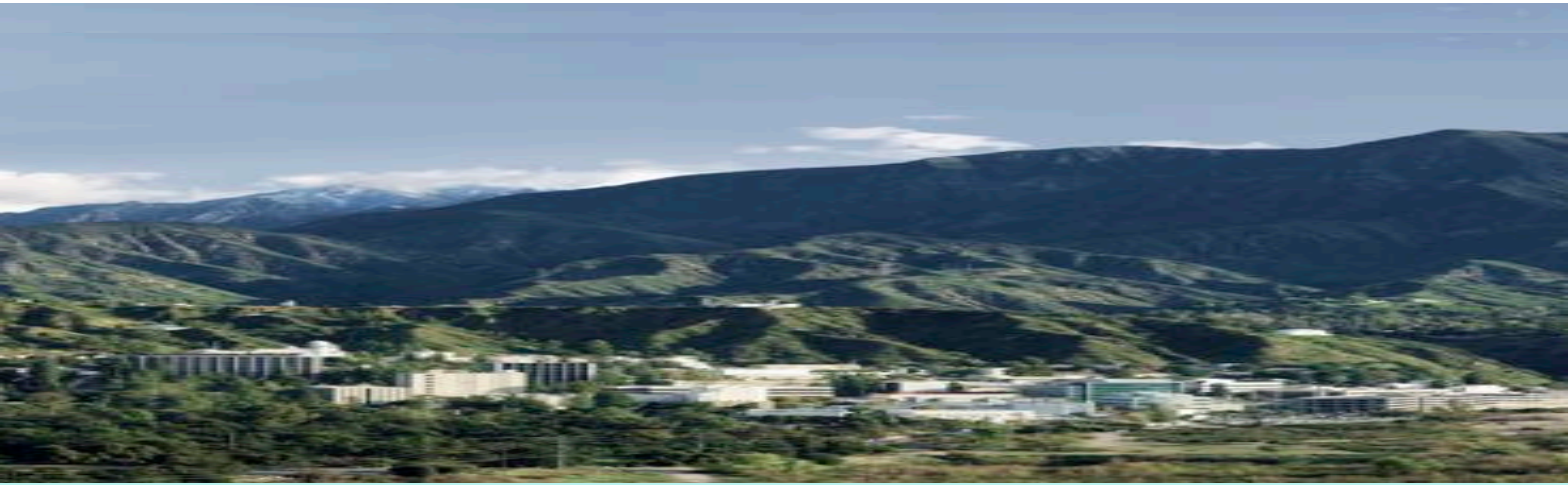

New Power Technologies for Venus Low-altitude and Surface Missions

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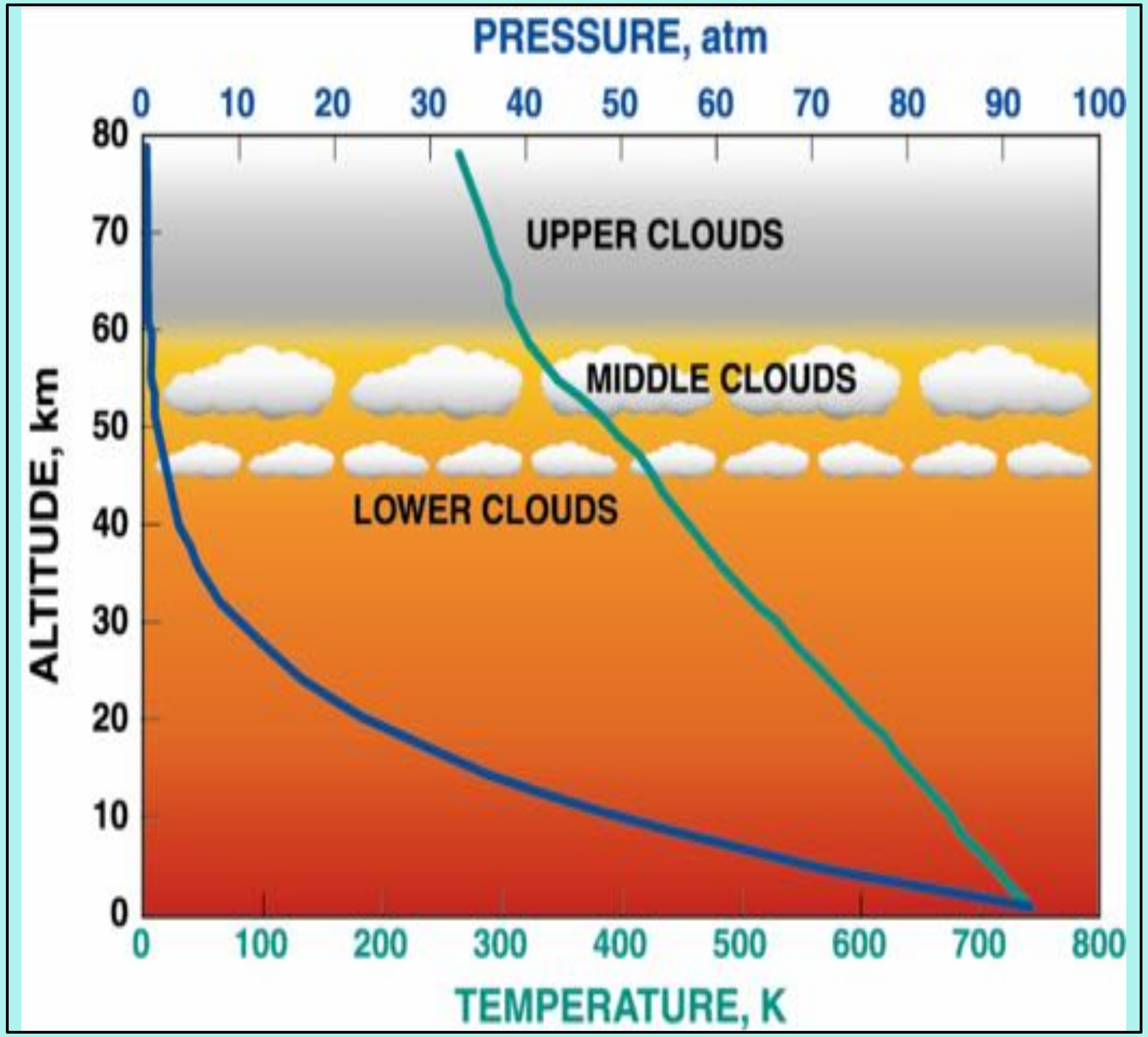
Hostile Venus Environment

- Of all the solar system's planets, Venus is the closest to a twin of Earth.
  - The two bodies are nearly of equal size, and Venus' composition is largely the same as Earth's.
  - The orbit of Venus is also the closest to Earth's of any solar system planet.
  - Both worlds have relatively young surfaces, and both have thick atmospheres with clouds (however, Venus' clouds are mostly made of poisonous sulfuric acid).
- But not enough exploration, because of its hostile environment
  - High Temperature : 25°C at 55 km rapidly increasing to 465°C 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
  - No possibility of extant life,



Challenging environment for in-situ missions

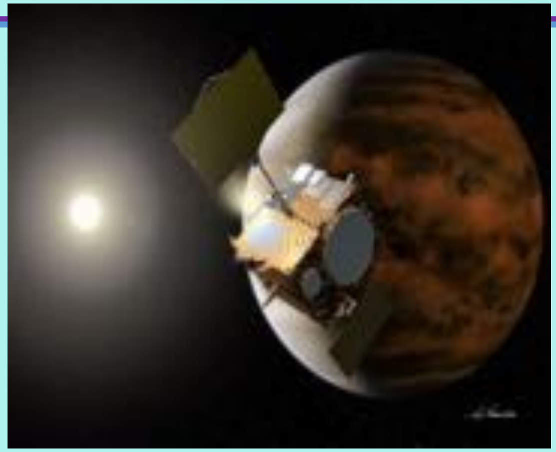
Prior Venus Missions

- **Orbiters**: Russian Venera (4-13) series [4], the US Magellan and the European Venus Express and Japan Akatsuki (2010)

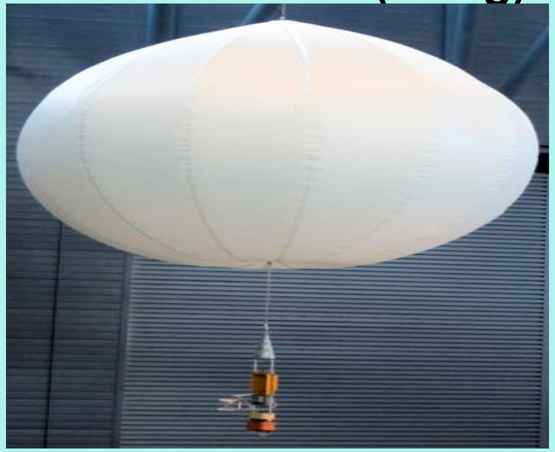
***In-situ* Missions**

- **Balloons**: Several missions have been implemented successfully, e. g., the Russian "VEGA" missions (1985).
  - Two balloons of 3.5m diameter super-pressure helium balloons with 7-kg instrumented payload were deployed into the atmosphere, and floated for 48 hours at about 54 km altitude.
  - Powered by primary batteries (1 kg of lithium batteries with 250 Wh), the VEGA balloons operated only in the benign temperature regime.
- **Surface missions (Lander/Surface Probes)**: Probes from the Venera series, Vega program and Venera-Halley probes.
  - Successfully landed on Venus and transmitted images of the Venus surface but lasted only <2 h due to the failure of batteries and electronics, even with extensive thermal insulation, phase-change materials and similar heat sinks.

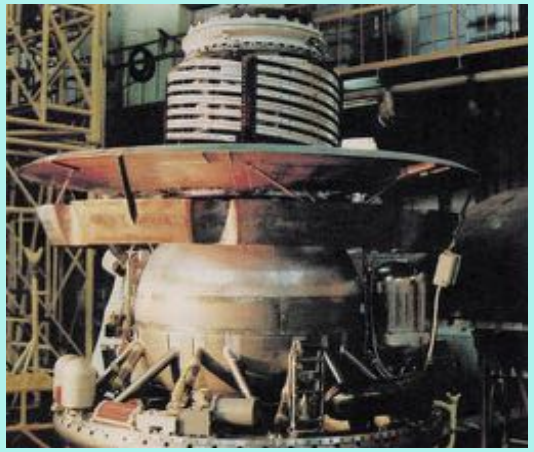
Japan Akatsuki Orbiter



VEGA balloon (21 kg)



VEGA lander (750 kg)



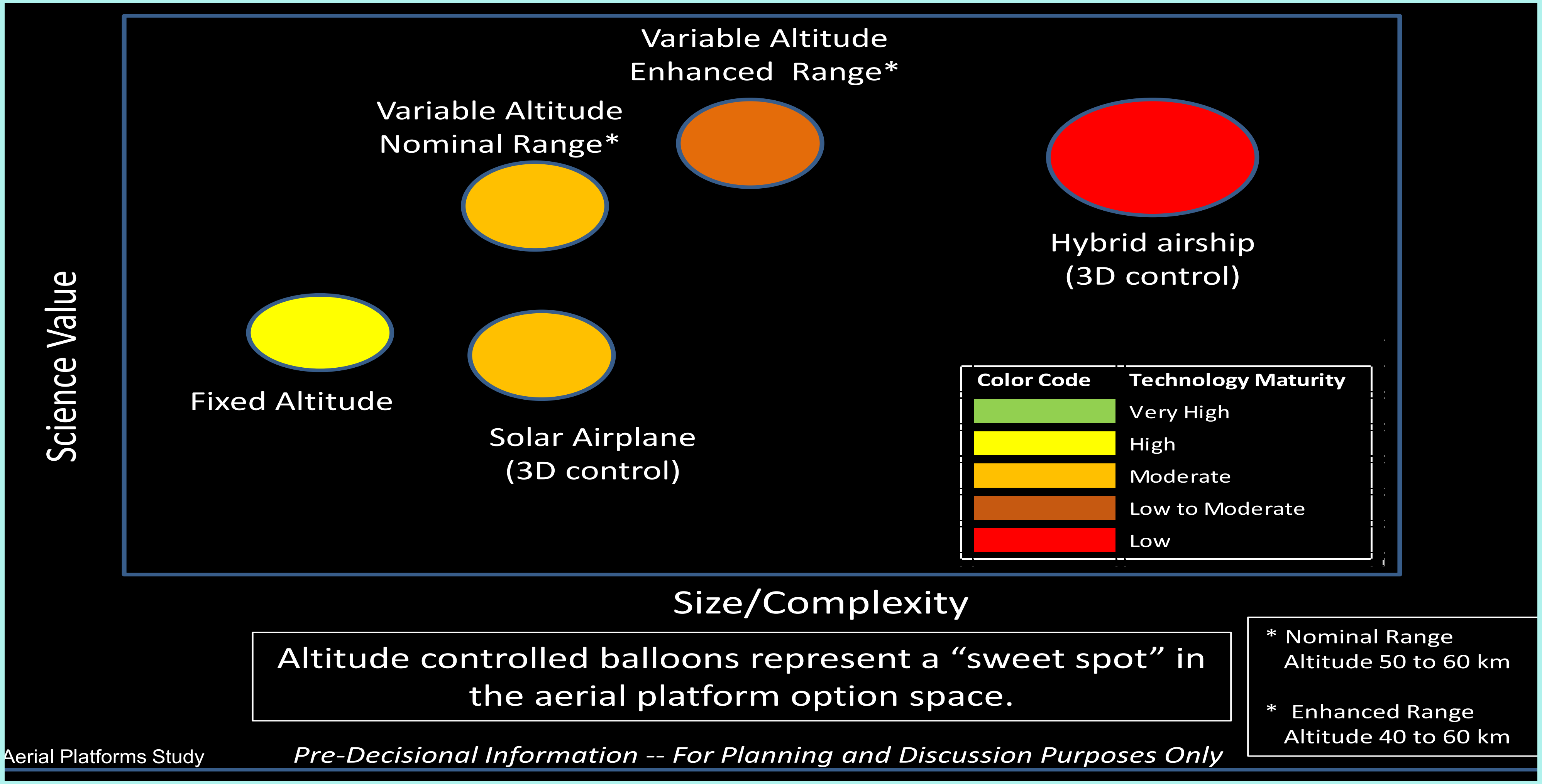
Venus Continues to be an Enigma

- Despite these missions, major questions remain:
  - What is the precise chemical composition of the atmosphere and how does it vary with location and altitude?
  - When and how did the runaway greenhouse effect occur on Venus?
  - How did the atmosphere of Venus form and evolve?
  - What are the morphology, chemical makeup and variability of the Venusian clouds and their impact on the climate?
  - What are the processes controlling the atmospheric super-rotation?
  - What are the processes governing Venus seismicity and its interior structure?
  - How have the interior, surface, and atmosphere interacted as a coupled system over time?
- The orbital and high-altitude (55-65km) balloon missions are stymied by the opaque clouds.
- **To address these questions and others, it is essential to have missions that allow long-term, *in situ* measurements at lower altitudes in the Venusian atmosphere.**

Recent VEXAG (Venus Exploration and Analysis Group) Study

Assessment of Different Aerial Platforms

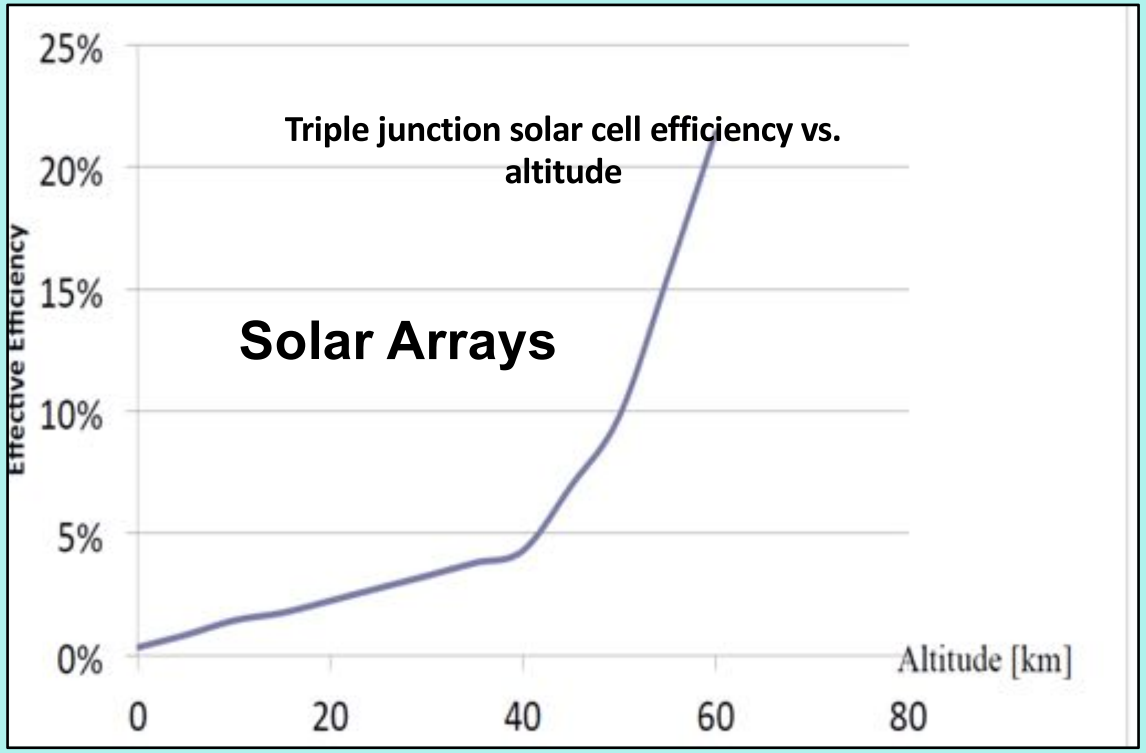
- **The variable-altitude balloons were determined to represent a scientific and technical “sweet spot”.**
- Have the potential for a substantial enhancement of the science without a commensurate increase in risk.
- Aerial platforms enable investigations of not only the atmosphere of Venus but also its interior and surface.

