



Short communication

Synthesis of Co_3O_4 /Carbon composite nanowires and their electrochemical properties

Peng Zhang^a, Zai Ping Guo^{a,b,*}, Yudai Huang^c, Dianzeng Jia^c, Hua Kun Liu^a^a Institute for Superconducting & Electronic Materials, University of Wollongong, NSW 2522, Australia^b School of Mechanical, Materials & Mechatronic Engineering, University of Wollongong, NSW 2522, Australia^c Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, PR China

ARTICLE INFO

Article history:

Received 7 August 2010

Received in revised form 25 October 2010

Accepted 26 October 2010

Available online 3 November 2010

Keywords:

Electrospinning

Anode material

Cobalt oxide

Amorphous carbon

Coulombic efficiency

Lithium ion batteries

ABSTRACT

Porous nanowires of Co_3O_4 /Carbon composite have been synthesized by using a simple and inexpensive electrospinning technique. The as-prepared materials were investigated by X-ray diffraction and scanning electron microscopy. The electrochemical properties of the composite have been characterized using cyclic voltammetry and galvanostatic methods. The results show a remarkably improved electrochemical performance in term of reversible capacity, rate capability, and cycling performance.

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1. Introduction

Energy storage is one of the great issues in the 21st century [1]. The popularity of portable devices and electric cars means that reliable batteries are required with high energy density, excellent rate capability, and good cycling performance. In the last decade, rechargeable lithium ion batteries (LIBs) have been used to power portable devices. However, due to the limited gravimetric capacity of carbon (the anode material in commercial lithium ion batteries), alternative anode materials have been explored by researchers [2]. Poizot et al. reported that electrodes made of transition-metal oxides (Fe_2O_3 , CuO , CoO , NiO , etc.) demonstrated reversible capacities several times larger than that of graphite [3]. As the most stable phase of cobalt oxide, Co_3O_4 exhibits excellent reversibility and high specific capacity compared with other transition-metal oxides.

However, transition-metal oxides anodes normally show large irreversible capacity in the first charge/discharge cycle due to the side-effects, such as formation of a solid electrolyte interphase (SEI) film, loss of active materials during cycling, and the partially irreversible reaction to form Li_2O [4,5]. Compared to the corresponding bulk materials, nanoscale materials introduce innovative reaction

mechanisms and provide shorter ion diffusion paths and larger electrode/electrolyte contact areas in lithium ion batteries, which improve the electrochemical performance in terms of reversible capacity, high current charge/discharge ability, and cycling stability [6]. Various nanostructures of Co_3O_4 have previously been fabricated, such as nanoparticles [7], nanofibers [8], nanorods, and nanotubes [9,10]. Among these materials, one-dimensional (1D) cobalt oxides have received steadily growing interest.

Herein, we report on the fabrication of porous Co_3O_4 /Carbon composite nanowires by using a relatively simple electrospinning technique combined with subsequent thermal treatment. The electrochemical characteristics of the as-prepared composite nanowires were investigated using cyclic voltammetry and galvanostatic methods. The results show remarkably improved performance in terms of reversible capacity, rate capability, and cycling performance.

2. Experiment

Polyacrylonitrile (PAN) ($M_w = 150,000$, Sigma–Aldrich) was added into the solvent *N,N*-dimethylformamide (DMF) with mechanical stirring. The solution was heated at 100°C for 1 h to form a polymer solution. 20% mass weight of cobalt acetate (Sigma) was added into the polymer solution, and the mixture was stirred for 1 h.

* Corresponding author at: Institute for Superconducting & Electronic Materials, University of Wollongong, NSW 2522, Australia. Tel.: +61 2 4221 5225; fax: +61 2 4221 5731.

E-mail addresses: zguo@uow.edu.au (Z.P. Guo), jdz@xju.edu.cn (D. Jia).

