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Graphene-Based Ultra-Light Batteries for Aircraft

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NASA Aeronautics Research Mission Directorate (ARMD)

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The Team

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Outline

- The innovation
- Background
- Technical approach
- Impact of the innovation
- Results of the Seedling effort to date
- Distribution/Dissemination—getting the word out

The Innovation

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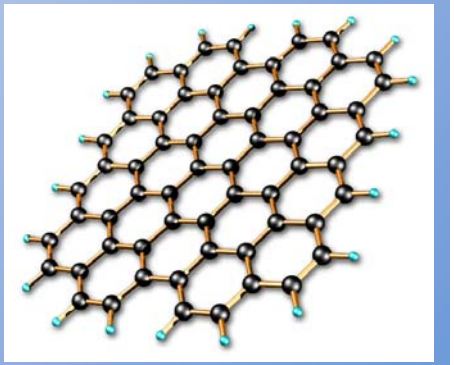
- Develop a graphene-based ultracapacitor prototype that is flexible, thin, lightweight, durable, low cost, and safe and that will demonstrate the feasibility for use in aircraft
- These graphene-based devices store charge on graphene sheets and take advantage of the large accessible surface area of graphene (2,600 m^2/g) to increase the electrical energy that can be stored.



- The proposed devices should have the electrical storage capacity of thin-film-ion batteries but with much shorter charge/discharge cycle times as well as longer lives
- The proposed devices will be carbon-based and so will not have the same issues with flammability or toxicity as the standard lithium-based storage cells.

Background

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There are two main established methods for the storage and delivery of electrical energy:

- Batteries
  - Store energy with electrochemical reactions
  - High energy densities
  - Slow charge/discharge cycles
  - Used in applications requiring large amounts of energy → aircraft

- Electrochemical capacitors
  - Store energy in electrochemical double layers
  - Fast charge/discharge cycles
  - Low energy densities
  - Used in electronics devices – Large capacitors are used in truck engine cranking

Current Aircraft Batteries

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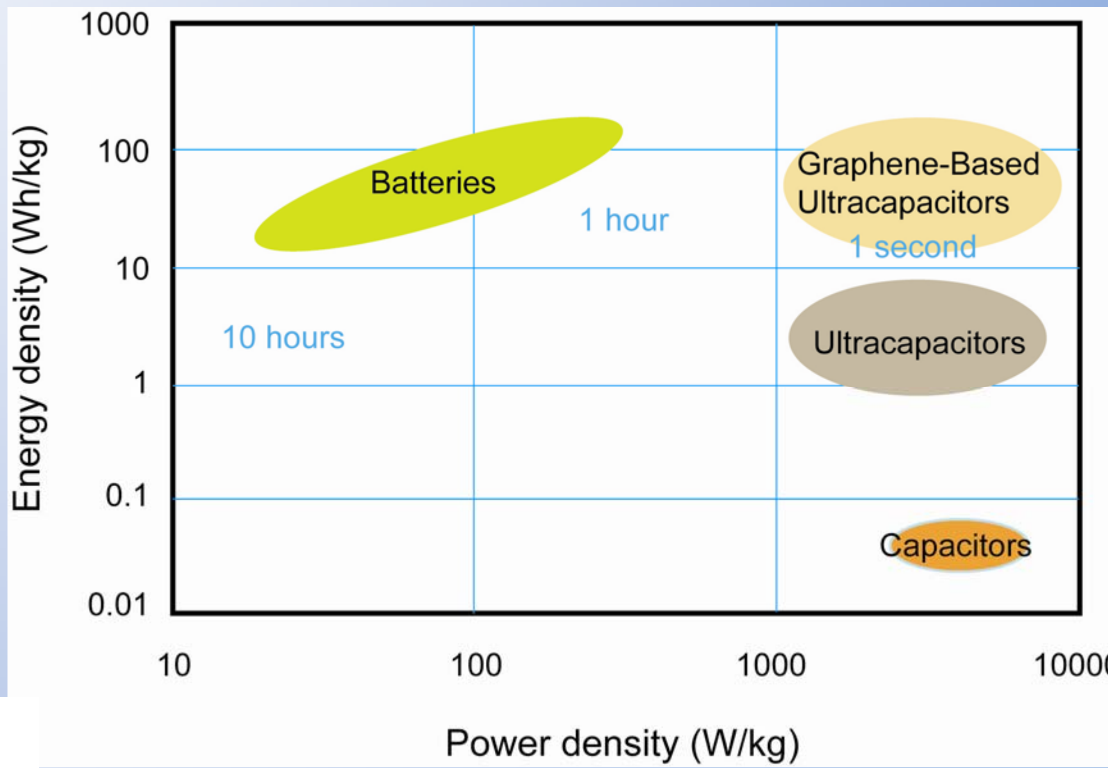
- General Aviation and Light aircraft → Lead acid batteries
- Larger aircraft and helicopters→ Nickel cadmium batteries
- Aircraft manufacturers are beginning to use Lithium Ion batteries due to their larger capacitances per unit weight.
  - Li-ion batteries still have low power densities
  - Performance is mainly controlled by
    - diffusion of Li ions
    - electron conductivity in the electrolyte
  - Recent approaches to increase performance involve
    - Use of nano-structured electrodes for shorter ion diffusion distances
    - Introduction of dopants to increase ion transport efficiency
  - However, stable performance over thousands of charge/discharge cycles has not been achieved.