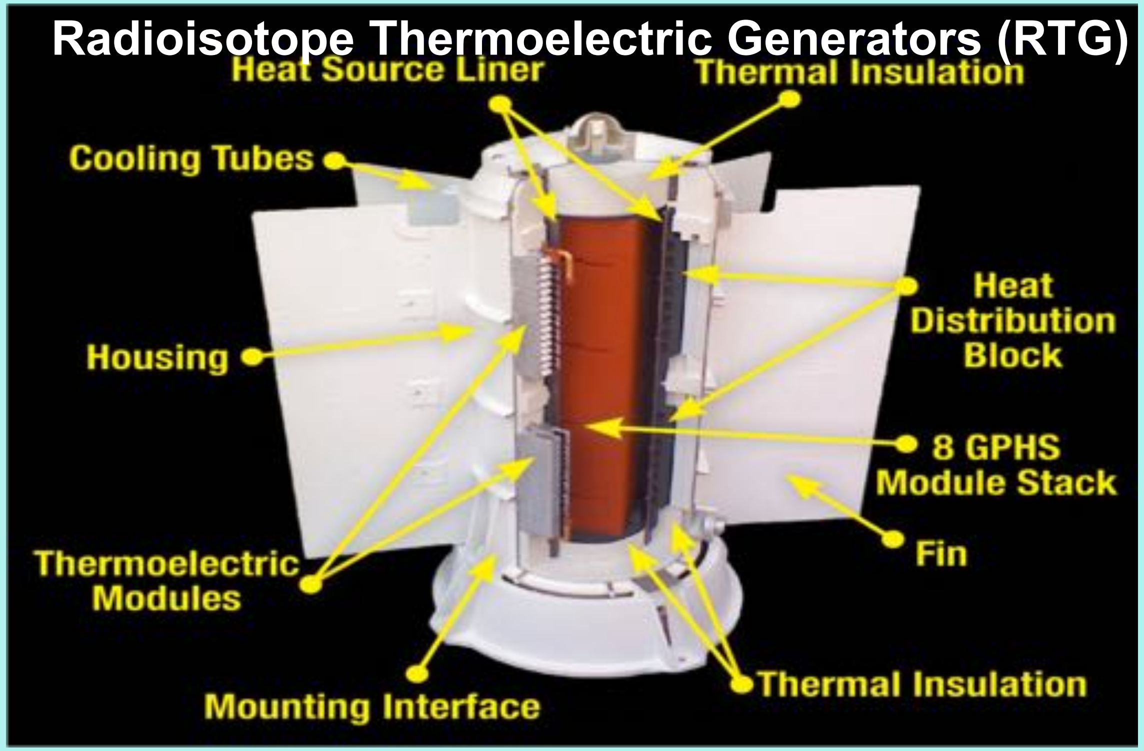


- Gas composition, especially the active species.
- Cloud and Haze Composition and Properties.
- Atmospheric Structure Investigations:
- Geophysical Investigations: Magnetic measurements and seismic infrasound experiments
- Surface Imaging

Pre-Decisional Information – for Planning and Discussion Purposes Only

Power Generation Challenges on Venus

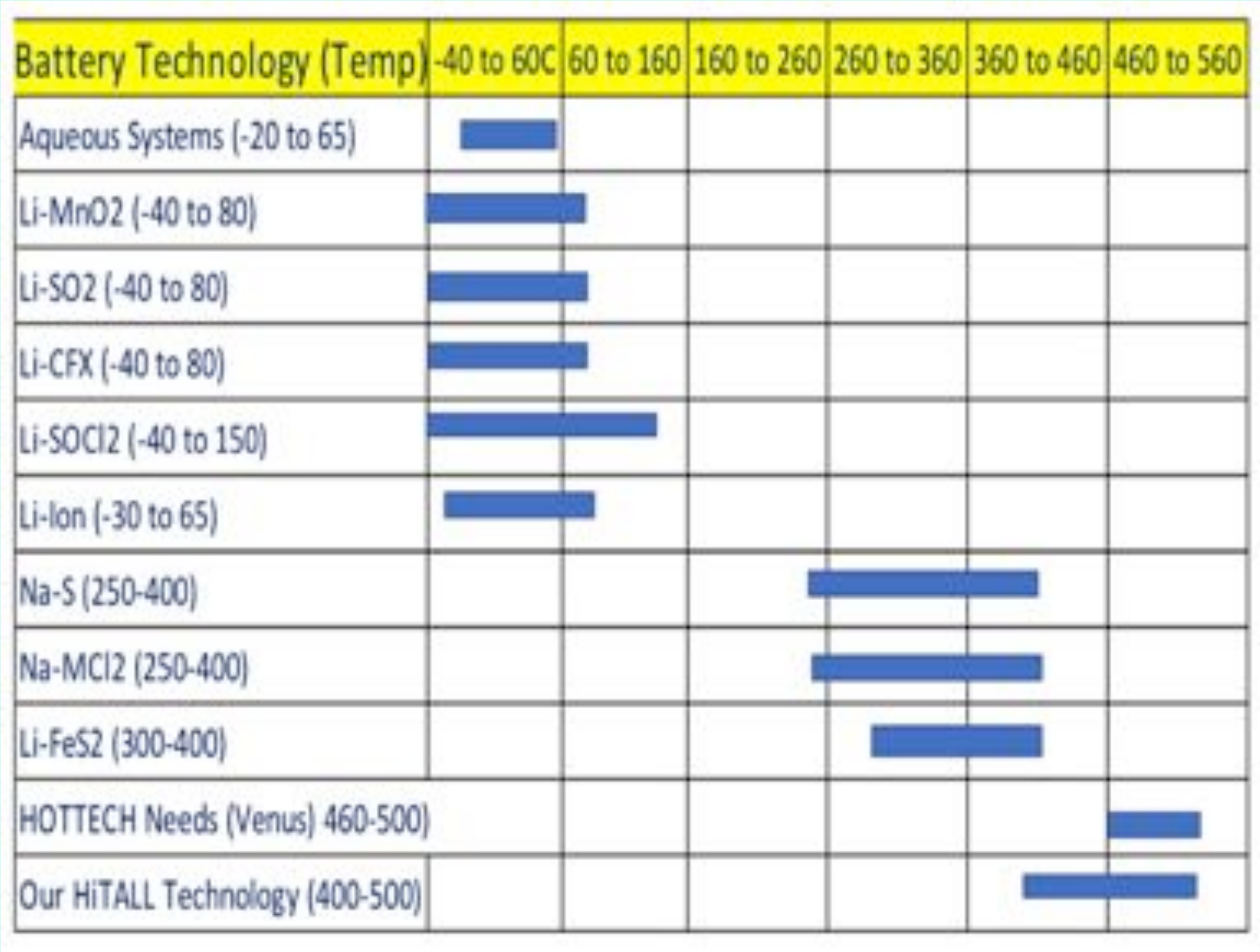




- Conventional long-duration power technologies, such as solar array or radioisotope power systems are challenging.
  - Reduced solar flux below the clouds and at the surface: 2600 W/m^2 (or roughly twice that of Earth's solar flux) at high altitudes and ~2-4 W/m^2 at the surface.
  - The current Multi-mission Radioisotope Thermoelectric Generator is not capable of operating at 90 bar pressure and a +465°C heat sink.
  - Dynamic RPS is promising but significant development is needed and also requires an energy storage device for load levelling

Battery Options Limited

- There is no battery system that can survive the Venus surface temperatures
  - Li-ion batteries: Not stable above 70C.
  - Li primary batteries (Li-CF_X, Li-$SOCl_2$): Not stable above 150ºC
  - Even with thermal management, the survivability life is limited to a few hours.
  - Thermal management system (phase change materials) would need considerable mass and volume at the expense of payload.
- High temperature sodium rechargeable batteries can't survive at >400º



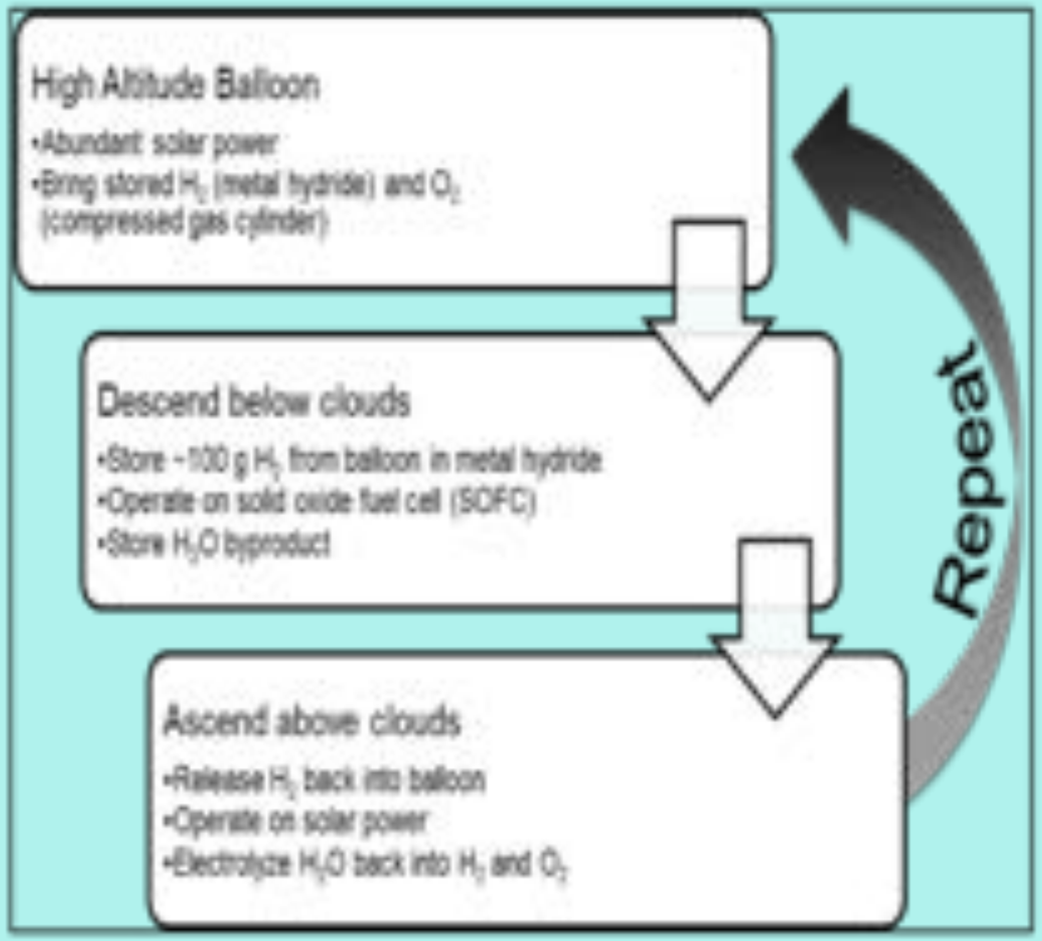
- **A new energy storage technology is required to enable an extended exploration of the Venus surface**

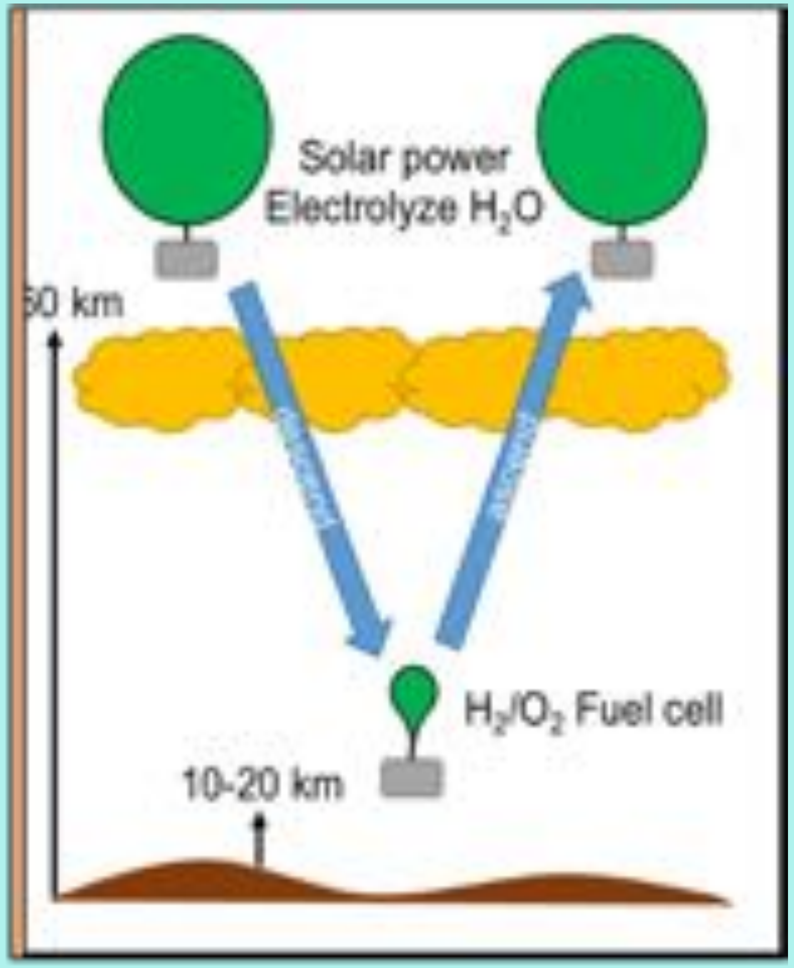
Venus Probe with In-situ Power Generation (VIP-INSPR)

- Venus Interior Probe based on in-situ resources (VIP-INSPR) for power generation (VIP-INSPR).
- Generation of hydrogen (fuel) and oxygen at high altitude from *in situ* resources, i.e., solar energy and water (from the Venus clouds or carried from ground) and generation of power at low altitudes utilizing fuel in a high temperature fuel cell.
- Hydrogen used as a lifting gas for buoyancy to navigate the probe across the Venus clouds.
- Can operate for extended durations (not limited by power or lifetime).

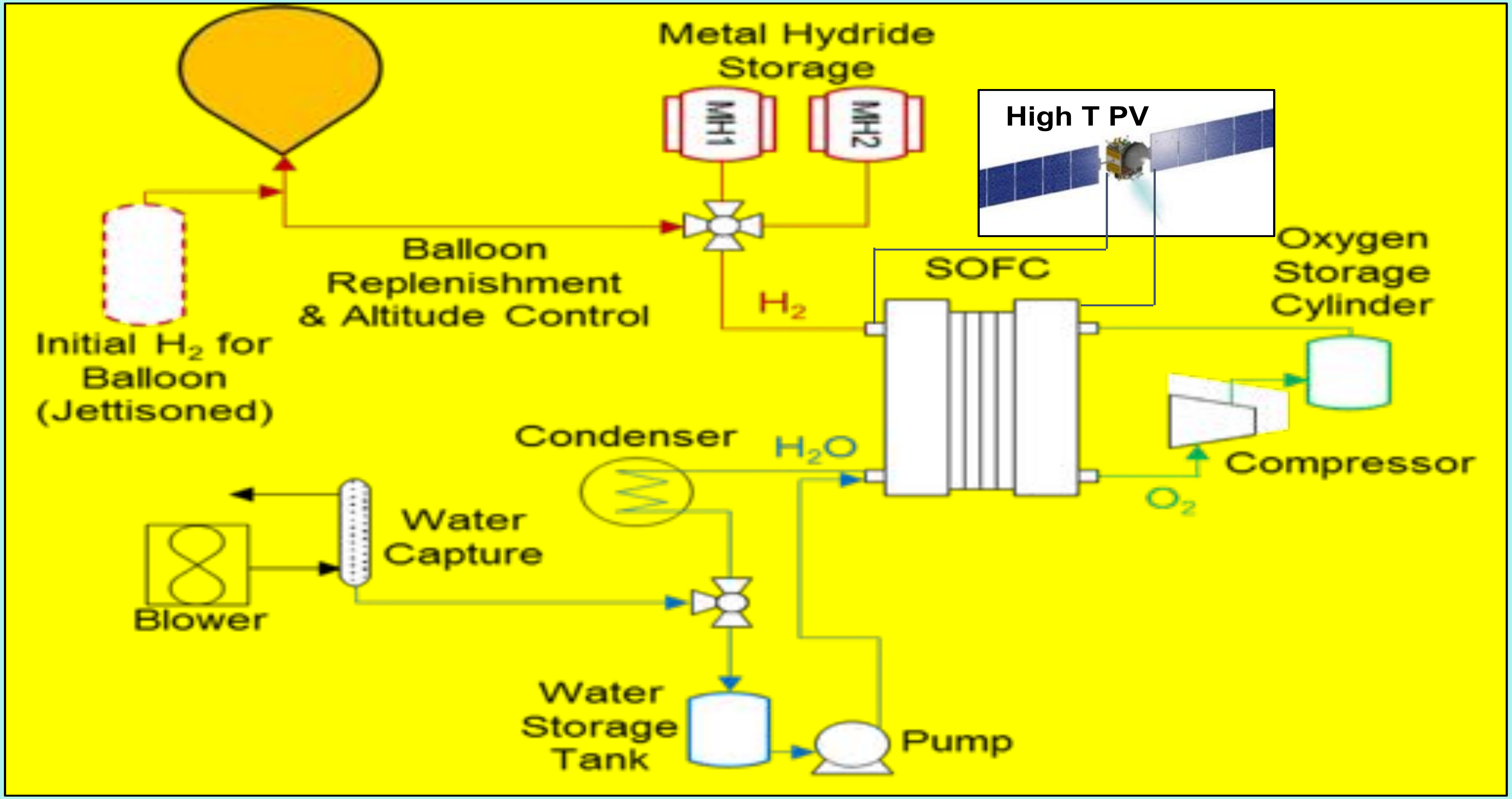
Approach

- Kapton balloon
- H_2 lifting gas & for energy storage
- Solar power at high altitude
- H_2 stored in metal hydrides
- Regen. solid oxide fuel cell (SOFC) power below clouds, at night, and regenerates H_2/O_2





Schematic of Power Architecture of Venus VAB

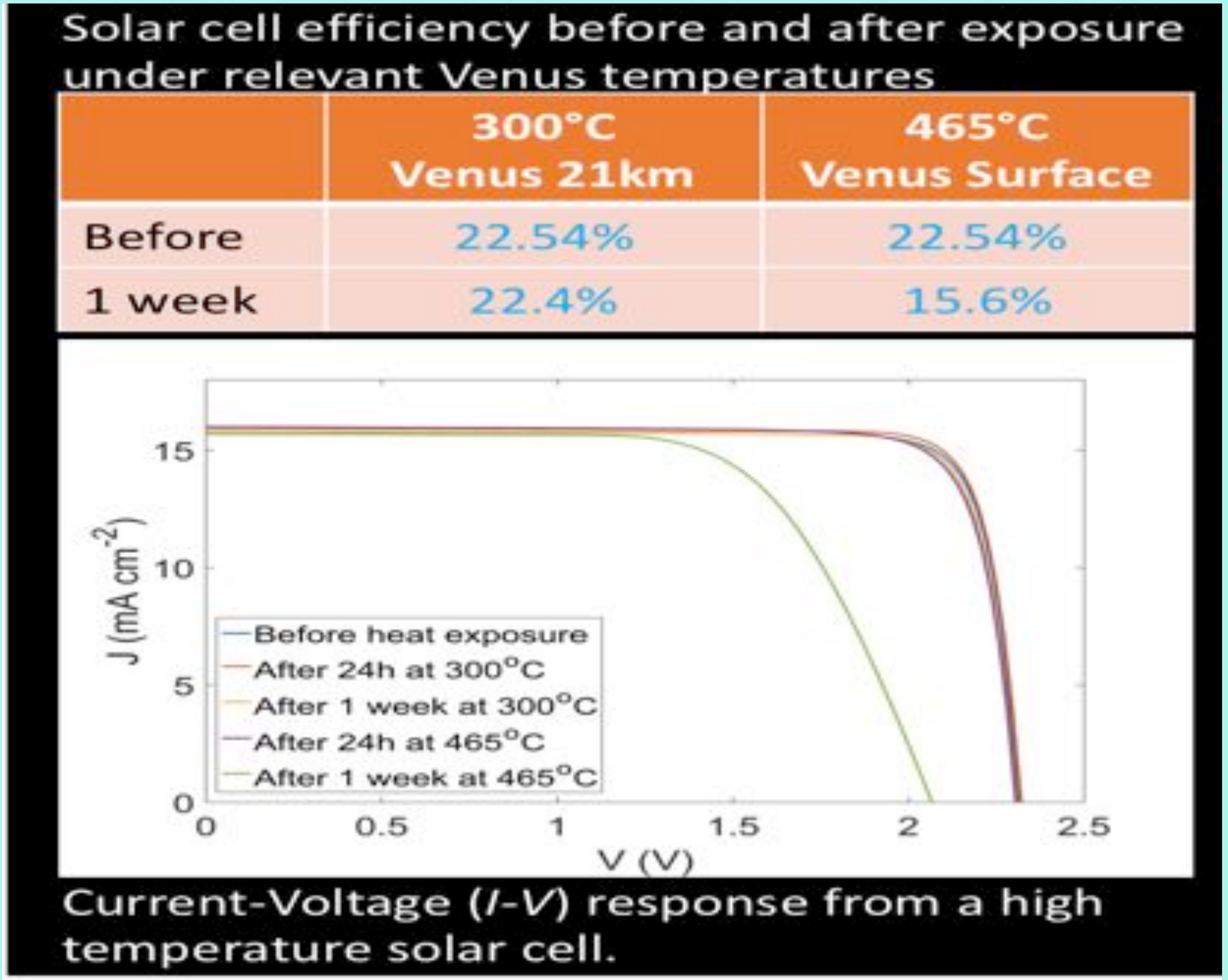


Simple architecture.

