Unveiling the dynamic capacitive storage mechanism of Co₃O₄@NiCo₂O₄ hybrid nanoelectrodes for supercapacitor applications

Yonghe Li, Yuefei Zhang, Yujie Li, Zhenyu Wang, Haoyu Fu, Xiaona Zhang, Yanhui Chen, Hongzhou Zhang, Xiaodong Li

A Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing 100124, P. R. China
b School of Physics and Centre for Research on Adaptive Nanomaterials and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Republic of Ireland
c Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia 22904, United States

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ABSTRACT

We report a simple and cost-effective approach to the synthesis of hierarchical mesporous Co₃O₄@NiCo₂O₄ nanoforests on Ni foam for supercapacitor (SC) electrode applications by a coupled one-step solution and annealing process. The synthesized electrode exhibits capacitive activation during charge-discharge cycling (from 0.73 F/cm² of the pristine state to the peak value of 1.12 F/cm² after 2000 cycles with only 1.8% loss compared to the peak capacitance after another 2000 cycles). We attribute such dynamic capacitive activation to (1) enlarged electroactive surface area through the formation of Co₃O₄@NiCo₂O₄ core-shell structure and (2) enhanced electrical conductivity by forming oxygen vacancies and hydroxyl groups during charge-discharge cycling. Our findings provide a scientific explanation for the capacitive activation in cobalt oxide-binary nickel cobaltite compounds, and a new design guideline for the development of capacitive activation enabled, high performance transitional oxide electrodes.

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1. Introduction

To meet urgent needs for sustainable and renewable power sources for high power electronic devices, back-up power supplies and electric vehicles, many efforts have been made in developing high performance batteries [1,2] and supercapacitors [3–5]. Traditional lithium-ion batteries suffer from a somewhat slow power delivery or uptake [6]. Faster and higher power energy storage systems are critical in a number of applications, such as uninterruptible power supplies used to protect against power disruption and airplane emergency doors, and this task has been assigned to supercapacitors [3]. Supercapacitors, also called ultracapacitors or electrochemical capacitors (ECs), have become some of the most promising candidates for next-generation power devices because of their overall advantages of high power density, fast charging/discharging rate, sustainable cycling life (millions of cycles) and excellent cycle stability [3,4]. Many materials have been explored for supercapacitor electrodes, including carbon-based materials, conducting polymers, and both noble and transition metal oxides. Among these candidate electrode materials, transition metal oxides, such as NiO [7,8] V₂O₅ [9] MnO₂ [10–12] etc, have attracted tremendous interest due to their low cost, high energy density, and environmental friendliness. Of particular interest, spinel cobalt oxides and binary nickel cobaltite compounds exhibit many exceptional characteristics, such as good redox activity, high capability and extremely high theoretical specific capacitance (3560 F/g) [13,14] suggesting them as the most promising electrode materials for next generation supercapacitors.

With all the excitement about new electrode materials, less attention has been paid to their dynamic storage mechanisms. It has been shown that nanomaterials of Co₂O₃ [15–20] and NiCo₂O₄ [21–29] exhibit intriguing capacitive activation during charge/discharge cycling. In the first cycle, only a fraction of the material is active, whereas in the subsequent cycles the electrolyte gradually penetrates into the nanomaterials, pushing up the capacitance to a higher level [15–29]. However, the mechanisms for such enhanced cycling capacitance remain, to a large extent, unknown. Several key questions are raised, yet left unanswered: What structural morphology renders the electrode such enhanced cycling capacitance? Does the microstructure of the electrode change during charge-discharge cycling? Does charge-discharge cycling generate new structure and/or materials? In this context, we have
a pressing need for a fundamental understanding of the correlation between the capacitive activation and microstructure of Co$_3$O$_4$ and NiCo$_2$O$_4$ electrodes during charge-discharge cycling.

In this paper, we report a simple and cost-effective approach to the synthesis of hierarchical mesoporous Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforests on Ni foam for SC electrode applications by a coupled one-step solution and annealing process. The synthesized electrode exhibits capacitive activation during charge-discharge cycling (from 0.73 F/cm$^2$ of the pristine state to the peak value of 1.12 F/cm$^2$ after 2000 cycles with only ca. 1.8% loss compared to the peak capacitance after another 2000 cycles). We attribute such dynamic capacitive activation to (1) enlarged electroactive surface area through the formation of Co$_3$O$_4$@NiCo$_2$O$_4$ core-shell structure and (2) enhanced electrical conductivity by forming oxygen vacancies and hydroxyl groups during charge-discharge cycling. Our findings provide a scientific explanation for the capacitive activation in cobalt oxide-binary nickel cobaltite compounds, and a new design guideline for the development of capacitive activation enabled, high performance transitional oxide electrodes.

