

Title of Grant / Cooperative Agreement:	
Type of Report:	
Name of Principal Investigator:	
Period Covered by Report:	
Name and Address of recipient's institution:	
NASA Grant / Cooperative Agreement Number:	

Reference 14 CFR § 1260.28 Patent Rights (*abbreviated below*)

The Recipient shall include a list of any Subject Inventions required to be disclosed during the preceding year in the performance report, technical report, or renewal proposal. A complete list (or a negative statement) for the entire award period shall be included in the summary of research.

Subject inventions include any new process, machine, manufacture, or composition of matter, including software, and improvements to, or new applications of, existing processes, machines, manufactures, and compositions of matter, including software.

Have any Subject Inventions / New Technology Items resulted from work performed under this Grant / Cooperative Agreement?	No	Yes
If yes a complete listing should be provided here: Details can be provided in the body of the Summary of Research report.		

Reference 14 CFR § 1260.27 Equipment and Other Property (*abbreviated below*)

A Final Inventory Report of Federally Owned Property, including equipment where title was taken by the Government, will be submitted by the Recipient no later than 60 days after the expiration date of the grant. Negative responses for Final Inventory Reports are required.

Is there any Federally Owned Property, either Government Furnished or Grantee Acquired, in the custody of the Recipient?	No	Yes
If yes please attach a complete listing including information as set forth at § 1260.134(f)(1).		

Attach the Summary of Research text behind this cover sheet.

Reference 14 CFR § 1260.22 Technical publications and reports (December 2003)

Reports shall be in the English language, informal in nature, and ordinarily not exceed three pages (not counting bibliographies, abstracts, and lists of other media).

A Summary of Research (or Educational Activity Report in the case of Education Grants) is due within 90 days after the expiration date of the grant, regardless of whether or not support is continued under another grant. This report shall be a comprehensive summary of significant accomplishments during the duration of the grant.

Info on Reference 14 CFR § 1260.27 Equipment and Other Property

Grant No. NNX13AB88A “Lightweight Supercapacitors with Porous Nanocarbon Platforms”

PI: Yi Lin (National Institute of Aerospace)

Instrument Name: **Biologic VMP3 Electrochemical Station**

Model: **VMP3-CHAS.**

Serial Number: **0684**

Accessories: **2 Potentiostat/galvanostat boards w/EIS (Model VMP3/Z-01) and 2 boards w/o EIS (Model VMP3-01).**

Total Purchasing Price: **\$30,874.05.**

Current Location:

Bldg 1293C, Rm 251, NASA Langley Research Center, Hampton, VA 23681

Lightweight Supercapacitors with Porous Nanocarbon Platforms

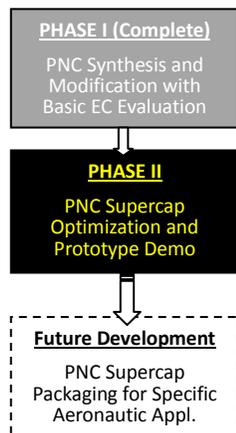
NASA Award Number: NNX13AB88A

Investigators: Dr. Yi Lin (PI) and Dr. Jae-Woo Kim (Co-I) (National Institute of Aerospace, 100 Exploration Way, Hampton, VA 23666)

Period Covered: 11/15/2012 – 12/31/2013

Purpose

The purpose of the proposed effort was to develop durable lightweight and low-volume supercapacitors with high power and energy density that can be used in aeronautic applications. We used our recently discovered porous nanocarbon (PNC) materials as platforms. Our Phase-I studies were devoted to obtain electrochemical (EC) performance – structure relationships of as-synthesized and modified PNC supercapacitor systems. If selected for Phase-II, we will seek the optimization of PNC electrode performance by using optimal material with suitable architecture designs toward a prototype demo.



Background

“Supercapacitors” (SC) is a common term referring to electrochemical capacitors, or more precisely, electrical double-layer capacitors (EDLCs). These devices are often of high power density with long cycling life but suffer from low energy density (see Fig.1). The uses of SCs have thus been restricted since they only function for a short period of time.

