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Capacitive characteristics of Ni–Co oxide nano-composite via coordination homogeneous co-precipitation method

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Abstract A series of Ni–Co oxide nano-composites were prepared by thermal decomposition of the precursors obtained via coordination homogeneous co-precipitation method. Thermogravimetric analysis (TGA), powder X-ray diffraction (XRD), and transition electron microscopy (TEM) tests were applied to investigate the thermal behavior, crystalline. and morphology of the Ni–Co oxide composites. The electrochemical properties of Ni–Co oxide electrodes were evaluated by cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance measurements. Results showed that the calcination temperature had great effect on morphology and specific capacitance of product. The effect of the molar ratios of Ni^{2+}/Co^{2+} in the reaction system on the electrochemical properties of Ni–Co oxide electrodes was also discussed.

Introduction

With increasing interest in high-power devices, especially for hybrid electric vehicles, electrochemical capacitors (ECs) have been studied extensively in recent years. The most widely used active electrode materials are carbon [1–3], transition metal oxides [4–6], and conducting polymers [7–9]. Among the various transition metal oxide materials, hydrous ruthenium oxide [10] exhibits prominent properties as a pseudocapacitor electrode material. However, its higher cost limits its commercial use. Recently, researchers found that other transition metal oxides, such as nickel oxide [11–13], cobalt oxide [14, 15], and manganese oxide [16–18] were prominent candidates for ECs because they are inexpensive and exhibit pseudocapacitance behaviors similar to that of ruthenium oxide. Among these candidates, nickel oxide has been widely studied and developed for applications in electrochemical energy conversion and storage system. Several methods have been developed for preparing nickel oxide, including sol–gel method [11, 19], electrochemical Route [12, 20], and Chemical precipitation method [21, 22].

Recently, it is reported that compounds of mixed oxides composites have superior capacitive performance to single transition metal oxide as electrode. It was found in the literature that Mn–Ni oxide composites [23], Mn–Co oxide [24], and Mn–Ni–Co oxide composites [25] were suitable materials for ECs. Cobalt oxide, though not extensively studied, is another candidate for electrochemical capacitors applications [26, 27]. But the electrochemical capacitive properties of binary Ni–Co oxides have been investigated few. Hu and Cheng [28] prepared hydrous nickel–cobalt oxides (denoted as $a\text{-(Co + Ni)(OH)}_2 \cdot n\text{H}_2\text{O}$) on graphite substrate by electrochemical anodic deposition method. However, the effect of different Ni/Co ratio on their capacitance has not been told.

In recent years, nanostructured electrode materials have attracted great interests, since the nanostructured electrodes show better rate capabilities than conventional electrodes composed of the same materials [21]. As for the fabrication of nanostructured materials, not only controlling the nanoscale size, the geometry, and chemical homogeneity should be considered, but also the simplicity and practicability of the synthesis methods.

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With these considerations, a coordination homogeneous co-precipitation method, which is different from the methods mentioned above, is applied to synthesize Ni–Co oxide nano-composites in this article. The method is facile, low-cost, easy to realize the scale production and it can also be extended to synthesize other nano-composites. The electrochemical properties of Ni–Co oxide nano-composites were investigated by cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance measurements. The effect of different Ni^{2+}/Co^{2+} molar ratio in the reaction system on capacitive properties of Ni–Co oxides was studied. Meanwhile, the effect caused by calcination temperature on specific capacitance was also investigated.

Experimental

Coordination homogeneous co-precipitation principle

The mechanism of coordination homogeneous co-precipitation method is as follows: first, two kinds of metal ions react with an appropriate coordination agent, forming a mixed complex solution coexisting with an appropriate precipitator. Subsequently, the complex dissociates to release the metal ions via changing the conditions of the solution, such as system concentration, reaction time, temperature and so on. Because the metal ions and the precipitator are dispersed in the solution homogeneously, the precipitation reaction of metal ions and precipitator can reach molecular level, which ensures the sedimentation of desired nanomaterials yielded and separated out homogeneously from the solution [29].

