

High Electrochemical Performances of LiFePO_4 Cathode Material Prepared from Surface Modification by Carbon Coating using Sucrose via Sol-gel Method

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Abstract: In this study, LiFePO_4 cathode was modified using the sucrose via sol-gel method. The carbon coated LiFePO_4 was characterized using XRD, SEM and EDS techniques. The XRD patterns of carbon coated LiFePO_4 revealed that the coating did not affect the crystal structure of the parent powder. The carbon coated LiFePO_4 has a discharge capacity of 143 mAh/g in the voltage range of 2.8-4.2V vs Li/Li^+ . The cathode exhibited a stable capacity on cycling, and a good rate capability in the current range of 0.1-4.0C. Additionally, the carbon coated LiFePO_4 compound exhibited a highly improved area-specific impedance (ASI), which is one of the most important properties for battery performances. The results indicated that this cathode material could be useful for lithium-ion cells because it has a much lower cost than LiCoO_2 -containing cells, and high safety.

Keywords: Cathode material; LiFePO_4 ; sol-gel; Sucrose; Lithium ion battery

1. INTRODUCTION

Li-ion batteries with high energy densities and power capabilities have become important power sources for portable electronic devices, such as cellular phones, computers and, more recently, hybrid electric vehicles (HEV) [1]. Most of the commercialized Li-ion batteries use LiCoO_2 as the cathode material because of its ease of production, stable electrochemical cycling, and acceptable specific capacity [2,3]. However, the relatively high cost of cobalt and the lure of a large capacity have led to the study of other possible alternatives [4-8].

In recent years, many research groups have developed secondary lithium batteries containing positive electrode materials made up of phospho-olivines. These cathode materials containing LiFePO_4 (olivine structure) possess a good thermal stability because of the P-O covalent bonding. Therefore, these materials are suitable for use in a number of applications ranging from cellular phones and notebook computers to hybrid electric vehicles. However, the electronic conductivity of LiFePO_4 is much lower than LiCoO_2 (10^{-3} Sm^{-1}) [9], which is currently used as the cathode material. Many attempts have been made to enhance the electronic conductivity of LiFePO_4 by optimizing the synthetic conditions. Carbon coating helps to retard the undesirable particle growth during the

thermal treatment, and also improves the electrical conductivity of the active material [10]. This carbon coating over the particle surface can significantly enhance the electrochemical performance of the LiFePO_4 cathode materials. However, a satisfactory approach to simultaneously solve the problems with the electrochemical properties and the economic process has not been developed yet.

In this work, a sucrose coating process was employed during the preparation of the active cathode materials. Sucrose is a very low cost carbon source material. Recently, some researchers have synthesized LiMn_2O_4 spinels with nano size particles through a combustion reaction with commercial sugar as the fuel [11,12]. Notably, sucrose serves as an electronic conductivity enhancing agent and a particle growth suppressant.

In this first study, a carbon coated LiFePO_4 cathode with sucrose was prepared because it (sucrose or Sugar) is very low-cost material in comparison to the other coating materials. Therefore, to depress particle growth and enhance electronic conductivity, surface modification of the particle using sucrose coating has been adapted in this work, and the electrochemical and structural properties were characterized.

2. EXPERIMENTAL

In this present study, a simple sol-gel process was adapted in order to synthesis LiFePO_4 from lithium acetate dihydrate

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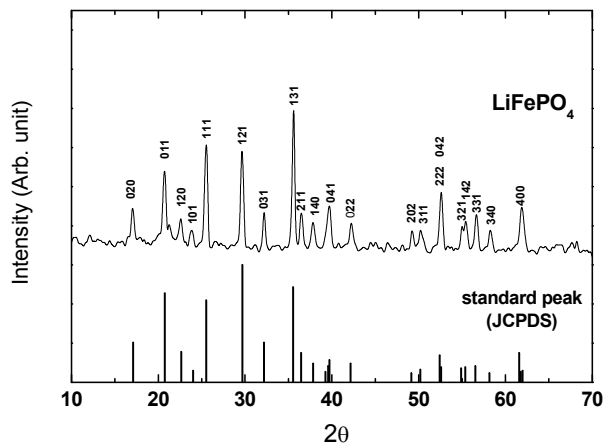


Figure 1. XRD spectra of LiFePO_4 in comparison to standard $Pnma$ orthorhombic LiFePO_4 .