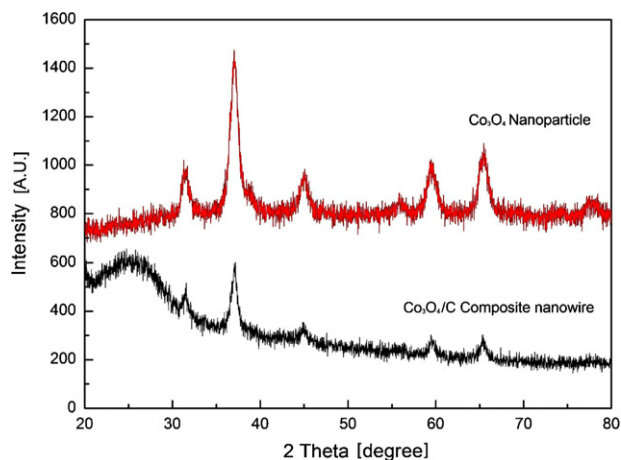


Fig. 1. XRD pattern of $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires and Co_3O_4 nanoparticles.

Details of the electrospinning device have been introduced in many previous works [11]. 14 kV DC voltage was applied between the needle and the collector. Copper foil was used as the collector. The as-prepared $\text{Co}^{2+}/\text{PAN}$ composite was heated at 250°C in air for 1 h and then at 500°C in an argon atmosphere for 3 h (heating rate: 1°C min^{-1}). The product is Co_3O_4 and amorphous carbon composite nanowires. For comparison, some products were treated at 360°C in air for 50 min after sintering in argon. The product is Co_3O_4 nanoparticles.

The product was evaluated by X-ray diffraction (XRD, Philip MMA) and field emission scanning electron microscopy (SEM, JEOL 7500). Electrochemical characteristics were examined by assembling a 2032 coin cell. The material was mixed with polyvinylidene

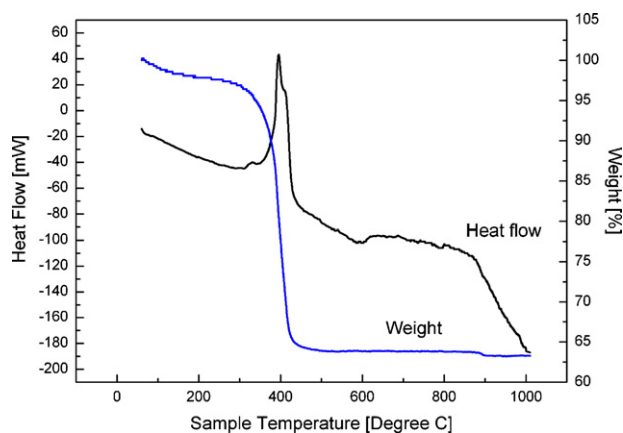


Fig. 2. TGA/DSC of $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires.

fluoride (PVDF), and the mixture was dissolved in *N*-methyl-2-pyrrolidone (NMP) solvent. Then, the slurry was cast on copper foil current collectors cut to a 1 cm^2 area. Lithium foil was used in this experiment as counter electrode. The electrolyte was 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 volume ratio (Zhangjiagang, PR China). The cells were assembled in an argon-filled glove box and tested at room temperature (20°C). Cyclic voltammograms (CV) were conducted in a Parstat 2273 Electrochemical System (Princeton Applied Research). The scan rate for CV was 0.1 mV s^{-1} with cut-off voltage of 0.01–3.0 V. For galvanostatic testing, the cells were discharged and charged at a current density of 100 mA g^{-1} with cut-off voltage of 0.01–3.0 V.

