

Research Article

Preparation and Characterisation of LiFePO₄/CNT Material for Li-Ion Batteries

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Li-ion battery cathode materials were synthesised via a mechanical activation and thermal treatment process and systematically studied. LiFePO₄/CNT composite cathode materials were successfully prepared from LiFePO₄ material. The synthesis technique involved growth of carbon nanotubes onto the LiFePO₄ using a novel spray pyrolysis-modified CVD technique. The technique yielded LiFePO₄/CNT composite cathode material displaying good electrochemical activity. The composite cathode exhibited excellent electrochemical performances with 163 mAh/g discharge capacity with 94% cycle efficiency at a 0.1 C discharge rate in the first cycle, with a capacity fade of approximately 10% after 30 cycles. The results indicate that carbon nanotube addition can enable LiFePO₄ to display a higher discharge capacity at a fast rate with high efficiency. The research is of potential interest for the application of carbon nanotubes as a new conducting additive in cathode preparation and for the development of high-power Li-ion batteries for hybrid electric vehicles.

1. Introduction

The exponential growth in portable electronic devices such as cellular phones and laptop computers in recent years has resulted in an enormous demand for compact and light-weight rechargeable batteries which can offer high energy densities. In addition, growing environmental concerns have simultaneously driven the development of advanced batteries for electric vehicles. Li-ion batteries are appealing candidates for these applications as they provide higher energy density compared to the other rechargeable batteries systems available, such as the lead acid, nickel cadmium (NiCd), and nickel-metal hydride (NiMH) batteries. Today, the Li-ion is the fastest growing and most promising rechargeable battery chemistry. The electrochemical performance of Li-ion batteries relies significantly on the properties of the cathode-materials, the anode materials, and the electrolytes. Carbon-based materials have been the material of choice for lithium storage in Li-ion batteries for some time [1, 2]. This paper focuses on our study of the development of new cathode materials which encompass carbon nanotubes (CNTs) to ideally produce highly specific capacities. LiFePO₄

has been reported to be an excellent cathode, but its high resistance limits the obtainable capacity. Recently, a variety of techniques have been attempted for the synthesis of high-performance LiFePO₄ [3, 4]. Mechanical activation, which involves the blending of ingredients by high-energy ball milling followed by thermal treatment at high temperature, has turned out to be a versatile technique with high capability for scale up [5, 6]. In this study, LiFePO₄/CNT composite cathode material has been synthesized via a novel synthesis technique and studied.

2. Experimental and Characterization

2.1. Experimental. LiFePO₄/CNT composite material was synthesised by growing carbon nanotubes onto LiFePO₄, via CVD using spray pyrolysis. Table 1 lists the experimental parameters employed in the CVD using spray pyrolysis technique.

LiFePO₄ material synthesised previously was placed into a quartz crucible and placed into a horizontal tube furnace. The furnace was then heated to 800°C under argon flow of

TABLE 1: Parameters employed for carbon nanotube growth via CVD using spray pyrolysis.

Flushing gas	Argon (UHP) obtained from Afrox
Carbon source	Ethylene Gas (UHP) obtained from Afrox
Deposition temperatures	800°C
Flushing gas flow rate	100 ml/min
Carbon source flow rate	100 ml/min
Times of deposition	30, 60, 90 minutes
Catalyst solutions	1.0 M NiSO ₄

100 ml/min. Once the set temperature was reached, a Ni mist was introduced to a tubular furnace apparatus. The mist was produced from a 1.0 M NiSO₄ solution. The argon gas flow was turned off, and ethylene gas was introduced into the furnace at a flow rate of 100 ml/min each for the desired deposition time. After the time elapsed, the final product was cooled to room temperature under an argon atmosphere.

