Challenge and Opportunity of Advanced Materials and Chemistries for Electrochemical Energy Storages Development of NASA Future Missions

James J. Wu, Ph.D.

NASA Glenn Research Center (GRC)

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University of California at Santa Cruz, California, April 2, 2018

Outline

- Introduction/NASA energy requirements
- Advanced materials for high energy Li-Ion batteries
- Beyond Li-ion battery chemistries
- Research opportunities for academia on NASA energy storage technique development
- Facilities and capabilities at NASA GRC
- Closing remarks

Energy Is an Important Business

- Energy is ranked #1 in humanity's top problems for next 50 years

- Electrochemical energy conversion and storage, such as batteries, play vital roles for energy security

- General strategies to improve battery energy
  - Improve/extend existing battery technology today
    - Optimization/maximum of existing materials and design
  - Develop new/advanced battery technology
    - New materials
    - New battery chemistries

Batteries: Important for NASA Missions

- **Batteries provide**
  - a versatile, reliable, safe and portable energy source, and are an essential component of the power system of virtually all NASA missions

  - Electrical energy storage options for NASA Space missions, such as:
    - Power during spacecraft eclipses
    - Peaking power for sort high power needs

Desired Battery Properties for NASA Missions

- Safe
- High in specific energy
- Light in weight
- Compact in volume
- Long in shelf life
- Durable in wide temperature range and harsh environment
- Reliable in meeting mission requirements

Battery Material Design and Selection

Voltage

Energy Density

Capacity

Power Density

Ionic conductivity

Rate Capability

Ionic mobile path length

Electronic conductivity

Cyclability

Structural stability

Safety

Thermal stability

Toxicity

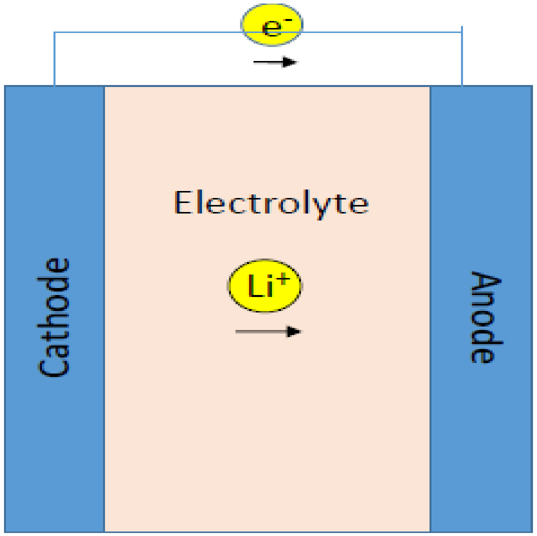
Availability

Cost

Processability

State-of-Art (SOA) Li-Ion Battery (LIB)

- **LIB Specs**:
  - Specific energy: 180-200 Wh/kg
  - Specific power: 300 W/kg
  - Cycles: 1000s (excellent)
  - Temp range: -20^{o}C to 60^{o}C
  - LIB has excellent rechargability



Anode: Graphite;
Cathode: Metal Oxide;
Electrolyte: Carbonate Liquids

- **Limitations**:
  - Maximum of energy density <250 Wh/kg
  - Electrolyte flammable and fire hazards

NASA Demands Very High Specific Energy Batteries

Electric Aviation

500 – 750 Wh/kg

- Green aviation – Less noise, lower emissions, high efficiency
- Hybrid / All-electric aircraft – Limited by mass of energy storage system
- Commercial aviation – Safe, reliable, lightweight on-board electric auxiliary power unit

Extravehicular Activities (Spacesuit power)

>400 Wh/kg

Required to enable untethered EVA missions lasting 8 hours within strict mass and volume limitations.

