Structure design of NiCo$_2$O$_4$ electrodes for high performance pseudocapacitors and lithium-ion batteries†

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High capacitance/capacity electrodes are in urgent demand to increase the charge storage capability of energy storage devices. However, there are some scientific and technical challenges for a large amount of charges to be transported through the devices because the kinetic resistances and volume change issues may limit the performance of devices. 3D conductive scaffolds are usually developed to build rapid electron/ion pathways and accommodate volume changes. Using a templated electrodeposition and hydrothermal synthesis technique, we developed a composite electrode consisting of NiCo$_2$O$_4$ nanowires on ultralight nickel foam. The NiCo$_2$O$_4$ nanowires provide a large surface for rapid charge transports. The ultralight nickel foam electrically wires NiCo$_2$O$_4$ and accommodates the volume expansion of NiCo$_2$O$_4$ during lithiation. The composite electrode demonstrates a high performance microstructure for ideal pseudocapacitors and lithium ion anodes. It not only enhances the utilization of active materials but also increases the electrode based specific capacitance by one order of magnitude as compared to the widely used nickel foam. More importantly, the ultralight nickel foam supported structure could further be extended to other high capacitance/capacity metal oxide materials for pseudocapacitors and lithium-ion battery applications.

Introduction

Pseudocapacitors and lithium-ion (Li-ion) batteries are two important devices for electrochemical energy storage.$^{1-6}$ The increasing demands for high energy and power characteristics are driving the research interest on energy storage to improve the energy density (per unit volume) and specific energy (per unit mass) of pseudocapacitors and Li-ion batteries. Among the extensively explored active materials, transition metal oxides (MO$_x$, M = Ni, Co, Mn, Fe etc.) have attracted increasing attention because they provide relatively high pseudocapacitance and Li-ion storage capability. Ternary metal oxides with two different metal cations exhibit high electrochemical activities because of their complex chemical composition and synergetic effects of multiple metal species.$^{7-9}$ For example, NiCo$_2$O$_4$ has higher electrical conductivity (2.5 S cm$^{-1}$) and electrochemical activity than monometal oxides of nickel or cobalt, resulting in an exceptionally high specific capacitance/capacity.$^{7,10,11}$ From the viewpoint of materials, NiCo$_2$O$_4$ has much larger potentials as active materials for pseudocapacitors and batteries than its corresponding monometal oxides. However, there are still many challenges to maximize the activities of NiCo$_2$O$_4$ in real pseudocapacitors and Li-ion batteries.

The pseudocapacitance of active materials is closely related to the surface area and solid/electrolyte interfaces because of the interface charge storage mechanism. Fine particles usually have large surface area and high capacitance. However, their aggregates lead to a lower conductivity than that of the bulk materials.$^{12,13}$ To obtain the large surface area and continuous electron transport network, the electrodes consisting of the electrically wired nanoparticles are highly desired especially for high power devices. The usage of percolating conductive networks such as in stainless steel mesh, nickel foam (NF), carbon nanotubes, graphene, and so on has been widely explored in high performance pseudocapacitors to that end. As a Li-ion anode material, NiCo$_2$O$_4$ is lithiated to generate the insulating Li$_2$O, which may shut off or slow down electron conduction. Meanwhile, its volume expands about 190% The large volume changes during cycling cause mechanical strains which may break the electron pathway and lead to the capacity loss. In order to address these issues, the three-dimensional (3D) conductive collectors are usually used to scaffold the active material NiCo$_2$O$_4$.$^{14-18}$ By using the good mechanical properties
of the 3D scaffold, the strains and adverse effect caused by the repeated volume change may be mitigated to a certain degree.