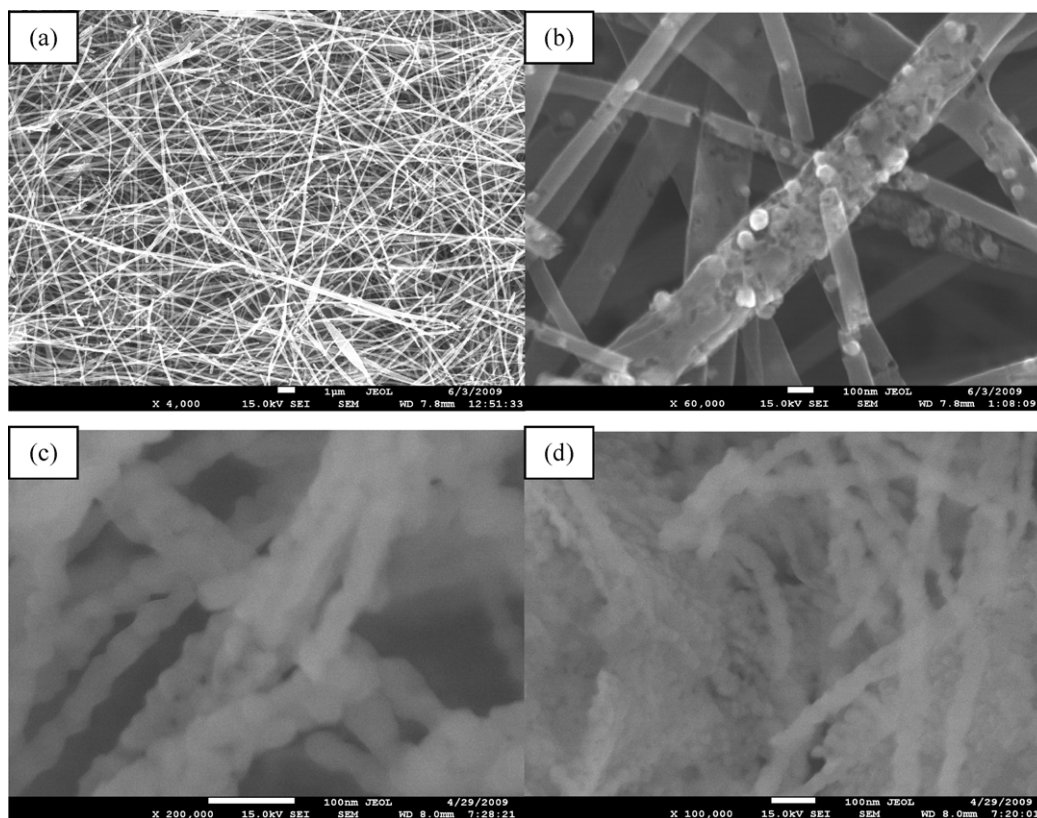


Fig. 3. SEM images of (a and b) $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires and (c and d) Co_3O_4 nanoparticles at different magnifications.

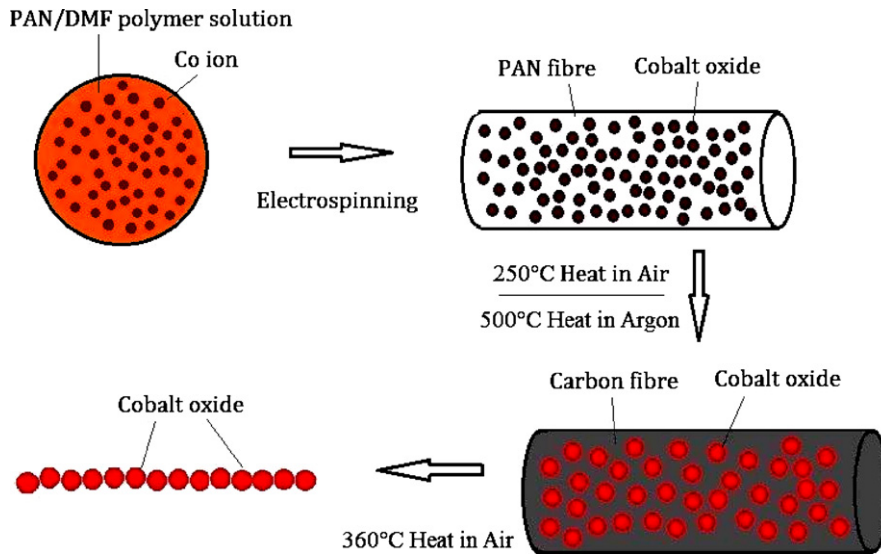


Fig. 4. Schematic illustration of the electrospinning of $\text{Co}_3\text{O}_4/\text{C}$ wires.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-synthesized $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires and Co_3O_4 nanoparticles. All peaks can be well indexed to the pure cubic phase of Co_3O_4 (JCPDS card no. 03-065-3103). No significant impurities or other phases were observed, indicating that the product is of high purity. The broadening of peaks for both products indicates a very fine grain size. Compared to the pure Co_3O_4 , an additional broad peak between 20° and 30° degree has appeared in the pattern of the as-prepared $\text{Co}_3\text{O}_4/\text{C}$ composite, which can be indexed to amorphous carbon.

Fig. 2 shows the thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) curves obtained for the as-spun $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires. The heating rate is $10^\circ\text{C min}^{-1}$. There is an endothermic peak at around 400°C , which indicates that amorphous carbon burns off at this temperature. According to the TGA curve, the weight of carbon is around 38% of the total active materials.

