Performance of High Energy/high Power Li-ion cells in Jovian Missions Encountering High Radiation Environments

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Singapore

June 23-28, 2019

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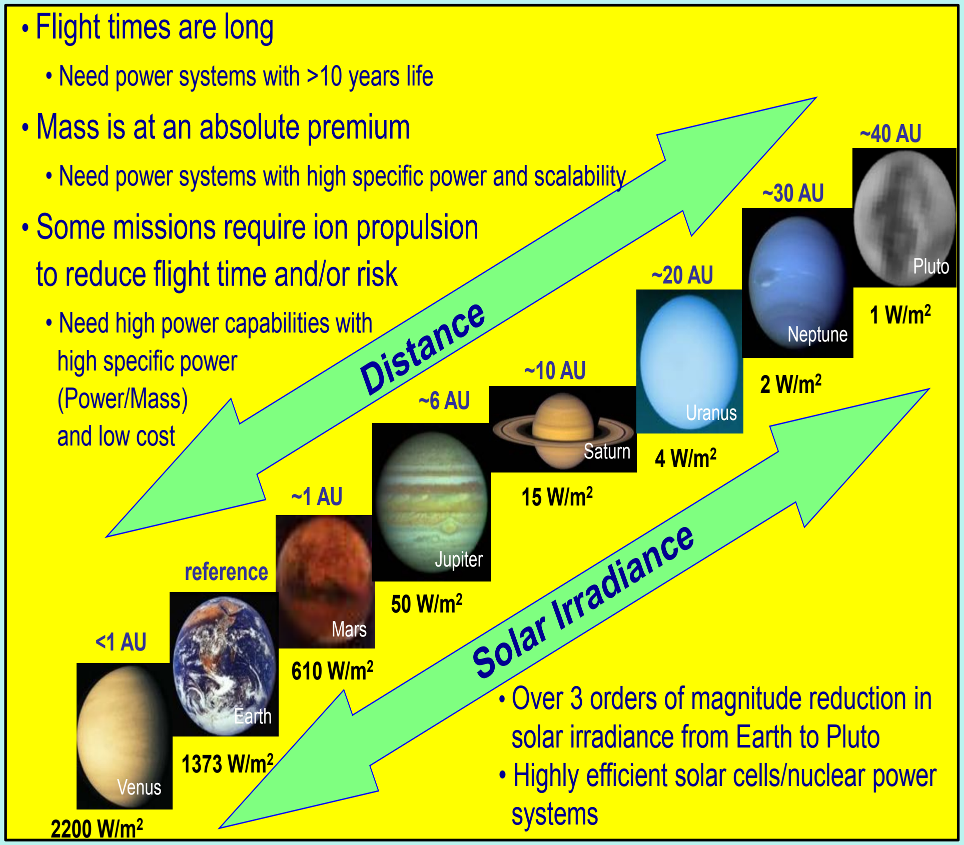
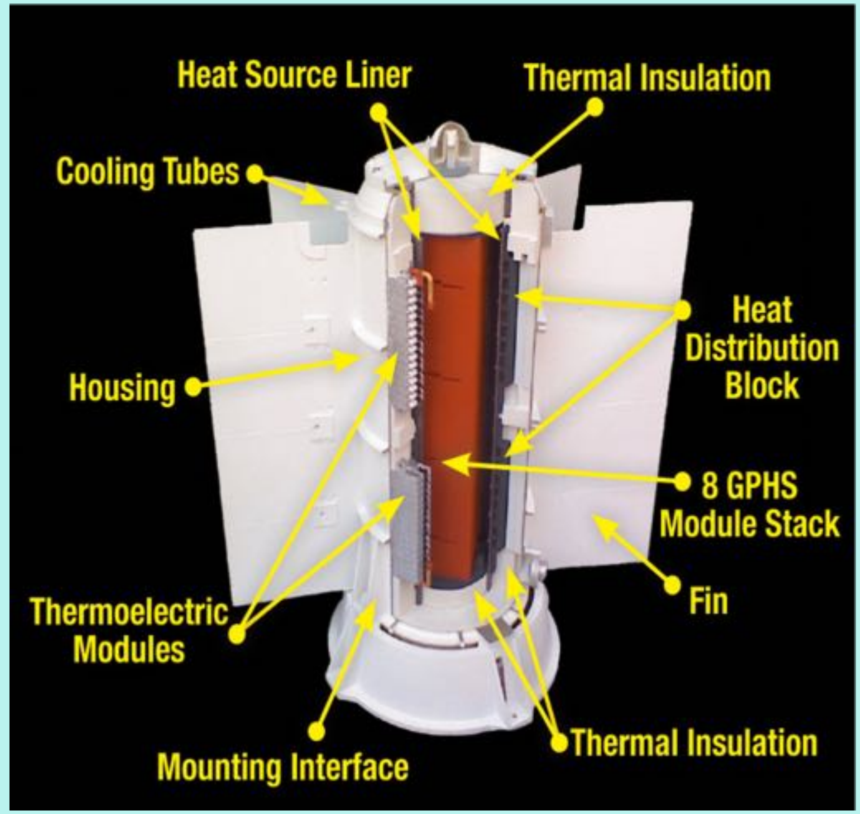
Power Generation Technologies in Planetary Missions

Solar Array for Near Planets



Radioisotope Thermoelectric Generators (RTG)



- Low solar irradiance at Jupiter and beyond.
- Most deep space mission concepts to Jupiter and beyond would use radioisotope power systems (Radioisotope thermoelectric generator or RTG)

Electrochemical Energy Storage Systems for Space Missions

- Primary cells: Non-rechargeable (Irreversible cell reactions)
  - Missions that require a single use of electrical power for a period of a few minutes to several hours (or even days, Europa Lander mission concept) and without any recharge option.
  - Missions include planetary probes (Galileo, Deep Impact, and Huygens), sample return capsules (Stardust and Genesis), Mars Landers (MER), and Mars Rovers (Sojourner)
- Secondary cells: Rechargeable
  - Reversible cell reactions; Multiple uses (Discharge and charge cycles)
  - Used in Orbiters, fly-bys Landers, Rovers, Aerial Vehicles
  - Power to the spacecraft during launch before deployment of the solar panels.
  - Power during cruise anomalies (Trajectory Control Maneuvers).
  - Power to the spacecraft, its equipment, and instrumentation during Sun eclipse periods.
  - For Load leveling during peak power operations such as telecoms, sample drilling and surface mobility.
- Capacitors
  - Charge separation across double layer or with the use of a dielectric layer (No electrochemical reactions) or from an electrochemical reaction.
  - Applications requiring repeated high power short duration pulses (seconds), e.g., Cassini

Battery Requirements of Space Missions

Requirements

- Operational under vacuum (microgravity) conditions
- Survive and Operate at planetary environments
  - Low temperature for outer planets (Mars and beyond)
  - High temperatures for Inner planets.
- Radiations for missions to Jupiter and Saturn
  - Radiation-hard PV, RTG and batteries
- High reliability and safety
- Resilience to shock and vibration

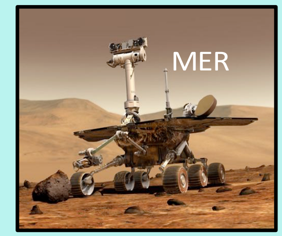
Types of Missions

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

Flyby

Orbiters

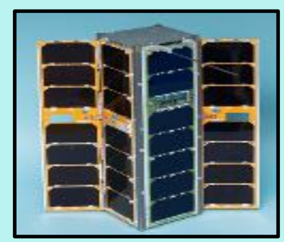
Landers

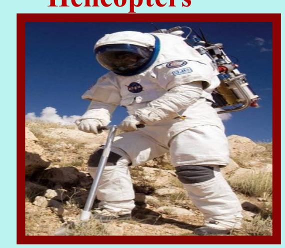


Rovers

Probes


Helicopters


Cubesats


Extra Vehicular Activities

Typical Space Battery Systems

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-CF_x or Li-ion,
	Sample Return Missions	Primary Long calendar life High specific energy and energy density	Li-CF_X and Li-$SOCl_2$,
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-CF_X and Li-$SOCl_2$,
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-MCl_2
	Surface	Primary High Temperature, high specific energy	Li-FeS_2
Mars	Sample Return Missions	Primary Long calendar life High specific energy and energy density	Li-CF_X and Li-$SOCl_2$,
	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-SO_2 Li-$SOCl_2$,
	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?

Two Approaches for Space Li-Ion Batteries

Custom Cell Designs

- Large-format, custom-size cells (5-60 Ah) in prismatic or cylindrical form
- Yardney/Eagle Picher, SAFT (US and France) or GS Yuasa
- Chemistry tunable to the environments (low temperature, long-life) and under configuration control).
- Cells have shutdown separators and pressure relief vents (no PTC or CID).
- Cells voltage monitoring and cell balancing during operating/non-operating conditions with a Battery Management System (BMS)..
- Due to their large capacities, their abuse tolerance is poor and it difficult to achieve thermal propagation resistant designs.

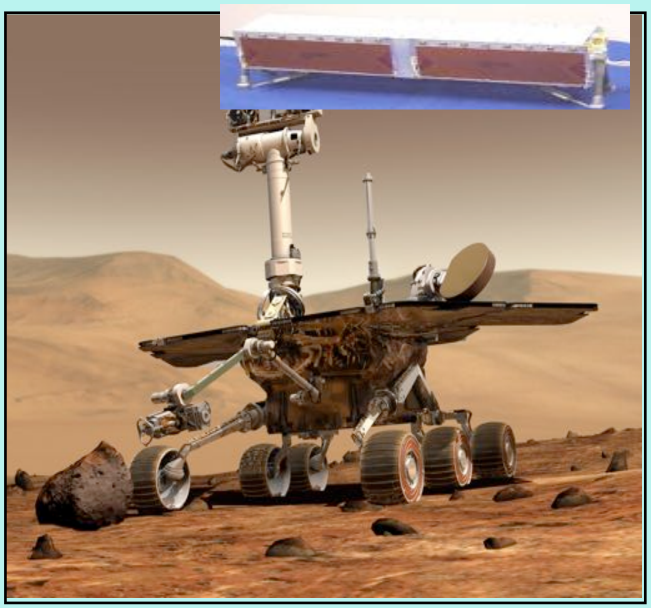
Batteries based on COTS Cells

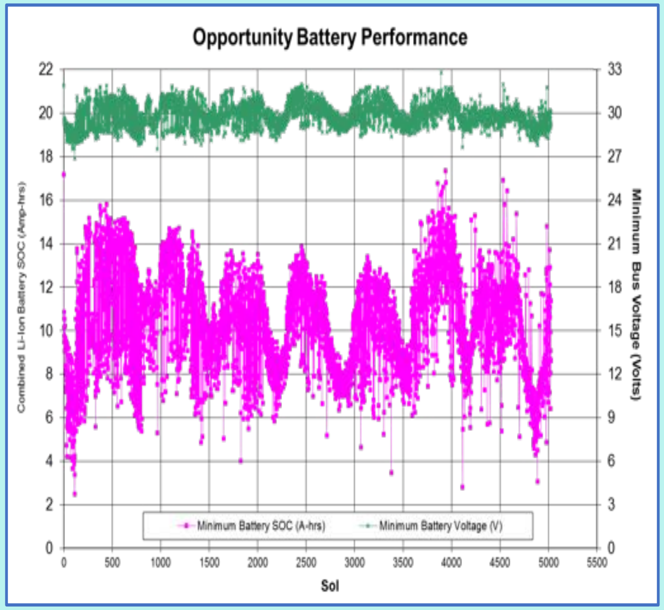
- Commercial Off-The Shelf (COTS) 18650 Li-ion cells (by Asian battery manufacturers)
- Higher specific energy and energy density than custom cells (~50-100%).
- Different chemistries from different sources and technologies are still being improvised
- Cells are safer with shutdown separators pressure relief vents, PTC and CID.
- Cells matched prior to assembly, and arranged in series/parallel configuration.
- Only battery voltages are monitored and controlled (No cell balancing)
- Highly modular designs
- Thermal propagation resistant designs are being developed.

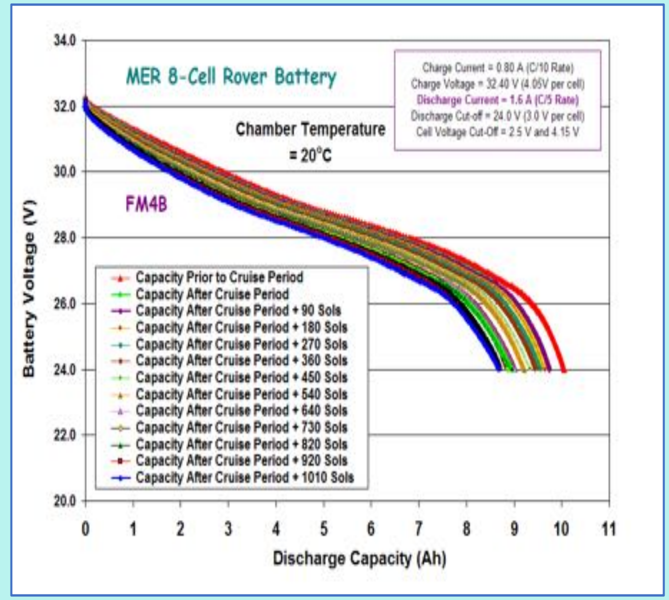
Long-Life Li-ion Batteries for Mars Missions

Mars Exploration Rovers (2003) – Spirit and Opportunity

~ 17 years of Operation from Opportunity







- Fabricated by Yardney with **JPL 1st Gen low temperature** electrolyte
  - Cell: Custom 10 Ah;
  - Battery: 32 V, 20 Ah;
  - Specific energy : 90 Wh/kg
  - Temperature:-20 to 30°

- Impressive performance of Li-ion batteries (30 V, 20 Ah) demonstrating great resilience and longevity
  - Opportunity survived through > 6000 sols
  - Stable voltages on spacecraft (45% Depth of discharge)
  - 70% capacity retention in laboratory tests.