It could be deduced that among the pseudocapacitors and Li-ion battery anodes, the conductive pathway or scaffold is of vital importance to the electrochemical properties of energy storage devices. However, the inactive scaffold usually does not contribute to the total capacitance/capacity but occupies the extra volume and mass of the whole electrode instead. The widely used Ni foam and Cu, Al foils actually decrease the total energy/power properties because of their electrochemically inactive nature. An ideal electrode requires a minimal amount of electron pathway or scaffold and the maximized rate capability and cycling stability by virtue of the appropriately designed electronic and mechanical properties of electrode microstructures.

In this work, we developed novel ultralight nickel foam (UNF) to scaffold NiCo₂O₄ nanowire arrays (NWAs) for better pseudocapacitors and Li-ion batteries instead of using conventional current collectors (see the ESI Fig. S1†). The UNF we developed could provide a rapid electron pathway to improve the power properties and also act as the mechanical support to accommodate the volume changes. The nanostructured NiCo₂O₄ morphology further increases the surface area and lowers the charge transfer resistances. Because of these advantages, the UNF@NiCo₂O₄ composite electrode delivers a capacitance of 1128 F g⁻¹ (electrode basis), which is one order of magnitude higher than that of a commercial NF supported sample. When used as a Li-ion anode, the UNF@NiCo₂O₄ composite electrode also shows a much higher capacity than that of NF@NiCo₂O₄. In general, our newly developed UNF@NiCo₂O₄ structure improves the configuration of composite electrodes and provides a rational design for high performance pseudocapacitors and Li-ion batteries.

Experimental

Preparation of 3D UNF

Commercial copper powder (Sinopharm Chemical Reagent Corp., China) was cast on a graphite plate to form a Cu layer. After annealing at 900 °C in forming gas (95% Ar and 5% H₂) for 2 h, the porous Cu layer was peeled off the graphite plate and then inserted into a Ni plating solution (Transene Company, USA). With a nickel plate as the counter electrode, Ni was electroplated onto the surface of the Cu template at a current density of ~5 mA cm⁻². After electrodeposition, the sample was rinsed with de-ionized water and etched by an aqueous solution containing 0.6 M Na₂S₂O₈, 1.92 M (NH₄)₂SO₄, and 3.5 M NaOH. The removal of the Cu template yields a highly porous UNF.

Growth of NiCo₂O₄ NWAs on 3D UNF

Typically, about 0.506 g CoCl₂·6H₂O, 0.254 g NiCl₂·6H₂O, and 0.96 g CO(NH₂)₂ were dissolved in 40 mL deionized water under stirring. The precursor solution and the UNF were placed into a Teflon-lined stainless steel autoclave. The autoclave was then heated in an oven at 100 °C for 8 h and cooled down to room temperature. The hydrothermally treated UNF was rinsed with deionized water and dried in a vacuum at 50 °C for 2 h. Finally, the sample was annealed at 300 °C for 2 h.

Materials characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX2500 V with Cu Kα radiation. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) images were obtained using a Zeiss Ultra 55 field-emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALab MKII X-ray photoelectron spectrometer with Mg Kα X-ray as the excitation source. The binding energies in XPS analyses were calibrated with C 1s at 284.6 eV. High resolution transmission electron microscopy (HRTEM) images were recorded on a FEI Tecnai G² 20 microscope at 200 kV. N₂ adsorption measurements were conducted on a Micromeritics ASAP 2020M+ volumetric adsorption equipment.

Electrochemical measurements

The pseudocapacitive properties of UNF@NiCo₂O₄ samples were measured in a 3 M KOH aqueous solution with a platinum wire and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. For Li-ion battery applications, the UNF@NiCo₂O₄ samples were assembled into coin cells with lithium foil in an Ar-filled glovebox. The electrolyte used was 1 M LiPF₆ in the 1 : 1 (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Two control samples were fabricated for comparison. The control sample with NF as the support was coated with NiCo₂O₄ nanowires using the same hydrothermal synthesis technique. The second control sample was fabricated by slurry-casting the mixture of hydrothermally synthesized NiCo₂O₄ acetylene black, polyvinylidene fluoride with a weight ratio of 75 : 15 : 10 on commercial NF (for pseudocapacitors) and Cu foil (for Li-ion batteries). The cells were galvanostatically cycled using a Land Battery Tester (Wuhan LAND electronics Corp. China). Cyclic voltammograms (CVs) and electrochemical impedance spectra (EIS) were recorded on a VSP potentiostat (Bio-Logic Corp. France).

