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Improvement of thermal stability and safety of lithium ion battery using SiO anode material



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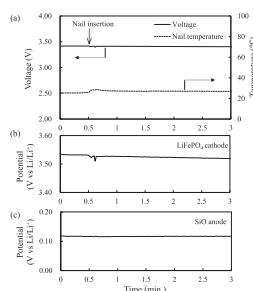
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HIGHLIGHTS

- Nanosized Si-rich and SiO₂-rich phases are uniformly mixed in SiO material.
- A LiFePO₄/SiO lithium ion battery exhibits high thermal stability at 80 °C.
- A 1.16 Ah laminated LiFePO₄/SiO cell remains safe after a nail penetration test.
- Li contents in Si-rich and SiO₂-rich phases are the same after a nail penetration.

GRAPHICAL ABSTRACT



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ABSTRACT

The thermal stability, in terms of cycle and rate performances at 80 °C, and its safety related to lithium ion batteries composed of a LiFePO₄ cathode and SiO anode are investigated. Based on an STEM-EELS analysis, the SiO powder is found to have an amorphous structure, in which nanosized Si particles (Si-rich phase) are uniformly dispersed in the SiO₂ matrix (SiO₂-rich phase). During the charge/discharge cycling, the cell exhibits a satisfactory cycle performance with a discharge capacity retention of 93.6% and a voltage retention of 93.9% at the 1500th cycle. Also, the charge and discharge capacity retentions at 10 C are 97.5% and 94.7%, respectively, together with a limited polarization, demonstrating its high rate performance. Furthermore, a 1.16 Ah LiFePO₄/SiO laminated cell shows negligible voltage and temperature changes during the nail penetration test. The Li concentration in the active material (Si-rich phase) is found to be almost the same as that in the SiO₂-rich phase after the test. This high thermal stability and safety may be due to the formed layer from the SiO₂ matrix, preventing any side reaction from occurring on the Si surface and isolating the internal current path during the nail penetration.

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1. Introduction

The lithium ion battery (LIB) has been widely utilized as an energy storage device in many electronic applications due to its favorable energy density and cycle performance. Especially, in recent years, with the rapidly growing market for the electric vehicle (EV), hybrid

electric vehicle (HEV) as well as stationary battery storage systems, the need for LIBs is thus shifting to larger scale applications [1–3]. Hence, not only improvement in battery performance, but also in its safety are imperative for large-scale LIBs because these batteries are more likely to be used in a hostile environment, such as high temperature, vibration and shock. To meet the severe safety requirement, a safe material should be chosen for the large-scale LIB design. Nowadays, lithium iron phosphate (LiFePO_4) is commonly used as a promising cathode material for the LIB due to its favorable thermal stability [4]. The release of oxygen from this cathode material at higher temperature can be prevented based on the strong P–O bonding in the crystalline structure [5], thus reducing the risk of thermal runaway. However, for the anode material, the commonly used graphite [6] is still not fully satisfactory because the formed solid electrolyte interface (SEI) on the graphite surface tends to decompose at a temperature of 60 °C [7], leading to a continuous exothermal reaction between the lithiated graphite and the electrolyte [8]. The accumulated heat would increase the battery's internal temperature resulting in the decomposition of the other battery materials, such as the electrolyte, separator, and electrode materials. Once the separator loses its function, the thermal runaway can be easily triggered by an internal short circuit between the cathode material and the carbonaceous anode material, which is an intrinsically good conductor of electricity. Therefore, safe anode materials should be the focus in developing large-scale LIBs.

As an alternative, SiO, composed of Si and SiO_2 , has attracted much attention among the anode materials due to the high theoretical specific capacity of Si, which is around ten times that of the conventionally used graphite [9–12]. Also, the SiO_2 matrix plays an important role in preventing the large volume change in Si during the charge/discharge processes, thus reducing the risk of structural pulverization and electrical disconnection between the active material and the current collector [12–15]. Miyachi et al. [16] reported that not only the strong Si–O bond, but also the formed Li-silicates after a full charge process can act as a buffer to compensate for the volume expansion, leading to a better cycle performance. Moreover, the SiO anode material has been reported to have an improved thermal stability and rate performance [17], showing that this material is a potential candidate for use in large-scale LIBs. Nevertheless, a long cycle performance at high temperature and safety issue, which are regarded as significant indices for the practical use of large-scale LIBs, have not been sufficiently investigated. In order to realize the practical use of SiO in large-scale LIBs, improvements in the battery thermal stability and safety are imperative.

