Iron-assisted carbon coating strategy for improved electrochemical LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ cathodes

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ABSTRACT

An iron-assisted carbon coating strategy is developed to guide the formation of uniform and highly graphitized carbon layers on surfaces of the LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ (LMFP) to yield cathode materials with improved electrochemical performance. A small amount of iron oxalate is added as a catalyst precursor, which decomposes into ferrous oxide (FeO) at high temperature. During the calcination process, FeO is reduced to iron (Fe) that helps to transform amorphous carbon into graphitized carbon which is deposited uniformly and tightly on surfaces of LMFP materials. The impact of Fe atoms on the formation of highly graphitized carbon layers as well as the electrochemical performances of the resulting LMFP/Fe/Carbon (LMFP/Fe/C), is evaluated. Compared to LMFP/C without iron oxalate, LMFP/Fe/C exhibited substantial discharge capacity and better rate and cycling performances. Discharge capacities of 152.3, 141.9, 132.1, 105.6 and 76.0 mAh g^{-1} are recorded at 0.2, 0.5, 1, 5 and 10 C, respectively. The retention capacity remained 78.6% at 10 C after 60 cycles. Furthermore, the conductivity and the lithium ion diffusion processes of LMFP/Fe/C are improved.

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1. Introduction

Lithium-ion batteries (LIBs) have gained great attention as renewable green energy and occupied a prime position in broad applications ranging from portable electronic devices to electric vehicles [1,2]. The cathode material is an important component in the successful operation of LIBs. The olivine-type LiMPO$_4$ (M = Fe, Mn etc.) cathode materials have been reported to exhibit higher capacity and superior safety coupled with low cost [3–5]. Compared with LiFePO$_4$ (LFP) material, the LiMnPO$_4$ (LMP) is considered as a better candidate for rechargeable LIBs because of its larger potential window of 4.1 V versus that of Li/Li$^+$ (3.4 V for LFP) [6]. However, the low electrical conductivity ($<10^{-10}$ S cm^{-1}) and the slow lithium-ion diffusion ($<10^{-16}$ cm^2 S^{-1}) have limited its practical applications [7,8]. To overcome the drawbacks of LMP, many modification methods have been attempted, including particle-size minimization [9–11], Mn-site doping [12–14], and carbon coating [15–18]. The particle-size minimization method shortens the lithium-ion diffusion path and increases the electrode surface area for interfacial charge transfer that leads to improved ionic diffusion efficiencies. Ye et al. [19] have synthesized nano LiMn$_{0.9}$Fe$_{0.1}$PO$_4$ by the solvothermal method and found that the introduction of cationic ions into the crystalline LMP can lead to stable crystal structure and excellent electrochemical performance. Hong et al. [20] have demonstrated the higher rate capability and cycle performance of LIBs cathode when Mn^{2+} is partially substituted by Fe^{2+}.

Carbon coating is an effective way to improve the electronic conductivity of LMP and its kinetic properties [21–24]. The carbon content, distribution and uniformity of the coverage, carbon surface area, and the degree of graphitization (the sp2/sp3 or graphitized/disordered ratio I$_G$/I$_D$) are the key factors to affect the electrochemical performance of LMP cathode [25–27]. However, the most conventional carbon sources and coating technologies are far from the requirements to yield high-performance cathodes. Graphene is alternatively exploited due to its high specific surface area and excellent conductivity [28], but graphene is difficult to be dispersed and its interaction with LMP particles is weak. Thus, direct mixing of graphene with LMP is not the best approach to improve the electrochemical performance of LMP cathodes.

Metal compounds such as iron oxides and iron sulfates can guide and catalyze the formation of graphitized carbon from various carbon sources [29–33]. Amorphous carbon could nucleate and grow into graphene layers depositing on metal surfaces [34].

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Furthermore, LiFePO$_4$/graphene was synthesized using glucose and FeSO$_4$ as the carbon source and catalyst precursor, respectively [35]. High-quality carbon layers were also coated on LiFe$_{0.6-}$Mn$_{0.4}$PO$_4$/C cathode material, where both the carbon and metal catalyst were mixed uniformly and were randomly distributed among the cathode particles. After the calcination process, the graphene layers were grown not only on the surface of the cathode particles but also in places among particles. Besides, some graphene sheets stretched out from the cathode particles yielding no positive contribution to the electrochemical performance [36]. Therefore, the adding and spatial sequence of the metal catalyst and carbon sources is a very important factor in acquiring highly graphitized carbon coatings only on the surface of cathode materials.

In this paper, LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ (LMFP) was synthesized by the solvothermal method. Iron oxalate was selected as metal catalyst precursor and mixed with LMFP for the synthesis of LMFP/Fe/Carbon (LMFP/Fe/C). By adding iron oxalate, and glucose in the desired order, the mechanism of forming the uniform and highly graphitized carbon layers was particularly investigated. The synthesized materials were characterized by various analytical methods and their electrochemical performances as LIBs cathodes were measured.