Results and discussion

Fig. 1 illustrates the fabrication procedure of 3D UNF@NiCo₂O₄. A commercial copper powder is slurry-cast on a graphite plate to form a 3D Cu template. Because the particles in the Cu template are loosely contacted, a heat treatment process is followed to enhance the interparticle connection, which is important to form a continuous network of the Cu phase in the porous template. The enhanced connection could be clearly seen by comparing the SEM images of the Cu template before and after sintering (Fig. 2a and b). After Ni is electroplated onto the surface of the template, Cu is selectively dissolved in an alkaline etchant solution under stirring. As shown in Fig. 2c, the obtained 3D UNF has an ~70 nm thick shell and the porosity of ~99.1%. An important feature of the 3D UNF is that all pores are highly interconnected, which is essential for rapid ion transport.
in the pseudocapacitor and battery applications. The formation of interconnected pores is caused by the sintered neck of Cu particles in the template (Fig. 2b). The high porosity and metallic conductivity make the unique UNF suitable to load energy storage materials, which usually require mechanical support and current collectors. More importantly, the pore size in UNF suits the requirements (tens of microns or less) of the characteristic length which electrochemical energy storage devices usually need.\textsuperscript{19} Fig. S2\textsuperscript{†} shows the cross-section SEM image of the UNF with about 40 μm thickness. The UNF has the areal mass of less than 2 mg cm\textsuperscript{-2} as shown in Fig. S3.\textsuperscript{†}

The hydrothermal synthesis and subsequent calcination are used to load the NiCo\textsubscript{2}O\textsubscript{4} NWAs on the UNF to form a monolithic electrode. Fig. 2d and e show that the nanowire arrays are vertically grown on the UNF surface. The EDX spectrum in Fig. 2f indicates that the monolithic electrode consists of Ni, Co, and O elements. The elemental mapping in the inset of Fig. 2f shows the uniform and continuous element distribution. The HRTEM image of a single nanowire in Fig. 2g reveals that the hydrothermally synthesized nanowire has a diameter of ~60 nm and actually consists of about 10–15 nm nanoparticles. Fig. S4\textsuperscript{†} shows that the NiCo\textsubscript{2}O\textsubscript{4} nanowires have the specific surface area of 34.9 m\textsuperscript{2} g\textsuperscript{-1}. The nanoparticle in Fig. 2h has the lattice fringe of 0.47 nm, which corresponds to the (111) plane of spinel NiCo\textsubscript{2}O\textsubscript{4}. The diffraction rings in the SAED pattern of Fig. 2i confirm that the nanowire is the polycrystalline aggregate of NiCo\textsubscript{2}O\textsubscript{4} nanoparticles.