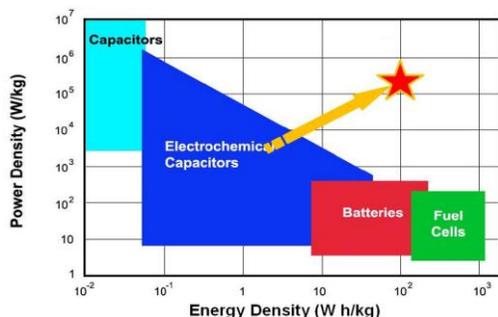


Fig.1. A Ragone plot showing the typical gravimetric power and energy density values for various electrochemical devices. The red-colored star indicates the targeted region of the next generation lightweight SCs that are suitable for aeronautics applications.

Compared to their use in electric vehicles for land and water, power devices for aeronautic applications [e.g., electric unmanned aerial vehicles (UAVs)] have even more demanding requirements in terms of weight and size reduction, life time cycles, reliability, and safety concerns. These requirements make it more imperative to develop electrochemical devices with both high gravimetric and volumetric energy and power. Although significant research

has been conducted on ultrahigh energy density batteries (e.g., lithium-sulfur (Li-S) batteries, theoretical energy density >2000 Wh/kg), it has been predicted that lightweight SCs with sufficiently high specific energy (to the level of Li-ion batteries) may negate the need for batteries in certain applications. By reducing weight/volume and complexity as well as potential explosion hazard (Li batteries), these devices can be useful for applications that require long operation duration such as the main power source for small UAVs or power sources for avionics.

One of the most important pathways toward the next generation SCs is the design of novel electrode platforms and architectures in order to obtain improved energy density while also improving or at least retaining the power density and cyclability. Activated carbon has been the standard EDLC electrode material; however various nanocarbon species including carbon nanotubes (CNTs) and graphene exhibit superior EDLC performance due to their very high surface area and high electrical conductivity. The effect of porosity on EDLC performance of carbon-based electrode materials is still not well understood. In general, improving the porosity of the electrode material leads to high ion transport rates during charging and discharging with reduced electrode weight and volume and consequently better EC performance. Manipulation of nanocarbon electrode porosity to obtain high accessible surface area while maintaining the electrical conductivity remains to be a significant challenge.

We recently discovered a facile and scalable catalytic method to produce a series of PNC [Fig.2, i.e., holey carbon nanotubes (hCNTs) and holey graphenes (hGs)] that led to the LEARN Phase-I support (patent application filed during Phase-I). The preliminary experiments showed that the electrochemical performance of PNC materials was significantly better than their parent non-porous

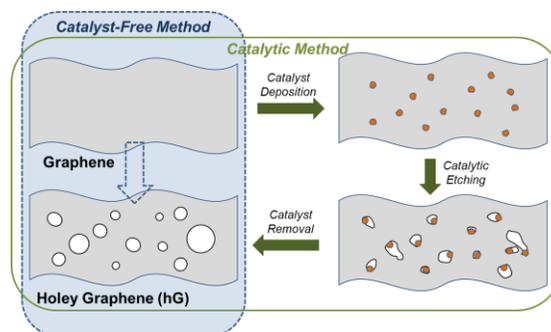


Fig.2. The catalytic and catalyst-free processes to synthesize hG. hCNTs can be similarly prepared.

counterparts. Thus, the project goal is to use these PNC platforms to develop lightweight, low volume electrical energy storage systems that have potentially breakthrough performances in energy/power density and thus are suitable for a broad array of aeronautics applications as discussed above. Our method is practical, scalable, and can create pores in a manner that allows for some control of pore size. These attributes make this technology highly suitable for TRL advancement and future industrial commercialization. The Phase-I study also allowed the discovery of another method to prepare hG and hCNT materials (Fig.2), for which a provisional patent was submitted. This method is catalyst-free and thus of lower cost. Details are discussed below in *Summary of Research*.

Approach

In order to obtain EC performance-structure relationships of basic and modified PNC SC platforms, the one-year Phase I effort was proposed to consist of: (1) synthesis and characterization; (2) modification and characterization; and (3) electrochemical evaluation of PNC materials.

