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Effects of Different Templates on Electrochemical Performance of $LiFePO_4/C$ Prepared by Supercritical Hydrothermal Method

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In this study, $LiFePO_4/C$ has been synthesized by supercritical-hydrothermal method followed with solid phase calcination using three different templates; hexadecyl trimethyl ammonium bromide (CTAB), sucrose and polyvinyl pyrrolidone (PVP). The effects of different templates on the properties of the synthesized $LiFePO_4/C$, including crystalline structure, particle size, morphology, and electrochemical performance, were examined. It was found that the use of the template of PVP led to better-crystallized and smaller-sized $LiFePO_4/C$ particles. As a result, a higher discharge capacity was observed with particles synthesized with PVP as template when compared with discharge capacities of those synthesized using CTAB and sucrose. The $LiFePO_4/C$ particles synthesized using the PVP as template delivered a relatively high specific discharge capacity of 141.2 mAh/g at 0.1 C, and good cycling performance.

Keywords: supercritical hydrothermal method; $LiFePO_4/C$; template; electrochemistry performance

1. INTRODUCTION

Since the pioneering works of Goodenough and his co-workers, olive structure lithium iron phosphate ($LiFePO_4$) was considered as attractive cathode material for lithium ion batteries, due to its high theoretical capacity (170 mAh/g), low raw materials cost, environmental benignity, high safety and long cycle stability [1, 2]. However, poor electronic conductivity and low lithium ion diffusion coefficient of $LiFePO_4$ hampered its practical application [3, 4]. Thus, many attempts have been made to overcome these two drawbacks, such as carbon coating [5], element doping [6, 7], minimizing particle size [8], preparing materials with porous or hollow structure [9].

To date, various methods have been proposed to synthesize $LiFePO_4$, such as solid-state reaction [10], sol-gel [6], hydrothermal/solvothermal [11], co-precipitation [12], microwave [13, 14], spray technology [15, 16], to name a few. Supercritical hydrothermal synthesis (SHS) is an effective, environmental-friendly and fast method to obtain well-crystallized cathode active materials with well-defined morphologies using either batch or continuous reactor system [17, 18]. More recently, Zhang *et al*. [19] showed that $LiFePO_4$ with particle size in the range of 100-300 nm can be synthesized using the batch SHS method, and Hong *et al.* [20] showed that the process parameters should be controlled within a rather narrow window to produce high-quality $LiFePO_4$ using the continuous SHS method. The effects of synthetic parameters such as temperature, pH, reaction time and reactant concentrations on the size and morphology of the $LiFePO_4$ particles produced via the batch SHS were investigated [21, 22]. However, the effects of different templates on electrochemical properties of the supercritical synthesized $LiFePO_4$ were not studied.

As well known, under hydrothermal processing, morphologies and sizes of particles can be readily tailored by employing appropriate template agent, owing to the adsorption of the assistant agent molecules onto the particle surface during the particle growth [23]. Meanwhile, some templates added into the hydrothermal solution can be used as the carbon source to coat $LiFePO_4$ particles with carbon films by calcination. Yu *et al.* [24] demonstrated that pyrogallic acid was added to serve as reducing agent, surface growth directing template and carbon source to synthesize craggy-faced $LiFePO_4/C$ composite materials.

This work is concerned with the effects of different templates (CTAB, sucrose, and PVP) on the electrochemical performance of $LiFePO_4/C$ particles prepared by supercritical hydrothermal method.

2. EXPERIMENTAL

2.1 Particles Production

$FeSO_4{\cdot}7H_2O$, ascorbic acid and template of hexadecyl trimethyl ammonium bromide (CTAB) were dissolved in deionized water to form a homogeneous solution. $LiOH{\cdot}H_2O$ and o-H_3PO_4 were then induced into the above solution under stirring. The precursor solution was adjusted to maintain the molar ratio of $FeSO_4{\cdot}7H_2O$:o-H_3PO_4:LiOH at 1:1:3 in the experiment. Afterwards, the obtained solution was transferred into the autoclave, kept for 1 min at 400 ^oC and 25 MPa, and then cooled down to room temperature by circulating cooling water through the jacket. The as-prepared precipitation was collected by filtrating, repeatedly washed by distilled water and absolute alcohol, and finally dried at 110 ^oC in a vacuum oven. The as-obtained $LiFePO_4$ material was followed by calcination in a tubular furnace at 700 ^oC for 1 h with a flow rate of 10% (volume ratio) hydrogen in argon. Under the identical experimental conditions, sucrose and polyvinyl pyrrolidone (PVP) were also used as templates to compare their effects with CTAB.

