Graphene-based Systems for Energy Storage

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• 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.
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 \( V > 25 \text{ V}, \ i_{\text{max}} = 22 \text{ A} \) 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 \( \geq 25 \text{ V} \)
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 m²/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 ~ 130 GPa (steel ~0.4 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.
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

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
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

Current (mA)
Potential (V)

0° 30° 60° 90° 120° 150° 180°

device
Bending angle
Tandem Supercapacitors
Cycling and Shelf-Life

Cycling life

![Cycling life graph]

Shelf life

![Shelf life graph]

Slide courtesy of UCLA, Kaner Laboratory
Comparison of LSG, AC, Thin-film Li

- 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

Concept for an oxygen and fuel production plant
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
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Thank you!