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Electrochemical Behavior of Spherical $LiFePO_4/C$ Nanomaterial in Aqueous Electrolyte, and Novel Aqueous Rechargeable Lithium Battery with $LiFePO_4/C$ anode

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A B S T R A C T

We designed a novel aqueous rechargeable lithium battery with $LiFePO_4/C$ (LFP) and $LiMn_2O_4/C$ (LMO) as the anode and cathode, respectively; then investigated the battery in Li_2SO_4 aqueous electrolyte. We also studied the electrochemical behavior of LFP in aqueous electrolyte using cyclic voltammetry (CV). The material exhibited excellent electrochemical performance in the aqueous electrolyte, including good oxidation/reduction reversibility and cycling stability; almost no decays were observable after 200CV cycles. The diffusion coefficients of Li ions through the interface between the liquid electrolyte and the solid $LiFePO_4$ in terms of intercalation and deintercalation were 1.22×10^{-14} and $9.97 \times 10^{-15}\,cm^2/s$, respectively. The material could be completely intercalated/deintercalated with Li ions in the aqueous electrolyte, indicating the excellent performance of LFP in an aqueous solution. Further, an aqueous rechargeable lithium battery (ARLB), which we fabricated using LFP as the anode and LMO as the cathode, also exhibited quite good performance in aqueous Li_2SO_4 solution: after 1,000 charge–discharge cycles at 2 C, the capacity loss was less than 30%, indicating that this type of ARLB has excellent cycling stability and may be promising for future research and application.

1. Introduction

Since Sony, in 1990, commercialized a lithium ion battery using an organic electrolyte [1], organic electrolyte lithium ion batteries have become one of the most important secondary batteries in the world, due to their long cycling capability and high energy density. However, these batteries have many disadvantages, including flammability, high toxicity, and high cost, which give rise to serious safety problems and limit their application in large-scale energy storage system like electric vehicles (EVs) and smart grids [2–4].

To tackle these problems at their root, the aqueous rechargeable lithium battery (ARLB) was first proposed in 1994, and it has drawn significant attention in recent years [5–8]. Using an aqueous electrolyte has many advantages, such as safety, low cost, and high ionic conductivity, which make the ARLB quite attractive, especially as a power source for EVs [9]. However, certain problems limit the practical application of ARLBs, including poor cycling stability, low energy density, and poor rate capability. Major efforts have been put into addressing these shortcomings, but significant challenges remain [10,11]. For example, Xia et al. [12] reported that eliminating oxygen in the electrolyte can raise the cycling stability of ARLBs. Wu et al. [13–15] reported that using coated Li metal as the anode and $LiMn_2O_4$ as the cathode can yield an ARLB with an average discharge voltage of about 4.0 V and an energy density of 446 Wh/kg, together with excellent cycling performance.

Other researchers have tried using novel materials for the ARLB electrode to improve the battery's electrochemical properties and performance [16–18], but few studies have referred to the electrochemical behavior of the electrode materials in an aqueous electrolyte solution. $LiFePO_4$ has been recognized as the most promising cathode material for organic electrolyte lithium ion batteries, especially for large-scale power systems, because it is inexpensive, nontoxic, and environmentally benign [19,20]. However, almost no investigations into its performance or electrochemical behavior in an aqueous electrolyte have been reported to date.

In this work, we prepared a spherical LFP nanomaterial using a spray-drying method. With this material as the anode, we designed and fabricated an ARLB with LMO as the cathode and

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used Li_2SO_4 aqueous solution as the electrolyte, then investigated the battery's capacity and stability. We also studied the electrochemical behavior of LFP in aqueous solution using cyclic voltammetry (CV).

2. Experimental

2.1. Synthesis and physical characterization of LFP material

The spherical $LiFePO_4$/C nanomaterial (LFP) was prepared using a spray-drying process previously reported by our group [21]. A typical preparation process was as follows. First, 0.300 mol $(FeNO_3)_3{\cdot}9H_2O$ (AR) and 0.2 mol citrate acid were dissolved in 100 mL deionized water (solution A); 0.300 mol $(NH_4)_2HPO_4$ (AR) and 50.0 g glucose were dissolved in 120 mL deionized (DI) water (solution B); and 0.300 mol LiOH (AR) was dissolved in 70 mL DI water (solution C). Under vigorous stirring, solution B was added dropwise to solution A, followed by the addition of solution C, yielding a gel-like mixture. Stirring continued for 24 h, followed by the addition of 10.0 mL ammonia solution (28 wt%). Then, the slurry was spray dried using a spray dryer with inlet and outlet temperatures of 180 °C and 70 °C, respectively. Finally, the resultant precursor powders were calcined from room temperature to 750 °C in a temperature-programmed tube furnace under a nitrogen atmosphere, then kept at the final temperature for 3 h.

The nanocomposite material was characterized by X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) using Cu-Kα radiation, and by scanning electronic microscopy (SEM, Hitachi S-4800, Japan).

