

Carbon coating by high-energy milling and electrochemical properties of LiMnPO_4 obtained in polyol process

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Abstract

LiMnPO_4 materials were synthesized via a polyol process and coated with conductive carbon black by using high-energy milling. We introduced two kind of synthesis process of LiMnPO_4/C according to carbon addition steps, which was carried out during high-energy milling or polyol process. The carbon addition during the polyol process followed by high-energy milling enabled carbon to be network with LiMnPO_4 particles and delivered an enhanced electrochemical rate capability. The result indicated that LiMnPO_4 particles were well coated with the conductive carbon.

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1. Introduction

Rechargeable lithium-ion batteries have attracted great attentions as energy storage devices for mobile devices and transportation [1]. Recently, LiMPO_4 have been widely investigated as a potential cathode for lithium-ion batteries due to their non-toxicity, cost effectiveness and better stability. Their three-dimensional olivine structure is stabilized by the covalent bonds between oxygen ions and P^{+5} resulting in PO_4^{+3} tetrahedral poly-anions. Of these LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}$) electrodes, particularly LiFePO_4 has been widely investigated and commercialized for high-power/large-format batteries [2].

Inspired by the achievement of LiFePO_4 , LiMnPO_4 especially has been investigated as a promising new cathode material because of higher theoretical energy density, higher redox potential and lower cost compared with LiFePO_4 . However, low charge-discharge current densities have rendered the practical use of LiMnPO_4 . The poor electrochemical performance of LiMnPO_4 is attributable to the low intrinsic electronic conductivity and the slow lithium diffusion kinetics within the grains [3–5]. Therefore, great efforts have been devoted to enhance its electrochemical properties by the

particle-size reduction [6,7], cation doping [8,9], the $\text{LiMnPO}_4/\text{carbon}$ composite [3,4,7,8] and carbon coating [5,10]. Murgan et al. [10] used hydrothermal method for carbon coating. The carbon layers on the surface of LiMnPO_4 were uniform. However, their procedures needed an additional heat treatment. It can cause a particle-size increase. And Yang et al. [5] applied sol-gel route for carbon coating. The procedure took a long time for aging the gel and needed further heating.

On the contrary, high-energy milling has been emphasized due to high rate coating at room temperature without further heat treatment. And it increases contact between materials in a short time and provides well-proportioned composite coating. Moreover, the milling process represents a low cost process with high flexibility for the production of nano-structured composites [11].

Diol used as a solvent is known to be a surfactant that effectively inhibits the aggregation of the colloidal particles. As a non-ionic surfactant, the diol with uniform and ordered chain structure is easily adsorbed onto the surface of particles. So, the carbon could be functionalized and well dispersed [12]. Based on the literature, diol was expected to help carbon dispersion, by which the LiMnPO_4 particles could be well coated during the following high-energy milling.

In this study, the LiMnPO_4/C powders were synthesized via a polyol process [13] and coated with carbon via high-energy milling [14]. In order to confirm the influence of diol, we

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introduced two synthesis methods. In each route, carbon was added during the polyol process or high-energy milling.

2. Experimental

The LiMnPO_4 was prepared by the following polyol method. 0.015 mol manganese acetate tetra hydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Aldrich, 99+%) was dissolved into 7.5 ml deionized water and poured into 50 ml 1,4-butanediol (Aldrich, 99%) in a three-neck flask. The solution was stirred and heated at 40 °C for 1 h and increases the temperature until 100 °C, kept for 1 h and then 7.5 ml 2 mol l^{-1} lithium dihydrogen phosphate (LiH_2PO_4 , 99%, Aldrich) aqueous solution was dropped into the flask with a speed of 0.5 ml min^{-1} . The diol suspension was kept for 5 h at 120 °C and cooled down to room temperature. And the LiMnPO_4 was washed with ethanol and deionized water. Finally the resultant products were dried at 80 °C overnight (A). For a preparation of LiMnPO_4/C synthesized with additional carbon in the polyol process (B), the procedures were similar to that of the former examples except that carbon black was added to the diol–water solution in proportion of 20 wt% of 0.015 mol LiMnPO_4 .