2. Experimental section

2.1. Materials synthesis

All solvents and chemicals were of reagent quality and were used without further purification. Cobalt nitrate, ammoniumfluoride and urea were obtained from Beijing Chemical Reagent Co. In a typical synthesis, Co(NO$_3$)$_2$$\cdot$6H$_2$O (2 mmol), NH$_4$F (8 mmol) and Co(NH$_2$)$_2$ (2 mmol) were dissolved in distilled water (40 mL) to form pink homogeneous solution. Then the homogeneous solution prepared above was transferred into Teflon-lined stainless steel autoclave liners (50 mL). Then, a piece of clean nickel foam (2 cm × 1 cm in area) was protected from solution contamination by uniformly coating the top with a polytetrafluoroethylene tape. The liner was sealed in a stainless steel autoclave and then held at 120 °C for 6 h. To study the growth mechanism, intermediate products were also obtained at the reaction time periods of 0.5, 1, 2, 3 h, 24 h. The Ni foam coated with a pink colour precursor was collected and rinsed with distilled water and ethanol several times before drying at 80 °C under vacuum for 2 h. Finally, the precursor was annealed at 300 °C in ambient atmosphere for 3 h, producing Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforests.

2.2. Structural characterization

The crystal structure of the as-synthesized samples were characterized by X-ray diffraction (XRD, SHIMADZU XRD-7000) using a CuK$_\alpha$ source (λ = 0.154056 nm) with step size of 0.02°. Energy dispersive X-ray spectrometry (EDS) with FEI TecnaiG20 was carried out to determine the molar ratio of the products. The morphology and structure of the prepared precursors and final products were studied by field emission scanning electron microscopy (FESEM, FEI Quanta 600 with an accelerating at 20 kV), and transmission electron microscopy (TEM, FEI Tecnai G20 with an accelerating at 200 kV), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F with an accelerating at 200 kV), and Fourier transform infrared spectroscopy (FTIR, Nicolet 6700 spectrophotometer). The in-situ electrical measurement experiments were performed using a commercial scanning tunneling microscope-transmission electron microscope (STM-TEM, NanoFactory Instruments) joint instrument insert into JEOL-2010 TEM. The chemical composition and oxidation state were characterized by Electron energy loss spectroscopy (EELS, FEI Titan 80-300(S)operating at 300 kV) and X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM with Al K$_\alpha$ radiation).

2.3. Electrochemical tests

The electrochemical measurements were carried out at room temperature in a three-electrode electrochemical cell containing 6 M KOH aqueous solution as electrolyte. Cyclic voltammetry (CV) measurements were performed with a PARSTAT2273 electrochemical workstation (Ametek, America), the Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest–Ni foam composite (1 cm$^2$ in area) as the working electrode, Hg/HgO as the reference electrode and Pt foil as the counter electrode. The galvanostatic charge-discharge tests were conducted using a LAND battery test system (Land, Wuhan). Electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential with an ac perturbation of 5 mV in the frequency range of 100 kHz–0.01 Hz.

