NASA Glenn Research Center Electrochemistry Branch Overview

This presentation covers an overview of NASA Glenn’s history and heritage in the development of electrochemical systems for aerospace applications. Current programs related to batteries and fuel cells are addressed. Specific areas of focus are Li-ion batteries and Polymer Electrolyte Membrane Fuel cells systems and their development for future Exploration missions. The presentation covers details of current component development efforts for high energy and ultra high energy Li-ion batteries and non-flow-through fuel cell stack and balance of plant development. Electrochemistry Branch capabilities and facilities are also addressed.
NASA Glenn Research Center
Electrochemistry Branch Overview

NASA Energy Storage Workshop

July 13, 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
- Electrochemistry Branch Capabilities and Facilities
- Overview of Current Projects
- Exploration Technology Development Program Energy Storage Project –
  - Space Rated Batteries – Concha Reid
  - Fuel Cells for Surface Power – Mark Hoberecht
RPC Electrochemistry Branch
Electrochemical Energy Storage Systems

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–H₂ 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
Li–Ion: Lithium–Ion
Ni–Cd: Nickel–Cadmium
Ni–H₂: Nickel–Hydrogen
Ni–MH: Nickel–metal hydride
Ni–Zn: Nickel–Zinc
Ag–Zn: Silver–Zinc
Na–S – Sodium Sulfur
LiCFx: Lithium–carbon monofluoride
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
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.

Experience
• 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

Products/Heritage
AFC – Alkaline Fuel Cell
PEM – Proton Exchange Membrane
SOFC – Solid Oxide Fuel Cell
RFC – Regenerative 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 setup of closed loop hydrogen oxygen regenerative fuel cell system

Conducted the first ever demonstration of closed-loop, hydrogen–oxygen regenerative fuel cell system
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
- 600 ft² 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

www.nasa.gov
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
RPC Electrochemistry Branch
Current Projects
RPC/Electrochemistry Branch
Current Projects

• Exploration Technology Development Program – Energy Storage Project – Lead Roles for Fuel Cell and Battery Development

• Support to Constellation Projects
  – CLV – Ares 1 Power System Development
  – Altair – Power System Development

• 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

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:
Fuel Cells: JSC, JPL, KSC
Batteries: JPL, JSC

Industry Partners, SBIR Partners, IPP Partners
Constellation Projects

• Ares 1 – CLV –
  – Battery Studies, specification, design – human rating
  – Project Closeout

• Altair Lunar Lander
  – Fuel Cell System studies, reliability analyses
  – Power System Lead
  – Propellant Scavenging Studies – Fuel Cell Performance
NESC Battery Working Group

- **Lead role for NESC Battery Working Group**
  - Multi center initiative – GRC, GSFC, JPL, JSC, MSFC, KSC
  - Government-wide participation

- **Recently completed suite of tasks addressing the following battery issues**
  - Wet Life of Ni–H₂ Batteries (GSFC)
  - Generic Safety, Reliability and Qualification Standards for Li–Ion batteries
    - Li–Ion Performance Assessment (GRC)
    - Generation of a Guidelines Document that addresses Safety and Handling and Qualification of Li–Ion Batteries (GRC)
    - Definition of Conditions Required for using Pouch Cells in Aerospace Missions (JSC/JPL)
    - High Voltage Risk Assessment: Limitations of Internal Protective Devices in High–Voltage/High–Capacity Batteries using Li–ion Cylindrical Commercial Cells (JSC)
    - Definition of Safe Limits for Charging Li–Ion Cells (JPL)
    - Availability of Source Materials for Li–Ion batteries (GRC)
  - Binding Procurements (GSFC)
International Space Station – Li–ion Risk Mitigation

- Extended Life of ISS requires battery replacement
  - Li–ion slated to replace Ni–H2 Batteries
- Selection of top cell designs for life testing is underway
  - Characterization Testing – Capacity, charged stand, soft short, thermal cycle, vibration testing – Mobile Power Solutions
  - Non-destructive analysis, DPA, and cross-sectional analysis – Exponent
- GRC – Life testing on top 3 or 4 vendors
- TIAAX – Determine safe zones of operation following selection of final cell
- Boeing – Working Change Request (CR) for battery development
  - Planning for 2014/2015 flight
Metal Air Battery Development

Human Research Program –
High energy battery to power Mobile Oxygen Concentrator for Spacecraft Emergencies

Li–Air System – candidate technology to meet high energy needs (>1850 Wh/kg)

Leverage SBIR program to support this development
Hydrogen Infrastructure for Renewable Energy

