Enhanced low-temperature performance of slight Mn-substituted LiFePO_4/C cathode for lithium ion batteries

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Received December 12, 2009; accepted May 27, 2010

Low temperature performance of LiFePO_4/C cathode was remarkably improved by slight Mn-substitution. Electrochemical measurements showed that about 95% of the discharge capacity of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ cathode at 20°C was obtained at 0°C , compared to 85% of that of LiFePO_4/C cathode. The $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ sample also presented enhanced rate performance at -20°C with the discharge capacities of 124.4 mA h/g (0.1C), 99.8 mA h/g (1C), 80.7mAh/g (2C) and 70 mA h/g (5C), respectively, while pristine LiFePO_4/C only delivered capacities of 120.5 mA h/g (0.1C), 90.7 mA h/g (1C), 70.4 mA h/g (2C) and 52.2 mA h/g (5C). Cyclic voltammetry measurements demonstrated an obvious improvement of the lithium insertion-extraction process of the LiFePO_4/C cathode by slight Mn-substitution. The results of FSEM observation and electrical conductivity measurement indicated that slight Mn-substitution minimized the particle size of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ and also obviously improved the electrical conductivity of the compound, thus obviously enhances the interface reaction process on the cathode.

low-temperature performance, Mn-substitution, LiFePO_4/C cathode, lithium ion batteries

Citation: Zeng L J, Gong Q, Liao X Z, et al. Enhanced low-temperature performance of slight Mn-substituted LiFePO_4/C cathode for lithium ion batteries. Chinese Sci Bull, 2011, 56: 1262–1266, doi: 10.1007/s11434-010-4097-0

Lithium ion phosphate has been intensively investigated in recent years as the most promising cathode material for large-scale lithium ion batteries (such as EV and HEV) due to its low cost, low toxicity, reasonable capacity and good thermal stability [1–4]. Commercial application of this material has made great progress. It has been successfully used in batteries for laptops, power tools and electric bicycles, etc. However, there are still a number of issues to work out before the batteries are suitable for EV and HEV application, such as high rate capability and low temperature performance. Several effective approaches such as carbon coating on the particle surface [5–8], minimizing the particle size [9–11], and cation substitution [12] have been applied to overcome the high rate problems at room temperature. However, efforts still need to be focused on enhancing low temperature performance of LiFePO_4 cathode. Although many efforts have been made on improving the low

temperature performance of lithium ion batteries by developing new low temperature electrolytes [13–15], improving the low temperature properties of the electrode materials is also imperative. In our previous work [16], we reported the low temperature performance of LiFePO_4/C cathode in a quaternary carbonate-based electrolyte. It was found that charge-discharge behavior of LiFePO_4/C cathode was obviously impeded at low temperature. The increase of charge-transfer resistance and the decrease of lithium ion diffusion capability were the main performance limiting aspects at low temperature. In our present work, we managed to improve the rate capability of LiFePO_4/C cathode at low temperatures by slight Mn-substitution of Fe-site in LiFePO_4 structure.

1 Experiment

$\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x=0, 0.02, 0.04, 0.06$) cathode materials

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were prepared by a mechanical/chemical reaction using a ball milling procedure as described in detail in another paper [17]. The starting materials were stoichiometric mixtures of Fe powder, iron phosphate ($\text{FePO}_4 \cdot 4\text{H}_2\text{O}$), lithium phosphate (Li_3PO_4) and manganese phosphate ($\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$). Sucrose was added as a conductive additive precursor. The precursor mixture powders were ball-milled for 24 h in a planetary mill (Pulverisett 6) with agate vessels. The resulting products were heat-treated under argon at 650°C for 30 minutes to obtain the final $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x=0, 0.02, 0.04, 0.06$) samples. The carbon content was about 2.7% by weight.