In this study, low-cost ammonia was chosen as the coordination agent, ammonium acid carbonate as a precipitator, nickel nitrate and cobalt nitrate as metal source. The mixture of the coordination compound $[Ni(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$ were formed first, then the coordination reaction moved in dissociation direction by diluting the complex solution with distilled water and heating, to remove ammonia from aqueous solution. As the ammonia concentration in the solution decreased, and the free nickel and cobalt ions increased, when the metal cations and precipitator anions reached a certain amount, precipitates of basic nickel carbonate and basic cobalt carbonate mixed precursors were yielded homogeneously in the solution. The precursors were gained by centrifugation, washing, and drying. The Ni–Co oxide nano-composites were finally obtained by calcining the precursors at an appropriate temperature. The reactions were as follows:

$$[Ni(NH_3)_6]^{2+} \rightarrow Ni^{2+} + 6NH_3 \quad (1)$$

$$[Co(NH_3)_6]^{2+} \rightarrow Co^{2+} + 6NH_3 \quad (2)$$

$$2Ni^{2+} + 2OH^- + CO_3^{2-} \rightarrow Ni_2(OH)_2CO_3 \downarrow \quad (3)$$

$$2Co^{2+} + 2OH^- + CO_3^{2-} \rightarrow Co_2(OH)_2CO_3 \downarrow \quad (4)$$

$$Ni_2(OH)_2CO_3 \xrightarrow{\Delta} 2NiO + H_2O + CO_2 \uparrow \quad (5)$$

$$3Co_2(OH)_2CO_3 + O_2 \xrightarrow{\Delta} 2Co_3O_4 + 3H_2O + 3CO_2 \uparrow \quad (6)$$

Materials preparation

All the chemical reagents used in this experiment were analytical grade and used without further purification. A certain amount of NH_4HCO_3 and concentrated ammonia (28 wt%) were added into a mixed solution which consisting of $Ni(NO_3)_2$ (1 mol L^{-1}) and $Co(NO_3)_2$ (1 mol L^{-1}) in a desired molar ratio, to form a mixed complex solution. Then the mixed solution was added into 7 times volume-distilled water, and the reaction was carried out under magnetic string at 70 °C for 1 h. The precipitated precursors were obtained by being filtered, washed with distilled water, and ethanol, respectively and dried in a vacuum at 60 °C for 12 h. The final black powders were obtained by calcination in air for a specified temperature and time. In this article, we chose Ni^{2+}/Co^{2+} molar ratios of 9:1, 7:3, 1:1, 3:7, and 1:9, respectively, and the corresponding Ni–Co oxides products were referred to as Ni–Co oxide (the molar ratio of Ni^{2+}/Co^{2+}), for example, Ni–Co oxide (1:1) indicated Ni–Co oxide with the molar ratio of Ni^{2+}/Co^{2+} was 1:1 in the reaction system.

Characterization and electrochemical tests

Thermogravimetric (TG) instrument (RAGIKU Jap.) was used to analysis the thermal behaviors. The structure of Ni–Co oxide composites was examined by Powder X-ray diffraction (XRD) measurements (SIEMENS D-5000 automatic X-ray diffractometer). (HITACHI)-600 transmission electron microscope (TEM) was used to characterize the morphology and microstructure of the products. Electrochemical study on Ni–Co oxide nano-composites was carried out on a CHI660A electrochemical working station. Electrodes were prepared by mixing the active materials with 20 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) of the total electrode mass. A small amount of alcohol was then added to this composite to make a more homogeneous mixture, which was pressed on nickel foam to fabricate the electrodes. A standard three-electrode cell was employed. The prepared electrode, Nickel foam sheet, and saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. The used electrolyte was 6 mol L^{-1} KOH.

Results and discussion

Thermal analysis

Thermogravimetric analysis was conducted for precursors to examine the conversion process during calcination. Figure 1 shows the TG curve and its differential curve (DTG) of Ni–Co oxide (1:1) as an example. The TG curve indicates obvious weight loss occur in two temperature regions: the first weight loss below 175 °C results from the removal of absorbed water, and the second step weight loss at 175–350 °C is due to the removal of chemically bound water and decomposition of precursors. And two peaks on the DTG curve correspond with these two stages. Because the decomposition temperature of basic nickel carbonate and basic cobalt carbonate is close to each other, only one endothermic peak appears during this stage. When the temperature is higher than 350 °C, the TG curves become nearly flat, which indicates that the precursor can be decomposed basically at 350 °C, and further heating could only make the structure of the products more crystalline. With this consideration, the calcination temperature was chosen as 350 °C in this study. In addition, to investigate the effect caused by calcination temperature, Ni–Co oxide (1:1) also calcined at 300, 350, 400, and 450 °C.