Astronaut life support
Safety and reliability are critical
100 cycles

Landers and Rovers, Robotic missions, In-space habitats

>500 Wh/kg

Batteries are expected to provide sufficient power for life support and communications systems, and tools including video and lighting

- >100 cycles

NASA future mission requirements far exceed the capabilities of lithium-ion chemistries

➢ Progress in these areas requires advances in safe, very high energy batteries

Advanced Safe, High Energy Li Batteries

- **Advanced electrode materials to improve Li-ion battery energy**
  - Anode active materials
  - Cathode active materials
- **Advanced electrolyte to improve safety**
  - Non-flammable additives
  - Ionic liquids
  - Solid state electrolyte
- **Beyond Li-ion battery chemistries**
  - Li-S Chemistry
  - Metal air batteries chemistries such as Li/O_2

Advanced Anode Development

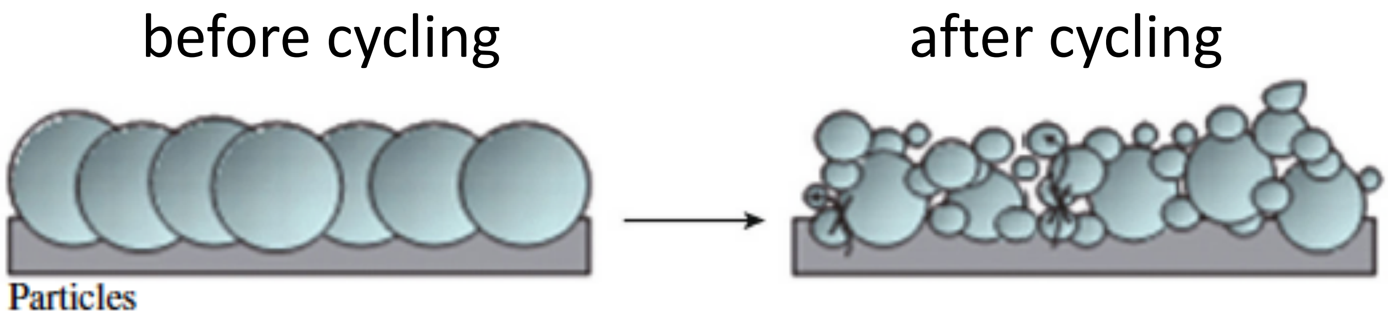
- **Silicon (Si) and lithium (Li) metal: promising as advanced anode materials**

  - **Very high theoretical capacity:**
    - Si (4200 mAh/g)
    - Li metal (3800 mAh/g)
    - 10x higher than SOA graphite (370 mAh/g) anode

  - **Additional advantages:**
    - Si: abundant element on Earth
    - Li: lightest metal, 100% active material, no binder needed

Challenges: Si as Advanced Anode Materials

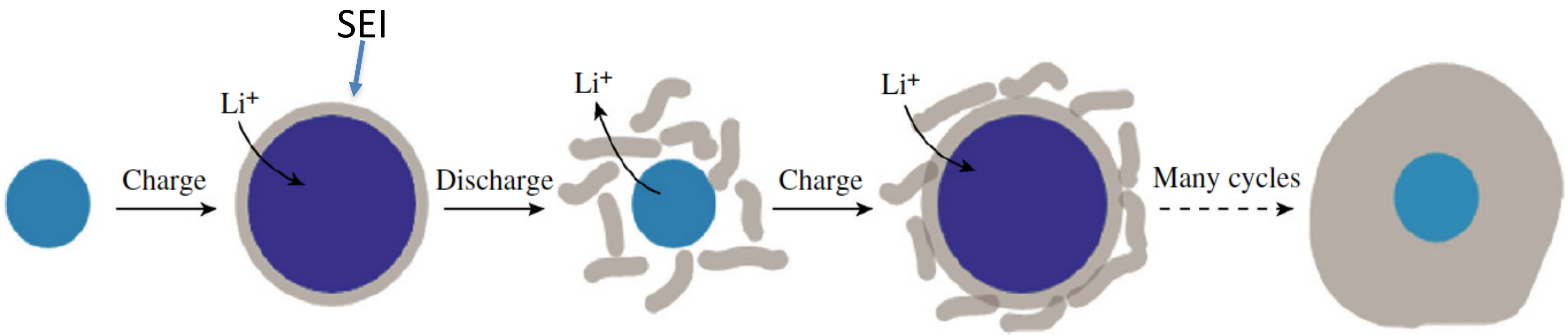
- **Challenges for Si:**
  - Poor electrical conductivity
  - Low diffusion coefficient of Li^+ in Si
  - High volume changes (up to ~400%) in Si particles upon lithiation and delithiation process, causing capacity fade



C.K. Chan et al Nat. Nanotechnol. 3(1), 31-35 (2008)

