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Prussian blue-derived Fe_2O_3/sulfur composite cathode for lithium–sulfur batteries

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ABSTRACT

Porous Fe_2O_3 was prepared by simple annealing of preformed Prussian blue that was synthesized from a wet chemistry method. The obtained porous Fe_2O_3 nanoparticles were then mixed with sulfur and used as cathode for lithium–sulfur batteries. The porous Fe_2O_3 acts as an internal polysulfide reservoir, and thus reduces the shuttle effect. Composite cathode containing 5% porous Fe_2O_3 shows improved cycling performance as compared to that without porous Fe_2O_3. A stable reversible discharge capacity of 574.3 mAh/g was obtained after 50 cycles at 0.5 C.

1. Introduction

Lithium–sulfur (Li/S) battery is a promising electrochemical system with possibility of achieving high-energy up to a theoretical capacity of 1675 mAh/g [1–4]. Combined with other advantages of sulfur such as low toxicity and natural abundance, it has attracted wide attention especially for applications of next generation energy storage and hybrid vehicles. However, the system suffers from several drawbacks particularly dissolution of intermediate polysulphide reaction species into electrolyte [5–10]. Thus, novel advances in materials design such as new electrolytes [11–20], polymer coated sulfur nanosphere core/cell structure and conductive mesoporous/nano carbon framework for constraining sulfur have been proposed [21–35]. These techniques significantly improve the cycling performance of Li/S batteries but falls short of completely controlling polysulphide dissolution. Recently, a new concept of embedding small fraction of porous silica particles (SBA-15) within carbon–sulfur nanocomposites which act as an internal polysulfide reservoir has been proposed by Nazar et al. to stabilize the system [36]. The results show greatly improved cycling stability and less polysulphide shuttle effect. In line with this concept, here we report the synthesis of porous Fe_2O_3 and the use of it as polysulfide reservoir in sulfur cathode to improve the performance of Li/S batteries. A doping of 5% porous Fe_2O_3 shows improved cycling performance with more stable reversible discharge capacity of ca. 574 mAh/g after 50 cycles.

2. Materials and methods

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Synthesis and characterization of porous Fe_2O_3: Porous microcubes Fe_2O_3 was prepared from annealing of preformed Prussian blue synthesized from precursors of Polyvineypirrolydone (PVP), potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) and HCl solution. Firstly, Polyvineypirrolydone (PVP, 15.2 g) and potassium ferrocyanide($K_4Fe(CN)_6 \cdot 3H_2O$, 0.44 g) were added to a HCl solution(0.1 M, 200 ml) under magnetic stirring to obtain a clear solution which was heated at 80 °C for 12 h. The solution was then washed several times with distilled water and ethanol solution and then centrifuged. The sediment was dried in a vacuum oven at 30 °C for 10 h. Finally, this product was heated at 500 °C for 5 h in air with a temperature ramp of 2 °C/min and naturally cooled to room temperature to obtain a porous micro boxes Fe_2O_3. The products were measured by X-ray diffraction (XRD, D8 Discover, Broker AXS), scanning electron microscopy (SEM, S-4800, Hitachi), transmissionelectronmicroscope (TEM, Tecnai F20, FEI) and thermogravimetric analysis (Pyris Diamond TG, Perkin-Elmer).

Electrode fabrication and electrochemical measurement: The electrochemical measurements were carried out using 2032-type coin cell system. S/Fe_2O_3 composite was prepared by simple mixing S and porous Fe_2O_3 particles at room temperature. Cathode electrodes were prepared by coating a mixture containing 70 wt% S/Fe_2O_3 (1% Fe_2O_3 doping=69.3 wt% sulfur loading, 5% Fe_2O_3 doping=66.5 wt% sulfur loading, 10% Fe_2O_3 doping=63 wt% sulfur loading) composite, 20 wt% conductive carbon black (super P), and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) to form a slurry onto Cu current collector. The test electrodes were dried at 50 °C in a vacuum for 20 h, the electrode film was cut into sheets of 14 mm in diameter, pressed and dried for another 2 h at 50 °C, and the composite loading is

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about 1.2 mg/cm^2. Then 2032-type coin cells were fabricated for electrochemical testing in an argon-filled glovebox which oxygen and moisture concentrations below 0.1 ppm. Metallic lithium was used as the counter/reference electrode, 1 M lithium bis (trifluoromethane sulfonimide)imide (LiTFSI) in dioxolane/dimethoxyethane solvent (DOL/DME, volume ratio=1:1) was used as electrolyte, and Celgard 2400 polypropylene as separator. Charge/discharge measurements were carried out galvanostatically at various current densities (1 C=1675 mAh/g) over a voltage range of 1.0–3.0 V(vs. Li/Li$^+$) using a battery test system(LAND model, CT2001A, Wuhan RAMBO testing equipment, Co. Ltd.) at 30 °C.

