



Carbon coated hollow $\text{Na}_2\text{FePO}_4\text{F}$ spheres for Na-ion battery cathodes

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HIGHLIGHTS

- ▶ $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ particles were synthesized using ultrasonic spray pyrolysis.
- ▶ $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ spheres can maintain 80% of initial capacity after 750 cycles.
- ▶ Electrochemical performance is comparable with cathodes for Li-ion batteries.
- ▶ Enhanced electrochemical performance is attributed to the unique structure.

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ABSTRACT

Carbon coated porous hollow $\text{Na}_2\text{FePO}_4\text{F}$ ($\text{C}/\text{Na}_2\text{FePO}_4\text{F}$) spheres with 500 nm diameter and 80 nm wall thickness are synthesized by a one-step template-free ultrasonic spray pyrolysis process using sucrose as the carbon source. Nano-sized porous hollow $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ spheres allow electrolyte to penetrate into the hollow structure, and thus the electrochemical reaction can take place on both the outside and inside surface and in the pores. Also, the carbon coating on $\text{Na}_2\text{FePO}_4\text{F}$ hollow spheres enhances the electronic conductivity and charge transfer reaction kinetics. The unique carbon coated porous hollow $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ cathodes deliver 89 mAh g^{-1} capacity at a low rate of 0.1C, and 75 mAh g^{-1} at 1C, and maintains 33% of capacity at 9C. After 750 cycles at 1C, $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ cathodes can still provide 60 mAh g^{-1} , which is 80% of initial capacity. The significant advance in electrochemical performance of hollow $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ spheres combined with mature aerosol spray synthesis technology make these carbon coated porous hollow $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ spheres very promising as cathode materials for practical applications in Na-ion batteries.

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1. Introduction

The sodium ion battery is a promising alternative to the widely studied lithium ion battery for smart electric grids that integrate discontinuous renewable energy sources due to low cost of sodium which is more abundant than Li [1]. Since the weight and footprint requirement for electrical grid storage is less important, the lower energy density of Na-ion batteries compared to that of lithium ion technology is not an issue [2]. However, Na-ions are about 55% larger in radius than Li-ions, which makes it difficult to find a suitable host material to accommodate Na-ions and allow reversible and rapid ion insertion and extraction. Only a few Li-ion battery cathode materials are suitable for the Na-ion battery. Among them, $\text{Na}_2\text{FePO}_4\text{F}$ can provide 124 mAh g^{-1} at a very low

charge/discharge rate, demonstrating potential as a cathode material for Na-ion cells. However, it can only provide 12% of 0.1C capacity at 8C and can maintain the capacity only in 20 charge/discharge cycles [3,4]. The rate performance and cycling stability of $\text{Na}_2\text{FePO}_4\text{F}$ need to be largely improved before practical application in Na-ion batteries.

A number of methods have been used for enhancing the cycling stability and rate performance of ion insertion materials. Among them, carbon coating and particle size reduction are the most common strategies to enhance both the cycling stability and rate performance of cathode electrodes due to low electronic conductivity and poor ion diffusivity. These two methods have been successfully adapted to $\text{Na}_2\text{FePO}_4\text{F}$ cathodes to improve the electrochemical performance in Na-ion batteries. The carbon coated nano-sized $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ cathodes prepared using solid-state reaction showed promising capacity of 110 mAh g^{-1} at a low rate of 1/20C [4]. However, it can deliver only 50% of 0.05C capacity at 1C and can only be charged/discharged for 20 cycles [4] even though the particle size of $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ was reduced to 30–200 nm and the particles were coated with carbon [4]. Therefore, reducing particle size and coating carbon, which are very effective for LiFePO_4 in

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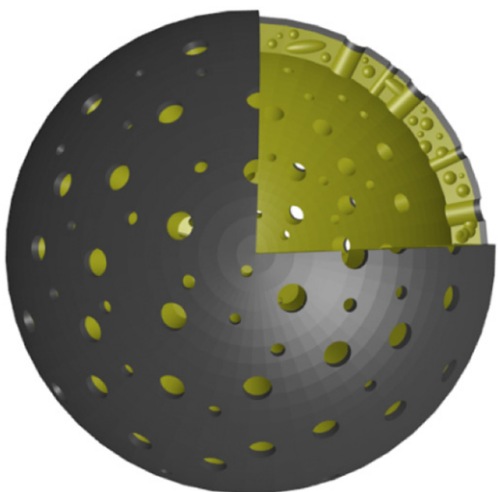


Fig. 1. Schematic of porous hollow C/Na₂FePO₄F.