Structure and morphology characterization

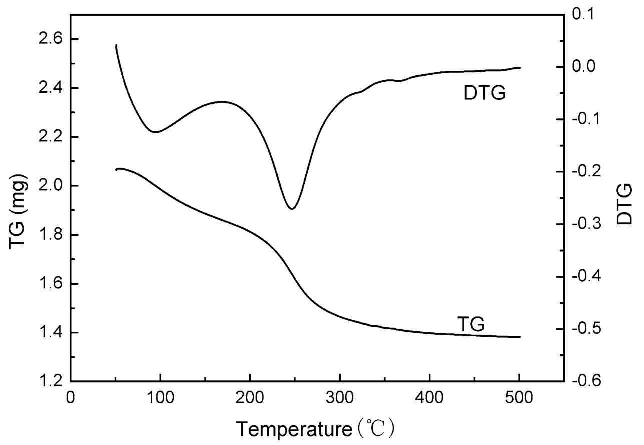

Fig. 1 TG and DTG curves of the precursor

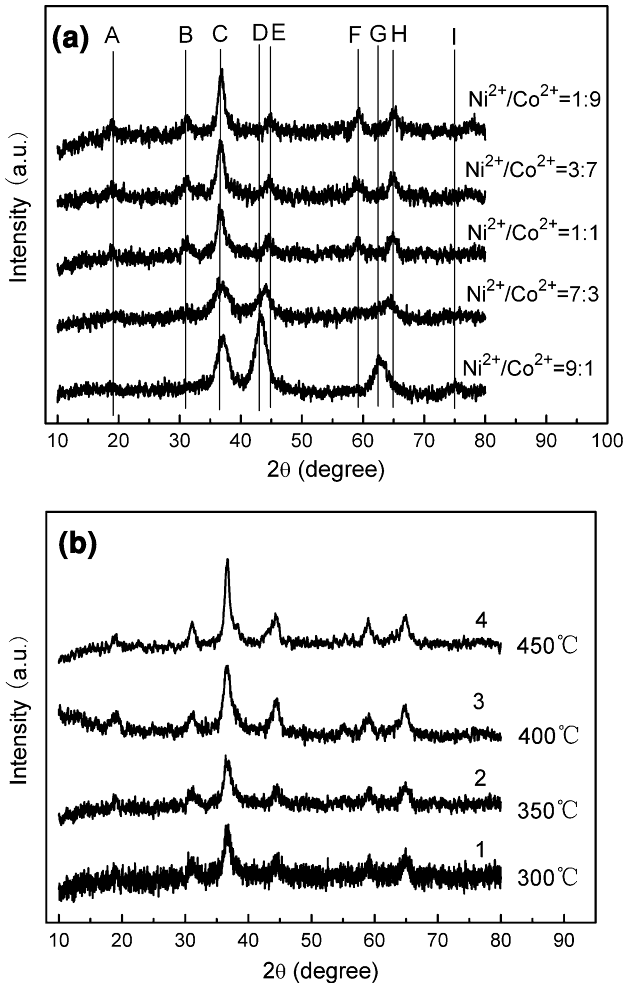

Fig. 2 **a** XRD patterns of Ni–Co oxides with different Ni^{2+}/Co^{2+} molar ratios; **b** XRD patterns of Ni–Co oxide (1:1) calcined at different temperature

The XRD patterns of all composites calcined at 350 °C for 2 h are shown in Fig. 2a. The corresponding results demonstrate that the nickel and cobalt oxides exist as NiO (JCPDS, No.47-1049) and Co_3O_4 (JCPDS, No.73-1701), respectively. The main diffraction peaks positions of NiO are lines C, D, G, and I, and the main diffraction peaks positions of Co_3O_4 are lines A, B, C, E, F, and H. The broad and low intense peaks may be related to the low crystallization degree and the small size of the crystalline grain. As the amount of Co_3O_4 in Ni–Co oxide (9:1) is small, the diffraction peaks of Co_3O_4 do not appear; only weak diffraction peaks of NiO are obtained. As the molar ratio of Ni/Co decrease, the diffraction peaks of Co_3O_4 appear gradually. Comparing these patterns, some peaks remain unchange (line C); some peaks position (lines D, E and G, H) shift in some sort; some peaks (line I) disappear gradually and some new peaks (lines A, B, and F) appear gradually with increase of Co content in the composites. On the other hand, the XRD patterns for Ni–Co oxide (1:1) calcined from 300 to 450 °C in air for 2 h are shown in Fig. 2b as examples of the structural transformations taking place in the composite. It is clearly seen that all these curves show very broad diffraction peaks, the peaks' intensities is not high even at high temperature, indicating that the as-calcined product has a low degree of crystallization. With increase in calcination temperature, the