The XRD analysis in Fig. 3a identifies the monolithic electrode as the mixture of nickel (JCPDS no. 87-0712) and NiCo\textsubscript{2}O\textsubscript{4} (JCPDS no. 73-1702). It indicates that the loaded material is crystalline NiCo\textsubscript{2}O\textsubscript{4}, which is in agreement with the electron diffraction in Fig. 2i. The surface composition of the monolithic electrode was further characterized by XPS. The inset of Fig. 3b shows the typical survey XPS spectra of the NiCo\textsubscript{2}O\textsubscript{4} sample in the range of 0–1200 eV. The O 1s spectrum is mainly composed of two peaks at 529.9 and 531.6 eV, which are related to lattice oxygen and hydroxyl species on surfaces, respectively.\textsuperscript{20–22} Fig. 3c presents the Ni 2p spectrum, which has a spin–orbit doublet around 855 and 873 eV and two strong satellite peaks. The Ni 2p\textsubscript{3/2} peak could be fitted with two components with the binding energies at 855.6 and 853.9 eV, which corresponds to Ni\textsuperscript{3+} and Ni\textsuperscript{2+}, respectively.\textsuperscript{22–24} Fig. 3d shows that the Co 2p spin–orbit doublet peaks are around 779.9 and 795 eV. The Co 2p\textsubscript{3/2}–1/2 separation of 15.1 eV and almost diminished satellites imply that most of the cobalt ions have a low-spin configuration (Co\textsuperscript{3+}), which are consistent with the literature.\textsuperscript{22,23,25–28}
The CV curves of UNF@NiCo2O4 (Fig. 4a) were scanned in 3 M KOH from 5 to 100 mV s⁻¹ between 0 and 0.4 V. At 5 mV s⁻¹, NiCo2O4 exhibits a broad oxidative peak around 0.33 V and a corresponding cathodic peak at about 0.23 V. With the increase of the scan rates, the peak currents rise and the gaps between redox peaks increase. The broadened peaks are associated with the faradaic redox reactions related to the Co and Ni.

Fig. 4b shows the galvanostatic charge/discharge curves between 0 and 0.4 V at varied current densities from 1 to 40 A g⁻¹ (based on the mass of NiCo2O4). A relatively symmetric shape indicates good pseudocapacitive behaviors.

To further understand what role UNF can play in the pseudocapacitive properties of the composite electrodes, three control samples with UNF, commercial NF, and acetylene black as the conductive scaffolds/agents were loaded with the same amount of NiCo2O4 nanowires (~6 mg cm⁻²), respectively. Despite the same areal loading of NiCo2O4 on the three samples, their capacitances differ at the same current density. Fig. 4c presents their specific capacitances at varied current densities. The UNF@NiCo2O4 NWAs show the highest specific capacitances of 1552 F g⁻¹ at 1 A g⁻¹ and 1460 F g⁻¹ at 2 A g⁻¹. Even when the current density increases to 40 A g⁻¹, their specific capacitance still remains at 643 F g⁻¹, which is higher than that of the commercial NF@NiCo2O4 sample (97 F g⁻¹). The sample containing acetylene black shows the lowest capacitance of 806 F g⁻¹ at 1 A g⁻¹. These data have been further compared and discussed with previously reported NiCo2O4 electrodes in ESI Table S1.* EIS measurements of the three samples were conducted at an open circuit voltage. Fig. 4d shows that the UNF has the lowest contact and charge transfer resistances. A vertical line in the low-frequency region indicates a more ideal capacitor behavior. Thus, one plausible reason for the varied capacitance may be that the kinetic resistances influence the utilization of active materials. Although commercial NF and our UNF can provide rapid pathways for both electrons and ions due to their metallic conductivity and porous structure, the UNF sample shows 11% higher capacitance (active material basis) than NF at 1 A g⁻¹. The enhanced performance is attributable to the high surface area and relatively thin coating of active materials on the UNF scaffold. A further investigation on the influence of surface area is discussed in Fig. 6e and f.

Fig. 4e shows the galvanostatic cycling properties of the monolithic UNF@NiCo2O4 electrode at 6 A g⁻¹. Its specific capacitance decreases from the initial 1080 F g⁻¹ to 976 F g⁻¹ in the first 1000 cycles. In the next 4000 cycles, it loses only 7.1% capacitance, which corresponds to 83% retention of its initial value. The coulombic efficiency remains at about 100% during cycling. The good rate capability and cyclability are related to the rapid charge transport pathways which the unique monolithic structures could provide. The large surface area of NiCo2O4 nanowires enables rapid interface charge transfer. The 3D continuous nickel scaffold electrically wires each NiCo2O4 nanowire and provides good electron conduction. Such an UNF@NiCo2O4 electrode is very suitable for electrochemical energy storage applications.