Fig. 3(a) shows SEM image of the electrospun nanowires. The wires are about 200–300 nm in diameter and exhibit a long and straight morphology. The nano-beads on the surfaces of the wires are uniform and about 50–100 nm in diameter (Fig. 3b).

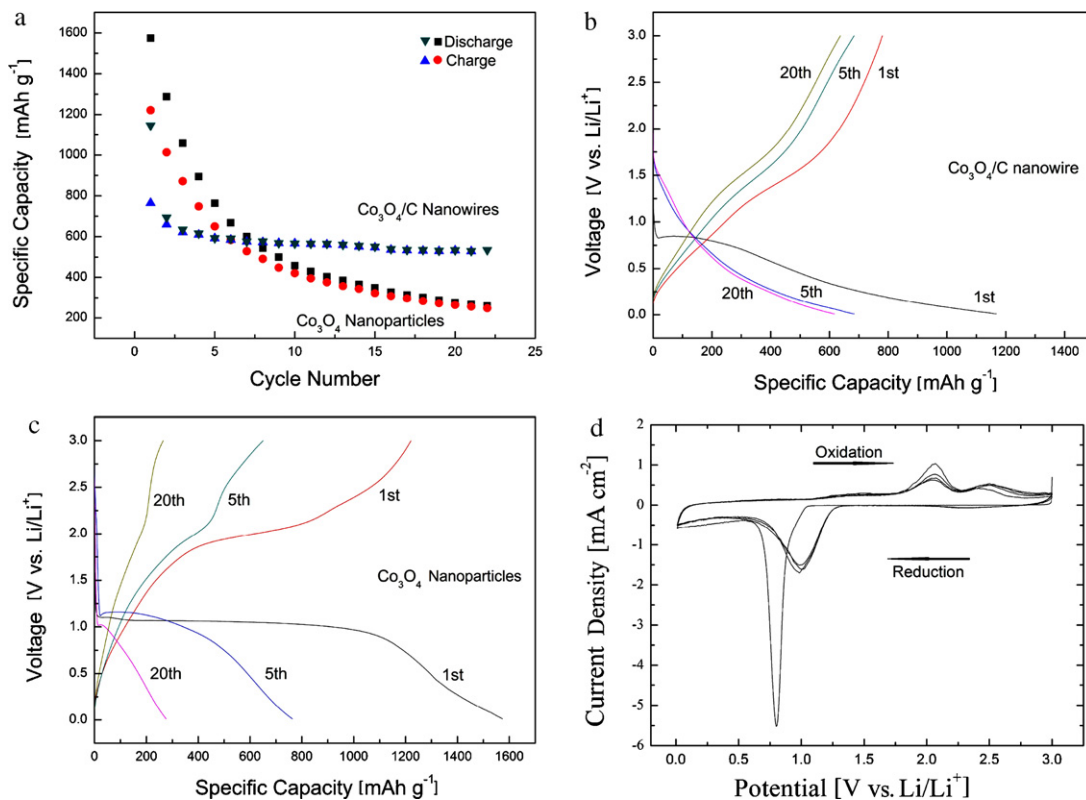


Fig. 5. (a) Cycling performance of as-prepared $\text{Co}_3\text{O}_4/\text{C}$ nanowires and Co_3O_4 nanoparticle electrodes, (b) charge/discharge profiles of $\text{Co}_3\text{O}_4/\text{C}$ nanowire electrodes for selected cycles, (c) charge/discharge profiles of Co_3O_4 nanoparticle electrodes for selected cycles, (d) CV of as-prepared $\text{Co}_3\text{O}_4/\text{C}$ nanowires.

Fig. 4 is a schematic illustration of the electrospinning of $\text{Co}_3\text{O}_4/\text{C}$ nanowires. During electrospinning, the cobalt ions are ejected from the nozzle and fully coated by the polymer solution. The original liquid jet splits into multiple branches because of the very high spinning frequency, and the jet is continuously elongated as it moves toward the collector [12]. Therefore, the diameter of the nanowire is greatly reduced, and the cobalt ions are encapsulated in the PAN wires. The electrospun wires are firstly stabilized at 250°C in air to create Co_3O_4 nanoparticles. Then, the wires are carbonized in argon to form the amorphous carbon matrix at 500°C . For comparison, some products are annealed in air. Fig. 3(c) and (d) shows that after the annealing in air, the amorphous carbon has been removed and the Co_3O_4 particles are agglomerated.