2.2. Morphological and Structural Analysis. SEM measurements were done using a Hitachi ×650 microscope. The microscope beam energy can be varied over the range from 5 to 40 KeV, with a maximum resolution of 10 nm. Transmission electron microscopy (TEM) analyses were done using a Tecnai G2 F20 X-Twin Mat FEG-TEM. X-ray diffraction (XRD) analyses were performed using a Bruker multipurpose powder diffractometer (D8 Advance). In this investigation, the surface area and porosity of the LiFePO₄/CNT cathode materials were investigated with high sensitivity using an accelerated surface area and porosity analyser (Micromeritics ASAP 2010).

2.3. Charge/Discharge Cycle Testing. The positive electrode consisted of 80% of the as-prepared composite, 15% acetylene black, and 5% polytetrafluoroethylene (PTFE) as a binder, and Al metal was used as the current collector. The electrolyte solution was 1.0 mol·L⁻¹ LiPF₆ in EC + DMC (1 : 1). Lithium metal foil was used as the counter electrode during electrochemical measurements. All cells were assembled in an argon-filled glovebox. Charge/discharge tests were carried out using a Land-BTL10 fully automatic program test instrument. For the novel Li-ion battery cathodes synthesised, tests were run at a voltage range of 2.40 to 4.10 V versus Li/Li⁺.

2.4. Electrochemical Conductivity. Electrochemical conductivity was calculated from the resistance values obtained from impedance measurements. Electrochemical impedance spectroscopy (EIS) measurements were carried out using an Eco Chemie Autolab PGSTAT 30. The amplitude of the AC signal was 5 mV over the frequency range between 100 kHz and 0.01 Hz.

3. Results and Discussion

Figure 1 illustrates the SEM images of LiFePO₄/CNT composite cathode materials synthesised. From these images, the presence of carbon nanotubes is clearly observed. A mat of carbon nanotubes covers the surfaces of the LiFePO₄ particles forming LiFePO₄/CNT composite material. The CVD of a carbon gas source generally yields carbon nanotubes having a wide range of carbon nanotube diameters, which is also confirmed by the SEM images.

Figure 2 displays TEM images of the LiFePO₄/CNT composite cathode material. From these HR-TEM images, we observe the presence of carbon nanotubes with thick walls, clear evidence that multiwalled carbon nanotubes have been successfully synthesised. Open cap ends are also observed in Figure 2(a). The dark particles were confirmed by EDS analysis to be that of the LiFePO₄ and also Ni particles, which is to be expected. It is also visible that the carbon nanotubes grow directly from the particles as evident from Figures 2(a) and 2(b). It is thus possible that this technique yields carbon nanotubes grown via the tip growth mechanism.

Figure 3 shows the XRD patterns of the obtained LiFePO₄/CNT composite cathode material. The diffraction peaks were confirmed to be that of olivine LiFePO₄, and no impurities were detected. The XRD pattern could be indexed to the orthorhombic *Pnma* space group (JCPDS card No. 40-1499) based on the well-ordered olivine structure. The intensity of diffraction peaks has a close relation to the crystallinity of the crystal particle. All the XRD peaks are quite sharp and narrow, indicating that highly crystallized LiFePO₄ phase is formed.

Li-ion intercalation/deintercalation reactions essentially depend on electronic conductivity, as the process is accompanied by electron removal at the same time [7]. The carbon nanotubes are added in order to enable the active material (LiFePO₄) to transport lithium ions and electrons at a fast rate. Furthermore, the diffusion of Li ions in the solid state, which is considered to be the slowest process, depends on the surface area [8], which as seen is higher for the LiFePO₄/CNT composites.

To effectively illustrate the effect of carbon nanotube addition on the electron conductivity of the composite materials, electron conductivity measurements were done on the pure LiFePO₄ and the LiFePO₄/CNT composite material. Figure 4 illustrates the electron conductivity results of the material as a function of CNT deposition time (which is directly proportional to CNT content). The increased electrical conductivity with increased CNT deposition time (and, hence, increased CNT content) for the LiFePO₄/CNT cathode material is due to presence of the carbon nanotubes which have higher electrical conductivity. As the CNT content increases, the poorly conductive LiFePO₄ grains are more surrounded by a widening “matrix” of fine, contiguous CNT networks. This is in agreement with the findings of Bewlay et al. [9] and Liu et al. [10] who increased the electrochemical conductivity of LiFePO₄ by the inclusion of carbon or CNT, respectively; however, our materials displayed better charge discharge capacities.

