A hollow Fe₃O₄-based nanocomposite anode for lithium-ion batteries with outstanding cycling performance

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Abstract. The fabrication of hybrid electrodes with conversion-type electrode materials has drawn growing interest in improving the capacity performance of lithium-ion batteries (LIBs) for many high-energy applications. However, as a typical conversion-type electrode material, Fe₃O₄ is usually restricted by large amount of volume change during repeated lithiation/delithiation course, which dramatically hinders the cycling stability of the constructed LIBs. We design a hybrid electrode of Fe₃O₄ nanospheres with a hollow structure wrapped by MnO₂ nanosheets (H-Fe₃O₄/MnO₂ NSs nanospheres). As a result of the synergetic effect of a high-capacity material coating and a robust hollow core, the H-Fe₃O₄/MnO₂ NS hybrid electrode delivers reversible capacity as high as 590 mAh g⁻¹ at a current rate of 0.1 C and maintains 92% of the initial reversible capacity after 1000 cycles at 1 C.

Keywords. Hollow Fe₃O₄; MnO₂; core-shell; hybrid electrode; lithium-ion battery.

1. Introduction

There has been a steady ever-increasing demand for rechargeable lithium-ion batteries (LIBs) with superb capacity and long lifespan in various high-energy applications, ranging from portable electronics to electric vehicles [1–5]. Considering that conventional carbon-based anode materials store energy stemming from classical intercalation reactions, a further capacity increase is difficult to achieve due to the limitation of intrinsic theoretical value [6,7], and thus, tremendous efforts have been made to exploit various conversion-type electrode materials to substitute the carbon materials, such as NiO, SnO₂, Fe₃O₄ and MnO₂ [8–13]. Among them, Fe₃O₄ is regarded as one of the most promising candidates of anode materials for LIBs by virtue of its relatively good electric conductivity of $2 \times 10^4 \text{ S m}^{-1}$ and theoretical capacity of 924 mAh g⁻¹, reacting with as many as eight Li ions per Fe₃O₄ unit [14–16]. However, during the lithiation/delithiation process, a huge volume change of ~200% for Fe₃O₄ dramatically hinders its widespread applications [17]. To be specific, LIBs assembled with the Fe₃O₄-based anode usually display a high initial capacity, but fade rapidly in a few cycles [17–19]. This phenomenon undoubtedly stems from the large volumetric expansion/shrinkage during lithiation/delithiation course which makes Fe₃O₄ to pulverize and delaminate from the current collector, leading to the degradation of mechanical and electrochemical performances of electrodes [20,21]. To relieve the large volume expansion of Fe₃O₄ nanostructures, numerous trials have been conducted, such as reducing the dimension, introducing a robust

coating, etc. [22]. Among them, constructing nanospheres with a hollow structure is considered as an effective method. The interior void of Fe₃O₄ can amortize the volume change and avoid the pulverization of nanospheres, which ensures the structural integrity and retains good cycling stability of the anode. In an effort to further raise the capacity, we wrapped the hollow Fe₃O₄ nanospheres with high-capacity MnO₂ nanosheets, thus constructing a hybrid anode with core/shell structure. MnO₂ nanosheets can contribute to high capacity caused by their sufficient active sites, which can provide short ion diffusion paths and facilitate fast Li⁺ intercalation/extraction.

In this study, we demonstrate a hybrid electrode design of MnO₂ nanosheets wrapped hollow Fe₃O₄ nanospheres (H-Fe₃O₄/MnO₂ NSs nanospheres). The whole synthesis approach is a facile template-free hydrothermal method. Benefiting from the hollow structure of Fe₃O₄ and MnO₂ coating layer, the well-designed H-Fe₃O₄/MnO₂ hybrid electrode exhibits a high reversible capacity of 590 mAh g⁻¹ at a current rate of 0.1 C and retains 92% reversible capacity relative to the initial reversible capacity after 1000 cycles at 1 C.

