BNL-114565-2017-JA

**High-rate and long-life lithium-ion
battery performance of hierarchically
hollow-structured NiCo₂O₄/CNT nanocomposite**

J. Wang, H. L. Xin

Published by Electrochimica Acta

Aug 2017

Center For Functional Nanomaterials

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (BES) (SC-22)**

Notice: This manuscript has been co-authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

High-rate and long-life lithium-ion battery performance of hierarchically hollow-structured NiCo₂O₄/CNT nanocomposite

Jie Wang^{a, 1}, Jianzhong Wu^{a, 1}, Zexing Wu^a, Lili Han^c, Ting Huang^a, Huolin L. Xin^b, and Deli Wang^{a,*}

^a Key laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

^b Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

^c School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China

Abstract

3D-transition binary metal oxides have been considered as promising anode materials for lithium-ion batteries with improved reversible capacity, structural stability and electronic conductivity compared with single metal oxides. Here, carbon nanotube supported NiCo₂O₄ nanoparticles (NiCo₂O₄/CNT) with 3D hierarchical hollow structure are fabricated via a simple one-pot method. The NiCo₂O₄ nanoparticles with interconnected pores are consists of small nanocrystals. When used as anode material for the lithium-ion battery, NiCo₂O₄/CNT exhibits enhanced electrochemical performance than that of Co₃O₄/CNT and NiO/CNT. Moreover, ultra-high discharge/charge stability was obtained for 4000 cycles at a current density of 5 A g⁻¹. The superior battery performance of NiCo₂O₄ nanoparticles is probably attributed to the special structural features and physical characteristics, including integrity, hollow structure with interconnected pores, which providing sufficient accommodation for the volume change during charge/discharge process. Besides, the consisting of ultra-small crystals enhanced the utility of active material, and intimate interaction with CNTs improved the electron-transfer rate.

Keywords: NiCo₂O₄ nanoparticles; Hierarchical hollow structure; interconnected pores; lithium storage; long-life stability

1. Introduction

Lithium ion batteries (LIBs) are regarded as one of the most promising renewable energy storage devices owing to their widely application in electric vehicles, portable devices and renewable energy integration. In the past years, the increasing demands for high-rate and long cycle life lithium ion batteries has stimulated the investigation of high theoretical capacity electrode materials[1], especially metal oxides (e.g. Co_3O_4 [2, 3], MnO_2 [4, 5], Fe_3O_4 [6, 7], Fe_2O_3 [8-10], SnO_2 [11, 12], TiO_2 [13, 14]), of which the theoretical capacity are larger than 700 mA h g^{-1} , much higher than graphite carbon (372 mA h g^{-1}). However, transition metal oxide anode materials with bulk structure are susceptible to cause large volume change during lithiation/delithiation and the low lithium diffusivity, which would lead to structure pulverization, even resulting in poor cycling stability and rate capability [15, 16]. Therefore, the investigation of transition metal oxide materials with different morphologies at micro- to nanoscales is noted to be one of the substantive solutions for the accommodation of volume change to some extent, which is attributed to their higher surface-to-volume ratio and short path length for Li-ion diffusion. Comparative study for recent references revealed that excellent battery performance for metal oxides with different nanostructure. Mesoporous peapod-like Co_3O_4 @carbon nanotube arrays has been reported as anode electrode material via a controllable nano-casting process, in which Co_3O_4 nanoparticles are confined exclusively in the intra tubular pores of the nanotube arrays [17]. The open pores between nanotubes render the Co_3O_4 nanoparticles accessible for effective electrolyte diffusion. As a result, such architecture exhibited excellent rate capacity, cycling performance as well as high specific capacity. One-dimensional (1-D) hierarchical NiO nanosheets covering bamboo-like amorphous CNT composites (NiO@CNT) were synthesized by using sulfonated polymeric nanotubes (PNTs) as both a template and a source of nano-structured carbon derived by low-temperature thermal carbonization treatment [18]. As an anode material, this hybrid material exhibited excellent electrochemical performance owing to the synergistic effects of the hollow amorphous CNT backbone and ultrathin NiO nanosheets.

Recently, binary transition metal oxides with controllable nanostructure such as $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ [19, 20], $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ [21, 22], $\text{Co}_3\text{V}_2\text{O}_8$ [23, 24], NiCo_2O_4 [25-27] et al have been reported in order to acquire the advantages of physical or electrochemical characteristics for two or more kinds of transition metal oxides. Among various binary metal oxides, NiCo_2O_4 is considered as a promising electrode material, in which one Co atom is replaced by Ni,

possessing much better electrical conductivity and higher electrochemical activity than nickel oxides or cobalt oxides [28, 29]. In addition, hollow structure with porous architecture could not only shorten the pathways for Li ion diffusion owing to the adequate interface contact between electrode and electrolyte, but also enlarge the surface area which is benefit to accommodate the volume change during the charge/discharge processes [30, 31]. In general, hollow structured materials are synthesized by template- or surfactants- directed methods [32-34] which is time consuming and costly, so far, a large scale production of hollow structured materials without using template- or surfactants is appealing via the widespread usage of low-cost raw transition metal materials.

