Energy Storage Technologies for Extreme Environments in NASA Missions

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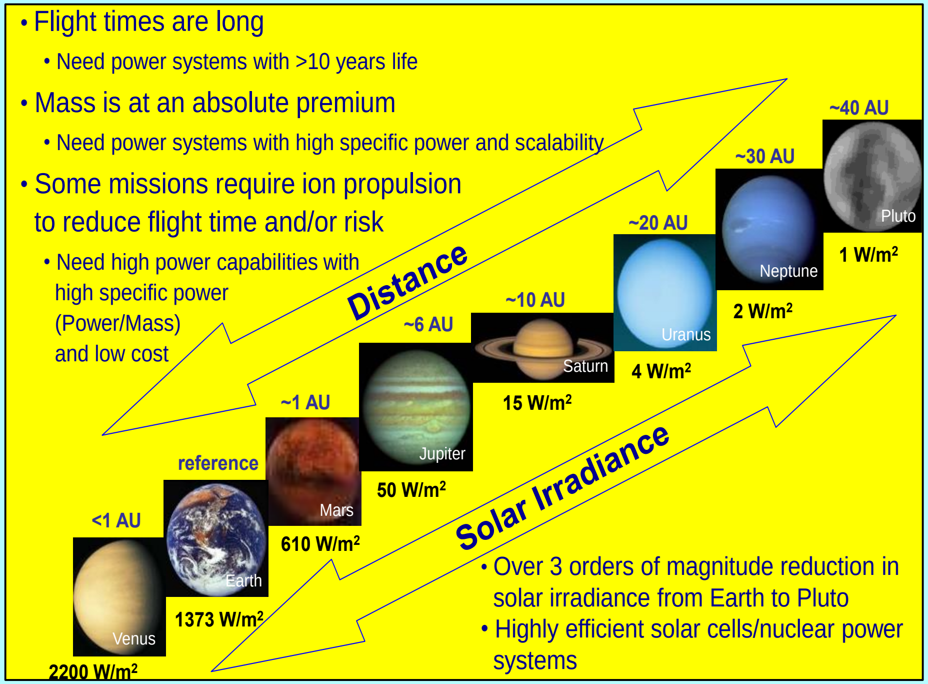
Power Challenges of Solar System Missions

Primary Power Source

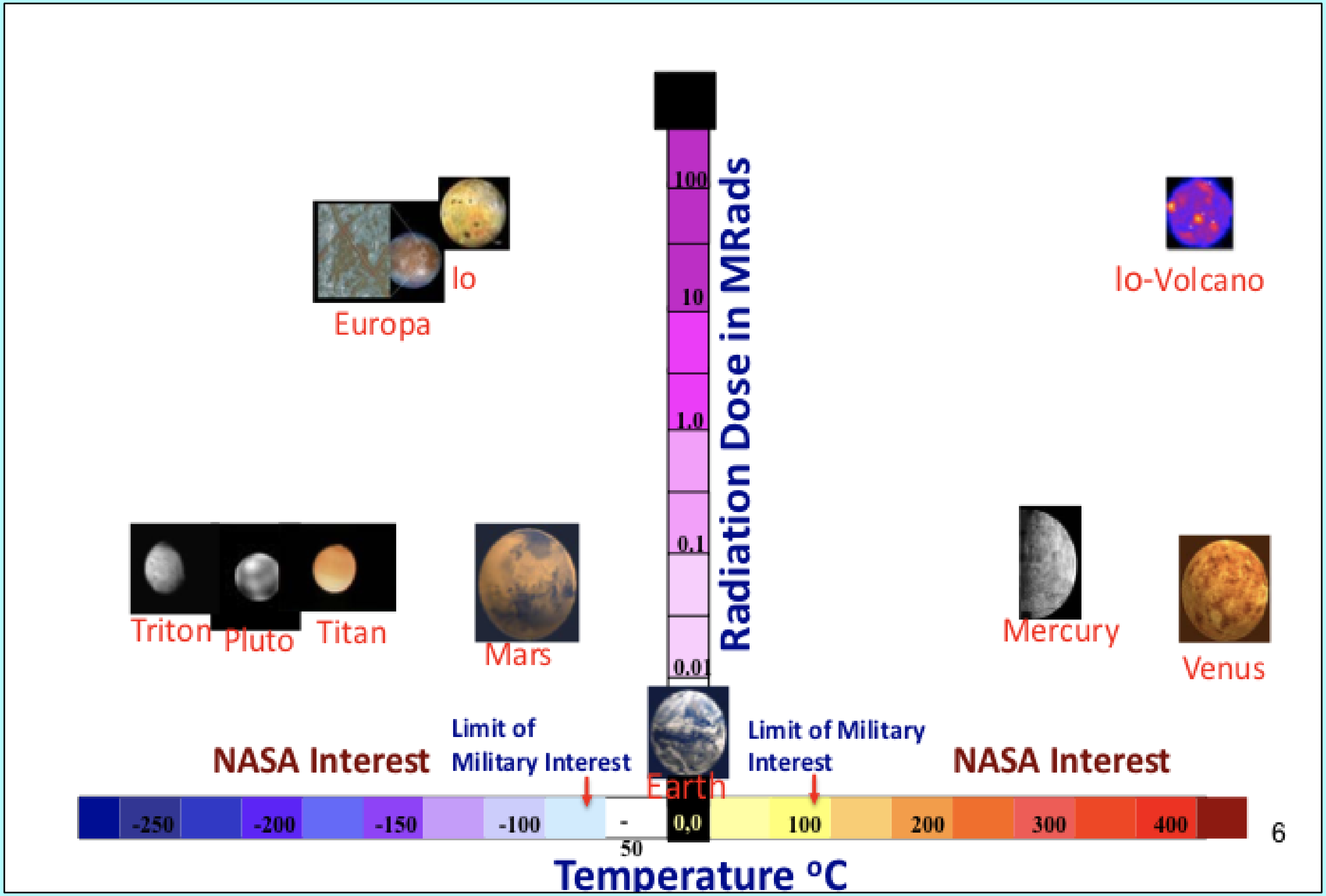


- Low solar irradiance beyond Mars (at Jupiter and beyond)
- Photovoltaic power sources commonly used out to Jupiter and nuclear power systems (Radio-isotope Thermoelectric Generators or RTGs) generally beyond Jupiter

Energy Storage options

- Rechargeable Batteries
  - To to provide power during eclipse periods for PVs and for load leveling with RTG
- Capacitors were used in conjunction with RTG for Deep Space Missions
- Primary Batteries, whenever rechargeability option is not available
- Fuel Cells are still to make an entry in planetary missions!

Power Challenges of Solar System Missions



- Challenging environments (temperature and radiation)

Requirements of Space Missions

- Operational under vacuum (microgravity) conditions
- Survive and Operate at Extreme Temperature
  - Low temperature for outer planets (Mars and beyond)
    - Low Temperature Low Intensity (LILT) Solar cells
    - Low temperature primary and rechargeable batteries
  - High temperatures for Inner planets.
    - High temperature low intensity solar cells
    - High Temperature primary and rechargeable cells and fuel cells
- Radiations for missions to Jupiter and Saturn
  - Radiation-hard PV, RTG and batteries

Types of Mission Concepts

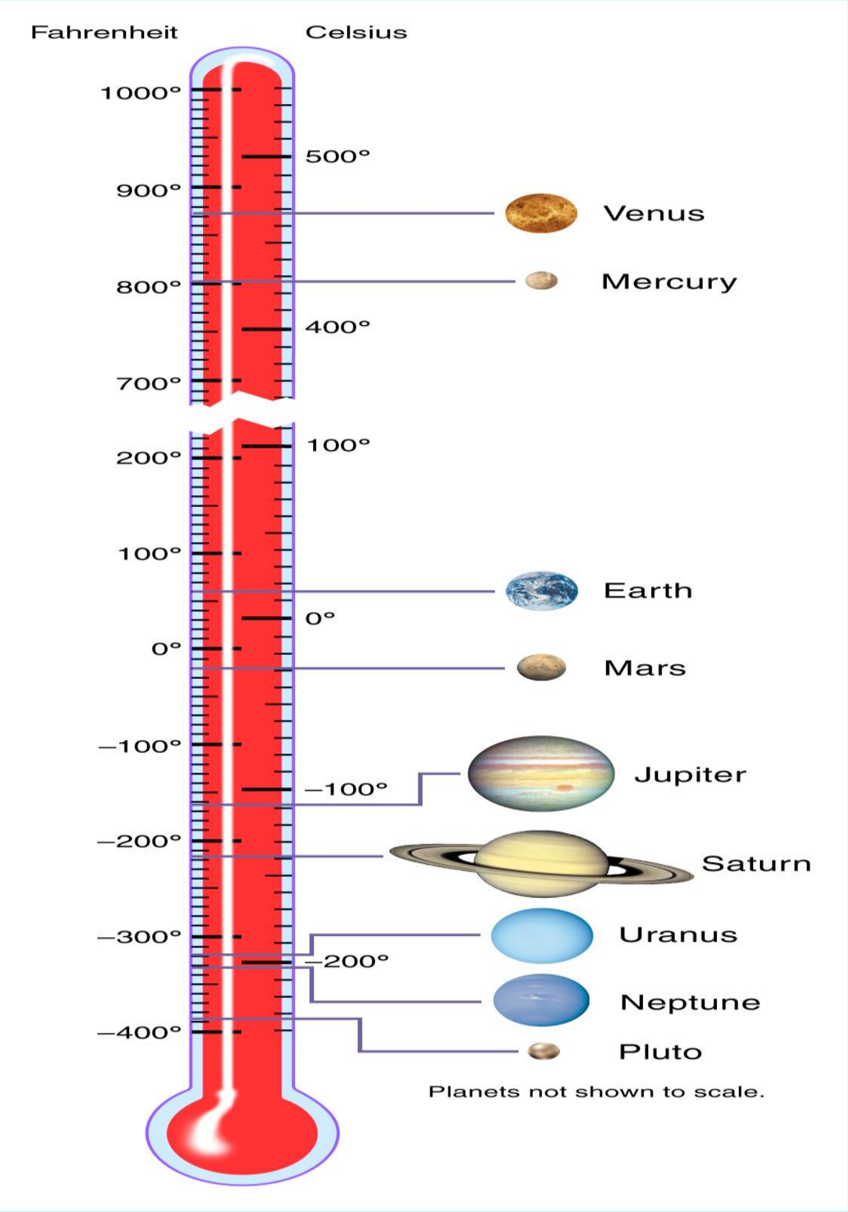
- Landers and Rovers
- Probes
- Flybys and Satellites
- Aerial missions, Balloons and Helicopters
- Sample Return missions
- Astronaut Equipment, Tools
- Space Station and Habitats

Batteries for Space Applications

Category	Mission	Battery Performance Drivers	Chemistry
Outer Planets: Ocean Worlds (Europa, Titan, Enceladus)	Orbital Missions	Long Cycle life (at partial depth of discharge)	Li-ion
	Surface Missions	Primary or rechargeable - high specific energy, long calendar life	$Li\text{-}CF_x$ or Li-ion,
	Sample Return Missions	Primary Long calendar life High specific energy and energy density	$Li\text{-}CF_X$ and $Li\text{-}SOCl_2$,
Outer Planets: ICE Giants (Neptune, Uranus)	Orbiters	Long Cycle life (at partial depth of discharge	Li-ion
	Probes	Primary - high specific energy, long calendar life	$Li\text{-}CF_X$ and $Li\text{-}SOCl_2$,
Inner Planets: Venus	Orbital	Long Cycle life (at partial depth of discharge	Li-ion
	Aerial	High Temperature, high specific energy and good cycle life	$Na\text{-}MCl_2$
	Surface	Primary High Temperature, high specific energy	$Li\text{-}FeS_2$
Mars	Sample Return Missions	Primary Long calendar life High specific energy and energy density	$Li\text{-}CF_X$ and $Li\text{-}SOCl_2$,
	Orbital Missions	Long Cycle life (at partial depth of discharge)	Li-ion
	Aerial Missions	High specific energy, energy density and high power density	Li-ion
	Surface Missions	High specific energy, energy density and low temperature performance	Li-ion
Small Bodies : Multi-asteroid rendezvous or flyby mission	Sample Return Missions	Primary Long calendar life High specific energy and energy density	$Li\text{-}SO_2$ $Li\text{-}SOCl_2$,
	Surface missions	Primary or rechargeable - high specific energy,	Li-ion or Li-S
Planetary Cube Sat/ Small Spacecraft		High specific energy, energy density and low temperature performance	Li-ion or Li-S
Interstellar Missions		Long Calendar life	Li-Solid State?

