AUV 2002

Silver/Zinc Batteries for AUV Applications

June 2002

SWRI, San Antonio

Contents

BST SYSTEMS, INC.

Submersible Applications

- AUVs
  - MK 30 - Torpedo Target (190AH)
  - MOSS - Mobile Submarine Simulator (140AH)
  - Draper/DARPA UUV (1200AH)
- Manned Submersible Applications
  - DSRV, Deep Submergence Rescue Vehicle (700AH)
  - DSV Deep Submergence Vehicle, Alvin (750AH)
  - NR-1, Nuclear Research Submarine (850AH)
  - SDV, Seal Delivery Vehicle (365AH)
  - ASDS, Advanced Seal Delivery Vehicle (740AH)

Ag/Zn Advantages

- High volumetric and gravimetric energy densities
- Excellent Power Density
- Stable voltage performance
- Excellent Charge Retention
- Excellent Electrochemical Efficiency
- Excellent Low Temperature Performance
- High discharge rate capability (up to 1 A/in2)
- Excellent Safety Record (benign failure)

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Ag/Zn Limitations

- Cycle life limit - 100 cycles
- Wet life limit - 12 to 18 months
- Current designs are vented
- Does not tolerate overcharge and over-discharge well

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Silver/Zinc Cell Characteristics

Parameter	Cell Model								
Nominal Capacity	140 AH	190 AH	365 AH	700 AH	740 AH	750 AH	850 AH	1200 AH	1800 AH
Initial Capacity	164 AH	200 AH	525 AH	920 AH	740 AH	950 AH	1100 AH	1300 AH	2250 AH
Height	17.4 cm	16.3 cm	18.7 cm	48.0 cm	18.7 cm	49.6 cm	48.0 cm	30.2 cm	58.9 cm
Width	8.4 cm	15.1 cm	14.8 cm	10.7 cm	16.0 cm	14.2 cm	12.0 cm	14.5 cm	13.6 cm
Depth	5.6 cm	3.9 cm	7.0 cm	10.7 cm	8.0 cm	9.7 cm	11.5 cm	10.8 cm	13.3 cm
Volume	0.82 L	0.96 L	1.94 L	5.49 L	2.39 L	6.79 L	6.62 L	4.71 L	10.65 L
Wet Weight	1.62 kg	2.00 kg	4.00 kg	11.70 kg	5.67 kg	12.50 kg	13.60 kg	11.40 kg	21.80 kg
Discharge Current	30 amps	47 amps	60 amps	140 amps	20 amps	150 amps	170 amps	60 amps	220 amps
Volumetric Energy Density	301 wh/L	313 wh/L	406 wh/L	252 wh/L	464 wh/L	210 wh/L	249 wh/L	414 wh/L	317 wh/L
Gravimetric Energy Density	152 wh/kg	150 wh/kg	197 wh/kg	118 wh/kg	196 wh/kg	114 wh/kg	121 wh/kg	171 wh/kg	155 wh/kg
Cell Type	std.	std.	std.	PC	std.	PC	PC	std.	std.

