Self-assembly of LiFePO₄ nanodendrites in a novel system of ethylene glycol–water

Fei Tenga,c, Sunand Santhanagopalan a, Anjana Asthana a, Xiaobao Genga, Sun-il Mohob, Reza Shahbazian-Yassara, Dennis Desheng Meng a,⁎

a Department of Mechanical Engineering-Engineering Mechanics, Michigan Technological University, Houghton, MI 49931, USA
b Division of Energy System research, Ajou University, Sawaon 443-749, Korea
c School of Environmental Science and Engineering, Nanjing University of Information Science and Technology Nanjing 210044, P.R. China

A R T I C L E   I N F O

Article history:
Received 24 March 2010
Received in revised form 9 July 2010
Accepted 2 September 2010
Communicated by M. Schieber

Keywords:
A1. Crystal morphology
A1. Crystal structure
A1. Nanostructures
A2. Self-assembly
B1. LiFePO₄

A B S T R A C T

In this work, a novel system of ethylene glycol/water (EG/W) was employed to synthesize LiFePO₄, in which dodecyl benzene sulphonic acid sodium (SDBS) was used as soft template to control particle morphology. The samples were characterized by X-ray diffractometer (XRD), field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX). The LiFePO₄ sample obtained by the reported method displays an interesting hierarchical nanostructure (i.e. nanodendrites), which was constructed by nanorods of 3–5 μm in length and ∼50 nm in diameter. The EG/W ratio, amount of SDBS added, hydrothermal temperature and duration played important roles in the assembly of the hierarchical nanostructures. A formation mechanism was proposed and experimentally verified. It is concluded that the nanodendrites were formed due to the end-to-end self-assembly of nanorods. Compared to previously reported methods, the reported approach shows obvious advantages of one-step synthesis, environmental friendliness and low cost, to name a few. The nanodendrites as a cathode material have a higher capacity, compared with the other samples.

