Binder-free Co–CoOₓ nanowire arrays for lithium ion batteries with excellent rate capability and ultra-long cycle life†

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Structure stability and fast charge–discharge capacity are highly desirable for electrode materials applied in lithium ion batteries (LIBs). In this report, binder-free Co–CoOₓ nanowire arrays (NWAs) were obtained by a simple H₂ reduction of Co₂O₄ NWAs. The resulting Co–CoOₓ NWAs were grown directly on the current collector with enough open space between each nanowire, which provides fast charge transfer channels and large accessible surface area to the electrolyte. More importantly, the introduction of electrochemically inactive Co without volume change during cycling for LIBs could improve the structural stability of the Co–CoOₓ NWA electrode and the high electronic conductivity of metallic Co in the array structure greatly enhances the electron transfer ability of Co–CoOₓ nanowires. Benefitting from those designed structural features, the binder-free Co–CoOₓ NWAs achieved remarkable electrochemical performances with excellent cycle stability at high rates and high rate capacity. The Co–CoOₓ NWA electrode maintains highly stable capacities of 990 and 740 mA h g⁻¹ after 1000 cycles at 10 and 20 A g⁻¹, respectively. At an ultrahigh rate of 50 A g⁻¹, a high reversible capacity of 413 mA h g⁻¹ is achieved. The result demonstrates that such a novel Co–CoOₓ nanowire array structure is a new strategy to design high performance anode materials for LIBs.

However, because of intrinsically low electronic conductivity and large volume change during cycling, CoOₓ materials often suffer from poor rate capacity and rapid capacity fading, hindering their practical applications.28–31 One promising strategy for handling those shortcomings is to design nanosized CoOₓ materials with a unique structure and smart hybridization of those with high conductivity materials such as graphene and carbon nanotubes.21–23 But traditional electrode preparation is usually accompanied by the use of insulating organic binders, which might affect the transport of electrons.24–26 Furthermore, the nanoparticles are easy to agglomerate during cycling which would also deteriorate the performance.27 Therefore, it is necessary to fabricate highly stable electrodes directly grown on current collectors without using insulating binders. Building upon this idea, grass-like Co₂O₃ NWAs were directly synthesized on the current collectors in our previous work, showing excellent electrochemical performance.28 However, the cycle stability at high rates is not satisfactory, which still needs to be improved.

Recently, nanowire array materials hybridized with highly conducting and electrochemically inactive materials have been considered as efficient anode materials to improve the rate capacity and cycle stability of LIBs.29–31 Within the free-standing array structures, the robust adhesion of active materials on current collectors shortens electron transport paths and ensures good conductivity of the integral electrode. And the open space between neighboring nanowires allows for easy

1. Introduction

To meet the growing demand for efficient mobile energy storage devices, lithium ion batteries (LIBs) with the merits of high energy density, safety and long cycle life have been considered as a promising power source for electric vehicles and portable electronic devices.1–3 The major challenge for the next-generation LIBs is to develop electrodes possessing high capacity, superior cyclic stability, and excellent rate capability.4–5

Transition-metal oxides have been considered as promising anodes for LIBs due to their abundance, low cost, and high theoretical capacity.6–11 Among them, cobalt oxides (CoO and Co₃O₄), possessing a high theoretical capacity of 716 and 890 mA h g⁻¹, have attracted much attention in the last decade.12–17

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†Electronic supplementary information (ESI) available: XRD patterns, H₂-TPR profiles, TEM and HRTEM images of Co-CoOₓ NWAs, the CV curves and charge and discharge curves for first three cycles of CoOs, capacity retention ratio of Co₂O₃ and Co-CoOₓ NWAs, cycling performance of Co₂O₃ and Co-CoOₓ at 10 A g⁻¹, and cycling performance of Co₂O₃ and Co-CoOₓ at 5 A g⁻¹ and 10 A g⁻¹ based on the total mass of the array electrode. SEM, XRD and TEM images of Co-CoOₓ NWAs from the side view after 200 cycles at 20 A g⁻¹. See DOI: 10.1039/c5ta02987b

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diffusion of the electrolyte into the inner region of the array electrode. Moreover, inactive materials like Co, Cu, and Ag metals acting as a good mechanically stable scaffold improve the cycle stability of the array electrode for LIBs. In this regard, it is assumed that hybrid CoOx NWAs with Co metal can effectively enhance the battery performance.

