Fabrication of Asymmetric Supercapacitors Based on Coordination Polymer Derived Nanoporous Materials

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Abstract

Considerable efforts have been devoted to the synthesis and characterization of novel nanoporous materials because of their versatile applications, such as gas storage, catalysis, and energy storage applications. Controllable synthesis of coordination polymers (CPs) with two- and three-dimensional architectures has given impetus to the development of nanomaterials with many exciting properties and applications. Here, we focus on CP-derived nanoporous materials and study their electrochemical performance as electrode materials in supercapacitors. Nanoporous carbon is prepared by direct carbonization of zinc-containing zeolitic imidazolate framework (ZIF-8). On the other hand, nanoporous nickel oxide (NiO) is prepared by thermal treatment of cyano-bridged CPs. By using the above two electrodes, we fabricate a novel asymmetric supercapacitor. These CP-derived nanoporous materials exhibit excellent electrochemical performance with high **specific energy and specific power**, and excellent cycling stability.

Keywords: coordination polymers, nanoporous carbons, nickel oxides, asymmetric supercapacitors

Table of Content

1. Introduction

Coordination polymers (CPs), such as metal-organic frameworks (MOFs), porous coordination polymers (PCPs), and Prussian blue analogues, are formed by strong chemical interaction between organic and inorganic units [1-3]. Various CP nanocrystals with ultra-high porosity and high thermal/chemical stability have been prepared by controlling the synthetic conditions, and interest in them has increased due to their unique size- and shape-dependent properties, which differ from those of bulk crystals. These unique characteristics make them ideal candidates for several applications in gas storage, separation, catalysis, and energy storage.

The supercapacitor is an energy storage device that stores charge and is intermediate between batteries having high energy density and capacitors having high power density [4]. In general, there are two types of supercapacitors: electrical double layer capacitors (EDLCs) and the pseudocapacitors. Double-layer capacitance is achieved by separation of charge at the interface between a conductive electrode surface and an electrolyte, while pseudocapacitance is achieved by faradaic electrochemical storage through redox reactions.

Nanoporous carbons (NPCs) possess large specific surface area, good electrical and thermal conductivity, and both chemical and mechanical stability, which facilitates their increasing use in EDLCs [5,6]. Recently, many efforts have been devoted to the development of NPCs (*e.g.*, activated carbons (AC), and microporous and mesoporous carbons prepared from zeolites and mesoporous materials) with controllable pore sizes [7-9]. MOFs, which are built from metal ions and organic ligands, can serve as sacrificial templates for the preparation of NPCs. Since the first report by Xu *et al.* [10], the preparation of NPCs directly from MOFs has emerged as a novel strategy and aroused widespread interest [11-13].

On the other hand, cyano-bridged CPs have recently gained attention as a new class of cathode materials for rechargeable batteries [14-18], which has motivated us to consider whether their derivatives can also be utilized for electrochemical supercapacitors. The organic parts in cyano-bridged CPs can be removed by optimized thermal treatment to prepare nanoporous metal oxides [19, 20]. The thus-obtained nanoporous metal oxides are useful electrode materials for pseudocapacitors.

The design of a facile and reliable method for the rational synthesis of nanoporous metal oxides as well as NPCs still remains a big challenge and may lead to great interest in the field of materials science. Based on above considerations, here, we have proposed a novel asymmetric supercapacitor (ASC) utilizing NPC [21] and nanoporous NiO (NPN, [22]) prepared from CPs (**Fig. 1**). The synergistic cooperation between pseudocapacitive NPN nanoflakes and highly porous NPC particles can provide high performance for energy storage. Our target is ‘all from CPs’ to fabricate ASCs. Our ASC is expected to offer promising supercapacitor performance by utilizing the advantages of both EDLC and pseudocapacitor materials.

2. Experimental

2.1 Chemicals Nickel (II) chloride hexahydrate, trisodium citrate dihydrate, polyvinylpyrrolidone (PVP, K30), hydrochloric acid solution, and methanol were purchased from Nacalai Tesque Reagent Co., Japan. 2-methylimidazole (MIM, purity 99%) and $\text{Zn}(\text{CH}_3\text{COO})_2$ (purity 97%) were purchased from Sigma-Aldrich Chemical Co. All the raw chemicals were used without any further purification.