Expected Performance

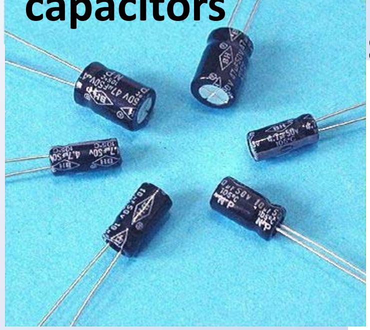
Our graphene-based ultracapacitors:

- High power densities of ultracapacitors
- High energy densities due to huge surface area of graphene

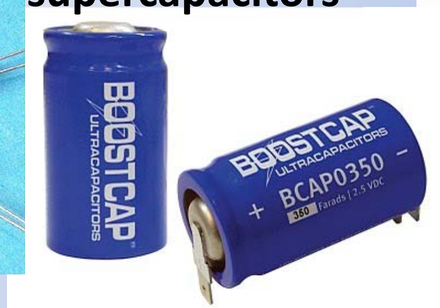


Energy and power density comparison for batteries, conventional ultracapacitors, and the expected performance of graphene-based ultracapacitors. Charging times are shown in blue.

capacitors



supercapacitors



batteries

Technical Approach

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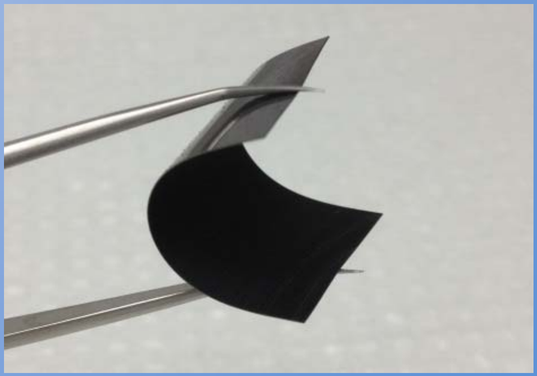
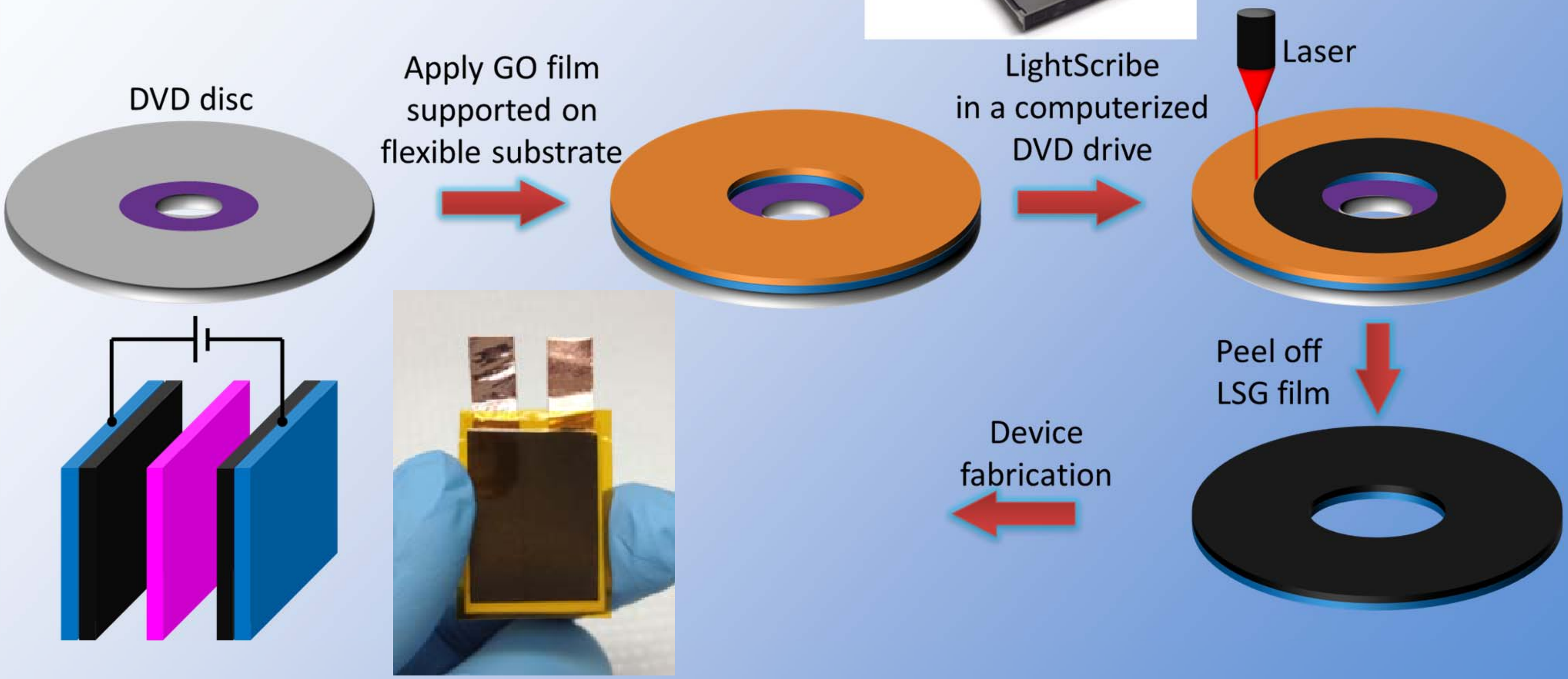
- Methods to reduce Graphene Oxide into graphene include chemical, thermal, and flash reduction
- UCLA Co-Investigator developed a light scribe lithography method that produces high quality graphene films that have high electrical conductivity and specific surface area, and can be used directly as electrodes in energy storage devices.*
- We are producing Laser Scribed graphene as well as direct laser reduced graphene.
- Ultracapacitors are assembled with graphene sheets using liquid electrolyte



