Ethanol-based synthesis of hierarchically porous carbon using nanocrystalline beta zeolite template for high-rate electrical double layer capacitor

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ABSTRACT

A porous carbon with a mesopore–micropore hierarchy has been synthesized using ethanol as a carbon source within a beta zeolite template, which possesses mesopores and micropores in a hierarchical manner. Various compounds have been evaluated as the carbon source in the carbon synthesis. The result indicates that ethanol vapor is suitable for the hierarchical carbon synthesis, as compared with propylene or acetylene gas. The advantage of ethanol is attributed to the formation of water from the ethanol decomposition during carbonization process. The water seems to assist in delaying the deposition of carbons at the exterior (or the mesopore walls). The resultant carbon after removal of the template is composed of regular micropores of 1-nm diameter and irregular mesopores of 10–30 nm arranged in a hierarchical manner. The hierarchical carbon exhibits a very high electrical double-layer capacitance both at low and high discharge current densities in galvanostatic measurements, as compared to solely microporous or solely mesoporous carbons. The high performance is attributed to facile transport of electrolytes in the hierarchically porous structure.

1. Introduction

The electrical double layer capacitor (EDLC) is a type of electrochemical supercapacitor, which stores electrical energy by the adsorption of ions on the electrode surface according to the electric potential applied to the electrode [1]. Since the energy storage process can rapidly be reversed, the EDLC exhibits superior power density (~10 kW kg−1) over conventional batteries. The EDLC also exhibits an excellent rate capability and a long cycle life (over 106 cycles). These advantages make the EDLC suitable for use as a next-generation energy storage device requiring high power, such as an auxiliary power supply for electrical vehicles, uninterruptible power supplies for computers, and load-leveling of electrical power [2,3]. The EDLC electrodes can be made of porous carbons, transition-metal oxides or conducting polymers [3]. Among them, porous carbons are considered the most suitable materials. Many porous carbons can be prepared with high electrical conductivity, surface area and stability at low cost [4]. Furthermore, in recent years, some porous carbons have been synthesized with a tailored pore structure. These carbons are suitable for investigating pore structure effects on the performance of the EDLC [5–8]. Application of templated nanocarbons, including zeolite-templated carbons, for electrochemical capacitors has been...
summarized in a recent review paper [9]. The paper shows that the EDLC performance depends markedly on the chemical properties of the surface, the surface area, the pore size and the pore connectivity of the porous carbons. Pore structure is critical to the electric current density because the ion accommodation capacity and diffusion rate are affected by porosity. In a low discharge current density, microporous (diameter < 2 nm) carbons have a much higher capacitance than mesoporous (2 < diameter < 50 nm) carbons. This is due to the higher specific surface areas that can accommodate relatively larger amounts of ions [5]. On the other hand, at high current conditions, mesoporous carbons can give better performance than the microporous carbons due to facile diffusion of the electrolyte ions (i.e., fast diffusion of electrolytes through large pores) [6]. However, neither the microporous nor the mesoporous carbons can achieve high energy density and high power density simultaneously.

In recent years, it was reported that carbons equipped with mesopes and micropores in a hierarchical manner could have the advantage in the EDLC, due to a synergistic combination of fast mass transport phenomena in the mesoporous structure and a high ion-accessible surface area in the microporous structure [10–14]. Such hierarchically porous carbons were prepared by various methods. For example, mesoporous carbons were activated with KOH or CO2 for the generation of micropores in the mesopore walls [10–12,15,16]. In other studies, phenol–formaldehyde resins were assembled into a mesostructured form. The polymeric resin was converted to a hierarchically porous carbon under carefully controlled carbonization conditions [13]. In another approach, silicon carbides or silicon carbonitrides were synthesized in a mesoporous form. The mesoporous materials were then treated with Cl2 gas. The reaction of Si with Cl2 led to the generation of micropores in the mesopore walls [14,17]. However, in this method, the original mesopes often collapsed before a sufficiently high content of micropores was generated by the activation process. Moreover, the micropore–mesopore connectivity was not fully guaranteed.

