Multi-walled carbon nanotubes composited with nanomagnetite for anodes in lithium ion batteries

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In this work, multi-walled carbon nanotube (MWNT) nanocomposites with homogenously anchored nanomagnetite of 10–20 nm prepared by a hydrothermal-annealing method have been demonstrated to serve as anode materials for lithium ion batteries (LIBs) with a specific capacity of 829 mA h g\(^{-1}\) after 50 cycles at a current density of 100 mA g\(^{-1}\) and a reversible capacity of 686 mA h g\(^{-1}\) at a current density of 200 mA g\(^{-1}\) for the nanocomposites with a weight ratio of 1 : 1, much larger than the specific capacity of 230 mA h g\(^{-1}\) after 50 cycles at a current density of 100 mA g\(^{-1}\) and a reversible capacity of 195 mA h g\(^{-1}\) at a current density of 200 mA g\(^{-1}\) for the MWNTs. The MWNTs in the nanocomposites could efficiently buffer the strain of volume change during lithiation/delithiation and greatly improve the electrical conductivity of the electrodes. The superior electrochemical performances of the Fe\(_3\)O\(_4\)/MWNTs were found to originate from the unique conductive network of the MWNTs in the nanocomposites as well as the high capacity from the nanomagnetite.

1. Introduction

Lithium ion batteries (LIBs) are becoming the most widely used energy resource in portable electronic devices due to their high energy density, fast charge-discharge rate, and excellent cycling performance. However, commercial graphene anode materials normally have low theoretical capacity (372 mA h g\(^{-1}\)), which severely limits the application of LIBs in electric vehicles and hybrid electric vehicles. Great efforts have been made to explore anode materials with high reversible capacity for LIBs. Recently, transition metal oxides, including Co\(_3\)O\(_4\), Fe\(_3\)O\(_4\), NiO, CuO, Mn\(_2\)O\(_3\), Cr\(_2\)O\(_3\), etc. have drawn growing attention to serve as anode materials due to their high theoretical capacity based on a unique conversion reaction with the formation of Li\(_2\)O during the discharge/charge processes. Among the aforementioned transition metal oxides, Fe\(_3\)O\(_4\) has been regarded as one of the most promising anode materials for LIBs owing to its high theoretical specific capacity (925 mA h g\(^{-1}\)), natural abundance and environmental benignity. However, similar to other metal oxides, Fe\(_3\)O\(_4\) anode materials suffer from poor cycling performance due to large volume shrinkage/expand during the charge/discharge processes, and low rate performance arising from the kinetic limitations, which severely restrict their applications. Generally, anode materials with high specific capacity tend to sustain considerable amount of volume changes during the lithiation/delithiation processes, which result in pulverization of the active materials and disintegration of electrode. Attempts have been made to deal with the volume change to improve the cycling performance of metal oxide anodes, such as minimizing the particle size or incorporating inert buffers to alleviate the fracture and pulverization of the electrode. Carbon nanotubes (CNTs) have attracted wide attentions as additives in constructing hybrid nanocomposites due to their superior electrical conductivity, high surface-to-volume ratio, ultrathin walls, and structural flexibility. Their large specific surface area ensures high contact area between electrolyte and electrode, and the ultrathin walls shorten the Li-ion diffusion distance. In addition, CNTs can be well connected to form unique conductive networks to provide continuous conductive pathways for electron transport. The CNTs can serve as not only conducting materials, but also an excellent inert confining buffer to accommodate the strain of volume change during the rapid charge/discharge processes. Therefore, enhanced electrode performance can be achieved through the application of these unique electrode structures by incorporating transition metal oxides with CNTs. The combination of conductive network of CNTs and high capacity of Fe\(_3\)O\(_4\) nanoparticles is a promising way to make anode materials with excellent electrode performance. The Fe\(_3\)O\(_4\)/CNTs nanocomposites have...
some potential applications in biomedicine, magnetic data storage, supercapacitor and fuel cell. For example, He et al. reported a method using polyvinyl alcohol (PVA) as a hydrogen bond functionalizing agent to modify CNTs to synthesize CNTs/Fe3O4 nanocomposites (656 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$) applied as anode materials for LIBs. Guo et al. synthesized Fe3O4–CNTs nanocomposites (702 mA h g$^{-1}$ at a current density of 50 mA g$^{-1}$ after 50 cycles) for application in LIBs by using Sn(OH)$_6^{2-}$ as inorganic dispersant. However, the electrode performances of Fe3O4/CNTs nanocomposites prepared by these methods need to be improved greatly to meet the demand of higher capacity and faster charge–discharge rate for current LIBs with larger scope of application.

