RAPID COMMUNICATION

Hierarchical mesoporous urchin-like \( \text{Mn}_3\text{O}_4 / \) carbon microspheres with highly enhanced lithium battery performance by in-situ carbonization of new lamellar manganese alkoxide (Mn-DEG)

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Received 20 October 2014; received in revised form 20 January 2015; accepted 26 January 2015
Available online 4 February 2015

KEYWORDS
Lamellar manganese alkoxide;
Carbonization;
Hierarchically porous \( \text{Mn}_3\text{O}_4 / \) carbon microspheres;
Anode materials;
Li battery

Abstract
Two types of hierarchical mesoporous urchin-like \( \text{Mn}_3\text{O}_4 / \) carbon microspheres (HM-MO/C-MS) have been prepared via the in situ carbonization of the newly synthesized lamellar manganese alkoxide (Mn-DEG) along with the crystallization of \( \text{Mn}_3\text{O}_4 \) in air (MO-A) and nitrogen (MO-N), respectively. Such unique HM-MO/C-MS with high surface area provides obvious advantages including a large contact area with electrolyte, a short transport path for \( \text{Li}^+ \) ions, a low resistance for charge transfer, and a superior structural stability. When used as an anode material for lithium ion batteries in the voltage range of 0.01 – 3 V, the HM-MO/C-MS obtained in nitrogen (MO-N) exhibits high lithium storage capacity (915 mA h g\textsuperscript{-1} at 100 mA g\textsuperscript{-1} for 50 cycles), great cycling stability (94.5% capacity retention versus the second cycle) and excellent rate capability (510 mA h g\textsuperscript{-1} at 1000 mA g\textsuperscript{-1}). In particular, when cycling at a high current density of 1500 mA g\textsuperscript{-1}, the reversible capacity of the MO-N sample can still be maintained as high as 480 mA h g\textsuperscript{-1} with a high capacity retention of 93.7% after 200 cycles. Even in a narrower voltage range of 0.01-1.5 V, the lithium storage capacity of the MO-N sample can

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http://dx.doi.org/10.1016/j.nanoen.2015.01.040
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reach 556 mA h g\(^{-1}\) at 100 mA g\(^{-1}\) with a very good cycling stability (over 91% capacity retention from the second cycle) and have an excellent rate capability of 269 mA h g\(^{-1}\) at 1000 mA g\(^{-1}\). Both MO-N and MO-A samples present a very high volumetric capacity of 741.2 mA h cm\(^{-3}\) and 647.4 mA h cm\(^{-3}\) at 100 mA g\(^{-1}\), respectively. Such high performances both in the voltage ranges of 0.01-3 V and 0.01-1.5 V are among the highest reported. Ex-situ SEM images showed clearly the excellent morphological and structural stability of our materials. The results demonstrate that the unique hierarchical mesoporous microspheres/carbon structure is favorable for improving the cyclability and rate capability in energy storage applications. Our effective synthesis strategy can be broadened to construct other mesoporous metal oxides/carbon composites for high-performance lithium ion batteries.

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Introduction

Lithium ion batteries (LIBs) are one of the most suitable candidates to satisfy the energy requirements and have been widely used in many portable electronic devices, such as mobile phones, laptops and cameras owing to their high energy and power densities and long cycle lifetime [1,2]. However, due to the relatively low capacity of 370 mA h g\(^{-1}\), low security, and poor cycling stability and rate capability, the commercial anode material of graphitic carbon could not meet the high power and energy density requirements of next-generation LIBs [3]. Transition metal oxides, since first reported by Tarascon and his co-workers [4], have attracted much more applications because of their extremely high reversible capacities and high energy densities.