In recent years, nanoporous carbon synthesis methods using sacrificial templates have been developed [18–22]. Various kinds of organic compound, such as ethylene, propylene, sucrose and furfuryl alcohol, can be used as the carbon sources [18–33]. These organic compounds can easily be converted to a self-supporting rigid carbon framework via pyrolysis if the template is composed of a three-dimensional (3-D) nanoporous network. The template walls can be removed by hydrofluoric acid or a hot NaOH solution after the formation of the carbon framework. The carbon, freed from the template in this manner, can retain by itself a nanoporous structure corresponding to a faithful replica of the template pore wall. This template synthesis method was reported to be suitable for various kinds of mesoporous carbons with well-defined pore diameters and connectivity [21–26]. Zeolite was also used as a template for the synthesis of microporous carbons [18–20,27–33]. However, as the template pore diameters decreased from the mesoporous to the microporous regions, the narrow pores made it progressively more difficult to generate rigid carbon frameworks [30]. So far, no zeolites with pore mouths equal to or less than 10-membered oxygen rings (<0.6 nm in diameter) were known to give a faithful carbon replica [20]. Successful carbon syntheses using 12-membered ring zeolites (e.g., beta, Y and EMC-2) were reported in the literature [20,27–33]. However, a significant fraction of the ordered microporous structure of zeolites was often lost during the replication process. This was because pore apertures in most zeolites were not sufficiently large or barely large enough for the formation of rigid carbon frameworks [30]. Moreover, it was a serious problem how to minimize the carbon deposition at external surfaces of the zeolite crystals.

In principle, the templating method should be applicable for the synthesis of hierarchically meso-/microporous carbons if templates with a suitable pore hierarchy are available, and also if the carbon can be selectively deposited in micropores (Fig. 1a). Luckily, such hierarchically meso-/microporous zeolites became available recently via various synthesis routes. For example, mesopores can be generated through an acid/base treatment of a bulk crystalline zeolite [34,35]. Nanoparticles can be used as a mesopore generator during a hydrothermal synthesis of zeolite [36,37]. Multi-ammonium compounds can be used as structure-directing agents for a nanocrystalline zeolite network [38,39]. Organosilane surfactants or polymers can be added to a zeolite synthesis composition [40,41]. It is also possible to synthesize the hierarchically porous zeolites directly by using surfactants functionalized with zeolite structure-directing groups [42,43]. However, the selective deposition of carbons in micropores of such hierarchical zeolites was not yet easy. The mesopore walls are normally the preferred carbon deposition site to the inside of micropores. The preferential filling of carbon in mesopores can block the accessibility of the carbon precursor into micropores, preventing the generation of rigid carbon frameworks inside the micropores. This problem often leads to only a partially successful synthesis result (Fig. 1b). For example, Yu et al. reported a synthesis of hierarchically porous carbon using alkaline-treated hierarchical beta zeolite as a template [44]. The resultant carbon after the removal of the zeolite template lost much of the original structural order corresponding to the zeolite. The carbon possessed a low micropore volume and Brunauer–Emmett–Teller (BET) surface area.

For the selective deposition of carbons in the micropores of the hierarchically meso-/microporous zeolites, the carbon deposition process should meet the following requirements: (1) an organic precursor should be sufficiently small for easy access to the zeolite micropores, (2) moderately hydrophilic organic precursors are desirable for high affinity to the hydrophilic zeolite frameworks, (3) carbonization of the organic precursor in mesopores (or the external surface of the zeolite) should be delayed until the precursor is diffused into the micropores. Organic compounds reported so far as carbon precursors in zeolite templates were propylene, acetylene, furfuryl alcohol and acetonitrile [20,27–34,44]. In the present work, we tested ethanol in addition to these organic compounds to synthesize carbon using hierarchically porous beta zeolite. We show that ethanol is particularly suitable as a carbon source for using the hierarchically meso-/microporous beta zeolites. Characterization by X-ray diffraction (XRD), Ar adsorption analysis and transmission electron microscopy (TEM) indicates that the carbon from ethanol can possess a high volume of ordered microporous structures and 3-D
connected open mesoporosity. Here, we also report on the charge-discharge property of the hierarchically meso-/microporous carbons in EDLC application in comparison with solely microporous or mesoporous carbon materials.

2. Experimental

2.1. Preparation of zeolite and mesoporous aluminosilicate templates

Hierarchically meso-/microporous beta zeolite (denoted as HR-ZT) was synthesized, following the procedure of Choi et al. [38]. Cyclic diammonium (CD) was used as a structure-directing agent, while water glass (29 wt.% SiO$_2$, Si/Na = 1.75) and Al$_2$(SO$_4$)$_3$·18H$_2$O were used as a silica and alumina source, respectively. In a typical synthesis, a synthesis gel with the composition $30\text{Na}_2\text{O} : 2.5\text{Al}_2\text{O}_3 : 100\text{SiO}_2 : 15\text{CD} : 6000\text{H}_2\text{O}$ was crystallized at 443 K for 3 d. After filtration and thorough washing with distilled water, the zeolites were calcined at 823 K for 2 h in air flow. The Si/Al of 16 was obtained by inductively coupled plasma atomic emission spectroscopy.