2.2 Particles characterization

The structure of the obtained particles was characterized by powder X-ray diffractometer (XRD, PW1825) with Cu K radiation at 40 kV and 40 mA at steps of 0.020°. The morphology and particle size of the samples were examined by field emission scanning electron microscopy (SEM, JEOL JSM-6390). The carbon content of the samples was measured by infrared carbon-sulfur analyzer (Eltar Co., CS800).

2.3 Electrochemical characterization

Electrochemical tests were conducted with two-electrode CR2025-type coin cells assembled in a dry glove box under protection of argon. For preparing the working electrodes, the prepared $LiFePO_4$/C as active material was mixed with acetylene black and polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) in a weight ratio of 8:1:1 to form slurry, and then the slurry was pasted onto aluminum foil, followed by drying at 110 ^oC for 12 h in a vacuum oven. A Celgard 2400 microporous membrane was used as a separator, and lithium foil was used as a counter electrode. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate (EC : DMC : EMC = 1:1:1 by volume) solvent.

The assembled cells were evaluated by using a commercial multichannel galvanostatic charge-discharge cycle in the potential range of 2.0-4.2 V versus Li^+/Li at different scan rates. Cyclic voltammetry (CV) tests were carried out using Zahner Zenniuma electrochemical working station with scan rates of 0.1 mV/s between 2.0 and 4.2 V. Electrochemical impedance spectroscopes (EIS) was also performed on a Zahner Zenniuma electrochemical working station with a frequency range from 10 mHz to 100 KHz.

3. RESULTS AND DISCUSSION

The XRD patterns of $LiFePO_4$/C particles prepared with different templates are shown in Fig. 1. The main diffraction patterns of the particles were indexed to orthorhombic $LiFePO_4$ olivine-type phase (JCPDS PDF number 83-2092). No impurity peaks are observed, suggesting that the existence of CTAB, sucrose and PVP did not induce impurity phase into the resulting $LiFePO_4$/C during the preparation process.

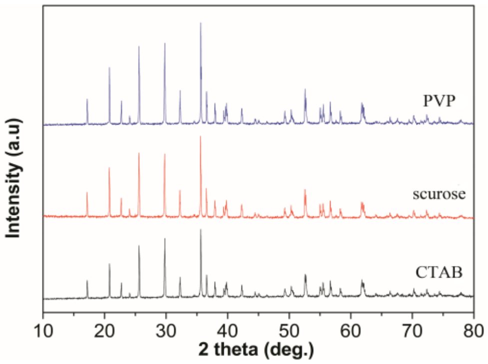

Figure 1. XRD patterns of $LiFePO_4$/C particles synthesized using different templates

No detectable reflections corresponding to carbon could be found in the XRD patterns, meaning that the carbon in the sample is not well crystallized [25]. A relatively stronger intensity of diffraction peaks is present in the samples synthesized with PVP as template when compared with those synthesized with CTAB and sucrose. This suggests that the use of the PVP template is more favorable for increasing the crystallinity of the $LiFePO_4/C$ when compared with the use of the CTAB and sucrose.

The SEM images of $LiFePO_4/C$ prepared with three different templates are shown in Fig. 2. The particle size distribution of the $LiFePO_4/C$ synthesized with CTAB, sucrose and PVP are 400–2000, 400–1000 and 200–600 nm, respectively. The $LiFePO_4/C$ particles obtained using PVP have a smaller particle size and more uniform particles in terms of size distribution. In batch hydrothermal synthesis, the nucleation step determines particle size at supercritical conditions [26]. So it is speculated that the function of template PVP with a long carbon chain and C=O groups has the capability for regulating nucleation of $LiFePO_4$ in SHS.

It is well known that annealing can transform these templates into carbon coating on the $LiFePO_4$ particles surface to enhance the electronic conductivity and improve the crystallinity [24]. The results measured show that the carbon contents of samples with CTAB, sucrose and PVP are 0.59%, 0.63% and 0.62% respectively, which indicates that the samples with different templates have almost the same carbon coating level to enhance electrochemical performances. We must state that these values of carbon contents are much lower than that in the most of previously reported studies. So it is necessary to increase the carbon content of the $LiFePO_4/C$ in the following research to further improve its electrochemical performance. In this paper, we primarily discuss the effect of three different templates on the electrochemical performance of $LiFePO_4/C$.

