

# Si–Mn composite anodes for lithium ion batteries

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Received 20 May 2005; received in revised form 10 July 2005; accepted 13 July 2005

Available online 24 August 2005

## Abstract

Si–Mn composites were prepared by mechanical ball milling for different periods. The microstructure and electrochemical performance of the composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical methods. XRD showed that the materials prepared by ball milling were composites consisting of Si and Mn powders. The particle size was about 1  $\mu\text{m}$  from the SEM images. The Si–Mn composites after 60 h ball milling showed the best performance, especially when annealed at 300 °C for 2 h, which had a reversible capacity of 455  $\text{mAh g}^{-1}$  and an initial Coulomb efficiency of 52%. Mn acted as an inactive buffer of the Si–Mn composite electrode and enhanced the cyclic performance of the active center (Si). It was also observed that nanosized Si–Mn particles merged together after the insertion/extraction of lithium ions, which decreased the electric contact between the active materials and copper substrate. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Si–Mn alloy; Secondary lithium batteries; Mechanical alloying

## 1. Introduction

In recent years, many new materials have been investigated in order to meet the need of high-energy density for lithium ion batteries. A glassy tin composite oxide (TCO) [1] as a negative electrode was announced at the commercialization of a new Li-ion technology (STALION) by Fuji Photo Film Co. in 1997. Moreover, Si-based materials as anode candidates have been studied widely because of the highest theoretical capacity of about 4000  $\text{mAh g}^{-1}$  corresponding to  $\text{Li}_{21}\text{Si}_5$  [2]. However, the materials encounter a pulverization as anode materials caused by their extreme changes with the insertion/extraction of lithium ions. Recently, several methods have been performed to relieve such morphological changes of these materials: nano-structural particles, single or multi-layer thin film and active–inactive matrix. Si thin films used as anode materials have reached a comparative level [3]. However, a Si thin film is hard to commercialize widely for Li-ion rechargeable batteries due to the expensive fabrication technology. Si-based alloys with active–inactive matrix have received more attention. Ni–Si and Fe–Si [4] alloy powders, which were synthesized by high-energy mechanical

ball milling, exhibited capacity retentions of 780  $\text{mAh g}^{-1}$  (Ni–Si) and 360  $\text{mAh g}^{-1}$  (Fe–Si) after 25 cycles. Kim et al. [5] have synthesized Fe–Si multi-layer films and concluded that these materials had a better electrochemical performance because of the lower volume changes caused by the Fe layers.  $\text{Mg}_2\text{Si}$  [6] alloy prepared by mechanical alloying exhibited a capacity of 100  $\text{mAh g}^{-1}$  after 25 cycles and its cyclability was improved significantly after annealing at 600 °C.

Thin films of Si–Al–Mn were fabricated using a vacuum sputtering system described by Fleischauer and Dahn [7] and a broad range of Si–Al–Mn compositions varied in a linear and orthogonal manner. It has shown that Mn content had a considerable effect on first discharge specific capacity and irreversible specific capacity. Moreover, Si–Mn composites have shown good cyclic performance compared with the conventional silicon anodes in our previous work [8]. In this work, Si–Mn composites were prepared by mechanical ball milling for various milling times and the electrochemical characteristics were investigated.

## 2. Experimental

A mixture of silicon (–325 mesh, 99.6%) and manganese (–325 mesh, 99.6%) with an atomic ratio of 3:5 were put into

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a stainless steel vial. The vial was evacuated and then purged with pure argon. The ball milling was carried out in a planetary ball milling machine (ND-6) for different milling times (30, 45, 60, 72, 84 and 96 h) of 200 rpm. The powders were characterized by XRD and SEM. XRD was performed using a D/Max-rB diffractometer equipped with Cu K $\alpha$  radiation. The particle size and microstructure of electrode materials were observed by SEM (Hitachi S-4700) with an EDAX equipment. The sample electrodes after cycling were soaked into DMC and then dried to observe the SEM images.

The electrodes were prepared by drying an electrode slurry (85% of active material, 5% acetylene black and 10% of PVDF dissolved in *N*-methyl-2-pyrrolidone) on a copper foil at 120 °C for 14 h under vacuum. Cells were assembled in a glove box filled with argon using a lithium foil as a counter and reference electrode. Heat treatment of the electrodes was performed in a tube stove with argon flow at 300 °C. Cyclic voltammograms were conducted in the cell at 0.2 mV s<sup>-1</sup> using CHI630A. A Neware BTS was used for galvanostatic cycling with a potential range of 1.5–0.02 V at 0.15 mA cm<sup>-2</sup>.

