High-Density Freestanding Graphene/Carbide-Derived Carbon Film Electrodes for Electrochemical Capacitors

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Abstract

Freestanding films of reduced graphene oxide (rGO) have attracted much attention as electrodes for electrochemical capacitors, especially for flexible device applications. Here, for the first time, we report binder-free supercapacitor electrodes made of highly porous carbide-derived carbon (CDC) nanoparticles as spacers between thermally reduced graphene oxide (rGO) sheets. The addition of CDC between the rGO layers increases the wettability and accessibility of active material to the electrolyte ions, which improves electrochemical performance. The resulting electrodes exhibit high capacitance of over 210 F/g, high power densities at 100 mV/s and 10 A/g charge/discharge rates, and long stability of over 10,000 cycles in an aqueous electrolyte. Moreover, hybrid rGO/CDC electrodes, in contrast to solely rGO-based counterparts, maintained high gravimetric capacitance as the electrode thickness increased from 5 μm to $\sim 50 \mu\text{m}$. This hybrid electrode material design is greatly viable in high-power energy storage devices.

Keywords:

Supercapacitors; carbide-derived carbon; graphene; nanopores; carbon composite; power density

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1. Introduction

The rapid boom in the electronics market, including wearable and portable devices, drives energy consumption and requires sustainable and portable energy storage devices [1-4]. Electrochemical capacitors (ECs), often called supercapacitors or ultracapacitors, are energy storage devices with higher power densities and faster charge/discharge times than conventional batteries [1, 5-7]. Distinct charge storage mechanisms separate ECs into two classes: electrical double layer capacitors (EDLC) and pseudocapacitors. In EDLCs, the ions adsorb onto electrodes with high specific surface areas and store charge in non-faradaic electrostatic attractions, while pseudocapacitors use fast chemical surface redox (faradaic) reactions to store charge [8]. Carbonaceous materials such as activated carbon [9], carbon black [10], carbon nanotubes [11, 12], carbide derived carbon (CDC) [13], and graphene [14, 15] are examples of electrode materials for EDLCs, whereas conducting polymers [16, 17] and transitional metals oxides [18] are examples of pseudocapacitor materials.

Graphene has been widely explored in EC applications due to its high conductivity and theoretical surface area approaching $2,600 \text{ m}^2/\text{g}$ [14, 19]. Due to its relatively low cost and high production volumes, reduced graphene oxide (rGO) has attracted significant attention as a graphene-based EC electrode material [14, 20, 21]. Despite their high specific surface area (SSA), the reported capacitive performance of rGO electrodes has, to date, not exceeded 130-200 F/g [20, 22, 23] in aqueous electrolytes. rGO sheets inherently tend to restack during synthesis and/or electrochemical cycling and minimize the SSA that is accessible to electrolyte ions [14, 23]. To overcome this issue, zero-dimensional carbon materials such as carbon onions [24] and one-dimensional carbon materials such as CNTs were utilized as nano-spacers between graphene sheets to increase electrolyte ion accessibility [25-29]. Although this strategy had prevented

restacking, the lower capacitance of CNTs or carbon onions, as compared to graphene sheets, limits the overall capacitance of the hybrid electrodes. Moreover, until now, this strategy has mostly been demonstrated for thin film electrodes ($< 10\ \mu\text{m}$), and the impact of nano-spacers on the performance of relatively thick binder-free graphene electrodes has not yet been systematically studied [28, 30, 31].

Carbide-derived carbons are three-dimensional microporous carbons that can be synthesized from carbide precursors (e.g., TiC, SiC, MoC) by selective removal of the metal atoms from their structures using either high-temperature halogen etching [13, 32, 33] or room-temperature electrochemical anodization [34]. Synthesis conditions can adjust the carbide precursor type, particle size (from 20 nm to 300 μm) [35, 36], and synthesis temperature to yield highly tunable, monodisperse porosities that precisely match the corresponding electrolyte ion dimensions [13, 37]. Unlike external surface carbons, such as CNTs and carbon onions, internal surfaces of microporous CDCs offer high surface areas greater than 1,500 m^2/g . Furthermore, nanosized CDC particles ($< 50\ \text{nm}$ in diameter) improve electrolyte transport rates and allow faster charge/discharge processes [38, 39]. Subsequently, CDCs offer high energy and high power densities as supercapacitor electrodes [40, 41]. However, to date, no attempts to integrate them as nanoscale spacers in binder-free, high-density composite freestanding films of nanoporous carbon and graphene have been reported.

