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The Electrochemical Behavior of LiFePO_4/C Cathode Materials Doped with Antimony

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Abstract

LiFePO_4 is considered as a practical cathode material because of low raw materials' cost, excellent thermal safety, environmental friendliness, and long operational life, despite obstacles such as low tap density, low electric conductivity and slow lithium-ion diffusion. To overcome these problems, we used an antimony-ion doping method to synthesize LiFePO_4/C with sebacic acid as a carbon source by a high-temperature solid-state reaction method. The effects of antimony concentration, sebacic acid content, calcination temperature, and calcination time on cell performance were investigated. After Sb^{3+} doping, LiFePO_4 was converted to a p-type semiconductor and demonstrated greater electric conductivity of about $10^{-3} \text{ S cm}^{-1}$. The 1.0 mol.% Sb-doped LiFePO_4/C synthesized with 36 wt.% sebacic acid delivered an initial discharge capacity of 154 mAh g^{-1} at a 0.2 C-rate between 4.0-2.8 V. The doped cathode materials were further characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), and high-resolution transmission electron microscope (TEM) techniques for structural analysis and confirmation.

Keywords: LiFePO_4 , antimony doping, sebacic acid, high-temperature solid-state method, Li-ion batteries

1 Introduction

In recent years, lithium-ion batteries have attracted significant interest in the energy storage of 3C applications, because of their high energy density, absence of memory effect, and long shelf life. The commercial cathode material of lithium-ion batteries, LiCoO_2 , provides high potentials (above 4 V vs. Li/Li^+) and good reversible capacities over

150 mAh g^{-1} in practical uses. However, safer, lower-cost and higher-power cathode materials are required for many applications such as EVs and HEVs. [1]

Olivine LiFePO_4 , which was first developed by Goodenough and his co-workers in 1997 [2], has been demonstrated as one of the most promising cathode materials due to its environmental friendliness, high theoretical capacity (170 mAh g^{-1}) [3-5], high charge/discharge potential (3.4 V

versus Li⁺/Li) [6,7], long cycle life [8-10], good thermal stability [11], low raw materials' cost [12-15], and high energy density [6,16].

It is known that Li_{1-x}FePO₄ compositions are composed of LiFePO₄ and FePO₄ phases, both of which seem to be insulating as a result of the single iron valency of Fe²⁺ and Fe³⁺, respectively [2,17]. Due to the intrinsic poor electronic conductivity (10⁻¹⁰ ~ 10⁻⁹ S cm⁻¹) [18] and low Li⁺ diffusion coefficient (1.8 × 10⁻¹⁴ S cm⁻¹) [19] of pristine LiFePO₄, it is difficult to reach its full theoretical capacity at useful rates. To overcome these problems, many research groups have used various methods, such as surface carbon coating [20-22], cation doping [23-25], and particle-size optimizing [26-28].

In 2002, Chung [23] converted LiFePO₄ to a p-type semiconductor to increase its electrical conductivity enormously by doping LiFePO₄ with polyvalent cations. Since then, various metal doping sources of LiFePO₄ have been widely studied, such as Co [29,30], Cr [31,32], Mg [33,34], Al [35,36], Mn [37, 38], Mo [39], Zn [40], Nb [23], Ti [23] and Zr [23]. However, there are no reports on the electrochemical properties of antimony-doped LiFePO₄.

In this work, we have prepared LiFe_{1-x}Sb_xPO₄/C (x=0.008, 0.010, 0.012, 0.014) composites by using a simple high-temperature solid-state method in the presence of sebacic acid as a carbon source. The electrochemical behavior of the Sb-doped LiFePO₄/C composites was investigated.

2 Experimental

2.1 The in-house synthesis of LiFe_{1-x}Sb_xPO₄

The LiFe_{1-x}Sb_xPO₄ powders were prepared using lithium carbonate (Merck, 99%), iron(II) oxalate dehydrate (Showa, 98%), antimony oxide (Sigma, 99%), and ammonium dihydrogen phosphate (Sigma, 99%) in a stoichiometric molar ratio (1.03 : 1-x : x : 1). The starting materials were mixed and ground in a planetary ball-mill with a rotation speed of 250 rpm for 3 h in acetone under an argon atmosphere. Then, the mixture was preheated at 593K at a 5 K min⁻¹ heating rate and held at 593 K for 10 h under an Ar/H₂ (v/v 95:5) atmosphere, in order to obtain gray LiFe_{1-x}Sb_xPO₄ precursor powders. Before final sintering, we mixed the precursor of LiFe_{1-x}Sb_xPO₄ with a proper quantity of sebacic acid (Acros, 98%), and then the mixture was heated in a quartz-tube furnace at 873

K under a flowing Ar/H₂ (v/v 95:5) atmosphere for 12 h.

