A facile route to synthesize multiporous MnCo$_2$O$_4$ and CoMn$_2$O$_4$ spinel quasi-hollow spheres with improved lithium storage properties

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A facile and general way for the synthesis of porous and hollow complex oxides is highly desirable owing to their significant applications for energy storage and other fields. In this contribution, uniform Mn$_{0.33}$Co$_{0.67}$O$_3$ and Co$_{0.33}$Mn$_{0.67}$O$_3$ microspheres are firstly fabricated solvothermally just by tuning the molar ratio of Mn and Co. Subsequently, the growth of multiporous MnCo$_2$O$_4$ and CoMn$_2$O$_4$ quasi-hollow microspheres by topotactic chemical transformation from the corresponding precursors are realized through a non-equilibrium heat treatment process. Topotactic conversion further demonstrated that the much larger CoMn$_2$O$_4$ pores than those of MnCo$_2$O$_4$ are possibly due to the longer transfer distance of ions. When evaluated as anode materials for LIBs (lithium ion batteries), after 25 cycles at a current density of 200 mA g$^{-1}$, the resultant MnCo$_2$O$_4$ and CoMn$_2$O$_4$ quasi-hollow microspheres possessed reversible capacities of 755 and 706 mA h g$^{-1}$, respectively. In particular, the MnCo$_2$O$_4$ samples could deliver a reversible capacity as high as 610 mA h g$^{-1}$ even at a higher current density of 400 mA g$^{-1}$ with excellent electrochemical stability after 100 cycles of testing, indicating its potential application in LIBs. We believe that such good performance results from the appropriate pore size and quasi-hollow nature of MnCo$_2$O$_4$ microspheres, which can effectively buffer the large volume variation of anodes based on the conversion reaction during Li$^+$ insertion/extraction. The present strategy is simple but very effective, and due to its versatility, it can be extended to other binary, even ternary complex metal oxides with high-performance in LIBs.

1 Introduction

Among rechargeable batteries, lithium-ion batteries (LIBs) is currently incomparable according to energy and power densities. The performance of LIBs is determined mainly by the choice of anode and cathode materials with the specific morphology, size, and porous distribution. Micro-/nano-structured simple metal oxides such as manganese oxide, iron oxide, cobalt oxide, and tin oxide have been among the most widely investigated alternative anode materials for use in LIBs over the last decade because of their high specific capacity (500 to 1000 mA h g$^{-1}$), compared with the 372 mA h g$^{-1}$ for conventional graphite. These nano-/micro-sized oxides have the advantages of a high surface-to-volume ratio and a short path length for Li ion diffusion in comparison with their bulk counterparts. However, most of these materials show rapid capacity fading due to their intrinsically low conductivity and habitual aggregation during the cycling process.

Interestingly enough, complex oxides from combination of two transition metal oxides, or a transition metal oxide and a post-transition metal oxide, such as ZnFe$_2$O$_4$, CuCo$_2$O$_4$, ZnCo$_2$O$_4$, ZnMn$_2$O$_4$, CoMn$_2$O$_4$, have shown good capacity cycling because of their complementarity and synergy in the Li$^+$ charge–discharge process for the two transition metal oxides. For instance, cobalt shows a higher oxidation potential than manganese, while manganese can transport more electrons and bring in higher capacity than cobalt. On the other hand, it is reported that complex binary or ternary transition metal oxides possess better electronic conductivity. For example, NiCo$_2$O$_4$ holds much better electronic conductivity, at least two orders of magnitude higher, and higher electrochemical activity than nickel oxides and cobalt oxides. In addition, the rate capability of electrode materials is mainly determined by the kinetics of ion diffusion and electronic conductivity. Therefore, there is still space for improvement in the case of the energy and power densities of LIBs.

In general, these complex oxides can be roughly divided from the view of the structure into two categories: namely a tetragonal spinel structure, such as CoMn$_2$O$_4$, ZnMn$_2$O$_4$, which are...
isomorphous to the $\text{Mn}_6\text{O}_4$ crystal structure, and a cubic spinel structure belonging to the $\text{Co}_3\text{O}_4$ type, including $\text{CuCo}_2\text{O}_4$, $\text{MnFe}_2\text{O}_4$, and $\text{ZnCo}_2\text{O}_4$ et al. Among them, $\text{ZnMn}_2\text{O}_4$ is the most widely studied because of its good cyclability and outstanding rate capability, as it can store Li ions through both conversion and alloying reactions. Excitingly, the $\text{MnCo}_2\text{O}_4$ quasi-hollow microspheres reported by this work are superior or at least equal to $\text{ZnMn}_2\text{O}_4$ nanostructures.\(^{9,11}\) Moreover, to the best of our knowledge, this is the first report of the performance of multiporous $\text{MnCo}_2\text{O}_4$ hollow structures as an anode material for LIBs.

