NASA Glenn Research Center

Electrochemistry Branch Battery Overview

This presentation covers an overview of NASA Glenn's history and heritage in the development of electrochemical systems for aerospace applications. Specific areas of focus are Li-ion batteries and their development for future Exploration missions. Current component development efforts for high energy and ultra high energy Li-ion batteries are addressed.

NASA Glenn Research Center
Electrochemistry Branch Overview

Original Equipment Suppliers Association (OESA) Technology Forum

Ohio Aerospace Institute (OAI)

October 5, 2010

Michelle A. Manzo
Chief, Electrochemistry Branch
michelle.a.manzo@nasa.gov
216-433-5261

Electrochemistry Branch Overview

- GRC Electrochemistry Branch – Energy Storage System Background and Heritage
- Current Projects – focus on Battery Efforts
- Electrochemistry Branch Capabilities and Facilities
- Concluding Remarks

RPC Electrochemistry Branch

Electrochemical Energy Storage Systems

Background and Heritage

Electrochemistry Branch – Batteries

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 for Battery Development Efforts under NASA Exploration Technology Development and Enabling Technology Development and Demonstration Programs
- 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 and bipolar nickel hydrogen battery designs
- Jointly sponsored Li-ion battery development program with DoD that developed Li-Ion cells used on Mars Exploration Rovers
- Lead for NASA Aerospace Flight Battery Systems Working Group
- Conducted electric vehicle battery programs for ERDA/DOE

Products/Heritage

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

Terrestrial Applications - Batteries for Electric Vehicles

Late 1970's Battery and Cell Development for Electric Vehicles

- Spin off of space battery developments
- Space expertise with nickel-cadmium and silver-zinc chemistries applied to nickel-zinc development

Electrochemistry Branch
Fuel Cells and Regenerative Fuel Cells

Overview

- Fuel cells provide a primary source of power that can support a wide range of aerospace applications.
- Regenerative fuel cells combine a fuel cell with an electrolyzer that is capable of converting the fuel cell products into reactants when energy is supplied and thus function much like a battery.
- Fuel cell based systems offer long run times in a portable, lightweight system and can enable extended operations.

Products/Heritage

AFC – Alkaline Fuel Cell

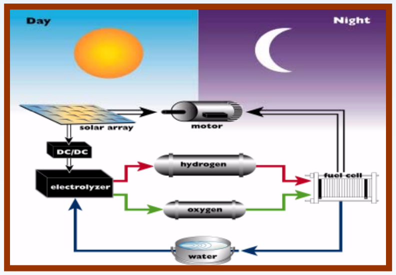
PEM – Proton Exchange Membrane

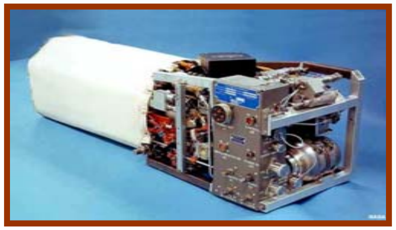
SOFC – Solid Oxide Fuel Cell

RFC – Regenerative Fuel Cell Systems

Experience

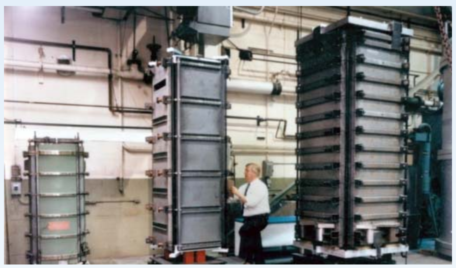
- Lead for Fuel Cell Development Efforts under NASA Exploration Technology Development and Enabling Technology Development and Demonstration Programs
- Gemini, Apollo, and Shuttle technology development
- Terrestrial energy program management for Fuel Cell systems for Stand Alone Power
- PEM fuel cell powerplant development for launch vehicles and Exploration Missions
- Fuel cell demonstration for high altitude scientific balloons
- Fuel cell development for Helios
- RFC Development for High Altitude Airships





