Graphene-Based Ultra-Light Batteries for Aircraft

Project WBS Number: 694478.02.93.02.13.55.76

Investigators: Carlos I. Calle, Ph.D., NASA Kennedy Space Center and Richard B. Kaner, Ph.D., University of California Los Angeles

Team Members: Paul J. Mackey, NASA Kennedy Space Center; Maher El-Kady, Ph.D., University of California, Los Angeles; Michael R. Johansen; Michael D. Hogue, Ph.D., NASA Kennedy Space Center; Lisa Wang, Jee Youn Hwang, University of California, Los Angeles

Purpose

The purpose of this project is to develop a graphene-based battery/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 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

There are two main established methods for the storage and delivery of electrical energy: batteries and electrochemical capacitors. Batteries store energy with electrochemical reactions that produce high energy densities with slow charge/discharge cycles. Electrochemical capacitors store energy in electrochemical double layers that allow for fast charge/discharge cycles but with low energy densities. Batteries are then widely used in applications that require relatively large amounts of energy. Electrochemical capacitors are used in applications that require fast charge/discharge cycles without the need for large amounts of energy, such as electronic devices.

Because of their need for high energy densities, aircraft use batteries rather than capacitors. Most aircraft batteries use nickel cadmium or lead acid chemistries. Lead acid batteries are typically used in light and general aviation aircraft while nickel cadmium batteries are used in larger aircraft and in helicopters [1]. Aircraft manufacturers are beginning to use lithium ion batteries due to their larger capacitances per unit weight. But even these larger capacitance batteries suffer from their low power densities. The performance of lithium ion batteries is mainly controlled by the diffusion of Li ions and by electron conductivity in the electrolyte. Recent approaches to increase their performance involve the use of nano-structured electrodes that provide shorter ion diffusion distances and the introduction of dopants to increase ion transport efficiency. However, stable performance over thousands of charge/discharge cycles has not been achieved [2].

The graphene-based ultracapacitors that we are developing with this project use graphene electrodes in an electrolyte. They retain the high power densities of standard ultracapacitors but, due to the increased surface area of graphene (up to 2630 m^2/g [3]), they achieve energy densities that approach those of the best performing thin-film ion batteries. Fig.1 illustrates the expected performance of our graphene-based ultracapacitors in comparison with the performances of standard ultracapacitors and lithium ion batteries.

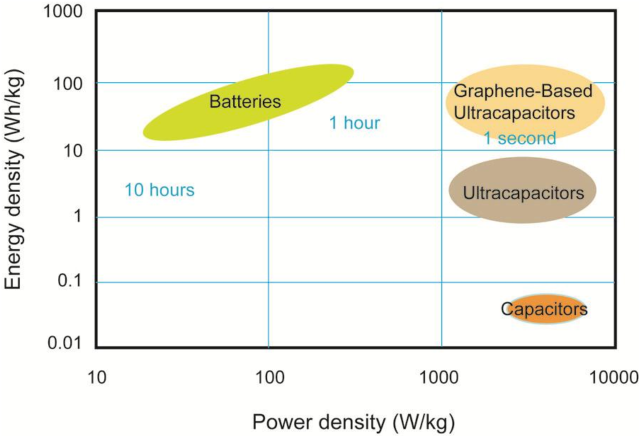

Figure 1. Energy and power density comparison for batteries, conventional ultracapacitors, and the expected performance of graphene-based ultracapacitors. Charging times are shown in blue. (Based on a Ragone plot in [4]).

Construction of graphene-based ultracapacitors requires the production of high quality graphene in sheets large enough to generate suitable electrodes. Several methods for the production of graphene have been developed in recent years. The most promising techniques for the production of high-quality bulk graphene-based devices begin with graphene oxide (GO). Several methods to reduce GO have been developed, including chemical [5], thermal [6], and flash [7] reduction. Not all of these methods produce high quality graphene and the ones that do, use relatively expensive equipment. A new and inexpensive solid state method developed by this proposal's co-investigator at UCLA [3] produces high quality graphene films with a surface area of 1500 m^2/g, which is much larger than that reported for thermally or chemically converted graphene. Oxygen reduction with this method reaches much higher values than the more widely used chemical reduction method. These graphene sheets are mechanically strong, have high electrical conductivity, and can be used directly as electrodes in energy storage devices. This form of graphene is potentially useful for ultracapacitors with remarkable energy and power densities.