Among the various transition metal oxides, manganese oxides (MnO [5,6], MnO\(_2\) [7,8], Mn\(_2\)O\(_3\) [9,10], Mn\(_3\)O\(_4\) [11,12]) have attracted considerable attention because of their excellent electrochemical properties. As one of the manganese oxides, hausmannite Mn\(_3\)O\(_4\) has high theoretical capacity, low toxicity, low price, thermal stability and natural abundance, which is a promising anode material for LIBs [13-15]. However, previous reports on Mn\(_3\)O\(_4\) have suggested that this pure material has poor lithiation activity due to its low electrical conductivity (10\(^{-7}\)–10\(^{-8}\) S cm\(^{-1}\)) and poor cycle stability [16]. To date, numerous strategies have been developed to solve these intrinsic drawbacks of Mn\(_3\)O\(_4\). An effective method is preparing nano-scaled materials with special morphologies to decrease the electrons and lithium ions diffusion length, which can improve the electroactivity and rate capability of electrode materials [17,18]. The second approach is constructing nanocomposites with a carbonaceous matrix to enhance the electrical conductivity, as well as buffer the volume expansion/contraction during the cycling process [19-22]. Another very significant strategy is designing hollow or porous micro/nanosstructures which can provide more active sites and suppress volume changes and resulting pulverization [13,23].

Nowadays, most of researches focus on only one of the above strategies to improve the electrochemical properties of Mn\(_3\)O\(_4\), there are few reports on the fabrication of hierarchical mesoporous Mn\(_3\)O\(_4\)/carbon materials combining the advantages of the three above effective strategies for LIBs. For such hierarchical mesoporous Mn\(_3\)O\(_4\)/carbon materials, the conductive carbon can provide electronic network that facilitates the charge transfer. The mesoporous Mn\(_3\)O\(_4\) with self-assembled three dimensional structures can further enhance the electrochemical kinetics, shorten the diffusion distance for lithium ions and accommodate the volume change during the cycling process [23,24]. Therefore, synthesis of hierarchical mesoporous Mn\(_3\)O\(_4\)/carbon composite for high performance LIBs is highly desirable. Generally, the mesoporous materials compositied with carbon have been synthesized via nanocasting method [25-28]. However, the complex process including multistep synthesis or using hard templates may increase preparation costs [29]. Therefore, it is of significance to develop a facile method for synthesizing mesoporous Mn\(_3\)O\(_4\)/carbon compositions [30]. To the best of our knowledge, a rational in situ synthesis of hierarchical mesoporous Mn\(_3\)O\(_4\)/carbon microspheres is not reported and remains largely unexplored.

In this work, a new type of lamellar manganese alkoxide (Mn-DEG) was first synthesized via a solution-phase reaction. Then two types of hierarchical mesoporous Mn\(_3\)O\(_4\)/carbon microspheres were obtained via the in situ carbonization of Mn-DEG under air or nitrogen atmosphere, respectively, as shown in Scheme 1a. The DEG is used as both solvent and structure-directing agent for Mn-DEG synthesis. Simultaneously, the DEG ligand in Mn-DEG acts as carbon sources to form the carbon scaffolds along with the crystallization of Mn\(_3\)O\(_4\). The novel HM-MO-N/C-MS material obtained in nitrogen demonstrates a high reversible capacity (915 mA h g\(^{-1}\) at 100 mA g\(^{-1}\)) and an excellent rate capability (510 mA h g\(^{-1}\) at a high current density of 1000 mA g\(^{-1}\)), which are related to the special hierarchical mesoporous microspheres/carbon structures.

Experimental sections

Material synthesis

All the reactants and solvents were analytical grade and used without any further purification. The preparation of the precursor manganese alkoxide (Mn-DEG) is very facile and depicted as followed: 0.004 mol of KMnO\(_4\) was dispersed in 80 mL diethylene glycol (DEG) and stirred for 30 min; subsequently, the brown solution was transferred into a thermostatic oil bath and heated to 230 °C with vigorous stirring for 3 h. The obtained brown precipitate was washed with ethanol repeatedly until the organic reagents were
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The working electrodes were fabricated by using the HM-MO/C-MS as the active materials, conductive carbon blacks (Super-P) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:10:10. The slurry was coated on a copper foil and dried in a vacuum oven at 120°C for 12 h. Electrochemical measurements were carried out via CR2025 coin type cell using lithium pellets as the counter electrode and the reference electrode, a 1 M solution of LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 w/w) as electrolyte. The cells were assembled in an argon-filled glove-box. Cyclic voltammetry (CV) measurements were carried out using a CHI 660D electrochemical workstation at a scanning rate of 0.2 mV s$^{-1}$. Galvanostatic charge/discharge cycling was studied in a potential range of 0.01-3 V and 0.01-1.5 V vs Li/Li$^+$ with a multichannel battery testing system (LAND CT2001A), respectively. Electrochemical impedance spectra (EIS) were measured with an electrochemical workstation (Autolab PGSTAT 302N) in the frequency range from 100 kHz to 10 mHz.