*El-Kady, M.F., V. Strong, S. Dublin, and R.B. Kaner, *Science* 335 (2012) 1326-1330

UCLA Laser Scribe Method

Making graphene supercapacitors
is as easy as burning a DVD



M.F. El-Kady, V.Strong, S.Dubin, R.B. Kaner, *Science* 335, 1326-1330 (2012)

Impact of the Innovation

- A robust, lightweight, flexible, thin, and inexpensive energy storage device with energy and power densities superior to those of state-of-the-art lithium-ion batteries will greatly benefit NASA and the nation's aeronautics.
- Such revolutionary energy storage devices will radically reduce the mass and weight of energy storage and supply devices resulting in more efficient aircraft.
- GO, the precursor for the production of graphene, is manufactured on the ton scale at low cost as opposed to lithium, which is a limited resource that must be mined throughout the world.

What is Graphene?

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- **Graphene is a revolutionary new allotrope of carbon (a single atomic layer of graphite) with extraordinary properties:**
  - ***Surface area*: 2630 m^2/g**
  - ***Electrical conductivity*: $10^6\ \Omega^{-1}cm^{-1}$ (Cu: $0.6 \times 10^6\ \Omega^{-1}cm^{-1}$)**
    π-electrons act like photons – mobility is determined by graphene quality
  - ***Thermal conductivity*: 5000 $Wm^{-1}K^{-1}$ (Cu: 401 $Wm^{-1}K^{-1}$)**
  - **Strongest material ever discovered: Tensile strength ~ 130 GPa (steel ~0.4 GPa)**
  - **"Graphene is complicated and expensive to make in large sheets" *Nature*, Nov. 20, 3013**

Results: XPS Analysis

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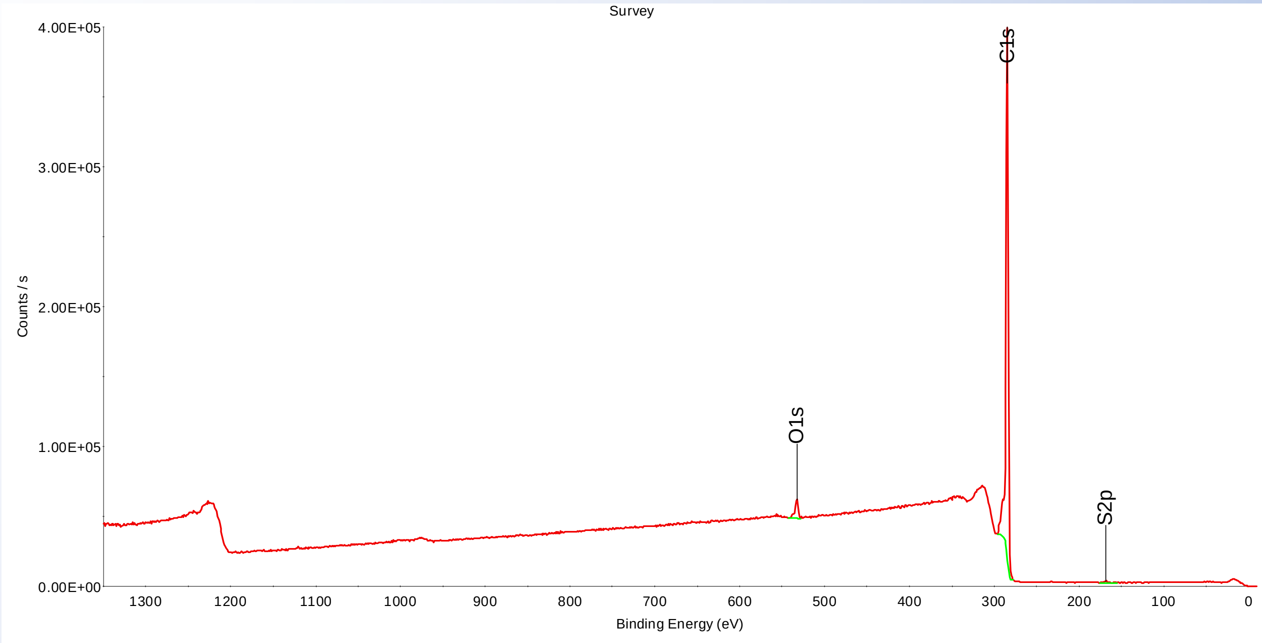

XPS survey scan of a representative graphene sample showing the relative presence of carbon (C1s peak) and oxygen (O1s peak).

