Hierarchical MnCo$_2$O$_4$ nanosheet arrays/carbon cloths as integrated anodes for lithium-ion batteries with improved performance

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To solve the reduced output voltage caused by the high lithium redox potential of Co$_2$O$_4$ when applied as an anode material in full cells, an effective strategy is to partially replace Co by Mn to form MnCo$_2$O$_4$ without changing the original crystal structure. Herein, 3D hierarchical MnCo$_2$O$_4$ nanosheets arrays grown via a hydrothermal method on carbon cloths, as binder-free anodes for lithium-ion batteries, exhibit a high areal capacity of 3.0 mA h cm$^{-2}$ at a current density of 800 mA cm$^{-2}$, excellent cycling stability, good rate performances and a discharge voltage plateau of 0.25 V which is lower than that of their Co$_2$O$_4$ nanosheet counterparts. Due to the increased output voltage of the full cell induced by the introduction of Mn species with a lower lithium extraction potential, MnCo$_2$O$_4$ based full cells display higher or comparative capacity in a certain voltage range compared with Co$_2$O$_4$, while still retaining the excellent conductivity of Co$_2$O$_4$ electrodes. Our work here paves the way for the design of high performance full cells with Co-based oxide electrodes.

Introduction

In recent years a great deal of effort has been directed towards the design of rechargeable lithium-ion batteries due to their advantages such as high energy density, long lifespan and environmental benignity and their wide application as power sources for portable electronic devices.$^{1-5}$ A major research direction is the exploitation of anode materials with high reversible capacity, high rate performance and long cycle life.$^{6-9}$ Amongst the available materials, Co$_2$O$_4$ has received much attention because of its high theoretical capacity of 890 mA h g$^{-1}$. However, its high lithium redox potential would generate a high average voltage, thus leading to the reduced output voltage when applied as an anode material in full cells, which may have poor performances at a relatively high potential when tested in a certain potential range. Meanwhile, the high cost of the cobalt element also makes it not an ideal anode material in practical applications. Since manganese (Mn) is 20 times less expensive than cobalt, and is more abundant in nature and especially manganese-based oxides possess a lower operating voltage for lithium-ion batteries,$^{14-16}$ the introduction of Mn species into cobalt-based oxide electrodes may be an effective strategy to improve the performance of lithium-ion batteries, while still retaining the excellent conductivity of cobalt-based oxides.$^{17}$

Recently, many research studies have confirmed that complex oxides containing two or more types of metal ions show good electrochemical performances because of their synergetic effects during the charge–discharge process.$^{18-24}$ Therefore considering the advantages and disadvantages of both Co-based and Mn-based electrode materials, as well as MnCo$_2$O$_4$ possessing better performances than CoMn$_2$O$_4$ under the same conditions according to the previous reports,$^{17,20}$ we choose MnCo$_2$O$_4$ as the anode material, adopting the excellent half cell performances of Co$_2$O$_4$ and the high output voltage of Mn species. Studies have found that the electrochemical performances of MnCo$_2$O$_4$ such as reversible capacity, cyclic stability or rate performance are not very good.$^{25-28}$ Therefore the MnCo$_2$O$_4$ electrodes with excellent performances are now highly desirable. In addition MnCo$_2$O$_4$ has the same crystal structure, approximate lattice constant with Co$_2$O$_4$. Therefore, MnCo$_2$O$_4$ can be regarded as the partial replacement of Co by Mn in Co$_2$O$_4$. With simple cubic structure, MnCo$_2$O$_4$ can provide sufficient space for lithium-ion insertion.

In this work, considering the superior performances of the hierarchical structure and MnCo$_2$O$_4$ substrates in energy storage,$^{31-33}$ hierarchical MnCo$_2$O$_4$ nanosheet arrays were grown...
on a textile carbon cloth via a simple hydrothermal method. When applied as a binder-free anode, the material displayed a high capacity of 3.0 mAh cm\(^{-2}\) at a current density of 800 \(\mu\text{A cm}^{-2}\), excellent cycling stability, good rate performances and a discharge voltage plateau of 0.25 V which is lower than that of their Co\(_3\)O\(_4\) counterparts fabricated under the same conditions. The lower average voltage of MnCo\(_2\)O\(_4\) electrodes leads to an increased output voltage of full cells, which makes the full cells exhibit superior performances in a certain voltage range as well.