2. Experimental

2.1 Synthesis of hierarchical H-Fe₃O₄/MnO₂ core/shell nanospheres

Fe₃O₄ nanospheres with a hollow structure were fabricated by a facile and economical hydrothermal method. Specifically,

1.0 g polyvinylpyrrolidone, 5 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 30 mmol NaAc were successively added to 40 ml ethylene glycol with vigorous stirring. After sequentially stirring for 15 min, the mixture was transferred to a 50 ml Teflon-lined stainless-steel autoclave and allowed to react at 200°C for 10 h. After cooling naturally to room temperature, the relevant product was centrifuged at 12,000 rpm through ethanol and deionized water washings several times, and was completely dried at 60°C for 10 h. The as-synthesized hollow Fe_3O_4 nanospheres were added into 40 ml 0.03 M KMnO_4 solution. After ultrasonic dispersion for 20 min, the solution was heated in a Teflon-lined stainless-steel autoclave at 160°C for 5 h. Finally, the resulting sample was filtered, washed and dried at 60°C to generate $\text{H-Fe}_3\text{O}_4/\text{MnO}_2$ core/shell nanospheres.

2.2 Microstructure characterization

The microstructures of the as-obtained samples were characterized by field-emission scanning electron microscopy (FESEM, JSM-6700F, 15 keV) and transmission electron microscopy (TEM, JEM-2100F). X-ray diffraction (XRD) measurements were investigated on a D/max 2500pc diffractometer using $\text{CuK}\alpha$ radiation at a scan rate of 4°min^{-1} . Raman analysis was conducted using a Raman spectrometer (Renishaw) with a laser wavelength of 532 nm. The chemical compositions were revealed by an X-ray energy-dispersive spectroscope (EDS) attached to a scanning electron microscope (JSM-7100F). Further constitution information was obtained by an X-ray photoelectron spectrometer (XPS, VG Scientific ESCA-lab220i-XL) using $\text{AlK}\alpha$ radiation.

2.3 Lithium-ion battery assembly and electrochemical measurement

Coin-type cells were packaged in an argon-filled dry glove box (control H_2O and O_2 levels below 1 ppm) using a commercial Li foil as a cathode. The anode on a Cu foil substrate consisted of the active material ($\text{H-Fe}_3\text{O}_4/\text{MnO}_2$ nanospheres), carbon black (super-P) and polymer binder (polyvinylidene difluoride) in a weight proportion of 7:2:1. The loading mass of the active material for the electrodes is

about 0.541 mg cm^{-2} . The cathode and anode were separated by porous polymer film in an organic electrolyte (1 M LiPF_6 in ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate mixture with equal volume ratios). Cyclic voltammetry (CV) was recorded on an IVIUM electrochemical workstation in the voltage scale of 0.01–3.0 V (vs. Li^+/Li) at a scan rate of 0.2 mV s^{-1} at room temperature. The rate capability and cycling performance were carried out on a battery test system.

3. Results and discussion

3.1 Design and structure of $\text{H-Fe}_3\text{O}_4/\text{MnO}_2$ NSs anode

For the purpose of gaining high-performance energy storage in practical LIBs, it is crucial to rationally design nanostructured hybrid electrodes for tackling the intrinsic barriers of conversion-type electrode materials, i.e., large volumetric expansion in lithiation course. The hollow structure of Fe_3O_4 could adapt for the volume expansion/contraction during cycling and avoid the pulverization of nanospheres to maintain the integrated structure, and ultimately achieve good cycling stability of the anode. Furthermore, MnO_2 nanosheets wrapped outside the Fe_3O_4 nanospheres can show high capacity due to the sufficient active sites in contact with the electrolyte, which can provide short ion diffusion paths and facilitate the fast Li^+ intercalation/extraction. A facile and scalable fabrication process of the $\text{H-Fe}_3\text{O}_4/\text{MnO}_2$ NS hybrid electrode is illustrated in figure 1, which mainly involves two hydrothermal steps, the synthesis of hollow Fe_3O_4 and MnO_2 coating layer.

Figure 2a and b shows typical FESEM images of the hollow Fe_3O_4 nanospheres, demonstrating that $\text{H-Fe}_3\text{O}_4$ nanospheres were synthesized in a large scale with a uniform diameter of $\sim 198 \text{ nm}$, which obeys the standardized normal distribution as shown in the inset of figure 2a. The inset TEM image displays the hollow structure of the Fe_3O_4 nanosphere. Figure 2c shows that MnO_2 nanosheets uniformly wrap on the external surface of $\text{H-Fe}_3\text{O}_4$ nanospheres. The $\text{H-Fe}_3\text{O}_4/\text{MnO}_2$ core/shell nanospheres show a uniform diameter of $\sim 216 \text{ nm}$ (inset of figure 2c). Figure 2d displays

Figure 1. Schematic illustration. The fabrication process of $\text{H-Fe}_3\text{O}_4/\text{MnO}_2$ NSs.