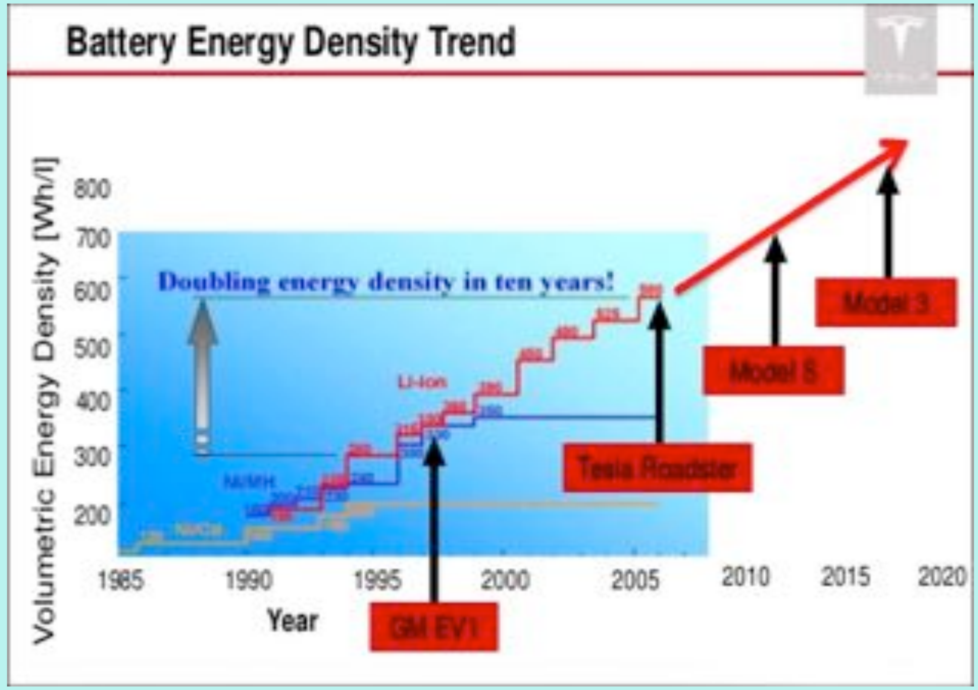
Missions With Batteries using Large Prismatic Cells

- Custom prismatic cells from 10-50 Ah from Yardney with JPL Gen-1 electrolyte
- Batteries successfully integrated with both both photovoltaic and nuclear power sources
- Chemistry (MCMB (graphite) anode, NCO cathode
- NCA cathode and/or JPL Gen-2 low temperature electrolyte in recent missions

Adaptation of Commercial Li-Ion Cells for Space Missions

Flight Batteries using COTS 18650 cells

- Long heritage with Sony Hard Carbon – Lithium Cobalt Oxide cells
  - No need for cell balancing electronics based on the cell uniformity as a result of consistent cell fabrication
- Several new high energy cells available (Specific Energy: 259-276 Wh/kg (4.2V) Energy Density: 704-735 Wh/l



Performance Characteristics

Characteristic	LG MJ1	Samsung 35E	Panasonic GA	Sony VC7
Capacity at C/10 at RT, Ah	3.41	3.49	3.34	3.5
Energy, Wh	12.46	12.7	12.16	12.72
DC Internal Resistance, mOhm	33	35	33	31
Mass, g	46.9	46	47	47.4
Specific Energy, Wh/kg	266	276	259	269
Energy Density, Wh/l	720	733	704	735

- Not quite Moore's Law (computing power tends to approximately double every two years) but impressive growth nonetheless (energy density doubles each ten years).

Planetary Missions with COTS Li-Ion Cells

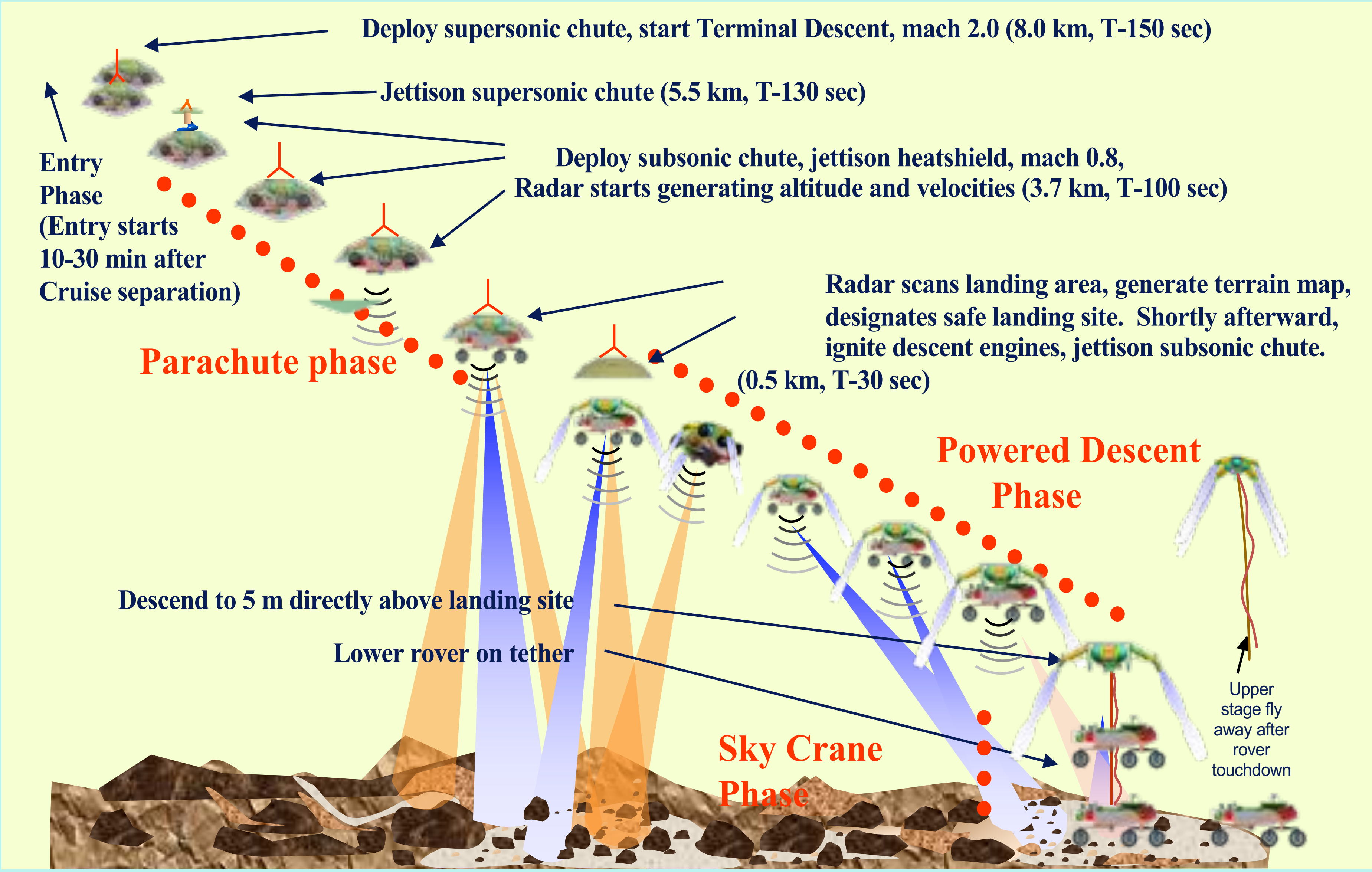
Previous Missions (Sony HC cells)

- Mars Express is the longest operating mission with COTS Li-ion batteries.
- ABSL/ Enersys developed robust batteries of different sizes (8SXP) with Sony HC or HCM with $LiCoO_2$ cathode. This technology has become obsolete

Upcoming Missions (New Technologies)

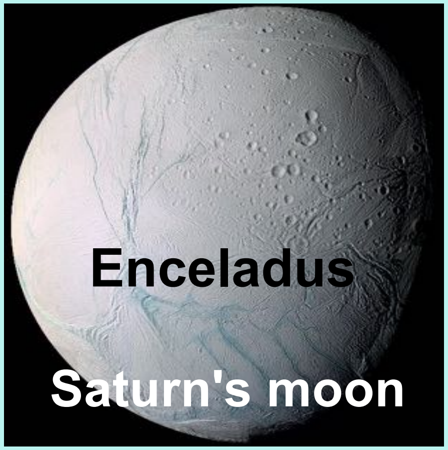
- For the upcoming Europa Clipper, we are planning to use LG Chem MJ 1 cells (250 Wh/kg)
- Other upcoming missions include: i) Cruise Stage and Descent Stage batteries for Europa Lander mission concept

Entry, Descent, and Landing (EDL) Sequence



- Thermal batteries, which are typically used to support the pyro-events, provide high power densities, but not high specific energies. Besides, their functionality is difficult assess before use.

Missions Encountering Radiation Environments

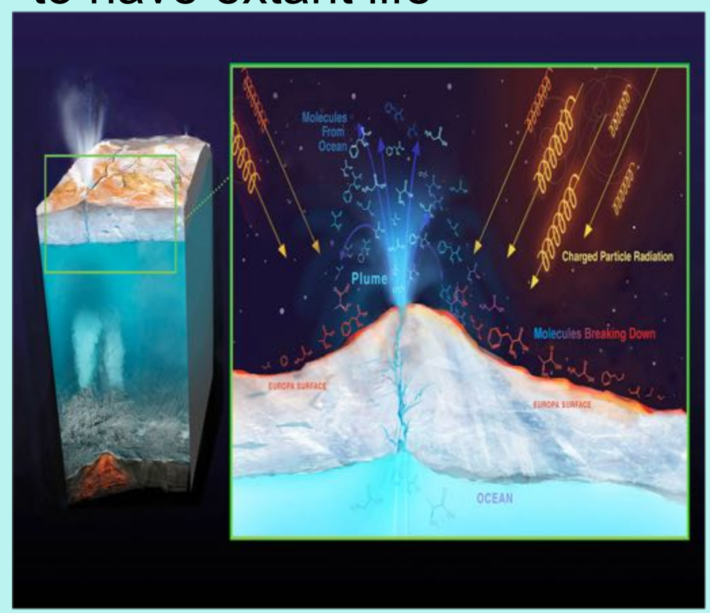


Magnetic Field Strength

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**

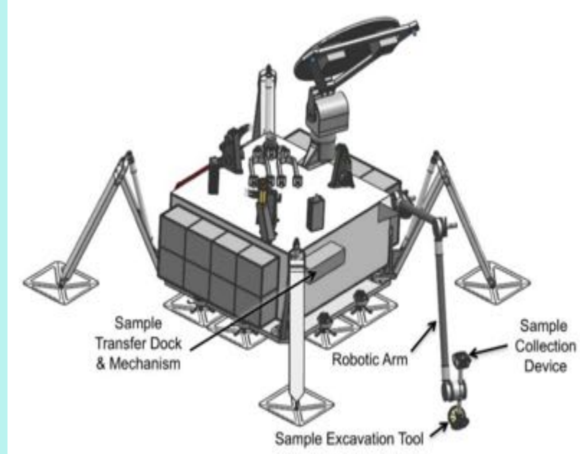
- Ocean Worlds with icy crust and subsurface water are likely to have extant life



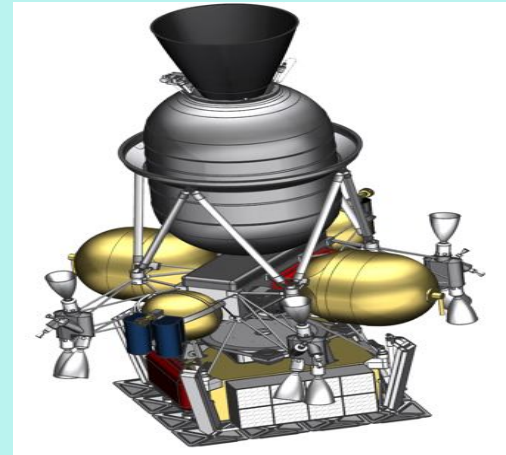
Descent Stage in Europa Lander Mission Concept

Mission Concept Requirement for Descent Stage

- Energy: ~2375 Wh
- Power: 3375 W (peak)
- 185 minutes
- Battery temperature 0-70ºC
- Approximately 20-25 kg



Notional Lander Design

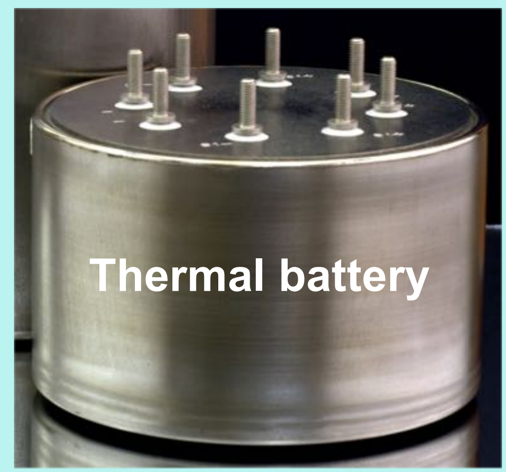


Notional Descent Stage Design

Descent Stage (Sky Crane)

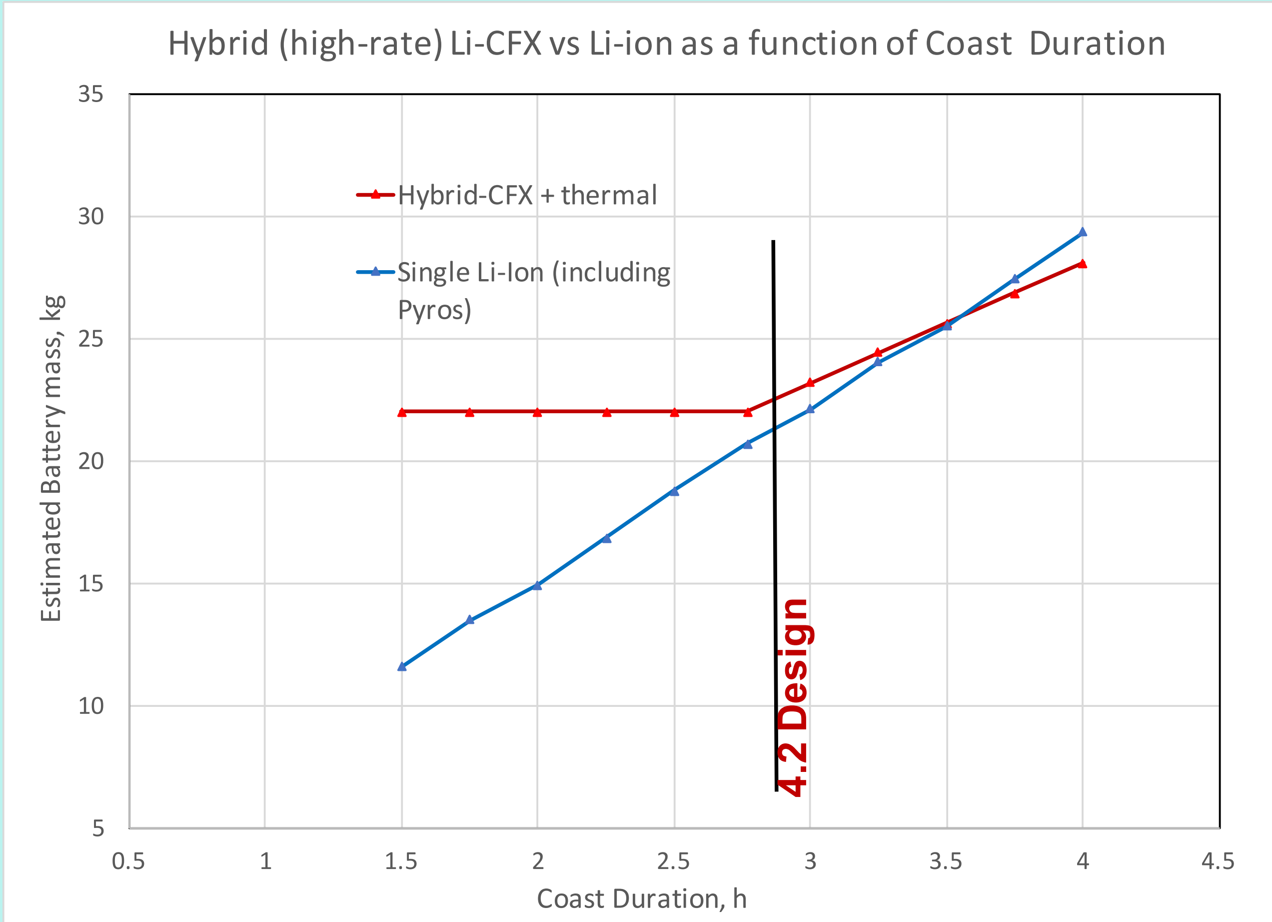
Original Battery Design Concept

- Combination of Primary Batteries and thermal batteries
- Primary Battery through 180 min
  - Li/CF_x–MnO_2 12s12p (144 D cells)
  - Power: 790 W; Energy: 2237 Wh
- Thermal Batteries (3) for high power
  - MSL Pyro batteries
  - Power: 3375 W; Energy: 138 Wh
  - Duration: 5 min
- Can be replaced by a single high energy and high power Li-ion battery



