



NASA Kennedy Space Center

# Graphene-based Filters and Supercapacitors for Space and Aeronautical Applications

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



# What is Graphene?

NASA Kennedy Space Center

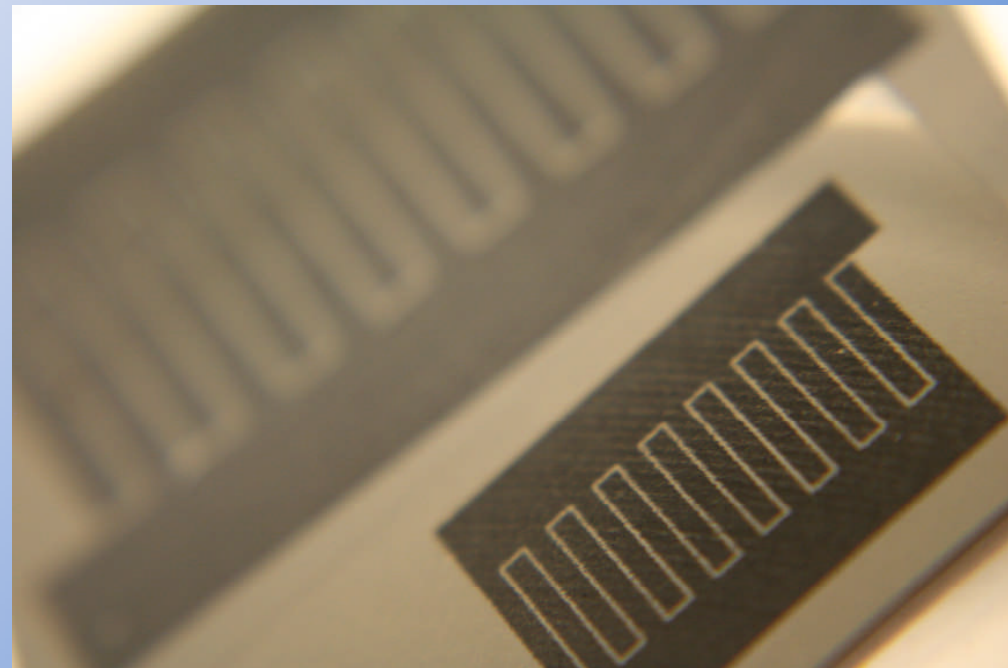
- **Graphene is a revolutionary new allotrope of carbon (a single atomic layer of graphite) with extraordinary properties:**
  - ***Surface area:* 2630 m<sup>2</sup>/g**
  - ***Electrical conductivity:* 10<sup>6</sup> Ω<sup>-1</sup>cm<sup>-1</sup> (Cu: 0.6x10<sup>6</sup> Ω<sup>-1</sup>cm<sup>-1</sup>)**  
π-electrons act like photons – mobility is determined by graphene quality
  - ***Thermal conductivity:* 5000 Wm<sup>-1</sup>K<sup>-1</sup> (Cu: 401 Wm<sup>-1</sup>K<sup>-1</sup>)**
  - **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**



# Laser Scribed Graphene

NASA Kennedy Space Center

- 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

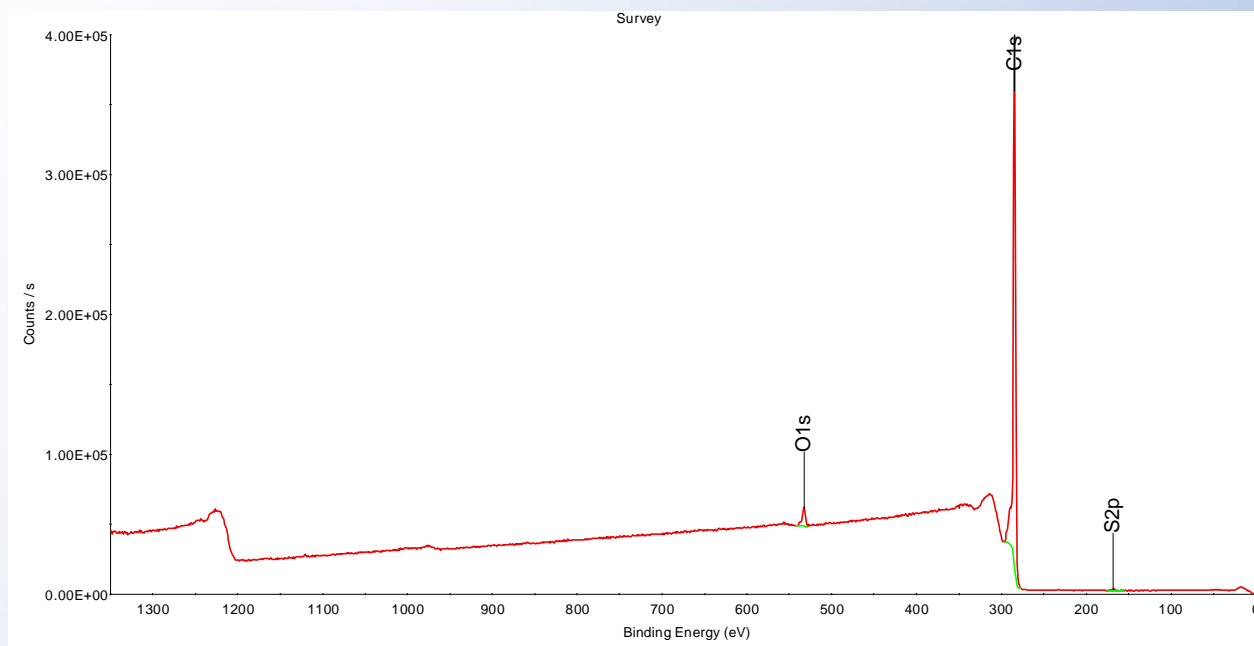


Picture credit: Rachel E Cox, NASA



# Our Results: XPS Analysis

NASA Kennedy Space Center



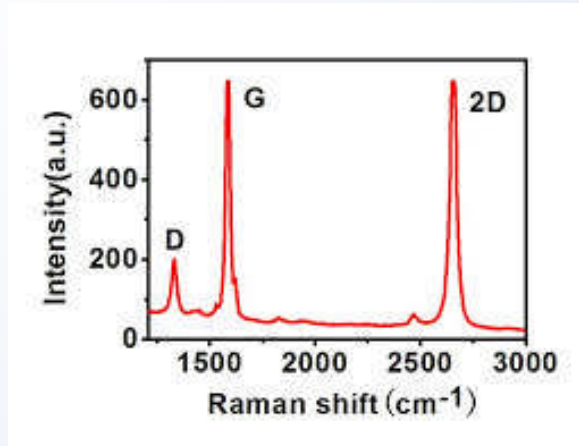
XPS survey scan of a representative graphene sample showing the relative presence of carbon (C1s peak) and oxygen (O1s peak).

- 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%.
- 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.