Conventional beta zeolite in H$^+$ form (denoted as ZT, Si/Al = 12.5) was purchased from ZEOCHEM. The zeolite samples were ion-exchanged with sodium ions and calcined at 673 K subsequently. KIT-6, an ordered mesoporous silicate with an $Ia_3d$ structure, was synthesized using Pluronic P123 and butanol as a mesoporogen [26]. Calcined KIT-6 was aluminate (Si/Al = 20) by the impregnation of ethanolic AlCl$_3$ and subsequent air calcination at 823 K.

2.2. Templated synthesis of carbon materials

In a typical carbon deposition process using ethanol as an organic precursor, 1 g templates were placed in a vertical quartz reactor equipped with a fritted disk (30 mm in diameter) and the reactor temperature was then raised to 1023 K under dry N$_2$ flow and kept. Then, N$_2$ flow was switched to an ethanol bubbler to saturate the gas with ethanol vapor at 298 K. An ethanol/N$_2$ gas mixture (7.6% ethanol in N$_2$) was pumped into the templates at a total flow rate of 120 ml min$^{-1}$. In the typical synthesis of carbon replica of HR-ZT and ZT, the gas flow was continued for 5 h. The amount of carbon deposited was 300 mg g$^{-1}$ zeolite in both HR-ZT and ZT. 'Over-deposited' replication of HR-ZT was prepared by elongated carbon deposition for 8 h (carbon deposition: 410 mg g$^{-1}$ zeolite). Ordered mesoporous carbon was synthesized by pyrolyzing ethanol (60 ml min$^{-1}$ flow) at 1073 K for 15 h (carbon deposition: 1200 mg g$^{-1}$ KIT-6). After the deposition of ethanol, the gas flow was switched to dry N$_2$ and the temperature was raised to 1173 K. After 1 h, the reactor was cooled to room temperature. Template-free carbon replicas could be generated by the repeated treatment of carbon/template composites in HF/HCl solution, or by digesting the zeolite template in a hot NaOH solution. Hereafter, the carbon replica of HR-ZT, ZT and KIT-6 will be denoted as HR-ZTC, ZTC and MC, respectively. For comparative study, propylene and acetylene were also carbonized in HR-ZT template at 973 and 873 K, respectively, by pumping in the carbon precursor/N$_2$ gas mixture (4% carbon precursor in N$_2$, total flow 120 ml min$^{-1}$). After carbon deposition, the subsequent annealing and template removal procedure is same as the method above mentioned.

For investigating the effect of water on carbonization, ethylene with and without the water vapor were carbonized in HR-ZT template at 1023 K by pumping in the ethylene/N$_2$ gas mixture (7.9% ethylene in N$_2$, total flow 120 ml min$^{-1}$). The water vapor was saturated at 313 K. The carbonization with and without the water vapor was carried out for 5 and 3 h, respectively (carbon deposition amount in both cases: 300 mg g$^{-1}$ zeolite).

Fig. 1 – (a) A scheme for successful synthesis of hierarchical carbons through selective carbon deposition on the micropores of hierarchical beta zeolite. (b) Unsuccessful synthesis of hierarchical carbons due to non-selective carbon deposition in zeolite mesopores.
2.3. Characterization

The contents of elemental analysis were determined by an elemental analyzer (FLASH 2000 series, Thermo Scientific). Powder X-ray diffractograms were recorded on Rigaku Multiplex instrument using Cu Kα radiation (30 kV, 40 mA). Argon adsorption–desorption isotherms were measured at liquid argon temperature (87 K) with Micromeritics ASAP 2020 after vacuum sample degassing for 3 h at 573 K. BET surface areas were determined using the data points in a relative pressure range of 0.05–0.2 and the external surface areas were determined by a t-pot analysis at a thickness range from 3.5 to 7.5 Å. Pore size distribution and pore volume were determined using nonlocal density functional theory (DFT) method, assuming a slit-shaped geometry. The micropore and mesopore volumes were determined from the DFT cumulative volume in the pore diameter ranges of d < 2 and 2 < d < 50 nm, respectively. Total pore volumes were estimated at P/P0 = 0.95. TEM micrographs were collected by Tecnai G2 F30 (FEI) at 300 kV acceleration voltages after mounting the samples on a carbon grid (300 mesh) using ethanol dispersion. Thermogravimetric analysis (TGA) was carried out by increasing the temperature up to 1073 K (ramp: 20 K min−1) under flowing air (60 ml min−1).