**Experimental section**

**Material synthesis**

All of the reagents were of analytical purity grade and were used without further purification. Before use, the commercially available textile carbon cloths were cut into desired sizes and treated with acetone, water and ethanol in sequence. In a typical process, 2 mmol Co(CH\(_3\)COO)\(_2\) and 1 mmol Mn(CH\(_3\)COO)\(_2\) were dissolved in 40 ml ethylene glycol to form a clear solution, and then the mixture and a piece of carbon cloth were put into a 60 ml Teflon-lined stainless steel autoclave at 200 °C for 6 h. After being cooled down to room temperature, the carbon cloths with the deposited samples were washed several times with ethanol and dried in air at 60 °C. The final products were obtained after calcination at 400 °C for 2 h in air. The Co\(_3\)O\(_4\)/carbon cloths were synthesized under the same conditions except that only Co(CH\(_3\)COO)\(_2\) was used instead of the mixture of Co(CH\(_3\)COO)\(_2\) and Mn(CH\(_3\)COO)\(_2\). The mass loading of the active material is calculated to be about 3 mg cm\(^{-2}\).

**Materials characterization**

The phase purity of the product was identified by using an X-ray diffractometer (X'Pert PRO, PANalytical B.V., The Netherlands) with radiation from a Cu target (K\(_\alpha\), \(\lambda = 0.15406\) nm). The morphology was characterized by using a scanning electron microscope (SEM, FEI Sirion 200 (10 kV)). XPS measurements were performed on a VG Multilab 2000 system with a monochromatic Al K\(_\alpha\) X-ray source.

**Cell assembly and electrochemical measurements**

The electrochemical performances of the electrode were measured by assembling CR2032 coin-type half cells consisting of lithium foil as the counter electrode and reference electrode, Celgard 2300 as the separator membrane, and 1 M LiPF\(_6\) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (v/v = 1 : 1) as the electrolyte, and the as-prepared cloths were directly used as working electrodes without any conductive agents or a polymeric binder. The coin-type full cells were fabricated with the commercial LiCoO\(_2\)/Al foil as the cathode, and the other conditions are the same as those used for the half cells. Cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. Cyclic voltammetry (CV) measurements were performed on an electrochemical station (CHI 760D, CH Instruments Inc., Shanghai) at different scanning rates. The galvanostatic discharge–charge measurements were carried out on a Land Battery Measurement System (Land, China) at different current densities with a voltage window of 0.01–3.00 V for the half cells and 1.8–4.00 V for the full cells. Electrochemical impedance spectroscopy (EIS) measurements were conducted on an electrochemical workstation in a frequency range from 0.1 Hz to 100 kHz.

**Results and discussion**

The compositions of the as-prepared products were studied by XRD, energy dispersive spectroscopy (EDS) and XPS. Fig. 1a shows the corresponding XRD pattern. All the peaks in this pattern can be indexed to face-centered-cubic (fcc) spinel MnCo\(_2\)O\(_4\) (JCPDS no. 1-1130) except for the peaks marked with “★”, coming from the carbon cloth. In order to eliminate the influence of the carbon cloth, the powers in the same reaction system were also checked by XRD and the corresponding XRD pattern is shown in Fig. S1,† where all the peaks can be indexed to pure spinel MnCo\(_2\)O\(_4\), further confirming the formation of the pure product. EDS microanalysis of the products is shown in Fig. 1b, displaying the compositions of Co, Mn and O elements with a Mn/Co ratio of approximately 1/2. In order to demonstrate the detailed valence states of Mn and Co, we also carried out the XPS (Fig. 1c and d) analysis. All of the binding energies were corrected for specimen charging by referring them to the C 1s peak (284.6 eV). By using a Gaussian fitting method, the Co 2p spectrum was best fitted considering two spin–orbit doublet characteristics of Co\(^{2+}\) and Co\(^{3+}\) and some shake-up satellites, while the Mn 2p spectrum features two main spin–orbit lines and little satellite structure could be observed. After refined fitting, the spectrum can be deconvoluted into four peaks. Fig. 1c and d display the fitting results, which clearly show the peak positions of the different valence states of Mn and Co. The results are in agreement with the previous reports about MnCo\(_2\)O\(_4\). Therefore it is reasonable that Mn exists as Mn\(^{2+}\) and Mn\(^{3+}\), meanwhile Co exists as Co\(^{2+}\) and Co\(^{3+}\). In conclusion, the solid-state redox couples of Mn\(^{2+}/\text{Mn}^{3+}\) and Co\(^{2+}/\text{Co}^{3+}\) are

![Fig. 1](image-url)
grown product at 400°C. Fig. 2a–c show the SEM images at different magnifications of the products after hydrothermal reaction, where uniform hierarchical nanosheet arrays were successfully grown on the entire carbon microfibers. Typical nanosheets are several micrometers in size and 100–200 nm in thickness. Fig. 2d–f show the SEM images of the products after calcination of the hydrothermally grown product at 400°C for 2 h in air. From these images, we can see that the hierarchical nanosheet array structures of the precursors were well preserved. The thickness of the nanosheets was reduced a little because of the calcination effects at high temperature.

