

Electrochemical performance of lithium iron phosphate cathodes at various temperatures



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ABSTRACT

The delithiation–lithiation process of C-coated olivine LiFePO₄ (C/LFP) cathodes with the temperature range between 25 and 55 °C has been investigated using cyclic voltammetry, charge–discharge cycling, and ac impedance spectroscopy. Using polyethylene glycol as carbon precursor, the C/LFP powders are synthesized by an efficient calcination/pyrolysis method at 650 °C. The experimental results reveal that the high-temperature operation of C/LFP cathodes shows an improved capacity at 0.1–5C but negative effect on high-rate cyclic stability. The ac impedance spectroscopy incorporated with equivalent circuit indicates the decrease in equivalent series resistance and the increase in diffusion coefficient (D_{Li}) with operating temperature. The D_{Li} value achieved is as high as $1.49 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at 55 °C according to the Randles plot, and the apparent activation energy for the ionic diffusion in the C/LFP cathode is approximately 110 kJ mol^{-1} , determined from the Arrhenius plot. On the basis of the results, the improved performance is attributed to high ionic conductivity, high ionic migration rate in solid electrolyte interphase film, high electronic conductivity, and high diffusion rate.

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1. Introduction

For their promising potential to be used as power sources for electric vehicles (EVs), so far, Li-ion batteries have captured a large share of the rechargeable battery market [1–3]. It is generally recognized that the battery performance strongly depends on the development of electrode materials [4]. Recently, olivine lithium iron phosphate (LiFePO₄, LFP) has emerged as one of the most promising cathode materials because of its low cost, safety, low toxicity, and high specific capacity of 170 mA h g^{-1} with a flat discharge–charge potential at 3.45 V vs. Li/Li⁺ owing to the Fe²⁺/Fe³⁺ redox couple [5–8]. However, one challenging issue regarding LFP cathode is its extremely poor conductivity, which induces lower rate capability. Accordingly, the LFP cathodes cannot satisfy the required power density in Li-ion battery for end-customer need [7,9]. Some effective routes have been investigated to circumvent this drawback by synthesizing nanosized LFP particles and by forming an electronic coating, that being often a carbon coating over the surface of LFP [4,8,10–12]. The carbon coating technique exhibits great potential to improve the rate capability of LFP cathodes due to its low cost, high electrical conductivity, and large-scale feasibility.

On the basis of previous studies, optimized C/LFP cathode materials have shown highly reversible capacity at room temperature, approximately similar to the theoretical one (i.e., 170 mA h g^{-1}) [4,8]. During charge/discharge cycling, the lithium insertion/extraction reaction takes place as a two-phase solid solution between a Li-rich and a Li-deficient phase at a certain potential of 3.45 V vs. Li/Li⁺ under ambient-temperature operation [13,14]. In fact, high-temperature operation of C/LFP cathodes is a crucial factor of performance, stability and safety for various applications of Li-ion batteries, such as EVs and drilling tools [15]. It is known that elevating the battery operation temperature is capable of activating electrode materials with higher electronic, ionic, and interfacial conductivities, whereas the decomposition of materials and side reactions would occur at electrode/electrolyte interface [16]. To examine the optimal operation, a better understanding on raising C/LFP cathode performance is required. However, to our best of knowledge, there are few reports focusing on the electrochemical performance of C/LFP cathodes at high temperatures.

To inspect the temperature effect, the present work reports a facile synthesis of C/LFP cathode materials at 650 °C using Li₂CO₃ and FePO₄ as precursors, as published previously [4]. Herein polyethylene glycol (PEG) serves as carbon precursor for preparing uniform carbon coating over the surface of LFP powders, forming C/LFP composite materials. The electrochemical performance of C/LFP cathodes was systematically investigated within the

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temperature range of 25–55 °C. The experimental results allow us to address in an appropriate operation to identify the relative influence of temperature on the mechanisms of Li⁺ insertion/extraction into/from the C/LFP cathodes.

2. Experimental

To ensure the accurate stoichiometric ratio, a dehydration treatment was adopted to heat FePO₄·2H₂O and Li₂CO₃ precursors at 190 °C for 2 h. In a typical procedure, FePO₄, Li₂CO₃, PEG, were dissolved in distilled water at room temperature. The molar ratio of Li:Fe:P in the precursor solution was fixed to 3:1:1, and the ratio of carbon additive, PEG (molecular weight: 2000) was set at 20 g PEG/1 mol FePO₄, according to our previous study [4]. The solution precursor was well mixed by using a planetary ball mill, forming mushy slurry. The slurry was then placed in an oven and dried at 120 °C overnight. The dried samples were grounded and sieved (Mesh No. 200). After that, the fine powders were calcined and carbonized at 650 °C in a furnace for 12 h under high-purity N₂ atmosphere.

The electrochemical performance of C/LFP cathodes was carried out using CR2032-type coin cells. For the cell assembly, the C/LFP powders were mixed with a binder (poly-vinylidene fluoride) and two conducting media (Super-P and KS-4) at a weight ratio of 80:10:5:5 in *N*-methyl pyrrolidinone (NMP) solvent to form the electrode slurry. The mixture was blended by a three-dimensional mixer using Zr balls for 1 h to form the uniform slurry. The resultant slurry was then uniformly pasted on an Al foil substrate with a doctor blade, followed by evaporating the solvent, NMP, with a blow dryer. The prepared cathode sheets were dried at 80 °C in a vacuum oven for 12 h and pressed under a pressure of ~200 kg cm⁻². The electrode layers were adjusted to control a thickness of ~100 μm. The coin cells were assembled in a glove box for the electrochemical measurements. In the coin cells, the Li foil and the porous polypropylene film were used as the counter electrode and the separator, respectively. The electrolyte solution was 1.0 M LiPF₆ in a mixture of ethylene carbonate (boiling point = 248 °C), propylene carbonate (boiling point = 242 °C), and dimethyl carbonate (boiling point = 109 °C) with a weight ratio of 1:1:1. Herein the LiPF₆ salt exhibited good thermal stability (melting point: 193 °C), analyzed by differential scanning calorimetry [17].