2.4. Electrochemical measurements

Specific capacitances were measured in a 2-electrode cell, operated in a galvanostatic charge/discharge mode (WBCS3000 battery cycler, WonaTech). Two film electrodes (area = 0.78 cm2) were separated by a porous polypropylene sheet (Celgard), and sandwiched between current collectors. 2 M sulfuric acid aqueous solution was used as an aqueous electrolyte, and organic electrolyte, capacitances were measured by charging to charged at a target current density (1–50 mA cm−2) and the external surface areas were determined by a t-pot analysis at a thickness range from 3.5 to 7.5 Å. Pore size distribution and pore volume were determined using nonlocal density functional theory (DFT) method, assuming a slit-shaped geometry. The micropore and mesopore volumes were determined from the DFT cumulative volume in the pore diameter ranges of d < 2 and 2 < d < 50 nm, respectively. Total pore volumes were estimated at P/P0 = 0.95. TEM micrographs were collected by Tecnai G2 F30 (FEI) at 300 kV acceleration voltages after mounting the samples on a carbon grid (300 mesh) using ethanol dispersion. Thermogravimetric analysis (TGA) was carried out by increasing the temperature up to 1073 K (ramp: 20 K min−1) under flowing air (60 ml min−1).

3. Results and discussion

3.1. Effect of carbon precursors

The hierarchical beta zeolite (HR-ZT) used as carbon template in the present was composed of tiny nanocrystals about 20 nm in diameter. As depicted in Fig. 1 (see also the TEM image in Fig. 5a), the zeolite nanocrystals were aggregated in a manner that retains intercrystalline mesopores of around 10–40 nm diameters. The mesopores were interconnected in a 3-D disordered way. The nanocrystalline zeolite synthesis, detailed structure analysis by TEM, and pore size determination by nitrogen gas adsorption were described elsewhere [38]. As briefed in the Section 2, the zeolite was synthesized using a laboratory-made cyclic diammonium compound as the zeolite structure-directing agent. This synthesis method is very cost-effective since the ammonium can be reused by ethanol extraction after the zeolite synthesis. Cheap water glass can be used as a silica source to the zeolite. Moreover, the silica source can be recovered as a sodium silicate solution if NaOH is used to release the carbon product.

In Fig. 2, the XRD pattern of the beta zeolite is compared with XRD patterns of the three carbon products which were obtained using acetylene, propylene and ethanol. The XRD pattern of the template HR-ZT sample was identical to that of a typical beta zeolite, except that the diffraction peaks coming from nanocrystals were broader than those for conventional bulk beta zeolites (Figure S1) [38]. As shown in Fig. 2, the template-free carbon product (HR-ZTC) from acetylene did not exhibit well-resolved XRD peaks. This result indicates a total loss of the micro-structural order which were originally present in the zeolite template. In contrast, the carbon products from propylene and ethanol showed a resolved peak at 2θ = 7°. The peak position was corresponding to the (100) or (101) diffraction of the beta zeolite structure. As judged by this XRD peak [20], ethanol gave the most faithful replication result among the three used carbon sources. Note that the ethanol-derived HR-ZTC carbon also had a second-order peak at 2θ = 15°, which corresponded to the (201) or (202) diffraction of the beta zeolite structure. In the case of the ethanol-derived carbon, the XRD pattern could even exhibit some high order diffraction peaks in the 2θ region between 21° and 27°. The presence of these peaks indicates that there remained quite a long-range structural order in this carbon replica.

To understand the difference between ethanol and propylene in the carbonization process, the microporosity of the
carbon/zeolite composite (i.e., before releasing the zeolite) was analyzed as a function of the carbon deposition amount (Fig. 3). The dashed line in Fig. 3a and b indicates a theoretical microporosity change in the composite samples during the carbon deposition. The theoretical values were calculated under the assumption that all carbons could be deposited inside zeolite micropores at a density of 1.5 g cm$^{-3}$ [29]. In the case of ethanol (Fig. 3a), the experimental plot between the remaining microporosity and carbon deposit quantity showed remarkable similarity with the theoretical values (dashed line) until less than 200 mg g$^{-1}$ deposition. The result indicates that the carbon was selectively deposited inside the zeolite micropores in this regime, rather than on the external surfaces. Above 200 mg g$^{-1}$ carbon deposition, the experimental microporosity decreased more slowly than the theoretical one. This seemed to be due to the increasing diffusion hindrance for ethanol as the zeolite micropores became almost completely filled with carbon.