In this study, we focused on the thermal stability and safety of LIBs using LiFePO_4 cathode and SiO anode materials. Particularly for the SiO, its properties were investigated through TEM analysis. Since the PI binder was reported to be advantageous for the cycling stability of SiO^{17} , it was thus adopted in preparing the anode. The developed LIB showed an improved long cycling stability (over 1000 cycles) and rate performance at 80 °C. Its safety was also confirmed by the nail penetration test. The reasons for the high thermal stability and safety were discussed.

2. Experimental

To determine the characteristics of the SiO powder (Osaka Titanium Technologies Co., Ltd.) used as the anode material, its microstructure was analyzed by transmission electron microscopy (TEM, JEM-ARM200F, JEOL). Electron energy-loss spectroscopy (EELS) along with a scanning transmission electron microscopy (STEM) was also performed to specify the chemical state of the Si. As for preparing the cathode, LiFePO_4 (Sumitomo Osaka Cement Co., Ltd.) powders were mixed with conductive agents including 2 wt% vapor growth carbon fiber (VGCF), 2 wt% acetylene black (AB) and 2 wt% active carbon, together with a 4 wt% water-based acrylic binder

to form the slurry. The prepared slurry was then pasted on a carbon coated aluminum foil sheet functioning as the current collector. The coated sheet was then preheated at 80 °C for 10 min before sending it to roller-press. After drying the sheet under vacuum at 160 °C for 6 h, the cathode was obtained. For preparing the anode, a mixture containing 79 wt% SiO powders, 1.5 wt% vapor growth carbon fiber (VGCF), 1.5 wt% acetylene black (AB) and 18 wt% PI binder (Ube Kosan Co., Ltd.) was dispersed in *N*-Methyl-2-pyrrolidone (NMP) to form a slurry before coating it on a stainless steel foil sheet. This coated layer was then preheated at 80 °C for 10 min, followed by vacuum drying at 300 °C for 9 h, to obtain the anode.

To investigate the electrochemical characteristics of the LIB composed of the LiFePO_4 cathode and SiO anode, a coin-type test cell (CR2032) was used. The anode was pre-doped with lithium ions to compensate its irreversible capacity of the SiO. The electrolyte in the test cell was 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) at the ratio of 1:1 (v/v) (Kishida Chemicals) with 1 wt% vinylene carbonate (VC). Also, a glass filter was used as the separator. The N/P ratio, based on the electrode capacity, was designed to be 2.8 for the cell in order to avoid the risk of lithium dendrite formation during the charge process. The cycling and rate tests were performed at 80 °C in the voltage range of 4–2 V using a charge–discharge machine (BLS series, Keisokuki Center Co., Ltd.). For the nail penetration test, a 1 Ah class laminated-type cell composed of LiFePO_4 cathode and SiO anode sheets was used. The details of the laminated cell are listed in Table 1. Before carrying out the safety test, the cell was charged to 4 V at the current rate of 0.1 C. A stainless steel nail, 3 mm in diameter, was used to penetrate the cell at a constant speed of 0.1 mm/s. To monitor the nail temperature during penetration, a thermocouple was located inside the center of the nail. Also, a reference electrode composed of Li metal was inserted inside the test cell in order to individually monitor the cathode and anode potentials.

3. Results and discussion

3.1. Characteristic of SiO anode material

Fig. 1(a) shows a TEM image of a SiO particle used for preparing the anode. No lattice fringe was observed in the microstructure, but uniformly distributed fine spots. The transmission electron diffraction (TED) pattern (inset) confirms that this particle has an amorphous structure. A magnified HAADF-STEM image of the SiO particle is shown in Fig. 1(b). Clearly, two separated phases exist in the SiO microstructure, which are indicated by the black and white areas. These two phases uniformly mix, and the particle size of each phase is around 2 nm. The black and white areas, which are respectively marked by 1 and 2 were further analyzed by EELS along with the spectra of the standard samples of Si and SiO, as shown in Fig. 1(c). It was found that the black area in Fig. 1(b) can be identified as the SiO_2 -rich phase, while the white one should be Si-rich phase. EELS mapping of Si (green) and O (red) elements is also shown in Fig. 1(d). This also suggests the uniform separation of the

Table 1
Details of the laminated lithium ion cell.

Cathode (size)	LiFePO_4 (83 × 51 mm)
Area specific capacity of cathode	4.6 mAh/cm ²
Number of cathode sheet	5
Anode (size)	SiO (86 × 54 mm)
Area specific capacity of anode	9.7 mAh/cm ²
Number of anode sheet	6
Separator	alumina-coating nonwoven separator
Electrolyte	LiPF_6 EC:DEC (1:1 vol%)
Discharge capacity (at 0.1 C)	1.16 Ah
Midpoint voltage	3.4 V (charge), 3.1 V (discharge)

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