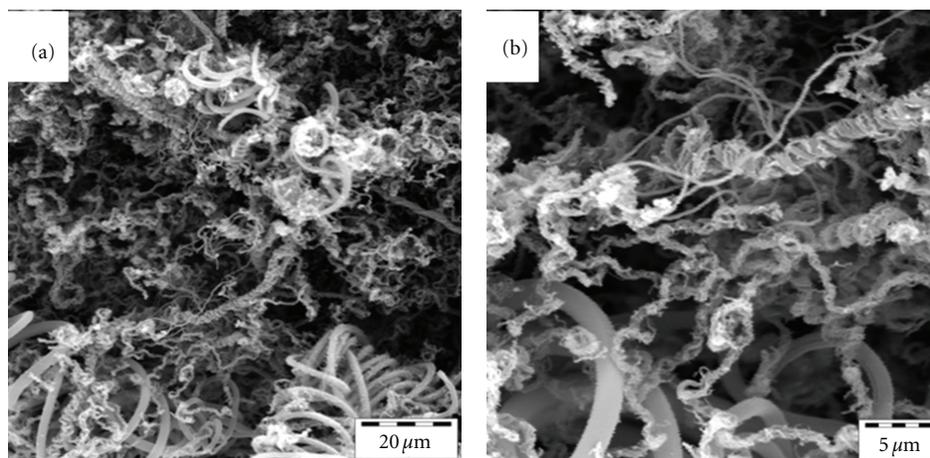


FIGURE 1: SEM images of LiFePO₄/CNT composites synthesised with (a) Ni mist, 60 min deposition at 1000x and (b) Ni mist, 60 min deposition at 3000x magnification.

