

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Topochemical synthesis of Bi₂O₃ microribbons derived from bismuth oxalate precursor as high-performance lithium-ion batteries†

Hai Wang, Hongxing Yang,* and Lin Lu

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Bismuth oxides (α -Bi₂O₃) microribbons are prepared from a precursor of Bi(C₂H₄)OH (BICH) with ribbon shape. The as-prepared BICH is obtained through a facile hydrothermal procedure of the mixture of bismuth nitrate and oxalic acid aqueous solution. XRD, FESEM, TEM and TG-DTG are used to characterize the BICH. The obtained BICH precursor consists of one-dimensional crystal structure, and has a width of 1 to 2 μ m, a thickness of 200 to 400 nm, and a length of 5 to 20 μ m. The thermal decomposition of the BICH microribbons leads to the formation of well-defined Bi₂O₃ microribbons structure without morphology change. Compared to commercial Bi₂O₃ powder, the as-prepared Bi₂O₃ acted as anode of lithium-ion batteries (LIBs) shows a higher capacity of about 1047 mAh g⁻¹ at 150 mA g⁻¹ after 100th cycle. The good performance of the Bi₂O₃ microribbons can be attributed to better charge transfer properties, and shorter lithium-ion diffusion path. Owing to their excellent cyclability and rate performance, the Bi₂O₃ microribbons may become promising candidates for high-performance LIBs application in the future.

1. Introduction

Over the last decade, lithium-ion batteries (LIBs) have received considerable attention due to their wide range of applications, such as cell phones and hybrid vehicles.^{1,2} Among the increasing demands of LIBs performance, higher energy density, power density and more stable cycle performance are a prerequisite to the scientific consideration of practice application. Metal oxides, as one of the most promising candidates to graphite anode materials of LIBs, have been extensively carried out due to their high capacity, low cost and superior cycle performance.³⁻⁶ Among these metal oxides anodes of LIBs, for example, TiO₂, SnO₂ have been the main research focus.^{4,7} Currently, the TiO₂, SnO₂ and their corresponding hierarchical nanostructured materials, nanocomposites, et al have been reported separately.^{4,5,8-10} Simultaneously, great efforts have recently been devoted to exploring new electrode materials with new functionalities in academia and innovative industrial application. For example, element semiconductor Si and metal Sn were also widely studied.¹¹⁻¹⁴

Drawing inspiration from the Sn and Si anode materials, Bi has been believed to act as an anode material for LIBs as well.^{15,16} Considering its quite high volumetric capacity (about 3765 mAh cm⁻³), the bismuth based compounds, such as bismuth telluride, bismuth sulphide have been studied as novel anode materials of LIBs.¹⁵⁻¹⁷ Very recently, Luo, et al reported that the direct growth of Bi₂O₃ on the surface Ni foam via a facile polymer-assisted solution approach and made an elegant comparative

electrochemical analysis with commercial Bi₂O₃ powder.¹⁸ These studies were interesting and meaningful works and, indeed, improved the capacity and stable performance obviously. From the point of view of microstructure of materials, their work main focused on the Bi₂O₃ nanocrystals. It is well-known that the anode materials morphology is an important feature for the development of high-performance LIBs. How to synthesis appropriate microstructure of materials is nowadays a hot topic. Previously, we demonstrated that TiO₂ anode materials with various hierarchical structures delivered superior electrochemical performance.^{5,9,19} Therefore, exploring new Bi₂O₃ structure is both an extremely meaningful and imperative for LIB applications in the future.

According to the formula $t=L^2/D$, where L is the diffusion length, D is the diffusion coefficient for lithium ion and charge, the size of nanocrystals is an important factor for the improvement of LIBs performance, as shown in Scheme 1. However, too small nanocrystals also would lead to some unexpected results thus caused poor cycling performance.¹⁻² Currently, one-dimensional (1-D) nanostructures, for example, nanotubes, nanorods and nanowires, have been attracting much attention owing to their effective charge transfer capability, and potential applications in LIBs.^{3,20-23} Other shapes, particularly, ribbon-shaped structures with rectangular cross-sections, have been synthesized and used as LIBs anodes.²⁴⁻²⁶ It is believed that the unique morphology of electrode materials is favourable for charge transfer and lithium ion diffusion owing to the high interfacial contact area between the electrodes and the electrolyte, and good mechanic accommodation of strain and volume change caused during

charge-discharge process. Therefore, the development of 1-D Bi_2O_3 ribbon-like structure with conductive layer is highly desired for high performance anode in practical LIBs.

Currently, Bi_2O_3 nanocrystals with irregular morphology have also been synthesized recently by a solution-based approach.^{27, 28} However, to meet the demands of ribbon-like Bi_2O_3 anodes in LIBs, there are two prerequisites, one is stable material microstructure, the other is its conductivity. For former, it is difficult to synthesis due to the monoclinic crystal structure of Bi_2O_3 ; for latter, it is still great challenge for one-step solution process due to the limited approaches, although much efforts had been devoted to developing the carbon-coated techniques.