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1. Introduction

Since the pioneering work of Padhi et al. [1], LiFePO₄ has been intensively investigated as one of the most promising cathode materials in rechargeable lithium batteries [2,3]. The main advantages of LiFePO₄ include flat voltage plateau (3.4 V versus Li⁺/Li), moderate theoretical specific capacity (170 mAh g⁻¹), high thermal stability, long cycling life, environmental friendliness and abundance of iron (Fe) resources in nature. Moreover, LiFePO₄ is considered to be much safer than other cathode materials (e.g., LiCoO₂ and LiMn₂O₄) due to its outstanding stability upon overcharging and overdischarging [1–3]. For example, metastable LiCoO₂ can easily lose oxygen while overcharging, which increases the probability of oxygen liberation. Hence, LiFePO₄ is expected to be the most promising cathode material for large-size lithium-ion batteries in electrical vehicles (EVs) and hybrid electric vehicles (HEVs) that demand both fast charging and strict safety regulation [1,4]. However, bulk LiFePO₄ electrodes are limited on its rate capability, due to its intrinsic low electrical conductivity and limited Li ion diffusion rate [2,3,5–7]. Its electrical conductivity (10⁻⁹–10⁻¹⁰ S cm⁻¹) is by several orders of magnitude lower than that (e.g., ca. 10⁻³ S cm⁻¹) of LiCoO₂ cathode materials, which prevents achievement of full theoretical capacity (170 mAh g⁻¹) at very high rates [3,7]. To date, most attempts have been carried out to overcome the electronic and lithium-diffusion limitations, such as coating of carbon [3,7,8], cationic supervalent substitution [3,7,9,10] and addition of conductive materials (Cu, Ag, carbon black) [11–13]. During the last decade, it has also been demonstrated that size reduction of LiFePO₄ micro- or nanoparticles can effectively enhance Li diffusion rate and significantly improve performances [3,14]. Another significant challenge is the large-scale synthesis of high-purity LiFePO₄ nanoparticles with uniform morphology, which is essential for their commercial applications. To date, various methods have been proposed to synthesize LiFePO₄ such as solid-state reaction [15], sol–gel [16], hydrothermal [17,18], co-precipitation [7], vapor deposition [8], microwave [19], spraying technology [20], to name a few. Of these, hydrothermal synthesis is an effective method to obtain well-crystallized materials with well-defined morphologies, where no additional high-temperature annealing is needed [17,21]. To date, synthesis of di-element materials with various morphologies by a hydrothermal route has been a fairly common practice. Nevertheless, morphosynthesis of multi-element LiFePO₄ represents significant challenges and thus has been reported...
only scarcely. This situation has been attributed to the fact that the different precursor chemicals generally have different reactivities, which is not favorable for crystal growth or formation of pure products. In the past years, Nazar et al. investigated the influence of hydrothermal conditions and additives on the morphology of LiFePO₄ crystals [18]. Chen et al. [22] prepared the large diamond-shaped LiFePO₄ sample by the hydrothermal method. Sides et al. [23] synthesized LiFePO₄ nanofibers with polycarbonate membranes template. They reported that the nanofibers showed an excellent rate capacity because the nanofiber morphology mitigates the problem of slow Li ion-transport in solid state. Vittal et al. also synthesized LiFePO₄ nanorods with high rate capability [24]. Their results showed that particle morphology or architecture has a great influence on the performances of materials [25]. Although significant efforts have to be made to synthesize LiFePO₄ nanostructures, designing or controlling new and advanced nanostructures with enhanced performances is always of most interest to materialists. Recently, Rangappa et al. [26] synthesized LiFePO₄ flowers using the solvothermal method. However, the preparation was performed at a very high temperature (400°C) and pressure (40 MPa), which limits its practical production. Yang et al. [27] synthesized LiFePO₄ dumbbell-like microstructures composed of nanoplates via a solvothermal route, which showed an excellent cycling stability. In their work, nevertheless, expensive benzyl alcohol and LiI were used, and a long reaction time (48 h) was required. Hence, the preparation is costly and time-consuming. Much effort is still needed to develop a more economically efficient route to synthesize LiFePO₄ with well-defined morphology. Although the hydrothermal method has shown its potential to provide such a route, it has not been reported as a feasible approach to synthesize LiFePO₄ nanodendrites.

In this work, a novel system of ethylene glycol/water (EG/W) was developed to synthesize LiFePO₄ nanodendrites under hydrothermal conditions. Lithium hydroxide was used as a precursor and dodecyl benzene sulphonic acid sodium (SDBS) was used as a soft template to control crystal growth. LiFePO₄ samples have been prepared under various synthesis conditions to reveal the influences of EG/W volumetric ratio, amount of SDBS added, hydrothermal temperature and time. Table 1 shows the results. The samples were characterized by XRD, FE-SEM, HRTEM, ED and EDX. A formation mechanism of LiFePO₄ nanodendrites was proposed based on the time-dependent results. The reported approach shows significant advantages over the state of the art, such as one-pot synthesis, environmental friendliness and low cost, which are mainly attributed to the employed inexpensive precursors and solvent, as well as the short synthesis time.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>EG/W&lt;sup&gt;b&lt;/sup&gt;</th>
<th>SDBS/Fe&lt;sup&gt;c&lt;/sup&gt;</th>
<th>T/t (°C/h)</th>
<th>Crystal phases</th>
<th>Particle shape&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-1</td>
<td>1/1</td>
<td>1/1</td>
<td>140/6</td>
<td>LiFePO₄ +Li₃PO₄ +Fe₄(PO₄)₃(OH)₃</td>
<td>–</td>
</tr>
<tr>
<td>S1-2</td>
<td>1/1</td>
<td>1/1</td>
<td>160/6</td>
<td>LiFePO₄</td>
<td>Nanodendrites</td>
</tr>
<tr>
<td>S1-3</td>
<td>1/1</td>
<td>1/1</td>
<td>180/6</td>
<td>LiFePO₄</td>
<td>Irregular</td>
</tr>
<tr>
<td>S1-4</td>
<td>1/1</td>
<td>1/1</td>
<td>200/6</td>
<td>LiFePO₄</td>
<td>Irregular</td>
</tr>
<tr>
<td>S1-5</td>
<td>1/1</td>
<td>1/1</td>
<td>160/2</td>
<td>LiFePO₄ (Little) +Fe₄(PO₄)₃(OH)₃</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>S1-6</td>
<td>1/1</td>
<td>1/1</td>
<td>160/4</td>
<td>LiFePO₄</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>S1-7</td>
<td>1/1</td>
<td>1/1</td>
<td>160/12</td>
<td>LiFePO₄</td>
<td>Nanodendrites</td>
</tr>
<tr>
<td>S1-8</td>
<td>1/1</td>
<td>1/1</td>
<td>160/24</td>
<td>LiFePO₄</td>
<td>Nanodendrites</td>
</tr>
</tbody>
</table>