- **Renewable Hydrogen Today: Phase 1 of A Clean Energy Program for Economic Development**
  - Deploy a hydrogen powered fuel cell RTA bus
  - Build a hydrogen refueling station at GLSC
  - Convert Lake Erie water into hydrogen using an electrolyzer powered by GLSC wind and solar

**Technologies**
- Proton-exchange-membrane (PEM) fuel cells
- High-pressure PEM electrolyzers
- Hydrogen refueling station system development
- System deployment

**Outcomes**
- Design study completed; awaiting additional funding for system development and deployment

**Partners**
- NASA GRC, GLSC, OAI, RTA, CSU, Sierra Lobo, Parker Hannifin, Hamilton Sundstrand, UTC; numerous other collaborators and funders

![Artist’s conception of an articulated hydrogen fuel cell bus in front of the Great Lakes Science Center, Cleveland, Ohio](image-url)
Summary Remarks

• NASA Glenn has a long, successful heritage with batteries and fuel cells for aerospace applications
• GRC current plays a role in the development of electrochemical systems for a wide range of applications
  − Capabilities and expertise span basic research through flight hardware development and implementation
• Electrochemical energy storage systems are critical to the success of future NASA missions
• There is a great deal of synergy between energy storage system needs for aerospace and terrestrial applications
Exploration Technology Development Program
Energy Storage Project
Space-Rated Lithium-ion Battery Development

- Concha Reid, Co-Principal Investigator,
  - NASA GRC, 216-433-8943
- Thomas Miller, Co-Principal Investigator,
  - NASA GRC, 216-433-6300
<table>
<thead>
<tr>
<th>Customer Need</th>
<th>Performance Parameter</th>
<th>State-of-the-Art</th>
<th>Current Value</th>
<th>Threshold Value</th>
<th>Goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safe, reliable operation</td>
<td>No fire or flame</td>
<td>Instrumentation/controllers used to prevent unsafe conditions. There is no non-flammable electrolyte in SOA</td>
<td>Preliminary results indicate a small reduction in performance using safer electrolytes and cathode coatings</td>
<td>Tolerant to electrical and thermal abuse such as over-temperature, overcharge, reversal, and short circuits with no fire or flame***</td>
<td>Tolerant to electrical and thermal abuse such as over-temperature, overcharge, reversal, and short circuits with no fire or flame***</td>
</tr>
<tr>
<td>Specific energy</td>
<td>Battery-level</td>
<td>90 Wh/kg at C/10 &amp; 30°C 83 Wh/kg at C/10 &amp; 0°C (MER rovers)</td>
<td>160 at C/10 &amp; 30°C (HE) 170 at C/10 &amp; 30°C (UHE) 80 Wh/kg at C/10 &amp; 0°C (predicted)</td>
<td>135 Wh/kg at C/10 &amp; 0°C “High-Energy”** 150 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”***</td>
<td>150 Wh/kg at C/10 &amp; 0°C “High-Energy” 220 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”</td>
</tr>
<tr>
<td>Landers: 150 – 210 Wh/kg 10 cycles</td>
<td>specific energy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rover: 160-200 Wh/kg 2000 cycles</td>
<td>Cell-level</td>
<td>130 Wh/kg at C/10 &amp; 30°C 118 Wh/kg at C/10 &amp; 0°C</td>
<td>199 at C/10 &amp; 23°C (HE) 213 at C/10 &amp; 23°C (UHE) 100 Wh/kg at C/10 &amp; 0°C (predicted)</td>
<td>165 Wh/kg at C/10 &amp; 0°C “High-Energy” 180 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”</td>
<td>180 Wh/kg at C/10 &amp; 0°C “High-Energy” 260 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”</td>
</tr>
<tr>
<td>EVA: 270Wh/kg 100 cycles</td>
<td>Cathode-level</td>
<td>180 mAh/g</td>
<td>252 mAh/g at C/10 &amp; 25°C 190 mAh/g at C/10 &amp; 0°C</td>
<td>260 mAh/g at C/10 &amp; 0°C</td>
<td>280 mAh/g at C/10 &amp; 0°C</td>
</tr>
<tr>
<td>Energy density</td>
<td>Battery-level</td>
<td>280 mAh/g (MCMB)</td>
<td>330 @ C/10 &amp; 0°C (HE) 1200 mAh/g @ C/10 &amp; 0°C for 10 cycles (UHE)</td>
<td>600 mAh/g at C/10 &amp; 0°C “Ultra-High Energy”</td>
<td>1000 mAh/g at C/10 0°C “Ultra-High Energy”</td>
</tr>
<tr>
<td>Landers: 311 Wh/l</td>
<td>energy density</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating environment</td>
<td>Operating Temperature</td>
<td>-20°C to +40°C</td>
<td>0°C to +30°C</td>
<td>0°C to 30°C</td>
<td>0°C to 30°C</td>
</tr>
<tr>
<td>0°C to 30°C, Vacuum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.
Exploration Technology Development Program
Energy Storage Project Advanced Li-ion Cell Development