2.2 Characterization

We used a powder X-ray diffractometer (XRD), Siemens D-5000, Mac Science MXP18, equipped with a nickel-filtered Cu K radiation source (λ= 1.5405 Å), to analyze the structure of materials. The diffraction patterns were recorded between scattering angles of 15° and 80° in steps of 0.05°. The morphology of the LiFe_{1-x}Sb_xPO₄/C composite was observed with a scanning electron microscope (SEM; Hitachi S-3500V) and high-resolution transmission electron microscope (HR-TEM; Jeol TEM-2000FXII). Electron diffraction patterns were obtained through selected area electron diffraction (SAED). The chemical composition of the separated phases was determined by nano beam energy dispersive spectroscopy (EDS). For these experiments, samples were previously dispersed in acetone and deposited on a holey silicon grid. Carbon content analysis of the products was investigated on a OIA Model Solids module as the total organic carbon (TOC) analyzer. Conductivity was measured by four-point conductivity measurements with a Keithley Model 2400S source meter.

2.3 Electrochemical characterization

The cathode was prepared by mixing 85 wt.% carbon-coated LiFe_{1-x}Sb_xPO₄ powder with 10 wt.% conductive carbon black and 5 wt.% polyvinylidene fluoride (PVDF) in n-methyl-2-pyrrolidone (NMP) solution. The as-prepared slurry was applied to cover an etched aluminum foil current collector and dried at 393 K for 12 h in an oven. Lithium metal (Foote Mineral) was used as the anode and a 1 M solution of LiPF₆ in EC:DEC(1:1 v/v) (Tomiyama Chemicals) was used as the electrolyte with a Celgard membrane as the separator. The cells were assembled in an argon-filled (VAC MO40-1 glove box). The cells were galvanostatically charged and discharged between 2.8 and 4.0 V at a 0.2 C-rate or 2.0 and 4.6 V at different current densities on the electrochemical instrument (Maccor 4000).

3 Results and discussion

3.1 XRD analysis

The XRD patterns of LiFe_{1-x}Sb_xPO₄/C composites (x= 0, 0.008, 0.010, 0.012, 0.014) are shown in Fig.1. The Sb-doped samples are consistent with the standard JCPDS pattern of LiFePO₄ (JCPDS (40-1499) LiFePO₄), and there was no impurity peaks such as Fe₂O₃ or Fe₂P detected on the LiFe₁₋

x Sb $_x$ PO $_4$ /C samples, which reveals that the original olivine structure remained crystalline and intact during the doping process [41]. By using the Scherrer's formula:

$$\beta \cos(\theta) = k\lambda/D \quad (1)$$

We can calculate the grain size (D), where β is the full-width-at-half-maximum length of the (0 2 0) reflection [42] and k is a constant here close to unity. The mean values (D) of LiFePO $_4$ /C and LiFe $_{0.99}$ Sb $_{0.01}$ PO $_4$ are 29.3 and 23.6 nm, respectively, which shows that the particle size of the doped composite powder was restrained in our doping process.

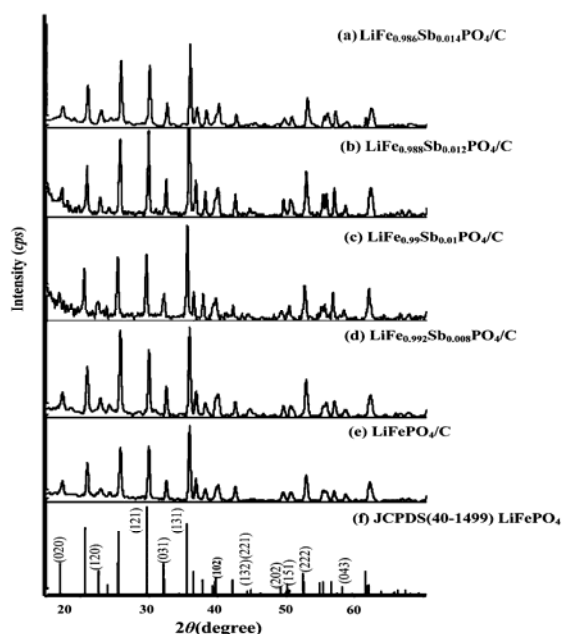


Figure 1: XRD patterns of 36 wt.% sebacic acid-coated LiFe $_{1-x}$ Sb $_x$ PO $_4$. (a) $x=0.014$, (b) 0.012, (c) 0.010, (d) 0.008, (e) 0.000, (f) JCPDS pattern (40-1499) of LiFePO $_4$

X-ray diffraction patterns of LiFe $_{0.99}$ Sb $_{0.01}$ PO $_4$ /C powders sintered for 12 h at different temperatures from 823 K to 973 K are shown in Fig. 2. It is obvious that the peaks become sharper when temperature increases due to the highly crystalline structure. From Scherrer's formula, the grain sizes of the LiFe $_{0.99}$ Sb $_{0.01}$ PO $_4$ /C samples with different sintering temperatures ($T=823, 873, 923, 973$ K) were 17.0, 23.6, 24.6, and 26.5 nm, respectively. The grain sizes show that higher temperatures result in larger grain size. However, the impurity phase Fe $_2$ P around $2\theta=45^\circ$ and 50° was detected in the sample prepared above 923 K (see Fig. 2 (c) and (d)). Ojczyk et al.[43] have reported that Fe $_2$ P can enhance the electronic conductivity and rate performance of LiFePO $_4$ /C.