High-Temperature Tolerant Solar Cells

Jet Propulsion Laboratory
California Institute of Technology

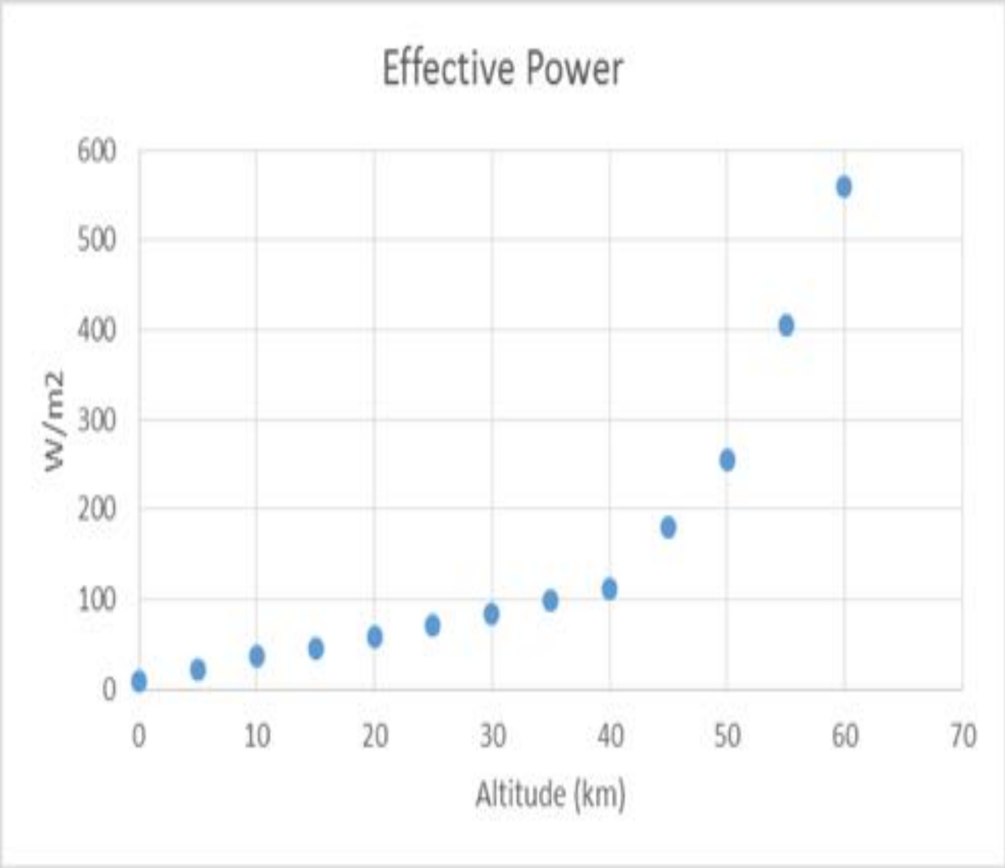
- JPL (Grandidier et al.) is developing high temperature tolerant solar cells under NASA's HOTTECH Program, using wide bandgap materials, since the higher voltage of wide bandgap solar cells results in less degradation.
    - Si solar cells (1.1 eV) lose ~ 0.45% /°C increase in operating temperature. GaAs cells (1.4 eV) lose about 0.21% per °C.
- For our Venus VAB, however, it is the lifetime that is crucial, since power at low altitudes is provided by fuel cell.


Solar cell efficiency before and after exposure under relevant Venus temperatures

	300°C Venus 21km	465°C Venus Surface
Before	22.54%	22.54%
1 week	22.4%	15.6%

Current-Voltage (*I-V*) response from a high temperature solar cell.

For 300W at 60km altitude we need: **0.536 m^2** solar cells



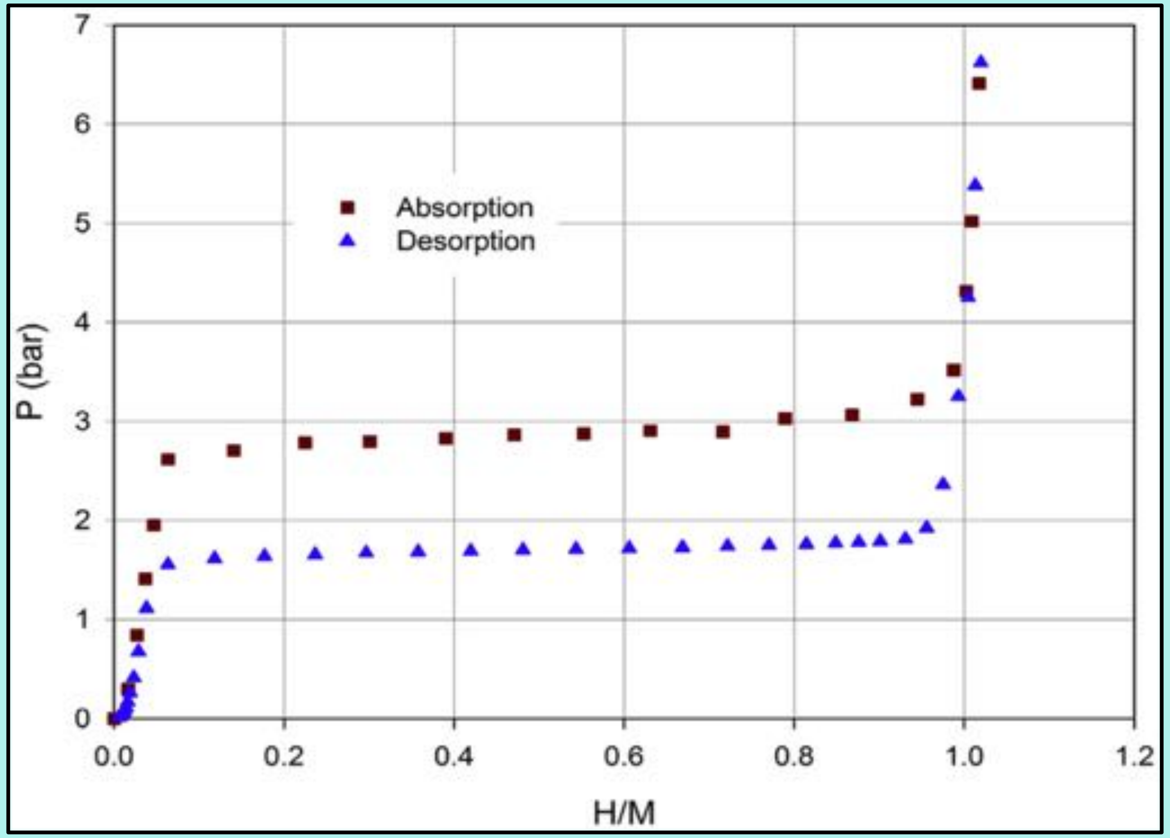
Power available for that size at other altitudes:

Altitude (km)	Solar cell Power (W)
0	4.7
5	11.8
10	20.1
15	24.5
20	31.4
25	38.6
30	45.7
35	53.1
40	60.2
45	97.3
50	137.3
55	217.0
60	300.0

Hydrogen Storage Using Metal Hydrides

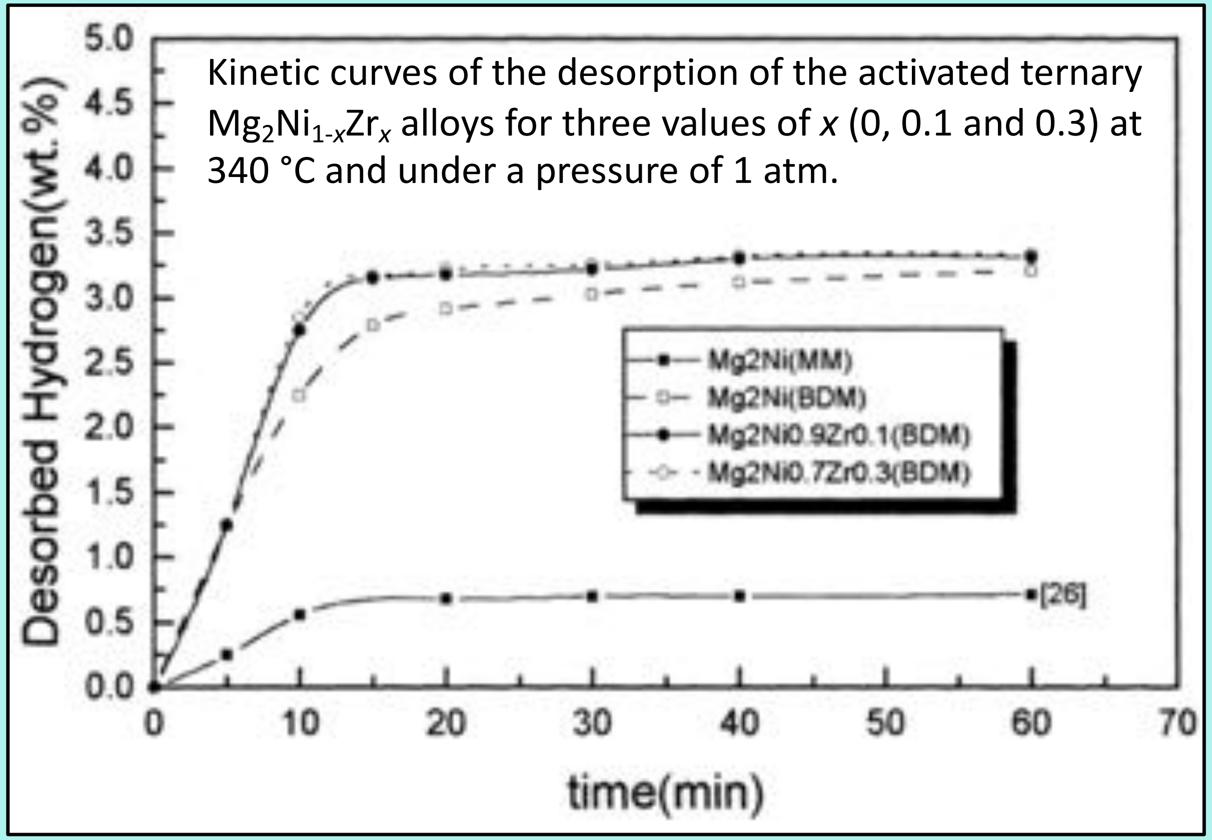
- Metal hydrides are attractive materials for hydrogen storage.
  - No need for compressors and volumes are considerably lower than real gas law requirements
  - Several materials exist with different amount of hydrogen absorption capacities and plateau pressures.

Pressure-Composition-Temperature (PCT) curves



- Absorption/desorption pressures are characteristic of materials

Hydride kinetics

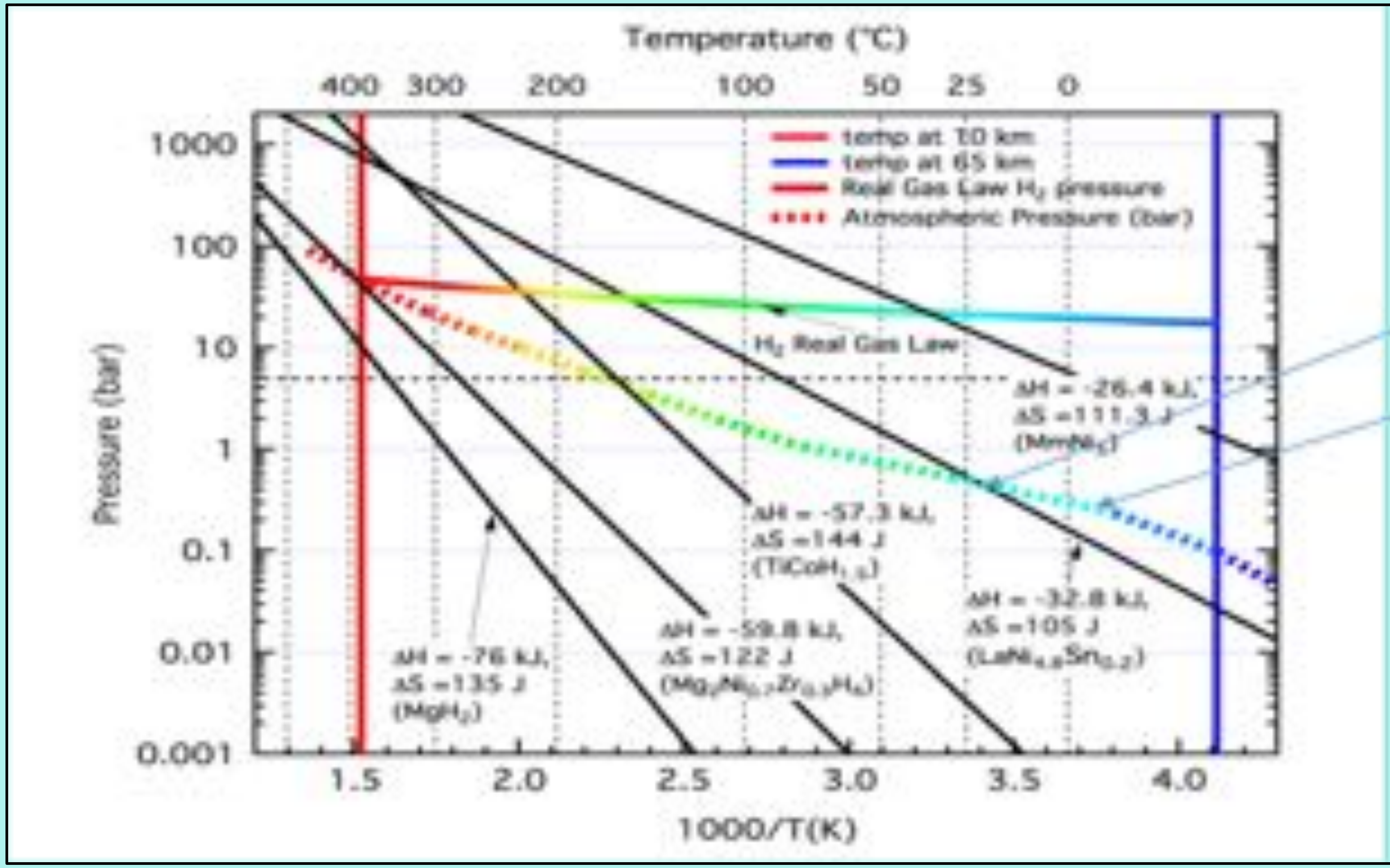


- Absorption/desorption kinetics are rapid both at 25- 300°C.

H_2 Transfer from MH into Balloon

- Absorption/desorption kinetics are rapid both at 25-300°C, about 90% within 10 minutes.
- Desorption is endothermic. Provides cooling at low altitudes

Van't hoff plot



$$\ln\left(\frac{P}{P_0}\right) = -\frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT}$$

Absorption at <25 °C temp (above 55 km).

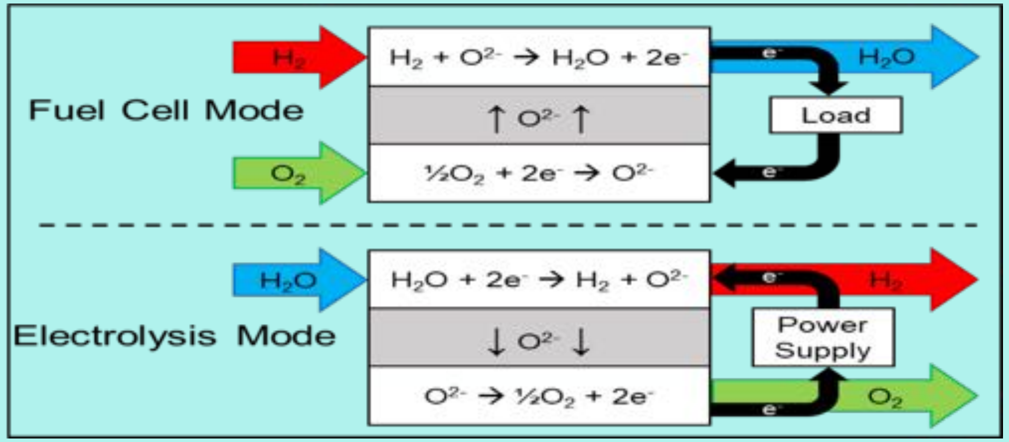
Equilibrium pressure of hydride low at 0 °C.