**High Energy Cell**
- Development targeted for Lunar Surface Systems (Lunar Electric Rover, Portable Utility Pallet)
- Lithiated mixed-metal-oxide cathode / Graphite anode

- Li(LiNMC)O₂ / Conventional carbonaceous anode
- **180** Wh/kg (100% DOD) @ cell-level, 0°C and C/10
- 80% capacity retention at ~2000 cycles


**Ultra High Energy Cell**
- Development targeted for EVA spacesuit and Altair Lunar Lander
- Lithiated-mixed-metal-oxide cathode / Silicon composite anode

- Li(LiNMC)O₂ / silicon composite
- **260** Wh/kg (100% DOD) @ cell-level, 0°C and C/10
- 80% capacity retention at ~200 cycles

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

Advanced electrolyte with additives provides flame-retardance and stability at high voltages without sacrificing performance.
Example: LiPF₆ 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

Layered Li(NMC)O₂ cathode particle
• Varying composition and morphology to improve capacity and charge/discharge rate

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

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[LiₓNiₓMnₓCo₁₋ₓ₋ₙ₋ₚ]O₂) to improve capacity
Li-Ion Cell Development

Combination of in-house, contractor and leveraged efforts targeted for development of advanced materials for High Energy and Ultra High Energy Cells and their design and development

### NASA In-House Efforts

**GRC**
- Si-based Composite Anode Development
- Separator Assessments
- Cell Development
- Cell Integration
- Analytical and Thermal evaluations
- Modeling

**JPL**
- Layered Metal Oxide Cathode Development
- High Voltage, Flame Retardant Electrolyte Development

**JSC**
- Safety Assessments

### NASA Research Announcement NNC08ZP022N Research and Development of Battery Cell Components

- 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”
- 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 Design and Development

- Saft America

### Leveraging

- NASA SBIR/STTRs
- NASA EPSCoR
- Interagency Advanced Power Group
- NASA Innovative Partnership Program
Anode Development
Led by William Bennett, ASRC at NASA GRC, 216-433-2486

- Develop silicon-based carbon composite materials
  - Much higher theoretical capacity than carbonaceous materials

- Development focus on:
  - Decreasing irreversible capacity loss
  - Increasing cycling stability by reducing impact of volume expansion
  - Improving cycle life

- Anode Development at:
  - Georgia Tech Research Institute
  - Lockheed Martin
  - Glenn Research Center

Silicon-based anodes: Specific capacity vs. cycles for three materials at C/10 and 23°C in coin cell half cell.
GRC In-House Anode Synthesis
PI: Jim Woodworth, NPP, NASA GRC, 216-433-5246

Resorcinol Formaldehyde (RF) Gels
- Resorcinol- formaldehyde resin formed in water
- Formed into monoliths
- Formed into microspheres
- Silicon or other materials may be added to the material
- Materials are freeze dried and pyrolyzed to form the carbonaceous anode material

Silicon Sputter Coated Carbon Fiber Paper
- Apply Si to an active support material that is also capable of acting as a current collector
- 50 nm Si Coating

Silicon Sputter Coated Copper
- 50 nm Si coating
- Used to study lithiation of silicon
Separators
Led by Richard Baldwin, NASA GRC, 216-433-6156

Goals
- Separators with improved safety
- Shutdown separators
- Optimized for ETDP chemistry

Significance
- The function and reliability of the separator are critical for optimal lithium-ion cell 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

Approach
- Assess and compare separator material properties
  - Emphasis on mechanical and thermal properties which strongly impact safety
- Leverage existing “second party” data on candidate materials
- Conduct laboratory and prototype full-cell testing
  - Integrated cell component compatibility
  - Cell charge/discharge cycle performance
  - Mechanical, thermal and electrical abuse testing
Separator Evaluation

Led by Richard Baldwin, NASA GRC  216-433-6156

Commercial Polyolefin Lithium-ion Battery Separator Comparisons - Tonen E20 Baseline and Celgard Separator Materials

Tonen E20 Polyethylene (PE) Separator Microstructure

Similar bulk porosity and ionic conductivity

Celgard 2500 Polypropylene (PP) Separator Microstructure

Wet-process
Non-oriented
Tortuous pore structure
~137°C melting point

Dry-process
Highly-oriented
~165°C melting point

DMA melt integrity data for Tonen E20 and Celgard 2325 separators
[the Celgard trilayer “shutdown” material retains mechanical integrity after the current flow in a cell is terminated as a result of the PE layer melting]
Cell Development
Led by Tom Miller, NASA GRC, 216-433-6300

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

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

- Build and test evaluation cells (10 Ah):
  - Determine component interactions
  - Determine cell-level performance

- Design lightweight cells (35 Ah)
  - Identify high risk elements early
Component screening:
UT Austin increased the tap density of their cathode to provide manufacturability; Saft modified their electrode processing to be compatible with Giner’s thermal switch; Georgia Tech will modify their binder additives to be compatible with Saft’s anode manufacturing process. Toda-9100 identified as baseline cathode.

