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Functionalization of MWCNTs by plasma treatment and use as conductive additives for $LiFePO_4$ electrode

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ABSTRACT

The application of $LiFePO_4$ in high power battery is limited by its low conductivity. MWCNTs as conductive additives were functionalized with maleic anhydride (MA) using the plasma-induced grafting technique. A series of $LiFePO_4$/MWCNTs-MA composite electrodes with 1.7 wt%, 2.7 wt%, 4.7 wt%, and 9.7 wt% of MWCNTs-MA were fabricated to improve conductivity and to investigate the effects of MWCNTs-MA on $LiFePO_4$ electrode performance. X-ray diffraction analysis of $LiFePO_4$/MWCNTs-MA cathodes showed that crystallinity and lattice spacing of $LiFePO_4$ were not altered by incorporation of MWCNTs-MA. Field-emission scanning electronic microscopy showed that 4.7 wt% MWCNTs-MA dispersed well in $LiFePO_4$ particle matrix. Electrochemical impedance spectroscopy showed that charge transfer resistance was decreased by increased amount of MWCNTs-MA. The specific capacity, cyclic stability, and rate performance of $LiFePO_4$ coin cells were enhanced by increased amount of MWCNTs-MA, and reaching optimal performance at 4.7 wt%. The $LiFePO_4$/MWCNTs-MA (4.7 wt%) battery had rate capacity of 114 mAh g^{-1} at 1 C with a capacity retention ratio of 75.6% after 200 cycles.

1. Introduction

Lithium-ion batteries (LIBs) are rechargeable batteries in which lithium ions move between the anode and the cathode. LIB uses an intercalated lithium compound instead of metallic lithium anode used in lithium battery [1]. LIB cell is composed of two electrodes and the electrolyte that allows ions move between two electrodes. Much effort has been focused on exploring materials used in electrode to optimize the energy density, operating temperature, durability, charging time, high input/output power, and cost [2]. Currently, cathode materials are generally made of lithium cobalt oxide ($LiCoO_2$) [3], lithium manganese oxide ($LiMn_2O_4$) [4], and lithium iron phosphate ($LiFePO_4$) [5].

$LiFePO_4$ batteries are environmentally friendly and have long cycle life with relatively low cost compared to other batteries due to their stable olivine structure and the ease of acquiring transition metals [6,7]. $LiFePO_4$ material has the theoretical capacity of 168 mAh g^{-1} and discharge plateau at 3.4 V vs. Li/Li^+. Thus, $LiFePO_4$ batteries are popular in electric vehicles and backup power applications. However, the application of $LiFePO_4$ in high power battery [8] is somewhat limited by its low conductivity 10^{-9} S cm^{-1} and low lithium-ion conductivity 10^{-5} S cm^{-1}.

There are two approaches to increase the conductivity of $LiFePO_4$ electrode, *i.e.* by preparing metal doping $LiFePO_4$ or by making $LiFePO_4$/carbon composite electrode [9,10]. To manufacture $LiFePO_4$/carbon composite electrode, one could try coating a layer of carbon on $LiFePO_4$ particles to allow mixture of $LiFePO_4$ and carbon source and then sintering at high temperature in vacuum [11]. Another way is mixing $LiFePO_4$ with carbon additives, such as multi-wall carbon nanotubes (MWCNTs) or graphene, to form cathode material slurry and spread on the metal substrate [12,13].

MWCNTs have many unique advantages such as large surface area, excellent thermal and electrical conductivity, good mechanical strength, and are lightweight [14]. MWCNTs have been investigated to serve as electric transporter to enhance $LiFePO_4$ battery performance [15–19]. For example, addition of MWCNTs at 5 wt% improved capacity retention ratio from 91.7% to 97.8% at 0.1C for 100 cycles in $LiFePO_4$ battery composed of 15 wt% Super P conductive agent [20]. Addition of 3.6 wt% MWCNTs to $LiFePO_4$ battery composed of 10 wt% carbon black improved the capacity from 127.2 mAh g^{-1} to 158.1 mAh g^{-1} at 0.5 C, and from 118 mAh g^{-1} to 155.3 mAh g^{-1} at 1C [21]. Accordingly, the capacity loss from 0.5 C to 1 C was cut down from 7.23% to 1.77%.