Pre-Decisional Information — For Planning and Discussion Purposes Only

Trade off: Li-ion Battery vs Hybrid Li-CFX primary + Thermal



- Baseline system (CFx + thermal) doesn't decrease with the coast duration (battery size driven by the power of hybrid CFX battery, not energy).
- Li-ion battery size decreases almost linearly with the coast duration, since the size is driven by the energy (considerable power margin)
- Easier flexibility and modularity and testability

High Energy and High Power COTS LI-Ion Cells

- **18650 Cells cells being evaluated (259- 276 Wh/kg and 704-735 Wh/l)**

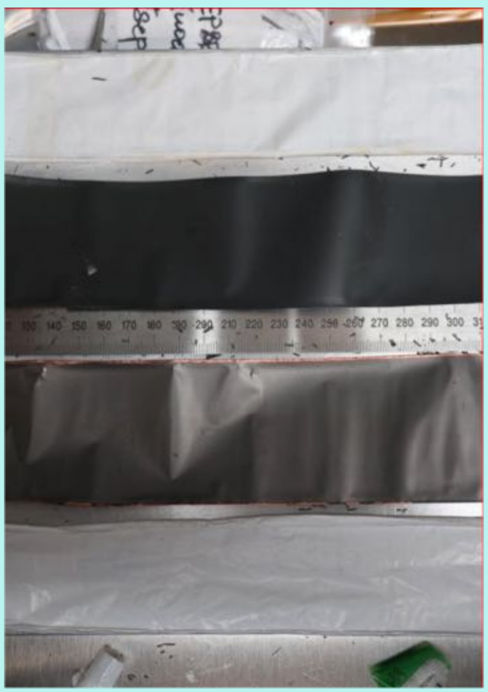
Batch 1 cells	Batch 2 cells
• LG M36	LG M36
• LG MJ1	LG MJ1
• Panasonic BJ	Panasonic/Sanyo GA,
• Samsung 35E	Samsung 3
• Sony VC7 (Bottom Vent)	Samsung 36G

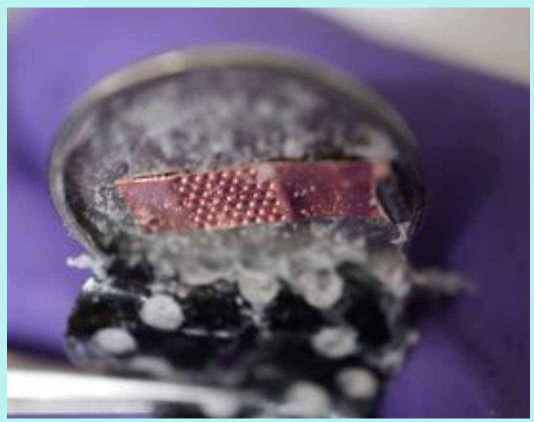
- **Types of Tests**
  - Initial Characterization
  - Rate characterization
    - ➢ At different rates and temperatures
    - ➢ High rate testing
  - EIS (Electrochemical Impedance) during cycling and radiation
  - Cycle life testing at different temepartures
  - Radiation exposure to 18 Mrad (gamma radiation using Cobalt-60 source)
    - ➢ Post radiation cycling and rate characterization
  - High rate characterization
  - Tear-down analyses

DPA of High Energy and High Power Li-Ion Cells

Identification and characterization of various elements

Cell Type	Anode		Cathode		Separator
	L (mm)	W (mm)	L (mm)	W (mm)	Thickness (mm)
Panasonic BJ	603.3	60.32	584.2	54.77	0.018
LG M36	653.2	60.32	606.4	59.63	0.02
LG MJ1	660.4	60.32	609.6	58.74	0.015
Samsung 35E	603.3	60.32	615.9	57.94	0.015
Sony VC7	603.3	59.53	615.9	59.53	0.018





Evidence of some corrosion in Sony VC7 cells

- CID (shown in 35E):

- Bottom vent (VC7, 36G):

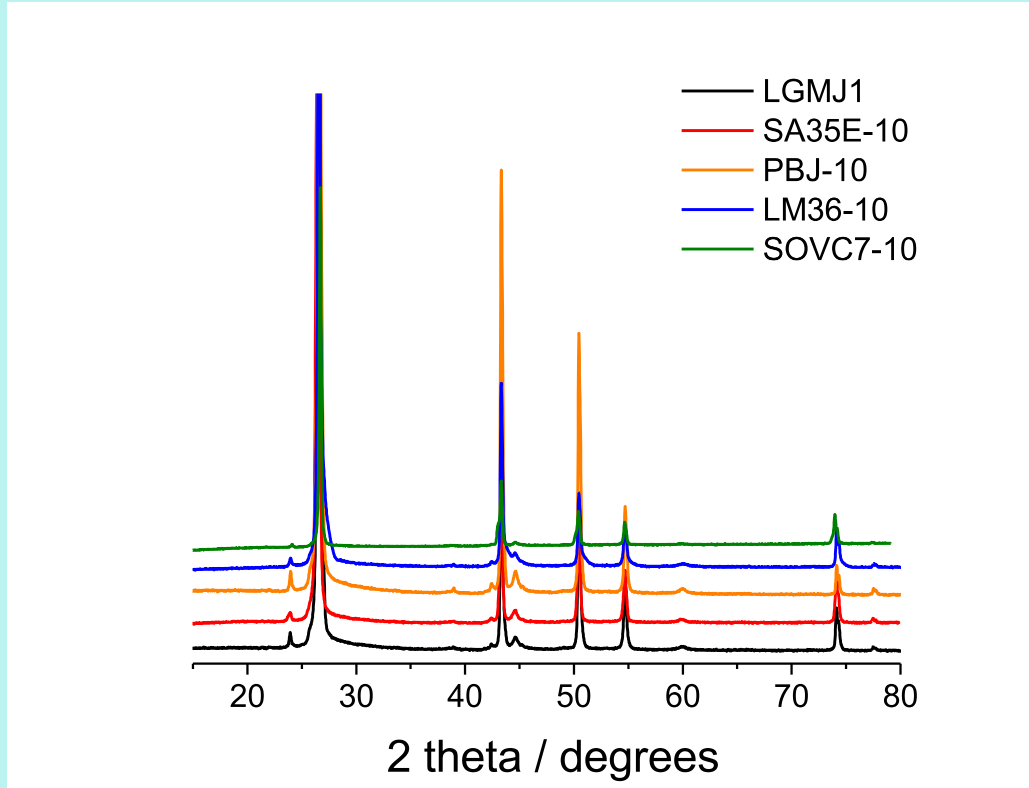
- Mandrel (shown in 35E):

DPA of High Energy and High Power Li-Ion Cells

Cells Chemistries

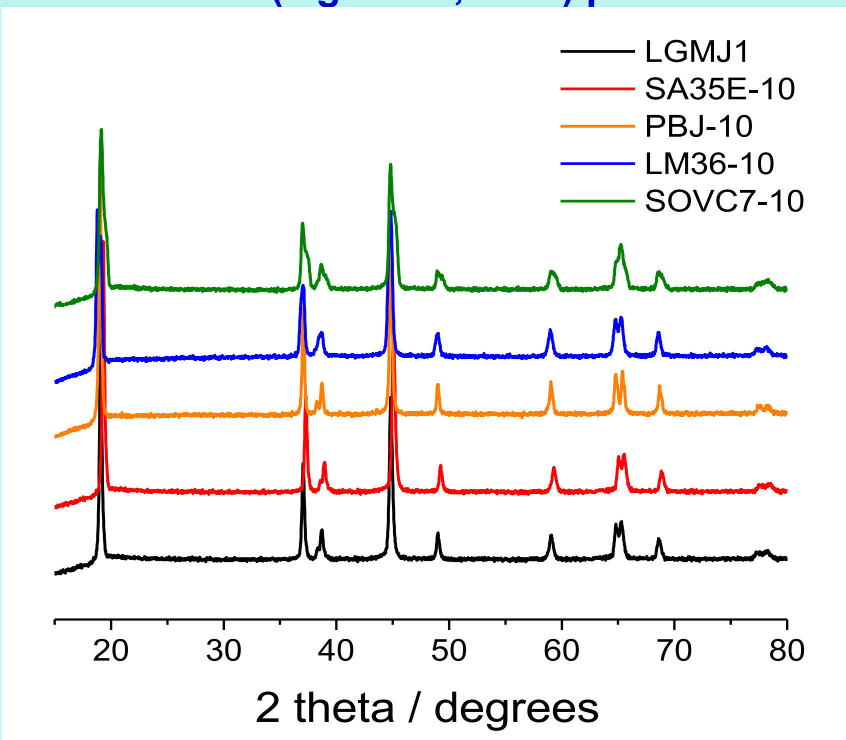
Anodes

- Cells dissected in the discharged state and the components were subjected to ex-situ analyses
  - XRD for cathodes and anodes
  - SEM and EDAX
  - NMR and MS for electrolyte