To investigate the possible application of the as-grown MnCo2O4 nanostructures in lithium-ion batteries, we studied their corresponding electrochemical properties by the assembly of CR2032 coin cells by using the MnCo2O4/carbon cloths as binder-free anodes. It should be noted that the direct growth of well assembled nanosheet arrays on the carbon cloth ensures robust mechanical adhesion and good electrical contact with the current collector (carbon cloth) in such additive-free electrodes. The corresponding electrochemical performances of the MnCo2O4-based electrodes for lithium storage are shown in Fig. 3. Fig. 3a demonstrates the first five consecutive cyclic voltammogram (CV) curves of the electrode at a scanning rate of 0.5 mV s⁻¹ in the voltage window of 0.01–3.00 V. The first CV curve is obviously different from the following cycles and the following CV curves are almost overlapped from the second to the fifth cycle, presenting excellent reversible performances except for the irreversible reactivity in the first cycle. In the first cycle, as shown in Fig. 3a, there is an obvious reduction peak around 0.5 V, which can be assigned to reduction of the metallic cation to metallic Co and Mn. In the anodic scan, two of the oxidation peaks are observed at 1.5 V and 2.0 V, corresponding to the oxidation of the transition metal to the metallic cation, while the peak around 0.4 V is ascribed to the co-efficiency between the carbon cloth and the electrode material. During the following cycles, the reduction peak is moved to 0.75 V and the oxidation peaks are almost unaltered. The slight shift of the reduction peak to higher potential in the following cycles might be related to some activation process caused by the Li⁺ insertion in the first cycle, indicating the slightly easier reduction in the subsequent cycles.

The galvanostatic discharge–charge profiles for the 1st, 2nd, 30th and 60th cycles at a current density of 800 mA cm⁻² are shown in Fig. 3b. The initial charge and discharge capacities are 3.9 and 3.05 mA h cm⁻², corresponding to a coulombic efficiency of 78%. The irreversible capacity loss during the first cycle is likely to be due to the incomplete decomposition of Li₂O and the difficult dissolution of the SEI, similar to other reported results. The discharge capacities of the representative cycles except for the first cycle are almost around 3.0 mA h cm⁻², displaying little capacity loss. Fig. 3c shows the discharge–charge capacities versus the cycle number at a rate of 800 mA cm⁻², which clearly reveals that the capacity is slightly decreased, then slightly increased and at last stable around 3.0 mA h cm⁻² even after 60 cycles. In order to get rid of the influence of the carbon cloth, the pure carbon cloth based electrode was also analysed, exhibiting a capacity of 0.7 mA h cm⁻² under the same test conditions (Fig. S27). When coated with the electrode material, the carbon cloth has relatively little contact with the electrolyte. Therefore the substrate contributes little to the whole capacity, consistent with the results of Fig. 3b, suggesting that the main capacity can be ascribed to the voltage plateau. In addition, to the best of our knowledge the high areal capacity obtained from the MnCo2O4/carbon cloth electrode is much higher than that reported in previous studies about other materials or substrates, such as MnCo2O4 nanowire arrays on stainless steel foil (0.175 mA h cm⁻²) after 30 cycles at

Fig. 2 SEM images of the precursor (a–c) and the final nanosheet-assembled MnCo2O4/carbon cloth (d–f) at different magnifications.