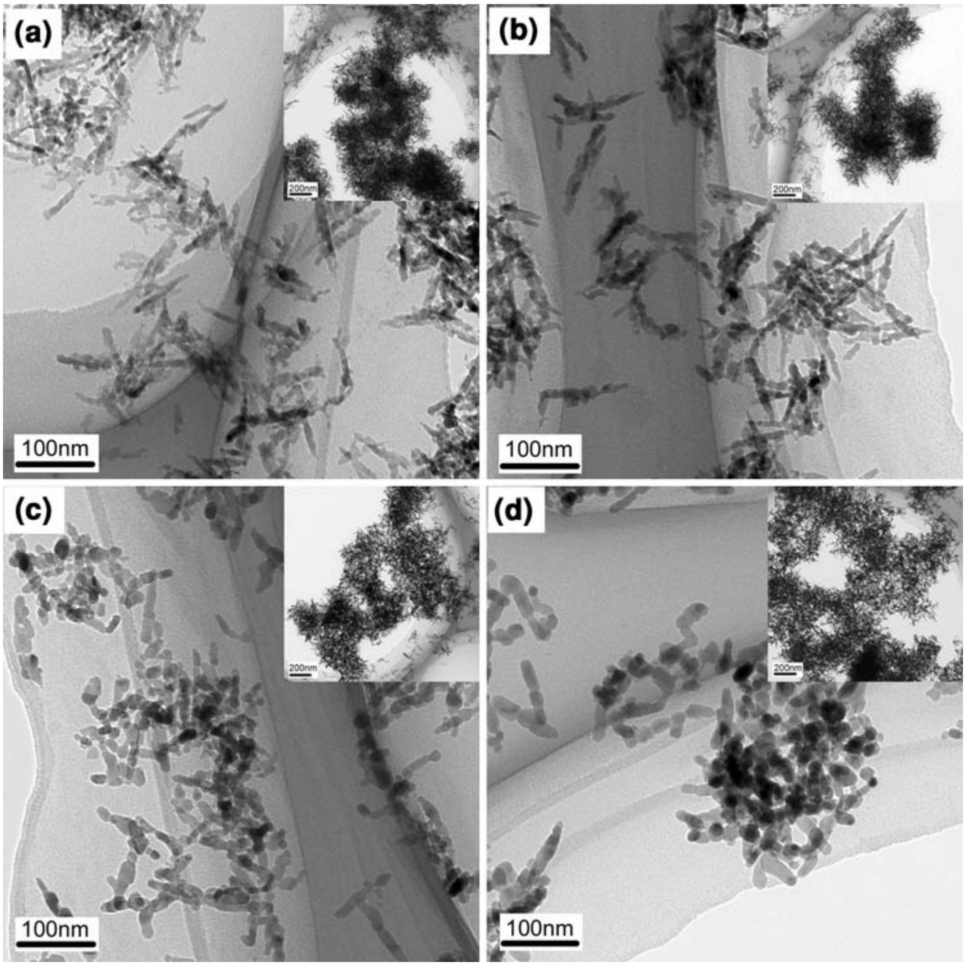

Fig. 3 TEM of Ni–Co oxide (1:1) nano-composite calcined at **a** 300 °C; **b** 350 °C; **c** 400 °C; **d** 450 °C

diffraction peaks become visible gradually and the peaks' intensities increase too, which indicates that the degree of crystallization of Ni–Co oxide increases and the grain sizes of the nanomaterials growing bigger.

Figure 3a–d illustrates the morphology of the Ni–Co oxide (1:1) composite calcined at different temperatures (300–450 °C). The right upper insert in each figure shows the TEM image under the lower magnification, and it can be found that all these samples are actually made up of small nanoparticles that agglomerate with each other to form the clusters. From the magnified images, we can see that the major morphology of the samples calcined at 300 and 350 °C is nanowires with the diameter about 10–15 nm and length up to 100 nm. Nevertheless, when heated above 350 °C, the morphology seems to change from nanowires to nanocolumns, which can be observed in Fig. 3c, d. The average size of the product calcined at 400 °C is about 20 nm and 25 nm at 450 °C. The average particle size increases gradually with increasing calcination temperature, suggesting a gradual growth of the nanoparticle during the heating process.

The effect of calcination temperature on specific capacitance

Figure 4 shows the charge–discharge curves of Ni–Co oxide (1:1) calcined at various temperatures. The potential behavior of composites calcined at 300, 350, 400, and 450 °C is approximately linear, which exhibits the response of electrochemical capacitor. It can be seen that the profile of all curves are almost the same, but the charge–discharge time changes much. The corresponding specific capacitance values can be calculated by the following relationship [30, 31]:

$$C_m = \frac{I \times \Delta t}{\Delta V \times m} \tag{7}$$

where I is the current of charge/discharge, Δt is the time of discharge, and ΔV is the potential range (in this article $\Delta V = 0.5$ V), m is the mass of active electrode materials.

