



Synthesis and electrochemical characterizations of dual doped $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$

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ABSTRACT

Dual doped $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$ material was synthesized at 660 °C in Ar atmosphere by a solid-state method. It showed well developed XRD patterns without any impurity peaks such as FeP or metallic Fe_2P at $2\theta=41^\circ$, which enhance the electrochemical capacity of the $\text{Li}/\text{LiFePO}_4$ system. $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$ was composed of many large polycrystalline-type particles with sizes between 200 and 300 nm and small particles from 20–50 nm distributed among the larger particles. The $\text{Li}/\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$ cell showed the highest initial discharge capacity, greater than 145 mAh/g, which was substantially higher than the $\text{Li}/\text{LiFePO}_4$ cell, 19 mAh/g, under the same test conditions. This might result from enhancement of the contact area and electrical conductivity between the small particles in the $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$ from the small amount of Li and Cu substitution.

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1. Introduction

The presently commercialized lithium secondary batteries use a layer-structured LiCoO_2 cathode material and the presumptive power sources for small portable electronic devices in the near future given their stable charge/discharge profile and excellent cyclability. However, they suffer from the disadvantages of high cost and cobalt toxicity [1–3]. Recently, it has become painfully evident that new cathode materials are required for large-scale battery operations that meet the dual requirements of cost and safety in order to successfully commercialize hybrid electric vehicles (HEVs).

Since LiFePO_4 was first reported by Goodenough et al., it has attracted a great deal of interest as an alternative to LiCoO_2 due to its low cost, nontoxicity, and safety merits [4–7]. Nevertheless, the low electrical conductivity of LiFePO_4 has been a serious obstacle to the development of practical cathode materials. Chung et al. reported a remarkable improvement in its electrical conductivity by doping with Zr, Nb, and W metal ions [8] and has thus brought LiFePO_4 into the spotlight and resulted in intensification of studies on this material.

Recently, Kim et al. also reported that the electronic conductivity was remarkably improved by controlling the lithium content within the lithium sites of the LiFePO_4 structure. They presented the electronic conductivity of Li-deficient (10^{-3} S/cm) and Li-rich (10^{-1} S/cm) samples in Li_xFePO_4 , respectively [9]. Moreover, Croce et al. presented an interesting result in which a Cu-added LiFePO_4 material showed an

increased discharge capacity greater than 137 mAh/g and a higher kinetic conductivity compared to the original LiFePO_4 material [11].

From previous reports, we concluded that lithium and Cu transition methods are quite effective tools in order to improve battery performance of the $\text{Li}/\text{LiFePO}_4$ cell. We firstly report the synthesis of a dual doped $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$ material to enlarge the merit of lithium rich ($\text{Li}_{1.05}\text{FePO}_4$) and copper substitution ($\text{LiFe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$) in the original LiFePO_4 structure. We suggest that substitution of Li and Cu metal ions in the LiFePO_4 structure resulted in a small change of the powder morphology, which improved the electric conductivity and battery performance of the LiFePO_4 electrode.

2. Experimental

Carbon-free LiFePO_4 , $\text{Li}_{1.05}\text{FePO}_4$, $\text{LiFe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$, and $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$ materials were synthesized from Li_2CO_3 (Sigma-Aldrich, USA), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich, USA), CuO (Aldrich, USA), and $(\text{NH}_4)_2\text{HPO}_4$ (Sigma-Aldrich, USA) using a conventional solid-state method. A stoichiometric amount of each material was ground and calcined at 400 °C for 1.5 h and then at 660 °C for 2.5 h in an Ar atmosphere using a tubular furnace. The Li, Fe, and Cu contents in the resulting materials were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP, OPTIMA 4300 DV, Perkin Elmer, USA) after dissolving the powders in dilute nitric acid. Powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) using $\text{CuK}\alpha$ radiation was used to determine the crystalline phase of the prepared material. The particle morphologies of the resulting compounds were observed using a scanning electron microscopy (FE-SEM, S-4700, Hitachi, Japan). The electrochemical characterizations were performed using a CR2032 coin-type cell. The cathode was fabricated with 20.0 mg of accurately