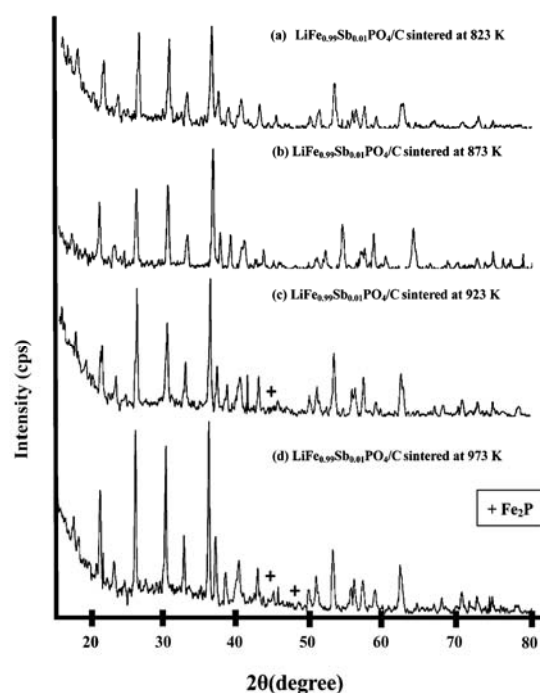


Figure 2: XRD patterns of 36 wt.% sebacic acid-coated LiFe $_{0.99}$ Sb $_{0.01}$ PO $_4$ at different sintering temperatures.

3.2 Carbon content analysis

The real carbon content in the LiFe $_{0.99}$ Sb $_{0.01}$ PO $_4$ /C composite was analyzed by total organic carbon (TOC) determination. Samples were pressed into disk-shaped pellets and their electronic conductivity was measured by the four-point dc method. Table 1 shows the comparison of TOC, initial discharge capacity, and conductivity of the LiFe $_{0.99}$ Sb $_{0.01}$ PO $_4$ /C composites when different quantities of sebacic acid were used. We can see that when more sebacic acid used, more real carbon content was obtained. In addition, the conductivity of the sample had an increasing trend with higher carbon content. However, the initial discharge capacity didn't follow this trend.

Table 1: A comparison of total carbon content, initial discharge capacity, and electronic conductivity of LiFe $_{0.99}$ Sb $_{0.01}$ PO $_4$ /C composites treated with different quantities of sebacic acid.

Sebacic Acid Concentration	TOC	Initial Discharge Capacity	Electronic Conductivity	Preparation Condition
	[wt.%]	[mAh g $^{-1}$]	[S cm $^{-1}$]	
34 wt.% Sebacic Acid	2.13	146	4.84×10^{-4}	1.0 mole% Sb 873 K 12 h
36 wt.% Sebacic Acid	2.73	154	9.81×10^{-4}	
38 wt.% Sebacic Acid	3.32	146	1.25×10^{-3}	
40 wt.% Sebacic Acid	3.94	143	2.33×10^{-3}	

3.3 Morphology

The size distribution and morphology of the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ particles were studied by a scanning electron microscope (SEM) on a Hitachi model: S-3500N equipped with an energy dispersive spectrometer, which was used to determine the elemental distribution. Fig. 3 (a) and (b) show SEM images of the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ composite sintered at 873 K for 12 hours. The samples were mainly fine particles between 150 and 200 nm in size, and we can find some agglomerations of the sample due to the formation of secondary particles.

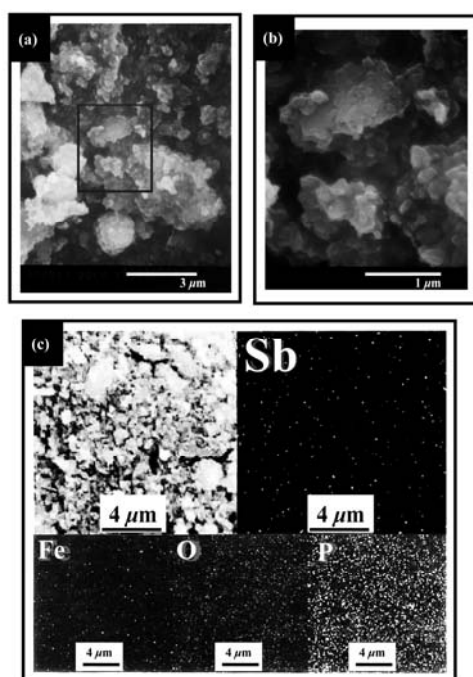


Figure 3: (a)-(b) SEM micrographs of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ powders; (c) elemental mapping of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ powders