2.2 Synthesis of NPC particles Firstly, in one beaker, $\text{Zn}(\text{CH}_3\text{COO})_2$ (175 mg) and PVP (300 mg) were dissolved in methanol (20.0 ml) to form a solution. In another, 2-methylimidazole (2.63 g) was dissolved in methanol (20.0 ml) to generate another clear solution. Then, both solutions were mixed together and stirred for 5 min. This mixed solution was aged at room temperature for 30 h. After that, white powders were precipitated. The powders were washed carefully with methanol and dried completely. The obtained zinc-containing zeolitic imidazolate framework (ZIF-8) particles were directly carbonized under flowing nitrogen gas at 800 °C. The temperatures inside the furnace were gradually increased from room temperature to the target temperature with a heating rate of 5 °C·min⁻¹. After the target temperature was reached, the powders were annealed for 5 h and then cooled down to room temperature. The obtained particles were collected and carefully washed with HF aqueous solution (10 %) to remove the Zn nanoparticles. The sample was stirred in the HF solution for 24 h. Finally, the sample was

2.3 Synthesis of NPN nanoflakes. In a typical experimental process, 0.4 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.3 mM dihydrate tri-sodium citrate were dissolved in 20 ml pure water to form a clear solution. Meanwhile, 0.4 mM $\text{K}_2[\text{Ni}(\text{CN})_4]$ was added to 20 ml pure water to prepare another clear solution. After that, the two solutions were mixed together and aged at room temperature for 30 h. Then, the precipitate was collected by centrifugation and washed using pure water and ethanol several times, and finally dried at a

room temperature in air for subsequent characterization. To convert Ni-CP nanoflakes to NPN nanoflakes, these samples were calcined at 300 °C for 1 h with a heating rate of 5 °C·min⁻¹ in air. Finally, the obtained samples were washed 5 times with distilled water and dried under vacuum conditions for 24 h at 60 °C.

2.4 Electrochemical measurements The electrochemical measurements were conducted on a three-electrode system using Pt as the counter electrode and Ag/AgCl as the reference electrode in 6 M KOH solution. Graphite substrate coated with NPC or NPN (1 mg) was used as the working electrode (The graphite substrate serves as the current collector). The graphite substrates were firstly polished under flowing water using a fine polisher. Then, they were washed with deionized water, etched in a 0.1 M HCl solution at room temperature for 10 min, and finally washed with deionized water in an ultrasonic bath for 30 min. The mass of the electrodes was measured using an ultra-microbalance (METTLER TOLEDO). The active electrode sample was mixed with poly(vinylidene difluoride) (PVDF, 20%) in N-methyl 2-pyrrolidinone (NMP) solvent. The resulting slurry was homogenized by ultrasonication and coated onto a graphite substrate, which was followed by drying at 80 °C for 2 h in a vacuum oven. Cyclic voltammograms (CV curves) were obtained using an electrochemical workstation (CHI 660E CH Instruments, USA). For every experiment, the typical area under consideration was 1 × 1 cm².

