High-performance energy storage is crucial to realize our sustainable society, and electrochemical capacitors (or ‘supercapacitors’) are promising due to their fascinating characteristics, such as large power density, high-speed charging, long durability and relatively low cost. A redox capacitor is a sort of supercapacitor that stores electrical energy as chemical energy via a reversible redox reaction near the interface between an electrode active material and an electrolyte solution. The redox capacitor is considered to store electric charge by stepwise changing the valence of the electrode active material. Despite having a redox capacity, its discharge-charging behavior is similar to that of an electric double layer capacitor (EDLC). Therefore, the redox capacitor is also called a ‘pseudocapacitor’. A redox capacitor generally has a high specific capacity because all the electrode surfaces in contact with the electrolyte serve as ion adsorption/desorption points. Among them, hydrous RuO₂ systems have particularly high capacity, and it has been reported that the redox capacitor with RuO₂·nH₂O nanotube array electrode achieved even ~1300 F/g. However, since RuO₂-based redox capacitor is much more expensive than a conventional carbon-based EDLC, alternative electrode active materials for redox capacitors have been eagerly investigated. For example, Co-containing spinel-type oxides, such as Co₃O₄ and NiCo₂O₄, are promising alternatives to RuO₂, but cobalt is still an expensive rare metal element.

To realize the further cost reduction of the electrode active materials, NiMn₂O₄ has attracted much attention due to its low cost and non-toxicity. NiMn₂O₄ has an inverse spinel structure, similarly to NiCo₂O₄, but NiMn₂O₄ is much cheaper than Co₃O₄ and NiCo₂O₄. Hence, many research groups have synthesized various types of NiMn₂O₄ nanostructures via wet chemical processes, and used them as redox capacitors. Despite the promising results on high specific capacitance, many of these works used toxic or less environmentally-friendly ingredients, such as oxalate, nitrates and chlorides. Meanwhile, some of them used eco-friendly precursors, e.g., acetates. In these studies with acetates ingredients, however, somewhat costly organic additives were utilized, such as polyvinylpyrrolidone (PVP), polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP).

We think that NiMn₂O₄ nanoparticles can be synthesized from eco-friendly acetates ingredients with eco-friendly and low-cost citric acid. Here, we report synthesis, microstructure and electrochemical characterization of NiMn₂O₄ nanoparticles via a simple citric acid method.

**Synthesis, microstructure and electrochemical characterization of NiMn₂O₄ nanoparticles via a simple citric acid method**

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NiMn₂O₄ has an inverse spinel structure similarly to Co₃O₄ and NiCo₂O₄, but NiMn₂O₄ is much cheaper than these cobalt containing materials. Here, we report synthesis, microstructure and electrochemical characterization of NiMn₂O₄ nanoparticles via a simple citric acid method. Ni(CH₃COO)₂·4H₂O (1.5 mmol) and Mn(CH₃COO)₂·4H₂O (3.0 mmol) were dissolved in distilled water (25 mL), and citric acid (3.75 mmol) was added and stirred for 2 h to obtain transparent blue-green solution. The solution was open-heated at 90 °C for 24 h, and heated at 170 °C for 2 h to obtain a xerogel. The xerogel precursor was pestled and calcined at 400 °C for 4 h in air to obtain a NiMn₂O₄ powder. X-ray diffraction, N₂ adsorption/desorption and transmission electron microscopy with energy dispersive X-ray spectroscopy revealed that single-phase NiMn₂O₄ mesoporous nanoparticles were successfully synthesized from eco-friendly acetates ingredients by the low-cost citric acid method. The specific surface area and pore size of the NiMn₂O₄ mesoporous nanoparticles were 211.3 m²/g and ~4 nm, respectively. The NiMn₂O₄ electrode successfully worked as a supercapacitor.

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**Figure 1** shows the sample preparation procedure. Commercially available nickel(II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O, >98%, Fujifilm Wako, Japan), manganese(II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O, >99%, Fujifilm Wako), and citric acid (HOOCCH₂C-(OH)(COOH)CH₂COOH, gelation/chelating agent, >98%, Fujifilm Wako) were used without additional purification. Typically, 1.5 mmol of Ni(CH₃COO)₂·4H₂O, 3.0 mmol of Mn(CH₃COO)₂·4H₂O and 3.75 mmol of citric acid were carefully weighed. First, Ni(CH₃COO)₂·4H₂O and Mn(CH₃COO)₂·4H₂O powders were dissolved in 25 mL of distilled water by magnetic stirring for 10 min. Then, citric acid powder was added and further stirred for 2 h to obtain transparent blue-green solution. The solution was open-heated (without sealing) in an oven at 90 °C for 24 h, and then successively heated at 170 °C for 2 h to obtain a xerogel. The xerogel precursor was pestled with agate mortar for 10 min, and then the precursor powder was calcined at 400 °C for 4 h in air to obtain a NiMn₂O₄ powder. The sample was named as ‘ca’ (= citric acid added sample).

