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Original Article

Synthesis of FeF₂/carbon composite nanoparticle by one-pot solid state reaction as cathode material for lithium-ion battery

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ABSTRACT

FeF₂/carbon composite nanoparticle was prepared by a one-pot thermal reaction using a mixture of ferrous oxalate and PTFE as precursor. FeF₂ was obtained as the main phase according to the XRD patterns of the samples prepared in the present study. Furthermore, the FeF₂ particle has a size of 50–100 nm. Its electrochemical properties were studied in the 4.2–1.3 V region at a current density of 60 mA g⁻¹. It exhibited an initial discharge capacity of 503.394 mA h g⁻¹ and still reserved discharge capacity of about 268.478, 211.34, 193.817 and 183.328 mA h g⁻¹ at the 2nd, 3rd, 10th, and 20th cycles, respectively.

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1. Introduction

Lithium-ion batteries (LIBs) are important energy storage devices, and they are required with higher energy density for usage in electric/hybrid vehicle and grid scale storage [1]. As the commercial cathode material LiCoO₂ or LiFePO₄ has a capacity of 150 or 170 mA h g⁻¹, the key to improve the energy density of LIBs is looking for electrode materials with higher energy density [2]. Metal fluoride can store more than one lithium per molecule or per molecular unit a multi-electron

conversion reaction, so its theoretical capacity can be very high. Besides, metal fluoride has a high voltage potential brought by high ionicity of M-F bond [3]. Iron fluoride is one of the most potential candidates used as cathode materials due to its high specific capacity, low cost, and low toxicity [4–6]. FeF₂ has a capacity of 571 mA h g⁻¹ and thermodynamic reduction potential with Li is 2.66 V [7–9]. So it is a good candidate for high energy density LIBs.

FeF₂/carbon nanoparticles were prepared by a one-pot thermal reaction using a simple procedure based on the thermal decomposition and reaction of a mixture of ferrous oxalate

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and PTFE. The composite's electrochemical property as cathode electrode is tested.

2. Material and methods

2.1. Experiment

The ferrous oxalate powder (FeC_2O_4) and PTFE ($(\text{C}_2\text{F}_4)_n$) powder were utilized as experimental raw materials. First, ferrous oxalate and PTFE were mixed using mortar and pestle. The weight ratio of $[\text{FeC}_2\text{O}_4]:[\text{PTFE}]$ was varied from 10:2.78 to 10:4.17, in which amount of PTFE are larger than that of a stoichiometric ratio. The PTFE is decomposed at low temperature between 400 and 600 °C [10]. Then, the homogeneous mixture was heated in an Ar atmosphere at a rate of 8 °C/min up to 500, 550 and 650 °C, This temperature was kept for 1 h and cooled to room temperature naturally. Finally, the product was collected and then subjected to structure and property characterization.

2.2. Characterization

The crystal structure of the product was characterized by X-ray diffraction using Bruker D8 with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscope with an accelerating voltage of 200 kV.

The electrodes were prepared by mixing active materials (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP). After the above slurries were uniformly spread onto an aluminum foil, the electrodes were dried at 100 °C in vacuum for 24 h. Then electrodes were pressed and cut into disks before transferring into an Argon-filled glove box. Coin cells (CR2025) were assembled using lithium metal as the counter electrode, Celgard 2400 membrane as the separator and LiPF_6 (1 M) in ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate (EC/DMC/EMC, 1:1:1 vol%) as the electrolyte. The cells were tested at current density of 60 mA g^{-1} between 4.2 V and 1.3 V with a Neware battery testing system.

3. Results and discussion

Fig. 1 shows the XRD patterns of FeF_2 with a ratio of $[\text{FeC}_2\text{O}_4]:[\text{PTFE}] = 10:4.17$ synthesized for 1 h under 500, 550 and 650 °C. It showed that the diffraction peaks corresponding to FeF_2 observed as a main phase in the sample synthesized at 500, 550 and 650 °C, although weak impurities corresponding to Fe_2O_3 and Fe_3O_4 . However, the peak intensity of FeF_2 was decreased with the increase in the calcination temperature. In addition, XRD patterns of the nanocomposites did not show C peaks, suggesting that the C sheets are amorphous. This can be attributed to the decomposition temperature of PTFE, in which a drastic weight loss leading to the decomposition of PTFE was confirmed over 400 °C and PTFE is completely decomposed at 600 °C [10].