In this paper, a novel hydrothermal method in methanol–glycerol solvent followed by an annealing process in argon atmosphere was used to prepare Fe3O4/multi-walled carbon nanotubes (MWNTs) nanocomposites. The X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM) are used to characterize the structure and morphologies of the obtained Fe3O4/MWNTs nanocomposites. X-ray photoelectron spectroscopy (XPS) is carried out to determine the elemental composition. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are used for weight percentage determination and thermal property investigation. The electrochemical performances of the prepared Fe3O4/MWNTs nanocomposites as anode materials for LIBs are evaluated by cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) measurement techniques.

2. Experimental

2.1. Materials

Iron chloride hexahydrate (FeCl$_3$·6H$_2$O), sodium hydroxide (NaOH), methanol (CH$_3$OH), glycerol (C$_3$H$_8$O$_3$), PVDF (C$_5$H$_9$NO, 99.0%), N-methyl-2-pyrrolidone (NMP) and concentrated nitric acid (65–68%) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. The MWNTs (20–50 nm in diameter) were purchased from Shenzhen Nanotech Port Co., Ltd, China. Carbon black, Li foil and Celgard 2300 were purchased from Hefei Kejing Material Technology Co., Ltd, China. LiPF$_6$ (dissolved in ethylene carbonate, dimethyl carbonate, and ethylene methyl carbonate with a volume ratio of 1 : 1 : 1) was purchased from Shenzhen Biyuan Technology Co., Ltd, China. All the chemicals were analytical grades and used as received without any further purification.

2.2. Preparation of acid-treated MWNTs

The purchased MWNTs were treated in concentrated nitric acid (65–68%) at 140 °C for 6 hours in a Teflon-lined stainless steel autoclave. After that, the acid-treated MWNTs were centrifuged and washed with deionized water and ethanol until the pH value of filtrate was around 7, then dried in vacuum for 24 hours.

2.3. Synthesis of Fe$_3$O$_4$/MWNTs nanocomposites with different weight ratios

The Fe$_3$O$_4$/MWNTs nanocomposites were synthesized as follows. The acid-treated MWNTs (0.1 g) were dispersed in a mixed solution of glycerol (10 mL) and methanol (15 mL) at room temperature for one-hour sonication, in which 0.4 g FeCl$_3$·6H$_2$O was dissolved under the magnetic stirring for 30 min. 25 mL 0.5 mol L$^{-1}$ NaOH methanol solution was slowly added into the above solution and stirred for additional 30 min. After that, the solution was sealed in a Teflon-lined stainless autoclave and maintained at 200 °C for 12 h. After reaction, the product was centrifuged and washed with methanol for 5 times. The obtained powders were dried in vacuum at 60 °C for 12 h. In order to obtain highly crystallized structure of Fe$_3$O$_4$ nanoparticles, the black product was treated at 500 °C for 2 h under argon atmosphere with a heating rate of 2 °C min$^{-1}$ in a quartz tube furnace. The weight ratio of Fe$_3$O$_4$ and MWNTs in these nanocomposites was estimated to be 1 : 1 (indexed as Fe$_3$O$_4$–MWNTs (1 : 1)). The Fe$_3$O$_4$/MWNTs nanocomposites with a Fe$_3$O$_4$–MWNTs weight ratio of 1 : 3 were prepared following the same procedures for comparison (indexed as Fe$_3$O$_4$–MWNTs (1 : 3)).

2.4. Characterizations

The crystal structure of the obtained products was determined by a Rigaku D/Max-RC X-ray diffractometer with Ni filtered Cu Kα radiation ($\lambda = 0.1542$ nm, $V = 40$ kV, $I = 50$ mA) in the range of 10–90° at a scanning rate of 4 °C min$^{-1}$. The morphology and microstructure of the products were observed by a JSM-6700F field emission scanning electron microscopy (SEM, accelerating voltage of 20 kV and electric current of 1.0 $\times$ 10$^{-10}$ A), and a JEOL JEM-2100 transmission electron microscopy (TEM, accelerating voltage of 200 kV). X-ray photoelectron spectroscopy (XPS) was recorded by a Kratos Analytical spectrometer using Al Kα ($\hbar\nu = 1486.6$ eV) radiation as the excitation source under an anode voltage of 12 kV and an emission current of 10 mA. To evaluate the content of MWNTs in the nanocomposites, TGA measurements were performed on a SDT thermal-microbalance apparatus from room temperature (about 20 °C) to 800 °C in air condition at a heating rate of 10 °C min$^{-1}$.

