



High microporosity of carbide-derived carbon prepared from a vacuum-treated precursor for energy storage devices



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ARTICLE INFO

Article history:

Received 7 July 2016

Received in revised form

2 March 2017

Accepted 18 March 2017

Available online 20 March 2017

ABSTRACT

Carbide-derived carbon (CDC) is an attractive electrode material for electrochemical applications because diverse pore textures and structures can be controlled by changing the properties of the precursor template and the synthesis conditions. Upon the tailoring of the micro-pore texture and graphitic structure of CDCs via a pre-vacuum treatment of a carbide precursor, the electrode shows a greatly high increased capacitance under a range of scan rates from 2 mV/s to 10 mV/s. The specific capacitance of a CDC chlorinated at 1000 °C from a pre-vacuum-treated at 1700 °C was 150 F/g at 2 mV/s, which is approximately 60% higher than that of a CDC chlorinated at 1000 °C.

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1. Introduction

Various types of carbonaceous materials have been studied extensively for use as electrodes in energy storage devices for transportation and renewable energy storage applications [1,2]. Capacitive electrodes (CEs) are used in a broad range of systems related to both energy and water infrastructure across the globe. Supercapacitor electrodes, traditionally associated with portable electronics [3], are emerging in grid-level energy storage applications [4,5], in capacitive deionization desalination methods [6], and in energy generation systems [7].

Supercapacitors occupy a region between batteries and dielectric capacitors on the Ragone plot, which describes the relationship between energy and power. They have served as a solution to the mismatch between the rapid growth in power as required by devices and the inability of batteries efficiently to discharge power at high rates [8]. This high performance requirement for high power discharge is directly related to the absence of charge-transfer resistances, which is a characteristic of battery Faradaic reactions and which subsequently leads to better performance at low

temperatures as compared to a battery system. Supercapacitors have received considerable attention in recent years due to their high pulse power supply, rapid charging capabilities at high current levels, long cycleability, and safe and reliable performance compared to battery systems [9]. Supercapacitors are usually connected to high-energy batteries or fuel cells to serve as a temporary energy storage device with high-power capabilities because the discharge time is too short for them to be used in independent power sources given their inherently low energy density levels [10,11].

Improvements have been made in cell packaging and electrolytes [12], but a lack of substantial progress in terms of carbon material designs has limited the energy density, effectively preventing the wide-scale usage of supercapacitors. Moreover, a new systemic approach beyond merely finding new electrode materials has been introduced [4,13–15]. To overcome the limitation of the low energy density, numerous new active materials for electrodes have been developed to realize high capacitance, ranging from carbon-based materials to metal-oxide composites [3,13,16–19]. Particularly, for the application of electrochemical double-layer capacitors (EDLCs), the study of electrochemical double layers is a key issue when attempting to overcome the present low capacity levels, representing a complex problem associated with the solid/electrolyte interface between the pore diameter of the solid

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electrode and the ion size of the electrolyte [20]. At high EDLC capacitance levels, the preparation of nanoporous carbon with uniform porosity suitable for the size of an ion is important, as ion-size tuned porous carbon can lead to an increase in the capacitance by increasing the confinement of the ions. For example, in the 1.0 M TEA-BF₄/ACN electrolyte system with a single associated solvent molecule of tetraethylammonium tetrafluoroborate (TEA-BF₄) that is a common electrolyte system in EDLCs owing to its high conductivity and the relatively small ion size, the carbon with micro-sized pore has more of an effect on the high capacitance performance than that with meso-sized pores. Therefore, the control of micro-sized pores is a more important factor than ensuring meso- or macro-pores in EDLC applications [21].

Carbide-derived Carbon (CDC), a carbon material suitable for supercapacitor applications, has been investigated due to its simple preparation and easy control of structures and properties, such as its graphitization and porosity. CDCs possess high porosity levels, a tunable pore size, and a narrow pore size distribution. A chemical etching method using chlorine gas can generate micro- and mesoporosity, leading to large adsorption capacities of target molecules matching the pore sizes due to the controlled pore size and high specific surface areas [22]. In previous reports, mesoporous CDCs produced by binary and ternary carbides (B₄C and TiC₇N₃ carbide precursors, respectively) showed significantly improved electrochemical capacities as lithium negative electrodes [23]. In addition, unique cyclic performance imparted by high mesoporosity was demonstrated in an electrode through the post-treated CDC by O₂ activation [24]. However, most post-activation processes also contribute to greater rates of mesopore development. When considering a commercial electrolyte such as TEABF₄/acetonitrile in a CDC electrode, a preparation method which increases the degree of microporosity represents an applicable spin-off technology for high storage capacitance in EDLC systems.

In this work, we demonstrate the significantly improved electrochemical capacitance of the CDCs through control of the micro-pore texture and amorphitization through the pre-vacuum and heat treatment of a carbide precursor. The origin of the changes in

the properties of the CDCs by the pre-vacuum treatment of the carbide precursor was investigated by means of an analysis of the structural changes and electrochemical performance capabilities of supercapacitors.

