This presentation covers an overview of NASA Glenn’s history and heritage in the development of electrochemical systems for aerospace applications. Current developments 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.
Electrochemistry Branch Overview

- GRC Electrochemistry Branch – Energy Storage System Background and Heritage
- Overview of Battery and Fuel Cell Development Efforts
- Electrochemistry Branch Capabilities and Facilities
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.
• Advanced battery technologies are needed to meet the challenges of future NASA missions.

Experience
• Lead battery development effort for Exploration Technology Development and Demonstration Program, High Efficiency Space Power Systems
• Developed and validated component and advanced designs of Ni–Cd and Ni–H₂ cells adopted by NASA, cell manufacturers and satellite companies.
• Developed lightweight nickel electrodes, bipolar nickel hydrogen battery designs
• Evaluated flight battery technologies for ISS
• Jointly sponsored and conducted Li–ion battery development program with DoD that developed Li–ion cells used on Mars Exploration Rovers
• Lead NASA Aerospace Flight Battery Systems Working Group – 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
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.
• Fuel cell/electrolysis based systems are enabling for various aspects of future NASA missions.

Experience
• Lead fuelcell/electrolysis development effort for Exploration Technology Development and Demonstration Program, High Efficiency Space Power Systems Project
• Gemini, Apollo, and Shuttle technology development
• Terrestrial energy program management for Fuel Cell systems for Stand Alone Power
• SOFC and PEM Fuel Cell development for aeronautics applications
• Alkaline fuel cell upgrades for Shuttle
• PEM powerplant development for launch vehicles
• Fuel cell demonstration for high altitude scientific balloons, Helios
• RFC Development for High Altitude Airships
• Conducted first ever demonstration of a closed loop hydrogen–oxygen regenerative fuel cell system

Products/Heritage
AFC – Alkaline Fuel Cell
PEM – Proton Exchange Membrane
SOFC – Solid Oxide Fuel Cell
RFC – Regenerative Fuel Cell Systems

www.nasa.gov
Exploration missions require advanced electrochemical energy storage devices to meet power requirements and enable various mission scenarios.

**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:** Landers, Rovers, Orbiters.

**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:** Landers, EVA, rovers, base power, orbiters.

**Overall Objectives:**
- Mature advanced technologies to TRL 6
- Integrate component technologies into prototype systems to validate performance
- Transition technology products to future Exploration Missions

**Participants:**
- GRC – Lead
  - Fuel Cells: JSC, JPL, KSC
  - Batteries: JPL, JSC

**Industry Partners, SBIR Partners, IPP Partners**

www.nasa.gov
Li–Ion Cell/Battery Development
Li-Ion Battery Development

Objectives: Develop Flight Qualified, Human-Rated Li-Ion cells with increased safety and reliability and mass and volume reductions

Approach:
• Identify chemistries most likely to meet overall NASA goals and requirements within allotted development timeframe
  - “High energy” and “ultra high energy” chemistries identified and targeted to meet customer requirements.
• 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
  - Design and optionally manufacture flightweight cells that address NASA’s goals
• Complete TRL 5 and 6 testing at NASA
• Leverage outside efforts
  - SBIR/IPP efforts, DoE and other government programs

Cell development TRL definitions

TRL 4: Advanced cell components integrated into a flight design cell
TRL 5: Performance testing on integrated cell shows goals met
TRL 6: Environmental testing on cell (vibration, thermal) shows robust performance
Chemistry Identification – Feasibility Study to Determine Ultra High Energy Chemistry

Customers’ top priority is safety. Based on customer requirements, team determined safety goals: No fire or thermal runaway at the component level.

No chemistry exists that can meet customers’ aggressive specific energy goals. Desire for a safer chemistry presents a set of conflicting objectives – Safer chemistry combined with ultra high specific energy.

