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# Ultralong cycling stability of carbon-nanotube/$LiFePO_4$ nanocomposites as electrode materials for lithium-ion batteries

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ABSTRACT

We developed a method to make CNTs fully coated by polyvinylpyrrolidone (PVP), which acts as an agent to effectively combine CNTs and $LiFePO_4$ to form a nanocomposite. In this nanocomposite, unbreaking and non-entangling CNTs forms a highly conductive 3D CNTs network that can significantly improve both the electrical conductivity of $LiFePO_4$ and the diffusion coefficient of Li ions and electrons. As a result, our CNTs/$LiFePO_4$ nanocomposite exhibited an excellent high-rate capacity and an ultralong cycling stability, i.e., a high discharge capacity of 123 mAh $g^{-1}$ and an extremely low loss in capacity of 1.6% could be achieved after 1000 cycles at 10C. A capacity of ~100 mAh $g^{-1}$ (corresponding to a capacity retention of 80%) could still be achieved after 3400 cycles at 10C. The loss in capacity of our $LiFePO_4$/CNTs is ~four to eight times smaller than that of previously studied $LiFePO_4$/CNTs and $LiFePO_4$/graphene nanocomposites. Our simple but powerful synthetic techniques should be beneficial to the application of lithium-ion batteries based on $LiFePO_4$ electrode materials in such electric vehicles as PHEVs, AEVs, and HEVs.

## 1. Introduction

Lithium-ion batteries are used in most of today's plug-in hybrid electric vehicles (PHEVs) and all electric vehicles (AEVs), as well as some hybrid electric vehicles (HEVs). For electrode materials, improving cycle stability is of immense technological significance [1–3]. Current EV batteries are often guaranteed for 8–10 years whereas the PHEV battery goals of the United States Council for Automotive Research LLC (USCAR) require batteries guaranteed for 15 years, or 5000 cycles, in 2020 [4]. Therefore, capacity loss through cycling at a high current density is a major challenge. The stable structure and the effective conductivity of the electrode materials are two major factors critical to cycle stability. As one of the most competitive candidate electrode materials of Li-ion batteries, the olivine-type $LiFePO_4$ has attracted extensive research interests [5–8]. As compared with other advantages such as nontoxicity, abundant resources along with a good security, the amazing structural similarity between $LiFePO_4$ phase and $FePO_4$ phase is more exciting [9]. It is undoubtedly that the same olivine structure of $LiFePO_4$ and $FePO_4$ is beneficial to maintaining the stability of crystal structure, avoiding capacity fading resulting from the volumetric changes during the charge/discharge process, and, hence, developing electrode materials with a superior cycling stability.

Researches have focused on their attention on increasing the effective conductivity of $LiFePO_4$ electrode materials for improving their superior cycling stability [10–14]. Usually, to maintain a long-term effective conductivity, the conductive agent must have an excellent electrical conductivity, a stable structure, a high strength and toughness, as well as the intimate contact between conductive agent and $LiFePO_4$. In the past years, many efforts have been made to increase the electrical conductivity by fabricating 3D conductive networks using 1D, 2D and 3D carbon [15–20]. As an 1D conductive material, carbon nanotubes (CNTs) with a large length-to-diameter ratio can significantly improve the cycle stability and rate capability of $LiFePO_4$ [21–28]. However, the aggregation resulting from the strong Van-der-Waals interactions between carbon nanotubes, the insolubility or poor dispersibility in organic solvents, and the intimate contact between $LiFePO_4$ and CNTs are of major obstacles to prepare uniformly distributed CNTs in $LiFePO_4$ electrode materials. Many synthetic techniques, such as surface functionalization, fabricating interface bonding, and designing $LiFePO_4$/CNTs with core-shell structures, have been developed to address these major obstacles, and most of the

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**Table 1**
Details of the freezing-thawing-drying method for making polyvinylpyrrolidone (PVP)-coated CNTs.

| Steps | Procedure | Quantity | T/K | t/min | Other conditions |
|---|---|---|---|---|---|
| 1 | Using $H_2O$ | 20 mL | 298 | / | Beaker (50 mL) |
| 2 | Adding PVP | 2 g | 298 | / | Beaker (50 mL) |
| 3 | Adding CNTs | 0.5 g | 298 | / | / |
| 4 | Sonicating | / | 298 | 30 | 200 watts, 20 kHz |
| 5 | Agitating | / | 323 | 240 | Magnetic stirrer |
| 6 | Centrifugating | / | 298 | 5 | At 3000 rpm |
| 7 | Freezing | 20 g | 77 | 10 | Drying flask (50 mL) In liquid nitrogen |
| 8 | Thawing | / | 298 | / | / |
| 9 | Heating | 20 g | 323 | 40 | In water bath |
| 10 | Repeating steps 7-9 | / | / | / | Four times |
| 11 | Freezing | 20 g | 77 | 10 | In liquid nitrogen |
| 12 | Drying | 20 g | 233 | 960 | At a pressure <10 Pa |

techniques provide $LiFePO_4$ electrodes with a good cycle stability [24,29–31]. For example, Chen et al. have demonstrated that their $LiFePO_4$/CNTs electrode materials exhibit a capacity retention of above 90% after 1000 charge/discharge cycles at 10C [24].