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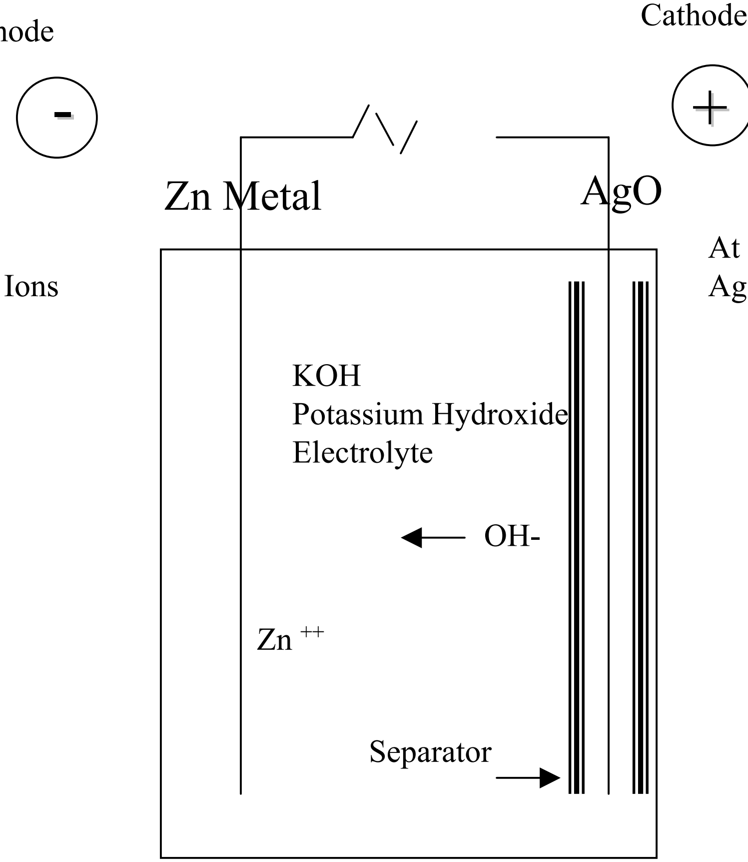
Rechargeable Cell Energy Densities

Chemistry	Gravimetric (Wh/kg)	Volumetric (Wh/l)
Pb-Acid	30-45	60-100
Ni-Cd	40-65	70-100
Ni-H2	40-60	70-90
Ni-MH	60-80	100-140
Ni-Zn	60-80	120-160
Ag-Cd	70-100	140-200
Li-Ion	115-160	250-360
Ag-Zn	140-200	400-510

Schematic and Operation of a Silver Zinc Cell

At the anode
Zn Metal $\rightarrow$ Zn^{++} Ions



At the cathode
AgO $\rightarrow$ Ag Metal

Overall Reaction : $Zn + AgO + H_2O \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Ag + Zn(OH)_2$

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Oxidation-Reduction
How It Works in the Silver Zinc Cell

Oxidation:

At the Zn Electrode: $Zn \xrightarrow{\text{discharge}} Zn^{++}$ ions $+ 2e^-$

Reduction:

At the AgO Electrode: $AgO + H_2O + 2e^- \xrightarrow{\text{discharge}} Ag + 2OH^-$

Overall Cell Reaction:

$$Zn + AgO + H_2O \longrightarrow Zn(OH)_2 + Ag$$

Silver Electrodes

- Uncharged
  - Silver powder, pressed and sintered
  - Silver powder, rolled and sintered
  - Pasted Ag_2O, sintered
- Charged
  - Sintered electrodes electrolytically formed
  - Pasted Ag_2O with binder
  - Pasted AgO with binder
  - Roll bonded AgO with binder

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Zinc Electrodes

- Uncharged
  - ZnO with binder, dry pressed
  - Pasted ZnO slurry with binder
- Charged
  - Zn metal powder with binder
  - Plated zinc metal sponge
  - Electroformed ZnO plates
  - Electrolysis of ZnO Slurry
  - Electroformed pasted ZnO

Separator Materials

- Cellulosics
  - Cellophanes
  - Fiber reinforced sausage casing
- Polymers
  - PVA
  - Polypropylene
    - Grafted
    - Irradiated

Potassium Hydroxide Electrolyte

The temporary disappearance of electrolyte

$$Zn + AgO + \underbrace{2KOH + H_2O}_{\text{electrolyte}} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} K_2Zn(OH)_4 + Ag$$

Electrolyte is used up on discharge

Electrolyte is reformed on charge

Another soluble form of zinc hydroxide

The permanent disappearance of electrolyte or water

1. Gassing on open circuit stand
2. Over charge
3. Over discharge

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Gassing

- All silver zinc cells generate gas:
- During Charge and Stand majority of gas is hydrogen
  - At end of charge, oxygen becomes the main constituent of the evolved gas
- During discharge, majority of gas is hydrogen, with a minimal amount of oxygen

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Mechanisms for Gassing (during stand)