3. Results and discussion

Fig. 1 shows the structural characteristics of the as-prepared hybrid Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest–Ni foam composite. Fig. 1a presents the typical XRD spectrum of the as-prepared product. The diffraction peaks, except for the three typical peaks from the Ni foam, can be indexed to spinel Co$_3$O$_4$ (JCPDS no 42-1467) and NiCo$_2$O$_4$ (JCPDS no 20-0781), which originated from the respective Co(OH)$_2$F precursor and (Ni, Co) (CO$_3$)$_{0.5}$OH)·0.11H$_2$O precursor (see Fig. S1 in Supporting Information for details). The SEM images (Fig. 1b–c) reveal that the Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforests were radially grown on the Ni foam. The nanoforests (Fig. 1d) exhibit a hierarchical nanorod@nanonoodle architecture with a clear boundary between the nanorod segment and nanoneedles (indicated by the dash line in Fig. 1d). The evolution process of the hierarchical nanoforests at different reaction stages can be found in Fig. S2 in Supporting Information. The EDS result (Fig. 1e and f) further unveil that the cycled area e’ in Fig. 1d is rich in Co and O (Fig. 1e) with the ratio close to that of Co$_3$O$_4$. Note that Cu peaks came from the TEM grid and the small Ni peak originated from the Ni foam. Ni, Co and O were detected (Fig. 1f) in the corresponding cycled area f’ (see Fig. 1d) and their atomic ratio is close to that of NiCo$_2$O$_4$. The EDS results validate the findings from the XRD in Fig. 1a. The close-up TEM view (Fig. 1g) reveals that an individual NiCo$_2$O$_4$ nanonoodle consists of nanoparticles that are assembled into the mesoporous structure, which should facilitate electrolyte and electron transport. The crystalline NiCo$_2$O$_4$ nanoparticles have a size of 10 nm and the inter-particle mesopores range from 2 to 5 nm in size. Fig. 1i shows the close-up HRTEM image of the single nanoparticle selected from Fig. 1h, revealing that both d-spacings of 0.203 nm are attributed to the (400) and (040) crystal planes of spinel cubic NiCo$_2$O$_4$, respectively. Fig. 1j presents the EDS elemental maps of Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest, showing that the elements of Ni, Co are uniformly distributed in the nanoforest. To better describe the elemental distributions, we used a dash line to indicate the boundary between the nanoneedles and the nanorod segment. Cleary, Co and O are rich in the nanorod segment. A small amount of Ni in the nanorod segment originates from the Ni foam. Ni, Co and O are homogeneously distributed in the nanonoodle part.

Cyclic voltammery (CV) tests were performed on the mesoporous Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest–Ni foam composite. It is of interest to note that it takes approximately 2000 cycles for the mesoporous Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest–Ni foam composite to achieve the peak capacitance. The CV curves of the 1st cycle and after 4000th cycle at a scan rate of 5 mV/s are depicted in Fig. 2a for comparison. The enclosed separation area was much increased after 4000 cycles. Both curves exhibit a pair of broad redox peaks, which are the
characteristic peaks of faradic reaction for M-O/M-O-OH (M represents Ni or Co) in KOH electrolyte [15,22].

Rate capability is one of the important factors to evaluate the power applications of SCs. The galvanostatic charge-discharge curves and calculated specific capacitance of the as-prepared Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest–Ni foam composite at different discharge current densities are shown in Fig. 2b-c. The pristine Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest–Ni foam composite exhibits a
The mesoporous Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest–Ni foam composite shows high electrochemical performance. The CV curves in Fig. 2a demonstrate the electrochemical behavior. The specific capacitance was measured to be 0.89 F/cm$^2$ at 1.6 mA/cm$^2$. After 4000 cycles, the specific capacitance increased to 1.32 F/cm$^2$ at the same current density. The Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest–Ni foam composite also exhibits good rate capability, with 73% retention at 12 times the current density compared to 0.97 F/cm$^2$ at 19.2 mA/cm$^2$.

The Nyquist plots in Fig. 2d reveal the electron conductivity of the electrode. The Rs value decreased from 1.96 to 1.81 ohm after 4000 cycles, indicating improved electronic conductivity.

The cycling performance and coulombic efficiency are shown in Fig. 2f. The capacitance increased by 57.8% after 2000 cycles. The enhanced electronic conductivity is likely another critical factor in the observed activation effect.

The Galvanostatic charge-discharge curves in Fig. 2b and Fig. 2f show the charge-discharge behavior of the electrode at different current densities.

The obtained Nyquist plots consist of a depressed arc in the high frequency region and an inclined line in the low frequency region. The value of Rs (internal resistance) of the pristine electrode is 1.96 Ω. Notably, after 4000th cycle, the Rs value decreased to 1.81 Ω, showing that the electronic conductivity of the electrode increased after long-term cycling. Such an enhancement in the electronic conductivity is probably another important factor for the fact that activation takes a certain
Fig. 3. Ex-situ HRTEM characterization of (a, b, c) pristine, (d, e, f) 850th cycle and (h, i, g) 2000th cycle at current density of 8 mA/cm², the insets are the corresponding SAED patterns. (j) Schematic illustration of morphology evolution of Co₃O₄@NiCo₂O₄ nanoforests during activation process.
period of time to occur. Accordingly, the $R_{ct}$ (pseudo charge transfer resistance) changed subtly after 4000 cycles, demonstrating the good retention capability.