- The carbon content of the graphene sheets ranges from 96% to 98.5% while the oxygen content is in the range of 1.4% to 3%.
- The carbon and oxygen content of the unreduced graphene oxide ranges between 66% to 70% and 29% to 32% respectively.

Results: Raman Spectrum

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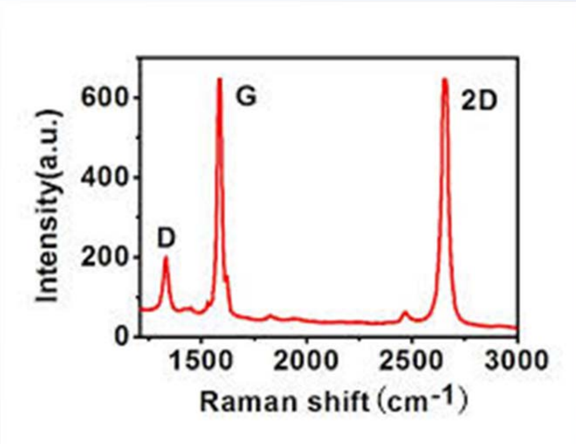
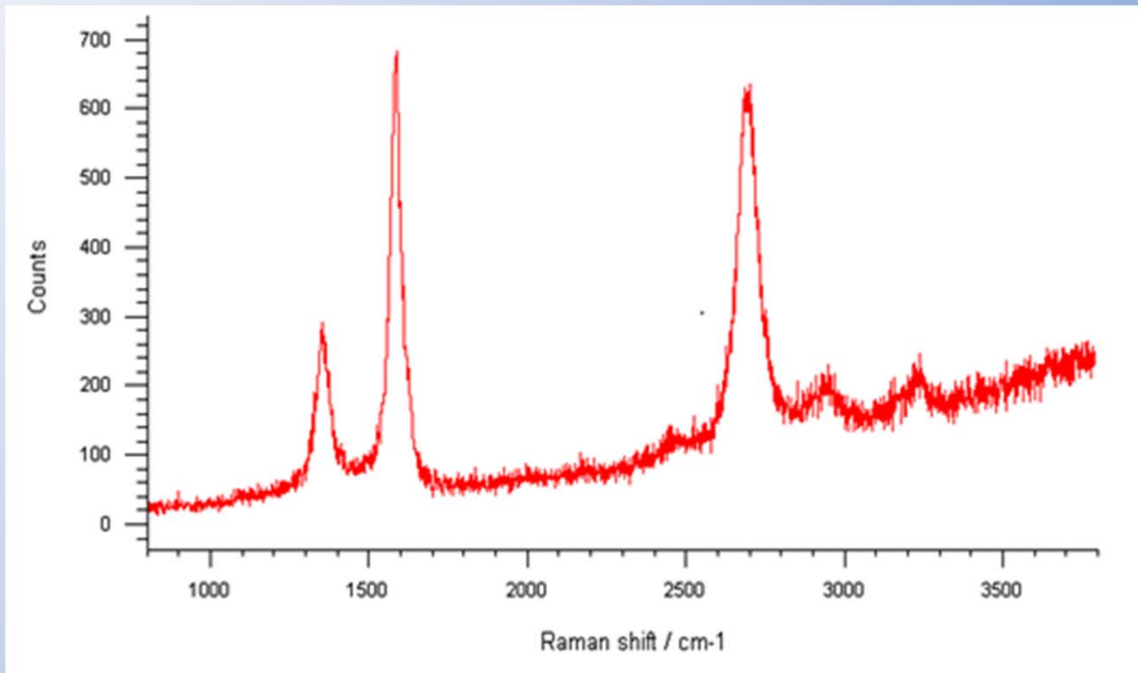


Ideal Raman spectrum of graphene.



Actual Raman spectrum of a graphene sheet.