1) Corrosion of the zinc:

$$Zn + 2KOH + 2H_2O \longrightarrow K_2Zn(OH)_4 + H_2 \uparrow \text{ gas}$$

Rate is inhibited with additives to the negative electrode

2) Decomposition of the silver peroxide:

$$2\,AgO \longrightarrow Ag_2O + 1/2\,O_2 \uparrow \text{ gas}$$

Rate is temperature dependent and enhanced at temperatures > 110 ºF

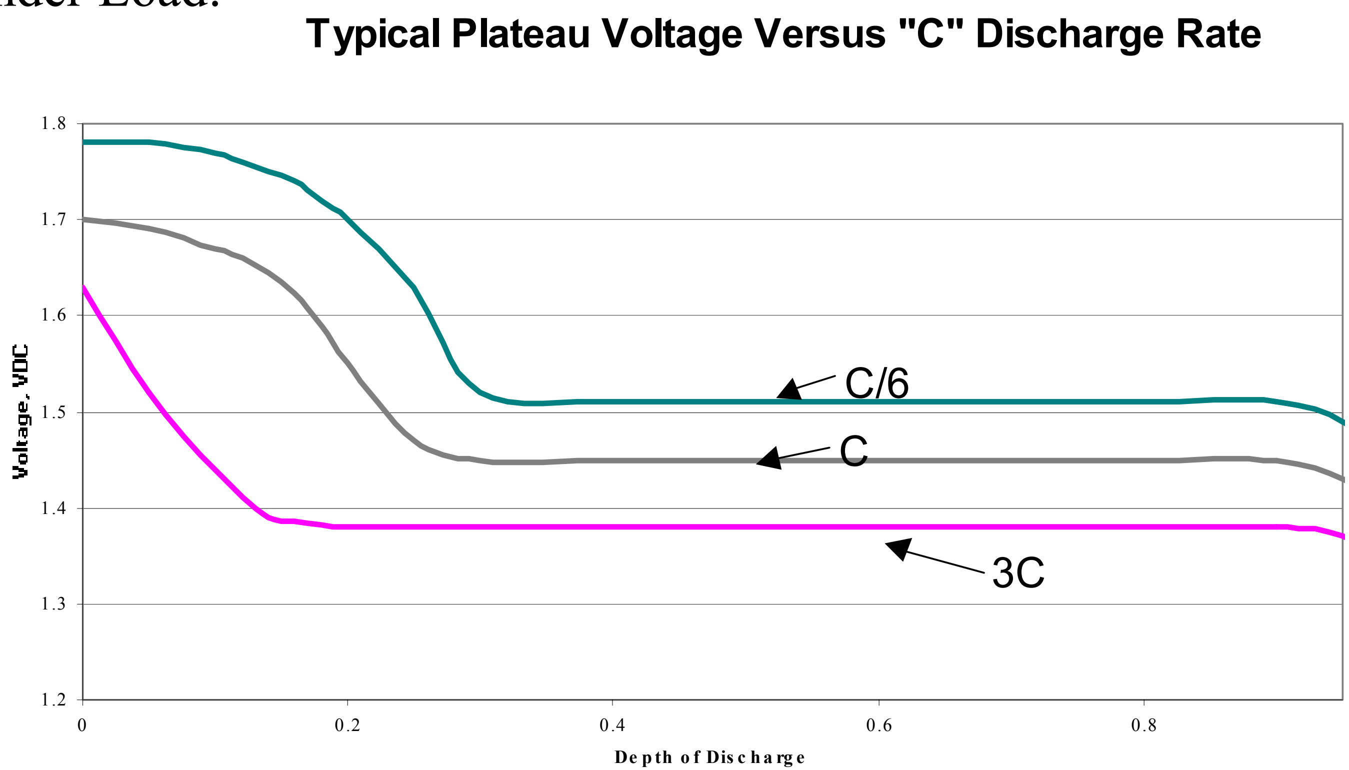
Two reactions do not occur at equal rates, therefore, cell, over time, becomes "silver limited"

Contents

Voltages of the Silver Zinc Cell

(open circuit & discharge)

