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Effects of α-Fe_2O_3 size and morphology on performance of $LiFePO_4$/C cathodes for Li-ion batteries

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ABSTRACT

In this study, carbon-coated lithium iron phosphate ($LiFePO_4$/C, denoted as LFP/C) composite cathode materials were prepared through wet ball milling and spray drying. Ground and spherical α-Fe_2O_3 precursors were used to synthesize LFP samples. Wet ball milling and a solvothermal method were used to prepare α-Fe_2O_3 particles with a smaller size and spherical morphology, respectively. The as-prepared α-Fe_2O_3 was used to synthesize LFP/C composites in order to investigate the effects of α-Fe_2O_3 size and morphology on the electrochemical performance of LFP/C cathode materials. Charge–discharge measurements revealed that the LFP/C cathode materials prepared from the ground and spherical α-Fe_2O_3 precursors delivered a similar specific discharge capacity of approximately 150 mAh/g at 0.1 C and 96 mAh/g at 10 C, which was higher than that of the LFP/C cathode materials prepared using the irregular and unground α-Fe_2O_3 (the discharge capacity was 135 mAh/g at 0.1 C and 62 mAh/g at 10 C). The results reveal that the size and morphology of iron precursors have a profound influence on the electrochemical properties of LFP/C materials. The results obtained in this study can serve as a reference in the use of the solid-state method to produce low-cost LFP/C cathode materials with favorable consistent properties and high electrochemical performance.

1. Introduction

Lithium iron phosphate (LFP) has been considered a viable cathode material for lithium-ion (Li-ion) batteries because of its high theoretical capacity, low cost, and environmental friendliness. LFP has an olivine structure, which is built from corner-sharing FeO_6 octahedral and PO_4 tetrahedral anions [1]. This olivine is more stable for Li-ion insertion and extraction, which affords excellent long-term cycle life [2]. However, the rate capability of pristine LFP samples in a Li-ion battery has shown limitations, because the electronic conductivity of pristine LFP is considerably low (ca. 10^{-9} S/cm). Thus, several methods have been reported to enhance the inherent electronic conductivity of pristine LFP, which include performing carbon coating [3,4], reducing particle size to the nanometer scale [5,6], and performing metal-ion doping [7,8]. After much research, LFP/carbon (LFP/C) composite cathode materials have been widely accepted as safe and cost-effective cathode materials with great promise for use in energy storage systems and electric vehicles.

Many methods have been employed to synthesize LFP/C cathode materials, including solid-state [9], precipitation [10], hydrothermal and solvothermal [11,12], sol–gel [13], and pyrolysis [14] approaches. Among these methods, the solid-state method is the most suitable for large-scale industrial production [15]. However, raw materials in the solid-state method are generally mixed inhomogeneously, which leads to an impurity phase and uncontrollable particle size, resulting in poor electrochemical performance. The choice of precursor material is a critical consideration in the preparation of a high-performance LFP/C cathode material by using the solid-state method. A perfect precursor can allow a lower sintering temperature and shorter sintering time, which improves the electrochemical performance of a product. Huang et al. reported that raw materials of iron and lithium sources were crucial for the preparation of high-performance cathode materials for Li-ion batteries [16]. A LFP/C material was synthesized at 750 °C through a solid-state reaction using LiH_2PO_4 and FeC_2O_4, and the material showed a specific discharge capacity of 152 mAh/g at 0.2 C [17]. Zhi et al. synthesized a LFP/C composite using LiH_2PO_4 and Fe_2O_3, and the composite delivered a specific discharge capacity of 145 mAh/g at 1 C [18]. Liu et al. reported a LFP/C cathode material synthesized from Li_2CO_3 and Fe_2O_3, with the samples having a highly uniform small particle size; the delivered capacity was approximately 145.8 mAh/g at 0.2 C, with good reversibility and high capacity retention [19]. Furthermore, many types of iron precursors have been used in the synthesis

