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Electrochemical properties of LiFePO$_4$/C synthesized by mechanical activation using sucrose as carbon source

Jae-Kwang Kim · Gouri Cheruvally · Jou-Hyeon Ahn

Abstract Olivine lithium iron phosphate (LiFePO$_4$) is attracting much attention as a safe, low cost and high capacity cathode material for lithium batteries, especially for applications in electric and hybrid-electric vehicles. In the present work, carbon-coated LiFePO$_4$ (LiFePO$_4$/C) materials are synthesized from lithium carbonate, ferrous oxalate, ammonium dihydrogen phosphate, and sucrose (varying content) as starting materials, by the process of mechanical activation followed by thermal treatment. A uniform, in situ coating of carbon surrounding the crystals of LiFePO$_4$ is achieved by the pyrolysis of sucrose during the thermal treatment. The structural properties of LiFePO$_4$/C are characterized by X-ray diffraction, and the morphological characteristics are studied by electron microscopy methods. Phase-pure particles of approximately 100 nm size and a homogeneous particle size distribution are obtained with 6 wt% carbon content. The electrochemical properties are evaluated at room temperature by cyclic voltammetry and charge–discharge performance in coin cells fabricated with lithium metal anode, LiFePO$_4$/C cathode, and 1 M LiPF$_6$ in ethylene carbonate (EC)/ dimethyl carbonate (DMC) electrolyte. LiFePO$_4$/C containing 6 wt% of carbon exhibits high discharge capacity of 165 mAh/g (corresponding to 97% of theoretical capacity) at 0.1 C-rate and 145 mAh/g at 1 C-rate. Good rate capability and stable cycle performance are realized for lithium cells employing LiFePO$_4$/C prepared by adding the cheap and easily available sucrose as carbon source during the synthesis of LiFePO$_4$.

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Introduction

Lithium iron phosphate (LiFePO$_4$) belonging to the family of phosphate-olivines is considered a very promising cathode active material for lithium batteries. Being a safe and low cost material that can offer a relatively high theoretical capacity of 170 mAh/g, it is attracting much attention for applications in lithium batteries, especially suitable for electric and hybrid-electric vehicles. LiFePO$_4$ offers good thermal stability and a stable charge/discharge property at ~3.4 V vs Li$^+$/Li, which provides safety margin in terms of electrolytic decomposition for many of the organic electrolytes used in batteries. In spite of the several advantages of this material, earlier studies have demonstrated its incapability in achieving high material utilization at lower temperatures and/or higher current densities [1, 2]. The rate-capability limitation of LiFePO$_4$ results from the low electronic conductivity of the material (~10^{-9} S/cm) and slow lithium ion diffusion across the phase boundary between FePO$_4$ and LiFePO$_4$. The studies that are undertaken in recent years focus to overcome these bottlenecks so as to develop LiFePO$_4$ into a mature cathode active material [3–10].

The poor conductivity limitation of LiFePO$_4$ is usually overcome by coating the active particles with conductive materials like carbon [2–12], dispersing metal particles [13] or solid-solution doping by cations [2]. Carbon-coating as a

means to enhance the electrochemical performance of LiFePO$_4$ was first demonstrated by Ravet et al. [14]; since then, several studies have focused on different means to achieve an efficient coating. In addition to enhancing the electronic conductivity of the material, carbon coating helps to block the inter-particle contact and disturbs the subsequent undesirable particle growth. Carbon can also function as a reducing agent avoiding the formation of trivalent phases during sintering of the material. There are essentially two methods followed for coating with carbon: (1) by incorporating carbon black powder along with other precursors during the synthesis of LiFePO$_4$ [8, 11, 12] and (2) by pyrolyzing suitable organic/polymeric compounds during synthesis [2–4, 9, 10, 14–20]. Different compounds have been evaluated for their suitability in providing an efficient coating of carbon by pyrolysis and thus to synthesize carbon-coated LiFePO$_4$ (hereafter referred to as LiFePO$_4$/C).