Carbon-coated products were prepared by the following process. High-energy milling was carried out with as-synthesized LiMnPO_4 (A), carbon black (20 wt% of LiMnPO_4) and zirconia balls (ball-to-powder weight ratio = 15:1) in Teflon jaw for 3 h at room temperature by using vibration mill (C). And as-synthesized LiMnPO_4/C (B) was milled according to the former high-energy milling process without an additional carbon black (D).

Phase of samples was analyzed by an X-ray diffraction (XRD) (Rigaku, D/MAM2500). The microstructures of each specimen were observed using a scanning electron microscopy (SEM), (Philips XL30) and transmission electron microscopy (TEM) (JEOL, JEM-3010).

To prepare the cathodes, three kinds of LiMnPO_4/C powders (B, C and D), carbon black and poly(vinylidene fluoride) (PVDF, Aldrich) binder were mixed in 80:15:5 weight ratio in *N*-methylpyrrolidone (NMP) to make a viscous slurry that was cast on aluminum foil and dried at 90 °C in air condition for 12 h. The formed cathodes were assembled into coin batteries. 1 M LiPF_6 in ethylene carbonate (EC):dimethyl carbonate (DMC) [1:1 (vol%)] electrolyte and a separator (polypropylene film, Celgard Inc.). The electrochemical performance of the cells was tested by a high precision battery performance testing system. The galvanostatic charge–discharge cycling performance of the cells was tested in the range of 2.70–4.40 V at room temperature. Until the fifth cycle, the cells were charged with a C/20 rate to 4.4 V, kept at 4.4 V until C/100 rate, then discharged to 2.7 V at C/20 ($=7.5 \text{ mA g}^{-1}$). Next five cycles, the cells were charged at C/10 until 4.4 V, kept at 4.4 V to C/100, and then discharged to 2.7 V at C/10. The electrochemical capacity of samples was evaluated on the active material. And electrochemical impedance spectroscopy was characterized using 2-probe AC impedance spectroscopy (Solartron 1260) in an AC voltage of 5 mV in the frequency range from 10^6 to 5 Hz.

3. Results and discussion

The XRD spectra of the synthesized LiMnPO_4 and LiMnPO_4/C matched the standard X-ray patterns of LiMnPO_4 as shown in Fig. 1. In comparison to the reference (JCPDS#74-0375), the products are pure phase LiMnPO_4 with olivine structure indexed in Pnma of orthorhombic system. Fig. 2 shows SEM images of prepared LiMnPO_4 and LiMnPO_4/C samples. SEM images of as-synthesized powders (A and B) illustrate platelet shape. In the case of B, well-dispersed carbon was expected due to the diol effects. Contrary to our expectation, distribution of LiMnPO_4 particles and carbon are non-uniform and segregated each other. SEM images of high-energy milled samples (C and D) show different shape from the as-synthesized samples (A and B). It is speculated that the milling process affected the morphology change. This is confirmed by sample E: high-energy milling was carried out with as-synthesized LiMnPO_4 (A) only. In the SEM image of the resultant products, there is no platelet shape.

In standard XRD patterns of LiMnPO_4 , the peak intensity ratio of (0 2 0) and (3 1 1) is 0.78. However, the highest XRD peak of the as-synthesized LiMnPO_4 (A) is (0 2 0), 1.29 times stronger than the peak of (3 1 1) plane. And as-synthesized LiMnPO_4/C (B) has similar ratio, 1.28. It was reported that intensity of diffraction peaks changed by the platelet morphology, which accustomed to the ac plane [15]. In the case of milled products, intensity of (3 1 1) peak is higher than that of (0 2 0) peak. It is due to the morphology change via high-energy milling. And E presents a similar ratio with C and D, 0.87. The results are consistent with SEM analysis.