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of LFP/C cathode materials, including $Fe(OH)_3$, $FeC_2O_4{\cdot}2H_2O$, α-Fe_2O_3, Fe_3O_4, and $FePO_4$. Gao et al. demonstrated that LFP/C composite materials obtained from $Fe(OH)_3$ at 800 °C and $FeC_2O_4{\cdot}2H_2O$ at 700 °C had similar electrochemical performance. The initial discharge capacities of LFP/C synthesized from $Fe(OH)_3$ and $FeC_2O_4{\cdot}2H_2O$ were 134.5 and 137.4 mAh/g at 0.2 C, respectively [20]. Wang et al. synthesized LFP/C composites by using Fe_2O_3 as an iron source at a relatively low temperature (600 °C). The highest discharge capacity (156 mAh/g) was obtained at 0.1 C by using sucrose as a carbon source [21]. Gao et al. used different iron precursors—namely α-Fe_2O_3, Fe_3O_4, $FePO_4$, and NH_4FePO_4—to prepare LFP/C cathode materials. The results showed that LFP/C obtained from the $FePO_4$ precursor delivered excellent electrochemical performance, with a discharge capacity of 152 mAh/g. The higher capacity was obtained because of smaller particles and grain size [22]. Most of the aforementioned studies concentrated on comparing the effects of different iron sources on the performance of LFP/C cathode materials. Few studies have examined the performance of the same iron sources with different particle sizes and morphologies.

Fe_2O_3 is a cheap iron precursor that is very stable and environmentally friendly. In this study, several types of α-Fe_2O_3 were used to prepare low-cost and high-performance LFP/C cathode materials. The crystal structure, particle size, and morphology of the iron precursors and LFP/C samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and micro-Raman spectroscopy. The results revealed that the size and morphology of the iron precursor played a crucial role in improving the electrochemical properties of the LFP/C cathode materials.

2. Experimental details

2.1. Preparation of ground Fe_2O_3 precursor

In a typical synthesis of ground α-Fe_2O_3, 30 g of a commercial unground α-Fe_2O_3 powder was mixed with 500 g of zirconia balls (200 μm diameter) and dispersed in 220 mL of ethanol. The mixture was wet ball milled at 2500 rpm for 4 h. The resulting stable suspension was placed in a rotary concentrator to remove the ethanol at 55 °C and then dried in an oven at 100 °C for 12 h to obtain the ground α-Fe_2O_3. Ground α-Fe_2O_3 powder of smaller size was used to synthesize LFP/C cathode composites to investigate the particle size effect of iron oxide on the electrochemical property of the LFP/C cathode materials.

2.2. Preparation of spherical Fe_2O_3 precursor

First, 50 mmol of $FeCl_3$-$6H_2O$ was dissolved in 400 mL of ethylene glycol to form a clear solution, followed by the addition of 36 g of NaAc and 10 g of polyethylene glycol. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (600 mL capacity). The autoclave was heated and maintained at 180 °C for 8–10 h and then washed with ethanol and deionized water several times. The precursor mixture was sintered at 400 °C for 3 h. The product was γ-Fe_2O_3. Conversely, if the calcination temperature was raised to 600 °C, α-Fe_2O_3 was obtained. The crystal structure was confirmed through XRD. The lattice parameters of the iron oxides were determined to be consistent with those reported in the literature [23]. The material spherical morphology was confirmed using SEM. A spherical α-Fe_2O_3 precursor was used in the synthesis of LFP/C to investigate the effect of iron oxide morphology on the electrochemical performance of LFP/C cathode materials.