2. Experimental

To produce CDC material, TiC was purchased from Alfa Aesar, USA. Vendor-furnished Purity is 99.5%, particle size is ~5 μm, Formula weight is 59.91 g/mol, and density is 4.93 g/cm³. Fig. 1 shows the schematic process used to obtain the micro/mesoporous CDC from the TiC carbide, which underwent a vacuum (10⁻⁵ torr) and heating (1500 °C and 1700 °C) pre-treatment process before a chlorination process to form the CDC with various pores. The TiC carbide during the pre-vacuum annealing treatment was placed into a graphite crucible at the center of a high-vacuum furnace (Solar Atmosphere, Hermitage, PA), heated to 1500 °C or 1700 °C, annealed at these temperatures for 4 h, and slowly cooled down to room temperature. The heating rate and the pressure in the vacuum chamber (at the highest temperature) were 10 °C/min and 10⁻⁵ torr, respectively. The as-received TiC powder with particle size ~5 μm became hard and a mass of TiC after vacuum-annealing process. The vacuum-treated TiC sample was crushed in a diamond mortar and then separated with stainless steel sieves into of 5–10 μm size. The vacuum-annealing process induce conglomeration of the crystalline as-received TiC powder. As shown in Rietveld Refinement in next section, while the basic structure, such as space group, was not changed, there was a little change in lattice parameter after vacuum-annealing process. These prepared carbon samples were denoted as TiC@1500Vac and TiC@1700Vac, respectively. Carbide-derived carbon (CDC) powders were produced using the chlorine of the as-received TiC and vacuum-annealed TiC powders. These TiC powders were placed into a horizontal tube furnace, purged under an argon flow, and heated to 1000 °C and 1200 °C under flowing chlorine (10–15 cm³ min⁻¹) for 3 h.

The normal CDC has high specific surface area (SSA) with pore sizes that can be fine-tuned by controlling the chlorination

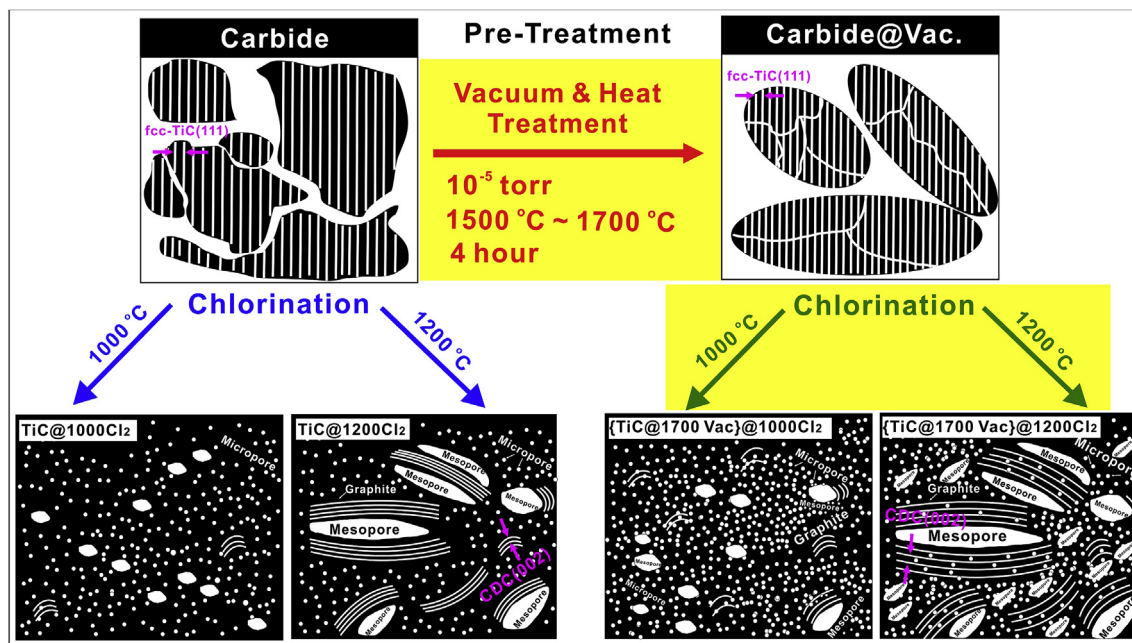


Fig. 1. Illustration of synthetic procedure of the micro/meso-porous vacuum-treated-TiC CDC. The crystalline carbide (TiC) as a precursor for vacuum-treated-TiC CDC sample expresses the fcc crystalline structure. After vacuum (10⁻⁵ torr) and heat (1500 °C and 1700 °C) treatments for 4 h, the carbide was transformed to large spherical aggregated particles. After chlorination process, the pre-treated carbide was transformed to CDC with high micro-porosity property. (A colour version of this figure can be viewed online.)

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