



Symmetric supercapacitors based on porous 3D interconnected carbon framework



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ABSTRACT

The construction and design of novel porous carbons for electric double-layer capacitors (EDLCs) application to meet the increasing demand and supply of energy is eminent. This is important because the pore volume (PV)/micropore volume (MV) in the porous network architecture of the carbon is mostly responsible for the ion traps in energy storage. Three dimensional carbon materials based on graphene materials with relatively high specific surface area (SSA) represents a promising material candidate for EDLCs applications. In this work, we synthesized highly porous carbon from graphene foam (GF) and polyvinyl alcohol PVA as a sacrificial template, and investigate their performance as electrodes for EDLCs applications. The as-produced carbons present a fairly large surface area ($502 \text{ m}^2 \text{ g}^{-1}$), and a highly porous interconnected framework with mesopore walls and micropore texture which are suitable as electrode for energy storage. As electrode material in a symmetric configuration the activated graphene foam (AGF) showed a specific capacitance of 65 F g^{-1} , energy density of 12 Wh kg^{-1} , power density of 0.4 kW kg^{-1} , good rate performance and excellent long term stability in $1 \text{ M Na}_2\text{SO}_4$ aqueous with no capacitance loss after 3000 cycles.

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1. Introduction

Electric double-layer capacitors (EDLCs) are charge-storage devices with a high power density, long cyclic life and low maintenance cost that have found applications in portable electronics, memory backup sources, hybrid electric vehicles, regenerative and renewable energy systems [1]. The storage mechanism of EDLCs is based on reversible adsorption of ion across the interface of electrode and electrolyte when a voltage is applied [2]. In practice, most EDLCs make use of carbon due to their low cost, excellent conductivity, chemical stability, and adjustable structural properties and specific surface area (SSA). Other carbon-based materials, metal-oxides, and conducting polymers are also considered due to their pseudocapacitive properties. Commercially, the most commonly used material for EDLCs application is the activated carbon due to its fairly high electrical conductivity, high surface area and are usually operated with organic electrolyte [3]. The use of organic or ionic electrolyte increases the energy density of the EDLC devices because the energy is a function of the voltage

squared. It has also been shown that organic electrolyte can operate up to 3.5 V and ionic liquids up to 5.0 V [4]. However, there are many disadvantages associated with them: some of which include low ionic conductivity (high internal resistance), highly flammable, high electrolyte leakage and are quite expensive. On the other hand aqueous electrolytes have high ionic conductivity and high mobility of proton transport mechanism which are required to achieve low internal resistance for development of high performance supercapacitor devices. Therefore, most research activities are focussed on the use of aqueous electrolyte for commercial application by trying to extend the potential window of their electrode materials [5,6].

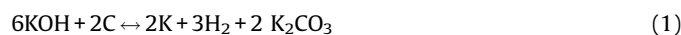
Recently the developments of high performance EDLCs have been based on porous carbons because of the fact that the porous morphology provides adequate mesopores and micropores, the Brunauer–Emmett–Teller (BET) specific surface area (SSA), pore size distribution (PSD) and other surface functionalities of the porous carbon combined with size of the ion from the electrolyte provide improved performance. Although, It has been shown that a large SSA with adequate distribution of mesopores and micropores is one of the most important parameters that is necessary to understand the performance of porous EDLCs carbon electrode but a definite relationship between the capacitance and SSA has not been clearly shown [7,8]. Using porous carbon is favourable

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because the pore structure governs the measured capacitance, energy storage and power delivery capability of the material. These result from contribution due to the total surface of micropores (S_{micro}) and the surface of larger pores (mesopores and macropores) [7]. It is worth stating that the macropores (>50 nm) makes virtually no contribution to the total capacitance but act as the ion buffering reservoir [9], while micropores (<2 nm in size) serve as the ion traps for energy storage, and mesopores (2 < 50 nm) act as the ion transport pathways for power delivery [9,10].

Several synthesis techniques for porous carbons have been explored for different applications [11–14]. Template-based approaches are the most widely used as an efficient technique for production of porous carbon with highly tunable properties such as pore distributions, pore textures, optimized hierarchical structures and surface functionalities [14,15]. The main challenge with template synthesis is that it relies on the use of inorganic materials sources such as silica and zeolite, which are expensive and has hindered this technique in large scale production [16,17]. An alternative approach to the template method in preparing porous carbon materials is the direct use of chemical and physical methods which have emerged as a novel strategy and raised considerable interests amongst researchers because they are well known techniques and allow synthesis of materials with tunable properties [18,19]. The chemical treatment usually results in the formation of aerogel or hydrogel materials and the physical treatment (activation) mostly with KOH, ZnCl_2 , and H_3PO_4 leads to the formation of porous carbons [20–22]. The formation mechanism of porous carbon with KOH has been attributed to carbon gasification by the removal of CO_2 and the oxygen related material contained in the matrix. During the activation process, CO_2 formed from K_2CO_3 in the heat treatment is released and becomes significant at high temperatures. The released CO_2 then react with carbon atoms to open up closed pores and enlarge existing micropores. Meanwhile, the potassium-containing compounds, such as K_2O and K_2CO_3 , can be reduced by carbon to form K metal, thus causing the carbon gasification and hence the formation of pores [22]. The activation process takes places according to the following reaction [22]