Approaches to Overcome Si Challenges

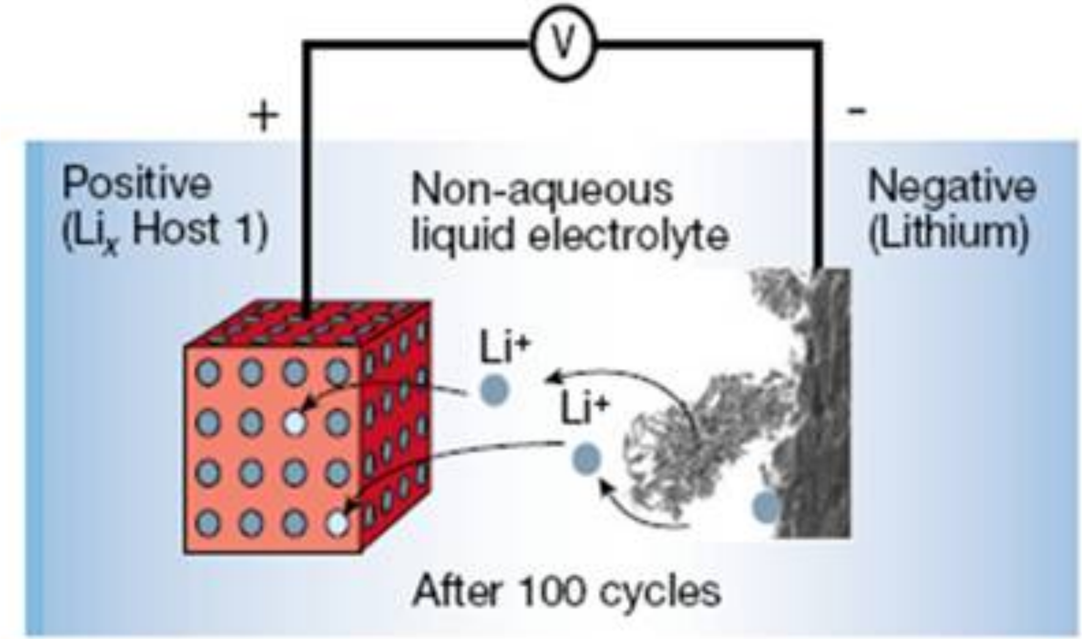
- with conductive materials (typical carbon) to form composite
- Nanosized Si particles/C composite, Si nanowire
- Nanostructured Si/CNF
- Improve Si electrode/electrolyte interphase: such as fast forming and stabilizing solid electrolyte interphase (SEI)



H. Wu et al Nat. Nanotechnol. 7(5), 310-315

Challenges: Li Metal as High Capacity Anode

- **Very reactive, parasite reactions, resulting in low coulombic efficiency (CE)**
- **Shape changes during cycling, causing poor cyclicability**
- **Dendrite growth to cause safety concern**



(Tarascon, J. M. et al, Nature, 2001, 414, 359-366)

Approaches for Li Metal Safe Cycling

- **Ways to overcome:**
  - Ionic liquid in electrolyte
  - High concentration Li salts
  - Solid state electrolyte
    - Ceramic
    - Solid polymer nanocomposite

- **Research on Li metal cycling at NASA**
  - NASA ARMD award to combine MD computational with experimental to study ionic liquid on Li metal (NASA Ames with GRC) John Larson in ARC, James Wu et al in GRC
  - CIF awards to solid polymer nanocomposite to make Li metal cycle safely (PI James Wu, 2016, 2018)

Advanced Cathode Development

- **Develop Li(NMC) Materials**
  - Offer higher capacity (>280 mAh/g) and enhanced thermal stability over conventional $LiCoO_2$ (170 mAh/g) cathodes
  - High voltage materials

- **Major Challenge:**
  - Voltage fade during cycling

- **Development Focus on:**
  - Increasing specific capacity
  - Improving rate capability
  - Stabilizing materials for higher voltage operation
  - Reducing irreversible capacity loss
  - Increasing tap density

Advanced Electrolyte Development

- **Develop advanced electrolytes with additives**
  - Non-flammable electrolytes and flame retardant additives
  - Stable at potentials up to 5V
  - Compatible with the NASA chemistries
  - **Development focus on:**
    - Reducing flammability
    - Stabilizing materials for higher voltage operation
    - Compatibility with mixed-metal-oxide cathodes and silicon composite anodes