In 2008 a feasibility study was initiated to determine the best advanced chemistry to meet EVA and Altair’s requirements on the established schedule (in time for customer System Design Reviews) and within available resources.
Study Goal:
Determine the best advanced chemistry to develop for EVA and Altair who require safe, reliable energy storage systems with extremely high specific energy as compared to today’s state-of-the-art (SOA) batteries.
Safety target: No fire or thermal runaway at the component level.
Specific energy target: 160–220 watt-hours per kilogram delivered at the battery level at C/10 and 0°C.
Process: Assessed 31 chemistries, selected 7 as feasible, ranked those 7 using an Analytical Hierarchy Process (pairwise comparison against 10 weighted attributes)
<table>
<thead>
<tr>
<th>Attribute</th>
<th>Final Weight</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safety</td>
<td>17.9</td>
<td>The likelihood that a cell made from these components can be made to be safe. Included safety under normal operation and abuse conditions</td>
</tr>
<tr>
<td>Rate Capability up to C/5</td>
<td>15.6</td>
<td>Likelihood that the technology can meet a C/5 continuous discharge rate</td>
</tr>
<tr>
<td>Specific Energy</td>
<td>15.0</td>
<td>Projected specific energy of the technology (calculated under a standard set of conditions)</td>
</tr>
<tr>
<td>Storage and Calendar Life</td>
<td>12.2</td>
<td>Projected storage + calendar life, where calendar life includes the operating time plus periods at open circuit between active charging and discharging</td>
</tr>
<tr>
<td>Energy Density</td>
<td>10.2</td>
<td>Projected energy density of the technology (calculated under a standard set of conditions)</td>
</tr>
<tr>
<td>Manufacturability</td>
<td>8.3</td>
<td>The projected level of ease or difficulty associated with working with materials, scaling up batches of materials, and manufacturing cells of practical capacity made from these components, and the projected adaptability of materials to large scale processing</td>
</tr>
<tr>
<td>Schedule</td>
<td>8.0</td>
<td>Likelihood that TRL 6 cells can be delivered by March 2104</td>
</tr>
<tr>
<td>Cost to TRL 6</td>
<td>6.5</td>
<td>The cost to develop the technology to TRL 6, including costs attributed to costly manufacturing processes or processes that cannot be automated</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>3.8</td>
<td>Projected cycle life of the technology</td>
</tr>
<tr>
<td>Rate Capability up to C/2</td>
<td>2.5</td>
<td>Likelihood that the technology can meet a C/2 continuous discharge rate</td>
</tr>
</tbody>
</table>
### Advanced Chemistry Options and Ranking

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Anode</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(Ni(<em>{0.33})Mn(</em>{0.33})Co(_{0.33}))O(_2)</td>
<td>Si-based Composite</td>
<td>20.2</td>
</tr>
<tr>
<td>Li(LiNMC)O(_2) (ETDP)</td>
<td>Si-based Composite</td>
<td>17.0</td>
</tr>
<tr>
<td>LiNiMn(_2)O(_4)</td>
<td>Li metal</td>
<td>15.3</td>
</tr>
<tr>
<td>Li(Ni(<em>{0.33})Mn(</em>{0.33})Co(_{0.33}))O(_2)</td>
<td>Li metal</td>
<td>13.9</td>
</tr>
<tr>
<td>Li(LiNMC)O(_2) (ETDP)</td>
<td>Li metal</td>
<td>13.1</td>
</tr>
<tr>
<td>(Li(_2))S</td>
<td>Li metal</td>
<td>11.5</td>
</tr>
<tr>
<td>LiCoPO(_4)</td>
<td>Li metal</td>
<td>9.1</td>
</tr>
</tbody>
</table>

**Projected Specific Energy in 35 Ah Cells**

![Graph showing projected specific energy](https://www.nasa.gov)

- Li(NMC) cathode with Si–based composite anode offers:
  - Higher safety, manufacturability and rate capability
  - Lower specific energy
- Li(LiNMC) (ETDP) cathode with Si–based composite anode offers:
  - Higher specific energy
  - Lower safety, manufacturability and demonstrated rate capability