Baseline cells: graphite anode (MPG-111), nickel-cobalt cathode (NCA) 
DD cells (10 Ah, cylindrical): fabricated and under test. 
34P cells (45 Ah, prismatic): fabricated, activated, and delivered.

Flightweight cells (35 Ah, prismatic): PDR held May, 2010

<table>
<thead>
<tr>
<th>Saft Contract Tasks</th>
<th>Basic (34 months)</th>
<th>Option 1 Flightweight Cell Fabrication (18 months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Component material scale-up</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electrode optimization</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Flightweight Cell Design</td>
<td></td>
</tr>
</tbody>
</table>
Cell Integration
Led by William Bennett, ASRC at NASA GRC, 216-433-2486

Objectives

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

Full cell testing with LM Si-based anode and Saft LiNiCoAl cathode

Increasing polarization at the cathode observed over 100 cycles

Electrochemical impedance after 100 cycles - Cathode impedance is greater than anode impedance, Si-based anode shows inductive loop
Analytical and Thermal Safety Evaluations
Led by Eunice Wong, ASRC at NASA GRC, 216-433-9823

- 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)

DSC analysis on anode, cathode, and electrolyte.
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

<table>
<thead>
<tr>
<th>Component Weight Fraction</th>
<th>User Pos</th>
<th>User Neg</th>
<th>LiPF6/EC-DMC</th>
<th>Celgard 2500</th>
<th>Kynar</th>
<th>Super-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total electrode mix (%)</td>
<td>66.0 (%)</td>
<td>33.2 (%)</td>
<td>5.00%</td>
<td>65.00%</td>
<td>8.00%</td>
<td>20.00%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrochemical Properties</th>
<th>T</th>
<th>HE</th>
</tr>
</thead>
<tbody>
<tr>
<td>current density (mA/cm²)</td>
<td>0.859</td>
<td>3.49</td>
</tr>
<tr>
<td>Energy Density (Wh/liter)</td>
<td>594.1</td>
<td>3930.9</td>
</tr>
<tr>
<td>Specific energy (Wh/kg)</td>
<td>110.46</td>
<td>1152%</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>LiPF6/EC-DMC</td>
<td>46.9994</td>
</tr>
<tr>
<td>Separator film</td>
<td>Celgard 2500</td>
<td>6.9485</td>
</tr>
<tr>
<td>Positive collector</td>
<td>Super-P</td>
<td>0.40</td>
</tr>
<tr>
<td>Negative collector</td>
<td>Al</td>
<td>24.8981</td>
</tr>
<tr>
<td>Positive mix 1</td>
<td>280.0</td>
<td>4.89</td>
</tr>
<tr>
<td>Negative mix 1</td>
<td>1000.0</td>
<td>23.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>grams wt%</th>
<th>vol% W h/ k g</th>
<th>Cu</th>
<th>vol-% Wh/ k g</th>
</tr>
</thead>
<tbody>
<tr>
<td>user Pos</td>
<td>182.0728</td>
<td>52%</td>
<td>41.1584</td>
<td>7%</td>
</tr>
<tr>
<td>user Neg</td>
<td>50.9804</td>
<td>14%</td>
<td>46.9994</td>
<td>12%</td>
</tr>
<tr>
<td>LiPF6/EC-DMC</td>
<td>46.9994</td>
<td>13%</td>
<td>347.10</td>
<td>0.859 mA/cm²</td>
</tr>
<tr>
<td>Celgard 2500</td>
<td>6.9485</td>
<td>2%</td>
<td>704.1</td>
<td>2.735 g/cc</td>
</tr>
<tr>
<td>Al</td>
<td>24.8981</td>
<td>7%</td>
<td>347.10</td>
<td>0.859 mA/cm²</td>
</tr>
<tr>
<td>Cu</td>
<td>41.1584</td>
<td>12%</td>
<td>704.1</td>
<td>2.735 g/cc</td>
</tr>
<tr>
<td>Super-P</td>
<td>0.40</td>
<td>7%</td>
<td>347.10</td>
<td>0.859 mA/cm²</td>
</tr>
<tr>
<td>Kynar</td>
<td>2.33</td>
<td>4%</td>
<td>347.10</td>
<td>0.859 mA/cm²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Battery</th>
<th>prismatic cell</th>
<th>cylindrical cell</th>
<th>prismatic cell</th>
<th>cylindrical cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive mix 1</td>
<td>280.0</td>
<td>214.3</td>
<td>273.85</td>
<td>544.0</td>
</tr>
<tr>
<td>Negative mix 1</td>
<td>1000.0</td>
<td>765.0</td>
<td>270.53</td>
<td>524.4</td>
</tr>
<tr>
<td>Electrode mix</td>
<td>381.1</td>
<td>1152%</td>
<td>343.82</td>
<td>652.4</td>
</tr>
<tr>
<td>Separator thk. (mils)</td>
<td>0.79</td>
<td>14%</td>
<td>3.49</td>
<td>7.85</td>
</tr>
<tr>
<td>Positive collector thk. (mils)</td>
<td>0.40</td>
<td>7%</td>
<td>0.40</td>
<td>7%</td>
</tr>
<tr>
<td>Negative collector thk. (mils)</td>
<td>0.20</td>
<td>4%</td>
<td>0.20</td>
<td>4%</td>
</tr>
<tr>
<td>Total weight (g)</td>
<td>353.06</td>
<td>1152%</td>
<td>39.00</td>
<td>2600%</td>
</tr>
<tr>
<td>Total volume (cm³)</td>
<td>129.18</td>
<td>1006%</td>
<td>381.12</td>
<td>1166%</td>
</tr>
<tr>
<td>Specific energy (Wh/kg)</td>
<td>110.46</td>
<td>1152%</td>
<td>343.82</td>