Herein, we first synthesized the bismuth oxalate precursor $\text{Bi}(\text{C}_2\text{O}_4)\text{OH}$ (BICH). The effect of hydrothermal reaction time on the formation of bisuth oxalates was investigated. It was found that the reaction time had an obvious effect on the dimensions of the precursor. Then the precursor was transformed into Bi_2O_3 microribbon via the simple thermal decomposition process. To the best of our knowledge, it is also a first report on the controlled dimensions of Bi_2O_3 with ribbon-like structure via the combination of chelation process and thermal decomposition. Most importantly, the amorphous carbon coated on the surface of the as-synthesized Bi_2O_3 microribbons was also obtained simultaneously during the thermal treatment. This method is completely different from the previously reported carbon-coated method, which may find new application in other transition metal oxides electrode materials, such as, Fe_3O_4 , NiO , and et al. The Bi_2O_3 microribbons can deliver a capacity of about 1047 mAh g^{-1} after 100 cycles at 150 mAh g^{-1} and a stable capacity of 672 mAh g^{-1} even at a higher rate of 450 mAh g^{-1} .

2. Experimental section

2.1 Materials synthesis

Bismuth nitrate pentahydrate, anhydrous oxalic acid were of analytical grade and were used without further purification. In a typical procedure, 3 g of oxalic acid was dissolved in 60 mL DI water. After stirring for about 15 min, a transparent colorless aqueous solution was obtained. Then, 0.5 g of bismuth nitrate pentahydrate was slowly added the above solution. After stirring for about 30 min, the resulting solution was transferred into an autoclave and then sealed and heated at 170 °C for 14 h. After cooling down to room temperature, the as-formed precipitate was harvested by filtration and was washed several times with DI water and ethanol before it was dried in a vacuum oven at 80 °C for 2 h. The as-prepared Bi_2O_3 (denoted as A- Bi_2O_3) was obtained via thermal decomposition of BICH at 300 °C for 1 h. The electrochemical properties of A- Bi_2O_3 was further investigated and compared to commercial Bi_2O_3 powder (denoted as C- Bi_2O_3).

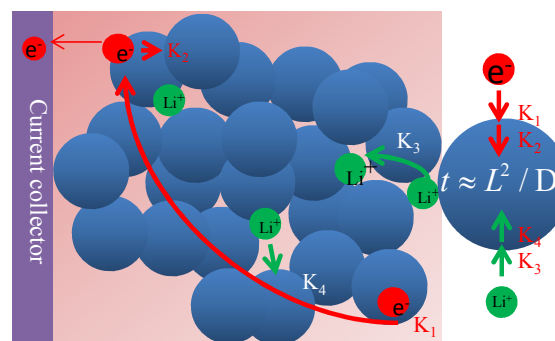
2.2 Material characterizations

The crystal phase was carried out by X-ray diffraction (XRD) analysis with a PANalytic X'Pert spectrometer using Cu K_α radiation, $\lambda=0.15405$ nm. The morphologies of the as-made samples were observed on field-emission scanning electron microscope (JEOL JSM-7000F, Japan). The high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL JEM-2010F microscopy operating at 200

Kv equipped with an energy dispersive X-ray spectrometry (EDX). The thermal decomposition behaviour of BICH microribbons was analysed by NETZSCH TG 209F1 Iris in N_2 atmosphere, Pt crucible, temperature range 30-800 °C (10 °C/min).

2.3 Electrochemical Measurements

The Bi_2O_3 electrodes were fabricated by spreading a mixture of 75 wt% Bi_2O_3 active material, 15 wt% a conductive agent (carbon black, Super-P-Li), and 10 wt% polymer binder polyvinylidene difluoride, PVDF on to a aluminum foil current collector. The mass loading of active material on each anode was about 3 mg. The as-made anodes were dried at 80 °C in vacuum oven for 24 h and pressed under 8 MPa. The electrodes were measured using coin cells (type CR2025) with pure lithium metal as both the counter electrode and the reference electrode at room temperature. Celgard 3400 membrane was used as a separator and 1.0 M LiPF_6 in a mixture of ethylene carbonate and diethyl carbonate (1: 1 volume, Novolyte Technologies, USA as the electrolyte). Cell assembly was performed in an Ar-filled glove box with concentrations of moisture and oxygen below 1.0 ppm. The charge-discharge cycling performance and cyclic voltammetry (0.05-2.5 V, 0.2 mV s^{-1}) was performed at room temperature on an electrochemical workstation (CHI 660 C) at different cycle number with a voltage window of 0.05-2.5 V. The impedance measurements were performed at frequencies ranging from 10^{-2} to 10^5 Hz.



K_1 : charge transfer kinetics (electrode surface)
 K_2 : charge diffusion kinetics (crystal lattice)
 K_3 : lithium-ion diffusion kinetics (electrolyte)
 K_4 : lithium-ion diffusion kinetics (crystal lattice)

Scheme 1. Schematic illustration of the transfer and diffusion principle of both charge and lithium ion of the aggregated nanocrystals electrodes.

3. Results and discussion

To understand the crystal phase of C- Bi_2O_3 and A- Bi_2O_3 and the transformation process of BICH precursor, the crystal structures of the three samples A- Bi_2O_3 , C- Bi_2O_3 and precursor BICH were characterized by XRD, as shown Fig. 1. From the XRD patterns, we can draw two conclusions. One is the A- Bi_2O_3 is transformed from the decomposition of the precursor BICH. In addition, the crystal phase of A- Bi_2O_3 and C- Bi_2O_3 is identical and both the XRD patterns matched well with JCPDS card no. 71-0465 for monoclinic Bi_2O_3 with $a = 5.8496$, $b = 8.1648$ nm and $c = 7.5101$ nm. The same crystal phase is favourable for the comparison of the electrochemical performance of the two samples since the crystals structure and morphology are two important features for

the LIBs performance. We noted that the crystallinity of C-Bi₂O₃ is better than that of A-Bi₂O₃. Generally speaking, under identical conditions, poor crystallinity will deteriorate the cycling performance of LIBs. However, our experimental results show that the electrochemical properties of A-Bi₂O₃ electrode exhibited superior performance compared to the C-Bi₂O₃ electrode; detail discussion will be described later.