However, MWCNTs tend to form agglomeration, due to van der Waals force and hydrophobic interaction between adjacent

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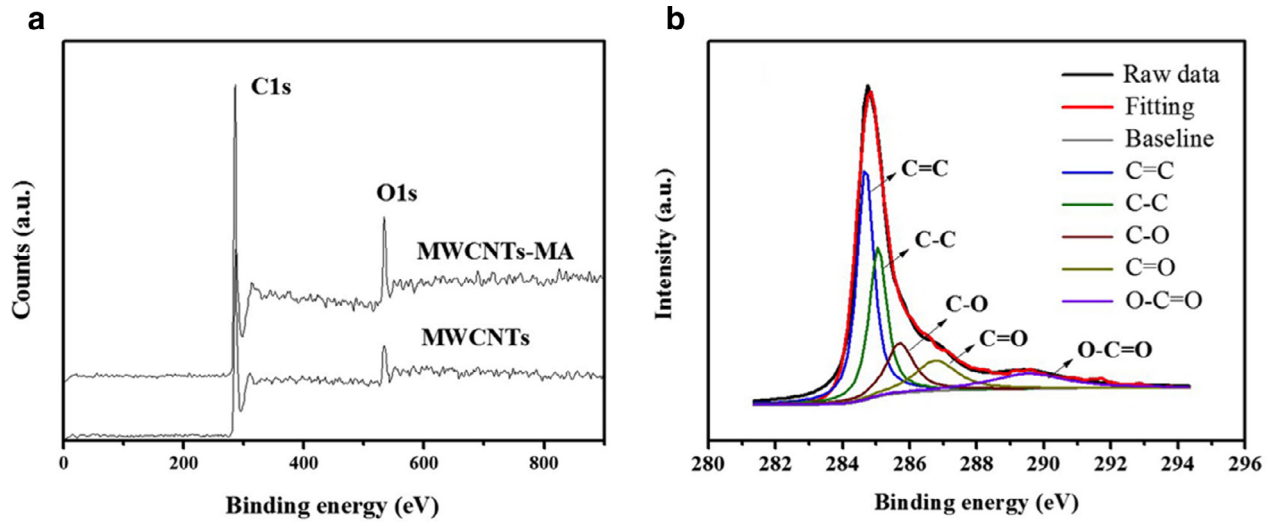

Fig. 1. (a) XPS spectra of MWCNTs and functionalized MWCNTs-MA, and (b) deconvolution spectra of C1s peak of MWCNTs-MA.

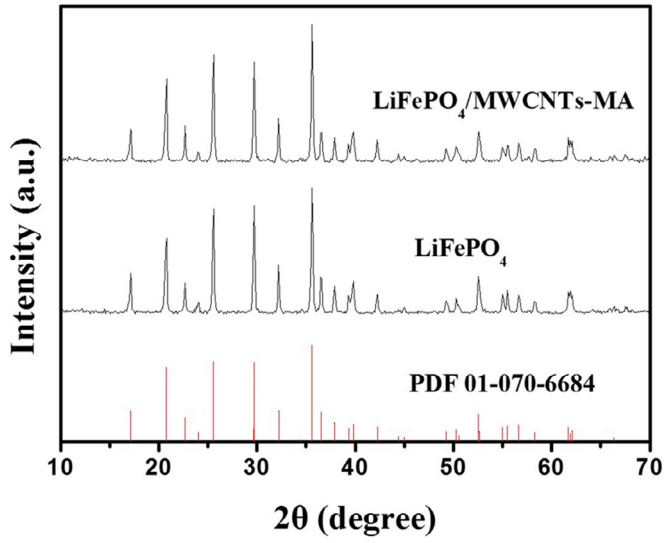

Fig. 2. XRD diffraction patterns of $LiFePO_4$ thin film and the $LiFePO_4$/MWCNTs-MA (4.7 wt%) composite film.