Compared to ethanol, the propylene carbonization (Fig. 3b) resulted in an abrupt decrease in microporosity even in the early carbonization period, exhibiting a sizable difference from the theoretical values. The large difference means that a large number of micropores became empty but still undetected when the micropore volume was measured by Ar adsorption. Compared to ethane, the propylene carbonization (Fig. 3b) resulted in an abrupt decrease in microporosity even in the early carbonization period, exhibiting a sizable difference from the theoretical values. The large difference means that a large number of micropores became empty but still undetected when the micropore volume was measured by Ar adsorption. This result could be attributed to the preferred carbon deposition at the zeolite external surfaces (i.e., the mesopore wall surfaces), blocking the access of propylene before the carbon formation inside micropores was completed. Therefore, the replication of the zeolite microporous structure became partially successful. The propylene-derived carbon after the template removal exhibited much lower microporosity (0.27 cm$^3$ g$^{-1}$) than the ethanol-derived carbon (0.62 cm$^3$ g$^{-1}$) (Figure S2). Quite often in propylene-derived carbons, the zeolite template became encapsulated by the external carbon deposition. It was difficult to remove the encapsulated template completely.

It should be noted that such a dramatic difference between the two carbon precursors was only observed for the HR-ZT template composed of small zeolite crystallites (~20 nm), not in a bulk beta zeolite. Both ethanol and propylene could successfully generate highly ordered carbon replicas for conventional beta zeolites (see XRD patterns in Figure S1) with larger crystallites. The results indicate that selective carbon deposition inside nano-sized zeolite crystallites is more difficult and requires the use of the suitable precursor with relevant physicochemical properties. Previously we reported that coke (or carbons) was selectively formed at the external surface of ultra-thin zeolite crystallites during acid catalysis, while internal coke was preferably formed in large zeolite crystals [42]. The difficulty of internal carbon deposition in ultra-small zeolite crystallites could be attributed to the extremely short diffusion path length, and thus the fast diffusion of the carbon intermediate species (e.g., aromatics) out of the zeolite micropores. We suppose that ethanol-derived carbon intermediate species could have stronger interaction with a zeolite micropore surface than propylene-derived ones although the polar interaction could be weakened at high temperature. Accordingly, the ethanol-derived intermediates seemed to grow more easily than the propylene-derived intermediates in the small zeolite crystallites before freely diffusing out.

At the carbonization temperature (1023 K), thermal decomposition of ethanol could occur before ethanol reached the zeolite pores. Hence, the decomposition products, ethylene and the water vapor, could be present during the carbonization process. In this sense, the water vapor generated from ethanol could assist in alleviating carbon formation at the external surface, contributing to the faithful replication of HR-ZT. To clarify the speculation, the selective replication of HR-ZT was carried out using the carbon precursor of ethylene with and without water vapor. Fig. 4 shows the XRD patterns...
obtained from the resultant carbons. The hierarchical carbons synthesized in the presence of the water exhibited well resolved first- and second-order peaks, which were very similar to XRD peaks for the ethanol-derived HR-ZTC (Fig. 2). As shown in Fig. 4, however, the carbon obtained using ethylene without H$_2$O had a poor micro-structural order. The result indicates that the water vapor generated by the decomposition of ethanol could play a decisive role in the selective carbon deposition inside zeolite micropores. A significantly long carbonization time was required in the case of using ethylene with water vapor, as compared to the case without H$_2$O (see Section 2). Thus, the deposition of carbon was retarded by water. This result is comparable to the work of Huang et al. [45] who reported that high-quality carbon nanotubes could be prepared using ethanol. They attributed the result to the effect of water vapor that could act as a mild oxidant in the growth of nanotubes and therefore lead to the formation of clean nanotubes. If this is the case, in the carbonization process involving H$_2$O, some carbon species could be oxidized by water. Such oxidation might delay carbon formation at the external surface of the hierarchical zeolites. More detailed studies using carbon precursors with the water would be required to clarify the role of water in the carbon replication of zeolite frameworks.

To check the ethanol effect for other zeolites, carbons were synthesized using conventional zeolite Y and zeolite EMC-2. The resultant carbons exhibited well resolved XRD patterns (Figure S3). The structural order of the carbons was similar to previous results that were obtained using other organic compounds in these zeolites [27,28]. Such results suggest that it is reasonable to synthesize hierarchically porous carbons using 12-membered ring zeolites if such zeolites as Y or EMC-2 zeolites are available with hierarchical pores.