Figure 2. Morphology characterization. (a) Low magnitude FESEM image of H-Fe₃O₄ NSs. Inset: size distribution of the H-Fe₃O₄ NSs. High-magnitude FESEM images of H-Fe₃O₄ NSs (b) before and (c) after MnO₂ coating. Inset: TEM image of H-Fe₃O₄ and size distribution of H-Fe₃O₄/MnO₂ NSs. (d) TEM image of H-Fe₃O₄/MnO₂ NSs.

a detailed TEM image of H-Fe₃O₄/MnO₂ core/shell nanospheres, from which we can see that the coating of MnO₂ is uniform and integrated and the thickness of the MnO₂ shell can be measured as ~ 9 nm. The uniform and integrated coating of MnO₂ is advantageous to the electrochemical performance.

XRD patterns were analysed to characterize the structures of H-Fe₃O₄ and H-Fe₃O₄/MnO₂ NS hybrid electrodes. As shown in figure 3a, eight obvious diffraction peaks of (111), (220), (311), (222), (400), (422), (511) and (440) can be well-fit to the magnetic cubic structure of Fe₃O₄ (JCPDS 19-0629) [18,19,23]. After coating with MnO₂, the additional XRD peaks at $2\theta = 12.6$ and 25.2° correspond to the (001) and (002) reflections of layered crystalline birnessite (δ -MnO₂) (JCPDS 80-1098), which has a two-dimensional lamellar structure with an interlayer spacing of ~ 7 Å, containing abundant water and stabilized hydrated alkali cations distributed in the layers of MnO₆ octahedra [24–26]. By virtue of offering a more complete and reliable

reflection of poorly crystalline components, Raman scattering spectroscopy was performed to probe the local structure at a very low excitation power of 0.1 mW. Raman spectrum for the as-prepared H-Fe₃O₄ nanospheres in the wavelength range of 100–1000 cm⁻¹ is dominated by four peaks located at 665, 524, 350 and 192 cm⁻¹, respectively, as shown in figure 3b. The peaks can be assigned to A_{1g}, T_{2g}, E_g and T_{2g} modes of Fe₃O₄, respectively [27]. By comparison, Raman spectrum of H-Fe₃O₄/MnO₂ NS electrode shows an extra distinct band at 574 cm⁻¹ and a weak band at 629 cm⁻¹, which originate from the layer-structured birnessite-type MnO₂ nanoshell [28]. The peak at 573 cm⁻¹ can be assigned to the $\nu(\text{Mn}-\text{O})$ stretching vibration with F_{2g} symmetry modes in the MnO₆ group, and the peak at 629 cm⁻¹ is usually attributed to the intrinsic vibrational frequency in the presence of Mn⁴⁺ ions. Thus, the spectrum of H-Fe₃O₄/MnO₂ NSs includes characteristic peaks of Fe₃O₄ and MnO₂, revealing the presence of both components. The chemical compositions of H-Fe₃O₄/MnO₂ NS electrode were examined by EDS.

Figure 3. Composition analysis. (a) XRD patterns of H-Fe₃O₄ and H-Fe₃O₄/MnO₂ NSs. (b) Raman spectra of the H-Fe₃O₄ and H-Fe₃O₄/MnO₂ NSs. (c) EDS spectrum of the H-Fe₃O₄/MnO₂ NSs. Inset: table of the element composition.

The EDS spectrum of the H-Fe₃O₄/MnO₂ NS electrode in figure 3c reveals that the molar proportion of Fe to Mn is $\sim 2.77:1$, which is in accordance with the composition of H-Fe₃O₄/MnO₂ NSs.

To further explore the chemical states of H-Fe₃O₄/MnO₂ NSs, XPS results are analysed in figure 4. The survey scan XPS of the as-prepared sample is displayed in figure 4a, demonstrating the existence of element iron, manganese and oxygen. Figure 4b reveals the core level binding energy of Fe 2p peaks, in which two distinct peaks with the binding energy of 710.9 and 724.7 eV could be assigned to Fe 2p_{3/2} and Fe 2p_{1/2} in the Fe₃O₄, respectively [29,30]. Moreover, nonexistence of the charge transferred satellite peak of Fe 2p_{3/2} at 720 eV manifesting the formation of a blended oxide of Fe(II) and Fe(III) [31]. Figure 4c shows the high resolution spectrum of Mn 2p, exhibiting two dominant peaks at the binding energy of 654.3 and 642.5 eV with a spin energy separation of 11.8 eV, which conformed well with Mn 2p_{3/2} and Mn 2p_{1/2} for MnO₂ in the literature [32,33]. The appropriate O 1s spectrum is displayed in figure 4d. The characteristic peak is wide and asymmetric, which can be dissolved into three peaks based on Gaussian and Lorentzian functions. The peak located at the binding energy of 529.7 eV is ascribed to lattice oxygen of the metal oxide bonding. Peaks at 531.6 and 532.2 eV are assigned to defective oxides with hydroxide bonding and absorbed oxygen species, such as H₂O and CO₂ molecules, respectively [34].