To further observe the morphology and carbon coating condition in the B, C and D, TEM images and EDS analysis are taken and shown in Fig. 3. As illustrated in Fig. 3(a), carbon is segregated with LiMnPO_4 in B. And the partial surface of the particles of B is covered with carbon layers that exposed the rest of the surface. A section of C is shown in Fig. 3(b), which indicated that carbon layer seems continuous, but most of carbons are aggregated by the side of LiMnPO_4 . A closer TEM imaging and EDS analysis in Fig. 3(c) illustrates the presence of

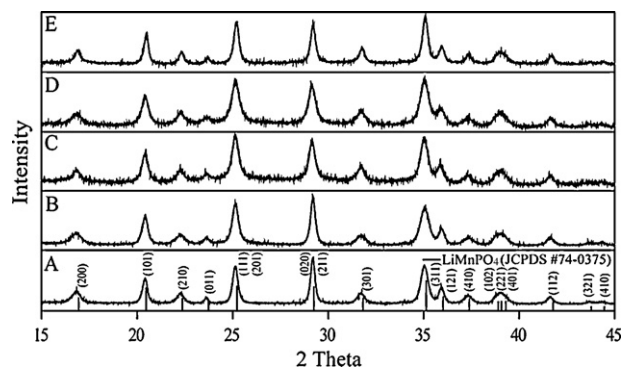


Fig. 1. XRD spectra of resultant materials [(A) as-synthesized LiMnPO_4 , (B) as-synthesized LiMnPO_4/C , (C) LiMnPO_4/C synthesized by high-energy milling from sample A, (D) LiMnPO_4/C synthesized by high-energy milling from sample B, (E) LiMnPO_4 synthesized by high-energy milling from sample A without carbon.].

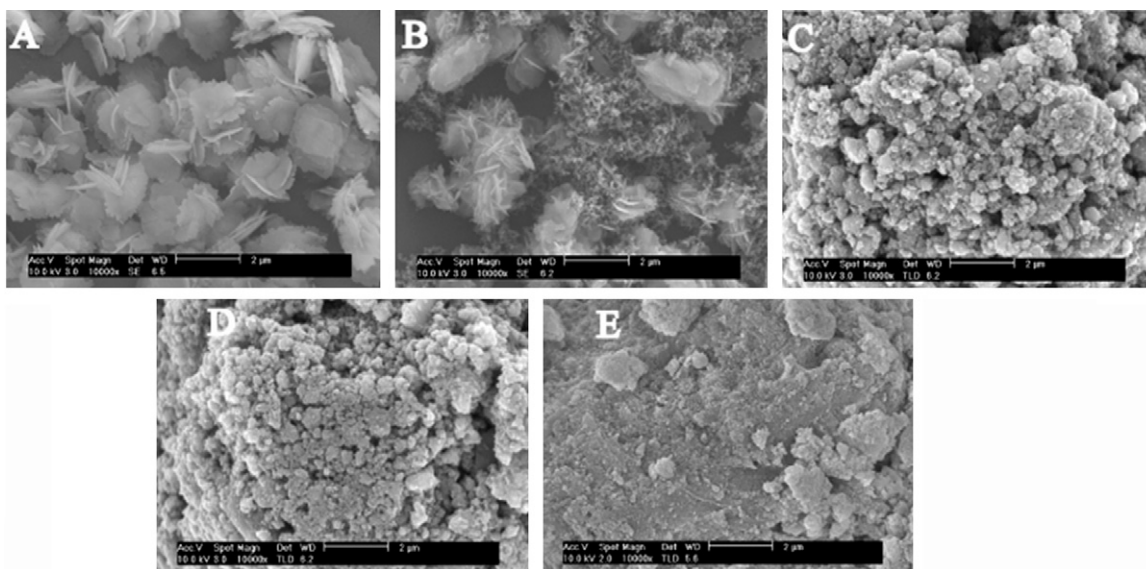


Fig. 2. SEM images of resultant materials [(A) as-synthesized LiMnPO₄, (B) as-synthesized LiMnPO₄/C, (C) LiMnPO₄/C synthesized by high-energy milling from sample A, (D) LiMnPO₄/C synthesized by high-energy milling from sample B, (E) LiMnPO₄ synthesized by high-energy milling from sample A without carbon.].

