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High volumetric energy density of $LiFePO_4$/C microspheres based on xylitol-polyvinyl alcohol complex carbon sources

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ABSTRACT

High volumetric energy density $LiFePO_4$/C electrode was synthesized by wet ball-milling, spray drying and carbothermal reduction using xylitol-polyvinyl alcohol (PVA) as complex carbon sources. The fused xylitol with certain viscosity is readily coated on the surface of ferric phosphate ($FePO_4$) during ball milling. PVA hydrogel not only forms a film on the surface of $FePO_4$, which fixes the coating of xylitol to form a gel network, but also acts as a dispersing agent to make the precursor particles disperse more uniformly. The unique properties of the complex carbon sources result in a homogenous carbon-coating all over the primary submicron $LiFePO_4$ particles (100–200 nm in diameter) to form a core-shell structure, and the regular microsphere particles (2–10 μm in diameter) are composed of the primary particles connected by a gel-conductive carbon network. This unique structure provides a Li^+ diffusion channel and improves the electronic conductivity. The synthesized $LiFePO_4$/C exhibits high electronic conductivity ($2 \times 10^{-1}\ S\,cm^{-1}$) and high tap density ($1.6\ g\,cm^{-3}$) with excellent electrochemical performance (at room and low temperatures) and high volumetric energy density ($617.8\ Wh\,L^{-1}$ at 10 C rate).

1. Introduction

As one of the most promising cathode materials, the olivine-structured lithium iron phosphate ($LiFePO_4$) has been widely used in the fields of pure electric vehicles (EV), plug-in hybrid vehicles (PHEVs) and energy storage systems (ESS) [1–4]. Since the first report by Goodenough in 1997, it has been widely studied due to high specific capacity ($170\ mAh\ g^{-1}$), high thermal stability, low cost and environmental friendliness [5–8]. The promising approaches to enhance the electrochemical performance are particle size nanocrystallization and carbon coating technology. Reducing particle size can increase the diffusion of Li^+ into one-dimensional channels of $LiFePO_4$ phase [9]. However, nano-scale $LiFePO_4$ exhibits low tap density ($<1.0\ g\,cm^{-3}$), resulting in low volumetric energy density [10]. Moreover, reducing particle size can provide Li^+ from the electrolyte to the electrode surface rapidly, thus causing undesirable side reactions at the electrolyte interface, which has an adverse on cycle performance [11]. Additionally, carbon coating can not only enhance electrical conductivity, inhibit crystal growth, reduce electrode polarization, but also provide channels to facilitate Li^+ intercalation/deintercalation [12–15]. Nevertheless, a lot of carbon agglomerates can be formed by excessive carbon, thus reducing volumetric energy density and hindering Li^+ diffusion [16]. On the contrary, less carbon content may lead to incomplete carbon coating around $LiFePO_4$, resulting in a limitation of ion migration and charge compensation, which in turn affects the discharge capacity [17]. Furthermore, the carbon source is one of the key factors of the carbon coating technology. The carbon layer on the particle surface has a significant influence on the electrochemical performance of $LiFePO_4$, which is closely related to the electrical conductivity, structure and order of carbon [15,18,19]. Moreover, the uniform distribution of carbon promotes the electrode reaction kinetics due to the full contact of active particles with each other [20–23]. Good electrical contact allows Li^+ and electrons to be simultaneously obtained at the same position during charging/discharging process [24–27].

In recent years, the core-shell microsphere structure, in which primary particles are loosely aggregated by van der Waals interaction to form secondary micron-sized particles, has received

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considerable attentions. This structure can not only facilitate Li^+ diffusion and increase electrode-electrolyte contact area, but also be beneficial to the volumetric energy density [28–31]. Since the internal electrical conductivity of the microspheres is the key factor in achieving good rate and cycle performance, it is crucial to establish a good conductive network within them [32]. However, it is found that $LiFePO_4/C$ secondary microspheres prepared by using conventional organic carbon sources have limited particle size control, and the carbon is extremely difficult to cover each primary particle, resulting in electrode polarization and poor rate performance [33–35]. A complete conductive network can be obtained by polymer coating. However, the conventional ball-milling method is used to add a lot of volatile organic compounds, resulting in low density and poor conductive network to prolong the conduction path in the microspheres, which in turn impacts rate performance and green environment [36–38].

In this work, the high-performance $LiFePO_4/C$ composites were synthesized by wet ball-milling, sprary drying and carbothermal reduction with xylitol-PVA as complex carbon sources. The surface of ferric phosphate is coated by fused xylitol during wet ball-milling, and the PVA hydrogel immobilizes the coated xylitol to form a gel network. Moreover, PVA is beneficial to the precursor particles disperse more uniformly. A homogenous carbon-coating all over the primary submicron $LiFePO_4$ particles (100–200 nm in diameter) to form a core-shell structure, and the regular microsphere particles (2–10 μm in diameter) are composed of the primary particles connected by a gel-conductive carbon network. This unique structure provides a channel of Li^+ diffusion and improve the electronic conductivity. The electronic conductivity and tap density of synthesized $LiFePO_4/C$ were measured, and the electrochemical performance at room and low temperatures were also tested. At the same time, xylitol was used as a single carbon source in the same synthesis as a control group.