A variety of synthesis methods has been reported for LiFePO$_4$, including solid state reactions and solution methods. Among these methods, a mechanical activation (MA) method, which involves the blending of ingredients in a high energy ball mill followed by thermal treatment at high temperature, has been found to be very promising [8–10]. The ball milling step results in an intimate mixture of the reactants leading to a reduction in the thermal treatment time and temperature; thus, undesirable particle growth is effectively avoided. MA process has been adopted in our laboratory for synthesizing small and phase-pure particles of LiFePO$_4$. The processing conditions have been optimized for attaining the maximum performance in using this material as a cathode in room temperature lithium metal batteries [11]. A modified MA process was subsequently developed for achieving a uniform coating of carbon over LiFePO$_4$ particles using carbon black powder as the precursor [12]. In this work, LiFePO$_4$/C composites with different carbon contents were prepared by the modified MA process using sucrose as the carbon precursor, and their structural and electrochemical properties are evaluated.

Experimental

Preparation

LiFePO$_4$/C was synthesized by a modified MA process from Li$_2$CO$_3$, FeC$_2$O$_4$·2H$_2$O and NH$_4$H$_2$PO$_4$ (all chemicals of 99% purity from Aldrich) taken in stoichiometric quantities. Sucrose was added in proportions of 6, 12, and 22 wt% with respect to the total weight of other chemicals to prepare three samples of LiFePO$_4$/C with varying carbon contents. The process consisted of the following steps: (1) magnetic stirring of all the ingredients together with 60 wt% of triply distilled water at room temperature for 7 h, (2) rotary evaporator drying

of the blend at 70 °C for 2 h at 60 rpm to yield a fine solid powder, (3) high energy ball milling of the powder at room temperature for 15 h in Ar atmosphere, (4) conversion of the powder into pellets by mechanical pressing, and (5) thermal treatment at 600 °C for 10 h in N$_2$ atmosphere [11, 12].

Characterization

The crystallographic structure of the synthesized material was analyzed by X-ray powder diffraction (XRD, D8 Advance, Bruker AXS) using CuK$_\alpha$ radiation. Morphology of the powder was examined by scanning electron microscopy (SEM, JEOL JSM 5600), and the homogeneity of chemical composition was determined by combined SEM imaging and energy dispersive X-ray (EDX) mapping (Philips XL30 S FEG). The nature of carbon coating was observed by high resolution transmission electron microscopy (HR-TEM, JEM-3010, JEOL). The particle size range and average particle size of the samples were estimated based on the SEM images. The specific surface area of the samples was measured by the Brunauer, Emmett, Teller (BET) method (ASAP 2010 Analyzer). The carbon content of the material was determined by elemental analyzer (CHNS-932, LECO), and the electrical conductivity was measured by a four-point probe method using LORESTA-GP (MCP-T600).

Electrochemical evaluation

To prepare the cathode, the active material powder, carbon black, and poly(vinylidene fluoride) (PVdF, Aldrich) binder were mixed in the ratio 80:10:10 by weight, and a viscous slurry in N-methylpyrrolidone (NMP) solvent was cast on aluminum foil and dried at 95 °C under vacuum for 12 h. The film was cut into circular discs of area 0.95 cm^2 and mass ~3.0 mg for use as cathodes. Two-electrode electrochemical coin cells were assembled with lithium metal anode, Celgard®-2200 separator, a 1 M LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by vol) electrolyte and LiFePO$_4$/C cathode. Cyclic voltammetry (CV) was performed at a scan rate of 0.1 mV/s between 2.0 and 4.5 V. Electrochemical performance tests were carried out in an automatic galvanostatic charge–discharge unit, WBCS3000 battery cycler, between 2.0 and 4.6 V at room temperature (25 °C). The experiments were done at different current densities.