Herein, a simple strategy for the synthesis of multi-walled carbon nanotubes supported three dimensional hierarchical hollow structured NiCo_2O_4 binary nanocomposites ($\text{NiCo}_2\text{O}_4/\text{CNT}$) is developed. The formation of hollow structure is based on the Kirkendall effect [35], in which no template or surfactant is needed. The hollow shell, composed of small nanocrystals, leave small interspaces for accommodating volume change during lithiation/delithiation and making full contact between electrolyte and active materials. When evaluated as anode materials for LIBs, the Li^+ ions can diffuse into the NiCo_2O_4 hollow structure through these pores within short distance and small resistance, favorably enhancing the electrochemical behaviors. It has been found that the $\text{NiCo}_2\text{O}_4/\text{CNT}$ composite with hierarchical hollow structure, interconnected pores and high electronic conductivity, delivered a high reversible capacity of 892 mAh g^{-1} at a current density of 1 A g^{-1} even after 200 charge/discharge cycles and still retained the hollow morphology, indicating its good potential application for high power applications in LIBs. Moreover, the $\text{NiCo}_2\text{O}_4/\text{CNT}$ also showed high reversible capacity of 500 mAh g^{-1} even after 4000 cycling with the average Coulombic efficiency above 99%, confirming the excellent high-rate stability.

2. Experimental part

2.1. Materials synthesis

The synthesis of $\text{NiCo}_2\text{O}_4/\text{CNT}$ was based on the simple impregnation-reduction-oxidation method. In detail, 0.90 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.45 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 mmol of MWCNTs were added into a 25 mL baker, then 10 mL purified water was poured into the baker followed by magnetic stirring at 60°C along with ultrasonic dispersion until the solution evaporated to form a thick slurry. The composite was then transferred into a vacuum drying oven at 40°C overnight. After milled in agate mortar[36], the resulting powder was annealed at 400°C

°C for 3 h under flowing Ar/H₂ atmosphere. In the end, the binary metallic composites were calcined in air condition at 350 °C for 10 hours.

The synthesis of hollow structured Co₃O₄/CNT and NiO/CNT nanoparticles was conducted via the same approach. The synthesis of hollow structured NiCo₂O₄ nanoparticles was conducted via the same approach, but the oxidation temperature was changed to 500 °C.

2.2. Material Characterization

Powder X-ray diffraction (XRD) was performed by using an X'Pert PRO diffractometer, and diffraction patterns were collected at a scanning rate of 4 ° min⁻¹. Thermal gravimetric analysis (TGA) was conducted on TA-Q500 Instrument at a heating rate of 10 °C min⁻¹. SEM images were obtained by using Nova NanoSEM 450. X-ray fluorescence (XRF) results were obtained via EAGLE III. ADF-STEM/TEM images were obtained using 200 and 300 keV field-emission S/TEMs. Electron Energy Loss Spectroscopy (EELS) data were acquired using a Gatan Tridiem spectrometer.

2.3. Electrochemical Measurements

For the electrochemical measurements, the working electrode was consisted of active material, electrical conductor (carbon black) and PVDF (in a weight ratio of 8: 1: 1) on a copper foil. For lithium-ion batteries, pure lithium foil was used as the counter electrode and a 1.0 M LiPF₆ in 1:1 v/v ethylene carbonate (EC)/dimethyl carbonate (DMC) as the electrolyte. The 2032 coin cells were assembled in an Ar-filled glovebox. Galvanostatic cycling results were obtained by using a Neware battery test system from 0.05 to 3.0 V. Cyclic voltammetry (CV) measurements were tested using a CHI 1040 with a potential range from 0.01 to 3.0 V.

3. Results and discussion

The hollow structured NiCo₂O₄/CNT nanoparticles with three dimensional interconnected pores were obtained via a simple two-step method. NiCo₂/CNT alloy composite was first formed by using an impregnation reduction method [37, 38], where the homogeneous mixture of NiCl₂, CoCl₂, and MWCNTs slurry was reduced under Ar/H₂ atmosphere at 400 °C for 3 h. The NiCo₂ alloy particles with smooth surface are uniformly distributed on multi-

walled carbon nanotubes (MWCNTs) with particle size ranging from 70 to 90 nm from the scanning transition electron microscopy (STEM) image in Figure 1a. The high-resolution TEM (HRTEM) image from the selected area (red dashed line frame) of one particle (inset of Figure 1b) in Figure 1b shows the arrays of lattice fringes. The inter-planar spacing between adjacent fringes are measured to be 0.204 nm and 0.176 nm, corresponding to (111) and (200) planes, respectively. The corresponding crystal planes in HRTEM image are consistent with the theoretical inter-planar spacing of NiCo₂/CNT from the XRD patterns (Figure S1c) where (111) and (200) lattice planes were detected at 44.3 ° and 51.7 °. According to Debye–Scherrer equation [39], the average crystal size of (111) plane for NiCo₂/CNT is 25.6 nm. Two pristine solid particles with different facet exposure are presented from the dark-field STEM image (DF-STEM) in Figure 1c. The corresponding STEM-electron energy loss spectroscopic (EELS) mapping from the two particles reveals the intermixing of nickel and cobalt in an ensemble of particles with nickel-rich surface, suggesting a surface segregation took place in Ar/H₂ atmosphere during the Ni-Co alloy formation [40]. Moreover, Co/CNT and Ni/CNT were obtained via the same method for comparison. The XRD patterns in Figure S1(a, b) confirmed the formation of pure metal phase.

Figure 1 (a) Overview STEM image NiCo₂/CNT nanoparticles; (b) high resolution TEM image of part of one NiCo₂ particle (inset, scale bar is 20 nm); (c) elemental mappings of NiCo₂/CNT particles (scale bar is 50 nm).