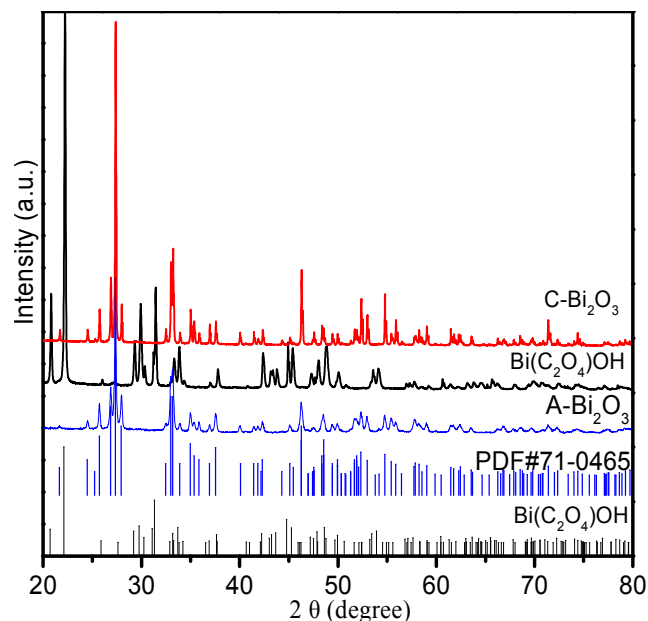


Fig.1 XRD patterns of the precursor BICH, A-Bi₂O₃ and C-Bi₂O₃. The bars are from Bi₂O₃ (JCPDS card no. 71-0465) and precursor BICH.

In addition, the morphology is another important factor for determining the LIBs performance. Currently, various morphologies had been extensively studied for the improvement in LIBs performance.^{9, 17, 21, 23} In comparison, the FESEM images of C-Bi₂O₃ and A-Bi₂O₃ at different magnification is presented in Fig. 2. It can be readily observed that the microstructure of C-Bi₂O₃ is randomly microparticles, as shown in Fig. 2 (a)-(c), whereas the obtained A-Bi₂O₃ consists of one-dimensional crystal structure, exhibits a ribbon-like morphology, and has width of 1 to 2 μm, thickness of 200 to 400 nm, and length of 5 to 20 μm, as shown in Fig. 2 (d)-(f). It should be noted that the morphology of A-Bi₂O₃ is well preserved after the thermal decomposition of BICH. To reveal the evolution process of ribbon-like structured materials, the time-dependant experiments were carried out. Interestingly, it was found that the ribbon-like materials are readily formed in the early stage during the hydrothermal process. Moreover, an interesting phenomenon was observed that the dimension of ribbon-like materials is successfully increased with the increase of reaction time, as shown in Fig. S1. Further detailed investigations on the reaction time dependence on the dimension change and the electrochemical behaviour of ribbon-like Bi₂O₃ are currently in progress. In addition, considering the similar morphology, we made a comparison analysis of crystal structures of BICH and Bi₂O₃, as shown in Fig. S2. Interestingly, the arrangement of BiO₆ octahedrons is similar to that of Bi₂O₃. The detailed 1D BICH structure had been well elucidated in previously literature.²⁹ Compared to BICH, zigzaglike chain connected to BiO₆ octahedrons only occurred a little distorted.

According to the experimental results, the 1D BICH are readily transformed to 1D Bi₂O₃ without the structure change. In addition, the comparison of the crystal structures shown in Tab. S1 means that the phase transformation of BICH from tetragonal phase to monoclinic phase (Bi₂O₃) occurs, moreover, the unit cell volume shrinks obviously during the thermal treatment process. In addition, it is worthwhile to note that significant changes of (*hkl*), for example, there are a shrinkage of the *a*-axis and *b*-axis and a significant increase of *c*-axis. As the unique ribbon-like structure, the increase of *c*-axis and the decrease of *a*-axis and *b*-axis may increase the lithium-ion diffusion coefficient due to the 1D pore channel structure, as shown Fig. S2 and Scheme.2.

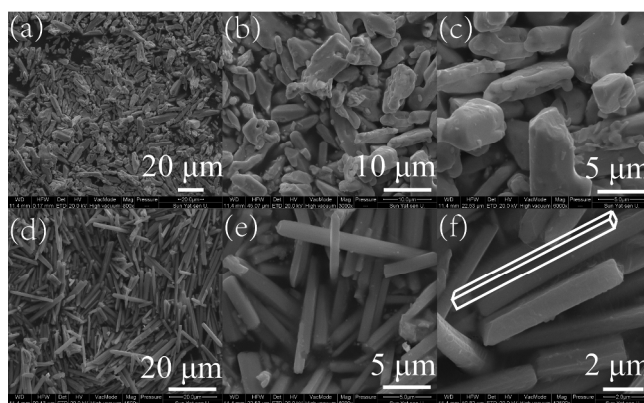


Fig. 2 Typical FESEM images of the C-Bi₂O₃ (a)-(c) and A-Bi₂O₃ (d)-(f) at different magnifications. A schematic image was shown in the inset of Fig. 2 (f).