Results and discussion

Carbon content in LiFePO$_4$/C

The samples of LiFePO$_4$/C synthesized with the addition of 6, 12, and 22 wt% of sucrose as carbon precursor contain

3.8, 6.0, and 10.2 wt% carbon, respectively. These are further referred to as LiFePO$_4$/C(X), where X denotes the carbon content in the sample. Under the conditions of high temperature sintering, sucrose gets decomposed to form the porous structure of carbon along with gaseous products of CO and/or CO$_2$ [16]. Sucrose to carbon conversion efficiency f (f denotes 1/12 the number of moles of carbon produced per mole of sucrose) calculated for LiFePO$_4$/C (3.8), LiFePO$_4$/C(6.0), and LiFePO$_4$/C(10.2) are 0.74, 0.60, and 0.59, respectively. Sucrose alone under the conditions of firing adopted in this study yields f=0.59, and hence, ~40% of carbon is lost in the form of gaseous products. The efficiency of sucrose as carbon precursor depends appreciably on the processing conditions, especially the firing temperature and duration [6, 15]. Thus, Spong et al. [15] achieved f=0.40 for LiFePO$_4$/C prepared with a solution precursor process using varying amount of sucrose additive and under firing at 700 °C for 10 h. The data given by Chen et al. for LiFePO$_4$/C prepared by solid state reaction correspond to (1) f=0.55 for post-synthesis impregnation with sucrose followed by firing at 700 °C for 4 h and (2) f= 0.43 for the sample prepared by the addition of sucrose at the start of the process itself with a final firing condition of 800 °C for 4 h [6]. The comparatively higher conversion efficiency obtained in our study could be due to the lower firing temperature adopted. We also observe that f is relatively high for the sample prepared with low sucrose content. This indicates that in addition to processing conditions, f is dependent on sucrose content and the particle size of the material.

Structure and morphology of LiFePO$_4$/C

The crystalline structure of LiFePO$_4$/C prepared with sucrose as carbon precursor has been identified to be the ordered olivine indexed to orthorhombic Pnma space group. The XRD spectra obtained for the LiFePO$_4$/C samples are shown in Fig. 1. The patterns show good correspondence with the reference LiFePO$_4$ spectrum, which is also included in the figure. There are no significant peaks arising from any impurity phase in the sample. Thus, as reported by earlier researchers, sucrose addition as carbon precursor in the starting material is effective in inhibiting the formation of Fe^{3+} impurities [9, 15–17].

Figure 2 shows the SEM images and Table 1 lists the properties of the three LiFePO$_4$/C samples containing varying carbon contents. It is observed from Fig. 2 that with an increase in carbon content from 3.8 to 6.0%, the average particle size decreases and a better uniformity of size distribution is achieved. BET surface area measurements also show higher surface area for LiFePO$_4$/C(6.0) than LiFePO$_4$/C(3.8). When the carbon content is further increased to 10.2%, the particles become quite large and the
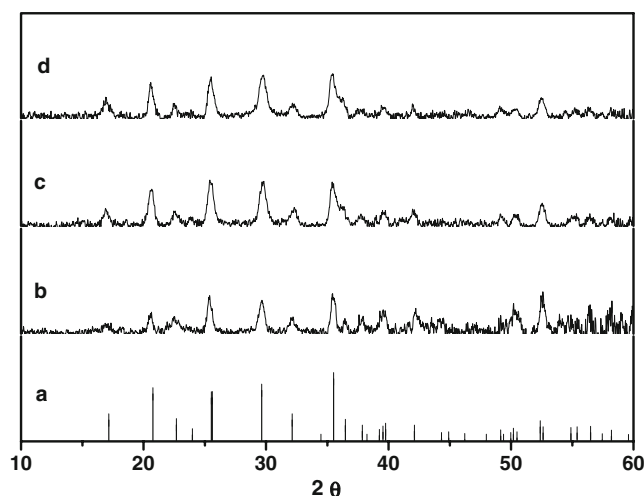

Fig. 1 XRD: **a** Standard Pnma orthorhombic LiFePO$_4$, **b** LiFePO$_4$/C (3.8), **c** LiFePO$_4$/C(6.0), and **d** LiFePO$_4$/C(10.2)

homogeneity of the sample is highly disturbed. The specific surface area also decreases significantly. Inclusion of sucrose as carbon precursor during the synthesis of LiFePO$_4$ has been reported to be advantageous in reducing the particle size effectively [6, 9, 15]. Carbon coating stabilizes the small crystals and avoids inter-particle contacts to a great extent, thus preventing their enlargement at high temperatures by coalescence [15]. In the present study, we observe that 6% carbon coating is the optimum in providing the smallest particles with the highest surface area and uniform morphology. The higher particle size observed for LiFePO$_4$/C(10.2) might be the result of a thicker and non-uniform carbon coating formed from a higher carbon content in the sample. Electrical conductivity (at 25 °C) of the samples shows a systematic enhancement with increase in carbon content as given in Table 1.