Results and discussion

Fig. 1a shows the X-ray diffraction (XRD) pattern of the Mn-DEG, which is similar to the XRD patterns of the previously reported Mn-Gly [31], Co-EG [32], Mn-EG [33]. The XRD results demonstrate that the Mn-DEG product could be formed and crystallized together with organic ligands in an alkaline environment under the solvothermal conditions [34]. The Mn-DEG sample exhibits a strong low-angle reflection (around 0.92 nm) related to interlayer spacing in lamellar structures, and basically, these structures are described as stacked metal-oxygen sheets separated by bonded alcololate anions [35,36]. According to Bragg equation, the interlamellar spacing is around 0.92 nm. FT-IR has also been used to further reveal the chemical composition and bonding situation of the Mn-DEG sample (Fig. 1b). The wide hump centered at 3288 cm$^{-1}$ is attributed to the O-H stretching vibration. The sharp band at 2835 cm$^{-1}$ is a characteristic of the C-H symmetric stretching vibration and the sharp and strong band located at 1458 cm$^{-1}$ is associated with the C-H asymmetric bending vibration. Apart from the above vibrations, all the bands located below 1300 cm$^{-1}$ are attributed to C-O stretching vibration, C-OH stretching vibration and manganese-O bond. The FT-IR investigation clearly reveals the bonding situation of the Mn-DEG amine and demonstrates that the DEG is alcoholhylized and coordinated with manganese ions. The crystal structure of Mn-DEG is illustrated in Scheme 1b, where the DEG anionic species are located in interlayer space, similar to another lamellar material Mn(OH)$_2$ with OH$^-$ locating in interlayer space [9].

The low magnification SEM image (Fig. 1c) shows that the Mn-DEG sample is consisted of well dispersed microspheres with a diameter of 600 nm-1 μm. The high-magnification SEM image of a single sphere displayed in Fig. 1d depicts an urchin-like microsphere composed of many radially orientated nanorods.
with a diameter of 40 nm. TEM image (Fig. 1e) further reveals that the microspheres are constructed from many radially orientated nanorods. HRTEM image (Fig. 1f) reveals the amorphous nature of the manganese-oxygen layer structure. The diffused ring of selected area electron diffraction (SAED) pattern in Fig. 1f inset confirms the amorphous nature of Mn-DEG layer structure.

The TGA and DSC curves of the Mn-DEG sample from 30 to 800 °C under air (5 °C/min) are shown in Fig. S1, which displays a very significant weight loss and a sharp DSC exothermic peak between 200 and 300 °C, corresponding to the decomposition of the DEG ligand. It is interesting to note that the TGA/DSC plot exhibits a small weight gain around 500 °C with a weak DSC exothermic peak, which can be associated with the phase transformation from Mn$_3$O$_4$ to Mn$_2$O$_3$ [31]. Therefore, the temperature of 400 °C was selected in this experiment to convert the Mn-DEG to Mn$_3$O$_4$/carbon composites. On one hand, such temperature can allow the conversion of the manganese compound only to Mn$_3$O$_4$. On the other hand, such temperature can ensure that there is still carbon left after the carbonization of the Mn-DEG in air.

Fig. 2a presents the XRD patterns of the products carbonized in air (MO-A) and in nitrogen (MO-N), respectively. All the reflections of the two samples are in good agreement with the standard pattern of the tetragonal Mn$_3$O$_4$ ((JCPDS card no. 80-0382). No other phases or impurities are detected in the patterns. In particular, the MO-N sample shows sharper and stronger diffraction peaks than the MO-A sample, indicating a better crystallization. Fig. S2 shows the FT-IR spectra of the MO-A and MO-N samples, from which no noticeable organic bonds can be observed comparing with the Mn-DEG sample, demonstrating that the DEG ligand has fully been carbonized during the heat-treating process.