To test and verify whether the rapid and stable electrochemical properties of the UNF composite structure are applicable to other energy storage systems, a monolithic electrode of UNF@NiCo2O4 NWAs was assembled with lithium foil into coin cells. The CV curves were scanned between 0.01 and 3.00 V at a scan rate of 0.1 mV s⁻¹. The first scan in Fig. 5a shows different cathodic curve, implying an activation process. The cathodic peaks at ~0.95 and ~0.62 V are mainly related to the...
reduction of NiCo$_2$O$_4$ to metallic Ni and Co and the formation of the solid electrolyte interface (SEI) layer.\textsuperscript{33-49} Two poorly defined anodic peaks at about 1.41 and 2.25 V can be attributed to the oxidation of metallic Ni and Co to metallic cations.\textsuperscript{2,36,40} In the next few cycles, the redox peaks overlap, indicating good electrochemical reversibility. The first galvanostatic lithiation curves in Fig. 5b show a distinguishable plateau at \textasciitilde1.0 V, which does not appear in the next cycles. It may be related to the activation reaction of NiCo$_2$O$_4$ and Li$^+$. The NiCo$_2$O$_4$ electrode delivers the discharge capacity of 1098 mA h g$^{-1}$ in the first cycle with an irreversible capacity loss of 26% between the first and second cycles. The loss can be mainly ascribed to the SEI formation on the surface and some undecomposed Li$_2$O phase due to kinetic hindrance.\textsuperscript{41-46} In the following cycle, the average potential of the discharge plateau slightly increases with a sloping voltage profile. The specific capacity decreases to 815 mA h g$^{-1}$.

The rate and cycling properties of the UNF@NiCo$_2$O$_4$ electrode are compared with the two control samples in Fig. 5c and e. The specific capacity of the slurry-based NiCo$_2$O$_4$ electrode decreases rapidly with the increase of current density. The UNF@NiCo$_2$O$_4$ nanowires demonstrate the highest rate properties. They deliver a capacity of 815 mA h g$^{-1}$ at 100 mA g$^{-1}$ and maintain 50.2% of their low-rate capacity even at 800 mA g$^{-1}$. The NF@NiCo$_2$O$_4$ electrode shows a relatively modest rate capability. It is understandable that metallic nickel scaffolds are able to efficiently conduct electrons and porous structures provide rapid ion transport channels compared to slurry-based NiCo$_2$O$_4$. Fig. 5d presents the Nyquist plots of the three electrodes. The UNF@NiCo$_2$O$_4$ electrode shows the lowest high frequency intercept (2.48 $\Omega$, Fig. S5†), indicating the most conductive electron pathway among the three samples. The smallest diameter of the medium frequency semicircle shows the lowest charge transfer resistance or the highest exchange current for the UNF@NiCo$_2$O$_4$ electrode. These results are basically in agreement with the pseudocapacitor applications, indicating that the UNF structure is able to enhance energy storage processes compared to the widely used conventional NF.

The galvanostatic cycling properties in Fig. 5e show that the UNF@NiCo$_2$O$_4$ sample has an initial capacity of 718 mA h g$^{-1}$, which decreases to 601 mA h g$^{-1}$ in the next cycle and retains 459 mA h g$^{-1}$ in the 150th cycle. The coulombic efficiency increases from the initial 86% to almost 100% in the next 5
cycles. In contrast, the slurry-based and NF@NiCo2O4 electrodes only deliver a modest initial capacity and then decrease rapidly. Especially, the slurry-based NiCo2O4 only retains 85 mA h g\(^{-1}\) in the 100th cycle. The rapid capacity decay may be related to the volume changes which are not effectively mitigated in conventional NF and slurry-based samples. In conjunction with the performance analysis of pseudocapacitor applications, our UNF@NiCo2O4 generally provides much better electro-chemical properties than conventional NF.