Till now, one popular way to prepare complex oxides is coprecipitation of their carbonate counterparts followed by high-temperature pyrolysis.\(^{9,12}\) Nevertheless, there have been no reports to date on synthesizing complex oxides by employing a facile solvothermal method, in spite of its great popularity in the synthesis of nanomaterials. Herein, in this article, a general solvothermal route is exploited to fabricate the carbonates used as precursors to obtain certain complex oxides. For example, uniform $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$ and $\text{Co}_{0.33}\text{Mn}_{0.67}\text{CO}_3$ microspheres were prepared solvothermally by just tuning the molar ratio of Mn and Co. After a topochemical conversion from the corresponding precursors at 600 °C in laboratory air, $\text{MnCo}_2\text{O}_4$ and $\text{CoMn}_2\text{O}_4$ quasi-hollow microspheres were harvested. It is noteworthy to point out that the present modified solvothermal method is also applicable for other complex oxides, such as $\text{NiCo}_2\text{O}_4$, $\text{NiMn}_2\text{O}_4$, $\text{ZnMn}_2\text{O}_4$, $\text{CuCo}_2\text{O}_4$, and so forth, which will be reported elsewhere. Furthermore, the electrochemical performance of both the resultant $\text{MnCo}_2\text{O}_4$ and $\text{CoMn}_2\text{O}_4$ quasi-hollow microspheres as anode materials for LIBs application were evaluated, which demonstrated that the two quasi-hollow structures, especially $\text{MnCo}_2\text{O}_4$ quasi-hollow microspheres, present high reversible discharge capacity, good rate capability and excellent cycling stability after prolonged testing.

2 Experimental

Chemicals: ethylene glycol ($\text{HOC}_2\text{H}_2\text{OH}$, absolute for analysis), are bought from Wuxi Zhanwang Chemical Reagent Co. Ltd in China. All the other reagents, including $\text{CoCl}_2\cdot\text{6H}_2\text{O}$ (99%), $\text{MnCl}_2\cdot\text{4H}_2\text{O}$ (99%), and ammonium hydrogen carbonate ($\text{NH}_4\text{HCO}_3$, 99%), were supplied by Shanghai Sinopharm Chemical Reagent Co. Ltd and used after manually grinding for several minutes to accelerate the dissolution rate in the solvent.

Preparation of the $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$ and $\text{Co}_{0.33}\text{Mn}_{0.67}\text{CO}_3$ precursors

In a typical synthesis of $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$, for example, 1 mmol of $\text{MnCl}_2\cdot\text{4H}_2\text{O}$ and 2 mmol of $\text{CoCl}_2\cdot\text{6H}_2\text{O}$ were dissolved into 40 mL of ethylene glycol under magnetic stirring. Then, 30 mmol of $\text{NH}_4\text{HCO}_3$ powder was added to the above mixture. The resultant mixture was continually stirred for 30 min to obtain a homogeneous solution and then transferred into a Teflon lined stainless-steel autoclave (capacity of 60 mL). The autoclave was sealed and maintained at 200 °C for 20 h in an electron oven. The system was then cooled to ambient temperature naturally. The final product of $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$ was collected and washed with distilled water and absolute alcohol several times, followed by vacuum-drying at 60 °C. The sample was then ready for further processing and characterization. For the synthesis of $\text{Co}_{0.33}\text{Mn}_{0.67}\text{CO}_3$, the procedures were carried out in the similar way with the above except that the molar ratio of $\text{MnCl}_2\cdot\text{4H}_2\text{O}$ and $\text{CoCl}_2\cdot\text{6H}_2\text{O}$ was 2 : 1. Several control experiments were also carried out with the same procedures.

Preparation of multiporous $\text{MnCo}_2\text{O}_4$ and $\text{CoMn}_2\text{O}_4$ quasi-hollow microspheres

Multiporous $\text{MnCo}_2\text{O}_4$ and $\text{CoMn}_2\text{O}_4$ quasi-hollow microspheres were prepared in the following steps: heating the corresponding precursors in a tube furnace in laboratory air at a ramping rate of 4 °C min\(^{-1}\) to 600 °C, then keeping at 600 °C for 10 h, followed by a natural cooling to room temperature.

Instrumentation and sample analysis

The crystallographic information of the prepared samples was established by powder XRD (XRD, Philips X’Pert Pro Super diffractometer with Cu Kz radiation (λ = 1.54178 Å)). Field Emission Scanning Electronic Microscopy (FESEM, JSM-6700F) was employed to examine the morphologies of the products. Structural and compositional investigations by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) instruments, operated with an electron kinetic energy of 200 kV. Surface analysis of the studied samples was performed using XPS (VGESCA-LABMKIIX-ray photoelectronic spectrometer). TGA (TGA-2050 (TA Corp.)) was also conducted to determine the composition of samples. The TGA measurements were carried out at a heating rate of 10 °C min\(^{-1}\) from 20 to 800 °C with an air flow-rate of 100 mL min\(^{-1}\). The measurements of the specific surface area and the analysis of the porosity of $\text{MnCo}_2\text{O}_4$ and $\text{CoMn}_2\text{O}_4$ products were performed through measuring $\text{N}_2$ adsorption–desorption isotherms at 77 K, using a Micrometrics ASAP 2020M system.

Electrochemical measurements

The electrochemical tests were performed under ambient temperature using two-electrode coin cells (size: 2016) with lithium serving as both the counter electrode and the reference electrode. The working electrode was composed of 60 wt% active material (e.g., our $\text{MnCo}_2\text{O}_4$ and $\text{CoMn}_2\text{O}_4$ quasi-hollow microspheres), 25 wt% conductivity agent (acetylene black, Super-P Li), and 15 wt% binder (polyvinylidene difluoride, PVDF, Aldrich). During the electrode-prepared process, we adopted a copper foil with the size of 12 mm, coated the active materials with the thickness of ~200 μm and the mass of about 2 mg. The electrolyte used in the cells was 1.0 M LiPF\(_6\) in a 50 : 50 (w/w) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The cell assembly was carried out in an argon-filled glove box with both the moisture and the oxygen content below 2 ppm. Galvanostatic charge–discharge was conducted using a battery tester (LAND-CT2001A) with a voltage window of 0.01–3.0 V at a current rate of 200–400 mA g\(^{-1}\). The cyclic
voltammetry (CV) test was carried out in the potential window of 0.01 V to 3.0 V by an electrochemical workstation (CHI 660). Electrochemical impedance spectroscopy (EIS) was carried out on an electrochemical workstation (Materials Mates 510, Italia) in the frequency range from 0.1 MHz to 0.01 Hz.