The higher sucrose to carbon conversion efficiency f of LiFePO$_4$/C(3.8) compared to that of LiFePO$_4$/C(6.0) could be due to its lower carbon content and its larger particles with lower exposed surface area resulting in lower loss of carbon as gaseous oxidation products. Similarly, when compared to LiFePO$_4$/C(6.0), LiFePO$_4$/C(10.2) has comparable f, which can be attributed to the bigger particles of the latter resulting in lower surface area, although the sample has higher carbon content.

The elemental mapping obtained for LiFePO$_4$/C(6.0) with SEM-EDX analysis is shown in Fig. 3. The images of the elements Fe and P closely match with the corresponding SEM image indicating the homogenous chemical composition of the sample. The nature of carbon coating achieved for LiFePO$_4$/C(6.0) was analyzed by TEM and is presented in Fig. 4. The crystals of LiFePO$_4$ appear dark, and the carbon coating appears gray in the TEM pictures. The presence of a nanometer-sized coating of carbon around the crystalline LiFePO$_4$ particles is clear from the figure.
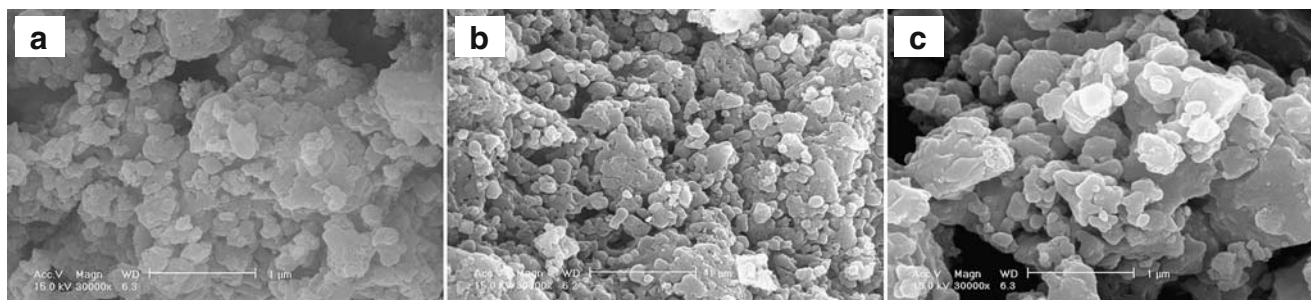
Fig. 2 SEM images of the three LiFePO$_4$/C samples containing varying carbon contents: **a** LiFePO$_4$/C(3.8), **b** LiFePO$_4$/C(6.0), and **c** LiFePO$_4$/C(10.2)

The carbon coating thickness varies between 2–10 nm, and it appears as an envelope surrounding the whole crystal. Chung et al. [17] prepared LiFePO$_4$/C with a nano-web of carbon using sucrose as precursor, and with energy dispersive X-ray spectrometry analysis showed that the web was composed of amorphous carbon. The coating achieved in the present study is also similar in characteristics.

Electrode properties

The electrochemical behavior of LiFePO$_4$/C with different carbon contents during the first cycle of CV is compared in Fig. 5. A single redox reaction pair, characteristic of Li$^+$ ion insertion and extraction in the material, is observed, with the redox potential centering at ~3.4 V. The carbon content in the material alters the anodic and cathodic peak positions slightly. The potential separation between the anodic and cathodic peaks (ΔV) are 1.1, 0.9, and 1.1 V for LiFePO$_4$/C (3.8), LiFePO$_4$/C(6.0), and LiFePO$_4$/C(10.2), respectively. Thus, when increasing the carbon content from 3.8 to 6.0%, ΔV gets reduced by 200 mV, whereas on further increase in carbon content, ΔV again increases. Evidently, the redox behavior is influenced by the carbon content of LiFePO$_4$. This results from the variation of the particle size, which determines the ease of lithium ion diffusion in the particle, as well as electrical conductivity of the material, which facilitates the electron transfer. LiFePO$_4$/C(6.0) possessing a well-controlled morphology with small particles and a sufficiently high carbon content for adequate electrical conductivity shows the best reversibility for the redox process in the CV studies.