Hollow structured NiCo₂O₄ particles with interconnected pores were formed via oxidizing the NiCo₂ alloy particles at 350 °C in air atmosphere. As shown from the XRD pattern (Figure S1c), the NiCo₂ particles were fully

oxidized to form oxides. Diffraction peaks at 18.9° , 31.2° , 36.7° , 44.6° , 59.1° , 64.9° correspond to (111), (220), (311), (400), (511) and (440) lattice planes, which are consistent with the standard diffraction pattern of NiCo_2O_4 (JCPDS No. 02-4211). Compared with the XRD pattern of NiCo_2/CNT , the crystal size decreased obviously, and the main crystal size of (311) plane is calculated to be 7.1 nm. The TGA curves (Figure S1d) showed that the weight percentage of the metal oxides were approximately 56%. The main atomic percentage of Ni and Co (Table S1) obtained from XRF results is about 35% and 65%, which is approximately 1 : 2, thus, the binary catalyst was definite as $\text{NiCo}_2\text{O}_4/\text{CNT}$. The hollow structure of NiCo_2O_4 particles were verified by STEM images in Figure 2a and TEM image in Figure S2. It can be seen that the 3D nanostructure of the NiCo_2O_4 particles featured by a series of internal cavities and hollow voids. The rough surface of NiCo_2O_4 is contrary to the NiCo_2 particle (smooth in surface). The average particle size is calculated to be about 80 nm by measuring more than 200 particles. Moreover, scanning electron microscopy (SEM) image in Figure S3 depicts that the particles are surrounded by CNTs which would enhance the electric-conductivity of the $\text{NiCo}_2\text{O}_4/\text{CNT}$ composite. The inter-planar spacing between adjacent fringes in Figure 2b from part of a NiCo_2O_4 particle (inset of Figure 2b) are measured to be 0.287 nm, 0.245 nm and 0.203 nm, corresponding to (220), (311) and (400) planes, respectively. The enlarged TEM images in Figure 2e and the inset of Figure 2b reveal that the particles are likely to consist of small individual particles. The main crystal size was measured to be 7 nm (inset of Figure 2f), which is greatly consistent with the calculating results of (311) plane of $\text{NiCo}_2\text{O}_4/\text{CNT}$ from the XRD patterns. The phenomenon is verified by the HRTEM image in Figure 2f which demonstrates that different adjacent fringes region (the white dotted line) can be clearly distinguished, indicating good crystal structure of NiCo_2O_4 particles. While the region with different adjacent fringes (Figure 2f) is probably caused by overlapping of different ultra-small particles. The formation of hollow structure was based on the Kirkendall effect, where the internal metal elements of NiCo_2 alloy would transfer to the outside and react with the oxygen outside the particle at proper temperature, and then after NiCo_2 particle was completely oxidized, the morphology was transformed into hollow structure. The formation of interconnected pores experienced two stages during the oxidation step according to the report of Xin and co-workers [41], in which hollow structure was first obtained via the oxidation step (left particle in Figure 2c) and then the subsequent immigration between Ni, Co and O atoms resulted in interconnected pores (right particle in Figure 2c). The chemical distribution of Ni and Co in the two particles (Figure 2c and Figure 2d) indicates that the oxidized particles are wrapped by a Co-rich surface layer. The different surface composition for NiCo_2 and NiCo_2O_4 particle is possibly due to the different reaction

atmosphere during the synthetic process [42]. $\text{Co}_3\text{O}_4/\text{CNT}$ and NiO/CNT were obtained by oxidizing Co/CNT and Ni/CNT . The XRD patterns in Figure S1a shows characteristic diffraction peaks at 18.9° , 31.3° , 36.8° , 38.5° , 44.8° , 59.3° and 65.3° , and XRD patterns in Figure S1b exhibits featured diffraction peaks at 36.9° , 43.2° , 62.8° , 75.3° and 79.4° , which are consistent with the standard diffraction pattern of Co_3O_4 (JCPDS No. 42-1467) and NiO (JCPDS No. 01-0269), respectively. The morphology for the as-prepared $\text{Co}_3\text{O}_4/\text{CNT}$ and NiO/CNT are proved to be hollow structure (Figure S4a and Figure S5a) with main particle size of 124 nm and 110 nm, respectively. The HRTEM image (Figure S4b) of $\text{Co}_3\text{O}_4/\text{CNT}$ shows obvious (311) lattice planes with inter-planar spacing of 0.243 nm. Moreover, uniformly distribution of Co and O element can be detected from the Co_3O_4 particles in Figure S4c. The measured inter-planar spacing value of 0.208 nm and 0.147 nm from the HRTEM image of NiO/CNT (Figure S5b) are corresponding to (200) and (220) lattice planes, respectively.

Figure 2 (a) Overview STEM image of $\text{NiCo}_2\text{O}_4/\text{CNT}$ nanoparticles; (b) high resolution TEM image of part of one NiCo_2O_4 particle (inset, scale bar is 20 nm); (c-d) enlarged STEM images of two single particles and the corresponding elemental mappings (scale bar is 50 nm); (e) enlarged TEM image of $\text{NiCo}_2\text{O}_4/\text{CNT}$ nanoparticles; (f)

enlarged area of high resolution TEM image from the inset NiCo_2O_4 particle image in Figure 2b and the insets is the corresponding crystal size distribution histogram.