3 Results and discussion

3.1 Synthesis of Mn_{0.33}Co_{0.67}CO_{3} and Co_{0.33}Mn_{0.67}CO_{3} precursors

Fig. 1a shows the X-ray diffraction (XRD) patterns of the carbonate precursors prepared through our ammonium hydrogen carbonate-assisted solvothermal process with the molar ratio of Mn and Co (denoted as Mn/Co) being 1 : 2 and 2 : 1 (see Experimental section), respectively. By comparison with MnCO_{3} or CoCO_{3}, all the diffraction peaks could be indexed on the basis of the hexagonal phase with the space group R3c (no. 167). In this structure, cobalt and manganese occupy the octahedral sites randomly but totally proportionally, as illustrated in Fig. 1b. Table 1 further shows the detailed cell parameters for the corresponding carbonates. With the proportion of manganese element increasing, the c axis becomes longer, originating from the larger radius of manganese cation. The morphologies of the as-prepared carbonate precursors were investigated by Field Emission Scanning Electronic Microscopy (FESEM), and the panoramic views (Fig. 1c and d) revealed monodisperse sphere-like structures for both samples. According to the statistic data of one hundred particles, the average diameter of Mn_{0.33}Co_{0.67}CO_{3} microspheres is about 3.2 μm, larger than that of Co_{0.33}Mn_{0.67}CO_{3} microspheres (1.5 μm) (inset in Fig. 1c and d, respectively).

In order to have greater understanding of the structural formation, the influence of synthetic conditions on the morphology of the corresponding precursors were also experimentally investigated. We found that the molar ratio of CoCl_{2} and MnCl_{2}, the solvent and reaction temperature played paramount roles in the synthesis. A higher or lower temperature (such as 220 °C or 180 °C) cannot obtain the uniform carbonate microspheres; and when the solvent of ethylene glycol was replaced by distilled water, irregular particles and microspheres were obtained (Fig. S1–S3, in the ESI†). All these results illustrated that the optimal conditions of the formation of the pure and uniform corresponding precursors are the molar ratio of CoCl_{2}:MnCl_{2} = 1 : 2 or 2 : 1, and 200 °C in the ethylene glycol solvent. With our starting chemical precursors, the formation reactions of the Mn_{0.33}Co_{0.67}CO_{3} and Co_{0.33}Mn_{0.67}CO_{3} phases can be described in the following steps:

\[
2\text{NH}_4\text{HCO}_3 \rightarrow \text{H}_2\text{CO}_3 + 2\text{NH}_4^+ + \text{CO}_3^{2-} \quad (1)
\]

\[
0.33\text{Mn}^{2+} + 0.67\text{Co}^{2+} + \text{CO}_3^{2-} \rightarrow \text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3 \quad (2)
\]

\[
0.33\text{Co}^{2+} + 0.67\text{Mn}^{2+} + \text{CO}_3^{2-} \rightarrow \text{Co}_{0.33}\text{Mn}_{0.67}\text{CO}_3 \quad (3)
\]

It should be mentioned that the ammonium hydrogen carbonate used in the present synthesis mainly serves as a source for the generation of carbonate, as explained in eqn (1), while the divalent cobalt and manganese cations required in eqn (2) and (3) are from chloridates.

3.2 Formation of spinel structured MnCo_{2}O_{4} and CoMn_{2}O_{4}

The investigations of the thermal behavior of Mn_{0.33}Co_{0.67}CO_{3} and Co_{0.33}Mn_{0.67}CO_{3} solid phases by the thermogravimetric analysis (TGA) are shown in Fig. 2. They may be categorized into two major weight loss steps: the first weight loss below 200 °C is attributed to the loss of physically and chemically adsorbed water, while the second prominent one is due to the thermal decomposition of these solid precursors into MnCo_{2}O_{4} or CoMn_{2}O_{4} and CO_{2} in the presence of an air stream used in the TGA measurement. For Mn_{0.33}Co_{0.67}CO_{3} and Co_{0.33}Mn_{0.67}CO_{3}, the value of the second weight loss is 33.53% and 35.50%, respectively, both of which are slightly larger than the theoretical value (32.7% and 33.3%), possibly due to the presence of tightly bound OH– and/or occluded water molecules and migration of atoms with the exception of CO_{2} release during the thermal decomposition. Note that the second major weight loss can also be divided into three steps, as shown in Fig. 2, because of the different thermal behaviors of MnCO_{3} and CoCO_{3}, and this phenomenon was also observed on the transformation of ZnCO_{3}–MnCO_{3} composite into ZnMn_{2}O_{4}.