We also investigated the use of a pulsed laser to reduce graphene oxide using a technique similar to the method developed by UCLA, but with a substantial decrease in reduction time and an increase in the area of the graphene sheets produced.

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.

Approach

We are reducing graphene oxide to form graphene electrodes for the assembly of our ultracapacitors. We are using the solid state method developed by UCLA using optical drive infrared lasers. We are also producing graphene electrodes with KSC's ultraviolet pulsed laser. The oxygen content of the graphene sheets produced by both methods is determined with X-ray Photoelectron spectroscopy (XPS). The presence of graphene is determined with Raman spectroscopy.

The graphene sheets are then used to assemble thin ultracapacitors using a liquid electrolyte and a separator. Testing of these devices is performed first at KSC using an LCR meter to measure the capacitance and subsequently with cyclic voltammetry at both KSC andUCLA, to characterize the devices.

Accomplishments

We have been able to produce high quality graphene by reducing graphene oxide with the optical drive infrared laser method developed by UCLA as well as with KSC's UV pulsed laser. We have successfully assembled prototype ultracapacitors using our graphene sheets in parallel plate configurations with a gel electrolyte composed of polyvinyl alcohol mixed with water and a concentrated sulfuric acid solution. Testing of these capacitors at UCLA and at KSC included electrical conductivity of the graphene electrodes and electrochemical impedance spectrometry and cyclic voltammetry of the ultracapacitors to determine the values of the capacitances.

Status of Research

Graphene production

A new experimental setup for the reduction of GO based on the UCLA LSG method was designed at the KSC laboratory. This new method uses a diode pumped laser system with tunable power and short wavelengths. After a few months of optimization, the method successfully produced high quality graphene electrodes. This process results in graphene with a reduction level that is superior to traditional methods for the reduction of GO. This low oxygen content is required for building durable supercapacitors.

Graphene sheet characterization

XPS analyses of the graphene sheets that we have produced show that the carbon content of the films 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. Figure 2 shows an XPS survey scan of one of the graphene sheets (sample P65-3A Pt 1) reduced with our UV pulsed laser. It is clear that most of the oxygen was removed.

Raman spectroscopy was also performed on the graphene sheets produced with the optical drive laser and with the UV pulsed laser. The electronic structure of graphene is captured in its Raman spectrum, which evolves with the number of layers [8]. The Raman spectrum of single-layer graphene has very distinct bands or peaks: the *G* peak, located at ~1580 cm^{-1}; the *2D* peak, at ~ 2650 cm^{-1}; a peak at ~2450 cm^{-1} labeled *D+D"*; and the 2*D'* peak at ~3200 cm^{-1}. The 2*D* band is the overtone of the *D* band. This band is due to breathing vibration modes of the six carbon rings and requires a defect for its activation. In addition, the 2*D'* peak is the overtone of the *D'*. The *D'* band is also activated by defects. However, the 2*D* and 2*D'* overtones originate with phonons with opposite wave vectors and as such conserve momentum. Thus, they do not require defects for their activation and are allowed in the Raman spectrum of graphene [9].

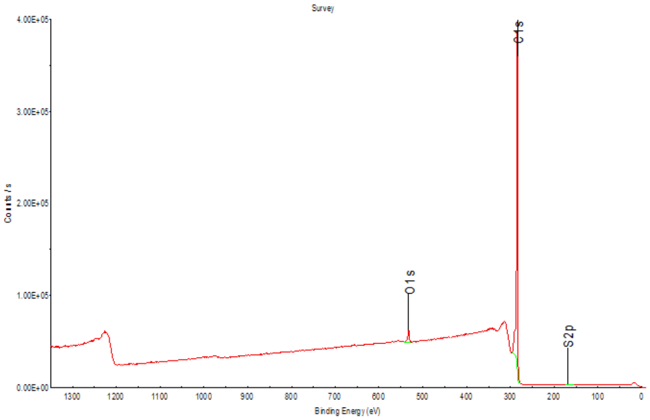

Figure 2. XPS survey scan of sample P65-3A, a representative graphene sample showing the relative presence of carbon (C1s peak) and oxygen (O1s peak).

Figure 3 shows the Raman spectrum of sample P65-3A. This spectrum 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. These defects could be edges, functional groups, or structural disorders [10].