Li-ion batteries, are not sufficient to enhance the performance of C/Na₂FePO₄F cathodes in Na-ion batteries due to the large size of Na-ions.

Recently, it was reported that porous materials with porous hollow structure (hollow spheres, nanotubes) have exceptional rate capability and cycling stability in Li-ion batteries, even for those materials which experience large volume change (270% for Si, Sn) during lithiation/delithiation [5,6]. Hollow and porous spheres offer several advantages over dense particles, including fast mass transfer and large reaction area, thus improving the electrochemical reaction kinetics. In addition, the interior void of hollow spheres can effectively accommodate the volume change, enhancing the structural stability by releasing the strain [6], thus improving the cycling stability.

Conventional methods for fabrication of hollow spheres utilize sacrificial templates [5,6]. However, template synthesis methods suffer from high cost and tedious synthetic procedures, which may prevent their use in large-scale applications. Ultrasonic spray pyrolysis (USP) is a one-step template-free synthetic method for the fabrication of hollow structure material [7]. In a typical process, ultrasonic waves are applied to precursor solution in order to create

an aerosol that is then swept through a furnace by a carrier gas. Upon heating, the precursor solvent evaporates and precursors decompose resulting in a product with a generally spherical shape. If the precursors also generate gas, it would escape from the product spheres to create a hollow structure or porous hollow structure, leaving large cavities and small pores. Since each droplet in the aerosol is an individual microreactor, the particle size, composition and structure can be controlled. USP has been widely used in industry for large-scale production of hollow particles.

In this paper, carbon coated porous hollow C/Na₂FePO₄F spheres with 500 nm diameter and 80 nm wall thickness (Fig. 1) are synthesized through an ultrasonic spray pyrolysis process using nitrates and sucrose as the gas and carbon source. Nano-sized pores crossing the C/Na₂FePO₄F wall allows electrochemical reaction to take place on the outside and inside surface and also inside of the wall, enhancing the rate capability, while the nanopores in the wall and micro-cavities in the center provide space to accommodate the volume change, thereby improving the cycling stability. The carbon coated porous hollow C/Na₂FePO₄F spheres can provide 89 mAh g⁻¹ at 0.1C, deliver 33% of capacity at a high rate of 9C, and maintain 80% of initial capacity after 750 full charge/discharge cycles at 1C, demonstrating a significant advance in cycling stability of C/Na₂FePO₄F cathode materials from 20 cycles (solid-state reaction) [4] to 750 cycles (aerosol spray).

2. Experimental

2.1. Ultrasonic spray pyrolysis (USP) reactor system

The ultrasonic spray pyrolysis (USP) reactor system is shown in Fig. 2. The system is composed of a precursor solution reservoir, an ultrasonic droplet generator (1.7 MHz), two tube furnaces in series, a quartz tube reactor (diameter 22/25 mm × 810 mm), and a filtration system for particle collection. Spray pyrolysis enables the production of spherical particles with compositional homogeneity with respect to the precursor solution. A frequency generator device is used to form ultrasonic vibrations, thereby creating fine aerosol droplets with stoichiometric composition. The fine aerosol is transported via carrier gas into a tubular furnace at a given temperature. Once in the furnace, processes of diffusion, dehydration, and decomposition occur simultaneously to form nanoparticles of controlled size, morphology, and composition.