### 3.2. Structure of ethanol-derived carbons

In addition to the ethanol-derived HR-ZTC carbon described in the previous section, we synthesized a solely microporous carbon (designated by ZTC) and a solely mesoporous carbon (MC) using ethanol as a carbon precursor (see Section 2). The ZTC carbon was synthesized using a conventional beta zeolite (designated by ZT as a sacrificial template). This zeolite consisted of bulk particles about 200 nm in diameter. For synthesizing the MC sample, an aluminated KIT-6 silica [26] with a cubic Ia3d mesoporous structure was used as a template. Fig. 5 shows TEM images taken from the aluminosilicate templates (HR-ZT, ZT and KIT-6) and their resultant carbon replicas (d) HR-ZTC, (e) ZTC and (f) MC.
replicas (HR-ZTC, ZTC and MC). The result shows that ~20 nm zeolite crystallites in HR-ZT were successfully replicated to carbon, while the original mesoporous structures corresponding to intercrystalline voids were well retained by the carbon framework. The zeolite and carbon exhibited remarkable similarities in particle sizes and morphologies, indicating that the process using ethanol successfully resulted in the selective carbon deposition inside zeolite crystallites and thereby faithful replication of the crystal morphology. Furthermore, the lattice fringes (1.2 nm d-spacing) for the HR-ZTC (inset of Fig. 5d) showed that the ordered microporous structure of the zeolite was successfully replicated to carbon. The result was consistent with a well-resolved XRD peak at 2θ = 7°. Similar to the result from the hierarchical zeolite, the template synthesis using bulk zeolite also produced a high-quality carbon sample exhibiting lattice fringes due to ordered microporous structure (ZTC in Fig. 5e). The ZTC carbon particles had the same crystal morphologies and sizes as those of the zeolite template. In the KIT-6 mesoporous template, the resultant carbon showed low-angle XRD peaks corresponding to the Ia3d symmetry, indicating the perfectly faithful replication (Figure S4) [24,26].

The structural properties of the aluminosilicate templates and their resultant carbon replicas were analyzed using Ar adsorption–desorption isotherms (Fig. 6 and Table 1). The HR-ZTC sample showed high microporosity (0.62 cm³ g⁻¹) as well as high mesoporosity (1.48 cm³ g⁻¹). The micropore diameters, determined using a nonlocal DFT method, gave a very sharp distribution around 1.2 nm. This is consistent with the literature value for the carbon replica of beta zeolite [8]. The mesopore size distribution was centered at 20 nm, which is almost the same as that of the HR-ZT template. The result indicates that carbon deposition occurred quite selectively inside zeolite micropores rather than on the external surface of

Fig. 6 – Ar adsorption–desorption isotherms at 87 K and the corresponding DFT pore size distributions: (a and b) the template aluminosilicate materials, (c and d) the resultant carbon replicas. For comparison, the isotherm and the pore size distribution for YP-17 (commercial activated carbon) were also given in (c and d). The isotherms for HR-ZT, ZT, YP-17, HR-ZTC and ZTC were offset by 200, 400, 200, 400 and 600 cm³ g⁻¹, STP, respectively.
crystals (mesopores). In the case of ZTC, the micropore volume (0.95 cm\(^3\) g\(^{-1}\)) was high, but the mesopore volume (0.10 cm\(^3\) g\(^{-1}\)) was small. The micropore size distribution was sharply centered at 1.2 nm in a similar way to the HR-ZTC, but had a shoulder at 1.5 nm. The shoulder was due to the formation of large micropores, which in turn were caused by the carbon incompletely filling the inside of the zeolite micropores [32]. The MC exhibited high mesopore volume (0.59 cm\(^3\) g\(^{-1}\)) with negligible microporosity (0.04 cm\(^3\) g\(^{-1}\)). The material showed a very narrow mesopore size distribution centered at 3.5 nm due to the ordered mesoporous structure.

### 3.3. Electrochemical properties

To estimate the electrochemical properties of the templated carbons in EDLC applications, the specific capacitances of each carbon were measured by the galvanostatic charge/discharge method using a 2-electrode system in organic and also aqueous electrolytes (Figure S5). In addition to the above synthesized carbons, a commercial activated carbon (YP-17) was purchased from Kuraray Chemical, Japan. Its electrochemical properties were measured by the same system we used for the reference carbon material. According to the Ar adsorption–desorption isotherm (Fig. 6c), the YP-17 reference carbon was mainly microporous (micropore volume = 0.55 cm\(^3\) g\(^{-1}\), and mesopore volume = 0.06 cm\(^3\) g\(^{-1}\)) with negligible microporosity (0.04 cm\(^3\) g\(^{-1}\)). The material showed a very narrow mesopore size distribution centered at 3.5 nm due to the ordered mesoporous structure.

