Carbon 141 (2019) 523–530

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Vertically edge-oriented graphene on plasma pyrolyzed cellulose fibers and demonstration of kilohertz high-frequency filtering electrical double layer capacitors

Nazifah Islam [a], Md Nadim Ferdous Hoque [a], Wenyue Li [a], Shu Wang [b], Juliusz Warzywoda [c], Zhaoyang Fan [a, *]

[a] Department of Electrical and Computer Engineering and Nano Tech Center, Texas Tech University, Lubbock, TX, 79409, USA
[b] Department of Nutritional Sciences, Texas Tech University, Lubbock, TX, 79409, USA
[c] Materials Characterization Center, Whitacre College of Engineering, Texas Tech University, Lubbock, TX, 79409, USA

ARTICLE INFO

Article history:
Received 3 July 2018
Received in revised form
23 September 2018
Accepted 4 October 2018
Available online 4 October 2018

ABSTRACT

High-frequency electrochemical capacitors or electrical double layer capacitor (HF-ECs) with large capacitance were developed from edge-oriented graphene (EOG) nanosheets perpendicularly grown around carbonized cellulose microfiber (CMF) sheets. Binder-free EOG/CMF electrodes were fabricated in a one-step 5-min plasma-enhanced chemical vapor deposition process, where cellulose fiber sheets were rapidly pyrolyzed by high-temperature plasma, while EOG simultaneously formed on the developing CMFs. Owing to combined unique characteristics of both EOG and CMF, such facilely produced electrodes exhibit excellent performance in terms of both high frequency response and high capacitance density. In aqueous electrolyte cells, 10 μm thick EOG/CMF electrode exhibits an areal capacitance of 1.07 mF cm^{-2} at 120 Hz along with a frequency of 13.8 kHz at −45° phase angle. ~3 V organic electrolyte cells show an areal capacitance of 0.49 mF cm^{-2} at 120 Hz, and a frequency of 1.47 kHz at −45° phase angle. Developed HF-ECs were successfully applied in practical applications as ripple current filter in line-frequency AC/DC conversion, and as pulse power storage/smoother in environmental energy harvesting for self-powered micro devices.

1. Introduction

There has been great interest in the study and development of ultrafast electrochemical capacitors (ECs) with response in kilohertz high frequency range, aiming to substitute them for the commonly used aluminum electrolytic capacitors (AECs) for current ripple filtering [1–3], pulse power storage and generation [4], and other similar functions. AECs have a low capacitance density, and their bulky size limits the downscaling of DC power modules and circuit boards for slim, compact and wearable electronics [5]. ECs have a larger capacitance density than AECs by several orders of magnitude; however, a maximum working frequency of conventional ECs is typically lower than 1 Hz [6,7]. They are only suitable as energy sources but not as conventional capacitors for filtering at high frequencies. Therefore, a performance gap exists between ECs and AECs in terms of frequency response and capacitance density. It has been envisioned that if high-frequency ECs (HF-ECs) with a compact size could be developed for filtering applications as the substitution for bulky AECs, circuit board form could be further scaled down for slim, small and light electronics. For the most common filtering application in the line-frequency AC/DC conversion, considering the harmonic frequencies, such HF-ECs should be able to respond in kilohertz (kHz) range.

Steady progress is being made toward developing kHz HF-ECs by tailoring different nanocarbon-based electrodes [3,4,8–16], prominently oriented graphene, carbon nanotube thin films, carbon nanofiber aerogel, and many others [2]. One key issue to achieve high frequency response is to minimize the equivalent resistance. This requires a minimized interfacial resistance between the current collector and the carbon material, high conductivity of the carbon material, and rapid electrolyte ion migration in the porous carbon electrode. Minimizing the electrode material resistance is critical by using highly conductive carbon materials, while tailoring the porous structure is equally, if not more important.

* Corresponding author.
E-mail address: Zhaoyang.Fan@ttu.edu (Z. Fan).

https://doi.org/10.1016/j.carbon.2018.10.012
0008-6223/

Based on de Levie's porous electrode model, the pore has a time constant $\tau = \frac{1}{4}z^2RC$, where z is the pore penetration depth, R and C are the pore resistance and capacitance per unit length [17]. This constant is further deduced as $\tau \propto z^2/d$, where d is the pore diameter. Clearly, high frequency response, or small pore time constant requires shallow pores and large pore size. Therefore, tailoring nanocarbon electrode structure by minimizing or eliminating micropores or even mesopores has been particularly interesting.

Achieving kilohertz response while maintaining large areal and volumetric capacitance densities for HF-ECs is a challenging goal. Usually, a high frequency response comes at the expense of low capacitance density since micropores and mesopores in the electrode must be sacrificed. Fast ECs have been obtained from a variety of carbon-based nanomaterials, but either their capacitance density is small or their frequency response is limited [18–20]. Another challenge for HF-ECs is their low operation voltage. Most studies explored aqueous electrolyte-based cells to achieve high-frequency response because aqueous electrolytes exhibit high ionic conductivity; however, such cells have a potential window smaller than 1 V, and this significantly limits their practical applications. HF-ECs with vertical graphene and organic electrolyte was first reported in Ref. [21]. Detailed presentation of frequency dependent behavior and other device characterizations were later on reported in Refs. [9,10].