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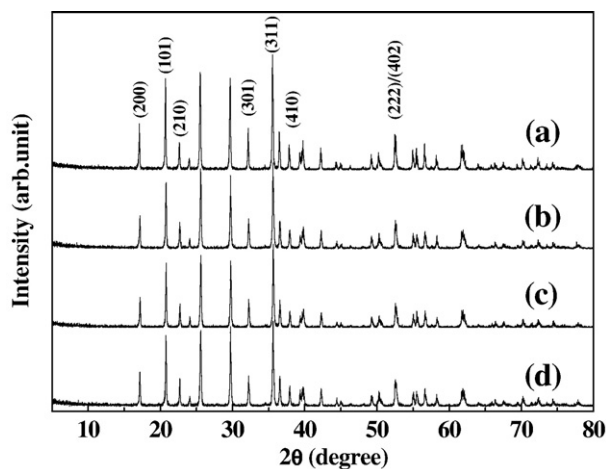


Fig. 1. XRD patterns of: (a) LiFePO_4 ; (b) $\text{Li}_{1.05}\text{FePO}_4$; (c) $\text{LiFe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$; and (d) $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$.

weighed active material, 3.0 mg of Ketzen black, and 3.0 mg of conductive binder (2.0 mg of Teflonized acetylene black (TAB) and 1.0 mg of graphite). It was then pressed onto a 200-mm² stainless steel mesh that 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 1.0 M LiPF_6 -ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1 v/v, Techno Semichem, Korea). The charge and discharge current density were 0.1 mA/cm² with a cut-off voltage of 2.8 to 4.0 V at 25 °C. A 3-

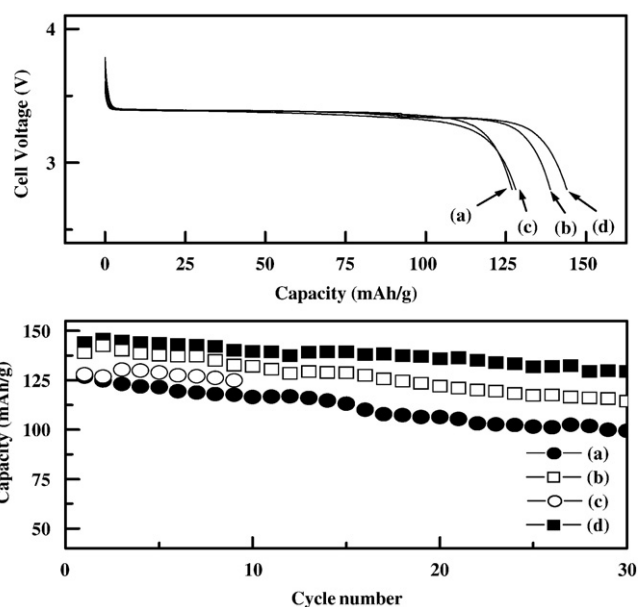


Fig. 3. Initial discharge curves and discharge capacities of Li: (a) LiFePO_4 ; (b) $\text{Li}_{1.05}\text{FePO}_4$; (c) $\text{LiFe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$; and (d) $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$ cells.

electrode glass cell was used for the cyclic voltammetry measurements. The working electrode consisted of 3.0 mg of the active material and 2.2 mg of conducting binder (TAB) pressed onto a stainless steel mesh. The counter and reference electrodes were prepared by pressing lithium foil onto stainless steel gauze. The CV measurements were performed with a cyclic voltammeter system (Hokutodenko, HSV-100,