<td>652.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effective Volts</th>
<th>SOA</th>
<th>HE</th>
</tr>
</thead>
<tbody>
<tr>
<td>voltage (V)</td>
<td>4.1</td>
<td>4.5</td>
</tr>
<tr>
<td>user Pos</td>
<td>280.0</td>
<td>4.89</td>
</tr>
<tr>
<td>user Neg</td>
<td>1000.0</td>
<td>23.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy Density (Wh/liter)</th>
<th>prismatic cell</th>
<th>cylindrical cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive mix 1</td>
<td>273.85</td>
<td>544.0</td>
</tr>
<tr>
<td>Negative mix 1</td>
<td>270.53</td>
<td>524.4</td>
</tr>
<tr>
<td>total electrode mix</td>
<td>66.0%</td>
<td>3930.9</td>
</tr>
<tr>
<td>Total weight (g)</td>
<td>353.06</td>
<td>3930.9</td>
</tr>
<tr>
<td>Total volume (cm³)</td>
<td>129.18</td>
<td>1006%</td>
</tr>
<tr>
<td>Specific energy (Wh/kg)</td>
<td>110.46</td>
<td>1152%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Voltage Efficiency</th>
<th>HE</th>
</tr>
</thead>
<tbody>
<tr>
<td>efficiency (%)</td>
<td>84</td>
</tr>
<tr>
<td>user Pos</td>
<td>182.0728</td>
</tr>
<tr>
<td>user Neg</td>
<td>50.9804</td>
</tr>
<tr>
<td>LiPF6/EC-DMC</td>
<td>46.9994</td>
</tr>
<tr>
<td>Celgard 2500</td>
<td>6.9485</td>
</tr>
<tr>
<td>Al</td>
<td>24.8981</td>
</tr>
<tr>
<td>Cu</td>
<td>41.1584</td>
</tr>
<tr>
<td>Super-P</td>
<td>0.40</td>
</tr>
<tr>
<td>Kynar</td>
<td>2.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component Weight Fraction</th>
<th>user Pos</th>
<th>user Neg</th>
<th>LiPF6/EC-DMC</th>
<th>Celgard 2500</th>
<th>Kynar</th>
<th>Super-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total electrode mix (%)</td>
<td>66.0 (%)</td>
<td>33.2 (%)</td>
<td>5.00%</td>
<td>65.00%</td>
<td>8.00%</td>
<td>20.00%</td>
</tr>
<tr>
<td>Positive mix 1</td>
<td>280.0</td>
<td>4.89</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Negative mix 1</td>
<td>1000.0</td>
<td>23.33</td>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrochemical Properties</th>
<th>T</th>
<th>HE</th>
</tr>
</thead>
<tbody>
<tr>
<td>current density (mA/cm²)</td>
<td>0.859</td>
<td>3.49</td>
</tr>
<tr>
<td>Energy Density (Wh/liter)</td>
<td>594.1</td>
<td>3930.9</td>
</tr>
<tr>
<td>Specific energy (Wh/kg)</td>
<td>110.46</td>
<td>1152%</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>LiPF6/EC-DMC</td>
<td>46.9994</td>
</tr>
<tr>
<td>Separator film</td>
<td>Celgard 2500</td>
<td>6.9485</td>
</tr>
<tr>
<td>Positive collector</td>
<td>Super-P</td>
<td>0.40</td>
</tr>
<tr>
<td>Negative collector</td>
<td>Al</td>
<td>24.8981</td>
</tr>
<tr>
<td>Positive mix 1</td>
<td>280.0</td>
<td>4.89</td>
</tr>
<tr>
<td>Negative mix 1</td>
<td>1000.0</td>
<td>23.33</td>
</tr>
<tr>
<td>Electrode mix</td>
<td>381.1</td>
<td>1152%</td>
</tr>
<tr>
<td>Separator thk. (mils)</td>
<td>0.79</td>
<td>14%</td>
</tr>
<tr>
<td>Positive collector thk. (mils)</td>
<td>0.40</td>
<td>7%</td>
</tr>
<tr>
<td>Negative collector thk. (mils)</td>
<td>0.20</td>
<td>4%</td>
</tr>
<tr>
<td>Total weight (g)</td>
<td>353.06</td>
<td>1152%</td>
</tr>
<tr>
<td>Total volume (cm³)</td>
<td>129.18</td>
<td>1006%</td>
</tr>
<tr>
<td>Specific energy (Wh/kg)</td>
<td>110.46</td>
<td>1152%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effective Volts</th>
<th>SOA</th>
<th>HE</th>
</tr>
</thead>
<tbody>
<tr>
<td>voltage (V)</td>
<td>4.1</td>
<td>4.5</td>
</tr>
<tr>
<td>user Pos</td>
<td>280.0</td>
<td>4.89</td>
</tr>
<tr>
<td>user Neg</td>
<td>1000.0</td>
<td>23.33</td>
</tr>
<tr>
<td>LiPF6/EC-DMC</td>
<td>46.9994</td>
<td></td>
</tr>
<tr>
<td>Celgard 2500</td>
<td>6.9485</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>24.8981</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>41.1584</td>
<td></td>
</tr>
<tr>
<td>Super-P</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>Kynar</td>
<td>2.33</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy Density (Wh/liter)</th>
<th>prismatic cell</th>
<th>cylindrical cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive mix 1</td>
<td>273.85</td>
<td>544.0</td>
</tr>
<tr>
<td>Negative mix 1</td>
<td>270.53</td>
<td>524.4</td>
</tr>
<tr>
<td>total electrode mix</td>
<td>66.0%</td>
<td>3930.9</td>
</tr>
<tr>
<td>Total weight (g)</td>
<td>353.06</td>
<td>3930.9</td>
</tr>
<tr>
<td>Total volume (cm³)</td>
<td>129.18</td>
<td>1006%</td>
</tr>
<tr>
<td>Specific energy (Wh/kg)</td>
<td>110.46</td>
<td>1152%</td>
</tr>
</tbody>
</table>
Cathode Development
Led by Kumar Bugga, NASA JPL, 818-354-0110