Herein, for the first time, we report the high performance of freestanding EDLC hybrid electrodes that rely on CDC nanoparticles as spacers between graphene sheets. Our results demonstrate high gravimetric capacitance ($> 200\ \text{F/g}$) and excellent charge retention at high voltammetry sweep rates and current loads. The electrodes yield high volumetric capacitance and

allow rapid ion transport even when electrode thickness increases tenfold. We demonstrate different CDC loading densities to underscore the benefits of these porous nanoparticles as spacers for graphene-based energy storage composite electrodes.

2. Materials and Methods

2.1 Materials:

Graphite (SP-Carbon) and activated carbon (YP50) were used as received. Potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), potassium hydroxide (KOH), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl) were purchased from Alfa Aesar. Hydrogen peroxide (H_2O_2) was purchased from Sigma Aldrich. All chemicals were used as received.

Synthesis of nano-CDC: CDC particles were synthesized according to a previously described procedure [42, 43]. Silicon carbide (SiC) nanoparticles (20 nm diameter, MTI Crystal) were loaded into a quartz furnace and treated with flowing Cl_2 gas at 800 °C for 5 hours. The resulting CDC material was, subsequently, annealed with H_2 gas at 600 °C for 2 hours [44].

Preparation of graphene oxide (GO): Graphite oxide was synthesized using modified Hummer's method [45]. Briefly, 2g of purified graphite powder (SP-1, Bay Carbon) and 1g of NaNO_3 were added to 50 ml of concentrated sulfuric acid under continuous stirring in an ice bath. After the temperature was brought down to 0 °C, 7 g of KMnO_4 was added gradually to ensure that the reaction temperature did not exceed 10 °C. The temperature was then brought to 35 °C, and the reaction allowed to proceed for an hour before slowly being quenched with 90 ml of deionized water ($\text{DI H}_2\text{O}$) while being kept below 98 °C. The dark brown solution allowed to mix at 98 °C for 15 min before adding 280 ml of $\text{DI H}_2\text{O}$ and 7 ml of H_2O_2 . The yellowish-

brown solution was filtered repeatedly with DI H₂O and further washed/centrifuged with DI H₂O and 1M HCl until the pH of the solution was ≥ 6 before being vacuum dried for 24 hours.

Preparation of GO-CDC composite and GO-CDC films: Aqueous dispersions of both GO (2 mg/ml) and CDC (1 mg/ml) were separately made by ultra-sonication (FB-505, Fischer Scientific, operating at 20 KHz and 500 Watts) for 60 min using a replaceable probe (13 mm titanium tip, Qsonica). Then, the GO-CDC composite was made by adding either 10 wt% or 20 wt% of the CDC solution to the GO dispersion and sonicating the composite once again for 1 hour. The resulting composite dispersion was made into a free-standing film via vacuum assisted filtration (VAF) through filter membranes (Durapore ©PVDF, Millipore) with a 0.1 μm pore size. The samples were denoted according to the amount of CDC added as GOC9010 (10 wt%) and GOC8020 (20 wt%).

Preparation of rGO-CDC (GCDC) electrodes: GO, GOC9010, and GOC8020 films were fixed between two glass plates and subjected to thermal treatment at 200 °C for 10 hours in an oven (KSL 1100X, MTI corp.). The resulting films were denoted as rGO, GC9010, and GC8020.