Raman scattering can probe the vibrational modes of both crystalline and amorphous materials in the two samples, providing complementary structural information to diffraction. Fig. 2b shows the Raman spectra of the MO-A and MO-N samples, respectively. Both spectra exhibit minor peaks at
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Fig. 2 The characterizations of the MO-A and MO-N samples: (a) XRD patterns; (b) Raman spectra, showing peaks of both crystalline Mn$_3$O$_4$ and amorphous carbon; (c) TGA curves under air at a rate of 5 °C min$^{-1}$ from 30 to 800 °C; (d-g) elemental mapping image of the MO-A sample; (h-k) elemental mapping image of the MO-N sample.

Fig. 3 The SEM, TEM and HRTEM images of the MO-A (a-d) and MO-N (e-h) samples.
308, 360, 473 cm\(^{-1}\), and a dominant peak at 647 cm\(^{-1}\), which match well with previously reported spectra for crystalline Mn\(_3\)O\(_4\) [12,37], indicating the pure Mn\(_3\)O\(_4\) phase of the two samples. Additionally, a weak peak locating at around 1250 cm\(^{-1}\) should correspond to the \(A_{1g}\) vibration mode of the disordered carbon [5], indicating the presence of amorphous carbon in both samples.

TGA was further employed to determine the content of carbon in the MO-A and MO-N samples under air from 30 to 800 °C, respectively (Fig. 2c). Two weight-losses are observed. As for the MO-A sample, the first weight loss around 2.1 wt% before 250 °C corresponds to the free water and physically adsorbed water. The second weight loss around 2.6 wt% after 300 °C can be attributed to the successive combustion of amorphous carbon. As for the MO-N sample, the second weight loss corresponding to the combustion of amorphous carbon is around 5.9 wt%, higher than that of the MO-A sample. The high carbon content in the MO-N sample is attributed to the only carbonization of DEG ligand in nitrogen, while the low content in the MO-A sample is attributed to the partial carbonization of DEG ligand due to the accompanying combustion process in air. Additionally, both of the TGA plots exhibit a small weight gain around 500 °C, similar to the TGA plot in Fig. S1, which is associated with the phase transformation from Mn\(_2\)O\(_3\) to Mn\(_3\)O\(_4\) as mentioned above.

Fig. 2d-k presents the typical elemental mapping images of the MO-A and MO-N samples, suggesting that both of the samples are composed of Mn, O and C elements with homogeneous distribution among the whole products. EDS spectra in Fig. S3 further demonstrate that the MO-N sample contains higher carbon content than the MO-A sample, which is in good agreement with the above TG results.

The morphology and structure of the MO-A and MO-N samples were further confirmed by SEM and TEM characterizations (Fig. 3). After carbonization in air, the size and spherical structure of the MO-A microspheres are still well maintained (Fig. 3a and Fig. S4a and b). Due to the severe combustion of organic group inside the stacked manganese-oxygen layers in air, some of the spheres are broken. The general low magnification TEM image shows the average size of the MO-A sample is around 600 nm (Fig. 3b and Fig. S5a), which is consistent with the SEM images (Fig. S4a and b). Fig. 3c shows the HRTEM image of the MO-A sample taken from the tip of one nanorod, which displays that the nanorods are composed of many crystallites, indicating the polycrystalline structure of the MO-A sample. This reveals that the nanorods in the spheres have changed into interconnected nanoparticles, indicating the severe carbonization of DEG ligands along with the crystallization of Mn\(_3\)O\(_4\). The lattice fringes with a spacing of 0.491 nm corresponds to the (1 0 1) plane of Mn\(_3\)O\(_4\) (Fig. 3d). Compared with the MO-A sample, when carbonization in nitrogen, the size and spherical structure of the microspheres also remain unchanged, with an urchin-like morphology about 600 nm (Fig. 3e and Fig. S4c and d). Upon our intensive observations, there are no broken microspheres can be found in the MO-N sample, indicating a moderate carbonization of DEG in nitrogen than that in air. The TEM image in Fig. 3f demonstrates that the nanorods of the MO-N sample are very complete without granulation, indicating the carbonization of DEG ligands in nitrogen is more favorable for the structure conservation. Fig. 3g depicts the HRTEM image of the MO-N sample taken from one nanorod, directly displaying the single crystal nature of the nanorod. From this image, one can observe that some amorphous materials exist on the surface of the MO-N sample (the white curves areas), corresponding to the amorphous carbon from the carbonization of DEG (the enlarged TEM image shown in Fig. 5e). Although amorphous carbon can affect the HRTEM observations, the interplanar distances of 0.288 nm and 0.245 nm can still be observed from the lattice fringe (Fig. 3h), corresponding to the (0 2 0) plane and (2 0 2) plane of the Mn\(_3\)O\(_4\) tetragonal crystalline structure, respectively.