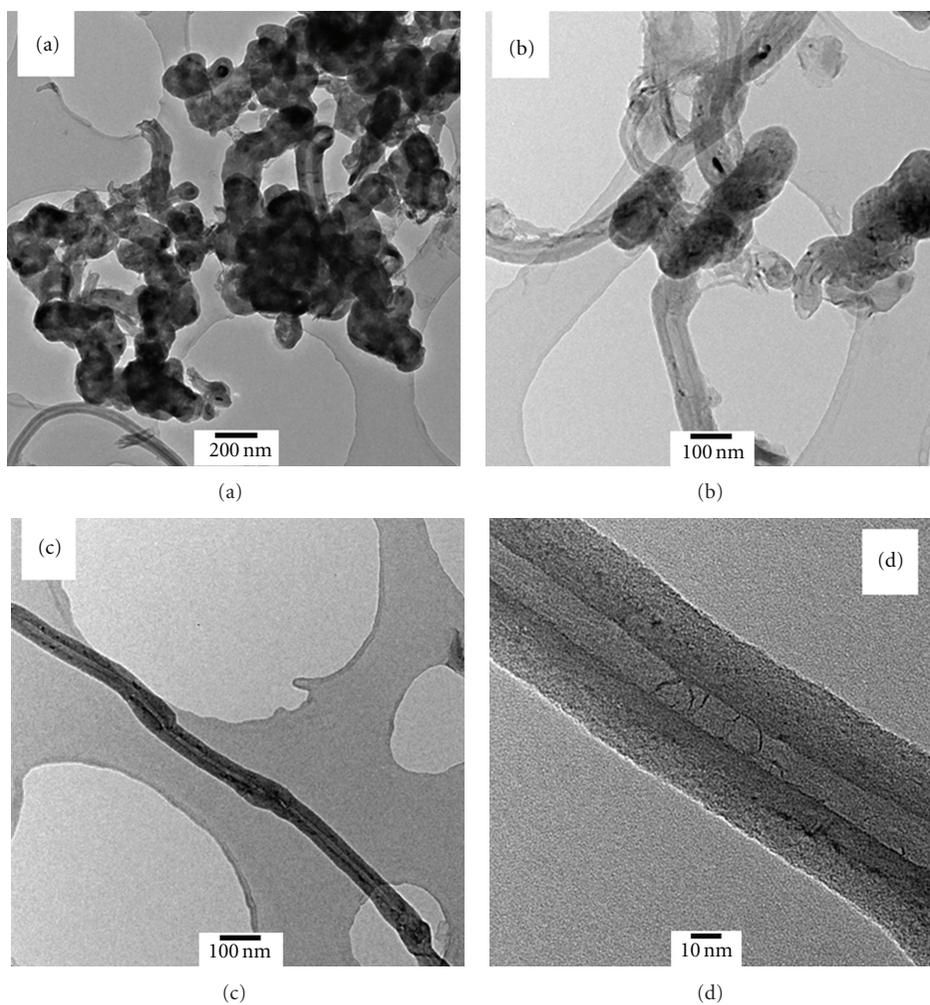


FIGURE 2: HR-TEM images of LiFePO₄/CNT synthesised using the spray pyrolysis-modified CVD technique at (a) 9000x magnification, (b) 17000x magnification, (c) 17000x magnification, and (d) 130000x magnification.

TABLE 2: Surface area and porosity data for the composite $\text{LiFePO}_4/\text{CNT}$ cathode material.

Material	Single-point BET surface area (m^2/g)	External surface area (m^2/g)	Internal pore area (m^2/g)	Pore volume (cm^3/g)	Average Pore diameter (nm)
$\text{LiFePO}_4/\text{CNT}$ Ni mist 60 min dep.	7.89	24.85	29.09	0.106	15.772

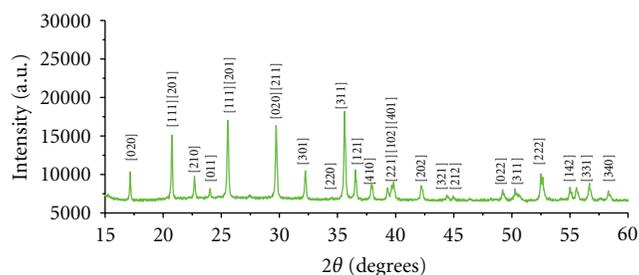
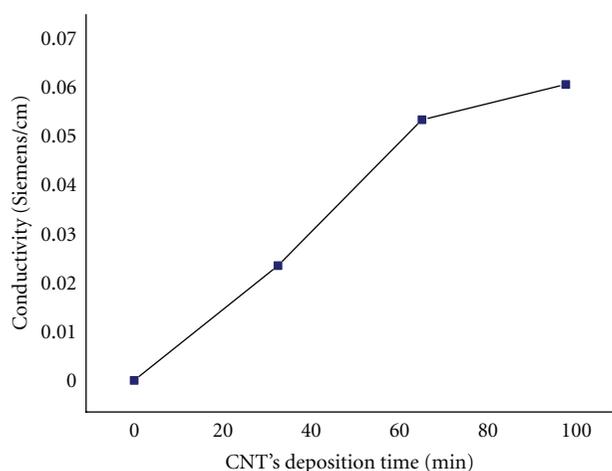
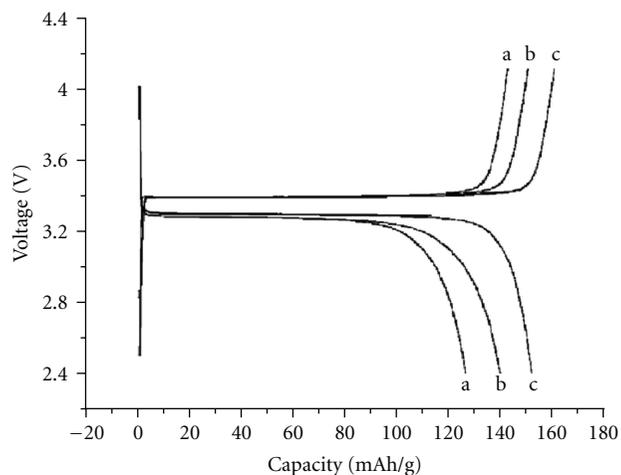
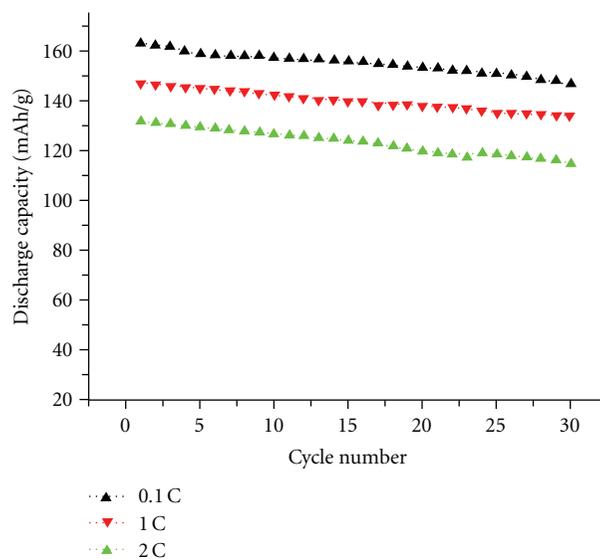
FIGURE 3: XRD patterns of $\text{LiFePO}_4/\text{CNT}$ composite cathode material. The surface area and porosity results obtained for the composite cathode materials are tabulated in Table 2.FIGURE 4: Room temperature conductivity of $\text{LiFePO}_4/\text{CNT}$ as a function of CNT deposition time.