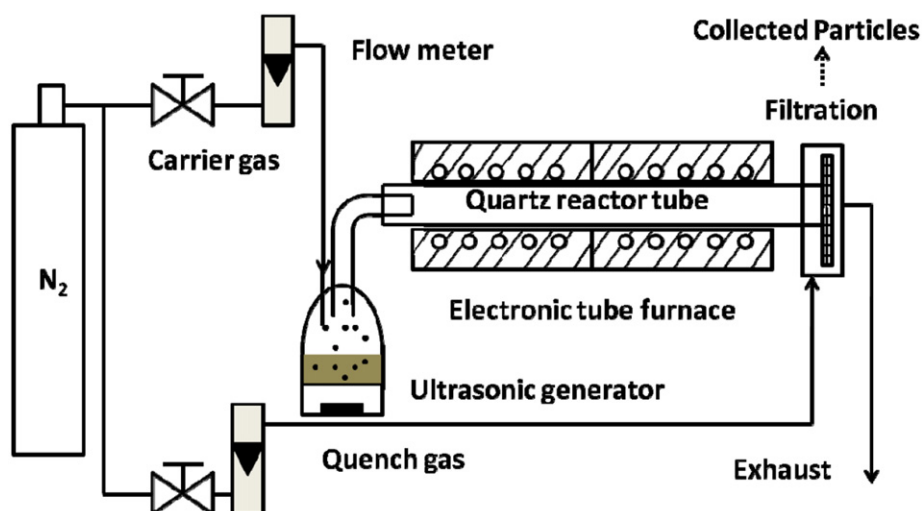


Fig. 2. Schematic of spray pyrolysis process.

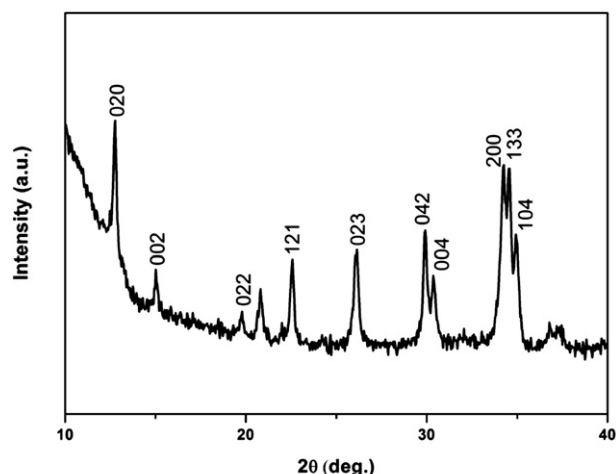


Fig. 3. XRD full-pattern fitting of C/Na₂FePO₄F sample.

2.2. Material synthesis

The synthesis of C/Na₂FePO₄F was carried out by mixing the stoichiometric amount of sodium fluoride, sodium nitrate, iron nitrate nonahydrate, phosphoric acid, and sucrose (35 wt%) dissolved in water. The species precursor molar concentration was 0.05 M, and the spray pyrolysis temperature was 500 °C, while nitrogen carrier gas and quench gas flow rates were held constant at 3 lpm and 10 lpm, respectively. 500 °C was chosen as the optimum pyrolysis temperature, which corresponds to a residence time of approximately 3 s. Particles were collected on a polytetrafluoroethylene (PTFE) filter using a brush. The as prepared materials were then annealed at 600 °C for 8 h in argon to obtain the desired phase.

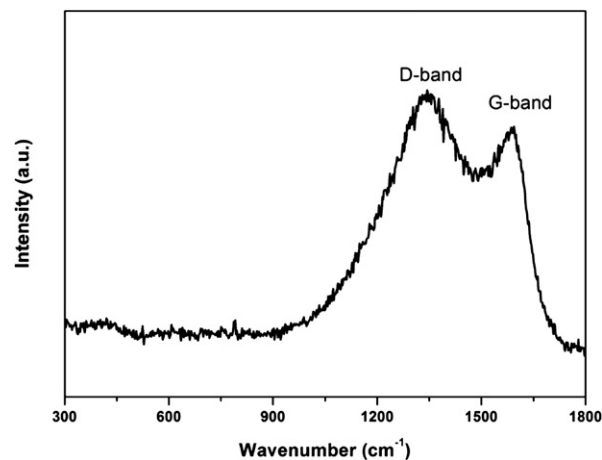


Fig. 5. Raman spectra of C/Na₂FePO₄F sample.

