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Ceramics International 34 (2008) 863–866

CERAMICS INTERNATIONAL

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High-rate properties of $LiFePO_4$/carbon composites as cathode materials for lithium-ion batteries

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Available online 29 September 2007

Abstract

Electrochemical properties of $LiFePO_4$/carbon composites were investigated to achieve a high-rate lithium electrode performance. $LiFePO_4$/carbon composites were synthesized by a hydrothermal reaction of a solution of $FeSO_4 \cdot 7H_2O$, H_3PO_4, and $LiOH \cdot H_2O$ mixed with carbon powders under nitrogen atmosphere followed by annealing under 1% H_2–99% Ar atmosphere. Particle size of the obtained $LiFePO_4$/carbon composites observed by scanning electron microscopy was less than 100 nm. At a high current density of 1000 mA g^{-1}, the $LiFePO_4$/carbon composites showed a high discharge capacity of 113 mA h g^{-1}, and a flat discharge potential plateau was observed around 3.4 V. The discharge capacity at the high current density, 85% of that at a low current density of 30 mA g^{-1}, is a quite high value for $LiFePO_4$ cathodes. Homogeneous microstructure consisting of small particles contributed to the high-rate properties of the $LiFePO_4$/carbon composites.

Keywords: E. Batteries; High-rate properties; $LiFePO_4$; Cathode

1. Introduction

The development of energy storage devices with a high energy density and a high power density is devoted for use as power sources of electric and hybrid vehicles. Lithium-ion batteries [1] have been applied in many portable electronic devices because of a high energy density. Lithium-ion batteries with a high energy density are required for an improvement of high-rate performance in order to use high power devices as power sources of electric and hybrid vehicles. Besides long cycle life, environmental safety and low cost are required. Lithium iron phosphate ($LiFePO_4$) is a promising candidate as a cathode material for lithium-ion batteries [2]. The olivine-based structure of $LiFePO_4$ consists of polyoxyanionic framework containing LiO_6 octahedra, FeO_6 octahedra and PO_4 tetrahedra [3]. $LiFePO_4$ has a high theoretical capacity of 170 mA h g^{-1} and a long cycle life [4]. A flat potential plateau is observed when the insertion/extraction of lithium proceeds via a two-phase of $LiFePO_4$/$FePO_4$. Moreover, $LiFePO_4$ is nontoxic and inexpensive material. However, discharge capacities of $LiFePO_4$ at high current densities decrease by a low lithium diffusion constant (approximately 10^{-14} to 10^{-16} cm^2 s^{-1}) [5] and a low electronic conductivity in the $LiFePO_4$ (approximately 10^{-9} to 10^{-10} S cm^{-1}) [6]. A low lithium diffusion constant and a low electronic conductivity in electrodes lead to capacity losses due to lithium diffusion limitations and ohmic drops. Many studies have been conducted in order to eliminate lithium diffusion limitations in $LiFePO_4$ by reducing particle size or enhance electronic conductivities by coating $LiFePO_4$ with conductive carbon. Yang et al. reported a hydrothermal synthesis method of $LiFePO_4$, and the hydrothermally synthesized $LiFePO_4$ showed a discharge capacity of 100 mA h g^{-1} at a low current density [7]. The particle size of $LiFePO_4$ synthesized by hydrothermal reactions was smaller than that of $LiFePO_4$ synthesized by solid-state reactions. Yamada et al. reported that $LiFePO_4$ with small particle size synthesized by a solid state reaction sintering at 550 °C showed a large discharge capacity of 162 mA h g^{-1} at a low current density [8]. Reducing particle size leads to a reduction of a lithium diffusion distance. Therefore, lithium diffusion limitations are eliminated by reducing particle size. They also analyzed the oxidation state of Fe with Mössbauer