The specific capacitance of Ni–Co oxide (1:1) calcined at 300, 350, 400, and 450 °C is calculated to be 272.3, 286.9, 180.0, and 123.7 F g^{-1}, respectively. It shows a

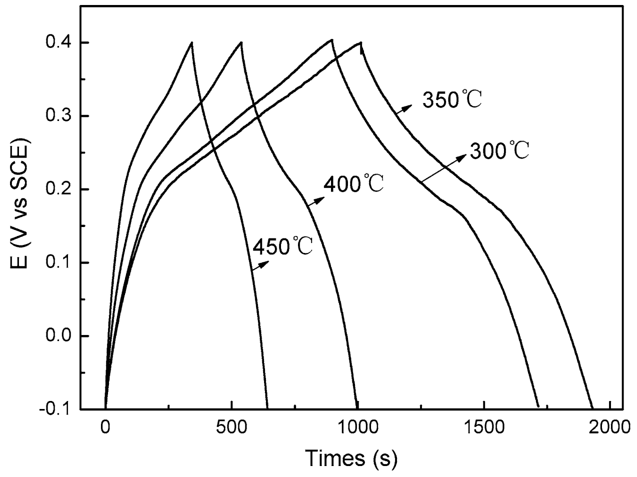

Fig. 4 Effect of calcination temperature on charge-discharge curves of Ni–Co oxide (1:1) electrodes measured at 0.2 A g^{-1} in 6 mol L^{-1} KOH

maximal capacitance value at 350 °C, and a slightly lower at 300 °C, which is expected to be due to the incomplete decomposition of precursor at 300 °C. When calcined above 350 °C, the specific capacitance decreases dramatically. It has been known that the capacitance of active materials is determined by two factors, namely, surface area and surface reactivity [5]. According to Fig. 2b, with increase in calcination temperature, the degree of crystallization increases, as well. It is expected that the Ni–Co oxide crystal phase becomes inert to the electrolyte with increasing degree of crystallization [32]. On the other hand, the decrease of specific capacitance is also supposed to be related to the morphology of the product. According to TEM results, the morphology changes from nanowires to nanocolumns when the temperature increase from 350 to 450 °C, and the particle size increase significantly, this may cause the decrease in specific surface area, and also possibly its reactivity for surface chemical process. So, the optimal calcination temperature is 350 °C in this article. At this temperature, the composite has higher surface reactivity and larger effective surface areas, this property can enlarge the contact areas and make the best use of the active materials and then enhance the electrochemical capacitance. All these results suggest that calcination temperature is an important factor for controlling the properties of Ni–Co oxide.

Cyclic voltammetry studies

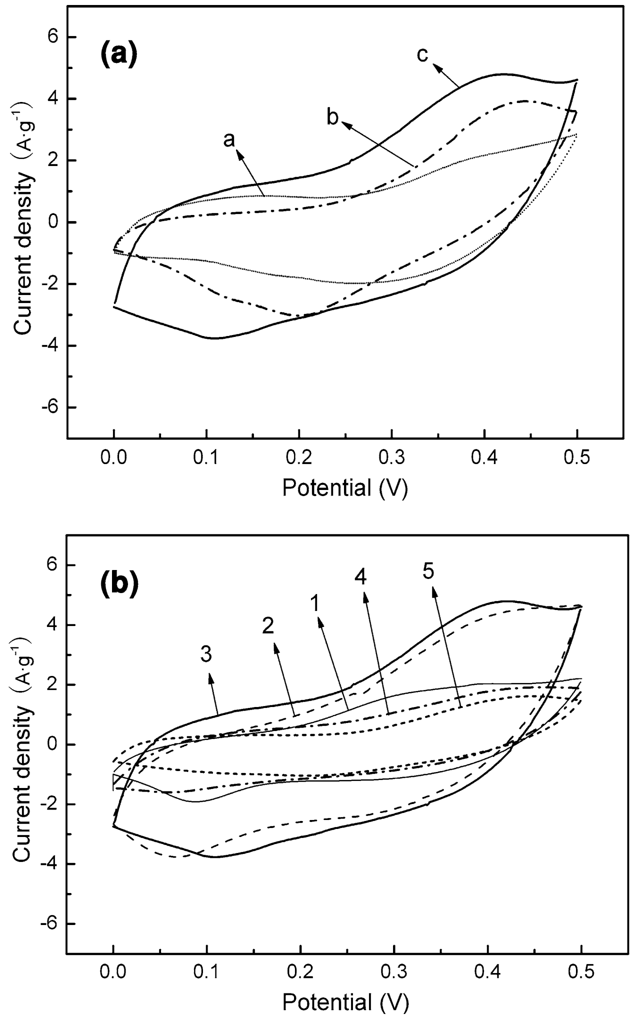

Fig. 5 **a** CV curves of pure NiO (curve a), Co_3O_4 (curve b), and Ni–Co oxide (1:1) composite (curve c) electrodes, respectively; **b** CV curves of all composite materials. 1, Ni–Co oxide (9:1) electrode; 2, Ni–Co oxide (7:3) electrode; 3, Ni–Co oxide (1:1) electrode; 4, Ni–Co oxide (3:7) electrode; 5, Ni–Co oxide (1:9) electrode