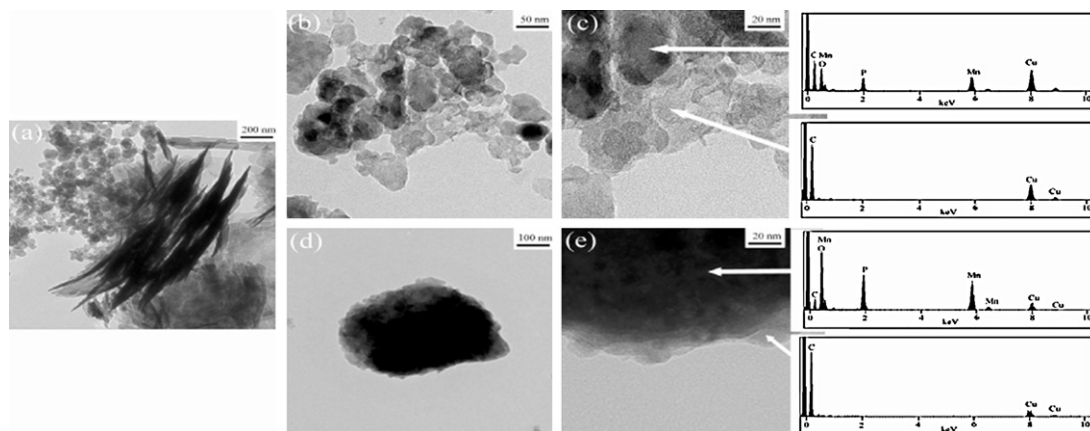


Fig. 3. TEM image and EDS analysis of the sample B (a), C (b and c) and D (d and e).

surface carbon layers, which show non-uniform. As illustrated in Fig. 3(d), LiMnPO₄ particles in D are well coated with carbon. Fig. 3(e) and EDS analysis showed thinner and uniform surface layers of carbon, which connect LiMnPO₄ particles intimately. Therefore, it can be speculated that high-energy milling facilitates intimate connection between carbon and LiMnPO₄ [7,16,17] and the improved distribution of carbons on the surface of LiMnPO₄ is probably related to the diol effect [12].

The cycling performance of B, C and D is shown in Fig. 4. The performance of D shows the highest. C is lower about 10 mAh g⁻¹ than D. And the electrochemical performance of B is severely lower than other sample. These result from the carbon coating and distribution, which is analyzed and concluded in the SEM and TEM images. Thin and uniform carbon arrangement probably leads to a good interparticle contact, which can advance the electronic conductivity of LiMnPO₄/C materials. In combination with the analysis of SEM and TEM, the cycling test results suggest that the uniformly coated LiMnPO₄ with carbon on can improve its

electrochemical performance. Well-coated LiMnPO₄/C exhibited a specific capacity of 61–68 mAh g⁻¹ at C/20, 49–52 mAh g⁻¹ at C/10 rate. The results were higher than that of literatures; 40–45 mAh g⁻¹ at C/20 in sol-gel process [5] and

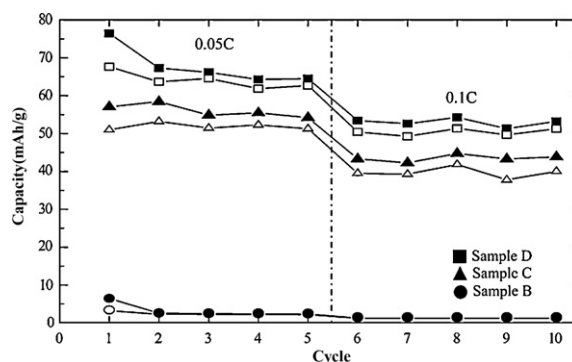


Fig. 4. The cyclability of LiMnPO₄/C composite at 0.05–0.1C (filled: charge, open: discharge).