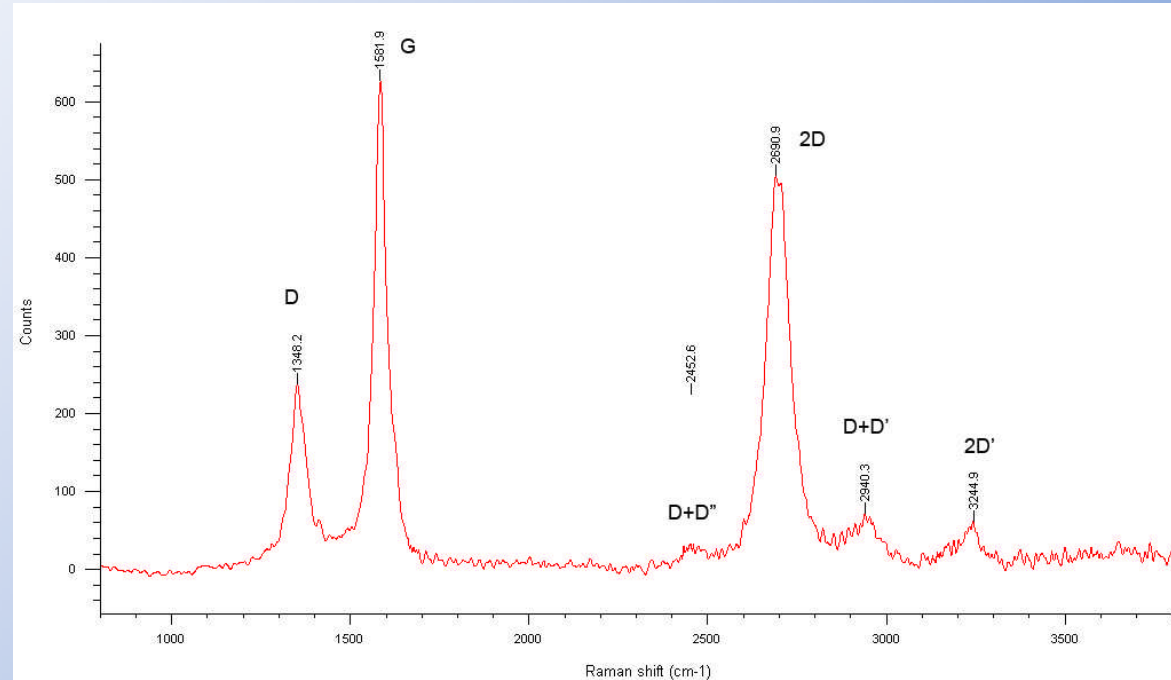


# Results: Raman Spectrum

NASA Kennedy Space Center



Ideal Raman spectrum of graphene.



Actual Raman spectrum of a graphene sheet.

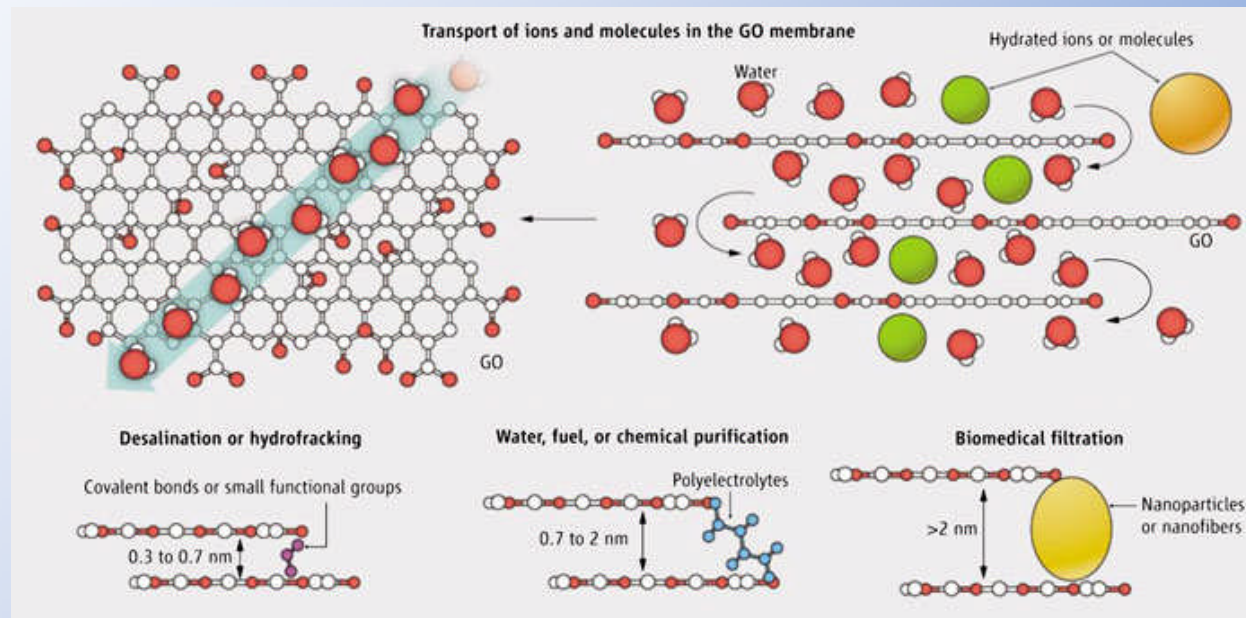
- Raman spectrum of the graphene sheet shows the  $G$ ,  $2D$ ,  $D+D''$ , and  $2D'$  bands that are characteristic of graphene, as well as a Raman-forbidden band,  $D+D'$ , that arises from defects.
- Defects could be edges, functional groups, or structural disorders



# Graphene Oxide Filters for Space

NASA Kennedy Space Center

- 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.



Water and small-sized ions and molecules permeate super fast in the graphene-oxide membrane, but larger species are blocked. The size of the membrane mesh can be tuned by adjusting the nanochannel size. (Courtesy: *Science*)



# GO Filters for Space

NASA Kennedy Space Center

- 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



# Energy Storage in Space

NASA Kennedy Space Center

- Desirable characteristics
  - High energy density
  - Stable, Reliable, Safe
  - Wide operating temperature
  - Rapid recharge







# Current Missions

NASA Kennedy Space Center

## Hubble



Nickel-hydrogen (Ni-H<sub>2</sub>)

Charge-use cycle of  
97 minutes

Reliable

Deep discharge capability



# Evolving Technology

NASA Kennedy Space Center

## Curiosity/Mars Science Laboratory



Lithium

Charge-use cycle  
multiple times per day

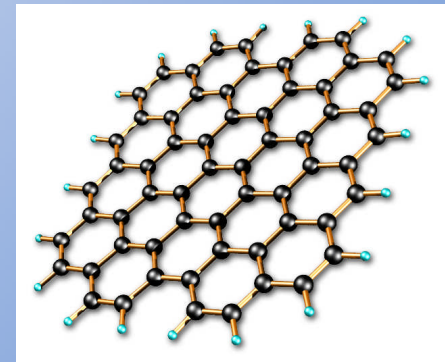
Peak power demands  
exceed MMRTG power  
Source



# The Innovation

NASA Kennedy Space Center

- 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 ( $2,600 \text{ m}^2/\text{g}$ ) 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.





# Impact of the Innovation

NASA Kennedy Space Center

- 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.





# Background

NASA Kennedy Space Center

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

NASA Kennedy Space Center

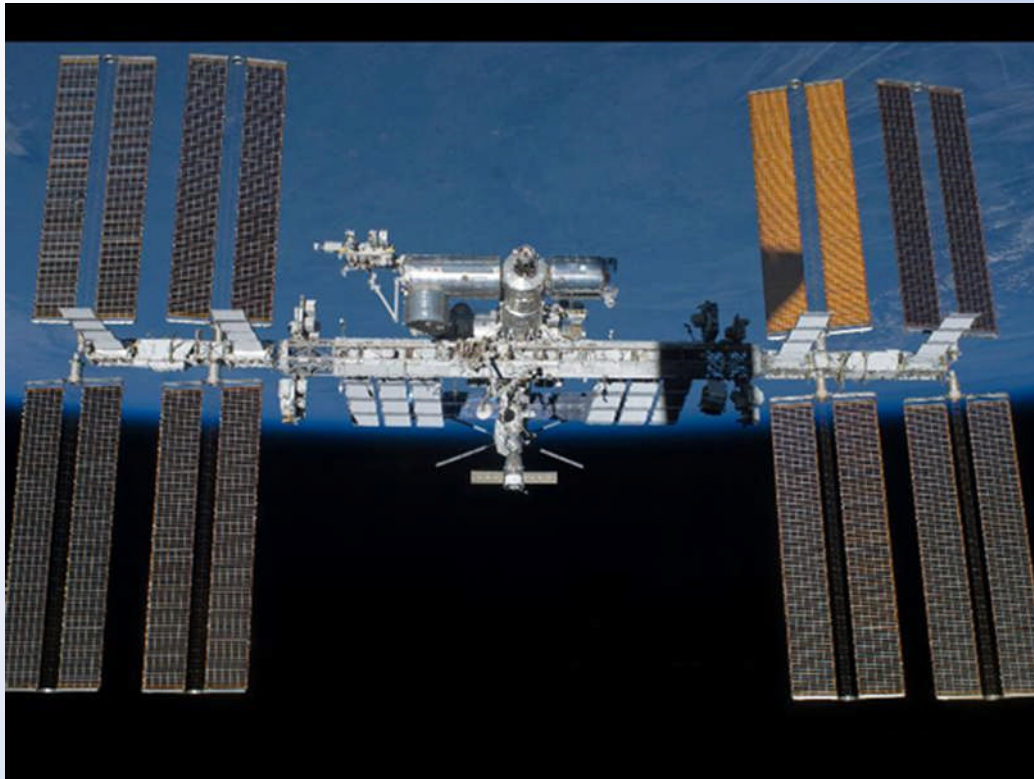
- General Aviation and Light aircraft → Lead acid batteries
- Larger aircraft and helicopters → Nickel cadmium batteries
- Aircraft manufacturers are beginning to use Lithium Ion batteries due to their larger capacitances per unit weight.
  - Li-ion batteries still have low power densities
  - Performance 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.