- Open Circuit:
  - Fully charged 1.86 vdc
  - Partially discharged 1.60 vdc
- Under Load:



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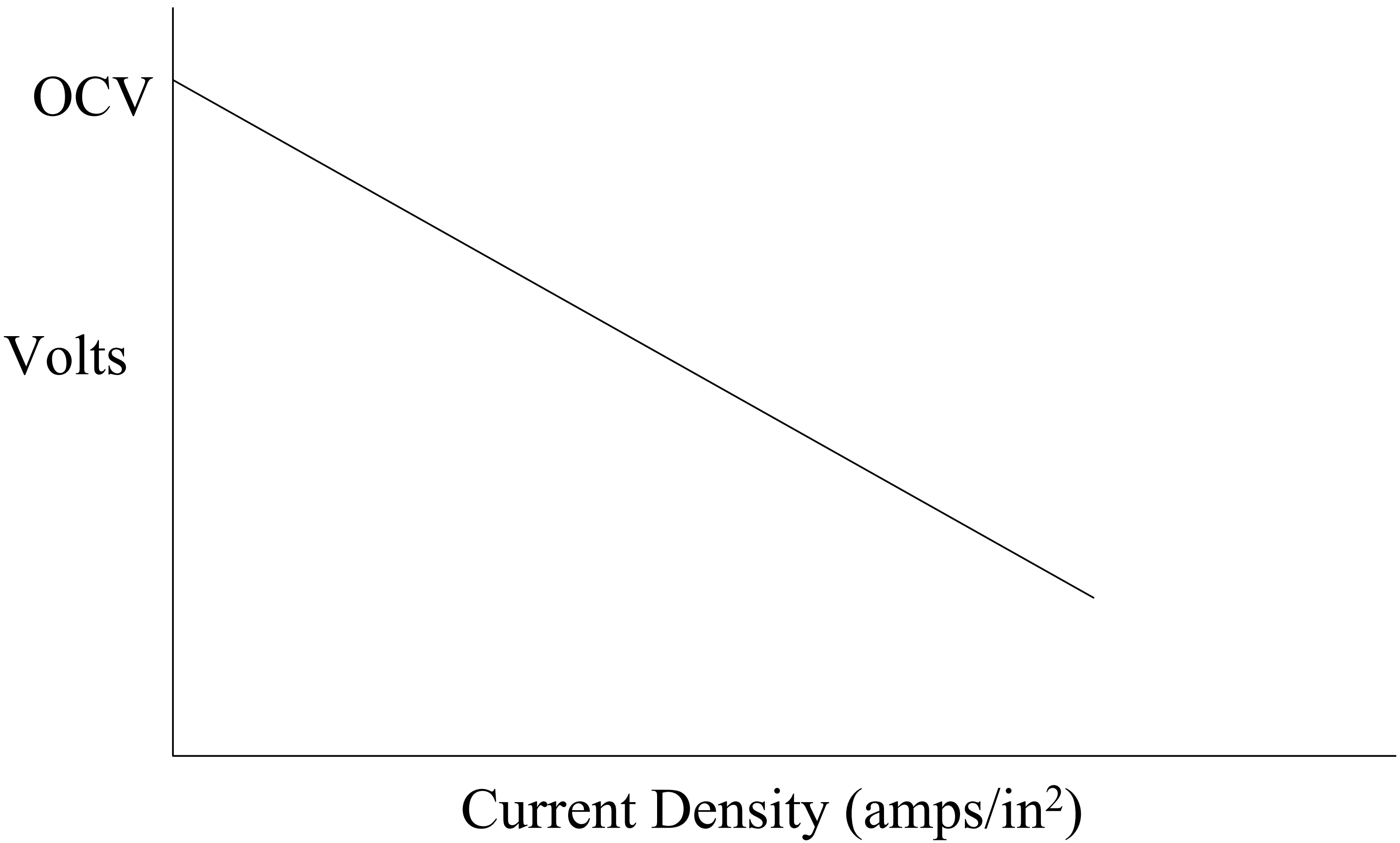
Polarization As a Function of Current Density