The electrochemical performance of the as-prepared $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires was evaluated by galvanostatic charge/discharge cycling at a current density of 100 mA g^{-1} (Fig. 5(a)). For comparison, we also evaluated the Co_3O_4 nanoparticles under the same electrochemical condition. Fig. 5(b) and (c) shows charge/discharge profiles of $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires and Co_3O_4 nanoparticles in the 1st, 5th, and 20th cycles. In the first discharge step, the nanowires and the nanoparticles exhibited long voltage plateaus at 0.8 V and 1.1 V , respectively, followed by a sloping curve down to 0.01 V . The first discharge and charge capacities for nanowires are 1146 mAh g^{-1} and 765 mAh g^{-1} , respectively. The specific capacities were calculated based on the weight of total active materials, i.e. $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires. The low initial coulombic efficiency may have resulted from the irreversible conversion reaction and the formation of the solid electrolyte interphase (SEI) layer [13]. $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires exhibited reversible capacity of 592 mAh g^{-1} at the 5th cycle and 534 mAh g^{-1} at the 20th cycle. By recalculating the specific capacity based on the weight of Co_3O_4 , the capacities are 954 mAh g^{-1} at the 5th cycle and 861 mAh g^{-1} at the 20th cycle at current density of 100 mA g^{-1} . The theoretical capacity of pure Co_3O_4 is 890 mAh g^{-1} . The extra capacity is attributed to the contribution of carbon and the reversible decomposition of electrolyte with formation of the SEI during cycling, along with extra absorption of Li ions in the porous architecture due to decomposition of PAN to carbon [3,14]. The coulombic efficiency rises from around 66.8% to 98.9% at the 5th cycle and 99.7% at the 20th cycle. In contrast, the capacity of the Co_3O_4 nanoparticles first increases to over 1574 mAh g^{-1} and then decreases significantly. After five cycles, the reversible capacity is around 763 mAh g^{-1} , and the coulombic efficiency is around 85.1%. After 20 cycles, the Co_3O_4 nanoparticle electrode only retains a capacity of 276 mAh g^{-1} . From the results, the $\text{Co}_3\text{O}_4/\text{C}$ composite nanowire electrode has better cycling performance. The reason could be the amorphous carbon in the composite, which forms a shell to coat the Co_3O_4 nanoparticles and is tolerant of the volume change of cobalt oxide during lithium ion insertion/extraction [15].

Fig. 5(d) shows cyclic voltammograms (CV) of electrode made from $\text{Co}_3\text{O}_4/\text{C}$ nanowires at a scan rate of 0.1 mV s^{-1} and a temperature of 20°C . In many previous works [16,17], the researchers proposed that the electrochemical reaction mechanism of Li with transition-metal oxides is different from that in the classical layered materials [3].

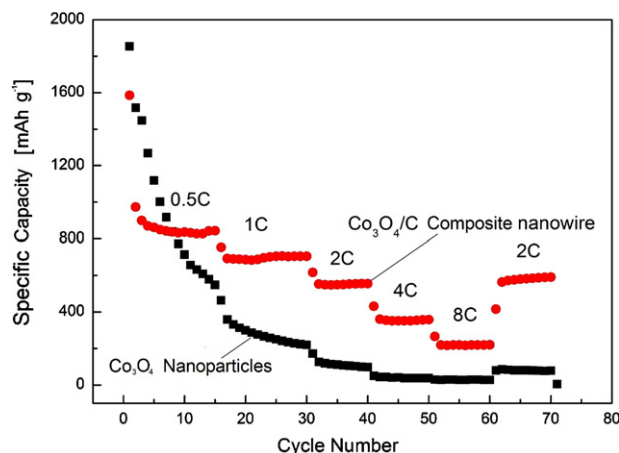
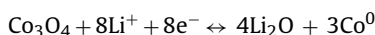


Fig. 6. Specific capacity of $\text{Co}_3\text{O}_4/\text{C}$ nanowires and Co_3O_4 nanoparticles at various current densities.