In Fig. 7, the specific capacitances of all the investigated carbon samples are given as a function of the discharge current density. In the organic electrolyte system (1 M tetraethylammonium tetrafluoroborate (Et\(_4\)NBF\(_4\))/anhydrous propylene carbonate (PC)), the specific capacitances of the carbon materials at low discharge density (1 mA cm\(^{-2}\)) were generally proportional to the BET surface area of the carbons (Fig. 7a). This seems natural since the amount of charge accumulation should be proportional to the specific surface area of an electrode. Accordingly, the HR-ZTC (BET area: 2220 m\(^2\) g\(^{-1}\)) and ZTC (2750 m\(^2\) g\(^{-1}\)) carbons with the largest surface areas showed highest capacitances of \(\sim 120\) F g\(^{-1}\). In comparison, the YP-17 (67 F g\(^{-1}\) at 1510 m\(^2\) g\(^{-1}\)) and MC (33 F g\(^{-1}\) at 520 m\(^2\) g\(^{-1}\)) carbons had low capacitances. The similar capacitances of HR-ZTC and ZTC, irrespective to the BET areas, can be attributed to a space constriction for charge accommodation inside the pores above the surface area of 1200 m\(^2\) g\(^{-1}\) in the same electrolyte system [46].

As the discharge density increased, the specific capacitance of all carbon materials generally decreased due to the resistance to electrolyte diffusion [1–6]. Such decreases in capacitance depended significantly on the pore size and the connectivity of carbon materials rather than on the surface areas. HR-ZTC, having 3-D interconnected meso- and micropores, showed a remarkably high capacitance even at high discharge conditions, while the ZTC with sole microporosity

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<th>Table 1 – Textural properties of carbons.</th>
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\(a\) BET surface area calculated at \(P/P_0 = 0.1–0.3.\)

\(b\) External surface area determined by t-plot analysis at thickness range from 3.5 to 7.5 Å.

\(c\) The total pore volume evaluated at \(P/P_0 = 0.95.\)

\(d\) Micropore and mesopore volumes determined from the DFT cumulative volume in the pore diameter ranges of \(d < 2\) and \(2 < d < 50\) nm, respectively.

![Fig. 7 – Specific capacitance per unit weight as a function of the discharge current density in (a) organic electrolyte (1 M Et\(_4\)NBF\(_4\)/PC), and (b) aqueous electrolyte (2 M H\(_2\)SO\(_4\)). The specific capacitance measured by 2-electrode system \(C_{\text{spec-2E}}\) was inter-calculated to the 3-electrode system \(C_{\text{spec-3E}}\) by the equation, \(C_{\text{spec-3E}} = 4 \times C_{\text{spec-2E}}\), because many literature values were reported in a 3-electrode system [5].](image-url)
exhibited a very fast decrease in capacitance with an increasing discharge rate. The capacitance of HR-ZTC more stable than ZTC should be attributed to the much smaller size of the microporous carbon domains of HR-ZTC (~20 nm) than ZTC (~200 nm), as confirmed by TEM (Fig. 5) and external surface areas (Table 1). The small carbon domain size of HR-ZTC could minimize the diffusion path length along the micropores and hence facilitate the electrolyte transport to and from the microporous channels. Due to large pore volume of HR-ZTC, however, the volumetric capacitance of HR-ZTC was lower than that of ZTC below a current density of 30 mA cm⁻² (Figure S6). Such low volumetric energy densities were commonly reported for highly mesoporous electrodes with large mesopore volume [9,33].

Another carbon sample (indicated by OD-HR-ZTC) was synthesized using the same HR-ZT template, but ethanol was overfed so that the carbon was excessively deposited on the boundary between the mesopores and micropores. That is, the connectivity between mesopores and micropores in OD-HR-ZTC was deliberately blocked. As shown in Figure S7, the OD-HR-ZTC exhibited an 85 F g⁻¹ capacitance at 1 mA cm⁻², which was smaller than that of the HR-ZTC (120 F g⁻¹). This is attributed to a low BET surface area (1610 m² g⁻¹). More notably, the carbon material showed a remarkably fast decrease in capacitances against increasing electrolyte density as compared to HR-ZTC. This result indicated that the carbon barrier between mesopores and micropores did not block the access to the micropores completely. The ionic access into the micropores seemed possible when the electrode was gradually charged. However, upon rapid discharge, the ionic diffusion seemed to be conspicuously hindered.