As shown in Fig. 3, the TG-DTG analysis of the precursor gave a direct evidence of how much temperature is appropriate to obtain Bi₂O₃. From the analysis of TG-DTG curves, about 274 °C is the crystal phase transition temperature. Therefore, we select 300 °C as the thermal decomposition temperature of the BICH. At high temperature, for example, at 400 °C, the ribbon-like structure is severely destroyed, as shown in Fig. S3. Therefore, the appropriate temperature should be optimized to obtain the proper ribbon-like structure.

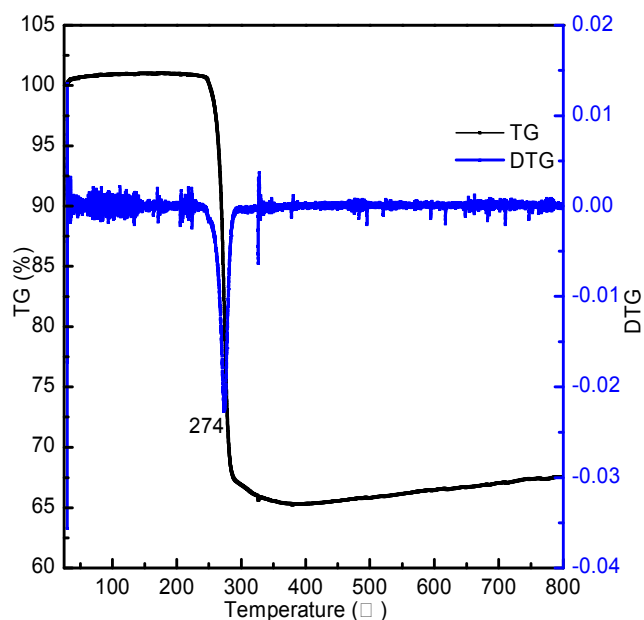


Fig. 3 TG-DTG curve of the BICH precursor. It can decompose completely at about 274 °C.

To further reveal the microstructure of A-Bi₂O₃, the TEM and HRTEM were carried out, as shown in Fig. 4. Fig. 4a shows an identical morphology presented in Fig. 2 (f). Interestingly, the HRTEM of end of ribbon revealed that amorphous carbon is uniformly coated in the surface of A-Bi₂O₃, which is rather favourable for high-performance LIBs. Currently, the carbon-coating technologies had been widely studied for improving the LIBs performance, to the best of our knowledge and this carbon-coated way had never been reported. Where is thin carbon layer from? It can be reasonably inferred that the carbon layer should be from the decomposition of Bi(C₂H₄)OH during the formation process of Bi₂O₃. Undoubtedly, the technology will provide new route for high-performance LIBs in the future. The clear lattice fringes, parallel to each other, show that the edge of A-Bi₂O₃ is well-crystallized, and the interplanar distance between adjacent lattice planes is 0.325 nm (Fig. 4(c)), corresponding to the d-spacing value of Bi₂O₃ (-121) planes. A. The corresponding SAED is shown in Fig. 4 (d), indicating a polycrystal structure of end of microribbons. The existence of white light circle also indicates that existence of the amorphous carbon layer. The stoichiometric composition of the A-Bi₂O₃ with amorphous carbon layer was further confirmed with our EDX analysis (atomic ratio of Bi/O, 2:3, Fig. S4).

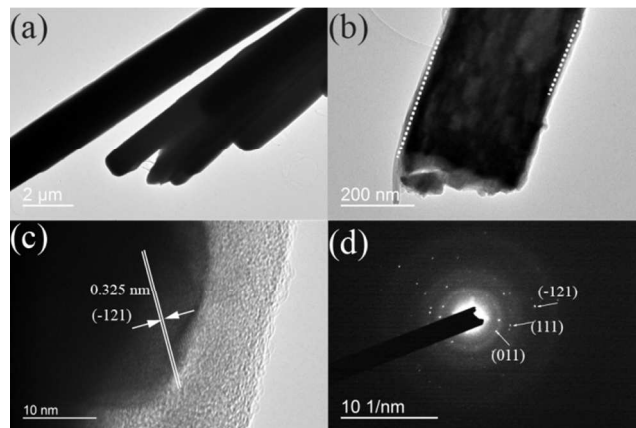


Fig. 4 Typical TEM images of the A-Bi₂O₃ (a) low magnification, (b) high magnification, (c) representative HRTEM image of the edge of A-Bi₂O₃ taken along [001] axis and its corresponding SAED (d).

In order to compare the electrochemical properties of the C-Bi₂O₃/Li and A-Bi₂O₃/Li half cells, the cycling performance of the fabricated half cells was carried out. Li-cycling in the voltage of 0.05-2.5 V vs Li at the current rate of 150 mA g⁻¹ are shown in Fig. 5(a), (b). For clarify, we selected the 1st, 2nd, 5th and 10th. For C-Bi₂O₃/Li half cell, as indicated, the initial charge-discharge capacities of ~759 mAh g⁻¹ and ~1272 mAh g⁻¹, respectively, with a Coulombic efficiency of 59.7 %. In the second cycle, a discharge capacity of 1010 mAh g⁻¹ indicated that 20.6 % of the initial discharge capacity is irreversible. This can be attributed to an inactive solid electrolyte interface (SEI) layer on the electrode surface and the decomposition of the electrolyte.³⁰ The discharge capacities of the 5th and 10th cycles remain large, ~971 and ~943 mAh g⁻¹, respectively, corresponding to the retention of 96.1 % and 93.4 % as compared to the second discharge capacity (1010 mAh g⁻¹). In comparison, the A-Bi₂O₃ has a much higher capacity, for the 1st, 2nd, 5th and 10th, the charge capacities are ~1195, 1176, 1074 and 984 mAh g⁻¹, respectively, whereas the discharge capacities are ~1598, 1470, 1323 and 1304 mAh g⁻¹, respectively. We believe that there are at least two reasons for A-Bi₂O₃ to deliver a significantly enhanced electrochemical performance. First microribbon structure can effectively accommodated the volume change during the charge-discharge process. Secondly, the amorphous carbon layer on the surface of the A-Bi₂O₃, acts a conductive pathway for effective charge transfer. This phenomenon has been observed on other anode materials as well.^{7, 31, 32} It should be noted, however, that the Coulombic efficiency of cycling in the current study is consistently low (around 75% for the first 10 cycles), which is much inferior as compared to many other anode materials.^{4, 5, 8-10}