Extreme Temperatures for (NASA) Space Missions

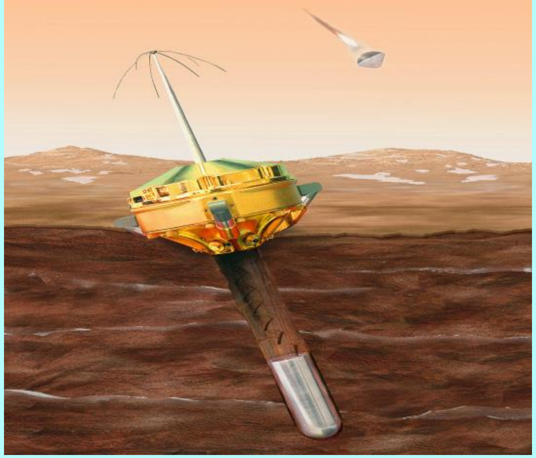
Planet/Moon	Surface, °C	Atmosphere, °C
Mars	-73	20
Europa	-160	
Titan	-179	-191
Venus	465	55-465
Asteroid	-73 to-108	-



Technologies Covered

- Low temperature Systems (for Mars and Beyond)
  - Primary batteries (80 to -115C to date)
  - Rechargeable Batteries (-70C to date)
- High Temperature Systems (Inner Planets)
  - Primary Batteries (465 C)
  - Rechargeable Batteries (350-400C)
  - Fuel Cell Based Systems
- High Intensity Radiation Environments
  - Primary batteries
  - Rechargeable Batteries

Mars Deep Space 2 (Microprobe)



- The probes were each powered by two non-rechargeable lithium-thionyl chloride batteries of 600 milliamp hours.
- 6 - 14 volts nominally from one to three days, but may have lasted longer.

Objectives

- Acceleration data during Entry and Descent
- Atmospheric pressure data
- Soil temperature data
- Soil water content - spectrometer and electromechanical drill incorporated in the forebody.

Battery

- 6- 12 V, 2 year life
- 2 Ahr capacity RT
- 0.5 Ahr at-80°C
- Survive impact 200 m/sec (80000g)

- Li-$SOCl_2$ is the most suitable system from the polarization curves and discharge tests at -80^{o}C.
- Lithium tetrachlorogallate gave improved discharge and voltage delay characteristics vs tetrachloroaluminate
- Lower salt concentrations (0.5M vs 1.0M improve electrolyte conductivity
- Pancake (flat plate) design in a sliced D cell

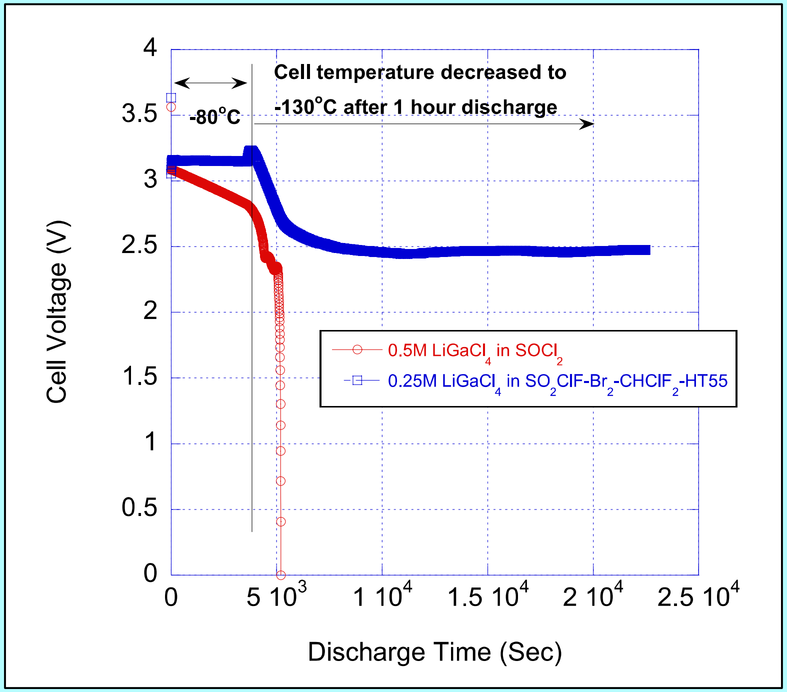
Materials Challenge: Electrolytes with low freezing point, ionic conductivity and stability with lithium

Design Challenge: Cells that can withstand high impact 80,000g

Status: Engineering batteries performed well, but mission was not successful

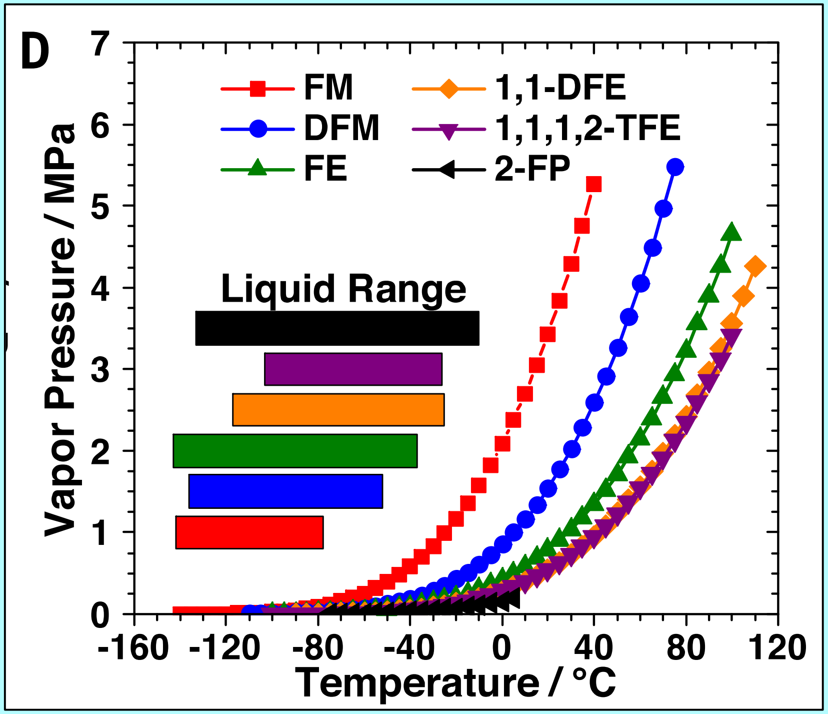
Ultra-low Temperature Liquid Cathode Primary Batteries

Sulfuryl and Thionyl Halide-Based Electrolyte



i) 0.5 M $LiGaCl_4$ in $SOCl_2$ cell and ii) Br_2-passivated 0.25 M $LiGaC_{l4}$ in 1:1 SO2ClF:$CHClF_2$ –HT55 cell. The cells were filled at −80°C, equilibrated for 1 h, discharged first at −80°C, and then cooled while discharging to −130°C

Electrolytes based on liquified gases



Examples: Fluoromethane (FM), difluoromethane (DFM), fluoroethane (FE), 1,1-difluoroethane (1,1-DFE), 1,1,1,2-tetrafluoroethane (1,1,1,2-TFE), and 2-fluoropropane (2-FP).

Partly funded by NASA

W. C. West et al., J. Electrochem. Soc., 157 5 A571 (2010)

Rustomji et al.,Science356, eaal4263 (2017)

SEI Holds the key for Li-Ion Cell Performance (at LT)

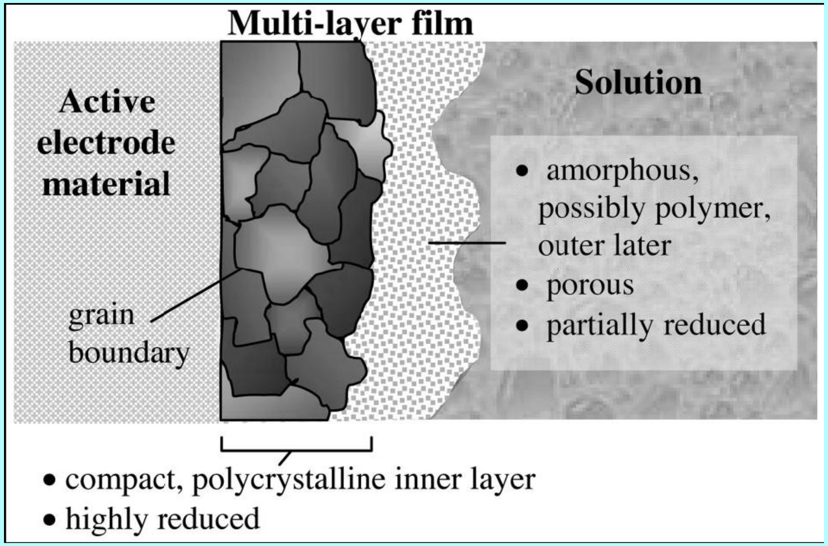
- The success of Li-ion batteries may be entirely attributed to the surface film on the (carbon) anode – termed as the "Solid Electrolyte Interphase", which provides kinetic stability to an otherwise (thermodynamically) unstable system.
- Similar surface films reportedly exist on the cathodes as well

Properties of SEI

- Nature of composition
- Morphology: Dual-layer with compact inner layer and diffused outer layer
- Ionic Resistivity and diffusivity
- Stability / Reactivity
- Coulombic Efficiency

Possible Surface Species

- Li_2CO_3
- Li_2O
- Li-O-R
- Li-OCO-R
- LiF
- Miscellaneous



SEI Impacts Cell Performance

- Low Temperature Performance
- High temperature resilience
- Kinetics (Rate Capability)
- Cycle Life Performance
- Reversible Capacity
- Self-Discharge
- Li Plating

SEI Determined by

- Solvent and salt Type
- Carbon Type

Low Temperature Li-Ion Cells

Material Challenges:

i) Electrochemical stability of electrolyte with carbon anode metal oxide cathode
ii) Stable SEI that facilitates charge transfer (and may be diffusion) at carbon anode
iii) Rapid cathode kinetics
iv) High conductivity for electrolytes
v) Lithium Plating