Similar to the case of ZTC, the conventional activated carbon, YP-17, also showed a fast decrease in capacitance at a high discharge density due to its mainly microporous structure. The fast capacitance loss (much faster than that of ZTC) can be attributed to irregular microporous structure of the conventional activated carbon. While the zeolite-templated ZTC had an ordered microporous structure with a fully 3-D connectivity, conventional activated carbons such as YP-17 have been known to have disordered pore structures and to contain a significant amount of dead-end pores that are disadvantageous for molecular diffusion [47]. On the other hand, the solely mesoporous carbons MC exhibited a stable capacitance behavior at a high discharge density, which could be attributed to fast diffusion of electrolytes into and from mesopores [6,7]. To summarize, the HR-ZTC carbon with hierarchically meso-/microporosity is most promising for EDLC electrodes. This material can show high capacities both at low and high discharge current densities. In comparison, a solely microporous carbon with a comparable surface area can have a high capacitance at a low current density, but the capacitance at high current density is decreased due to the hindered diffusion of electrolytes. A solely mesoporous carbon can exhibit a stable capacitance behavior even at a high current density, but its absolute capacitance value is relatively small due to the low surface area of its solely mesoporous structure. When an aqueous electrolyte system (2 M H₂SO₄) is used, the discharge trends are similar to those organic electrolytes. However, the effect of the mesopores is less pronounced, which can be attributed to the small size of the aqueous electrolytes [48].

Electrochemical impedance spectroscopy is a powerful tool for investigating capacitance behavior. This tool was used to check the electrochemical behavior of the carbon electrodes in this work. We used the complex impedance spectrum (Nyquist plot) of carbons in the organic electrolyte, to measure the resistances of a 2-electrode system. The spectrum can be divided into Rₑ and Rₑ as shown in Fig. 8a. Here, Rₑ is the combination of ohmic resistance of the electrolyte and separator, inter-particle resistance and contact resistance between the current collector and the electrode surface [1]. The Rₑ value was determined by the Z’-axis intercept in the Z’ vs. Z” plot while the frequency was decreased from 100 kHz to 1 mHz. Here, Z’ and Z” indicate the real and imaginary components of impedance [1]. The Rₑ values determined in this manner were almost the same for all porous carbons synthesized using porous templates. This is because the sample mounting and electrical measurements were performed with the same equipment. The slight variations of Rₑ might have resulted from the different contact areas between

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**Fig. 8** – (a) Complex-plane impedance plots of the cells in organic electrolyte. (b) Ragone plots of the templated carbons and YP-17 in the organic electrolyte.
the current collector and electrode particles [49], or the inter-particle resistance [50], owing to the different morphology of the carbon particles. On the other hand, $R_p$ in Fig. 8a indicates the resistance arising from the interior of porous carbons, such as current leakage (faradaic reaction of heteroatoms) and electrolyte resistance within pores [1]. The $R_p$ value was determined by the diameter of the $Z'$ vs. $Z''$ semicircle shown in Fig. 8a. Because a same carbon precursor was used, all the templated carbons should have a similar carbon surface nature (Table S1), and thus similar current leakages [1,51]. Accordingly, the $R_p$ values for HR-ZTC and MC smaller than for ZTC indicate a lower electrolyte resistance within the pores [52].

The electrochemical properties of all the carbon materials are summarized in the Ragone plot (Fig. 8b). In the Ragone plot, the power density of an electrode is reciprocally proportional to the energy density, where the degree of decreasing power density is affected by the total resistance [1]. HR-ZTC with a hierarchically meso-/microporous structure maintains a high energy density of 10 Wh kg\(^{-1}\) even at a high power density (3 kW kg\(^{-1}\)), while the energy density of ZTC and YP-17 with sole microporosity drops very rapidly with increasing power density due to slow electrolyte diffusion. The MC carbon, with solely mesoporosity, shows a relatively slow decrease in energy density with an increasing power density, but the absolute value is much smaller than HR-ZTC due to the low surface area. The Ragone plots clearly reveal that a hierarchical structure of the electrodes is highly desirable for simultaneously achieving high power and energy densities.

## 4. Conclusions

We synthesized hierarchically meso-/microporous carbons using a hierarchically meso-/microporous beta zeolite. Ethanol was superior as a carbon source to propylene and acetylene, which could be attributed to the effect of product H\(_2\)O to retard the carbon deposition on the mesopore walls. The carbon deposition using ethanol allowed quite selective carbon deposition inside the zeolite micropores and hence enabled the faithful replication of the beta zeolite structure, while the micropore entrances at the surface of the mesopore walls were still open. The hierarchically porous carbons exhibited a high BET surface area (2200 m\(^2\) g\(^{-1}\)), large micropore volume (0.62 cm\(^3\) g\(^{-1}\)) and mesopore volume (1.48 cm\(^3\) g\(^{-1}\)). In an EDLC application, the hierarchical pore structure has the advantage of facile transport of electrolytes to and from the high-surface micropores via mesopores. Such facile electrolyte diffusion leads to high specific capacitance even at high discharge conditions. The volumetric capacitance of HR-ZTC may be further improved if heteroatoms are incorporated to the hierarchically porous carbons [3,9].

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.04.011.

## References