The SEM and EDS mapping images (Sb, Fe, P, and O) of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ are shown in Fig. 3 (c). The distribution areas for elements (Sb, Fe, P and O) are homogeneous. There is also a uniform distribution of the Sb-dopant element on the surface of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$. Fig. 4 shows the SEM analysis of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ at various sintering temperatures. The particle sizes of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ treated at 823, 873, 923, and 973 K were 100-150, 150-200, 250-400, and 300-500 nm, respectively. It is clear that higher sintering temperature leads to larger average particle sizes, which is consistent with XRD analysis. However, these values are quite different from those calculated by Scherrer's formula, indicating the primary particles agglomerate to secondary particles. The same result was also

reported by Kwon et al. [44]. Larger grain size should lead to greater polarization and lower the capacity of LiFePO_4/C .

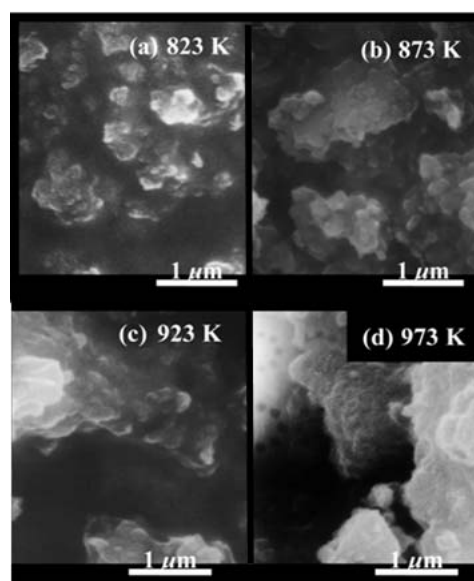


Figure 4: SEM micrographs of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ at different sintering temperatures.

3.4 TEM/SAED/EDS analysis

To analyze the morphology of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ particles and the carbon coating layer on the particle surface in detail, we used TEM in combination with SAED and EDS. Fig. 5 (a) and (b) display the TEM images of the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ samples. In the micrographs, we can see that independent particles are packed closely, and all of the samples are well-covered with a carbon layer. The average particle sizes of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ composites are around 100~ 150 nm with a carbon layer about 10~ 20 nm thick on the surface.

Fig. 5 (c) and (d) are the SAED analysis images of regions I and II in Fig. 5(b), respectively. Likewise, Fig. 5 (e) and (f) are the EDS analysis images of regions I and II in Fig. 5 (b), respectively.

The SAED analysis images show a bright spot on the outer carbon layer (region I) of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ in Fig. 5 (c), which indicates that the carbon layer had a disordered carbon structure. The dark region (region II) shows a bright spot pattern in Fig. 5 (d), which is typical for crystalline LiFePO_4 . From these results, we conclude that the outer layer (region I) is amorphous carbon, and the inner particle (region II) is crystalline LiFePO_4 , both of which are consistent with our previous findings [45].

To prove antimony doping in the LiFePO_4 particles, EDS analysis was used. The EDS images, Fig. 5 (e) and (f), confirmed that the transparent layer (region I) was mainly carbon (Fig. 5 (e)) and the dark area (region II) included the main elements such as Fe, P, O and Sb elements (Fig. 5 (f)).

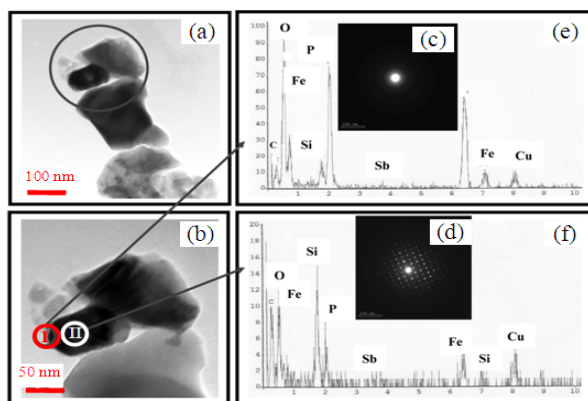


Figure 5: (a)–(b) TEM micrographs of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ powders; (c)–(d) SAED for the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ particles; (e)–(f) EDS analysis for the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ particles

3.5 Electrochemical properties

Table 2 shows a comparison of electronic conductivity and initial discharge capacity of $\text{LiFe}_{1-x}\text{Sb}_x\text{PO}_4/\text{C}$ composites treated with 36 wt.% sebacic acid at various Sb-doping concentrations ($x=0, 0.008, 0.010, 0.012, 0.014$). Conductivity increased with increasing antimony doping concentrations, which implies that antimony doping could improve the conductivity of the LiFePO_4 cathode material. However, the higher Sb-doping concentration did not result in higher initial discharge capacity. Therefore, an appropriate doping level is a very important consideration. According to Xie and Zhou [46], the multivalent metal ion locating in lithium sites improves electronic conductivity of the material, but lithium ion diffusion may be hindered if too many lithium sites are occupied with multivalent metal ion, so excess antimony doping would disturb the tunnels of lithium ions and impede Li^+ diffusion of LiFePO_4 .