$[\text{Li}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}]$, ammonium iron(II) sulfate $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2]$, phosphoric acid $[\text{H}_3\text{PO}_4]$, sucrose $[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$. Sucrose and stoichiometric amounts of Fe, P and Li were dissolved in distilled water at a molar ration of 0.1:1 (sucrose: LiFePO_4) were and continuously stirred at 80 °C for 4 hr until a transparent sol was obtained. The sol was heated at 100 °C for 3h to remove the water, turning the sol into a viscous brown gel. This gel was heated at 500 °C for 5h in an argon atmosphere, and then calcined at 800°C for 10h an argon atmosphere to obtain LiFePO_4 powder.

The X-ray diffraction patterns of the cathodes were obtained using a Bruker D8 diffractometer in the 2θ range from 10 to 70° with Cu K_α radiation ($\lambda = 1.5406\text{Å}$). The surface morphology and the composition of the carbon coated powder was observed using a scanning electron microscope (SEM) and energy dispersive X-ray microanalysis (EDAX) mapping.

To prepare the positive electrode, 80% LiFePO_4 powder., 10% super-P carbon black (Aldrich), N-methyl-2-pyrrolidone and 10% PVdF (Kureha KF100) binder were added in crucible. After two hours of grinding, the viscous slurry was coated on an aluminum foil using a doctor blade and a film with a uniform thickness was obtained. Then the film was then dried at 60 °C for 6 h and 120 °C for 6 h in a vacuum oven. The thickness of the cathode film was about 40 μm . The CR2016 type coin cell was assembled in a glove box using the above cathode film, lithium, a porous polyethylene film and 1.2M LiPF_6 solution in 1:1:3 volume ratio of ethylene carbonate (EC)/poly carbonate (PC) /dimethyl carbonate (DMC). The lithium metal foil was used as both the counter and reference electrode. After coin cell assembly, the test cells were charged to 4.2 versus Li/Li^+ at constant current density (170 mA g^{-1} was assumed to be 1C rate) and then discharged to 2.8 V with the same current density.

3. RESULTS

3.1. Powder characterization

The XRD pattern of the synthesized LiFePO_4 is presented in Fig. 1. The LiFePO_4 sample was well fitted well with orthorhombic olivine $Pnma$ space group. The LiFePO_4 pattern exhibited a good correspondence with the standard spectra which was also included

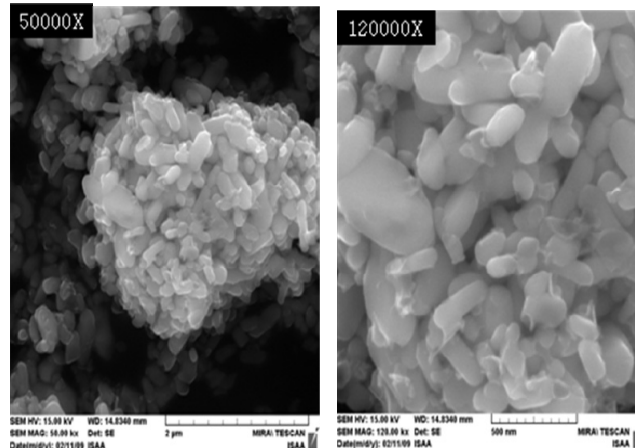


Figure 2. SEM images of LiFePO_4 powder.