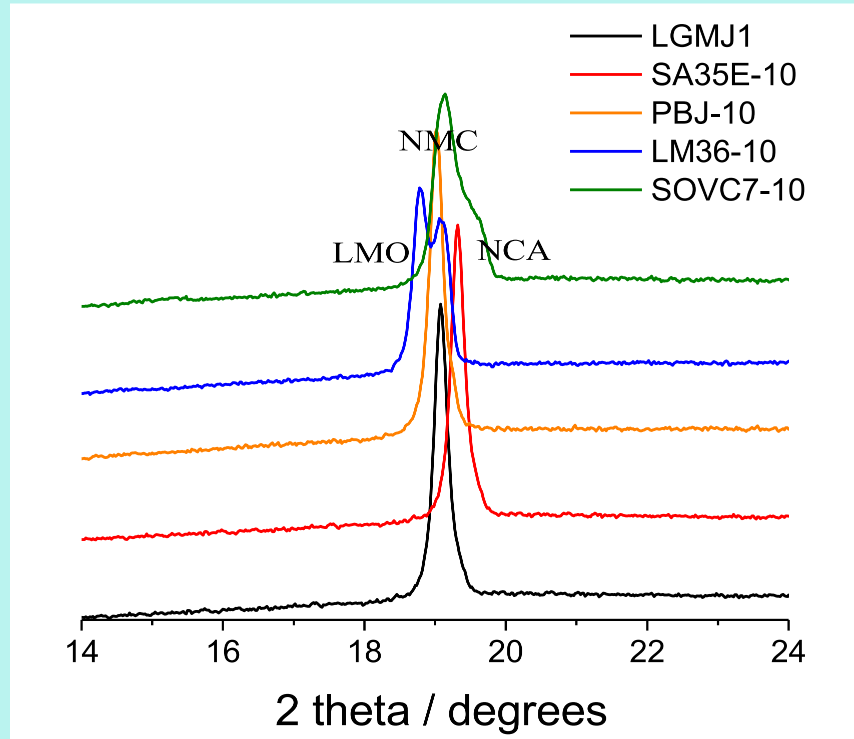


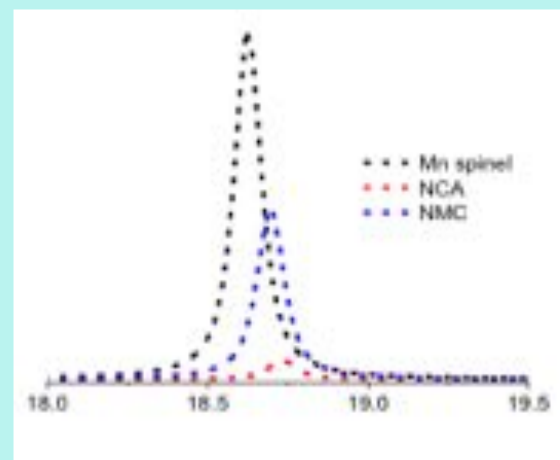
DPA of Li-Ion Cells - Cathodes

Diffraction typical for $LiMO_2$ layered structure (e.g. NMC, NCA) plus Al foil



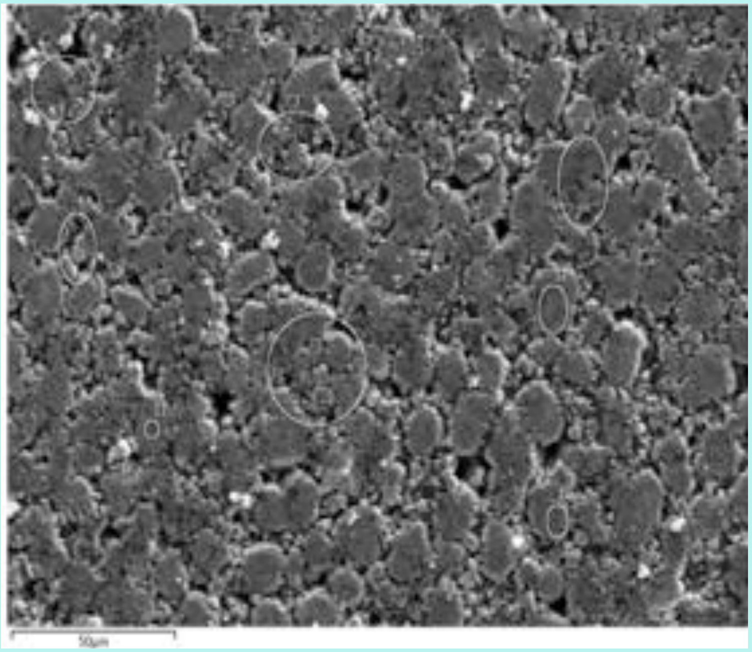
(111)/(001) peak shows variations

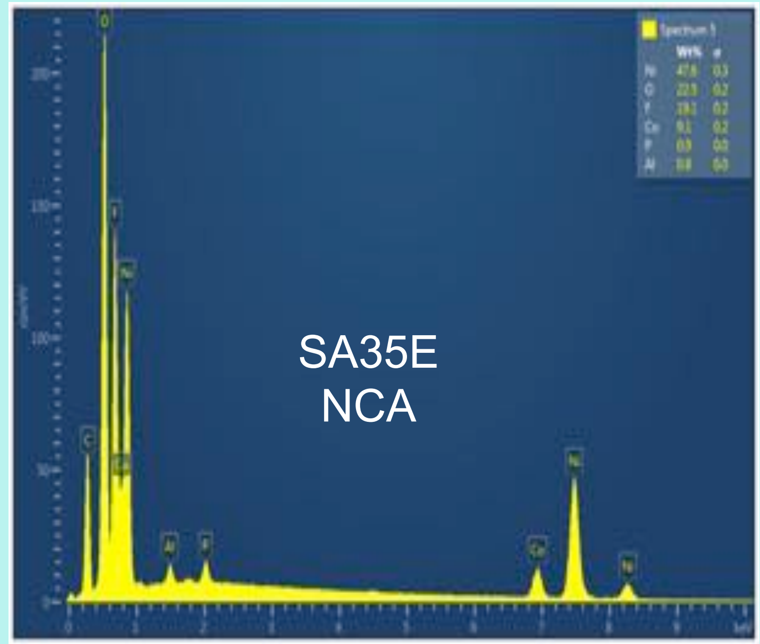


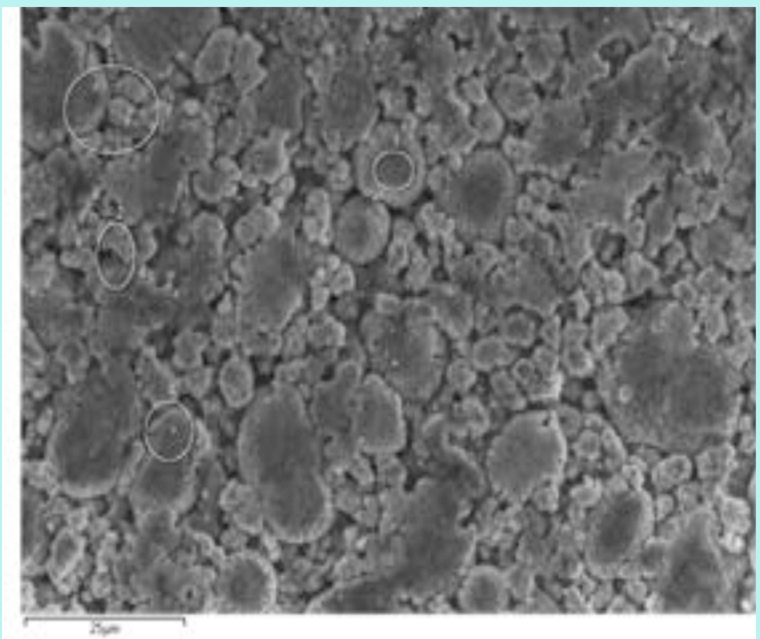


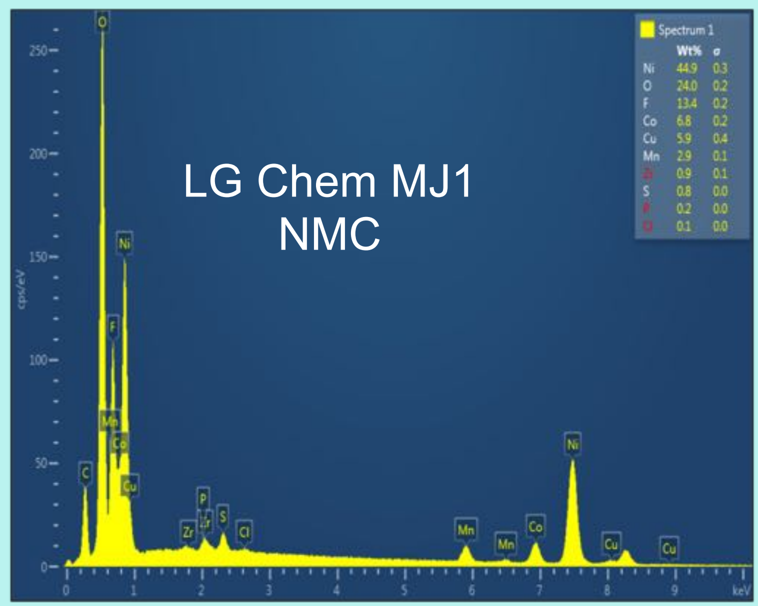
- NCA: Lithium Nickel Cobalt Aluminum Oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}$)
- LMO: Lithium Manganese Spinel Oxide ($LiMn_2O_4$)
- NMC: Lithium Nickel Manganese Cobalt Oxide ($LiNi_{1-x-y}Mn_xCo_yO_2$)

Cathode Analyses





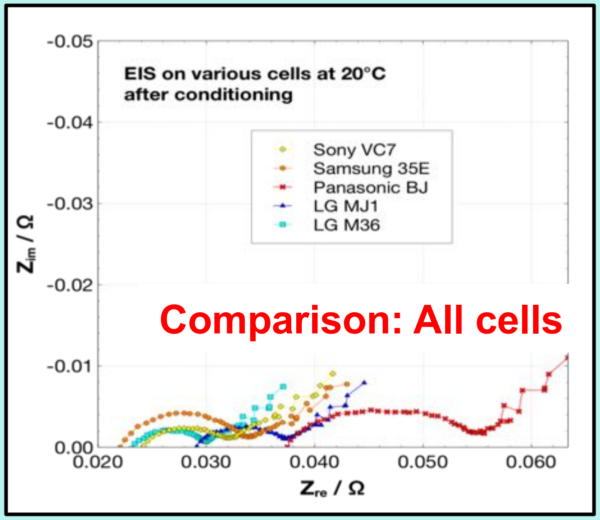


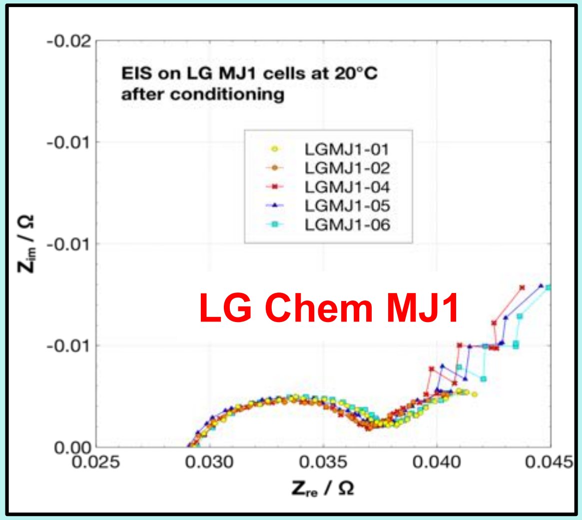


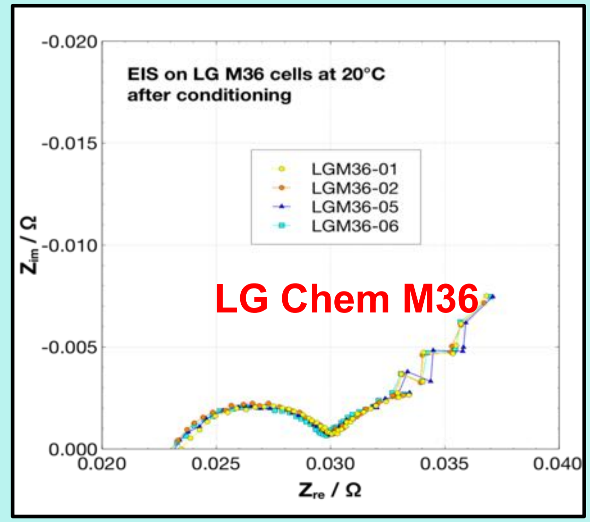
DPA of Li-Ion Cells- Summary

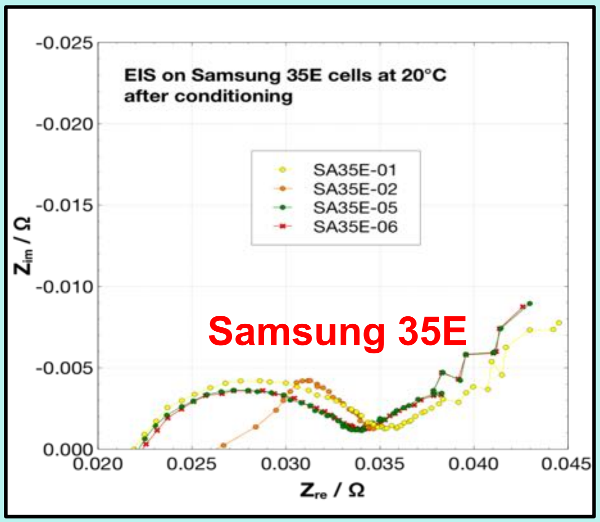
	Anode	Cathode	Electrolyte
LGMJ1	graphite	$Ni_{0.81}Co_{0.13}Mn_{0.06}$ by EDX*	EC, DMC, $LiPF_6$, LiFSI (lots)
SA35E-10	graphite, ~2% Si by EDX	$Ni_{0.83}Co_{0.15}Al_{0.02}$ by EDX	EC, DMC, additive, $LiPF_6$, LiFSI
PBJ-10	graphite	$Ni_{0.81}Co_{0.16}Al_{0.04}$ by EDX	EC, DMC (assumed), $LiPF_6$, LiFSI
LM36-10	graphite (less crystalline)	$Ni_{0.86}Co_{0.12}Al_{0.02}$ and $LiMn_2O_4$ (95:5)*	EC, DMC, $LiPF_6$, LiFSI (lots)
SOVC7-10	graphite (least crystalline)	$Ni_{0.90}Co_{0.08}Al_{0.02}$ by EDX$	EC, DMC (assumed), $LiPF_6$, LiFSI (least)

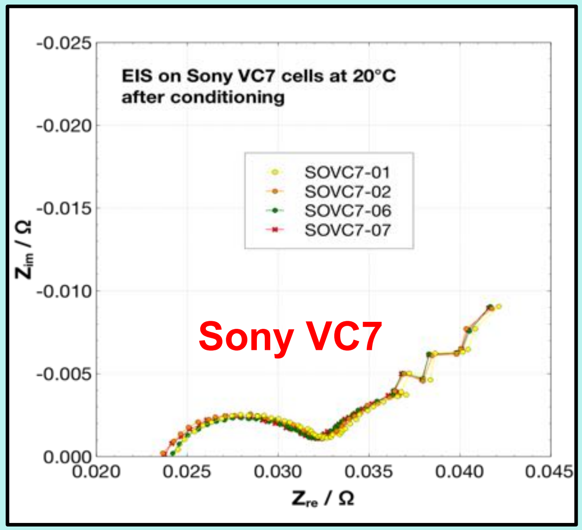
EIS after conditioning (Batch1 cells)

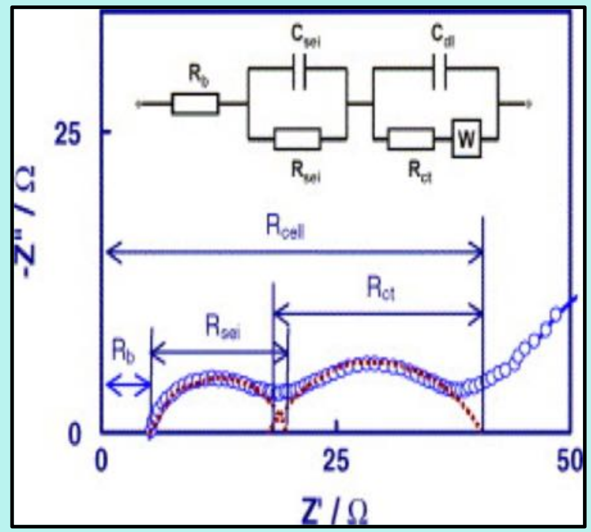












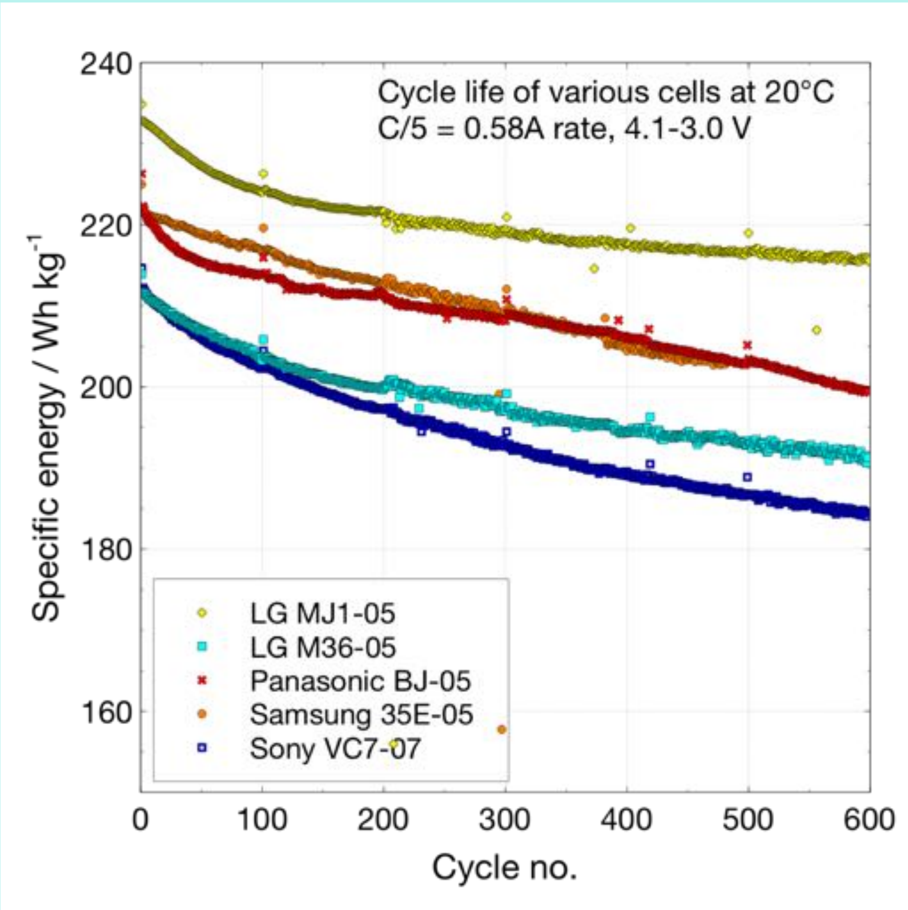
Typical Eq. Circuit

- Cells have very good cell-to-cell reproducibility in EIS spectra at +20 ºC
- Panasonic BJ cells appear to have greater film resistance, possibly due to suspected low-temperature optimized electrolyte
- LG M36 shows narrowest loop in BOL spectrum

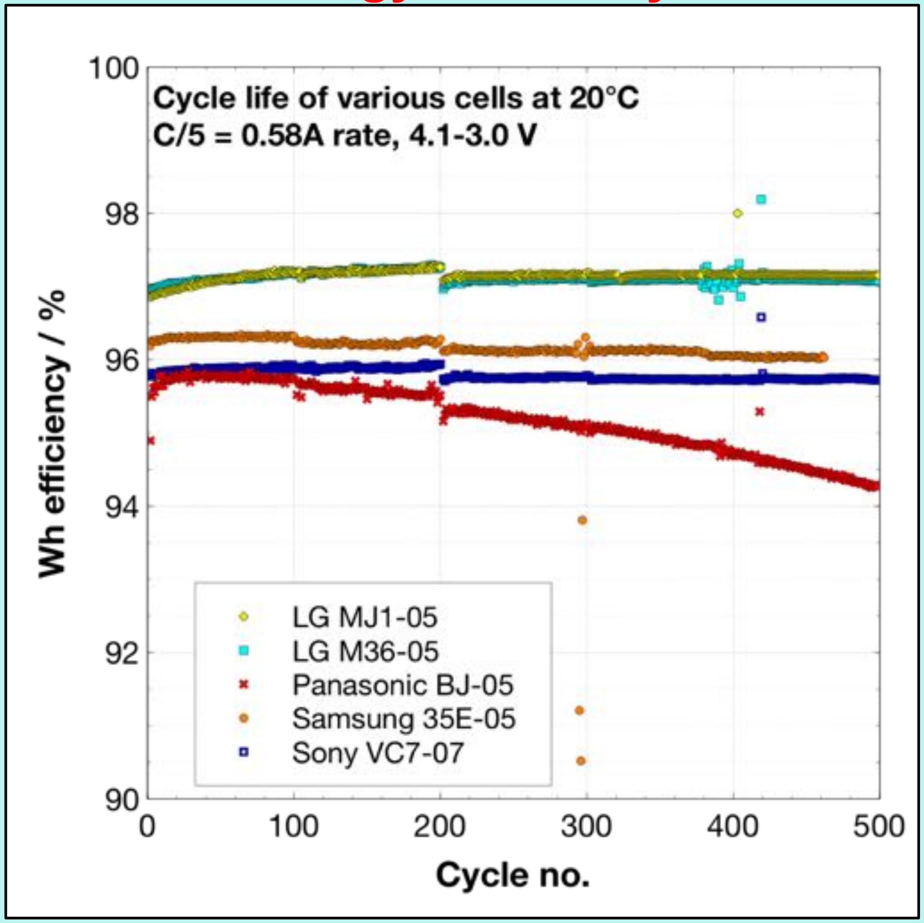
Cycle life at +20 ºC – Batch 1

100% DOD cycling at C/5, 4.10 – 3.00 V

Specific Energy, Wh/kg



Energy Efficiency



- All the cells have shown good cycle life
- LG Chem MJ1 cells exhibit the highest specific energy and efficiency