It has been reported that nanostructured materials can grow into self-assembled microstructures based on an oriented aggregation mechanism [38-41]. From the above SEM and TEM observations, the main formation process of the HM-MO/C-MS is illustrated in Scheme 1a. First, the Mn(II) could be easily formed in the solution via the redox reaction between KMnO\(_4\) and DEG (4MnO\(_2\) + C\(_8\)H\(_{16}\)O\(_3\) + 12H\(^+\) \rightarrow 4Mn\(^{2+}\) + 11H\(_2\)O\(_1\) + 4CO\(_2\)); then DEG can rapidly coordinate with Mn(II) to form Mn(DEG\(^2-\))\(_x\)(DEG\(^-\))\(_{2-x}\), similar to other metal alkoxides in previous work [31]. During the reaction process, numerous precursor nuclei form and grow into rod-like nanocrystals directed by DEG to form layered Mn-DEG nanorods. Finally, driven by minimization of the overall surface energy, these layered Mn-DEG nanorods self-aggregate and form urchin-like microspheres [39,42,43]. During the carbonization process, the mesoporous structure is directly in situ carbonized from the DEG ligand in lamellar Mn-DEG along with the crystallization of Mn\(_3\)O\(_4\).

Nitrogen adsorption-desorption analysis was carried out to study the as-prepared lamellar Mn-DEG, the MO-A and MO-N samples, respectively (Fig. 4). All three samples exhibit type IV \(N_2\) isotherms with type-H3 hysteresis loops, suggesting the presence of mesopores. The BET specific surface areas of the Mn-DEG, the MO-A and MO-N samples are measured to be about 179 m\(^2\) g\(^{-1}\), 105 m\(^2\) g\(^{-1}\) and 70 m\(^2\) g\(^{-1}\), respectively. The Mn-DEG sample demonstrates the highest BET surface area due to the amorphous structure. After carbonization, the lamellar Mn-DEG is transformed to Mn\(_3\)O\(_4\). Furthermore, the nanorods of the MO-A sample are composed of interconnected nanoparticles, largely contributing to the specific surface area; while the nanorods of the MO-N sample are kept unchanged and show single crystal structure, exhibiting lower specific surface area. The pore size distributions (Fig. 4b) calculated from adsorption branches visibly demonstrate the mesoporous structures of all the samples. As for Mn-DEG, the curve shows a narrow pore size distribution centering at 4.2 nm; after carbonization, the MO-A and MO-N deliver wider pore size distributions centering at 10.6 nm and 11.9 nm, respectively.

Although the Mn-DEG is a lamellar structure, most possibly, the lithium insertion mechanism should be a conversion reaction for manganese compounds as anode materials [3]. Our result indicates that the Mn-DEG delivers a very low specific capacity (77 mA h g\(^{-1}\) after 50 cycles) at a current density of 100 mA g\(^{-1}\) in the voltage range from 0.01 V to 3 V (Fig. 5f). Therefore, in the following text, we will only discuss the electrochemical properties of the MO-A and MO-N samples.