2.3. Cathode preparation

Electrochemical performance of C/Na₂FePO₄F was tested in a coin cell using sodium metal as the counter electrode and 1 M NaClO₄ in EC/DMC (1:1 by volume) as the electrolyte. C/Na₂FePO₄F cathodes consisted of 80 wt% C/Na₂FePO₄F, 10 wt% acetylene black, and 10 wt% poly(vinylidene fluoride), which were mixed with NMP and pasted on Al foil, and then dried at 80 °C in vacuum. The active material loading is 0.5–0.6 mg cm^{−2}. The charge/discharge behavior was tested using an ArbinBT2000 workstation (Arbin Instruments, TX, USA).

2.4. Cathode characterization

Structural studies were performed by X-ray diffraction (XRD) on D8 Advance with LynxEye and SolX (Bruker AXS, WI, USA) using

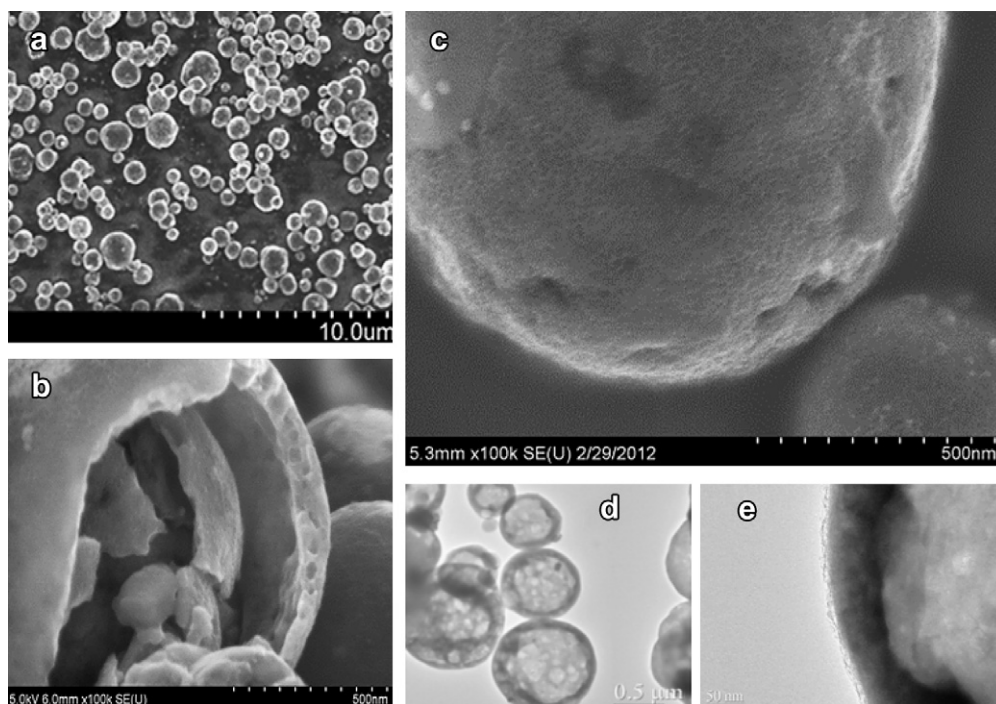


Fig. 4. (a) SEM image of C/Na₂FePO₄F particles prepared by USP with average particle size of 0.5 μm. (b) Broken shell depicting hollow nature of particles. (c) SEM image showing nanoporous structure of particles. (d) TEM image showing nanopores and aggregated nature of particle wall. (e) TEM image of particle edge depicting a thin carbon layer.

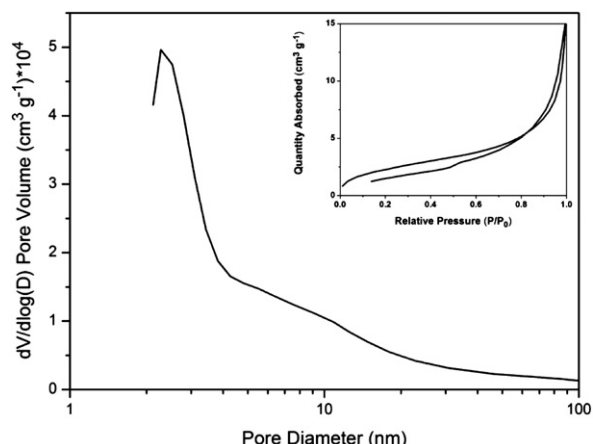


Fig. 6. Pore size distribution and N_2 adsorption–desorption isotherm (inset) of C/Na_2FePO_4F sample.