**✓** ETDP cathode with Si–based composite anode chosen as Ultra High Energy chemistry due to its potential to achieve much higher specific energy.
<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, over-charge, reversal, and short circuits with no fire or thermal runaway***</td>
<td>Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and short circuits with no fire or thermal runaway***</td>
</tr>
<tr>
<td><strong>Specific energy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lander: 150 – 210 Wh/kg 10 cycles</td>
<td>Battery-level specific energy* [Wh/kg]</td>
<td>90 Wh/kg at C/10 &amp; 30°C&lt;br&gt;83 Wh/kg at C/10 &amp; 0°C (MER rovers)</td>
<td>160 Wh/kg at C/10 &amp; 30°C (HE)&lt;br&gt;170 Wh/kg at C/10 &amp; 30°C (UHE)&lt;br&gt;80 Wh/kg at C/10 &amp; 0°C (predicted)</td>
<td>135 Wh/kg at C/10 &amp; 0°C “High-Energy”<strong>&lt;br&gt;150 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”</strong>&lt;br&gt;180 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”</td>
<td>150 Wh/kg at C/10 &amp; 0°C “High-Energy”&lt;br&gt;220 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”</td>
</tr>
<tr>
<td>Rover: 160-200 Wh/kg 2000 cycles</td>
<td>Cell-level specific energy [Wh/kg]</td>
<td>130 Wh/kg at C/10 &amp; 30°C&lt;br&gt;118 Wh/kg at C/10 &amp; 0°C</td>
<td>199 Wh/kg at C/10 &amp; 23°C (HE)&lt;br&gt;213 Wh/kg at C/10 &amp; 23°C (UHE)&lt;br&gt;100 Wh/kg at C/10 &amp; 0°C (predicted)</td>
<td>165 Wh/kg at C/10 &amp; 0°C “High-Energy”&lt;br&gt;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”&lt;br&gt;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 specific capacity [mAh/g]</td>
<td>180 mAh/g&lt;br&gt;252 mAh/g at C/10 &amp; 25°C&lt;br&gt;190 mAh/g at C/10 &amp; 0°C</td>
<td>260 mAh/g at C/10 &amp; 0°C&lt;br&gt;280 mAh/g at C/10 &amp; 0°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Energy density</strong></td>
<td>Anode-level specific capacity [mAh/g]</td>
<td>280 mAh/g (MCMB)&lt;br&gt;330 @ C/10 &amp; 0°C (HE)&lt;br&gt;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”&lt;br&gt;1000 mAh/g at C/10 0°C “Ultra-High Energy”</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rover: TBD</td>
<td>Cell-level energy density</td>
<td>320 Wh/l&lt;br&gt;n/a</td>
<td>385 Wh/l “High-Energy”&lt;br&gt;460 Wh/l “Ultra-High”&lt;br&gt;390 Wh/l “High-Energy”&lt;br&gt;530 Wh/l “Ultra-High”</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVA: 400 Wh/l</td>
<td>Operating Temp</td>
<td>-20°C to +40°C</td>
<td>0°C to +30°C</td>
<td>0°C to 30°C&lt;br&gt;0°C to 30°C</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.
Advanced Li–Ion Battery Cell Development

High Energy Cell

- Li(LiNMnC)O$_2$ • NASA Cathode
- Conventional Carbonaceous Anode

Lithiated–mixed–metal–oxide cathode – Li(LiNMnC)O$_2$

- Conventional carbonaceous anode

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

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

Ultra–High Energy Cell

- Li(LiNMnC)O$_2$ • NASA Cathode
- Si–composite NASA Anode

Lithiated–mixed–metal–oxide cathode – Li(LiNMnC)O$_2$

- Silicon composite anode

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

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

www.nasa.gov
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

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

Li-Metal-PO₄ Safety Coating for Thermal Stability

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[LiₓNiₓMn₂Co₃₋ₓ₋₂₋₂]O₂) to improve capacity

www.nasa.gov
Li–Ion Cell 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 Battery Cell Component Development Contracts**
- 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

www.nasa.gov
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

<table>
<thead>
<tr>
<th>Technology Challenges</th>
<th>Current Approaches to Address</th>
</tr>
</thead>
</table>
| 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 |
| Achieve 250 cycles | • Loss of contact with active particles reduces cycle life. Addressing volume changes and improvement of mechanical integrity will improve cycle life |
**Composite Anodes for Ultra-High Energy Batteries**

**Objective:**
- Develop anode materials capable of delivering 1000 mAh/g at 0°C and C/10 (10 hour rate), and 200 cycles to 80% of their original capacity.