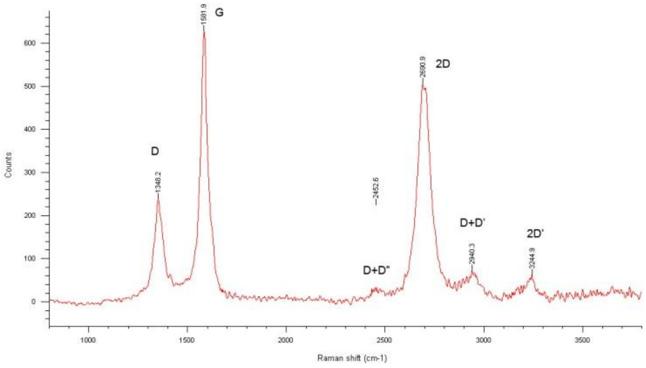

Figure 3. Raman spectrum of a graphene sheet showing the *G*, 2*D*, *D +D”*, and *2D’* bands that are characteristic of graphene, as well as a Raman-forbidden band, *D +D’*, that arises from defects.

Graphene Ultracapacitor Performance

Graphene electrode sheets were made into solid squares for parallel-plate laser-scribed electrochemical capacitors (LSG-EC). Parallel-plate LSG-EC prototypes using a 1.0 M sulfuric acid electrolyte were fabricated and tested at the KSC laboratory. Cyclic voltammetry (CV) measurements of these devices were performed (Fig. 3). These cyclic voltammetry profiles have a fairly rectangular shape, indicative of an efficient capacitor with fast charge/discharge cycles and low equivalent series resistance.

From the CV profiles in Fig. 3, a capacitance of 34 mF and specific capacitance of 29.5 F/g for the button cell LSG-EC were calculated. The energy and power densities were calculated to be 0.37 mWh/cm^3 and 136 mW/cm^3 respectively.

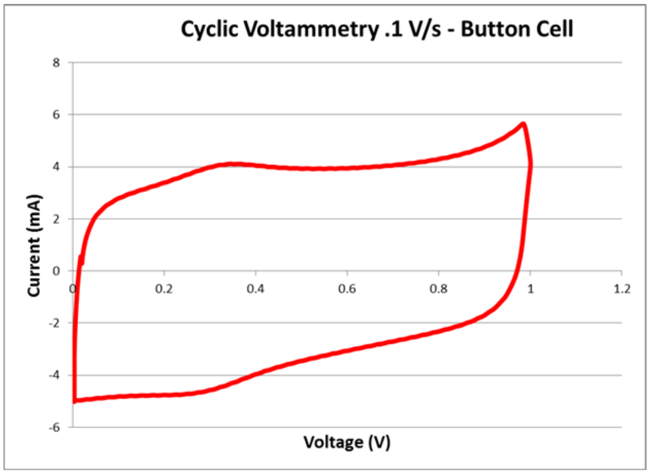

Figure 4. Cyclic voltammetry profile for a button cell graphene capacitor at 100 mV/s scan rate.

LSG-ECs were driven through multiple charge/discharge cycles at the UCLA laboratory. Figure 4 (top) shows that the device loses only about 3% of its capacitance after 10,000 cycles. The shelf life of these devices was also measured. Figure 5 (bottom) shows that the capacitance is retained after 120 days.