Accomplishments

- **Equipment:** Identified and purchased a state-of-the-art electrochemical station (Biologic VMP3) and essential electrochemical supplies and equipment for the project.
- **Experiments:** Synthesized and characterized various PNC materials, including both hGs and hCNTs (see details in *Summary of Research*). The results have confirmed the advantages of the importance of the pores/holes to the energy storage properties and elucidated a path to optimize performance.
- **Publication and Patent Applications:** 1 peer-reviewed journal article was published and featured as cover in a high impact journal (Fig.3); 1 patent application and 1 provisional patent application were filed. Notably, one of the reviewers rated our journal article being “extremely novel” and stated that “this manuscript represents the first example where holey graphene was prepared from a solid-phase graphene sheets”. The other reviewer complimented our work being “a major contribution with significant and wide-ranging impact” and “its broad application in the polymeric composites and energy storage communities”.
- **Collaborations:** (1) Prof. Liangbing Hu at University of Maryland at College Park is an expert on design and fabrication of nanocarbon-based energy storage devices using flexible substrates such as paper and textiles.



Fig.3. Our peer-reviewed article was published and featured on the cover of the September 7, 2013 issue of the Royal Society of Chemistry journal *Nanoscale* (impact factor 6.23).

Several PNC samples were sent to Prof. Hu for his team to evaluate these materials into full-cell supercapacitor devices. He has participated in our Phase-II LEARN proposal, which seeks to optimize and apply our PNC electrode architecture toward a prototype demo. (2) Dr. John Connell at NASA Langley Research Center has provided consultation to our project and directions of using various characterization instruments at LaRC. He is also a collaborator in our Phase-II proposal.

- **Personnel:** Recruited a summer student (Caroline Campbell; 05/20/13 – 07/26/13) under NASA LaRC’s LARSS intern program to conduct electrochemical characterization and PNC modifications.
- **Synergistic Activities:** The PI is organizing an upcoming symposium “Two Dimensional Materials for Energy and Fuel” for 247th American Chemical Society (ACS) National Meeting, Dallas, TX (March 2014).

Summary of Research

Effects of Holes on hG Performance: Experiments confirmed that the presence of holes on graphene surface resulted in improvement in capacitive performance. Fig.4a shows the normalized cyclic voltammetry (CV) curves of a hG sample (from 10 mol% Ag, or “hG₁₀”) matched one another at various scanning rates from 10 mV/s to as high as 1 V/s (distorted curves at high rates for starting graphene), indicating excellent rate performance due to improved electrolyte ion transport. Specific capacitance values improved from 45 F/g for starting graphene to 88 F/g for hG₁₀ (Fig.4b). Note the relative capacitance improvement is of more significance as the absolute values are strongly related to the conditions that they were measured (e.g., current density, scanning rate, electrolyte, etc.).

The specific capacitance of hGs increased with hole size (correlated with the starting catalyst amount) until an optimal value of ~22 nm average hole size (hG₁₀). The initial increase of hole size led to improvement of ion transport and accessibility to graphene surface, but larger holes diminished the usable graphitic surface which is needed for electric double layer formation, resulting in reduction in capacitance.

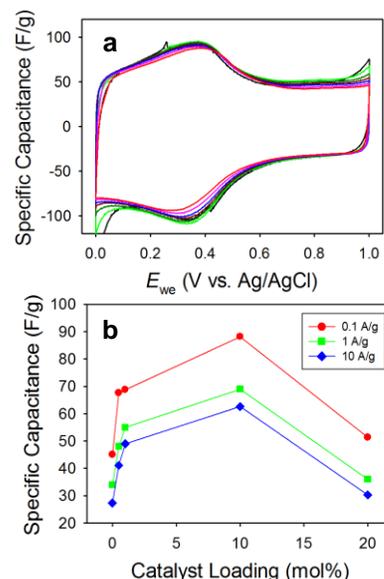


Fig.4. Effect of holes: (a) CV data (normalized to capacitance) of a hG₁₀ sample at various scanning rates (10, 20, 50, 100, 200, 500, and 1000 mV/s). (b) Dependence of specific capacitance vs. starting catalyst loading at various current densities. Electrolyte: 0.5 M H₂SO₄.