The reproducibility of CV curves during repeated cycling of LiFePO$_4$/C(6.0) is shown in Fig. 6. The electrode takes a few initial cycles to stabilize; thus, there is excellent reproducibility for the CV traces. As shown in the figure, overlapping CV curves are obtained for the fifth and tenth cycles. When compared to the first cycle, ΔV is higher for the subsequent cycles, which indicates a decreased efficiency for the electrochemical reaction with cycling. Nevertheless, the areas under the respective anodic and cathodic peaks remain nearly the same even on repeated cycling, indicating an equal amount of lithium ion insertion and extraction in the material.

Performance of LiFePO$_4$/Li cells

The samples of LiFePO$_4$/C have been evaluated as cathode materials for their electrochemical performance in lithium cells at room temperature (25 °C). The initial charge–discharge performances of the cells with LiFePO$_4$/C cathodes of varying carbon contents at a current density of 0.07 mA/cm^2 (corresponding to 0.1 C-rate) are compared in Fig. 7. Extremely flat voltage plateaus at ~ 3.50 V for charging and ~ 3.35 V for discharging are observed. The highest specific capacity is achieved for LiFePO$_4$/C(6.0) exhibiting a charge capacity of 168 mAh/g and a discharge capacity of 165 mAh/g, corresponding to 97% utilization of the active material. The discharge capacities for LiFePO$_4$/C(3.8) and LiFePO$_4$/C(10.2) are 136 and 110 mAh/g, respectively. The high performance of LiFePO$_4$/C(6.0) is attributed to its uniform morphology with small particles having a thin and efficient carbon coating. CV study also (as discussed earlier) has indicated a

Table 1 Properties of LiFePO$_4$/C samples containing varying carbon contents

	LiFePO$_4$/C(3.8)	LiFePO$_4$/C(6.0)	LiFePO$_4$/C(10.2)
Particle size range (nm)	60–300	80–250	120–420
Average particle size (nm)	200	100	300
Specific surface area (m^2/g)	16.7	17.9	7.4
Electrical conductivity (S/cm)	3.0×10^{-4}	5.7×10^{-4}	7.2×10^{-4}
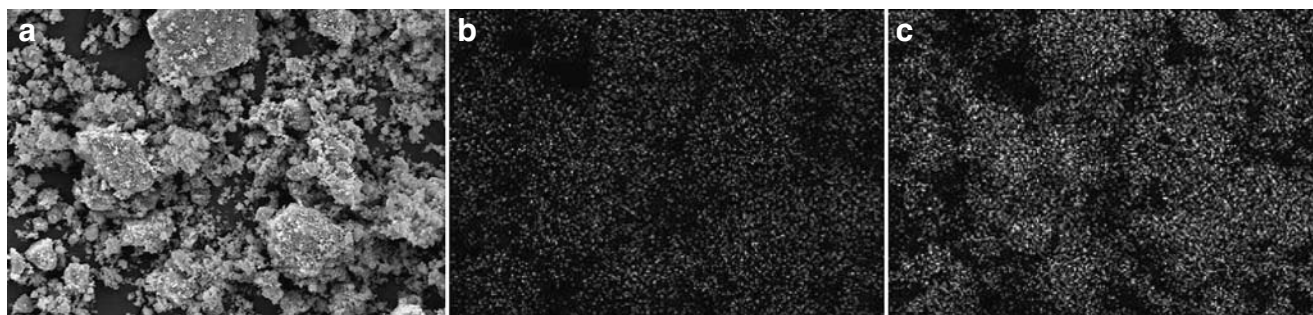
Fig. 3 SEM-EDX mapping for LiFePO$_4$/C(6.0): **a** SEM image, **b** and **c** corresponding EDX mapping of Fe and P, respectively

comparatively better property for LiFePO$_4$/C(6.0) than the others.