Terrestrial Programs –Fuel Cell Systems

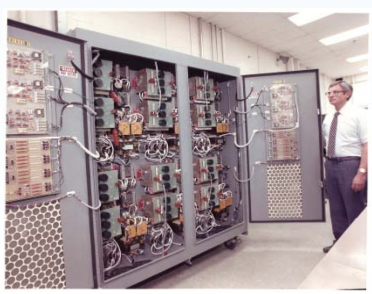
Fuel Cell Systems for Stand Alone Power



Fuel Cell Stacks

Gas Reformers

Power Management

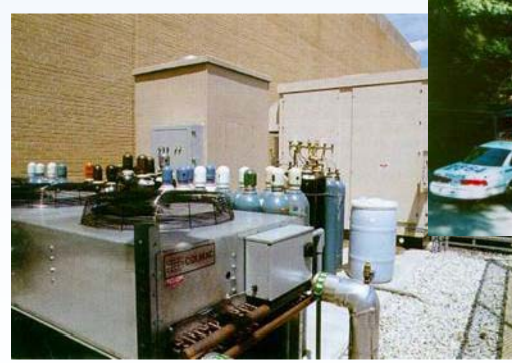


Commercial Installations of PC25 Phosphoric Acid Fuel Cell Systems

Bank in Omaha, NE

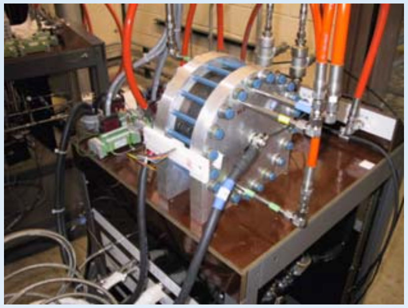
Verizon Telecommunications

Police Station Central Park, NY

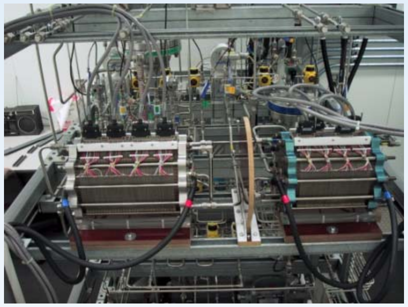


Sewage Treatment Facility

Fuel Cells and Regenerative Fuel Cells



Lynntech Generation III hydrogen-oxygen fuel stack



Fuel cell and electrolyzer stacks

Helios solar airplane

Integrated system test set up of closed loop hydrogen oxygen regenerative fuel cell system

First ever demonstration of closed-loop, hydrogen-oxygen regenerative fuel cell system

RPC Electrochemistry Branch
Current Projects

RPC/Electrochemistry Branch Current Projects

- Enabling Technology Development and Demonstration Program – High Efficiency Space Power Systems – Battery & Fuel Cell Development – Lead Roles
- Support to Constellation Projects
  - CLV – Battery Studies, specification, design – human rating
  - Altair – Power System Lead, Fuel Cell System studies, reliability analyses
- NASA Engineering Safety Center – Lead for Battery Working Group – Discipline Advancing Battery Tasks
- International Space Station – Li-ion Risk Mitigation – Life Testing Li-ion Batteries
- Human Research Program – Metal Air Battery Development
- Hydrogen Infrastructure for Renewable Energy

Exploration Technology Development Program

ENERGY STORAGE PROJECT

Fuel Cells For Surface Systems and Space Rated Lithium-Ion Batteries

Exploration missions require advanced electrochemical energy storage devices to meet power requirements

Program/Project Completed September 30, 2010 – Transition to Enabling Technology Development and Demonstration Program

Fuel Cells for Surface Systems:

Proton Exchange Membrane (PEM) fuel cell technology offers major advances over existing alkaline fuel cell technology

Objective: Develop Proton Exchange Membrane (PEM) Fuel Cell technology with enhanced safety, longer life, lower mass and volume, higher peak-to-nominal power capability, higher reliability compared to alkaline fuel cells

Customers: Altair and Lunar Surface Systems

Space Rated Lithium Ion Batteries:

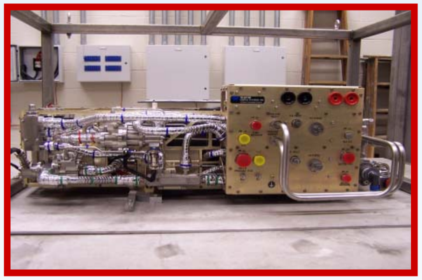
Lithium ion battery technology offers lower mass & volume, wider operating temperature range than alkaline battery chemistries (Ag-Zn, Ni-H2, Ni-Cd, Ni-MH)

Objective: Develop human-rated Li-ion batteries having high specific energy, energy density, long calendar life

Customers: Altair, EVA, and Lunar Surface Systems.