3. Results and discussion

Fig. 1(a) shows the SEM image of as-synthesized Prussian blue microcubes. Those microcubes are quite uniform with an average size of ca. 300 nm due to the face-centered-cubic (fcc) crystal structure of $Fe_4[Fe(CN)_6]_3$. These as-synthesized Prussian blue microcubes were transformed into porous Fe_2O_3 microcubes by annealing in air. As indicated by the thermogravimetric analysis (TGA) shown in Fig. 1(b), the Prussian blue microcubes underwent significant weight loss during heating. A loss of ~40% of weight was found under 320 °C, which is mainly due to the thermally induced oxidative decomposition. The decomposition process is accompanied by outward gas flow, which eventually resulted in formation of cavities.

From SEM image and TEM image shown in Fig. 1(c) and (d), it was found that highly porous cubic structures were obtained at 500 °C. These porous microcubes were consisted of Fe_2O_3 nanoparticles with sizes of tens of nanometeres and cavities with size in the range of 1–10 nm. At lower temperature, no porous structures were observed, while higher temperature heating resulted in the continued growth of Fe_2O_3 pore size and the aggregation of Fe_2O_3 nanoparticles.

The crystallographic structure of the porous structures annealed at 500 °C was further examined by powder X-ray diffraction (XRD). As shown in Fig. S1, although there are a few small peaks which are difficult to be assigned possibly due to incomplete oxidation of Fe_2O_3, most of the main diffraction peaks could be assigned to Fe_2O_3 as indicated in the figure.

To study the effects of porous Fe_2O_3 incorporation on electrochemical performance in Li–S batteries, sulfur and Fe_2O_3/S composite electrodes were prepared (see the experimental method). Fig. 2 shows the SEM images of sulfur cathode without Fe_2O_3

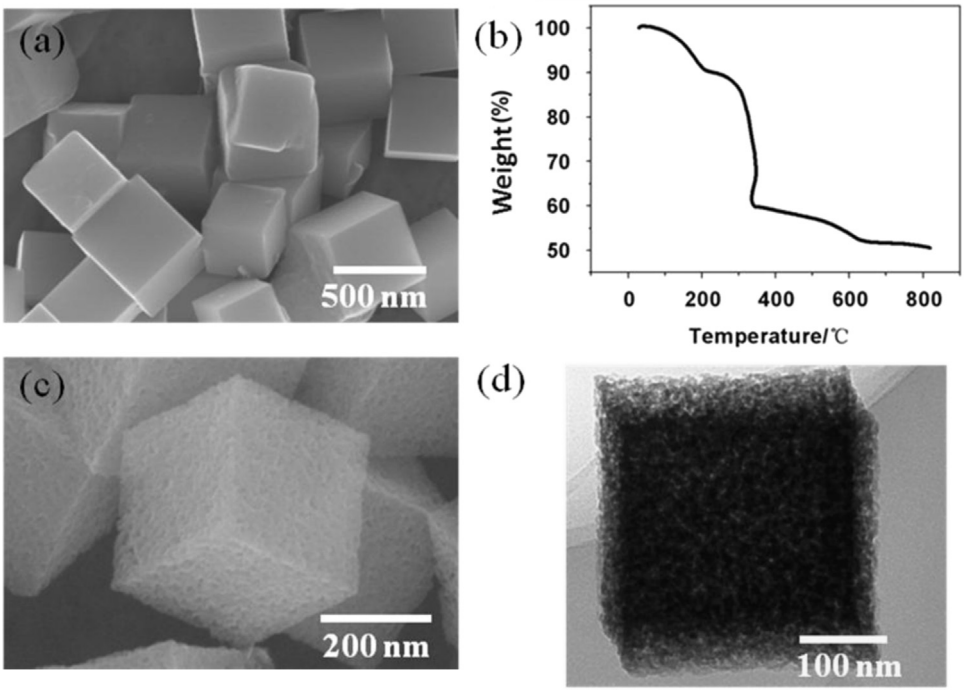

Fig. 1. (a) SEM image of as-prepared Prussian blue microcubes, (b) TGA of the as-prepared Prussian blue microcubes in air, (c) SEM image of Prussian blue microcubes annealed at 500 °C, and (d) TEM image of Prussian blue microcubes annealed at 500 °C.

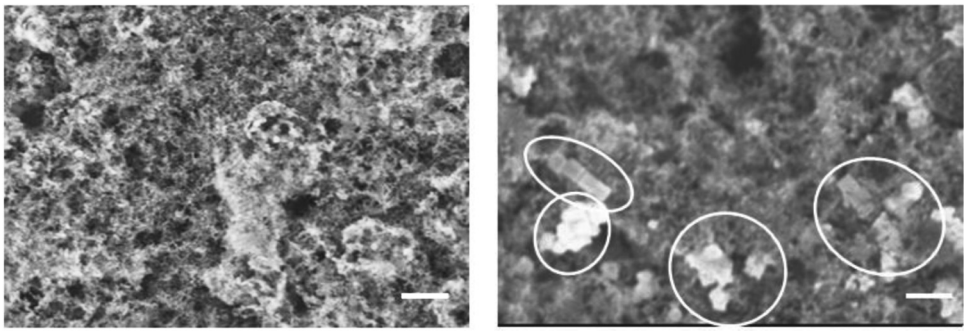

Fig. 2. SEM images of sulfur cathode without Fe_2O_3 (a), and composite electrodes with 5% Fe_2O_3 nanoparticles. Scale bar: 1 μm.