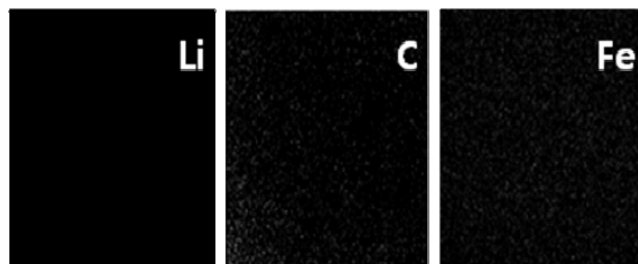


Figure 3. Carbon EDS map (50,000) of LiFePO_4 .

as reference. Therefore LiFePO_4 was successfully synthesized using the simple sol-gel method. The unit cell parameters for the hexagonal cell were $a = 10.2876\text{Å}$, $b = 6.0073\text{Å}$ and $c = 4.6714\text{Å}$.

In Figure 2, the morphology of LiFePO_4 was observed using a scanning electron microscope (SEM). The average particle size of the samples was in the range of 200–700 nm. Figure 3. shows the EDS dot map of the carbon, and the very small white dots indicated that the carbon was dispersed on the surface of the LiFePO_4 particles. Therefore, the LiFePO_4 particles were successfully coated with the electronically conductive carbon, and the silver was well distributed without aggregation.

3.2. Electrochemical behavior

Cyclic voltammetry is a complementary and well-suited technique for evaluating the cathodic performance and the electrode kinetics of oxide materials. The cyclic voltammograms (CV) of the LiFePO_4 cathode were recorded for the cells at room temperature with metallic lithium as the counter and reference electrodes from 2.5–4.2 V. Figure 4 shows the CV at a scan rate of 0.05 mV/s for 5 cycles. The important feature of the CV was the difference between the first and subsequent cycles. The first anodic scan contained one oxidation peak that was centered at 3.63 V. The peak at 3.63 V in the first anodic scan did not shifted to a lower voltage in the second anodic scan. On the subsequent cycles, the oxidation and reduction processes exhibited only one major anodic and one major cathodic

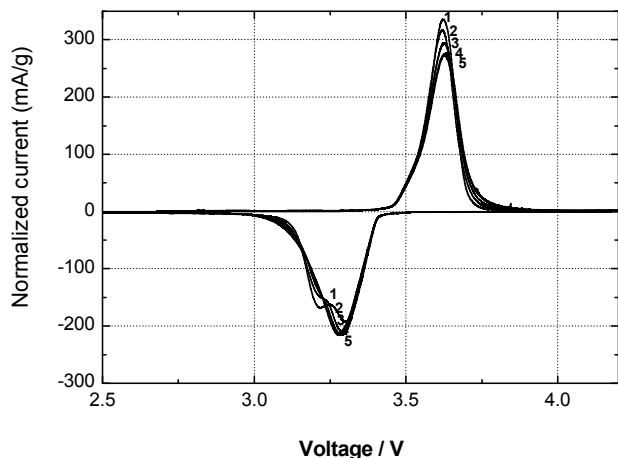


Figure 4. Cyclic voltammetry of the LiFePO₄ cell between 2.5 and 4.2 V at a scan rate of 50 μV s⁻¹.