Overall Objectives:

- Mature advanced technologies to TRL 6
- Integrate component technologies into prototype systems to validate performance
- Transition technology products to Project Constellation – Altair, Extravehicular Activities, Lunar Surface Systems



Participants:

GRC – Lead
_Fuel Cells:
JSC, JPL, KSC
Batteries:
JPL, JSC

Industry Partners, SBIR Partners, IPP Partners

Project Transition

Phased out September 30, 2010

Exploration Systems Mission Directorate

Exploration Technology Development Program

…

Energy Storage Project

Goal: To develop energy storage technologies for Lunar Exploration

…

New Project as of October 1, 2010

Exploration Systems Mission Directorate

Enabling Technology Development and Demonstration

…

High Efficiency Space Power Systems

Goal: To provide abundant and low-cost power where it is needed for power-rich exploration

…

Li-Ion Battery Development

Objectives:

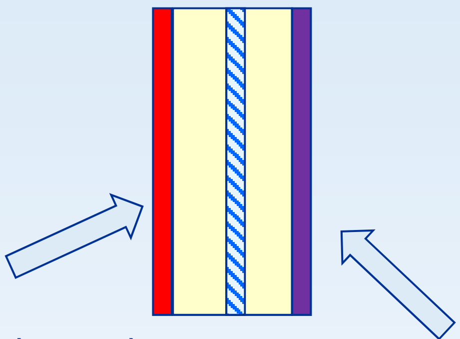
Improve performance of secondary (rechargeable) lithium-ion cells to meet the energy storage requirements of human missions

Approach:

- Develop "High energy" and "ultra high energy" cells to meet customer needs
- Utilize in-house and NRA Contracts to support component development
  - Develop components to increase specific energy (anode, cathode, electrolyte)
  - Develop low-flammability electrolytes, additives that reduce flammability, battery separators and functional components to improve human-safety;
- Engage industry partner – multi year contract
  - Provide recommendations for component development and screening
  - Scale-up components
  - Manufacture evaluation and screening cells with advanced chemistries
- Leverage outside efforts
  - SBIR/IPP efforts, DoE and other government programs

High-Efficiency Space Power Systems
Battery Cell Development

High Energy Cell

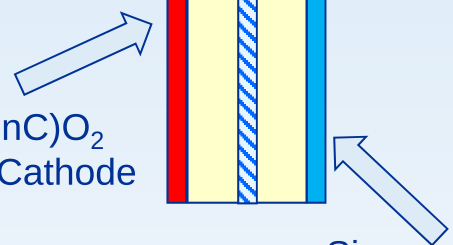


Li(LiNMnC)O_2
•NASA Cathode

Conventional
Carbonaceous Anode

Ultra-High Energy Cell

Li(LiNMnC)O_2
•NASA Cathode



Si-composite
NASA Anode

- Anode (commercial)
- Anode (NASA)
- Cathode
  Cathode (NASA)
- Electrolyte (NASA)
- Separator (commercial)
- Safety devices (NASA) Incorporated into NASA anode/cathode

Lithiated-mixed-metal-oxide cathode - Li(LiNMnC)O_2

Conventional carbonaceous anode

180 Wh/kg @ cell level
150 Wh/kg @ battery-level
At 0^0C C/10

~2000 cycles to 80% of original capacity at 100% DOD

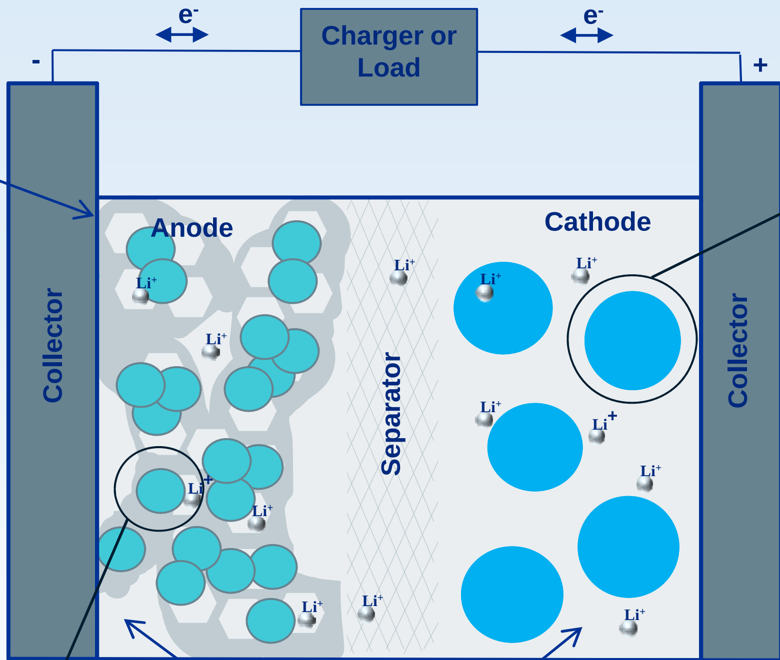
Lithiated-mixed-metal-oxide cathode /Li(LiNMnC)O_2