3. Results and discussion

NPC particles and NPN nanoflakes were prepared by calcination of ZIF-8 and cyano-bridged CPs, respectively. The detailed experimental procedure is described in the experimental section. The NPC particles and NPN nanoflakes were characterized by wide-angle X-ray diffraction (XRD) measurements. NPC exhibits one obvious broad peak at around 25° , corresponding to a typical (002) interlayer peak of graphite-type carbon (**Fig. 2a-1**). Whereas, NPN exhibits three characteristic peaks which are assignable to the (111), (200), and (220) peaks of cubic crystalline NiO phase (**Fig. 2a-2**). The nanoporous carbon retains the original highly-symmetric shape of ZIF-8 (**Fig. 2b-1, b-2**). The arrows in the high-resolution transmission electron microscope (TEM) image in **Fig. S1a** in the Supporting Information shows the presence of nanopores, although their arrangement is not ordered. The elemental mapping (**Fig. S2a-c**) confirms the presence of carbon and nitrogen in NPC. From the scanning electron microscope (SEM) image in **Fig. 2c-1**, the NPN particles are in nanoflake form, and their lateral size is about 100-300 nm. The obtained flakes are not stacked together, so the space between these flakes is helpful for fast movement of ions in the electrolyte for supercapacitor application. As shown in the TEM images in **Figs. 2c-2** and **S1b** and the high-angle annular dark-field (HAADF)-TEM image in **Fig. S2d**, highly crystallized NiO phase and well-developed nanoporous structure were observed. The corresponding elemental mapping (**Fig. S2e-f**) further confirms the presence of nickel and oxygen in the flakes. Nitrogen adsorption-desorption isotherms (**Fig. S3**) give a Brunauer-Emmett-Teller (BET) surface area of $1523 \text{ m}^2\cdot\text{g}^{-1}$ (for NPC) and $78 \text{ m}^2\cdot\text{g}^{-1}$ (for NPN), respectively. For realizing such high specific surface area, the contribution from the surface of the material is relatively less significant, with the major contribution from the nanopores inside the materials.

To evaluate the electrochemical potential window and to quantify the specific capacitances of the NPN and NPC electrodes, CV measurements were firstly performed in 6 M KOH aqueous electrolyte using a three-electrode system. The NPN electrodes were measured within a potential window of 0 to 0.5 V (vs. Ag/AgCl), and the NPC electrodes were measured in the potential window from -1.2 to 0 V (vs. Ag/AgCl) at various scan rates from 5 mV·s⁻¹ to 100 mV·s⁻¹ (**Fig. 3**). In the case of NPN (**Fig. 3a**), a pair of reduction and oxidation peaks were observed, due to the following reversible reaction: NiO + OH⁻ ↔ NiOOH + e⁻ [23,24]. As the applied scan rate is increased, the current increases and the oxidation peak shifts to the more positive potential side, while the reduction peak shifts to the more negative potential side. All the CV curves are symmetric with good reversibility, indicating ideal pseudocapacitive behaviour for the NiO electrode material. The specific capacitance value was calculated from the CV curve using the following equation,

$$C = \frac{1}{ms(V_f - V_i)} \int_{V_i}^{V_f} I(V) dv \quad (1)$$

where ‘*m*’ is the mass of active electrode material, ‘*s*’ is the potential scan rate, ‘*V_f*’ and ‘*V_i*’ are the integration limits of the voltammetric curve, and *I(V)* denotes the specific current, respectively. The specific capacitance of NPN as a function of scan rate is plotted in **Fig. 3b**. From the CV curves, the specific capacitance values were 533, 411, 393, 364, 342, and 325 F·g⁻¹ at different scan rates of 5, 20, 40, 60, 80, and 100 mV·s⁻¹, respectively. In contrast, the CV curve of NPC was in a quasi-rectangular shape with a wide potential window (1.2 V) (**Fig. 3c**). The specific capacitance values for NPC were 182, 111, 89, 78, 71, and 67 F·g⁻¹ at the different scan rates of 5, 20, 40, 60, 80, and 100 mV·s⁻¹, respectively (**Fig. 3d**).

Importantly, as the potential windows are quite stable, an operating cell potential can be envisioned to extend up to ~ 1.7 V. An ASC cell was fabricated by using NPN as the positive electrode and NPC as the negative electrode, as shown in **Fig. 4a**. A schematic illustration of our ASC device is presented in **Fig. 1**. To fabricate a stable ASC operating in a wide potential window, it is necessary to balance the charges (Q) that are stored at both positive and negative electrodes. The stored charge (Q) is proportional to the specific capacitance (C), the potential window (V), and the mass (m) of the electrode (*i.e.*, $Q = C \cdot V \cdot m$) [25, 26]. For the charge-discharge measurements, it is ideal that a two-electrode ASC cell is employed by using positive and negative electrodes with similar charge capacity. Considering this point, the optimized mass ratio of NPN and NPC can be calculated to be 0.7 mg and 1 mg, respectively, in the present ASC.

