

cient [40], when the electrode material is charged and discharged at lower rates, the diffusion time (τ) is longer than that at higher rates, which leads to the higher specific capacity. Meanwhile, the longer diffusion time (τ) can also inevitably cause the volume change of the electrode materials and the structure degradation. Therefore, the discharge capacity is fading fast with the increase of the cycle numbers. However, in the case of charging and discharging at higher rates, the Li^+ insertion/extraction just occurs near the surface of the electrode material and thus the Li^+ diffusion distance is much shorter, this induces the increase of kinetics performance and maintains the structure stable. Although the capacity is lower, the cycling stability of the electrode material is much better than that at lower rates. The rates and average reversible capacities at different rates are presented in Table S1. It can be seen that the average reversible capacities are 1064, 875, 771, 678, 568, and 379 mA h/g at the rates of 0.1 (step 1), 0.2 (step 2), 1 (step 3), 2 (step 4), 5 (step 5), and 10 C (step 6), respectively, which evidently demonstrates that the $\text{Fe}_3\text{O}_4/\text{C}$ nanospheres display superior capacity retention at higher rates. Even at a high rate of 10 C (9240 mA/g at step 6), charging/discharging finished within 6 min still gave a average reversible capacity to be 379 mA h/g, equivalent to about 35.6% of capacity using 0.1 C (step 1). Upon returning to 0.1 C (step 7), stable capacity of 870 mA h/g was resumed and negligible capacity loss was observed after another 10 cycles. Overall, this electrode retained about 82.1% of the capacity over 100 cycles. Such remarkable high-rate performance, high specific capacity and cycling stability at high charge/discharge rates are higher than in previously reported work on $\text{Fe}_3\text{O}_4/\text{carbon}$ composites [9–24].

TEM techniques were employed to examine the morphology evolution of the $\text{Fe}_3\text{O}_4/\text{C}$ anode under the severe volume expansion and contraction during lithium insertion/extraction. Fig. S2 shows the TEM images of the $\text{Fe}_3\text{O}_4/\text{C}$ anode after 100 charge/discharge cycles for rate performance test in Fig. 5(d). Compared with Fig. 3, the morphology of the $\text{Fe}_3\text{O}_4/\text{C}$ after 100 charge/discharge cycles was similar to that of the pristine one. Moreover, TEM images in Fig. S2(c) and (d) show that the carbon layer and the core-shell structure still maintained after charge/discharge cycling, and the thickness of the carbon layer was similar to that of before cycling. The similar morphology indicates that the $\text{Fe}_3\text{O}_4/\text{C}$ anodes can effectively decrease substantial aggregation and cracking upon cycling. In particular, thin carbon layer has good elasticity to effectively accommodate the mechanical stress caused by the large volume change of Fe_3O_4 during the charge–discharge process [10–14].

As shown in the results presented above, our $\text{Fe}_3\text{O}_4/\text{C}$ electrode displays superior electrochemical performance and structural stability. These outstanding properties arise from the structure advantages of the nanospheres: the nanosized Fe_3O_4 nanocrystals (~ 9 nm) encapsulated in interconnected conductive carbon nanospheres (~ 60 nm) not only endow large quantity of accessible active sites for lithium ion insertion but also good conductivity and short diffusion length for lithium ion transport, which are beneficial for high capacity and rate capability. Meanwhile, the interconnected carbon layer is a self-supporting framework, which can not only effectively inhibit the aggregation of Fe_3O_4 nanoparticles as well as simultaneously circumvent the severe volume expansion/contraction associated with lithium insertion/extraction, but also maintain structural integrity of the electrode during charge-dis-

charge process, which are favorable to high capacity as well as cycling stability. As a consequence, their original morphology in terms of shape, size, and structural integrity can be well preserved after being charged/discharged over 100 cycles (Fig. S2). Benefit from the enhanced structural stability and integrity and excellent kinetics for lithium ion and charge transport, the lithium storage properties of our $\text{Fe}_3\text{O}_4/\text{C}$ nanospheres are thus remarkably improved.

4. Conclusions

We have successfully synthesized homogeneous and small Fe_3O_4 nanocrystals (~ 9 nm) encapsulated in interconnected carbon nanospheres (~ 60 nm) for a high-rate LIB anode by an easy one-step hydrothermal process followed by annealing in argon atmosphere. The small size of the Fe_3O_4 nanocrystals in the nanospheres allows for fast lithium ion diffusion and the interconnected structure of the carbon nanospheres can effectively circumvent the severe volume expansion/contraction associated with lithium insertion/extraction and maintain structural integrity of the electrode during charge–discharge process. Therefore, this unique structure demonstrates high reversible capacity (784 mA h/g at 1 C, 1 C = 924 mA/g), high Coulombic efficiency ($\sim 99\%$), excellent cycling stability and superior rate capacities of 568 mA h/g at 5 C and 379 mA h/g at 10 C. Both the source materials (glucose and iron nitrate) and the preparation processes used in this work are cost-effective and easy to scale up. Therefore, it has a good potential to be used for large scale applications. Furthermore, the approach reported in this work is also applicable to other metal oxide nanocrystals encapsulated in interconnected carbon nanospheres, which may find important applications as electrodes, catalysts, adsorbents, and sensors in many scientific disciplines.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2013.01.056>.

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