Cyclic voltammetric experiments within a 0.0–0.5 V range (vs. SCE) at a scan rate of 10 mV s^{-1} were performed in 6 mol L^{-1} KOH electrolyte at room temperature. Figure 5a shows the comparison of the CV curves of pure NiO (curve a), Co_3O_4 (curve b), and Ni–Co oxide (1:1) composite (curve c) electrodes, respectively. A quasi-reversible electron transfer process is visible in these curves, indicating that the measured capacitance is mainly based on redox mechanism. The CV curve of NiO does not displays obvious redox peaks, which is the character of capacitive behavior of electrode materials [28]. The electrochemical redox reaction of NiO in alkaline solution has been expressed as follows [12, 20]

$$\mathrm{NiO} + \mathrm{OH^-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} \mathrm{NiOOH} + \mathrm{e^-} \tag{8}$$

For Co_3O_4 electrode, a pair of broad redox peaks can be seen at 0.22 and 0.42 V, respectively, which can be attributed to [6]

$$\mathrm{Co_3O_4} + \mathrm{H_2O} + \mathrm{OH^-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} 3\mathrm{CoOOH} + \mathrm{e^-} \tag{9}$$

For Ni–Co oxide (1:1) composite electrode, one very broad redox peak appears on the CV curve, this result is in agreement with that reported in literature [27]. Compared with the Co_3O_4 electrode, the anodic and cathodic peak potentials of Ni–Co oxide (1:1) electrode are shift in negative direction. In addition, the Ni–Co oxide (1:1) composite electrode has larger CV current response and CV areas than those of pure NiO and Co_3O_4 electrodes. CVs of all samples are presented in Fig. 5b (curve 1–5). It is clearly observed that the current response is affected by the molar ratio of Ni^{2+}/Co^{2+}. On curve 3, the voltammetric current density is much larger than that of other curves. These results indicate that the capacitive properties of nickel oxide (cobalt oxide) can be improved by adding a suitable amount of cobalt oxide (nickel oxide), and the electrochemical properties of the composites were strongly dependent on the molar ratio of Ni^{2+}/Co^{2+}.

The galvanostatic charge–discharge analysis

Figure 6a–e shows the galvanostatic charge–discharge curves of all samples at different current densities. By comparing all these curves, the discharge curves of Ni–Co oxide (1:1) are more symmetrical to their charge curves than those of other electrodes, which demonstrate that Ni–Co oxide (1:1) exhibits higher reversible characteristics. It can be found that, when molar ratio of Ni^{2+}/Co^{2+} below 1:1, the potential behavior is approximately linear during the discharge step, whereas, when molar ratio of Ni^{2+}/Co^{2+} above 1:1, the linear-ship of E–*t* is not so good. However, the reason is not yet clear. Further study is needed to address these issues. According to the linear part of the discharge curves, the average specific capacitance of these Ni–Co oxides electrodes can be estimated from Eq. 7. The relationship between the specific capacitance of Ni–Co oxide

