

Short communication

Innovative nanosize lithium storage alloys with silica as active centre

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Abstract

Two types of nanosize intermetallic alloy powders, NiSi and FeSi, are prepared by high-energy ball-milling. The alloys are used as electrode materials in lithium test cells. During lithium insertion into the alloy electrodes, Si acts as active centres, which react with Li to form Li_xSi alloys. A high lithium storage capacity of 1180 mA h g^{-1} is observed for the NiSi electrode, with some reversibility. A mechanism for the reaction of NiSi and FeSi with Li^+ is proposed. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The use of Li-alloys as anode materials in lithium-ion batteries could lead to improvements in specific energy and safety compared with carbonaceous materials [1–4]. The major drawback with Li-alloy electrodes, however, is their poor cycleability which is caused by mechanic cracking or crumbling due to volume expansion of the alloys on lithium insertion [5,6]. Recently, this problem has been largely overcome either by preparing ultrafine alloy powders (nanosize or amorphous) such as Sn and Sn–Sb [7–9] or by synthesizing intermetallic alloys with active and inactive elements such as FeSn and FeSn_2 [10–12]. In the latter case, the ductile inactive matrix is generated simultaneously with lithium insertion, which buffers volume changes of the alloys. Although most of these alloys have used Sn as the active element, Si can also alloy with Li to form Li_xSi to a maximum uptake of $\text{Li}_{21}\text{Si}_5$ with a theoretical capacity of 4000 mA h g^{-1} . It has been reported that a nano-Si composite electrode can deliver a large Li insertion capacity of 1700 mA h g^{-1} , but with the sacrifice of volumetric capacity due to the use of 40% carbon black to enhance the conductivity and provide a ductile matrix [13].

This investigation reports for the first time the preparation and lithium insertion properties of nanosize intermetallic alloys NiSi and FeSi with Si as the active centre.

These alloys demonstrate quite a large lithium storage capacity and some reversibility

2. Experimental

NiSi and FeSi alloy powders were prepared by high-energy ball-milling. Elemental powders of Si (–325 mesh, 99%, Aldrich), Ni (–100 mesh, 99.8%, Aldrich) or Fe (–325 mesh, 97%, Aldrich), as well as hardened steel balls, were put into a steel vial. The vial was initially evacuated and then filled with argon. Ball-milling was carried out in a Pulverisette-5 ball-milling machine (LABTECHNICS, Australia). The alloy powders were characterized by X-ray diffraction with a Phillips PW1730 diffractometer which used $\text{Cu-K}\alpha$ radiation, as well as by scanning electron microscopy.

The NiSi and FeSi electrodes were prepared by dispersing 80 wt.% active material, 18 wt.% carbon black and 2 wt.% polyvinylidene fluoride (PVdF) binder in dimethyl phthalate to form a slurry, which was then spread on to copper foil. CR2032 coin cells of Li/NiSi and Li/FeSi were assembled in an argon-filled glove-box (Mbraun, Unilab, USA). The electrolyte was 1 M LiPF_6 in a 1:1 (by volume) mixture of EC (ethylene carbonate) and DMC (dimethyl carbonate) provided by MERCK KGaA, Germany. The cells were galvanostatically charged and discharged at a current density of $80 \mu\text{A cm}^{-2}$ in the voltage range 0 to 2.5 V.

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3. Results and discussion

The X-ray diffraction patterns of the NiSi and FeSi alloy powders are shown in Fig. 1(a) and (b), respectively. The diffraction peaks are broad, which indicates small particle size and internal stress. A mixture of FeSi and Si was detected instead of a pure FeSi alloy. This is probably because it is more difficult to synthesize FeSi alloy through ball-milling than by conventional methods. From the width of the diffraction peaks, the average grain size was calculated according to the Scherrer equation (crystallite size = $k\lambda/\beta\cos\theta$) using the Traces Program [14]. The estimated average crystallite size for the NiSi and FeSi powders is about to 4 to 6 nm. Electron micrographs of the NiSi and FeSi–Si alloys are given in Fig. 2. The NiSi alloy powder produced by ball-milling is quite homogeneous (Fig. 2(a)). Due to the ultrafine nature of the grains, the particles tend to form large agglomerates, as shown in the micrograph. In the case of FeSi–Si powder, well-dispersed particles were observed together with large unalloyed Si particles. Energy dispersive spectroscopic (EDS) analysis confirmed that these large particles are elemental Si.