As anode materials for LIBs, the lithium storage properties of 3D $\text{NiCo}_2\text{O}_4/\text{CNT}$ was evaluated by cyclic voltammetry (CV) examination for the first five cycles in the potential range of 0.05 to 3 V at a scan rate of 0.1 mV s^{-1} (Figure 3a). The voltammogram for the first cycle is substantially different from those of the subsequent four cycles. An irreversible reduction cathodic peak was obtained at around 0.5 V, corresponding to the initial reduction of M^{2+} to M and the formation solid electrolyte interphase (SEI), while peaking at around 0.96 V is ascribed to the reduction of M^{3+} to M [43, 44]. The oxidation peak at 2.2 V in the anodic scan corresponds to the oxidation of metal to metal oxides and Li_2O decomposition. In the subsequent cycles, there remains only one cathodic peak which shifts to about 1.02 V due to the drastic Li^+ driven structural or textural modifications during the first lithiation process [45]. Figure 3b described the initial five charge/discharge curves of $\text{NiCo}_2\text{O}_4/\text{CNT}$ electrode at a current density of 0.2 A g^{-1} and potential window from 0.05 V to 3.0 V. Results showed that the charge/discharge potential platform for the five groups of curves was well consistent with the redox peaks in CV curves. The first discharge potential platform of $\text{NiCo}_2\text{O}_4/\text{CNT}$ was situated between the first discharge platform of $\text{Co}_3\text{O}_4/\text{CNT}$ (1.09 V, see in Figure S6a) and NiO/CNT (0.71 V, see in Figure S6b), indicating that the combination of Ni and Co made good influence for the electrochemical performance. The discharge plateau increased in the subsequent curves, whereas the overall trend maintained. The initial discharge and charge capacities of $\text{NiCo}_2\text{O}_4/\text{CNT}$ are 1656 mA h g^{-1} and 1024 mA h g^{-1} , respectively, with an initial Coulombic efficiency (CE) of 62%. The irreversible capacity between the first discharge and charge process may be ascribed to the decomposition of electrolytes and the SEI film formation on the electrode surface. Afterwards, the capacity was maintained at around 1000 mAh g^{-1} . In comparison, $\text{Co}_3\text{O}_4/\text{CNT}$ and NiO/CNT exhibited lower first discharge and charge capacities (1544 mAh g^{-1} and 912 mAh g^{-1} for $\text{Co}_3\text{O}_4/\text{CNT}$, 1434 mAh g^{-1} and 741 mAh g^{-1} for NiO/CNT , Figure S6a and Figure S6b) and CE (59% and 52% for $\text{Co}_3\text{O}_4/\text{CNT}$ and NiO/CNT , respectively) than $\text{NiCo}_2\text{O}_4/\text{CNT}$.

In addition, the rate performance of $\text{NiCo}_2\text{O}_4/\text{CNT}$ is shown in Figure 3c, in which the current density is increased stepwise from 0.2 A g^{-1} to 5 A g^{-1} . Impressive high reversible capacities of 1108, 1005, 915, 805 and 643 mAh g^{-1} were obtained at current densities of 0.2, 0.5, 1, 2 and 5 A g^{-1} . Notably, the capacity recovered and even exceeded the initial level when the current density is returned to 0.2 A g^{-1} . The increase of current density is mainly

attributed to the shorten of charge/discharge distance after transient activation process [21]. When compared with $\text{Co}_3\text{O}_4/\text{CNT}$ and NiO/CNT , the rate performance of $\text{NiCo}_2\text{O}_4/\text{CNT}$ exhibited much higher capacity and lower capacity change during current density change. Furthermore, the stability of the $\text{NiCo}_2\text{O}_4/\text{CNT}$ electrodes at current densities of 0.5 and 1 A g^{-1} are shown in Figure 3d. It can be seen that high reversible capacities of 1155 and 892 mA h g^{-1} are obtained after 200 cycles (higher than $\text{Co}_3\text{O}_4/\text{CNT}$ and NiO/CNT at a current density of 0.5 A g^{-1} , seen in Figure S6c), suggesting the excellent reversibility of discharge/charge properties under relative low/high current density. During the discharge/charge performance, the discharge capacity is nearly equal to the charge capacity at the same circle (CE value equals to ~99%), proving an excellent reversibility for the $\text{NiCo}_2\text{O}_4/\text{CNT}$. Meanwhile, the cycling stability of hollow structured NiCo_2O_4 and MWCNTs were also investigated as anodes for LIBs (Figure S7). The MWCNTs exhibited lower capacity of 155 mAh g^{-1} at 0.5 A g^{-1} . After deducting the capacity of MWCNTs, the $\text{NiCo}_2\text{O}_4/\text{CNT}$ also exhibited excellent cycling performance (higher than 900 mAh g^{-1}) at 0.5 A g^{-1} , higher than pure NiCo_2O_4 , indicating that the incorporation of MWCNTs with NiCo_2O_4 would effectively enhance the electron transfer rate and then increase the battery capacity. Long-life cycling performance for high-rate LIBs remains a great challenge which appeals excellent electrode materials to accommodate such fast charge/discharge rate [46, 47]. Based on the merits of porosity, hollow, excellent crystal structure, high electric conductivity via CNT support and good characteristics for the binding of Ni and Co, the $\text{NiCo}_2\text{O}_4/\text{CNT}$ exhibited excellent long-term cycling stability at a current density as high as 5 A g^{-1} for more than 4000 cycles. As is shown in Figure 3e, high reversible capacity of 500 mA h g^{-1} is obtained after 4000 cycles, with average CE value of above 99%, confirming the excellent high-rate stability performance during discharge/charge processes. Compared with the cycling performances at relative lower discharging/charging rate of the recent reported NiCo_2O_4 based electrodes as LIBs anode system listed in literatures (Table S3), the hollow structured $\text{NiCo}_2\text{O}_4/\text{CNT}$ presented are ranked in the front row. In addition, the excellent long-cycling life performance at high discharging/charging rate (5 A g^{-1}) of hollow structured $\text{NiCo}_2\text{O}_4/\text{CNT}$ showed great potential in next generation LIBs.

Figure 3 (a) Cyclic voltammogram curves of NiCo₂O₄/CNT at a scan rate of 0.1 mV s⁻¹; (b) discharge/charge profiles of NiCo₂O₄/CNT for the first five cycles at a current density of 0.2 A g⁻¹; (c) Rate performance of NiCo₂O₄/CNT at different current densities between 0.2 and 5 A g⁻¹; (d) Cycling performance of NiCo₂O₄/CNT at current densities of 0.5 A g⁻¹ and 1 A g⁻¹; (e) Long-term discharge performance of NiCo₂O₄/CNT at current density of 5 A g⁻¹ and corresponding CE value.