The morphology of the powder materials was observed with a field emission scanning electron microscope (JSM-7401F). X-ray diffraction (XRD) measurements were carried out over the two-theta range from 10 to 70° with a Philips 3100E diffractometer using filtered $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). The electrical conductivity was measured by four-probe dc method based on sintered bars of approximate dimensions $2 \text{ mm} \times 5 \text{ mm} \times 12 \text{ mm}$. The measurements were performed in air at room temperature. A constant current was applied to the two current wires and the voltage response on the two voltage wires was recorded using a Keithley 2420 sourcemeter.

Electrochemical testing for the samples were carried out using coin cells (R2016) with Li metal foil as counter electrode and $1.0 \text{ M LiPF}_6/\text{EC}+\text{DMC}+\text{DEC}+\text{EMC}$ ($1:1:1:3, \text{ v/v}$) electrolyte. The cathode was constituted from 75 wt% active material, 15 wt% carbon black and 10 wt% PVDF binder. The active material loaded on the electrode disks was about 4.5 mg/cm^2 . Charge-discharge performance of the cells was evaluated using a battery test system (LAND CT2001A model, Wuhan Jinnuo Electronics Co., Ltd). The cyclic voltammetry of the cells was performed on Solartron SI1287. A three-electrode electrochemical cell was employed for electrochemical impedance measurements. Lithium metal wire and foil were used for reference and counter electrodes. EIS measurements were carried out on Solartron SI1260/SI1287 test system.

2 Results and discussion

The phase composition of the prepared $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x=0, 0.02, 0.04, 0.06$) samples were characterized by XRD as shown in Figure 1. The diffraction patterns for the Mn-substituted samples are similar to that of undoped LiFePO_4/C . All the Bragg diffraction peaks of the compounds can be well indexed based on a single-phase olivine-type structure indexed to the orthorhombic $Pnmb$ space group. No impurity phases were detected by XRD. The single phase characteristic of the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ samples in the whole substitution range ($0 \leq x \leq 1$) was also reported by Molenda and coworkers [18]. Figure 2 presents the charge-discharge profiles of the prepared $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x=0, 0.02, 0.04, 0.06$) samples at 20°C , 1C rate. It can be seen that the voltage gaps

Figure 1 X-ray diffraction patterns of the prepared $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x=0, 0.02, 0.04, 0.06$) samples and standard LiFePO_4 . 1, Standard LiFePO_4 ; 2, $x=0.02$; 3, $x=0.04$; 4, $x=0.04$; 5, $x=0.06$.

between charge and discharge profiles of Mn-substituted samples were obviously reduced compared with pristine LiFePO_4/C . This phenomenon indicates decreased electrode polarization by Mn-substitution. Slightly substituted $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ sample demonstrated the best electrochemical performance with the discharge capacity of 137.8 mAh/g . As the Mn content increased, the charge and discharge capacities of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x=0.04, 0.06$) were decreased. In this paper we focused on the comparison of low temperature performance of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ sample and pristine LiFePO_4/C .

Figure 3 compares the charge-discharge characteristics of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ and LiFePO_4/C electrodes at four different temperatures under 1C rate. It can be seen that $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ sample showed substantially better low temperature performance than that of LiFePO_4/C sample. The voltage gap between charge and discharge profiles of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ is reduced and the decrease of charge and discharge capacities of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ electrode with the decrease of operation temperature is obviously alleviated compared with that of LiFePO_4/C electrode. The

Figure 2 Charge-discharge profiles of the prepared $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x=0, 0.02, 0.04, 0.06$) samples at 20°C at 1C rate, using $1.0 \text{ mol/L LiPF}_6/\text{EC}+\text{DMC}+\text{DEC}+\text{EMC}$ ($1:1:1:3, \text{ v/v}$) electrolyte.

Figure 3 Comparison of the charge-discharge characteristics of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ and LiFePO_4/C electrodes at different temperatures under 1C rate. (a) LiFePO_4/C ; (b) $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$.

discharge capacities of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ were 137.8 mAh/g (20°C), 131.0 mAh/g (0°C), 99.8 mAh/g (−20°C) and 70.5 mAh/g (−40°C), respectively, while LiFePO_4/C delivered capacities of 134.5 mAh/g (20°C), 113.8 mAh/g (0°C), 90.1 mAh/g (−20°C) and 69.0 mAh/g (−40°C). It is interesting to find that 95% of discharge capacities of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ cathode at 20°C was obtained at 0°C, compared to 85% of that of LiFePO_4/C . This is an attractive result for routine application of this material.