Silicon composite anode

260 Wh/kg @ cell level
220 Wh/kg @ battery-level
At 0^0C C/10

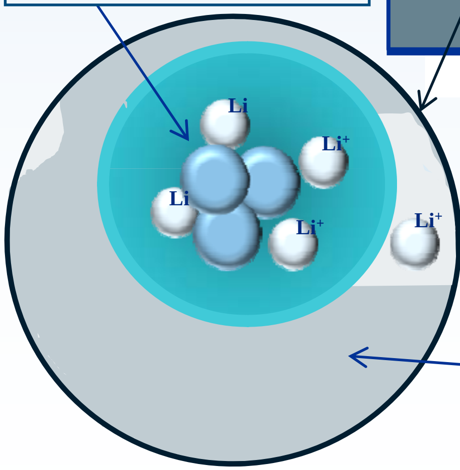
~200 cycles to 80% of original capacity at 100% DOD

Lithium Ion Battery Technology Development
Advanced Cell Components

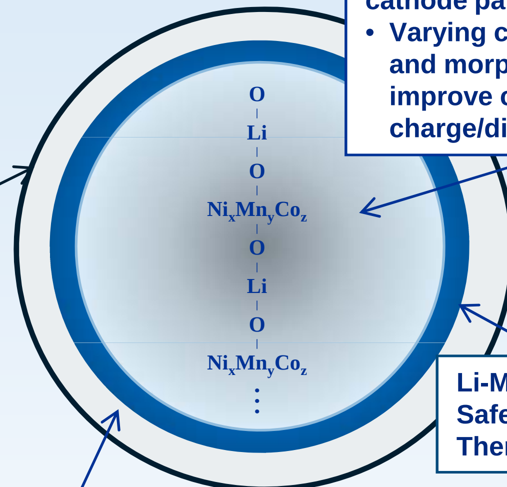


Nano-particle based circuit breaker

Silicon nano-particles alloy with Li during charge, lose Li ions during discharge
- **Offers dramatically improved capacity over carbon standard**



Layered $Li(NMC)O_2$ cathode particle
- **Varying composition and morphology to improve capacity and charge/discharge rate**



Li-Metal-PO_4 Safety Coating for Thermal Stability

Optimized Solid-Electrolyte interface Layer
- **Mitigates causes of irreversible capacity**

Advanced electrolyte with additives provides flame-retardance and stability at high voltages without sacrificing performance.
Example: $LiPF_6$ in EC+EMC+TPP+VC

- **Porous, elastomeric binder allows ionic transport and accommodates large volume changes during charge/discharge cycling**
- **Functionalized nanoparticles adhere to binder without blocking reactive silicon surface area**

Improving Cell-Level Safety

- ***Nano-particle circuit breaker, flame-retardant electrolytes, and cathode coatings to increase the thermal stability of the cell.***
  Goal: no fire or flame, even under abuse.

Providing Ultra High Specific Energy

- ***Silicon-composite anodes to significantly improve capacity; elastomeric binders and nanostructures to achieve ~200 cycles***
- ***Novel layered oxide cathode with lithium-excess compositions ($Li[Li_xNi_yMn_zCo_{1-x-y-z}]O_2$) to improve capacity***