Several coin cells were assembled to examine the lithium insertion properties of NiSi and FeSi–Si electrodes. The discharge curves of two of these cells are shown in Fig. 3. The open-circuit potentials of NiSi and FeSi–Si electrodes

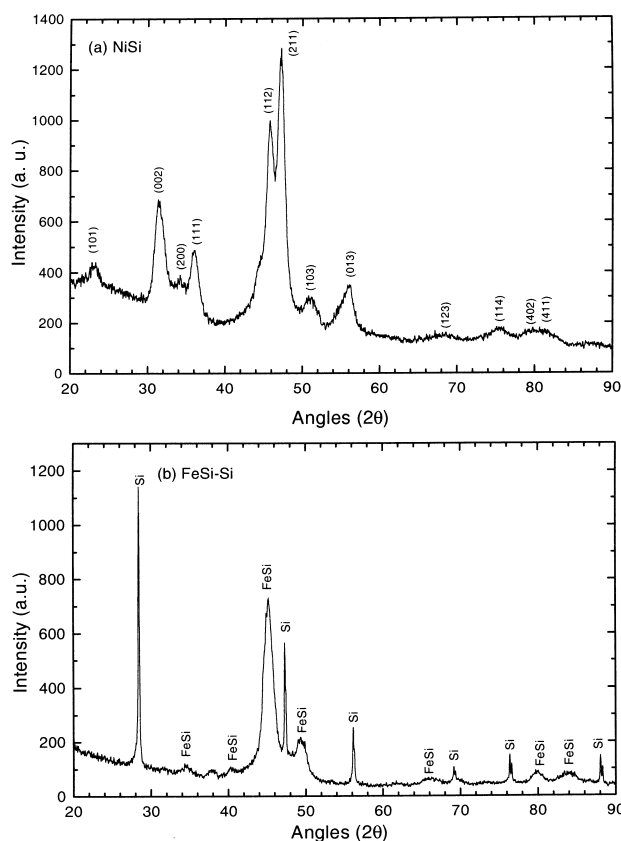


Fig. 1. X-ray diffraction patterns of: (a) NiSi powder; (b) FeSi–Si powder.

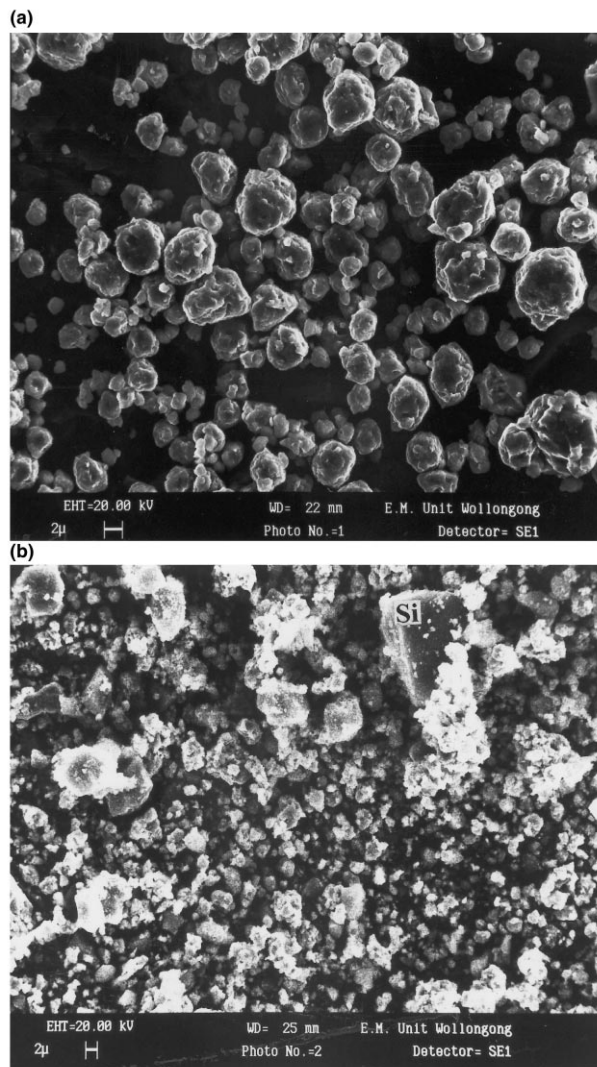
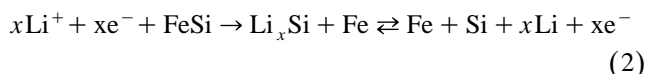
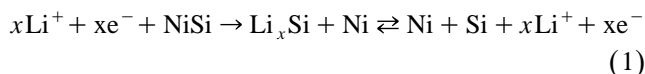


Fig. 2. Electron micrographs of ball-milled alloy powders: (a) NiSi powder; (b) FeSi–Si powder.

are in the range 2.8 to 3.2 V vs. Li/Li^+ in the un lithiated state. On discharge, the potential of the NiSi electrode rapidly falls to 2.0V and then follows an approximately half parabolic curve until the cut-off voltage of zero volts (Fig. 3(a)). No obvious discharge plateau was observed. The first discharge capacity is 1180 mA h g^{-1} , which corresponds to the insertion of 3.82 mol of Li/mol of NiSi. If all of the Si in the NiSi compound reacts with Li to form $\text{Li}_{4.2}\text{Si}$, the theoretical capacity for NiSi alloy would be 1297 mA h g^{-1} . Thus, the lithium storage capacity on the first discharge is close to the theoretical value. In the first charge, however, only 80% of the lithium ions were reversibly extracted. During subsequent discharge–charge cycles the capacity of the NiSi electrode gradually degraded. In general, the shape of the discharge curve for the FeSi–Si electrode is different from that of the NiSi electrode. When discharging, the voltage of FeSi–Si electrode drops to 0.3 V more rapidly than that of the NiSi

electrode. On the first discharge, there exists quite a large polarization resistance. This is probably related to the presence of Si. Since Si still retains a coarse particle size after ball-milling (as shown in Fig. 1(b)), it could participate in the lithiation reaction. The kinetics of the reaction of coarse Si with Li are slow.