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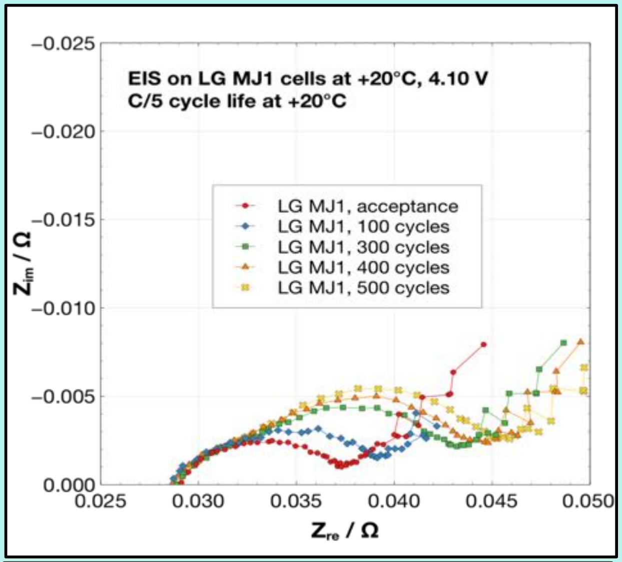
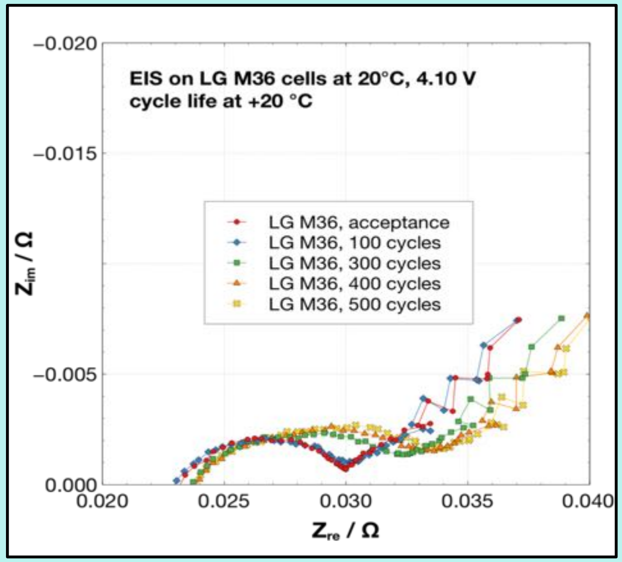
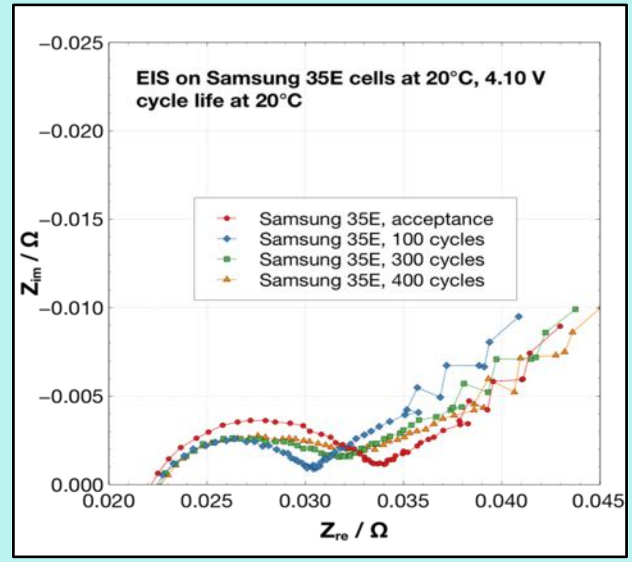
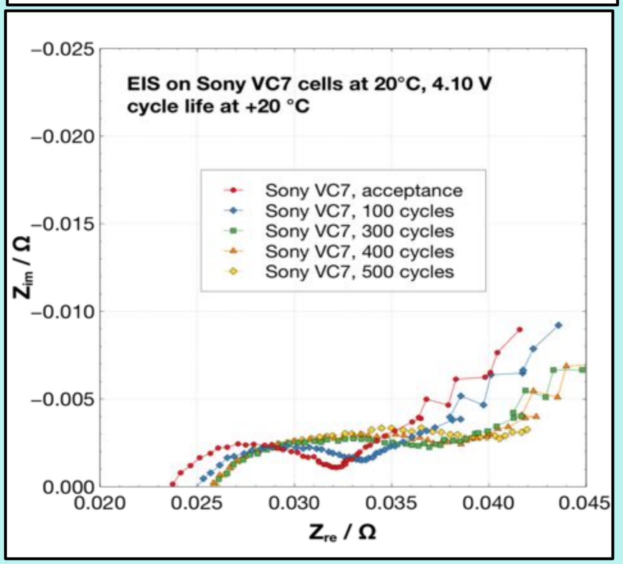
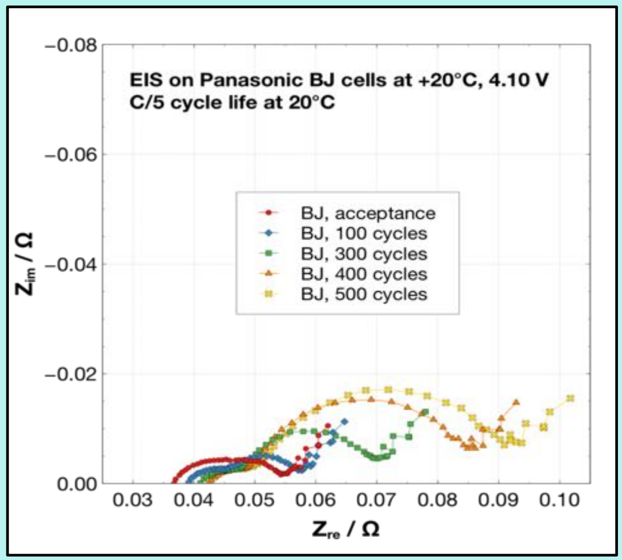
EIS vs. cycle life at +20 ºC

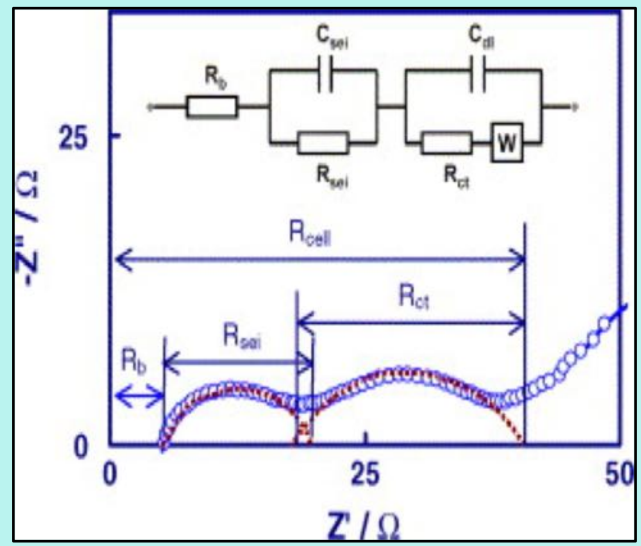










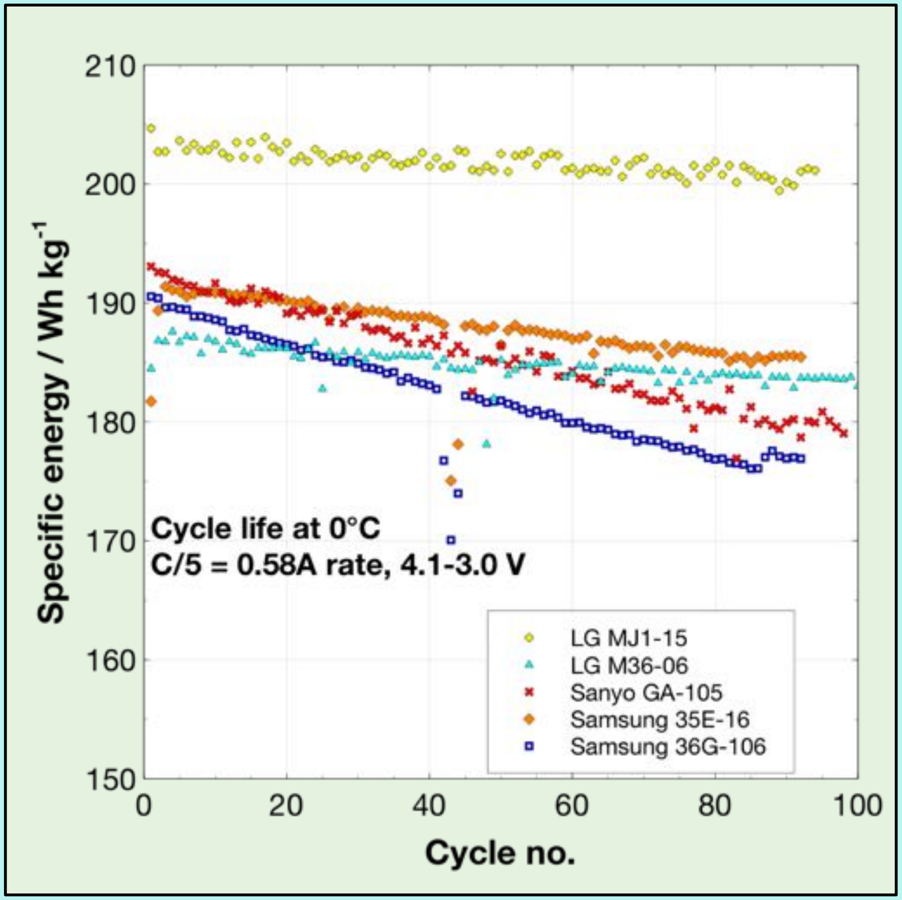


Typical Eq. Circuit

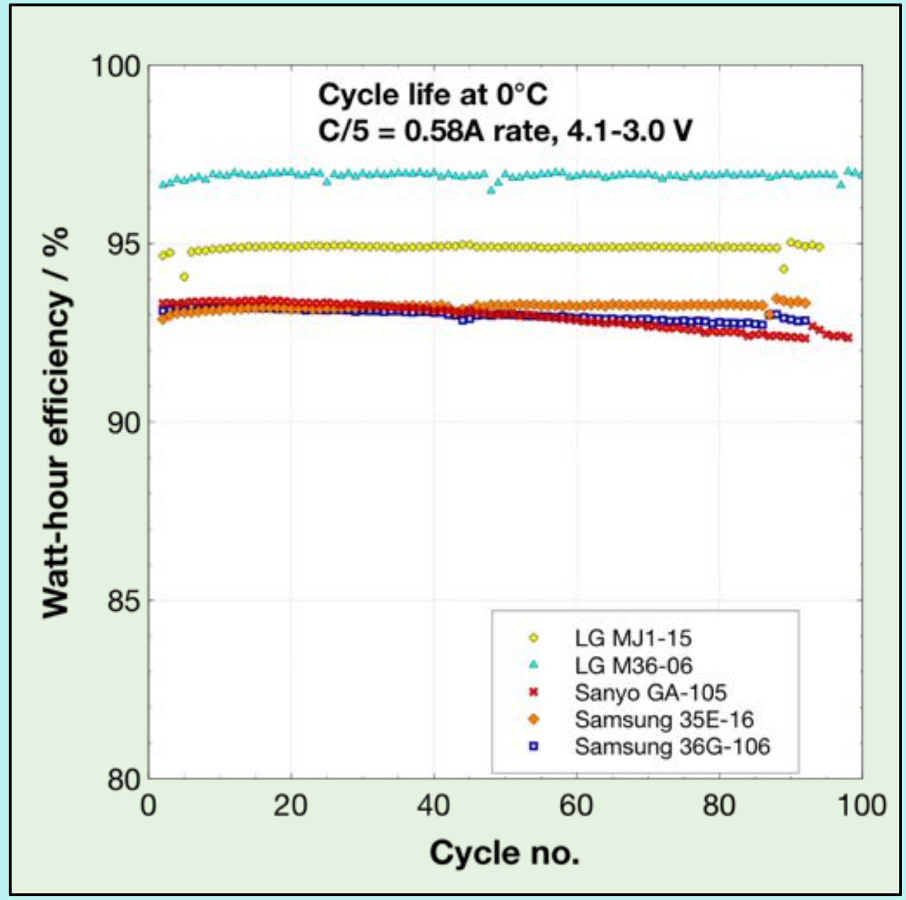
- All cells have shown some growth impedance over 500 cycles
- LG M36 and Samsung 35E cells had the least growth, while Panasonic cell shows the highest growth during cycling.
- Impedance from the second loop is dominant (Charge transfer kinetics of cathode)

Cycle life at 0 ºC - (Batch 2 cells)

Specific Energy, Wh/kg



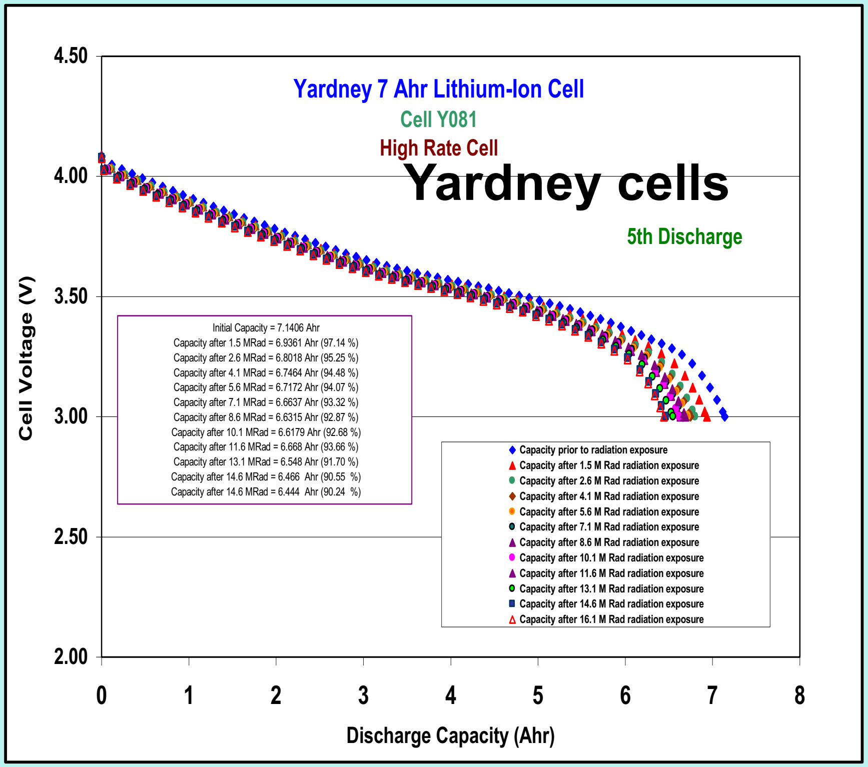
Energy Efficiency

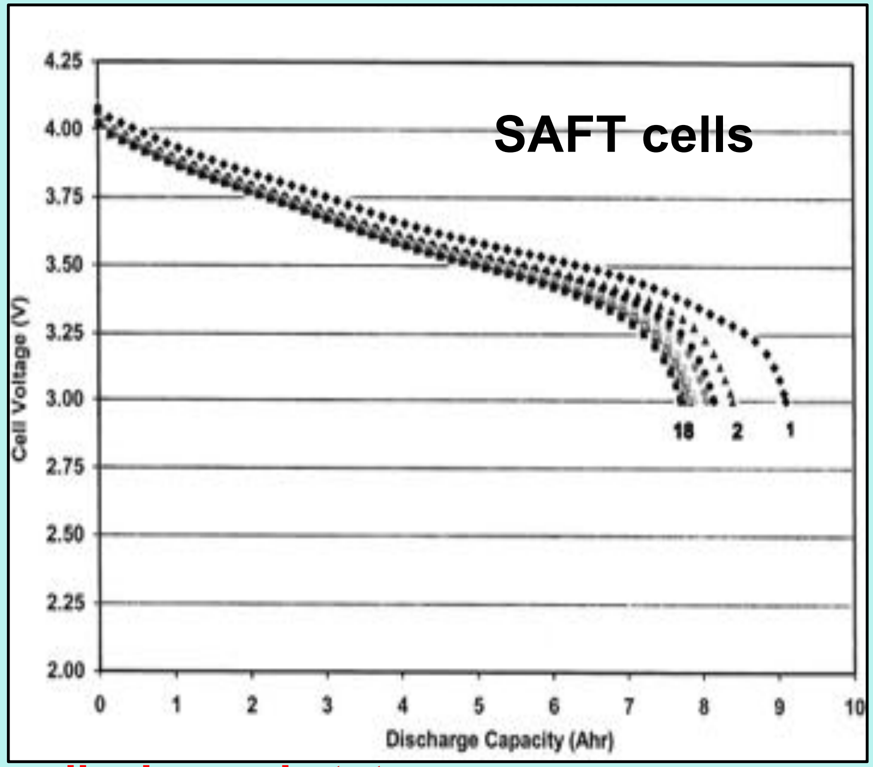


- All the cells have shown high specific energy of 190 Wh/kg at 0C, with LG Chem MJ1 cells offering the ~205 Wh/kg.