2.5. Electrochemical measurements

The anode electrodes were prepared as follows. Briefly, the active material, carbon black, and polyvinylidene fluoride (PVDF) were mixed at a weight ratio of 8 : 1 : 1 in N-methyl-2-pyrrolidinone (NMP) to form homogenous slurry. Then the slurry was deposited onto a copper foil substrate by the doctor-blade process followed by drying in vacuum at 120 °C for 12 h. And then the circular electrodes were punched out with a diameter of 14 mm. The CR2025-type cells were assembled using Li foil as counter and reference electrode, Celgard 2300 as separator, and 1.0 M LiPF$_6$ (dissolved in ethylene carbonate, dimethyl carbonate, and ethylene methyl carbonate with a volume ratio of 1 : 1 : 1) as the
electrolyte. The assembly was performed in an argon filled glove-box.

The galvanostatic charge–discharge cycles were recorded in a voltage range of 0.02 to 3 V at various current densities on a LAND CT2001A battery test system (Wuhan Lanhe Co., Ltd). The CV experiment was performed on an IviumStat electrochemistry work station with a scanning rate of 0.3 mV s$^{-1}$ and the potential vs. Li/Li$^+$ ranging from 0.01 to 3 V. The EIS was tested on the same instrument with an AC signal amplitude of 10 mV in a frequency range from 100 kHz to 0.01 Hz. The data were adopted to draw Nyquist plots using real part $Z$ as X-axis, and imaginary part $Z''$ as Y-axis.

3. Results and discussions

3.1. Characterizations of Fe$_3$O$_4$/MWNTs nanocomposites

Fig. 1 shows the XRD patterns of pure MWNTs and the as-prepared nanocomposites. Pure MWNTs are observed to display a broad diffraction peak centered at $2\theta = 22^\circ$, indicating the existence of amorphous carbon. The sharp peak at $26^\circ$ corresponds to the (0 0 2) plane of CNTs with layered and hexagonal structure. The XRD patterns of the nanocomposites correspond to the diffraction peaks of carbon ($2\theta = 26^\circ$) and Fe$_3$O$_4$ with spinel structure based on JCPDS file card no. 65-3107, indicating the prepared iron oxide is Fe$_3$O$_4$. The strong and sharp peaks of Fe$_3$O$_4$ suggest a high crystallinity of the as-prepared Fe$_3$O$_4$ nanoparticles. The peak intensity of carbon ($2\theta = 26^\circ$) in the Fe$_3$O$_4$–MWNTs (1 : 3) nanocomposites is much stronger than that in the Fe$_3$O$_4$–MWNTs (1 : 1) nanocomposites, which is in well agreement with the higher weight ratio of MWNTs in the Fe$_3$O$_4$–MWNTs (1 : 3).

Fig. 2a–f show the SEM and TEM images of the samples. The surface of pure MWNTs is very smooth, Fig. 2a and b. Fig. 2c–f shows the SEM and TEM images of the Fe$_3$O$_4$–MWNTs (1 : 1). The TEM image of the Fe$_3$O$_4$–MWNTs (1 : 1) nanocomposites, Fig. 2d, clearly shows the presence of Fe$_3$O$_4$ nanoparticles on the surface of MWNTs. A uniform distribution of Fe$_3$O$_4$ nanoparticles with size of ca.10–20 nm is observed on the surface of MWNTs, Fig. 2e. The small size of nanoparticles can facilitate the ions diffusion and the conductive network of MWNTs can accommodate large volume change and improve the electrical conductivity of the nanocomposites. Fig. 2f is a high resolution TEM (HRTEM) image of the Fe$_3$O$_4$/MWNTs nanocomposites, clearly demonstrating the Fe$_3$O$_4$ nanoparticles and the wall of MWNTs. There exists a clear boundary between the Fe$_3$O$_4$ nanocrystals and the MWNTs. The lattice distance of 0.338 nm corresponds to the (0 0 2) plane of graphitic carbon. The measured lattice distance for the Fe$_3$O$_4$ nanoparticles is around 0.257 nm, corresponding to the (3 1 1) plane of Fe$_3$O$_4$. The observed clear lattice fringe of Fe$_3$O$_4$ nanoparticles indicates a high crystalline structure of the as-prepared Fe$_3$O$_4$ nanoparticles.

