A Sol-Gel Process for the Synthesis of NiCo$_2$O$_4$ Having Improved Specific Capacitance and Cycle Stability for Electrochemical Capacitors

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High performance nickel cobaltite (NiCo$_2$O$_4$) with ultrahigh capacitance is synthesized by a facile sol-gel process and then calcined at 300°C. The structure and morphology is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), and nitrogen adsorption/desorption experiments. A mesoporous structure with high specific surface area is obtained. Electrochemical properties are investigated by cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS). The NiCo$_2$O$_4$ exhibits excellent electrochemical performance. The highest specific capacitance of 1128 F g$^{-1}$ is achieved at a current density of 5 mA cm$^{-2}$ and 92.5% of the initial specific capacitance remained after 1000 cycles. NiCo$_2$O$_4$ prepared by this scale-able route could be a promising electrode material for electrochemical capacitors.

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As energy storage devices having properties intermediate to those of batteries and electrostatic capacitors, electrochemical capacitors (ECs) exhibit the desirable properties of high power density, fast charging, excellent cycling stability, small size, and low mass, which make them one of the most promising candidates for next generation power devices.1-4 On the other hand, ECs deliver a low and unsatisfactory energy density.5 Current research work on ECs has been mainly focused on the enhancement of energy density to make it comparable to that of batteries.6-8 Generally, faradic pseudo capacitors based on metal oxides or conducting polymers that can be doped electrochemically have a higher energy density than electrochemical double-layer capacitors (EDLCs) based on carbon materials.9-11 Conducting polymer materials are considered to have relatively lower specific capacitances and also poor electrochemical stability.12,13 Metal oxides have been considered to be one of the most promising materials for ECs.14-16

As a typical metal oxide electrode material, RuO$_2$ has a high capacitance, reversible charge/discharge features, and good electrical conductivity, all of which make it the focus of research and development of supercapacitors having the potential to achieve higher energy and power densities.17-19 Unfortunately, its high cost renders this material unsuitable for commercialized in many applications. Thus, development of alternative electrode materials having improved characteristic and performance is the next logical step.20-22 Transition metal oxides possess multiple oxidation states/structures that enable rich redox reactions for pseudo capacitance and have drawn much attention in recent years.23 Interestingly, mixed metal oxides24-26 and binary metal oxide/hydroxides27-29, which have been reported to exhibit a higher performance than single component oxides/hydroxides, seem to be one of the most promising electrode materials for ECs.

One of the binary metal oxide, NiCo$_2$O$_4$ adopts a spinel structure in which nickel occupies the octahedral sites and cobalt distributes over both octahedral and tetrahedral sites.30 It is expected to offer rich redox reactions and is highly considered in energy-conversion/storage systems due to its better electronic conductivity and higher electrochemical activity than those of nickel oxides and cobalt oxides.30 Recently, some studies have been carried out on the supercapacitive performance of NiCo$_2$O$_4$.31,32 However, a high degree of crystallinity and low level of electrochemical active sites was introduced into the synthesis by the high calcination temperature used, which leads to a low specific capacitance. In contrast, Chen and co-workers33 have synthesized NiCo$_2$O$_4$ crystals by a sol-gel method then calcined the product at 400°C. The highest specific capacitance of 217 F g$^{-1}$ they achieved is, however, lower than that reported for NiO and Co$_3$O$_4$. Lu et al.21 have synthesized NiCo$_2$O$_4$ aerogels at 200°C and a specific capacitance of 719 F g$^{-1}$ was obtained. Unfortunately, the synthesized NiCo$_2$O$_4$ aerogel is a composite of Ni(OH)$_2$, NiO, Co$_3$O$_4$, and NiCo$_2$O$_4$ according to the XRD characterization. Its higher specific capacitance was not only contributed by the NiCo$_2$O$_4$ phase, but also by Ni(OH)$_2$, NiO, and Co$_3$O$_4$. Hence, the exploitation of pure NiCo$_2$O$_4$, using an sol-gel technique, raises the expectation of a facile and scale-able synthesis of a high specific capacitance NiCo$_2$O$_4$.

An appropriate mesostructure, which is expected to enhance the electrochemical performance owing to the shape-selective properties and large surface area,33-36 is essential to improve the performance of electrode materials. Here, we report a porous NiCo$_2$O$_4$ single phase fabricated by a sol-gel process then calcined at a moderate temperature of 300°C. The effects of calcination temperature on product phase were investigated. The as-prepared NiCo$_2$O$_4$ exhibits a higher specific capacitance than NiO and Co$_3$O$_4$, showing high performance electrode material of ECs. On the one hand, this can be attributed to the low crystallinity and large specific surface area of the as-prepared NiCo$_2$O$_4$, which result in a high activity and an effective utilization of the active materials. On the other hand, it benefits from feasible oxidation states/structures of NiCo$_2$O$_4$ contributed by both nickel and cobalt ions. Moreover, the excellent rate capability and cycle stability of the as-prepared material is also demonstrated.