<sup>a</sup> Crystal size calculated by the Sherrer equation basing on [0 0 2] plane.
<sup>b</sup> Ethylene glycol/deionized water volumetric ratio.
<sup>c</sup> Molar ratio; SDBS stands for dodecyl benzene sulphonic acid sodium.
<sup>d</sup> Observed by FE-SEM or HRTEM.

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Fig. 1. XRD patterns of the as-prepared samples at different hydrothermal temperatures corresponding to those in Table 1. (A) scanning in the range of 15–70°; (B) slow scanning in the range of 26–32°: (a) S1-1; (b) S1-2; (c) S1-3; (d) S1-4.
The novel nanodendrites are expected to present excellent electrochemical properties compared to other nanostructures, e.g., near-spherical nanoparticles.

2. Experimental section

2.1. Chemicals

In this work, all chemicals were used as purchased without further purification. Deionized (DI) water treated in-house by an ion-exchange system was used in the experiment. FeCl₂ · 7H₂O, LiOH, H₃PO₄ (85 wt% aqueous solution), L(+)-ascorbic acid, ethylene glycol (EG) and dodecyl benzene sulphonic acid sodium (SDBS, C₁₈H₂₉SO₃Na) were purchased from Sigma Aldrich.

2.2. Preparation of samples

The LiFePO₄ nanodendrites were prepared by a simple hydrothermal process, during which L-ascorbic acid was added as a mild reducing agent to prevent the oxidation of Fe(II). Typically, the appropriate quantities of LiOH, FeCl₂ · 7H₂O, H₃PO₄, L-ascorbic acid and SDBS with the molar ratios of 3:1:1:3:1 were added into 35 mL of EG/W mixture (1/1 volumetric ratio). After intensive magnetic stirring for 1 h at room temperature, a homogeneous solution was formed. The solution was then transferred into a 50 mL Teflon®-lined stainless steel autoclave, which was heated to 160 °C and kept at this temperature for 6 h. After being cooled naturally to room temperature, the product was centrifuged, washed at least six times with DI water and ethanol, and finally dried at 80 °C in a vacuum for 24 h. In order to investigate the effects of preparation conditions on the samples, several experimental parameters, such as the volumetric ratio of EG to W, the amount of SDBS added, hydrothermal time and temperature, were varied.

2.3. Characterization

Scanning electron microscopy (SEM) images were taken with a Hitachi S-4700 field emission scanning electron microscope (FE-SEM). Before FE-SEM inspection, the samples were coated with 5-nm-thick platinum/palladium layer by direct current (DC) sputtering. The acceleration voltage was 15 keV, and the acceleration current was 1.2 nA. The morphology, crystalline properties, surface structure and element composition of the samples were determined by using high-resolution transmission electron microscopy (HRTEM). We employed a JEOL JEM-4000FX system equipped with electron diffraction and energy dispersive X-ray spectroscopy (EDX) attachments with an acceleration voltage of 200 kV. The powders were first ultrasonically dispersed in ethanol, and then deposited on a thin amorphous carbon film supported by a copper grid. The crystal structures of the samples were characterized by an X-ray powder diffractometer (XRD, Rigaku D/MAX-RB), using graphite monochromatized Cu Kα.
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3. Results and discussion