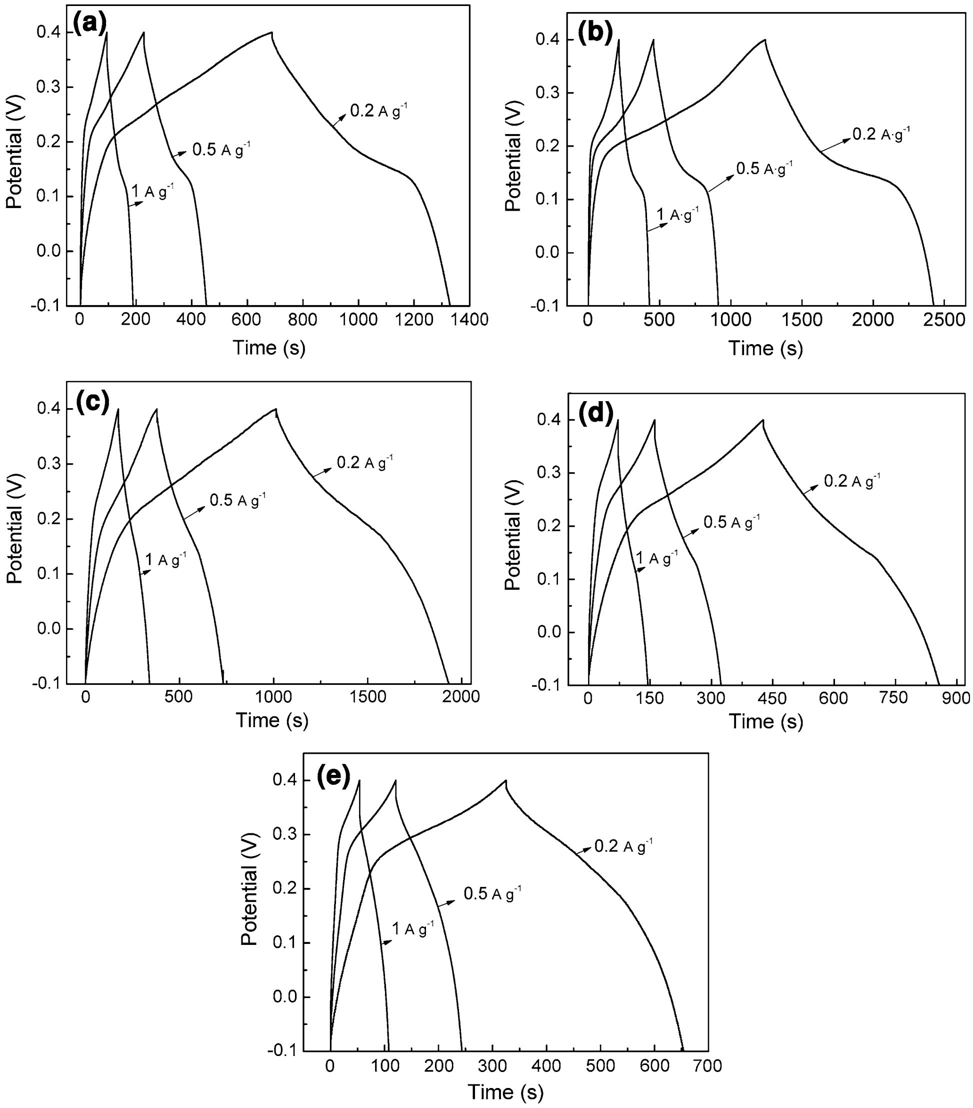

Fig. 6 Galvanostatic charge/discharge curves of all samples. **a** Ni–Co oxide (9:1); **b** Ni–Co oxide (7:3); **c** Ni–Co oxide (1:1); **d** Ni–Co oxide (3:7); **e** Ni–Co oxide (1:9)

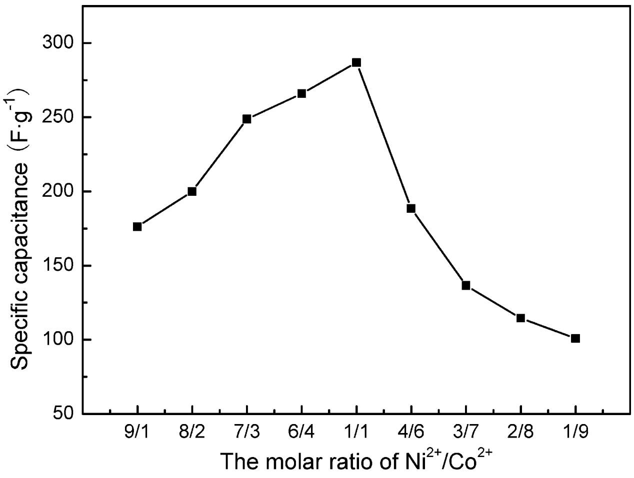

Fig. 7 Specific capacitance of Ni–Co oxide electrodes as the molar ratio of Ni/Co at the discharge current density of 0.2 A g^{-1}

electrodes at the discharge current density of 0.2 A g^{-1} and the Ni^{2+}/Co^{2+} molar ratio is plotted (Fig. 7). As seen in Fig. 7, Ni^{2+}/Co^{2+} molar ratio has great effect on specific capacitance. The specific capacitance increases significantly before the molar ratio of Ni^{2+}/Co^{2+} = 1:1, but after that it decreases sharply when Ni^{2+}/Co^{2+} = 6:4, then it decreases slowly to the lowest specific capacitance of only 100 F g^{-1} (Ni^{2+}/Co^{2+} = 1:9). From Fig. 7, it can be concluded that Ni–Co oxide (1:1) is more suitable for electrochemical capacitors than other samples. This result is consistent with that of CV studies. The specific capacitance of this composite could reach 286.9 F g^{-1} in 6 mol L^{-1} KOH solution at a discharge current density of 0.2 A g^{-1}.