To gain insight of the excellent electrochemical performance of 3D NiCo₂O₄/CNT nanocomposite, electrochemical impedance spectrometry (EIS) was performed. The Nyquist plots in Figure 4a clearly shows that the cell assembled by using NiCo₂O₄/CNT as electrode material exhibited the smallest semicircle diameter compared with Co₃O₄/CNT and NiO/CNT (the values can be seen from Table S2), indicating a better charge transfer

performance and electric-conductivity of 3D NiCo₂O₄/CNT (The equivalent circuit model can be seen in Figure S8). Compared with the semicircle diameter of NiCo₂O₄/CNT, bare NiCo₂O₄, MWCNTs and the mechanic mixture of NiCo₂O₄ and MWCNTs (Figure S9), the electric-conductivity of 3D NiCo₂O₄/CNT was situated much closer to MWCNTs than NiCo₂O₄ and the mechanic mixture of NiCo₂O₄ and MWCNTs, indicating the great significance of the combination of NiCo₂O₄ with MWCNTs. The results indicated that the combination of Ni and Co enhanced the electronic conductivity. Besides, the diameter of the semicircle remained slightly changed on NiCo₂O₄/CNT electrode after 200 cycles at a current density of 1 A g⁻¹ (Figure 4b), indicating the excellent charge transfer stability, which also explained the excellent long-term performance for 4000 cycles at high-rate current density of 5 A g⁻¹. In addition, CV measurements at scan rates ranging from 0.1 to 5 mV s⁻¹ were performed to better understand the underlying reasons for the superior high rate capability of 3D NiCo₂O₄/CNT [48]. As shown in Figure 4c, well-defined peaks at different scan rates are observed where the anodic peaks shift to the higher potential and the cathodic peaks move to the lower potential with the increasing of scan rates. The fitting line of log (i) to log (v) was plotted according to the CV curves in Figure 4c, where i represents the cathodic peak current, v is the scan rate. The relationship of current to scan rate comply with power law dependence function below:

$$i = av^b \quad (1)$$

According to equation (1), the power coefficient b is indicative of the charge storage kinetics in the electrode which also represents the slope value for the fitting line in Figure 4d. Thus, it clearly demonstrates that the cathodic current exhibits a linear dependence with a slope value of 0.71, indicating a fast, surface controlled kinetics corroborating the high counter-ion mobility and ultra-fast electron transfer kinetics of the electrode [49, 50]. Thus, it can be speculated that the excellent kinetics of the NiCo₂O₄/CNT electrode was ascribed to the high electronic conductivity of carbon nanotubes, the second-level structure of small crystals and the hollow structure with interconnected pores.

Figure 4 (a) Nyquist plots of fresh cell using $\text{NiCo}_2\text{O}_4/\text{CNT}$, $\text{Co}_3\text{O}_4/\text{CNT}$ and NiO/CNT as electrode materials; (b) Nyquist plots of $\text{NiCo}_2\text{O}_4/\text{CNT}$ electrode before and after 200 cycles at current density of 1 A g^{-1} ; (c) Cyclic voltammogram curves of $\text{NiCo}_2\text{O}_4/\text{CNT}$ at scan rates from 0.1 mV s^{-1} to 5 mV s^{-1} ; (d) Cathodic peak current function of the scan rate for the $\text{NiCo}_2\text{O}_4/\text{CNT}$ electrode.

According to the electrochemical performance of the 3D $\text{NiCo}_2\text{O}_4/\text{CNT}$ nanocomposite, the hollow structure with interconnected pores was speculated to play an important role in the whole process, which not only provided adequate space to accommodate the volume change during the lithiation process, but also maintained the structural integrity after delithiation process, shorten the lithiation distance (seen from the Schematic image in Figure 5a). In addition, the NiCo_2O_4 particles surrounded by high electric-conductive MWCNTs would enhance the electrons transfer rate. Therefore, to verify the speculation, the structural change on different lithiation and delithiation states for NiCo_2O_4 particles were monitored via ex-situ STEM study during the first cycle. As shown in Figure 5b, the original NiCo_2O_4 particle exhibited hollow structure and small holes, while after a half-lithiation process, the voids in the particle was fully filled with Li_2O and transition metal (Figure 5c), leading to the expansion of the particle size. After a whole discharging process, obvious small particle can be seen (Figure 5d) which may be caused by the

aggregation of transition metal or Li_2O via the further process of lithium insertion. The subsequent half-delithiation STEM image in Figure 5e shows a crescent shaped (red dashed box) bright area, which presents the remaining Li_2O in the particle. Therefore, it is concluded that the hollow structure of NiCo_2O_4 particle can be maintained after discharge/charge process. It should be noted from Figure 5f that the hollow structure was still maintained even after 200 cycles at a current density of 1 A g^{-1} . Furthermore, the lattice fringes can be seen clearly in Figure 5g and the measured inter-planar spacing value is 0.245 nm , corresponding to the (311) plane of NiCo_2O_4 , indicating a stable crystal structure of NiCo_2O_4 . Thus, it can be concluded that the hollow structure in the particles with interconnected pores not only provide enough apace for adapting the volume change, but also shorten the transport length for Li ions during lithiation/delithiation, favoring cycling stability and high-rate capability.

Figure 5 (a) Schematic of the lithiation and delithiation process of NiCo_2O_4 particle with interconnected pores. (b-g) STEM image of NiCo_2O_4 particle at different lithiation or delithiation state. Original hollow particle (b); half-discharge state (c); fully discharge state (d); half charge state (e); after 200 cycles at current density of 1 A g^{-1} (f); HRTEM image after 200 cycles at current density of 1 A g^{-1} (g).