3.1. Influences of hydrothermal temperature and duration

First, we investigated the influence of hydrothermal temperature on the sample (Table 1 S1-1 to S1-4). The hydrothermal temperature was varied from 140 to 160, 180 and 200 °C, while the other processing parameters were maintained the same. Fig. 1 gives the typical XRD patterns of the as-synthesized samples. After being processed at 140 °C for 6 h, no single-phase LiFePO₄ sample was obtained (S1-1). Instead, the sample contained significant amounts of impurity crystals (e.g., Li₃PO₄ and Fe₄(PO₄)₃(OH)₆). It could be assumed that the higher energy is necessary for the formation of LiFePO₄ crystals. Above 160 °C, the diffraction peaks become stronger and narrower with the increase of temperature. The mean crystallite size (D_{020}) was further calculated using Scherrer’s equation from the [0 2 0] diffraction peak (Fig. 1(B)). The mean D_{020} values for S1-2, S1-3 and S1-4 are 25.5, 37, and 42 nm, respectively. It is obvious that the hydrothermal temperature has a significant influence on the morphology and structure of the products. It is clear that the hydrothermal temperature has a significant influence on crystal growth. Further, the morphologies of the as-prepared samples (S1-2, S1-3, and S1-4) were characterized by FE-SEM. Interestingly, the as-prepared sample (S1-2) at 160 °C displays a hierarchical structure (Fig. 2). When observed at a low magnification (Fig. 2(a)), the particles displayed fairly uniform morphology, and each particle features a nanodendrite of 4–5 μm in length. As revealed in Fig. 2(b), the individual nanodendrite consists of nanorods of 100 nm in diameter and 2–5 μm in length. These nanorods seem to be attached end-to-end to form an ordered architecture. This novel hierarchical architecture of LiFePO₄ nanorods has not been reported previously. At higher temperatures (180 and 200 °C), however, the as-prepared samples display irregular morphologies (Fig. 2(c) and (d)). It is obvious that the hydrothermal temperature has a significant influence on the morphology and structure of the products. It could be concluded that there exists a critical temperature at which the nucleation and growth of crystals are too fast to form crystals with well-defined morphology. It is clear that the hydrothermal temperature played a key role in the formation of high crystallinity LiFePO₄ crystals. Our results have shown that an appropriate hydrothermal temperature (160 °C) can be chosen to synthesize LiFePO₄ nanorods. This mild temperature of the reported process is considered to be a major advantage over existing methods employing higher processing temperatures.

Hydrothermal time was then varied from 2, 6, 12 and 24 h to investigate the effect of reaction time while the hydrothermal...
LiFePO₄ nanorods that are 100 nm in length and 10–20 nm in diameter (Fig. 4(a)). On the other hand, when the processing time is longer than 6 h, the crystals grew at a fairly smaller extent. It is further confirmed that the as-obtained sample consists of many well-dispersed nanodendrites with uniform morphology. The length of those structures is again confirmed as of 4–5 μm (Fig. 4(c)). The results consistently agree with the FE-SEM images presented in Fig. 2(a) and (b). It is worth mentioning that these nanodendrites are sufficiently stable to withstand ultrasonic treatment for 30 min (or even longer) without being broken into fragments. We also observed that after being processed for 12 or 24 h, the nanodendrite architectures maintained their morphologies (Fig. 4(d)). The TEM image for sample S1-8 (24 h) is not shown herein. To exemplify the morphology of the sample obtained, the high-magnification image of an individual particle is shown in Fig. 4(d). The spiky structure on the edge of the particle indicates that the particles are composed of nanorods with a diameter of about 100 nm (Fig. 4(e)). The inset of ED patterns (Fig. 4(f)) shows clearly the single-crystalline nature of the nanorods. A HRTEM image (Fig. 4(g)) taken on the tip of an individual nanorod displays clear crystal lattices with d-spacing of 0.29 nm, corresponding to the (0 2 0) plane of orthorhombic LiFePO₄ crystals. The above time-dependent processes further confirm that the single-crystalline nature of the nanorods, and suggested that the crystal preferentially grow along the (0 2 0) direction. Fig. 4(h) provides the EDX spectra of the sample (S1-2). The peaks of copper are obviously caused by the copper grid, which is the carrier of the HRTEM samples. The peaks of Fe and P can be observed clearly, but the peaks of lithium did not appear in EDX spectra due to the light mass of lithium. The above time-dependent experiments suggest that at the beginning stage, the nucleation process takes place under hydrothermal conditions, leading to the formation of nanoparticles; then the nanoparticles grow into nanorods through a crystallization–dissolution–recrystallization process. Eventually, the nanorods organize into the hierarchical structures through an end-to-end self-assembly process. Extensive future research is still needed to clarify the details of the self-assembly process.