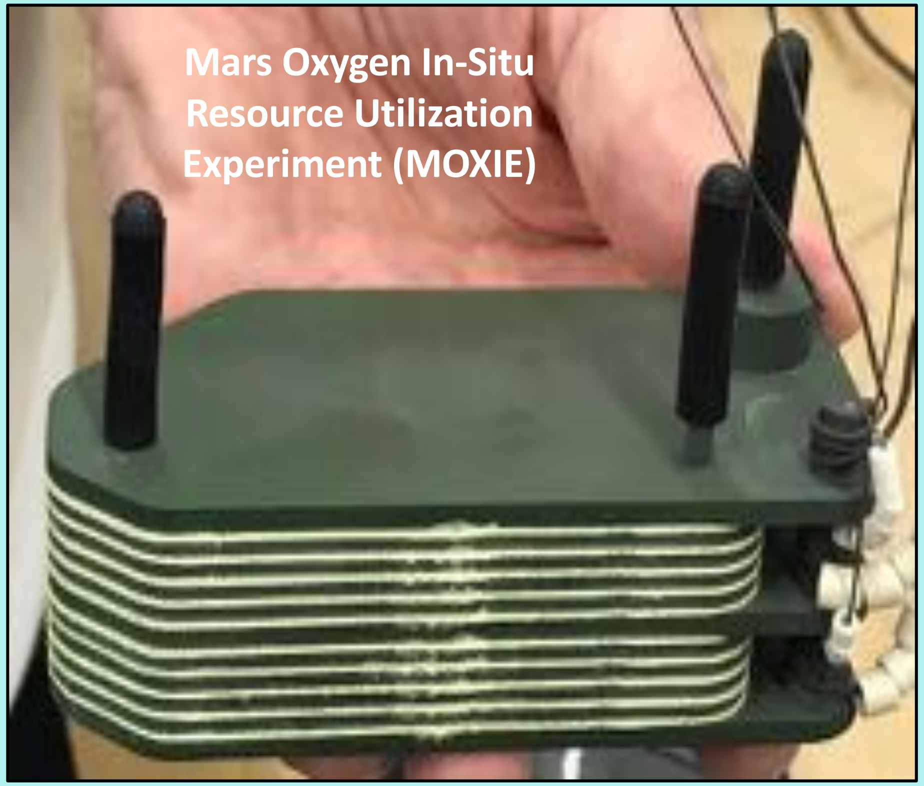
- Absorb H_2 at low temp/high altitude
- Release H_2 at high temp/low altitude (endothermic)
- Modulate altitude by adding or removing H_2 from balloon
- Store energy for fuel cell

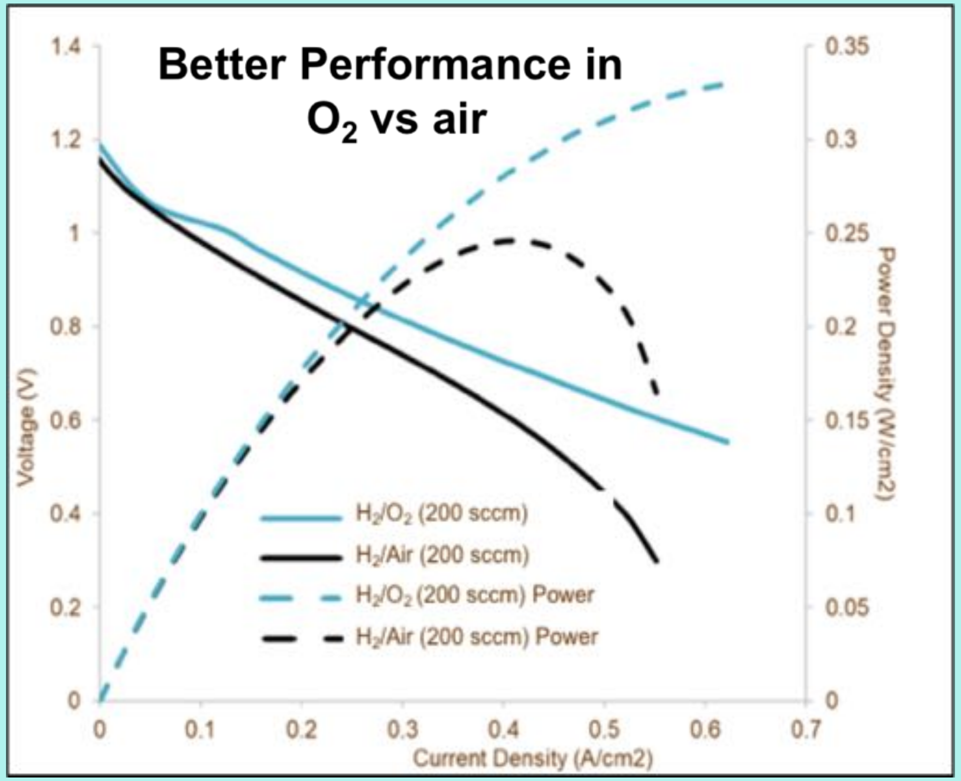
- Metal hydrides can be selected based on the temperature (altitude) range
- For 2 kWh of energy, ~100 grams or 42.4 moles of H_2 and 21.2 moles of O_2 would be required. Another 200 g of H_2 is required for altitude control (total of 15 kg of MH)
  - The initial fuel requirements will be part of the launch package
  - The system will be encased in a Titanium shell for stability against high pressure, temperature and H_2SO_4

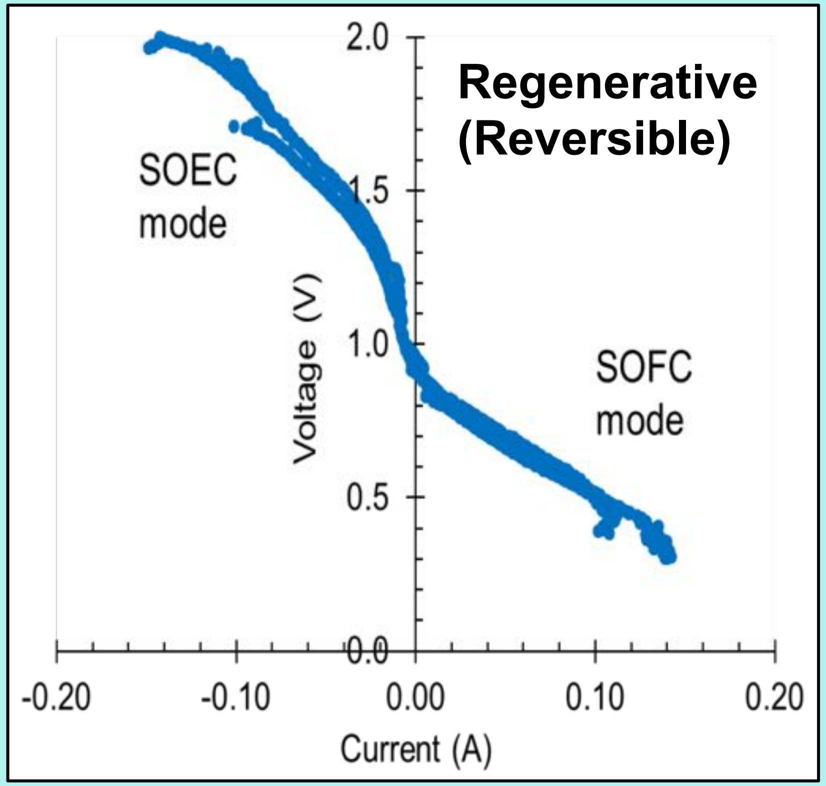
H_2/O_2 Solid Oxide Fuel Cell / Electrolyzer

- A reversible solid oxide fuel cell (RSOFC) is a device with a solid oxide electrolyte that operates efficiently at ~800°C as fuel cell and electrolysis cell, generating power from H_2 and O_2 (and produce H_2O) in fuel cell mode and generating H_2 and O_2 (from H_2O) during electrolysis.
- Standard Ni/YSZ/LSM SOFCs operate from 750-1000 °C
  - High reliability (>19,000 hr demonstrated)
  - High power density (0.75 W/cm^2)
- Planned demonstration on Mars 2020 (MOXIE)



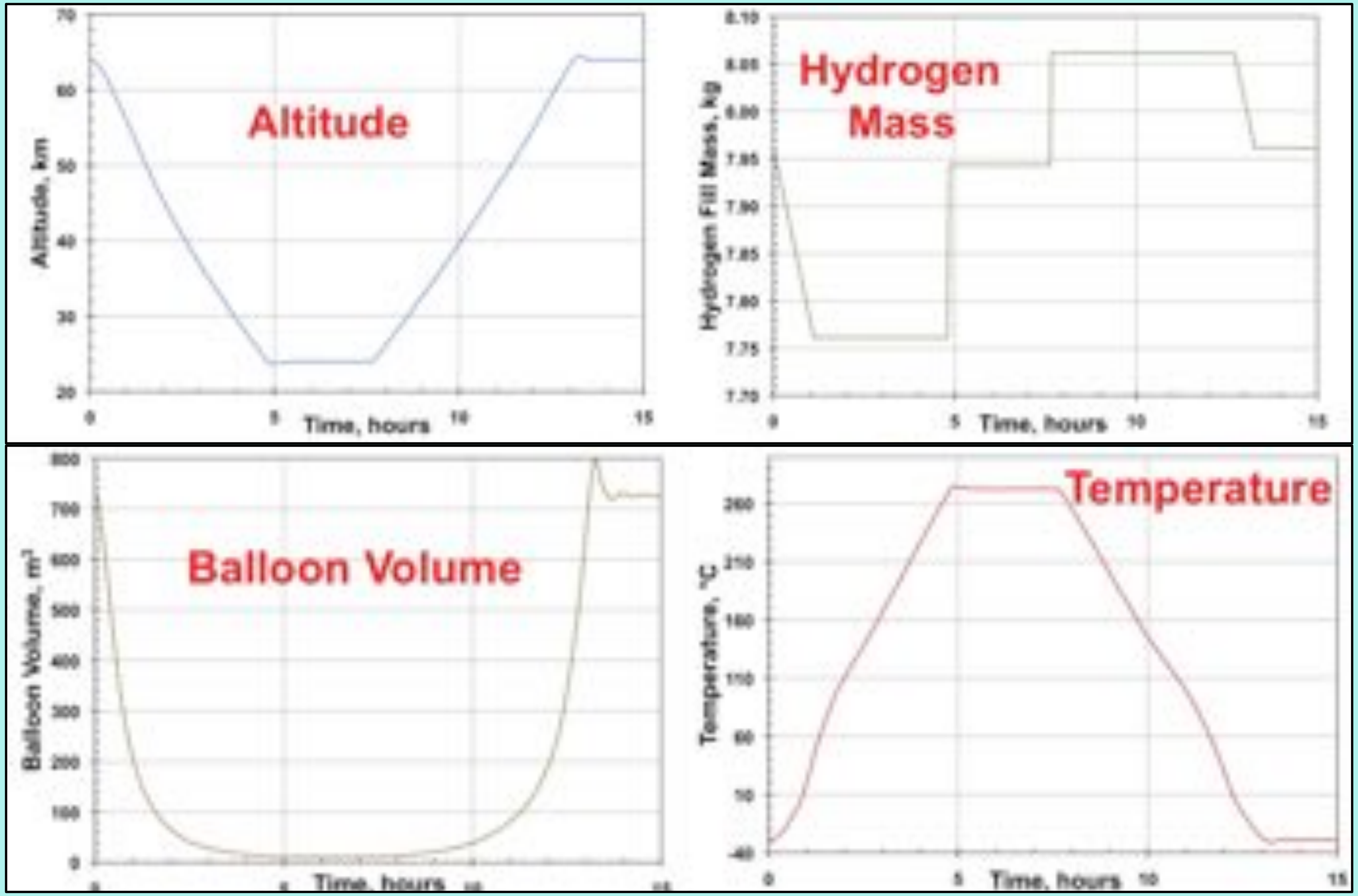






Notional Balloon Altitude Control

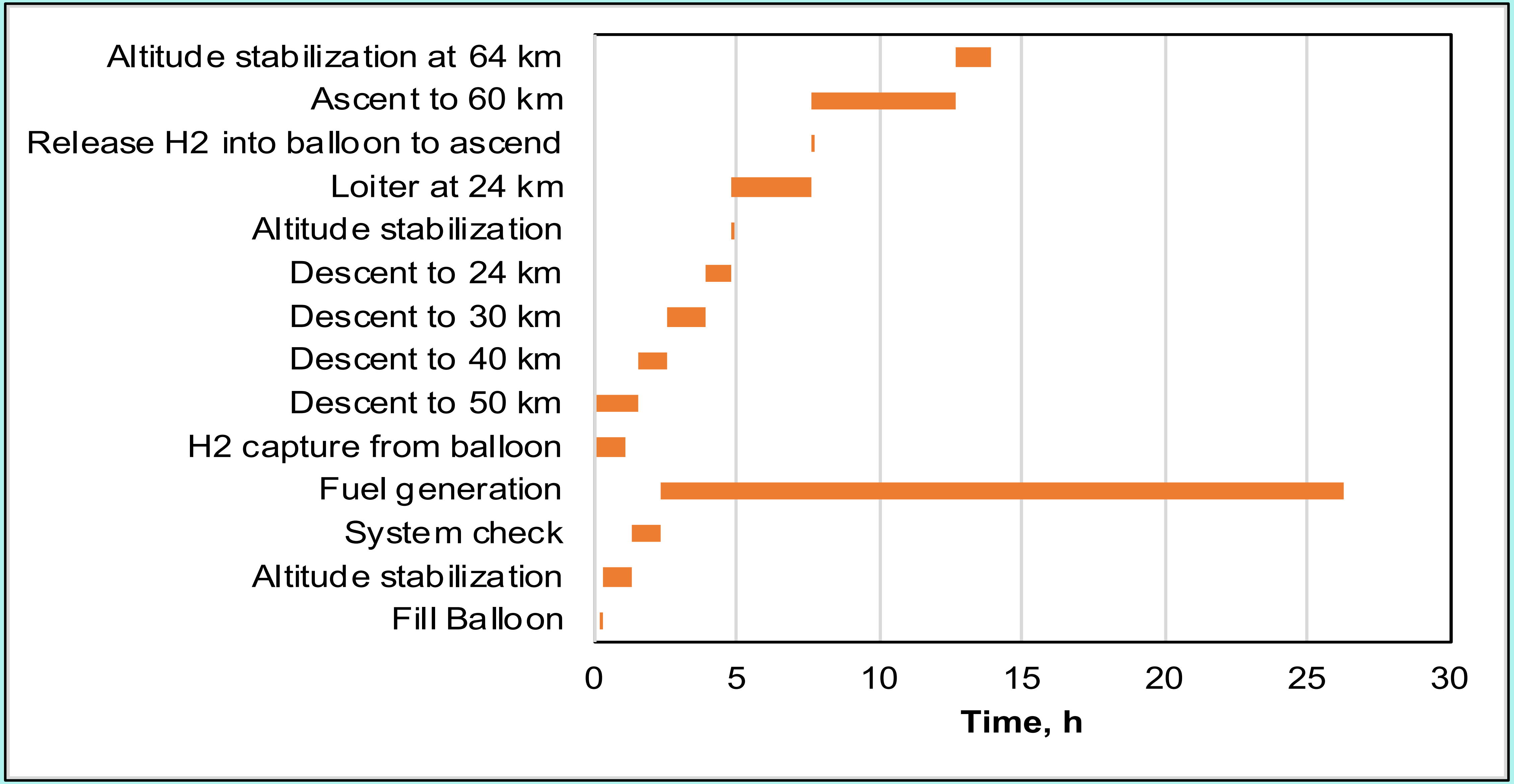
- Altitude cycling and control is achieved by means of buoyant gas storage.
- Taking as little as 200 g of H_2 gas from the envelope and storing it at much higher density than ambient (at lower altitudes), results in negative balloon buoyancy that causes the balloon to descend to 10 km in just over 7 hours.
- Withdrawing smaller amounts from the balloon results in longer descent times.
- Re-filling the balloon with stored gas allows the balloon to return to positive buoyancy and ascend.



- *Carried out by our collaborators at the Global Aerospace Corporation in Pasadena, CA*

Pre-Decisional Information – for Planning and Discussion Purposes Only

Venus Probe – Notional Operational Sequence



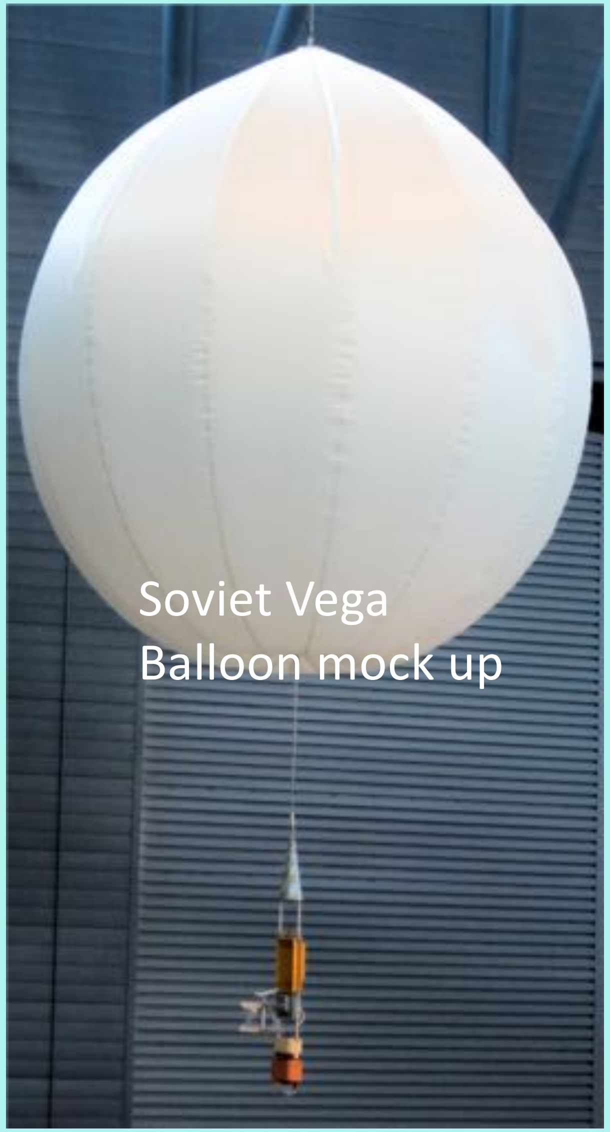
- 24 h required to generate adequate hydrogen for the fuel cell to support low altitude dive
- About 9 h to complete one altitude excursion (60-24 km) during daytime
- Another 24 h for regeneration of fuel for the fuel cell to support nighttime operations

Preliminary (VIP-INSPR) Balloon Design

- A balloon system design that can cycle in the range of 15 to 60 km.
- Assumed suspended mass is 100 kg; Pay load ~20 kg of science payload
- Single, near-spherical zero pressure balloon: simple and lightweight
  - 1 mil thick Polyimide (e.g. Kapton) or Polybenzimidazole (PBI) Film.
  - 0.5 mil Teflon coating, vapor deposited gold or SiO_2 for protection.
  - For 100 kg suspended mass, the envelope mass is 20.8 kg and diameters are 9.4 m (at 60 km) and 2.1 m (at 20 km).
  - Envelope needs to support suspended mass load in highest temp regime.
  - Venting and fill features.

