



Electrochemical properties of a full cell of lithium iron phosphate cathode using thin amorphous silicon anode



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ABSTRACT

Carbon-coated lithium iron phosphate (LiFePO₄/C) with uniform carbon coating was synthesized by a mechanical activation method. Silicon negative electrode material was obtained in the form of thin films of amorphous silicon on a Cu foil substrate by vertical deposition technique. The electrochemical performance of the full cell, LiFePO₄/C–Si, was tested with 1 M LiPF₆ in EC/DMC at 0.5 and 1 C-rates. The cell exhibited an initial discharge capacity of 143.9 mAh g⁻¹ at 0.5 C-rate at room temperature. A reasonably good cycling performance under a high current density of 1 C-rate could be obtained with the full cell.

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1. Introduction

Recently, olivine-LiFePO₄ has attracted much attention as a cathode material for lithium-ion batteries, especially for heavy-duty applications like electric and hybrid-electric vehicles. It has a high theoretical specific capacity of 170 mAh g⁻¹ and a perfect flat discharge voltage at 3.4 V vs. Li/Li⁺. The other attributes which make it an attractive choice as an active cathode material for use in a wide spectrum of applications include good reversibility of cathode reactions, high thermal and chemical stability, low material cost, low toxicity and improved safety, and choice of the use of organic electrolytes [1–3]. However, LiFePO₄ suffers from the limitations of poor electronic conductivity and slow lithium-ion diffusion [4–6]. The poor electronic conductivity and slow lithium-ion diffusion of LiFePO₄ are usually overcome by coating conductive materials like carbon and devising synthetic methods to design particles of small size [7–13]. In our earlier studies, we optimized the synthesis condition of the mechanical activation process and demonstrated that its electrochemical performance can be enhanced by carbon coating and reduction in the size of particles [14–18].

As commercial negative electrode material, graphite is extensively used for lithium-ion battery due to their flat potential profile and

structural stability during cycling. However, graphite suffers from a relatively small capacity (372 mAh g⁻¹). In recent years, silicon (Si) has been pointed out as an attractive negative electrode material for lithium-ion batteries because it has a low discharge potential and a theoretical charge capacity of 4200 mAh g⁻¹ on the basis of Li_{4.4}Si formation; this is 11 times higher than the capacity of graphite being used commercially. Despite such a huge theoretical charge capacity, a negative electrode material made of silicon has limited applications, because silicon undergoes a volume change by 300% upon insertion and extraction of lithium ions. Such a large volume change induces cracks in the electrode film and leads to an abrupt capacity fade [19–22]. Several attempts have been made to address the problem of volume expansion of Si anode. For example, the preparation of an electrode made of a thin film of amorphous silicon has been reported to exhibit stable capacity over cycling. The cycle stability was ascribed to a homogeneous volume expansion/contraction during charge–discharge and to multiple paths for lithium-ion diffusion [22,23].

In this article, a lithium ion battery comprising of a LiFePO₄ positive electrode and a Si negative electrode made of amorphous silicon thin film is reported. The Si negative electrode was prepared by the vertical deposition of Si on a Cu foil substrate using sputtering system to get the homogeneous film with good adhesion between the substrate and Si film. In 2005, Amine et al. reported the electrochemical performance of a LiFePO₄-graphite full cell [24]. The battery showed discharge capacity of ~140 mAh g⁻¹ and stable cycle performance at C/3 at room temperature. Reale et al. showed a stable cycle performance on LiFePO₄ and

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Li₄Ti₅O₁₂ cell with ionic liquid electrolyte, even though the cell had a low power density [25]. Here we investigate an electrochemical combination of LiFePO₄ and Si for lithium ion battery. To the best of our knowledge, till date, the report on full cells of LiFePO₄ positive electrode using silicon negative electrode is rare.

2. Experimental

2.1. Synthesis of LiFePO₄ cathode

LiFePO₄ was synthesized by a mechanical activation process from Li₂CO₃, FeC₂O₄·2H₂O and NH₄H₂PO₄ (all chemicals of 99% purity from Aldrich) taken in stoichiometric quantities, as reported elsewhere [14, 15]. Sucrose for carbon coating was added in proportion of 12% of the total weight of the other reactants. All starting materials were magnetically stirred with 60 wt.% of triple distilled water at room temperature for 7 h. Fine solid powder was obtained from the homogenous solution by rotary evaporator drying at 70 °C for 2 h at 60 rpm. The powder was subjected to high energy ball milling at room temperature for 15 h in argon atmosphere and then thermal treatment at 600 °C for 10 h in N₂ atmosphere.

2.2. Preparation of silicon anode

Amorphous silicon film was deposited on a Cu foil substrate using a sputtering system with a vertical deposition technique. The Cu foil was pre-cleaned using ultrasonic treatment and annealed in vacuum-sealed ampules at 300 °C for 30 min to remove any residual impurities attached on the surface. The film was grown in a vacuum chamber under a pressure of 5×10^{-3} Torr in argon atmosphere. The growth rate of the Si film was 3 nm min⁻¹. A cross-sectional analysis was performed to measure the thickness of the film with an alpha step profiler. In this study, 330 nm-thick Si film was fabricated.

