1. INTRODUCTION

The demand for high capacity, long life Li-ion battery has been steadily increasing for future power tools, such as portable electronics and electric/hybrid vehicles [1,2]. Recently, nano-sized 3d-metal oxides MO\textsubscript{x} (M= Fe, Co, Ni, etc.) have been extensively researched as anode materials in lithium-ion battery because of their high energy capacity [3,4]. The mechanism of Li react with MO\textsubscript{x} involves the formation and decomposition of Li\textsubscript{2}O, accompanying the reduction and oxidation of MO\textsubscript{x}. The reduction of lithium from Li\textsubscript{2}O was thought to be thermodynamically impossible before. However, it was demonstrated to become feasible when the size of MO\textsubscript{x} was reduced to nanoscale [4]. Among those transition-metal oxides, iron oxide is considered one of the most appealing anode materials due to its low cost, low environmental impact and abundance of the raw materials. The theoretical capacity of Fe\textsubscript{2}O\textsubscript{3} is as high as 1005 mAh g\textsuperscript{-1}, which is much higher than that of the current commercial graphite anode materials (372 mAh g\textsuperscript{-1}). MO\textsubscript{x}, including Fe\textsubscript{2}O\textsubscript{3}, reduction and oxidation with lithium are accompanied by enormous structural change, which induces fast capacity fading and hindrance of practical implementation.

To address this issue, an efficient approach is to design nanostructured Fe\textsubscript{2}O\textsubscript{3}, such as nanoflowers [5], nanowires [6], nanocapsules [7], nanoflakes [8,9] and nanotubes [10]. These investigations distinctly revealed that the morphology of the nanostructured Fe\textsubscript{2}O\textsubscript{3} particles, which enlarged the surface area and shortened the pathway for lithium ion migration. The appealing electrochemical capability indicated the potential implementation of hollow Fe\textsubscript{2}O\textsubscript{3} spheres as anode material for future lithium-ion battery.

In this paper, we prepare hollow α-Fe\textsubscript{2}O\textsubscript{3} spheres by the facile hydrothermal method and subsequent heat-treatment. The sample shows impressive high capacity and excellent cycling stability, which indicates the potential of their application as electrode mate-
28 mM Glucose was firstly dissolved in 30 mL deionized water, and then 5.6 mM (NH₄)₂Fe(SO₄)₂·6H₂O was dissolved in 15 mL deionized water. The carbohydrate:metal molar ratio was 5:1 as reported before [13]. The two solutions were mixed and sealed in an autoclave, which was hydrothermal heated at 160 °C for 24 h. The precipitate was then filtered and washed repeatedly with deionized water and ethanol. The products were then calcined at 600 °C for 5 h to form hollow metal oxide particles.

The working electrode was constituted by mixing Fe₂O₃ (active material), polyvinylidene fluoride (binder), and Super P (conducting material) with a weight ratio of 70:10:20. The galvanostatic measurements were carried out at room temperature. Cyclic voltammetry test was performed between 0 and 3 V at a scanning rate of 0.1 mV/s.

The hollow Fe₂O₃ were characterized by a field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and a field emission transmission electron microscope (FE-TEM, JEM-2100F). Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX 2000 PC diffractometer, using Cu Ka radiation (λ=1.5406 Å).

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of the final conducts after calcination at 600 °C for 5 h. The diffraction peaks are consistent with the standard hematite (α-Fe₂O₃) rhombohedral structure (JCPDS Card No. 33-0664). The sharp peaks suggest the high crystallinity of the product. Additionally, the broad peak from 15° to 30° is ascribed to the diffraction of the glass substrate which was used to hold the sample.

Fig. 2a shows SEM image of the as-prepared α-Fe₂O₃ products. It clearly certifies that porous hollow Fe₂O₃ spheres consisted of many nanoscale particles were formed after calcinations. In the hydrothermal processing, carbon spheres are formed with metal ion incorporated into their hydrophilic shell while the hollow Fe₂O₃ spheres were obtained after removal of carbon by calcination [13]. Fig. 2b is a low magnification TEM image, showing the hollow sphere structure with diameter about hundreds of nanometers. High magnification TEM image in Fig. 2c distinctly illustrates the individual hollow sphere is actually comprised of many nanoparticles with a size of a dozen nm. Fig. 2d exhibits a HRTEM image of Fe₂O₃ nanoparticles at the shell of the submicron hollow sphere, indicating the sample is well crystallized. The distance between the neighboring lattice planes is 0.270 nm as marked in Fig. 2d. The distance is in agreement with the (104) spacing of rhombohedral α-Fe₂O₃.