Experimental

Materials.— Analytical grade CoCl$_2$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, KOH, propylene oxide, and absolute alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received without any further purification.

Fabrication of the NiCo$_2$O$_4$.— The NiCo$_2$O$_4$ was synthesized using a modified version of the procedure described in a previous report.23 In a typical process, 0.225 g Ni(NO$_3$)$_2$·6H$_2$O and 0.37 g CoCl$_2$·6H$_2$O were dissolved in 2.5 mL ethanol and stirred for 5 min, then 2.0 g propylene oxide was added and the mixture was stirred at room temperature (25°C) for another 12 h. The resulting solution was then stirred at 75°C to promote gelation. The product was dried at 60°C for 12 h then heated in an air atmosphere at 200, 250, 300, or 350°C for 5 h. The resulting samples were washed with ethanol and distilled water several times then dried at 80°C for 12 h. For
comparison, NiO and Co$_3$O$_4$ were synthesized by the same procedure. The mechanism of gelation can be explained as the following reaction sequence:

\[
[M(H_2O)_6]^{2+} + A^- \xrightarrow{\text{ring opening}} [M(OH)(H_2O)_5]^{3+} + OH^{-}
\]

where M represents nickel or cobalt ions, A$^-$ represents Cl$^-$ or NO$_3^-$ ions. In this procedure, the propylene oxide acts as an acid scavenger through protonation of the epoxide oxygen and subsequent ring opening by the nucleophilic, anionic conjugate base.\(^{39}\)

**Structure characterization.**— The microstructure and morphology of the as-prepared NiCo$_2$O$_4$ was characterized by transmission electron microscope (TEM, JEOL, JEM-2010, Japan) and field emission scanning electron microscope (SEM, JEOL, JSM-6701F, Japan). The pore properties, including the BET surface area and pore size distribution were investigated volumetrically by nitrogen adsorption/desorption experiments (ASAP 2020). Crystalite structures were determined by X-ray diffraction (XRD) using a Rigaku D/MAX 2400 diffractometer (Japan) with Cu Ka radiation ($\lambda = 1.5418$ Å) operating at 40 kV and 60 mA.

Electrode preparation and electrochemical measurements.— The working electrodes were prepared as follows. 80 wt% of NiCo$_2$O$_4$ was mixed with 7.5 wt% of acetylene black and 7.5 wt% of conducting graphite in an agate mortar until a homogeneous black powder was obtained. To this mixture, 5 wt% of poly (tetrafluoroethylene) was added together with a few drops of ethanol. The resulting paste was pressed at 10 MPa into a nickel foam (ChangSha Lyrun New Material Co. Ltd., 90 PPI, 2 mm) then dried at 80 $^\circ$C for 12 h. Each carbon electrode contained approximately 8 mg of electroactive material and had a geometric surface area $\approx 1$ cm$^2$.

A typical three-electrode glass cell equipped with a working electrode, a platinum foil counter electrode, and a saturated calomel reference electrode (SCE) was used for electrochemical measurements of the as-prepared working electrodes. All electrochemical measurements were performed using an electrochemical working station (CHI660C, Shanghai, China) in 2 M KOH aqueous solution at 25 $^\circ$C. The corresponding specific capacitance was calculated from the following equation:

\[
C_m = \frac{I}{\Delta V \times m} \times \frac{l}{D_t}
\]

where $C_m$ (F g$^{-1}$) is the specific capacitance, $I$ (A) is discharge current, $\Delta V$ (V) represents the potential drop during discharge process, and $m$ (g) is the mass of the active material.