**Accomplishments:**
- Silicon anodes under development have demonstrated initial capacities of up to 1731 mAh/g.
- Novel silicon nanowire/carbon microfiber anode structure from Physical Sciences Incorporated produced over 1200 mAh/g for 110 cycles in room temperature testing at C/10 with good low temperature rate capability, achieving 83% of room temperature capacity at C/2 and 0 deg C.
- Full cell with Georgia Tech silicon anode and NCA cathode achieved satisfactory coulombic efficiency and maintained anode capacity above the threshold level of 600 mAh/g for over 200 cycles in an un-optimized cell.

**Current Challenges:**
- Specific capacity fade rates are still too high to meet the goal of 200 cycles at the cell level.
- Irreversible capacity is extremely high (>106% over 2 cycles in final contract deliverable)
- Limited capacity utilization after first cycle presents issue for positive electrode capacity matching
- Demonstrating performance at 0 deg C.
## 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

<table>
<thead>
<tr>
<th>Technology Challenges</th>
<th>Current Approaches to Address</th>
</tr>
</thead>
</table>
| 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 |
Cathodes

Objective:
• Develop cathode materials with improved thermal stability and specific capacity (to 3.0V)>280 mAh/g at C/10 and 0°C.

Accomplishments:
• Synthesized high voltage materials with significant gains in specific capacity and rate capability
• Tap density issues have been addressed – increased to 1.6 – 2 g/cc but specific capacity to 3.0V degraded (from 252 mAh/g to ~210 mAh/g)
• Surface modified samples demonstrate higher capacity, lower irreversible capacity loss, and more cycle stability than unmodified cathode sample.

Current Challenges:
• Low temperature(0°C) capacity
• Address rate capability issues
• High first cycle irreversible capacity loss –~30% at RT
• Scale up and coating of large batches of materials needs to be demonstrated

| Cathode Specific Capacity (mAh/g) – at C/10 Rate |
|-----------------|-----|-----|
| Sample          | 23°C| 0°C |
| UT Austin       | 231 | 208 |
| NEI–D (UT Austin scaled up by NEI) | 209 | 188 |
### Electrolytes

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

<table>
<thead>
<tr>
<th>Technology Challenges</th>
<th>Current approaches to address</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte that is stable up to 5V</td>
<td>Experiment with different electrolyte formulations and additives with potential to improve high voltage stability. Study interactions at both electrodes</td>
</tr>
<tr>
<td>Non-flammable or flame retardant electrolyte</td>
<td>Develop electrolytes containing additives with known flame retardant properties. Perform flame retardance assessments on developments that exhibit suitable electrochemical performance</td>
</tr>
<tr>
<td>High voltage stable, non-flammable or flame retardant electrolyte (combination of both properties in one electrolyte system)</td>
<td>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.</td>
</tr>
<tr>
<td>Electrolytes possessing the requisite physical properties to ensure good rate capacity (adequate conductivity) and electrolyte-wetting.</td>
<td>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.</td>
</tr>
</tbody>
</table>
**Objective:**
• Develop flame retardant electrolytes for Li-ion cells that are stable up to 5.0 volts and maintain electrochemical performance.

**Approach:**
• Determine best formulation for low-flammability that is consistent with high-voltage mixed-metal-oxide cathodes, and with graphite and silicon composite anodes:
  • Vary concentration of triphenyl phosphate additives
  • Test both linear and cyclic fluorinated carbonates as non-flammable solvents.

**Accomplishments:**
• JPL Gen #1 Electrolyte has <50% heat release, <25% pressure rise, and >33% faster flame extinction compared to Saft electrolyte, but showed poor compatibility with NMC cathodes.

• JPL Gen #2 electrolytes (containing LiBOB) shows good performance with graphite/NMC electrodes, and has lower flammability because of increased TPP content (10%).
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:**
  - 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.
    • 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

www.nasa.gov
Safety

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

<table>
<thead>
<tr>
<th>Technology challenges</th>
<th>Approaches to address</th>
</tr>
</thead>
</table>
| 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) |
**Physical Sciences – Coated Cathodes**

- Successfully coated TODA 9100 NMC
- Demonstrated reduced isotherms with coated Toda 9100
- Coated materials have higher capacity, higher tap density, lower irreversible capacity, and better cycling stability

**Giner – Composite Thermal Switch**

- Unoptimized materials with composite coating on current collector exhibits switching behavior at >60 °C.
- Unable to demonstrate consistent, repeatable switching behavior to date
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)