Radiation Tolerance of Li-ion Batteries

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





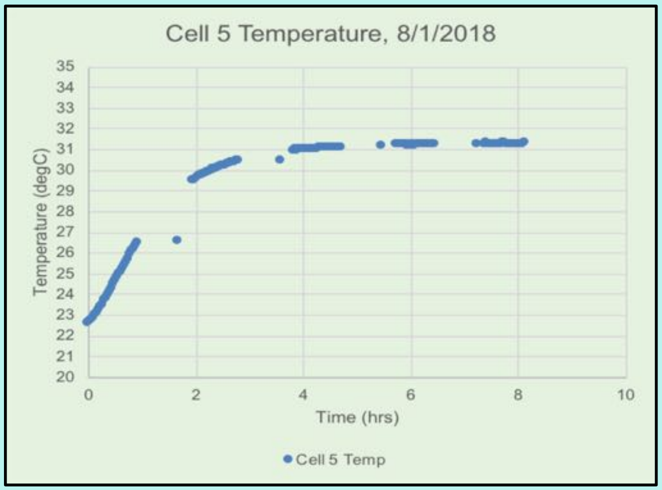
- **Cells tested in the discharged state**

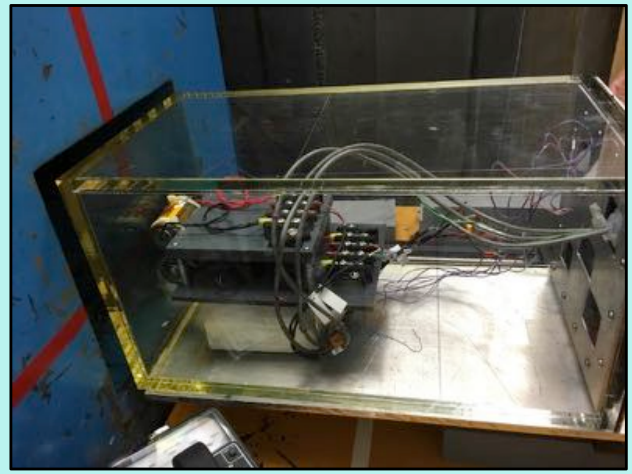
- Material Challenges: Radiation tolerance of polymers (including separators, seals and other components) and electrolytes
- Slight reduction of electrolyte conductivity and separator elasticity, but little to moderate loss in performance

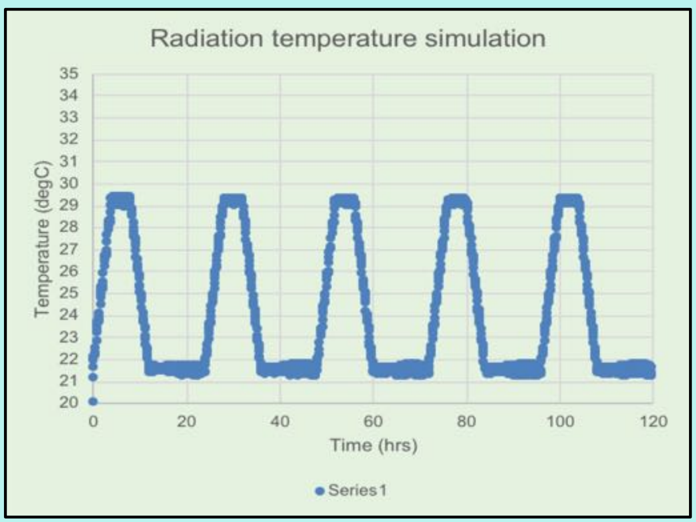
Ratnakumar et al, Journal of The Electrochemical Society, **151** 4 A652-A659 2004

Exposure to Cobalt-60 (^{60}Co) Radiation

- Two exposures: 12 Mrad and 8 Mrad for a total of 20 Mrad TID (12 MRad for planetary protection and 8 MRad 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

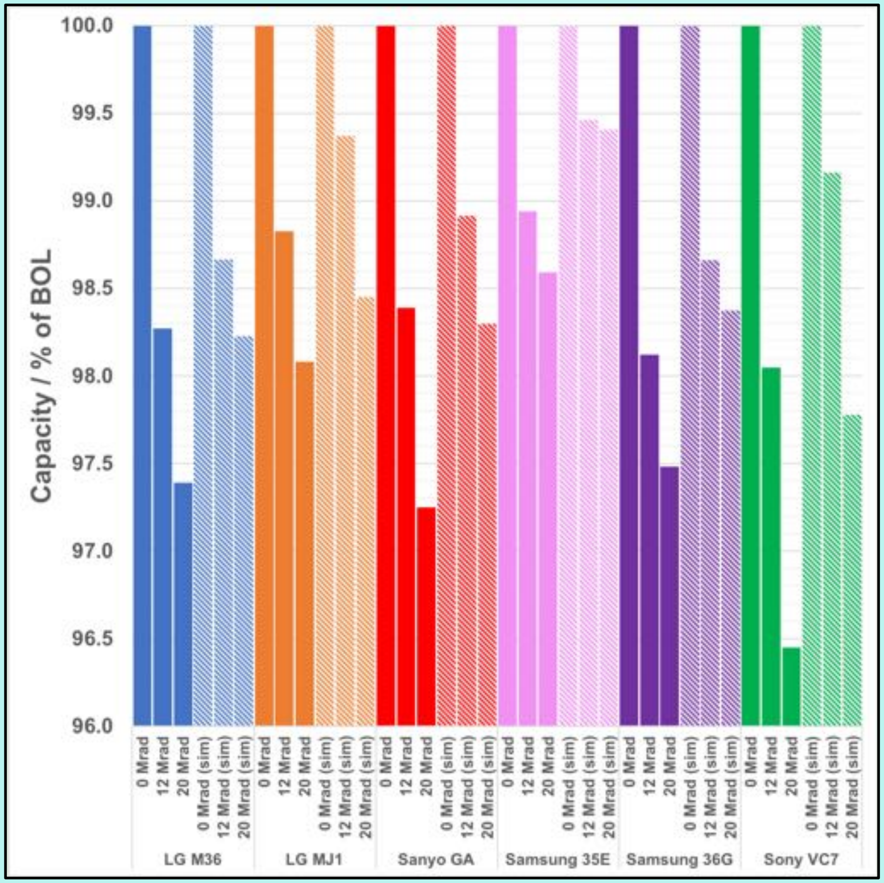






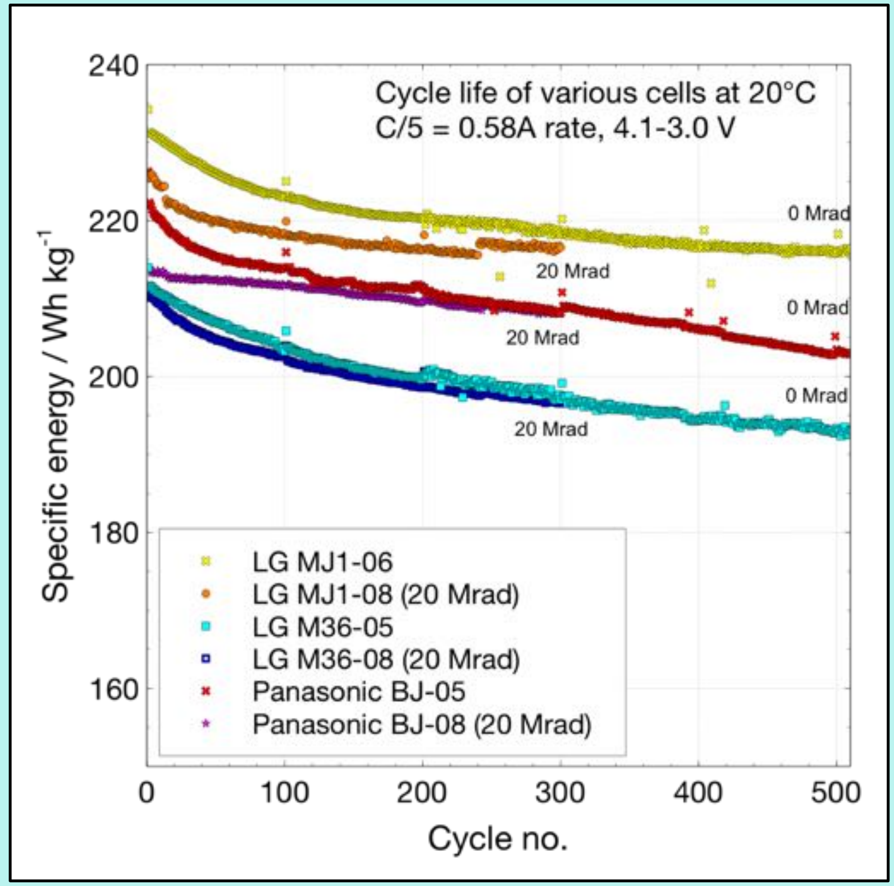
Irradiation of cells in two stages

Capacity vs Radiation dose



M36 MJ1 GA 35E 36G VC7

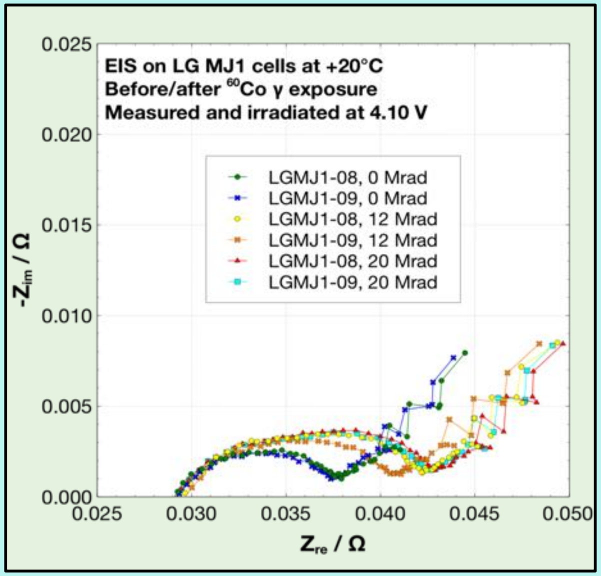
Cycling of radiated cells

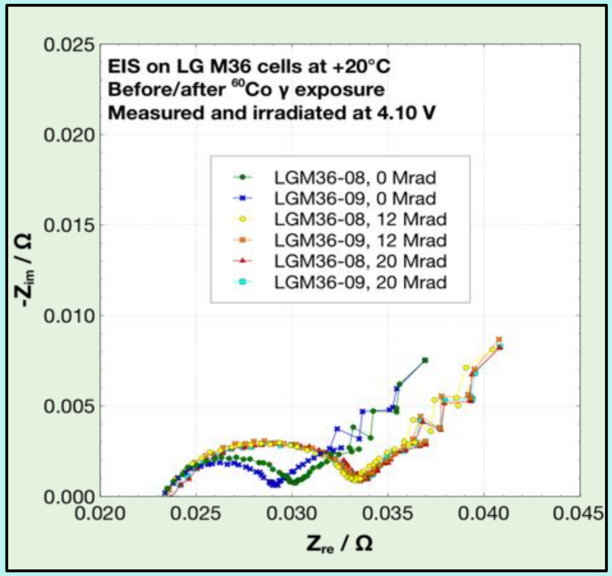


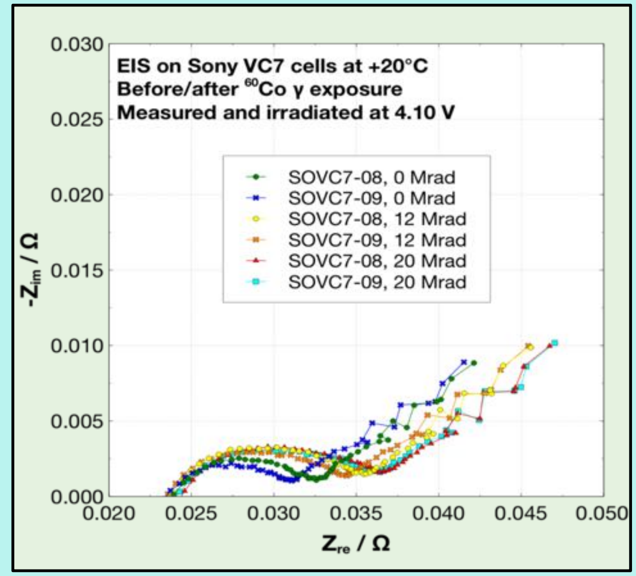
- Solid: radiation exposed; 0 Mrad, 12 Mrad, 20 Mrad
- hashed: 0 rad control group, after equivalent stand periods
- All the cells show impressive tolerance to radiation with <2% capacity loss (vs control cells) after 20 Mrad exposure.
- Again, LG Chem MJ1 cells have the highest specific energy

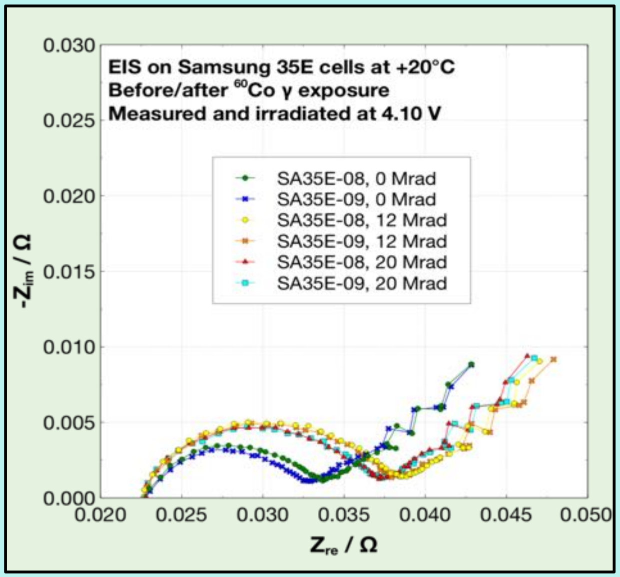
- Radiated cells are cycling well; slightly lower specific energy, but less fade rate.