The elemental composition of Fe$_3$O$_4$–MWNTs (1 : 1) was further investigated using XPS. The observed peaks of Fe$2p$, O$1s$, C$1s$ in the survey scan XPS spectrum, Fig. 3a, indicate the existence of Fe, O and C elements in the as-prepared Fe$_3$O$_4$/MWNTs nanocomposites. Deconvolution of the C$1s$ peak in the high resolution XPS spectrum, Fig. 3b, reveals three types of carbon bonds: C–C (284.6 eV), C–O–Fe (285.4 eV), and C=O (286.1 eV). The formation of C–O–Fe bond indicates the intimate attachment of the Fe$_3$O$_4$ nanoparticles on the walls of MWNTs. In the Fe$2p$ spectrum (Fig. 3c), the peaks at 710.2 and 723.8 eV correspond to Fe$2p_{3/2}$ and Fe$2p_{1/2}$, respectively, which are in agreement with the XPS of Fe$_3$O$_4$ in the previous report. The O$1s$ spectrum (Fig. 3d) can be deconvoluted into three peaks, indicating three different oxygen species existed. The peak at 529.9 eV is due to the O–Fe of Fe$_3$O$_4$. The peak at
532.0 eV can be attributed to the C–O bonds due to the surface oxidation of the MWNTs. The peak at 533.3 eV is assigned to the OH groups, arising from the moisture absorbed on the surface of the nanocomposites. The bond formation between MWNTs and Fe₃O₄ nanoparticles can not only accelerate the electron transfer but also stabilize the structure of nanocomposites during the charge/discharge process. According to the above analysis, the proposed formation mechanism of the prepared Fe₃O₄/MWNTs nanocomposites is given in Fig. 4.

To evaluate the content of MWNTs in the Fe₃O₄/MWNTs nanocomposites, TGA measurements were carried out in air up to 800 °C. The weight loss of 3.07 and 4.69% occurred separately in the Fe₃O₄–MWNTs (1 : 1) nanocomposites, Fig. 5a and Fe₃O₄–MWNTs (1 : 3) nanocomposites, Fig. 5b, between 20 and 170 °C, corresponding to the evaporation of water absorbed on the sample surface, which is consistent with the analysis of XPS. From 350 to 600 °C, the observed sharp exothermic peak, along with the intensive weight loss of 49.19% in the Fe₃O₄–MWNTs (1 : 1) nanocomposites and the weight loss of 77.02% in the Fe₃O₄–MWNTs (1 : 3) nanocomposites are attributed to the degradation of MWNTs. After 600 °C, no observed apparent exothermal peak or weight loss suggests the complete oxidation of the nanocomposites. The TGA results confirm that the MWNTs contents in the samples are in perfect accordance with the predetermined values before preparation.

3.2. Electrochemical performances of Fe₃O₄/MWNTs nanocomposites

The electrochemical performances of the prepared Fe₃O₄/MWNTs nanocomposites for LIBs were evaluated by galvanostatic charge–discharge, CV and EIS. Fig. 6a shows the selected discharge/charge voltage profiles of the Fe₃O₄–MWNTs (1 : 1) nanocomposite electrode between 0.01 and 3 V at a current density of 100 mA g⁻¹. There is a short voltage plateau around 1.0 V in the first discharge curve (Fig. 6a), corresponding the decomposition of electrolyte and the formation of solid electrolyte interphase (SEI) layer. The voltage decrease to 0.75 V refers to the formation of LiₓFe₃O₄, and the voltage plateau at 0.75 V suggests the reduction of Fe³⁺ and Fe²⁺ to Fe⁰ and the formation of amorphous Li₂O. With the voltage drop to 0.02 V, the first discharge cycle delivers a total capacity of 1184 mA h g⁻¹, much higher than the theoretical capacity of...
Fe$_3$O$_4$ (925 mA h g$^{-1}$). The first charge profile shows a slope from 1.5 to 2.0 V, suggesting the oxidation of Fe$^0$ to Fe$^{2+}$ and Fe$^{3+}$. The electrode exhibits a higher irreversible capacity in the first cycle, attributed to the formation of the SEI, the insertion of lithium-ions into the MWNTs, and the irreversible reaction of lithium-ions with Fe$_3$O$_4$ nanoparticles.