The charge-discharge cyclic stability of the Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest–Ni foam composite was also tested at 8 mA/cm$^2$. As can be seen in Fig. 2e, the cycling period can be largely divided into two regimes, i.e. the active stage and the stable stage. In the active stage, specific capacitance increased 57.8% from 0.73 F/cm$^2$ of the 1st cycle to the peak value of 1.12 F/cm$^2$ of the 2000th cycle. The stable stage, i.e. the period of the 2000th cycle to the 4000th cycle, characterizes a slow rate of decrease in specific capacitance from the peak value of 1.12 F/cm$^2$ down to 1.1 F/cm$^2$ of the 4000th cycle, 98.2% retention rate with reference to the peak value. The cycling performance of Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest arrays is much better than that of the other Co$_3$O$_4$ and NiCo$_2$O$_4$-based nanostructures, such as NiCo$_2$O$_4$@MnO$_2$ core/shell nanowire arrays (12% loss after 2000 cycles), [39] hierarchical porous NiCo$_2$O$_4$ nanowires (~6.2% loss after 3000 cycles), [22] Co$_3$O$_4$@NiMnO$_4$ nanowire arrays (~23% loss after 3000 cycles), [40] NiCo$_2$O$_4$ nanowires (~19% loss after 3000 cycles) [41]. The volumetric stability of the electrode in all cycling periods maintained nearly at 100%, showing an excellent reversibility of the electrode. Fig. 2f shows the charge-discharge cycling curves of 2th-11th cycles and 1990th-1999th cycles. It can be seen that both curves still kept near linear and symmetrical shape, implying that capacitive activation occurred.

To seek the underlying mechanism of the observed enhancement in specific capacitance during charge-discharge cycling, the crystal structure and morphology evolution of the electrode at different activation stages were characterized by XRD and HRTEM. Comparison of the XRD spectra of the 1st cycle and the 2000th cycle at the current density of 8 mA/cm$^2$ (see Fig. S3a in Supporting Information) suggests that phase transformation would not occur during this cycling period. Fig. 3a presents the TEM image of the pristine Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforests, showing a typical hierarchical mesoporous nanorod@nanoneedle structure. The close-up view (Fig. 3b) reveals that individual nanoneedles consist of numerous nanoparticles which have NiCo$_2$O$_4$ crystal structure (see the insert of Fig. 3b and the XRD pattern of Fig. S3a in Supporting Information). The HRTEM image of the nanoneedles (Fig. 3c) reveals that the d-spacings of both 0.203 nm crystal planes correspond to the (400) and (040) planes of cubic NiCo$_2$O$_4$, respectively. TEM images (Fig. 3d-e) further reveal that after 850th charge-discharge cycle, the Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforests were uniformly covered with a 20-50 nm layer, forming a core-shell nanostructure (see Fig. 3f). This layer consists of NiCo$_2$O$_4$ nanocrystals 2-5 nm in size originating from the core part of nanoneedles (see Fig. 3b in Supporting Information), which in turn suppresses the volume change of electrode during electrochemical de/alloying, leading to the inhibition of cracking and pulverization [30]. The measured-spacings of the (400) crystal planes in both core and shell are in consistent with the d-spacing of spinel cubic NiCo$_2$O$_4$. The TEM images of the sample after 2000th cycle (Fig. 3g-i) show that the shell layer grew to a length of ca. 100-200 nm, uniformly covering nanoforests to form Co$_3$O$_4$@NiCo$_2$O$_4$ core-shell structure with an enlarged surface area. The SAED pattern (insets in Fig. 3h) and the same d-spacings (Fig. 3i) show that both the core and shell have the same NiCo$_2$O$_4$ crystal structure. A schematic illustration (Fig. 3j) illustrates the morphology evolution and benefits of the Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforests during the activation process. The nanoﬂake shells ensure the full exposure of both active Co$_3$O$_4$ and NiCo$_2$O$_4$ to the electrolyte, thus enhancing both ion and electron diffusion [17,23]. The overall experimental evidences conclude that the self-developed core-shell structure with enhanced electrochemical sites facilitates the activation process.