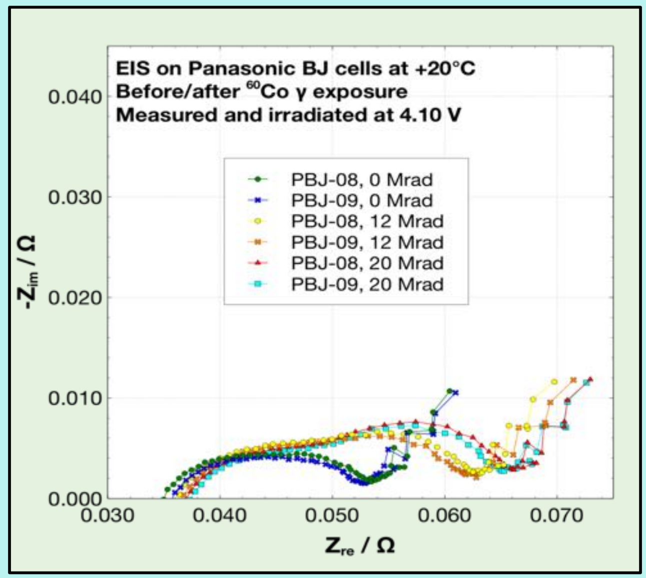
EIS (at 20C) after Radiation (Batch1)





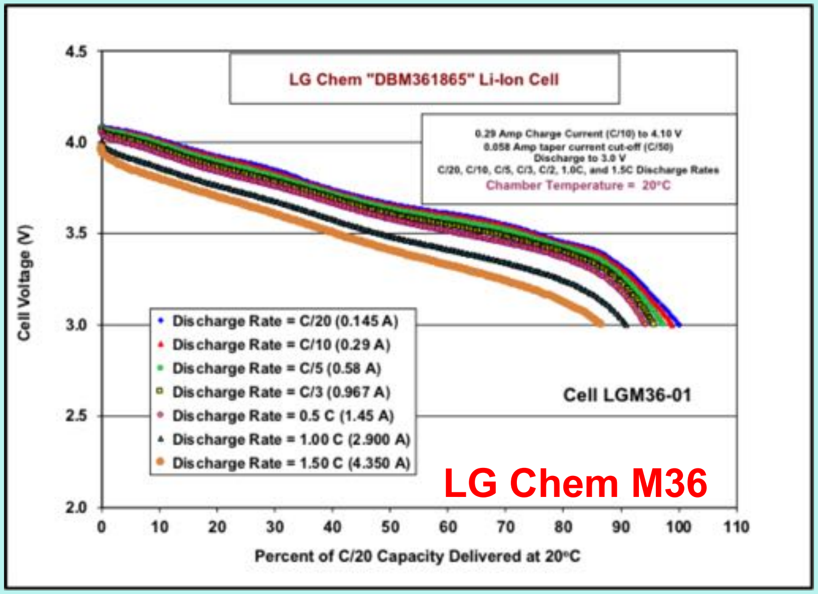


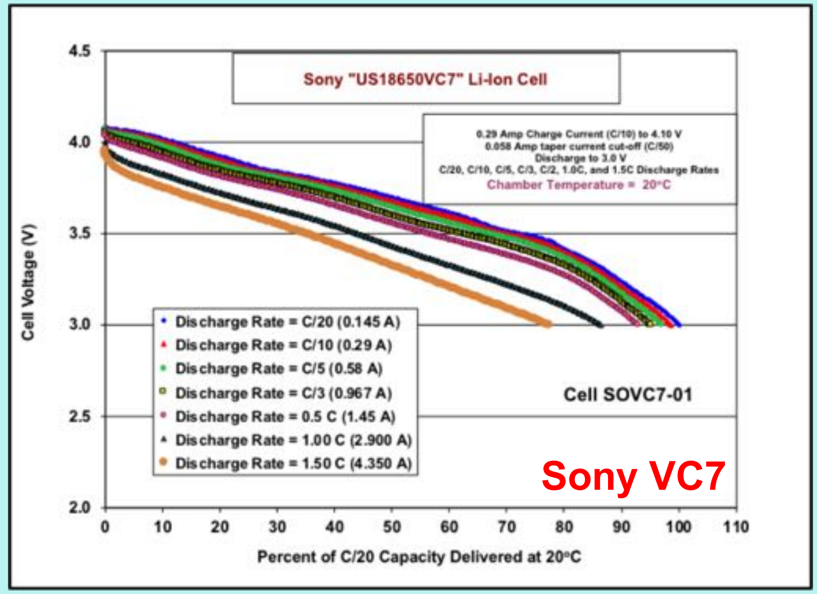


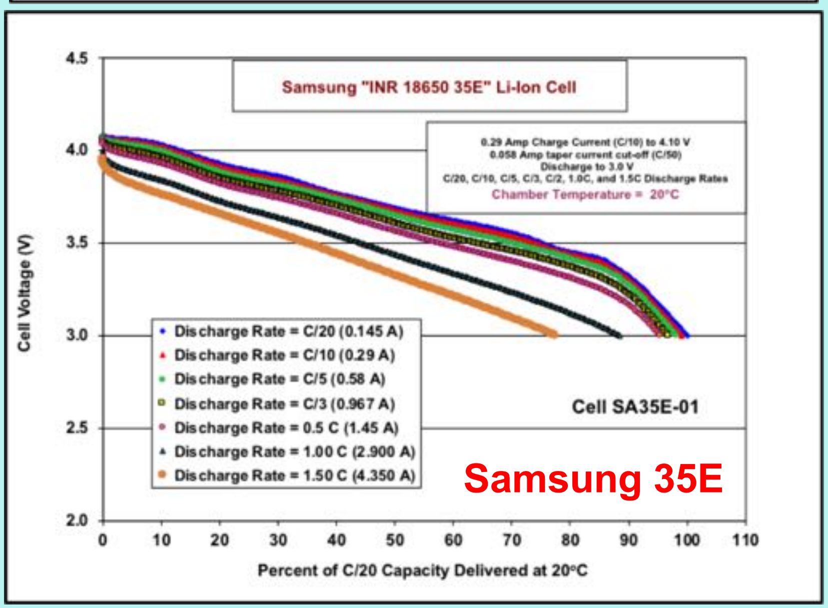


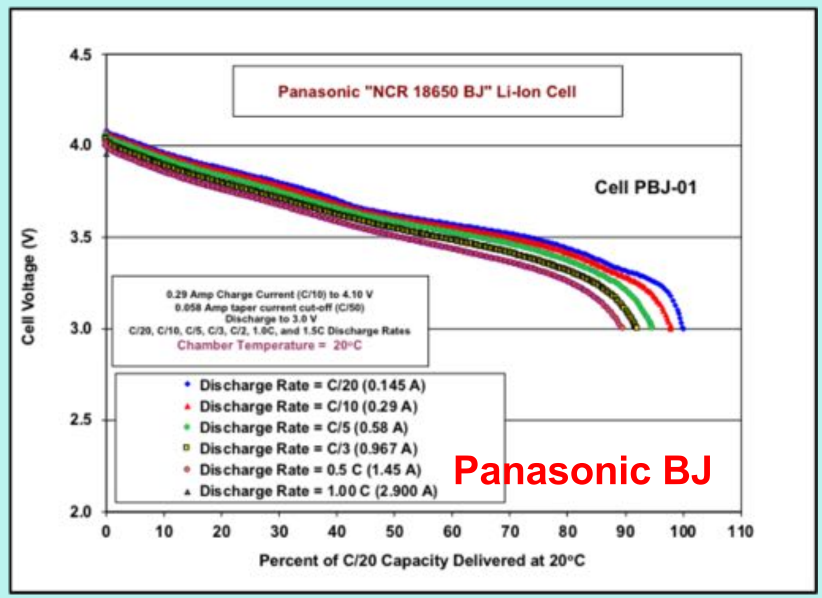
- Only very small increase in series resistance
- Increase in breadth of impedance loop
- Minimal change in Sony VC7 cells and maximum change in Panasonic BJ cells

Discharge rate test at +20 °C



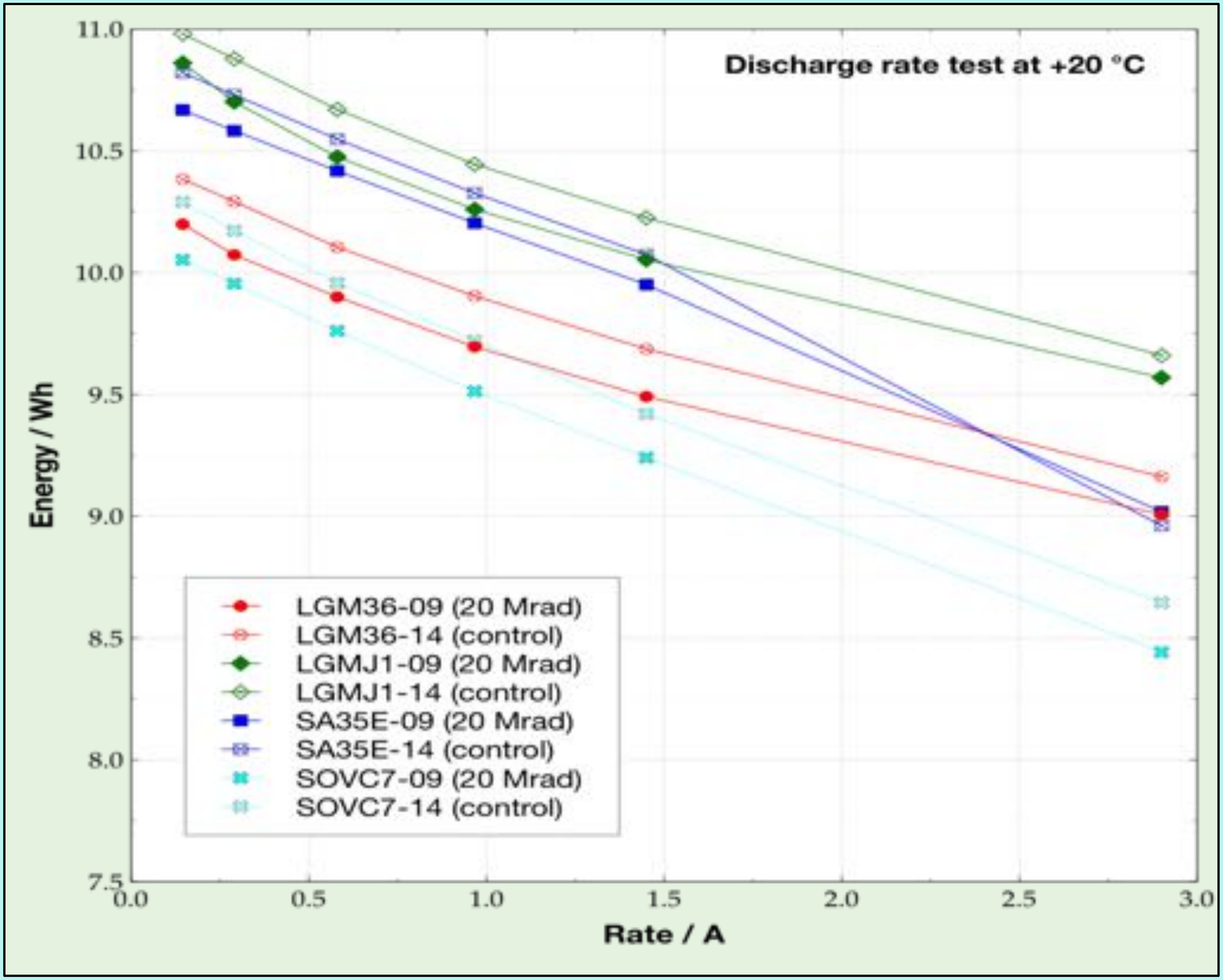






- Excellent rate capability with LG M36 Cells (90% of the capacity, 190 Wh/kg at 1.5C rate

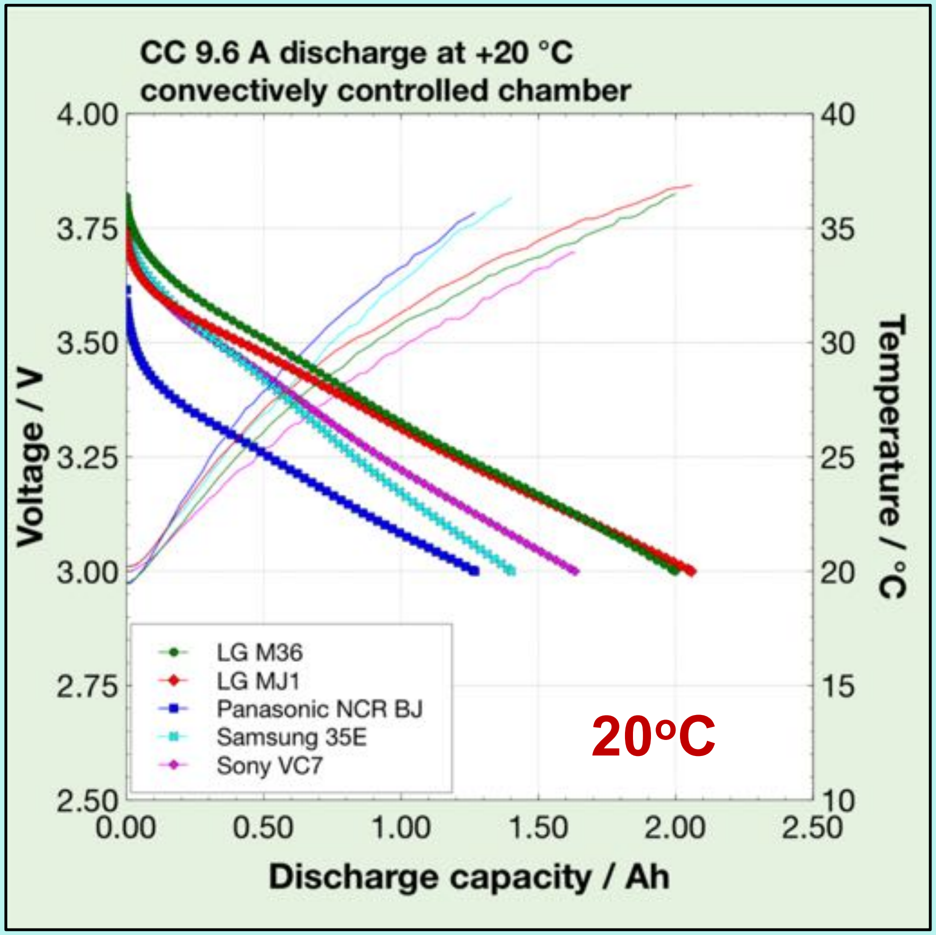
Discharge Rate Effect (20 ºC)-Radiated vs. Control