2.2 Methods:

Electrochemical cell setup: Electrochemical tests were done in a three-electrode configuration using a Swagelok cell in which the counter electrode was activated carbon (YP50) containing 5% wt. of polytetrafluoroethylene PTFE as a binder, and the reference electrode was Ag/AgCl in 3.5M KCl. rGO, GC9010, and GC8020 were separately used as the working electrode. Both counter and working electrodes had 0.9 cm diameter. The electrolyte was potassium hydroxide

(6M KOH), and 2 Celgard polypropylene membranes (0.064 μ m pore size and 1.2 cm in diameter) were used as the separator.

Electrochemical measurements: Cyclic voltammetry (CV), galvanostatic cycling (GC), and electrochemical impedance spectroscopy (EIS) measurements were done using a VMP3 potentiostat (Bio-Logic, USA).

Film characterization: Electrical conductivities were measured using four probes conductivity meter (ResTest v1, Jandel Engineering Ltd., Bedfordshire, UK) with a distance of 1 mm between each probe. Scanning electron microscopy (SEM) was performed on a Zeiss Supra 50VP (Carl Zeiss SMT AG, Oberkochen, Germany) equipped with an energy-dispersive spectroscope (Oxford EDS, with INCA software). X-ray diffraction (XRD) patterns were recorded with a powder diffractometer (Rigaku SmartLab) using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) with 0.02° 2θ steps and 0.5 s dwelling time. Raman spectra were collected using Confocal Raman Spectroscopy (Renishaw inVia, UK) with He-Ne laser (632.8 nm wavelength and spot size of $\sim 1\mu\text{m}$). X-ray photoelectron spectroscopy (XPS) survey scan were done using (Kratos AXIS Ultra^{DLD}, Manchester, U.K.) with monochromatic Al-K α (1486.6 eV). Specific surface area for each film were calculated by fitting the N₂ adsorption-desorption data using the Brunauer-Emmett-Teller (BET) theory. Pore size distributions for each film were determined by Quenched Solid Density Functional Theory (QSDFT) slit pore fitting of the gas sorption data. These results are shown in Fig. S2.

Fig. 1 Schematic of synthesis process for rGO and rGO-CDC films

3. Results and Discussions:

Aqueous dispersions of GO and CDC were used as precursors toward the fabrication of the rGO/CDC composite film. A schematic of the synthesis process for film fabrication is shown in Fig. 1, in which freestanding and flexible films of GO and GOC9010 were made using VAF techniques before being thermally converted to rGO and GC9010. The electrical conductivity of rGO, GC9010, and GC8020 films are 555 ± 10 S/m, 181 ± 8 S/m, and 166 ± 5 S/m respectively. TEM images reveal that CDC particles are uniformly distributed on a sheet of graphene. The resulting structure is more accessible to ions than the sealed, stacked structure of standard collapsed rGO sheets. SEM images in Fig. 2 show how the open layered structure of GO film (Fig. 2a) became sealed as seen in Fig. 2c. The graphene sheets restacked during thermal reduction. However, the presence of interstitial CDC space-separating particles (Fig. 2b)

prevented GO sheets from restacking even after thermal treatment (Fig 2d), making the surface

Fig 2. Cross sectional SEM images of (a) GO, (b) GOC9010, (c) rGO, and (d) GC9010 films. Insets are photos of (a) GO film and (b) GOC9010 (diameter of 4 cm). area more accessible compared to rGO alone.

Raman spectra in Fig. 3a show the D and G bands of carbon, which are centered at ~ 1330 cm^{-1} and ~ 1580 , respectively. The results underscore structural changes that occur during the thermal reduction of GO to rGO. The degree of disorder in graphitic materials is measured by the intensity ratios of the D band to the G band (I_d/I_g) [46], which increased as a result of GO reduction. CDC is a 3D-disordered carbon [33], and its presence has a greater influence on the I_d/I_g ratio in GC8020 than in GC9010, as expected.