The performance of the assembled NPN//NPC ASC cell with the optimal mass ratio was measured at different potential windows in a 6 M KOH aqueous electrolyte at $40 \text{ mV} \cdot \text{s}^{-1}$, and the obtained CV curves are shown in **Fig. 4b**. The CV curves are very rectangular and symmetric in shape, even when the potential is extended to 1.6 V, indicating ideal capacitive behavior with good reversibility. This also implies that this ASC cell can be operated in a wide and stable operating potential window that is extended up to 1.6 V in an aqueous medium. Thus, the wide potential window of 1.6 V is chosen to further investigate the electrochemical performance.

Galvanostatic charge/discharge curves of our ASC cells were recorded with various current densities. These typical triangular-shape discharge curves (**Fig. 4c, 4f** inset) exhibit good symmetry in shape and fairly linear discharge slopes at different current densities, again demonstrating the ideal capacitive characteristics for an ASC cell. The specific capacitance of the NPN//NPC ASC cell was calculated by the following equation.

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

where I is the discharge current at a discharge time Δt (s), ΔV is the potential window, and m is the mass of the electrode. The specific capacitance (C) based on the discharge curve is calculated to be $71 \text{ F} \cdot \text{g}^{-1}$ at $1 \text{ A} \cdot \text{g}^{-1}$, and even at high specific current ($20 \text{ A} \cdot \text{g}^{-1}$), $38 \text{ F} \cdot \text{g}^{-1}$ is retained. In addition, the initial voltage loss (*i.e.*, IR drop) observed on the discharge curves is small, even at high current densities, indicating the fast I - V response and low internal resistance characteristic of supercapacitors, similar to previous reports [11]. The capacitance values calculated are 71, 70, 68, 63, 59, 54, 50, 47, 41, and $37 \text{ F} \cdot \text{g}^{-1}$ at different current densities of 1, 2, 3, 4, 5, 6, 8, 10, 15, and $20 \text{ A} \cdot \text{g}^{-1}$, respectively. (**Fig. 4d** and **Table 1**).

The Ragone plot is a performance indicator for energy storage devices (specific power against specific energy) and is commonly used to evaluate the electrochemical properties of a supercapacitor cell (**Fig. 4e**). The specific energy (SE , $\text{W} \cdot \text{h} \cdot \text{kg}^{-1}$) and specific power (SP , $\text{kW} \cdot \text{kg}^{-1}$) were calculated from the discharge curves at different current densities by the following equations, respectively.

$$SE = \frac{\frac{1}{2}CV^2}{3.6} \quad (3)$$

$$SP = \frac{3600 \times SE}{t} \quad (4)$$

where ‘ C ’ is the specific capacitance obtained from the above Equation (2), ‘ V ’ is the width of the potential window, and ‘ t ’ is the discharge time, respectively. Our ASC cell shows the best performance with **specific energy** of $26 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$ at a **specific power** of $809 \text{ W}\cdot\text{kg}^{-1}$ (at $1 \text{ A}\cdot\text{g}^{-1}$), and still a high retention of $14 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$ at an ultra-high **specific power** of $16100 \text{ W}\cdot\text{kg}^{-1}$ (at $20 \text{ A}\cdot\text{g}^{-1}$). Thus, even at very high **specific current**, our device shows high specific power without much loss in specific energy. **The specific energy obtained from this ASC is much higher than the symmetric supercapacitor based on NPC ($10.86 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) reported previously [27].** The maximum **specific energy** obtained in the present study surpasses the previously reported symmetric supercapacitors, such as NPC//NPC ($19.6 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [28], RuO_2 // RuO_2 ($18.77 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [29], mesoporous carbon sheet-like framework (MCSF)//MCSF ($9.6 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [30], NiO-AC//NiO-AC (polymer-gel electrolyte, $26 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$) [31], $\text{Co}(\text{OH})_2$ -Ni foam (NF)// $\text{Co}(\text{OH})_2$ -NF ($11.95 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [32], and other carbon-based symmetric supercapacitors ($< 10 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [33]. Even when compared to the previously reported ASCs, the energy densities in our ASC cell are significantly higher than those of NiO//porous carbon ($\sim 13 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [34] and RuO_2 - TiO_2 nanocomposite//AC ($12.5 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [35], and are comparable to those of MnO_2 //porous carbon ($15.3 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [36] and NiCo_2O_4 //AC ($17.72 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [37]. Thus, our CP-derived nanoporous materials serve as very promising electrodes for ASC application. **The main problem in achieving superior energy density performance is the low surface area ($78 \text{ m}^2\cdot\text{g}^{-1}$) of the pseudocapacitive NiO material used in this study. Although the performance demonstrated by this ASC is comparable to previous reports, it should be considered to develop new pseudocapacitive materials with high surface area. Such pseudocapacitive materials will provide more reaction sites, which eventually leads in achieving much higher energy density for ASC. On the other side, nanoporous carbons with**