The capacity and cyclability of $\text{LiFe}_{1-x}\text{Sb}_x\text{PO}_4/\text{C}$ samples ($x=0, 0.008, 0.010, 0.012, 0.014$) were determined between 4.0 and 2.8 V by galvanostatic charge/discharge tests at a 0.2 C-rate. Fig. 6 demonstrates the effect of antimony concentration on discharge capacity, while Fig. 7 shows the charge/discharge voltage profiles at the first cycle. At the optimum Sb-doping concentration ($x=0.01$)

in Fig. 6, the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ sample shows the highest initial discharge capacity of 155 mAh g^{-1} due to the appropriate antimony content that increased electronic conductivity (see Table.1, $8.76 \times 10^{-4} \text{ S cm}^{-1}$) and minimized the polarization between lithium extraction and insertion. In this case, the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ composite delivered a high capacity because its conductivity was improved by a conversion to p-type semi-conductivity via a dopant effect [23].

Table 2: A comparison of initial discharge capacity and electronic conductivity of $\text{LiFe}_{1-x}\text{Sb}_x\text{PO}_4/\text{C}$ ($x=0, 0.008, 0.010, 0.012, 0.014$) composites treated with 36 wt.% sebacic acid.

Sb-doping Concentration	Electronic Conductivity	Initial Discharge Capacity	Preparation Condition
	$[\text{S cm}^{-1}]$	$[\text{mAh g}^{-1}]$	
0 mole% Sb-doped	5.87×10^{-5}	126	36 wt.% Sebacic Acid
0.8 mole% Sb-doped	1.84×10^{-4}	140	
1.0 mole% Sb-doped	8.76×10^{-4}	154	
1.2 mole% Sb-doped	9.81×10^{-4}	142	
1.4 mole% Sb-doped	2.33×10^{-3}	141	

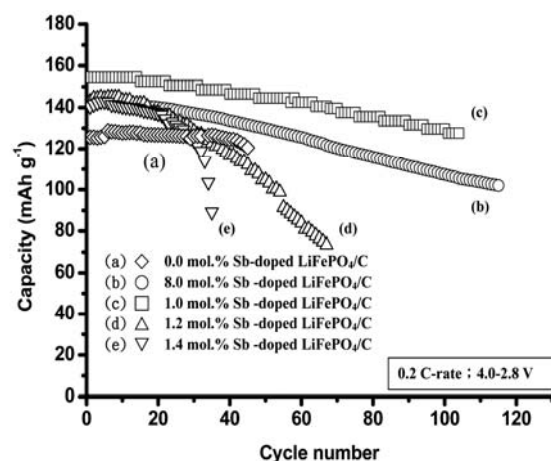


Figure 6: Galvanostatic cycling performance of $\text{LiFe}_{1-x}\text{Sb}_x\text{PO}_4/\text{C}$ ($x=0, 0.008, 0.010, 0.012, 0.014$) composites treated with 36 wt.% sebacic acid and doped with different Sb concentrations.

In Fig. 7, all the samples displayed flat charge and discharge voltage plateaus around 3.5 and 3.4 V, respectively. The voltage difference between charge and discharge plateaus (ΔV) is related to the polarization of the cell system. The lower polarization comes with the smaller ΔV . As shown in Fig. 7, an undoped sample exhibits the largest ΔV of 0.154 V compared to that of 0.097 V for $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$. The good cycling performance of the doped composite was partly attributed to its low polarization.

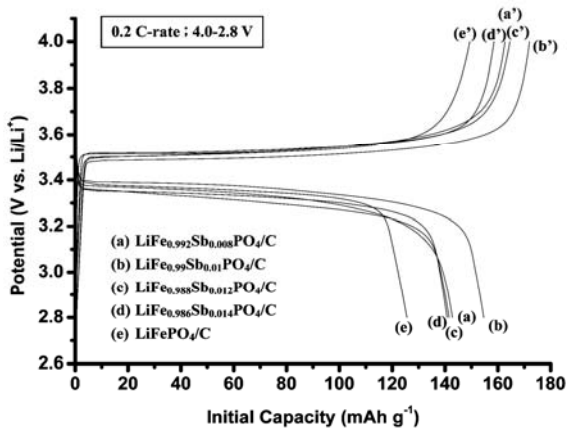


Figure 7: Initial charge and discharge curves for bare LiFePO_4 and $\text{LiFe}_{1-x}\text{Sb}_x\text{PO}_4/\text{C}$ materials treated with 36 wt.% sebacic acid. (a)–(e): discharge; (a')–(e'): charge

Sebacic acid was used as the carbon source for the preparation of composite cathode material and a proper quantity was critical to the electrode performance. Fig. 8 displays the effects of sebacic acid concentrations on the discharge capacities, while Fig. 9 shows the concentration effects on charge/discharge voltage profiles at the first cycle.

