Hydrothermal synthesis and electrochemical capacitor application of urchin-like NiCo$_2$O$_4$ particles: effect of urea concentrations

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NiCo$_2$O$_4$-based materials are promising for high-performance energy storage materials. Here, we report the synthesis of urchin-like NiCo$_2$O$_4$ particles via the hydrothermal urea precipitation process, and studied the effect of urea concentrations on phase purity, microstructure, and electrochemical capacitor performance. NiCl$_2$, 6H$_2$O, CoCl$_2$,6H$_2$O and urea, were weighed as Ni:Co:urea = 1:2:[5, 10 or 15] in molar fraction, and they were dissolved in distilled water and hydrothermally heated at 140°C for 6 h. The three precursors were calcined at 350°C for 3 h in air atmosphere. The three products were mainly composed of 3–10 μm sized urchin-like particles. All the final samples had 5–20 nm sized mesopores and ~50–70 m$^2$/g of specific surface area, but the distributions of Ni and Co in the urchin-like particles were affected by the starting urea concentration. The sample of single-phase NiCo$_2$O$_4$ from Ni:Co:urea = 1:2:15 showed the best electrochemical capacitor performance among the three urea concentrations.

Key-words : NiCo$_2$O$_4$, Electrochemical capacitor, Supercapacitor, Hydrothermal treatment, Urea, Spinel

1. Introduction

Development of high-performance energy storages is urgent to realize our sustainable societies, and in that sense, electrochemical capacitors (or ‘supercapacitors’) are considered to be promising devices, because of their favorable electrochemical characteristics, such as large energy storage, relatively high-speed charging performance and low cost.\(^1\),\(^2\) Recently, electrochemical capacitors using transition metal oxides (viz., redox capacitors or pseudocapacitors) attract much attention due to their relatively high performance compared with conventional electric double-layer capacitors.\(^3\)

NiCo$_2$O$_4$ has an inverse-spinel-type crystal structure,\(^4\) and it is a candidate material not only for electrochemical capacitors,\(^5\) but also for biosensors,\(^6\) electrocatalysts,\(^7\) and lithium ion batteries.\(^8\) For the synthesis of NiCo$_2$O$_4$ particles, post-thermal decomposition of Ni and Co mixed precursors is widely used, and NiCo$_2$O$_4$ fine particles with various morphologies have been reported.\(^9\),\(^10\) Typically, precursors for NiCo$_2$O$_4$ are prepared via hydrothermal or solvothermal methods, and then the precursors are postthermally treated. During the post-thermal treatment, decomposed H$_2$O and CO$_2$ gases act like pore-forming agents, and thus NiCo$_2$O$_4$ particles with uniform meso-/nanoporous microstructures are obtained. These porous structures enable sufficient electrochemical reactions for the electrochemical capacitor applications.

To obtain uniformly-precipitated precursors for NiCo$_2$O$_4$, urea is widely used in the hydrothermal route.\(^11\),\(^12\) Wang et al.\(^11\) recently reported the synthesis of urchin-like NiCo$_2$O$_4$ nanostructures, and pointed out that urea plays an important role to determine the morphology of the products and a “rods-to-straw-bundles-to-urchins”. In fact, urea has been used to obtain metal oxide co-precipitates by controlling the hydrothermal conditions since early studies,\(^13\) and this process is specifically called as ‘low-temperature hydrothermal urea precipitation process’.\(^14\) Although some research groups also have utilized this hydrothermal urea precipitation process to obtain the precursors for NiCo$_2$O$_4$,\(^15\)–\(^17\) the effect of urea concentration on phase purity, microstructure, and electrochemical capacitor performance of final NiCo$_2$O$_4$ particles is not completely clarified.

In this study, we have synthesized urchin-like NiCo$_2$O$_4$ particles via the low-temperature hydrothermal urea precipitation process, and have studied the effect of urea concentrations on phase purity, microstructure, and electrochemical capacitor performance of urchin-like NiCo$_2$O$_4$ particles. Just by changing the amount of urea, urchin-like particles composed of core–shell like NiO–Co$_3$O$_4$ mixture (at low urea concentration) or single-phase NiCo$_2$O$_4$ (at high urea concentration) were obtained.
2. Experimental

2.1 Synthesis of NiCo$_2$O$_4$ particles

Commercially available nickel chloride hexahydrate (NiCl$_2$·6H$_2$O, >98%, Wako, Japan), cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O, >99%, Wako), and urea (NH$_2$CONH$_2$, >99%, Wako) were used without additional purification. Typically, 1.5 mmol of NiCl$_2$·6H$_2$O, 3.0 mmol of CoCl$_2$·6H$_2$O and [7.5, 15 or 22.5] mmol of urea were dissolved in 30 mL of distilled water. The molar ratio of Ni source:Co source:urea was 1:2:[5, 10 or 15]. Each of three powders was dissolved in 30 mL of distilled water by magnetic stirring for ~10 min. The obtained homogenous pink-colored solution was transferred into a 50 mL Teflon-lined stainless autoclave and hydrothermally heated at 140°C for 6 h. Each precipitate was washed with distilled water and ethanol for several times and dried in an oven at 80°C for ~6 h. The three precursors were calcined at 350°C for 3 h in air with the heating rate of 5 °C/min, resulting in three post-thermal decomposition products. Hereinafter, the three compositions with different amount of urea are denoted as U-5, U-10, and U-15, respectively.

