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High performance carbon supercapacitor electrodes derived from a triazine-based covalent organic polymer with regular porosity

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ABSTRACT

A series of highly microporous carbon materials was produced by carbonization of a triazine-based covalent organic polymer (TCOP) followed by carbonization and CO_2 physical activation. The N-containing porous COP was prepared from easily available economic monomer precursors via a simple Friedel-Crafts reaction, which produced a predominantly microporous structure with a high surface area. Carbonization at 600–900 °C produced predominantly microporous carbons with a narrow pore size distribution in the range of 0.5–1.5 nm. Upon further activation using CO_2, more micropores were formed, accompanied by an increase in the surface area (to 2003 $m^2 g^{-1}$) and the nitrogen level in the carbon structure was maintained at ca. 2 wt%. The electrochemical properties of the samples were measured by employing a three-electrode system with 6 M KOH electrolyte. Among the prepared carbon samples, the electrode fabricated using the carbon activated at 900 °C (AC-900) had a specific capacitance of 278 F g^{-1} at a current density of 1 A g^{-1}, which is significantly higher than that of a commercial activated carbon (130 F g^{-1}) and ranks among the highest reported so far. This improved performance was attributed to the highly microporous structure of the nitrogen-doped carbon with a narrow pore size distribution.

1. Introduction

Supercapacitors (also referred to electrical double layer capacitors; EDLCs) have attracted considerable interest for energy storage because of their product safety, excellent reversibility, discharge-charge capability, high power density, and cycle life stability [1–3]. Owing to these unique advantages, supercapacitors have been considered for many applications, such as digital devices, pulsing techniques, electrical vehicles, and most importantly, for energy storage devices [4,5]. Porous carbon materials have mainly been used as supercapacitor electrodes due to their high electrical conductivity, ease of processability, controllable heteroatom doping, excellent electrochemical stability, and high surface area/pore volume [6,7]. Despite these desirable features, the low energy density of carbon materials is a still major problem that must be overcome to achieve efficient carbon-based supercapacitor electrodes [8,9] (see Scheme 1).

Generally, the electrochemical reaction in supercapacitors takes place between the electrode surface and the electrolyte interface according to the following equation: $E = 1/2\ CV^2$ [10]. The energy density (E) of a supercapacitor is dependent on its nominal open voltage window (V) and capacitance (C). Various approaches have been developed to enhance the supercapacitor energy density based on the above relationship [10,11]. Typically, V is determined by the stability of the electrolyte in the system, and ionic liquid electrolytes have recently been shown to exhibit a high open voltage window (>3 V) because of their chemical stability, non-volatility, and high ionic conductivity [12]. The capacitance, on the other hand, is primarily governed by the carbon/electrolyte interface parameters [13]. Therefore, the rational design of new carbon materials and optimizing their surface structures/functionality are major research issues [13], which may be addressed by the introduction of heteroatoms into the carbon skeleton, improving the pore size distribution and increasing the effective surface area [13,14].

Improvement of the capacitance by increasing the carbon surface area was actively investigated preferentially, but was

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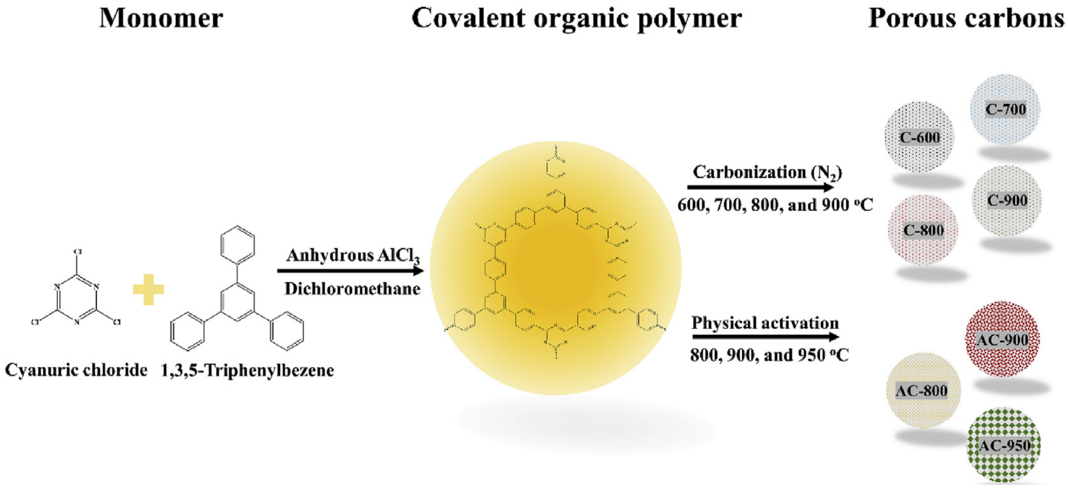