nanotubes. One way to overcome this limitation is to add dispersing agent to facilitate dispersion of carbon additive into $LiFePO_4$ slurry [22]. Alternatively, one could try to functionalize the surface of MWCNTs with tiny polymer to provide steric hindrance between MWCNTs so that agglomeration can be prevented and MWCNTs dispersion can be enhanced [23]. To functionalize MWCNTs, it often needs to be treated with acid, yet acid treatment can cause significant damage on surface and structure of MWCNTs which decreases the conductivity of MWCNTs. To address this issue, our group has been successful in applying plasma-induced grafting method to functionalize the surface of MWCNTs with polymer or molecular to improve MWCNTs dispersion without compromising the conductivity of MWCNTs [24].

Generally, $LiFePO_4$ cathode is composed of $LiFePO_4$ active materials along with polymer binder and 10–15 wt% of carbon black or Super P. In this study, we proposed to investigate if functionalized MWCNTs could serve as an effective conductive agent for $LiFePO_4$ battery. To minimize the resistance of electron transfer from $LiFePO_4$ to MWCNTs, small molecule maleic anhydride (MA) was chosen as the grafting agent for MWCNTs (MWCNTs-MA). Series of $LiFePO_4$/MWCNTs-MA composite electrodes with different weight ratios (wt%) between $LiFePO_4$ and MWCNTs-MA were manufactured to investigate the effect of MWCNTs-MA on the performance of batteries and to determine the optimal wt% of MWCNTs-MA within $LiFePO_4$ electrode. Galvanostatic battery testing and electrochemical impedance spectroscopy (EIS) were used to obtain the capacity, operating voltage, cycle life, rate performance and charge transfer resistance of $LiFePO_4$/MWCNTs-MA batteries.

2. Experimental section

2.1. Functionalization of MWCNTs with MA by plasma induced grafting technique

To facilitate MWCNTs dispersion homogeneously into cathode slurry, MWCNTs were functionalized with maleic anhydride (Aldrich Co.) using plasma induced grafting process [24]. MWCNTs (Industrial Technology Research Institute, Taiwan), which have diameter of 10–90 nm and length of 3–5 μm, were placed in the stainless vacuum chamber with a volume of 6×10^3 cm^3. The distance of a pair of parallel circular copper (Cu) electrodes was 3 cm. Atmospheric pressure in the stainless chamber was reduced from 760 torr to 10^{-5} torr using mechanical pump and diffusion pump and filled to 10^{-1} torr with 99.999% argon gas (Yun Shan Gas Co.). MWCNTs were plasma pre-treated between circular copper electrodes with a power of 50 W and a frequency of 13.56 MHz for 10 min. Subsequently, 0.1 M solution of MA in 95% cyclohexanone (Fisher Scientific Taiwan Co.) was injected into chamber. The temperature of grafting reaction was controlled at 60 °C for 2 h. After functionalization, MWCNTs grafted with MA were washed with 95% cyclohexanone by centrifugation and heated subsequently in the oven at 70 °C for 1 h. For commercialization, we have established the necessary means for mass production of MWCNTs grafted with MA. The patent abstract associated with photos of apparatus is shown in supplementary S1.

2.2. Preparation of lithium ion batteries with $LiFePO_4$/MWCNTs-MA composite cathodes

The cathode slurry was prepared by mixing with $LiFePO_4$ particles (Advanced Lithium Electrochemistry Co., Ltd.) and Solef 6020 polyvinylidene fluoride (PVDF) of MW~30,400 as binder in the weight ratio of 95:5 in the N-methyl-2-pyrrolidone (NMP) solvent (Merck KGaA). One kind of MA grafted level on MWCNT was