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



- Carried out by our collaborators at the Global Aerospace Corporation in Pasadena, CA

Batteries for Venus Surface Missions

Objective

- Develop an enabling advanced primary battery technology resilient to the high-temperature environments of Venus surface, Mercury, or the deep atmosphere of gas Giants and operational for 30 days at 475°C (and 92 bar pressure).

Previous Venus Surface Missions

- Probes from the Venera series, Vega program and Venera-Halley probes.
- Successfully landed on Venus but lasted only <2 h due to the failure of batteries and electronics, even with extensive thermal insulation, phase-change materials and similar heat sinks.

Notional battery powered version of the Long-Life In-situ Solar System Explorer Venus Probe (~20 cm cube)

High Temperature Battery Chemistry

- High capacity anode (Li alloys, e.g., Li-Si, Li-Al alloy)
- High energy cathodes
  - Metal chalcogenides, Disulfides: FeS_2, CoS_2, NiS_2, ZrS_2, TiS_2
  - Metal Phosphorous Trisulfides: $FePS_3$, $MnPS_3$, $CoPS_3$ and $NiPS_3$
  - Metal Halides ($FeCl_2$ and $NiCl_2$ and CF_X
- Molten salt electrolyte with low vapor pressure (mixed alkali metal halides)
  - Standard LiCl-KCl (44 wt% LiCl and 56 wt% KCl) (359°C)
  - LiBr–KBr–LiF and LiBr–KBr–LiCl eutectics (melt at 324.5 and 321°C)
  - LiCl:LiBr:KBr (12.05 wt% LiCl and 36.54 wt% LiBr and 51.41wt% KBr)
  - LiF:NaF:KF eutectic.(29.2 wt% LiF, 11.7 wt% NaF and 59.1 wt% KF)
- Separators that minimize self-discharge.
  - MgO, Al_2O_3, Li_2O

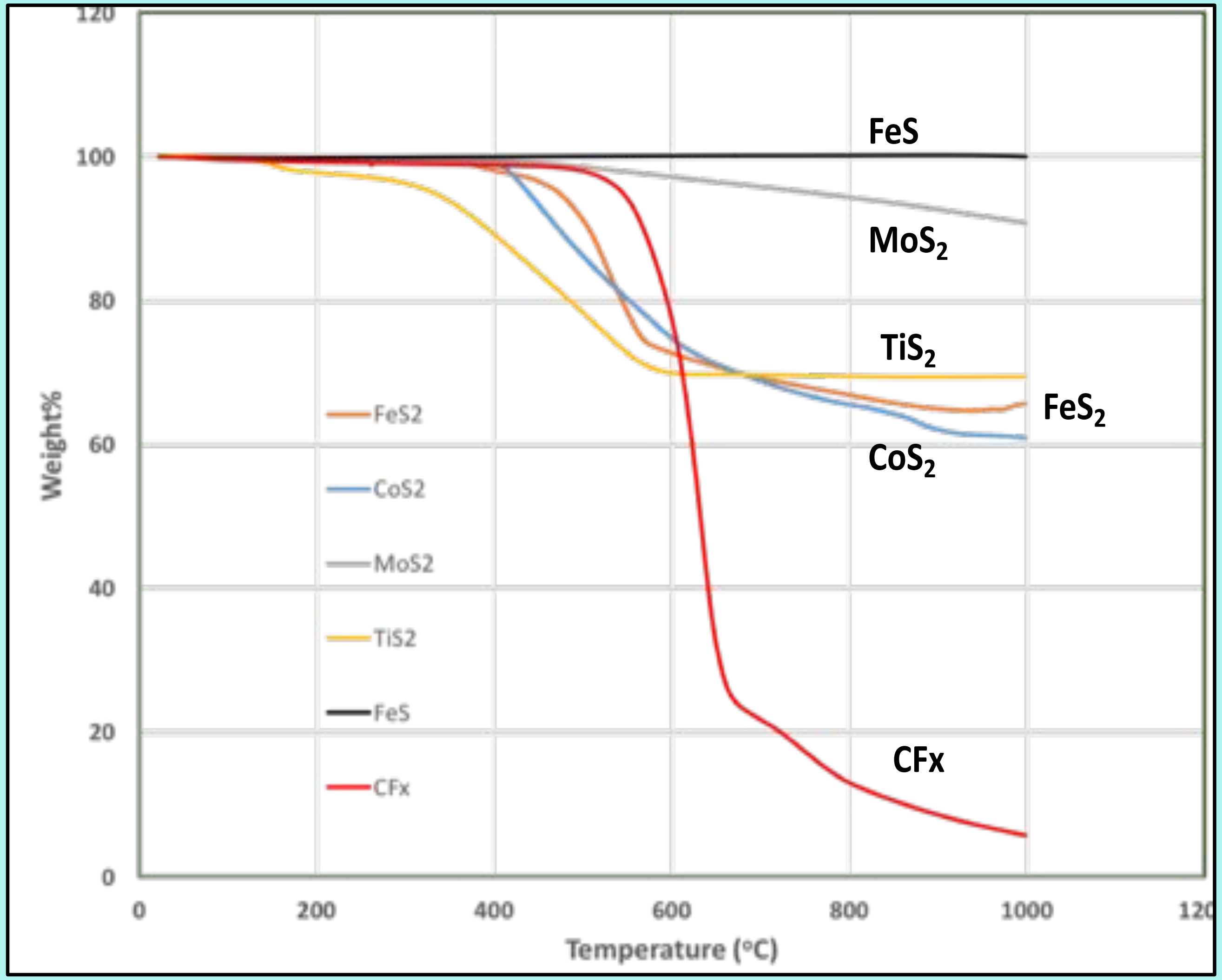
Cathode Materials for High Temperature Batteries

Electrochemical Characteristics

Cathode		Voltage, vs. Li	Sp. Capacity, mAh/g	Sp. Energy, Wh/kg
Metal Disulfides	FeS2	1.7	894	1520
	FeS	1.7	610	1036
	CoS2	1.6	870	1392
	NiS2	1.7	873	1484
	TiS2	2.6	240	624
	MoS2	1.6	642	1027
	ZrS2	1.6	690	1104
Metal Chlorides	NiCl2	2.6	413	1074
	FeCl2	2.3	423	973
Metal Phosphorous Trisulfides	FePS3	1.6	1318	2109
	CoPS3	1.6	1248	1997
	NiPS3	1.7	1255	2134
Fluorides	CFX	2.5	810	2025

$MS < MS_2 < MPS_3 < CF_X$

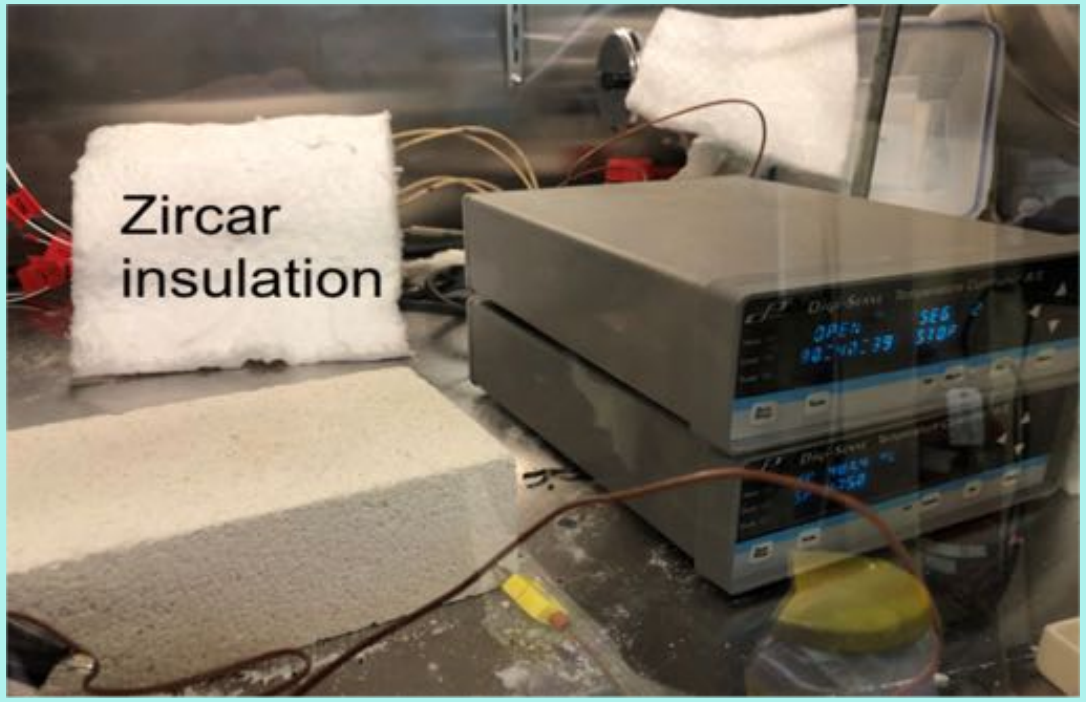
Thermal Stability from TGA

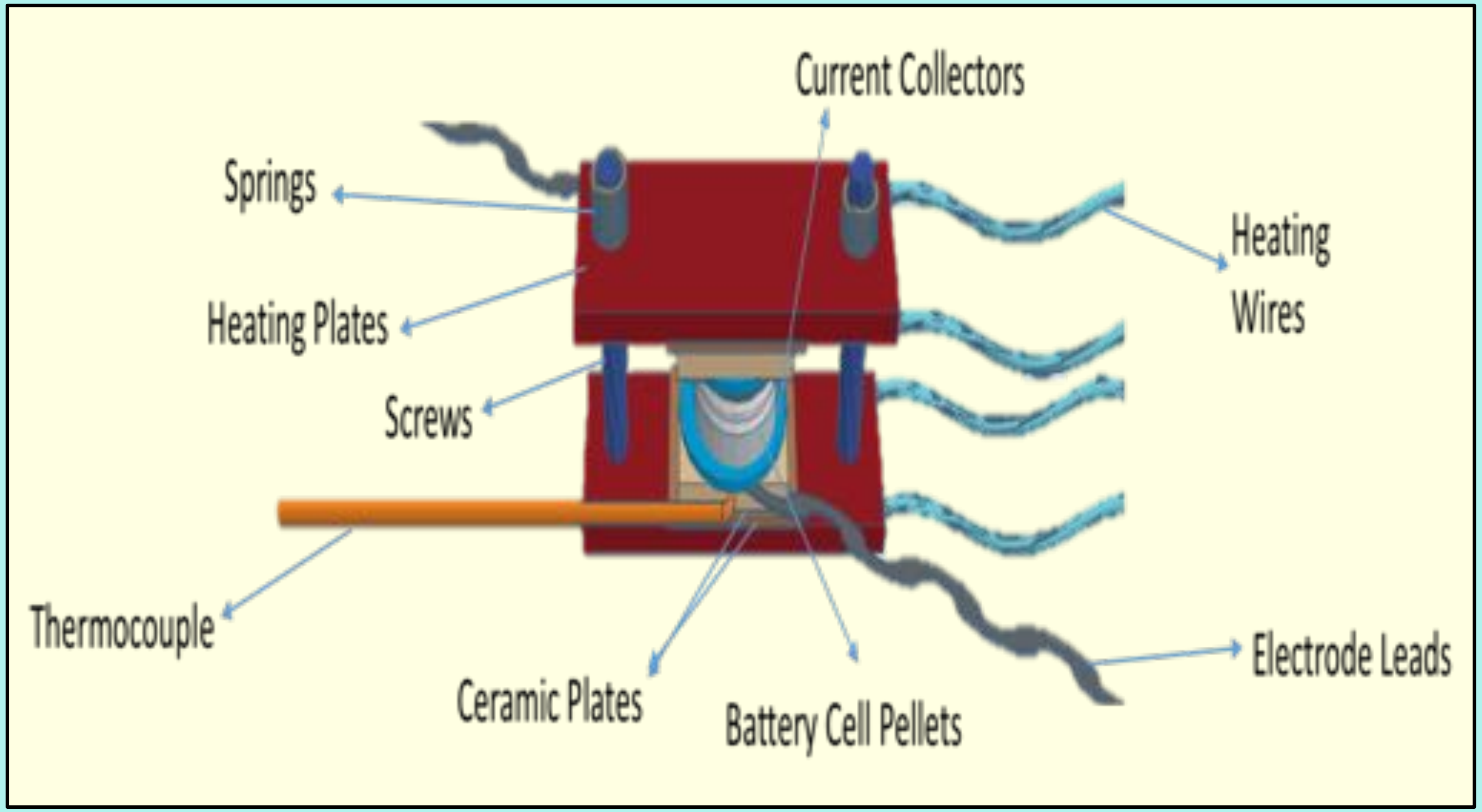


- Also made TGA measurements under isothermal conditions at different temperatures
- Thermal stability decreases as $FeS > MoS_2 > CF_x > CoS_2 > FeS_2$ TiS_2

Laboratory High Temperature Cells

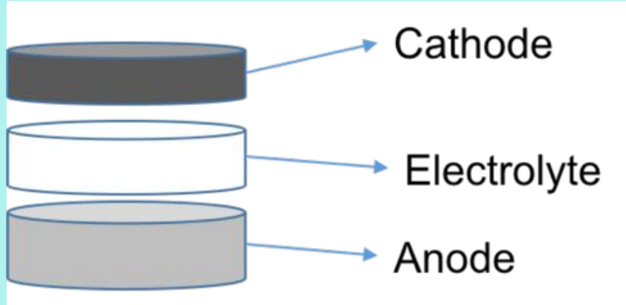
- Test conditions:
  - Cell operation temperature → 475 ^{O}C
  - Cell discharge time → 1 month(C/720 rate). We also used C/20 discharge rate to screen changes.
- Pellets prepared (13 mm die 8 metric tons) and cells assembled in dry room
- Tested in glove box with ultra-low oxygen and moisture content (<10ppm)