JPL Low Temperature Electrolytes

- Ternary Solvent Mixture - Generation-1
  - 1.0 M LiPF6 EC+DEC+DMC (1:1:1 V/V)-Used in Mars Rovers, Landers
- Low EC- Quaternary carbonate Mixtures -Gen-2
  - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:2 v/v)
  - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:3 v/v)
  - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4 v/v)
- Low-EC mixtures with Ester Co-solvents- Gen 3
  - 1.0 M LiPF6 EC+EMC+MP (20: 60:20 v/v %) – Used in Mars Insight Lander
  - 1.0 M LiPF6 EC+EMC (1:9 v/v %)
  - 1.0 M LiPF6 EC+EMC (1:9 v/v %)
  - 1.0 M LiPF6 EC+EMC+EB (1:1:8 v/v %)
  - 1.0 M LiPF6 EC+EMC+MB (1:1:8 v/v %)
- Low-EC mixtures with substituted-Ester Co-solvents Gen-4
- Low Temperature Electrolytes with additives for High temperature resilience
  - VC, VEC, LiBOB and LiFSI additives for anode SEI (and CEI) formation

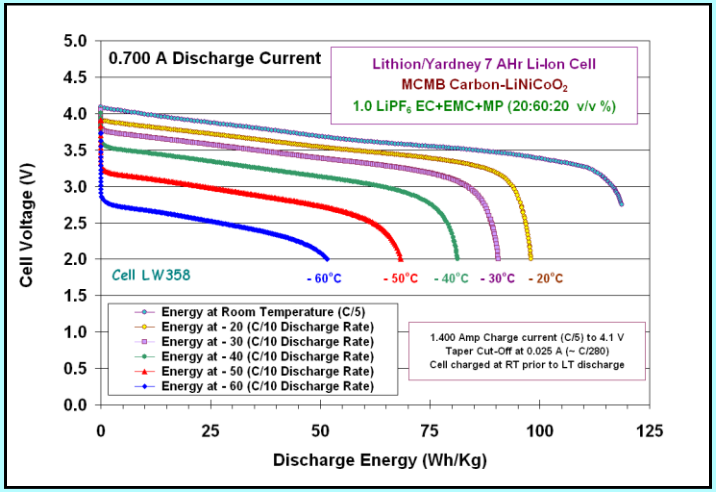
Major Missions with Low Temperature Electrolytes

Gen-1 Electrolyte 1.0 M $LiPF_6$ in EC+DEC+DMC(1:1:1) (-20 to +40 C)

1.0 M LiPF6 EC+EMC+MP (20:60:20) (-30 to +30 C)

Low temperature Li-ion cells

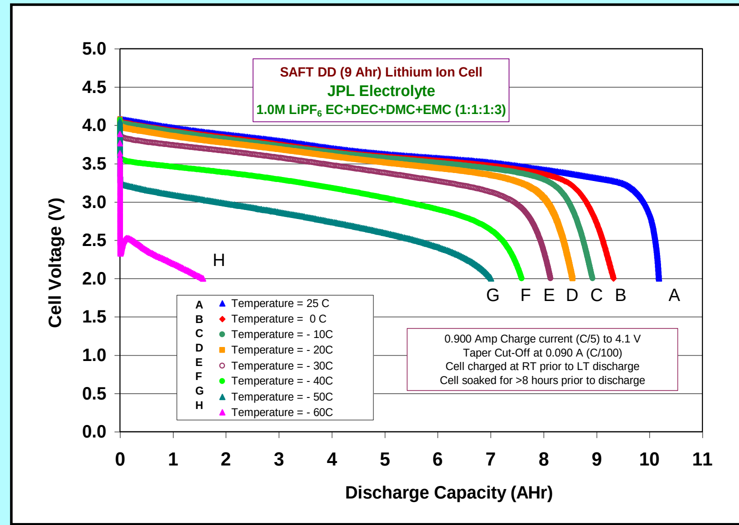
Ester Blends-Yardney Cells



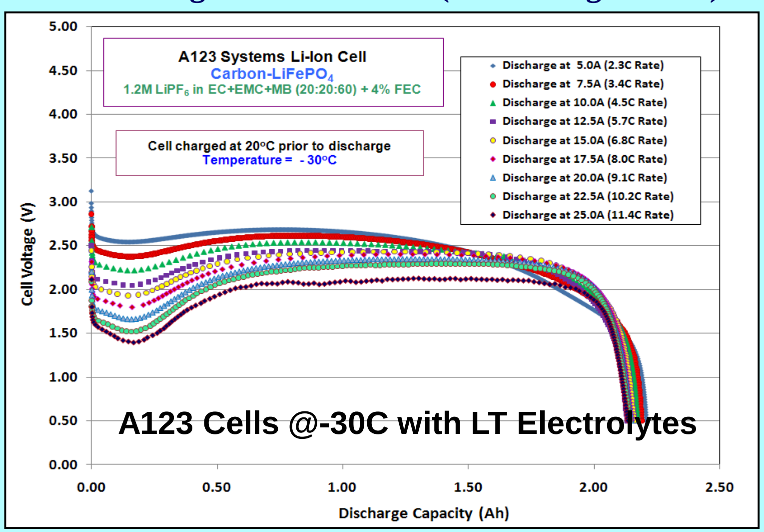
M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, J. Electrochem. Soc., 157 (12), A1361-A1374 (2010).

- **50 Wh/kg at -60°C at C/10 (vs 5 Wh/kg in SOA)**

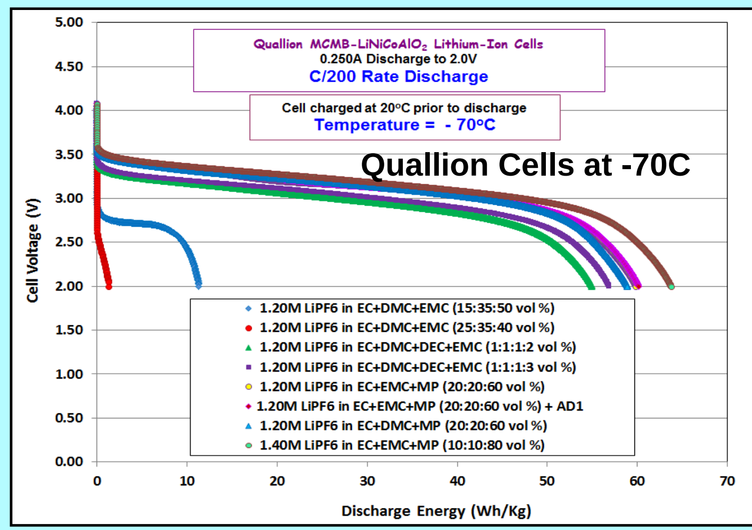
Low-EC All Carbonate -Cells



M. C. Smart, B. V. Ratnakumar, L. Whitcanack, K. Chin, and S. Surampudi, H. Croft, D. Tice and R. Staniewicz,, J. Power Sources, 119-12, 349-358 (2003).



M. C. Smart, C. L. Fuller, F. C. Krause, J. –P. Jones, L. D. Whitcanack, B. V. Ratnakumar, M. R. Tomcsi and V. Visco, 2016 Prime Pacific Rim Meeting on Electrochemical and Solid-State Science, Honolulu, HI, October 2-7, 2016.

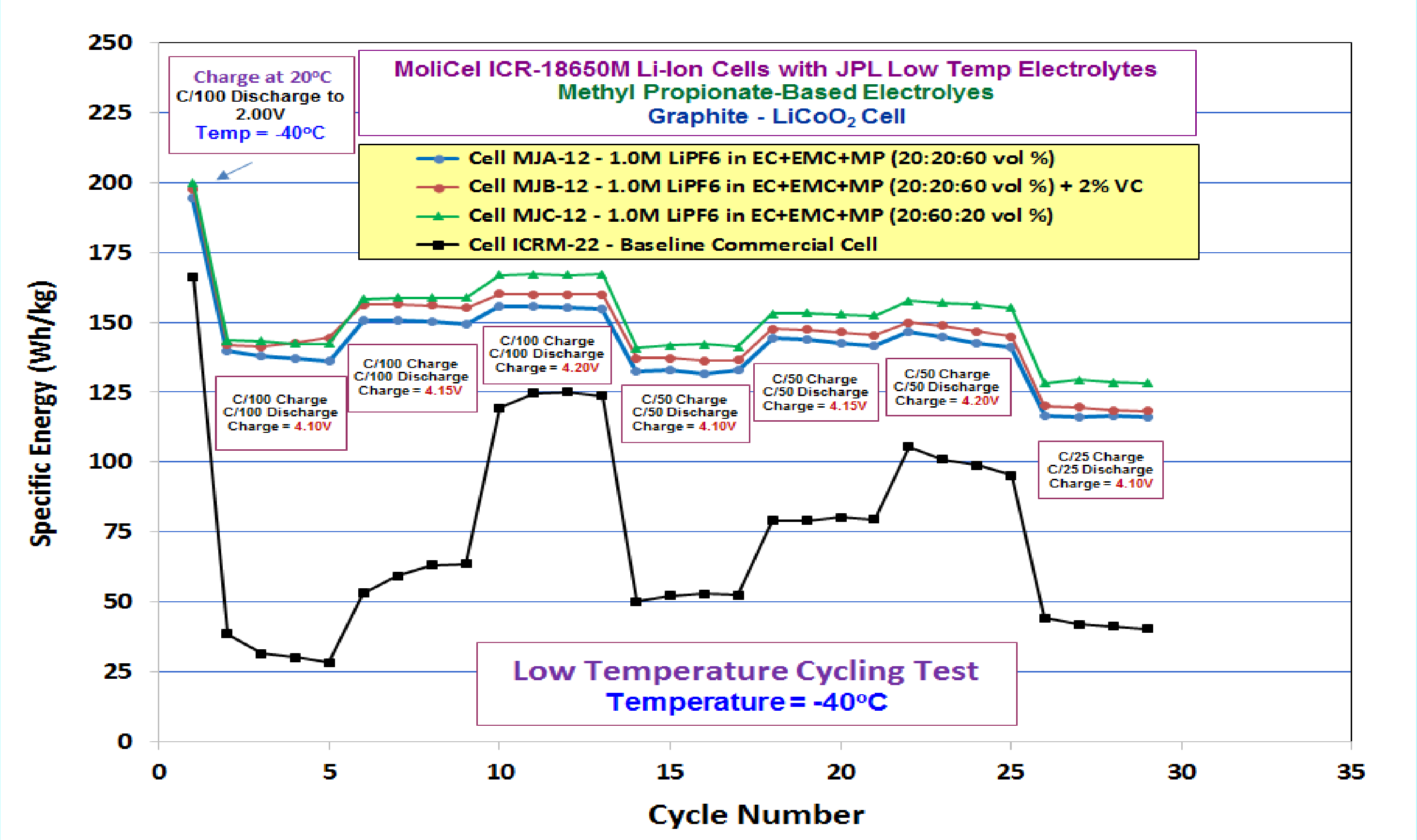


- Operational at -70C at C/200

M. C. Smart, A. S. Gozdz, L. D. Whitcanack, and B. V. Ratnakumar, 220th Meeting of the Electrochemical Society, Boston, MA, October 11, 2011.