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doi:10.1016/j.ceramint.2007.09.037

spectroscopy and indicated that the oxidation state of Fe was Fe^{2+} in the most part of the $LiFePO_4$. Preventing the formation of Fe^{3+} in $LiFePO_4$ contributes to achieve a high lithium intercalation charge/discharge capacity. Chen et al. reported that $LiFePO_4$ particle coated with a carbon synthesized by sintering with sugar showed a large capacity of 125 mA h g^{-1} at a high current density of 850 mA g^{-1} [9]. The electronic conductivity in electrodes was enhanced by coating $LiFePO_4$ with conductive carbon. The enhanced electronic conductivity contributed to the high discharge capacity at the high current density. Kudo et al. reported sufficient high-rate charge/discharge performances for V_2O_5/carbon composites, prepared by mixing V_2O_5 sol and carbon powders followed by heat treatment [10]. Thin V_2O_5 layers on carbon particles can lead to high discharge capacities at sufficient high current densities for the following reason. The formation of such a homogeneous composite contributes to a reduction of lithium diffusion distance and an increase of a specific surface area as is the case with reducing particle size and an enhancement of an electronic conductivity in electrodes.

Kimura et al. reported that a homogeneous $LiFePO_4$/carbon composite based on the microstructure of the composite suggested by Kudo et al. [10] showed high-rate charge/discharge properties, synthesized from an aqueous solution mixed with carbon powders by hydrothermal reactions followed by annealing [11]. Discharge capacities of the $LiFePO_4$/carbon composite were 90 mA h g^{-1} at a high current density of 1000 mA g^{-1}. However, the discharge capacity of the $LiFePO_4$/carbon composite was 120 mA h g^{-1} at a low current density, and Fe^{3+} contents as impurities produced through oxidation of Fe^{2+} by oxygen dissolved in the aqueous solution would exist in $LiFePO_4$. Preventing the oxidation to Fe^{3+} is required in a synthesis of a homogeneous $LiFePO_4$/carbon composite in order to achieve high capacities and high-rate properties.

In this work, hydrothermal reactions of $LiFePO_4$ precursor mixed with carbon powders under nitrogen atmosphere were conducted in order to synthesize a homogeneous $LiFePO_4$/carbon composite without oxidation of Fe^{2+} by oxygen dissolved in an aqueous solution and to achieve a high-rate lithium intercalation/deintercalation properties. The detailed structure and lithium intercalation properties of the $LiFePO_4$/carbon composite were evaluated.

2. Experimental procedure

$LiFePO_4$/carbon composites were synthesized by hydrothermal reactions [11] under nitrogen atmosphere. $FeSO_4\cdot 7H_2O$ (Wako Chemicals), H_3PO_4 (Wako Chemicals), and $LiOH\cdot H_2O$ (High Purity Chemicals) with molar ratio 1.0:1.0:3.0 were dissolved in deionized water under nitrogen atmosphere. Polyethylene glycol (Wako Chemicals) was added to the solution by a half volume of the mixture solution in order to obtain fine particles [7]. Acetylene black (Denki Kagaku Kogyo) was added to the solution and dioxane (Kanto Chemical) as a surfactant between the aqueous solution and carbon particles was added by a same volume of the mixture solution. The carbon was added by the same weight as that of $LiFePO_4$ to be yielded. A homogeneous dispersion obtained by stirring for 24 h and the nitrogen gas were put into Teflon crucible, and the sealed Teflon crucible was set in pressure-resistant container. Hydrothermal reactions were performed for 3 h at 150 °C under nitrogen atmosphere, and obtained $LiFePO_4$/carbon composites were annealed under 1% hydrogen–99% argon atmosphere for 1 h at 500 °C. The crystal structure of the $LiFePO_4$/carbon composites was evaluated by X-ray diffraction methods using Cu Kα radiation (Bruker AXS, D8 diffractometer). The X-ray diffraction data were corrected in the angle interval from 15° to 55° (2θ) at steps of 0.02° (2θ). The local structure of the $LiFePO_4$/carbon composites was characterized by diffuse reflectance Fourier transform infrared spectroscopy (Shimadzu, IR Prestage-21). The particle sizes of the $LiFePO_4$/carbon composites were observed by scanning electron microscopy (Hitachi, S-4500). The specific surface areas of the $LiFePO_4$/carbon composites were evaluated by nitrogen adsorption–desorption measurements (Micromeritics, TriStar3000). The weight ratio of carbon in the $LiFePO_4$/carbon composites was evaluated by thermogravimetry (Rigaku, TG8120).