The CV profiles for the initial three cycles of the Fe$_3$O$_4$–MWNTs (1 : 1) nanocomposites are shown in Fig. 6b. The observed peaks at 0.6 and 0.9 V in the first cathodic process are ascribed to the lithiation reaction of Fe$_3$O$_4$ to Li$_x$Fe$_3$O$_4$ and Li$_x$Fe$_3$O$_4$/Fe$^0$ + Li$_2$O, electrolyte decomposition and SEI formation, respectively. The peak at 0.9 V disappears in the subsequent cycles, in accordance with the aforementioned irreversible process. Meanwhile, two peaks at about 1.7 and 1.8 V in the anodic curve correspond to the oxidation of Fe$^0$ to Fe$^{2+}$ and Fe$^{3+}$ during the anodic process.

From the second cycle, both the cathodic peaks and the anodic peaks shift to higher potential positions, consistent with the results obtained from their discharge and charge curves. Similar peak shift towards high voltage has also been observed in other transition metal oxides, due to the polarization of active material in the first cycle.

There are no large position shift and intensity change for the main peaks in the 2nd and 3rd scans, indicating a good electrochemical reversibility of the Fe$_3$O$_4$/MWNTs electrode.

The electrochemical performances of the Fe$_3$O$_4$–MWNTs (1 : 3) nanocomposites and pure MWNTs electrode were also investigated under the same electrochemical conditions for comparison. Fig. 7a shows the cyclic performance of different electrodes at a current density of 100 mA g$^{-1}$. The Fe$_3$O$_4$–MWNTs (1 : 1) and Fe$_3$O$_4$–MWNTs (1 : 3) nanocomposite electrodes exhibit an initial specific capacity of 1184 and 782 mA h g$^{-1}$, which are stabilized to 829 mA h g$^{-1}$ and 584 mA h g$^{-1}$ after 50 cycles, respectively. It is observed that a stable reversible capacity of 230 mA h g$^{-1}$ is observed for the pure MWNTs electrode within the cycling tests. These results demonstrate that the Fe$_3$O$_4$–MWNTs (1 : 1) nanocomposite electrode shows a better cycling performance than the Fe$_3$O$_4$–MWNTs (1 : 3) nanocomposite electrode. Theoretically, the capacity in these Fe$_3$O$_4$–MWNTs nanocomposites is mainly contributed by Fe$_3$O$_4$ due to the aforementioned low capacity of the MWNTs. The theoretical capacity can be estimated to be 648.5 mA h g$^{-1}$ for the Fe$_3$O$_4$–MWNTs (1 : 1) and 510.3 mA h g$^{-1}$ for the Fe$_3$O$_4$–MWNTs (1 : 3). Obviously, the obtained capacity is consistent with the theoretical expectations.

Fig. 7b shows the rate performances of the electrodes. The Fe$_3$O$_4$–MWNTs (1 : 3) nanocomposite electrode possesses a reversible capacity of 439, 414, 371, 280, 196 and 131 mA h g$^{-1}$ at a current density of 100, 200, 400, 800, 1600 and 3200 mA g$^{-1}$, respectively. The Fe$_3$O$_4$–MWNTs (1 : 1) nanocomposite electrode markedly delivers higher reversible capacity of 714, 686, 624, 541, 408 and 294 mA h g$^{-1}$ at the corresponding current densities, Fig. 7b. These results indicate that the Fe$_3$O$_4$–MWNTs (1 : 1) nanocomposite electrode demonstrates the best electrode performance among these three electrodes. It is noticed that
when the current density returns to 100 mA g⁻¹ after the rate performance test, the discharge capacities of the Fe₃O₄–MWNTs (1 : 1) and Fe₃O₄–MWNTs (1 : 3) nanocomposites are 803 and 502 mA h g⁻¹, respectively, higher than those obtained at an initial density of 100 mA g⁻¹. Similar phenomena have also been found in other anode materials, which were ascribed to the formation of polymer/gel-like films due to the decomposition of electrolyte driven by the active metal nanoparticles. It also indicates that the integrity of the structure and the electrical contact are well maintained in the electrodes even under high charge/discharge rates. The fascinating electrochemical performance may originate from the unique architecture of the nanocomposites as well as the contribution of high capacity from the Fe₃O₄ nanoparticles. The electrode performance of the as-prepared Fe₃O₄/MWNTs nanocomposites is better than those of the reported CNTs–66.7 wt% Fe₃O₄ nanocomposite (636 mA h g⁻¹ at a current density of 100 mA g⁻¹) synthesized through a method using polyvinyl alcohol (PVA) as a hydrogen bond functionalizing agent to modify multi-walled carbon nanotubes and the reported 2 : 1 Fe₃O₄–CNTs electrode (702 mA h g⁻¹ at a current density of 50 mA g⁻¹ after 50 cycles) prepared by an inorganic dispersant assisted hydrothermal synthesis.