the high surface area will provide superior stability to the device by fast charge-discharge through appropriate pore structure.

To further demonstrate the advantages of our ASC cell, long-term galvanostatic charge-discharge measurements were carried out, as shown in **Fig. 4f**. More interestingly, these electrodes exhibit highly stable capacitance over long-term charge-discharge measurements. Even after 5000 cycles, the capacitance almost recovers the initial value, with negligible loss of 2 %. These results highlight the merits of the NPN//NPC ASC cell, such as high energy/power delivery and good cycling performance, which points to a new era for researchers to explore new high-performance electrochemical energy storage devices based on CP-derived nanoporous materials.

4. Conclusions

We have developed an efficient approach for the development of nanoporous materials from CPs as starting precursors. This bottom-up approach to the design of nanoporous materials is a facile, low-cost, and safe-solution method. Our NPN//NPC ASC cell exhibits high energy/power delivery and long term cycling stability, which gives researchers a new opportunity to explore high-performance electrochemical energy storage devices based on ‘CP-derived nanoporous materials’. We anticipate that the low-cost and convenient method reported in this work could be extended to the fabrication of other metal oxides that may hold promise for the construction of advanced electrodes for energy storage and conversion. Furthermore, this simple method developed in this work can be extended to larger devices by scaling up electrode surface area and other throughput techniques that are suitable for mass production.

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Fig. 1

Fig. 1 Schematic illustration of ASC based on CPs. NPN derived from cyano-bridged CPs is used as the positive electrode, whereas NPC derived from ZIF-8 is used as the negative electrode.

Fig. 2

Fig. 2 Wide-angle XRD pattern for a-1) NPC particles and a-2) NPN nanoflakes, (b) SEM and TEM images of NPC particles, and (c) SEM and TEM images of NPN nanoflakes.

Fig. 3

Fig. 3 Three-electrode electrochemical measurements of NPN and NPC in 6 M KOH aqueous solution: (a) CV curves at different scan rates for NPN, (b) specific capacitance of NPN as a function of the scan rate, (c) CV curves at different scan rates for NPC, and (d) specific capacitance of NPC as a function of the scan rate.

Fig. 4

Fig. 4. CV curves of NPN//NPC asymmetric supercapacitor, where NPN is used as the positive electrode and NPC is used as the negative electrode: (a) Comparative three-electrode CV curves for NPN and NPC, showing their potential limits, (b) CV curves of asymmetric supercapacitor measured with different potential windows (at 40 mV·s⁻¹), (c) galvanostatic charge-discharge curves at different specific currents, (d) variation of specific capacitance with specific current, (e) Ragone plot of ASC based on the NPN//NPC cell (The blue disks are for the present ASC), and (f) stability study for NPN//NPC ASC, with the inset showing the cell potential vs. time for individual cycles.

Table 1. Various parameters of the ASC: discharge time, specific capacitance, specific energy, and specific power at different **specific current** from charge/discharge measurements.

Specific current (A·g⁻¹)	Discharge time (s)	Specific capacitance (F·g⁻¹)	Specific energy (W·h·Kg⁻¹)	Specific power (W·Kg⁻¹)
1	113.9	71.18	25.60	809
2	56.0	70.00	25.00	1609
3	36.7	68.81	24.46	2399
4	25.3	63.70	22.64	3221
5	18.9	59.50	21.15	4018
6	14.6	54.75	19.46	4798
8	10.1	50.87	18.08	6448
10	7.6	47.85	17.01	8066
15	4.4	41.55	14.77	12804
20	3.0	37.77	13.42	16104