Abstract
The template carbonization technique enables the production of porous carbons and carbon-based composites with precisely designed, controlled pore structures. The resulting templated carbons are therefore useful to investigate and understand the relation between carbon nanostructure and electrocapacitive properties. In this short review paper, we introduce our works on electrochemical capacitance using zeolite-templated carbons and carbon-coated anodic aluminum oxide.

1. Introduction
An electrochemical capacitor is an electric storage device which can be repeatedly charged and discharged. Compared with secondary batteries, the capacitor has several advantages such as higher power density and longer cycle life, though its energy density is much lower than those of the secondary batteries. There are mainly two strategies in the development of the capacitor electrode materials; focusing on the increase of (i) the power density and (ii) the energy density. In this short review, we introduce our previous works regarding these two strategies, using uniform porous materials prepared by the templated carbonization technique.

2. Electrochemical properties of zeolite-templated carbons
Our group has developed the templated carbonization technique which allows to produce carbon materials having well-tailored nanostructures [1-4]. When a zeolite, a microporous inorganic crystal, is used as a template, an ordered microporous carbon, zeolite-templated carbon (ZTC) can be produced [1, 4-6], according to the scheme shown in Figure 1.

ZTC consists of single-layer graphene nanoribbon (Figure 1), and its graphene framework is fully exposed without any stacking. In addition to both faces of the basal plane of the graphene (theoretical surface area is 2627 m² g⁻¹), the contribution of the edge sites to surface area is significant, and thus ZTC has very high surface area of 3000-4000 m² g⁻¹ [7]. Accordingly, ZTC shows a high electric double-layer capacitance [8-10]. A valuable advantage of ZTC is its excellent rate performance [8-10]. The three-dimensionally arrayed and interconnected carbon framework of the ZTC is responsible for its high energy density and stability.

Figure 1. A synthesis scheme of ZTC together with TEM images of zeolite Y and ZTC. Scale bars in the TEM images are 10 nm. Black, blue, and red spheres in the models correspond to carbon, hydrogen, and oxygen atoms, respectively. Reprinted with permission [4]. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figura 1. Esquema de la preparación de ZTC mostrando las imágenes TEM de la zeolita Y y el ZTC. La barra de escala en las imágenes es 10 nm. En los modelos moleculares, las esferas negras, azules y rojas corresponden a átomos de carbono, hidrógeno y oxígeno, respectivamente.
pores realize a fast ion-transfer despite its small pore size (1.2 nm). Many people believe that mesoporous, macroporous, or hierarchical porous carbons could be good electrode materials for high-power supercapacitors. However, the introduction of such large pores seriously decreases the packing density of the electrode layer, resulting in a low volumetric capacitance. ZTC is able to achieve both a good rate performance and a high volumetric capacitance, the latter of which comes from the fact that ZTC does not possess unnecessary meso- nor macropores. Figure 2 shows the volumetric capacitance versus current density for ZTC and reference activated carbons (MSC30 and A20) [9]. It is found that ZTC shows a high volumetric capacitance and a good rate performance.

Figure 2. Volumetric capacitance versus current density for ZTC and activated carbons (MSC30 and A20). Reprinted with permission [9]. Copyright 2011 American Chemical Society.

We have prepared also a binderless thin-film electrode consisting of ZTC, formed directly on a current collector film [11]. The obtained film electrode exhibits a high area capacitance (10–12 mF cm⁻²), compared with other microcapacitors. In addition, the film electrode is free from inter-particle resistance, and ultrahigh rate capability is achieved: the formation of double-layer capacitance could be confirmed at an ultra-high scan rate of 10000 mV s⁻¹.

ZTC has another interesting feature as a pseudocapacitive material. ZTC has a very large amount of edge sites [6], which is about 10-times larger than conventional activated carbons, and a large number of oxygen functional groups can be easily introduced into the edge sites by electrochemical oxidation [12]. By tuning the oxidation condition, it is possible to introduce electrochemically active quinone groups with a high selectivity [8]. Figure 3 shows cyclic voltammogram of ZTC in 1M H₂SO₄ electrolyte. In an acidic electrolyte, ZTC is significantly oxidized and a large amount of quinone groups are introduced into the edge sites, without serious damage to its nanographene framework [8]. Thus, ZTC exhibits very high capacitance (ca. 500 F g⁻¹).

Despite its high capacitance and excellent rate capability, ZTC unfortunately suffers from intense hydrogen evolution at a negative potential range in an acidic electrolyte. To take advantage of the ability of ZTC, we constructed an asymmetric capacitor in which ZTC and an ultrastable KOH-activated carbon are used as a positive electrode and a negative one, respectively [13]. The latter was prepared by KOH activation of Spanish anthracite [14]. The asymmetric capacitor can be operated with the working voltage of 1.4 V, and exhibits an energy density that is comparable to those of conventional capacitors utilizing organic electrolytes, thanks to the large pseudocapacitance of ZTC. Thus, ZTC is advantageous to construct asymmetric capacitors, as a high-capacity positive electrode in acidic electrolytes.

3. Investigation of the effect of N- and B-doping by using a model porous material

It is well known that doping of heteroatoms, such as B, N, and P, into porous carbons is an effective way to enhance the electrochemical capacitance.
So far, many research groups have indeed reported a positive effect of such heteroatom doping in both aqueous and organic electrolyte solutions [4]. However, heteroatom doping usually alters the pore structure of a carbon matrix, and this makes it difficult to assess the sole effect of heteroatom doping, because the pore structure is also one of the crucial factors affecting electrochemical capacitance. To acquire better understanding about the effect of the heteroatom doping, we have prepared model porous materials by uniform carbon coating on anodic aluminum oxide (AAO), as shown in Figure 4 [15]. Carbon-coated AAO thus prepared has uniform-sized cylindrical mesopores with a diameter of 16 nm, and is free from any other pores, such as ultramicropores and micropores. In addition, it is possible to introduce B or N into the carbon layer. Thus, a series of mesopores completely coated with pure-, N-doped, or B-doped carbon layer were prepared, and their electrochemical properties were systematically examined both in aqueous (Figure 5) and organic electrolyte solutions [15]. It was revealed that the improvement in electrocapacitive properties due to the heteroatom doping is caused by its pseudocapacitance, not by other factors, such as the increase in wettability, conductivity, and space-charge-layer capacitance, in a large mesopores.

**References**