The rate capabilities of the $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ and LiFePO_4/C electrodes at −20°C are displayed in Figure 4. The cells were firstly charged to 4.2 V at a constant current of 34 mA/g (0.2C), and then discharged to 2.0 V at different current densities. It can be seen that at a low discharge current of 17 mA/g (0.1C), the $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ and LiFePO_4/C electrodes showed discharge capacities of 124.4 mA h/g and 120.5 mA h/g respectively. As discharge current increased, the $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ sample demonstrated obviously enhanced rate performance with discharge capacities of 99.8 mA h/g (1C), 80.7 mA h/g (2C) and 70 mA h/g (5C), respectively, while pristine LiFePO_4/C only delivered capacities of 90.7 mA h/g (1C), 70.4 mA h/g (2C) and 52.2 mA h/g (5C). Furthermore, the discharge voltage plateaus of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ sample were enhanced compared with that of LiFePO_4/C , indicating a decreased electrochemical

Figure 4 Rate performance of (a) $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ and (b) LiFePO_4/C samples at −20°C using 1.0 mol/L LiPF_6 / EC+DMC+DEC+EMC (1:1:1:3, v/v) electrolyte.

polarization.

Figure 5 exhibits cyclic voltammograms of the LiFePO_4/C and $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ samples at −20°C. The LiFePO_4/C sample showed broad redox peaks with the anodic peak at 3.77 V and cathodic peak at 3.16 V (vs. Li^+/Li), respectively. The $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ sample showed narrower peak separation and the peak shape was slightly sharper compared with that of LiFePO_4/C . These results are consistent with the charge-discharge performance, indicating an easier lithium insertion and extraction behavior of the slightly Mn-substituted sample.

In order to further understand the effects of Mn-substitu-

Figure 5 Cyclic voltammograms of LiFePO_4/C and $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ cathode materials at −20°C at a sweep rate of 0.1 mV/s.

tion on the electrochemical behavior of LiFePO_4/C material, electrochemical impedance spectra of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ and LiFePO_4/C cathodes were measured at different temperatures using a three-electrode electrochemical cell. The tests were carried out at a 20% depth-of-discharge (DOD) state of the cathodes after 60 cycles. The results were shown in Figure 6. All the Nyquist plots showed two overlapped semicircles at high and medium frequency range and a straight line at low frequency range. The intercept of the high frequency semicircle with the real impedance axis refers to R_s , corresponding to the sum of electrolyte and conducting substrate resistances. The semicircle at high frequencies is probably due to the contact resistance R_p including current collector-to-particles and the particle-to-particle contact resistance of the cathode and corresponding constant phase element Q_p . The semicircle at medium frequencies reflects the charge-transfer reaction resistance R_t and corresponding constant phase element Q_t . The straight

line at low frequencies represents lithium ion diffusion resistance in electrode matrix. By fitting the Nyquist plots with the equivalent circuit as shown in Figure 6(c), the impedance parameters R_s , R_p and R_t at different temperatures can be derived. The results are listed in Table 1.

The linear part in Nyquist plot is related to Lithium ion diffusion in electrode bulk. The lithium diffusion coefficient in the LiFePO_4/C and $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ electrode can be calculated using the following equation [19]:

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}, \quad (1)$$

here, R is the gas constant, T is the absolute temperature, A is the surface area of the cathode, n is the number of electrons involved in reaction ($n=1$), F is the Faraday constant, C is the concentration of lithium ion, and σ is the Warburg factor which has the relationship with Z_{re} :

$$Z_{re} = R_s + R_p + R_t + \sigma \omega^{-1/2}, \quad (2)$$

here, Z_{re} is real part of impedance, R_s is the resistance of electrolyte and conducting substrate, R_p is the resistance of current collector-to-particles and the particle-to-particle contact resistance of the cathode, R_t is charge-transfer reaction resistance, σ is the Warburg factor, and ω is angular frequency.