In NiSi and FeSi–Si electrodes, elemental Ni and Fe are inactive to Li. By contrast, Si reacts with Li to form Li_xSi alloys. Thus, the following mechanism is proposed for the reaction of NiSi and FeSi with Li, based on the reaction mechanism of Sn and Sn–Sb with Li in lithium cells [15].



After the first discharge, when lithium is extracted from the alloy electrode, it is assumed that Ni or Fe and Si are retained in their elemental state. In this case, Ni or Fe will act as a buffering matrix for the formation of Li_xSi on the subsequent cycle.

The degradation of the discharge capacity of NiSi and FeSi–Si electrodes with cycle number is shown in Fig. 4. The FeSi–Si electrode reached its maximum capacity on

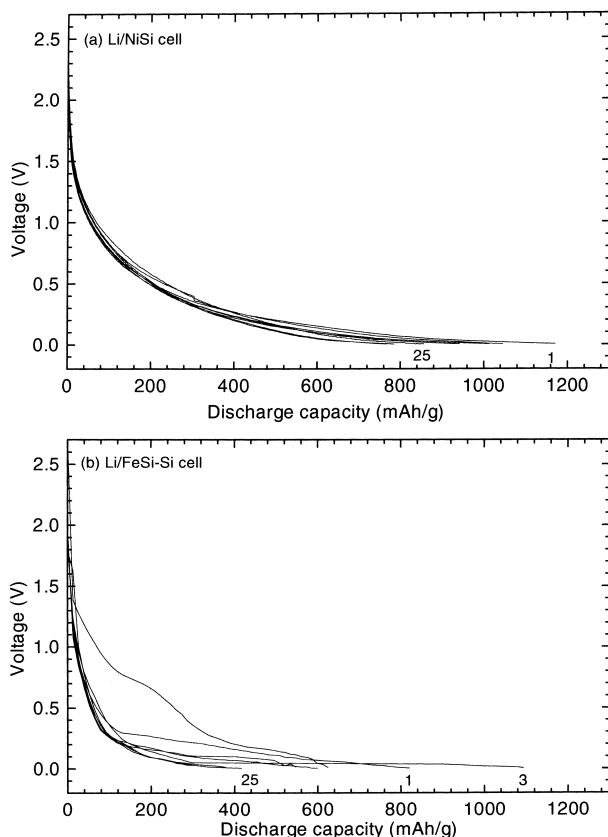


Fig. 3. Discharge curve of: (a) Li/NiSi cell; (b) Li/FeSi–Si cell.

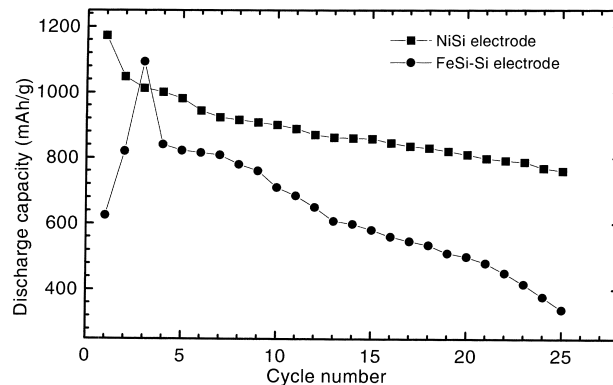


Fig. 4. Discharge capacities of NiSi and FeSi–Si electrodes

the third cycle instead of on the first cycle for the NiSi electrode. The rate of capacity decrease for the FeSi–Si electrode is faster than that of the NiSi electrode, which could possibly be related to the presence of large particles of Si in the FeSi–Si electrode. The cycling behaviour of the NiSi electrode appears reasonable. Nevertheless, it still cannot compete with commercial carbon materials. During the charge–discharge cycle, some Li is trapped with Si in the electrode. It is critical to utilize all of the Li source in the battery system. This could be realized through optimization of the crystal structure and morphology of the electrode materials. To this end, nano NiSi or FeSi could be a choice as an anodic material for lithium-ion batteries with double or even triple the capacity of carbonaceous materials.

4. Conclusions

Nanosize NiSi and FeSi–Si powders can be synthesised via high energy ball-milling. When NiSi is used as an electrode in lithium cells, it provides a high lithium storage capacity of 1180 mA h g^{-1} on the initial discharge, in which Si acts as an active element to combine with Li to form Li_xSi . This reaction is partially reversible and its capacity declines with each cycle. Further optimization of the synthesis of NiSi could lead to the improvement of the electrochemical performance of this electrode material.

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