$CuK\alpha$ radiation, scanning electron microscopy on a Hitachi (Tokyo, Japan) SU-70 HR-SEM with FFT images, and transmission electron microscopy on a JEOL 2100F field emission TEM (Tokyo, Japan). Raman spectra of the material were collected using a Raman microscope. Energy dispersive X-ray spectroscopy (EDS) and thermogravimetric analysis (TGA) were carried out to determine the amount of carbon. BET measurements were performed using a Micromeritics physisorption analyzer.

3. Results and discussion

3.1. Structural and morphological analysis

The crystal structure of C/Na_2FePO_4F hollow particles after annealing in argon at $600^\circ C$ for 8 h were analyzed by X-ray diffraction. XRD patterns of the annealed sample (Fig. 3) demonstrates single phase Na_2FePO_4F , which is isostructural to both Na_2FePO_4OH and Na_2CoPO_4F .

Fig. 4 shows typical particle morphology after annealing in argon at $600^\circ C$ for 8 h. Na_2FePO_4F particles prepared using USP are spherical in shape with average particle size of 500 nm (ranging from 100 nm to 1 μm , Fig. 4a). A hollow structure inside of C/Na_2FePO_4F spherical particles can be clearly observed by a broken hollow sphere and fragments (Fig. 4b). The thickness of the wall is around 80 nm. The wall is formed by sintering of aggregated nanoparticles (Fig. 4b and d) thus leaving many micro-sized cavities (Fig. 4b) and nanopores inside the wall. The nanopores with size of around 2.5 nm can be more clearly observed in SEM images of the

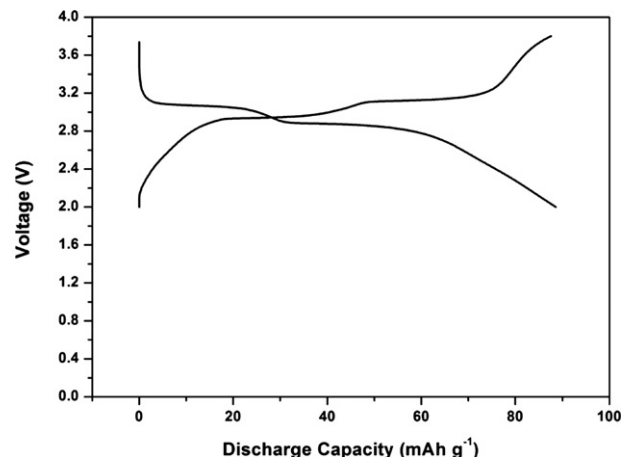


Fig. 8. Galvanostatic charge/discharge curves of a Na/Na_2FePO_4F cell cycled at a rate of 0.1C.

C/Na_2FePO_4F particle surface (Fig. 4c). Fig. 4e clearly shows the presence of a thin layer of carbon coated on the surface of the C/Na_2FePO_4F particle. The carbon coating thickness is about 10 nm. According to energy dispersive X-ray spectroscopy (EDS) and thermogravimetric analysis (TGA), the amount of carbon is between 6 and 8 wt%. Raman spectroscopy was used as an additional measurement to confirm the presence of carbon on C/Na_2FePO_4F hollow particles (Fig. 5). Strong D and G-bands from elemental carbon on the materials are observed at 1330 cm^{-1} and 1570 cm^{-1} , respectively.

The pore size distribution and specific surface areas of hollow C/Na_2FePO_4F particles were characterized using BET (Fig. 6). The BET specific surface area of the particles is $8.7\text{ m}^2\text{ g}^{-1}$. The Barret–Joyner–Halenda (BJH) desorption shows that most of the pores are 2.5 nm and some large pores with average size of 10 nm also exist, which is consistent with SEM observations in Fig. 2b and c. The pores in the wall will allow the liquid electrolyte to penetrate through the wall to the inside of the hollow sphere. Therefore, the electrochemical charge transfer reaction can take place on both sides of the wall and in the pores.