Fig. 3 Electrochemical properties of the MnCo2O4/carbon cloth for lithium storage. (a) The first five consecutive CVs at a scanning rate of 0.5 mV s⁻¹. (b) 1st, 2nd, 30th and 60th charge–discharge curves. (c) Cycling performance at a current density of 800 μA cm⁻². (d) The impedance spectra after different cycles of discharge–charge at 200 μA cm⁻². (e) The galvanostatic charge–discharge curves at different current densities. (f) Rate performance at different current densities.
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In order to further reveal the transport kinetics, electrochemical impedance spectra were measured after different cycles of discharge and charge at 200 μA cm⁻² (Fig. 3d). The plots consist of a depressed semicircle in the high and middle frequency regions and a straight line in the low frequency region. The semicircle at high frequency can be assigned to the SEI film and the contact resistance ($R_{SEI}$), while that at middle frequency is attributed to the charge-transfer impedance at the electrode–electrolyte interface ($R_{ct}$). Small changes of $R_{SEI}$ and $R_{ct}$ have been shown from the plots, implying the reversible reactivity in the discharge–charge cycles. In addition, from the low frequency inclined line, the lithium-ion diffusion process is easier with the increasing cycle number, which is likely to be an activated process. Therefore, this fact again confirms the excellent reversible reactivity during the insertion/desertion of the lithium-ion in the assembled-nanostructure.

Since the rate capability is also an important parameter for lithium-ion batteries, we also investigate the rate performances of the MnCo₂O₄-based electrodes by charging–discharging at different rates ranging from 200–1600 μA cm⁻². From Fig. 3e and f, it can be seen that the capacity decreases from 3, 2.8, 2.25 to 2 mA h cm⁻² on increasing the rate from 200, 400, 800, to 1600 μA cm⁻². The capacity is then increased reversibly back to 3 mA h cm⁻² once the charge–discharge rate was set back to 200 μA cm⁻² again. The corresponding ratios of the charge–discharge capacity as well as the coulombic efficiency are almost approaching 100%, which can be concluded from the approximate capacity of charge and discharge, presenting the excellent battery performance. Based on the above results, it can be concluded that the MnCo₂O₄ with mixed valence states of Co and Mn is an excellent anode material.

Since Co₃O₄ has the same crystal structure and approximately the same lattice constant as that of MnCo₂O₄ and the only difference is the partial substitution of Co with the Mn cation, it is quite important to compare the electrochemical properties between Co₃O₄ and MnCo₂O₄. Hierarchical Co₃O₄ nanosheet arrays were first grown on a carbon cloth via a similar hydrothermal and annealing process. Fig. 4a shows the XRD pattern of the annealed sample, where all the peaks, except those marked with *asterisk* coming from the carbon cloth, can be indexed to pure spinel Co₃O₄ (JCPDS no. 42-1467). Fig. 4b and c show the SEM images of the products at different magnifications. Similar to the MnCo₂O₄ samples, the Co₃O₄ products also have the nanosheet morphology, which were grown uniformly on the whole carbon microfiber, forming a hierarchical structure. The electrochemical performances of the Co₃O₄/carbon cloth electrodes were also investigated by configuring them as CR2032 coin cells. The galvanostatic discharge–charge profiles for the 1st, 2nd, 30th and 60th cycles at a current density of 800 μA cm⁻² are shown in Fig. 4d. The initial charge and discharge capacities are 4.25 and 3.4 mA h cm⁻² presenting a coulombic efficiency of 80%. The discharge capacities of the representative cycles except for the first cycle are almost around 3.5 mA h cm⁻² with little capacity loss. Fig. 4e shows the discharge–charge capacities versus the cycle number at a rate of 800 μA cm⁻², which clearly reveals that the capacity is slightly increased and is then stable around 3.5 mA h cm⁻² even after 60 cycles. Fig. 4f shows that the capacity decreases from 3.5, 3, 2.7, 2.5 to 2 mA h cm⁻² on increasing the rate from 200, 400, 800, 1600 to 3200 μA cm⁻², and the capacity could be increased reversibly back to 3.5 mA h cm⁻² once the charge–discharge rate is set back to 200 μA cm⁻² again. The capacities remain stable almost at every current density.

In order to further investigate the MnCo₂O₄ performances, which could be considered as the partial replacement of Co by Mn in Co₃O₄, the first charge–discharge capacity versus voltage profiles are presented in Fig. 5a and b. Both of the two products have an obvious plateau, indicating the main capacity around the plateau voltage. However it is also evident that after the introduction of Mn species the voltage plateau becomes lower, whatever the current density, 200 or 800 μA cm⁻². In addition to the current density of 800 μA cm⁻² the voltage drops to a plateau at about 0.25 V. Meanwhile the capacities of MnCo₂O₄ are comparable to those of Co₃O₄, displaying only a slightly lower capacity. As it is well known that the Mn-based metal oxides have worse performance than the Co-based metal oxides due to their bad conductivity. Nonetheless here in our research the performances of MnCo₂O₄ are almost well compared to Co₃O₄. Considering the reduced average voltage of MnCo₂O₄ leading to an increased output voltage of a lithium-ion full cell, the full cells were also assembled with commercial LiCoO₂/Al foil as the cathode. The cycling performance of the commercial cathode is shown in Fig. S3† displaying a capacity of 2.5 mA h cm⁻² after 80 cycles at a current density of 800 μA cm⁻². The capacity versus voltage profiles of the full cells are shown in Fig. 5c and d displaying cathode-limited capacities. The results show that the capacities of MnCo₂O₄ are obviously higher than Co₃O₄ likely due to the fact that in the certain voltage window of 1.8–4.0 V MnCo₂O₄ has a slightly lower average voltage as well as higher

