Graphene-based Systems for Energy Storage

Carlos I. Calle, Ph.D.
NASA Kennedy Space Center

Paul J. Mackey
Michael R. Johansen
James Phillips III
Michael Hogue, Ph.D.
NASA Kennedy Space Center

Richard B. Kaner, Ph.D., Maher El-Kady, Ph.D.,
University of California Los Angeles
• Every exploration plan calls for a sustainable exploration architecture.
• Living in space requires supplies of energy, air, water, and food
• We can initially supply our habitat with those commodities, but we must have systems able to regenerate some of those essential items.
Current Spacecraft Batteries

Hubble Space Telescope

- Nickel-hydrogen (Ni-H$_2$)
- Charge-use cycle of 97 minutes
- Reliable
- Deep discharge capability
Evolving Technology

Curiosity/Mars Science Laboratory

- Lithium-ion
- Charge-use cycle:
  - multiple times per day
- Peak power demands exceed the Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) power source
The MSL rover uses a Multi-Mission Radioisotope Thermoelectric Generator (MMRTG). To augment the MMRTG, a rechargeable Li-ion battery is being used.

**Li-ion Battery Functions to Augment MMRTG throughout Mission**
- Provide power during launch
- Assist thermal batteries during entry, descent, and landing (EDL)
- Support power loads on the Mars surface that exceed the Multi-Mission Radioisotope Thermoelectric Generator (MMRTG)

**Mission Requirements for the Li-ion Battery**
- Ability to be stored for 6-12 months
- Provide 920 Wh with $V > 25$ V, $i_{\text{max}} = 22$ A during launch
- Survive cruise phase at 50-75% State of charge (SOG), $-20^\circ\text{C} \leq T \leq +40^\circ\text{C}$
- Support backup power: 30A pulses at 100% SOC
- Support EDL loads: 25A pulses
- Augment MMRTG during surface operations for at least 670 sols

**Operational Requirements on the Mars Surface**
- Charge and discharge at $-20^\circ\text{C} \leq T \leq +30^\circ\text{C}$
- Operate for $>2000$ cycles with depth-of-charge $\leq 45$
- Operating voltage $\geq 25$ V
Potential Future Missions

- Future missions will require higher energy and power density to enable:
  - High power robotics
  - In-Situ Resource Utilization (ISRU)
  - Exploration

Space Exploration Vehicle (SEV)  
Resource Prospector  
RASSOR
Future Power Requirements

- Higher specific energy rechargeables
  - long life (500 Wh/kg, 5000 cycles)
  - low temperature (200 Wh/kg, -100°C)
  - High temperature (450°C)
- High specific energy primary storage
  - low temperature (1000 Wh/kg, -160°C)
  - high temperature (1000 Wh/kg, 450°C)
- Green battery materials and processes
- Advanced electronics to implement optimized charge methodologies to enhance life and safety.
New Materials

• New nanomaterials offer possibilities for new technologies
• Graphene, a one-atom-thick, two-dimensional array of carbon atoms is one of the most promising materials
What is Graphene?

- 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*: \(10^6\ \Omega^{-1}\text{cm}^{-1}\) (Cu: \(0.6 \times 10^6\ \Omega^{-1}\text{cm}^{-1}\))
    - \(\pi\)-electrons act like photons – mobility is determined by graphene quality
  - *Thermal conductivity*: \(5000\ \text{Wm}^{-1}\text{K}^{-1}\) (Cu: \(401\ \text{Wm}^{-1}\text{K}^{-1}\))
  - Strongest material ever discovered: Tensile strength \(\sim 130\ \text{GPa}\) (steel \(\sim 0.4\ \text{GPa}\))
  - “Graphene is complicated and expensive to make in large sheets” *Nature*, Nov. 20, 2013
The Innovation

• 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 m²/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.

Theoretical surface area = 2630 m²/g
Laser Scribed Graphene

• UCLA and NASA: Use of laser to reduce Graphene Oxide
  • Exfoliates layers while removing oxygen
  • Result is a large surface of area of graphene crystals

Picture credit: Rachel E Cox, NASA
LaserScribe: Graphene in a DVD

NASA Kennedy Space Center

780 nm laser

graphite oxide film

laser scribed graphene film

www.lightscribe.com
Our Results: XPS Analysis

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%.

In comparison, more widely used chemical reduction methods reduce oxygen content to 10% or higher. Our laser reduction method produces a more pure graphene sample.

The carbon and oxygen content of the unreduced graphene oxide ranges between 66% to 70% and 29% to 32% respectively.

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

Raman spectrum of the graphene sheet shows the \( G, 2D, D+D'' \), and \( 2D' \) bands that are characteristic of graphene, as well as a Raman-forbidden band, \( D+D' \), that arises from defects.