In this paper, binder-free CoOx NWAs were synthesized by a one-step hydrothermal method, and then Co–CoOx NWAs were obtained by a simple H2 reduction of Co3O4 NWAs. The as-prepared Co–CoOx NWAs combine the advantages of array structures and metal doping. As shown in Fig. 1, the newly introduced metallic Co plays a key role in achieving extraordinary battery performance. Firstly, the good conductivity of Co provides a fast electronic conductivity pathway in the integral array electrode, which is beneficial for the high rate performance. Secondly, the inactive Co acts as a skeleton structure remitting the structural deterioration and enhancing the structural stability, which finally prolongs the cycle life. Based on the above advantages, Co–CoOx NWAs achieved an excellent electrochemical performance for LIBs. Remarkable capacities of 990 and 740 mA h g−1 are obtained after 1000 cycles at 10 and 20 A g−1, respectively. Even at a high rate of 50 A g−1, Co–CoOx NWAs can still maintain a capacity of 413 mA h g−1.

2. Experimental section

2.1 Preparation of Co–CoOx NWAs on Ti substrates

Co3O4 nanowire arrays were synthesized according to our previous work. In brief, 1 mmol Co(NO3)2, 2 mmol NH4F and 5 mmol urea were dissolved in 70 mL of deionized water, and then transferred to a 100 mL Teflon-lined stainless autoclave; a piece of Ti foil (1 cm × 1 cm) was suspended in the reaction solution. The autoclave was sealed and maintained in an electric oven at 110 °C for 5 h, and then cooled down to room temperature. The precursor was taken out and washed with deionized water. Finally, the Co3O4 NWAs were obtained by annealing at 350 °C in Ar for 2 h. Co–CoOx NWAs were obtained by a simple reduction of Co3O4 NWAs in Ar/H2 (8%) at 400 °C for 2 h. The loading of the Co–CoOx mixture on the Ti foil is about 0.4 mg cm−2, while CoOx accounts for 40% of the total mass of the Co–CoOx array.

2.2 Material characterization

The structure and morphology were characterized by scanning electron microscopy (SEM, NOVA NANOSEM 430) and transmission electron microscopy (TEM) (TEM, JEM-2010HR). The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using filtered Cu Kα radiation. The acc. voltages of the SEM and TEM are 10 kV and 200 kV, respectively. The X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer using an Al Kα X-ray source. All XPS spectra were calibrated using the C 1s line at 284.6 eV. And curve fitting was performed using XPSPEAK41 based on the peak area. H2 temperate programmed reduction (H2-TPR) experiments were performed using a TP-5080 Multi-functional Automatic Adsorption Instrument from Tianjin Xianquan Company.

2.3 Electrochemical measurements

The electrochemical performances of Co–CoOx and Co3O4 NWAs were measured using half coin cells (CR2025). Co–CoOx and Co3O4 NWAs were directly used as the working electrodes without addition of any binders and conducting carbon black. Pure Li foil was used as the counter electrode. A Whatman GF/B glass fiber membrane was used as the separator. The electrolyte consisted of a solution of 1 mol L−1 LiPF6 in ethylene carbonate (EC)/diethylcarbonate (DEC) (1 : 1 by volume). The coin cells were assembled in an argon-filled glovebox (Mikrouna, super 1220) where the oxygen and moisture contents are less than 1 ppm. Galvanostatic charge–discharge cycles were tested using a Battery Testing System (Neware Electronic Co., China) between 0.01 and 3.0 V. Cyclic voltammetry (CV) measurements were carried out on an electrochemical workstation (CHI660D, Chenhua, Shanghai, China) over the potential range of 0.01–3.0 V vs. Li/Li+ at a scanning rate of 0.2 mV s−1. The impedances of the batteries were measured on the Zahner IM6ex electrochemical workstation. The frequency range was set from 0.01 Hz to 1 MHz with a potential amplitude of 5 mV.

3. Results and discussion

Fig. 2 shows the typical SEM images of Co3O4 (a, c, and e) and Co–CoOx (b, d, and f) NWAs. After a simple hydrothermal synthesis, Ti foil is covered with grass-like Co3O4 NWAs (Fig. 2a). The as-prepared Co3O4 NWAs with a length of 5 μm and a diameter of 70–100 nm grow on Ti foil in a random orientation (Fig. 2c and e). The direct attachment of the Co3O4 nanowire on the current collector provides a fast charge transfer pathway, and helps to improve the rate capability. Notably, after
H₂ reduction, the Co–CoOₓ NWAs are also uniformly distributed on the Ti foil, although the nanowire partly crosslinks together and the surface of the nanowire becomes rough. On the basis of our previous work about Co₃O₄ NWAs, it is confirmed that the crosslinking of nanowires is beneficial for improving the structure stability and electronic conductivity. Moreover, the buffer space between each nanowire still exists after H₂ reduction, which contributes greatly to enlarging the electroactive surface between active materials and the electrolyte. The thickness of the Co–CoOₓ array on Ti foil is still about 5 µm.