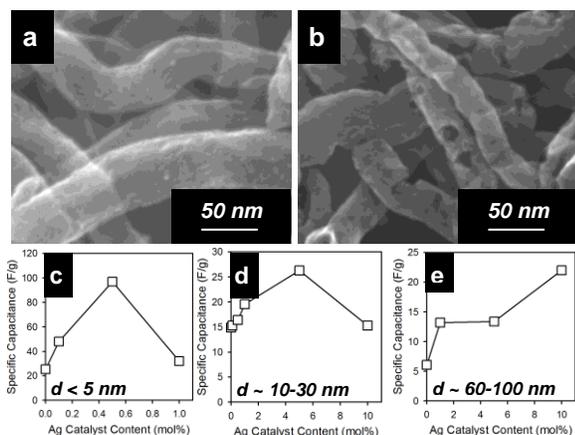


Fig.5. Examples of SEM images of hCNTs from different catalyst loading: (a) 0.1 mol% Ag for CNTs of $d \sim 60-100$ nm and (b) 1 mol% Ag for CNTs of $d \sim 40-60$ nm. (c-e) Dependence of specific capacitance values (@ 1A/g in 6 M KOH) on the catalyst loading for hCNTs with various diameters as indicated.

Diameter-Dependence of hCNTs: Our catalytic synthesis methods are equally applicable to graphene and CNTs. CNTs of various diameter ranges (single-walled: ~ 1.5 nm; few-walled: < 5 nm; multi-walled: < 8 nm, 10-30 nm, 40-60 nm, and 60-100 nm) were used as starting materials to prepare hCNTs from various catalyst amounts (Fig.5). Similar to the case of hGs, comprehensive evaluation with a large set of hCNT samples indicated that there is an optimum catalyst amount (thus hole size) for capacitance improvement. Interestingly, this improvement is diameter dependent: smaller-diameter CNTs needed less catalysts for hole generation to maximize capacitance (Fig.5-c-e). In some cases, such improvement was quite dramatic. For example, with suitable catalyst amount (0.5 mol% Ag), the specific capacitance value of few-walled CNTs (diameter < 5 nm, “hFWNT_{0.5}”) improved from 25 to 97 F/g.

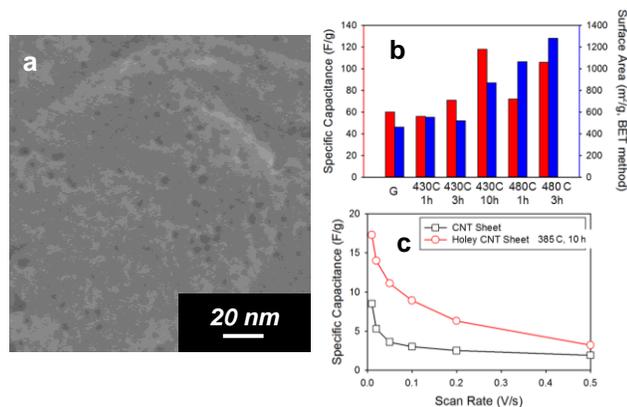


Fig.6. (a) SEM of a hG₀ sample from catalyst-free preparation by simply heating graphene in air at 430 °C for 3 h; (b) Specific capacitance and corresponding BET surface area values measured for hG₀ samples prepared at various conditions; (c) specific capacitance values measured at different scanning rates for a CNT sheet sample (from Nanocomp) measured before (black) and after (red) the catalyst-free hole generation process.

PNCs from Catalyst-Free Synthesis: In Phase-I, we discovered an alternative, single-step, and catalyst-free method to prepare PNCs (Figs.2&6).¹⁵ Without the use of catalyst, nanocarbons were directly heated in air but at a controlled heating rate, temperature, and period to yield

PNC products. The catalyst-free hGs (“hG₀”) had much improved Brunauer-Emmett-Teller (BET) surface area (as high as ~ 1300 m²/g vs. ~ 500 m²/g of starting graphene sample) and, more importantly, significantly enhanced capacitive and retained cycling performance (a few thousand cycles were measured) – comparable to that from catalytically prepared hGs. Advantages of the catalyst-free method compared to the catalytic one include: (1) excludes the use of noble metal catalyst and reduces the number of process steps, thus leading to a much lower production cost; (2) versatility as it is non-invasive to nanocarbon materials in various forms, such as commercially available CNT sheets (Fig.6c), graphene paper, vertically aligned graphene sheets, CNT fibers and yarns, CNT arrays, etc. The current limitation for catalyst-free PNC synthesis is that the hole sizes are in a rather limited range (< 10 nm), while the catalytic approach afforded a greater breadth of sizes.