The (002) peaks of XRD are centered at 12° (Fig. 3b) and 24° (Fig. S1a) for GO film and CDC powder, respectively, which translates to interlayer spacing (d_{002}) of $8.1\text{\AA}$ and $3.7\text{\AA}$ for rGO and

Fig 3. (a) Raman spectra of GO, rGO, GC9010, and GC8020 films. XRD patterns of (b) GO, GOC9010, and GOC9010 before thermal reduction and (c) rGO, GC9010, and GC8020 after thermal reduction. All films are 30 μ m-thick.

CDC respectively. No shifts in 002 peaks occurred for both GO9010 and GO8020 films; however, the peaks broadening and the decrease in their intensity (Fig. 3b) suggest that CDC is sandwiched between GO sheets. During thermal reduction of GO sheets, the (002) peak shifted to higher angles (Fig. 3c) and consisted of two peaks (I) and (II). The evolution of these peaks during thermal reductions was previously reported [47, 48], and it is attributed to partial reduction of GO and to the fast vaporization of intercalated water molecules in GO films during thermal reduction (10 °C/min in this case). In region (I), the broad (002) peaks shown at (2 θ) angles of 22.0° (for rGO) and 20.8° (for GC9010 and GC8020) correspond to interlayer spacing (d_{002}) of 4.02 Å and 4.26 Å films respectively. However, all three films in regions (II) have the same d_{002} of 3.69 Å. From SEM images (Fig. 2) and XRD analysis, CDC particles are intercalated/sandwiched between rGO sheets and can act as spacers.

The nano-CDC powder possesses high surface area ($\sim 1164 \text{ mg/cm}^2$)[43], while it's 9.5 mg/cm^2 for rGO film as shown in Fig S.2. Hence, it's expected for GC8020 film (370 mg/cm^2) to have

Fig 4. CV curves of rGO, GC9010, and GC8020 at (a) 2 mV/s, (b) 20 mV/s, and (c) 500 mV/s. (d) Specific capacitance at different scan rates calculated from CV curves.

higher surface area than GC9010 film (18 mg/cm^2).

Fig 5. CV curves of rGO, GC9010, and GC8020 at (a) 2 mV/s, (b) 20 mV/s, and (c) 200 mV/s. (d) Specific capacitance at different scan rates calculated from CV curves.

To investigate the effect of CDC spacer incorporation on the energy storage capability of rGO, we studied the electrochemical performance of all three electrodes as a function of thickness. 5 μm -thick electrodes of rGO, GC9010, and GC8020 were made and electrochemically tested at different scan rates (Fig. S3) including 2 mV/s (Fig. 4a), 20 mV/s (Fig. 4b), 500 mV/s (Fig. 4c), and 1000 mV/s (Fig. S3d). CV curves of all three electrodes exhibit a rectangular-like shape which suggests a double layer capacitive behavior. Moreover, all CVs have obvious humps between -0.7 V and -0.8 V, which are typical features for partially reduced rGO [14, 49, 50] as a result of pseudocapacitive contribution of oxygen containing groups on both rGO and CDC due to the fact that thermal treatment was performed in air. Table S1. Shows the content of carbon and oxygen for each film were measured by XPS (see Fig. 1Sb). For these *very thin* electrodes, rGO performs slightly better than both GC9010 and GC8020 as

shown in Fig. 4d. However, the performance of these thin electrodes (mass loading < 0.1

mg/cm²) is not comparable to the performance of much thicker commercial supercapacitor

electrodes. It is well-known that the thickness of the electrode can have a very high impact on its

performance [51]. To examine the effect of electrode thickness on electrochemical performance,

we increased the electrode thicknesses to 30 μm . All three electrodes retained high capacitance

and rapid ion transport (Fig. S4) and exhibited comparable capacitive performances at 2 mV/s