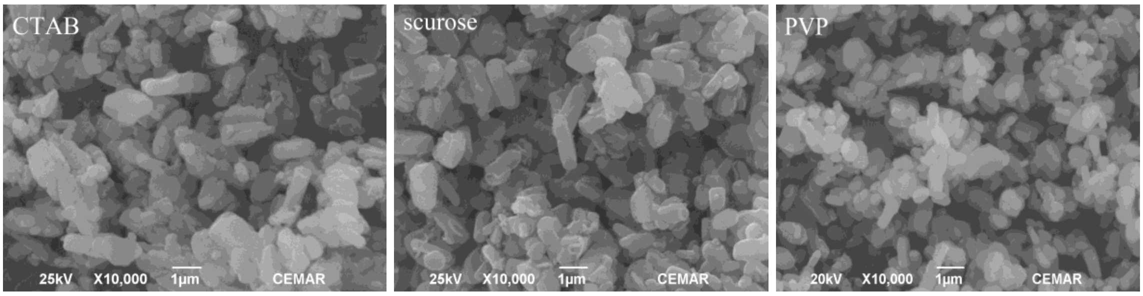

Figure 2. SEM images of $LiFePO_4/C$ particles synthesized using different templates

Figure 3 and Figure 4 show the charge-discharge curves and cycling performances of the $LiFePO_4/C$ particles prepared with different templates, respectively. As seen from Fig.3, all samples show a flat voltage plateau at around 3.4 V at 0.1 C, which corresponds to the characteristics of Li-ion extraction and insertion reactions between $LiFePO_4$ and $FePO_4$ phases [27]. The initial discharge specific capacities of samples synthesized with CTAB, sucrose and PVP are 84.9, 114.5 and 141.2 mAh/g at 0.1 C, respectively. The sample synthesized using PVP as template has higher capacity than others, which means that the optimal template is PVP. The distinct capacity skip may be attributed to the well-distributed and good crystallinity of the $LiFePO_4/C$ particles synthesized with PVP [25]. It is also seen from Fig.4 that all of the samples exhibit high capacity retention throughout the continuous charge discharge process. The capacity retention rates of the samples synthesized using CTAB, sucrose and PVP are 94.6%, 95.1% and 96.0% after 100 cycles at 1.0 C, respectively. This observation suggests that our $LiFePO_4/C$ materials prepared by supercritical-hydrothermal combined with solid phase calcination route show good cycle performance.

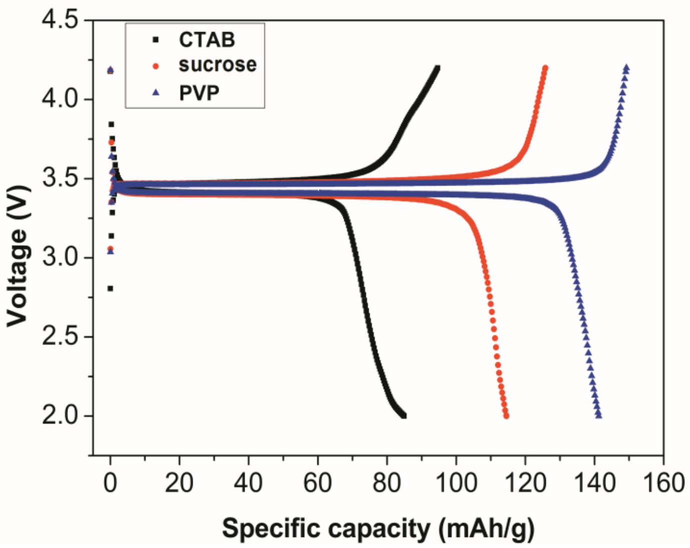

Figure 3. Charge-discharge curves of $LiFePO_4/C$ particles synthesized using different templates at 0.1 C

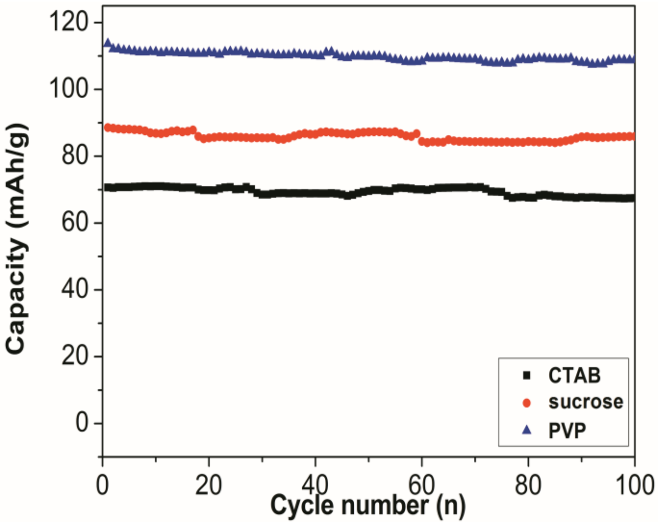

Figure 4. Cycling performances of $LiFePO_4/C$ particles synthesized using different templates at 1.0 C

Figure 5 compares the rate performance of samples synthesized with different templates. The sample synthesized using CTAB as template, compared to the samples synthesized using sucrose and PVP, shows lower rate capacity with a significant fade. The capacity fade could be due to its lower crystallinity and larger particle size resulting in the difficulty of lithium ion insertion/de-insertion during the charge/discharge process.