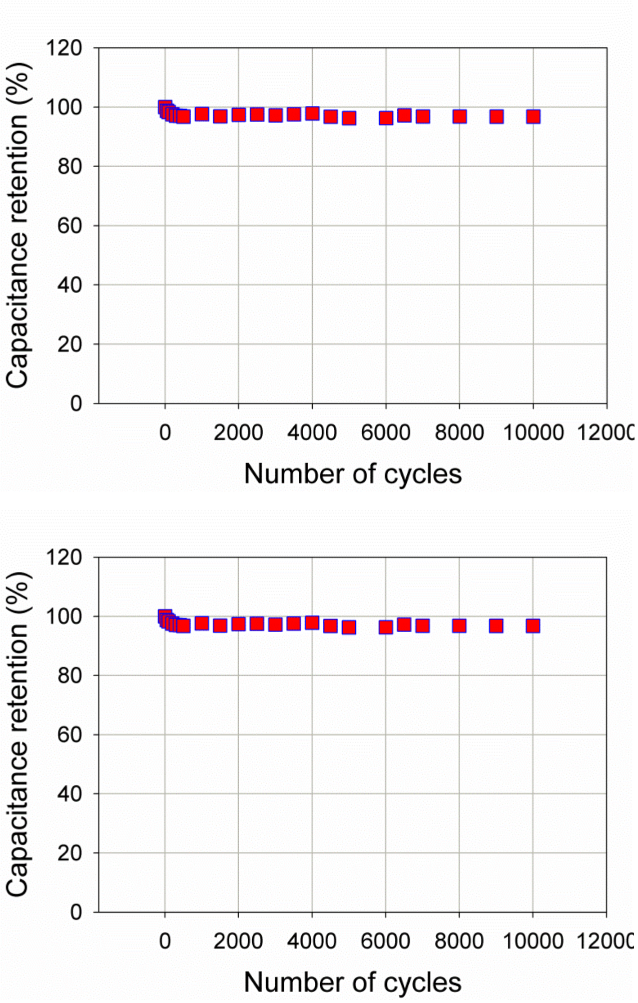

Figure 5. Cycling stability and shelf life of a graphene ultracapacitor.

Energy storage devices usually contain individual cells connected in series, parallel, or series-parallel combinations. Four LSG-ECs with gel electrolytes (with poly(vinyl alcohol) (PVA)-H_3PO_4 polymer) operating at 1.0 V were connected in series at the UCLA laboratory. Galvanostatic charge/discharge curves for the single device and for the series connection operating at the same constant current conditions show that the voltage was increased to 4.0V (Fig. 6, top). In the series-parallel connection, the output voltage and current were both doubled (Fig. 6, bottom).

LSG-ECs with an organic electrolyte commonly used in commercial devices, tetraethylammonium tetrafluoroboate (TEA-BF_4) dissolved in acetonitrile (CH_3CN), were also fabricated and tested at UCLA [3]. These devices showed better performance than the aqueous and gelled electrolytes and reached a voltage of 3V. Finally, we manufactured and tested devices with the room-temperature ionic liquid 1-ethyl-3methylimidazolium tetrafloroborate ($EMIMBF_4$).

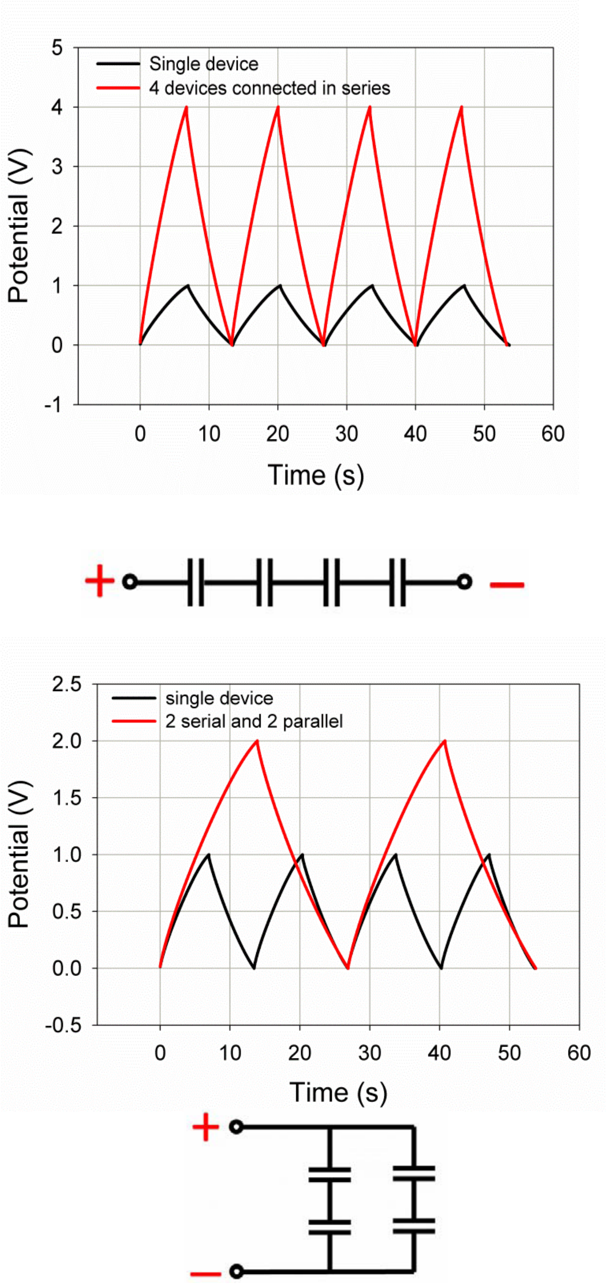

Figure 6. Increasing the output voltage and current with serial and serial/parallel combinations.