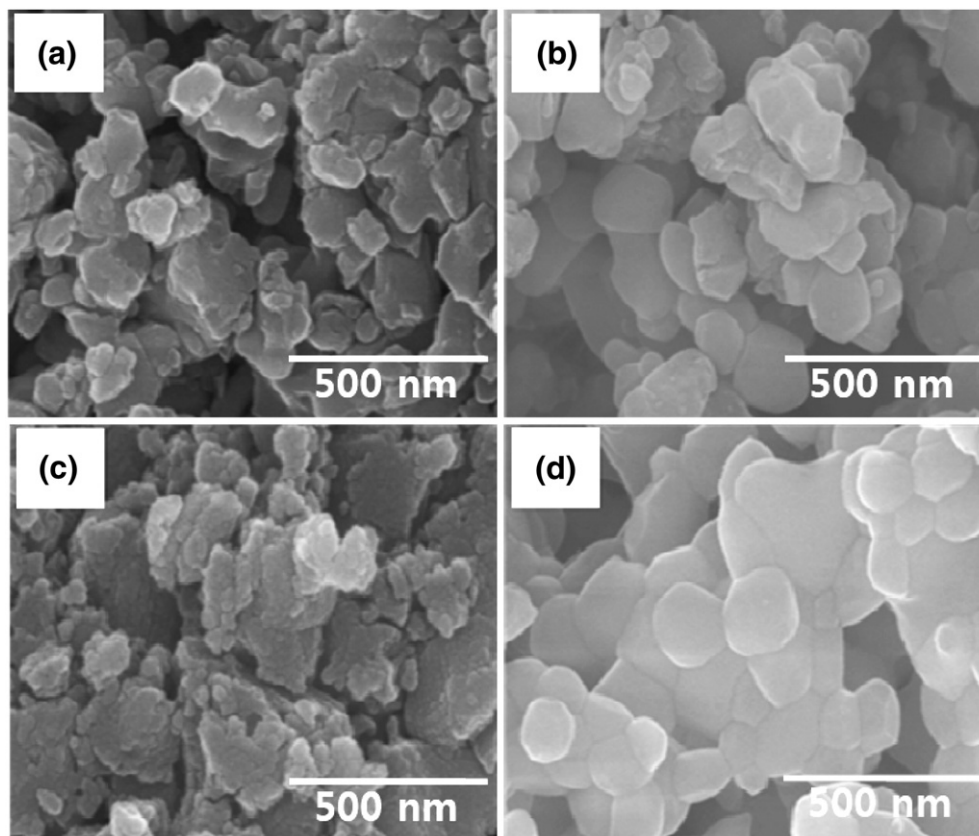


Fig. 2. SEM images of: (a) LiFePO_4 ; (b) $\text{Li}_{1.05}\text{FePO}_4$; (c) $\text{LiFe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$; and (d) $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$.

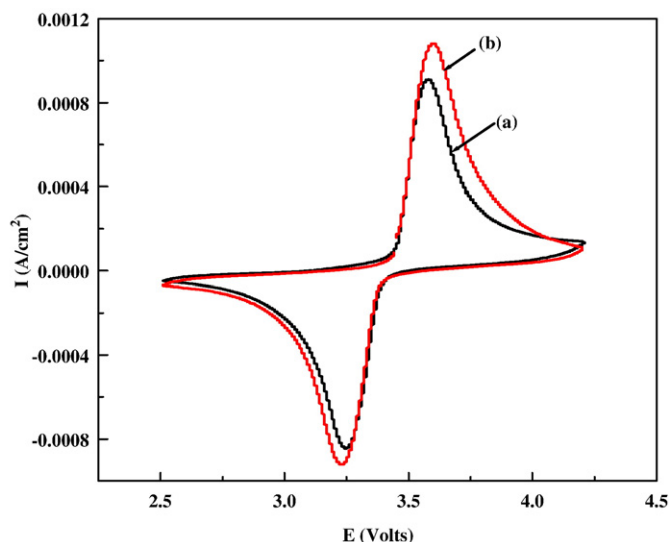


Fig. 4. Cyclic voltammetry of (a) LiFePO₄ and (b) Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄.

Japan) at a scan rate of 0.2 mV/s between the voltage limit of 2.5 and 4.2 V. The assembly of the cell was carried out in a dry box under argon gas.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the LiFePO₄, Li_{1.05}FePO₄, LiFe_{0.997}Cu_{0.003}PO₄, and Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ materials, which were calcined at 400 °C for 1.5 h and then at 660 °C for 2.5 h in an Ar atmosphere. All materials showed an orthorhombic structure with the Pnam space group without any impurities. These materials contained almost no FeP or metallic Fe₂P impurities, as confirmed by the absence of peaks at $2\theta = 41^\circ$, which enhanced the electrochemical capacity of the Li/LiFePO₄ cell [10]. The lattice constants of the stoichiometric LiFePO₄ material were: $a = 10.347$ Å; $b = 6.019$ Å; and $c = 4.699$ Å. These values were similar to those previously reported [14]. However, the Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ material showed slightly decreased values ($a = 10.323$ Å, $b = 6.006$ Å, and $c = 4.692$ Å) to those of the parent LiFePO₄. There was also a small decrease in the a -axis and no remarkable change of the lattice constants in the other axes between the two materials.