The possible formation mechanism of C/Na_2FePO_4F porous hollow particles is shown in Fig. 7. The initial step in the spray pyrolysis process is the evaporation of a solution droplet. As precursor droplets move through the furnace (dotted line), water evaporates and solute concentration is higher at the surface than at the center since evaporation occurs from the droplet's surface. Therefore, the precursor solution becomes supersaturated and solute precipitation at the droplet's surface forms a viscous shell on

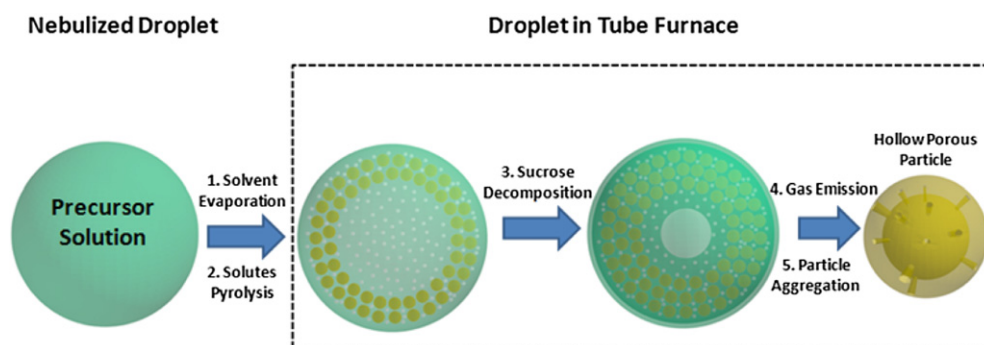


Fig. 7. Schematic illustration of the formation process of hollow C/Na_2FePO_4F spheres fabricated by USP. The dotted line represents inside the furnace. Yellow spheres are the particles while white spheres are the gaseous species. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

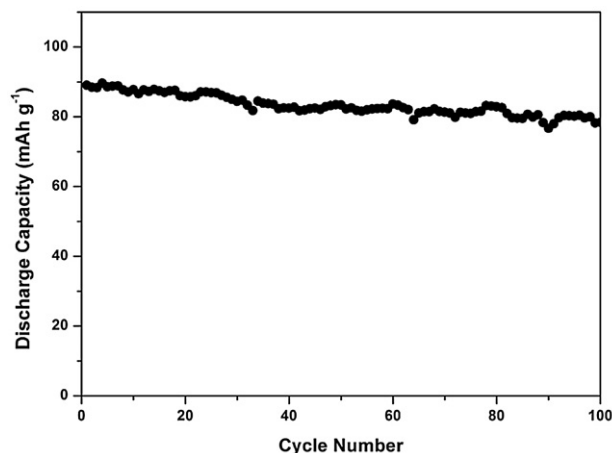


Fig. 9. Capacity retention of C/Na₂FePO₄F cycled at a rate of 0.1C.

the surface of the precursor droplet [8]. During the formation of C/Na₂FePO₄F shell, the large amount of gas generated in the center of C/Na₂FePO₄F shell due to solvent evaporation and CO and CO₂ generation from decomposition of sucrose in the droplet at high temperatures, results in high internal gas pressure. When the internal pressure is greater than the mechanical strength of the C/Na₂FePO₄F shell, the shell breaks resulting in gas escaping from the C/Na₂FePO₄F spheres to form an inner hollow structure and small pores in the wall of hollow C/Na₂FePO₄F spheres [9]. The decomposition of sucrose also forms carbon, which is coated on the surface of hollow C/Na₂FePO₄F spheres.