- **Develop Li(NMC) materials**
  - Offer enhanced thermal stability over conventional cobaltate cathodes
  - High voltage materials

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

- **Cathode Development at:**
  - University of Texas at Austin
  - NEI Corporation
  - JPL

Synthesis methods affect tap density
Electrolyte Development
Led by Marshall Smart, NASA JPL, 818-354-9374

- 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

- Electrolyte Development at:
  - JPL
  - Yardney Technical Products/University of Rhode Island

<table>
<thead>
<tr>
<th>Description</th>
<th>Electrolyte</th>
<th>Percentage Flame Retardant Additive (%)</th>
<th>SET, S</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yardney/URI GEN #1 Electrolyte</td>
<td>1.0M (95% LiPF6+5% LiBOB) in EC/EMC/DMMP (8/3/3/1.5)</td>
<td>15% DMMP</td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td>JPL Electrolyte</td>
<td>1.0M LiPF6 in EC/EMC/TPP (2/6/3/1.5) + 2% VC</td>
<td>15% TPP</td>
<td>3.78</td>
<td>1.2</td>
</tr>
<tr>
<td>JPL Electrolyte</td>
<td>1.0M LiPF6 in EC/EMC/TPP (2/7/1) + 2% VC</td>
<td>10% TPP</td>
<td>9.57</td>
<td>0.9</td>
</tr>
<tr>
<td>JPL GEN #1 Electrolyte</td>
<td>1.0M LiPF6 in EC/EMC/TPP (2/7.5/0.5) + 2% VC</td>
<td>5% TPP</td>
<td>22.45</td>
<td>2.3</td>
</tr>
<tr>
<td>&quot;Baseline&quot; Electrolyte</td>
<td>1.0M LiPF6 in EC/EMC (8:7)</td>
<td>None</td>
<td>33.4</td>
<td>3.4</td>
</tr>
<tr>
<td>Yardney/URI GEN #1 Electrolyte</td>
<td>1.0M (95% LiPF6+5% LiBOB) in EC/EMC/DMMP (8/3/3/1.5)</td>
<td>20% DMMP</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Self-extinguishing time (SET) flammability tests show excellent flame retardance in JPL and Yardney/URI electrolytes.
Safety Component Development
Led by Judy Jeevarajan, NASA JSC, 281-483-4528