# International Space Station

NASA Kennedy Space Center



Nickel-hydrogen (Ni-H<sub>2</sub>)

Charge-use cycle of  
90 minutes

Expected replacement to  
lithium in 2017

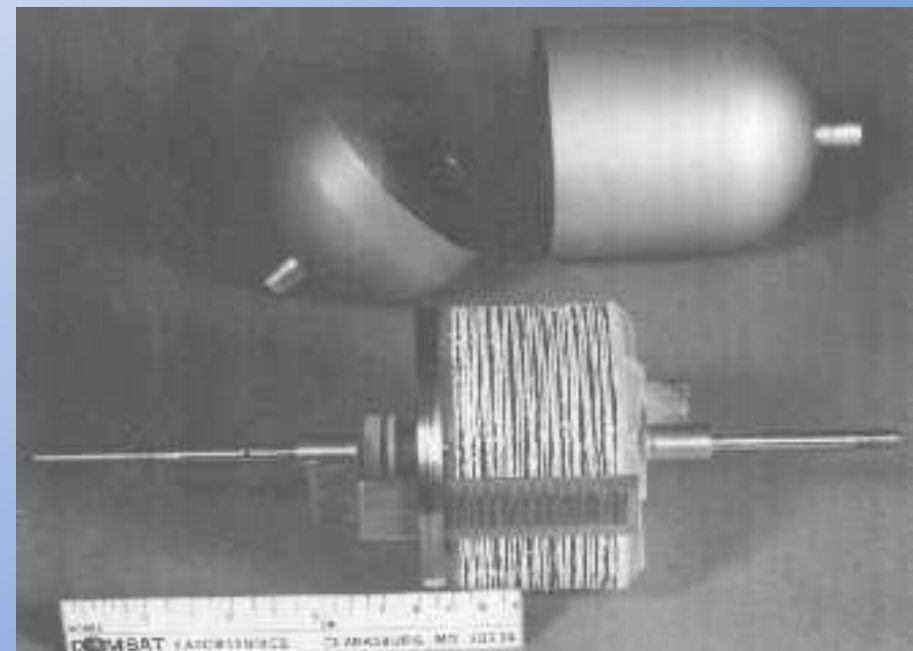
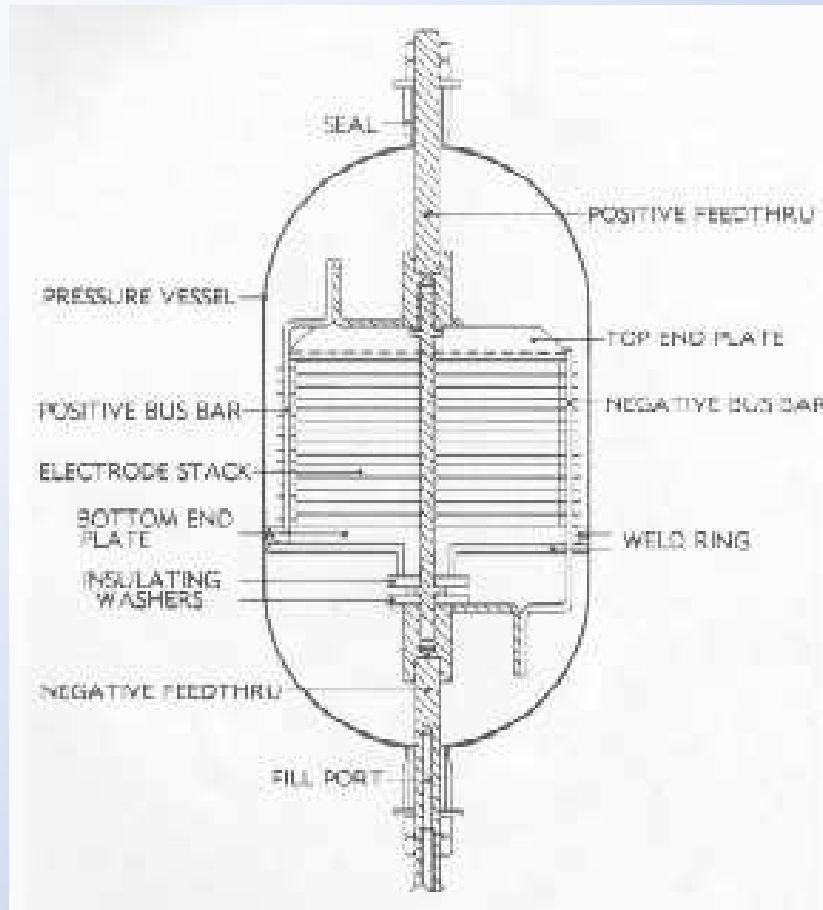
One lithium ORU to  
replace two nickel-  
hydrogen ORU's



# ISS Batteries: Nickel-Hydrogen Batteries

NASA Kennedy Space Center

- The complex Electric Power System (EPS) onboard the International Space Station (ISS) provides all the power vital for the continuous, reliable operation of the spacecraft.
- Actually generate hydrogen gas during charge and use up the hydrogen gas during discharge. The hydrogen pressures inside the ISS batteries can reach 850 psi. That's why the battery cells are contained in pressure vessels.



Individual Battery Cell (diagram and photo)





# NiH<sub>2</sub> Advantages

- High Specific Energy (60 Wh/kg)
- Long life cycle: over 40,000 cycles at 40% Depth of Discharge (DOD) for LEO applications
- Long lifetime in orbit - over 15 years

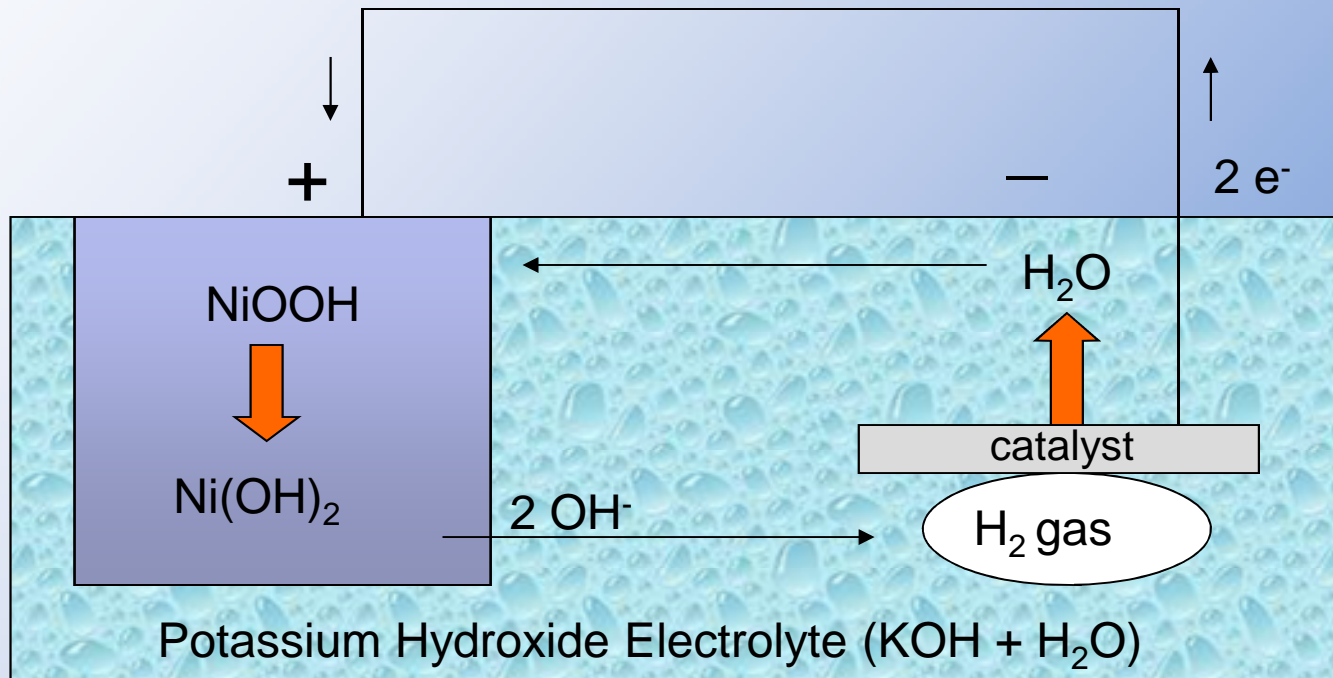


# Ni-H<sub>2</sub> Batteries

NASA Kennedy Space Center

They work like a Ni-Cad at the nickel (positive) electrode and a fuel cell at the hydrogen (negative) electrode.