3.2. Electrochemical characterization

Galvanostatic charge/discharge performance of carbon coated C/Na₂FePO₄F cathode materials was tested in a voltage range of 2.0–3.8 V in a Na-ion coin cell. Fig. 8 shows the typical voltage profiles of C/Na₂FePO₄F cathode during the 5th cycle at a rate of 0.1C. Two well-defined reversible voltage plateaus are evident at 2.9 V and 3.1 V, which represent two reversible phase transformations of Na₂FePO₄F ↔ Na_{1.5}FePO₄F and Na_{1.5}FePO₄F ↔ NaFePO₄F. An intermediate phase Na_{1.5}FePO₄F has lattice parameters between the two end members, and its structure undergoes a slight change in symmetry to a monoclinic unit cell [2]. Due to the unique carbon

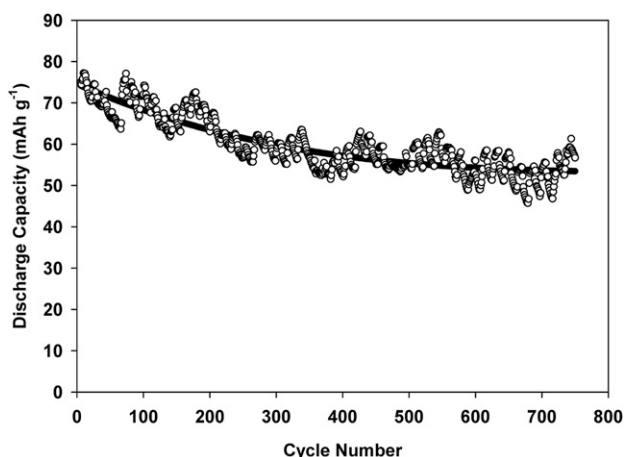


Fig. 10. Capacity retention of C/Na₂FePO₄F cycled at a rate of 1C.

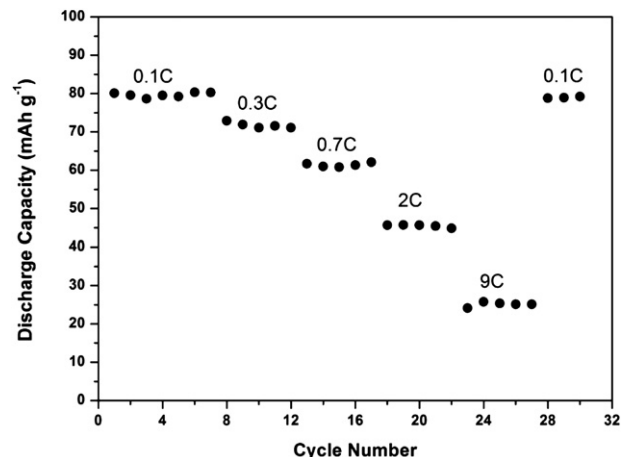


Fig. 11. Rate capability of C/Na₂FePO₄F. Before rate capacity test, the C/Na₂FePO₄F cathode was charged and discharged at 0.1C for 100 cycles.

coated porous hollow structure, C/Na₂FePO₄F shows exceptional cycling stability as demonstrated in Fig. 9. C/Na₂FePO₄F can deliver approximately 90 mAh g^{−1} of reversible capacity and retain 90% of capacity after 100 cycles. Because of the excellent stability of the material at a low C-rate (0.1C), much longer charge/discharge cycles were tested for C/Na₂FePO₄F cathodes at a high rate of 1C and also shown in Fig. 10. The initial capacity of C/Na₂FePO₄F is 75 mAh g^{−1} at 1C. After 750 cycles, the capacity decreases to 60 mAh g^{−1} which corresponds to capacity retention of 80%, while the C/Na₂FePO₄F synthesized using solid-state reaction can retain 75% of capacity after only 20 cycles. This work represents a significant advance in C/Na₂FePO₄F cathode materials for Na-ion batteries.

The C/Na₂FePO₄F cathodes after experiencing 100 charge/discharge cycles at 0.1C (the sample in Fig. 9) were subjected to a rather abusive high rate testing protocol in which the cells were both charged and discharged at the same high rates. As shown in Fig. 11, under this stringent condition, C/Na₂FePO₄F can deliver approximately 80 mAh g^{−1} of reversible capacity at 0.1C and 26 mAh g^{−1} at 9C. Even after 100 charge/discharge cycles, C/Na₂FePO₄F can still provide 33% of the capacity at 9C. The C/Na₂FePO₄F synthesized using solid-state reaction can only provide 15 mAh g^{−1} at the rate of 8C [4]. The discharge curves at the various C-rates are given in Fig. 12. Such a high rate capability and long cycling stability of C/Na₂FePO₄F cathodes in Na-ion cells have not