Based on the TGA results, the optimal temperature for obtaining composite oxides is 600 °C. As a result, the thermal decomposition of the corresponding precursors was carried out

<table>
<thead>
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<th>Sample</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Ref.</th>
</tr>
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<td>15.64</td>
<td>JCPDF. 86-0172</td>
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<tr>
<td>Co_{0.33}Mn_{0.67}CO_{3}</td>
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<td>15.41</td>
<td>This work</td>
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<td>15.28</td>
<td>This work</td>
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<tr>
<td>CoCO_{3}</td>
<td>4.661</td>
<td>14.96</td>
<td>JCPDF. 78-0209</td>
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</table>

Table 1 Comparisons of cell parameters for carbonates
at 600 °C in air for 10 h. The XRD patterns of the as-decomposed products are displayed in Fig. 3. After the pyrolysis of the Mn_{0.33}Co_{0.67}CO_3, all of the reflections could be indexed as face-centered-cubic (fcc) MnCo_2O_4 (a_0 = 8.269 Å; space group Fd_3m (227), JCPDS no. 23-1237) with a spinel structure, as illustrated in Fig. 3b. Whereas, under the same reaction conditions, including temperature, reaction time and heating rate, tetragonal CoMn_2O_4 was obtained by thermal decomposition of Co_{0.33}Mn_{0.67}CO_3, which can be indexed as body-centered-tetragonal (bct) phase (a = 5.784 Å, c = 9.091 Å; space group I_4_1/amd) with a distorted spinel structure owing to the well-known Jahn–Teller effect of manganese (Fig. 3d). Both the two structures are regarded as mixed valence oxides that adopt spinel structures in which manganese and cobalt ions are distributed over octahedral and tetrahedral stacking interstices.

In this work, we also carried out an X-ray photoelectron spectroscopy (XPS) analysis of both the MnCo_2O_4 and CoMn_2O_4 quasi-hollow microspheres, and the results are shown in Fig. 4. All of the binding energies (BEs) in this XPS analysis were corrected for specimen charging by referencing them to the C 1s peak (set at 284.6 eV). By using a Gaussian fitting method, both the Co 2p spectrum (Fig. 4a and c) was best fitted considering two spin–orbit doublets characteristic of Co^{2+} and Co^{3+} and two shakeup satellites.14–17 Whereas, in the Co 2p spectrum of Fig. 4c, the two Co 2p_3/2 and Co 2p_1/2 peaks located at 780.2 and 795.7 eV are accompanied by two prominent shake-up satellite peaks (786.3 and 802.9 eV), which distinctly verifies the dominating presence of the Co(II).18 On the other hand, the Mn 2p spectrum features two main spin–orbit lines of 2p_3/2 at ~642.0 eV and 2p_1/2 at ~653.5 eV with separation of 11.5 eV. Little satellite structure could be observed. After refined fitting, the spectrum can be deconvoluted into at four peaks. Among them, 641.5 and 653.0 eV can be assigned to the existence of Mn(II), while other two peaks at 642.9 and 653.7 eV are characteristic of Mn(III) cation.19 It is reasonable, therefore, to conclude that the Mn element exists as Mn^{2+} and Mn^{3+} in both MnCo_2O_4 and CoMn_2O_4 microspheres. In conclusion, the solid-state redox couples Mn^{3+}/Mn^{2+} and Co^{3+}/Co^{2+} (the ratio are shown in Table S1† based on the area of deconvoluted peaks) are present in these two structures, which may provide a notable electrochemical activity. In addition, the chemical compositions of the MnCo_2O_4 and CoMn_2O_4 hollow microspheres are also confirmed by energy-dispersive X-ray spectroscopy (EDX) analysis (Fig. S4†), which indicates Mn/Co of ~0.5 and 2, respectively.

3.3 The morphologies and topotactic transformation of porous MnCo_2O_4 and CoMn_2O_4 quasi-hollow microspheres

The morphologies and microstructures of the as-prepared microspheres were further investigated by FESEM and
transmission electron microscopy (TEM). The typical low magnification FESEM image of the resultant MnCo2O4 in Fig. 5a shows that the product is composed of uniform microspheres with a diameter of 2.5–3.5 μm. A representative broken MnCo2O4 microsphere is shown in higher-magnification Fig. 5b, where the hollow interior can be identified from the broken part. The hollow interior of MnCo2O4 microspheres can be detected by the contrast between the center and the edge in the TEM image (Fig. 5c). However, the wall of the hollow structures is so thick that it is not very obvious. Thus, we named them as “quasi-hollow” microspheres. The representative high-resolution TEM (HRTEM) image of Fig. 5d displays distinct lattice fringes with an interplanar distance of 0.48 nm and 0.42 nm, corresponding to the spacings of (111) and (200) planes of MnCo2O4 crystals. The angle between the two planes is 54.8°, which is very consistent with the calculated value (54.7°). Slightly different from MnCo2O4 microspheres, the surface of CoMn2O4 microspheres is quite rough and the nanosized building blocks can be clearly observed under low and high magnification SEM images, as illustrated in Fig. 5e and f. From the cracked parts of the microspheres, the inner hollow structures can be observed in Fig. 5f. As shown in TEM images in Fig. 5g, each microsphere is composed of numerous primary particles with sizes of tens of nanometers and the contrast inside the microsphere confirms the porosity and hollow interior. A representative HRTEM image is shown in Fig. 5h, from which lattice spacing of 0.27 nm, resulting from (103) planes of tetragonal CoMn2O4, can be clearly observed. The porosity and internal quasi-hollow structures mainly attributed to the heterogeneous contraction, determined by non-equilibrium heat-treatment approaches, originated from release of CO2 during the transformation of Mn0.33Co0.67CO3 and Co0.33Mn0.67CO3 precursors into MnCo2O4 and CoMn2O4. At the initial stage of calcination, the adhesive force (σ_{ad}) exceeds the cohesive force (σ_{co}) between the inner carbonates and the outer complex oxides, generated by the high ramping rate, which results in the formation of porous and inner hollow structures with continuing calcination.