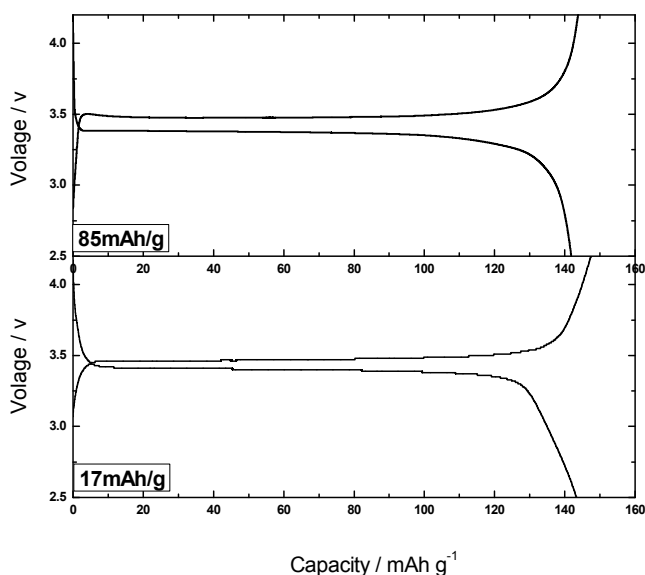


Figure 5. First charge-discharge curves for LiFePO₄ sample cycled in various current range at a constant voltage ranges between 2.5–4.2 V.

peak that were centered 3.63 and 3.29 V, respectively. This behavior implied that structural degradation was not expected during the lithium extraction/insertion process of the LiFePO₄ electrode unlike LiNiO₂. The multi-phase reactions that exhibit three peaks for LiNiO₂ lead to the structural change, resulting in the eventual degradation of electrode performance [13]. Figure 5 shows the typical initial charge and discharge curves of the cathodes for the LiFePO₄ cell that contained 1.2M LiPF₆-EC/PC/DMC(1:1:3) at various current densities. These curves showed that both charge and discharge cathode polarization was substantially reduced by the carbon (sucrose) coating. The discharge capacity and the irreversible capacity were also improved by the carbon coating. The carbon coated LiFePO₄ compound had a relatively large initial discharge

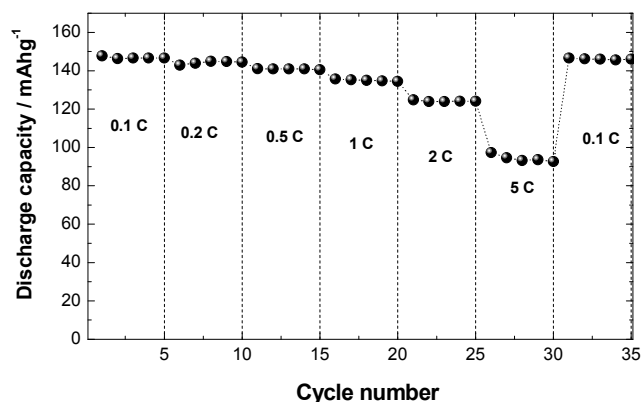


Figure 6. Discharge capacities and cyclic performances of LiFePO₄ electrodes in the voltage range of 2.5–4.2 V at 0.1, 0.2, 0.5, 1, 2, 5 and 0.1 C rates.

capacity of 143.3 mAh/g with an irreversible capacity loss of 29 mAh/g at the current range 4.2 mA/h/g. On the other hand, the carbon coated LiFePO₄ compound exhibited a discharge capacity of 139.1 mAh/g at the current density 85 mA/h/g. These results suggested that the discharge capacity was improved by the coating at the high rate current density. The increased discharge capacity of the electrode was caused by the presence of the well distributed carbon on the surface of the particles. This coated layer minimized the cell polarization because of its high electronic conductivity. The minimized cell polarization was observed in the cyclic voltammetry in Figure 4 and the charge-discharge curve in Figure 5.

Figure 6 shows the discharge capacity and cyclic performance of the LiFePO₄ electrodes as a function of the charge-discharge rates. The measurement were carried out at 0.1C, 0.2C, 0.5C, 1C, 2C, 5C and 0.1C rates in the voltage range of 2.5–4.2 V. The discharge capacity of the LiFePO₄ electrodes was clearly enhanced by sucrose coating at high C rates. Therefore, the sucrose coating effectively improved the rate capability of the LiFePO₄ cathode.