The charge/discharge cycling test at different *C* rates (from 0.1 to 5 C) was performed within the voltage region of 2.0–4.0 V vs. Li/Li⁺ at 25, 40, and 55 °C. It was worth noting that all electrolyte components are stabilized under the operation temperatures. An electric oven was used to accurately control the surrounding temperatures for all electrochemical measurements. Cyclic voltammetric (CV) analysis on C/LFP cathodes was performed within the potential range of 2.0 to 4.0 V vs. Li/Li⁺ at the sweep rate of 0.1 mV s⁻¹. An ac impedance analysis was performed in the frequency range of 100 kHz to 0.01 Hz at open circuit potential with an alternating current perturbation of 5 mV. The analysis of cathodes was also carried out at various temperatures (i.e., 25, 40, and 55 °C) using an impedance analyzer (CH Instrument, Inc., CHI 608), and the equivalent circuit was analyzed by computer software (Z-view).

Field-emission scanning electron microscope (FE-SEM, JEOL JSM-5600) and high-resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100) were used to observe the microstructures of the C/LFP powders. The HR-TEM observation was performed using a microscope operating at 200 kV. The C/LFP sample was prepared by ultrasonically dispersing the composite in ethanol. A drop of the suspension was applied onto a copper grid and was dried in air. An X-ray diffraction (XRD, Shimadzu Labx XRD-6000) spectroscopy, equipped with Cu-Kα radiation

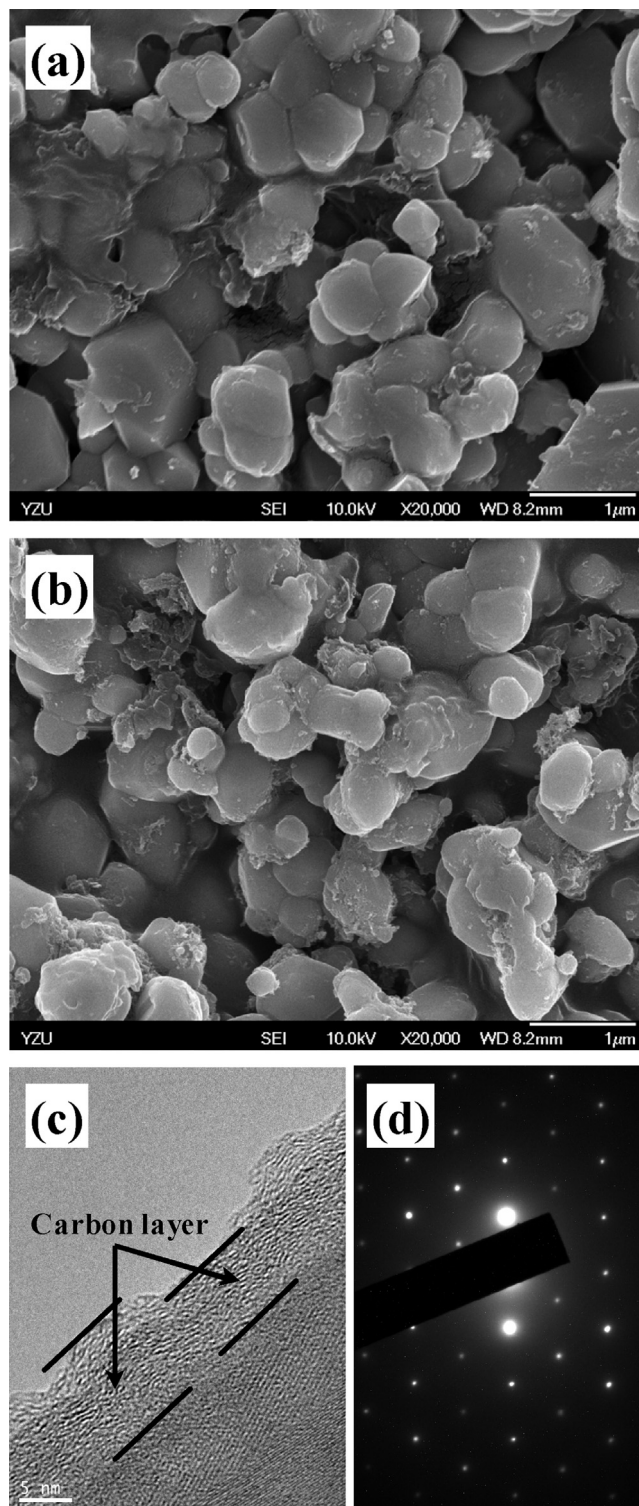


Fig. 1. (a) FE-SEM image of bare LFP powders. (b) FE-SEM image and (c) HR-TEM micrograph of as-prepared C/LFP powders. (d) SAD pattern focusing on the individual LFP crystal.

emitter, was used to characterize the crystalline structures of C/LFP sample.

3. Results and discussion

Fig. 1(a) and 1(b) displays FE-SEM images of bare LFP and as-grown C/LFP composites, showing that the LFP particles with

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