### 3. Results and discussion

Fig. 1 shows that the XRD patterns of the powder composites prepared by mechanical milling for various periods.

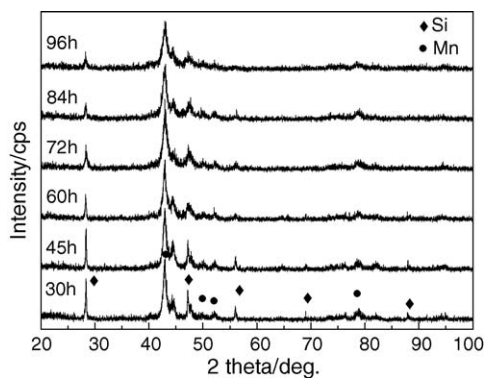


Fig. 1. XRD patterns of powders of Si–Mn composite for a variety of milling periods.

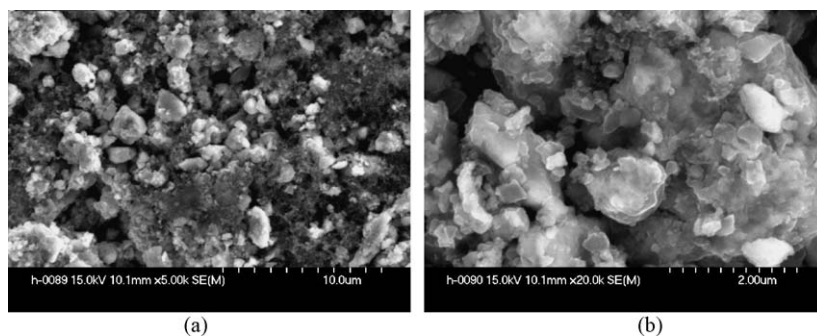


Fig. 2. SEM of the composite electrode: (a) electrode prepared by a mixture of Si–Mn composite milled after 60 h, acetylene black and PVDF and (b) zoom part of (a).

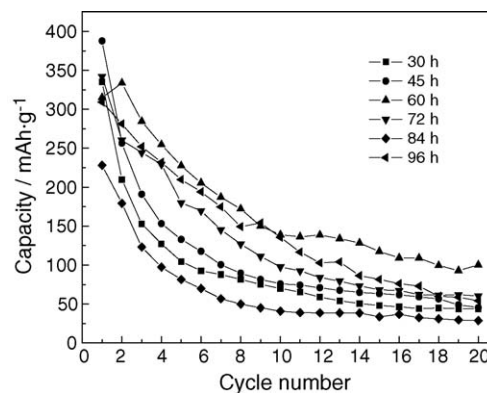


Fig. 3. Discharge capacity vs. cycle number of Si–Mn composite for a variety of milling periods.

From the result, we can conclude that the prepared materials are mixtures of Si and Mn powders. These peaks become broadened with increase of the milling period and almost disappear after milling for 84 and 96 h, especially the Si. Fig. 2(a) shows an image of the Si–Mn composite electrode in which the Si–Mn powders prepared by ball mill for 60 h was mixed with acetylene black (AB). The average particle size of the composite is 1  $\mu$ m. From the zoom image as shown in Fig. 2(b), it can be seen that Si–Mn composite particles are interspersed uniformly among (AB).

Fig. 3 shows that the composite material obtained after a milling time of 60 h exhibits good electrochemical properties. This material shows a specific capacity of about 315 mAh g<sup>-1</sup> and a retention capacity of 100 mAh g<sup>-1</sup> after 20 cycles. It is believed that decreasing the particle size could improve the performance of these materials. However, especially in the case of silicon, the cyclability of nanoparticles will decrease obviously due to the high surface energy of nanoparticles. That is why the cyclabilities of the composites ball milled for 84 and 96 h are less than that for 60 h. So, the composite with an appropriate particle size can retain morphological stability and achieve an excellent cyclability.

To improve the affinity of active materials and current collector, a heat treatment for the electrode at 300 °C for 2 h was

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