A Ragone plot comparing the performance of the different devices that were manufactured and tested with that of commercial ultracapacitors is shown in Fig. 7. The commercial devices are a 2.75V, 44 mF activated carbon electrochemical capacitor (AC-EC); a 500-µAh thin film lithium-ion battery; and a 3V, 300 µF aluminum electrolytic capacitor. The Ragone plot shows that the LSG-EC with the ionic liquid electrolyte has volumetric energy densities as high as 1.36 mWh/cm^3, twice as high as that of the commercial AC-EC. With these ionic liquid electrolytes, our devices also have power densities of about 20 W/cm^3, three orders of magnitude higher than the thin film lithium ion battery.

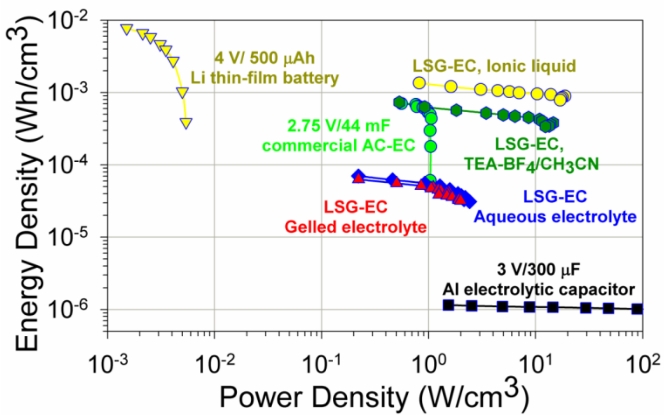

Figure 7. Ragone plot, showing the volumetric energy density vs. volumetric power density for four types of laser-scribed graphene electrochemical capacitors (LSG-EC) with different electrolytes (aqueous, gelled, organic, and ionic liquid) and for three commercial devices [3].

These results are very encouraging and show that we should be able to demonstrate that our graphene-based ultracapacitors can achieve the high power and energy densities that would make them feasible for use in aircraft.

Current TRL: 4.

Applicable NASA Programs/Projects

There has been a great deal of interest on this technology from the NASA ISRU project, the NASA Game Changing Development Program, and the NASA Mars Exploration Program.

Publications and Patent Applications

New Technology Report (NTR) entitled “Method for the Production of Graphene for Use in Graphene-Based Ultracapacitors for Space Applications” was filed on August 23, 2013. A second NTR entitled “Optical Method for the production of Long Graphene Sheets of Use in Graphene-Based Ultracapacitors” was filed on March 24, 2014. A papers entitled “Graphene-based ultracapacitors for aeronautics applications” was submitted to the Two-Dimensional Materials for Energy and Fuel of the Division of Energy and Fields at the 247th American Chemical Society Meeting in Dallas, TX, March 2014. Additional papers describing our work will be submitted to refereed journals.

References

1. 1.N. Thomas, http://www.aviationpros.com/article/10371585/aircraft-batteries, September 17, 2010
2. R. Mukherjee et al, *ACS Nano*, 2012, 6(9), 7667-7878B
3. El-Kady, M.F., V. Strong, S. Dublin, and R.B. Kaner, *Science* 335 (2012) 1326-1330

4. Chen, *Energy Storage Workshop*, Santa Clara, CA, May 7, 2010
5. Stankovich, S. *et al., J. Mater. Chem*. 16 (2006) 155-158
6. McAllister, M.J. *et al*., *Chem. Mater.* 19 (2007) 43-96-4404
7. Gilje, S. *et al*., *Adv. Mater.* 22 (2010) 419-423
8. A.C. Ferrari *et al*., *Physical Review Letters*, (2006) 97, 187401
9. J. Hwang et al., *Nanotechnology* 21 (2010) 465705
10. A.C. Ferrari and D.M. Basko, *Nature Nanotechnolgy* 8 (2013) 235-246