2.2 Materials characterization

Phase compositions of precursors and post-thermal treated powders were characterized by X-ray diffraction (XRD, Multiflex, Cu-Kα, 40 kV and 40 mA, Rigaku). Microstructures were observed by scanning electron microscopy (SEM, JSM-5600U, JEOL) and by transmission electron microscopy (TEM, JEM-2100F, JEOL). Specific surface areas and pore-size distributions of the post-thermal treated powders were measured by nitrogen adsorption/desorption (Autosorb-3-AG, Quantachrome) and analyzed by BET and BJH methods. Thermal decomposition behavior of precursors was evaluated by thermogravimetric-differential thermal analysis (TG–DTA, Seiko, TG/DTA7300, 50–550°C, 5 °C/min, air atmosphere). The thermal decomposition behavior of the U-5 and U-15 precursors was certainly different to each other, and that of the U-10 should be an intermediate of these. Moreover, the total weight losses by thermal decomposition gradually increased from U-5 (~24%) to U-15 (~28%), which reflects the quantity of gasifiable species in the precursors. By using the TG–DTA results, the sample annealing for the electrochemical measurement was set at 350°C for 3 h.

Figure 2 shows TG–DTA curves of the U-5, U-10 and U-15 precursors. As shown in Fig. 2(a), two (or more) weight-loss steps were observed in 250–370°C, which suggests that the conversion into NiO and Co$_3$O$_4$ occurred separately. TG curve of U-15 in Fig. 2(c), on the other hand, showed nearly one-step thermal decomposition, and its moderate decomposition curve suggests the successful conversion into NiCo$_2$O$_4$. The thermal decomposition behavior of the U-5 and U-15 precursors was certainly different to each other, and that of the U-10 should be an intermediate of these. Moreover, the total weight losses by the thermal decomposition gradually increased from U-5 (~24%) to U-15 (~28%), which reflects the quantity of gasifiable species in the precursors. By using the TG–DTA results, the sample annealing for the electrochemical measurement was set at 350°C for 3 h.

2.3 Electrochemical characterization

As an example of electrochemical properties, supercapacitor properties were evaluated. A three-electrode method was used for the evaluation with an electrochemical analyzer (660A-G, ALS), saturated calomel electrode was used as a reference electrode, Pt plate was used as a counter electrode, and a 3 M KOH aqueous solution was used as an electrolyte. The working electrodes were prepared with these sample powders on a Ni foam (2 cm × 1 cm). The Ni foam was immersed in a 3 M HCl solution and cleaned by an ultrasonication for 20 min to remove the impurity layer. It was carefully washed with distilled water, ethanol and acetone. Then, each precursor powder was loaded on the cleaned Ni foam with ethanol, and was annealed at 350°C for 3 h in air atmosphere. Obtained electrodes were carefully washed with ethanol. The sample mass of U-5, U-10 and U-15 on the Ni foam was determined to be ~0.8, ~1.1 and ~3.1 mg/cm$^2$-Ni foam, respectively. These working electrodes were evaluated by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) test, similarly to our recent report on Co$_3$O$_4$.

3. Results and discussion

3.1 Constituent phase of post-thermal treated products

Figure 1 shows XRD patterns of the post-thermal treated powders. As shown in Fig. 1, the U-5 and U-10 samples were most probably composed of NiO (JCPDS No. 47-1049), Co$_3$O$_4$ (JCPDS No. 42-1467) and NiCo$_2$O$_4$ (JCPDS No. 20-0781), which indicates that these hydrothermal conditions were insufficient for synthesizing single-phase NiCo$_2$O$_4$. On the other hand, the urea-rich U-15 sample was composed of single-phase of NiCo$_2$O$_4$.

In order to elucidate the thermal decomposition behavior of the precursors, TG–DTA analysis was conducted. Figure 2 shows the TG–DTA curves of the U-5, U-10 and U-15 precursors. As shown in Fig. 2(a), two (or more) weight-loss steps were observed in 250–370°C, which suggests that the conversion into NiO and Co$_3$O$_4$ occurred separately. TG curve of U-15 in Fig. 2(c), on the other hand, showed nearly one-step thermal decomposition, and its moderate decomposition curve suggests the successful conversion into NiCo$_2$O$_4$. The thermal decomposition behavior of the U-5 and U-15 precursors was certainly different to each other, and that of the U-10 should be an intermediate of these. Moreover, the total weight losses by the thermal decomposition gradually increased from U-5 (~24%) to U-15 (~28%), which reflects the quantity of gasifiable species in the precursors. By using the TG–DTA results, the sample annealing for the electrochemical measurement was set at 350°C for 3 h.