### 3.2. Influence of reaction medium composition

We have also investigated the effect of reaction medium on the samples. EG/W volumetric ratio was varied at 0/1, 1/1, 2/1, 4/1 and 1/0 while other preparation parameters were maintained the same (Table 2). The typical XRD patterns and FE-SEM images of the as-prepared samples are shown in Figs. 5 and 6, respectively. At the EG/W ratios of 0/1, the sample obtained is mainly composed of LiFePO₄ crystals accompanied by a very small amount of Fe₂PO₄·(OH)₃ impurity crystals (Fig. 5(a)). At the EG/W ratios of 1/1 and 2/1, single-phase LiFePO₄ crystals were obtained, while no other impurity crystals were observed (Fig. 5(b), S1-2 in Fig. 2). At the EG/W volumetric ratio of 0/1, the obtained sample is composed of plates with a thickness of 100–150 nm and a width of 1 μm (S2-1 in Fig. 6). The nanodendrite structure was obtained at an EG/W volumetric ratio of 1/1, as shown in Fig. 5. When the volumetric ratio of EG/W was changed to 2/1, the sample obtained consists of...

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**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>EG/W*</th>
<th>SDS/Fe⁵</th>
<th>T (h)</th>
<th>Crystalline phases</th>
<th>Particle shape⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2-1</td>
<td>0/1</td>
<td>1/1</td>
<td>160/6</td>
<td>LiFePO₄+Fe₂PO₄·(OH)₃ (Little)</td>
<td>Plates</td>
</tr>
<tr>
<td>S1-2</td>
<td>1/1</td>
<td>1/1</td>
<td>160/6</td>
<td>LiFePO₄</td>
<td>Nanodendrites</td>
</tr>
<tr>
<td>S2-3</td>
<td>2/1</td>
<td>1/1</td>
<td>160/6</td>
<td>LiFePO₄</td>
<td>Large shuttles</td>
</tr>
<tr>
<td>S2-4</td>
<td>4/1</td>
<td>1/1</td>
<td>160/6</td>
<td>LiFePO₄+Li₃PO₄ Fe₂PO₄·(OH)₃</td>
<td>Large rods</td>
</tr>
<tr>
<td>S2-5</td>
<td>1/0</td>
<td>1/1</td>
<td>160/6</td>
<td>LiFePO₄+Li₃PO₄ Fe₂PO₄·(OH)₃</td>
<td>Irregular particles</td>
</tr>
</tbody>
</table>

* Volumetric ratio.
⁵ Molar ratio.
⁶ Observed by FE-SEM.

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**Fig. 5.** XRD patterns of the as-prepared samples at different volumetric ratios of EG/W corresponding to those in Table 2: (a) S2-1, (b) S2-3, (c) S2-4 and (d) S2-5.

