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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 ~50 μm. This hybrid electrode material design is greatly viable in high-power energy storage devices.

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 2600 m^2/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 μm), 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].

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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 1500 m^2/g. Furthermore, nanosized CDC particles (<50 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 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.

2.1.1. 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 h. The resulting CDC material was, subsequently, annealed with H_2 gas at 600 °C for 2 h [44].

2.1.2. Preparation of graphene oxide (GO)

Graphite oxide was synthesized using modified Hummer's method [45]. Briefly, 2 g of purified graphite powder (SP-1, Bay Carbon) and 1 g 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 (DI H_2O) while being kept below 98 °C. The dark brown solution allowed to mix at 98 °C for 15 min before adding 280 ml of DI H_2O containing 7 ml of H_2O_2. The yellowish-brown solution was filtered repeatedly with DI H_2O and further washed/centrifuged with DI H_2O and 1 M HCl until the pH of the solution was ≥6 before being vacuum dried for 24 h.

2.1.3. 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 h. 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%).

2.1.4. 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 h in an oven (KSL 1100X, MTI corp.). The resulting films were denoted as rGO, GC9010, and GC8020.

2.2. Methods

2.2.1. 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 3.5 M 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 (6 M KOH), and 2 Celgard polypropylene membranes (0.064 μm pore size and 1.2 cm in diameter) were used as the separator.

2.2.2. Electrochemical measurements

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

2.2.3. 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 Kα radiation ($\lambda = 1.54$ Å) 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 ~1 μm). 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 N_2 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.

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