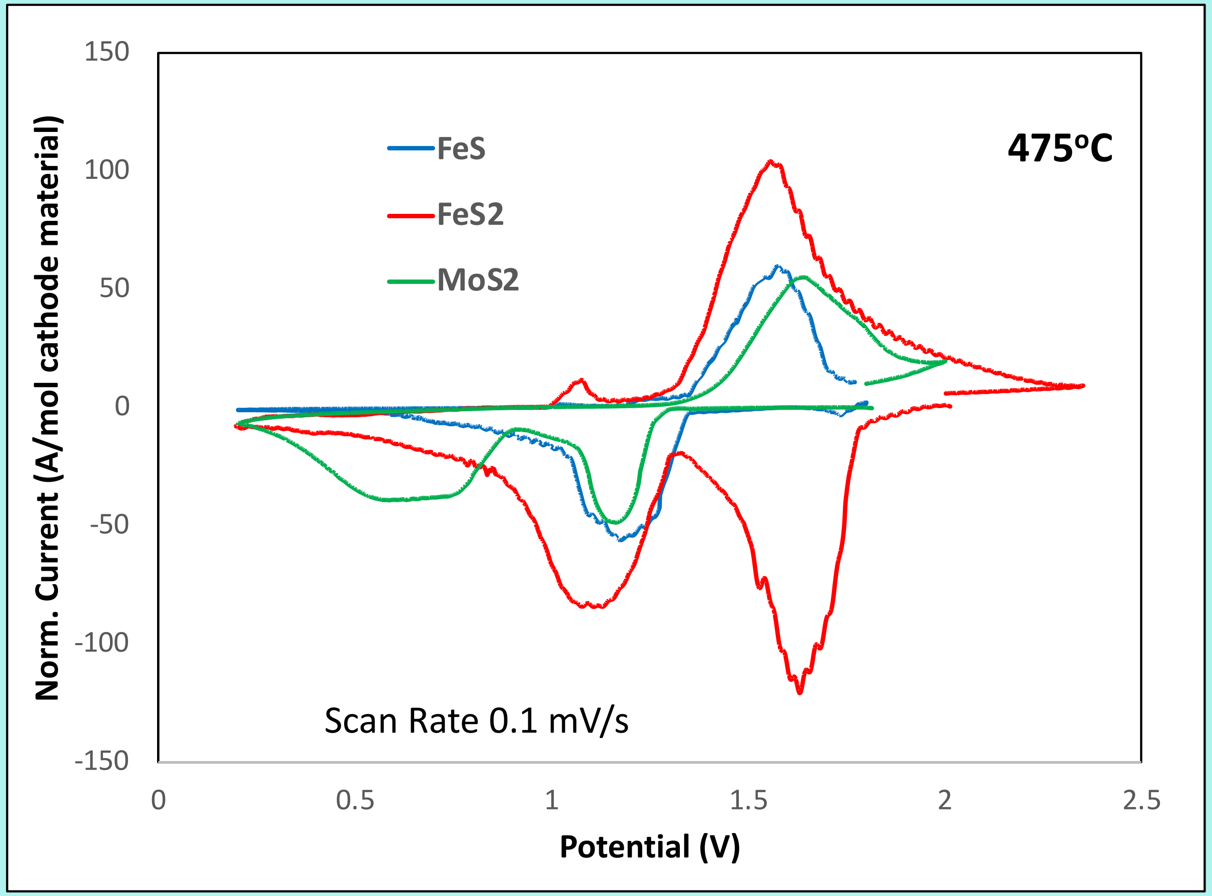


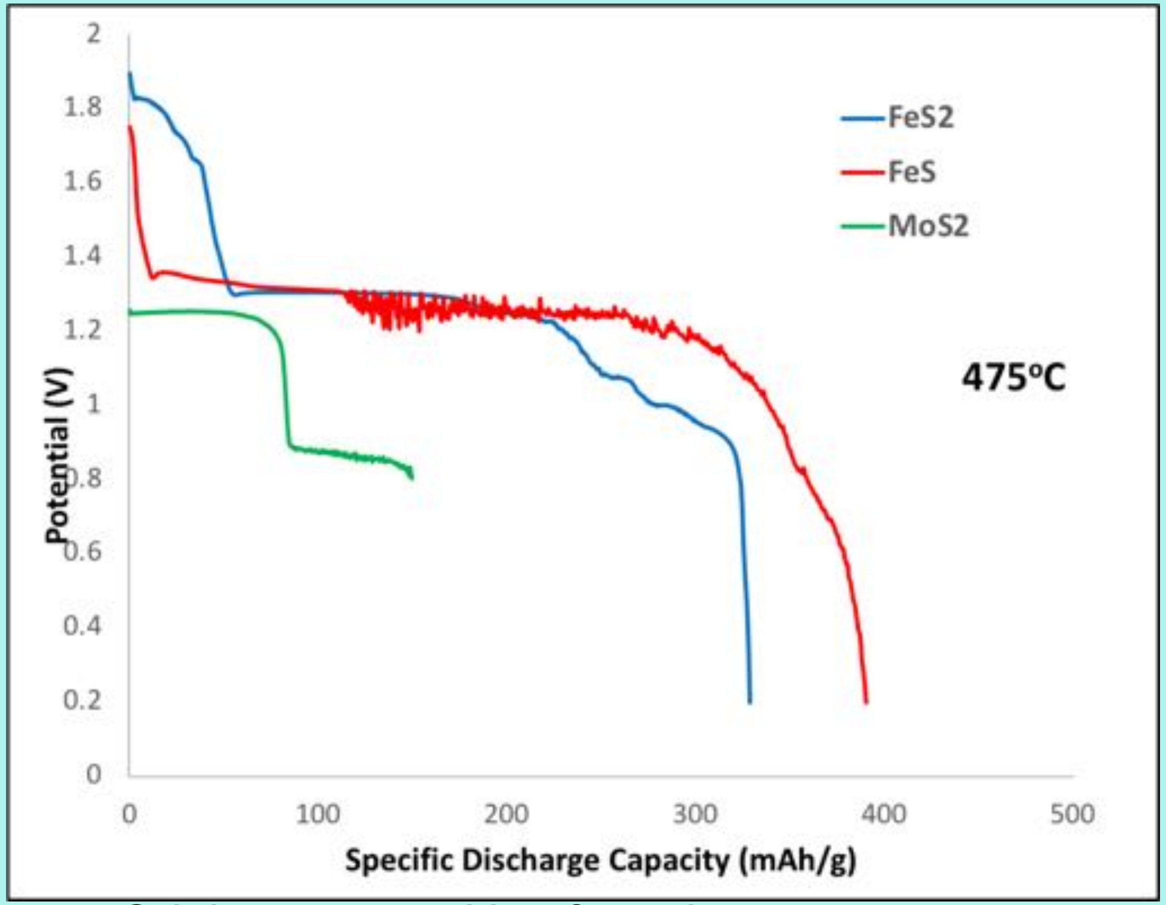
Anode	Electrolyte	Cathode

LiAl : LiCl-KCl 65:35	LiCl-KCl-MgO 60:40	FeS2: LiCl-KCl-MgO 70:20:10



Electrochemical Characteristics of Cathodes



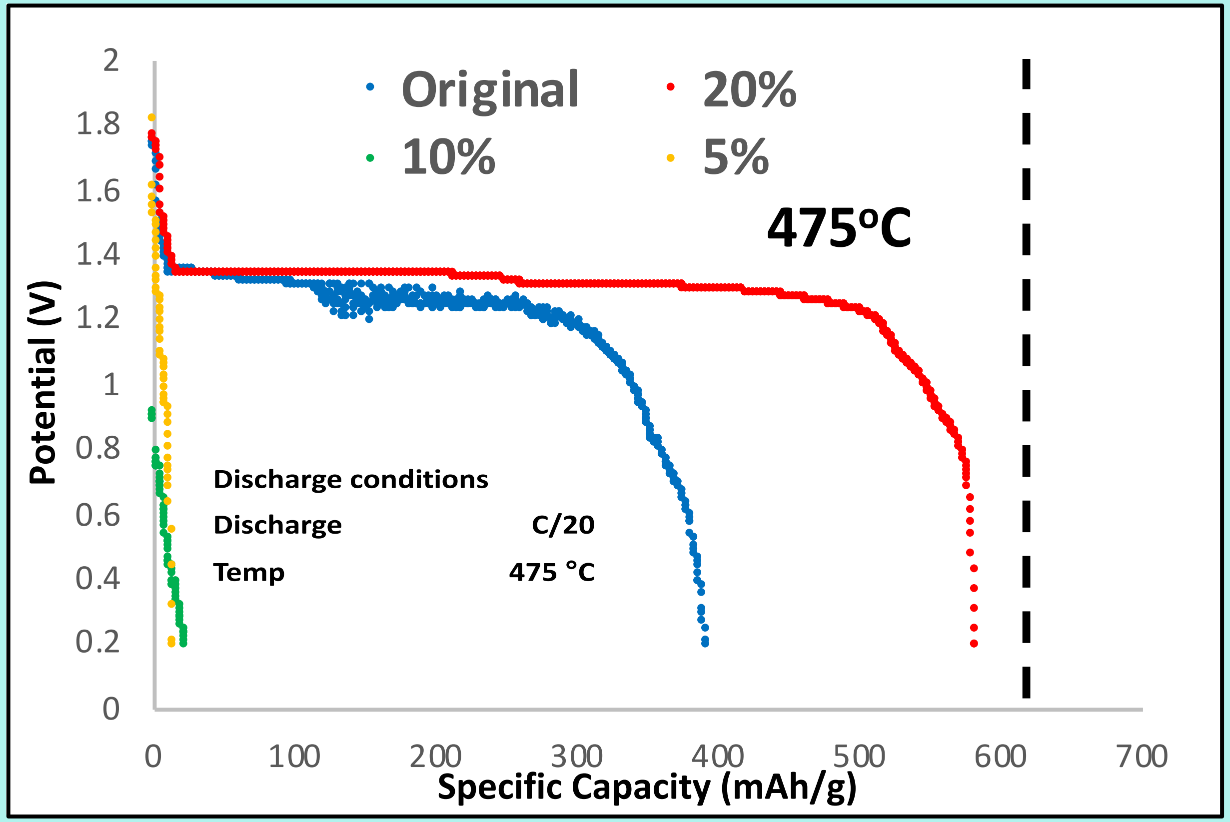


- FeS_2 & MoS_2 have two discharge peaks
  - 1st Li^+ intercalation and Fe/Mo reduction
- FeS has only one discharge peak
  - Fe reduction
- MoS_2 peaks downshifted → less discharge potential

- Original composition from literature:
  - Anode → LiAl:LiCl-KCl 65:35
  - Cathode → MS_x:MgO:LiClKCl 70:10:20
  - Electrolyte → LiClKCl:MgO 60:40
- FeS_2 and MoS_2 display multiple potential drops
  - Li_2TMS_2 intermediates
- FeS displays smooth discharge curve
  - Higher specific capacity

Optimization of Electrolyte : Binder Ratio

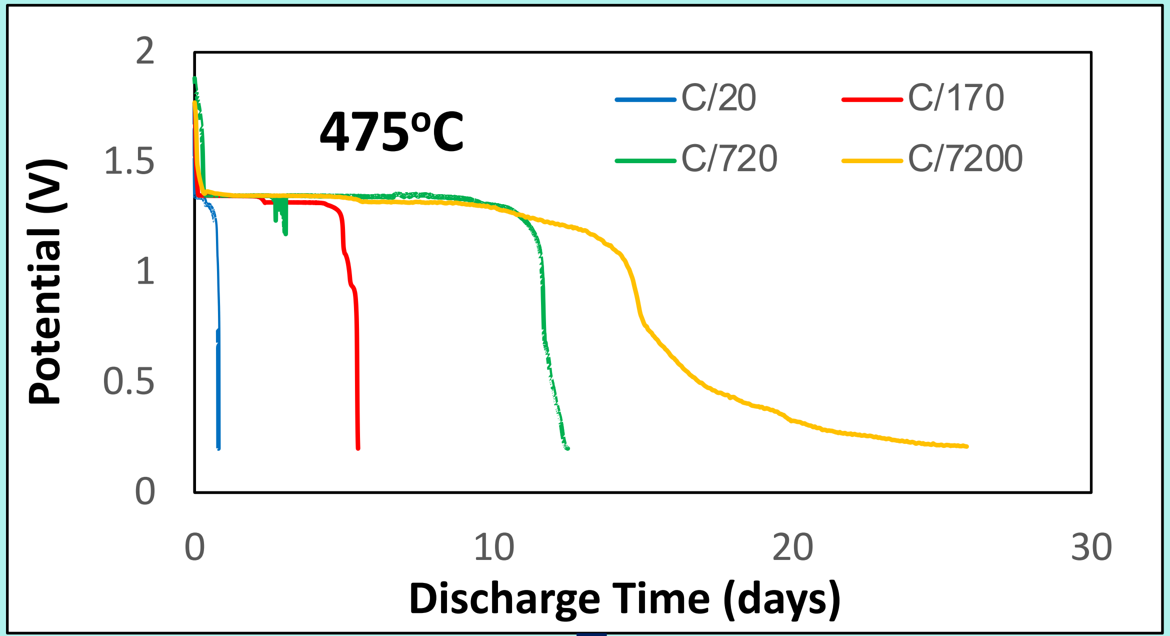
- Used LiCl-KCl eutectic blend
- Varied electrolyte concentration for electrodes
  - Electrolyte leakage from cell
  - Soft shorts
- Lower concentrations → not enough conductivity
- 20% electrolyte→ 95.6% discharge capacity

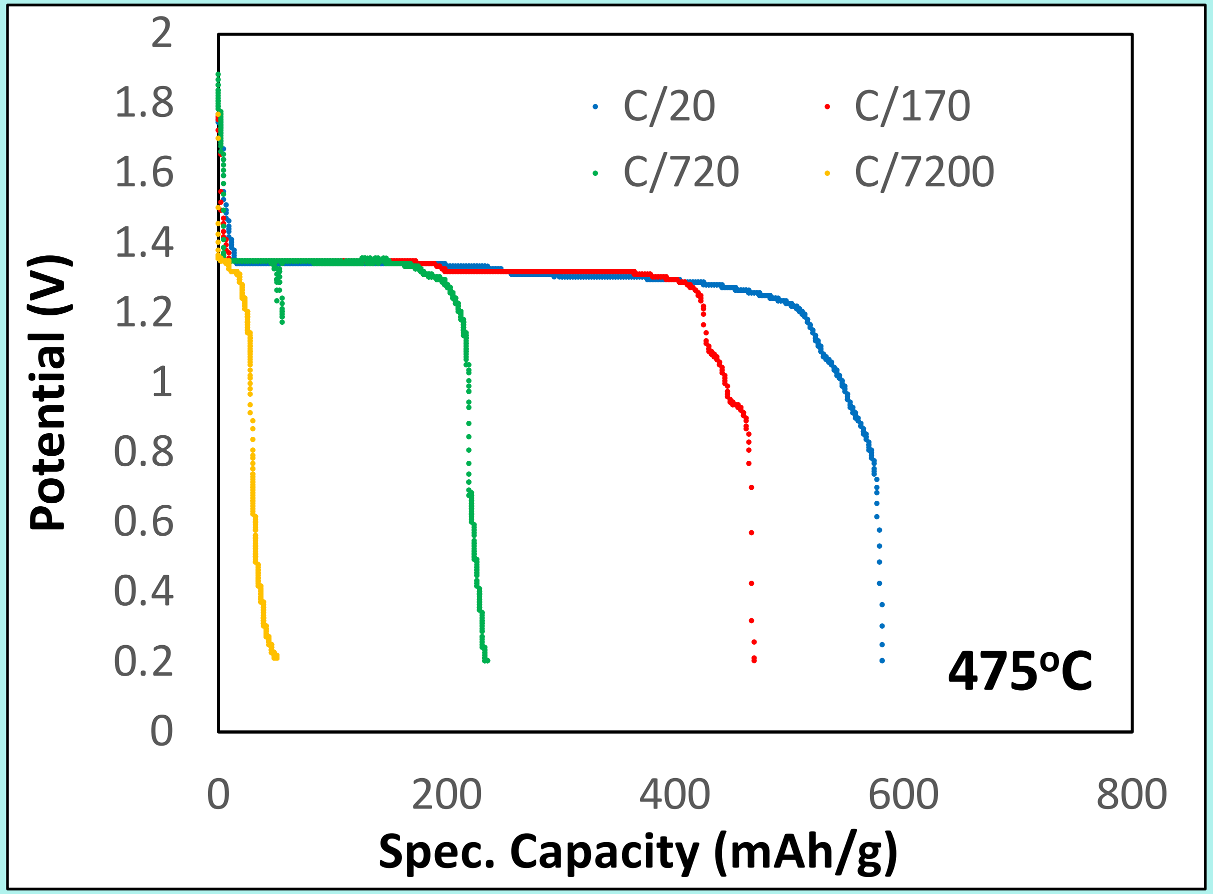


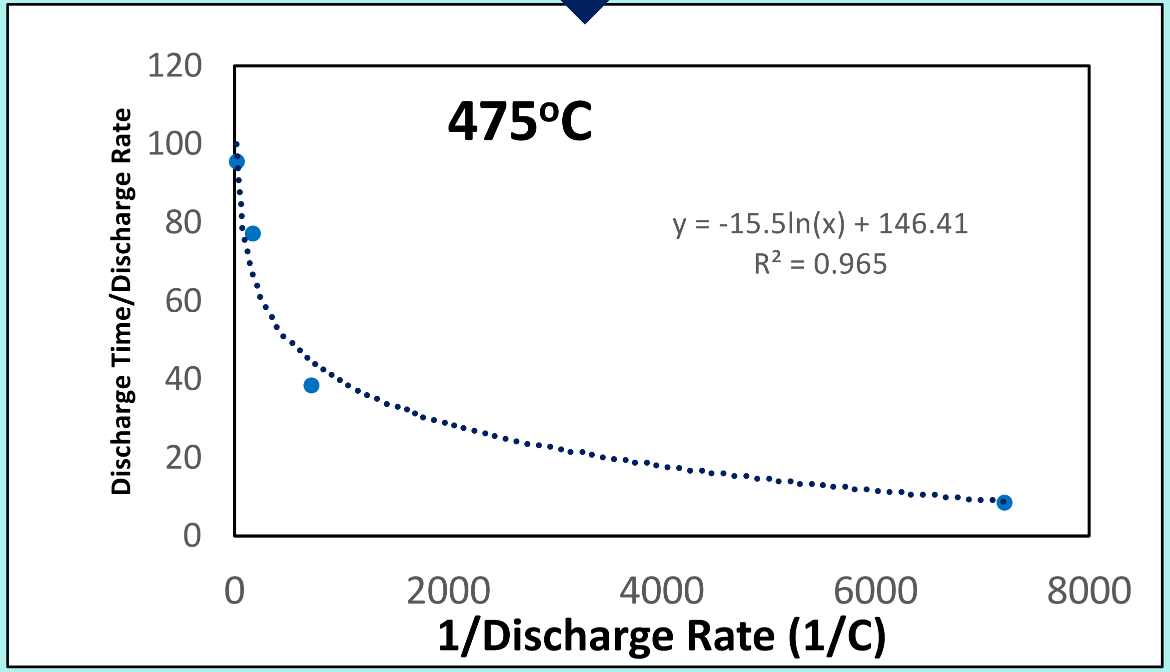
Electrode	60% Electrolyte (wt-%)	20% Electrolyte (wt-%)	10% Electrolyte (wt-%)	5% Electrolyte (wt-%)
Anode	LiAl:LiCl-KCleu	LiAl:LiCl-KCleu	LiAl:LiCl-KCleu	LiAl:LiCl-KCleu
	(65:35)	(80:20)	(90:10)	(95:5)
Electrolyte / Separator	LiCl-KCleu:MgO	LiCl-KCleu:MgO	LiCl-KCleu:MgO	LiCl-KCleu:MgO
	(60:40)	(20:80)	(10:90)	(5:95)
Cathode	MS_x:MgO:LiCl-KCleu :: 70:10:20 (M = Mo or Fe and x = 1 or 2)			

Stability of Cathode in the Electrolyte melt

- 20% electrolyte blend tested for stability over a range of discharge rates
- Cathode capacity decrease with increase discharge duration
  - Trend follows logarithmic decay
  - Stability is an issue at longer discharge rates