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Please cite this article as: F. Teng, et al., J. Crystal Growth (2010), doi:10.1016/j.jcrysgro.2010.09.005
large spindle-shaped particles with a length of 2 \( \mu \text{m} \) and a center diameter of 1 \( \mu \text{m} \) (S2-3 in Fig. 6). When the volumetric ratio of EG to W was further increased to 4/1 and 1/0, high-purity LiFePO\(_4\) crystals were not obtained. Instead, the impurity crystals (Li\(_3\)PO\(_4\), FeFe\(_3\)(PO\(_4\))\(_3\)(OH\(_3\)) and unknown phases) started to appear in these samples. FE-SEM images show that both samples consist of large rods and irregular particles (S2-4 and S2-5 in Fig. 6). It is obvious that reacting medium composition has a significant influence on phase composition and morphology of the samples. Two aspects of the new mixture medium are assumed to be very important in this process. First of all, a high enough solubility of the precursor chemicals in the EG/W medium needs to be guaranteed to ensure the formation of proper LiFePO\(_4\) crystal structure. As the EG content in the mixture increases, the solubility of the precursor chemicals decreases. As a result, the precursor chemicals cannot be mixed homogeneously at higher EG content, which does not favor the formation of pure LiFePO\(_4\) crystals. On the other hand, it is well known that the viscosity of EG (\( \eta = 21 \) mPa s, 20 °C) is much higher than that of water (\( \eta = 1.0087 \times 10^{-3} \) mPa s, 20 °C). The mobility or reactivity of ions in solvent has an important influence on the crystal growth. Too higher EG content may lead to very slow mobility or reactivity of ions in the medium, which does not favor to form the final product. At an appropriate content of EG (i.e. 1/1 volumetric ratio of EG to W), the reactivity of the precursors may match one another, which does favor to form the final product. Although those two factors can explain our experimental results well, further investigations are still needed to confirm our hypothesis and reveal the fundamental physical and chemical interactions in our process.

### 3.3. Influence of the amount of surfactant added

To investigate the influence of the added amount of SDBS on the self-assembly behavior of LiFePO\(_4\) nanostructures, this particular processing parameter (SDBS amount) was changed while others were maintained the same, as shown in Table 3. Fig. 7 indicates high-purity LiFePO\(_4\) structures of the as-prepared

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**Table 3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>EG/W (^a)</th>
<th>SDBS/Fe (^b)</th>
<th>T/t (°C/h)</th>
<th>Crystalline phases</th>
<th>Particle shape (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3-1</td>
<td>1/1</td>
<td>0/1</td>
<td>160/6</td>
<td>LiFePO(_4)</td>
<td>Large spheres+irregular particles</td>
</tr>
<tr>
<td>S1-2</td>
<td>1/1</td>
<td>1/1</td>
<td>160/6</td>
<td>LiFePO(_4)</td>
<td>Nanodendrites</td>
</tr>
<tr>
<td>S3-3</td>
<td>1/1</td>
<td>2/1</td>
<td>160/6</td>
<td>LiFePO(_4)</td>
<td>Rods+dumbbells</td>
</tr>
<tr>
<td>S3-4</td>
<td>1/1</td>
<td>4/1</td>
<td>160/6</td>
<td>LiFePO(_4)</td>
<td>Large bones</td>
</tr>
</tbody>
</table>

\(^a\) Volumetric ratio.  
\(^b\) Molar ratio.  
\(^c\) Observed by FE-SEM.
samples with different amounts of SDBS. Fig. 8 shows the FE-SEM images of these samples. When no SDBS was added to the system, large nearly spherical particles were obtained (Fig. 8(a)). In this case, neither the hierarchically assembled structure (i.e. nanodendrites) nor the nanorod building blocks were observed, although the final samples seem to be composed of high-purity LiFePO₄ crystals. Under an SDBS/Fe molar ratio of 1/1, the optimal synthesis conditions in our research, a number of well-defined hierarchical structures of nanorods are observed, as exemplified by sample S1-2 in Fig. 2. When the molar ratio of SDBS/Fe was further increased to 2/1, relatively larger dumbbells of 10 µm in length are observed, consisting of 3–4 µm long microrods (S3-3 in Fig. 8(b)). When the volumetric ratio of SDBS/Fe was further increased to 4/1, coarse bone-shaped microparticles of 10 µm in length were obtained (S3-4 in Fig. 8(c) and (d)). The blow-up view of those nanorods in S3-4 is shown in Fig. 8(d). It appears that they are assembled by nanorods, similar to the building blocks of nanodendrites in S1-2. These observations clearly establish that the presence of SDBS plays a key role in the formation of nanorod building blocks, as well as the self-assembly process. Additionally, the amount of SDBS is a crucial factor for the control of the hierarchical structures. We further conjecture that SDBS may act as a soft template to direct the growth of nanoparticles into nanorods at the early stage of the process through a preferential bonding to certain crystal planes. Later on, these nanorods are further aligned tightly and assembled end-to-end under the guidance of the soft template to form various forms of hierarchical structures (e.g., nanodendrites or bones).