We think that the Bi₂O₃ microribbons were not electrochemically active before 10 cycles, which may be due to its unique micrometer and one-dimensional structure characteristics. From the SEI point of view, there may be some changes of the interface between the electrodes surface and the electrolyte. The main reason was currently under progress.

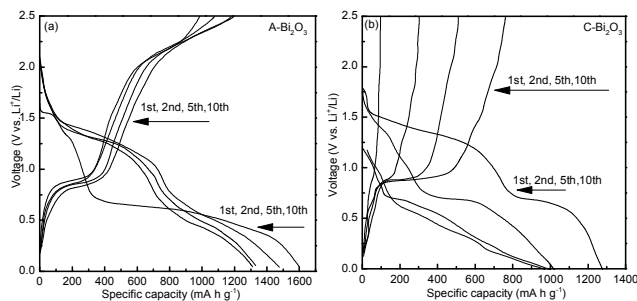


Fig. 5 Charge-discharge profiles of A-Bi₂O₃/Li and C-Bi₂O₃/Li half cells at a constant current density of 150 mA g⁻¹.

Fig. 6 shows the cycling performance of A-Bi₂O₃/Li and C-Bi₂O₃/Li half cells. Compared to C-Bi₂O₃/Li, the A-Bi₂O₃/Li half cell displays superior cycling performance, for which it can deliver stable discharge capacities of ~1047, 849 and 672 mAh g⁻¹, respectively, after 100 cycles at different current density (150, 300, 450 mA g⁻¹) (**Fig. 6 (a)**), whereas for the C-Bi₂O₃/Li half cell, under the identical conditions, it only deliver discharge capacities of ~853, 615 and 248 mAh g⁻¹ (**Fig. 6 (b)**). The rate performance of C-Bi₂O₃/Li and A-Bi₂O₃/Li half cells is also tested to study the fast discharge behaviour. As shown in **Fig. 7**, the discharge rates are increased successively from 150 to 750 mA g⁻¹ for each 10 cycles. For the A-Bi₂O₃/Li half cell, as shown in **Fig. 7 (a)**, the average discharge capacities for each 10 cycles at 150, 300, 450, and 600 mA g⁻¹ are ~1137, 831, 607 and 386 mAh g⁻¹, respectively. At a high rate of 750 mA g⁻¹, it can still deliver a discharge capacity of ~248 mAh g⁻¹. When the rate is decreased back to 150 mA g⁻¹, 80% discharge capacity of the initial 10 cycles at 150 mA g⁻¹ has been recovered, indicating a superior rate capability. Obviously, the A-Bi₂O₃/Li half cell exhibits a superior rate performance in comparison with C-Bi₂O₃/Li half cell (**Fig. 7 (b)**). Moreover, the morphology of A-Bi₂O₃ can be well preserved during lithium intercalation/deintercalation process even under the current density of 450 mA g⁻¹ for 100 cycles (**Fig. 8**), which are helpful in improving the electrochemical performance of the electrode. The superior rate capability exhibited by A-Bi₂O₃ suggests them as promising anode material for lithium ion battery with large power densities.

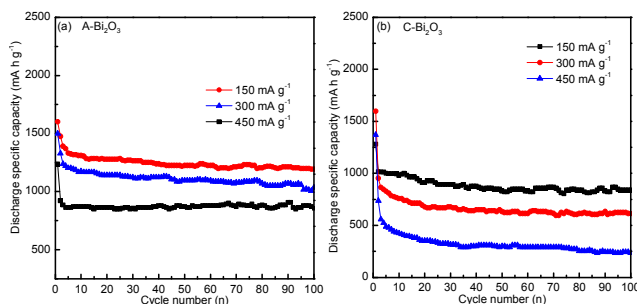


Fig. 6 The cycle performance of A-Bi₂O₃/Li half cells. (a) and C-Bi₂O₃/Li (b) at different current density.

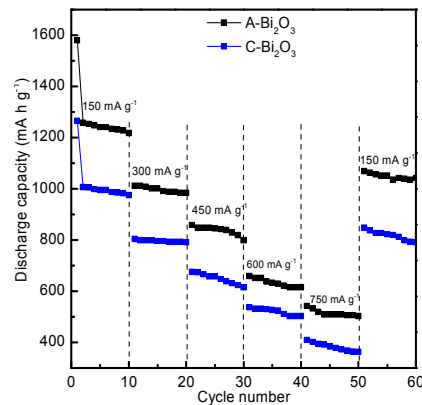


Fig. 7 Rate performance of A-Bi₂O₃/Li and C-Bi₂O₃/Li half cells.

