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Preparation and Characterization of Porous Li_2FeSiO_4/C Microsphere via a Spray Drying-Assisted Technique

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Porous spherical Li_2FeSiO_4/C microscale secondary particles have been synthesized by a spray drying-assisted process using citric acid as chelating agent and carbon source. The spherical Li_2FeSiO_4/C microscale particles (1–5μm) with porous structures consist of carbon-coated primary nanoparticles (20-40 nm), which promises high electronic conductivity and short lithium ion diffusion paths. The as-prepared Li_2FeSiO_4 sample exhibits desirable electrochemical performance, At 0.2 C and 5 C rates, the capacities of 150 mAh g^{-1}, 94 mAh g^{-1} are observed, respectively. Meantime, good cycling stability is achieved with a capacity retention of 98.4% at high current density of 1C after 300 cycles.

Keywords: Li-ion battery; Cathode material; Li_2FeSiO_4/C composite; porous sphere; spray drying

1. INTRODUCTION

The orthosilicate family of Li_2MSiO_4, where M is some transition-metals Fe, Mn or Co, are highlighted as interesting candidates for lithium battery cathodes by virtues of their potential ability to facilitate the extraction of more than one Li ions per transition metal, low cost and high safety[1-2]. Among them, Li_2FeSiO_4 has been proposed as one of the most promising candidate for the cathode material of lithium-ion batteries due to its low cost, high safety, environmental benign, and high theoretical capacity (332mAhg^{-1}) [3-6]. Unfortunately, as the intrinsic characteristics of polynomic materials, Li_2FeSiO_4 also suffers from the problems of small lithium ion diffusion coefficient and poor electronic conductivity, which have been the main obstacle to its applications[7]. Therefore, much effort has been made to to solve this problem, such as synthesis of the nanosized particles via various methods[8-12], conductive carbon coating on Li_2FeSiO_4 particle surface[13-15] and cation doping in Fe and Si sites [16-18].

Recently, constructing Porous spherical particles (e.g., $Li_3V_2(PO_4)_3$ [19] and $LiFePO_4$ [20]) have been considered as a good strategy for effectively improving the electrochemical behavior of cathode materials. It is well accepted that porous sphere structure provides good contact with electrolyte, high specific surface area, quick Li^+ permeation and easier to bind than isolated nanosized particles [19]. These advantages generally promise good cycling stability and high rate performance, both of which are required for electric vehicle applications [21]. To date, few works on preparation of porous spherical Li_2FeSiO_4/C particles with excellent electrochemical properties has been reported. In this work, we present a novel and facile approach to obtain porous spherical Li_2FeSiO_4/C microscale secondary particles by spray drying assisted method. The as-synthesized materials are easy to contact with electrolyte and give good electrochemical characteristics because of its large surface area and evenly carbon coated.

2. EXPERIMENTAL

The preparation of Li_2FeSiO_4/C composite was performed through a spray drying-assisted method. Firstly, Fe powder and citric acid were mixed in deionized water under vigorous magnetic stirring at 80 °C, resulting in a light green solution with release of H_2. Secondly, lithium acetate and PVP were dissolved gradually into the solution, then NH_3 solution was added in order to keep the pH at 7.0-8.0. Thirdly, silica solution was added into the solution and stirred for 1 h, and then spray-dried at 108°C to form green powder. The green powder was heated in a horizontal quartz tube oven under flowing argon gas at 700 °C for 10 h to obtain the final Li_2FeSiO_4.

The phases in the as-received sample were characterized by X-ray powder diffraction analysis (XRD) with Cu Kα radiation (DX 2700). Particle morphology of the sample was examined by field emission scanning electron microscopy (SEM FEI INSPECT-F).The specific surface area was measured by nitrogen adsorption/desorption at -196 ℃ using a Builder SSA-4200 apparatus. Thermal gravimetry (TG) was carried out with a NETZSCH STA 449C differential scanning calorimeter under N_2 atmosphere at a ramping rate of 10 ◦C min^{-1}.

The electrochemical properties of the sample were assessed using CR2032 coin cells. The electrodes were prepared by casting and pressing a mixture of 80 wt% of active material, 10 wt% of Super-P carbon, and 10 wt% of LA-132 binder in water on aluminum foil followed by drying in vacuum at 100 °C for 10 h. The cells were assembled in an argon-filled glove box, using lithium foil as the counter electrode, Celgard 2400 as the separator, and 1 mol/L $LiPF_6$ dissolved in a mixture of EC, DEC, DMC with a volume ratio of 1:1:1 as the electrolyte. Galvanostatic charge and discharge measurements were performed in a potential range of 1.5-4.8 V at room temperature.