Electrochemical impedance spectroscopy (EIS) analysis

Figure 8 shows the typical electrochemical impedance plots for each sample. All the plots are composed of a semicircle and a straight line. The straight line at lower frequency region should be ascribed to the diffusion process, and the semicircle at higher frequency region should be attributed to the charge transfer process at electrode/electrolyte interface. It can be seen that the semicircle of Ni–Co oxide (1:1) electrode is the smallest, which indicates that its charge transition resistance is the smallest. From the point intersecting with the real axis in the range of high frequency, we can evaluate the internal resistances. It can be seen from the insert, the internal resistances of Ni–Co oxide with Ni^{2+}/Co^{2+} molar ratio 9:1, 7:3, 1:1, 3:7, and 1:9 are 1.8, 1.5, 1.0, 3.2, and 3.6 Ω, respectively. It is obvious that Ni–Co oxide (1:1) electrode has the best conductivity.

From all the results, we can conclude that the molar ratio of Ni^{2+}/Co^{2+} plays an important role in the electrochemical properties of Ni–Co oxide nano-composites. This may be related to the difference of electrochemical reversibility and conductivity in each electrode. The following are the reasons for the superior pseudocapacitative nature of Ni–Co oxide (1:1).

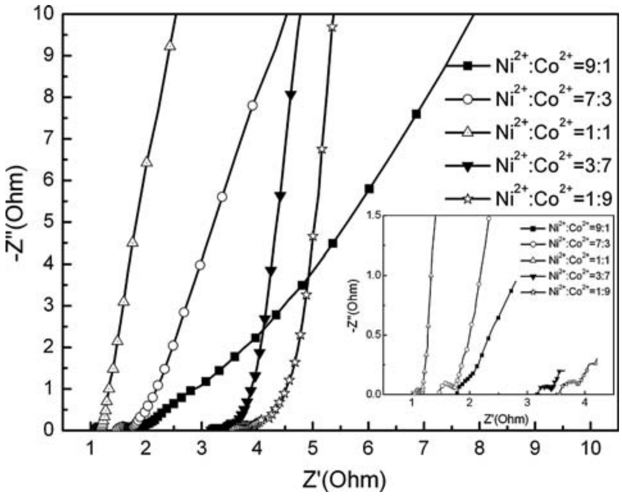

Fig. 8 The ac impedance plots of all samples

(1) It has been known that the pseudocapacitance mainly comes from the electrochemical energy stored by the fast, reversible Faradaic redox reactions occurring at or near a solid electrode surface. High electrochemical activity and reversibility are necessary properties for such electrode materials. With adding a certain amount of cobalt ions (nickel ions) into the nickel oxide (cobalt oxide) matrix, the electrochemical activity and reversibility of the composites change much. From CV and charge–discharge results, a higher electrochemical activity and reversibility can be observed in the Ni–Co oxide (1:1) electrode, and thus, more capacitance was stored in this electrode.

(2) Large internal resistance will limit the function of ECs only to low-current applications [11]. With the variety of molar ratios of Ni^{2+}/Co^{2+}, the internal resistance of composite electrodes changes too. Ni–Co oxide (1:1) electrode has the smallest internal resistance, it is obvious that the conductivity of Ni–Co oxide (1:1) was enhanced by reducing the internal resistance and its capacitance performance improves. All these properties made Ni–Co oxide (1:1) more suitable for ECs in practical use.

Therefore, due to low-cost, simple preparation, and excellent capacitive properties, Ni–Co oxides nano-composite electrode is highly promise for application in electrochemical capacitors.

Conclusions

In this article, a series of Ni–Co oxides composites were prepared by thermal decomposition of the precursors obtained via coordination homogeneous co-precipitation method. TEM analysis shows that the morphology of the product changes from nanowires to nanocolumns with increasing the calcination temperature. The results of electrochemical tests suggest that the capacitive behaviors of Ni–Co oxide are affected by calcination temperature. The specific capacitance decreases dramatically as the temperature increases from 350 to 450 °C. And the optimal molar ratio of Ni^{2+}/Co^{2+} in the reaction system is 1:1,the electrochemical reversibility and conductivity are the best at this ratio. A maximal specific capacitance of 286.9 F g^{-1} in 6 mol L^{-1} KOH solution is obtained.

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