Performance of E-One Moli ICR-18650 M Custom Cells

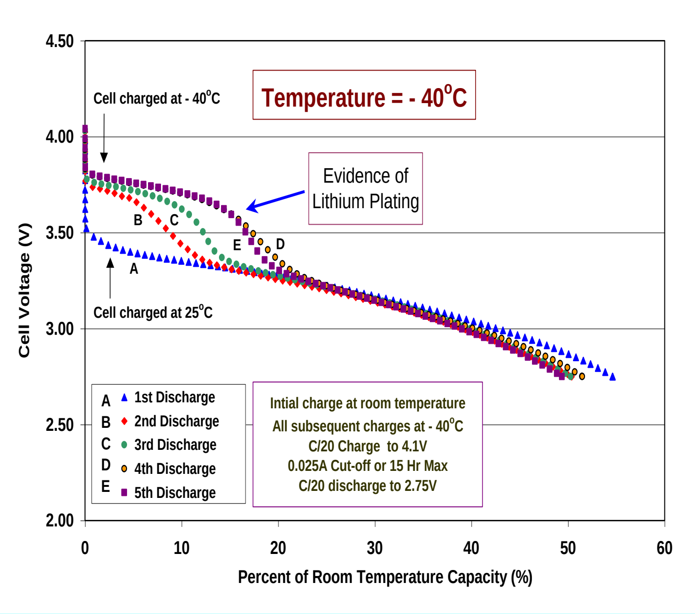
Continuous cycling at -40°C: Effect of charge voltage and charge rate

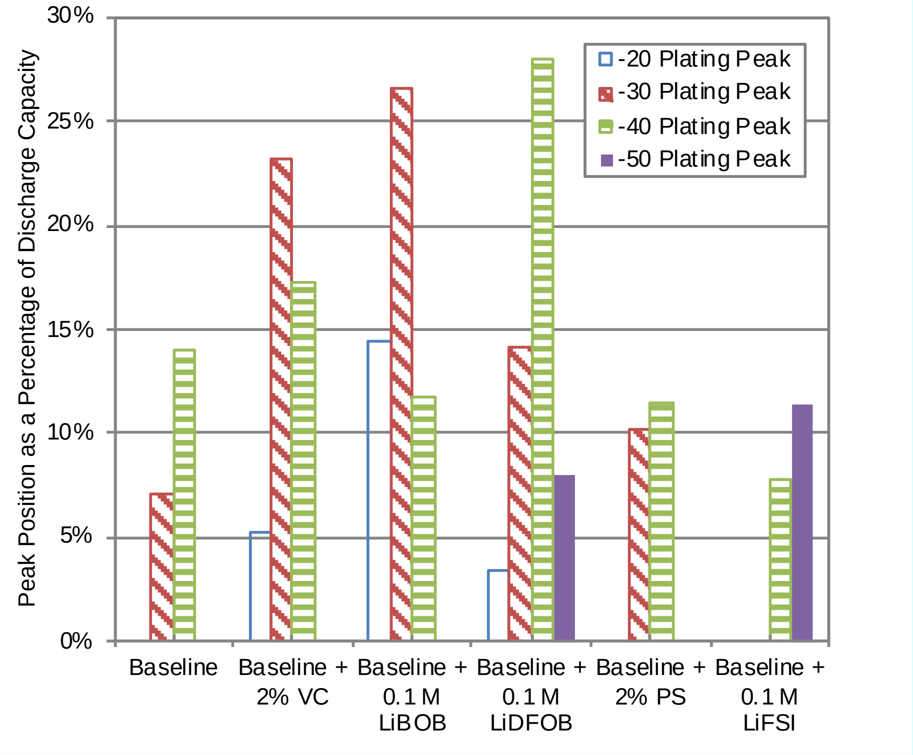


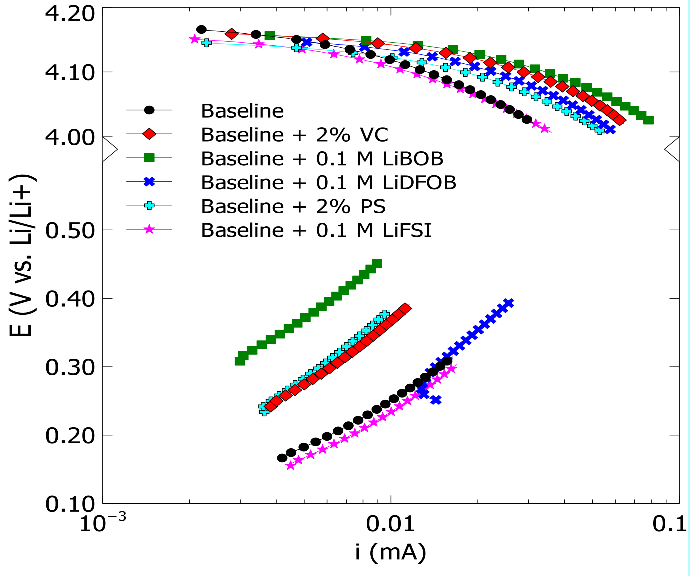
- Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 167 Wh/kg).
- Cells have been continuously cycled at -40°C since 10/22/2015 (over 5.5 months of operation)
- **The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of cells containing JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).**

M. C. Smart, F. C. Krause, J. –P. Jones, L. D. Whitcanack, B. V. Ratnakumar, E. J. Brandon, and M. Shoesmith,, 2016 Prime Pacific Rim Meeting on Electrochemical and Solid-State Science, Honolulu, HI, Oct. 2016.

Li Plating at Low Temperatures







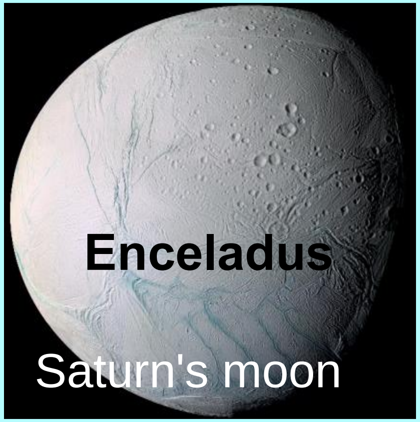
Electrolytes with additives: Lithium bis(oxalato)borate (LiBOB), vinylene carbonate (VC), 1,3-propanesultone (PS), lithium difluoro(oxalato)boarte (LiDFOB) and lithium bis(Fluoro sulfonyl)imide (LiFSI)

- LiFSI>PS> baseline> LiDFOB>LiBOB

- Anode kinetics become sluggish at low temperatures, leading to Li deposition

J. –P. Jones, M. C. Smart, F. C. Krause, B. V. Ratnakumar, and E. J. Brandon, ECS Trans., 75 (21), 1-11 (2016).

Missions Encountering Radiation Environments

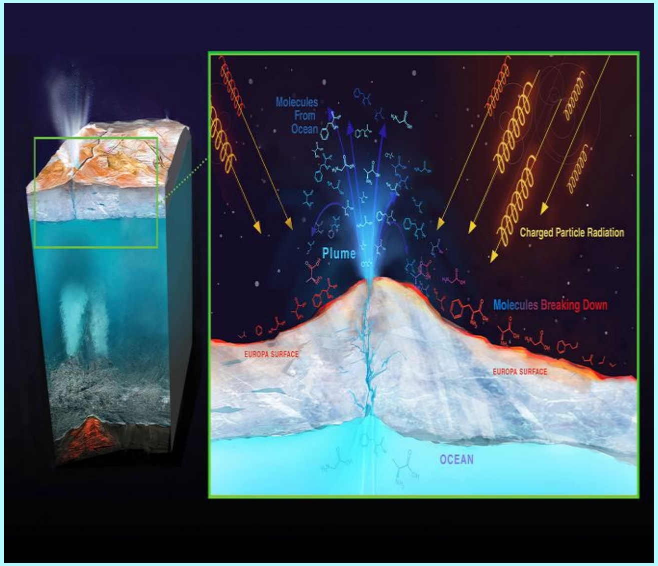


- Ocean Worlds with icy crust and subsurface water are likely to have extant life

Magnetic Field Strength

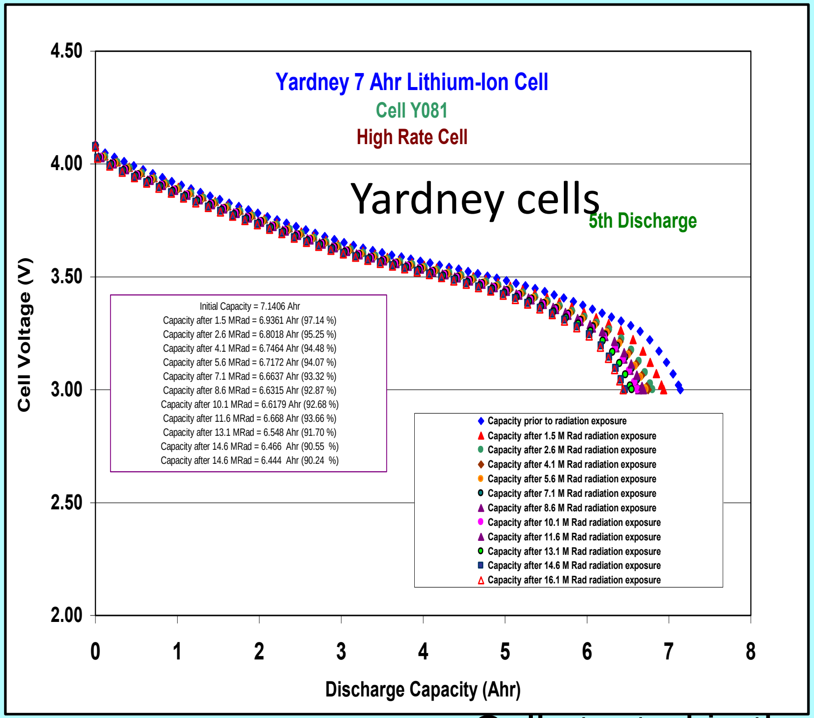
Planet	Magnetic Field Strength vs Earth
Earth	1
Saturn	600
Uranus	50
Neptune	25
Jupiter	20,000

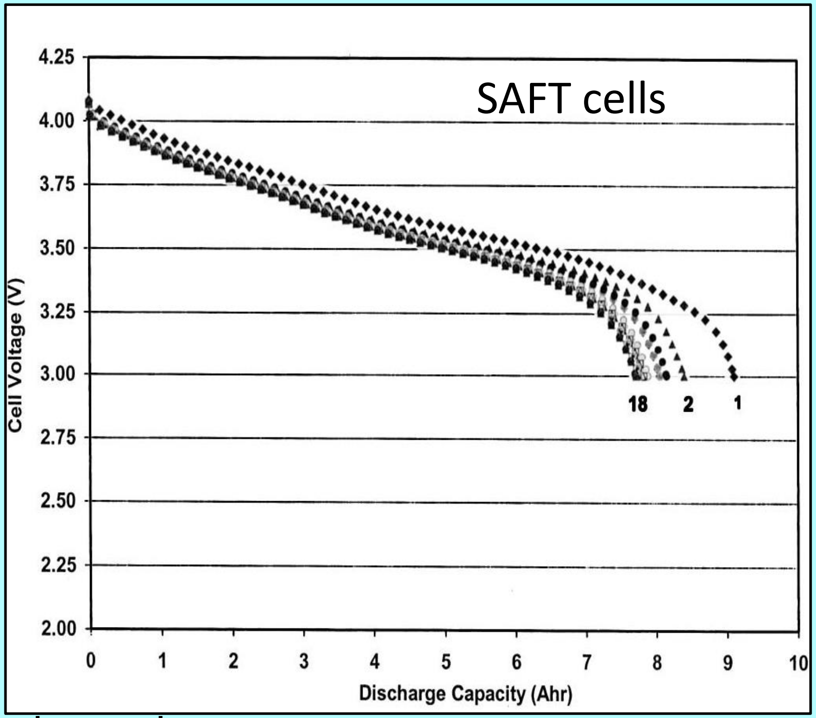
- **Jupiter** is surrounded by an enormous magnetic field and charged particles are trapped in the magnetosphere and form intense **radiation belts ten time stronger than Earth's Van Allen belts**