Key Performance Parameters for Battery Technology Development

Customer Need	Performance Parameter	State-of-the-Art	Current Value	Threshold Value	Goal
Safe, reliable operation	No fire or flame	Instrumentation/controllers used to prevent unsafe conditions. There is no non-flammable electrolyte in SOA	Preliminary results indicate a small reduction in performance using safer electrolytes and cathode coatings	Tolerant to electrical and thermal abuse such as over-temperature, overcharge, reversal, and short circuits with no fire or thermal runaway***	Tolerant to electrical and thermal abuse such as over-temperature, overcharge, reversal, and short circuits with no fire or thermal runaway***
Specific energy Lander: 150 – 210 Wh/kg 10 cycles Rover: 160-200 Wh/kg 2000 cycles EVA: 270Wh/kg 100 cycles	**Battery-level** specific energy* [Wh/kg]	90 Wh/kg at C/10 & 30°C 83 Wh/kg at C/10 & 0°C (MER rovers)	160 at C/10 & 30°C (HE) 170 at C/10 & 30°C (UHE) 80 Wh/kg at C/10 & 0°C (predicted)	**135** Wh/kg at C/10 & 0°C "High-Energy"** **150** Wh/kg at C/10 & 0°C "Ultra-High Energy"**	**150** Wh/kg at C/10 & 0°C "High-Energy" **220** Wh/kg at C/10 & 0°C "Ultra-High Energy"
	Cell-level specific energy [Wh/kg]	130 Wh/kg at C/10 & 30°C 118 Wh/kg at C/10 & 0°C	199 at C/10 & 23°C (HE) 213 at C/10 & 23°C (UHE) 100 Wh/kg at C/10 & 0°C (predicted)	**165** Wh/kg at C/10 & 0°C "High-Energy" **180** Wh/kg at C/10 & 0°C "Ultra-High Energy"	**180** Wh/kg at C/10 & 0°C "High-Energy" **260** Wh/kg at C/10 & 0°C "Ultra-High Energy"
	Cathode-level specific capacity [mAh/g]	180 mAh/g	252 mAh/g at C/10 & 25°C 190 mAh/g at C/10 & 0°C	**260** mAh/g at C/10 & 0°C	**280** mAh/g at C/10 & 0°C
	Anode-level specific capacity [mAh/g]	280 mAh/g (MCMB)	330 @ C/10 & 0°C (HE) 1200 mAh/g @ C/10 & 0°C for 10 cycles (UHE)	**600** mAh/g at C/10 & 0°C "Ultra-High Energy"	**1000** mAh/g at C/10 0°C "Ultra-High Energy"
Energy density Lander: 311 Wh/l Rover: TBD EVA: 400 Wh/l	**Battery-level** energy density	250 Wh/l	n/a	**270** Wh/l "High-Energy" **360** Wh/l "Ultra-High"	**320** Wh/l "High-Energy" **420** Wh/l "Ultra-High"
	Cell-level energy density	320 Wh/l	n/a	**385** Wh/l "High-Energy" **460** Wh/l "Ultra-High"	**390** Wh/l "High-Energy" **530** Wh/l "Ultra-High"
Operating environment 0°C to 30°C, Vacuum	Operating Temperature	-20°C to +40°C	0°C to +30°C	**0°C** to **30°C**	**0°C** to **30°C**

Assumes prismatic cell packaging for threshold values. Goal values include lightweight battery packaging.

* Battery values are assumed at 100% DOD, discharged at C/10 to 3.0 volts/cell, and at 0°C operating conditions

** "High-Energy" = mixed metal oxide cathode with graphite anode

** "Ultra-High Energy" = mixed metal oxide cathode with Silicon composite anode

*** Over-temperature up to 110°C; reversal 150% excess discharge @ 1C; pass external and simulated internal short tests; overcharge 100% @ 1C for Goal and 80% @ C/5 for Threshold Value.

NASA Enabling Technology Development and Demonstration Program
High-Efficiency Space Power Systems – Battery Development Effort

NASA In-House Efforts

- Layered Metal Oxide Cathode Development – JPL
- High Voltage, Flame Retardant Electrolyte Development – JPL
- Si-based Composite Anode Development – GRC
- Safety Assessments – JSC
- Separator Assessments – GRC

NASA Research Announcement – Battery Cell Component Development Efforts

- NEI Corp., “Mixed Metal Composite Oxides for High Energy Li-ion Batteries”
- University of Texas at Austin, “Development of High Capacity Layered Oxide Cathodes”
- Physical Sciences, “Metal Phosphate Coating for Improved Cathode Material Safety”
- Yardney, “Flame-retardant, Electrochemically Stable Electrolyte for Lithium-ion Batteries”
- Lockheed Martin Space Systems Company, “Advanced Nanostructured Silicon Composite Anode Program”
- Georgia Tech Research Corp. & Clemson University, “Design of Resilient Silicon Anodes”
- Giner, “Control of Internal and External Short Circuits in Lithium-Ion Batteries”

Component Scale-up and Cell Development for High Energy and Ultra High Energy Cells

- Saft America

Projections

New materials have promise for greatly increased specific energy and energy density relative to state-of-the-art Li-ion

