



Porous glassy carbon formed by rapid pyrolysis of phenol-formaldehyde resins and its performance as electrode material for electrochemical double layer capacitors



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ABSTRACT

In this article, we report a modified pyrolysis technique featuring an ultra-fast pyrolysis for obtaining a new type of high surface area glassy carbon (GC) from lithographically patterned novolac type phenol-formaldehyde resin, SU8. The fast-pyrolysis chemistry of SU8 is responsible for the formation of bubbles in the carbonizing matrix, which ultimately leads to the observed morphological changes. This porous glassy carbon (PGC) pyrolyzed at a heating rate of 50 °C/min has been evaluated as an electrode material for electrochemical double layer capacitors employing electrochemical techniques such as cyclic voltammetry (CV) and chronoamperometry. The electrochemically available surface area of PGC electrodes is found to be ~3 times greater compared with flat GC electrodes, and the electrode and specific capacitance improvements are 15 and 5 times, respectively. We describe possible mechanisms that may influence the enhanced capacitor performance of PGC electrodes, and compare their capacitance at five different potential scan rates ranging from 5 to 75 mV/s. In addition, the effect of H₂SO₄ surface treatment on the electrochemistry of the thus pyrolyzed carbons is investigated. Other possible applications of the thus obtained PGC are also discussed in the concluding remarks.

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1. Introduction

Electrochemical capacitors (ECs) are energy storage and delivery devices that store charges in the electrical double layer (Helmholtz layer) set up by ions in a liquid electrolyte compensating for the electronic charges in a high surface area electrode [1–4]. Based on the principle of operation involved, ECs are classified into electrochemical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs store charge non-faradaically, while in the case of pseudocapacitors charge is stored through faradaic surface redox processes [2,5]. The performance of both types of ECs depends upon establishing charge-storage processes on high specific area electrodes.

Carbon materials feature the desired specific surface area for electrodes employed for EC applications. Carbon also exhibits good corrosion resistance, is low-cost, has excellent physicochemical and electrochemical stability, and exhibits a wide range of electrical properties owing to its availability in a variety of allotropes

[4,6]. Recently, carbon MEMS (CMEMS) and carbon NEMS (CNEMS) technology have enabled the fabrication of miniature carbon electrodes that are lithographically patterned on to a photosensitive polymer, often a phenol-formaldehyde resin, SU8. The SU8 patterns are subsequently pyrolyzed at 900 °C in an inert environment. This pyrolysis process yields glassy carbon (GC), which is one of the most suitable materials for electrochemical applications [2,4,5]. It has been established that GC electrodes in an electrolyte commonly adapt the EDLC mechanism for charge storage [7].

Among the various carbon materials, porous carbon materials feature the largest surface area. However, the electrochemical stability window of GC is wider than that of the porous carbons. Based on the device requirements one can therefore choose the appropriate carbon type. For porous carbon electrode fabrication the methodologies most extensively researched include catalytic activation of carbon precursors employing metal salts or organometallic compounds [8], carbonization of polymer blends [9,10], chemical or physical activation of carbon precursors [11,12], and carbonization of a polymer aerogel synthesized under supercritical drying conditions [13]. These methods and resulting materials have their own advantages in terms of cost, scalability

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or ease of processing however, they are more suitable for bulk manufacture of porous carbon and do not have the flexibility of creating enhanced surface area film electrodes of a pre-defined geometry. Also, many of these methods involve mixing of two or more components, such as two polymers or an organometallic catalyst in a matrix, which may leave behind impurities in the resulting porous carbon [14]. Polymer blends, in particular, are not the materials of choice for photolithography, the most common fabrication technique for CMEMS and CNEMS, because photoresists typically lose their photosensitivity upon mixing with another polymer. Yet another drawback of porous carbons is that the microstructure, electrical conductivity and surface chemistry of the thus obtained carbons often vary depending upon their provenance, conditioning treatment and the underlying microstructure that influences the electrochemical response [5].

On the other hand, GC derived from the pyrolysis of an organic resin precursor exhibits very high purity. Polymer derived GC features randomly oriented graphitic crystallites arranged in an interconnected ribbon-like geometry, and therefore has a high sp^2 (graphitic) carbon content [15]. The graphitic content in GC can be further enhanced by increasing the pyrolysis temperature [16]. Since it is the sp^2 fraction that predominantly controls the electron transport properties of the material and enables their use for applications involving electrical conductivity and electrochemical reactions, GC is considered more suitable than porous carbons [17].

In this contribution, we introduce a new type of high surface area porous glassy carbon (PGC) material for EC applications. PGC is obtained from lithographically patterned SU8 by a modified 'rapid' pyrolysis technique featuring an ultra-fast temperature ramp rate. SU8 is the commercial name for an epoxy based phenol-formaldehyde type negative tone photoresist whose chemical structure is illustrated in Fig. 1(a). SU8 has several attributes that make it suitable for the fabrication of high aspect ratio MEMS structures. It is photosensitive in the 300–400 nm range, is biocompatible, and features high thermal and chemical stability after cross-linking and development. SU8 yields an extremely low-porosity graphitic GC when slowly pyrolyzed at 900 °C. The long polymer chains with aromatic carbon backbone facilitate C–C bond formation during pyrolysis, which results in GC with greatly improved ordering of the graphite crystallite than that obtained from other polymers.