3. RESULTS AND DISCUSSION

The XRD patterns of as-synthesized Li_2FeSiO_4/C sample are shown in Fig. 1. As illustrated, the main diffraction peaks can be indexed to a single-phase material having an monoclinic structure (space group $P2_1$), which are the same as the standard value (PDF card number: 97-024-0207). No crystalline carbon can be obviously detected in the XRD pattern, revealing that the as-formed carbon layer is probably in the amorphous state [22].

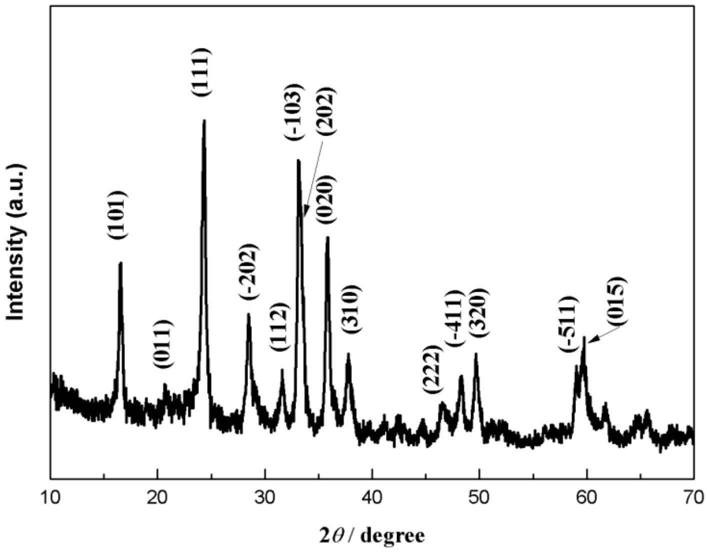

Figure 1. XRD profiles of as-obtained Li_2FeSiO_4 sample

The weight ratio of carbon in the Li_2FeSiO_4/C composite was evaluated by using TG method. The TG curve for the Li_2FeSiO_4/C composite performed in a flowing N_2 atmosphere is shown in Fig. 2. There is no extremely distinct weight loss on the TG curve after 500 ◦C. Thus, the carbon content in the Li_2FeSiO_4/C composite is turned out to be approximately 17.3 %. It is well accepted that the carbon in the Li_2FeSiO_4/C composite is created from the pyrolysis of citric acid.

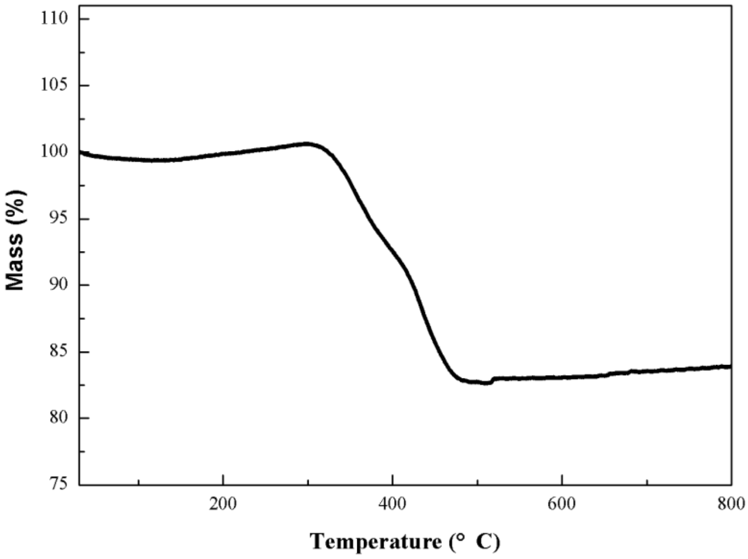

Figure 2. TG curve of Li_2FeSiO_4/C composite

Fig. 3 shows the SEM images of Li_2FeSiO_4/C powders. As seen in Fig. 3 A, the Li_2FeSiO_4 microspheres are composed of densely aggregated nanoparticles with grain diameter of 20-40 nm, which interweave together forming porous structure [23]. It is further confirmed by the BET measurements (Fig. 4). As well known, the porous structure can promote good electrical contact among the Li_2FeSiO_4 particles and help the electrolyte to penetrate the material, thus highly favors the solid-state diffusion kinetics and improves the capacity of the electrode material [19]. Fig. 3B displays that most of the Li_2FeSiO_4 secondary particles are mono-disperse microspheres with a diameter of 1-5 μm.