• Development of internal cell materials (active or inactive) designed to improve the inherent safety of the cell

• Functional components

• Safety Component Development at:
  – Physical Sciences, Inc.
  – Giner
Energy Storage Workshop
Fuel Cell Technical Capabilities

• Mark Hoberecht / NASA GRC
• Principal Investigator, Fuel Cell Systems

• July 13, 2010
Energy Storage: Fuel Cells
Technical Objectives and Approach

Objectives:
Increase system lifetimes (10,000 hours) and reduce system mass, volume and parasitic power for primary and regenerative fuel cells, and
Enable the use of regenerative fuel cells including the use of high pressure (>2000 psi) reactants to reduce tankage mass and volume.

Focus is exclusively on Hydrogen/Oxygen Proton Exchange Membrane fuel cells and regenerative fuel cell systems

Technical Approach is to develop:
“Non-flow-through” proton exchange membrane stack and balance-of-plant technology;
Advanced membrane-electrode-assemblies for both fuel cells and electrolyzers,
Balanced high-pressure electrolyzers; and
Thermal and reactant management technologies for electrolyzer/fuel-cell integration into regenerative fuel cell systems.
Fuel Cell Technical Approach

Technical approach: Develop “non-flow-through” proton exchange membrane fuel cell technology for a system improvement in weight, volume, reliability, and parasitic power over “flow-through” technology.

Flow-Through components eliminated in Non-Flow-Through system include:
- Pumps or injectors/ejectors for recirculation
- Motorized or passive external water separators

Non-Flow-Through PEMFC technology characterized by dead-ended reactants and internal product water removal
- Tank pressure drives reactant feed; no recirculation
- Water separation occurs through internal cell wicking
Balance-of-Plant: developing universal system to test cells from many vendors, and lightweight, low power system for demos.

Fuel Cell Stacks from several vendors incorporate advanced water removal, thermal management, and manufacturing processes.

Electrolysis development focuses on balanced, high pressure operation.

Test facilities at NASA GRC, JSC and JPL augment industrial capability.

MEA development improves system efficiency.
Vendor Partners in Fuel Cell Development

Non-Flow-Through Fuel Cell Stacks
• Infinity (baseline technology)
• ElectroChem
• Proton
• Teledyne

Electrolysis Stacks
• Hamilton Sundstrand (active liquid feed)
• Giner (active liquid feed, vapor feed)
• Infinity (vapor feed)
• Potential SBIR vendors (passive liquid feed)

Passive Thermal Control
• Thermacore (titanium flat-plate heat pipes)

Electrical Control
• Ridgetop (integrated circuit development for extreme environments)
Non-Flow-Through Common Test Bed
Balance-of-Plant Scope

• Develop Test Platform
  – Configurable to test stacks provided by multiple vendors
  – Capable of testing total output power of 1 kW_e
  – Capable of testing stacks of up to 40 Cells
  – Capable of conducting un-attended life testing
  – Developed and built using COTS hardware
Non-Flow-Through Common Test Bed Overview

- Reactant Management
- Power Interface Module
- Electronics Module
- Fuel Cell Stack

- External System
- Common Test Bed (CTB)

- Reactants (H₂ & O₂)
- Heat
- Water/Coolant
- Communication Bus
- Sensor/Actuator
- Power

110 Vac
DC
Non-Flow-Through Common Test Bed System
Passive Thermal Management

The objective of the advanced thermal management work is to develop a passive means of fuel cell thermal management that can eliminate system components within the conventional pumped loop cooling systems used presently. This will reduce mass and improve reliability.
Advanced Thermal Management Materials

Testing of new ultra-high thermally conductive materials shows thermal conductivity 4 to 15 times that of copper and should be satisfactory for extracting heat from the core of the fuel cell stack.