Obviously, it can be observed that the size distribution of porosity between the two structures is very different. Therefore, herein from the viewpoint of crystal-lattice matching, a topotactic phase transformation from the corresponding precursors is further proposed. As for the topotactic conversion from Mn0.33Co0.67CO3 to MnCo2O4, the transformation basis from hexagonal to cubic structures is the [1000]_{H} parallel with [111]_{C}. According to the structural illustration of Fig. 6a and b, in the Mn0.33Co0.67CO3 structure, the basic stacking hedra is the oxygen octahedra occupied by some metal ions, while the
tetrahedra and octahedra are incorporated in the structure of MnCo$_2$O$_4$. Therefore, it is reasonably concluded that the transformation of partial oxygen octahedra to tetrahedra will take place in the topotactic conversion from Mn$_{0.33}$Co$_{0.67}$O$_3$ to MnCo$_2$O$_4$, accompanied by the shift of some ions. As illustrated in Fig. 6a and b, two topotactic models can be proposed for the transformation process. On the one hand, the edge length of three octahedra labeled in the purple triangle of Fig. 6a is $a = 4.61 \, \text{Å}$ and the green central octahedron in the lower layer will convert to a tetrahedron by atom shifting. On the other hand, the edge length labeled in the black triangle of Fig. 6a is $3^{1/2} \, a = 7.98 \, \text{Å}$ and thus the octahedron located in the center of the triangle will convert to a tetrahedron. By comparing with the edge length labeled in Fig. 6b ($3^{1/2} \, a/2 = 7.20 \, \text{Å}$), the similar length could more favorably pave the way to the topotactic transformation. At the same time, the conversion to tetrahedron from central octahedron could more easily happen because of no shifting due to the central location on the same layer. As demonstrated in Fig. 6c and d, via comparing the two structures of Co$_{0.33}$Mn$_{0.67}$O$_3$ and CoMn$_2$O$_4$, the basis of the transformation could be the six octahedra stacking. The edge length of the component octahedra in Fig. 6c is $a = 4.61 \, \text{Å}$ and $a/2 = 2.90 \, \text{Å}$ in Fig. 6d. During the transformation process, the ions will move for a longer distance to transform into the pattern and at the same time pores will form in the obtained complex oxides. As a result, the resultant pores will be much larger in CoMn$_2$O$_4$ than MnCo$_2$O$_4$, possibly due to the longer transfer distance of ions, consistent with the pore size investigation observed in SEM and TEM images (Fig. 5).

### 3.4 Textural characteristics and electrochemical properties

To further investigate the specific surface areas and porous nature of MnCo$_2$O$_4$ and CoMn$_2$O$_4$ quasi-hollow microspheres, Brunauer-Emmett-Teller (BET) gas-sorption measurements were performed. N$_2$ adsorption–desorption isotherms at 77 K are reported in Fig. 7, with the insets showing their corresponding Barrett–Joyner–Halenda (BJH) pore-size distribution. The MnCo$_2$O$_4$ and CoMn$_2$O$_4$ samples exhibit distinct isotherms. The isotherm of MnCo$_2$O$_4$ hollow microspheres can be classified as type IV with a type H1 hysteresis loop, determining this structure to be mesoporous (Fig. 7a). According to the corresponding BJH plots (the inset) recorded from the nitrogen isotherms of the MnCo$_2$O$_4$ samples, the average pore size is about 48.0 nm, confirming that the sample contains mesoscale pores. On the other hand, the CoMn$_2$O$_4$ microspheres exhibit a typical type II with a type of H3 hysteresis loop, which is characteristic of macroporous materials. The larger pore size of the CoMn$_2$O$_4$ sample is attributed to the longer transfer distance from Co$_{0.33}$Mn$_{0.67}$O$_3$ as discussed above, which is consistent with the results observed by FESEM/TEM images (Fig. 7b). The BET specific surface areas and pore volumes of the samples were 18.0 m$^2$ g$^{-1}$ and 0.174 cm$^3$ g$^{-1}$ for MnCo$_2$O$_4$ quasi-hollow microspheres, 8.0 m$^2$ g$^{-1}$ and 0.0194 cm$^3$ g$^{-1}$ for CoMn$_2$O$_4$ quasi-hollow microspheres, respectively. The porous quasi-hollow structures suggest advantages in buffering the large volume variation of anodes based on the conversion reaction during Li$^+$ insertion/extraction, thus partly mitigating the quick capacity fading issue.