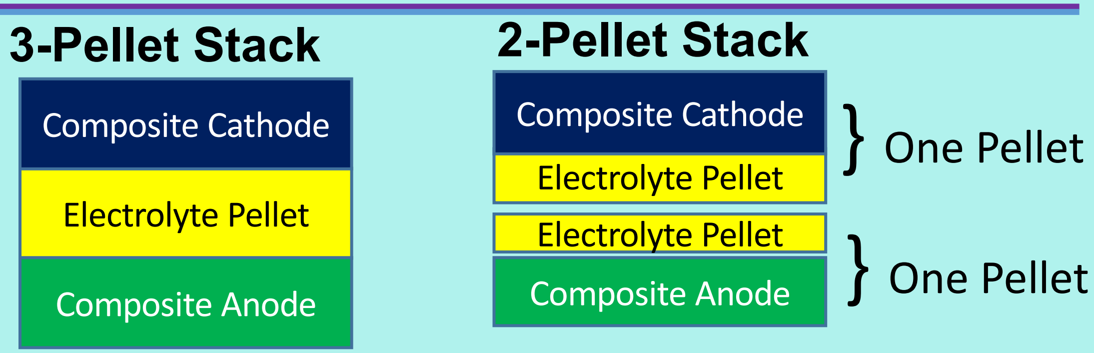


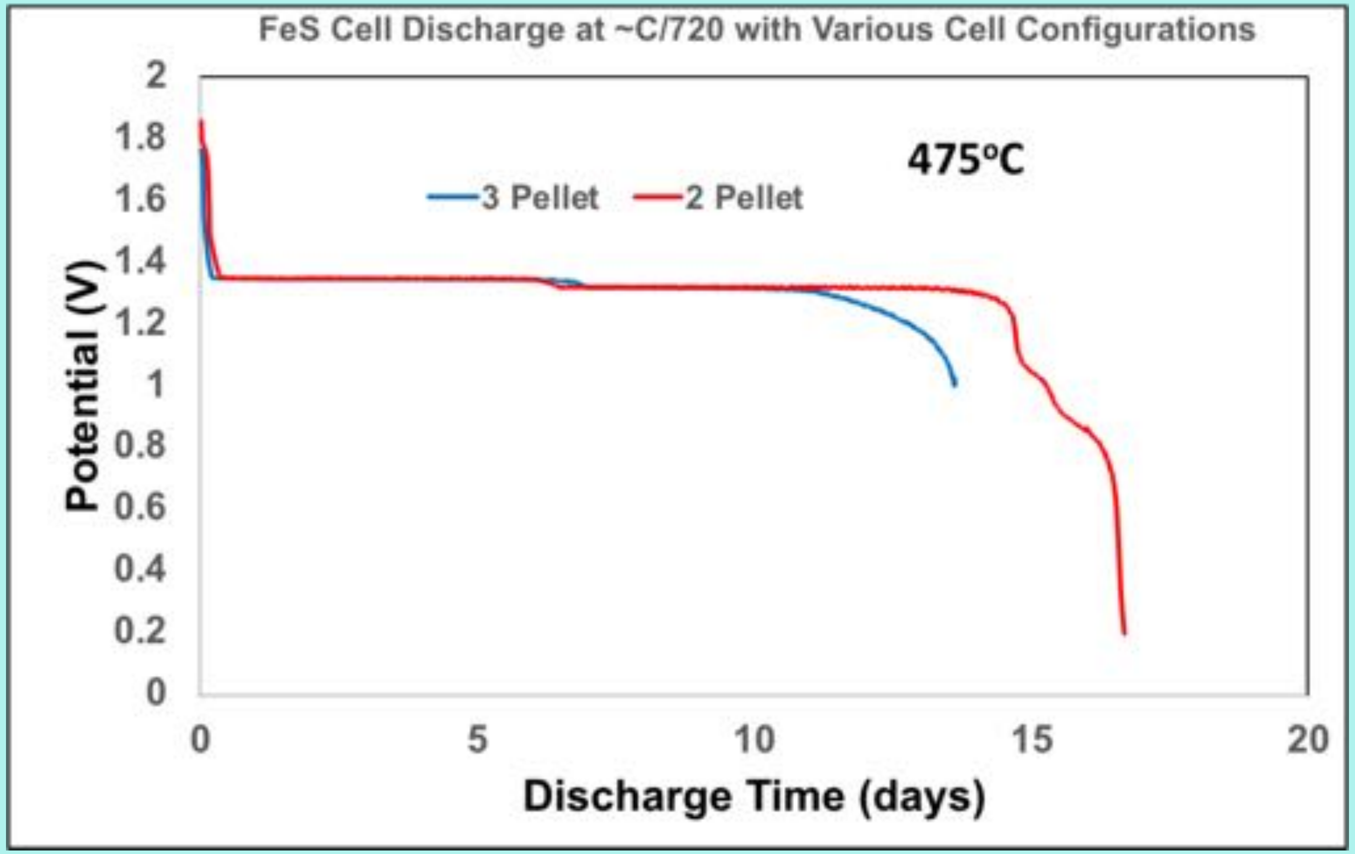


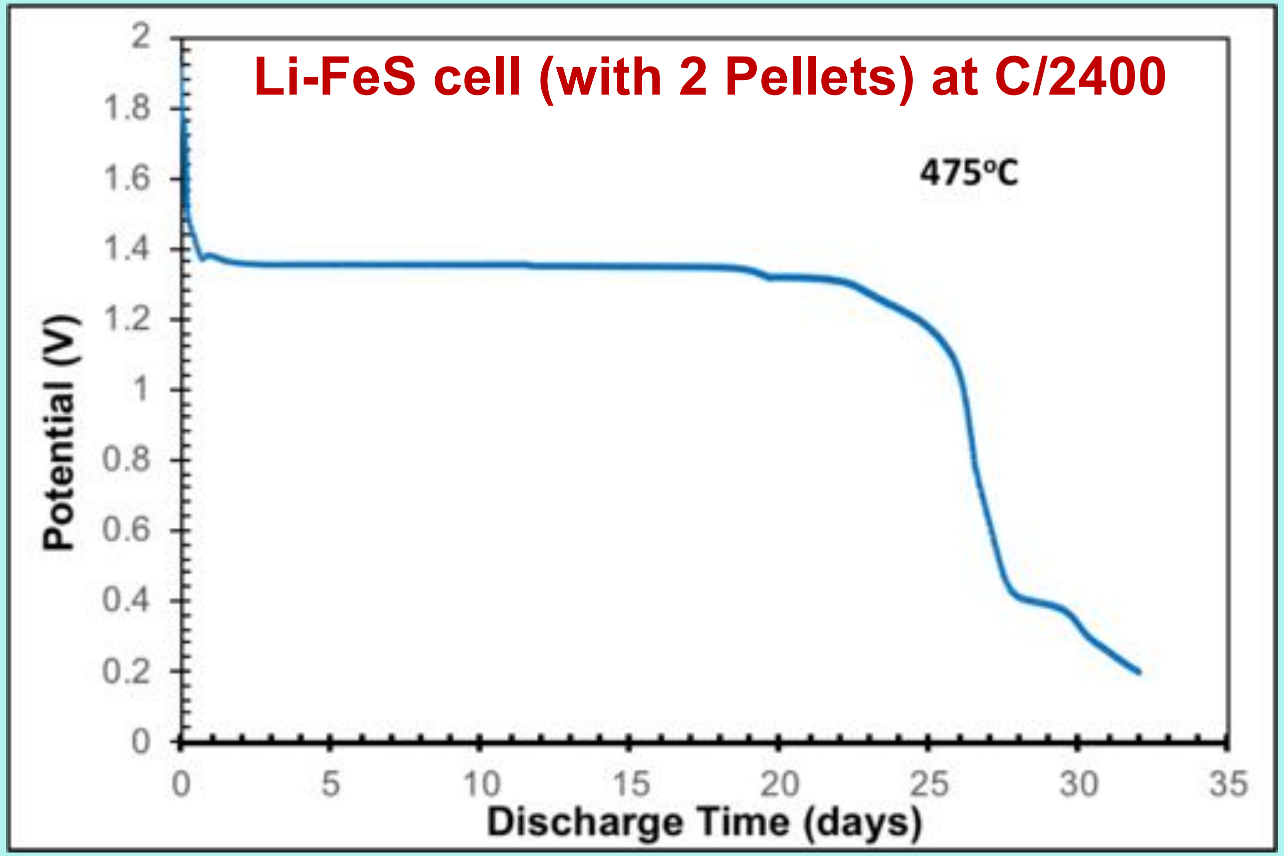


Cell Design Modifications

- 2 Pellet design:
  - Press anode and electrolyte together
  - Press cathode and electrolyte together
- ~13% enhancement discharge capacity vs. 3 pellet design







26 days of operation on the Venus Surface!

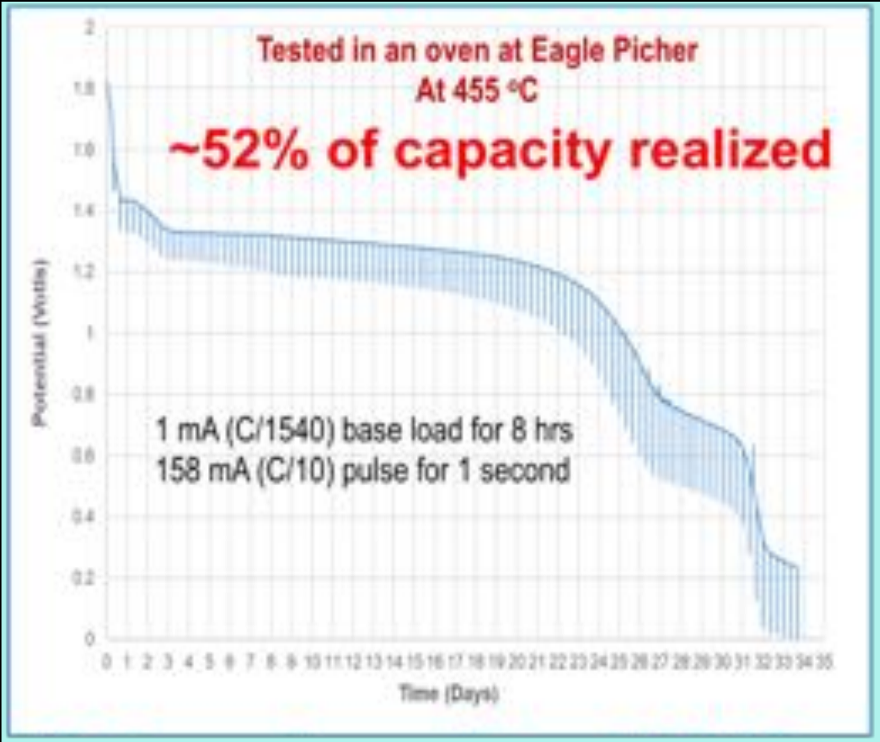
Prototype Venus Lander Cell Data

(Cells fabricated by EaglePicher w/JPL recipe)

Prototype Cells

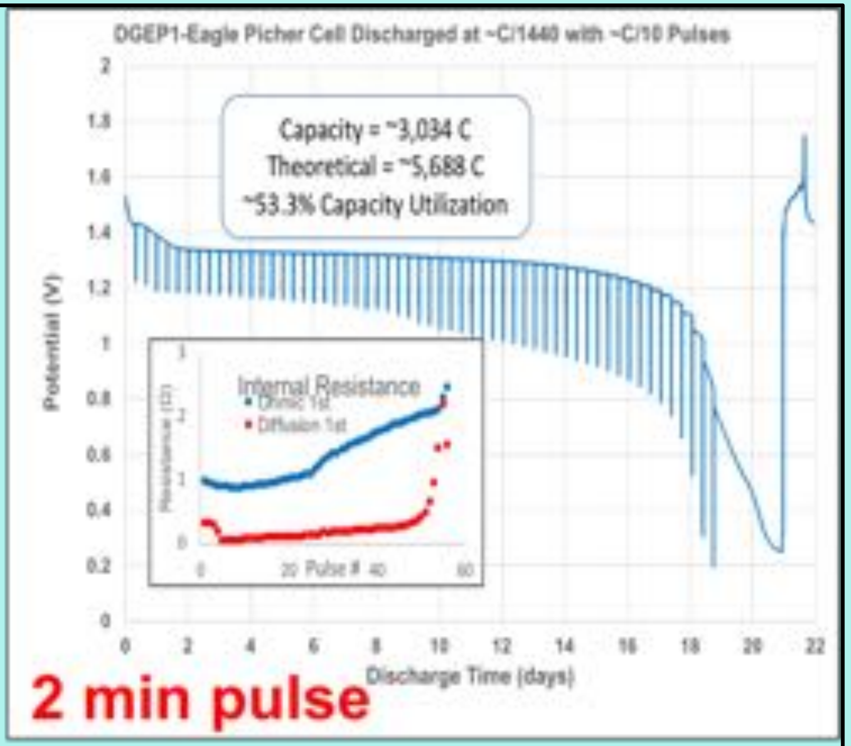
- Prototype Cells manufactured by EaglePicher Technologies with JPL materials and recipe
- Stainless steel can and header and proprietary Seal
- Capacity: 1.58 Ah (Anode limited)

Tested in air at 455C



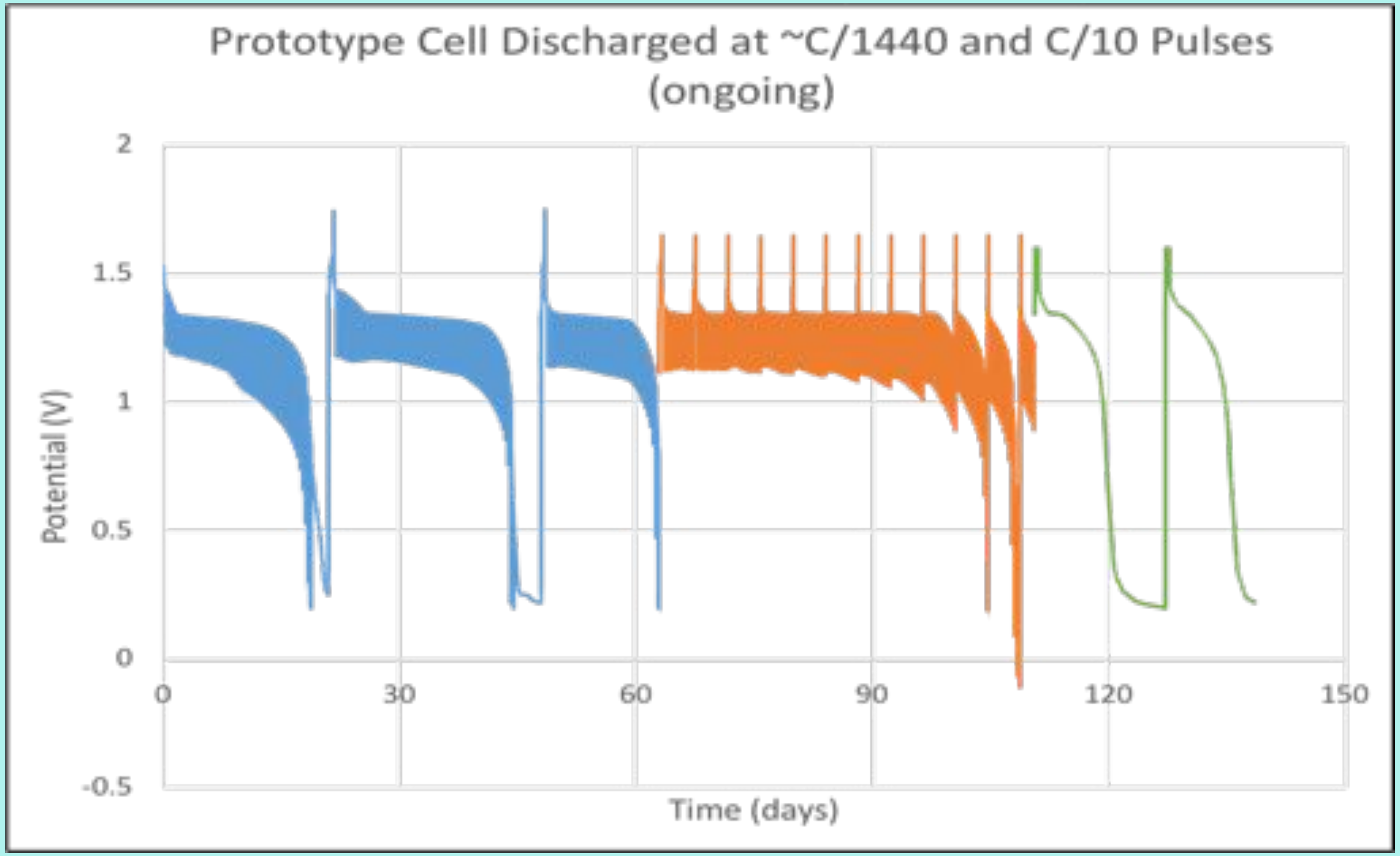
26 days of operation at 455°C

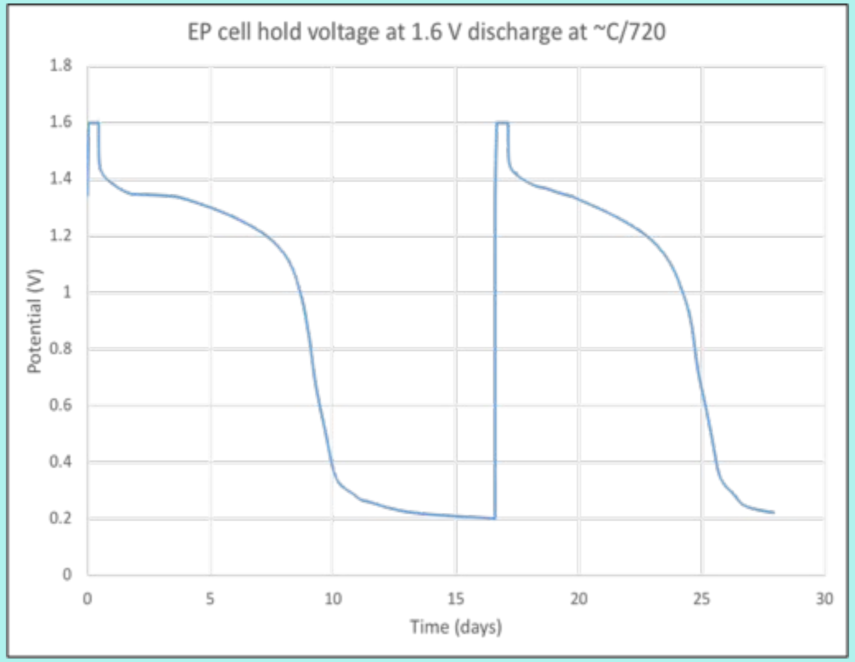
Tested in Ar at 475C



19 days of operation at 475°C

Prototype Venus Lander Rechargeable Cell
(Operating over 100 days at 475^{o}C)



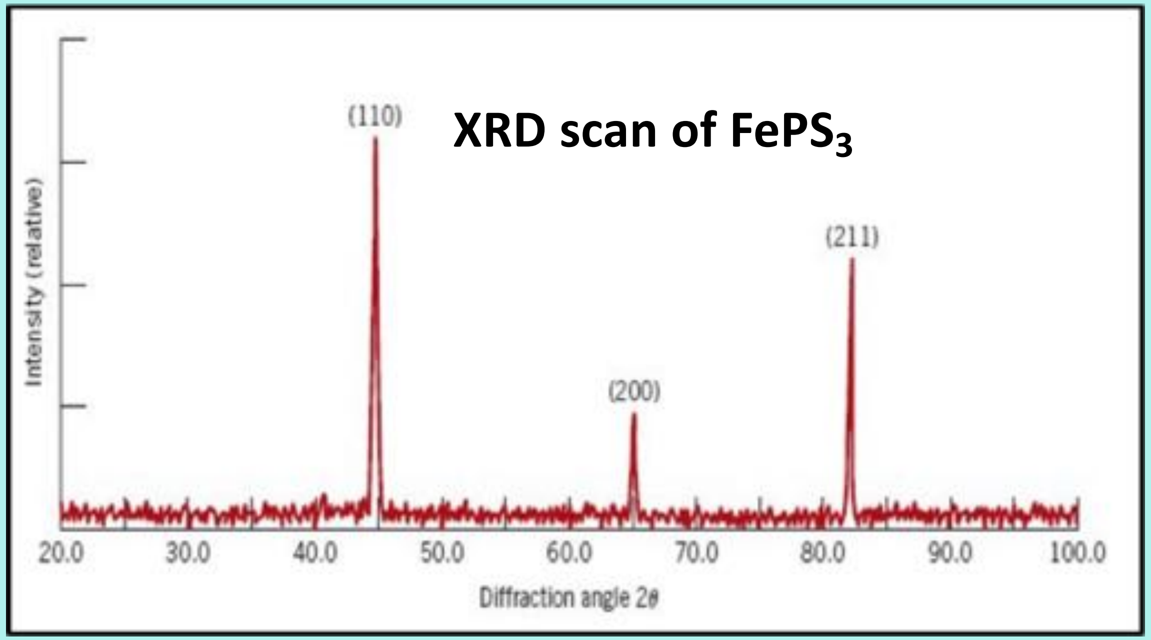


- Cell was discharged at C/1440 with C/10 pulses for 2 min after each 8h and charged at C/20 in the first three cycles.
- Subsequently, the cell was recharged after 10 pulses. In the last charge the cell was charged at CC-CV, i.e., with tapered current