The electrochemical performance of the FeF_2 /carbon composite as cathode was evaluated at room temperature. Fig. 2 shows the initial charge and discharge curves of the FeF_2 in the 4.2–1.3 V region at a current density of 60 mA g^{-1} . The

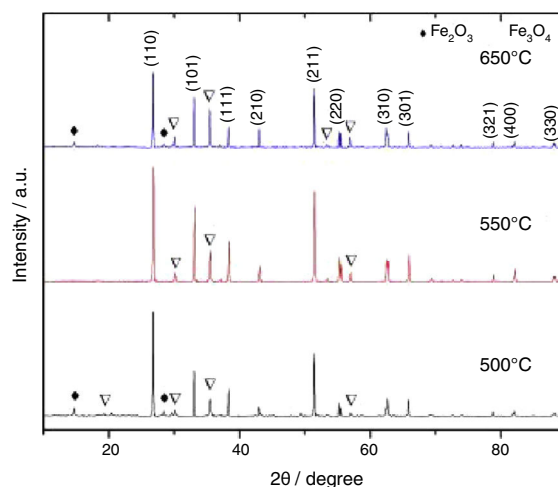


Fig. 1 – XRD patterns of FeF_2 with a ratio of $[\text{FeC}_2\text{O}_4]:[\text{PTFE}] = 10:4.17$ synthesized for 1 h under 500, 550, and 650 °C.

initial discharge capacity of the FeF_2 at 500, 550 and 650 °C can reach 212.67, 503.394 and 333.327 mA h g^{-1} , respectively. The reversible capacity of the FeF_2 obtained in this study was lower than that of the theoretical specific capacity (571 mA h g^{-1}). These results may be due to the Fe_2O_3 and Fe_3O_4 impurity phases observed in the sample, which would decrease the discharge capacity. However, the reversible capacity of the obtained FeF_2 was higher than that of the FeF_2 -carbon composite reported by Zhang et al. (345 mA h g^{-1}) [2]. The high discharge capacity is attributed to incorporation of carbon that might facilitate charge transfer at the interface. These results indicate that the optimum temperature is 550 °C.

Fig. 3 shows the XRD patterns of the sample synthesized at 550 °C for 1 h with function of different weight ratio of $[\text{FeC}_2\text{O}_4]:[\text{PTFE}]$. It is obvious that the optimum weight ratio of $[\text{FeC}_2\text{O}_4]:[\text{PTFE}]$ for synthesis of FeF_2 as a single phase is 10:4.17. There is a weak impurity corresponding to Fe_3O_4 with

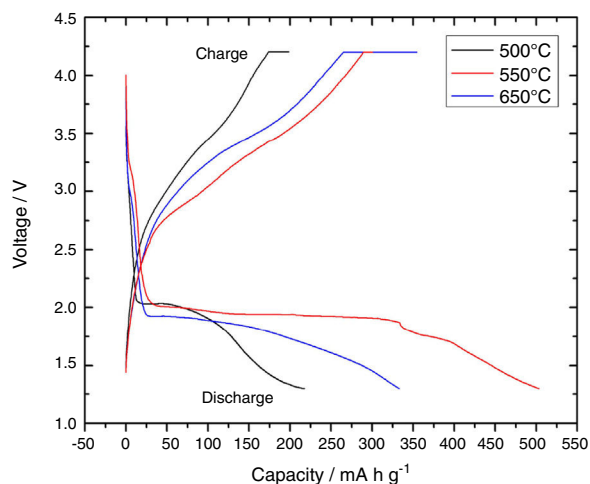


Fig. 2 – Initial charge and discharge curves of FeF_2 with a weight ratio of $[\text{FeC}_2\text{O}_4]:[\text{PTFE}] = 10:4.17$ synthesized at 500, 550, and 650 °C for 1 h in the 4.2–1.3 V region at a current density of 60 mA g^{-1} .