3.2 Electrochemical properties of the H-Fe₃O₄/MnO₂ NSs hybrid electrode

The anode electrochemical behaviour of the as-obtained H-Fe₃O₄/MnO₂ NSs for LIBs was investigated by CV and galvanostatic charge/discharge cycling in classic two-electrode coin-type cells. Figure 5a reveals the first four typical CV curves of the anode in the scale of 0.01 and 3.0 V (vs. Li⁺/Li) at a scanning rate of 0.2 mV s⁻¹. For the first discharge scan, H-Fe₃O₄/MnO₂ anode shows three well-defined cathodic peaks at 1.50, 0.70 and 0.29 V, which is quite distinct from

that of the following cycles possessing only two peaks at 0.70 and 0.29 V. The cathodic peak at 1.50 V is related to the generation of a solid electrolyte interphase (SEI) layer on electrode surface and the absence of this peak from the second discharge cycle infers that the generation of SEI only occurs during the first cycle, which benefits from the presence of the static δ -MnO₂ interface with the electrolyte, possessing the capability to fully adapt to the volume change of Fe₃O₄ in the lithiation/delithiation course so that it does not break the shell structure and contact with the electrolyte. The peak at 0.70 V in the first discharge scan is attributed to the lithiation of Fe₃O₄, i.e., $\text{Fe}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow 3\text{Fe}^0 + 4\text{Li}_2\text{O}$ [24,25,27], while the one at 0.29 V can be assigned to the reductions of MnO₂ to Mn⁰, $\text{MnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Mn}^0 + 2\text{Li}_2\text{O}$ [35]. Notably, the CV curves from the second cycle are almost coinciding, proving excellent reversible phase transformation and cycle stability of the core/shell H-Fe₃O₄/MnO₂ NS hybrid electrode [35]. The galvanostatic charge/discharge profile of this core/shell H-Fe₃O₄/MnO₂ anode was performed in the voltage scale of 0.01–3.0 V at a current rate of 0.1 C as given in figure 5b. The first discharge and charge section exhibit specific capacity values of 1657 and 723 mAh g⁻¹, respectively, with a columbic efficiency of 43.6% and reaches 86.9% in the subsequent cycles. For clarity, all the capacity values in the figure were computed based on the total mass of electrochemically active core/shell H-Fe₃O₄/MnO₂ NSs. Remarkably, the larger value than the theoretical capacity of MnO₂ (1230 mAh g⁻¹) and Fe₃O₄ (924 mAh g⁻¹) in our calculation could be attributed to the decomposition of electrolyte at a low voltage in the generation of SEI layer, which dedicated extra lithium storage at the metal/Li₂O interface [14,15,35,36]. However, the generation of SEI and the decomposition of electrolyte also cause irreversible capacity loss, resulting in the relatively low initial columbic efficiency, which are usual for most anode materials [37–40]. Moreover, this feature also fits well to the CV results for the discharge voltage plateaus at 1.50 V in the first cycle, absent afterwards, further revealing that irreversible reactions occurred during the first cycle. Rate capability of H-Fe₃O₄/MnO₂ NS

Figure 4. XPS analysis. (a) Typical XPS survey spectrum for as-prepared H-Fe₃O₄/MnO₂ NSs. (b) High-resolution XPS spectrum of Fe 2p. (c) High-resolution XPS spectrum of Mn 2p. (d) High-resolution XPS spectrum of O 1s.