Fig. 2 shows the scanning electron microscopy (SEM) images of the prepared materials. All materials showed similar particle sizes and particle distributions. LiFePO₄, Li_{1.05}FePO₄, and LiFe_{0.997}Cu_{0.003}PO₄ were composed of many large polycrystalline type particles ranging from 100–200 nm and small particles from 20–50 nm distributed among the larger particles. Each particle was completely separated and located alone without any linkage. However, Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ showed a slightly increased particle size (200–300 nm) and different particle morphology from other materials. The particles of Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ seemed to melt and combine together during the synthetic process, connecting with each other to form micrometer size lumps. We suggest that a small amount of Li and Cu substitution in the LiFePO₄ changes its structural properties and particle morphology and enhances the contact area between the particles and improves electrical conductivity of the electrode, although only partially in this material.

Fig. 3 shows the results of cyclic behaviors of the Li/LiFePO₄, Li_{1.05}FePO₄, LiFe_{0.997}Cu_{0.003}PO₄, and Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ cells. The first discharge curves of the cells, as shown in Fig. 3(a), exhibit the typical electrochemical behavior of lithium iron phosphate with a long, distinct voltage plateau at 3.4 V. The Li/LiFePO₄ cell showed a small, initial discharge capacity of 126 mAh/g. As expected, the Li/Li_{1.05}FePO₄ and LiFe_{0.997}Cu_{0.003}PO₄ cells commonly present an increased initial discharge capacity of 138 and 128 mAh/g, respectively [9,11]. However, Li/Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ showed the highest discharge capacity of 145 mAh/g and an excellent cycle retention rate over 90% after 30 cycles. We strongly suggest that this material was easily prepared without any

additional treatment for improving cycle performance, such as carbon coating and ball milling, which was reported by many research groups for improving battery performance [9–13]. The difference in initial discharge capacities between the LiFePO₄ and Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ materials was 19 mAh/g, which is quite large when the practical discharge capacity of the Li/LiFePO₄ cell in this study (>15%) is considered.

In order to investigate the relation between the particle properties and electrochemical properties of the prepared materials, cyclic voltammetry analysis was carried out at a sweep rate of 0.2 mV/s between the voltage limit of 2.5 and 4.2 V (Li/Li⁺) as shown in Fig. 4. The cyclic voltammogram of the Li/LiFePO₄ cell in this study shows 2 clear oxidation/reduction peaks at approximately 3.5 and 3.3 V, which are related to the reaction of the Fe²⁺/Fe³⁺ redox couple. The Li/Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ cell also clearly shows enlarged oxidation and reduction peaks at 3.53 V and 3.3 V, respectively. It can be considered that the substituted Li and Cu ions play an important role to improve battery performance of the LiFePO₄ material, which can improve the kinetics of lithium oxidation/reduction on the electrode by enlarging the contact area of the particles. We propose that the advanced battery performance of the Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ material resulted from the use of optimum synthetic conditions as well as properly doped metal and content. A more detailed electrochemical discussion regarding the role of the Li and Cu ions in the Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ material, using extended X-ray absorption fine structure (EXAFS) and XPS, will be reported elsewhere.

4. Conclusion

Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ material synthesized at 660 °C in an Ar atmosphere using a solid-state method. It showed well developed XRD patterns without any impurity peaks. This material was composed of many large polycrystalline-type particles with sizes between 200 and 300 nm and small particles from 20–50 nm distributed among the larger particles. The Li/Li_{1.05}Fe_{0.997}Cu_{0.003}PO₄ cell showed the highest initial discharge capacity of 145 mAh/g, which was substantially higher than the Li/LiFePO₄ cell, 19 mAh/g, under the same test conditions.

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