- Raman spectrum of the graphene sheet shows the *G*, 2*D*, and *D+D"* bands that are characteristic of graphene, as well as two Raman-forbidden bands, *D* and *D+D'*, that arise from defects.
- Defects could be edges, functional groups, or structural disorders

Results: Ultracapacitor Performance

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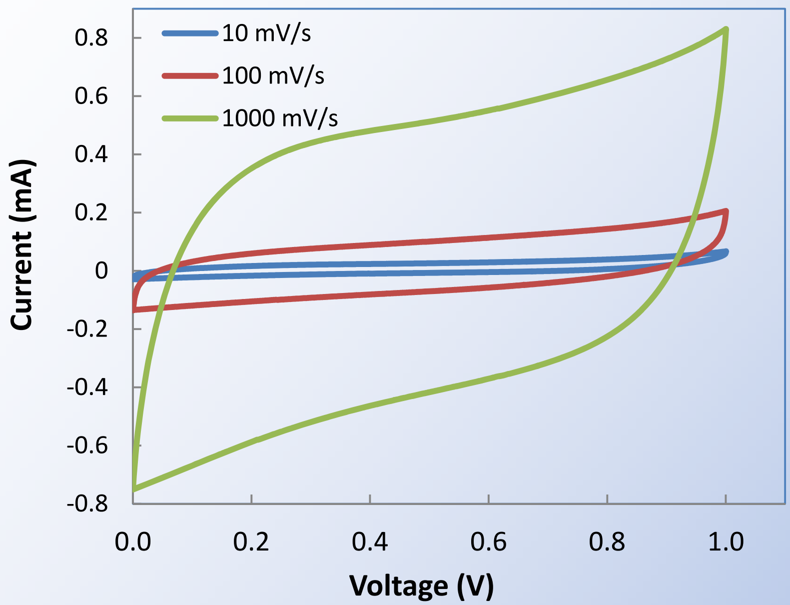
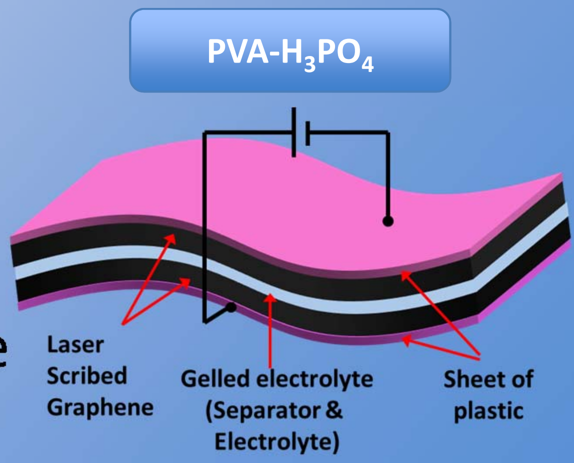


Cyclic voltammetry profiles for parallel-plate graphene capacitor prototypes.



- Cyclic voltammetry (CV) measurements of parallel-plate capacitors made with our graphene sheets were performed.
- CV profiles for 10, 100, and 1000 mV/s indicate that the charge/discharge rates are good but need to be improved (**need to update this**).

Ultracapacitor

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Current Density (mA/cm^3)	dV/dt (V/s)	Capacitance (F)	Volumetric Capacitance (F/cm^3)	Energy Density (Wh/cm^3)
3333.33	-27.968	1.79E-04	1.19E-01	4.87E-06
2666.67	-16.082	2.49E-04	1.66E-01	9.17E-06
1333.33	-4.9644	4.03E-04	2.69E-01	2.47E-05
666.67	-1.951	5.13E-04	3.42E-01	3.89E-05
533.33	-1.4548	5.50E-04	3.67E-01	4.35E-05
400.00	-0.9818	6.11E-04	4.07E-01	5.03E-05
266.67	-0.5539	7.22E-04	4.81E-01	6.19E-05
133.33	-0.1924	1.04E-03	6.93E-01	9.27E-05
66.67	-0.0593	1.69E-03	1.12E+00	1.53E-04
53.33	-0.0453	1.77E-03	1.18E+00	1.61E-04
40.00	-0.0291	2.06E-03	1.37E+00	1.89E-04
26.67	-0.0161	2.48E-03	1.66E+00	2.29E-04
13.33	-0.0043	4.65E-03	3.10E+00	4.29E-04

- Capacitance and volumetric capacitance values were obtained from galvanostatic curves at different current densities.
- Specific volumetric capacitances were calculated by considering the volume of the active material.
- Energy densities were obtained from cyclic voltammetry measurements.
- Volumetric capacitance reaches 3.1 F/cm^3 at 13.33 mA/cm^3
- Decreases only to 1/3 of its highest value at 133 mA/cm^3 and has a value of 0.1 F/cm^3 at an extremely high current density of 3.3 A/cm^3
- Results are very encouraging and show that we should be able to demonstrate we can achieve the high power and energy densities that would make them feasible for use in aircraft

Tandem Supercapacitors

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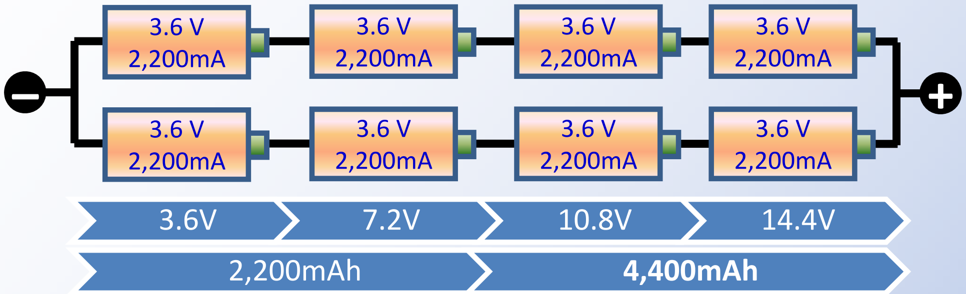