The area specific impedance (ASI) was measured as a function of the depth of discharge (DOD) in order to understand the superior electrochemical property of the carbon coated LiFePO₄ cell. During the lithium insertion/extraction, a combination of electrode kinetics, the ohmic drop and the Li⁺ ion diffusion caused a change in the overall cell voltage [14]. The area specific impedance (ASI) was determined using the equation $(A \cdot \Delta V) / I$ [15], where A is the cross-sectional area of the electrode (1 cm²), ΔV is the voltage variation during the current interruption for 60s at each DOD, and I is a constant current density of 0.1 mA/cm² (The thickness of cathode film was about 40 μm). In Figure 7, the carbon coated LiFePO₄ cathode (300–900 Ωcm²) exhibited much lower ASI values than the commercialized LiFePO₄ cathode like the one that was made by Sudchem and A123 (>1000 Ωcm²) [16]. Again, the improved ASI characteristics were ascribed to the reduced interfacial impedance between cathode and electrolyte, which confirmed that the carbon coated layer on the surface of the LiFePO₄ cathode acted as an interfacial stabilizer. However, the mechanisms that were involved with the carbon coating, such as interactions with the electrolyte, still need to be identified.

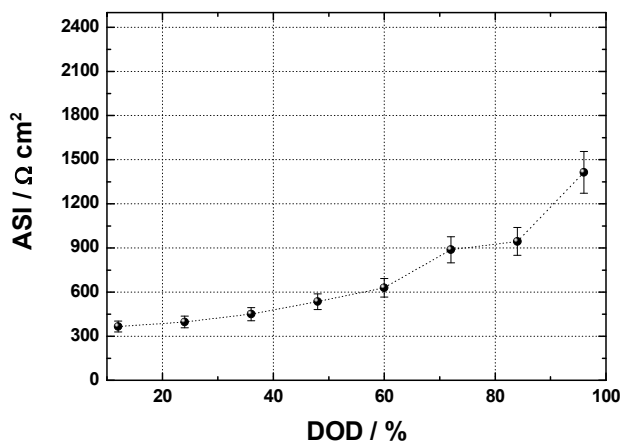


Figure 7. Area specific impedance (ASI) of carbon coated LiFePO₄ as a function of state of discharge (DOD).

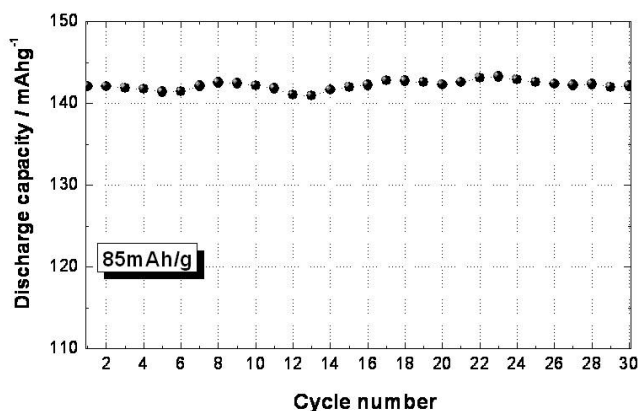


Figure 8. Cycle performance of bare and the LiFePO₄ samples at a constant current density of 85 mA/g (0.5 C).

The cycle performance of the cells with the bare LiFePO₄ cathode material is presented in Figure 8 as a function of the cycle number for a cell that was operated at 85 mA/g and cycled between 2.5-4.2 V. For the carbon coated electrode, the discharge capacity gradually decreased with the cycle number and reaches 141 mAh/g from 2.5-4.2V at the end of 30 cycles. Thus, capacity retention seems to be perfect. Therefore, the carbon coating with sucrose did not effectively increase discharge capacity but did increase the cycle performance.

4. CONCLUSIONS

We show for the first time in this study that the cycling behavior of the LiFePO₄ material is improved without sacrificing discharge capacity by coating carbon particles on the surfaces using sucrose. Additionally, both the charge and discharge cathode polarization were substantially reduced by the carbon coating. The improved electrochemical performance of the carbon coated LiFePO₄ electrode with sucrose was partly attributed to the minimized cell polarization and the decreased ASI value, which was caused by the uniform carbon coating.

5. ACKNOWLEDGEMENT

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