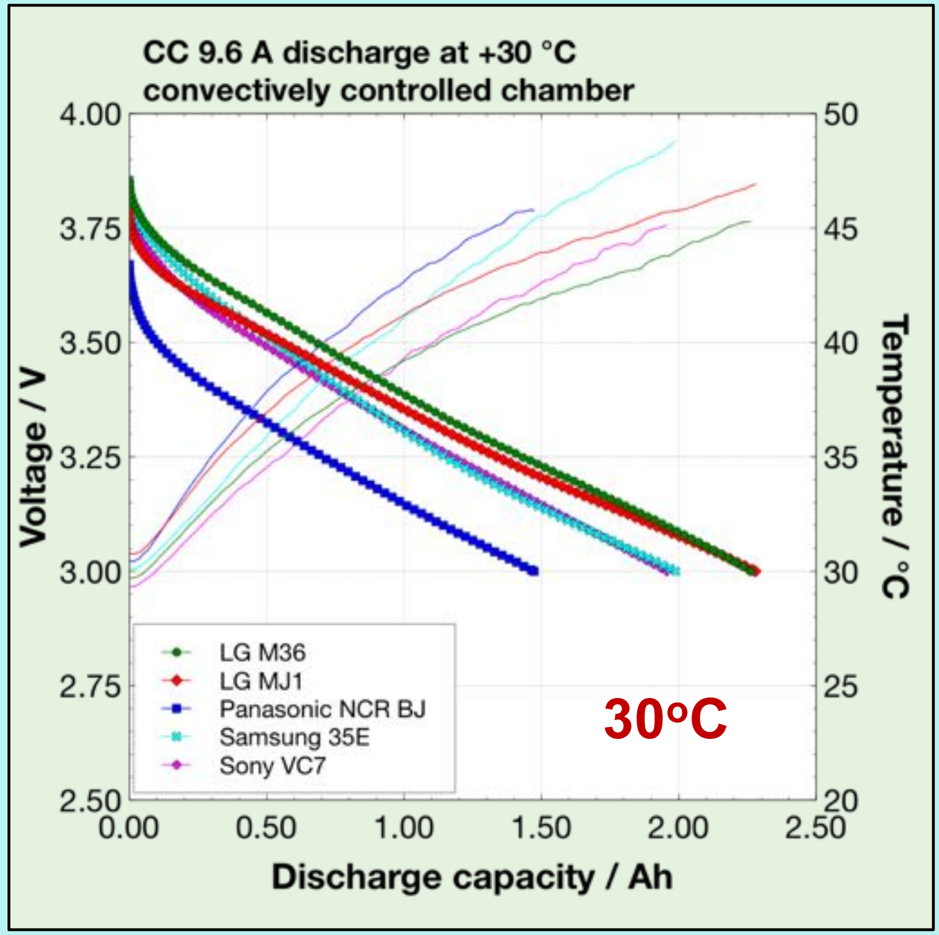


- No change in the rate capability after radiation exposure (20 Mrad)

High Rate Testing (9.6 A)

Discharge profiles at 9.6 A - Comparison of cells

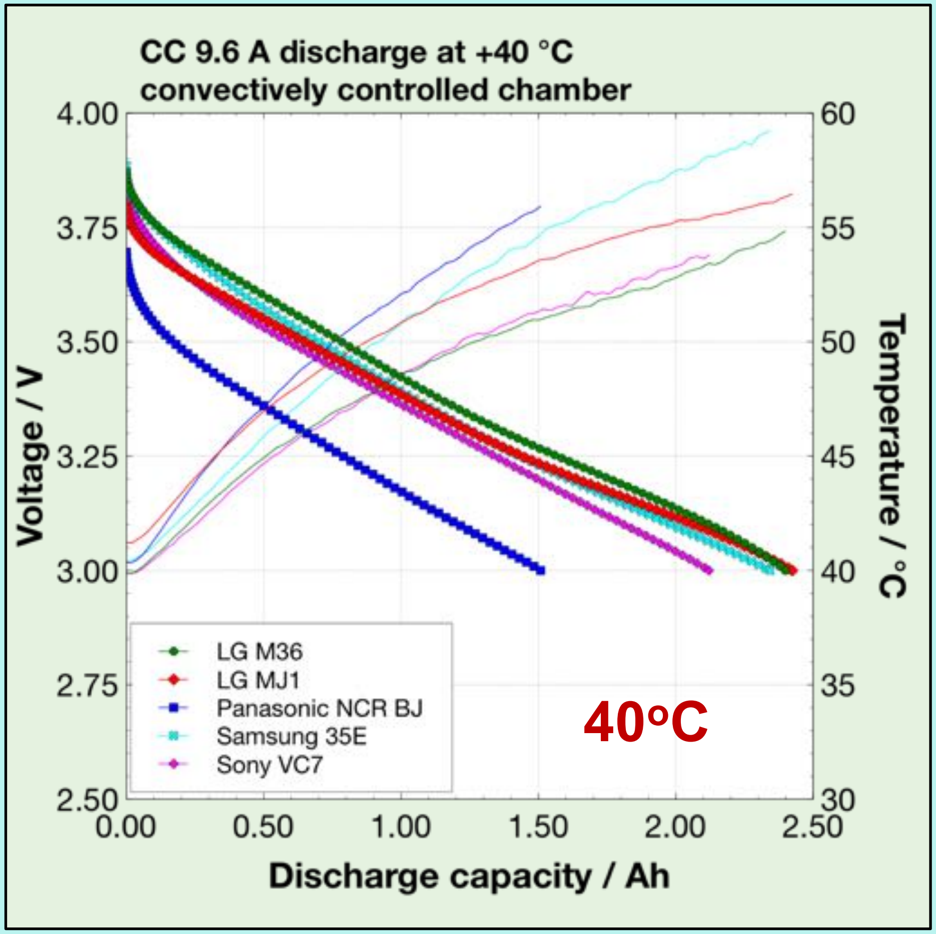


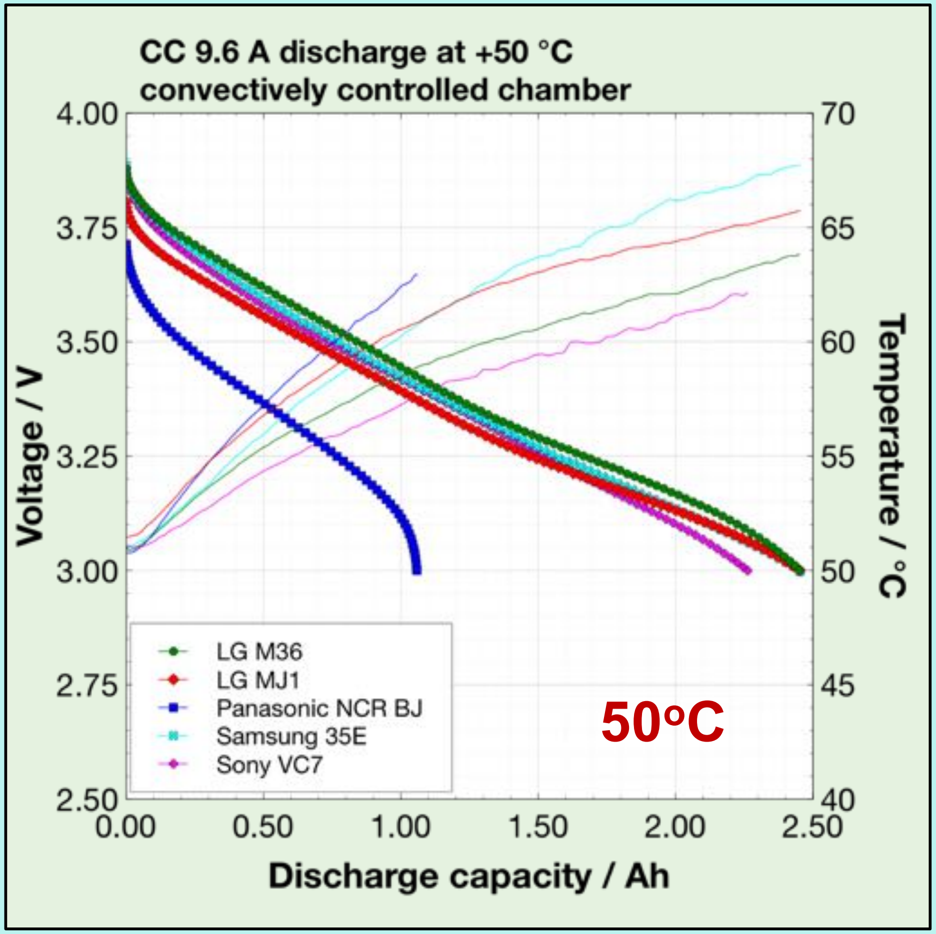


- Considerable cell warm up in a convectively controlled chamber

High Rate Testing (9.6 A)

Discharge profiles at 9.6 A - Comparison of cells





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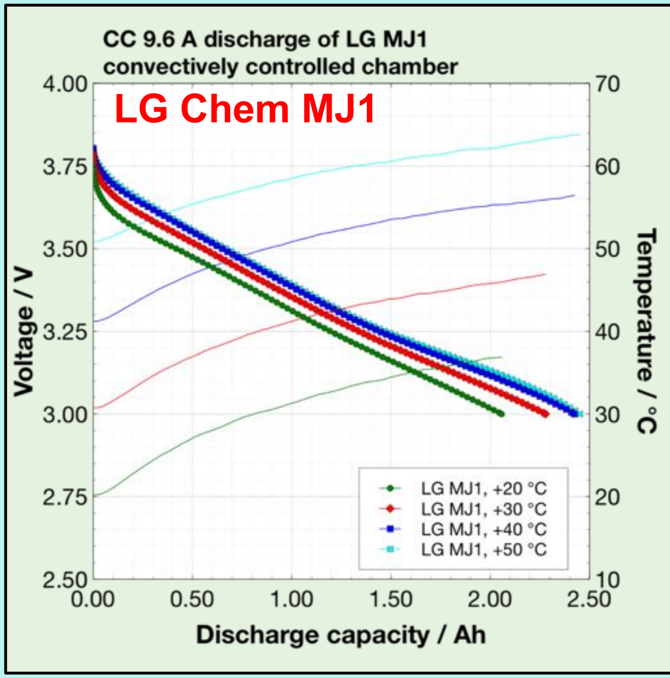
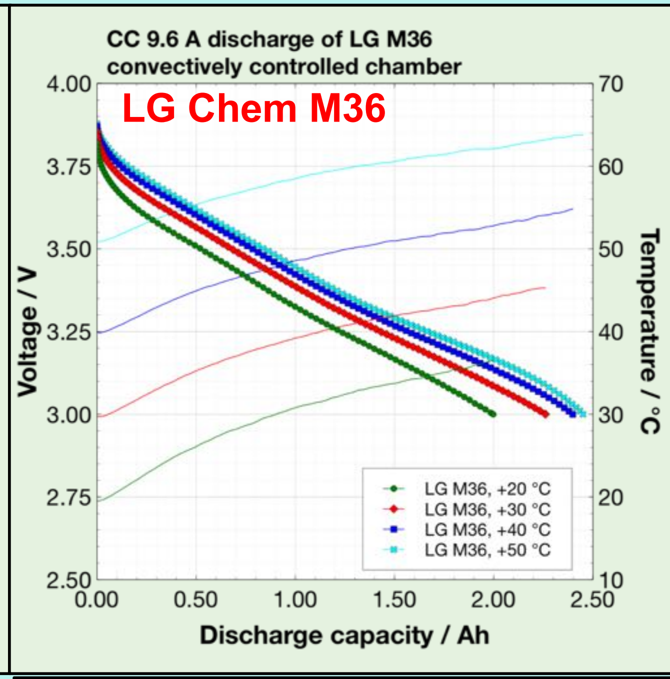
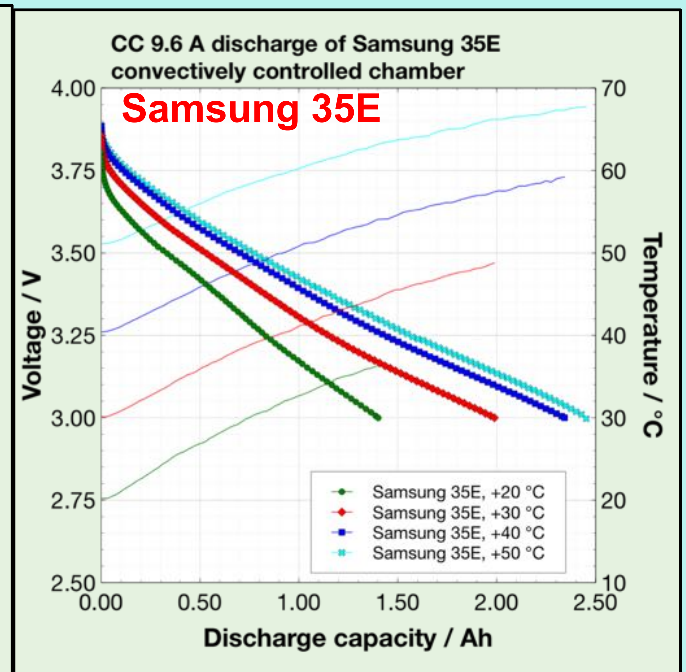
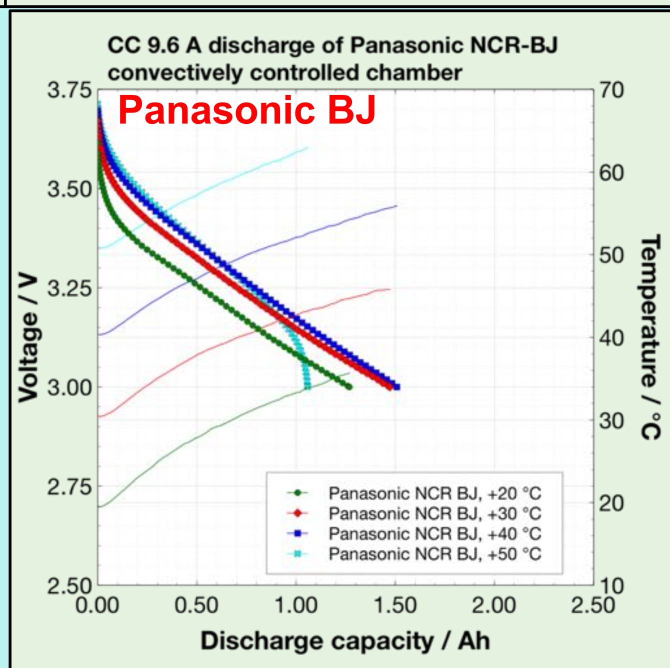
High Rate Testing (9.6 A)

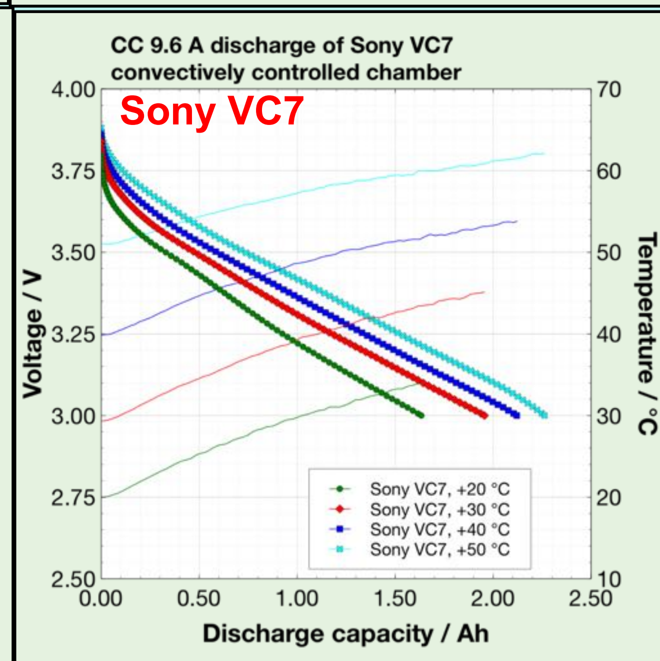






- LG Chem cells provide high power densities at 20-50C, while other chemistries provide only at warm temperatures.





Conclusions and Future Plans

- **Conclusions**
  - Recent Li-ion 18650 COTS cells provide high specific energy and high power density, good cycle life and resilience to high-intensity radiation environments.
  - LG Chem MJ1 cells show impressive performance in all the categories.
- **Future Plans**
  - Testing of multi-cell modules (8S5P) for cell divergence during cycling and storage
  - Capacity retention during (cruise) at different States of Charge
  - Post-radiation performance (storage and cycling)
  - Destructive Physical Analysis of irradiated cells for an understanding of radiation effects

Acknowledgements

This research was carried out at the Jet Propulsion Laboratory (JPL), California Institute of Technology under a contract with the National Aeronautics and Space Administration and supported by NESC and JPL's Europa Lander project.

Disclaimer