Fig. 3a shows the X-ray diffraction (XRD) patterns of Co₃O₄ NWAs and Co–CoOₓ. As can be seen, after annealing in Ar at 350 °C, Co₃O₄ is well formed. There are five diffraction peaks that can be indexed to pure spinel phase Co₃O₄. However, after the H₂ reduction the diffraction peaks of Co₃O₄ disappeared entirely. Instead, four diffraction peaks of metallic Co appeared. The XRD analysis confirmed that Co₃O₄ was reduced to Co via annealing in a H₂ atmosphere. But the existence of CoOₓ could not be observed by the XRD analysis, which can be explained by the small amount of CoOₓ or the amorphous state of CoOₓ.

In order to confirm the existence of CoOₓ, X-ray photoelectron spectroscopy (XPS) was carried out. As presented in Fig. 3b, the survey spectrum primarily shows the presence of Co and O, along with a small quantity of C from the reference. For the Co 2p spectrum in Fig. 3c, two major peaks with BE values at 779.5 and 794.5 eV are assigned to the Co 2p 3/2 and Co 2p 1/2, respectively. After deconvolution of the Co 2p 3/2 branch, two peaks at 779.4 and 780.6 eV belong to Co³⁺ and Co²⁺, respectively. Notably, compared to Co₃O₄ NWAs in our previous work, the content of Co²⁺ is sharply increased, and the content of Co³⁺ is greatly decreased. It means that Co³⁺ is partly reduced to Co²⁺ due to the reduction process. The synthetic nanowire after H₂ reduction contains CoO. The O 1s spectrum in Fig. 3d can be deconvoluted into two peaks at 529.7 and 531.1 eV, which generally belong to lattice oxygen in CoOₓ and the oxygen in hydroxide ions. Beyond that, the mass change data by H₂-TPR (Fig. S2†) also show that the nanowire after H₂ reduction contains CoOₓ. The CoOₓ content in Co–CoOₓ can be deduced from H₂-TPR, which is around 40%. As is well known, the XPS analysis can only detect the surface region about the thickness of 5–10 nm. From the HRTEM image in Fig. S3,† it can be seen that the surface region of the Co–CoOₓ nanowire is mainly composed of CoOₓ. So in the XPS data (Fig. 3c), metallic Co cannot be detected.

The microstructure of the Co–CoOₓ NWAs was further investigated by TEM and HRTEM in Fig. 4. As seen in Fig. 4a and 4d, the Co–CoOₓ nanowire is composed of numerous nanocrystals with a size of 5–10 nm, and disordered pores exist among the primary nanoparticles. From the HRTEM images in Fig. 4b, two calculated interplanar distances of 0.204 nm and 0.246 nm correspond to the lattice plane spacing of Co and CoOₓ, which reveals that the as-prepared nanowire is composed of Co and CoOₓ. This result is in accord with XRD and XPS analysis. Besides, energy filtered TEM (EFTEM) images in Fig. 4c and d show that the O element is unevenly distributed in the as-synthesized Co–CoOₓ nanowire, and the amount of the O element is far less than that of the Co element in a single Co–CoOₓ nanowire. The EFTEM results are further evidence that the as-obtained nanowire after H₂ treatment is composed of cobalt
metal and CoO₂. The unique structure constructed by Co and CoO₂ combines the high electronic conductivity of Co and the high lithium storage capacity of CoO₂, which may have a promising application in energy storage.