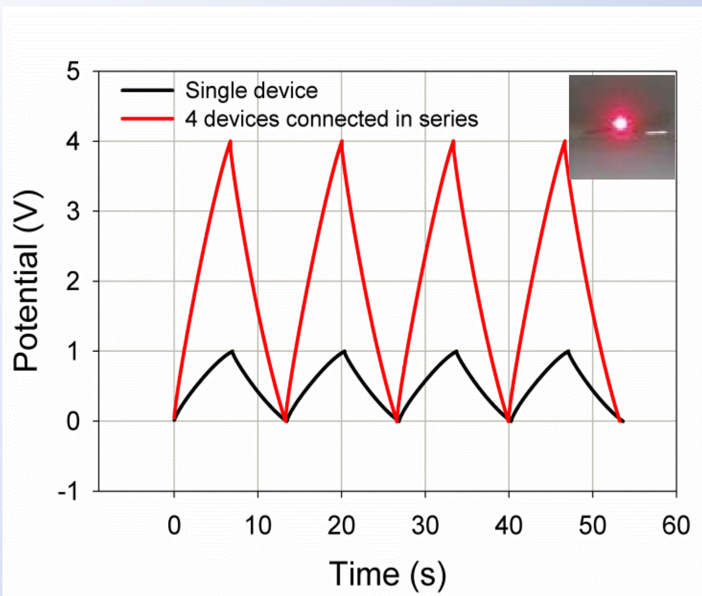

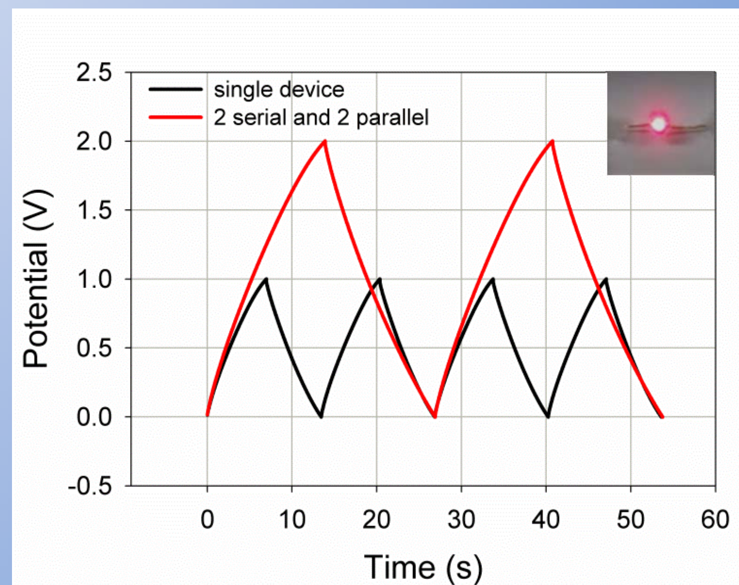

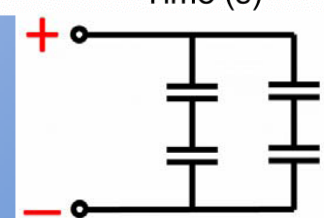

Cycling and Shelf-Life

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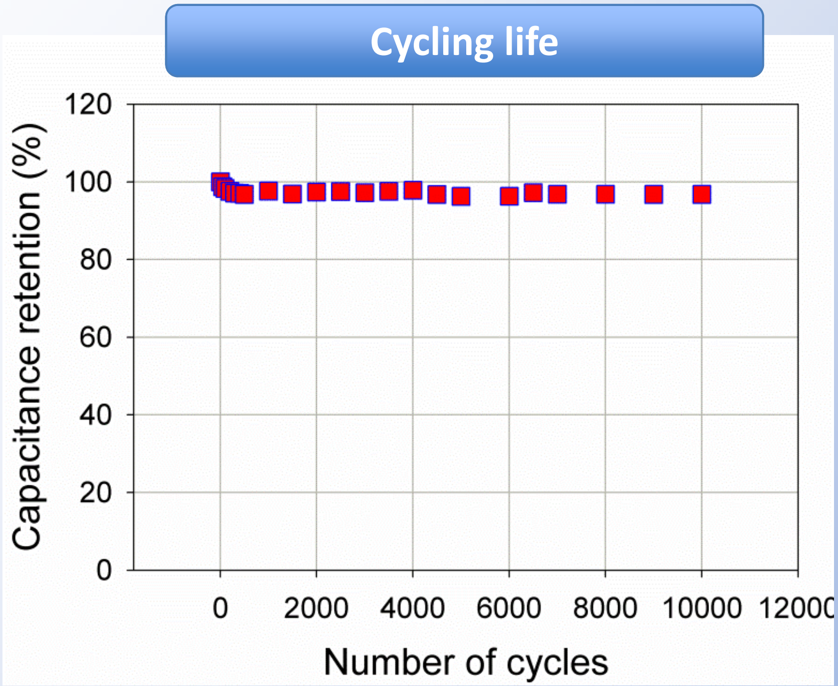