2.3. Characterizations of synthesized materials

The crystallographic structural characterization by X-ray powder diffraction (XRD) and Rietveld refinement was carried out on a SIMENS D5005 X-ray diffractometer using CuK α radiation (35 mA/40 kV) and a graphite monochromator. Scanning electron microscopy (SEM) imaging was done using FE-SEM (Philips XL30 S FEG). The nature and thickness of the carbon coating and amorphous silicon film were observed with field emission transmission electron microscopy (FE-TEM) (JEM-2100F, JEOL). The chemical composition of active materials was obtained from inductively coupled plasma (ICP) analysis (Atomscan 25, Optima 4300DV), and carbon content of LiFePO₄/C was obtained by elemental analyzer (CHNS-932, LECO). A Dilor (LabRam) Raman spectrometer operating with a 632.8 nm He–Ne laser and a 100 \times NA objective were used to investigate the vibrational properties of coated carbon.

2.4. Electrochemical evaluation

To prepare the positive electrode, LiFePO₄/C powder, super-P carbon black (Alfa) and poly(vinylidene fluoride) (Aldrich) as binder were mixed in 80:10:10 weight ratio, and a viscous slurry in *N*-methylpyrrolidone 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 cm² and mass ~2.5 mg for use as positive electrodes. The coin type LiFePO₄–Si cell was fabricated by amorphous silicon film as the negative electrode and LiFePO₄/C as the positive electrode with Celgard®-2400 separator film. 1 M LiPF₆ in EC/DMC (1:1 by vol.) was used as liquid electrolyte. The cell assembly was performed under argon atmosphere in a glove box. Cyclic voltammetry (CV) of LiFePO₄/C and amorphous Si thin film was performed at a scan rate of 0.1 mV/s between 2.0 and 4.5 V and 0.0 and 2.0 V, respectively. The charge–discharge and cycling properties of Si/LiFePO₄ full-cells were evaluated between 2.5 and 4.4 V at 0.5

and 1 C-rates using an automatic galvanostatic charge–discharge unit (WonA Tech. Co.) at room temperature. The practical weight balance in the full-cell was ~2:1 for LiFePO₄:Si.

3. Results and discussion

Based on a number of experiments, the optimal conditions of the mechanical activation process was found to be ball milling for 15 h at room temperature followed by the thermal treatment for 10 h at 600 °C [13]. The mechanical activation process yielded a composite sample with high purity, small particle size and uniform particle size distribution [14, 18]. The ICP analysis showed that the chemical composition of the composite matched the theoretical molar ratio of Li:Fe:P in the sample as 1:1:1. The elemental analysis revealed that the LiFePO₄/C composite has 6.0 wt.% carbon.

XRD patterns of the synthesized LiFePO₄/C and amorphous Si/Cu film are shown in Fig. 1. The crystal phase of LiFePO₄/C was identified from the XRD pattern to be orthorhombic, with an ordered olivine structure belonging to space group *Pnma* having a good correspondence with the standard LiFePO₄ pattern. The lattice parameters of $a = 10.314(4)$ Å, $b = 6.002(3)$ Å, $c = 4.694(2)$ Å correspond to a volume of 290.66 (2) Å³. No parasitic peaks corresponding to impurities of Fe³⁺ compounds were present in the XRD pattern. The addition of sucrose as carbon precursor effectively reduced any Fe³⁺ to be formed, resulting in the formation of a single-phase material. XRD patterns of Si thin film deposited on Cu substrate were also examined. All the diffraction peaks corresponded to those of Cu substrate. No peak was observed that could be assigned to silicon. It is considered from the result that the Si thin film has an amorphous structure.

The morphologies of LiFePO₄/C particle and amorphous Si thin film as revealed by scanning electron microscopy (SEM) are shown in Fig. 2. The typical particle size observed for LiFePO₄/C (Fig. 2a) is in the range of 70 to 250 nm. The particles have a specific surface area of 17.9 m² g⁻¹ [15]. Inclusion of sucrose as carbon precursor during the synthesis of LiFePO₄ has been reported to be advantageous in reducing the particle size effectively. Although a few particles do aggregate to yield different sizes, the primary particles are almost of the same size and have similar morphology. The surface of the directly deposited Si film on Cu substrate (Fig. 2b) is nearly flat. The morphology of Si film appears as embossing when examined in high scale. Such a surface appearance resulted from relatively low diffusivity of silicon during the growth of film. The average size of silicon lumps is about 110 nm and embossing-like structure also exists in the silicon lump.

Fig. 3a and b are FE-TEM images (the insets are SAED patterns) of LiFePO₄/C particle and Si/Cu thin film. Fig. 3a shows a TEM image and the electron diffraction patterns of LiFePO₄/C composite. Only the lattice line of LiFePO₄ is observed in the images and from this observation it can

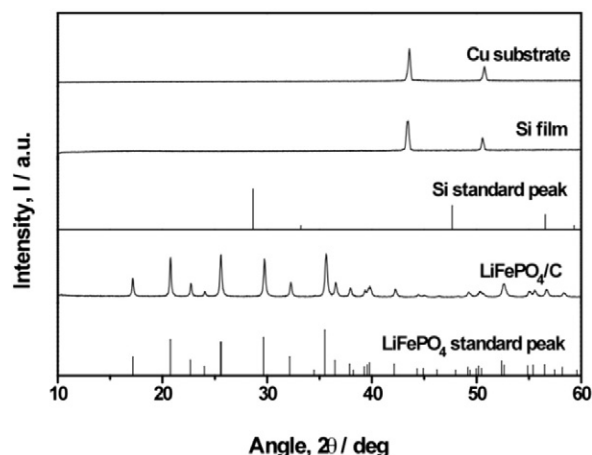


Fig. 1. XRD patterns of LiFePO₄/C and thin film of amorphous Si deposited on Cu substrate.

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