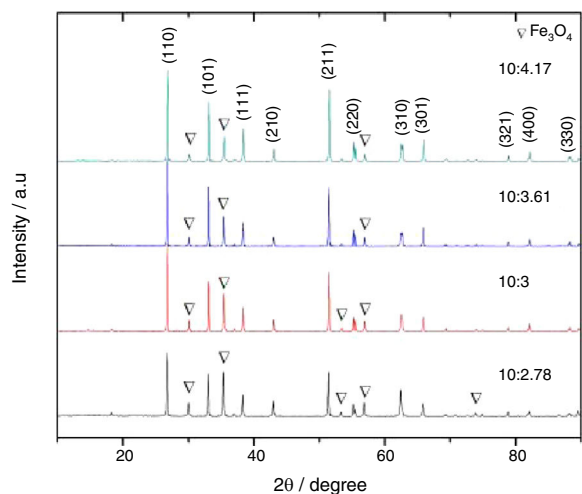


Fig. 3 – XRD patterns of FeF₂ synthesized at 550 °C for 1 h with function of different weight ratio of [FeC₂O₄]:[PTFE].

different weight ratio of [FeC₂O₄]:[PTFE]. The peak intensity of FeF₂ was increased and the impurity phase was decreased with the increase of PTFE. It is indicated that the optimum conditions of synthesis of FeF₂ using PTFE as a fluorine source are flowing that; i) weight ratio of [FeC₂O₄]:[PTFE] is 10:4.17, ii) calcination temperature is 550 °C.

Fig. 4a shows a TEM image of the synthesized FeF₂/carbon nanoparticle. The image clearly shows that the obtained FeF₂ sample has granular particle morphology and a particle size of 50–100 nm. The carbon layer coated on the FeF₂ shows thickness less than 20 nm, providing a good electrical conduction path. Fig. 4b shows the clearly observable lattice fringes of the carbon layer, which correspond to an inter-planar (*d*) spacing of 0.5 nm. This result suggests that the particle growth of FeF₂ was effectively suppressed by using PTFE as the fluorine source due to the low decomposition temperature and high activation rate, which led to the short reaction time and low reaction temperature for synthesis of the FeF₂ sample.

Fig. 5a shows the initial charge and discharge curves of the FeF₂ in the 4.2–1.3 V region. The initial discharge capacity of the FeF₂ with a weight ratio of [FeC₂O₄]:[PTFE] = 10:2.78, 10:3, 10:3.61, 10:4.17 can reach 136.032, 168.098, 303.835 and 503.394 mA h g⁻¹, respectively. It is due to the Fe₃O₄ impurity phase observed in the sample, which would decrease the discharge capacity. These results indicate that the optimum weight ratio of [FeC₂O₄]:[PTFE] is 10:4.17. Fig. 5b shows the charge–discharge curves as a weight ratio of [FeC₂O₄]:[PTFE] = 10:4.17 at a current density of 60 mA g⁻¹. During the first cycle, the composite delivers a discharge capacity of 503.394 mA h g⁻¹, the reversible specific charge capacity is 300.427 mA h g⁻¹. The reversible capacity of charge and discharge also decreased with increasing cycle number. The