Inspired by the fascinating structure, the Co–CoO₂ NWAs were tested as an anode material for LIBs. For comparison, the electrochemical performance of Co₃O₄ NWAs was also investigated. It is worth noting that the capacity calculated below is based on the active CoO₂. The cyclic voltammetry (CV) profiles of Co–CoO₂ (Fig. 5a) and Co₃O₄ (Fig. S5a†) were obtained for the initial three cycles in the voltage range of 0.01–3.0 V at a scan rate of 0.2 mV s⁻¹, respectively. As shown in Fig. 5a, in the first cycle, the cathodic peak at 0.7 V is ascribed to the formation of a solid electrolyte interface (SEI) film and the reduction of CoO₂ to Co.⁸⁻¹⁹ And then the cathodic peak shifts to 0.9 V in the following cycles, in addition, a new cathodic peak appears at 1.9 V. During the anodic scan, two broad peaks located at 1.3 V and 2.1 V are recorded, which can be attributed to the oxidation of Co to CoO₂. Fig. 5b and S5b† show the charge–discharge profiles of Co–CoO₂ NWAs in the initial three cycles at a current density of 500 mA g⁻¹, respectively. In the first cycle, a plateau below 1 V was observed, which is consistent with the above CV measurements. The initial discharge and charge capacities of Co–CoO₂ NWAs are 1361 and 1027 mA h g⁻¹, respectively, and the first columbic efficiency is 75%. The potential difference between the charge and discharge potential is commonly observed in transition metal oxide anodes.⁴⁶⁻⁴¹ This phenomenon is related to the large electrode polarization.⁴⁰

Fig. 5c displays the rate capability of Co₃O₄ and Co–CoO₂ NWAs under various current densities ranging from 0.5 to 50 A g⁻¹. As can be seen, Co–CoO₂ NWAs deliver the reversible capacities of 925 and 865 mA h g⁻¹ at a low rate of 0.5 A g⁻¹ (0.6C) and 1 A g⁻¹ (1.2C), respectively. When the current density increases (2 A g⁻¹ to 50 A g⁻¹), the Co–CoO₂ NWA electrode shows a much better rate capability than the Co₃O₄ NWA electrode; it delivers reversible capacities of 827, 756, 678, and 568 mA h g⁻¹ at 2, 5, 10, and 20 A g⁻¹, respectively. Even at a ultrahigh rate of 50 A g⁻¹, the Co–CoO₂ NWA electrode can still achieve a high capacity of 431 mA h g⁻¹. When the current density comes back to 0.5 A g⁻¹, a capacity over 1200 mA h g⁻¹ is obtained. The phenomenon of increasing capacity is commonly observed in transition metal oxide anodes.⁴³⁻⁴⁴ The high specific capacity is likely assignable to the reversible growth of a polymeric gel-like film resulting from the decomposition of electrolytes.⁴³⁻⁴⁴ In contrast, Co₃O₄ NWAs exhibit an undesired rate performance at high rates (≥5 A g⁻¹), the capacities of Co₃O₄ NWAs decline sharply by the increment of current density. It delivers a low capacity less than 100 mA h g⁻¹ at a high rate of 50 A g⁻¹ (56C), showing almost inability for Li⁺ storage. For a better understanding of the gap of their rate capabilities, capacity retention ratios (defined as the capacity at every current density over that at 0.5 A g⁻¹) at different rates are shown in Fig. S6.† Obviously, Co–CoO₂ NWAs maintain higher capacity retention ratios than Co₃O₄ NWAs at various rates, and the disparity between Co–CoO₂ and Co₃O₄ NWAs is widened with the increase of current density. The above results confirm the improved rate performance of Co–CoO₂ NWAs. To the best of our knowledge, this kind of superior rate capacity about Co₂O₃ array materials for LIBs has not been reported before. The main reason for the outstanding performance is the special structure constructed by Co and CoO₂. The advantages of Co–CoO₂ NWAs include: (1) the 3D array architecture provides easy access for the electrolyte to the active materials, and the strong adhesion of nanowires on the current collector guarantees good conductivity. (2) The metallic Co acts as a good electrical conductor to enhance the electronic conductivity of the integral electrode and a buffer to avoid the volume expansion of Co–CoO₂ nanowires, which finally becomes a huge booster for the excellent rate capacity.