## Discharge (consuming hydrogen gas)

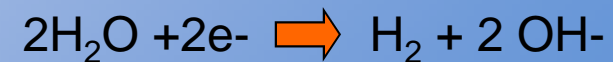
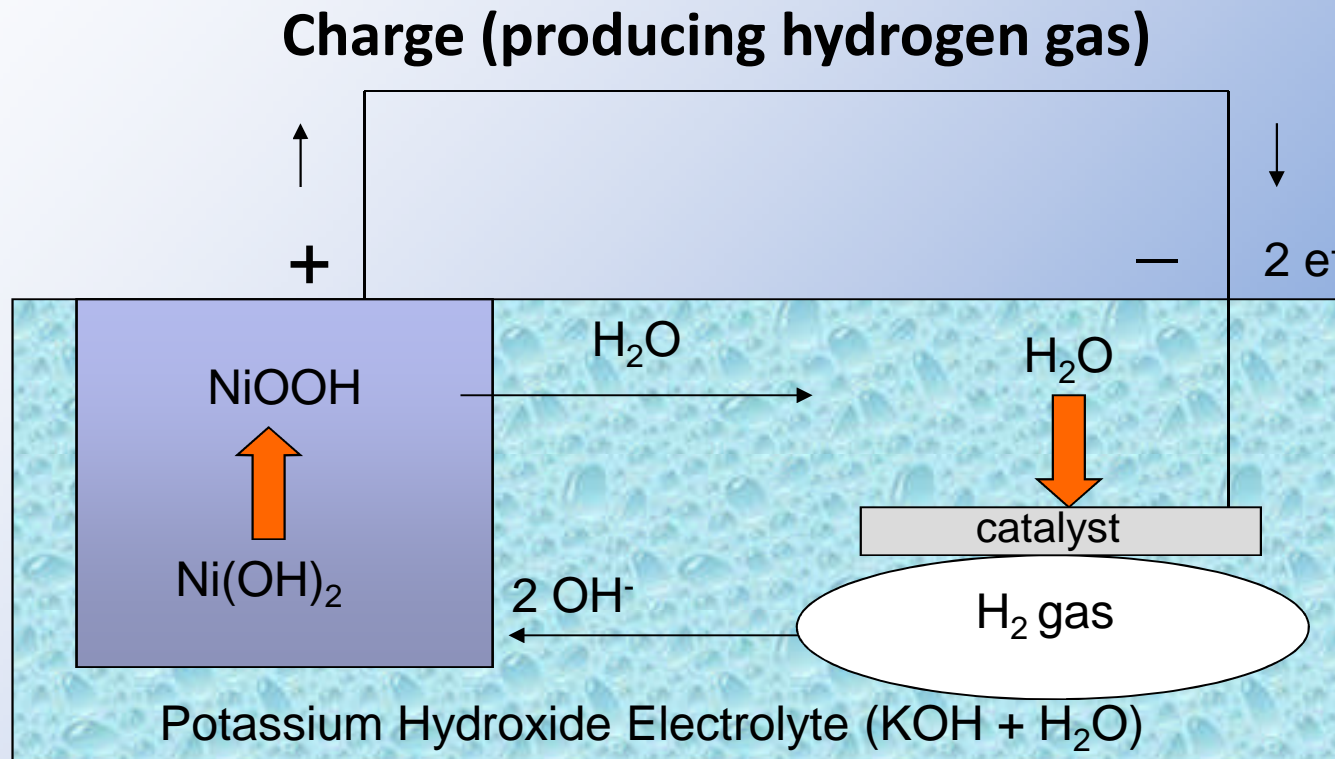


Nickel-hydrogen battery reactions during discharge.



# Ni-H<sub>2</sub> Batteries

NASA Kennedy Space Center



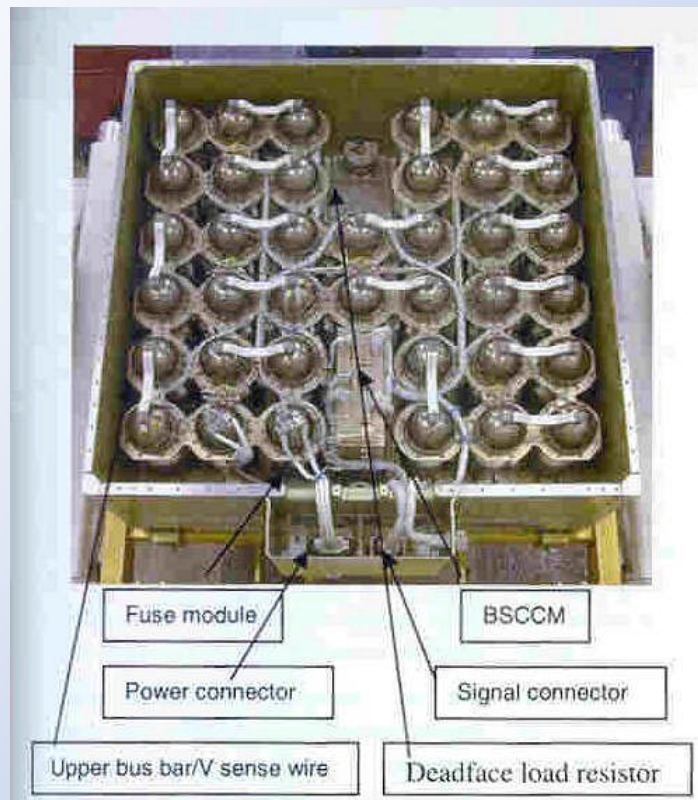
Nickel-hydrogen battery reactions during charge.



# ISS Batteries

NASA Kennedy Space Center

- ISS batteries are made up of 38 individual cells (1.25 volts each) wired together.
- The EPS consists of several hardware components called Orbital Replacement Units (ORU).
- Each ORU is considered a subsystem of the entire EPS and can be replaced upon failure either robotically or by Extra-Vehicular Activity (EVA).



ISS Battery ORU Interior



ISS Battery ORU Exterior

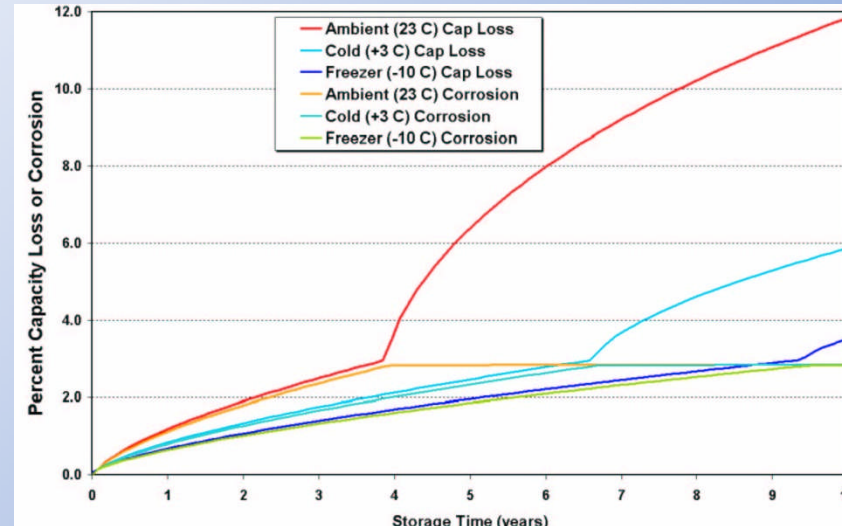


# ISS Battery Storage

NASA Kennedy Space Center

## Why They Lose Capacity Over Time

- Even though NASA uses positive precharge on its batteries (which gives longer storage), there are still slow reactions at lower voltages which take place on the battery electrodes that cause loss of capacity. One process is the actual corrosion of the nickel electrode, reducing the positive precharge. The other is the build up of oxides on the electrodes that increase the resistance of the battery. These oxides can be broken up though, buy repeated overcharging – resulting in buying back that part of the lost capacity. With enough time however, the positive precharge will be lost due to the corrosion of the nickel electrode and the battery will change to that of a negative precharge and really start degrading rapidly if the electrode voltages remain low. Of course, cold storage temperatures slow the reactions.