Radiation Tolerance of Batteries

- A total of 20 MRad TID (12 MRad for planetary protection and 8 MRad from environment
- Simulated by ^{60}Co source





Cells tested in the discharged state

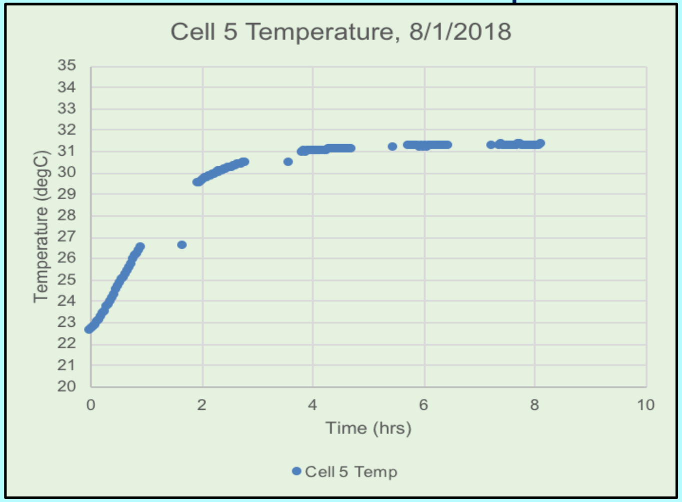
- Slight reduction of electrolyte conductivity and separator elasticity, but little to moderate loss in performance

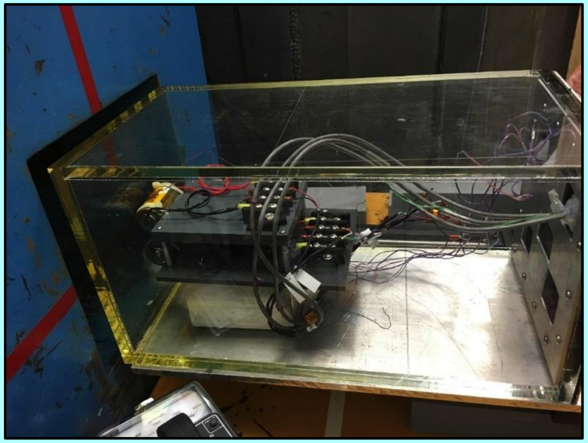
Material Challenges: Radiation tolerance of polymers (including separators, seals and other components) and electrolytes

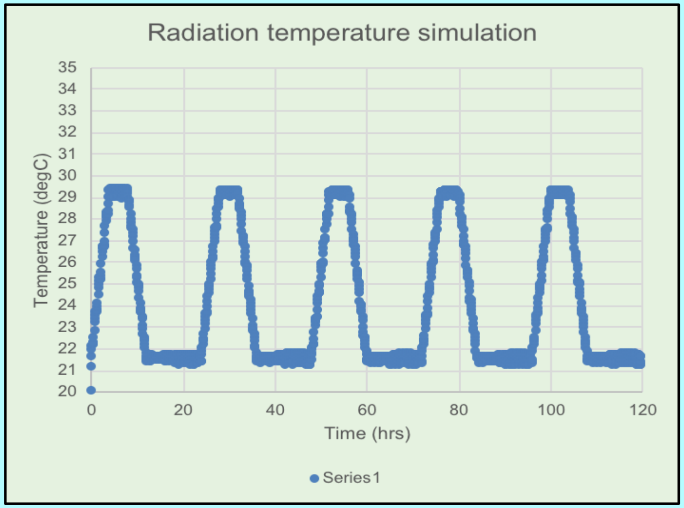
Ratnakumar et al, Journal of The Electrochemical Society, **151** 4 A652-A659 2004

Radiation Tolerance of High Energy Li-Ion cells

- Two exposures: 12 Mrad and 8 Mrad for a total of 20 Mrad TID (12 MRad for planetary protection and 8 MRad (2x of flight level of 4Mrad) from the Jupiter/Europa environment
- Cells were at full SOC (4.10 V) during exposure
- Control cells: At the same temperatures the radiation cells experienced during irradiation