4. Conclusions

In conclusion, 3D NiCo₂O₄/CNT bimetallic oxide materials have been successfully prepared via a simple two-step method. The NiCo₂O₄/CNT electrode material present hollow structure with interconnect pores and consists of small individual particles with good crystal structure. The unique structure shortened the pathways for Li ion diffusion and provided sufficient surface area to accommodate the volume change during the charge/discharge processes. Such a 3D hollow structure maintained the electrode material electrochemically active without sacrificing template or using surfactants during the synthetic approach. As a result, benefiting from such unique structure and Ni-Co incorporation, the 3D NiCo₂O₄/CNT outperformed Co₃O₄/CNT and NiO/CNT, exhibited superior rate performance and long-term high-rate stability at current density of 5 A g⁻¹ for more than 4000 cycles as anode material for LIBs.

Acknowledgements

This work was supported by the National Natural Science Foundation (21573083), the Program for New Century Excellent Talents in Universities of China (NCET-13-0237), the Fundamental Research Funds for the Central University (2013TS136, 2014YQ009), 1000 Young Talent (to Deli Wang), and initiatory financial support from Huazhong University of Science and Technology (HUST). The authors thank the Analytical and Testing Center of HUST for XRD, STEM measurements. S/TEM and EELS work was carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704.

References

- [1] Roy, P.; Srivastava, S. K., Nanostructured anode materials for lithium ion batteries. *J. Mater. Chem. A* **2015**, *3*, 2454-2484.
- [2] Yan, C.; Chen, G.; Zhou, X.; Sun, J.; Lv, C., Template-based engineering of carbon doped Co₃O₄ hollow nanofibers as anode materials for Lithium-ion batteries. *Adv. Funct. Mater.* **2016**, *26*, 1428-1436.
- [3] Wang, D.; Yu, Y.; He, H.; Wang, J.; Zhou, W.; Abruna, H. D., Template-free synthesis of hollow-structured Co₃O₄ nanoparticles as high-performance anodes for lithium-ion batteries. *ACS Nano* **2015**, *9*, 1775-1781.

- [4] Wang, G.; Sun, Y.; Li, D.; Wei, W.; Feng, X.; Müllen, K., Constructing hierarchically hollow core-shell MnO_2/C hybrid spheres for high- performance lithium storage. *Small* **2016**, *12*, 3914-3919.
- [5] Chae, C.; Kim, K. W.; Yun, Y. J.; Lee, D.; Moon, J.; Choi, Y.; Lee, S. S.; Choi, S.; Jeong, S., Polyethylenimine-mediated electrostatic assembly of MnO_2 nanorods on graphene oxides for use as anodes in Lithium-ion batteries. *ACS Appl. Mater. Interfaces*. **2016**, *8*, 11499-11506.
- [6] Zhao, L.; Gao, M.; Yue, W.; Jiang, Y.; Wang, Y.; Ren, Y.; Hu, F., Sandwich-structured graphene- Fe_3O_4 @carbon nanocomposites for high-performance Lithium-ion batteries. *ACS Appl. Mater. Inter.* **2015**, *7*, 9709-9715.
- [7] Li, L.; Kovalchuk, A.; Fei, H.; Peng, Z.; Li, Y.; Kim, N. D.; Xiang, C.; Yang, Y.; Ruan, G.; Tour, J. M., Enhanced cycling stability of Lithium-ion batteries using graphene-wrapped Fe_3O_4 -graphene nanoribbons as anode materials. *Adv. Energy Mater.* **2015**, *5*, 1500171.
- [8] Cao, K.; Jiao, L.; Liu, H.; Liu, Y.; Wang, Y.; Guo, Z.; Yuan, H., 3D Hierarchical porous $\alpha\text{-Fe}_2\text{O}_3$ nanosheets for high- performance Lithium-ion batteries. *Adv. Energy Mater.* **2015**, *5*, DOI: 10.1002/aenm.201401421.
- [9] Wang, J.; Gao, M.; Pan, H.; Liu, Y.; Zhang, Z.; Li, J.; Su, Q.; Du, G.; Zhu, M.; Ouyang, L., Mesoporous Fe_2O_3 flakes of high aspect ratio encased within thin carbon skeleton for superior lithium-ion battery anodes. *J. Mater. Chem. A* **2015**, *3*, 14178-14187.
- [10] Wang, Y.; Yang, L.; Hu, R.; Sun, W.; Liu, J.; Ouyang, L.; Yuan, B.; Wang, H.; Zhu, M., A stable and high-capacity anode for lithium-ion battery: Fe_2O_3 wrapped by few layered graphene. *J. Power Sources* **2015**, *288*, 314-319.
- [11] Huang, B.; Li, X.; Pei, Y.; Li, S.; Cao, X.; Massé, R. C.; Cao, G., Novel carbon- encapsulated porous SnO_2 anode for Lithium-ion batteries with much improved cyclic stability. *Small* **2016**, *12*, 1945-1955.
- [12] Xia, L.; Wang, S.; Liu, G.; Ding, L.; Li, D.; Wang, H.; Qiao, S., Flexible SnO_2/N -doped carbon nanofiber films as integrated electrodes for Lithium-ion batteries with superior rate capacity and long cycle life. *Small* **2016**, *12*, 853-859.