3.4. Formation mechanism of nanodendrites

From the results obtained in this research, it can be concluded that the EG/W mixture system and SDBS are essential for the formation of novel hierarchical LiFePO₄ structures. First of all, the reactivity of all the precursor chemicals can be reduced in this mixture solvent medium. At an optimal EG content (EG/W = 1/1 in our experiment), the differences among the reactivity of the precursors would be reduced significantly so that their reactivity can match each other, which will facilitate the formation of the desired olive-structure crystal instead of the impurity crystals, such as Li₂PO₄ and Fe₄(PO₄)₃(OH)₃. Secondly, the solubilities of the precursors in EG/W would be smaller than those in deionized water, which will lead to a more homogeneous nucleation process. Finally, the presence of SDBS acts as a soft template to direct the growth of nanoparticles into nanorods at the early stage of the process through a preferential bonding to certain crystal planes. Later on, these nanorods are further aligned tightly and assembled end-to-end under the guidance of the soft template to form various forms of hierarchical structures (e.g., nanodendrites or bones).
water, i.e. the precursor chemicals in EG/W could have a higher degree of supersaturation than they do in deionized water if the same amounts of precursors are used. Consequently, the EG/W system would favor the nucleation and growth processes of crystals. At too high an EG content, the precursors cannot be mixed homogeneously due to the lower solubility of the precursors. For the process reported herein, the mixture system turns out to be a promising reaction medium to provide well-controlled crystallization. Moreover, a proper surfactant present in the system can be used to adjust the size and morphology of the particle being produced by binding SDBS molecules onto the newly formed surfaces during crystal growth [18,28–31]. The formation mechanism of the hierarchical structures was proposed and described in Fig. 9. The time-dependent experiment results presented in Table 1 and Fig. 4 reveal the evolution of the hierarchical nanostructures, while the results at various SDBS content (Table 3 and Fig. 8) have revealed the critical role played by this surfactant in the formation of the hierarchical structure. As we concluded in the previous section, SDBS, an anionic surfactant, was used to both guide the growth of the crystalline LiFePO4 nanorods and template their self-assembly. During crystal growth, the surfactant acted as strong coordinating agents by binding to some crystal faces, and accordingly inhibited the crystal growth along the other defined crystal plane. As a result, at the early stages of the process, SDBS directs crystals to grow along the crystal direction whose crystal plane weakly bonds with the surfactant molecules. As a result, nanorods are formed, as was observed and described in the former parts. In comparison, in the absence of SDBS, no nanorods building blocks were found in the final product (Fig. 8(a)). In addition, it is conjectured that the SDBS molecules also act as a soft template to assemble the nanorod building blocks into the final hierarchical structures, in which the nanorods are tightly attached together by their ends. We assume
that the end-to-end self-assembly results from the Van der Waals attraction of hydrophobic interaction of the surfactant molecules bonded to the end of the nanorods. Since surfactant molecules preferentially and strongly adsorbed on the nanorod side, the stronger electrostatic force exists on the nanorod side than that on the end. It seems that there is a balance between electrostatic repulsion interaction and hydrophobic attraction interaction. Hence the electrostatic repulsion interaction on the side is stronger than that on the end between nanorods, which refines the side-by-side attachment. The long hydrophobic chains of the SDBS molecules bonded on the nanorods will be attracted to one another through hydrophobic interaction. As a result, the nanorods are attached with each other by their ends to form hierarchical structure. Note that this hypothetic formation mechanism still needs to be confirmed by direct proof. Summarily, the reported approach demonstrates obvious advantages, such as one-step synthesis, environmental friendliness, and low cost. The methodology will also inspire a similar route to prepare other phospholines, e.g., LiMnPO₄. Most importantly, nanodendrites have been recently identified as one of the most promising morphologies for ultrahigh electrochemical/catalytic activity [32]. The synthesized LiFePO₄ nanodendrites could be a promising electrode material for lithium-ion batteries.