Increasing nickel corrosion and capacity loss during continuous open circuit NiH<sub>2</sub> cell storage at different temperatures, starting with 12% nickel precharge. The loss of the positive precharge is apparent where the slopes change.



# New ISS Batteries for 2017

NASA Kennedy Space Center

- Starting in 2017, the nickel-hydrogen battery ORUs will be replaced by Lithium-ion batteries.
- The design and development of the new Li-ion batteries started in 2011.
- One of the advantages of the Li-ion over the Ni-H<sub>2</sub> is that it has a higher specific energy, thus two nickel-hydrogen ORUs will be replaced by one Lithium-ion battery.
- To maintain the integrity of the thermal control loop that runs underneath the EPS ORUs, the empty Ni-H<sub>2</sub> ORU slots will be covered by an adapter plate.
- Each Li-ion battery will weigh about 425 lb, and each adapter plate will weigh 65 pounds, for a weight savings of 299 lb.



# Graphene for Energy Storage

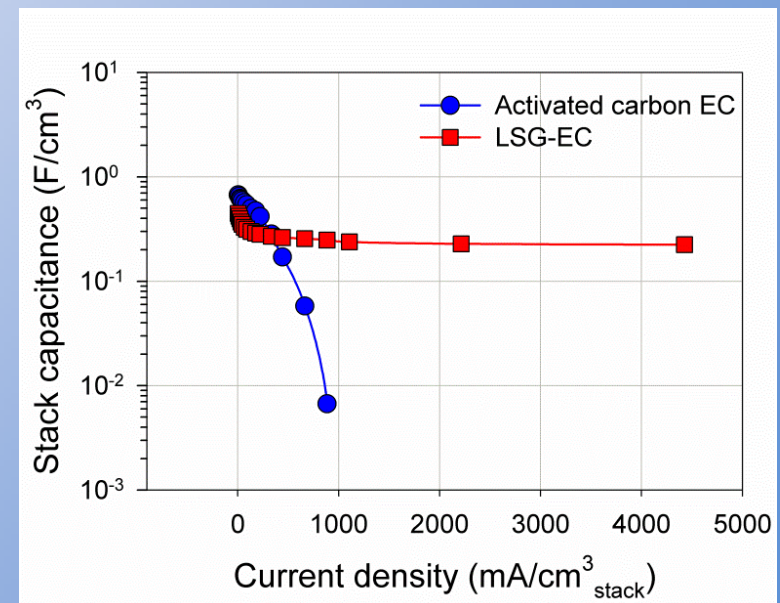
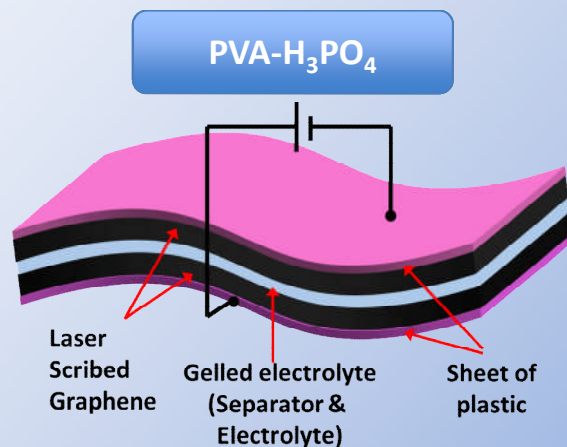
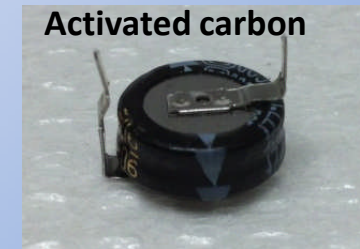
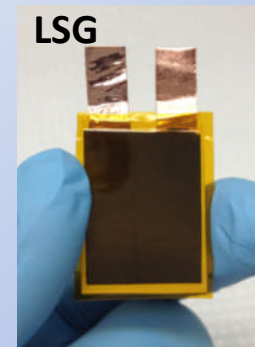
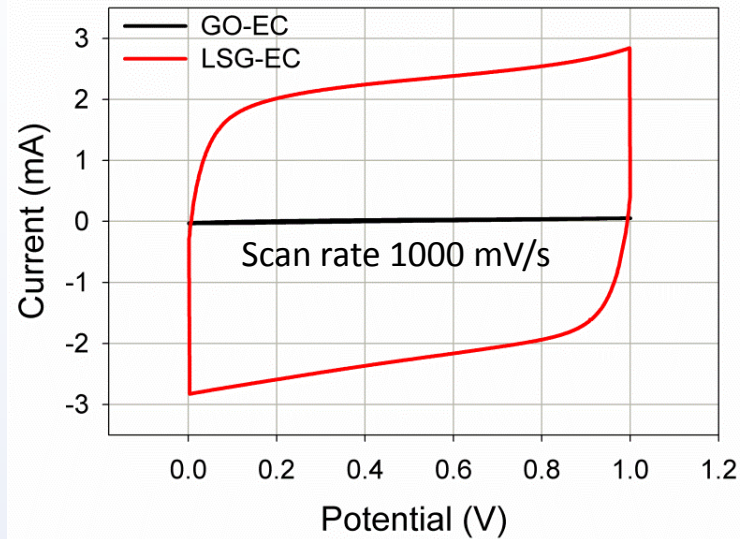
NASA Kennedy Space Center

- High intrinsic capacitance
  - $21 \mu\text{F}/\text{cm}^2$
- Large surface area
  - $\sim 2,600 \text{ m}^2/\text{g}$
- Versatile
  - Grown on or transferred to a wide variety of substrates
- High temperature and chemical stability



# Ultracapacitor Performance

NASA Kennedy Space Center

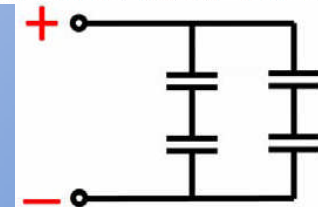
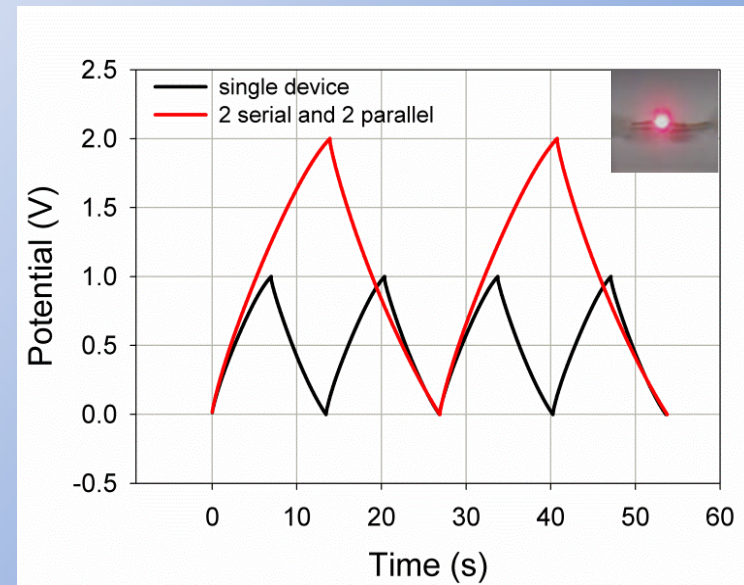
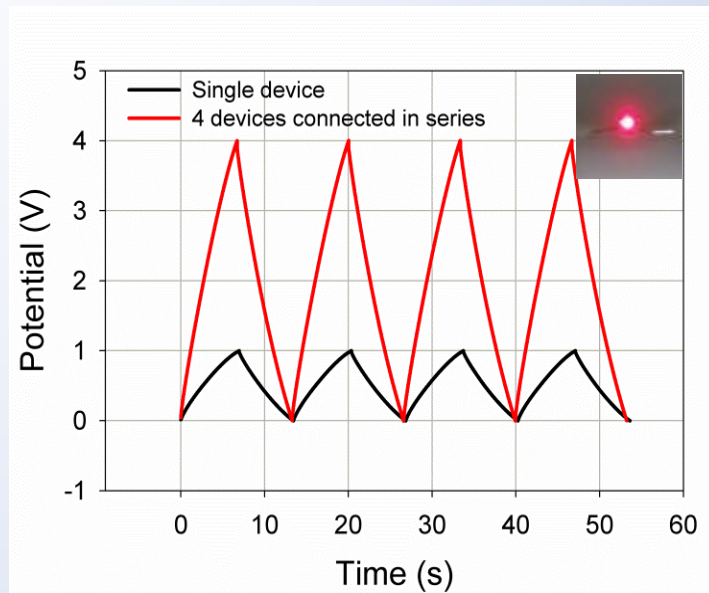