The electrochemical properties of the as-prepared quasi-hollow microspheres were initially analyzed by cyclic voltammetry (CV). Fig. 8a and b shows the CV curves of electrodes made of the MnCo$_2$O$_4$ and CoMn$_2$O$_4$ quasi-hollow microspheres at a scan rate of 0.2 mV s$^{-1}$ in the potential range 0.01–3.0 V, respectively. The CV curves for the first cycle are obviously different from those for the following cycles, and no significant alteration is seen from the second cycle onwards. In the first cycle, as shown in Fig. 8a, there is a broad peak at ~1.25 V and a sharp reduction peak at ~0.58 V in the cathodic process, which can be assigned to the reduction of Co$^{3+}$ to Co$^{2+}$, Co$^{2+}$ and Mn$^{2+}$ to metallic Co and Mn, respectively. Two broad oxidation peaks are observed at 1.55 and 2.05 V in the anodic scan, corresponding to the oxidation of Mn to Mn$^{2+}$ and Co to Co$^{3+}$. In the second and third cycles, it can be observed that the reduction peak is gradually moved to about 0.9 V and becomes much broader, which is different from the irreversible electrochemical reaction during the first discharge cycle. Different from the electrochemical behavior of MnCo$_2$O$_4$, the CoMn$_2$O$_4$ electrode exhibits two obvious peaks at 1.30 V and 0.29 V in the first cathodic sweep, as shown in Fig. 8b, which could be assigned to the reduction of Mn$^{2+}$ to Mn$^{2+}$, and the further reduction of Mn$^{2+}$ and Co$^{2+}$ to metallic Mn and Co, respectively. In the following anodic process, two peaks at 1.40 V and 2.05 V could be observed, due to the oxidation of Mn and Co to Mn$^{2+}$ and
Co\textsuperscript{2+}, respectively. From the second cycle onwards, the repeated reduction–oxidation of MnO and CoO results in two pairs of redox peaks at 0.51/1.45 V and 1.15/2.05 V, respectively. Furthermore, for both the MnCo\textsubscript{2}O\textsubscript{4} and CoMn\textsubscript{2}O\textsubscript{4} electrodes, from the second cycle onward, the reduction peaks in the cathodic scan and the oxidation peaks in the anodic scan overlap very well, demonstrating that these two electrodes exhibit good stability and cyclability for the insertion and extraction of lithium ions. On the basis of the cyclic voltammograms, the entire electrochemical process can be classified as follows:

\[
\text{MnCo}_2\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow \text{Mn} + 2\text{Co} + 4\text{Li}_2\text{O} \quad (4)
\]

\[
\text{Mn} + 2\text{Co} + 3\text{Li}_2\text{O} \leftrightarrow \text{MnO} + 2\text{CoO} + 6\text{Li}^+ + 6\text{e}^- \quad (5)
\]

\[
\text{CoMn}_2\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow \text{Co} + 2\text{Mn} + 4\text{Li}_2\text{O} \quad (6)
\]

\[
\text{Co} + 2\text{Mn} + 3\text{Li}_2\text{O} \leftrightarrow \text{CoO} + 2\text{MnO} + 6\text{Li}^+ + 6\text{e}^- \quad (7)
\]

When the MnCo\textsubscript{2}O\textsubscript{4}/CoMn\textsubscript{2}O\textsubscript{4} microspheres are electrochemically discharged with lithium metal, crystal structure destruction occurs, followed by the formation of nanosized Mn, Co, and Li\textsubscript{2}O, as shown in eqn (4) and (6). Then, the consequent electrochemical process may be the combined reaction, based on the MnO (eqn (5)) and CoO (eqn (7)), respectively. Individual MnO and CoO components, as the anode materials of Li-ion batteries, have been detailed clearly in many papers.

Electrochemical capacity tests are then performed using both MnCo\textsubscript{2}O\textsubscript{4} and CoMn\textsubscript{2}O\textsubscript{4} quasi-hollow microsphere electrodes. The galvanostatic discharge–charge profiles for the first five cycles at a current rate of 200 mA g\textsuperscript{-1} are exhibited in Fig. 8c and d. The first discharge capacity is 1473 mA h g\textsuperscript{-1} for MnCo\textsubscript{2}O\textsubscript{4}, 1427 mA h g\textsuperscript{-1} for CoMn\textsubscript{2}O\textsubscript{4}, respectively, which is higher than the theoretical values (906 and 921 mA h g\textsuperscript{-1}) based on eqn (4) and (6). The formation of solid electrolyte interphase (SEI) layers on the electrolyte interface may contribute to the extra capacity at the first discharge. The first charge process of the MnCo\textsubscript{2}O\textsubscript{4} sample delivered a lower capacity of 954 mA h g\textsuperscript{-1} than the first discharge, showing an irreversible capacity shift of 519 mA h g\textsuperscript{-1} with the ratio of the charge retention of 64.8%. The large, irreversible capacity loss arising during the first cycle is likely to be due to the incomplete decomposition of Li\textsubscript{2}O and the difficult dissolution of the SEI, as well as other factors, such as the intrinsic nature of the materials, kinetic limitations and cation deficient. During the fifth charge–discharge cycle of the MnCo\textsubscript{2}O\textsubscript{4} sample, a discharge capacity of 958 mA h g\textsuperscript{-1} and a charge capacity of 920 mA h g\textsuperscript{-1} were exhibited, together with an increased charge retention ratio to 96.0% (Fig. 8c).