The electrodes for electrochemical measurements were fabricated by pressing the mixture of the $LiFePO_4$/carbon composites with 10 wt.% Teflon binder (Du Pont) onto Nickel mesh. The mass loading of $LiFePO_4$ in the electrodes was approximately 1×10^{-2} g cm^{-2}. The thickness of the electrodes was approximately 0.3 mm. Electrochemical measurements were performed using a three-electrode cell with a counter electrode and a reference electrode of lithium metal. An electrolyte was 1 M $LiClO_4$ in propylene carbonate (Kishida Chemical). The cells were assembled in an argon-filled glove box at room temperature. Cyclic voltammetry measurements were carried out at a sweep rate of 0.1 mV s^{-1}, and galvanostatic charge and discharge measurements were carried out in a current density range of 30–2000 mA g^{-1}. All measurements were performed in the voltage range of 2.7–4.3 V with potentiostat/galvanostat (Hokuto Denko, HAG-5001) at room temperature.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns for the $LiFePO_4$/carbon composites. The figure also shows the position

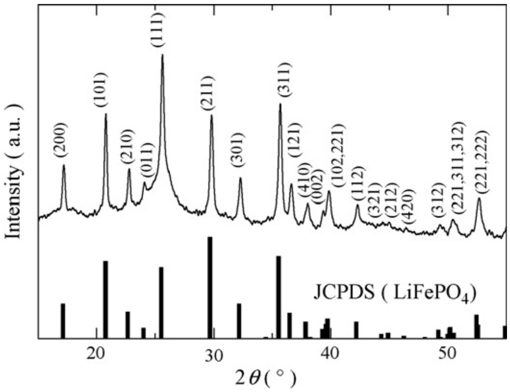

Fig. 1. X-ray diffraction patterns for the $LiFePO_4$/carbon composites.

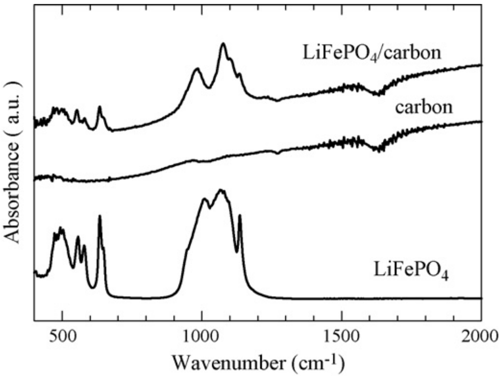

Fig. 2. Fourier transform infrared spectra for the $LiFePO_4$/carbon composites. The spectrum in the middle represents the patterns of acetylene black. The spectrum on the bottom represents the patterns of $LiFePO_4$.

and the relative intensity of peaks for $LiFePO_4$ (JCPDS, No. 40-1499). The XRD pattern of the $LiFePO_4$/carbon composites included broad peak originated from carbon around 26°. All sharp peaks of the $LiFePO_4$/carbon composites were indexed to $LiFePO_4$. Therefore, no impurities in the $LiFePO_4$/carbon composites were detected by X-ray diffraction measurements.

The impurity nano-sized phases can be detected by Fourier transform infrared spectra [12]. Fig. 2 shows the Fourier transform infrared spectra for the $LiFePO_4$/carbon composites, acetylene black and $LiFePO_4$. The intramolecular vibrations of the $(PO_4)^{3-}$ appear in the wavenumber range of 372–1139 cm^{-1} [13]. Symmetric and antisymmetric O–P–O bending modes exist in the range of 372–647 cm^{-1}. Symmetric and antisymmetric P–O stretching modes exist in the range of 945–1139 cm^{-1} [13]. In Fig. 2, these bending and stretching modes in the $LiFePO_4$/carbon composites and $LiFePO_4$ were observed. Additional peaks in the $LiFePO_4$/carbon composites compared with the peaks in $LiFePO_4$ were not observed. Therefore, no inclusions as impurities were detected by Fourier transform infrared spectra in the $LiFePO_4$/carbon composites.