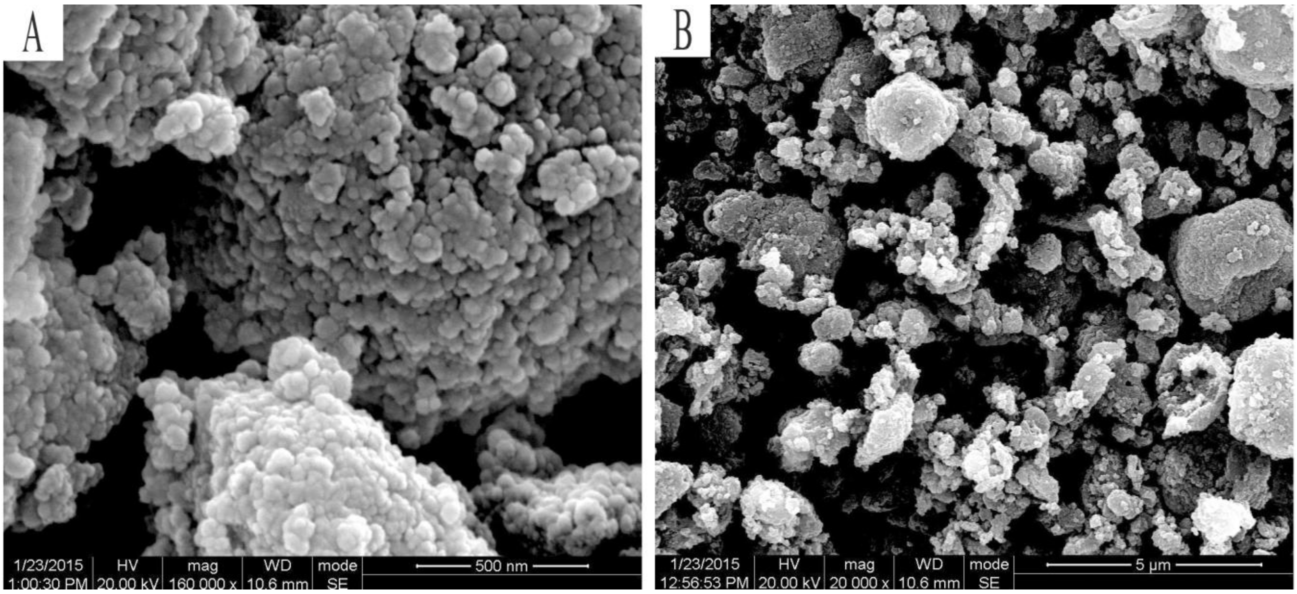

Figure 3. SEM images of the Li_2FeSiO_4 sample

The porous structure was further supported by the nitrogen adsorption desorption measurement. The Brunauere Emmette Teller (BET) surface area for the Li_2FeSiO_4/C composite is ca. 76 m^2 g^{-1}. The corresponding pore size distributions, calculated from desorption isotherms, is given in Fig. 4. It exhibits a narrow porous distribution centred at 2 nm and 5 nm, respectively, confirming that the Li_2FeSiO_4/C composite was typical mesoporous and microporous structures. The porous structures are mainly produced because of the release of gases from the decomposition of the organic precursor [22].

Fig.5 presents the excellent charge–discharge curves of Li_2FeSiO_4/C composite at various current rates. Clearly, the retaining capacity of Li_2FeSiO_4 decreases quickly from 148 mAh/g (0.2 C) to 94 mAh/g (5 C) as the rate increases. Even at a rate as high as 5 C, the as-synthesized sample exhibits a flat voltage plateau , indicating that the porous spherical Li_2FeSiO_4/C composite possessed lower polarization and would be well suited for cathode materials of high-power lithium batteries [24].