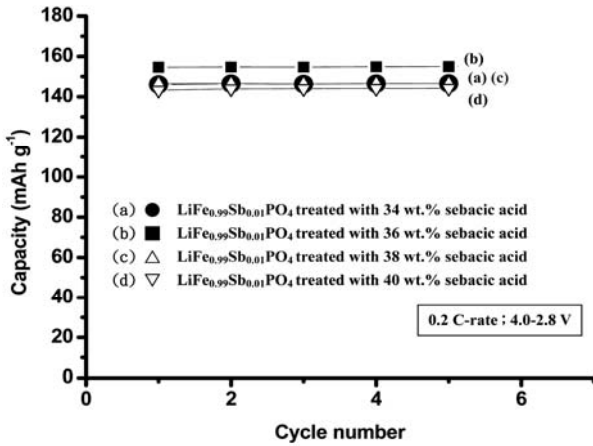


Figure 8: Discharge capacity vs. cycle number for $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ treated with various wt.% of sebacic acid.

The $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ samples were individually treated with 34, 36, 38, and 40 wt.% sebacic acid. It is clear from these figures that $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ treated with 36 wt.% sebacic acid exhibited the best discharge performance and the smallest ΔV between charge and discharge plateaus. However, the best discharge capacity did not come with the highest electronic conductivity, as shown in Table 1, probably due to the large amount of electro-inactive material.

The influence of sintering temperature and duration on $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4$ with 36 wt.% sebacic acid is shown in Fig. 10 and Fig. 11. $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4$ sintered at 873 K had the highest capacity of 154 mAh g^{-1} during the first five cycles. Based on the work of Yamada et al. [26] and Kwon et al. [44], the LiFePO_4 particles would agglomerate under a high temperature environment and particle growth led to a smaller surface area on $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ and an increase in polarization due to the diminishing $\text{LiFePO}_4/\text{FePO}_4$ interface. On the other hand, lower temperatures resulted in finer particles, but influenced the crystallinity of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$.

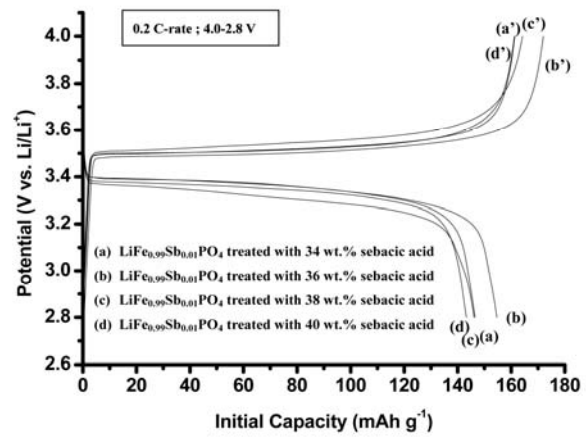


Figure 9: Initial charge and discharge curves for $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ composites treated with various wt.% of sebacic acid. (a)–(d): discharge; (a')–(d'): charge

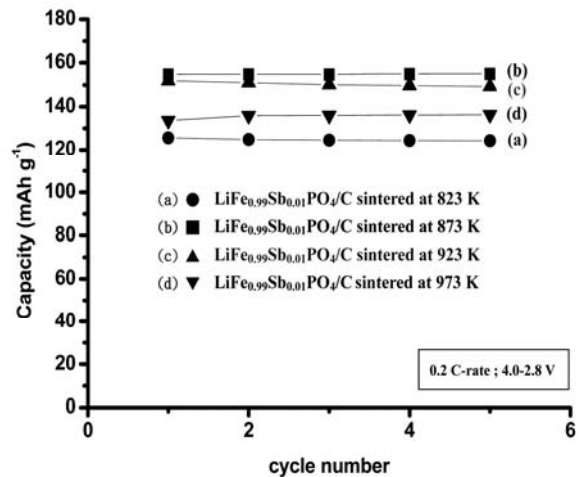


Figure 10: Discharge capacity vs. cycle number for $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4$ at different sintering temperatures.

In addition, sintering time also plays an important part on particle size and crystallinity. Fig. 11 exhibits a comparison of the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ composites treated with various sintering durations (4, 8, 12, 16, 20 h). Longer sintering time led to larger particle size and better crystallinity. However, this does not mean that long sintering time produces a better cathode material, because large particles cause a reduction in surface area and a diffusion limit of lithium ions. Based on the data from Fig. 11, a suitable sintering time might be 8 h for synthesizing $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$.