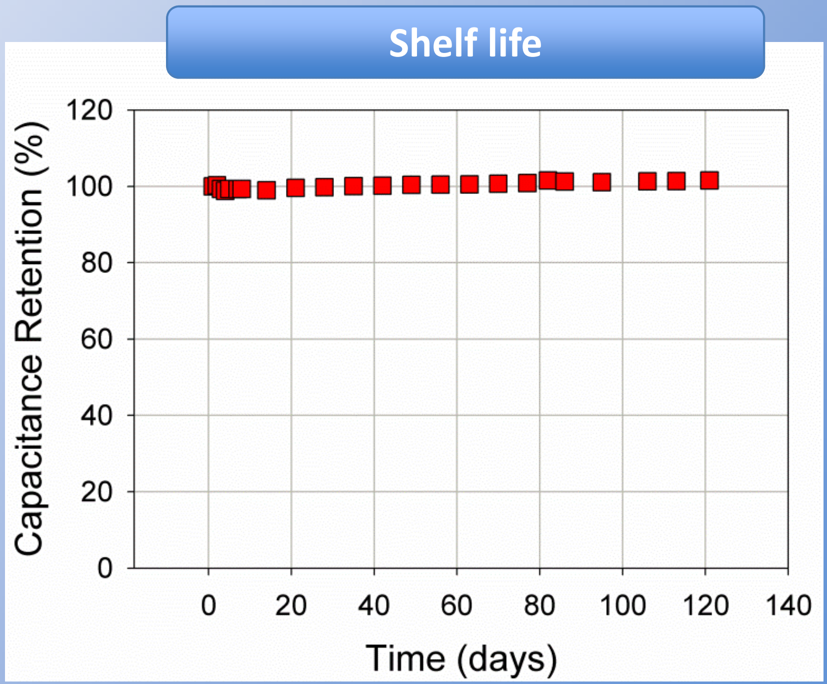

LSG vs. Commercial Supercapacitors

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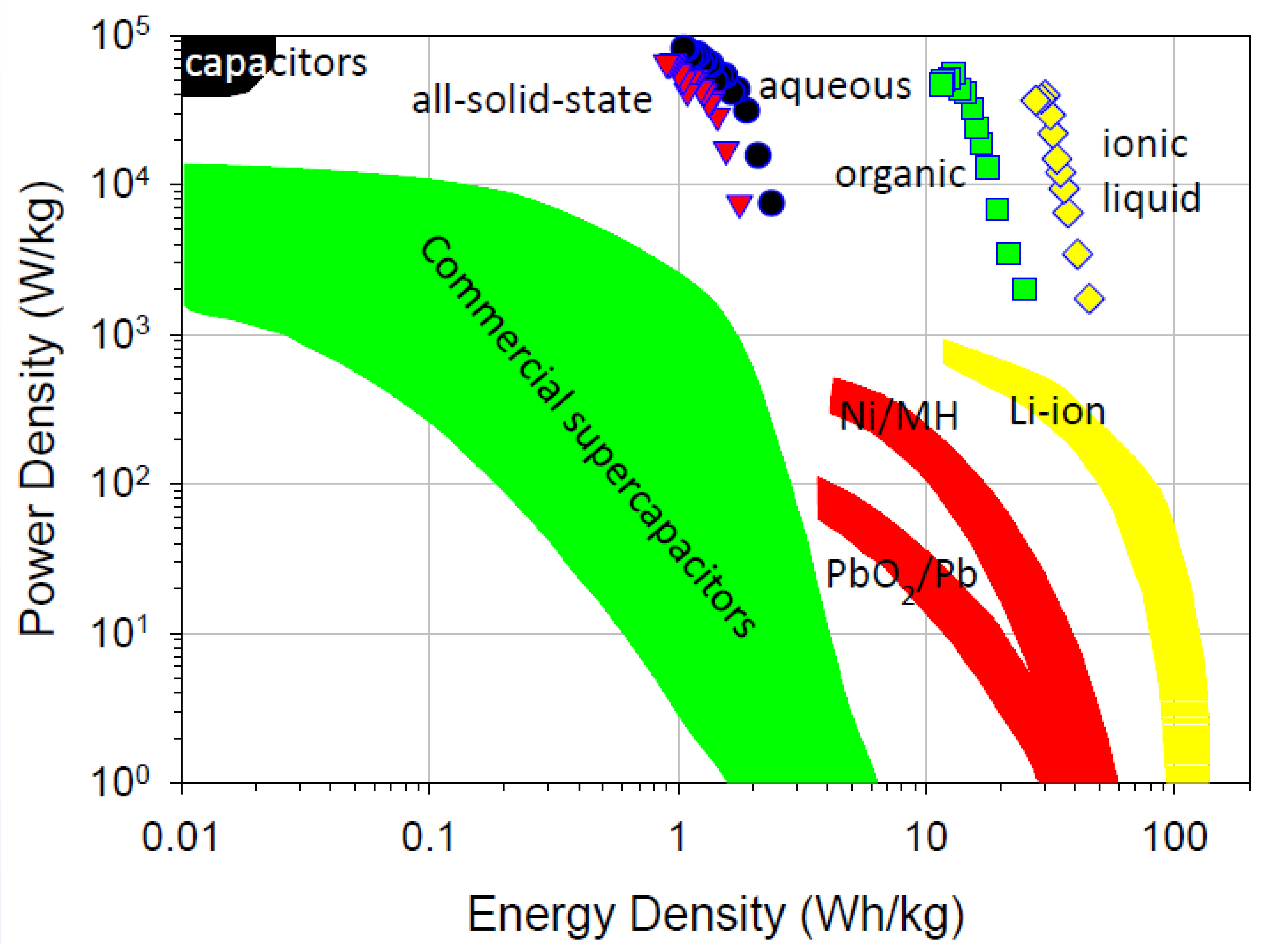