Fig. 3 shows the scanning electron microscopic images for (a) the $LiFePO_4$/carbon composites and (b) acetylene black using as carbon sources. The particle size of the $LiFePO_4$/carbon composites was less than 100 nm. The particle size of acetylene black was approximately 50 nm, and this particle size of acetylene black was smaller than that of the $LiFePO_4$/carbon composites. Then, the $LiFePO_4$/carbon composites are expected to have a microstructure where each carbon particles with a size of approximately 50 nm would be covered with thin $LiFePO_4$ layer or buried in $LiFePO_4$ aggregates, as reported previously [11].

The Brunauer–Emmett–Teller (B.E.T.) surface area of the $LiFePO_4$/carbon composites was 39 $m^2 g^{-1}$ measured by nitrogen adsorption–desorption measurements. A specific surface area of the $LiFePO_4$/carbon composites estimated in the ideal state in which carbon with a diameter of 50 nm was uniformly coated with $LiFePO_4$ is 40 $m^2 g^{-1}$. The estimated surface area was nearly equal to the measured B.E.T. surface area. These results of scanning electron microscopic images and B.E.T. surface area indicated that the $LiFePO_4$/carbon composites were constructed with carbon particles covered with a thin $LiFePO_4$ layer. A thickness of the $LiFePO_4$ layer denoted a lithium diffusion distance for the $LiFePO_4$/carbon composites, and the layer thickness could be estimated to be a few nanometer.

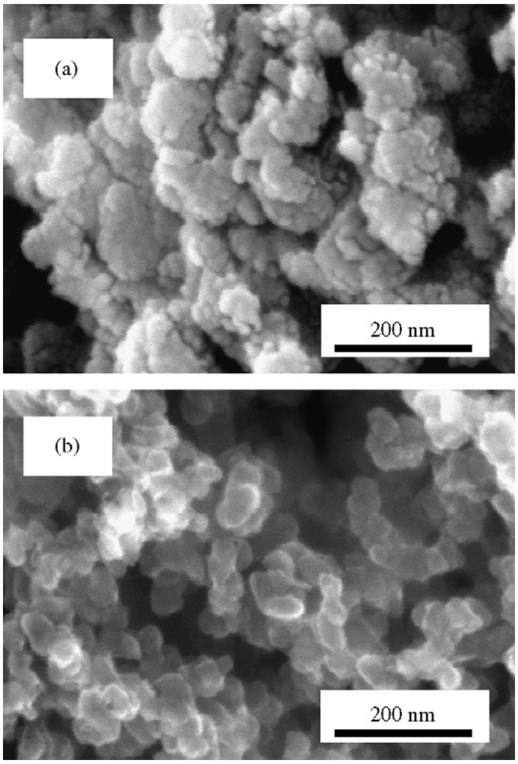

Fig. 3. SEM images for $LiFePO_4$/carbon composites and acetylene black using as carbon sources. (a) $LiFePO_4$/carbon composites and (b) acetylene black.

The weight ratio of carbon in the $LiFePO_4$/carbon composites was evaluated by using thermogravimetry. Fig. 4 shows the thermogravimetric curves for the $LiFePO_4$/carbon composites and $LiFePO_4$. The amount of weight change in the $LiFePO_4$/carbon composites and $LiFePO_4$ was evaluated by heating in air at 800 °C. The difference of weight change in the $LiFePO_4$/carbon composites and $LiFePO_4$ denoted the mass of carbon content in the composites as the carbon in the composites was burned off by heating in air at 800 °C. The mass of $LiFePO_4$ increased approximately 3% by an oxidation of Fe^{2+} in $LiFePO_4$. The carbon in the $LiFePO_4$/carbon

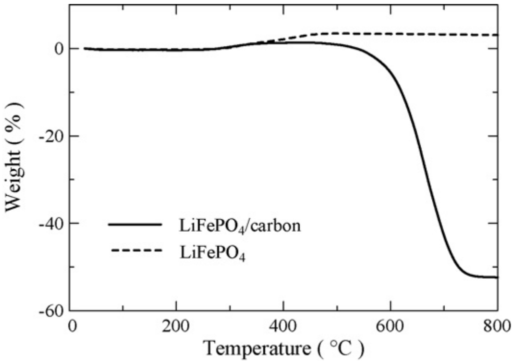

Fig. 4. Thermogravimetric curves for the $LiFePO_4$/carbon composites and $LiFePO_4$. Heating rate was 10 K min^{-1}.