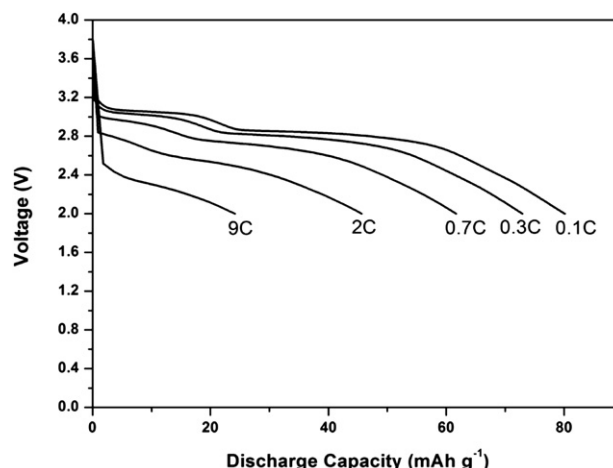


Fig. 12. Discharge curves of C/Na₂FePO₄F at various C-rates after 100 cycles at 0.1C.

been reported before, demonstrating a great potential for commercialization of Na-ion batteries.

Although the Na^+ ion is much larger than Li^+ the carbon coated hollow $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ cathode materials synthesized using an USP process demonstrated a high rate capability and long cycling stability in Na-ion batteries, which is comparable to the lithium ion batteries. The high rate performance of $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ is attributed to (1) high interface area between liquid electrolyte and $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ due to penetration of the liquid electrolyte into pores and center hole of hollow $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$, (2) carbon coating increasing the charge transfer reaction kinetics, and (3) hollow structure shortening the diffusion length of Na^+ ion. Hollow $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ is also structurally very robust to withstand the volume change during Na^+ insertion/extraction, resulting in a long cycling life.

4. Conclusions

In summary, carbon coated hollow $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ particles with pores in the shell were synthesized using an USP process. The $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ cathodes can deliver 89 mAh g^{-1} capacity at a low rate of 0.1C, and 75 mAh g^{-1} at 1C, and maintains 33% of capacity at 9C. After 750 cycles at 1C, $\text{C}/\text{Na}_2\text{FePO}_4\text{F}$ cathodes can still provide 60 mAh g^{-1} , which is 80% of initial capacity. This enhanced electrochemical performance is attributed to the unique hollow spherical and porous structure of the material inherent to the spray

pyrolysis process. Additionally the presence of a thin carbon layer acts to enhance the rate capability and cycling stability.

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References

- [1] B. Dunn, H. Kamath, J.M. Tarascon, *Science* 334 (2011) 928–934.
- [2] V. Palomares, P. Serras, I. Villaluenga, K.B. Hueso, J. Carretero-Gonzalez, T. Rojo, *Energy Environ. Sci.* 5 (2012) 5884–5901.
- [3] C. Vidal-Abarca, P. Lavela, J.L. Tirado, A.V. Chadwick, M. Alfredsson, E. Kelder, *J. Power Sources* 197 (2012) 314–318.
- [4] Y. Kawabe, N. Yabuuchi, M. Kajiyama, N. Fukuoka, T. Inamasu, R. Okuyama, I. Nakai, S. Komaba, *Electrochem. Commun.* 13.11 (2011) 1225–1228.
- [5] Y. Yao, M.T. McDowell, I. Ryu, H. Wu, N. Liu, L. Hu, W.D. Nix, Y. Cui, *Nano Lett.* 11 (2011) 2949–2954.
- [6] H. Wu, G. Chan, J.W. Choi, I. Ryu, Y. Yao, M.T. McDowell, S.W. Lee, A. Jackson, Y. Yang, L. Hu, Y. Cui, *Nat. Nanotechnol.* 7 (2012) 310–315.
- [7] F. Dong, Y. Huang, S. Zou, J. Liu, S.C. Lee, *J. Phys. Chem. C* 115 (2011) 241–247.
- [8] J. Ortega, T.T. Kodas, *J. Aerosol Sci.* 23 (1992) 253–256.
- [9] L.A. Patil, M.D. Shinde, A.R. Bari, V.V. Deo, *Sens. Actuators B Chem.* 143 (2009) 316–324.