Based on our patented technique [32], we developed a method to make CNTs fully coated by PVP, which acts as an agent to effectively combine CNTs and $LiFePO_4$ to form a nanocomposite. We first modified CNTs by making PVP/CNTs/water dispersions and repeatedly freezing and heating the dispersions. The modified CNTs are dry, amphiphilic, and PVP-coated powders that can be re-dispersed in both aqueous and organic solvents to form stable and uniform dispersions with a high concentration of CNTs. We then prepared $LiFePO_4$ particles with an average particle size of ~35 nm. We finally combined our PVP-coated CNTs and $LiFePO_4$ particles to make $LiFePO_4$/CNTs nanocomposite electrode materials, where the PVP acts as the dispersant, the surfactant and the binder. The obtained $LiFePO_4$/CNTs cathode materials exhibit an excellent high-rate capacity and an ultralong cycling stability, i.e., after 1,000 charge (1C)/discharge (10C) cycles, a high discharge capacity of 123.0 mAh $g^{-1}$ and an extremely low loss in capacity of 1.6% can be achieved. Moreover, the cathode materials can maintain a discharge capacity of about 100 mAh $g^{-1}$ (corresponding to a capacity retention of 80%) after 3400 cycles at 10C. To our best knowledge, these are the best rate and cycling performances achieved with the $LiFePO_4$-based electrode materials [33–39]. The breakthrough can be ascribed to the combined effect of the large Li-ion diffusion coefficient achieved in $LiFePO_4$ particles and the highly conductive 3D networks composed of monodispersed CNTs free from breaking and entangling effects.

## 2. Experimental

### 2.1. Synthesis of PVP-coated CNTs

CNTs synthesized by a CVD method were commercially available from Nanostructured & Amorphous Materials, Inc. (Houston, USA). These CNTs are with a purity of >95 wt.%, an outer diameter of ~40 nm, an inner diameter between 5 and 15 nm, and a length between 10 and 20 $\mu$m. The CNTs contain such impurities as Cl (0.20 wt%), Fe (0.55 wt%), Ni (1.86 wt%), and S (0.02 wt%) which were measured by an Energy Dispersive X-ray Spectroscopy, as suggested by the supplier's Certificate of Analysis. PVP-coated CNTs powders were prepared with the following procedures: (1) Adding 20 mL deionized water in a beaker (50 mL) at room temperature (25 °C); (2) Dissolving 2 g PVP (M. W. = 40,000) in deionized water to form a solution; (3) Adding 0.5 g CNTs to the above solution to form a mixture; (4) Sonicating the mixture with a sonicator supplied by Ningbo Scientz Bio-Tech Co., Ltd. and equipped with an ultrasonic probe operated at a power of 200 watts and a frequency of 20–25 kHz for 30 min; (5) Agitating the mixture with a conventional magnetic stirrer at 50 °C for 4 hours; (6) Centrifugating the mixture with a conventional centrifuge at 3000 rpm for 5 minutes to separate the non-dispersed CNTs and such impurities as metallic catalysts and amorphous carbon from the CNTs/water mixture to form a stable and uniform PVP/CNTs dispersion; (7) Freezing the PVP/CNTs dispersions transferred to a vacuum drying flask (50 mL) in liquid nitrogen (−196 °C) for 10 min; (8) Thawing the frozen dispersion at room temperature; (9) Heating the thawed dispersion in a warming water bath (50 °C) for 40 min; (10) Repeating the above

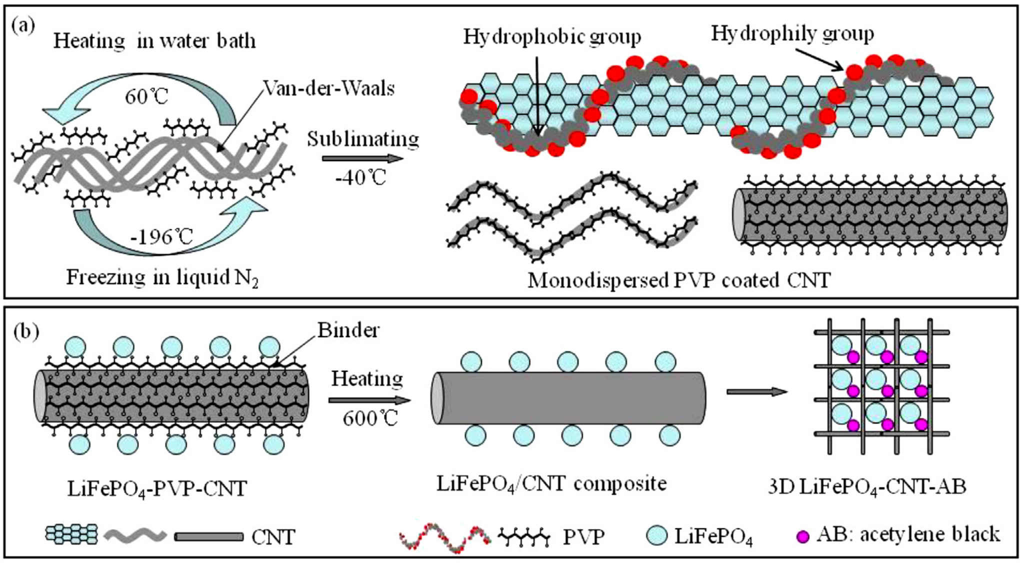

**Fig. 1.** Schematic description of three-dimensional conductive network of monodispersed CNTs. (a) PVP-coated CNTs; (b) Three-dimensional conductive network with CNTs and acetylene black.