2.3. Preparation of carbon-coated LFP/C composite material

To synthesize the LFP/C composites, desired amounts of α-Fe_2O_3, Super P (carbon ball), and Li_2CO_3 with a constant molar ratio of 1:1:1 (Li:Fe:P) were mixed in a beaker. Subsequently, H_3PO_4 aqueous solutions (85 wt%) were slowly added to the beaker at 85 °C with stirring. Next, the precursor mixture was wet ball milled in acetone with a ball (0.5 mm)-to-powder weight ratio of 5:1 at 250 rpm for 3 h. The slurry was then placed in a rotary evaporator to remove the acetone at 45 °C and dried in an oven at 100 °C for 12 h. The obtained powder was heated in a tube furnace at 350 °C for 6 h and then 600–700 °C for 10 h in a 95% Ar/5% H_2 atmosphere to obtain a LFP powder. The LFP powder was mixed with an aqueous glucose solution and then wet ball milled again at 250 rpm for 2 h. The slurry, containing 10 wt% of LFP as-prepared powders, was dried in a spray dryer at 180 °C. The as-prepared powder was transferred to a tube furnace and heated to 600 °C for 10 h in a 95% Ar/5% H_2 atmosphere to obtain a microspherical LFP/C composite material.

2.4. Physical characterization

The crystal structure of the as-prepared LFP/C composite powder was characterized through XRD with a Philip/X-pert diffractometer using Cu Kα radiation (λ = 1.54443 Å). Bragg–Brentano geometry was used in the XRD measurement processes. The diffraction angle was scanned from 10° to 70° at a scanning speed of 0.02°/s. An SEM instrument (S-2600H) (Hitachi, Tokyo, Japan) and TEM instrument (JEM-2100) (JEOL Ltd., Tokyo, Japan) were used for examining the particle size and morphology of the samples. The operating voltages of the SEM and TEM instruments were 15 and 200 kV, respectively. TEM was applied to study the thin carbon layer coated on the LFP surface. Selected area electron diffraction (SAED) was used to examine the crystal structure, and energy-dispersive X-ray spectroscopy (EDS) was used to perform elemental analysis. SAED and EDS were both performed inside the TEM instrument. The structural variations of carbonaceous materials in the carbon-coated LFP particles were identified using micro–Raman spectroscopy, with the spectra recorded on a confocal micro-Renishaw with a 632 nm He–Ne laser excitation.

2.5. Electrochemical measurement

Electrochemical measurements were completed using CR2032-type coin cells with lithium anodes assembled in an argon-filled glove box. For the preparation of a LFP cathode electrode, the LFP/C composite material and Super P were blended. Polyvinylidene fluoride (PVDF) (7 wt%) dissolved in *N*-methyl-2-pyrrolidone was then added and stirred for 2 h. The weight ratio of the active material, conductive additive, and PVDF was 85:5:10 (in wt%). The resultant slurry was subsequently pasted on aluminum foil, which was dried at 120 °C in a vacuum oven for 2 h. The electrolyte used in this study was 1.0 M $LiPF_6$ in ethylene carbonate and dimethylcarbonate (1:1, v/v). Li foil (Aldrich) served as the counter and reference electrodes, and a polyethylene microporous film (Celgard) served as the separator. The cells were charged and discharged over a voltage range of 2.0–3.8 V at different rates from 0.1 to 10 C.

3. Results and discussion

3.1. Material characterization

Fig. 1a–d shows the XRD patterns of the four types of iron sources (Fe_2O_3) used in this study, namely unground commercial α-Fe_2O_3, ground α-Fe_2O_3, spherical α-Fe_2O_3, and γ-Fe_2O_3. The XRD patterns of LFP/C powders prepared from the unground α-Fe_2O_3, spherical α-Fe_2O_3, and ground α-Fe_2O_3 precursors are also shown in Fig. 1e–g. The relevant lattice parameters are listed in Table 1. From the XRD pattern of the unground Fe_2O_3 powder, refractive peaks of 2θ were observed at 24.2°, 33.1°, 35.6°, 40.8°, 49.5°, 54.1°, 57.5°, 62.4°, and 64.1°, corresponding to the (012), (104), (110), (113), (024), (116), (018), (214), and (300) planes, which can be indexed to the pure rhombohedral phase of hematite, α-Fe_2O_3 (Joint Committee on Powder Diffraction