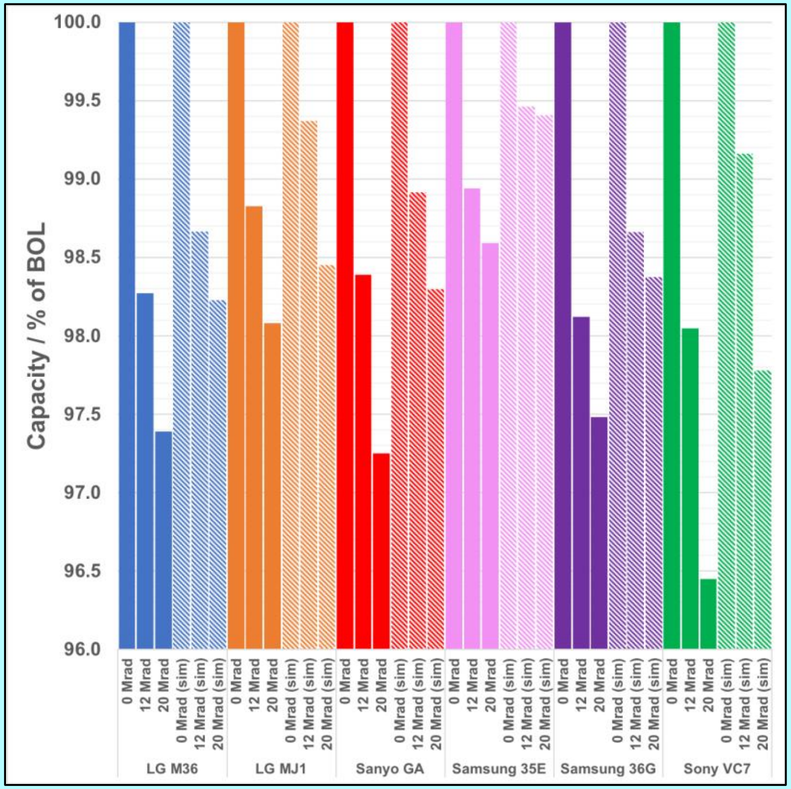




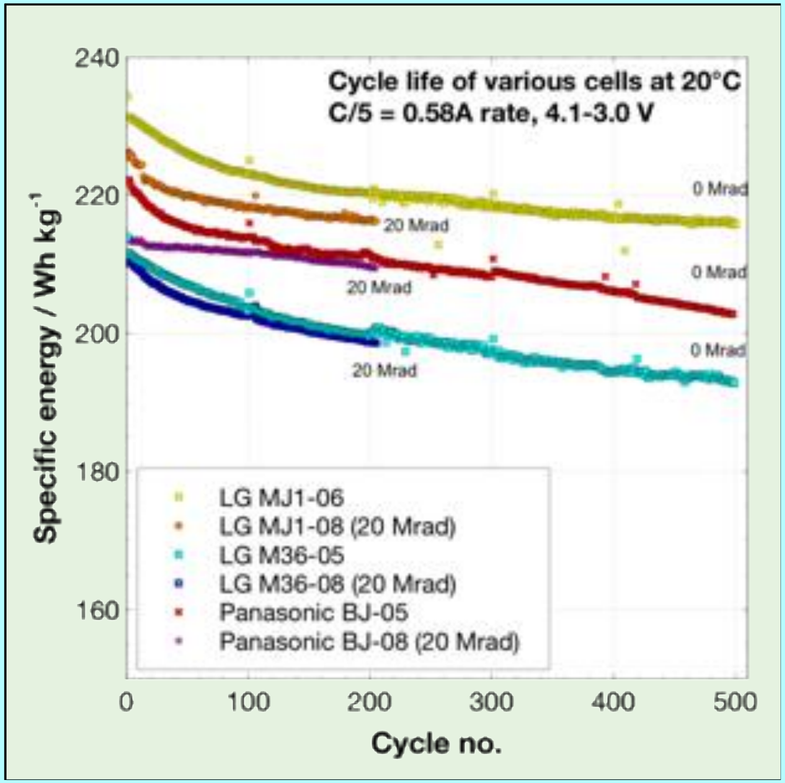


Radiation Tolerance of High Energy Li-Ion Cells

Capacity vs Radiation dose



Cycling of Radiated Cells

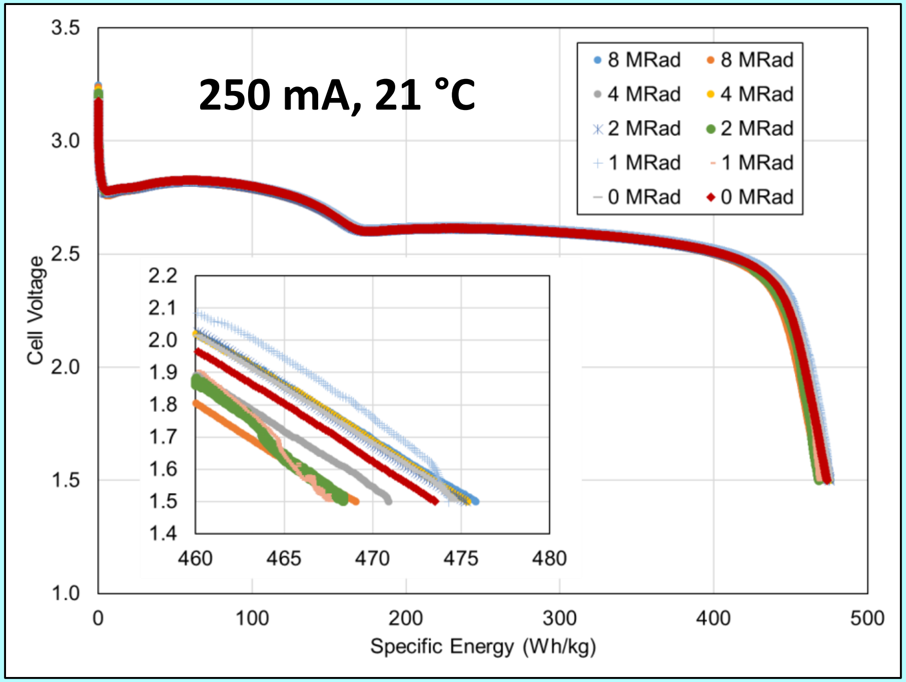


M36 MJ1 GA 35E 36G VC7

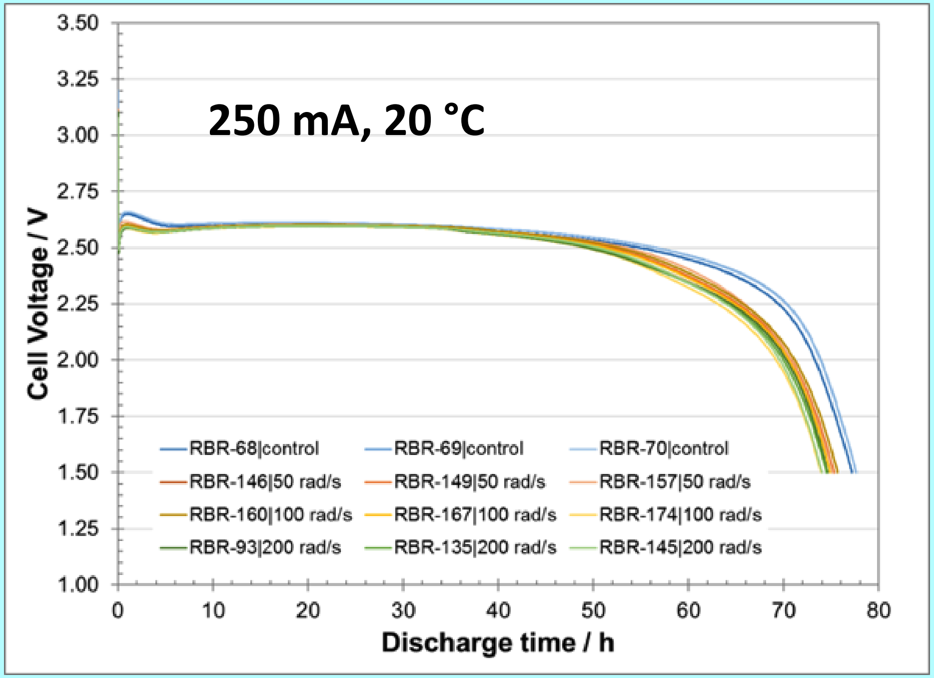
- Solid: radiation exposed; 0 Mrad, 12 Mrad, 20 Mrad
- hashed: 0 rad control group, after stand periods equivalent to irradiation duration
- All the cells show impressive tolerance to radiation with about <2% capacity loss (compared to control cells) after 20 Mrad exposure.
- Again, LG Chem MJ1 cells have the highest specific energy

Radiation Tolerance of High Energy Li Primary Cells

Li/CF_X-MnO_2 Hybrid Cell



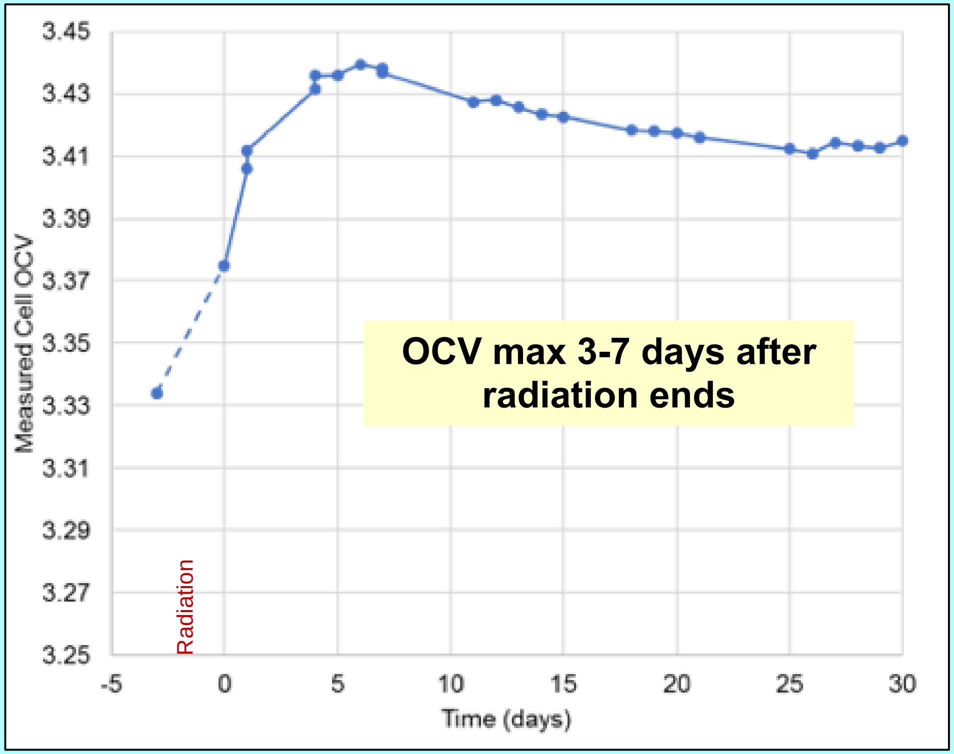
Li/CF_X Cell

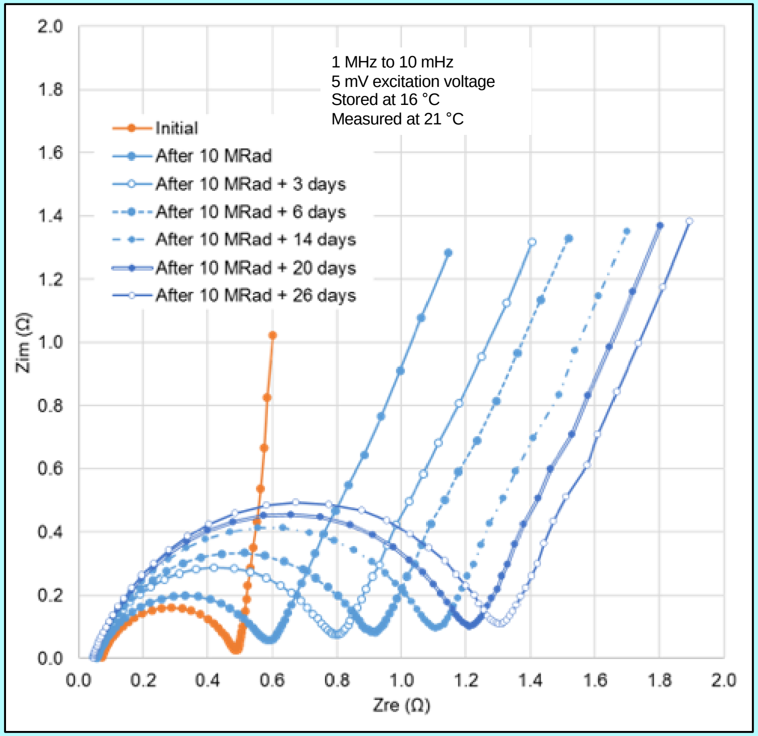


- Little change in the performance even at high intensities

Radiation Effects on Li Primary Cells

- **OCV and Impedance change drastically for Li/CF_x D-cell after 10 MRad**

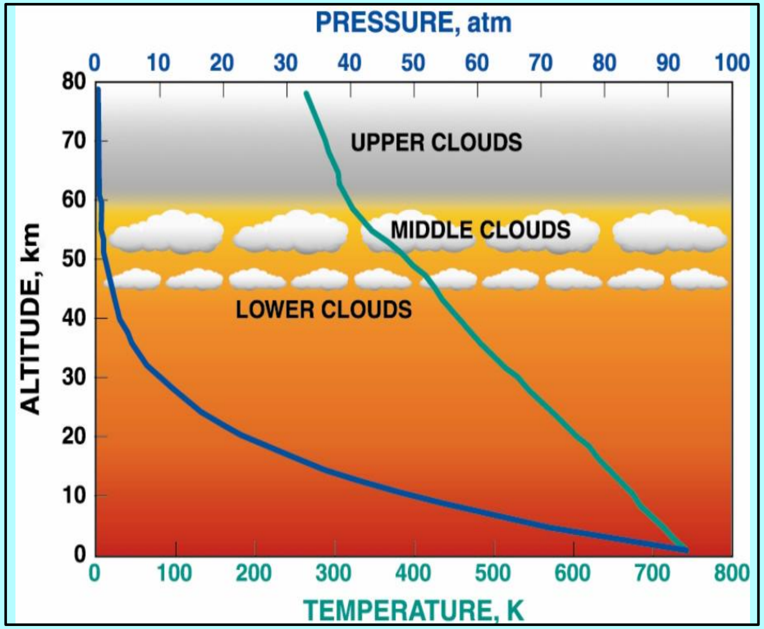




- Radiation is inducing
  - Interfacial changes
  - Loss of strength in separator

Power Technologies for Venus Missions

- High temperatures: 25ºC at 55 km rapidly increasing to 465ºC at the surface
- High pressure: CO_2 pressure (90 atm) at the surface
- Corrosive environment: Concentrated H_2SO_4 droplets in or above the clouds and sulfur compounds
- Due to the opacity of the Venus atmosphere, orbital/balloon observations are inadequate for a detailed study of Venus inner atmosphere and surface and there is a need for long-duration low-altitude aerial platforms or surface lander and probes.
- Current photovoltaic or nuclear power systems (radioisotope thermoelectric generators) are currently inapplicable at low altitudes or at the surface.



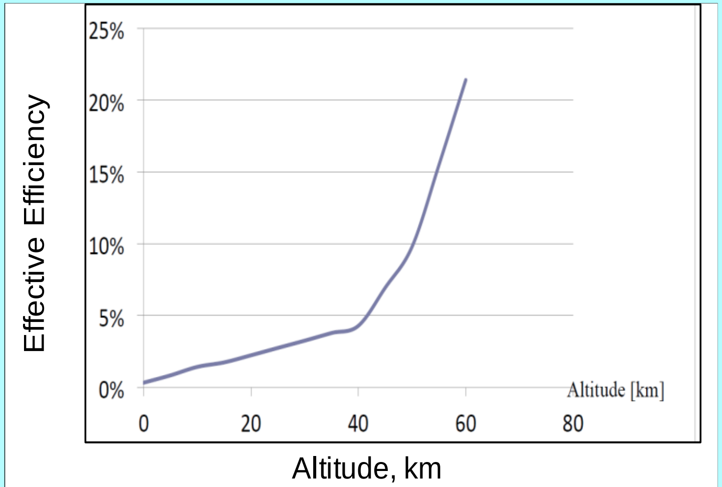


Fig. 2 Triple junction solar cell efficiency vs. altitude

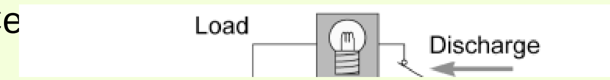
Characteristics of High Temperature Rechargeable Batteries

Characteristic	$LiAl\text{-}FeS_2$	$Na\text{-}NiCl_2$	Na-S
Operating Temp Range, °C	400-475	250-500	290-450
Open Circuit Voltage, Volts	1.73	2.58	2.08
Theoretical Specific Energy, Wh/kg	490	800	755
Specific Energy for Cells, Wh/kg	90-130	100-130	130-180
Specific Energy for Batteries, Wh/kg	100	90-110	80-120
Energy Density for Cells, Wh/l	150-200	150-190	180
Energy Density for Batteries, Wh/l	Near 150	70-130	90-150
Cycle Life, cycles	>1000	>2000	2000

- Sodium-sulfur has been replaced by Sodium-Metal halide batteries and $Li\text{-}FeS_2$ development was discontinued (by DoE) after 1990s.