Cyclic voltammetry was performed to understand the electrochemical behavior of the sample as shown in Fig. 3a. A substantial difference is clearly exhibited between the first and the subsequent cycles. In the first cathodic process, a sharp peak is recorded at ~0.63 V accompanied by two small peaks at ~0.91 V and ~1.58 V. This is consistent to the mechanism of the first lithium intercalation to α-Fe₂O₃, as reported before [14]. The two small peaks are ascribed to the lithium insertion into the crystal structure of α-Fe₂O₃ and the formation of cubic Li₂Fe₂O₅. The sharp peak corresponds to the thorough reduction of iron from Fe³⁺ to Fe⁰. Meanwhile, in the anodic process, two broad overlapping peaks were observed at ~1.69 V and ~1.88 V as a consequence of the oxidation of Fe³⁺ to Fe⁵⁺ and further oxidation to Fe⁷⁺ [15]. In the following cycles, both the cathodic and anodic peak potentials shift to ~0.79 V and ~1.73 V, respectively. The cathodic/anodic peak pair is assigned to the reversible oxidation/reduction reaction between α-Fe₂O₃ and Li. It is noticed that the peak current and the integrated area of the peaks are similar. These results reveal the good stability of the...
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lithium intercalation/de-intercalation process in the hollow Fe₂O₃ spheres, due to the hollow structure and nanoscale particles in the shell layer, which shortened the diffusion length of the Li⁺ and enhanced the reactivity of iron oxides.

Fig. 3b depicts the voltage profiles of hollow Fe₂O₃ spheres electrodes cycled over a voltage range of 0.01–3 V at 0.2 C rate. In the first discharge curve, the voltage initially drops rapidly to approximately 1.5 V followed by a small slop at 1.5–1.1 V and a wide slop at 1.1–0.8 V. The two slopes are attributed to the insertion of lithium to α-Fe₂O₃ as discussed in the CV results. The extended plateau at 0.8 V is ascribed to the reduction of Fe²⁺ to Fe⁰ [14]. The first discharge capacity is 1336 mAh g⁻¹, which is higher than the theoretical value of Fe₂O₃ (1005 mAh g⁻¹). The excess capacity is probably owing to the formation of a solid electrolyte interphase (SEI) layer because of decomposition of electrolyte on the Fe₂O₃ surface (generally below 0.8 V vs Li⁺/Li) [10]. In the following cycles, the lithium intercalation/de-intercalation voltage shifts higher than the first cycles.

Fig. 4 depicts the charge/discharge (rate = 0.2 C) capacity and Coulombic efficiency versus cycle number plots, providing a direct evidence of the excellent lithium storage performance. Despite the low value of 70% in the first cycle due to the decomposition of electrolyte, the Coulombic efficiency increases quickly in the following cycles (ca. 96% for cycles 7–50). The reversible capacity for the first cycle is 934 mAh g⁻¹, and for the 50th cycle is 840 mAh g⁻¹ with retention of 90%. This remarkable enhancement of electrochemical properties can be assigned to the hollow structure and the nanoscale particles in the shell of the sphere. The porous hollow sphere allows complete penetration of the electrolyte, while the nanoscale particles afford short diffusion length of lithium ions and accommodation of volume change during charging/discharging process.

4. CONCLUSIONS

In summary, hollow spheres with nanoscale α-Fe₂O₃ particles in the porous shell have been successfully synthesized and applied into lithium-ion batteries. Electrochemical measurements of the sample show high capacity and excellent cycle stability. A large capacity of 840 mAh g⁻¹ and an appealing capacity retention rate of 90% are accomplished after 50 cycles. This indicates the hollow Fe₂O₃ spheres material is an attractive candidate anode material for future lithium-ion battery.

5. ACKNOWLEDGEMENTS

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