# Tandem Supercapacitors

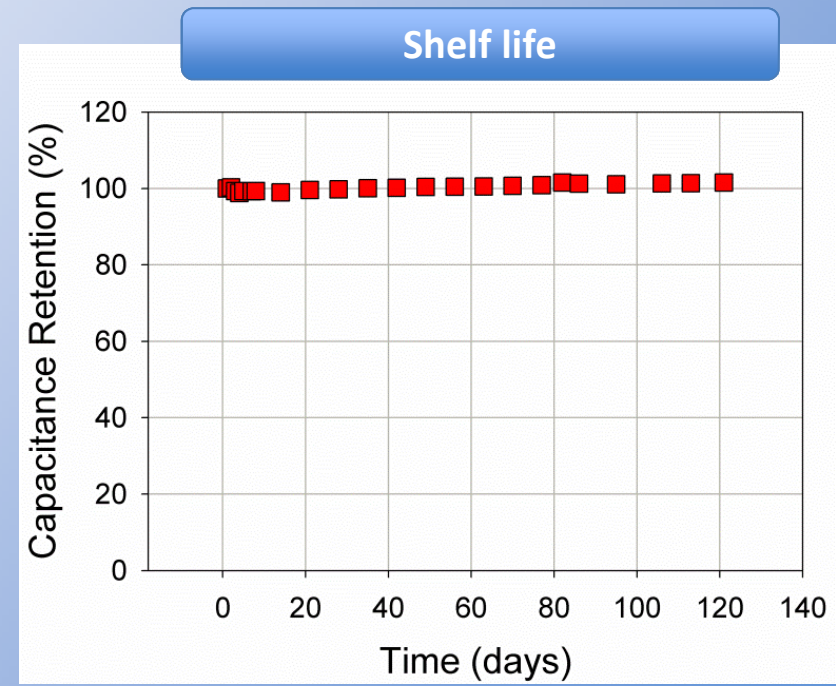
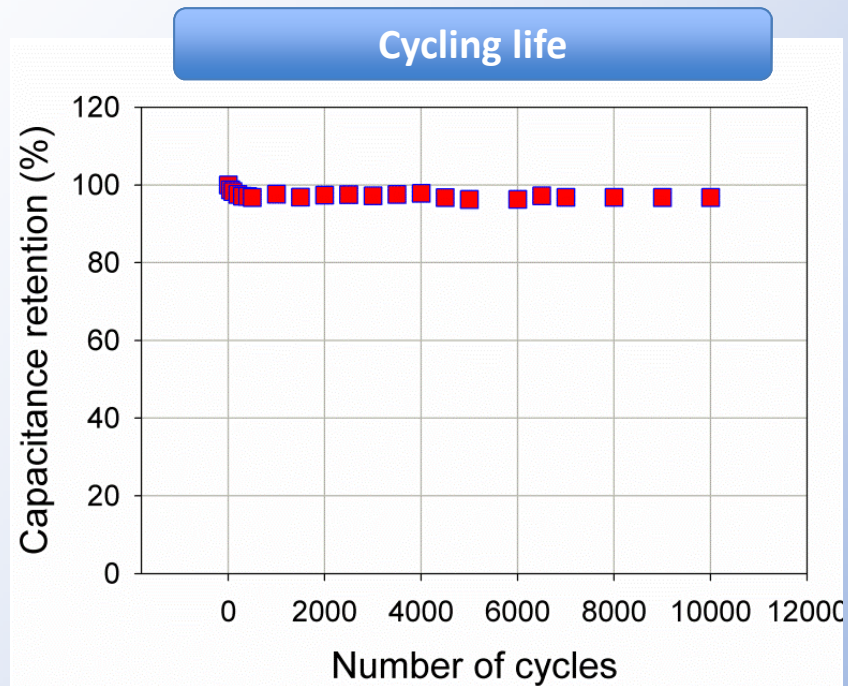
NASA Kennedy Space Center





# Cycling and Shelf-Life

NASA Kennedy Space Center



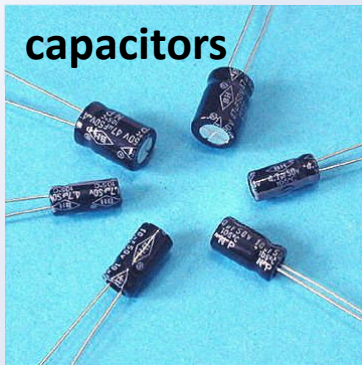
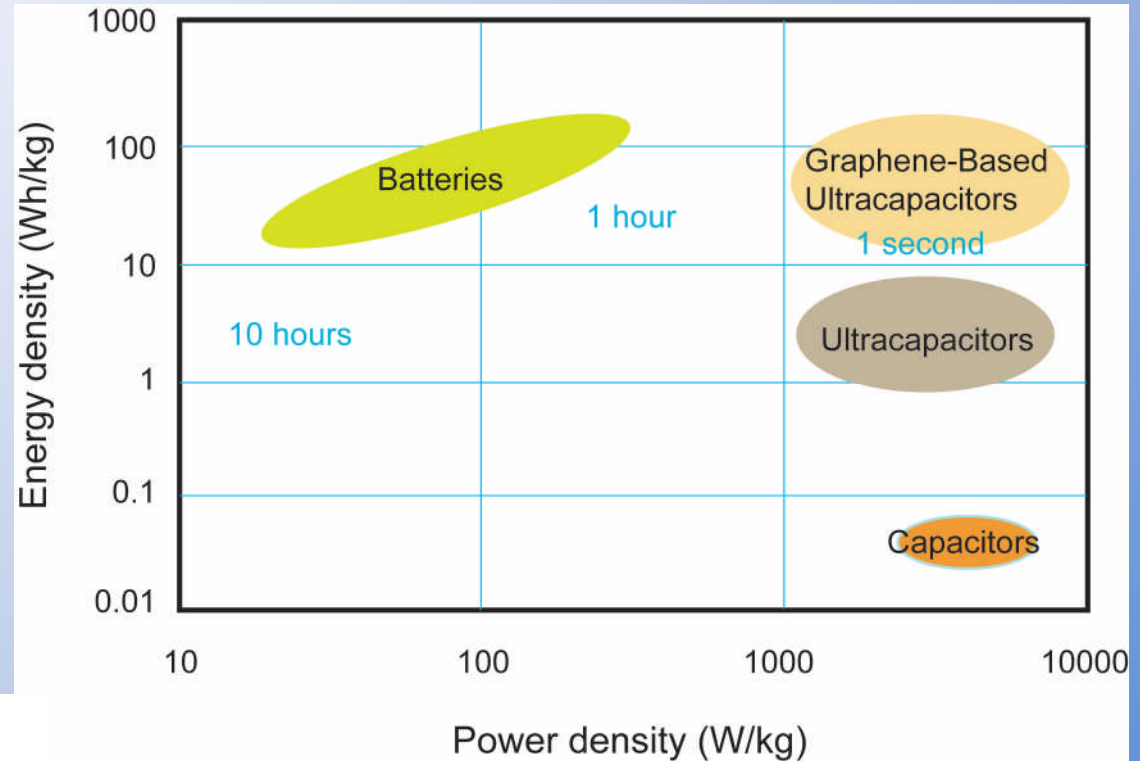