- [13] Liu, H.; Li, W.; Shen, D.; Zhao, D.; Wang, G., Graphitic carbon conformal coating of mesoporous TiO₂ hollow spheres for high-performance lithium ion battery anodes. *J. Am. Chem. Soc.* **2015**, *137*, 13161-13166.
- [14] Han, C.; Yang, D.; Yang, Y.; Jiang, B.; He, Y.; Wang, M.; Song, A.-Y.; He, Y.-B.; Li, B.; Lin, Z., Hollow titanium dioxide spheres as anode material for lithium ion battery with largely improved rate stability and cycle performance by suppressing the formation of solid electrolyte interface layer. *J. Mater. Chem. A* **2015**, *3*, 13340-13349.
- [15] Jiang, Y.; Li, Y.; Sun, W.; Huang, W.; Liu, J.; Xu, B.; Jin, C.; Ma, T.; Wu, C.; Yan, M., Spatially-confined lithiation–delithiation in highly dense nanocomposite anodes towards advanced lithium-ion batteries. *Energy Environ. Sci.* **2015**, *8*, 1471-1479.
- [16] Lu, Z.; Liu, N.; Lee, H.-W.; Zhao, J.; Li, W.; Li, Y.; Cui, Y., Nonfilling carbon coating of porous silicon micrometer-sized particles for high-performance lithium battery anodes. *ACS Nano* **2015**, *9*, 2540-2547.
- [17] Gu, D.; Li, W.; Wang, F.; Bongard, H.; Spliethoff, B.; Schmidt, W.; Weidenthaler, C.; Xia, Y.; Zhao, D.; Schüth, F., Controllable synthesis of mesoporous peapod-like Co₃O₄@Carbon nanotube arrays for high-performance Lithium-ion batteries. *Angew. Chem. Int. Ed.* **2015**, *54*, 7060-7064.
- [18] Xu, X.; Tan, H.; Xi, K.; Ding, S.; Yu, D.; Cheng, S.; Yang, G.; Peng, X.; Fakeeh, A.; Kumar, R. V., Bamboo-like amorphous carbon nanotubes clad in ultrathin nickel oxide nanosheets for lithium-ion battery electrodes with long cycle life. *Carbon* **2015**, *84*, 491-499.
- [19] Yu, L.; Zhang, L.; Wu, H. B.; Zhang, G.; Lou, X. W., Controlled synthesis of hierarchical Co_xMn_{3-x}O₄ array micro-/nanostructures with tunable morphology and composition as integrated electrodes for lithium-ion batteries. *Energy Environ. Sci.* **2013**, *6*, 2664-2671.
- [20] Mondal, A. K.; Su, D.; Chen, S.; Ung, A.; Kim, H.-S.; Wang, G., Mesoporous MnCo₂O₄ with a Flake-Like Structure as Advanced Electrode Materials for Lithium-Ion Batteries and Supercapacitors. *Chem. – Eur. J.* **2015**, *21*, 1526-1532.

- [21] Wang, D.; He, H.; Han, L.; Lin, R.; Wang, J.; Wu, Z.; Liu, H.; Xin, H. L., Three-dimensional hollow-structured binary oxide particles as an advanced anode material for high-rate and long cycle life lithium-ion batteries. *Nano Energy* **2016**, *20*, 212-220.
- [22] Li, Z. H.; Zhao, T. P.; Zhan, X. Y.; Gao, D. S.; Xiao, Q. Z.; Lei, G. T., High capacity three-dimensional ordered macroporous CoFe_2O_4 as anode material for lithium ion batteries. *Electrochim. Acta* **2010**, *55*, 4594-4598.
- [23] Yang, G.; Cui, H.; Yang, G.; Wang, C., Self-assembly of $\text{Co}_3\text{V}_2\text{O}_8$ multilayered nanosheets: Controllable synthesis, excellent Li-storage properties, and investigation of electrochemical mechanism. *ACS Nano* **2014**, *8*, 4474-4487.
- [24] Luo, Y.; Xu, X.; Tian, X.; Wei, Q.; Yan, M.; Zhao, K.; Xu, X.; Mai, L., Facile synthesis of a $\text{Co}_3\text{V}_2\text{O}_8$ interconnected hollow microsphere anode with superior high-rate capability for Li-ion batteries. *J. Mater. Chem. A* **2016**, *4*, 5075-5080.
- [25] Shen, L.; Yu, L.; Yu, X.-Y.; Zhang, X.; Lou, X. W., Self-templated formation of uniform NiCo_2O_4 hollow spheres with complex interior structures for Lithium-ion batteries and supercapacitors. *Angew. Chem. Int. Ed.* **2015**, *54*, 1868-1872.
- [26] Mondal, A. K.; Su, D.; Chen, S.; Kretschmer, K.; Xie, X.; Ahn, H.-J.; Wang, G., A microwave synthesis of mesoporous NiCo_2O_4 nanosheets as electrode materials for Lithium-ion batteries and supercapacitors. *ChemPhysChem* **2015**, *16*, 169-175.
- [27] Huang, G.; Zhang, F.; Du, X.; Qin, Y.; Yin, D.; Wang, L., Metal organic frameworks route to in situ insertion of multiwalled carbon nanotubes in Co_3O_4 polyhedra as anode materials for lithium-ion batteries. *ACS Nano* **2015**, *9*, 1592-1599.
- [28] Shen, L.; Che, Q.; Li, H.; Zhang, X., Mesoporous NiCo_2O_4 nanowire arrays grown on carbon textiles as binder-free flexible electrodes for energy storage. *Adv. Funct. Mater.* **2014**, *24*, 2630-2637.
- [29] Wei, T.-Y.; Chen, C.-H.; Chien, H.-C.; Lu, S.-Y.; Hu, C.-C., A cost-effective supercapacitor material of ultrahigh specific capacitances: Spinel nickel cobaltite aerogels from an epoxide-driven sol-gel process. *Adv. Mater.* **2010**, *22*, 347-351.