The Effect of Over Discharge (Reversal) on the Silver Zinc Cell

At the AgO Electrode: $2H_2O + 2\ e^- \xrightarrow{\text{reduction}} H_2\uparrow + 2\ OH^-$

At the Zn Electrode: $2\ OH^- - 2\ e^- \xrightarrow{\text{oxidation}} 1/2\ O_2\uparrow + H_2O$

- Net Result: $H_2O \longrightarrow H_2\uparrow + 1/2\ O_2\uparrow$ (idealized)

  Again, one electrode may start gassing before the other, thus changing the ratio between hydrogen and oxygen

  In overdischarge, results are the same as in overcharge, except that gasses are evolved at different electrodes

- Weakening of Separator

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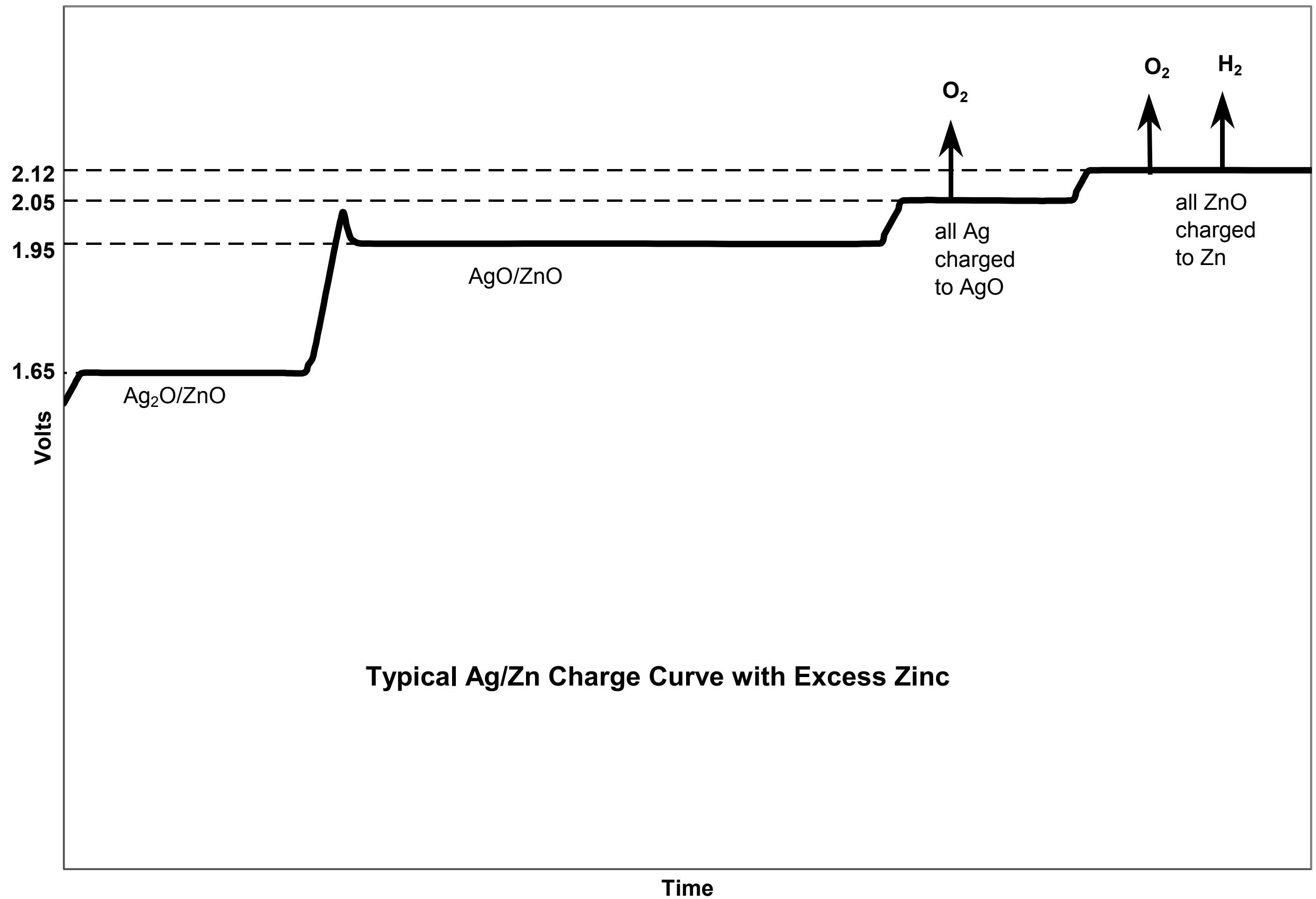
Charge Voltages of the Silver Zinc Cell