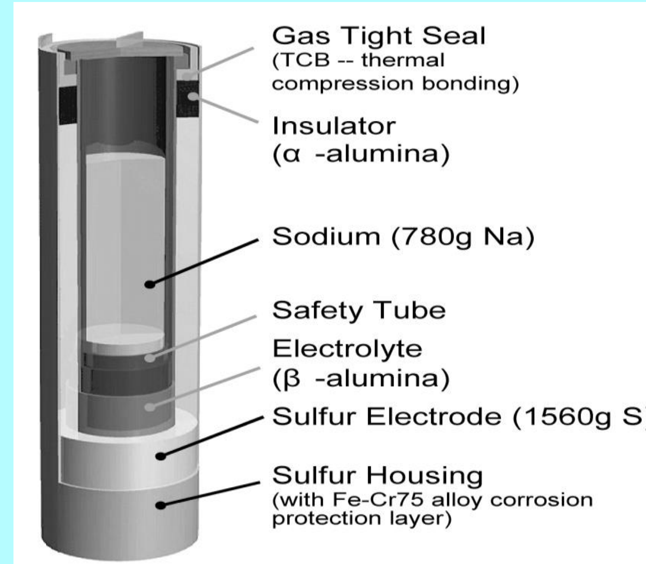
Sodium-Sulfur Batteries (Na-S)

- Chemistry
  - Uses (molten) sodium as the anode and (molten) sulfur as the cathode, and sodium-ion-conductive β-alumina ceramic as the electrolyte/separator.
  - Operate at ~300-350°C
  - Ce

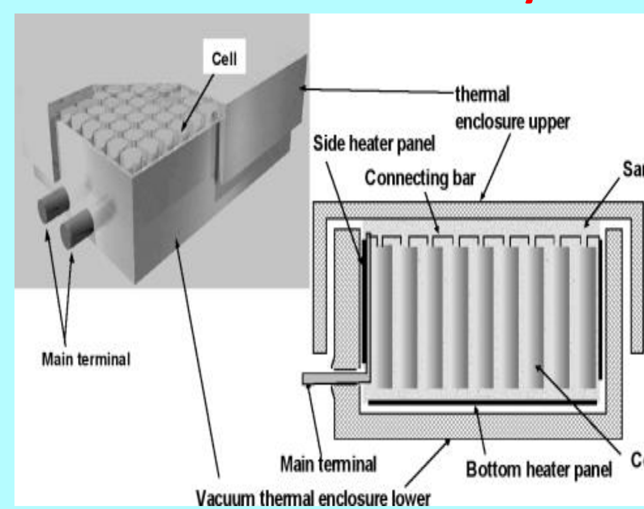


- Performance
  - High specific energy (150 Wh/kg)
  - 100% coulombic efficiency, i.e. no self- discharge.
  - Excellent cycle life: 40,000+ cycles to 20%, 4500 cycles to 90%, and 2500 cycles to 100% depth of discharge.
  - Comparable to Li-ion, which cannot survive > 65°C.
- Status
  - Currently used in stationary applications 1.5 to 35MW (manufacturers: NGK Insulators (Japan); Ford aerospace (past)
- Issues
  - Reliability and safety issues emanating from the failure of the brittle ceramic separator (beta alumina).
- TRL
  - 6-7 for terrestrial applications However, the TRL is only 3-4 for temperatures exceeding 350°C.

Sodium-Sulfur Cell



Sodium-Sulfur Battery

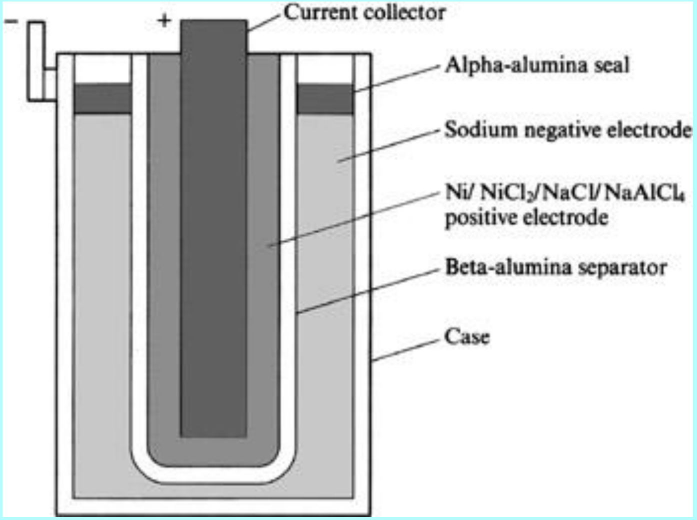


Sodium-Metal Chloride Batteries (Na-MCl_2)

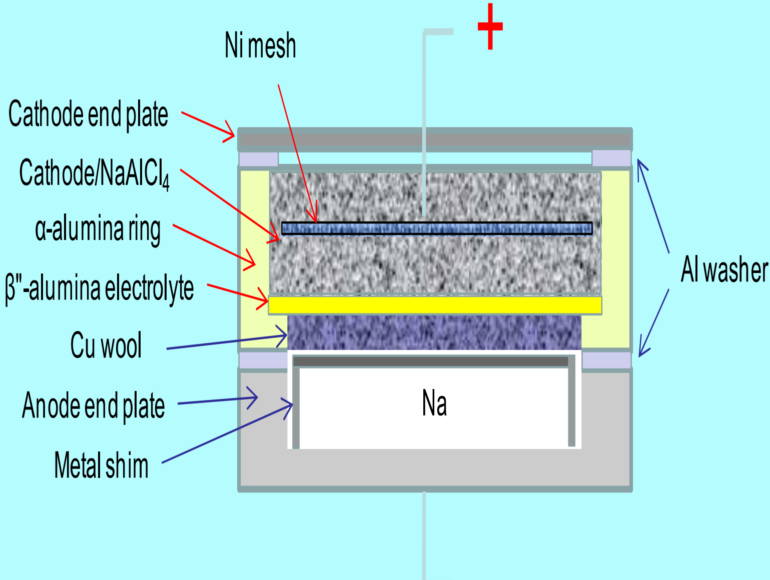
- Chemistry
  - Uses (molten) sodium as the anode and solid metal chloride (iron or nickel) as cathode in sodium tetrachloro-aluminate melt and with Na^+-ion-conductive β-alumina ceramic as the separator electrolyte.
  - Operate at ~300-400°C
  - C elopment of a Ni,Ni(

    2.6 V
- Performance
  - Specific energy: 115 Wh/kg; Energy density: 160 Wh/L
  - Cycle Life: > 2000 cycles at 100% DOD and >3,000 cycles at 80% DOD.
  - Safer and more reliable than Na-S
  - Can be operated at higher temperatures (Venus: 475oC) due to the low vapor pressure of the molten salt.
  - Comparable to Li-ion, which cannot survive > 65°C.
- Status
  - Currently used in stationary applications 1.5 to 35MW (manufacturers: NGK Insulators (Japan); Ford aerospace (past)
- Issues
  - Reliability and safety emanating from the failure of the ceramic separator (beta alumina).
- TRL
  - 6-7 for terrestrial applications

Sodium- Nickel Chloride Cell



Planar Sodium- Nickel Chloride Cell



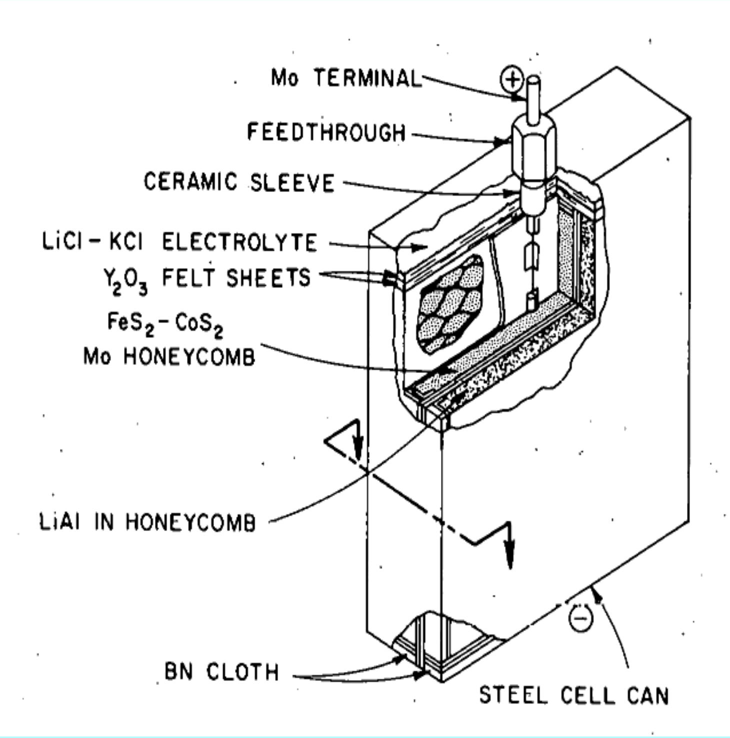
Lithium-Iron Disulfide ($Li-FeS_2$)

- Chemistry
  - Uses Li-Al alloy as anode and iron disulfide as cathode in a molten salt containing LiCl-KCl eutectic.
  - Operate at ~375-425°C
  - Chemistry similar to the (proven) thermal batteries
  - Cell Reaction:

    $4\,Li + FeS_2 = Fe + 2Li_2S$ 2.6 V

- Performance
  - Specific energy: 160 Wh/kg demonstrated in cells/ stacks l
  - Suitable high pulse power applications (150-900 W/kg)
  - Cycle Life: > 500 cycles at 100% DOD
  - Can be operated at higher temperatures (Venus: 475°C) with CoS_2 cathode, which has better thermal stability
  - Prismatic bipolar configurations (of 20-35 Ah) developed and large stacks were built.
  - Comparable to Li-ion, which cannot survive > 65°C.
- Status
  - Developed by Argonne National Laboratory, Westinghouse and SAFT America; Currently not in production/use.
- Issues
  - Operational/safety issues related to high temperature
- TRL
  - 5 for terrestrial applications However, The TRL is 3-4 for temperatures exceeding 450°C.