hG Modification with Oxygen Functional Groups: The presence of heteroatom (e.g. N, O, S, etc.) functional groups can further improve the capacitive performance of nanocarbons. The abundance of oxygen functional groups on hGs (typically at the sheet and hole edges) was tuned by varying their reflux time in a nitric acid (more oxygen with longer reflux). The electrochemical results confirmed that such modifications generally improved the specific capacitance values. There was an optimal treatment time; for example, ~ 24 h reflux

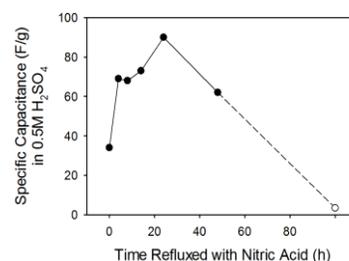


Fig.7. Optimization of hG₁₀ capacitance by modification with oxygen functional groups via refluxing in nitric acid.

in dilute (2.6 M) nitric acid of a hG₁₀ sample resulted in significantly improved capacitance values several times over the same sample with minimal treatment (i.e., room temperature acid wash, Fig.7). The modifications were carried out for hGs from both catalytic and catalyst-free methods. For the former, this was done simultaneously with the catalyst removal step during the synthesis. Over-functionalization with oxygen functional groups (e.g. prolonged reflux at 48 h or preparation of “holey graphene oxide (hGO)” with KMnO₄ oxidation) deteriorated the capacitive performance because the excessive oxidation damaged the graphitic surface conjugation.

Modification with Conductive Polymers and Metal Oxides: The hG samples were modified to introduce additional charge storage pathways known as pseudocapacitance by using polyaniline (PANI) and manganese dioxide (MnO₂). The capacitance improvement of hGs by modification of MnO₂ was only marginal ($\sim 30\%$) possibly due to insufficient loading. In comparison, the synthesized PANI-modified hGs via in-situ polymerization performed significantly better (Fig.8). The capacitance values of one of the PANI-hG samples (PANI:hG = 9:1 by weight) reached over 250 F/g, several times that of the

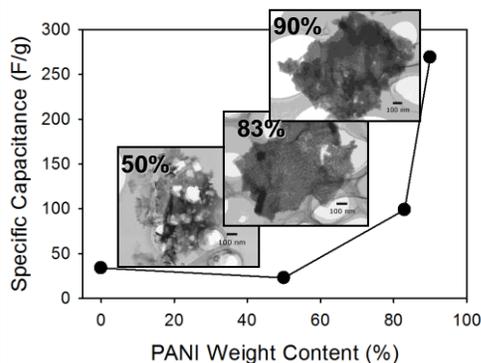


Fig.8. Improvement of capacitance of hGs by modification with different amount of PANI (weight percentages shown in the images).

starting hG sample. Electron microscopy images showed that PANI polymers exhibited partial to complete coverage on hG sheets from lower to higher weight loadings, consistent with continuous capacitance improvement with PANI loading. It should be noted that the incorporation of pseudocapacitance often significantly improves the energy density (capacitance increase) but reduces power density (conductivity loss). Therefore, a balance in the modification degree needs to be achieved for specific performance requirements.