In recent time there have been reports on activation of graphene based materials, for examples Yanwu Zhu et al. have produced carbon materials assisted by microwave-expansion called a-MEGO with exceptional properties and demonstrated excellent electrochemical properties in ionic electrolytes [23,24]. Recently Zhang et al. [25] produced porous 3D graphene-based bulk materials with exceptional supercapacitor performance in ionic liquid with a specific capacitance of 92 F/cm^3 and energy density of 39 Wh/liter in EMIMBF₄ electrolyte respectively. However, it is worth stating that most of these activations are based on graphene oxide obtained from the usual Hummer's method and to the best of our knowledge there has been no report on the activation of graphene foam derived from the chemical vapor deposition technique (CVD) and this is the first report on a

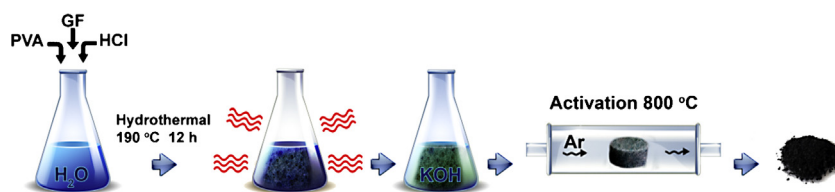
symmetric supercapacitors based on activated graphene foam operating at 1.6 V in a neutral aqueous electrolyte.

2. Experimental

Scheme 1 shows the schematic route used to prepare the porous carbon in this study. Briefly, graphene foam (GF) and polyvinyl alcohol (PVA) were used as starting material for the production of hydrogel, which was then used to produce porous carbon materials after the activation process. Graphene foam (GF) was prepared by chemical vapour deposition (CVD) onto a catalytic nickel foam (Alantum Innovations in Alloy Foam Munich, Germany) as reported in our previous work [26], and 100 mg of the GF was dispersed in 0.1 g/ml of (PVA) in a vial glass by ultrasonication followed by addition of 1.5 ml of hydrochloric acid (HCl) to the solution as a cross linker and the resultant mixture was hydrothermally treated in an autoclave heated up to 190°C and maintained at this temperature for 12 h to polymerize the mixture [25]. The resulting hydrogel was washed with deionized water and dried for 6 h. The as-prepared hydrogel was then soaked in aqueous KOH solution with a KOH/hydrogel mass ratio of 7 for 24 h [24]. The composite mixture was then placed in a horizontal tube furnace ramped from room temperature to 800°C at 10°C/minute under argon gas flow for 1 hour of activation. This procedure transforms the composite hydrogel into carbon materials consisting of a continuous pore network distribution. The activated material denoted as AGF was neutralized with 0.1 M HCl, washed with deionised water and dried at 120°C for 12 h after which samples were characterized.

2.1. Material Characterization

Raman spectroscopy measurements was carried out using a Jobin Yvon Horiba TX 6400 micro-Raman spectrometer equipped with a triple monochromator system to eliminate contributions from Rayleigh lines and using LabSpec (Ver. 5.78.24) analytical software. All the samples were analyzed with a 514 nm argon excitation laser (1.5 mW laser power on the sample to avoid possible thermal effects and beam damage). The sample was also characterized using powder X-ray diffraction (XRD). An XPERT-PRO diffractometer (PANalytical BV, Netherlands) with theta/theta geometry, operating a cobalt tube at 35 kV and 50 mA, was used. The XRD patterns of all specimens were recorded at room temperature in the 20.0° – 80.0° 2θ range with a counting time of 15.240 s per step. Qualitative phase analysis of the sample was conducted using the X'pert Highscore search match software. Nitrogen sorption isotherms were obtained using Micromeritics TriStar II 3020 (version 2.00), the samples were outgassed for 12 h at 150°C . BET surface areas were calculated from the relative pressure range $0.01 < P/P_0 < 0.2$ of the adsorption branch for the activated carbon. Pore size and pore volume were obtained using Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm. Scanning electron microscopy (SEM) was carried out with a Zeiss Ultra Plus 55 field emission scanning electron



Scheme 1. Preparation of porous carbon from GF and PVA.

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