Fig. 8e and f shows the discharge capacity versus cycle number at the current density of 200 and 400 mA g\textsuperscript{-1}, respectively. The specific capacity is also maintained at ca. 755 mA h g\textsuperscript{-1} for MnCo\textsubscript{2}O\textsubscript{4}, 706 mA h g\textsuperscript{-1} for CoMn\textsubscript{2}O\textsubscript{4} after cycling 25 times, respectively, as shown in Fig. 8e. The reversible capacities are also higher than the theoretical values (681 mA h g\textsuperscript{-1} for MnCo\textsubscript{2}O\textsubscript{4} and 691 mA h g\textsuperscript{-1} for CoMn\textsubscript{2}O\textsubscript{4}) considering the
reversible reaction (eqn (5) and (7)) on the oxidation of metallic Co and Mn to CoO and MnO during the discharge process, respectively. The large reversible capacities of our samples could be attributed to the reversible formation/dissolution of organic polymeric/gel-like layer by electrolyte decomposition, which could deliver extra capacity through a so-called “pseudocapacitance-type behavior,” similar to that reported in nano-sized MO/Li cell systems. In addition, the unique porous structures of the MnCo\(_2\)O\(_4\) and CoMn\(_2\)O\(_4\) quasi-hollow microsphere is considered as another important factor. At a higher current density of 400 mA g\(^{-1}\), the MnCo\(_2\)O\(_4\) electrode stabilized at 610 mA h g\(^{-1}\) with the percentage of theoretical capacity of 89.7% after 100 cycles. Fig. 8e and f unambiguously shows that the capacity of MnCo\(_2\)O\(_4\) is much higher than that of CoMn\(_2\)O\(_4\). FESEM analysis revealed some partial deconstruction of the CoMn\(_2\)O\(_4\) nanostructures after 100 cycles (ESI, Fig. S5c and S5d†). This result could interpret its lower electrochemical performance than MnCo\(_2\)O\(_4\) of which no structural changes were observable after 100 cycles (ESI, Fig. S5a and b†). In addition, we made a comparison of the electrochemical performance between our quasi-hollow microspheres and complex oxide nanostructures previously reported, as summarized in Table 2. It is obvious that the multiporous MnCo\(_2\)O\(_4\) and CoMn\(_2\)O\(_4\) quasi-hollow microspheres both exhibit significant improvement, especially for MnCo\(_2\)O\(_4\), either in cycling performance, or in discharge–charge capacity. Significantly, to the best of our knowledge, this is the first time to report MnCo\(_2\)O\(_4\) quasi-hollow microspheres as an anode material for LIBs with such excellent performance.

In addition to the high specific capacity and good cyclability, both samples were also tested for their rate performances at various current density from 200 mA g\(^{-1}\) to 800 mA g\(^{-1}\), and the results were plotted in Fig. S6.† It can be seen that the discharge capacity for MnCo\(_2\)O\(_4\) electrode slightly reduced to 964, 781, 633, and 571 mA h g\(^{-1}\) at current densities of 200, 400, 600, and 800 mA g\(^{-1}\), respectively. Even at the rate as high as 800 mA g\(^{-1}\), the electrode can still deliver a capacity higher than 571 mA h g\(^{-1}\), which is higher than the theoretical capacity of the graphite anode (372 mA h g\(^{-1}\)). More importantly, when the current rate returns to 200 mA g\(^{-1}\), the electrode resumes its original capacity of about 676 mA h g\(^{-1}\). On the other hand, by comparison with the MnCo\(_2\)O\(_4\) sample, CoMn\(_2\)O\(_4\) exhibits a slightly weak performance of the rate capability, and recovers the original capacity of only about 410 mA h g\(^{-1}\) when the current rate returns to 200 mA g\(^{-1}\). One possible reason may be due to the larger pore size for CoMn\(_2\)O\(_4\), which is apt to collapse and disintegrate after long term cycling, as illustrated in Fig. S5a and S5b†.

AC impedance measurements, as shown in Fig. 9, were performed to further understand the good performance of the porous MnCo\(_2\)O\(_4\) quasi-hollow microspheres. The Nyquist plots obtained for the MnCo\(_2\)O\(_4\) and CoMn\(_2\)O\(_4\) electrodes after 2 and 50 cycles (at 400 mA g\(^{-1}\)) in the fully charged state were collected for comparison. The Nyquist plots of both the electrodes consist of a depressed semicircle where a high-frequency semicircle and a medium-frequency semicircle overlap each other and a long low-frequency line. The intercept on the Z* real axis in the high-frequency region corresponds to the resistance of electrolyte (R\(_e\)). The semicircle in the middle frequency range indicates the charge-transfer resistance (R\(_ct\)), relating to charge transfer through the electrode–electrolyte interface. The inclined line in the low-frequency region represents the Warburg impedance (Z\(_w\)), which is related to solid-state diffusion of Li\(^+\) in the electrode materials. As one can observe, from 2 to 25 cycles, there are obvious decreases of R\(_ct\) for both the electrodes. However, the value of R\(_ct\) of MnCo\(_2\)O\(_4\) electrode is always lower than that of CoMn\(_2\)O\(_4\), which indicates the electrons and Li\(^+\) can transfer.