- **Develop ionic liquids, solid polymer nanocomposite electrolyte and solid state electrolyte**

Solid State Electrolyte: Improve Safety

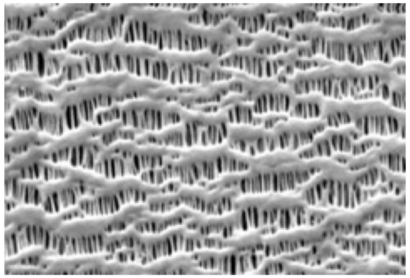
- **Solid state electrolyte enhances safety**
  - Ceramic type such as Garnet type
  - Solid polymer nanocomposite electrolyte

- **Challenges in Solid State Electrolyte Development**
  - Low ionic conductivity at room temperature ($<10^{-3}$ S/cm)
  - High contact/interfacial resistance issues)
  - Processing/fabrication issues

- **Approaches to Overcome**
  - 3D design of electrodes
  - Thin layer of electrolytes
  - Hybrid w/polymer, ionic liquid & nanomaterials

Advanced Separator Development

- **Significance**
  - The function and reliability of the separator are critical for optimal cell/battery performance and safety
  - Affects internal cell resistance, stability, cycle-life, operating temperature range and rate kinetics and intrinsic cell safety, especially under abuse or elevated-temperature conditions



- **Technology Challenges**
  - Design optimization for high porosity and low ionic resistance to facilitate ionic conductivity while maintaining mechanical strength
  - Shutdown separators must "shutdown" cell reactions at optimum temperature without shrinking or losing mechanical integrity

NASA Advanced Space Power System Program (ASPS)
(2008-2014)

- Partnered with University/Industry for Advanced components development
  - Si as advanced anode – Georgia Tech, Physical Science Inc.
  - NMC as advanced cathode – University of Texas at Austin
  - Low-flammable electrolyte: NASA JPL

- Although NMC cathode was difficult to scale up, NASA worked with industrial partners (PSI/Yardney) for scale-up Si production and the use of Si as anode in large format flight-type prismatic cells (35Ah)

Beyond Li-Ion Battery Chemistries

- **Li/S Battery Chemistry:**
  - **Advantages**
    - Very high theoretical specific energy: 2680 Wh/kg
    - abundance
    - Non-toxic
    - Environmentally benign
  - **Challenges**
    - Poor electronic conductivity
    - Low voltage
    - Short cycle life.
    - Li dendrite growth
    - Polysulfide shuttle causing short shelf life
- **Metal-Air Batteries Chemistries, e.g. Li/O_2**
  - Very high theoretical specific energy (17000 Wh/kg)
  - Li at 13 kWh/kg, Carbon is light, O2 from air or cylinder
  - Battery depends on environment e.g. O2, humidity, air flow, temperature

  - air cathode is "open" to environmental;
  - Complex discharge products, high overpotential during cycling
  - Safety, Li dendrite growth

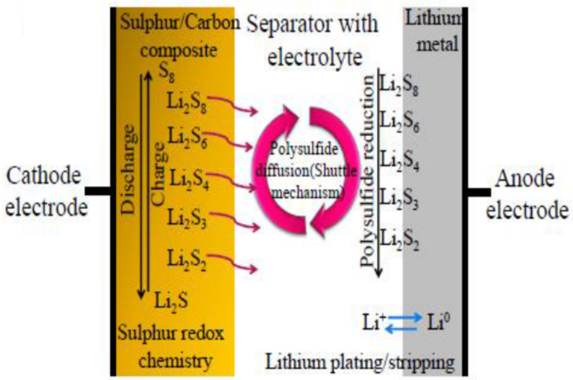
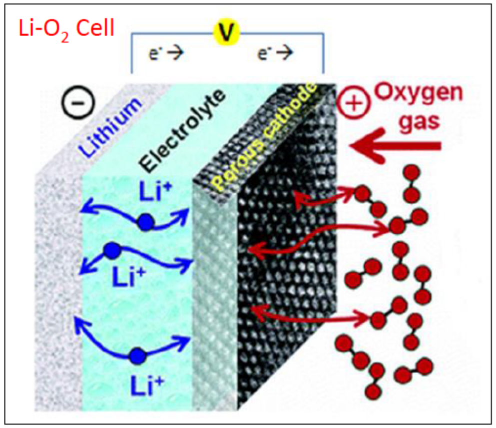