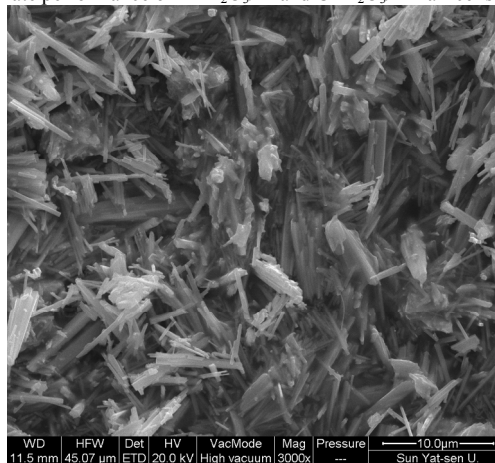
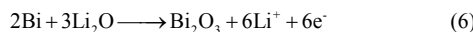
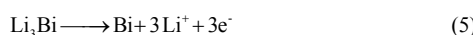
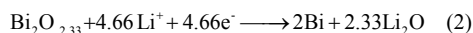


Fig. 8 FESEM image of the Bi₂O₃ microribbons after 100 cycles of charge and discharge process under the current density of 450 mA g⁻¹.

The electrochemical behavior of A-Bi₂O₃/Li half cell is characterized by cyclic voltammetry (CV) at the scanning rate of 0.2 mV s⁻¹ between 0.05 and 3.5 V, as shown in **Fig. 9**. **Fig. 9** shows CV curves of the A-Bi₂O₃ and C-Bi₂O₃ electrodes, respectively, both first three cycles. On the basis of the CVs, the lithium insertion and extraction reactions for A-Bi₂O₃/Li half cell are believed to proceed as follows:



For A-Bi₂O₃/Li half cell, each peak position shown in **Fig. 9 (a)** is analyzed as follows. Anodic peak of 0.44 V corresponds the alloying reaction of Bi and Li, and the formation of SEI layer.³³ During the subsequent cycle, namely, the 2nd cycle, the peak is replaced by other two minor peaks, 0.75 V and 0.64 V, indicating the formation of LiBi and Li₃Bi, which correspond to the electrochemical lithium insertion reaction of eqn (3) and (4), respectively. The cathodic peak of 1.24 V is associated with the reduction of Bi₂O₃ to metal Bi (eqn 1) while the peak at 1.45 V may correspond to reduction of tetragonal Bi₂O_{2.33} (eqn 2).³⁴ The small anodic peaks of 2.24 V and 1.77 V are associated with the oxidation of Bi to Bi₂O₃, which correspond to eqn (6). The

obvious anodic peak at 0.97 V is associated with the de-alloying process. For comparison, the C-Bi₂O₃/Li half cell was also evaluated under identical conditions. In comparison with the C-Bi₂O₃ electrode (Fig. 9 (b)), the A-Bi₂O₃ electrode exhibits sharper peak and higher current intensity, suggesting that good kinetic behaviors of both lithium ion diffusion and charge transfer of A-Bi₂O₃ electrode during the charge-discharge process.

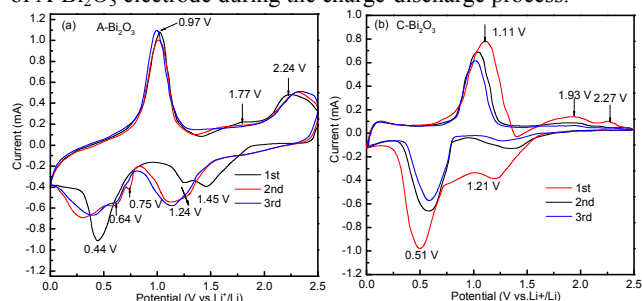


Fig. 9 Cyclic voltammetry for the first three cycles of A-Bi₂O₃/Li half cell (a) and C-Bi₂O₃/Li half cell (b) at scan rate of 0.2 mV s⁻¹.

Electrochemical impedance spectroscopy (EIS) measurements are carried out in order to evaluate the electrode kinetic behaviour of as-prepared C-Bi₂O₃/Li and A-Bi₂O₃/Li half cells. The impedance measurements are performed after charge-discharge for 5 cycles at a discharge potential of 0.75 V vs. Li/Li⁺. The Nyquist plots of the two electrodes are shown in Fig. 10. Both of the fresh cells display a high charge-transfer resistance. It can be seen clearly that the R_{ct} is much smaller for the A-Bi₂O₃/Li half cell (about 297 Ω) electrode than for the C-Bi₂O₃/Li half cell (about 212 Ω) electrode after the 5th cycle, which indicates that the ribbon structure could enable faster charge transfer at the electrode/electrolyte interface and favor in reducing electrode polarization and therefore, decrease the overall LIBs internal resistance. Moreover, the ribbon-like structure can also lead to better accommodation of the strain and change of volume change induced during charge-discharge process, which is favour for the cycle life of LIBs, which had been demonstrated in other ribbon-like anode materials.^{24, 26} In addition, the amorphous carbon coating significantly enhances the conductivity of the A-Bi₂O₃ material, since the conductive amorphous coating layer facilitates electronic conductive paths in the A-Bi₂O₃ belts, which is considered a key factor in improving the performance of LIBs, in particular, the charge-discharge capacity and rate capability of the A-Bi₂O₃/Li half cell. The following factors can account for this result: (1) the ribbon structure and open spaces can not only provide more sites for the adsorption of lithium ions, but also facilitate the fast their intercalation and deintercalation of active species; (2) the conductive layer of amorphous carbon directly formed on the surface of the A-Bi₂O₃ is favorable for electron collection and transfer (Scheme 1). Therefore, the A-Bi₂O₃ exhibited superior rate and cycling performance.