Graph showing DSC analysis on anode, cathode, and electrolyte.
Accelerating Rate Calorimetry

Blast enclosure and control rack of the Thermal Hazards Technology ARC

ARC data and voltage of Panasonic 18650 cell (100% SOC)

ARC/Self-heat data of Panasonic 18650 Li-ion cell (100% SOC)

The cell went into thermal runaway at 160°C with a maximum heating rate of 95.87°C/min. at 200°C
Cell Integration

Objectives

- Assess performance of integrated components
- Determine anode:cathode materials balance
- Predict full cell performance
- Determine formation procedures to maximize 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
• 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
Cell Development Contract with Saft America

Contract Tasks:

- Component screening and evaluation
  - Build and test electrodes and screening cells
  - Provide manufacturing perspective and feedback to component development efforts
- Scale-up promising NASA-developed components
- Transition components from the lab to the manufacturing floor
- Optimize electrode parameters
- Build and test evaluation cells (10 Ah):
  - Determine component interactions
  - Determine cell-level performance

Optional Tasks
- Design flightweight cells (35 Ah)
- Fabricate flightweight cells

Accomplishments:

- Evaluated and screened cathodes, anodes, electrolytes from component developers
- Guided cathode development efforts to produce materials with suitable tap density
- Provided guidance to align materials selections and processing parameters with manufacturing considerations
- Conducted studies to address materials balance in cells
- Established parameters for initial DD evaluation cells
- Fabricated and delivered DD and 34P cells with baseline chemistry
Cell Testing and Evaluation

- Evaluate cells produced under contract with Saft America
  - DD cells
  - 34P, prismatic, ~35Ah cells

- Survey commercial technology options for products that address NASA goals
  - Obtain and evaluate commercial products against NASA KPP’s

- Assessments include:
  - Cell characterization at projected rates and temperatures
  - Life testing
  - Safety Testing
    - Overcharge tolerance
    - Overdischarge tolerance
    - Overtemperature tolerance
    - Crush test
Battery Related Efforts

- **Li–Air System** – Initiating effort that addresses the development of a primary battery system to meet high energy needs (>1850 Wh/kg)
  - SBIR supported efforts to begin soon

- **Human Rating Process for Li–Ion Batteries for Launch Vehicle applications**

- **NASA Engineering and Safety Center – Battery Technology Discipline Advancing Efforts**

- **International Space Station – Low Earth Orbit Life Test**
PEM Fuel Cell Development
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.
Benefits of Non-Flow-Through Technology

**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

![Diagram showing the comparison between Flow-Through and Non-Flow-Through PEMFC technology]

**Flow-Through**
- MEA
- Active water separator
- Gas recirculation pump
- H₂, O₂

**Non-Flow-Through**
- MEA
- Hydrophilic membrane
- H₂, O₂
# Key Performance Parameters for Fuel Cell Technology Development

<table>
<thead>
<tr>
<th>Customer Need</th>
<th>Performance Parameter</th>
<th>SOA (alkaline)</th>
<th>Current Value* (NFT 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>Fuel Cell RFC (without tanks)</td>
<td>49 W/kg n/a</td>
<td>44 W/kg n/a</td>
<td>88 W/kg 25 W/kg</td>
</tr>
<tr>
<td>Lunar Surface Systems: TBD kW for 15 days continuous operation</td>
<td>Fuel Cell Stack power density</td>
<td>n/a</td>
<td>51 W/kg</td>
<td>107 W/kg</td>
<td>231 W/kg</td>
</tr>
<tr>
<td>Rover: TBD</td>
<td>Fuel Cell Balance-of-plant mass</td>
<td>n/a</td>
<td>2 kg</td>
<td>21 kg</td>
<td>9 kg</td>
</tr>
<tr>
<td></td>
<td>MEA efficiency @ 200 mA/cm²</td>
<td>For Fuel Cell</td>
<td>73%</td>
<td>72%</td>
<td>73%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Individual cell voltage</td>
<td>0.90V</td>
<td>0.89V</td>
<td>0.90V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>For Electrolysis</td>
<td>n/a</td>
<td>83%</td>
<td>84%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Individual cell voltage</td>
<td>n/a</td>
<td>1.48</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>For RFC (Round Trip)</td>
<td>n/a</td>
<td>60%</td>
<td>62%</td>
</tr>
<tr>
<td></td>
<td>System efficiency @ 200 mA/cm²</td>
<td>Fuel Cell</td>
<td>71%</td>
<td>64%</td>
<td>71%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Parasitic penalty</td>
<td>2%</td>
<td>8%</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Regenerative Fuel Cell***</td>
<td>n/a</td>
<td>n/a</td>
<td>43%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Parasitic penalty</td>
<td>n/a</td>
<td>n/a</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High Pressure penalty</td>
<td>n/a</td>
<td>n/a</td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td>Maintenance-free lifetime</td>
<td>Altair: 220 hours (primary)</td>
<td>Fuel Cell MEA</td>
<td>2500 hrs n/a</td>
<td>13,500 hrs n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrolysis MEA</td>
<td>n/a</td>
<td>n/a</td>
<td>5,000 hrs 220 hrs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fuel Cell System (for Altair)</td>
<td>2500 hrs n/a</td>
<td>n/a</td>
<td>5,000 hrs 5,000 hrs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Regenerative Fuel Cell System</td>
<td>n/a</td>
<td>n/a</td>
<td>5,000 hrs</td>
</tr>
</tbody>
</table>