The reasons for good electrochemical properties are further investigated by comparing the microstructures of composite electrodes as shown in Fig. 6a and b. Because of the relatively small pore size and large surface area per unit mass, our UNF needs only a thin layer of NiCo2O4 (~1 μm) to obtain the same areal loading of active materials. In contrast, the nanowires on conventional NF in Fig. 6a and b are about 10 μm long to match the same areal loading as that of the 1 μm long nanowires on UNF. The comparison of charge storage capabilities in Fig. 6c and d clearly shows that the electrode based capacitance of 612 mA h g\(^{-1}\), which is much higher than that of NF@NiCo2O4 (46.1 mA h g\(^{-1}\)).

For a practical application, the capacity per unit volume or mass is important. It is desired to load as much active materials as possible per unit volume or mass. However, the increased load of active materials in the entire pores (50–500 μm in Fig. 6a) of conventional NF slows down the charge/discharge rates due to the long transport length in large NiCo2O4 crystals. To maintain a reasonable rate capability, the large void space in Fig. 6b is usually left without filling active materials as most reports demonstrated. The capacitance/capacity of electrodes using conventional current collectors is significantly low. Thus, the small pore sizes of the UNF scaffold are much favorable for electrochemical energy storage applications as compared to the conventional NF.

The most important advantage of the UNF scaffold is its ultralight mass and relatively large specific surface area. We employed the double layer capacitance to compare the surface areas of NF and UNF scaffolds according to the previous report. CVs were scanned at 200 mV s\(^{-1}\) between 0 and 50 mV in acetonitrile containing 0.1 g mL\(^{-1}\) tetrabutylammonium.
perchlorate. It is usually assumed that the measured capacitance is due to the electric double layer mechanism and is proportional to the surface area.\textsuperscript{52} Fig. 6e and f show the large difference in CV currents of the two samples. A comparison of their voltammetric charges in Fig. 6f indicates that UNF has about 216 times higher specific surface area than conventional NF. The high surface area significantly increases the charge storage capability per unit mass.

Metallic foils as current collectors are also used for NiCo$_2$O$_4$ pseudocapacitors and Li-ion anodes.\textsuperscript{53} We have summarized the previously reported NiCo$_2$O$_4$ electrodes using NF and metal foils in ESI Tables S1 and S2.\textsuperscript{†} The capacitance/capacity based on active materials and electrodes are both listed. The UNF realizes the maximum loading and the best utilization of active materials. Especially, the electrode based capacitance/capacity of UNF-supported NiCo$_2$O$_4$ electrodes far exceeds the previous reports as shown in Fig. 6c and d (see the ESI\textsuperscript{†} for the complete summary and details).\textsuperscript{29,30,47–51,53} Thus, our UNF scaffold seems to meet both requirements of space utilization and active material loading per unit electrode mass.

Conclusions

In summary, UNF is developed by a templated electrodeposition technique. The resultant UNF has high porosity, small pore sizes, and interconnected pore structures. Such a unique microstructure meets the demands of conducting and mechanical scaffolds for high performance energy storage devices. NiCo$_2$O$_4$ NWAs are grown on the surface of UNF and used for pseudocapacitors and Li-ion battery anodes. Our UNF could significantly improve the utilization of active materials in comparison to conventional NF, metallic foils, and acetylene black as conductive scaffolds/agents. The UNF@NiCo$_2$O$_4$ composite electrode demonstrates a high specific capacitance
of 1128 F g_{gel}^{-1} for pseudocapacitors. When used as the Li-ion battery anode, it delivers a capacity of 612 mA h g_{gel}^{-1}. Due to the ultrathin porous microstructures, our composite electrodes show about one order of magnitude higher charge storage capability for both pseudocapacitors and Li-ion batteries. Such an UNF@NiCo_{2}O_{4} configuration demonstrates the significant improvement in the electrode based performance and could be also extended to other important energy storage materials.

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**Notes and references**


