested that tin atoms aggregate into clusters and the size of these clusters increases upon cycling[2]. R. Retoux et al. identified the increase of tin cluster upon cycling for thin film tin oxide electrode and suggested that the increase in cluster size results in an increase in void space and a possible loss of electrical contact[3]. Our HRTEM results clearly show the formation of tin clusters and increase of their size upon cycling. It appears that the growth of tin particles has a detrimental effect on this anode material. And the possible ways for avoiding tin aggregation have been suggested as using nanosized particles, adding foreign atoms to electrode or adjusting the cut-off voltage range [2].

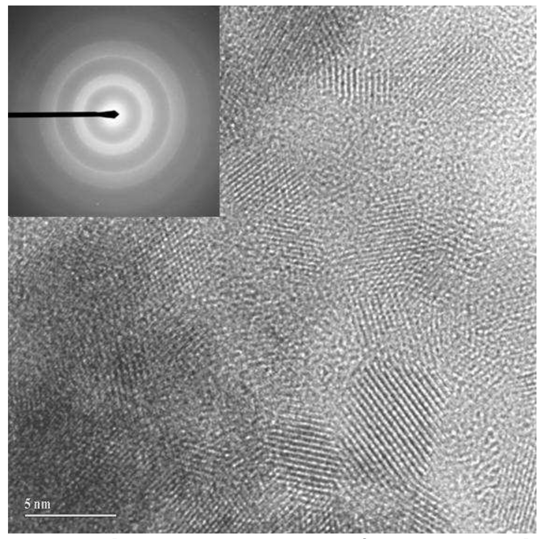

Fig. 1 The HRTEM image of HRTEM and SADP of pristine $Sn_3O_2(OH)_2$ powders

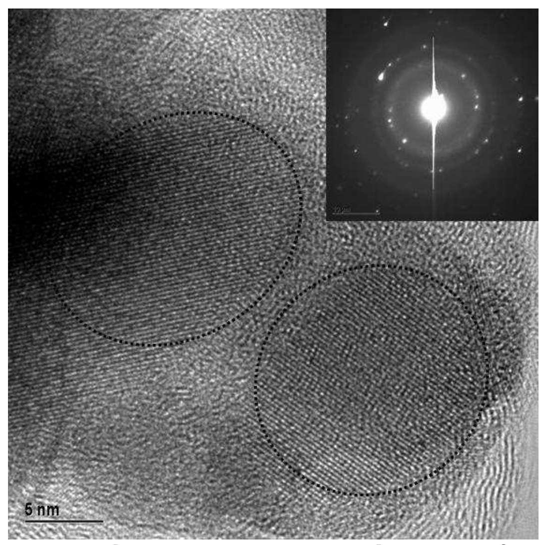

Fig. 2 The HRTEM image and SADP of $Sn_3O_2(OH)_2$ electrodes after 20 cycles

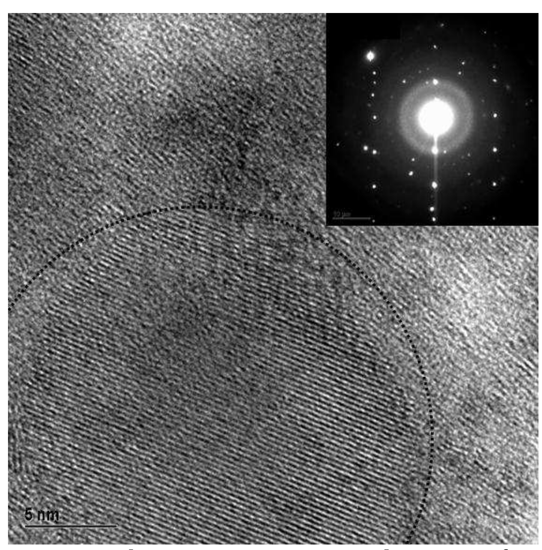

Fig 3. . The HRTEM image and SADP of $Sn_3O_2(OH)_2$ electrodes after 40 cycles

References

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[3] R. Retoux, T. Brousse, and D.M. Schleich, J. Electrochem. Soc., 146, 2472 (1999)