<table>
<thead>
<tr>
<th>Complex oxide</th>
<th>Reversible capacity (mA h g(^{-1}))</th>
<th>Current density (mA g(^{-1}))</th>
<th>Percentage of theoretical capacity (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCo(_2)O(_4) quasi-hollow microspheres</td>
<td>755/25th cycle</td>
<td>200</td>
<td>108.5%</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>738/25th cycle</td>
<td>400</td>
<td>111.0%</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>610/100th cycle</td>
<td>400</td>
<td>89.7%</td>
<td>This work</td>
</tr>
<tr>
<td>CoMn(_2)O(_4) quasi-hollow microspheres</td>
<td>706/25th cycle</td>
<td>200</td>
<td>102.1%</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>628/25th cycle</td>
<td>400</td>
<td>90.9%</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>426/100th cycle</td>
<td>400</td>
<td>61.6%</td>
<td>This work</td>
</tr>
<tr>
<td>Double-shelled CoMn(_2)O(_4) hollow microcubes</td>
<td>624/50th cycle</td>
<td>200</td>
<td>90.3%</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>406/50th cycle</td>
<td>800</td>
<td>58.8%</td>
<td>12</td>
</tr>
<tr>
<td>CoMn(_2)O(_4) powders</td>
<td>330/50th cycle</td>
<td>80</td>
<td>47.8%</td>
<td>27</td>
</tr>
<tr>
<td>CoMn(_2)O(_4) bulks or powders</td>
<td>&lt;400/50th cycle</td>
<td>691</td>
<td>&lt;57.9%</td>
<td>28</td>
</tr>
<tr>
<td>MnCo(_2)O(_4) bulks or powders</td>
<td>494/50th cycle</td>
<td>681</td>
<td>72.3%</td>
<td>28</td>
</tr>
<tr>
<td>ZnMn(_2)O(_4) hollow microspheres</td>
<td>607/100th cycle</td>
<td>400</td>
<td>77.4%</td>
<td>9</td>
</tr>
<tr>
<td>ZnMn(_2)O(_4) powders</td>
<td>490/25th cycle</td>
<td>80</td>
<td>62.5%</td>
<td>27</td>
</tr>
<tr>
<td>ZnMn(_2)O(_4) nanocrystalline</td>
<td>560/50th cycle</td>
<td>100</td>
<td>72.6%</td>
<td>10</td>
</tr>
<tr>
<td>ZnMn(_2)O(_4) nanowires</td>
<td>450/40th cycle</td>
<td>500</td>
<td>65.1%</td>
<td>29</td>
</tr>
<tr>
<td>Nano-ZnMn(_2)O(_4)</td>
<td>600/50th cycle</td>
<td>100</td>
<td>76.3%</td>
<td>11</td>
</tr>
<tr>
<td>Flower-like ZnMn(_2)O(_4) superstructures</td>
<td>626/50th cycle</td>
<td>100</td>
<td>79.8%</td>
<td>30</td>
</tr>
<tr>
<td>ZnFe(_2)O(_4) powder</td>
<td>615/50th cycle</td>
<td>60</td>
<td>79.1%</td>
<td>6</td>
</tr>
<tr>
<td>NiMn(_2)O(_4) powders</td>
<td>210/20th cycle</td>
<td>80</td>
<td>30.3%</td>
<td>27</td>
</tr>
<tr>
<td>ZnCo(_2)O(_4) nanoflakes</td>
<td>750/50th cycle</td>
<td>80</td>
<td>98.8%</td>
<td>8</td>
</tr>
<tr>
<td>Nano-phase CuCo(_2)O(_4)</td>
<td>705/50th cycle</td>
<td>60</td>
<td>88.1%</td>
<td>7</td>
</tr>
</tbody>
</table>
more effectively in the interface of active materials and electrolyte, thus resulting in the enhanced electrode reaction kinetics and better cycling performance of the cells during the charge–discharge process as mentioned above.

The superior and excellent electrochemical performance for these two multiporous microspheres, especially MnCo2O4 quasi-hollow microspheres, could be attributed to the following factors. First, the specific porosity of the structures shortens diffusion length of the lithium ion, and offers a large-area material–electrolyte contact. Their relatively large surface areas can also benefit the charge-transfer rate and thus enhance the rate capability.12,13 Second, the cavities in hollow structures may provide extra space for the storage of Li ions, beneficial for enhancing specific capacity. The void space buffers against the local volume change during Li insertion/desorption and alleviates pulverization and aggregation of the electrode material demonstrated by preservation of the hollow spherical morphology after 100 charge–discharge cycles at 400 mA g−1 (see ESI, Fig. S5†), hence improving cycling performance.22 Consequently, besides their intrinsic nature of the materials, the superior electrochemical properties of these structures originate from their porosity and hollow interior. However, the phenomenon that the large capacity loss in the initial cycle is a major obstacle for potential applicability of most conversion oxides. To overcome the limitation and avoid the drawback, pre-lithiation14,15 and film nanostructuring48 are preferred, and more detailed and further investigation are under the way.

4 Conclusions

In summary, we have devised a facile solvothermal route to fabricate uniform Mn0.33Co0.67O4 and Co0.33Mn0.67O4 microspheres by just tuning the molar ratio of Mn/Co, for the first time. When calcined at 600 °C for 10 h, these solid microspheres were transformed into MnCo2O4 and CoMn2O4 quasi-hollow microspheres. Topotactic conversion demonstrated that the much larger CoMn2O4 pores than those of MnCo2O4 are possibly due to the longer transfer distance of ions. It is worth pointing out that these two structures belong to the mixed valence compounds, which provide notable electrochemical activity in lithium ion batteries. When evaluated as anode materials for LIBs, the resultant MnCo2O4 samples could deliver reversibly as high a capacity as 610 mA h g−1, the Independent Innovation Foundations of Shandong University (2012DD008), and the National Natural Science Fund of China (no. 91022033), and Postdoctoral Innovation Foundations of Shandong Province (201203051).

Notes and references


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