- Defects could be edges, functional groups, or structural disorders.
Problem: Achieving both high energy and high power density
Solution: Electrodes with high surface area and high conductivity

HEV = hybrid electric vehicles
Expected Performance of Graphene devices

Graphene-based ultracapacitors:
- High power densities
- High energy densities

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

Making graphene supercapacitors is as easy as burning a DVD.

1. DVD disc
2. Apply GO film supported on flexible substrate
3. LightScribe in a computerized DVD drive
4. Peel off LSG film

- Substrate
- LSG
- Separator & Electrolyte
High-Performance Laser Scribed Graphene Electrodes

<table>
<thead>
<tr>
<th></th>
<th>Activated Carbon</th>
<th>LSG</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity (S/m)</td>
<td>10-100</td>
<td>1740</td>
<td>High power density</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>1000-2000 (micropores)</td>
<td>1520 (accessible)</td>
<td>High energy density</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>Powder</td>
<td>Flexible electrodes</td>
<td>Flexible devices</td>
</tr>
<tr>
<td>Binders and current collector</td>
<td>Yes</td>
<td>No</td>
<td>Simple fabrication</td>
</tr>
</tbody>
</table>
Need for Flexible Energy Storage

LG Electronic Newspaper
Flexible keyboard
Wearable electronics (ECG patch)
Flexible polymer solar cell
Samsung flexible AMOLED display
Flexible, All-Solid State Supercapacitors

PVA-H$_3$PO$_4$

Laser Scribed Graphene  Gelled electrolyte (Separator & Electrolyte)  Sheet of plastic
Tandem Supercapacitors

- Single device
- 4 devices connected in series

- Single device
- 2 serial and 2 parallel
Cycling and Shelf-Life

**Cycling life**
- Capacitance retention (%)
- Number of cycles

**Shelf life**
- Capacitance retention (%)
- Time (days)

Slide courtesy of UCLA, Kaner Laboratory
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
Impact of the Innovation

- Commercial ultracapacitors are currently being used in transportation. A fleet of buses near Shanghai has been running on ultracapacitors for the past several years. Only disadvantage: frequent stops due to low energy densities.

- Graphene-based ultracapacitors promise energy densities greater than existing commercial electrochemical ultracapacitors by an order of magnitude. They also have greater power densities than lithium-ion batteries by an order of magnitude.

- 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.

- A robust, lightweight, flexible, thin, and inexpensive energy storage device with energy and power densities superior to those of state-of-the-art energy storage devices 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.
Application to Space

• Higher power density will enable a new class of operations

• Potential for much wider temperature operation: carbon melting point (4900K)

• Increased safety-margin due to reduced fire and toxicity risk

• In-situ resource available from regolith or waste stream
Next Steps

- Increase in voltage produces a substantial increase in the energy density of a supercapacitor \( E = \frac{1}{2} CV^2 \)
- Investigate new solvents and electrolytes with higher ion conductivity that would yield voltages suitable for aeronautics applications
- Investigate combinations of these electrolytes for higher performance
- Scale up graphene sheet production with our laser system
- Build prototypes to demonstrate feasibility of graphene-based ultracapacitors for aeronautics applications
III. Filtration Systems

• Filtration Systems for ISRU:
• Living off the Land: ISRU-
  Production of
  – mission consumables
  – construction
  – manufacturing and repair
  – Energy and utilities
• Production of oxygen, methane, and water from the Martian atmosphere requires dust removal
• Electrostatic Precipitator capable of working at 1/100 atm
Graphene Oxide Filters for Liquids and Gases

• Andre Geim at the University of Manchester showed that membranes of stacked graphene oxide (GO) sheets are impermeable to all gases and vapors except for water.
• The graphene-oxide sheets are arranged in such a way that there is room for only one layer of water molecules.
• In the absence of water, however, the capillaries shrink and do not let anything through, thus making the material impermeable to everything but water.
GO Filters for Space

• GO membranes immersed in water block all molecules or ions with a hydrated size larger than 9 Å.

• Ions pass through the membrane 1000 times faster than expected by diffusion

• Capillaries between graphene oxide flakes act as powerful vacuum cleaners

• We are looking at its feasibility for space applications
In Summary

• Graphene offers exciting possibilities for future space applications

• We are taking advantage of its properties to develop technologies for
  – High energy density/Power density energy storage devices that are flexible and safe
  – Filters for space habitats
Acknowledgments

• Dra. Gabriela Karina Pedraza-Basulto
  Profesor-Investigador
  Facultad de Ingeniería y Tecnología
  Universidad Autónoma del Carmen

• Dr. José Luis Rullan
  Director
  Facultad de Ingeniería y Tecnología
  Universidad Autónoma del Carmen

Thank you!