*Based on non-flow-through test hardware with 4-cells and heavy end plates, scaled to 3 kW

**Threshold and Goal values based on full-scale (3 kW, 300 cm²) fuel cell and RFC technology.

***Includes high pressure penalty on electrolysis efficiency 2000 psi
Balance-of-Plant: developing universal system to test cells from many vendors, and lightweight, low power system for demos.

**Focus is reliable, 10,000 hours, operation**

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

Electrolysis development focuses on balanced, high pressure operation.

NASA Test facilities (GRC, JSC, JPL) augment industrial capability.

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

Non-Flow-Through Fuel Cell Stacks

- Infinity – baseline stack technology
- ElectroChem
- Proton
- Teledyne
- EIC, Giner – membranes
- Lynntech – catalysts

Electrolysis Stacks

- Hamilton Sundstrand (active liquid feed)
- Giner (active liquid feed, vapor feed)
- Infinity (vapor feed)
- Sustainable Innovations (passive liquid feed)
- Electrochem (liquid feed)

Cross Cutting Stack Developments

- Electrochem (coatings)

Passive Thermal Control

- Thermacore (titanium flat-plate heat pipes)

Electrical Control

- Ridgetop (integrated circuit development for extreme environments)
Infinity Non-Flow-Through Fuel Cell Stack Progression
Non-Flow-Through Fuel Cell Performance Demonstrated in Full Size (150cm²) Hardware

Key Accomplishments:

- 4-cell, 150 cm² non-flow-through fuel cell stack incorporating advanced manufacturing process demonstrated 100 hours of continuous testing
- Performance exceeded all prior small area (50 cm²) stacks.

Significance:

- Demonstrates the feasibility of non-flow-through fuel cell technology for Exploration missions
- Eliminates a substantial program risk associated with scale-up of non-flow through fuel cell technology from a laboratory size to the final flight hardware active area.
- Validates the decision to develop non-flow-through fuel cell technology over the previous flow-through technology.
- The 150 cm² cell size is optimum for full-size stacks anticipated for 120VDC Exploration missions

Future Work:

- Build ¼-scale breadboard, then 3-kW Engineering Model

Lab-scale non-flow-through fuel cell stack under test

Schematic image of future 3kW non-flow-through fuel cell stack
Non-Flow-Through Fuel Cell Common Test Bed

- Configurable to test stacks provided by multiple vendors
- Capable of testing total output power of 1 kWe
- Capable of testing stacks up to 40 cells
- Capable of conducting un-attended life testing
- Developed and built using COTS hardware
Integrated Balance-of-Plant Components for Fuel Cells

- Integrated balance-of-plant demonstrated in conjunction with the laboratory scale fuel cell stacks
- Balance-of-plant ran on a battery source consuming less than 10 watts of parasitic power to operate the fuel cell system
- Project that a full-scale (3-kW fuel cell system) balance-of-plant will operate on less than 50 watts of parasitic power
  - Significant reduction from flow-through systems –
  - A 2–12 kW flow-thru fuel cell system tested at GRC required hundreds watts of parasitic power during operation
- That difference in parasitic power translates to significant reductions in reactant mass over the course of a mission
Membrane Electrode Assembly Accomplishments:
MEAs performance exceeds minimum success criteria