**Results and Discussion**

**Structure characterization.**— XRD was employed to determine optimum calcination temperature of the pure NiCo$_2$O$_4$ phase. Fig. 1 shows XRD patterns of four samples calcined at various temperatures. When samples were calcined at 200 or 250 $^\circ$C, the (111) peak and (400) peak of NiCo$_2$O$_4$ (JCPDS No. 20-0781) were observed, indicating that the NiCo$_2$O$_4$ phase was successfully obtained. Unfortunately, the diffraction peaks of NiO (JCPDS No. 04-0835) and Co$_3$O$_4$ (JCPDS No. 42-1467) also appeared, i.e. the as-fabricated samples were a NiO/NiCo$_2$O$_4$/Co$_3$O$_4$ composite rather than the pure NiCo$_2$O$_4$ phase sought. A pure NiCo$_2$O$_4$ crystalline phase was obtained at a calcination temperature of 300 $^\circ$C. The resultant diffraction peaks were in good accordance with the standard pattern for face-centered cubic spinel NiCo$_2$O$_4$, the absence of NiO and Co$_3$O$_4$ characteristic peaks affirming phase-purity of NiCo$_2$O$_4$ crystal and suggesting that 300 $^\circ$C is optimum suitable temperature for fabricating pure NiCo$_2$O$_4$. On further increasing the calcination temperature to 350 $^\circ$C, the NiCo$_2$O$_4$ coexists with NiO and Co$_3$O$_4$ phases, the Co$_3$O$_4$ crystalline phase even becoming dominant due to its sharper and narrower diffraction peaks compared to NiCo$_2$O$_4$. Appearance of the diffraction peaks for NiO and Co$_3$O$_4$ show that 350 $^\circ$C is too high for formation pure NiCo$_2$O$_4$ crystal, or else that a higher calcination temperature may lead to the decomposition of NiCo$_2$O$_4$ to NiO and Co$_3$O$_4$ phases and also the growth of the resulting Co$_3$O$_4$ crystals. The unit cell dimension of the spinel structure NiCo$_2$O$_4$ crystal, $a$, was determined from the observed d-spacing for the (111) and (400) planes using the formula for a cubic lattice:

\[
a = d\sqrt{h^2 + k^2 + l^2}
\]

where $h$, $k$, and $l$ are the Miller indexes. The calculated value of $a$ corresponding to (111) and (400) planes, which ranges between 0.8080 and 0.8238 nm, is very close to that of 0.8110 nm given in the JCPDS 20-0781 file for NiCo$_2$O$_4$.

The surface morphology of the fabricated NiCo$_2$O$_4$ was investigated by SEM measurement. As shown in Fig. 2a, a loosely packed porous structure consisting of interconnected nanoparticles, tens of nanometers in size, was clearly visible. This is in accordance with

![Figure 1. XRD patterns of the NiCo$_2$O$_4$ following calcination at various temperatures.](image1)

![Figure 2. (a) SEM image of NiCo$_2$O$_4$. (b, c) TEM and (d) HRTEM images of porous NiCo$_2$O$_4$.](image2)
the results of TEM imaging shown in Fig. 2b. Fig. 2c exhibits the porous structure of NiCo$_2$O$_4$ with a pore size approximately 10 nm. The high-resolution TEM (HRTEM) image shown in Fig. 2d reveals an interplanar spacing of 0.2803 nm for the (220) plane of spinel NiCo$_2$O$_4$, which is close to that of 0.2869 nm given in the JCPDS 20-0781 file. The results suggest that the as-fabricated NiCo$_2$O$_4$ has a porous structure which will enhance the facility of ion transportation and maintain the smooth electron pathways facilitating rapid charge/discharge reactions and is a promising candidate for EC electrode materials.

The porous characteristics of NiCo$_2$O$_4$ were further investigated by N$_2$ adsorption/desorption. Fig. 3a and 3b show the N$_2$ adsorption/desorption isotherms and corresponding BJH pore size distributions. As seen from Fig. 3a, the existence of the hysteresis loops indicates the porous structure of NiCo$_2$O$_4$. In Fig. 3b, NiCo$_2$O$_4$ exhibits a narrow pore-size distribution at 3.28 nm and a wide pore size distribution around 6.24 nm, suggesting a hierarchical porous structure. The sample shows a specific surface area of 32.7 m$^2$ g$^{-1}$ and an average pore size of 11.1 nm.

Electrochemical characterization.— CV, chronopotentiometry, EIS, and cycle measurements were employed to evaluate electrochemical capacitive performance of NiCo$_2$O$_4$ electrodes. Fig. 4a shows the CV of a pure NiCo$_2$O$_4$ electrode at different scan rates. A pair of redox peaks is visible in each voltammogram, suggesting that the measured capacitance is mainly based on the redox mechanism. The anodic peak current is increasing at 0.2 V, and that for the corresponding cathodic peak is evident at approximately 0.18 V, indicating that the oxidation reaction and reduction reaction of active material began at 0.2 and 0.18 V, respectively. This was attributed to the redox reactions of Ni (II)/Ni (III). According to the literature, anodic peaks located at approximately 0.35 V in the CV curves at a scan rate of 10 mV s$^{-1}$ was also contributed.
by the transition of the redox couple Co (II)/Co (III), indicating that both nickel and cobalt ions were involved in energy storage.

