



Synthesis of LiFePO_4 material with improved cycling performance under harsh conditions

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ABSTRACT

LiFePO_4 material was synthesized at 670 °C in an Ar atmosphere using a sol-gel method. This material showed a well developed XRD pattern (orthorhombic structure, $Pnma$) without any peaks at $2\theta = 41^\circ$, indicating the absence of FeP or metallic Fe_2P impurities. The $\text{Li}/\text{LiFePO}_4$ cell showed a high initial discharge capacity of more than 150 mA h/g and no capacity decrease until the 70th cycle (>99.9%). This cell also exhibits excellent cycle performance at high current densities of over 30C, without any surface treatment or carbon coating onto the LiFePO_4 particles.

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1. Introduction

Iron-based cathode materials are ideal for future lithium-ion batteries because of their low cost and environmental friendliness. Many research groups recently focused on a group of lithium- and iron-containing compounds incorporating polyanions of the class XO_4^{3-} ($\text{X} = \text{S}, \text{P}, \text{As}, \text{Mo}$) [1–3]. These large polyanions can stabilize the structure and tune the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential to a useful level. Among them, LiFePO_4 was proposed by Goodenough and co-workers [4] and has sparked renewed interest in the search for the desirable cathode material for next generation lithium secondary batteries. The electrochemical charge/discharge potential profile of $\text{Li}/\text{LiFePO}_4$ cells is very flat and located at 3.45 V vs. Li/Li^+ , moreover, its theoretical capacity is relatively high (170 mA h/g) compared with those of other cathode materials. However, LiFePO_4 has low electrical conductivity, which poses a great challenge for battery applications. Numerous researchers have attempted to increase the electric conductivity by coating the surface of the LiFePO_4 particles with carbon [5–9]. At the same time, many research groups focused on the synthesis of LiFePO_4 with a small particle size in order to improve the electrical properties using various synthetic methods [10]. The ability to control the size and crystallinity of the particles during the synthetic process is crucial, since a small

particle size is very effective to promote the diffusion of lithium ions in the LiFePO_4 electrode [11–15].

In order to improve the electrochemical properties of the LiFePO_4 powder by controlling the particle size, the sol-gel method was adopted for the synthesis of LiFePO_4 in this study. We report the synthesis and electrochemical characterization of LiFePO_4 material prepared by an adipic acid-assisted simple sol-gel method without any additional treatment to improve the cycle performance, such as carbon coating, the use of additives or ball milling, which have been employed by many research groups for the purpose of enhancing the battery performance.

2. Experimental

Nano-crystalline LiFePO_4 was synthesized from LiCH_3COO (Sigma-Aldrich, USA), $\text{Fe}(\text{CH}_3\text{COO})_2$ (Sigma-Aldrich, USA), H_3PO_4 (Sigma-Aldrich, USA), and $\text{C}_6\text{H}_{10}\text{O}_4$ (Sigma-Aldrich, USA) using a conventional sol-gel method. A stoichiometric amount of each material was dissolved in ethanol and mixed well with an aqueous solution of adipic acid as a chelating agent. The solution was evaporated at 90 °C for 4 h to form a transparent sol. The sol was then dried at 90–100 °C for 24 h in a vacuum oven to yield the gel precursors. The resulting gel powder was ground and calcined at 400 °C for 1.5 h and then at 670 °C for 2.5 h in an Ar atmosphere using a tubular furnace.

Powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) using $\text{Cu K}\alpha$ radiation was used to determine the crystalline phase of

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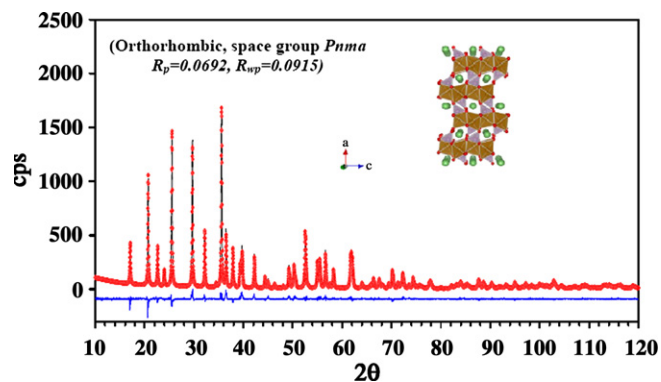


Fig. 1. X-ray diffraction and Rietveld analysis of LiFePO₄ obtained by sol-gel method.

the prepared material. The particle morphology and particle size distribution of the resulting compound were observed using a scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan) and Laser Zeta-Potential Analyzer (ELS-8000, Otsuka Electronics, Japan), respectively. The electrochemical characterizations were performed using a CR2032 coin-type cell. The cathode was fabricated with 20 mg of accurately weighed active material, 3 mg of Ketjen black and 3 mg of conductive binder (2 mg of Teflonized acetylene black (TAB) and 1 mg of graphite). It was pressed on a 200 mm² stainless steel mesh which was used as the current collector under a pressure of 300 kg/cm² and dried at 130 °C for 5 h in an oven. The test cell was made of a cathode and a lithium metal anode separated by a porous polypropylene film (Celgard 3401). The electrolyte used was a mixture of 1 M LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by Vol., Techno Semichem Co., Ltd, Korea). The charge and discharge current density was 0.1 mA/cm² with a cut-off voltage of 2.8–4.0 V. It also conducted the cycling test at the same test condition with various current densities (0.1–30C).

