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Microstructure of high battery-performance Li_2FeSiO_4/C composite powder synthesized by combining different carbon sources in spray-freezing/freeze-drying process

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ABSTRACT

Spray-freezing/freeze-drying technique was applied to the synthesis of Li_2FeSiO_4/C composite powders using solutions containing various carbon sources, water-soluble and colloidal carbon, followed by heat treatment. The effects of the carbon sources on the microstructure and battery performance of the synthesized composite powders were investigated. The microstructures of the composite powders were clearly different when different carbon sources were used, ascribed from the thermal behavior of the carbon sources during the heat treatment. It was possible to control the microstructures of Li_2FeSiO_4/C composite powders by combining different carbon sources, and the synthesized composite powders exhibited high discharge capacities by mixing with only a binder for cathode. The composite powders using glucose and Ketjenblack dispersion as carbon sources delivered 165 mAh/g at first discharge capacity at 0.1 C. The developed chain structure suitable for conducting paths in the electrodes and a higher-specific BET surface area, attributed from Ketjenblack, were likely responsible for the higher performance.

1. Introduction

Batteries have been experiencing dramatic development in the last several years. In particular, lithium-ion batteries (LIBs) have gained a significant position in the market and are the most promising and fastest growing battery technology. The main application targets of LIBs are moving from small-scale portable devices to large-scale electric vehicles (xEV) and energy storage systems (ESSs) in off-grid renewable energy. Although they are suitable for small-scale devices, LIBs do not offer sufficient capacity or lifetime for use in vehicles or for energy storage. It is essential to develop the capabilities to serve these uses as soon as possible [1–4].

The performance of a LIB strongly depends on its component materials, in particular the properties of its cathode active material [5]. The need for large batteries offering higher performance has driven the development of new cathode active materials for LIBs; in recent years, interest has focused on the lithium transition-metal orthosilicates (Li_2MSiO_4, where M = Mn, Fe or Co), which are materials of the polyoxyanion-type [6]. The orthosilicates are quite attractive candidates, since they include two Li^+ ions, as indicated by their chemical formula; these confer a theoretical capacity of over 330 mAh/g [7,8]. The most commonly studied orthosilicates are Li_2FeSiO_4 (LFS). Iron and silicon are inexpensive elements, existing in the Earth's crust in large quantities, so research on LFS serves well for developing economical, safe and sustainable cathode active materials that can realize the manufacture of LIBs on a large commercial scale. Nevertheless, LFS has the drawbacks of extremely low electrical conductivity (about 10^{-14} S/cm at room temperature) [9,10] and low diffusivity of the Li^+ ion (approximately 10^{-14} cm/S [11]). Consequently, despite its chemical formula, its actual capacity goes down to 1 Li^+ ion per formula unit. The corrective strategies to improve the poor electrical characteristics of LFS have focused on coatings with conductive materials like carbon [12–14], reducing the particle size [15–17], and doping with hypervalent cations [18–20]; carbon coatings have been most widely examined of these methods [21]. Carbon coatings or containing carbon in a precursor can prevent the growth and agglomeration of LFS particles and oxidation of Fe^{2+} [22].

Control and design of the morphology of electrode materials have

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been reported to be of beneficial effects on their electric and chemical properties [23–25]. Similarly, a wide spectrum of forms of LFS have also been investigated, including ultra-thin nanosheets [26], hierarchical shuttle-like forms [27], nanoworm-like forms [28], and hollow spheres [29]. Among them, morphology control of materials using the shape of carbon added to enhance the conductivity is one of the ideas for designing higher performance LFS/carbon (LFS/C) materials. The 3DOM-LFS/C-NF reported by Li et al. was successfully designed using a soft template strategy and demonstrated the excellent lifetime performance of 1500 cycles [30]. Rangappa et al. used carbon nanosheets for morphology design of LFS/C [21,26]. We have reported LFS/C composite powders with unique structures by a spray-freezing/freeze-drying (SF/FD) method using a solution containing two types of carbon sources and subsequent heat treatment [31].

SF/FD has been already reported as a useful method to synthesize uniform superconductive powders [32], fine perovskite-phase particles for applications in solid oxide fuel cells (SOFCs) [33], and non-oxide ceramic products such as silicon carbide [34]. Despite the practical advantages of this method, there are few reports on the synthesis of LIB materials using SF/FD other than those on $LiFePO_4$/carbon composite powder by Palomares et al. [35,36]. Since the starting solution provided for spray-freezing is a homogeneous solution, the element distribution throughout the obtained composite powder is homogeneous, and a high-purity material can be synthesized. Additionally, if a starting solution containing carbon sources is used, a composite material can be synthesized with just a single heat treatment, and the heat-treated carbon originating from the carbon sources improves the conductivity of LFS. In addition to water-soluble carbon, colloidal carbon was employed in our study as the source; the LFS/C composite powder obtained had a unique structure consisting of LFS nanoparticles coated with a thin carbon layer coexisting with carbon nanoparticles. Here, we describe the effect of differing types of carbon sources on the morphology and battery performance of the resulting LFS/C composite powders.