Fig. 1(b) represents the microstructure of the GC derived from pyrolysis of SU8 at 900 °C with a temperature ramp rate (room temperature to 900 °C) of 2 °C/min. If the temperature ramp up is rapid, *i.e.*, is maintained above 25 °C/min, we obtain a bubble containing GC material (PGC) that features the GC microstructure, but with a much enhanced surface area due to the morphological changes resulting from the presence of bubbles.

PGC features hemispherical pores on its surface created by the bursting of bubbles (~5 μm wide) generated due to the release of the indigenous O and H of SU8 during pyrolysis (for details see Section 3, also see Fig. 2). The bubble generation renders the carbon surface rough and leads, as we shall see below, to a three-fold increase in the electrode surface area. We performed a reactive ion etch (RIE) employing oxygen plasma and calculated the electrical resistance for PGC to confirm that the microstructure and electrical conductivity of PGC remain the same as that of the flat GC obtained from SU8 via standard pyrolysis (performed at lower than 10 °C/min temperature ramp rate).

Rapid pyrolysis (ramp rate ≥ 25 °C/min) is a one-step carbonization approach that enables the manufacture of enhanced surface area carbon with tunable bubble density from SU8 films of pre-defined dimensions. This technique does not require any modifications in the composition of SU8, or any change in the pyrolysis environment and thus offers a highly pure material. We carried out a study on pyrolysis at three different temperature

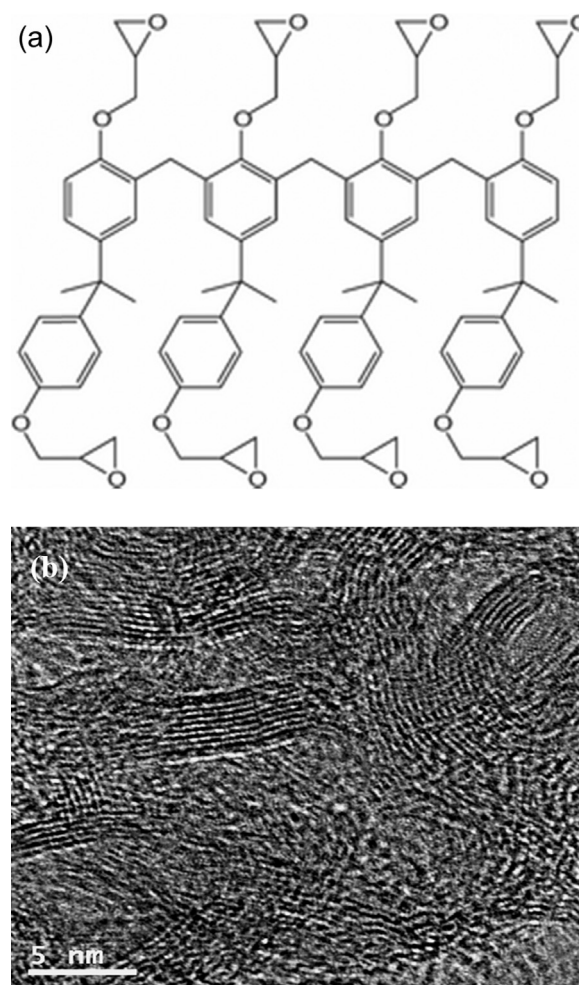


Fig. 1. (a) Chemical structure of SU8, (b) TEM micrograph of GC derived from pyrolysis of SU8 at 900 °C at a ramp rate of 5 °C/min.

ramp rates (25, 50 and 75 °C/min) and determined the surface area of the thus fabricated PGC employing chronoamperometry. Unlike other surface area measurement techniques such as gas adsorption isotherms that utilize the Brunauer–Emmett–Teller (BET) theory to obtain the specific surface area irrespective of its wetting during the electrochemical tests, chronoamperometry measures only the electrochemically available (wetted) surface. Therefore, we evaluated the specific capacitance of PGC based on its chronoamperometric surface area, which is more pertinent to electrochemical applications reported here.

The wetting of the electrodes during CV is extremely important in order to completely utilize the extended surface for electrochemical measurements. Even for a very low density/high surface area carbon, the capacitance may not increase as expected if the electrolyte cannot access the entire surface. Wetting of carbon electrodes has been extensively studied by electrochemists, and various physical and chemical pathways for improving the electrochemically accessible area have been suggested. After determining which pyrolysis ramp rate yielded the highest electrochemically available surface area carbon based on chronoamperometry we tested these same electrodes for their capacitance values as determined from cyclic voltammetry (CV) in a voltage region where there are no faradaic reactions.

High surface area carbons are known to have complicated kinetics due to the presence of various surface functional groups [18]. These surface groups contain functionalities such as quinoid, quinhydrone, phenolic, carboxyl, carbonyl and lactone depending upon

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