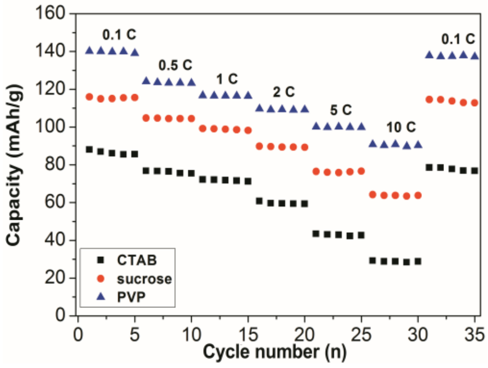

Figure 5. Rate and cycling performances of $LiFePO_4/C$ particles synthesized using different templates

Cyclic voltammograms (CVs) of the three $LiFePO_4/C$ composite electrodes are shown in Fig. 6. The $LiFePO_4/C$ sample synthesized with PVP as template shows the highest peak current density, the narrowest voltage separation and the best peak symmetry. This observation shows the sample obtained using PVP as template had the less polarization and better electrochemical reversibility than those obtained using CTAB and sucrose, which is in well agreement with the charge/discharge result.

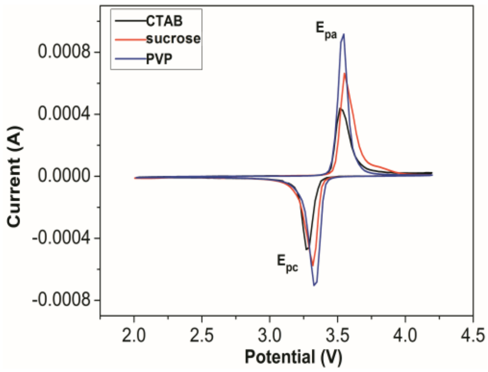

Figure 6. Cyclic voltammograms of $LiFePO_4/C$ particles synthesized using different templates

EIS was carried out for further electrochemical investigation, as shown in Fig. 7. All samples exhibit a depressed semicircle in the high-middle frequency region and a straight line in the low frequency region. The semicircle in the high-middle frequency is related to charge-transfer resistance for lithiation reaction at the interface of electrolyte and cathode. The inclined line in the low-frequency range is corresponding to Warburg impedance, which is associated with the diffusion of lithium ion in the electrolyte to the bulk electrode material [28]. From the AC impedance spectroscopy of Fig. 7, we can see that the $LiFePO_4/C$ sample synthesized using PVP has the smallest charge-transfer resistance than the $LiFePO_4/C$ samples synthesized using CTAB and sucrose, which indicates that the polarization of former is much less than that of latter.

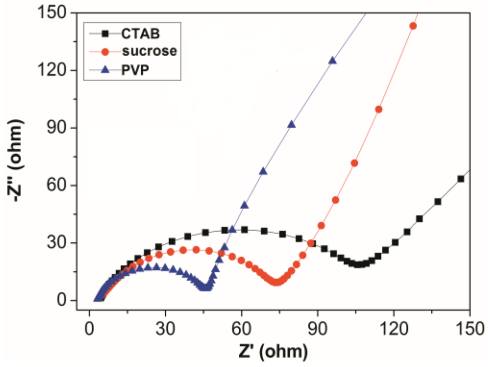

Figure 7. The EIS plot of three cells with $LiFePO_4/C$ particles synthesized using different templates

4. CONCLUSIONS

$LiFePO_4/C$ particles have been prepared through a supercritical-hydrothermal combined with solid phase calcination route with the assistance of three different templates, namely, CTAB, sucrose and PVP. It is found that the templates introduced during supercritical hydrothermal synthesis play an important role in the formation of $LiFePO_4/C$ particles with different crystallinities and sizes. The $LiFePO_4/C$ composite synthesized using PVP as template exhibits the most desirable electrochemical performance due to its stable crystalline structure and small particle size. So it is concluded that PVP used as template is preferred during synthesis of $LiFePO_4/C$ by supercritical hydrothermal method.

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