- NASA fuel cell and electrolysis MEA performance exceeds best performance of industry vendors

JPL MEAs supplied to Teledyne, Infinity, and Proton Energy

Comparison of JPL’s best iridium-doped ruthenium with the latest vendor supplied MEA shows substantially better (30 mV) performance by the NASA material.
**Objective:**
Develop balanced high-pressure (≥ 2,000 psi) electrolysis technology for Exploration missions. Incorporate advanced membrane-electrode-assemblies (MEAs) with better electrical performance into high-pressure electrolyzers.

**Accomplishment:**
- JPL-developed MEA 86% efficient at 1.48V
- Hamilton Sundstrand modified existing International Space Station electrolyzer (liquid-feed) for high-pressure operation.
- Testing at JPL showed good voltage performance to 2000 psi H2 and 1000 psi O2 with Nafion MEA.

**Significance:**
- Advanced electrolysis MEAs will deliver more H2 and O2 gases with less electrical power input, reducing the required size of a solar array for a regenerative fuel cell system.
- Balanced high-pressure operation permits operation within an architecture having smaller tanks, reducing launch mass and volume requirements

**Future Work:**
- Vapor-feed and passive liquid-feed electrolyzers are being investigated to reduce the significant parasitic power draw of the pumps and water/gas separators required for liquid feed systems.
Passive cooling plates replace internal active pumped-liquid cooling loop resulting in reduced mass and volume, lower parasitic power, increased reliability, longer life.

Pyrolytic graphite cooling plates have 4x the conductivity of copper.

Flat-plate heat pipes have 30–40x the conductivity of copper.
Fuel Cell Technology Progression to Simpler Balance-of-Plant

Active Mechanical Component (pump, active water separator)

Passive Mechanical Component (injector/ejector, passive water separator)
PEMFC System Comparison

1-kW Flow-Through PEMFC System

3-kW Non-Flow-Through PEMFC System (mock-up)
Fuel Cell Predicted Performance

- **Test data shows** that even with existing heavy endplates, power density of current hardware nearly matches that of SOA Shuttle alkaline flight hardware:
  - 59 kg non-flow-through stack (endplates 17 kg) + 10 kg BoP @ 3 kW = 44 W/kg
  - SOA Shuttle alkaline @ 6 kW = 49 W/kg

- Note: KPP threshold and goal power density values are based on 300 cm² hardware (for 30V systems), which is more mass efficient than smaller 150 cm² hardware (for 120 V systems). Our current expectations for 3kW performance are based on test results from 4-cell stacks, and assume a 4-screen design, 4 kg lightweight endplates, and a 10 kg BOP. **The expected 3 kW performance ranges from:**
  - 66 W/kg for the stack and 54 W/kg for the system, assuming a 4-chamber cell (separate cavities for coolant and product water); to
  - 125 W/kg for the stack and 88 W/kg for the system, assuming a 3-chamber cell (combined water/coolant cavity) and additional mass optimization.

- Next steps are to build successively taller stacks to move toward 1/4 scale breadboard (40 cells, 1 kW, 150 cm²) while retaining the excellent power density.

- Voltage, lifetime, and some mass KPP’s not specifically addressed in current fiscal year
  - Optimization for voltage not in current year scope, although some conductive coatings will be investigated
  - Lifetime testing not in current year scope
  - Mass optimization not in current year scope, although replacing metallic porous plate with Supor membrane for mass reduction will be investigated
Fuel Cell Related Efforts

• Unique SOFC design innovation for fuel cell and electrolysis systems is being pursued at GRC
  – Bi-Supported Cell Technology
  – Operate with High Specific Power 1kW/kg

• Hydrogen Infrastructure for Renewable Energy
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
RPC Electrochemistry Branch
Facilities and Capabilities
Electrochemistry Branch – Batteries

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

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
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 – 3 test cells for large-scale (up to 125kW) fuel cell and regenerative system evaluation and life testing, 2 independent control rooms
• 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

• 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