Thermal Conductivity Tests in VF-15

Heat Pipes and Pyrolytic Graphite have high enough thermal conductivity to be acceptable lightweight cooling plates for fuel cells while copper does not.
The Ti heat pipes have been fabricated and tested at GRC. Their thermal conductivity ranged from 3500 to 6300 w-m/K. (copper is 400 w-m/K)

The Ti heat pipes were delivered to Infinity Fuel Cells for integration into the stack.

The HX Interface plate hardware has been fabricated and will be delivered to Infinity for final stack assembly.

The integrated FC stack is to be delivered to GRC by February 2009 for testing.

Preparations are being made for this testing to occur in the GRC Bldg 309 Fuel Cell Laboratory.
<table>
<thead>
<tr>
<th>Customer Need</th>
<th>Performance Parameter</th>
<th>SOA (alkaline)</th>
<th>Current Value* (PEM)</th>
<th>Threshold Value** (@ 3 kW)</th>
<th>Goal** (@ 3 kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altair: 3 kW for 220 hours continuous, 5.5 kW peak.</td>
<td>System power density</td>
<td>49 W/kg</td>
<td>n/a</td>
<td>88 W/kg</td>
<td>136 W/kg</td>
</tr>
<tr>
<td>Fuel Cell RFC (without tanks)</td>
<td></td>
<td>n/a</td>
<td>n/a</td>
<td>25 W/kg</td>
<td></td>
</tr>
<tr>
<td>Fuel Cell Stack power density</td>
<td></td>
<td>n/a</td>
<td>n/a</td>
<td>107 W/kg</td>
<td>231 W/kg</td>
</tr>
<tr>
<td>Fuel Cell Balance-of-plant mass</td>
<td></td>
<td>n/a</td>
<td>n/a</td>
<td>21 kg</td>
<td>9 kg</td>
</tr>
<tr>
<td>Lunar Surface Systems: TBD kW for 15 days continuous operation</td>
<td>MEA efficiency @ 200 mA/cm²</td>
<td>73%</td>
<td>72%</td>
<td>73%</td>
<td>75%</td>
</tr>
<tr>
<td>For Fuel Cell Individual cell voltage</td>
<td></td>
<td>0.90V</td>
<td>0.89V</td>
<td>0.90V</td>
<td>0.92V</td>
</tr>
<tr>
<td>For Electrolysis Individual cell voltage</td>
<td></td>
<td>n/a</td>
<td>86%</td>
<td>84%</td>
<td>85%</td>
</tr>
<tr>
<td>For RFC (Round Trip)</td>
<td></td>
<td>n/a</td>
<td>1.48</td>
<td>1.46</td>
<td>1.44</td>
</tr>
<tr>
<td>System efficiency @ 200 mA/cm²</td>
<td>Fuel Cell Parasitic penalty</td>
<td>71%</td>
<td>65%***</td>
<td>71%</td>
<td>74%</td>
</tr>
<tr>
<td>Regenerative Fuel Cell**** High Pressure penalty</td>
<td></td>
<td>n/a</td>
<td>n/a</td>
<td>43%</td>
<td>54%</td>
</tr>
<tr>
<td>Parasic penalty</td>
<td></td>
<td>n/a</td>
<td>n/a</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td>Maintenance-free lifetime</td>
<td>Maintenance-free operating life</td>
<td>2500 hrs</td>
<td>13,500 hrs</td>
<td>5,000 hrs</td>
<td>10,000 hrs</td>
</tr>
<tr>
<td>Altair: 220 hours (primary) Surface: 10,000 hours (RFC)</td>
<td>Fuel Cell MEA</td>
<td>2500 hrs</td>
<td>n/a</td>
<td>5,000 hrs</td>
<td>10,000 hrs</td>
</tr>
<tr>
<td>Electrolysis MEA</td>
<td></td>
<td>n/a</td>
<td>n/a</td>
<td>220 hrs</td>
<td>220 hrs</td>
</tr>
<tr>
<td>Fuel Cell System (for Altair) Regenerative Fuel Cell System</td>
<td></td>
<td>n/a</td>
<td>n/a</td>
<td>5,000 hrs</td>
<td>10,000 hrs</td>
</tr>
</tbody>
</table>

*Based on limited small-scale testing.
**Threshold and Goal values based on full-scale (3 kW) fuel cell and RFC technology.
***Teledyne passive flow through with latest MEA
****Includes high pressure penalty on electrolysis efficiency 2000 psi
Concluding Remarks

- ETDP/Energy Storage Project is a prime example of successful intercenter collaborations in the development of electrochemical systems
  - Relationships built and fostered working on joint projects provide sound basis for future work
- GRC capabilities and expertise compliment and reinforce capabilities at other NASA Centers
- Current project serves as model for teaming to advance energy storage technologies