To understand the obtained $I$-$V$ curves under different cycles (1st cycle and 2000th cycle), the electrical conductivity of the as-prepared Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforests was studied in-situ using a Nanofactory Instruments scanning tunnelling microscope (STM)-transmission electron microscope (TEM) electrical probing system. An experimental setup is sketched in Fig. 4a. An Au rod was attached to a fixed electrical sensor, and the as-synthesized Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest sample was adhered to the piezomovable side of Au rod. Then the position of the W tip and an individual Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest were coordinately adjusted through the nanoscale precision piezo-driven manipulator of STM-TEM holder to realize a bridge (Fig. 4b). The electrical properties ($I$-$V$ curves) of this bridged Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest were measured, as shown in Fig. 4c. The current value of the pristine Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest varies from -5.23 nA to 4.8 nA, while after charge-discharge 2000 cycles at 8 mA/cm$^2$, the current value varies from -805.7 nA to 801.6 nA. The cycled Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest possesses more than two orders of magnitude electrical conductivity compared with the pristine one, which could significantly improve the pseudocapacitance based on Faradic reaction process during charge-discharge cycling.

The structural evolution of the Co$_3$O$_4$@NiCo$_2$O$_4$ nanoforest during charge-discharge cycling was studied by in-situ electron energy loss spectroscopy (EELS) (Fig. 5). Fig. 5a-b show the $L_3/L_2$ lines ratios for Co L-edge and Ni L-edge (determined by directly integrating the individual peaks [31]). The calculated $L_3/L_2$ ratios for Co L-edge and Ni L-edge in the pristine pattern are 1.8 and 2.0, respectively, while the corresponding ratios respectively increased to 2.8 and 2.2 for the samples after 2000 cycles. The increased average (Co, Ni) $L_3/L_2$ ratio indicates a valence decrease of Co (Co$^{3+}$ to Co$^{2+}$) while a little change of Ni$^{3+}$ to Ni$^{2+}$ [32] after 2000 charge-discharge cycles. This findings validated by the change of oxygen K-edge structure. The O K-edges for the pristine sample and the
sample after 2000 cycles (Fig. 5c) show three characteristic peaks, labeled correspondingly as a, b and c. Peak a located in 532.7 eV is referred to as the O K-edge pre-peak, which is attributed to the hybridization of O 2p-state with the transition metal-3d, and is correlated with the 3d-band unoccupied of transition metal [33]. Peaks b and c stem from hybridized O2p–transition metal 4sp band [33]. The two spectra show a difference in the relative height of the pre-peak with respect to the first peak b. The decrease in height for the pre-peak in the sample after 2000 cycles indicates the formation of oxygen vacancies in conjunction with the decrease in valence state, as observed from Co L-edge and Ni L-edge. This result agrees with the previously reported results for similar CoOx materials [34,35]. The formation of oxygen vacancies and functional hydroxyl groups during long-term charge–discharge cycling is also validated by X-ray photoelectron spectroscopy (XPS) (see Fig. S4 in Supporting Information). Previous studies [36–38] showed that more oxygen vacancies and functional hydroxyl groups, which lead to increased carrier density (better electrical conductivity), facilitate the transport of charge carriers, thereby enhancing the capacitive storage of cycling Co3O4@NiCo2O4 nanoforests.

4. Conclusions

A coupled one-step solution and annealing process has been developed to synthesize hierarchical mesoporous Co3O4@NiCo2O4 nanoforests on Ni foam for SC electrode applications. The synthesized Co3O4@NiCo2O4 nanoelectrode exhibits a dynamic capacitive storage behavior during charge–discharge cycling (from 0.73 F/cm2 of the pristine state to the peak value of 1.12 F/cm2 after 2000 cycles with only ca.1.8% loss compared to the peak capacitance after another 2000 cycles). We attribute such dynamic capacitive activation to (1) enlarged electroactive surface area through the formation of Co3O4@NiCo2O4 nanoforest core–shell structure and (2) enhanced electrical conductivity by forming oxygen vacancies and hydroxyl groups. The change in microstructure during charge–discharge cycling promote the transport of charge carriers, thereby enhancing the capacitive storage of cycling Co3O4@NiCo2O4 nanoforests. The discovered electrochemical induced microstructure change during charge–discharge cycling creates new opportunities for developing high performance sustainable energy storage devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2014.06.168.

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