LSG vs. Commercial Supercapacitors

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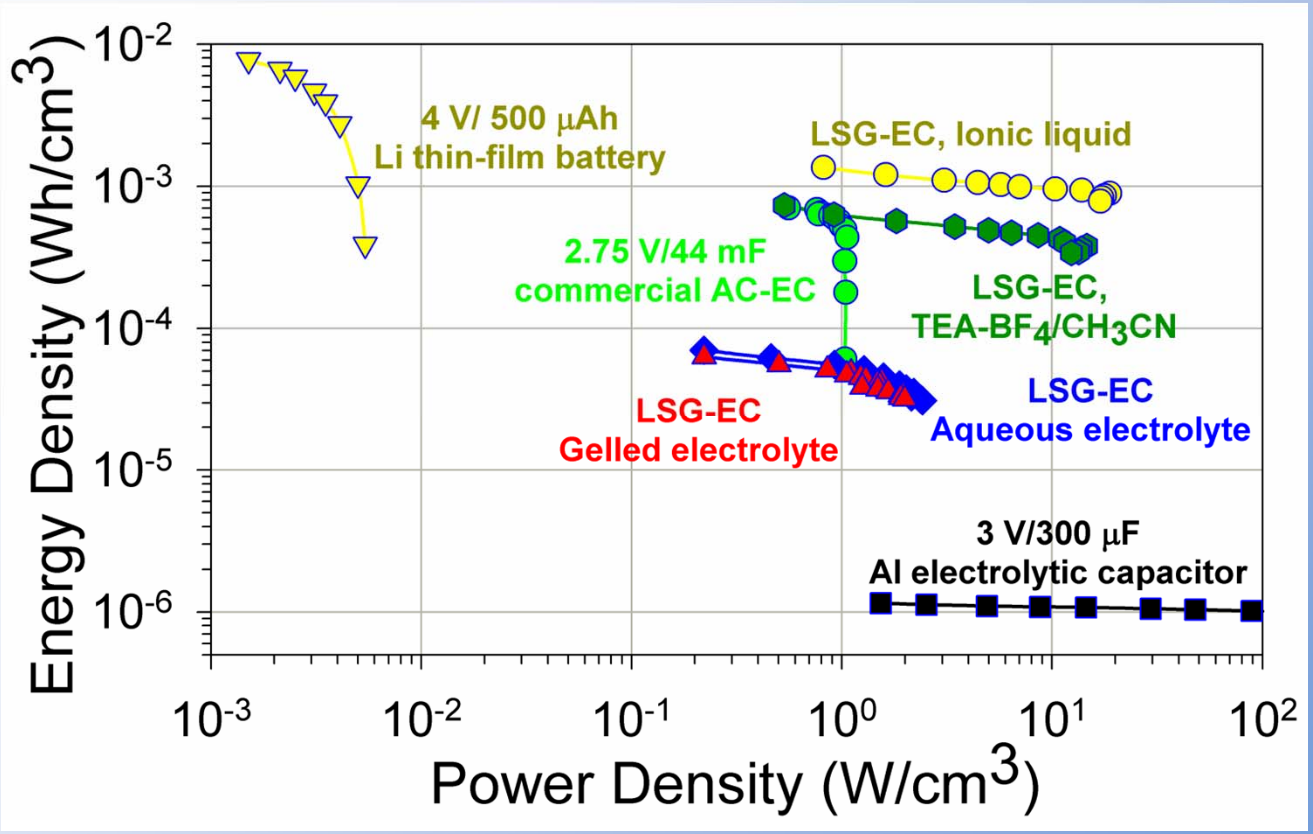

- The plot shows the energy density and power density of the stack for all the devices tested (including current collector, active material, electrolyte and separator).
- Additional features: flexible, lightweight, current collector free and binder free

Distribution/Dissemination

- Graphene-based unltracapacitors for aeronautics applications
  - Invited paper to be presented at the 247th ACS National Meeting, Dallas, TX, March 16-20, 2014