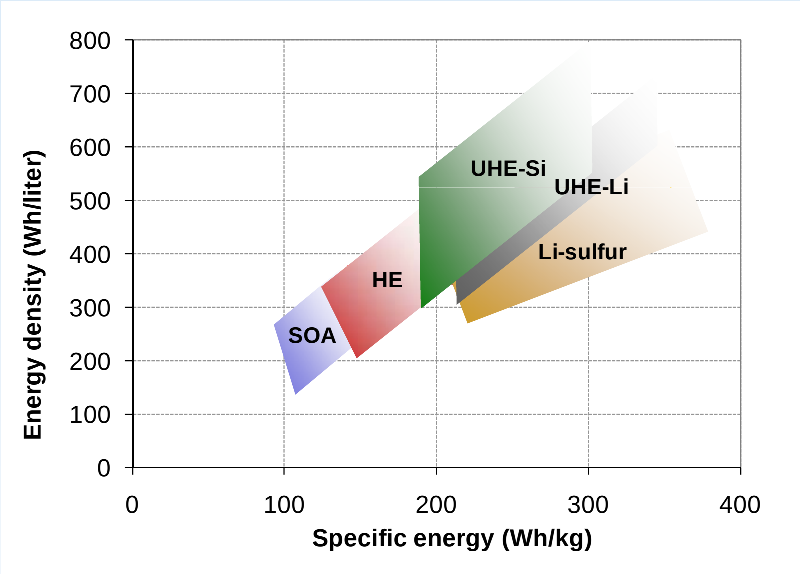
High energy and Ultra-high energy Li-ion chemistries are under development

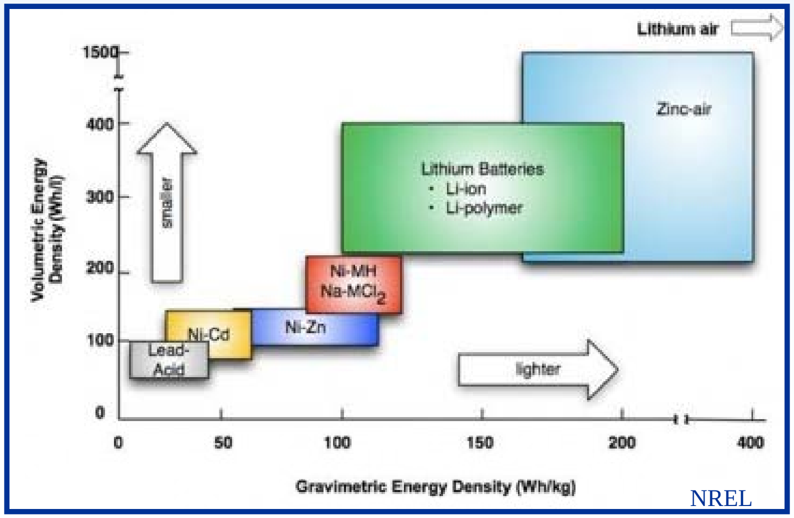
New electrode materials with challenging performance goals are required