Fig. 5a represents the CV curves of the MO-A and MO-N electrodes conducted in the range of 3.0 and 0 V at a scan rate of 0.2 mV s\(^{-1}\). In the first cycle, there are one weak and broad cathodic peak locating at around 0.7 V for both
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Fig. 4 The nitrogen adsorption-desorption isotherms (a) and the corresponding pore size distribution curves (b) of the Mn-DEG, MO-A and MO-N samples, respectively.

samples, which are related to the decomposition of electrolyte and formation of solid electrolyte interphase (SEI) layer on the surface of the samples [19]. The intensive peaks in both samples appear in the low potential are assigned to the reduction of Mn$_3$O$_4$ into metallic Mn accompanying with Li$_2$O formation [24]. During the following anodic sweep, strong peaks at around 1.3 V in both samples can attribute to the oxidation of metallic manganese to Mn(II) and decomposition of Li$_2$O. In the second cycle, it is noticed that the reduction peaks of both samples are shifted to 0.25 V related to the reduction of Mn(II) to Mn(0), which is in good agreement with the CV analysis. The whole reaction can be depicted as Mn$_3$O$_4$ + 8 Li$^+$ + 8 e$^-$ → 3 Mn + 4 Li$_2$O. In the first charge curve, an apparent voltage plateau around 1.3 V can be observed for each sample, corresponding to the reversible oxidation of Mn(0) to MnO during the anodic process, which is consistent with CV test. An additional shoulder peak is observed when the two electrodes are charged above 2.2 V, which is the further oxidation of MnO to Mn$_3$O$_4$ [18]. It is notable that the first charge capacities of both samples are lower than the first discharge capacities. The large irreversible capacity decay of the first cycle is common for the transition metal oxides because of the formation of the SEI film and the irreversible phase transformation [45,46].

In the second charge curves, only one voltage plateau around 0.5 V can be observed, suggesting that the lithium reaction of the second cycle is easier, which is often the feature of a single phase reaction. While the tendency of the second charge profiles of both samples is very similar to the first ones, indicating the good reversibility after the first discharge.

Fig. 5c displays the cycling performance of the MO-A and MO-N samples at a current density of 100 mA g$^{-1}$ in the voltage range from 0.01 V to 3 V. After carbonization, the cycling performance of the MO-A and MO-N samples significantly improves. It can be found that the MO-N sample delivers a better cycling stability and a higher reversible specific capacity of around 915 mA h g$^{-1}$ after 50 cycles of discharge and recharge, close to the theoretical capacity of Mn$_3$O$_4$ (937 mA h g$^{-1}$). By comparison, the MO-A sample exhibits less stable cycling performance, with the specific capacity decreases rapidly to 600 mA h g$^{-1}$ and then gradually increases to 830 mA h g$^{-1}$ after 50 cycles. This special cycling behavior is usually observed for some transition metal oxides and can be attributed to the reversible growth of a polymeric gel-like film resulted from kinetically activated electrolyte degradation [47-49]. Additionally, the coulombic efficiency results (Fig. S8) demonstrate that the MO-N sample displays a high initial coulombic efficiency of about 66.5%. After the first cycle, the coulombic efficiency of the MO-N sample reaches to 95.6%, higher than that of the MO-A sample, and it remains steady at a value >96% after the second cycle. To calculate the volumetric capacities, the tap densities of the MO-A and MO-N samples were measured, as high as 0.78 g cm$^{-3}$ and 0.81 g cm$^{-3}$, respectively. The higher tap density of the MO-N sample may be ascribed to its lower BET surface area (70 m$^2$ g$^{-1}$ vs. 105 m$^2$ g$^{-1}$ of the MO-A sample). Herein, the reversible volumetric capacities of the MO-A and MO-N samples are calculated to be 647.4 mA h cm$^{-3}$ and 741.2 mA h cm$^{-3}$, respectively. Although the MO-A sample possesses higher BET specific surface area than the MO-N sample, the former exhibits poor cycling performance, which should be attributed to the more stable hierarchical framework of the MO-N sample that can bear repeated lithiation and delithiation reaction and the single crystalline nanorods that can facilitate the charge transfer on the electrode/electrolyte interface.