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of the LiFePO₄ material, which was calcined at 400 °C for 1.5 h and then at 670 °C for 2.5 h in an Ar atmosphere. This material showed an orthorhombic structure with the *Pnma* space group without any impurities. This material contained no FeP or metallic Fe₂P impuri-

ties, as confirmed by the absence of peaks at $2\theta = 41^\circ$, which enhanced the electrochemical capacity of the Li/LiFePO₄ cell [16]. The lattice constants of the LiFePO₄ material are $a = 10.3228 \text{ \AA}$, $b = 6.0049 \text{ \AA}$, and $c = 4.6913 \text{ \AA}$. These values are similar to those of the previously reported LiFePO₄ material ($a = 10.3308 \text{ \AA}$, $b = 6.0081 \text{ \AA}$, and $c = 4.6994 \text{ \AA}$). There is a small decrease in the a -axis parameter, however, no remarkable change of the lattice constants in the other axes was observed compared to the previously reported material.

Fig. 2 shows the scanning electron microscopy (SEM) image and particle size distribution of the LiFePO₄ material obtained by the sol-gel method. LiFePO₄ was composed of many small polycrystalline particles with a size of about 50–100 nm and a small proportion of large particles with a size of about 200–300 nm, which were distributed among the smaller particles. The LiFePO₄ material in this study shows a very even particle morphology, which can provide it with a high surface area and improve the electrical conductivity of the electrode. Recently, many research groups have reported the preparation of various LiFePO₄ materials with a very small particle size using different wet methods, because the particle size was suggested to be a key parameter to enhance the electric conductivity of LiFePO₄ at a high current density due to the short diffusion length of lithium ions [11–15]. We also expect that the synthesis of good material with an adequate particle size (about 100 nm) is very important to produce a powerful Li/LiFePO₄ battery system able to operate at a high current density.

Fig. 3 shows the result of the electrochemical characterization of the Li/LiFePO₄ cell. The Li/LiFePO₄ cell shown in Fig. 3a exhibits typical electrochemical behavior with a long distinct voltage plateau at 3.4 V in the first charge/discharge process. This cell shows a high initial charge capacity of more than 159 mA h/g, however, it presents a slightly reduced discharge capacity of 150 mA h/g. It was considered that the mismatched charge/discharge curve results from the non-optimized test condition, such as the powder morphology and electrolyte condition. On the other hand, the Li/LiFePO₄ cell (Fig. 3b) presents a slightly increased discharge capacity of 153 mA h/g until the 3rd cycle and exhibits an excellent cycle performance during the cycling test. There is no capacity fading until 70 cycles (>99.9%), which is a very remarkable cycling result considering that the material was synthesized by the sol-gel method.

Many research groups have tried to adopt the sol-gel process in order to achieve an Li/LiFePO₄ cell with a high initial discharge capacity (>150 mA h/g) as well as an excellent cycle retention rate [17–19]. Especially, Kumta et al. reported a new type of LiFePO₄

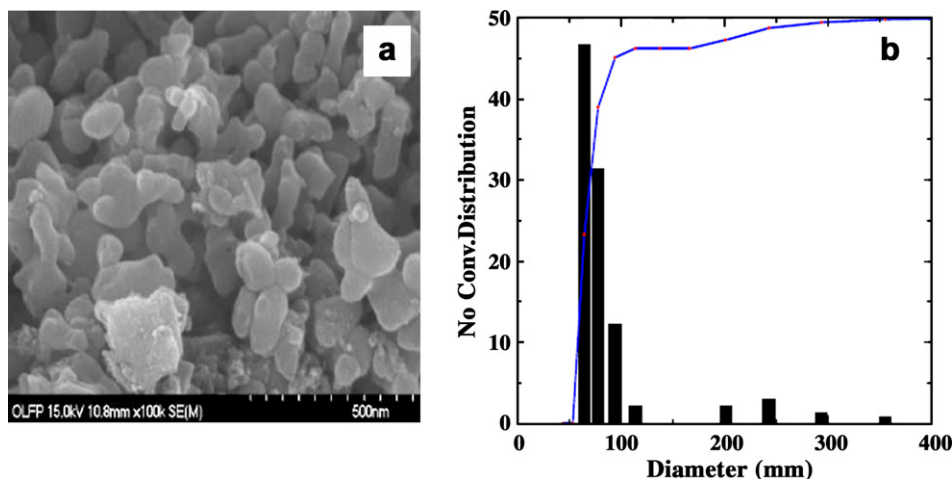


Fig. 2. (a) SEM image and (b) particle size distribution of LiFePO₄ obtained by sol-gel method.