2. Experimental

2.1. Synthesis of Li_2FeSiO_4/C composite powders

The LFS/C composite powders were synthesized by the SF/FD method reported in our previous study [31]. The materials were used as received without any special processing. The starting materials were lithium acetate (98% purity), iron acetate dihydrate (93% purity), iron nitrate 9-hydrate (98% purity), and colloidal silica (amorphous silicon oxide, 10 wt%). They were dissolved in distilled water to prepare the Li:Fe:Si molar ratio of 2:1:1. The molar ratio of iron acetate and iron nitrate in the starting solution was 1:3. Next, glucose, commercial Indian ink (carbon colloid, 6.8 wt%, Kuretake Co., Ltd.), which is known to be a water-based carbon colloidal dispersion, or Ketjenblack dispersion (KB, 8.1 wt%) were added as the carbon source, and the solutions were used as starting solutions. Then, the solutions were sprayed in a nitrogen atmosphere and freeze-dried for 24 h. The obtained precursors were heated under an argon atmosphere for 5 h at 700 °C or 800 °C with an intermediate holding step for 30 min at 450 °C. That is, the heat treatment was performed in a single step. The amount of glucose added to the starting solution was decided by measuring the weight change of the glucose with temperature; when glucose was the carbon source, 0.7160 g was added for per gram of LFS. The added amounts of Indian ink and KB were set according to their carbon content to be 3.550 g and 3.7570 g, respectively, for per gram of LFS. When the carbon sources were combined, 0.5560 g of glucose and either 2.9850 g of Indian ink or 1.8840 g of KB were added for per gram of LFS.

2.2. Materials characterization

The crystalline structures of the synthesized powders were identified using a powder X-ray diffractometer with Cu Kα radiation (Ultima IV, Rigaku). The morphology and microstructure of the powders were observed with a scanning electron microscope (FE-SEM; JSM-7600F, Jeol) and with a high resolution transmission electron microscope (HRTEM; Tecnai F20, FEI) equipped with an energy dispersive spectrometer (EDS). The carbon content in the powders was examined with an organic elemental analyzer (Micro Order JM10, J-Science Lab Co., Ltd.). The weight change of glucose with temperature was measured under an Ar atmosphere from room temperature to 700 °C with a thermogravimetric-differential thermal analyzer (TG-DTA; TG-DTA2000SA, Bruker). Raman spectrometry was conducted with a laser Raman spectrometer (NRS-3100, JASCO Corporation) in the range of 700–1700 cm^{-1}. Nitrogen adsorption/desorption isotherms were determined using an automatic specific surface area measurement system (Gemini V, Micromeritics), and the specific surface area of the powders was calculated based on the standard Brunauer-Emmett-Teller (BET) equation.

2.3. Electrochemical measurements

The electrochemical tests were conducted with CR2025 coin cells. Metallic lithium foil, which was used as the counter electrodes, was cut into 12 mm circles (rounds) and pressed onto stainless steel plate of 14 mm in diameter. Glass fiber filter paper was used as separators and 1 mol/L $LiPF_6$ ethylene carbonate/dimethyl carbonate solution (volume ratio 3:7) was employed as the electrolyte. The working electrodes were made of the as-synthesized powder and polytetrafluoroethylene (PTFE) binder in a weight ratio of 93:7. For each cell, the mixture containing 5 mg LFS was pressed onto aluminum mesh. After drying for 10 h at 220 °C in a vacuum, the working electrodes were transferred into a glovebox filled with Ar and the coin cells were assembled. The charge-discharge test was conducted at 30 °C on an Auto Battery Evaluation System (AEB1024-5V, Electrofield). The first cycle was conducted in the range of 1.5–4.8 V, and for the subsequent cycles the charge cut-off voltage was reset to 4.5 V to minimize degradation of the electrolyte. The current density and charge/discharge capacities were calculated based on the LFS weight, excluding the carbon weight.

3. Results and discussion

Fig. 1 presents XRD patterns and Raman spectra of the powders synthesized with the different carbon sources at 800 °C. LFS has been reported to form a monoclinic ($P2_1/n$ or $P2_1$) or an orthorhombic structure ($Pmn2_1$ or $Pmnb$) [7,37–39]. From Fig. 1(a), the main diffraction peaks of the synthesized composite powders, regardless of the carbon source used, match those reported by Nishimura et al. in PDF#01-016-1988, and were identified as those of a monoclinic structure with space group $P2_1/n$. This result indicates that the carbon source, whether water-soluble or colloidal carbon, has no effect on the crystalline structure of LFS. No peak originating from the carbon was found from any of the carbon sources; either the carbon was in amorphous form or its particle sizes were too small. Li_2SiO_3 was also detected only when KB was the source. Dominko [40] and Dahbi [41] have reported that Li_2SiO_3 is detected when large quantities of carbon are present. The carbon content in the synthesized powders was 2.5 wt%, 11.8 wt% and 22.8 wt%, respectively, when glucose, Indian ink and KB were used. The fact that the powders synthesized using KB had so much higher carbon content than that from the other two carbon sources may have affected the production of impurities.

The graphitization degrees of the carbon in the synthesized powders were compared using the R value ($R = I_D/I_G$) calculated with the intensity of peaks from the Raman spectra in Fig. 1(b); the R value is the ratio of the intensity at the 1335 cm^{-1} peak (I_D) to the intensity at the