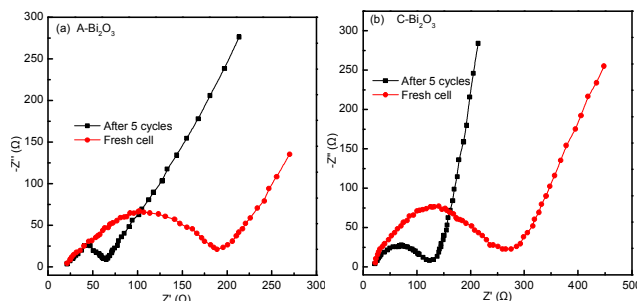
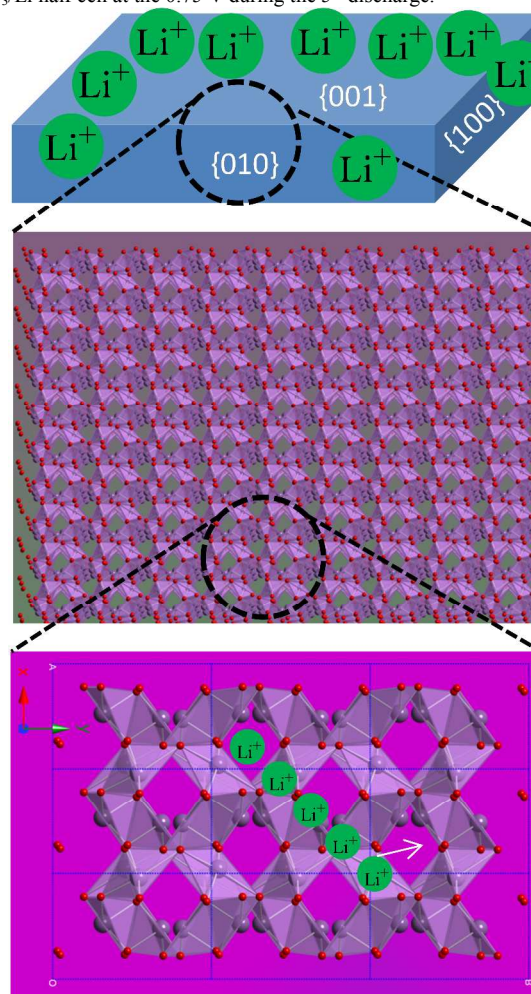


Fig.10 Nyquist plots of Bi₂O₃/Li cells. (a) A-Bi₂O₃/Li half cell, (b) C-Bi₂O₃/Li half cell at the 0.75 V during the 5th discharge.



Scheme 2 Simple schematic representations of Li-ion diffusion paths in A-Bi₂O₃ microribbons.

4. Conclusions

In summary, we have synthesized Bi₂O₃ microribbons through facile thermal decomposition and morphologically conserved transformation of Bi(C₂O₄)OH synthesized by topochemical synthesis. It was found that the amorphous carbon was uniformly coated on the surface of the Bi₂O₃ microribbons without extra carbon-coated process. We have further investigated the prospect of using the carbon-coating microribbons as an anode for LIBs and demonstrated high reversible capacity and good cyclability. The enhanced electrochemical performance can be attributed to the synergistic

effects of the carbon layer and microribbon structure. The experimental results further demonstrated that the microribbon is an effective structure for high-performance LIBs. This work provides new opportunities for the development of high-performance anode materials for LIBs.

Acknowledgements

We gratefully acknowledge financial support from National Natural Science Foundation of China (No. 41272064), Department of Education, Guangxi Zhuang Autonomous Region of China (Nos. 200103YB061 and 201010LX188) and PolyU's Postdoctoral Dean Reserve Project (1-ZV9F).

Notes and references

Renewable Energy Research Group (RERG), Department of Building Services Engineering, The Hong Kong Polytechnic University, Room: ZN816, Kowloon, Hong Kong, China. Fax: +852-27746146; Tel: +852-27665863; E-mail: bxhxyang@polyu.edu.hk.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

