Synthesis and Electrochemical Properties of Sn-Fe-P anode for Lithium ion Batteries

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Introduction

Transition metal phosphides have attracted much interest as alternatives to graphite anode material for Lithium ion batteries due to their reversibility and large amount of lithium uptake at relatively low potential. [1] Kim et al. reported electrochemical properties and reaction mechanism of tin phosphide material prepared by mechano-milling method.[2] However, major problems of tin phosphides are their poor cycle performance because of change in morphology of tin phosphides induced lithium uptake and removal.[3]

In this work, we have introduced a novel ternary Sn-Fe-P anode material in other to improve the cycle performance. We will also discuss physical and electrochemical properties of Sn-Fe-P anode for lithium ion batteries.

Experimental

The Sn-P and Sn-Fe-P anode materials were prepared by solvothermal process. Tin metal, Iron metal, and red phosphorous were mixed with ethylendiamine in PTFE vessel of stainless steel reactor. The reactor was sealed and kept 200 °C for 20h. The product obtained washed several times by using distilled water, ethanol, and HCl solution. The physical and electrochemical properties of Sn-Fe-P and are examined by powder XRD, SEM, XPS, TEM and galvanostatic test. The Sn-P and Sn-Fe-P electrodes were prepared with a mixture of active material, Super P conductive agent and PAI binder. The charge-discharge tests were performed using a CR2032 coin-type cell. The Sn-Fe-P electrode tested using lithium foil as counter electrode. 1M LiPF₆-EC/DEC/DMC (3:5:2 by vol) with 10 wt% FEC. The charge and discharge rate was 0.1C with a cut-off voltage of $5 \sim 2000 \text{ mV}$.

Results and Discussion

Fig. 1 shows shows the typical XRD results of the (a) Sn-P and the (b) Sn-Fe-P compound powders prepared by solvothermal method. All peaks of obtained samples by solvothermal synthesis could be indexed as Rhombohedral Sn_4P_3 phase of $R\overline{3}m$ with small mixture of metallic tin. These compounds are layered structure consisting of Sn layers and P layers located alternately. It means that substitution of Sn with Fe cannot change the basic Sn₄P₃ structure, but slightly changes the intensity of Sn_4P_3 and metallic tin. By substituting Sn with Fe, the intensity of Sn₄P₃ peaks are weaken and increased the intensity of metallic tin compared with that of pristine Sn₄P₃, indicating the reduction of the average crystallite size of Sn₄P₃. The changes in intensity of these peaks assure that Fe has entered the Sn₄P₃ crystal without any other impurities.

Fig. 2 shows the cycle performances of (a) Sn-P (b) Sn-Fe-P half cells at 0.1C rate with voltage range from 2000 to 5 mV. The Sn-Fe-P anode exhibited a much

higher initial charge capacity than that of pristine Sn-P. Moreover, the charge capacity of Sn-Fe-P anode retained 420 mAhg⁻¹ after the 100th cycle, which was higher than that of the Sn-P. This demonstrated that substituting Fe in Sn-P structure could remarkably improve the structure stability and the cyclability of Sn-Fe-P anode.

References

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Fig. 1 The XRD results of the (a) Sn-P and the (b) Sn-Fe-P prepared by solvothermal method.



Fig. 2 The cycle performance of the (a) Sn-P/Li and the (b) Sn-Fe-P/Li cells with charge and discharge rate of 0.1C.