Figure 3 shows EPMA elemental mapping images of horizontal fracture surface of the post-thermal treated U-5 and U-15 particles. From Fig. 3(a) for U-5, the EPMA images can be interpreted that NiO tends to locate at the center of urchin-like particles, and Co$_3$O$_4$ tends to surround...
NiO. This interpretation agrees with the results of XRD (i.e. multiphase) and TG–DTA (i.e. multi-step decomposition). From Fig. 3(b) for U-15, on the other hand, Ni and Co distributed almost homogeneously in the urchin-like particles, which supports the formation of single-phase of NiCo$_2$O$_4$ for U-15. Semi-quantitative analysis results are given in Supporting Information (Figure S1 and Table S1).

3.2 Nanostructure and powder properties of post-thermal treated products

Figure 4 shows high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) images of the post-thermal treated U-15 sample. In Fig. 4(a), interplanar spacing of 0.16, 0.26, and 0.28 nm were observed, corresponding to the (511), (311) and (220) planes of spinel-

![Fig. 2. TG–DTA curves of the precursor powders: (a) U-5, (b) U-10, and (c) U-15.](image1)

![Fig. 3. EPMA elemental mapping images of the post-thermal treated powders: (a) U-5 and (b) U-15.](image2)

![Fig. 4. TEM images of NiCo$_2$O$_4$ (post-thermal treated U-15 sample): (a) HRTEM and (b) SAED.](image3)
Figure 5 shows $N_2$ adsorption/desorption isotherms and BJH pore-size distribution. In Fig. 5(a), all post-thermal treated products show IUPAC type-IV isotherms, which indicate that they were mesoporous materials. From Fig. 5(a) insert, the specific surface areas for U-5, U-10, and U-15 were 46.6, 59.4 and 69.1 m$^2$/g, respectively. With increasing NiCo$_2$O$_4$ phase, the specific surface area was enlarged. Pore-size distributions were calculated from desorption isotherms by using the BJH method as shown in Fig. 5(b). The pore-size distribution curves clearly show the existence of mesopores. The typical pore sizes for all samples are estimated to be 5–20 nm. The formation of mesopores in the post-thermal treated powders is mainly attributable to the emission of H$_2$O and CO$_2$ gases during the thermal decomposition of precursors. As compared with Fig. 2 (TG–DTA), smaller pores at ~8 nm might be attributable to the decomposition at lower temperatures (~300°C), and larger pores at ~10–20 nm might be attributable to the decomposition at higher temperatures (~350°C). Further studies, such as thermogravimetry mass spectrometry or temperature programmed desorption, are needed to clarify the pore-formation mechanism in detail.

3.3 Microstructure of NiCo$_2$O$_4$ electrodes on Ni form

Figure 6 shows microstructures of the post-thermal treated particles on the Ni foam. In the low magnification images, Figs. 6(a)–6(c), three sample powders were well-fixed on the Ni foam. In the high magnification images, Figs. 6(d)–6(f), urchin-like particles of 3–10 µm were observed; microstructural difference among these three samples was apparently not so prominent. We expect some advantages from the spherical urchin-like morphology, such as (1) good fluidity as powders, (2) good crystallinity of each microcrystal, and (3) easy penetration of the liquid electrolyte into the spheres.

3.4 Supercapacitor properties

Figure 7 shows CV curves with different scan rates at 5, 10, 20, 40 and 50 mV s$^{-1}$ in the potential from −0.3 to 0.7 V for prepared three-type electrodes. According to their constituent phases, prepared electrodes exhibited pairs of charge–discharge reactions as follows:

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\begin{align*}
\text{NiO} + \text{OH}^- & \leftrightarrow \text{NiOOH} + e^- \\
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} & \leftrightarrow 3\text{CoOOH} + e^- \\
\text{NiCo}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} & \leftrightarrow \text{NiOOH} + 2\text{CoOOH} + e^- \\
\text{CoOOH} + \text{OH}^- & \leftrightarrow \text{Co}_2\text{O}_3 + \text{H}_2\text{O} + e^-
\end{align*}
\]

Moreover, the anodic and cathodic peaks shifted as the increase of the scan rate in the both samples. This indicates the quasi-reversible redox features. The CV curves were gradually widened from U-5 to U-15 corresponding to the increase of NiCo$_2$O$_4$ phase.

Figure 8 shows GCD curves for three sample electrodes in the potential from 0 to 0.38 V at the different current concentrations.
Fig. 7. CV curves with different scan rates of the sample electrodes: (a) U-5, (b) U-10 and (c) U-15.

Fig. 8. GCD curves with the different current densities of the prepared electrodes: (a) U-5, (b) U-10 and (c) U-15.
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