The rate capability of the MO-A and MO-N samples were also evaluated in the voltage range from 0.01 V to 3 V (Fig. 5d). For the MO-N sample, one can see the discharge
capacity approaches 980 mA h g⁻¹ at a current density of 50 mA g⁻¹ and then slightly decreases to 900, 810, 650 and 510 mA h g⁻¹ at the current densities of 100, 200, 500 and 1000 mA g⁻¹, respectively, demonstrating excellent rate capability. Even at a high current density of 1500 mA g⁻¹, the electrode can still deliver a high reversible capacity of 460 mA h g⁻¹ (50–59 cycles), which is still higher than the theoretical capacity of graphite (372 mA h g⁻¹). Moreover, at the high current density of 1500 mA g⁻¹, the MO-N sample shows superior cycling performance and when cycling for 200 cycles, the specific capacity can still maintain as high as 480 mA h g⁻¹, with high coulombic efficiency nearly 100%. Such superior rate performance of the MO-N sample is ascribed to the attractive structure of this material: hierarchical three dimensional frameworks, high porosity distribution and composited with conducted carbon, which is very important for high-power application. Compared with the MO-N sample, the MO-A sample also displays good rate capability (900, 700, 580, 430, 300 and 290 mA h g⁻¹ at the current densities of 50, 100, 200, 500, 1000 and 1500 mA g⁻¹, respectively) with lower capacity comparing with the MO-N sample at each rate.

Electrochemical impedance spectroscopy (EIS) measurements were also carried out to provide further information on the electrochemical kinetics of the MO-A and MO-N samples. Fig. 5 shows the Nyquist plots of the MO-A and MO-N samples over the frequency range from 100 kHz to 0.01 Hz at 100 mA g⁻¹. In general, the EIS curves display three main frequency regions: low, middle and high frequency regions, which correspond to resistance of the electrolyte, charge-transfer resistance and solid-state diffusion of Li ions, respectively. Apparently, in Fig. 5e, the charge-transfer resistance \( R_{ct} \) value of the MO-N sample is much lower than that of the MO-A sample, indicating that the charge-transfer process of MO-N on the electrode/electrolyte interface is more facile than that of MO-A. This can be attributed to the higher carbon content and single crystal nature of the MO-N, providing improved conductivity and enhanced reaction kinetics, thus leading to higher cycling stability and reversible capacity.

It can be found the main discharge/charge voltage plateaus of Mn₃O₄ electrodes are around 0.5 V and 1.2 V, respectively (Fig. 3b). From the realistic point of view on anode application, it should be interesting to study the electrochemical properties at a narrower voltage window of 0.01–1.5 V. Applying narrow voltage ensures the structural stability upon cycling but of course sacrifices capacity [50]. Fig. 6 shows that the initial discharge/charge specific capacities of the MO-A and MO-N samples are 1215/499 mA h g⁻¹ and 1175/556 mA h g⁻¹, with a very low coulombic efficiencies of 41% and 47.4%, respectively. The low coulombic efficiencies can be ascribed to the high first discharge capacity, which is tested from the open-circuit voltage (around 2.7 V) to 0.01 V. This discharge process contains the whole reduction reaction of Mn₃O₄ to Mn(0), as well as the formation of SEI film, resulting in a high consumption of Li in the first discharge. From the second cycle, the coulombic efficiencies reach a high level over 91% for both samples. The corresponding first and second charge/discharge profiles of the MO-A and MO-N samples are displayed in Fig. S9. Fig. 6a also demonstrates that the MO-N sample delivers a higher reversible
capacity (around 376 mA h g\(^{-1}\) after 50 cycles with 66.5% capacity retention vs. 2nd cycle) than that of the MO-A sample (around 327 mA h g\(^{-1}\) after 50 cycles with 64.5% capacity retention vs. 2nd cycle), consistent with the tendency of cycling performance in the voltage range of 0.01-3 V as shown in Fig. 5c. Furthermore, the rate capability of the MO-N sample is also better than that of the MO-A sample, as demonstrated in Fig. 6b. At 50, 100, 200, 500 and 1000 mA g\(^{-1}\), the specific capacities of the MO-A sample are 625, 436, 357, 285, 232 mA h g\(^{-1}\), while for the MO-N sample, the specific capacities can reach 648, 502, 417, 328, 269 mA h g\(^{-1}\), respectively, indicating the excellent rate capability of the two samples in the voltage range of 0.01-1.5 V.