Image- courtesy of Storagenergy Technologies Inc



NASA Advanced Energy Storage System (AESS) Project under Game Change Program (2014-2017)

- **Phase I**: 8 month, 4 awards were given:
  - 1 award (Category I) on Si Anode based Li-ion battery (Amprius)
  - 3 awards (Category II) on Li/S battery development (JPL/CIT, IUPIU, University of Maryland (UMD)
- **Phase II**: 12 month, 2 award were given:
  - **Amprius**: **Silicon Anode Based Cells for High Specific Energy Systems**
    - Commercial standard cathode paired with Amprius' silicon anode
    - Phase I: Deliverables with >300 Wh/kg after 225 cycles (pouch cell)
    - Phase II: Scale-up cells (2X size in phase I) with >300 Wh/kg over 200 cycles
      - Additional temperature & safety evaluations at cell & battery levels
      - Battery pack brassboard delivering > 250 Wh/kg
  - **University of Maryland**: **Garnet Electrolyte-Based Safe Lithium-Sulfur Energy Storage**
    - All solid state battery with unique and scalable trilayer(porous-dense-porous) solid state electrolyte (SSE) structure.
    - Phase I: demonstrated the feasibility in lab cells (coin cell)
    - Phase II: optimize the parameters and scale up to 5cm x 6cm sizes with targeted energy density ~500 Wh/kg

Supercapacitor vs. Battery

- **Two major types of electrochemical-based energy storage devices**
  - **Battery:** Faradic/exothermal redox reaction (many different varieties)
High energy density
Electrode degradation
Limited cycle life
  - **Capacitor:** Electrostatic/capacitive interaction
High power density
Electrode structural integration
Long cycle life

How to Improve Both Power Density and Energy Density of Battery

- **New materials with high specific capacity**

- **Novel architectures: 3D design of electrode**
  - **Thinner electrode (fast ionic transport)**
  - **High electronic conductivity (fast e^- transport)**
  - **High electrode/electrolyte interfacial area (fast charge transfer across the interface)**

How to Improve Both Energy Density and Power Density of Capacitor

- One approach is to hybrid the capacitor electrode with one battery electrode i.e. asymmetric supercapacitor

- One electrode (as cathode) from capacitor (i.e. active carbon w/high porosity and high surface area) undergoes electrostatic interaction

- The other electrode (as anode) from battery (i.e. silicon with high specific capacity) undergoes electrochemical redox reaction

NASA GRC Capabilities Related to Batteries

- ***To support the development advanced cells and batteries for aerospace applications:***
  - Development and characterization of materials, advanced battery components, and battery cells
  - Integration of advanced components and study of interactions
  - Development and application of modeling tools
  - Performance evaluations of cell and battery systems
  - Validation and verification of aerospace and flight cells and batteries
  - Li-ion battery/power system test bed development
  - Design support for battery/power systems for flight vehicles
  - Guidelines and requirements development and documentation for batteries for use in flight systems
- **Capabilities to address all levels of advanced battery design and development, ranging from component-level to cell-level to battery level**

NASA GRC Battery Energy Storage System – Background and Heritage

Overview

- Batteries provide a versatile, reliable, safe, modular, lightweight, portable source of energy for aerospace applications.
- Batteries have demonstrated the life and performance required to power current missions.
- Li-Ion batteries offer improvements in specific energy, energy density, and efficiency

Experience

- Lead battery development effort for Exploration Technology Development Program, Energy Storage Project
- Developed and validated advanced designs of Ni-Cd and Ni-H_2 cells adopted by NASA, cell manufacturers and satellite companies.
- Evaluated flight battery technologies for ISS
- Developed lightweight nickel electrodes, bipolar nickel hydrogen battery designs
- Jointly sponsored Li-ion battery development program with DoD that developed Li-Ion cells used on Mars Exploration Rovers
- Led NASA Aerospace Flight Battery Systems Steering Committee –agency-wide effort aimed at ensuring the quality, safety, reliability, and performance of flight battery systems for NASA missions.
- Conducted electric vehicle battery programs for ERDA/DOE