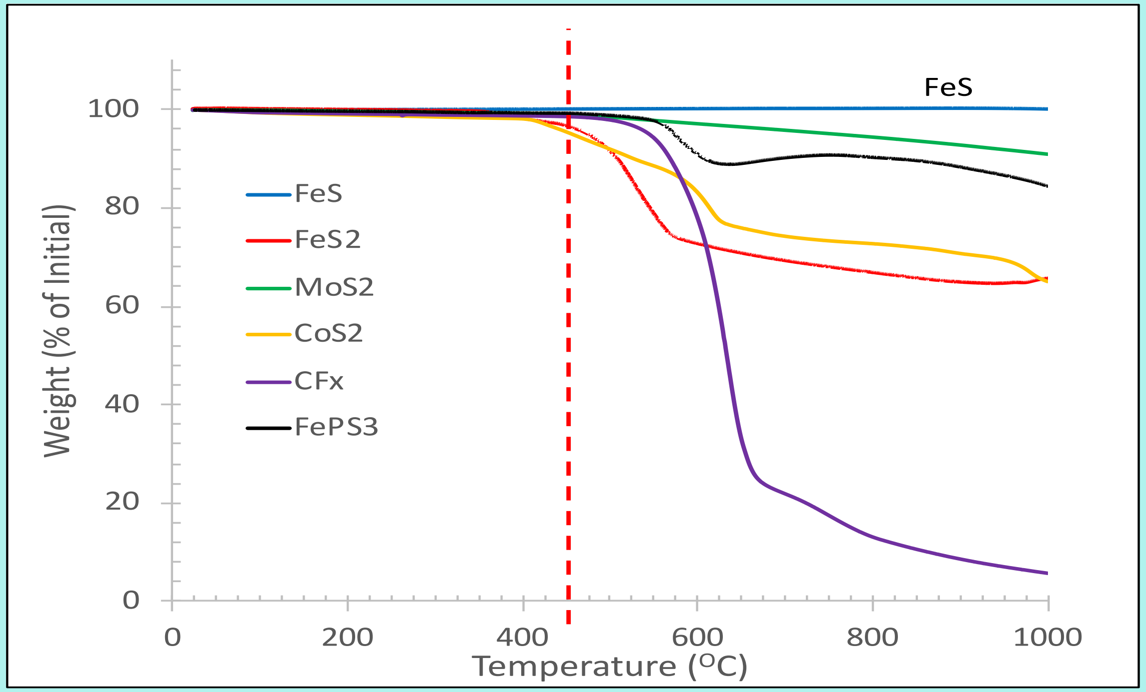
High Capacity Cathodes

- Transition Metal Phosphorous Trisulfides have higher specific capacity than Disulfide counterparts
- Can transfer ~9 Li^+ per mole vs. 4 Li^+ for disulfides.
- Synthesized by mixing stoichiometric amounts of highly pure metal powder (Fe or Ni), red phosphorous and sulfur and placed in quartz tube, which was then evacuated and heated to 970-1070k for one week
- Synthesized both $FePS_3$ and $NiPS_3$ and characterized them using XRD

Compound		Voltage (V vs. Li)	Spec. Capacity ($mAh\ g^{-1}$)
Metal Sulfides	FeS_2	1.7	894
	FeS	1.7	610
	CoS_2	1.6	870
	NiS_2	1.7	873
Metal Phosphorous Trisulfides	$FePS_3$	1.6	1318
	$CoPS_3$	1.6	1248
	$NiPS_3$	1.7	1255

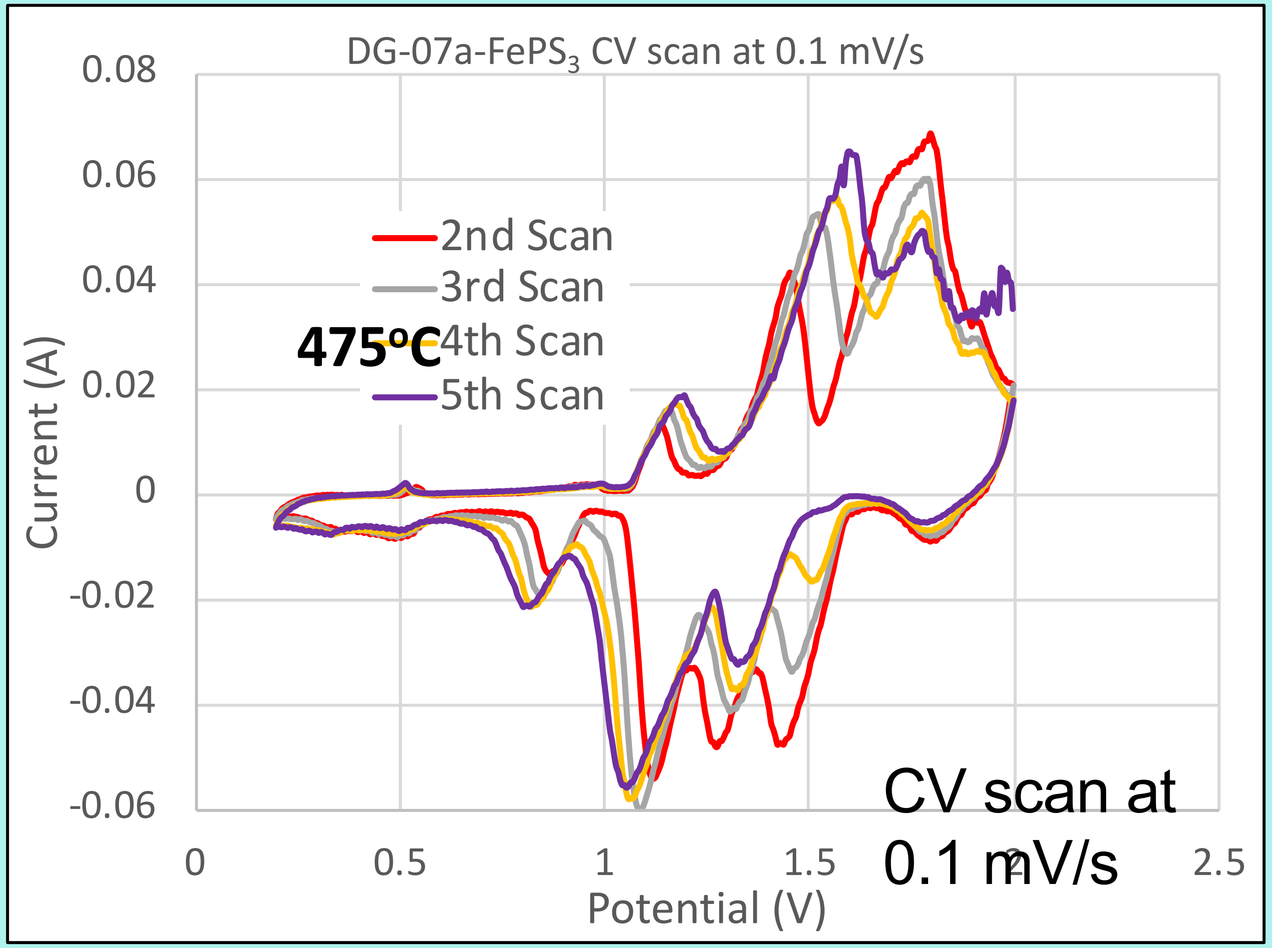


TGA of Cathode Materials at 10 °C/min



$FePS_3$ and $NiPS_3$ Cathode Materials

Cyclic Voltammetry

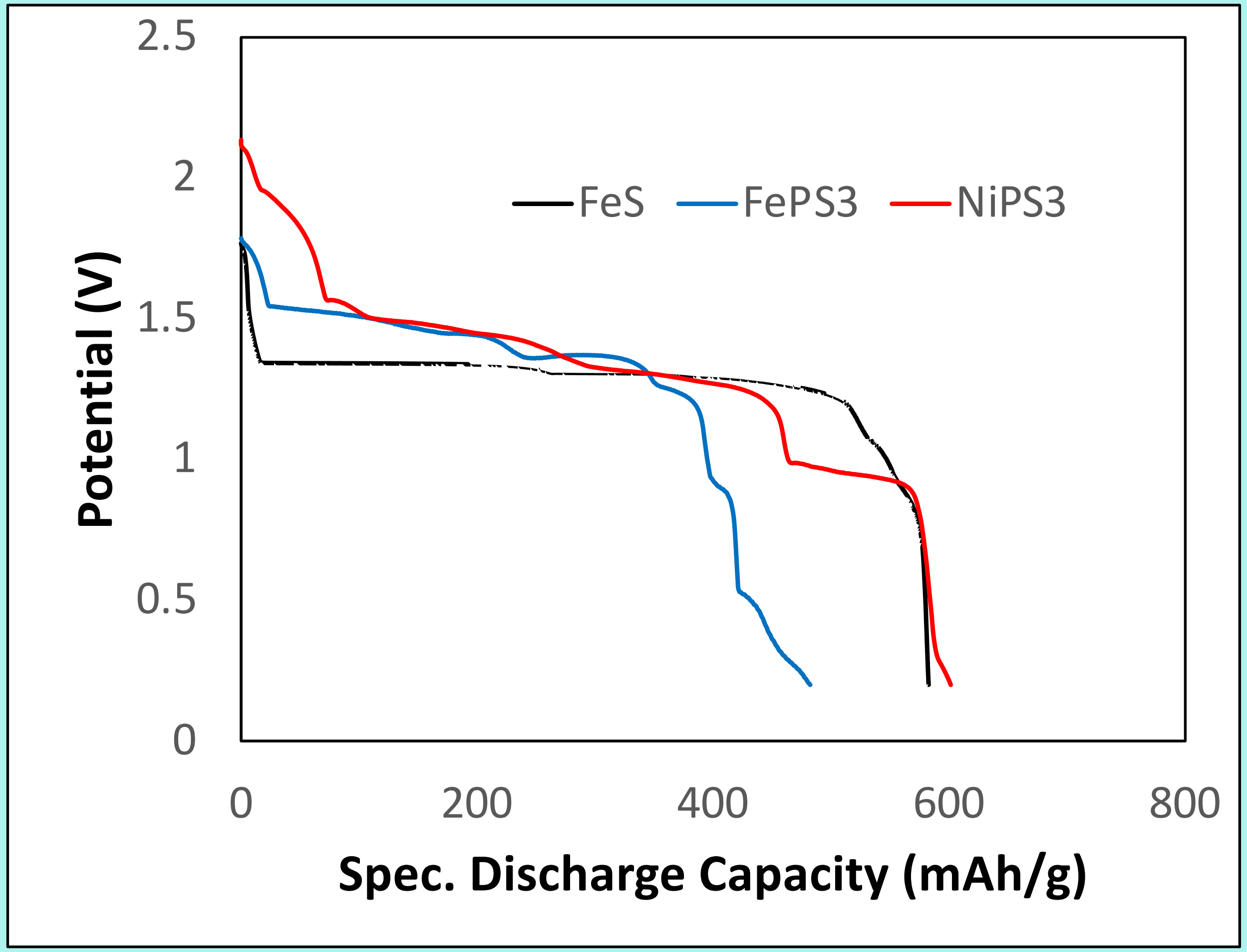


- Multiple lithiums intercalated/reduced

1) $FePS_3 + 1.5Li^+ + 1.5e^- \leftrightarrow Li_{1.5}FePS_3$
2) $Li_{1.5}FePS_3 + 4.5Li^+ + 4.5e^- \rightarrow 3Li_2S + Fe + P$
3) $P + 3Li^+ + 3e^- \rightarrow Li_3P$

Pre-Decisional Information – for Planning and Discussion Purposes Only

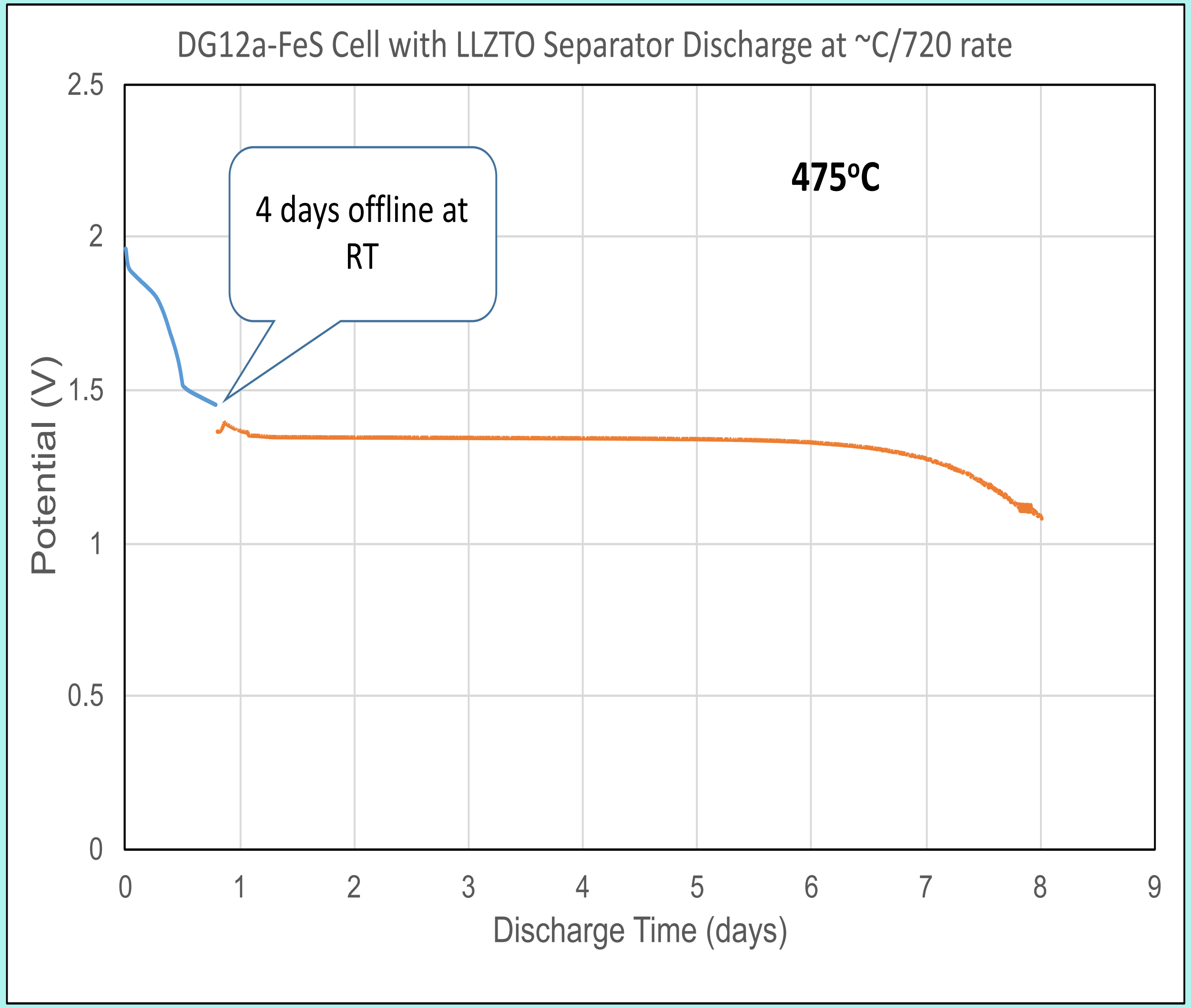
Preliminary Discharge Curves

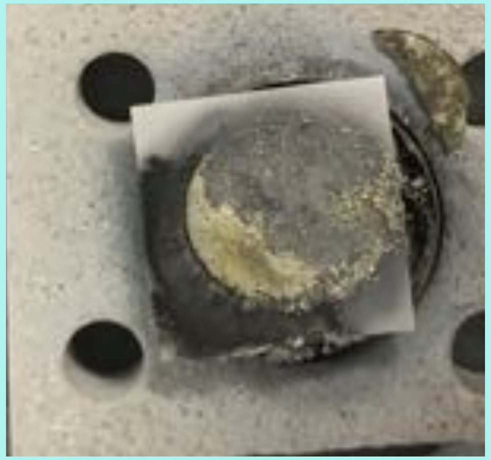


- FeS: ~95% discharge capacity at C/20 rate
- **$NiPS_3$: ~50% discharge capacity at C/20 rate. Higher voltage**
  - **Equivalent to spec. discharge capacity (in mAh/g) of FeS**
- $FePS_3$: ~35% discharge capacity at C/20 rate
- Different plateaus from different phases during discharge

Solid Electrolytes for Cathode and Separator

- Motivation: Use a solid electrolyte as a separator (in place of electrolyte-binder pellet to minimize sulfide solubility
- Solid electrolytes:
  - Oxide based solid electrolytes (Garnets)
    - LLZO ($Li_7La_3Zr_2O_{12}$)
    - Lithium-Lanthanum-Zirconium-Tantalum-Oxide from Toshima, Japan
  - Sulfide glasses
    - LGPS ($Li_{10}GeP_2S_{12}$
  - Phosphate based LiSICONs
    - Lithium Aluminum Titanium Phosphate (Ohara)





- LLZTO intact and easily Separated from pellets

Summary

Venus Aerial Missions

- The new power technology concept developed here, involving a combination of high temperature PV, Metal Hydrides and Regenerative Solid Oxide Fuel Cells enable sustained *in situ* exploration of Venus over a wide range of altitudes.
- Although the VAB technology for the simplest type of missions is ready now, a multi-year investment program focusing on variable altitude capability would enhance the science capability of these platforms

Venus Surface Missions

- Molten salt based batteries with Li alloys and metal sulfide cathode with optimized cell design have lifetimes of ~30 days at Venus surface temperatures.
- These systems have shown good rechargeability and may be coupled with an energy generation source (e.g., wind power, solar, RTG) for extended surface studies on Venus
- Strategies to improve operational life and specific energy include: New cathodes; Surface coatings on FeS, New Electrolyte with reduced cathode dissolution, Solid electrolytes
- These batteries enable new missions with enhanced and detailed scientific studies on the surface of Venus.

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