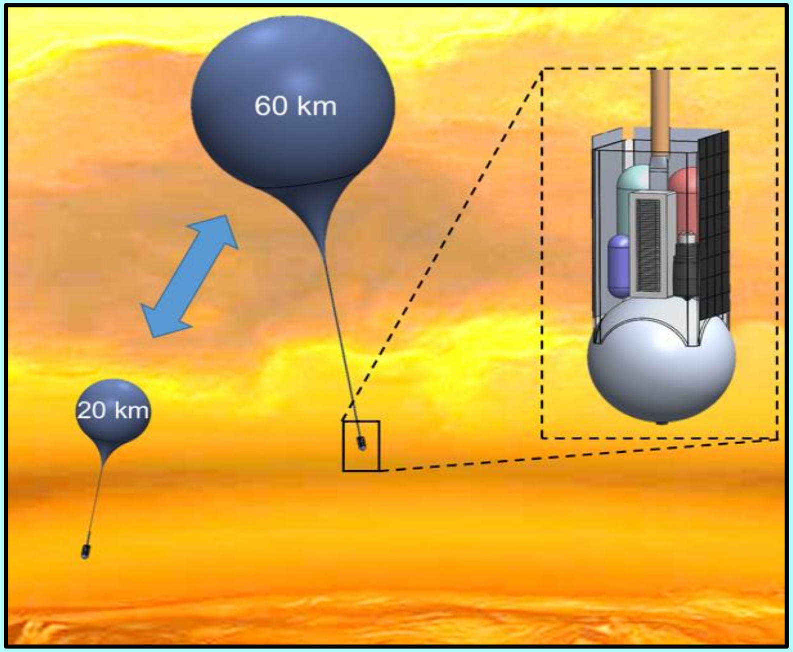
Li-FeS2 Cell



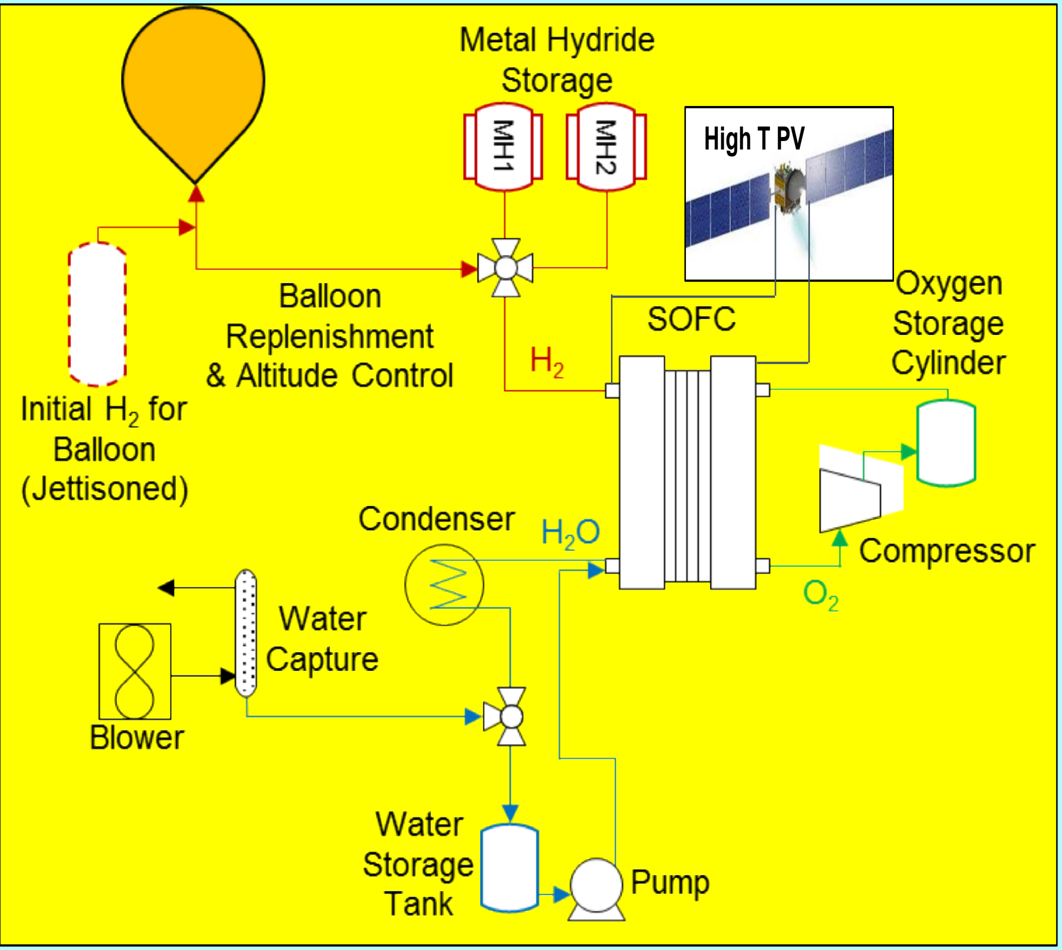
New Architecture for Venus with In-situ Probe

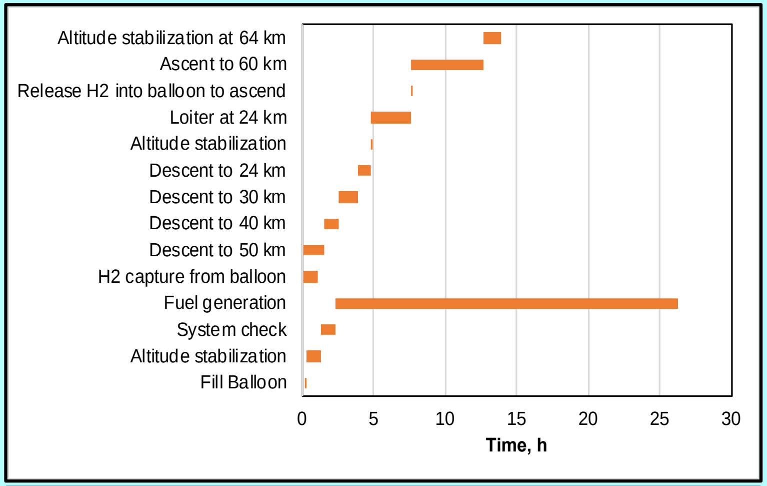
VIP-INSPR- Venus Interior Probe using In-Situ Power -NIAC Project

- The Venus Interior Probe Using In-situ Power and Propulsion (VIP-INSPR) is a novel architecture for Venus Interior Probe based on in-situ resources for power generation (VIP-INSPR) and navigation.
- A Reversible Solid Oxide Fuel Cell (RSOFC) for electrolysis at high altitudes and power generation at low altitudes.
- High temperature tolerant solar array to provide power to the balloon and to the RSOFC to generate H_2 and O_2 at high altitudes
- Harvesting in-situ resources in the upper atmosphere for electrolysis (generation of H_2 and O_2) from water carried from ground or formed at low altitudes) and generation of power at low altitudes utilizing these resources in a high temperature fuel cell.
- Hydrogen storage in a multi-system wide-temperature metal hydride (MH) (absorption at low T and desorption at high T)
- Balloon altitude control system using MH to store H2 for descent to low altitudes for subsequent power generation.



New Architecture for Venus with In-situ Probe





Initial Design Comparison

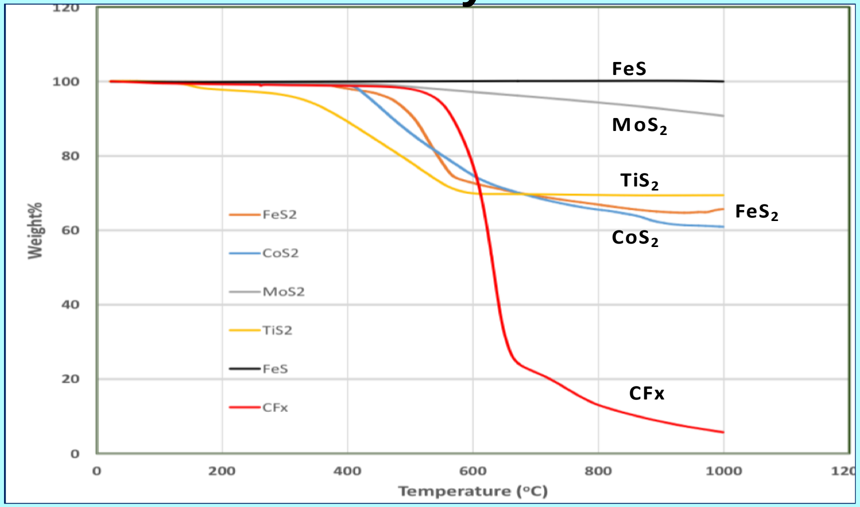
	VIP-INSPR	Vega Aerostats
Type	ZPB	Spherical SPB
Gas	8.1 kg of Hydrogen	2.1 kg of Helium
Volume	855 m^3	20.6 m^3
Diameter	11.8 m (65 km) 1.1 m (10 km)	3.4 m
Envelope Material	1 mil coated Kapton	Teflon Laminate
Envelope Density	37.8 g/m^2	300 g/m^2
Envelope Mass	16.6 kg	12.5 kg (Includes 13 m tether
Payload Mass (Science)	20 kg	6.9 kg
Design Altitude	10-65 km	54 km

Challenges: Compatibility of the materials (balloon, instruments and electronics) to temperature, pressure and corrosive environments

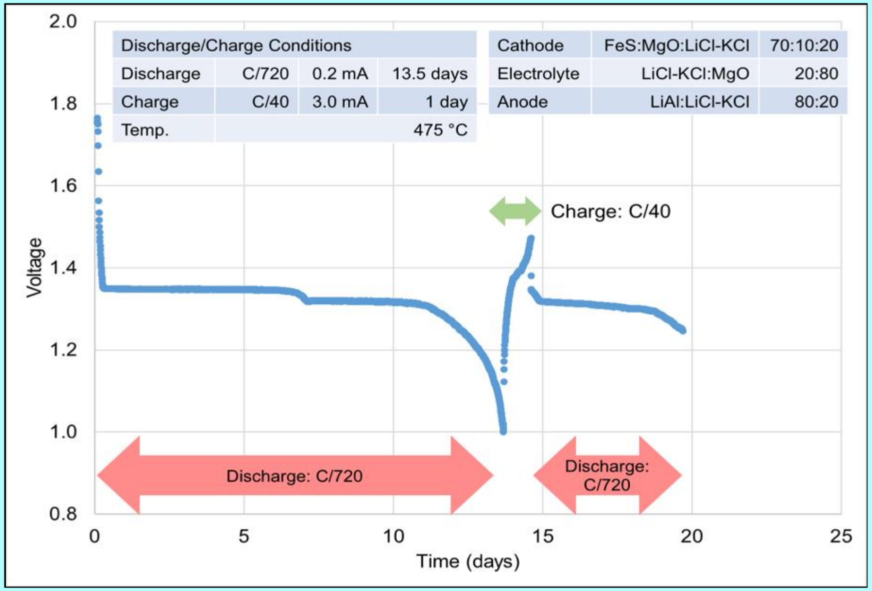
Venus Surface Missions High Temp Primary Batteries (465°C)

- A battery thermally stable on the Venus surface for extended durations and providing high specific energy.
- Configuration:
  - Similar to the current thermal batteries, but with longer life (days vs. minutes).
- Chemistry
  - High capacity anode (Li alloy),
  - High energy cathode (metal chalcogenides) with improved stability (no stability / decomposition)
  - New molten salt electrolyte with low pressure (mixed alkali metal halides)
  - Separators with low self-discharge.
- Goals: Sp. energy: >150 Wh/kg, energy density: >200Wh/l, long calendar life (>5y) and low self-discharge (<1%/day) at 500°C.
- Benefits: Lightweight, compact and will support Venus/Mercury surface missions for long durations (>30 d vs < 2h for SOA).
- Being developed under NASA-HOTTech program

Thermal Stability of Cathodes



Thermal Stability of Cathodes



Summary

- Many future NASA's mission concepts require energy storage devices that can survive and operate at extreme temperatures and high-intensity radiation environments:
  - Enable new in-situ mission concepts (surface and atmospheric missions) to explore planets with challenging environments
  - Inherent thermal and radiation stability simplifies battery designs, eliminates the need for thermal management and allows increased science payload
  - Improvements are underway in low-intensity and low temperature solar cells, which combined with batteries are able to support deep space missions (to Jupiter).
  - Recent developments extend low temperature operations to ~-100C for primary batteries and -60 to -70C for Li-ion batteries. New electrolyte materials are needed to extend the temperature range for future deep space missions.
  - Development is underway for new high temperature systems for Venus surface and atmospheric missions. Material compatibility with the hostile Venus environment is still a challenge
  - Both Li primary and Li-ion rechargeable systems seem to have good resilience to high intensity radiation environments, yet there are some radiation-induced effects on the cell components (electrolytes, separators and binder) that are still to be understood.

Acknowledgements

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