(Fig. 5a) and at 20 mV/s (Fig. 5b). Interestingly, both GC9010 and GC8020 showed better high rate performance at 200 mV/s (Fig. 5c) and 1000 mV/s (Fig. S4d), while the capacitance of rGO electrodes dropped drastically at scan rates higher than 100 mV/s. As shown in Fig. 5d, rGO and GC8020 have relatively similar gravimetric capacitances, about 180 F/g, at 100 mV/s, whereas GC9010 has a capacitance of 200 F/g at this high rate. When the electrode thicknesses increased to 50 μm , GC9010 with density of 0.932 g/cm³ showed even better comparative performance at all scan rates (Fig. S5). The CVs displayed superior capacitive performance for GC9010 versus rGO at 20 mV/s (Fig. 6a). rGO showed a resistive CV curve at higher rate of 200 mV/s (Fig. 6b), while GC9010 still exhibited a standard rectangular cyclic voltammogram shape. Interestingly, GC9010 has a specific capacitance of 208 F/g at 100 mV/s (Fig. 6c), outperforming some of

Fig 6. CV curves of rGO and GC9010 at (a) 20 mV/s and (b) 200 mV/s. (c) specific capacitance of rGO and GC9010 at different scan rates calculated from CV curves and (d) specific capacitance at different electrode thickness.

rGO-carbon composites based electrodes despite having a thickness 10 times higher (see Table S2). Moreover, a specific capacitance >200 F/g was maintained for GC9010 despite increasing electrode thickness from $5\text{ }\mu\text{m}$ to $50\text{ }\mu\text{m}$ as shown in Fig. 6d, while the rGO electrode was dramatically affected by such thickness variation.

Nyquist plots from electrochemical impedance spectroscopy of all $30\text{ }\mu\text{m}$ -thick electrodes are shown in Fig. 7a. The graphs show the typical small semicircles (charge transport

Fig 7. Electrochemical analysis of 30 μm thick electrodes shown by (a) Nyquist plots, (b) galvanostatic charge-discharge cycles at 10A/g and their internal resistance (IR) drops (inset). (c) IR drops are shown at different discharge current densities. (d) Long-term cycling performance at 10A/g (see inset), for 10,000 cycles, shows capacitance retention.

resistance) at low frequencies and an almost vertical line at high frequencies (ionic impedance) [52]. In the low frequency region, rGO, GC9010, and GC8020 exhibit almost the same

equivalent series resistance (ESR) ($\sim 0.1\Omega$), exhibited by the x-intercept of the Nyquist plot. However, GC9010 and GC8020 demonstrate a reduced charge transfer resistance, exhibited by the size of the semicircle before the curve transitions to the 45° region. Moreover, both GC9010 and GC8020 have a more vertical 45° region which indicates better ion diffusion and can be attributed to the porosity of the electrode with added CDC [53]. Fig. 7b displays galvanostatic cycling between -0.1 V and -1.1 V at a high discharge current density of 10 A/g. Although all three electrodes possessed small IR drops, rGO has the largest IR drop which dramatically increases with increasing discharge current density in contrast to the minimal IR drops for both GC9010 and GC8020 even at 100 A/g as seen in Fig. 7c.

Cycling performance of the three electrodes was tested for 10,000 cycles at 10A/g in the same voltage range shown in the inset in Fig. 7d. rGO, GC9010, and GC8020, showed 100% columbic efficiency (Fig. S6) and specific capacity retention rates of 87%, 94%, and 90% respectively.

4. Conclusions

Binder-free hybrid electrodes were made by the incorporation of porous CDC into rGO which showed excellent capacitive performance at high rates for both composites with 10 wt% and 20 wt% of CDC added. Increasing the electrode thickness from 5 μm to 50 μm revealed the capacity dependence of rGO on thickness, which was significantly improved when CDC was present. In fact, the sample with 10 wt% showed a specific capacitance larger than 200 F/g at 100 mV/s despite changes in electrode thickness, rendering it a potential candidate in applications that require high power.

Acknowledgements:

We acknowledge Kathleen Maleski for assistance with schematic design and BET measurements, Taron Makaryan for help with Raman spectra, and Patrick Urbankowski with

XPS. SEM and TEM characterization were done at the Central Research Facilities (CRF) at Drexel University. This work was supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

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