Fig. 5d is the cycling performance of Co₃O₄ and Co–CoO₂ NWAs at a current density of 20 A g⁻¹. In the first cycle, Co₃O₄ NWAs have a high reversible capacity of 700 mA h g⁻¹. But the Co₃O₄ NWA electrode almost loses its ability for Li⁺ storage after only 100 cycles. The reason for the capacity fading of Co₃O₄ NWAs might be attributed to the large volume change during cycling which induced the loss of contact between the active materials and current collector. During repeated discharge and charge processes, the Co₃O₄ nanowire lost its contact with the Ti foil, even fall off from the Ti foil, which ultimately results in capacity fading. By contrast, the cycle performance of Co–CoO₂ NWAs is much better. Co–CoO₂ NWAs deliver a discharge capacity of 540 mA h g⁻¹ in the first cycle at 20 A g⁻¹ (24.6C) and maintain a reversible capacity about 740 mA h g⁻¹ after 1000 cycles. It should be noted that a capacity increase in the first 400 cycles occurs in Co–CoO₂ NWAs. The increased capacity in cycle performance is commonly observed in transition metal oxide anodes, which is similar to the capacity increasing in the rate capability.⁷⁻¹⁰⁻⁴₅ In addition, the cycle performance of Co–CoO₂ and Co₃O₄ NWAs at 10 A g⁻¹ is demonstrated in Fig. S7;† this battery performance is similar to the case at 20 A g⁻¹. Co–CoO₂
NWAs maintain a capacity of 755 mA h g\(^{-1}\) at 10 A g\(^{-1}\) (12.3C) after 1000 cycles, while Co\(_3\)O\(_4\) NWAs exhibit a poor cycle performance at 10 A g\(^{-1}\) (11.2C). The reason for the superior cycle performance of Co–CoO\(_x\) NWAs can be explained as follows: with cycles going on, the inactive metallic Co in the Co–CoO\(_x\) nanowire can effectively reduce the electron-transfer resistance, showing a superior rate capability. Meanwhile metallic Co serves as a structural skeleton which effectively prevents the structure destruction caused by repeated volume expansion and shrinkage during cycling, displaying an excellent cycle performance.

The Co\(_3\)O\(_4\) NWA and Co–CoO\(_x\) NWA electrodes were also characterized by electrochemical impedance spectroscopy (EIS) to evaluate their conductivities. The Nyquist plots shown in Fig. 6 contain a semicircle in the high frequency region and a sloped line in the low frequency region. The impedance data were fitted using an equivalent electrical circuit, where \(R_s\) is the total resistance of the electrochemical system, \(R_{ct}\) is the charge transfer resistance, \(W_0\) is the Warburg impedance, and CPE is the constant phase element which involves the double layer capacitance.\(^{46,47}\) The charge transfer resistance \(R_{ct}\) of Co–CoO\(_x\) NWAs (56 \(\Omega\)) is much smaller than that of Co\(_3\)O\(_4\) NWAs (314 \(\Omega\)). The results show that the Co–CoO\(_x\) NWA electrode has a faster charge transfer capability, and the introduction of metallic Co can enhance the conductivity of the array electrode.

In order to deeply understand the relationship of structure stability and battery performance, the surface morphologies of Co\(_3\)O\(_4\) NWAs and Co–CoO\(_x\) NWAs after 200 cycles at a rate of 20 A g\(^{-1}\) were investigated as shown in Fig. 7. A large number of cracks with the width less than 1 mm were observed on the anode surface of Co\(_3\)O\(_4\) NWAs, this phenomenon is also observed in other anode materials.\(^{48}\) Due to the structural deterioration, charge transfer is seriously impeded under prolonged cycling, which directly leads to the fading of cycle performance. However, the electrode of Co–CoO\(_x\) NWAs maintains its structural integrity without any cracks discovered. Due to the good maintenance of the structure, the electron can still transfer fast to the current collector after long term cycling; we believe that the remarkable structural stability is the main reason for the good cycle performance. Besides, after 200 cycles, the thickness of Co–CoO\(_x\) arrays changes to 6 \(\mu\)m [Fig. S9†]. The
change of the electrode thickness is related to the large volume change of Co–CoOx arrays during cycling, and the formation of the solid electrolyte interphase (SEI) film. Through the XRD and TEM analysis (Fig. S10 and S11†), it is validated that metallic Co still exists in the Co–CoOx nanowire after 200 cycles. The existence of metallic Co ensures the stable structure of the Co–CoOx array electrode, resulting in high battery performance.

4. Conclusions

In summary, binder-free Co–CoOx NWAs on Ti foil were successfully fabricated via a simple H2 reduction of Co3O4 NWAs obtained by a hydrothermal method. Benefiting from the design of the unique array structure and the introduction of inactive cobalt metal, the Co–CoOx NWA electrode exhibits improved rate capabilities and better cycle stability as compared to the Co3O4 NWA electrode. The Co–CoOx NWAs maintain high specific capacities of 990 and 740 mA h g–1 over 1000 cycles at 10 A g–1 and 20 A g–1, respectively. Even at a high rate of 50 A g–1, the discharge capacity still reaches 413 mA h g–1. The results show that in situ Co metal introduced into the array structure contributes significantly to improving the electrochemical performance. We believe that the obtained Co–CoOx array materials can provide an easy way to design anode materials for advanced high performance LIBs, and this method can be promoted to other similar material systems.

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Notes and references