Based on the results of Fig. 4a, it is evident that the CV curves of NiCo2O4 electrode at different scan rates display a high redox peak current.

To further understand the rate capability and to estimate the specific capacitance of the NiCo2O4 electrode, charge/discharge measurements were performed. Fig. 4b shows charge/discharge curves of the NiCo2O4 electrode at a current density ranging from 5 to 50 mA cm$^{-2}$. The calculated specific capacitances of NiCo2O4 electrode are 1128, 1068, 988, 937, 888, and 833 F g$^{-1}$, corresponding to the discharge current densities of 5, 10, 20, 30, 40, and 50 mA cm$^{-2}$, respectively. The specific capacitance gradually decreased at higher current density due to the incremental (IR) voltage drop and insufficient active material involved in redox reaction at a higher current density. However, the as-fabricated NiCo2O4 possesses excellent capacitance at all the current densities evaluated and shows a good rate capability. Even at a high current density of 50 mA cm$^{-2}$, nearly 74% of the initial capacitance value remains. We believed that the porous structure of NiCo2O4 provides a larger surface area and a high density of active sites. The porous structure also allows rapid transportation of electrolyte ions into bulk materials, improving the rate capability of the electrodes.

Figure 4c displays the EIS of NiO, NiCo2O4, and Co3O4 electrodes, respectively. The inset shows the semicircle evident at high frequency. All the impedance spectra were similar, being composed of one semicircle at high-frequency followed by a linear component at low frequency. The internal resistances ($R_\text{s}$) of Co3O4, NiO, and NiCo2O4 electrodes, obtained from the intercept of the plots on the real axis, are very similar (0.94, 1.07, and 1$\Omega$, respectively). However, the semicircle for the NiCo2O4 electrode is smaller than that of Co3O4 and NiO, revealing a lower pseudo charge transfer resistance ($R_\text{ct}$) which due to the good electrical conductivity of NiCo2O4. At lower frequencies, the straight line represents the diffusive resistance (Warburg impedance) of the electrolyte ions diffusion in host materials. Each spectrum has higher angles above 45°, corresponding to the effective porous structure of NiCo2O4 facilitating ionic transportation.

The excellent cycle stability of the as-fabricated NiCo2O4 electrode at a current density of 20 mA cm$^{-2}$ is demonstrated in Fig. 4d. The specific capacitance of the electrode increased over the first 100 cycles due to complete activation of the active materials. After 100 cycles, the capacitance gradually decreased at higher cycle numbers such that 92.5% of the initial specific capacitance was retained after 1000 cycles. The results reveal the excellent stability of the NiCo2O4 electrode as high-performance electrochemical pseudo capacitors.

To further illustrate the excellent electrochemical properties and the suitability of the synthesized NiCo2O4 as an electrode material for ECs, the specific capacitance of NiO and Co3O4 electrodes at various current densities were measured for comparison. As shown in Fig. 5, the specific capacitances of NiCo2O4 are much higher than that of NiO and Co3O4. There are three contributions to the excellent supercapacitive performance of NiCo2O4. The first is the high electrochemical performance of NiCo2O4 compared to NiO and Co3O4 because of the possible increase in feasible oxidation states contributed by both constituent metal ions. The second is the high utilization of active material and excellent reversibility in faraday reactions resulting from its unique morphology and hierarchical mesoporous structure. The third is the high electrical conductivity of NiCo2O4 which improves the rate capability of the electrodes. The highest specific capacitance of 1128 F g$^{-1}$ is relatively close to that of 1580 F g$^{-1}$ reported for RuO2. Taking advantage of its excellent electrochemical capacitive properties, low cost, and easy fabrication, sol-gel synthesized NiCo2O4 is a promising alternative material to RuO2 in next-generation supercapacitors.

Figure 5. Specific capacitances of Co3O4, NiO, and NiCo2O4 at a controlled current density.

Conclusion

A promising electrode material, NiCo2O4 is successfully synthesized by a sol-gel process followed by calcining at 300°C. It exhibits a high specific capacitance, excellent rate capability, and good cycle stability. A high specific capacitance of 1128 F g$^{-1}$ is achieved at a current density of 5 mA cm$^{-2}$ and 92.5% of the initial specific capacitance was remained after 1000 cycles. The excellent electrochemical capacitive performance, low cost, and easy fabrication of the as-prepared NiCo2O4 render it a promising electrode material for electrochemical capacitors.

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References

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