Metal-air and Li-S

Other challenges

- Cycle life
- calendar life
- safety



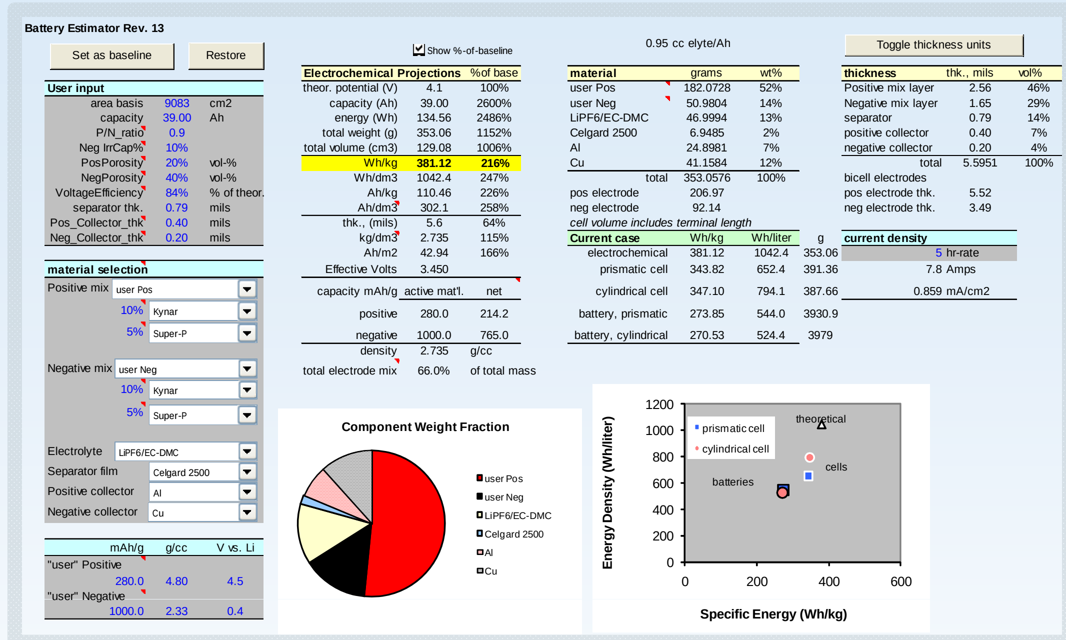


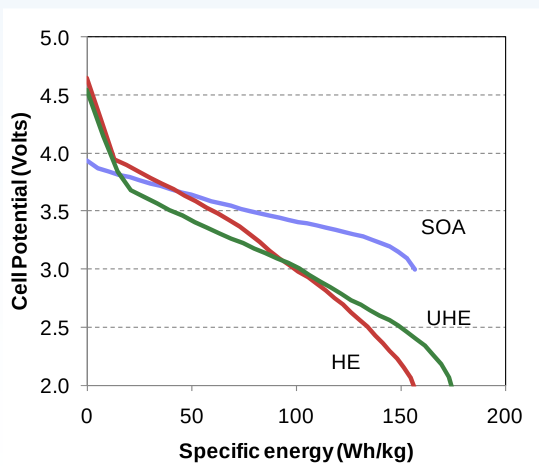
Modeling

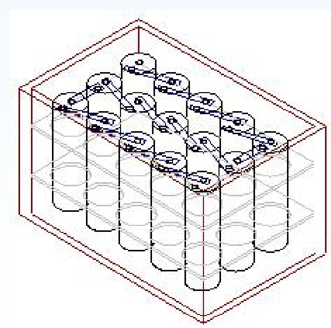
Spreadsheet-based models project cell and battery level characteristics

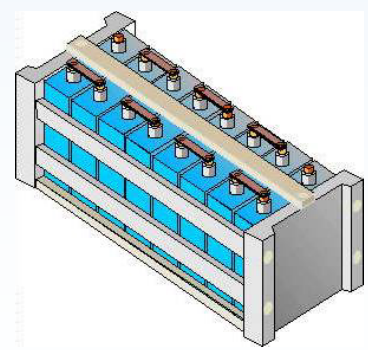
Tool for “what if?” analysis

Rate performance can be estimated from laboratory data for electrodes under relevant conditions









Cathodes

- **Goals:**
  - Specific capacity of 280 mAh/g at C/10 and 0°C to 3.0 V
  - High voltage operation to 4.8 V
  - Improved thermal stability over conventional Li-ion cathodes

Technology Challenges	Current Project Approaches to Address
High specific capacity at practical discharge rates	•Vary stoichiometry to determine optimum chemical formulation •Reduce particle size •Experiment with different synthesis methods to produce materials with physical properties such that their specific capacity is retained on production scale
Low volume per unit mass	•Vary cathode synthesis method to optimize properties that can: •Improve energy density •Improve ability to cast cathode powders •Facilitate incorporation of oxide coatings, which have the potential to increase rate capability and reduce capacity fade to extend cycle life
Minimize 1st cycle irreversible capacity loss and irreversible oxygen loss	•Surface modification via coatings to improve cathode-electrolyte interfacial properties •Improves capacity retention •Reduces capacity fade

Anodes

- **Goal:** 1000 mAh/g at C/10 (10 hour discharge rate) and 0°C
  - Over 3 times the capacity of SOA Li-ion anodes
  - Threshold value = 600 mAh/g at C/10 and 0°C

Technology Challenges	Current Approaches to Address
Minimize volume expansion during cycling	•Pursuing various approaches to optimize the anode structure to accommodate volume expansion of the silicon •Nano-structured Si composite absorbs strain, resists active particle isolation on cycling •Incorporation of elastic binders in Si –graphite and Si-C matrices •Improvement of mechanical integrity by fabricating structure to allow for elastic deformation
Minimize irreversible capacity loss	•Protection of active sites with functional binder additives •Pre-lithiation approaches are possible •Nano-structured Si resists fracture and surface renewal
250 cycles	Loss of contact with active particles reduces cycle life. Addressing volume changes and improvement of mechanical integrity will improve cycle life

Electrolytes

- **Goal:** Develop flame-retardant and/or non-flammable electrolytes that are stable up to 5V

Technology Challenges	Current approaches to address
Electrolyte that is stable up to 5V	Experiment with different electrolyte formulations and additives with potential to improve high voltage stability. Study interactions at both electrodes
Non-flammable or flame retardant electrolyte	Develop electrolytes containing additives with known flame retardant properties. Perform flame retardance assessments on developments that exhibit suitable electrochemical performance
High voltage stable, non-flammable or flame retardant electrolyte (combination of both properties in one electrolyte system)	Combine flame retardant additives with electrolyte formulations with high voltage stability. Operate systems to high voltages and investigate impacts on rate capability, specific energy, energy density and life.
Electrolytes possessing the requisite physical properties to ensure good rate capacity (adequate conductivity) and electrolyte-wetting.	Develop electrolytes that are not excessively viscous to ensure that the ionic conductivity is sufficiently high over the desired temperature range and the electrolyte-wetting is adequate.