Just as a comparison, another sample with a small amount of ethylene glycol was also tested, because ethylene glycol (ethane-1,2-diol) and other diols (e.g., butane-1,4-diol) also act as chelating agents (so called glycolate/chelating agent, >98%, Fuji Film Wako) were used without additional purification. For the supercapacitor properties measurement, a NiMn₂O₄ working electrode was prepared with the ‘ca’ sample powder on a Ni foam (1 cm × 1 cm). The Ni foam was immersed in a 3 M HCl solution and cleaned by an ultrasonification for 20 min to remove the impurity layer. It was carefully washed with distilled water, ethanol and acetone. Then, the ‘ca’ sample paste with some ethanol was loaded on the cleaned Ni foam, and was annealed at 200 °C for 2 h in air. The obtained electrode was carefully washed with ethanol. A three-electrode method was used for the evaluation with an electrochemical analyzer (660A-G, ALS); saturated calomel electrode (SCE) was used as a reference electrode, Pt plate was used as a counter electrode, and a 1 M KOH aqueous solution was used as an electrolyte. The sample mass on the Ni foam was measured by electronic balance. The working electrode was evaluated by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) test, similarly to our recent report on urchin-like NiCo₂O₄ particles.¹²

**Figure 2** shows XRD patterns of the NiMn₂O₄ powders. Both ‘ca’ and ‘caE’ samples consisted of spinel phase. But only from these XRD patterns, it is difficult to specify the real chemical compositions of these powders (viz., NiMn₂O₄, MnNi₂O₄, NiMn₂O₄–MnNi₂O₄ solid solution or NiMn₂O₄/MnNi₂O₄ mixture). Preliminary elemental analyses suggested that the ‘ca’ sample was composed of almost pure NiMn₂O₄ (slightly Ni-rich than the stoichiometry), but the ‘caE’ sample was composed of ‘near stoichiometric NiMn₂O₄/Mn-poor NiMn₂O₄ mixture’, and hence the further evaluations were mainly focused on the ‘ca’ sample. Detail of the sample analysis is given in the Supporting Information.

**Figure 3** shows N₂ adsorption/desorption isotherms and BJH pore-size distributions. Both ‘ca’ and ‘caE’ samples displayed IUPAC type-IV isotherms, which indicate that they were mesoporous materials. The specific surface areas for ‘ca’ and ‘caE’ were 211.3 and 99.1 m²/g, respectively, which were in good agreement with broad and
less-broad XRD patterns in Fig. 2. The BJH pore-size distribution curves clearly show the existence of mesopores. The typical pore sizes for these samples are estimated to be ~4 nm for ‘ca’ and ~5–10 nm for ‘caE’. The formation of mesopores in the sample powders is attributable to the emission of H2O and CO2 gases during the thermal decomposition of precursors. However, these pores are too small for the penetration of electrolyte solution in an actual supercapacitor device. Further study on pore-structure control must be needed.

Since the ‘ca’ sample had larger BET surface area and sharper BJH pore-size distribution, it was further analyzed by SEM, TEM and STEM-EDS analyses. Figure 4 shows SEM and low and high-resolution TEM images of the NiMn2O4 powder (‘ca’ sample). NiMn2O4 nanoparticles (typically ~50 nm) formed strongly aggregated secondary particles (SEM), and mesopores (~4 nm) were observed (TEM), which was in good agreement with the XRD and BJH analyses. Figure 5 shows STEM-EDS elemental mapping images of the NiMn2O4 powder (‘ca’ sample). Ni, Mn and O atoms were homogeneously distributed in the sample. From the XRD, BJH and STEM-EDS analyses, it is concluded that a single-phase NiMn2O4 nanopowder with mesopores was successfully synthesized by a simple citric acid method.

Then the supercapacitor properties of the NiMn2O4 electrode were evaluated. Figure 6 shows CV curves of the NiMn2O4 electrode with different scan rates at 5, 10, 20, 30, 40, 50, 75 and 100 mV s⁻¹.

Figure 7 shows GCD curves of the NiMn2O4 electrodes in the potential from 0 to 0.40 V at the different current densities. The specific capacitance can be calculated by the following formula: 33)

\[ C = \frac{I \times \Delta t}{m \times \Delta V} \]

where \( C \) (F/g) represents the specific capacitance of the working electrode, \( I \) (A) refers to the charge/discharge current, \( \Delta t \) (s) is the discharge time, \( m \) (g) is the mass of active material and \( \Delta V \) (V) is potential drop during discharge. The specific capacitances of the NiMn2O4 electrodes in this
study were 48.6, 42.4, 37.0, 32.8, 31.4, 30.2, 28.7 F/g at the current density of 1, 2, 4, 8, 10, 12, 15 mA/cm², respectively.

The curve shapes of the CV curves (Fig. 6) and GCD curves (Fig. 7) of the NiMn₂O₄ electrode in this study were similar to those of the NiCo₂O₄ electrode in our previous study (U-10 sample with moderate performance). In the previous study, urchin-like NiCo₂O₄ microstructure (in particular for the U-15 sample) is favorable for the penetration of liquid electrolyte, but in this study, such microstructure has not yet been realized. Actually, the current (Fig. 6) and the specific capacitance (from Fig. 7) of the NiMn₂O₄ electrode with equiaxed mesoporous (but microscopically aggregated) structure in this study were one-order smaller than those of the NiCo₂O₄ electrode with urchin-secondary particles. Although NiMn₂O₄ has a potential for a replacement of expensive NiCo₂O₄, further tuning of the NiMn₂O₄ particle structure as well as the optimization of electrode structure will be required.

In conclusions, single-phase NiMn₂O₄ mesoporous nanoparticles were successfully synthesized from eco-friendly acetates ingredients by a low-cost citric acid method. The specific surface area and pore size of the NiMn₂O₄ mesoporous nanoparticles prepared with citric acid were 211.3 m²/g and ~4 nm, respectively. The NiMn₂O₄ electrode in this study successfully worked as a supercapacitor, but the further tuning of the particle shape (e.g., urchin-like structure) is needed to further improve the electrochemical performance.

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