2. Experimental

2.1. Materials synthesis

For comparison, the xylitol powders (AR, Beisitian, Tianjin) were fused as a monomer carbon source at 95 °C in an electronic multipurpose furnace. The fused xylitol, stoichiometric amounts of nano-scale $FePO_4$ (AR, Qixing, Sichuan) and lithium carbonate (Li_2CO_3 AR, Zhongli, Sichuan) at molar ratio of 0.09: 1: 0.51 were ball-milled in a planetary mill with deionized water at 300 rpm for 2 h. The zirconia ball with a diameter of 0.8 mm was used for ball milling and the ratio of ball to material was 6: 1. The obtained slurry with a solid content of 40 wt.% was subjected to spray rapid dried at a rate of 100 mL min^{-1} with inlet and outlet temperatures of 325 and 110 °C, respectively. The nozzle has a diameter of 1 mm and an inlet pressure of 0.4 MPa, and then the precursor was transferred to a tube furnace at 750 °C for 4 h under the flowing nitrogen protection atmosphere with a heating rate of 8 °C min^{-1} to synthesize $LiFePO_4/C$ composites, which was marked as LFP-1.

$LiFePO_4/C$ composites were synthesized through the method using the complex carbon sources as follows: Firstly, the PVA hydrogel was obtained by a solid content of 5 wt% PVA powders (Wanwei Anhui, 1788) dissolved in deionized water at 90 °C in water bath. Especially, the fused xylitol and the PVA hydrogel were doped as the complex carbon sources in a molar ratio of 3: 1. A slurry containing the precursor to the $LiFePO_4/C$ composites were synthesized by mixing the stoichiometric nano-scale $FePO_4$, Li_2CO_3, the complex carbon sources at above the same molar ratio in a planetary mill at 300 rpm for 2 h. After then, the $LiFePO_4/C$ composites were synthesized by spray drying and carbothermal reduction with the same condition, which was marked as LFP-2.

2.2. Material characterization

The crystalline structures were analyzed by X-ray polycrystal diffractometer (XRD, D8 FOCUS Bruker AXS, Germany) with Cu Kα radiation in the 2θ scanning range of 10–80°. The surface morphology and microstructure were observed using Scanning Electron Microscope (SEM, FEI, Hong Kong) and Transmission Electron Microscope (TEM, JEOL). The carbon content was tested by the carbon sulfur tester (Eltra CS800). The particle size distribution was analyzed by the Laser Particle Sizer (LS609). The electronic conductivity was measured by two-point probe method. The tap density was tested by tap density meter (BT-301).

2.3. Electrochemical measurements

The electrochemical performance of the samples were measured using CR2032 coin-type half cells. The active material ($LiFePO_4/C$), the conductive agent (acetylene black, AR, Xinlian, Henan) and the binder (polytetrafluoroethylene, AR, Chenguang, Sichuan) were uniformly mixed according to the weight ratio of 80:15:5 in absolute ethyl alcohol. After ultrasonic dispersion, a positive electrode film with a thickness of 0.14 mm was rolled. Finally, 10 mm diameter films were dried at 120 °C for 12 h under vacuum conditions. With a lithium foil as the counter and reference electrodes, CR2032 coin-type cells were assembled with a solvent mixture of 1 M $LiPF_6$/ethyl carbonate (EC) + diethyl carbonate (DEC) (1:1, v/v) as the electrolyte (AR, Jinniu, Tianjin) under argon circulation protection in glove box. The galvanostatic charge/discharge tests were performed at the voltage range from 2.3 to 4.2 V (vs. Li/Li^+) on a battery test system (LAND CT2001A, Wuhan, China) at 25 °C. Low temperature electrochemical tests were performed in a high-low temperature box (Ronglixin Shenzhen, China) as follows: Firstly, after the initial two charge and discharge cycles at 0.2 C and 25 °C and fully charging, then the cells were placed in the set low temperature environment (−20 °C) for 15 h. Finally, the low-temperature discharge (cut-off voltage is 2.0 V) test was at 0.2 C and 0.5 C. The cyclic voltammetry (CV) tests were performed at a scanning rate of 0.1–1.0 mV s^{-1} between 2.3 and 4.2 V on a CHI660C electrochemical workstation (Chenhua Shanghai, China) at 25 °C. After two charge and discharge cycles at 0.2 C and 25 °C, the cells were charged to 50% DOC for electrochemical impedance spectroscopy (EIS) tests over the frequency range $0.1–1 \times 10^5$ Hz on the electrochemical workstation at 25 °C.

3. Results and discussion

3.1. Sample characterization

Under the sintering conditions of this study, both precursors have been successfully converted to an olivine structure, as shown in Fig. 1. Both samples exhibit the ideal orthorhombic olivine structure (JCPDS card number: 83–2092) without any impurity phase. The lattice parameters of both samples are close to the standard parameters (a = 1.0334 nm, b = 0.6010 nm, c = 0.4693 nm, V = 0.29147 nm^3) in Table 1. The strong and sharp peaks indicate a high crystallinity of synthesized $LiFePO_4$. Additionally, the carbon contents of both samples are approximately 2.6 wt%, but no diffraction peak of carbon is found due to its existence in an amorphous form, which indicates that the presence of carbon has no effect on the crystal structure of $LiFePO_4$.

The distribution of carbon has a significant effect on the morphology and microstructure of $LiFePO_4/C$, as shown in Figs. 2 and 3. The precursor microspheres obtained by spray drying is displayed in Fig. 2a and b. The precursor of LFP-1 sample exhibits a loose spherical morphology, while that of LFP-2 sample