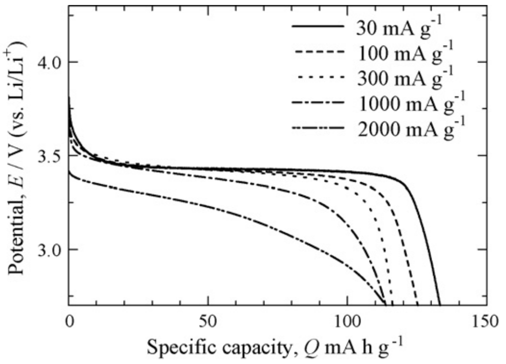

Fig. 5. Discharge curves for the LiFePO$_4$/carbon composites. Current density range was 30–2000 mA g^{-1}.

composites was burned off at 600 °C, and the total mass of the composites decreased by 52%. As a result, the carbon weight ratio in the LiFePO$_4$/carbon composites was 52 wt.% as against a total mass of the composites.

Fig. 5 shows the discharge curves for the LiFePO$_4$/carbon composites in a current density range of 30–2000 mA g^{-1}. Current densities and discharge capacities were normalized to the mass of LiFePO$_4$. A discharge capacity for the LiFePO$_4$/carbon composites was 133 mA h g^{-1} at a low current density of 30 mA g^{-1} and a flat discharge potential plateau was observed around 3.4 V. Discharge capacities for the LiFePO$_4$/carbon composites decreased with increasing current density, however significant capacity losses were not observed. Discharge capacities for the LiFePO$_4$/carbon composites were 125 mA h g^{-1} at a current density of 100 mA g^{-1}, 116 mA h g^{-1} at 300 mA g^{-1}, 113 mA h g^{-1} at 1000 mA g^{-1} 1 and 113 mA h g^{-1} at 2000 mA g^{-1}, respectively. In a current density range of 30–1000 mA g^{-1}, flat discharge potential plateaus were observed around 3.4 V, and the discharge capacity at the high current density was approximately 85% of that at the low current density in the LiFePO$_4$/carbon composites. The flat discharge potential plateaus around 3.4 V in a current density range of 30–1000 mA g^{-1} indicates that the LiFePO$_4$/carbon composites has a high electronic conductivity and a low lithium diffusion distance in the electrodes. The homogeneous microstructure of the LiFePO$_4$/carbon composites led to an increase in an electronic conductivity by close contact of LiFePO$_4$/carbon interface and a reduction of a lithium diffusion distance in the LiFePO$_4$ layer with a few nanometer thickness as shown above. The discharge capacity at the highest current density of 2000 mA g^{-1}, 85% of that at a low current density of 30 mA g^{-1}, is a quite high value for LiFePO$_4$ cathodes. Then, high-rate lithium intercalation/deintercalation performances for the LiFePO$_4$/carbon composites were achieved. On the other hand, a volumetric capacity for the LiFePO$_4$/carbon composites was approximately 50 mA h cm^{-3}. The small volumetric capacity is due to a high carbon content, which is necessary for preparing such homogeneous LiFePO$_4$/carbon composites. Improvement of composite microstructure such as use of smaller carbon particles with a low content will enable an increase in volumetric capacity.

4. Conclusions

LiFePO$_4$/carbon composites were synthesized by hydrothermal reactions under nitrogen atmosphere and their electrochemical properties were investigated. The particle size of the LiFePO$_4$/carbon composites was less than 100 nm. The LiFePO$_4$/carbon composites were constructed with carbon particles covered with a thin LiFePO$_4$ layer. At a high current density of 1000 mA g^{-1}, the LiFePO$_4$/carbon composites showed a high discharge capacity of 113 mA h g^{-1}, and the flat discharge potential plateau was observed around 3.4 V. The discharge capacity at the high current density was approximately 85% of that at the low current density in the LiFePO$_4$/carbon composites. The homogeneous microstructure of the LiFePO$_4$/carbon composites led to an increase in an electronic conductivity by close contact of LiFePO$_4$/carbon interface and a reduction of a lithium diffusion distance in LiFePO$_4$ layer with a few nanometer thickness. Therefore, high-rate lithium intercalation/deintercalation performances for the LiFePO$_4$/carbon composites were achieved.

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