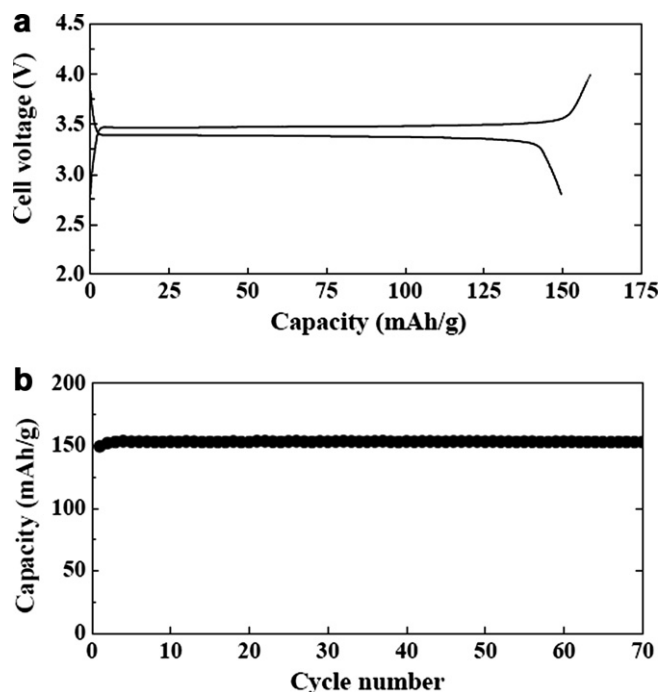


Fig. 3. (a) Initial charge/discharge curves and (b) capacity retention of Li/LiFePO₄ cell. The charge and discharge current density was 0.1 mA/cm² with a cut-off voltage of 2.8–4.0 V at 25 °C.

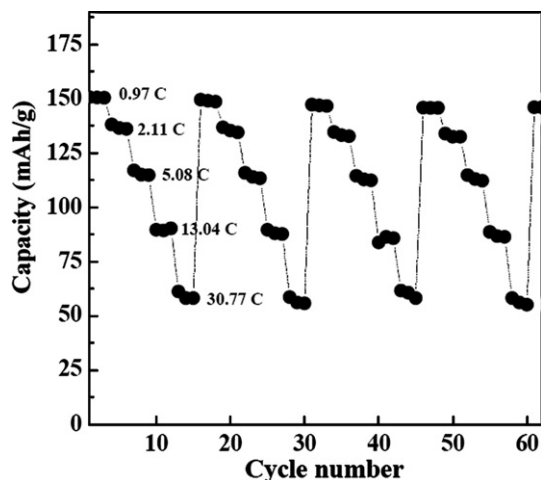


Fig. 4. The high rate cycling performance of Li/LiFePO₄ cell at various current densities (1–30 C).

material, which was treated with lauric acid as a surfactant using the sol–gel method. This material showed excellent battery performance at 10C (>125 mA h/g), which is one of the best results obtained so far for a Li/LiFePO₄ cell. Regrettably, no further cycling data was presented at rates over 10C and the Li/LiFePO₄ cell produced without the surfactant treatment presented an abrupt decline in its cycling performance even at a low current density (5C) [20].

Fig. 4 presents the result of the cycle characterizations of the Li/LiFePO₄ cell at various current densities (1–30C). The initial dis-

charge capacity of the Li/LiFePO₄ cell at 1C still presents a high value of 148 mA h/g and shows a similar value during the continuous cycling test. At a high current density of over 30C, the Li/LiFePO₄ cell also exhibits quite good cycle retention, although the discharge capacity is significantly reduced to 59 mA h/g, which is a small value compared with that of the Li/LiFePO₄ cell at a low current density (0.1C). From the results, we conclude that the LiFePO₄ material prepared by the adipic acid-assisted sol–gel method in this study presents excellent cell performance under harsh conditions (>30C). Moreover, it was easily synthesized without any complex or additional treatments for the purpose of improving the cycle performance, such as the use of a carbon coating, additives, or ball milling.

4. Conclusion

LiFePO₄ was synthesized at 670 °C in an Ar atmosphere using an adipic acid-assisted sol–gel method. It was composed of many polycrystalline particles with a small particle size of about 50–100 nm and a small proportion of large particles with a size of about 200–300 nm. The Li/LiFePO₄ cell showed a high initial discharge capacity of more than 150 mA h/g as well as good cycleability at a high current density of over 30C. We concluded that the excellent battery performance of the Li/LiFePO₄ cell in this study resulted from the small nanoparticles about 100 nm in size and homogeneous powder properties, which increased the electric conductivity and diffusion of lithium ions in the electrode.

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