The graph of Z_{re} against $\omega^{-1/2}$ in the low frequency region is a straight line with the slope of σ . The slope σ can be obtained and lithium ion diffusion coefficient D can be calculated. The results are listed in Table 1.

It can be seen from Table 1 that $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ cathode showed smaller R_p and R_t values than that of LiFePO_4/C cathode at low temperatures. The values of lithium ion diffusion coefficient D for $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ sample were also obviously enhanced compared with those of LiFePO_4/C sample. It can be said that slight Mn-substitution both decreased the interface charge transport resistance and enhanced lithium ion diffusion capability in the electrode bulk. The coexistence of Mn^{2+} with $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion pair in matrix structure improved the local charge transportation. Electrical conductivity measurement demonstrated that the $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4$ showed a spectacular increase in electrical conductivity which was $1.68 \times 10^{-6} \text{ S/cm}$ compared with the $1.08 \times 10^{-10} \text{ S/cm}$ of pure LiFePO_4 . Figure 7 shows the FSEM images of LiFePO_4/C and $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ samples. It can be seen that the particle size of $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ is

Figure 6 Impedance spectra of (a) LiFePO_4/C cathode (20%DOD); (b) $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ cathode (20%DOD) at different temperatures; (c) equivalent circuit model used for fitting of the impedance spectra.

Table 1 Impedance parameters derived using equivalent circuit model and lithium diffusion coefficient D for LiFePO_4/C and $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ electrodes (20%DOD)

Temperature ($^{\circ}\text{C}$)	LiFePO_4/C				$\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$			
	R_s (Ω)	R_p (Ω)	R_t (Ω)	D ($\text{cm}^2 \text{s}^{-1}$)	R_s (Ω)	R_p (Ω)	R_t (Ω)	D ($\text{cm}^2 \text{s}^{-1}$)
20	4.7	86.9	98.2	1.7×10^{-12}	11.1	38.3	90.43	5.5×10^{-12}
0	5.9	101.1	124.3	1.6×10^{-12}	13.2	43.1	104.3	4.8×10^{-12}
-20	7.9	120.0	315.1	2.1×10^{-13}	18.6	94.0	150.1	1.4×10^{-12}
-40	13.0	126.3	2005.4	2.1×10^{-14}	33.2	122.7	610.2	3.4×10^{-13}

Figure 7 FSEM images of (a) LiFePO_4/C ; (b) $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$.

smaller than that of pristine LiFePO_4/C . The smaller particle size may increase the active surface area of the $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ material and also shorten the lithium ion diffusion path in the particles thus contributes to better electrochemical performance of the $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ sample.

3 Conclusions

Improving low temperature performance of olivine lithium ion phosphate is an important issue for its successful commercialization. Slight Mn-substitution of the Fe-site was demonstrated to be an effective approach to improve the rate performance of LiFePO_4/C cathode at low temperatures. The discharge capacities of the prepared $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ cathode at -20°C were about 124.4 mA h/g (0.1C), 99.8 mA h/g (1C), 80.7 mA h/g (2C) and 70 mA h/g (5C), respectively, while pristine LiFePO_4/C only delivered capacities of 120.5 mA h/g (0.1C), 90.7 mA h/g (1C), 70.4 mA h/g (2C) and 52.2 mA h/g (5C). EIS measurements demonstrated that $\text{LiFe}_{0.98}\text{Mn}_{0.02}\text{PO}_4/\text{C}$ showed a smaller interface charge-transfer resistance and improved lithium ion diffusion capability than that of LiFePO_4/C .

This work was supported by the National Natural Science Foundation of China (20773087), the National Basic Research Program of China (2007-CB209705) and the Science and Technology Commission of Shanghai Municipality (09XD1402400, 09DZ1203603 and 09HJS000100).

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