# Expected Performance

NASA Kennedy Space Center

Graphene-based ultracapacitors:

- High power densities
- High energy densities



supercapacitors



batteries



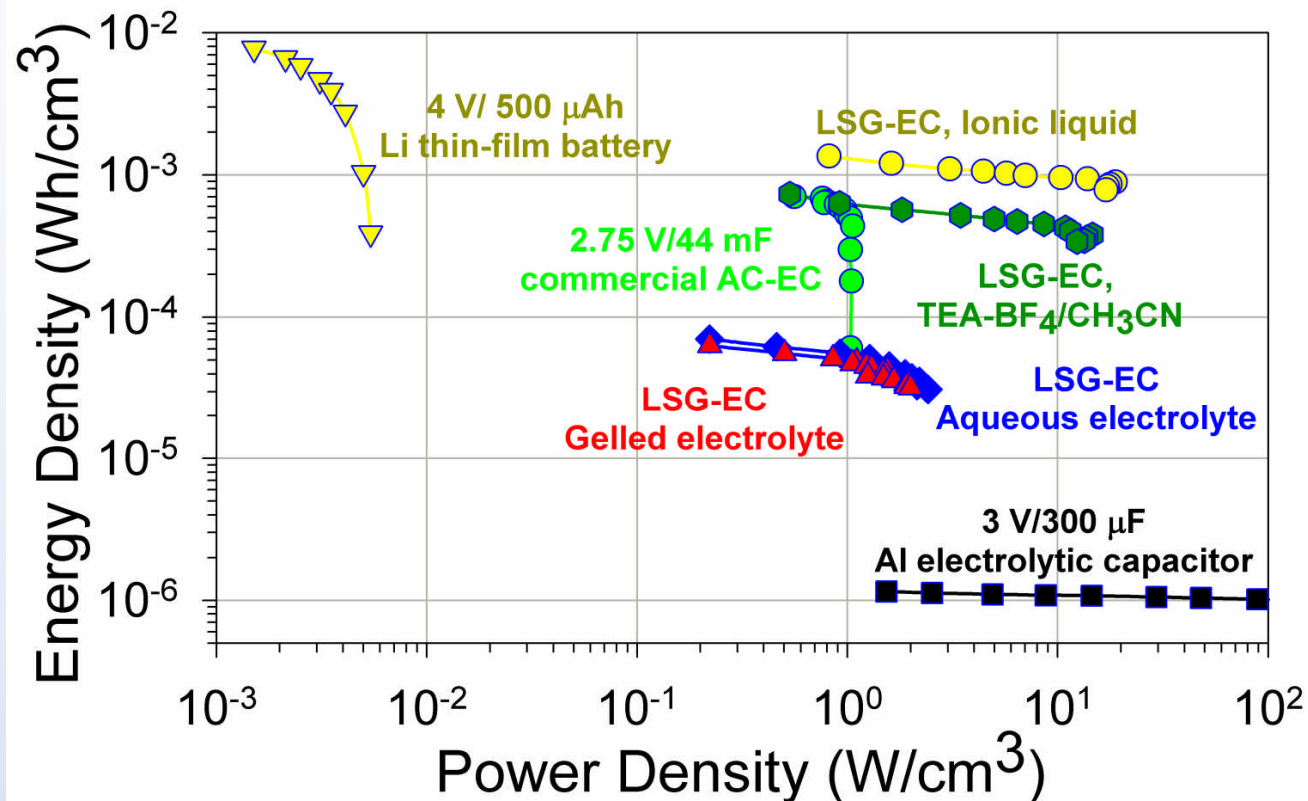
Energy and power density comparison for batteries, conventional ultracapacitors, and the expected performance of graphene-based ultracapacitors. Charging times are shown in blue.

Slide courtesy of UCLA, Kaner Laboratory



# Comparison of LSG, AC, Thin-film Li

NASA Kennedy Space Center



- 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

Slide courtesy of UCLA, Kaner Laboratory



# Current Work

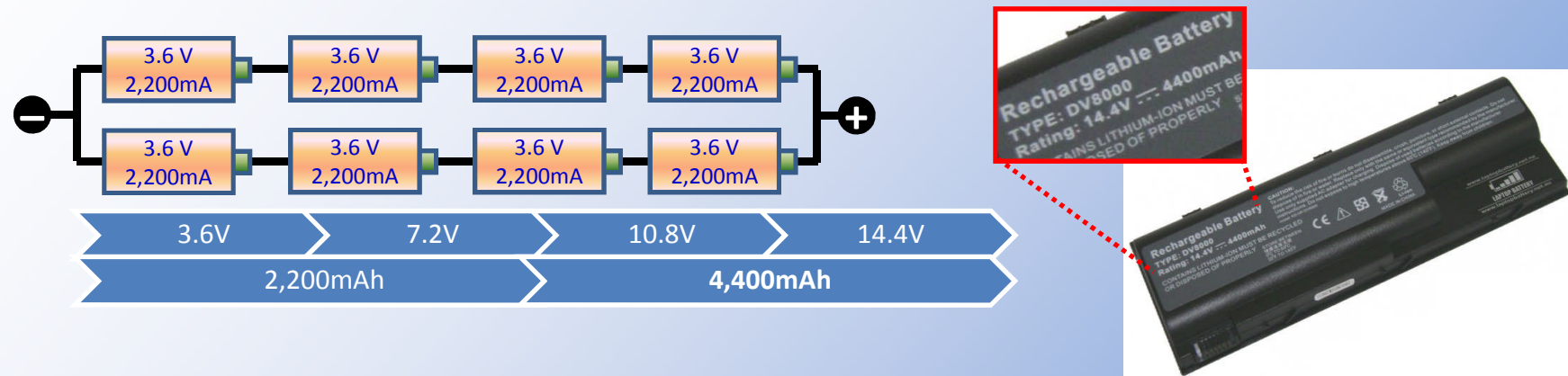
NASA Kennedy Space Center

- Increased surface area
- Conductive substrates
- Better electrolytes
- Operating voltage primarily a limitation of the electrolyte
- Ionic liquids can offer exceptionally high thermal stability to 200°C [Kolmulski *et al.* 2004]



# Next Steps

NASA Kennedy Space Center



- 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



# Future Work

NASA Kennedy Space Center

## RASSOR



Regolith Advanced  
Surface Systems  
Operations Robot

Regolith includes dust,  
sand and rock

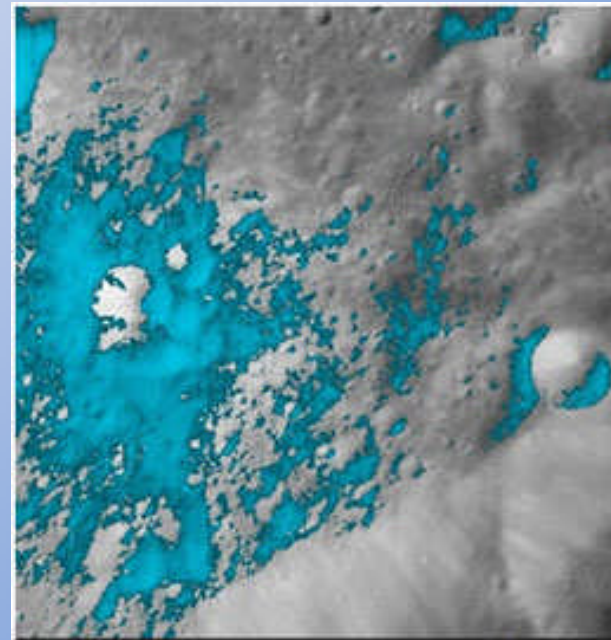
High power robotics  
designed to extract  
compact and icy regolith  
frozen mixtures



# ISRU

NASA Kennedy Space Center

- In-Situ Resource Utilization (ISRU) is the identification, acquisition, and utilization of in-situ resources whether they be naturally occurring or man-made.
- This lunar crater image from the M3 mapper shows water-rich minerals in blue.