As incorporation of low density carbon in the cathode adversely affects its tap density and volumetric energy density, it is of primary importance to optimize the composition so as to obtain the maximum performance with the minimum carbon content as possible [6]. In the present study with the cathode formulation consisting of the active material, carbon, and binder in the ratio 80:10:10, the total carbon content in the electrode for LiFePO$_4$/C (3.8), LiFePO$_4$/C(6.0), and LiFePO$_4$/C(10.2) are 13.0, 14.8, and 18.2%, respectively. LiFePO$_4$/C(3.8) is preferred over LiFePO$_4$/C(6.0) in terms of carbon content, which is lower by 1.8%; however, it has a discharge capacity lower by 17.6%. LiFePO$_4$/C(10.2) is evidently not preferred, as it has a high carbon content and also it performs the least in electrochemical tests compared to the other two samples. It is inferred that the particle size plays a more crucial rule in determining the electrochemical property once the sample has the minimum carbon coating necessary to make it sufficiently conductive.

The rate capability of LiFePO$_4$/C cathodes of varying carbon content are compared in Fig. 8. A gradual decrease of discharge capacity with increase in C-rate is evident, as is generally the case for LiFePO$_4$ cathodes, attributed to limitation of lithium ion diffusion to meet the fast reaction kinetics at higher C-rates, especially at low temperature. The discharge capacities of LiFePO$_4$/C(3.8), LiFePO$_4$/C

(6.0), and LiFePO$_4$/C(10.2) at the high, 3 C-rate are 63, 110, and 59 mAh/g, respectively. The comparatively better rate capability shown by LiFePO$_4$/C(6.0) is evidently supported by the small particles, high surface area, uniform morphology, and better conductivity with a moderate carbon content. The material is thus able to exhibit a reasonably high active material utilization of 64.7% at 3 C. LiFePO$_4$/C(10.2) exhibits lower discharge capacities at all C-rates compared to the other two samples resulting mainly from its large particle size and lower surface area. However, with a higher carbon content and electrical conductivity, it offers a good retention of its 0.1 C capacity at higher C-rates as well. Thus, at 3 C, LiFePO$_4$/C(10.2) retains 54% of its capacity at 0.1 C, compared to 46% by LiFePO$_4$/C(3.8).

A comparison of the discharge capacities so far reported for LiFePO$_4$/C synthesized using sucrose as the carbon precursor showed that the material made by mechanical activation method [9] exhibited higher performance than those made by solid-state [6] and solution/co-precipitation methods [15–17]. Thus, Liao et al. [9] reported a high performance of 164 mAh/g at 0.1 C and 138 mAh/g at 1 C at room temperature using LiFePO$_4$/C synthesized by ball-milling followed by thermal treatment at 600 °C. The discharge capacity obtained in the present study using
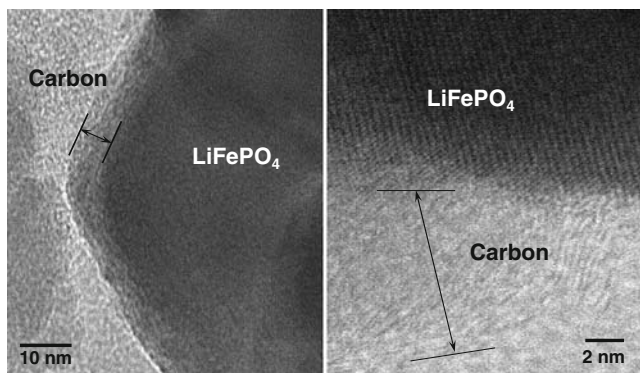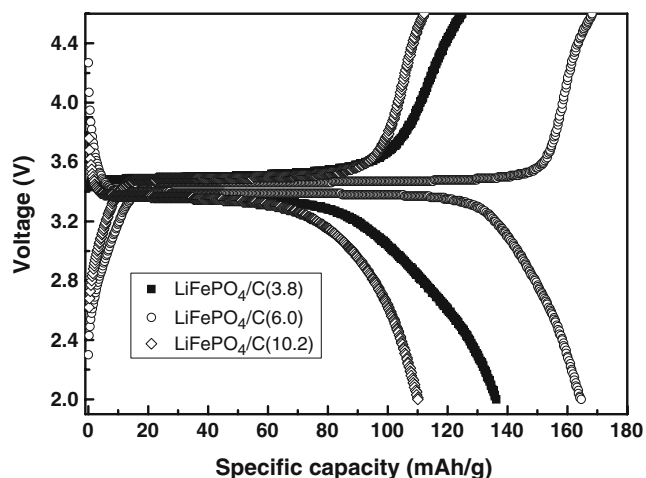