Scheme 1. Schematic illustration of the fabrication of porous carbons derived from a triazine-based covalent organic polymer.

hampered by certain limitations. It was reported that the specific capacitance of activated carbon with a high surface area ($1500\ m^2\ g^{-1}$) is limited to less than $150\ F\ g^{-1}$ due to the isolated and irregular pore tunnels that are inaccessible to the electrolyte ions [15,16]. However, recent studies on the relationship between the carbon structure and the capacitance indicated that the specific capacitance of a supercapacitor exhibits a sharp increase in carbon materials with a pore size of <2 nm (micropore region), whereas mesopores and macropores (>2 nm) provide only a minor contribution [17,18]. Moreover, functionalization of various carbon materials such as carbon nanofibers (CNFs), graphene, carbon nanotubes (CNTs), and carbon shells with nitrogen moieties has proven to be a promising approach for achieving improved surface wettability, electrical conductivity, and electrochemical properties, leading to enhanced capacitance [19–24]. Therefore, current research efforts have focused on the synthesis of highly microporous carbons having a narrow micropore size distribution and nitrogen functionalization in order to obtain carbon electrodes with high capacitance, good rate performance, and long cycle life [25,26].

Nitrogen-functionalized porous carbons have been produced through complicated procedures [27–30]; however, recent research employs simpler methods using nitrogen-containing polymers as the carbon precursor. Liu et al. fabricated a nitrogen-rich porous carbon shell, derived from a porous organic framework (POF), which featured a microporous hollow structure and a nitrogen-doped structure, resulting in good supercapacitor performance ($210\ F\ g^{-1}$ at $1\ A\ g^{-1}$) [31]. Han et al. synthesized porous nitrogen-doped carbon microspheres from POF, where the structure facilitated the rapid diffusion of electrolyte ions, leading to excellent capacitive performance ($240\ F\ g^{-1}$ at $1\ A\ g^{-1}$) [32]. Zhao et al. also fabricated nitrogen-functionalized microporous carbon nanoparticles for high-performance supercapacitor electrodes ($254\ F\ g^{-1}$ at $1\ A\ g^{-1}$) having a large surface area, unique porosity, and distinctive morphology, as well as nitrogen functional groups [33]. Zhu et al. investigated high-nitrogen carbon microspheres (NCMs) with a microporous structure, which showed good electrochemical properties ($228\ F\ g^{-1}$ at $1\ A\ g^{-1}$) [34]. Despite the promising results, many carbonized and activated carbons derived from various precursors exhibit a wide and irregular pore size distribution (micro/meso), which decreases the ion accessibility at the carbon surface, thereby hampering the formation of the electrical double-layer [35].

In this study, an alternative triazine-based covalent organic polymer (TCOP) with high specific surface area, pore volume, and narrow pore size distribution is used as a carbon precursor. After carbonization and physical activation process, this carbon materials showed the high surface area and nitrogen species. Also, the activated carbon at 900 °C (AC-900) featured the superior high surface area and regular microporous structure, resulting in excellent capacitive behavior owing to good ion accessibility. It is shown that the carbon sample optimized by controlling the carbonization/activation parameters is highly microporous with sufficient incorporated nitrogen species, leading to excellent electrochemical performance.

2. Experimental

2.1. Materials

1,3,5-Triphenylbenzene, cyanuric chloride, anhydrous aluminum chloride, dichloromethane (DCM), and polytetrafluoroethylene (PTFE, 60 wt% dispersed in water) were purchased from Sigma Aldrich (USA). Carbon black (Vulcan XC 72) was acquired from Cabot (USA). Ethyl alcohol and potassium hydroxide (KOH) were supplied by Duksan Pure Chemical (South Korea). The chemicals were used as received without further purification.

2.2. Synthesis of triazine-based covalent organic polymer (TCOP)

Firstly, cyanuric chloride (1.48 g, 8 mmol) and 1,3,5-triphenylbenzene (2.45 g, 8 mmol) were charged into a 250 mL round bottom flask filled with dichloromethane (DCM; 100 mL); anhydrous aluminum chloride (3.00 g, 24 mmol) was then added slowly. This reaction mixture was connected to a condenser and heated at 70 °C for 16 h. When the reaction was completed, the resulting mixture was cooled to room temperature and the solid brownish-black precipitate was collected by filtration, washed with dichloromethane (DCM), methanol, and water several times to remove the unreacted precursors. Finally, the brownish-black solid was dried under vacuum for 24 h to obtain the solvent-free final product (88% yield).

2.3. Preparation of microporous and activated carbons

To fabricate the microporous carbons, the synthesized polymer was subjected to carbonization at four different temperatures, 600, 700, 800, and 900 °C, in a tubular furnace (Korea Furnace