Safety

- **Goal:** Cells that are tolerant to electrical and thermal abuse

Technology challenges	Approaches to address
Safe electrodes	•Develop materials to improve tolerance to an electrical abuse condition •Approach 1: Develop a high-voltage stable (phosphate) coating on cathode particles to increase the safe operating voltage of the cell and reduce the thermal dissipation by the use of a high-voltage stable coating material (cobalt phosphate). •Approach 2: Develop a composite thermal switch to shutdown cell reactions safely using coatings on the current collector substrates
Safe electrolyte	•Development of advanced high voltage, non-flammable/flame-retardant electrolytes (via electrolyte task)

Separators

- **Goals:**
  - Identification of Li-ion cell separator materials that are compatible with the ETDP chemistry and provide an increased level of safety over SOA Li-ion cell separators
  - Current efforts are focused on assessment of developmental (i.e., company IRAD materials) and commercial separator materials
- **Technology Challenges:**
  - No significant technology challenges
  - Design optimization for high porosity and low ionic resistance to facilitate ionic conductivity while maintaining mechanical strength
  - Must “shutdown” cell reactions below 130°C without shrinking or losing mechanical integrity
- **Significant results to date:**
  - Baseline separator identified (Tonen E20) and evaluated
    - Physical, thermal, electrical and mechanical properties measured and documented
  - Several promising commercial and IRAD materials identified and evaluated. Procured, obtained, or negotiating for additional samples to evaluate for our purposes
    - Physical Sciences, Inc.
    - Exxon Mobil
    - Kynar PVDF resins
    - Porous Power Technologies Symmetrix separators
    - Tonen polyethylene (PE)
    - Celgard polypropelene (PP)
    - Celgard PP/PE/PP trilayer
    - Saft America

RPC Electrochemistry Branch Facilities and Capabilities

Electrochemistry Branch – Batteries

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

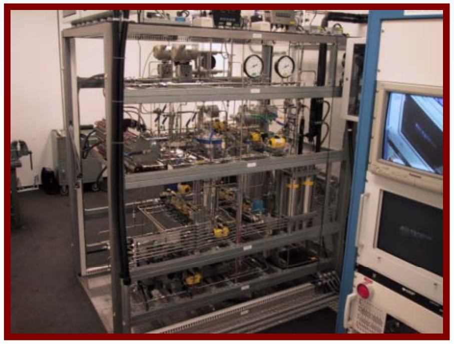
Facilities:

- Development Laboratories – SOA equipment for materials and component development, and analytical and electrochemical characterization
- 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

National Aeronautics and Space Administration

Electrochemistry Branch
Fuel Cells and Regenerative Fuel Cells

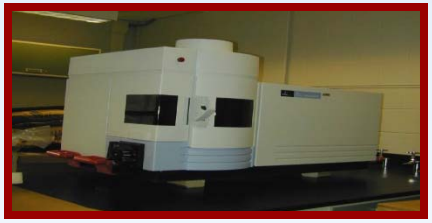
Capabilities
- Fundamental electrochemical research – component development and characterization with state-of-the-art analytical test capability
- Design and development of fuel cell and regenerative fuel cell systems, including ancillary components and reactant storage systems
- Fuel Cell System Modeling
- Fuel Cell System Performance and Life Testing and Evaluation



Fuel Cell Facilities
- Fuel Cell Development Laboratories with SOA equipment for materials and component development, and analytical and electrochemical characterization capabilities
- Fuel Cell Testing Laboratory large-scale (up to 25kW) fuel cell and regenerative system evaluation and life testing
- Regenerative Fuel Cell Test Facility component and system design evaluation

Electrochemistry 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 Spectrometer
- Thermogravimetric Analyzer (TGA)
- Raman Spectrometer
- Particle Size Analyzer


Concluding Remarks

- Electrochemical systems are critical to the success of Exploration, Science and Space Operations missions
- NASA Glenn has a long, successful heritage with batteries and fuel cells for aerospace applications
- GRC Battery capabilities and expertise span basic research through flight hardware development and implementation
- There is a great deal of synergy between energy storage system needs for aerospace and terrestrial applications