Herein, aiming at achieving both high response frequency in kHz range and a large capacitance density, as well as a wider voltage window, we investigated edge-oriented multilayer graphene (EOG) network grown on carbonized cellulose microfiber (CMF) sheets, which were used as a binder-free electrode for development of kilohertz frequency HF-ECs, as illustrated in Fig. 1. Both aqueous electrolyte cells and organic electrolyte cells are reported. The rationale to adopt such an EOG/CMF electrode is based on the following considerations.

In terms of tailoring the pore structure of an electrode for high frequency response, vertically oriented multilayer graphene (VOG) on a flat surface [1], which is produced in a plasma enhanced chemical vapor deposition (PECVD) process, with its fully exposed graphene edges and oriented channels between graphene sheets, seem to be an ideal electrode structure for kHz HF-ECs. As schematically highlighted in Fig. 1b: (1) the aligned multilayer graphene sheets are rooted in the surface or subsurface of the substrate with a trivial interfacial resistance; (2) graphene sheets have reasonably large conductivity; (3) the aligned channels between sheets allow electrolyte ions to migrate rapidly for charge and discharge; and (4) the fully exposed graphene edges and steps can be easily accessed by electrolyte ions as adsorption sites. For this last point, it should be emphasized that the capacitance at the edge plane is much larger than at the basal plane [22]. However, on a flat substrate, the achievable VOG surface area is limited, resulting in a small areal capacitance density, and therefore oriented graphene network grown perpendicularly around a 3D porous scaffold, i.e. EOG, was further investigated [23,24].

The conventional carbon cloth is too thick to be used as a 3D scaffold for HF-ECs. Here, we carbonized very thin cellulose wiper sheet into 10 μm thick carbon microfiber sheet for use as the 3D scaffold for EOG deposition. As the most common polymer and a renewable resource with large scale annual production, cellulose fibers are being exploited as carbon fiber precursor for electrochemical energy storage due to their abundance, low-cost, and high content of carbon [25,26]. Time- and energy-consuming thermal pyrolysis of polymer fiber sheets at high temperatures for several hours or even longer, in an inert or active gas environment, is commonly applied to obtain carbon fiber sheets with abundant micro- and meso-porous structures [27–30], which, however, are not suitable as electrodes for HF-EC. For this study, in a 5-min rapid PECVD process, EOG nanosheets with fully exposed graphene edges were grown perpendicularly wrapped around carbon microfibers, which were rapidly formed by pyrolysis of cellulose microfibers in the same PECVD process to minimize micropore generation (Fig. 1a). Plasma pyrolysis is a technique used to produce high quality carbon fiber networks from natural or artificial polymer fibers, and has previously been identified as a key process for producing highly conductive non-porous carbon fibers for HF-ECs [4,31].

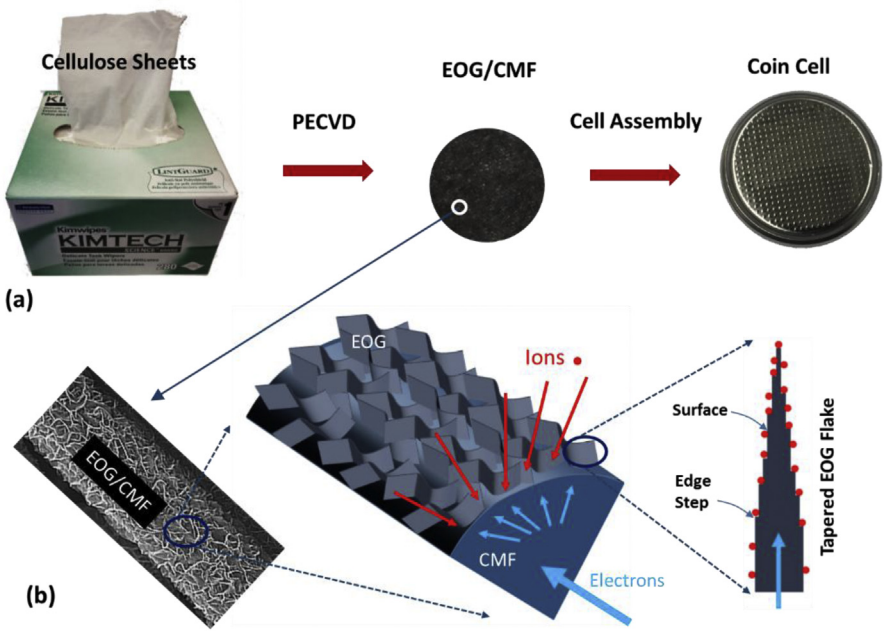

Fig. 1. Schematics illustrating (a) the one-step process from cellulose paper to EOG/CMF binder-free electrode, which was then studied in a coin cell, and (b) EOG network on carbon fiber with fully exposed graphene edges along the tapered perpendicular graphene sheet for easy access, and inter-sheet channels facilitating rapid electrolyte transport. (A colour version of this figure can be viewed online.)