anode at different current rates (increased from 0.1 to 32C) is demonstrated in figure 5c. The discharge capacity of the H-Fe₃O₄/MnO₂ anode reaches 590 mAh g⁻¹ at a low current rate of 0.1C and still maintains 118 mAh g⁻¹ at the extremely high discharge rate of 32C. Furthermore, when the current rate returns to the initial value of 0.1C, the discharge capacity can return to the initial or even higher value because of the activation process [41]. To demonstrate the contribution of the capacity from support material of Cu foil, LIB based on bare Cu foil is also assembled and tested under the same conditions. The inset in figure 5c shows that at the current rate of 0.1C, the areal discharge capacity from the Cu substrate is 0.0091 mAh cm⁻², accounting for only 2.8% of the total areal capacity of H-Fe₃O₄/MnO₂ NSs. Even when the current rate increases to 32C, the contribution from Cu is <9.8%. Figure 5d demonstrates the cycling performance of the H-Fe₃O₄/MnO₂ NS anode at a current rate of 1C in the voltage scale of 0.01–3.0V. During the whole process, outstanding cycling capability of H-Fe₃O₄/MnO₂ anode is observed, delivering high discharge capacity of 257 mAh g⁻¹

after 1000 cycles, which is ~92% of the initial reversible capacity. The gradual increase of discharge capacity is mainly attributed to the activation of the Fe₃O₄/MnO₂ electrode, in addition to the formation of reversible polymeric gelatinous SEI layer due to the electrolyte degradation, which can be commonly seen in other metal oxide materials [42–44]. Besides, the coulombic efficiency dramatically rises from 81.5% of the initial cycle to 96% of subsequent cycles, indicating a facile lithiation/delithiation process correlative to efficient ion/electron transportation in the electrode. The outstanding cycling performance in H-Fe₃O₄/MnO₂ NS electrode arises from the hollow structure of Fe₃O₄, as well as the presence of the δ -MnO₂ coating, which can not only elevate the cell specific capacity, but also improve superiorly the cycling stability.

The well-performed H-Fe₃O₄/MnO₂ NS hybrid electrode can be attributed to the hollow structure of Fe₃O₄ and presence of δ -MnO₂ coating. First, the Fe₃O₄ nanosphere core can offer not only a large surface area and high capacity, but also tremendous robust backbone with relatively good

Figure 5. Electrochemical performance of H-Fe₃O₄/MnO₂ NS anode. **(a)** Representative CV curves of H-Fe₃O₄/MnO₂ NS anode acquired at a voltage scope of 0.01–3.0 V (vs. Li⁺/Li) and voltage scan rate of 0.2 mV s⁻¹. **(b)** Voltage–time profile of the first four cycles at a voltage range of 0.01–3.0 V (vs. Li⁺/Li) and current density of 0.1 C. **(c)** Charge/discharge capacity at various current densities range from 0.1 to 32 C. Inset: comparison of areal discharge capacities for H-Fe₃O₄/MnO₂ NSs with Cu substrate. **(d)** Cycling performance of H-Fe₃O₄/MnO₂ NS anode at a current rate of 1 C.

electronic conductivity for the MnO₂ shell. Second, the hollow structure of Fe₃O₄ can relieve the volume change and circumvent the pulverization of nanospheres and the integrated structure could benefit good cycling stability of the anode. Third, high capacity could primarily contribute to MnO₂ nanosheets with sufficient active sites, providing short ion diffusion paths and facilitating fast Li⁺ intercalation/extraction.

4. Conclusions

In summary, we have successfully designed and synthesized a hybrid electrode of MnO₂ wrapped H-Fe₃O₄/MnO₂ NSs as anode for LIBs. The hollow structure of Fe₃O₄ can relieve the volume change in repeated charge/discharge course and circumvent the pulverization problem of the nanospheres, which endows excellent cycling performance. The MnO₂ coating layer can supply sufficient active sites for contact with electrolyte, shorten ion diffusion paths and facilitate fast Li⁺ intercalation/extraction. As a consequence of the

rational design, H-Fe₃O₄/MnO₂ NS hybrid electrode exhibits exceptional electrochemical performances in a quite wide current rate span (0.1–32 C), exhibiting a high reversible capacity of 590 mAh g⁻¹ at 0.1 C and maintains ~92% of the initial reversible capacity after 1000 cycles at 1 C (lasting for more than a 83-day period and only 0.008% loss per cycle). Although the specific capacity achieved by the H-Fe₃O₄-based hybrid anode (590 mAh g⁻¹) is slightly lower than the theoretical value of 924 mAh g⁻¹ for the dominant material Fe₃O₄, the low-cost and superb performance (including rate and cycling) endow it to be qualified to fulfil the need of rechargeable LIBs in various applications. The novel design concept of transition metal oxide wrapped hollow structure can shed light on the utilization of conversion-type electrode materials in next-generation LIBs.

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