Products/Heritage

Beyond Li-ion: Li/S, Li/O2

Li-Ion: Lithium-Ion

Ni-Cd: Nickel-Cadmium

Ni-H_2: Nickel-Hydrogen

Ni-MH: Nickel-metal hydride

Ni-Zn: Nickel-Zinc

Ag-Zn: Silver-Zinc

Na-S – Sodium Sulfur

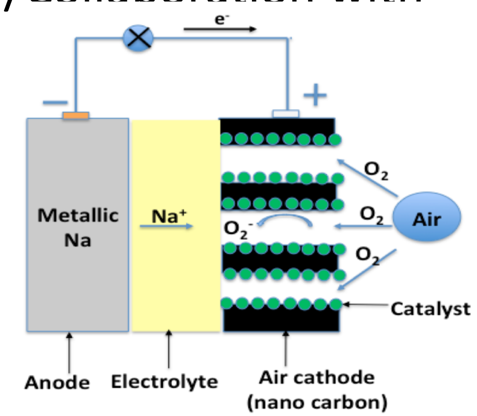
LiCFx: Lithium-carbon monoflouride

Advanced Battery Component/System Development

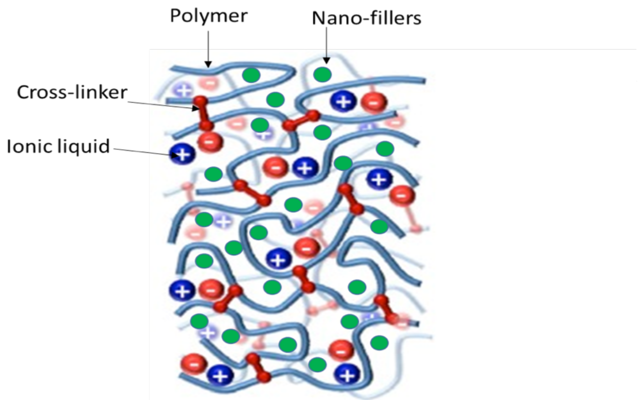
- **Convergent Aeronautics Solution (CAS) Projects**
  - High risk/high return projects
  - University/industry partners
- **Center Innovative Funds (CIF)**
  - seeding fund for support innovative ideas
- **Independent Research and Development (IRAD)**

NASA Center Innovative Fund (CIF)

- **CIF: seeding fund for support innovative ideas**
- **Previous/current awards:**
  - High Capacity Sulfur Cathode Development
    (PI James Wu, FY 12 CIF)
  - Safe and High Energy Density Na/O2 Development w/Collaboration with University of Akron (PI James Wu, FY 15 CIF)
    - Novel catalyst on carbon cathode to make a superior air-cathode
    - New electrolyte for long cycle life



  - Solid Polymer Nanocomposite Electrolyte
    (PI James Wu, FY16, FY18 CIF)
    - Polymers as host matrix
    - Integrated with ionic liquid and Li salt
    - Incorporated with nanomaterials to
      - Further improve ionic conductivity
      - Mitigate interface with Li metal
      - Enhance electrochemical stability
      - Improve mechanical strength



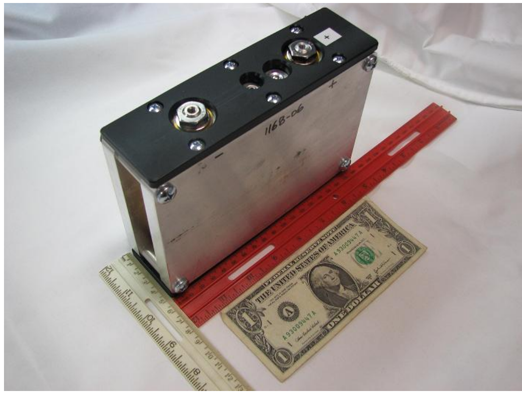
Cell Integration

- Assess performance of integrated components
- Predict full cell performance
- Determine optimum cycling parameters and cycling limitations
- Identify and understand performance and compatibility issues

Cell Development

- **Assess NASA-developed components**
  - Build and test electrodes and screening cells
  - Provide manufacturing perspective from the start

34PCell



- **Scale-up NASA-developed components**
  - Transition components from the lab to the manufacturing floor

- **Build and test evaluation cells:**
  - Determine component interactions
  - Determine cell-level performance