Figure 5 shows the charge/discharge curves at discharge/charge rates varied from 0.1 to 2 C of the $\text{LiFePO}_4/\text{CNT}$ composite material synthesised using the spray-modified CVD technique. In the potential range of 2.5–4.2 V, the composite cathode delivered 163 mAh/g with 94% cycle efficiency at 0.1 C rate in the first cycle. The cycling characteristics of the $\text{LiFePO}_4/\text{CNT}$ cathode material at different discharge rates are shown in Figure 6. The results showed an almost steady decrease in discharge capacity with cycle number, with a capacity fade of approximately 10% after 30 cycles. The cathode displayed discharge capacity of 163 mAh/g at 0.1 C rate and around 134 mAh/g at 2 C rate.

The optimal deposition time required was established from the subsequent charge-discharge testing of the resulting material. The optimal deposition time was found to be 60 minutes when this Ni spray technique was utilised. In this optimal method of $\text{LiFePO}_4/\text{CNT}$ synthesis, a higher

FIGURE 5: Charge/discharge curves of $\text{LiFePO}_4/\text{CNT}$ electrode, at different rates; (a) 2 C, (b) 1 C, and (c) 0.1 C.FIGURE 6: The discharge capacity versus cycle number plot for the $\text{LiFePO}_4/\text{CNT}$ electrode, at different rates.

surface area material was obtained. Well-crystallized carbon nanotubes can improve cycle efficiency due to the reduction of oxide group production and the increased surface area. The electron transport between the cathode-active materials and the current collector was improved due to the fact that the interface was filled with carbon nanotubes. Therefore, the rate capability of this $\text{LiFePO}_4/\text{CNT}$ composite cathode

material was enhanced effectively by the three-dimensional carbon nanotube network.

4. Conclusions

The composite cathode exhibited excellent electrochemical performances with 163 mAh/g discharge capacity at 0.1 C rate in the first cycle. The results indicate that carbon nanotube addition can enable LiFePO₄ to display a higher discharge capacity at a fast rate with high efficiency. The research is of potential interest to the application of carbon nanotubes as a new conducting additive in cathode preparation and for the development of high-power Li-ion batteries for hybrid electric vehicles.

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