Fig. 4 TEM images of LiFePO$_4$/C(6.0)
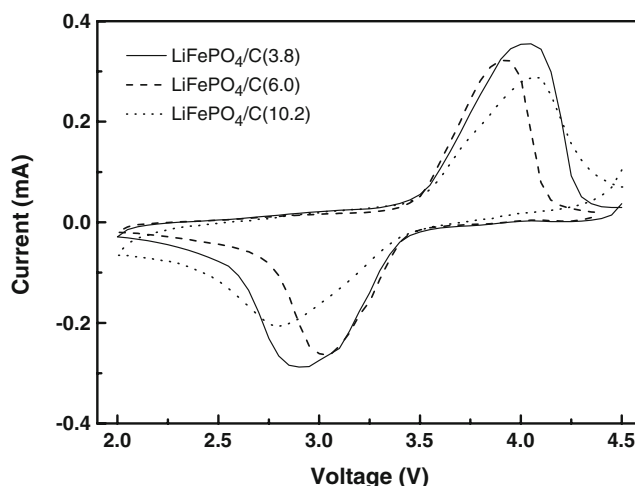
Fig. 5 CV curves of LiFePO$_4$/C cathodes with varying carbon contents (scan rate: 0.1 mV/s, voltage range 2.0–4.5 V)
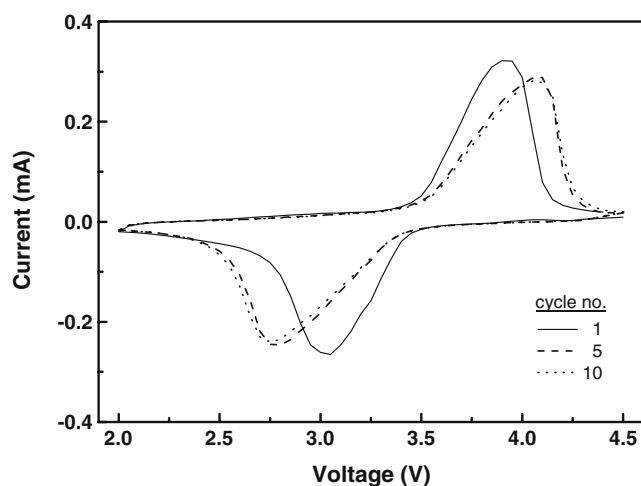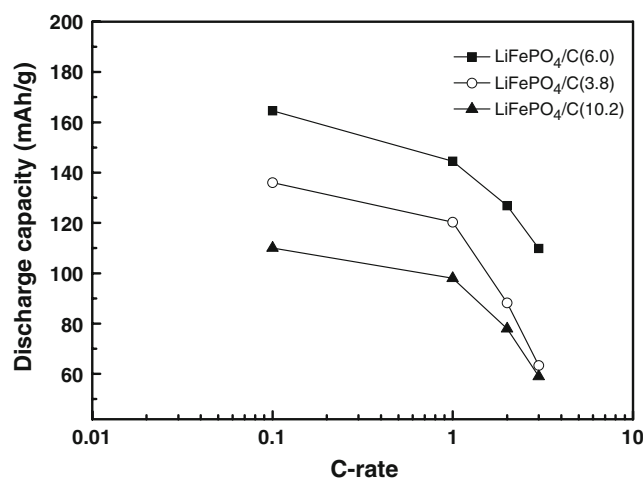
Fig. 6 CV curves during cycling of LiFePO$_4$/C(6.0) (scan rate: 0.1 mV/s, voltage range 2.0–4.5 V)