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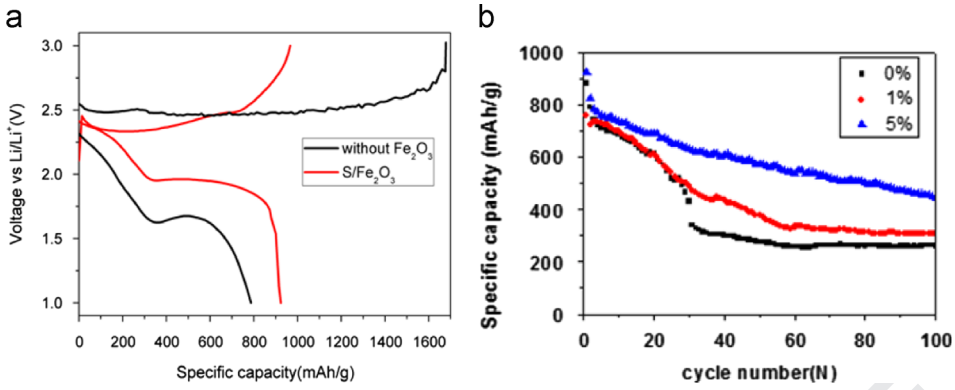

Fig. 3. Electrochemical data for Fe_2O_3/S composite electrode as compared to the sulfur electrode. Data were obtained on galvanostatic cycling at a C/2 rate (corresponds to a current density of 837.5 mA/g) and voltage window of 1.0–3.0 V. (a) Comparison of the charge–discharge profiles of the first cycle of Fe_2O_3 (5%, weight)/S composite electrode and pure S electrode system. (b) Electrochemical data for various Fe_2O_3/S composite electrodes compared with the sulfur electrode.

doping and with Fe_2O_3 doping. From Fig. 2b, it is clearly found that the cubic structure of porous of Fe_2O_3 (indicated in the white boxes as shown in Fig. 2b) is well-maintained after mixing with sulfur.

Electrochemical measurements of the assembled coin cells were then carried out in the voltage range of 1.0–3.0 V. As shown in Fig. 3(a), a discharge specific capacity of 787.2 mAh/g at a rate of 0.5 C was observed in the pure sulfur system. Meanwhile, the 5% Fe_2O_3/S composite electrode shows a higher specific capacity of 923.5 mAh/g under similar condition. The increment of the first discharge capacity from Fe_2O_3/S electrode could be due to contribution of the discharge capacity of Fe_2O_3. It was also found that both cells with or without porous Fe_2O_3 incorporation exhibited irreversible capacity in the first cycle. However, such effect is much lesser in cell with porous Fe_2O_3 incorporation (95.6% for Fe_2O_3/S vs. 46.9% for S electrode). This implies polysulphide shuttle mechanism is significantly mitigated due to the incorporation of porous Fe_2O_3, which acts as an internal polysulfide reservoir to reduce the shuttle effect.

The 5% Fe_2O_3/S composite system not only improved the first discharge capacity, but also shows an improved cycling stability as shown in Fig. 3(b). A reversible capacity of 574.3 mAh/g and 442.3 mAh/g were obtained after 50 cycles and 100 cycles, respectively. Other ratios of Fe_2O_3:sulfur composite electrodes were also tested. It was found that both the lower Fe_2O_3 doping (1% weight) and higher Fe_2O_3 doping (5% weight) Fe_2O_3/S composite systems have improved cycling stability (Fig. 3b), however, doping of over 10% of Fe_2O_3 resulted in low performance of batteries due to insufficient loading of the active element of sulfur. One should note that although Fe_2O_3 has long been reported as an anode material for lithium ion batteries, the use of Fe_2O_3 as cathode do not contribute significant capacity (only 50 mAh/g at 1 C) under the measured voltage range (1–3 V).

We noticed that in all cases of different amount of Fe_2O_3 doping, the shuttle effect still exists. This kind of composite electrodes seem unable to completely eliminate the polysulfide dissolution probably due to inhomogeneous of the Fe_2O_3 pore sizes. Further study on the effects of pore sizes on Li–S system is on the way to elucidate the shuttle effect. Stable metal–organic framework with tunable pore size could be a better candidate as polysulfide reservoir.

4. Conclusion

In summary, porous Fe_2O_3 with size of ~300 nm and cavities in the range of 1–10 nm was prepared from simple annealing of preformed Prussian blue. For the first time, we observed that porous Fe_2O_3 incorporation stabilized the cycling with a higher specific capacity than the pure sulfur cathode Li–S battery system. Our strategy based on the facile doping of porous structure rather than synthesis of complex S/C or other core/shell structures provides a new route for stabling the Li–S system and could be more practical for mass application with low cost and good repeatability.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.08.115.

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