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**Fig. 4** The XRD pattern (a) and SEM images (b and c) at different magnifications of the Co₃O₄/carbon cloth. Electrochemical properties of the Co₃O₄ nanosheets for lithium storage: (d) 1st, 2nd, 30th and 60th charge–discharge curves. (e) Cycling performance at a current density of 800 μA cm⁻². (f) Rate performance at different current densities.
output voltage in full cells. The rate performances of the two material based electrodes again demonstrate the superior properties of MnCo$_2$O$_4$, as shown in Fig. 5e. The capacities are higher at almost all of the current densities. Besides, it was found that the capacities slowly decrease in the first several cycles; this may be due to the wasting of the cathode material in full cells before reversible cycling as well as the irreversible reaction in the first several cycles.

The corresponding coulombic efficiency plots (Fig. 5f) are almost 100% except for the first cycle. Evidently owing to the special crystal structure of MnCo$_2$O$_4$, the performances of full cells are better when compared to Co$_3$O$_4$.

Fig. 6a shows the unit cell consisting of O$^{2-}$ (yellow) and cations of +2 (red) and +3 (blue) for MnCo$_2$O$_4$ or Co$_3$O$_4$, presenting the mixed valence oxides that adopt the same spinel structure. Fig. 6b clearly displays the detailed structure which can be regarded as the O atoms with cubic closest packing and the cations of +2 and +3 respectively distributed over tetrahedral and octahedral stacking interstices. Therefore MnCo$_2$O$_4$ could have the same excellent electrochemical performances as Co$_3$O$_4$. In order to further investigate the kinetics of lithium ion insertion/extraction at the electrode–electrolyte interface and the rate of lithium diffusion in the film we performed the CV measurements at different scanning rates. As the sweep rate increases the cathodic and anodic peaks move to lower and higher potentials, which clearly reflects the kinetics of lithium insertion/extraction at the electrode–electrolyte interface and the rate of lithium diffusion in the film. Fig. 6c and d show the CV curves of the MnCo$_2$O$_4$ and Co$_3$O$_4$ electrodes at scan rates of 0.2–0.8 mV s$^{-1}$ in the voltage range of 0.01–3.0 V after 5th, 10th, 15th and 20th cycles. The slopes for peak 1 and peak 2 of MnCo$_2$O$_4$ are almost the same as those of the Co$_3$O$_4$, revealing that even with the introduction of Mn species with poor performance there was little influence on the lithium diffusion coefficient, resulting in an excellent electrochemical performance for lithium storage.

Conclusions

In summary, we have developed a facile strategy for the preparation of hierarchical MnCo$_2$O$_4$ nanosheet arrays/carbon cloths...
exhibiting high capacity, excellent cycling stability and good rate performances. Using the flexible cloth directly as the anode, we fabricated binder-free coin cells with a high areal capacity of 3.0 mAh cm⁻² at a current density of 800 µA cm⁻², which is only slightly lower than those of the Co₃O₄/carbon cloth fabricated by the same method. Considering the reduced average voltage as well as increased output voltage of a full cell induced by the introduction of Mn species with a lower lithium extraction potential, the full cells of MnCo₂O₄ have demonstrated a higher or comparable capacity to Co₃O₄ in the potential range of 1.8–4.0 V. The capacity versus voltage curves of both half and full cells confirmed the lower voltage plateau and superiority performances of MnCo₂O₄. In addition the crystal structures have been analyzed, exhibiting a small difference on partially replacing Co by Mn. Meanwhile the lithium-ion diffusion has not been affected by the introduction of Mn with poor conductivity demonstrating the excellent electrochemical performances of MnCo₂O₄. This facile method of fabricating transition metal oxides may hold promise in the synthesis of multiphasic oxides such as Co or Mn based materials with any ratio and partial replacement of Co by Mn paves the way for high full cell performances of Co-based oxides.

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Notes and references