3.5. Electrochemical properties

The electrochemical properties of LiFePO₄ nanodendrites were investigated and compared with other three typical samples. Fig. 10 shows the charge/discharge profiles of the samples in the cutoff voltage range of 2.0–4.2 at 0.1C (17 mA g⁻¹). A flat plateau at 3.4–3.5 V can be observed obviously during the charge/discharge process, representing the typical electrochemical Li⁺ insertion/extraction behavior of LiFePO₄. This flat plateau is attributed to the two-phase reaction as follows (1) [33]:

\[
\text{LiFePO₄} + (1-x)\text{LiFePO₄} \rightarrow \text{xLiFePO₄} + x\text{Li}^+ + xe^- \quad (1)
\]

At 0.1C, the discharge capacity of LiFePO₄ nanodendrites (S1-2 sample) is determined to be 154 mA h g⁻¹ for the first cycle, which is much higher than those (103, 107, 110 mA h g⁻¹) of the S3-1, S3-3 and S3-4 samples. This difference may be explained by their different microstructures or textural properties. To further confirm it, the BET areas of the S1-2 and S3-4 samples have been tested with the isothermal sorption of nitrogen. The BET area of LiFePO₄ nanodendrites is determined as 32.6 m² g⁻¹. Furthermore, the higher BET area of the nanodendrites may also confirm the hierarchical microstructures constructed by the nanorods. These small nanorods may facilitate the intercalation processes of lithium ions, which may have improved the charge and discharge kinetics. Martin et al. have reported that the nanofiber morphology mitigates the slow transport problem of Li ions, because the diffusion distance of Li ions within the electrode material is minimized [34]. Therefore, the higher discharge capability of LiFePO₄ nanodendrites can be mainly ascribed to the shorter and easier diffusion path of Li ions in the material with small grain size [33,35]. Fig. 11(a) gives the charge/discharge curves of LiFePO₄ nanodendrites at different discharge rates from 0.1C to 5C. Its initial discharge capacity almost maintained 154 mA h g⁻¹ at 0.5C. Furthermore, the discharge capacities at the rates of 1C and 5C decreased to 145 and 141 mA h g⁻¹, respectively, corresponding to about 93% and 90% capacity retention, compared with that at a rate of 0.1C. It can thus be confirmed that the nanodendrites show good rate capacity. Fig. 11(b) gives the cycling stability of the nanodendrites at a 0.1C rate. There was almost no capacity fading after 50 cycles, indicating its good cycling stability. The good capacitive behavior of the hierarchical LiFePO₄ nanodendrites demonstrates its potential application as an excellent cathode material for lithium-ion batteries.

4. Conclusions

LiFePO₄ nanodendrites composed of nanorod building blocks have been successfully synthesized in the EG/W system using SDBS as the surfactant. The results indicate that both reaction medium (EG/W) and SDBS played an important role in the self-assembly of hierarchical nanostructures. Evidences show that the nanodendrite hierarchical structures are formed through the self-assembly of nanorods by their end-to-end attachment. The reported approach is simple and economical, which has simplified the traditional multi-step methods and will encourage the future applications of LiFePO₄ crystals, especially in lithium-ion batteries.

Acknowledgments

We would like to thank Mr. Nate Kroodsma for English improvement. This work was financially supported by the Michigan Tech Faculty Startup Fund, Michigan Tech Research Excellent Fund, and the Korea Research Foundation grant (KRF-2007-412-J04003).

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