- [30] Shin, H.; Lee, W.-J., Multi-shelled MgCo_2O_4 hollow microspheres as anodes for lithium ion batteries. *J. Mater. Chem. A* **2016**, *4*, 12263-12272.
- [31] Sun, X.; Zhang, H.; Zhou, L.; Huang, X.; Yu, C., Polypyrrole- coated zinc ferrite hollow spheres with improved cycling stability for Lithium-ion batteries. *Small* **2016**, *12*, 3732-3737.
- [32] Zou, F.; Hu, X.; Li, Z.; Qie, L.; Hu, C.; Zeng, R.; Jiang, Y.; Huang, Y., MOF-derived porous $\text{ZnO}/\text{ZnFe}_2\text{O}_4/\text{C}$ octahedra with hollow interiors for high-rate Lithium-ion batteries. *Adv. Mater.* **2014**, *26*, 6622-6628.
- [33] Jeong, J.-M.; Choi, B. G.; Lee, S. C.; Lee, K. G.; Chang, S.-J.; Han, Y.-K.; Lee, Y. B.; Lee, H. U.; Kwon, S.; Lee, G.; Lee, C.-S.; Huh, Y. S., Hierarchical hollow spheres of Fe_2O_3 @polyaniline for Lithium ion battery anodes. *Adv. Mater.* **2013**, *25*, 6250-6255.
- [34] Wang, J.; Yang, N.; Tang, H.; Dong, Z.; Jin, Q.; Yang, M.; Kisailus, D.; Zhao, H.; Tang, Z.; Wang, D., Accurate control of multishelled Co_3O_4 hollow microspheres as high-performance anode materials in Lithium-ion batteries. *Angew. Chem.* **2013**, *125*, 6545-6548.
- [35] Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P., Formation of hollow nanocrystals through the nanoscale Kirkendall effect. *Science* **2004**, *304*, 711-714.
- [36] Bindumadhavan, K., Srivastava, S. K., Mahanty, S. MoS_2 -MWCNT hybrids as a superior anode in lithium-ion batteries. *Chem. Commun.*, **2013**, *49*, 1823-1825.
- [37] Liu, S.; Xiao, W.; Wang, J.; Zhu, J.; Wu, Z.; Xin, H.; Wang, D., Ultralow content of Pt on Pd–Co–Cu/C ternary nanoparticles with excellent electrocatalytic activity and durability for the oxygen reduction reaction. *Nano Energy* **2016**, *27*, 475-481.
- [38] Xiao, W.; Zhu, J.; Han, L.; Liu, S.; Wang, J.; Wu, Z.; Lei, W.; Xuan, C.; Xin, H. L.; Wang, D., Pt skin on Pd–Co–Zn/C ternary nanoparticles with enhanced Pt efficiency toward ORR. *Nanoscale* **2016**, *8*, 14793-14802.
- [39] Shen, S.; Zhao, T.; Xu, J.; Li, Y., Synthesis of PdNi catalysts for the oxidation of ethanol in alkaline direct ethanol fuel cells. *Journal of Power Sources*, **2010**, *195*, 1001-1006.

- [40] Ruban, A. V.; Skriver, H. L.; Nørskov, J. K., Surface segregation energies in transition-metal alloys. *Phys. Rev. B* **1999**, *59*, 15990-16000.
- [41] Han, L.; Meng, Q.; Wang, D.; Zhu, Y.; Wang, J.; Du, X.; Stach, E.; Xin, H., Interrogation of bimetallic particle oxidation in three dimensions at the nanoscale, *Nat. Commun.*, **2016**, DOI: NCOMMS-16-10020B.
- [42] Wang, J.; Wu, Z.; Han, L.; Lin, R.; Xin, H. L.; Wang, D., Hollow-structured carbon-supported nickel cobaltite nanoparticles as an efficient bifunctional electrocatalyst for the oxygen reduction and evolution reactions. *ChemCatChem* **2016**, *8*, 736-742.
- [43] Gachot, G.; Grugeon, S.; Armand, M.; Pilard, S.; Guenot, P.; Tarascon, J.-M.; Laruelle, S., Deciphering the multi-step degradation mechanisms of carbonate-based electrolyte in Li batteries. *J. Power Sources* **2008**, *178*, 409-421.
- [44] Zhang, L.; Zhang, G.; Wu, H. B.; Yu, L.; Lou, X. W., Hierarchical tubular structures constructed by carbon-coated SnO₂ nanoplates for highly reversible lithium storage. *Adv. Mater.* **2013**, *25*, 2589-2593.
- [45] Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J. M., Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. *Nature* **2000**, *407*, 496-499.
- [46] Sun, T.; Li, Z. j.; Wang, H. g.; Bao, D.; Meng, F. l.; Zhang, X. b., A biodegradable polydopamine-derived electrode material for high-capacity and long- life Lithium-ion and Sodium-ion batteries. *Angew. Chem.* **2016**, *128*, 10820-10824.
- [47] Li, F. S.; Wu, Y. S.; Chou, J.; Winter, M.; Wu, N. L., A mechanically robust and highly ion- conductive polymer- blend coating for high- power and long- life lithium- ion battery anodes. *Adv. Mater.* **2015**, *27*, 130-137.
- [48] Simon, P.; Gogotsi, Y.; Dunn, B., Where do batteries end and supercapacitors begin? *Science* **2014**, *343*, 1210-1211.
- [49] Vlad, A.; Singh, N.; Rolland, J.; Melinte, S.; Ajayan, P. M.; Gohy, J. F., Hybrid supercapacitor-battery materials for fast electrochemical charge storage. *Sci. Rep.* **2014**, *4*, 4315-4321.

[50] Xu, G.-L.; Li, J.-T.; Huang, L.; Lin, W.; Sun, S.-G., Synthesis of Co_3O_4 nano-octahedra enclosed by {111} facets and their excellent lithium storage properties as anode material of lithium ion batteries. *Nano Energy* **2013**, 2, 394-402.

Carbon nanotube supported hollow structured NiCo_2O_4 nanoparticles with interconnected pores were fabricated via a simple one-pot method which possess excellent charge storage kinetics and exhibited ultra-high discharge/charge stability for 4000 cycles at a high-rate current density of 5 A g^{-1} , when used as anode material for the lithium ion battery.

TOC

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.