DD Cells

- **Design flightweight cells**
  - Identify high risk elements early

Analytical and Thermal Safety Evaluations

- **Analytical studies to assess component structures, particle size and distribution, morphology, elemental composition, electrode purity, etc.**

- **Characterization of thermal behavior of cell components by Differential Scanning Calorimetry (DSC)**
  - **Separators**
  - **Electrolytes**
  - **Electrodes harvested from fully charged cells**

- **Characterization of thermal stability of cells and components by Accelerating Rate Calorimetry (ARC)**

Capabilities and Facilities for Batteries Research

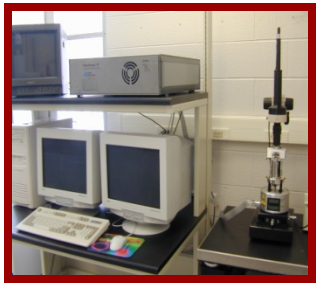
Capabilities

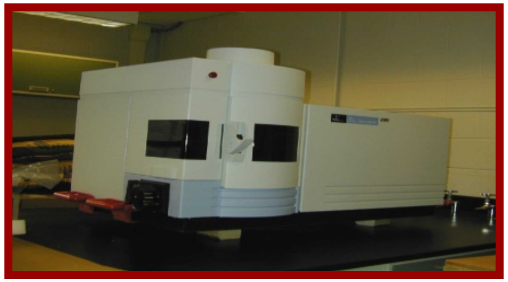
- Fundamental electrochemical research - component development and characterization with state-of-the-art analytical test capability
- Cell/Battery Design
- Cell/Battery Performance and Life Testing
- Cell/Battery Safety Testing
- Battery Performance Modeling
- Environmental Testing

Facilities:

- Development Laboratories - SOA equipment for materials and component development, and analytical and electrochemical characterization
- 600 ft^2 Dry room with 1% relative humidity for handling moisture sensitive materials used in lithium based batteries
- State-of-the-art battery cycling facilities with >100 independent test channels, 1-200 Ahr, 1-50 V
- Environmental chambers to evaluate performance as a function of temperature (-75°C to +200°C)
- Accelerating Rate Calorimeter

Branch Facilities





Imaging and Material Analysis Laboratory –

Surface and Thermal Analysis Capability

- Inductively Coupled Plasma Optical Emission Spectrometer
- Scanning Probe Microscope
- Scanning Electron Microscope Energy Dispersive Spectrometer
- Stereomicroscope
- BET Surface Area Analyzer

Thermal and Material Analysis Laboratory

Molecular analysis, particle size distribution, thermal property analysis

- Differential Scanning Calorimeter
- Fourier Transform IR Spectromete
- Thermogravimetric Analyzer (TGA
- Raman Spectrometer
- Particle Size Analyzer

NASA/University Program - Faculty

- **SBIR/STTR (Small Business Innovation Research/ Small Business Technology Transfer) program**

- **NASA EPSCoR (Experimental Program to Stimulate Competitive Research)**
  - Solicits topic-specific proposals addressing high-prority NASA research and technology needs, awards are up to $750K for a 3-year performance period

- **NASA MIRO program**
  Minority university research and education program **(**MUREP) Institutional Research Opportunity, up to 1 million/year for 5 years

- **Small Spacecraft Technology Program, Smallsat Technology Partnership**
  $200K for 2 years with NASA researcher is also covered

- **NASA early faculty proposal call**

- **NASA Summer Faculty Research Opportunity**

NASA/University Program - Students

- **NASA Student Internship**
  - NASA Interns, Fellows and Scholars (NIFS), One Stop Shopping Initiative (OSSI) https://intern.nasa.gov/solar/we/public/main

- **NASA Space Technology Research Fellowship (NSTRF)**

- **Aeronautics Scholarship and Advanced STEM Training and Research (AS&ASTAR) Fellowship (AS & ASTAR)**

Closing Remarks

- **Summary Statement**

  At NASA GRC, we have the capability to develop cell and battery technologies from fundamental research on battery components through the development, maintenance and management of flight battery systems

- **Area of Interest for Collaboration/Business Development**
  - **Advanced battery/capacitor technologies**
    - **Component Level**
    - **Cell Level**
  - **Next generation battery/capacitor technologies**
  - **Cell and battery safety**
  - **System level solutions to maximize energy**
  - **Charge control**

Acknowledgements

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Thank you!

Any Questions?