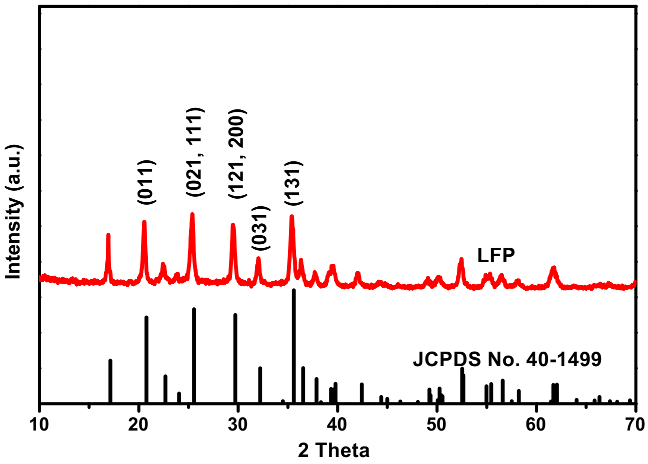

Fig. 1. XRD pattern of $LiFePO_4$/C prepared with a spray-drying method.

2.2. Electrochemical characterization of LFP material

We used a standard three-electrode electrochemical system to perform the electrochemical evaluation and characterization of the LFP material. The working electrode was prepared as follows. First, 20.0 mg LFP, 5.0 mg acetylene black, and 1 mL Nafion (5 wt%) ethanol solution were mixed using ultrasonication for 15 minutes to obtain a slurry. Next, 10 μL of the slurry ink was doped onto a clean glassy carbon electrode (GCE) surface with a diameter of 5 mm and left to dry under infrared illumination. Aqueous Li_2SO_4 solution (0.5 mol/L) was used as the electrolyte. An Ag/AgCl

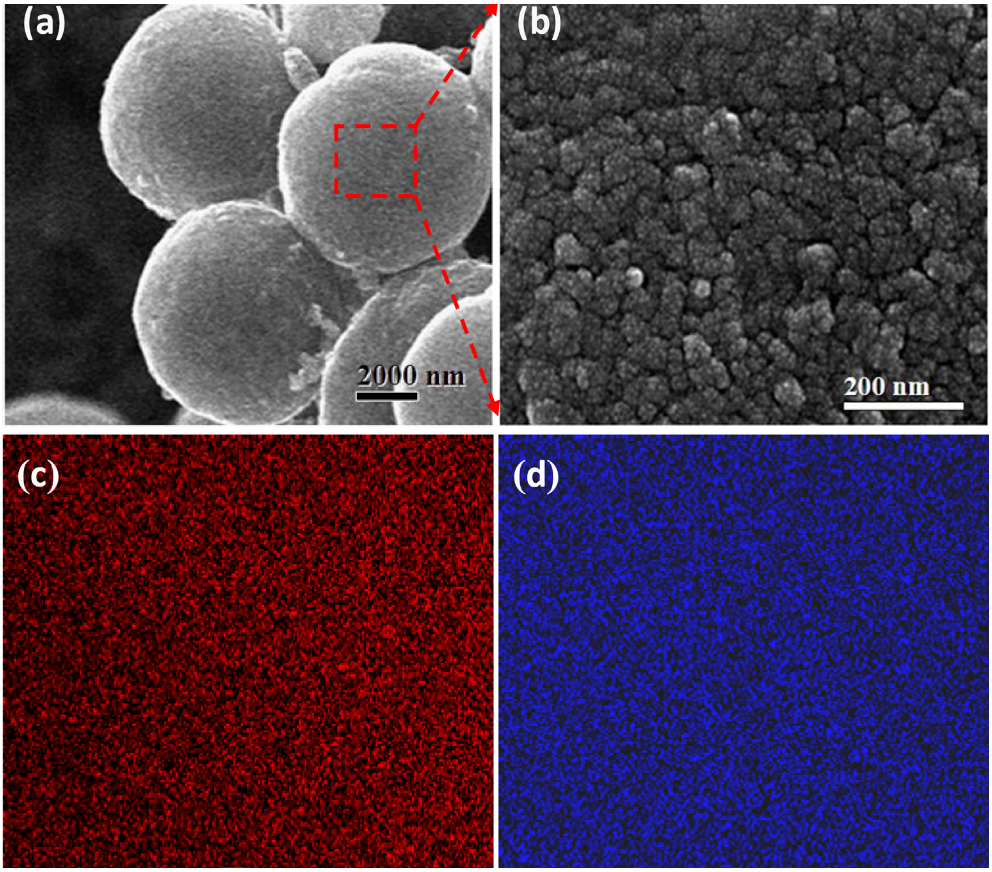

Fig. 2. SEM images of $LiFePO_4$/C prepared with dual carbon sources: (a) overall morphology; (b) the material's surface. Element mapping of $LiFePO_4$/C: (c) carbon; (d) iron.