To further investigate the electrochemical performances of the Fe₃O₄/MWNTs nanocomposites, EIS measurements, which were conducted on the samples fully-charged with an electrode potential of 3 V after 100 cycles at a current density of 100 mA g⁻¹, are shown in Fig. 8. The Nyquist plot of each sample is comprised of arc in the high-frequency region and the medium-frequency region, and an inclined line in the low frequency region. The diameter of the semicircle is in direct proportion to the impedance, which contains electrolyte resistance (Rₑ), surface film resistance (Rₐf) and charge transfer resistance (Rₑt). The inclined line is assigned to the lithium-ion diffusion process inside the electrode materials corresponding to the Warburg impedance. The impedance spectra can be fitted based on a reasonable equivalent circuit (inset of Fig. 8), in accordance with the physical mechanism of the Li-ion insertion/extraction for the electrodes. The fitted curves are in accord with the experimental data.

Fig. 7 (A) Cycling discharge performance for (a) Fe₃O₄–MWNTs (1 : 1), (c) Fe₃O₄–MWNTs (1 : 3) and (e) MWNTs, and charge performance for (b) Fe₃O₄–MWNTs (1 : 1), (d) Fe₃O₄–MWNTs (1 : 3) and (f) MWNTs at the current density of 100 mA g⁻¹. (B) Rate discharge performance for (a) Fe₃O₄–MWNTs (1 : 1), (c) Fe₃O₄–MWNTs (1 : 3) and (e) MWNTs and charge performance for (b) Fe₃O₄–MWNTs (1 : 1), (d) Fe₃O₄–MWNTs (1 : 3) and (f) MWNTs.

Fig. 8 The experimental Nyquist plots of (a) the MWNTs, (c) Fe₃O₄–MWNTs (1 : 3) and (e) Fe₃O₄–MWNTs (1 : 1). The fitted Nyquist plots of (b) the MWNTs, (d) Fe₃O₄–MWNTs (1 : 3) and (f) Fe₃O₄–MWNTs (1 : 1). The inset is the corresponding equivalent circuit.
nanocomposites and accommodates the large volume changes during the lithiation/delithiation processes; (2) the structure of well-dispersed Fe_{3}O_{4} nanoparticles anchored on MWNTs effectively prevents the aggregation of Fe_{3}O_{4} nanoparticles; (3) the small size of Fe_{3}O_{4} nanoparticles (ca. 10–20 nm) and the thin walls of MWNTs facilitate the ions diffusion in the electrode and increase the contact surface between the active materials and electrolyte; and (4) the good contact between Fe_{3}O_{4} nanoparticles and MWNTs has stabilized the structure of the nanocomposites during the charge/discharge process.

4. Conclusions

Uniform distribution of Fe_{3}O_{4} nanoparticles homogeneously anchored on MWNTs were fabricated by a novel hydrothermal method in methanol–glycerol solvent followed by an annealing process in argon atmosphere. The Fe_{3}O_{4}/MWNTs nanocomposites exhibited superior cycling performance (829 mA h g^{-1} after 50 cycles at a current density of 100 mA g^{-1}) and rate performance (686, 624, 451, 408, and 294 mA h g^{-1} at 200, 400, 800, 1600, and 3200 mA g^{-1}, respectively). The fascinating electrochemical performances originate from the network of MWNTs in the nanocomposites as well as the high capacity from nano-sized Fe_{3}O_{4} particles. The incorporation of the conductive MWNTs with transition metal oxides is proved to be a promising way to make anode materials with superior electrode performance.

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