Single-Cell Device Fabrication and Demonstration: In order to fully demonstrate the advantages of PNC materials (hG in particular) over conventional nanocarbons, we prepared single-cell devices by fabricating coin cells from a hG₀ sample (Fig.9). The electrodes were prepared by solution dispersion, filtration, drying, and precise cutting into disc shapes. Full-cell electrochemical evaluations (CVs, galvanometric charge/discharge, impedance, cycling, etc.) confirmed significant improvement of gravimetric capacitance performance (84 F/g) over starting graphene material (40 F/g) with retained conductivity (Fig.9c). The devices showed excellent energy and power density values ($E = 36 \text{ W h/kg}$; $P = 170 \text{ kW/kg}$). It is even more encouraging that the volumetric capacitance value (60 F/cm^3) exhibited more significant improvement (9 F/cm^3 for starting graphene) as higher electrode packing density

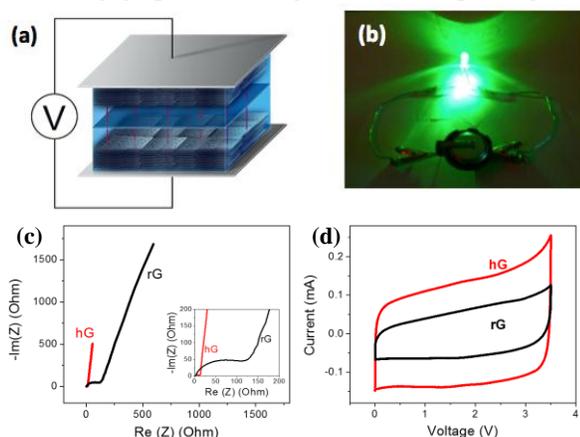


Fig.9. (a) Schematic of a single-cell supercapacitor device with hG electrodes. (b) A hG₀ coin cell supercapacitor (~0.4 mg total electrode weight) lit up an LED (model NTE30037). (c) Impedance and (d) CV data comparison of hG and raw graphene (rG) devices. Electrolyte: ionic liquid EMI-TFSI.

was achieved, strongly supporting the proposed ion transport scenario. This volumetric capacitance value (not yet optimized) is already on par with that of the SOA experimental material (Ruoff, et al. *Science* **2011**, *332*, 1537; “a-MEGO” from chemical activation of microwave-expanded graphene oxide; 60 F/cm^3) and better than a commercial activated carbon electrode (45 F/cm^3) (Huang et al. *ACS Nano* **2013**, *7*, 1464).

The success of this single-cell device fully demonstrated the advantages of these unique PNC materials. Based on our progress and knowledge, we have confidence that the potential for further optimization and development of our novel material and device architecture in future studies will be successful. All current results were achieved at essentially the material (or, to be more precise, “sub-architecture”) level. Our PNCs are compatible with the most recent nanocarbon electrode architectural designs, which will enable further improvements in the volumetric and gravimetric capacitance when combined with optimal starting graphene material and PNC structural motifs (i.e., hole size, hole-edge chemistry, etc.).

Current TRL: 3

Applicable Programs/Projects

Relevant NASA programs are Environmentally Responsible Aviation and Fundamental Aeronautics (Fixed Wing). Efforts will be made to contact the respective PIs to make them aware of this technology.

Public Distribution/Disseminations

Journal Publication:

Lin, Y.; Watson, K. A.; Kim, J.-W.; Baggett, D. W.; Working, D. C.; Connell, J. W. “Bulk Preparation of Holey Graphene via Controlled Catalytic Oxidation.” *Nanoscale* **2013**, *5*, 7814-7824 (Cover Article).

Patent:

Watson, K. A.; Lin, Y.; Ghose, S.; Connell, J. W. “Bulk Preparation of Holey Carbon Allotropes via Controlled Catalytic Oxidation.” Patent Application Filed on 04/01/2013 (LAR18110-1/0150238).

Provisional Patent:

Lin, Y.; Kim, J.-W.; Connell, J. W. Funk, M. R.; Campbell, C. J. “Single-Step, Solvent-Free, Catalyst-Free Preparation of Holey Carbon Allotropes.” Invention disclosure filed on 04/04/2013 (LAR-18334-1); provisional patent application filed on 10/14/2013.

Invited Talks:

Lin, Y.; Kim, J.-W.; Funk, M. R.; Connell, J. W. Lightweight Platforms toward Composite and Energy Storage Applications. 2nd International Symposium on Graphene for Energy. 246th American Chemical Society (ACS) National Meeting, Indianapolis, IN (September 2013).

Lin, Y.; Kim, J.-W.; Connell, J. W. Holey Graphene Supercapacitors. 247th ACS National Meeting, Dallas, TX (March 2014).