- 1 B. L. Ellis, K. T. Lee and L. F. Nazar, *Chem. Mater.*, 2010, **22**, 691-714.
- 2 J. B. Goodenough and Y. Kim, *Chem. Mater.*, 2010, **22**, 587-603.
- 3 Y. G. Li, B. Tan and Y. Y. Wu, *Nano Lett.*, 2008, **8**, 265-270.
- 4 G. F. Xia, N. Li, D. Y. Li, R. Q. Liu, N. Xiao and D. Tian, *Mater. Lett.*, 2011, **65**, 3377-3379.
- 5 J. Y. Shen, H. Wang, Y. Zhou, N. Q. Ye, G. B. Li and L. J. Wang, *RSC Adv.*, 2012, **2**, 9173-9178.
- 6 W. Tang, X. W. Gao, Y. S. Zhu, Y. B. Yue, Y. Shi, Y. P. Wu and K. Zhu, *J. Mater. Chem.*, 2012, **22**, 20143-20145.
- 7 J. W. Zhang, X. X. Yan, J. W. Zhang, W. Cai, Z. S. Wu and Z. J. Zhang, *J. Power Sources*, 2012, **198**, 223-228.
- 8 J. M. Ma, J. Zhang, S. R. Wang, Q. H. Wang, L. F. Jiao, J. Q. Yang, X. C. Duan, Z. F. Liu, J. B. Lian and W. J. Zheng, *CrystEngComm*, 2011, **13**, 6077-6081.
- 9 J. Y. Shen, H. Wang, Y. Zhou, N. Q. Ye and L. J. Wang, *CrystEngComm*, 2012, **14**, 6215-6220.
- 10 X. M. Wu, S. C. Zhang, L. L. Wang, Z. J. Du, H. Fang, Y. H. Ling and Z. H. Huang, *J. Mater. Chem.*, 2012, **22**, 11151-11158.
- 11 M. Wachtler, J. O. Besenhard and M. Winter, *J. Power Sources*, 2001, **94**, 189-193.
- 12 K. T. Lee, Y. S. Jung and S. M. Oh, *J. Am. Chem. Soc.*, 2003, **125**, 5652-5653.
- 13 J. W. Deng, H. X. Ji, C. L. Yan, J. X. Zhang, W. P. Si, S. Baunack, S. Oswald, Y. F. Mei and O. G. Schmidt, *Angew. Chem. Int. Ed.*, 2013, **52**, 2326-2330.
- 14 J. H. Kong, W. A. Yee, Y. F. Wei, L. P. Yang, J. M. Ang, S. L. Phua, S. Y. Wong, R. Zhou, Y. L. Dong, X. Li and X. H. Lu, *Nanoscale*, 2013, **5**, 2967-2973.
- 15 A. Finke, P. Poizot, C. Guery, L. Dupont, P. L. Taberna, P. Simon and J. M. Tarascon, *Electrochem. Solid-State Lett.*, 2008, **11**, E5-E9.
- 16 C. M. Park, S. Yoon, S. I. Lee and H. J. Sohn, *J. Power Sources*, 2009, **186**, 206-210.
- 17 J. M. Ma, J. Q. Yang, L. F. Jiao, T. H. Wang, J. B. A. Lian, X. C. Duan and W. J. Zheng, *Dalton Trans.*, 2011, **40**, 10100-10108.
- 18 Y. L. Li, M. A. Trujillo, E. G. Fu, B. Patterson, L. Fei, Y. Xu, S. G. Deng, S. Smimov and H. M. Luo, *J. Mater. Chem. A*, 2013, **1**, 12123-12127.
- 19 J. Y. Shen, H. Wang, Y. Zhou, N. Q. Ye, Y. H. Wang and L. J. Wang, *Chem. Eng. J.*, 2013, **228**, 724-730.
- 20 Q. S. Gao, L. C. Yang, X. C. Lu, J. J. Mao, Y. H. Zhang, Y. P. Wu and Y. Tang, *J. Mater. Chem.*, 2010, **20**, 2807-2812.

- 21 E. Hosono, T. Kudo, I. Honma, H. Matsuda and H. S. Zhou, *Nano Lett.*, 2009, **9**, 1045-1051.
- 22 J. Y. Liao, D. Higgins, G. Lui, V. Chabot, X. C. Xiao and Z. W. Chen, *Nano Lett.*, 2013, **13**, 5467-5473.
- 23 L. Q. Mai, F. Yang, Y. L. Zhao, X. Xu, L. Xu and Y. Z. Luo, *Nat. Commun.*, 2011, **2**.
- 24 J. S. Chen, Y. L. Cheah, S. Madhavi and X. W. Lou, *J. Phys. Chem. C*, 2010, **114**, 8675-8678.
- 25 Y. X. Sun, J. Wang, B. T. Zhao, R. Cai, R. Ran and Z. P. Shao, *J. Mater. Chem. A*, 2013, **1**, 4736-4746.
- 26 X. Y. Xue, Z. H. Chen, L. L. Xing, S. Yuan and Y. J. Chen, *Chem. Commun.*, 2011, **47**, 5205-5207.
- 27 J. L. Hu, H. M. Li, C. J. Huang, M. Liu and X. Q. Qiu, *Appl. Catal. B: Environ.*, 2013, **142**, 598-603.
- 28 B. Ling, X. W. Sun, J. L. Zhao, Y. Q. Shen, Z. L. Dong, L. D. Sun, S. F. Li and S. Zhang, *J. Nanosci. Nanotechnol.*, 2010, **10**, 8322-8327.
- 29 M. Rivenet, P. Roussel and F. Abraham, *J. Solid State Chem.*, 2008, **181**, 2586-2590.
- 30 Y. Z. Su, S. Li, D. Q. Wu, F. Zhang, H. W. Liang, P. F. Gao, C. Cheng and X. L. Feng, *ACS Nano*, 2012, **6**, 8349-8356.
- 31 J. Q. Zhao, J. P. He, J. H. Zhou, Y. X. Guo, T. Wang, S. C. Wu, X. C. Ding, R. M. Huang and H. R. Xue, *J. Phys. Chem. C*, 2011, **115**, 2888-2894.
- 32 J. Zhu, D. N. Lei, G. H. Zhang, Q. H. Li, B. G. Lu and T. H. Wang, *Nanoscale*, 2013, **5**, 5499-5505.
- 33 J. C. Perez-Flores, A. Kuhn and F. Garcia-Alvarado, *J. Power Sources*, 2008, **182**, 365-369.
- 34 G. Pistoia, M. Pasquali and F. Rodante, *J. Power Sources*, 1985, **16**, 263-269.