As shown above, the redox reaction of the phase transformation of cobalt is complex. In our experiment, the one broad cathodic current peak and two anodic peaks, shown in Fig. 5(d), indicate a multistep electron capture and loss procedure during the redox reaction [17]. Only one cathodic peak can be observed during the reduction process. The current density and potential are significantly different between the first cycle and the following cycles in the cathodic process. The reduction potential is 0.8 V for the first cycle and about 1 V for the following cycles. The current densities are 5.5 mA g^{-1} and about 2.83 mA g^{-1} for the first cycle and the following cycles, respectively. This higher peak intensity in the first cycle reveals a faster kinetics for the phase transformation of cobalt and the formation of the SEI film [18]. It also can be considered that the grain size of the product is very fine and the specific surface area is large, so the reaction is relatively severe, which results in a higher cathodic current in the first cycle [17]. During the anodic polarization, two peaks are observed. One is around 2.07 V and the other is around 2.5 V . The shape of the CV curves in the second and following cycles remain similar, and the potentials and current densities do not change too much in those cycles. This phenomenon indicates the reversible reduction and oxidation of the electrode material [18].

In addition, the $\text{Co}_3\text{O}_4/\text{C}$ composite nanowire shows better rate capability compared to the Co_3O_4 nanoparticle electrode at various rates from 0.5 C to 8 C (Fig. 6). The $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires deliver a capacity of 842.3 mAh g^{-1} after 15 cycles at 0.5 C , whereas the Co_3O_4 nanoparticle electrode retains only 582.9 mAh g^{-1} after 15 charge/discharge cycles. The subsequent capacity of the composite nanowire and the nanoparticle electrodes is 705.7 mAh g^{-1} and 218.6 mAh g^{-1} at the 30th cycle at 1 C ; 555.7 mAh g^{-1} and 98.6 mAh g^{-1} at the 40th cycle at 2 C ; 358 mAh g^{-1} and 37 mAh g^{-1} at the 50th cycle at 4 C ; 220 mAh g^{-1} and 28 mAh g^{-1} at the 60th cycle at 8 C , respectively. Moreover, when the current density returns to 2 C after 60 cycles, the $\text{Co}_3\text{O}_4/\text{C}$ composite nanowire electrode recovers its previous capacity at 2 C or even a slightly higher one (590.7 mAh g^{-1} at the 70th cycle). The good performance of the $\text{Co}_3\text{O}_4/\text{C}$ nanowires at various current densities can be attributed to the amorphous carbon shell and the one-dimensional morphology, which improve the electrode/electrolyte contact area and favour the diffusion of ions, resulting in a better rate capability [6].

Based on the results presented above, the $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires show better electrochemical performance than Co_3O_4 fabricated using the same technique. The most likely reasons

are discussed as follows. Firstly, in the composite, the Co_3O_4 nanoparticles are embedded in the amorphous carbon matrix, which not only provides a flexible buffer to accommodate the volume change during lithium insertion/extraction, but also prevents the aggregation and cracking or crumbling of the cobalt oxide nanoparticles [6,19]. Thus, the composite electrode exhibits excellent cycling performance compared to the bare Co_3O_4 electrode. Secondly, the lithium ion diffusion significantly depends on the transport length and specific surface area of the material [20]. In our experiment, the one-dimensional morphology and the nanoscale materials increase the proportion of atoms lying on the surface and decrease the ion diffusion length, which results in a large electrode/electrolyte contact area and a short average path length for Li-ion transport. Therefore the nanowires exhibit high rate capability and good coulombic efficiency [6]. Thirdly, the amorphous carbon has high electrical conductivity, which decreases the interior resistance of the electrodes and is good for balancing the electronic and ionic conductivity [21]. Considering its high electrochemical performance, the as-prepared $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires can be considered as a good candidate anode material for LIBs.

4. Conclusion

In this work, we reported unique 1D $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires and investigated their electrochemical properties. This material exhibited high rate capability and good cycling performance. The improved performance may be attributed to the effects of nanoscale grains, the carbon coating of the Co_3O_4 nanoparticles, and the 1D nanostructure. Because of the advantages shown above, $\text{Co}_3\text{O}_4/\text{C}$ composite nanowires have a potential application in high-performance LIBs.

Acknowledgements

The authors would like to thank Dr. Tania Silver for critical reading and correction of this manuscript. Financial support from the Australian Research Council (ARC) through Project LP0775456 is greatly appreciated.

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