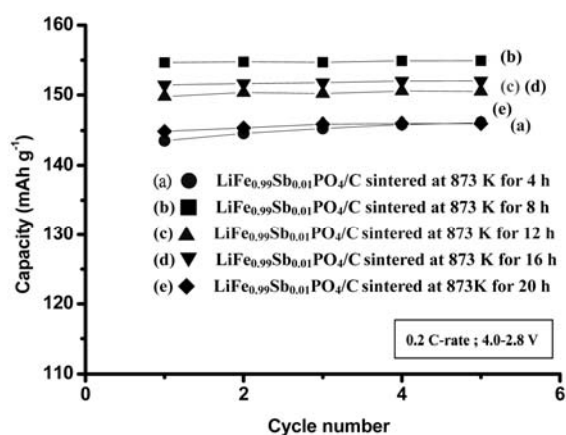


Figure 11: Discharge capacity vs. cycle number for $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4$ at different sintering duration conditions

Fig. 12 represents the rate capability of LiFePO_4/C and $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ samples between 4.0-2.8 V. The discharge capacities of LiFePO_4/C and $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ are 30 and 5 mAh g^{-1} at 4 C, respectively. We found that Sb-doping did improve the rate capability due to the enhanced electronic conductivity.

In Fig. 13, the discharge capacities of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ sintered at 823 K, 873 K, 923 K, and 973 K are 125, 154, 151 and 143 mAh g^{-1} at 0.2 C-rate, respectively, and 0, 0, 2, and 26 mAh g^{-1} at 8 C-rate, respectively. It was impressive that higher rate capability accompanied the higher sintering temperature between 823 K and 973 K. The $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ treated at 973 K has the best rate capability, since the formation of Fe_2P improved the electronic conductivity of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$. Even though the higher sintering temperature of LiFePO_4/C leads to larger particle size and loss of capacity as reported by our previous report [47], electronic conductivity is the main factor determining rate capability of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$. Kang [48] also reported that

the best sintering temperature of LiFePO_4/C was 973 K due to the formation of Fe_2P .

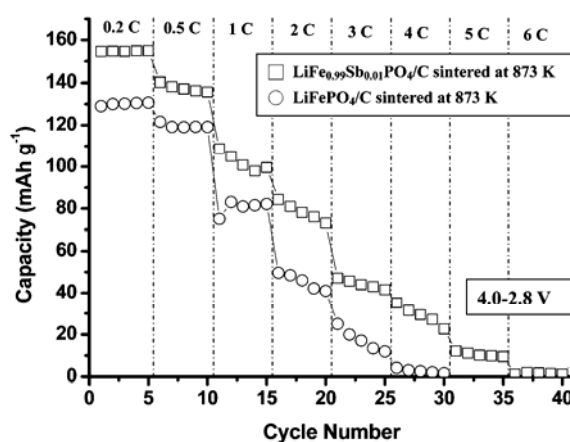


Figure 12: A comparison of the rate performance between Sb-doped and Sb-undoped LiFePO_4/C composites treated at 873K. (Charge/discharge: 4.0/2.8 V)

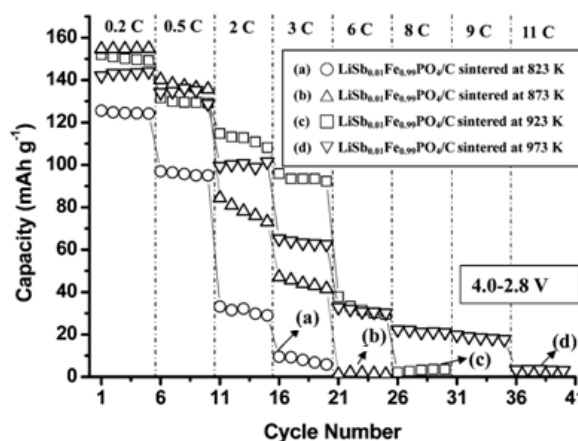


Figure 13: The rate performance of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ composites sintered at different temperatures. (Charge/discharge: 4.0/2.8 V)

Because high current density would increase the charge/discharge polarization voltage which could mask the true rate capability of the material, we changed the charge/discharge cut-off voltage range from 4.0-2.8 V to 4.6-2.0 V, as shown in Fig. 14. Again, this figure clearly demonstrates that Sb-doping can significantly improve the high rate performance of the material due to enhanced electronic conductivity.

Fig. 15 displays the discharge behavior of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ sintered at 973 K in the cut-off potential range of 4.6-2.0 V. After the first series of c-rate tests from 0.2 C to 28 C in Fig. 15, we continued the second series and found that the discharge capacity at a 0.2 C-rate was 150 mAh g^{-1} ,

which was almost the same as the first series. This means that the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ structure remained stable after high rate tests.