The Effect of Overcharge on the Silver Zinc Cell

At the Zn Electrode: $2H_2O + 2\,e^- \xrightarrow{\text{reduction}} H_2\uparrow + 2\,OH^-$

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Note: One electrode may start gassing before the other, thus changing the ratio between hydrogen and oxygen

- Weakening of Separator

Factors Influencing Battery Life

Increases Life

- Shallow Capacity Discharge Cycling < 75%
- Low Current Discharges--Less than C Rate
- Moderate Temperature Operation
- Low Temperature Storage < 40 ºF
- Full Charge Cut-off at Recommended Voltage
- Low Rate Charge
- Regular Maintenance

- Deep Capacity Discharge Cycling > 75 %
- High Current Discharge Over C Rate
- High Temperature Operation
- High Temperature Storage > 125 ºF
- Overcharge
- High Rate Charge
- Cell Reversal (overdischarge)

Decreases Life

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Failure Modes

- Capacity Loss
  - Mechanism - Negative electrode shape change
- Shorting
  - Mechanism -Zinc short, Silver short, Combination
  - Causes
    - Age (end of wet life--deterioration of the separator system)
    - Abuse
      - Over charging
      - Over discharging (reversal)
      - Improper storage
    - Manufacturing defect

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Cell Characteristics

- Prismatic cell geometry
- Good packing factor
- Plastic cell case and cover
  - Polysulfone - high temperature
  - ABS, SAN, Polypropylene
- Brass or steel terminals
  - Solder or crimp attachment to electrode leads
- Electrolyte - 40-45 weight % solution of potassium hydroxide
- Standard (pressurized) & Pressure Compensated

Standard Construction

- Must be within pressure hull
- Closed Cell with Vent Valve to relieve internal pressure
- Relatively short headspace
- Intercell connections are simple copper strip buss bars
- Dry Charged or Green

Pressure Compensated

- Open to ocean depth pressure - no relief valve
- Protected from seawater with mineral oil layer on top of cells and battery
- Taller head space to allow fluctuation in oil level without contaminating electrode pack
- Intercell connections are rubber coated cable with sealed contacts

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Battery Characteristics

- Case material
  - Fiberglass, Stainless Steel, Aluminum, Titanium
  - Simple restraint method
    - Wrap/Strap battery pack of cells
    - Install in vehicle battery compartment
- Series connected cells
- Power & ICVM connector assemblies
- Relief Valves
- Pressure Compensation System

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Performance Characteristics

- Temperature
  - low limit -20ºF
  - high limit +130ºF
  - end of discharge 180ºF
- Pressure
  - full vacuum to 20,000 ft H_2O
- Dynamic
  - tolerates standard transportation and shipboard vibration environments
- Orientation
  - Temporary Inversion OK for Discharge

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Operational Requirements

- Vehicle integration
  - Access to battery for re-charge
  - Thermal & Gas Management
  - Battery & Cell Monitoring
    - voltage
    - amp-hour gauge
- Support equipment
  - Vacuum system for activation/maintenance
  - Electronics capable of monitoring individual cells
  - Should top charge individual cells every 10 cycles

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User Selection Guidelines

- Off the Shelf designs
  - best cost and schedule
  - performance/fit compromise
- Tailored designs
  - use existing tooling and size
  - custom match performance
- Custom designs
  - best match to requirements
  - higher NRE costs
  - longer development cycle