Fig. 8 Variation of discharge capacity with C-rate of lithium cells with LiFePO$_4$/C(3.8), LiFePO$_4$/C(6.0) and LiFePO$_4$/C(10.2) as cathodes (room temperature, 2.0–4.6 V)

LiFePO$_4$/C synthesized by a similar mechanical activation process (but with different raw materials and processing conditions) is nearly the same at 0.1 C and higher at 1.0 C. When compared to LiFePO$_4$/C sample with sucrose as carbon precursor, reported by Chen and Dahn [6], the discharge capacity of LiFePO$_4$/C(6.0) is higher at 0.1 C and comparable at 2 C.

The lithium cell with LiFePO$_4$/C(6.0) as cathode shows stable cycle performance even at high C-rates, as depicted in Fig. 9. At the end of 50 cycles, the discharge capacities realized at 0.1, 1.0, and 2.0 C-rates are 154, 140, and 120 mAh/g, respectively. Thus, even at the high current densities of 1 and 2 C, the variation of discharge capacity during 50 cycles is <6%, compared to the initial capacity. The capacity fade per cycle at all the above C-rates is very low (~ 0.1%), making LiFePO$_4$/C a very promising cathode material capable of delivering satisfactory performance at room temperature.

Conclusions

Phase-pure, olivine LiFePO$_4$/C materials with carbon contents of 3.8, 6.0, and 10.2 wt% have been synthesized by a modified mechanical activation process followed by firing, using sucrose as the carbon precursor. The addition of sucrose initially along with the other ingredients results in nanometer-sized particles of active material with a thin coating of carbon. LiFePO$_4$/C(6.0) exhibits a uniform morphology with the smallest average particle size of 100 nm. Electrochemical property evaluation in lithium cells at room temperature shows an active material utilization of 97% at 0.1 C-rate with LiFePO$_4$/C(6.0). Stable cycle performances are also achieved even at the higher current densities of 1 and 2 C. LiFePO$_4$/C(10.2) shows a relatively lower performance attributed to the larger particles and non-uniform particle size distribution,
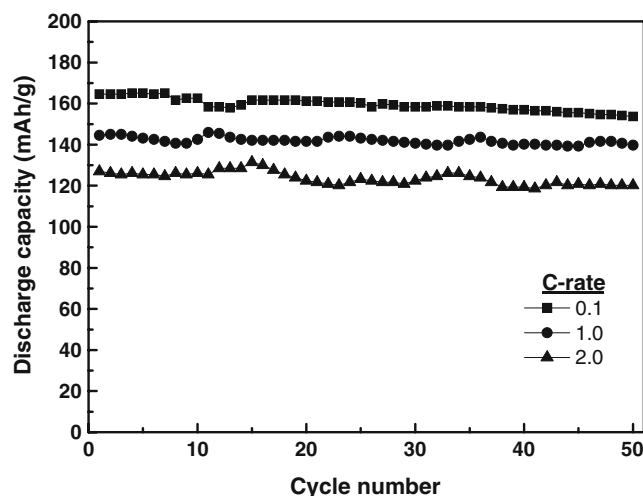

Fig. 7 Initial charge and discharge capacities of lithium cells with LiFePO$_4$/C samples with varying carbon contents as cathodes (room temperature, 0.1 C-rate)

Fig. 9 Cycle performance of lithium cells with LiFePO$_4$/C(6.0) as cathode at different C-rates (room temperature, 2.0–4.6 V)

which adversely affect the rate of lithium ion diffusion in the material. The study shows that sucrose is an effective carbon precursor for the synthesis of high-performance $LiFePO_4/C$ by mechanical activation process followed by firing, which results in nanometer-sized particles of active material with a thin coating of carbon.

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