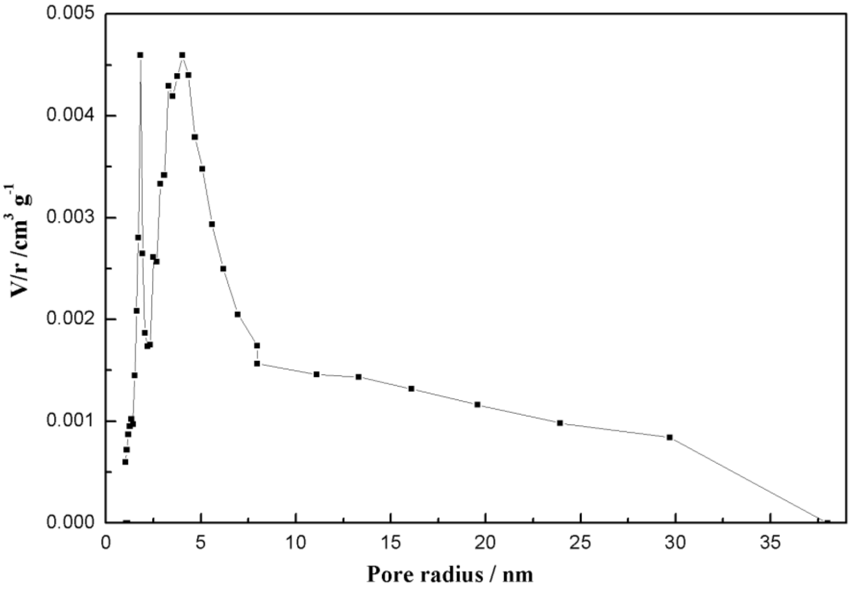

Figure 4. Pore size distribution of the Li_2FeSiO_4/C composite

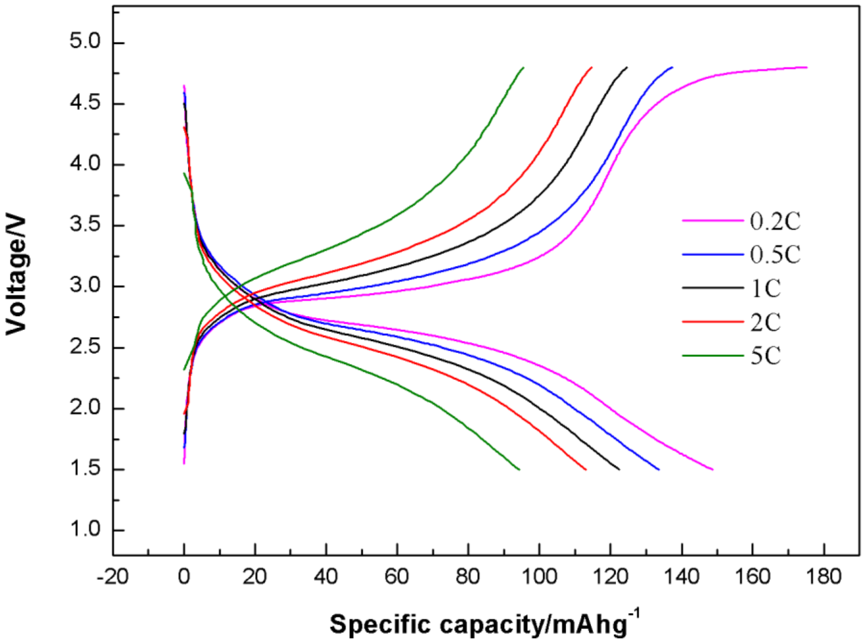

Figure 5. shows the charge-discharge profiles of as-prepared sample at different rates.

Rate performance of the Li_2FeSiO_4/C composite with various discharge current rates are presented in Fig. 6. It can be seen that the discharge capacity of the Li_2FeSiO_4/C composite gradually decreases with the increasing of the rate. This is because the utilization of the active material decreases as the rate increases [25]. The maximum discharge capacity measured for the Li_2FeSiO_4/C composite at a rate of 0.2 C, 0.5 C, 1C, 2 C and 5C is 150 mAh g^{-1}, 135 mAh g^{-1}, 124 mAh g^{-1}, 113 mAh g^{-1}, and 94 mAh g^{-1}, respectively. Hence, it can be concluded that porous spherical Li_2FeSiO_4/C possesses an excellent rate capability. The excellent preformance could be attributed to the morphology of porous microsphere and highly uniform distribution of carbon in the Li_2FeSiO_4 particles [26].