In order to verify the structural stability of the MO-A and MO-N anode electrodes, the post-mortem SEM images after 50 discharge-charge cycles were explored, as shown in Fig. 7. It can be seen the uniformity and spherical morphology of both the MO-A (Fig. 7a and b) and MO-N (Fig. 7c and d) materials have no change after cycling for 50 cycles, indicating the good structural stability of both materials and their robustness for lithium storage application.

To the best of our knowledge, such high performances both in the voltage ranges of 0.01-3 V and 0.01-1.5 V are among the highest values obtained for the power performance of Mn\(_3\)O\(_4\) reported in the literature\([51]\), which are superior to those of the previously reported spongelike Mn\(_3\)O\(_4\) \([12]\), Mn\(_3\)O\(_4\) nano-
octahedra [14], mesoporous Mn$_3$O$_4$ nanosheets [24], Mn$_3$O$_4$ nanorods/carbon [22], Mn$_3$O$_4$ nanoparticles/graphene [20]. The excellent electrochemical properties can be attributed to the hierarchical mesoporous microspheres composed with carbon, as illustrated in Scheme 2. On one hand, the mesoporous nature of the HM-MO/C-MS facilitates good contact of the electrode with electrolyte and further promotes the transportation of lithium ions, which can effectively relieve the pulverization issues and improve the cycling performance and rate capability. On the other hand, the presence of carbon in the HM-MO/C-MS can effectively buffer the structural strain and volume changes in the anode during repeated electrochemical reactions and greatly enhances the conductivity of the electrode material. Furthermore, the MO-N sample constructed by single crystalline nanorods can provide more stable structure and better conductivity than the MO-A sample constructed by nanoparticles, resulting in better cycling performance and rate capability.

Conclusion

We have developed an in situ strategy to fabricate two types of hierarchical mesoporous Mn$_3$O$_4$/carbon microspheres, where the mesoporous structure is directly carbonized from the DEG ligand in Mn-DEG along with the crystallization of Mn$_3$O$_4$. This approach is novel and facile without any templates and expensive surfactants. Such unique hierarchical mesoporous with single crystalline structure of the MO-N sample provides large electrode-electrolyte contact area, short Li$^+$ ions transport path, low charge transfer resistance, and superior structural stability upon prolonged cycling, leading to, in the voltage range of 0.01-3 V, the high lithium storage capacity (915 mAh g$^{-1}$ at 100 mA g$^{-1}$), great cycling stability (94.5% capacity retention from the second cycle) and excellent rate capability (510 mAh g$^{-1}$ at 1000 mA g$^{-1}$). Even in a very narrower voltage range of 0.01-1.5 V, the lithium storage capacity of the MO-N sample can reach 556 mAh g$^{-1}$ at 100 mA g$^{-1}$ with a cycling stability (over 91% capacity retention from the second cycle) and have an excellent rate capability of 269 mAh g$^{-1}$ at 1000 mA g$^{-1}$. This kind of mesoporous microspheres structure and the effective strategy can be further applied to other metal oxides for high-performance energy storage devices.

Acknowledgements

This work is realized in the frame of a program for Changjiang Scholars and Innovative Research Team (IRT1169) of Chinese Ministry of Education. B. L. Su acknowledges the Chinese Central Government for an “Expert of the State” position in the Program of the “Thousand Talents”. Y. Li acknowledges Hubei Provincial Department of Education for the “Chutian Scholar” program. This work is also financially supported by the National Science Foundation for Young Scholars of China (nos. 51302204 and 21301133) and Self-determined and Innovative Research Funds of the SKL WUT (2013-ZD-6). We also thank J. L. Xie, X. Q. Liu and T. T. Luo for TEM analysis from Research and Test Center of Materials at Wuhan University of Technology.

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.nanoen.2015.01.040.

References

Hierarchical mesoporous urchin-like $\text{Mn}_3\text{O}_4$/carbon microspheres with highly enhanced lithium battery performance

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