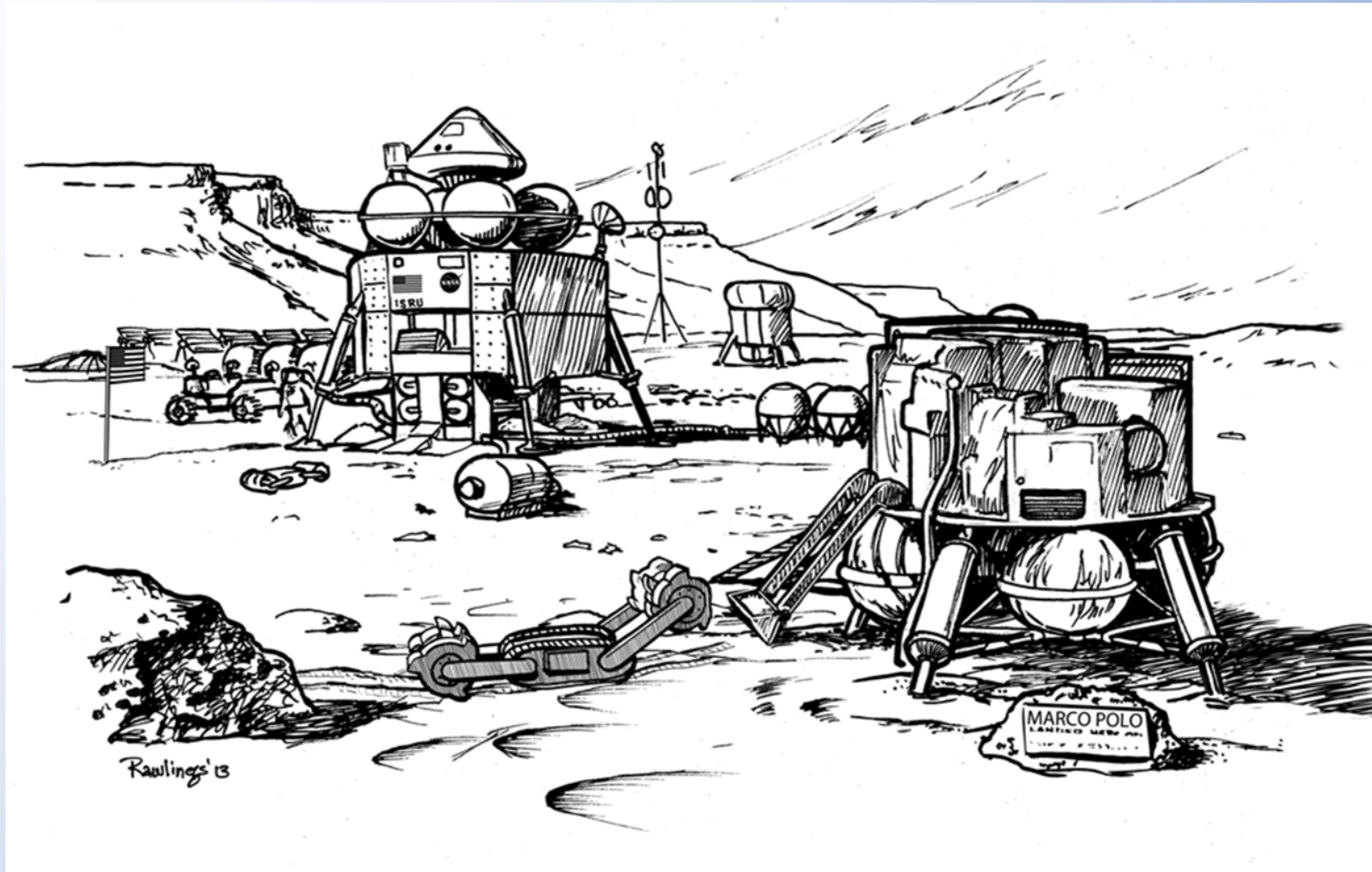
(Image: NASA/Brown University)





# End-to-End ISRU

NASA Kennedy Space Center



Excavation, collection and processing for methane/oxygen bipropellant



# Application to Space

NASA Kennedy Space Center

- 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



# The Vision

NASA Kennedy Space Center

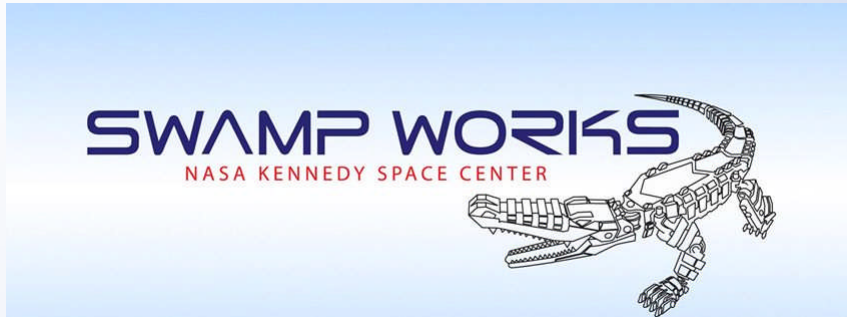
- Every exploration plan calls for a sustainable exploration architecture.





# Contributors

NASA Kennedy Space Center



## NASA KSC

Paul J. Mackey  
Michael R. Johansen  
James Phillips III  
Michael Hogue, Ph.D.

Richard B. Kaner, Ph.D.  
Maher El-Kady, Ph.D.  
Lisa J. Wang, Ph.D.  
Jee Youn Hwang



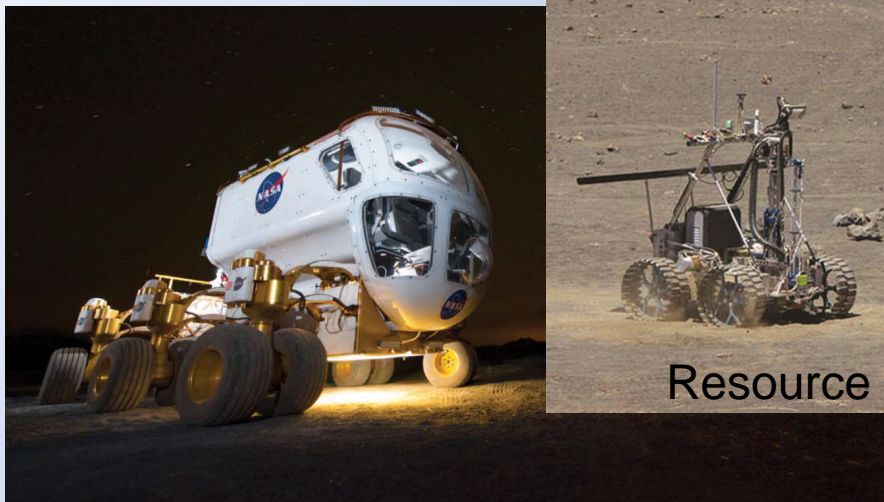
BACKUP



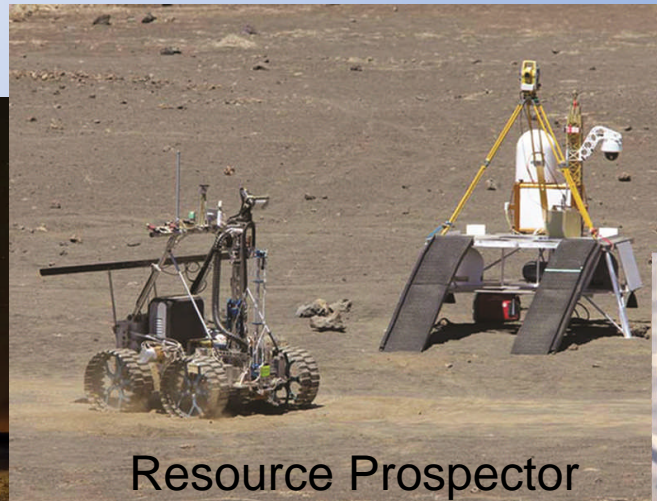
# Potential Future Missions

NASA Kennedy Space Center

- 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

NASA Kennedy Space Center

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