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Electrochemical and Physical Properties of La-Ion-Doped $LiFePO_4$ Coated with Different Carbon Sources as Cathode Materials for Lithium-ion Batteries

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Abstract

In lithium-ion batteries, olivine-type $LiFePO_4$ is a cathode material being most widely developed but its intrinsic properties of poor conductivity and low lithium-ion diffusion limit its practical applications. In order to improve electronic conductivity of $LiFePO_4$, it can be modified by carbon coating [1] and metal doping [2]. In this paper, the $LiFe_{0.99}La_{0.01}PO_4/C$ composites were prepared by the solid-state reaction method and treated with La-ion doping and different carbon sources by adding 1 mole% of La-ion and coating malonic acid or sebasic acid, respectively. The products of this work were investigated by XRD, DSC, BET, SEM/mapping, TEM/EDS/SAED, magneto-susceptometer and total organic carbon (TOC). Furthermore, their electrochemical properties were studied by cyclic voltammetry, four-point probe conductivity measurements, and a Maccor Series 4000 battery cycler.

The XRD results indicate that these La-ion dopants do not affect the structure of the $LiFePO_4/C$ composite but considerably improve its electronic conductivity from 3.97×10^{-7} to 3.17×10^{-5} S cm^{-1} as shown in Table 1. From TOC analysis, the residual carbon of the composites increased when increased amounts of carbon were used. Furthermore, the La-doped composite coated with malonic acid as a carbon source has an initial discharge capacity of 151 mAh g^{-1}. On the other hand, one with sebasic acid has a discharge capacity of 145 mAh g^{-1} between 2.8 and 4.0 V at a 0.2 C-rate. Both results of the La-doped samples demonstrate that their initial discharge capacity performance is much better than that of the undoped $LiFePO_4$, which is only 104 mAh g^{-1}in the first cycle.

Thermal stability is a useful indicator to study battery safety. Fig. 1 presents the DSC profiles of bare $LiFePO_4$ and $LiFe_{0.99}La_{0.01}PO_4$ coated separately with 60 wt.% malonic acid and 36 wt.% sebasic acid. The DSC patterns of these samples were recorded after these cells were fully charged to 4.5 V. The total exothermic heat for the sample coated with malonic acid as a carbon source is 103.9 mJ g^{-1} and with sebasic acid, it is only 93.7 mJ g^{-1}. Table 2 shows a comparison of DSC results for various cathode materials [3]. The thermal data indicate that the ΔH of $LiFePO_4$ (520 Jg^{-1}) is much lower than the other cathode materials, such as $LiCoO_2$ (1100 Jg^{-1}), $LiNiO_2$ (1300 Jg^{-1}), $LiMn_2O_4$ (860 Jg^{-1}), and $LiNi_{0.8}Co_{0.2}O_2$ (1600 Jg^{-1}). $LiFePO_4$ exhibits excellent thermal stability in term of battery safety. It is noteworthy that the DSC test conditions between two research teams are different and these data are used only for comparison purposes.

[1] Y.D. Cho, G.T.K. Fey, H.M. Kao, J. Power Sources 189 (2009) 256–262.
[2] Y.D. Cho, G.T.K. Fey, J. Solid State Electrochem. 12 (2008) 815-823.
[3] D.D. MacNeila, Z. Lub, Z. Chenb, J.R. Dahn, J. Power Sources 108 (2002) 8-14

Table 1. Comparison of conductivity, total carbon content, and first discharge capacity of La-doped samples.

The Amount of Coating Material	Conductivity ($S\ cm^{-1}$)	TOC (wt.%)	First Discharge Capacity ($mAh\ g^{-1}$)	Preparation Conditions
Carbon-free	3.97E-07	0.13	104	873 K 12 h
50 wt.% Malonic Acid	9.80E-06	0.96	148	1.0 mole% La
60 wt.% Malonic Acid	2.60E-05	1.65	151	873 K
70 wt.% Malonic Acid	8.27E-06	2.10	146	12 h
34 wt.% Sebasic Acid	3.17E-05	4.03	142	1.0 mole% La
36 wt.% Sebasic Acid	2.25E-05	4.69	145	873 K
38 wt.% Sebasic Acid	2.13E-05	4.99	140	12 h

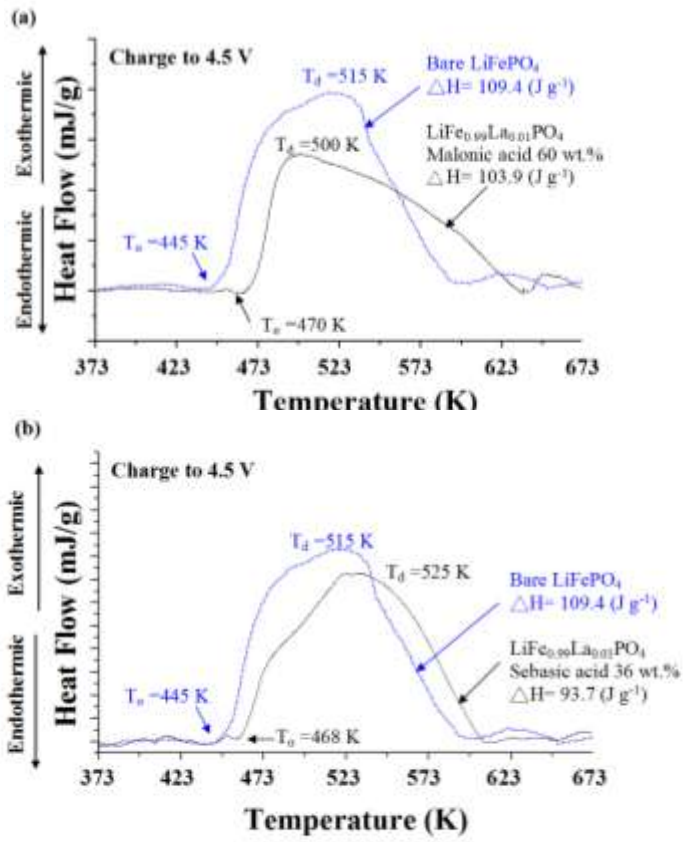

Figure 1. DSC profiles of La-doped $LiFePO_4/C$(a) malonic acid 60 wt.%；(b) sebasic acid 36 wt.%. Charged to 4.5 V.

Table 2. comparison of DSC results for various cathode materials.

Cathode materials	Charged to indicated voltage (V)	Onset tem. (K)	Peak tem. (K)	Total evolved heat ΔH (J/g)
In-house bare $LiFePO_4$	4.5	445	515	109
$LiFe_{0.99}La_{0.01}PO_4$ coated with 60 wt.% malonic acid	4.5	470	500	104
$LiFe_{0.99}La_{0.01}PO_4$ coated with 36 wt.% sebasic acid	4.5	468	525	94
$LiFePO_4$	4.4 [3]	494	525	520
$LiCoO_2$	4.4 [3]	454	529	1100
$LiNiO_2$	4.4 [3]	455	482	1300
$LiNi_{0.8}Co_{0.2}O_2$	4.4 [3]	470	501	1600
$LiMn_2O_4$	4.4 [3]	480	553	860

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