2. Experimental

2.1. Synthesis of LMFP and LMFP/Fe/C composite

The LMFP particles were synthesized by the solvothermal method. The Mn/Fe mixture (Mn/Fe = 4:1, n/n, MnSO$_4$·H$_2$O (AR grade), FeSO$_4$·7H$_2$O (AR grade)) and H$_3$PO$_4$ (85 wt%) were dissolved in a mixture of ethylene glycol-water (5:3, v/v) as the solvent in presence of ascorbic acid as the reducing agent. LiOH·H$_2$O was then added dropwise into the mixture with a molar ratio of Li:Mn/Fe:P fixed at 3:1:1. After vigorous stirring for 30 min under a nitrogen atmosphere, the resulting suspension was transferred into a 200 ml Teflon-lined stainless steel autoclave and was heated at 240 °C for 4 h. After the autoclave was cooled down to room temperature, the gray precipitate was washed off several times with water and ethanol.

To prepare LMFP/Fe/C, iron oxalate as the catalyst precursor was mixed with LMFP and the molar ratio between PO$_4^{3+}$ and iron oxalate was kept at 200:1. Subsequently, the mixture was dried at 200 °C in vacuum for 4 h. The obtained powder (LMFP/FeO) was then mixed with glucose and the mass ratio between the powder and carbon contained in glucose was kept to 93:7. Finally, the mixture was calcined at 650 °C for 8 h in a tube furnace under a nitrogen atmosphere. The composite material LMFP/Fe particles with carbon coating was abbreviated as LMFP/Fe/C. For comparative purposes, the LMFP particles with carbon coating (LMFP/C) without iron oxalate were also produced using the same method.

2.2. Characterization

The phase purity and crystal structure of the samples were characterized by X-ray diffraction (XRD) using a Bruker D8 X-ray diffractometer with Cu Kα radiation set between 5° and 80° at a scan rate of 5°/min. The morphology and structure were determined by a NanoSEM450 scanning electron microscope (SEM) and a Tecnai G2 F20 transmission electron microscopy (TEM). The carbon analysis was conducted by DXR Microscope Raman spectroscopy with a 532 nm wavelength laser.
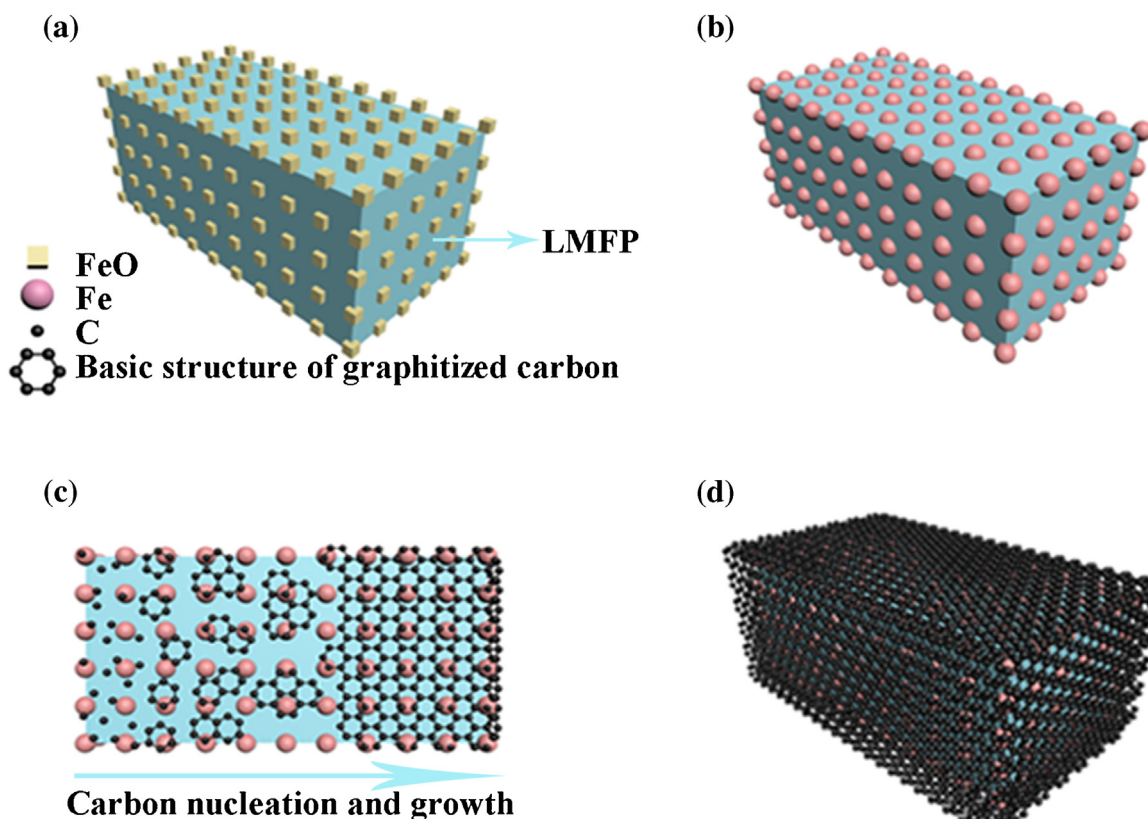

Fig. 1. The schematic preparation of the LMFP/Fe/C. (a) Iron oxalate was converted to ferrous oxide and attached on surface the of LMFP particles during the drying process, (b) ferrous oxides were reduced to iron atoms by carbon during the sintering process, (c) under the catalytic guidance of Fe atoms, carbon atoms nucleated and grew into graphitized carbon layers on surfaces of the LMFP particles, (d) LMFP was coated with uniform graphitized carbon layers.