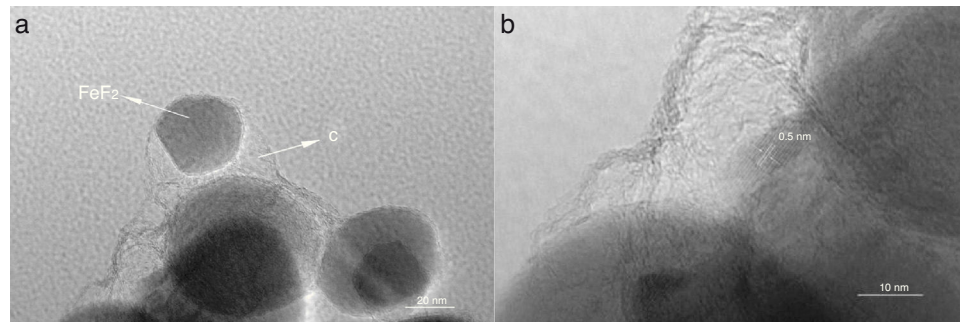


Fig. 4 – TEM image of FeF₂/carbon nanoparticle as with a weight ratio of [FeC₂O₄]:[PTFE] = 10:4.17 synthesized at 550 °C for 1 h.

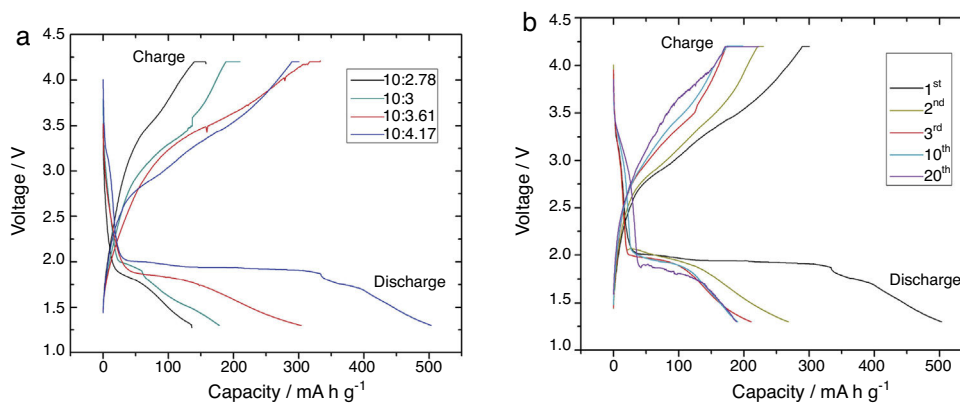


Fig. 5 – Initial charge and discharge curves of FeF₂ synthesized at 550 °C for 1 h with function of different weight ratio of [FeC₂O₄]:[PTFE] in the 4.2–1.3 V region at a current density of 60 mA g⁻¹ (a), and charge–discharge curves with a weight ratio of [FeC₂O₄]:[PTFE] = 10:4.17 at a current density of 60 mA g⁻¹ (b).

discharge capacities are found to be 268.478, 211.34, 193.817 and 183.328 mA h g⁻¹ at the 2nd, 3rd, 10th, and 20th cycles, respectively. In addition, the voltage plateau was confirmed in the 2.0 V in the discharge curves. This region involves the conversion reaction, accompanied by the formation of Fe and LiF. In the following cycles, the plateaus are almost the same, which may be attributed to the improvement on conductivity due to generation of iron nanoparticles in the conversion reaction. The voltage plateau is lower than the theoretical voltage (2.66 V). The possible reasons are as follows. The thick carbon layer presents a longer diffusion length, thus limiting Li⁺ diffusion and hindering electrolyte penetration. So, decreasing the thickness of carbon layer and the particle size of FeF₂ will be explored in further investigation.

4. Conclusions

In summary, FeF₂/carbon composite nanoparticle was synthesized successfully by a one-pot thermal reaction using polytetrafluoroethylene (PTFE) as a fluorine source. It is indicated that the optimum conditions of synthesis of a single phase FeF₂ are flowing that: a) calcination temperature is 550 °C; b) weight ratio of [FeC₂O₄]:[PTFE] is 10:4.17. The composite exhibits an initial discharge capacity of 503.394 mA h g⁻¹ at a current density of 60 mA g⁻¹ in voltage range of 4.2–1.3 V. The specific discharge capacities to be 268.478, 211.34, 193.817 and 183.328 mA h g⁻¹ at the 2nd, 3rd, 10th, and 20th cycles, respectively.

Conflicts of interest

The authors declare no conflicts of interest.

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