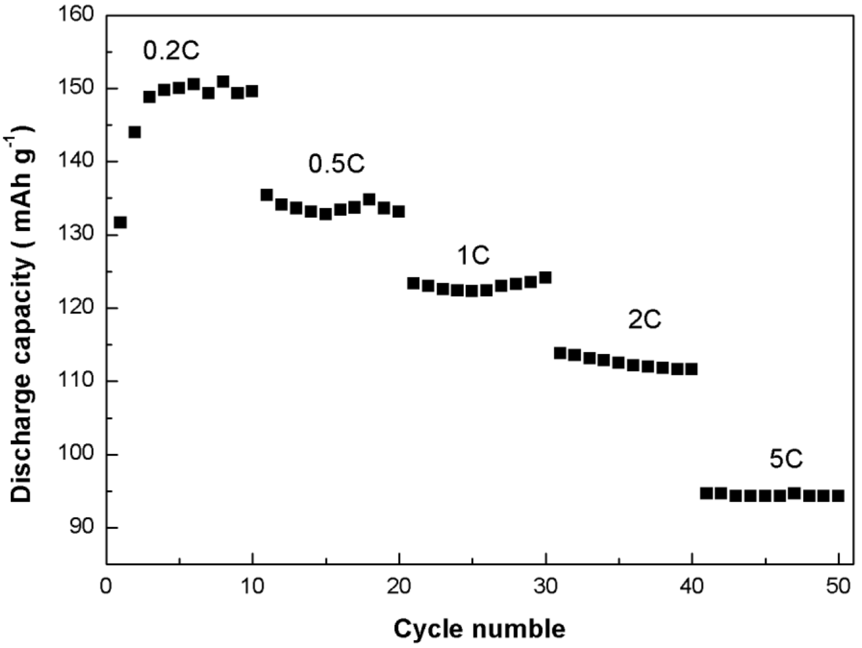

Figure 6. Cycle stability of Li_2FeSiO_4/C composite with various discharge current rates.

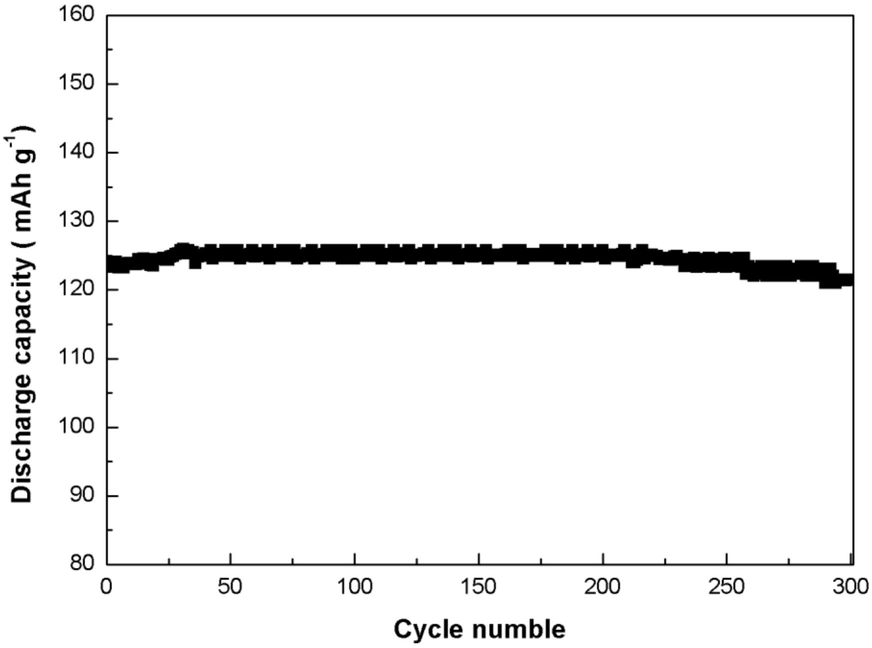

Figure 7. Cycle stability of Li_2FeSiO_4/C composite at 1C

The cycle performance of the cells with the Li_2FeSiO_4/C composite cathode was cycled 300 cycles at 1C, and the results are shown in Fig. 7. As seen, the initial discharge capacity of the Li_2FeSiO_4/C composite is 123 mAh g^{-1}, and 98.4% of the initial discharge capacity after 300 cycles is remained. So far, zhang and co-workers[27] have reported Li_2FeSiO_4/C/rGO via a solid-state reaction method, which exhibited an initial discharge capacity of 93 mAh g^{-1} at 1 C, 91.3% of its initial value is obtained after 60 cycles. Clearly, the as-prepared Li_2FeSiO_4/C composite has much better cycling performance.

4. CONCLUSIONS

Spray drying-assisted method was used to synthesize porous microsphere Li_2FeSiO_4/C composite. The as-prepared porous microsphere Li_2FeSiO_4 particles have a narrow porous distribution centred at 2 nm and 5 nm and give large specific surface area(76 m^2 g^{-1}). It delivers a discharge capacity of 123 mAh g^{-1} at 1 C, and after 300 cycles, 98.4 % of its initial capacity is retained. The excellent electrochemical performance should be contributed to the enhanced ionic/electronic conductivity by porous structure and carbon coating.

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