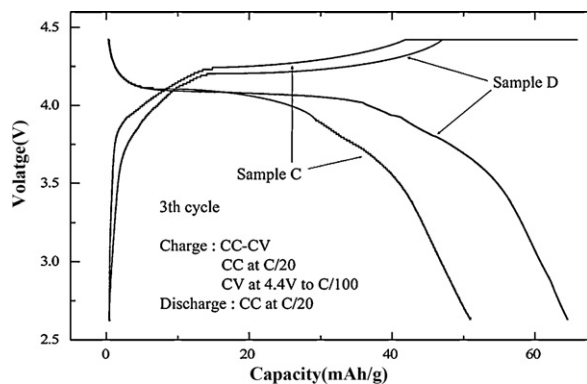


Fig. 5. The charge–discharge curves of LiMnPO_4/C composite at C/20 in third cycle.

20–25 mAh g^{-1} at C/10 in hydrothermal reaction [10]. It might be due to the combination of small particle size and carbon coating by high-energy milling. Size reduction of particle results in enhancement on ion transport [18] and high-energy milling makes uniform carbon network connection between carbon particles [7]. Though the agglomeration became marked, the particle size was decreased and carbon was intimately connected with LiMnPO_4 by high-energy milling. And Fig. 5 shows charge–discharge profiles of C and D at C/20 in third cycle. These two samples presented a reversible plateau around 4.1 V vs. Li/Li^+ , which is the typical redox potential of $\text{Mn(II)} \leftrightarrow \text{Mn(III)}$ in olivine manganese phosphate.

In order to verify the difference in the electrochemical performance between C and D, we conducted ac impedance measurement using the coin cells. Fig. 6 shows Nyquist plots obtained from the C and D. As shown in the Fig. 6, the resistivity ($R = R_{ct} - R_e$) [19] was obtained by fitting the impedance spectrum with an equivalent circuit model (inset model in Fig. 6.) using the non-linear least squares fitting program of the Z-view software. The semicircle size of the C is slightly larger than that of the D. When the semicircle size translates into charge transfer resistance, it demonstrates 195.18 and 179.32 Ω/cm^2 in the C and D, respectively. This is related to charge transfer through the electrode/electrolyte interface in fabricated LiMnPO_4 material matrix [20]. Hence, it is suggested that the electric conductivity of D was enhanced by better carbon distribution which resulted from adding carbon source during the polyol process.

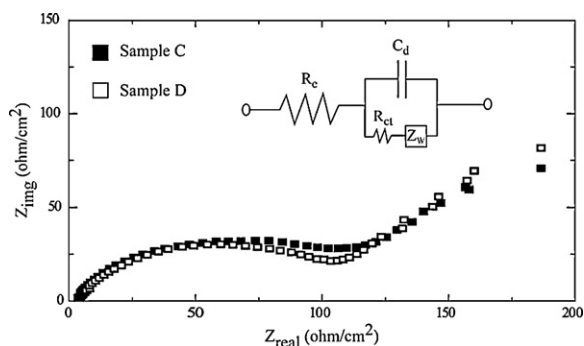


Fig. 6. Nyquist plots of the sample C and D.

4. Conclusion

A polyol method using 1,4-butanediol as a solvent and high-energy milling for carbon coating are developed for the synthesis of carbon coated LiMnPO_4 powders. As-synthesized LiMnPO_4 and LiMnPO_4/C by the polyol process present the platelet shape. Contrary to what would be expected because of the diol effects, the as-synthesized LiMnPO_4/C shows poor dispersed carbon segregated with LiMnPO_4 particles apparently. High-energy milling with as-synthesized samples forms the carbon coated LiMnPO_4/C materials. Evidently, more uniform and intimate coated material is formed from as-synthesized LiMnPO_4/C compared to as-synthesized LiMnPO_4 . The carbon arrangement improves the electronic conductivity of LiMnPO_4/C cathodes materials. Well-coated LiMnPO_4/C has presented the highest specific capacity: 61–68 mAh g^{-1} at C/20, 49–52 mAh g^{-1} at C/10 rate. The highest performance is attributed to the uniform distribution of coated carbon on the surface of LiMnPO_4 . It is probably due to the diol effect. However, the exact role of diol in this process is not established. Thus, further study for diol is necessary.

Acknowledgements

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