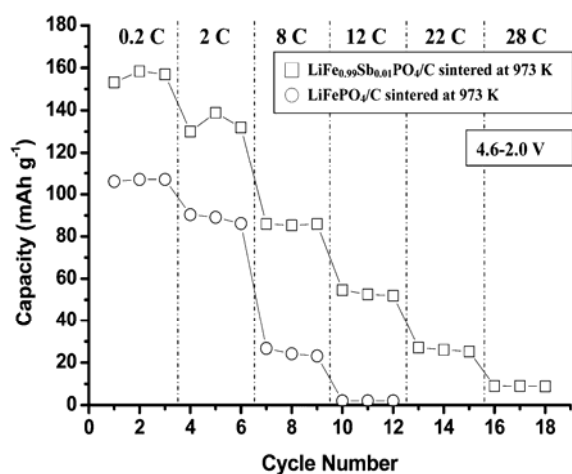


Figure 14: A comparison of the rate performance between Sb-doped and Sb-undoped LiFePO_4/C composites treated at 973K. (Charge/discharge: 4.6/2.0 V)

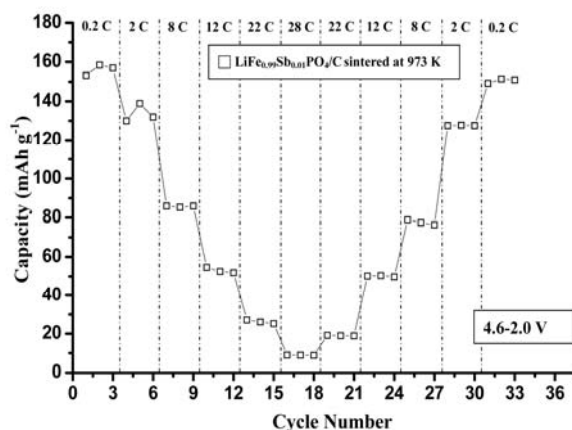


Figure 15: The rate performance of $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ at 973 K in the range of cut-off voltages: 4.6/2.0 V.

In Fig. 16, the charge/discharge voltage profile exhibits that the charge/discharge voltage plateaus for 0.2 C and 12 C are around 3.5/3.4 V and 4.0/3.0 V, respectively, which proves that the high charge voltage plateau can restrict the charge/discharge test, and this cut-off voltage range (4.6-2.0 V) was also used in Kim and his-co-worker's work [49].

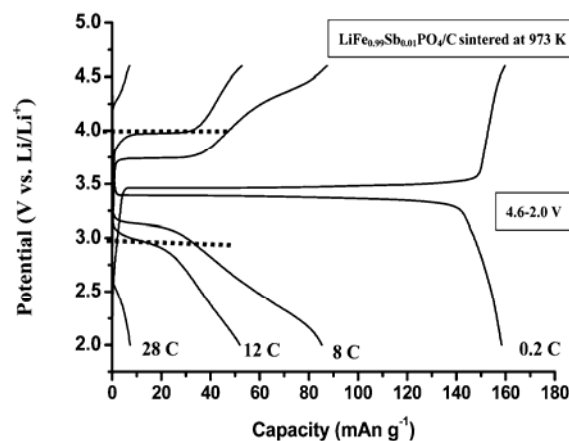


Figure 16: Initial charge and discharge curves for $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ composites sintered at 973 K under different rates.

4 Conclusions

LiFePO_4 was converted to a p-type semiconductor upon Sb-doping, resulting in enhanced electronic conductivity. Among the materials studied, the $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ composite treated with 36 wt.% sebacic acid demonstrated the best cell performance with a discharge capacity of 154 mAh g^{-1} cycled between 2.8 and 4.0 V at a 0.2 C-rate. Such a significant improvement was mainly attributed to enhanced electronic conductivity from 5.87×10^{-6} to $8.79 \times 10^{-4} \text{ S cm}^{-1}$ for the Sb-doped samples. The optimum sintering temperature and duration for preparing the Sb-doped composites were 873 K and 8 hours, respectively. Confirmation of carbon coating and Sb-doping in the composite products was achieved by elemental mapping and EDS analysis. The capacity loss at higher sintering temperatures was caused by the aggregation of composite particles, which decreased surface area and limited the diffusion of lithium ions. However, the in-situ formation of Fe_2P at high temperatures (above 923 K) in LiFePO_4 could enhance the discharge capacity at a high C-rate. The $\text{LiFe}_{0.99}\text{Sb}_{0.01}\text{PO}_4/\text{C}$ treated at 973 K could sustain a 28 C-rate between 4.6 and 2.0 V, and this rate capability is equivalent to charge or discharge in 129 seconds.

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