

Impact of Charge Methodology Upon the Performance of Lithium Ion Cells

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Outline

- Introduction
- Charge Characteristics of Lithium Ion Prototype Cells
 - Charge Rate Characteristics at Different Temperatures
 - Effect of Charge Methodology Upon Cycle Life Performance
 - Effect of Charge Voltage Upon Cell Performance
 - Impact upon Low Temperature Performance
 - Impact of Charge Voltage at High Temperature
- Charge Characteristics of Three-Electrode Cells
 - Charge Characteristics of Lithium-Ion Batteries
- Charge Characteristics of Lithium-Ion 8-Cell Battery
- Conclusions
- Acknowledgements



Lithium-Ion Cells for NASA and DoD Applications: Program Objectives

- Assess viability of using lithium-ion technology for future NASA and Air Force applications.
- Demonstrate applicability of using lithium-ion technology for future Mars Lander and Rover applications.



Lithium-Ion Cells for NASA and DoD Applications: Summary of General Characterization Tests On-Going at JPL

- Cycle life performance at room temperature (25°C)
- Cycle life performance at low temperature (-20°C)
- Discharge rate characterization (at 40, 25, 0, and -20°C)
- Charge rate characterization (at 40, 25, 0, and -20°C)
- Capacity retention characterization tests
- Storage characterization tests (cruise conditions)
- Pulse capability tests (Entry Descent and Landing)
- VT charge characterization tests
- Electrical characterization by a.c. impedance
- LEO and GEO characterization tests
- Thermal characterization (microcalorimetry)



Charge Characteristics of Prototype Lithium Ion Cells

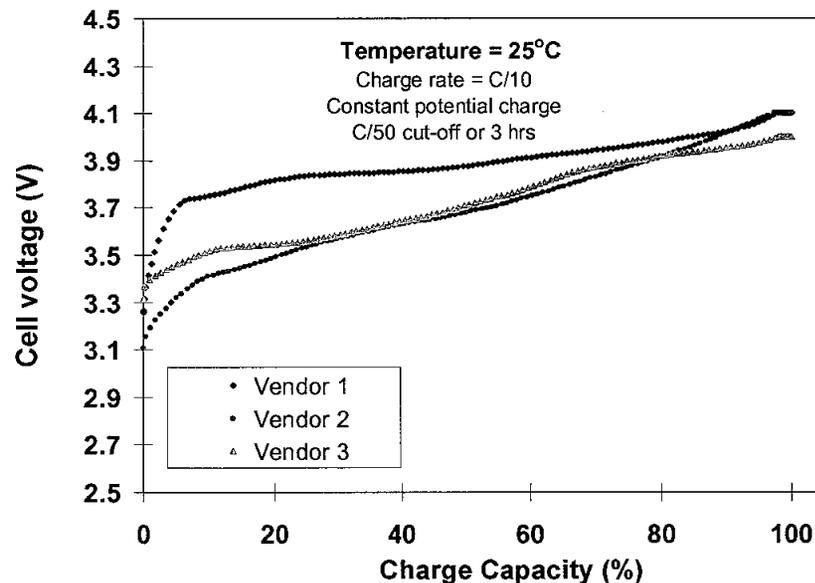
- **Charge acceptance at various rates and temperatures**
 - Various chemistries, cell designs and sizes
 - Range of charge rates investigated (C/20 to C rate)
 - Range of Temperatures investigated (-40° to +40°C)
- **Effect of Charge Methodology Upon Cycle Life Performance**
 - Effect of charge voltage
 - Effect of taper current cut-off
 - Effect of storage on the bus (float charging)
- **Effect of charge voltage upon cell performance**
 - V/T characterization



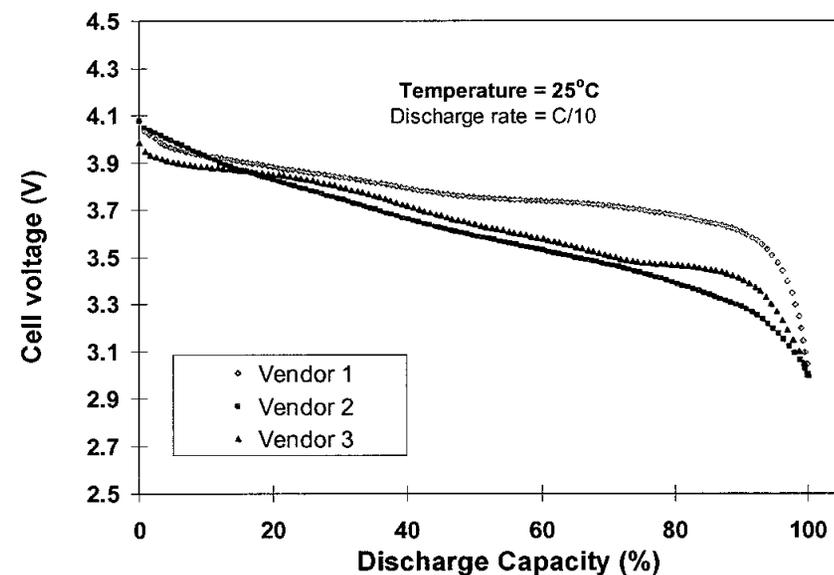
Large Capacity Lithium-Ion Cells for Future Mars Applications

Room Temperature Charge/Discharge Characteristics

Voltage Profile on Charge



Voltage Profile on Discharge

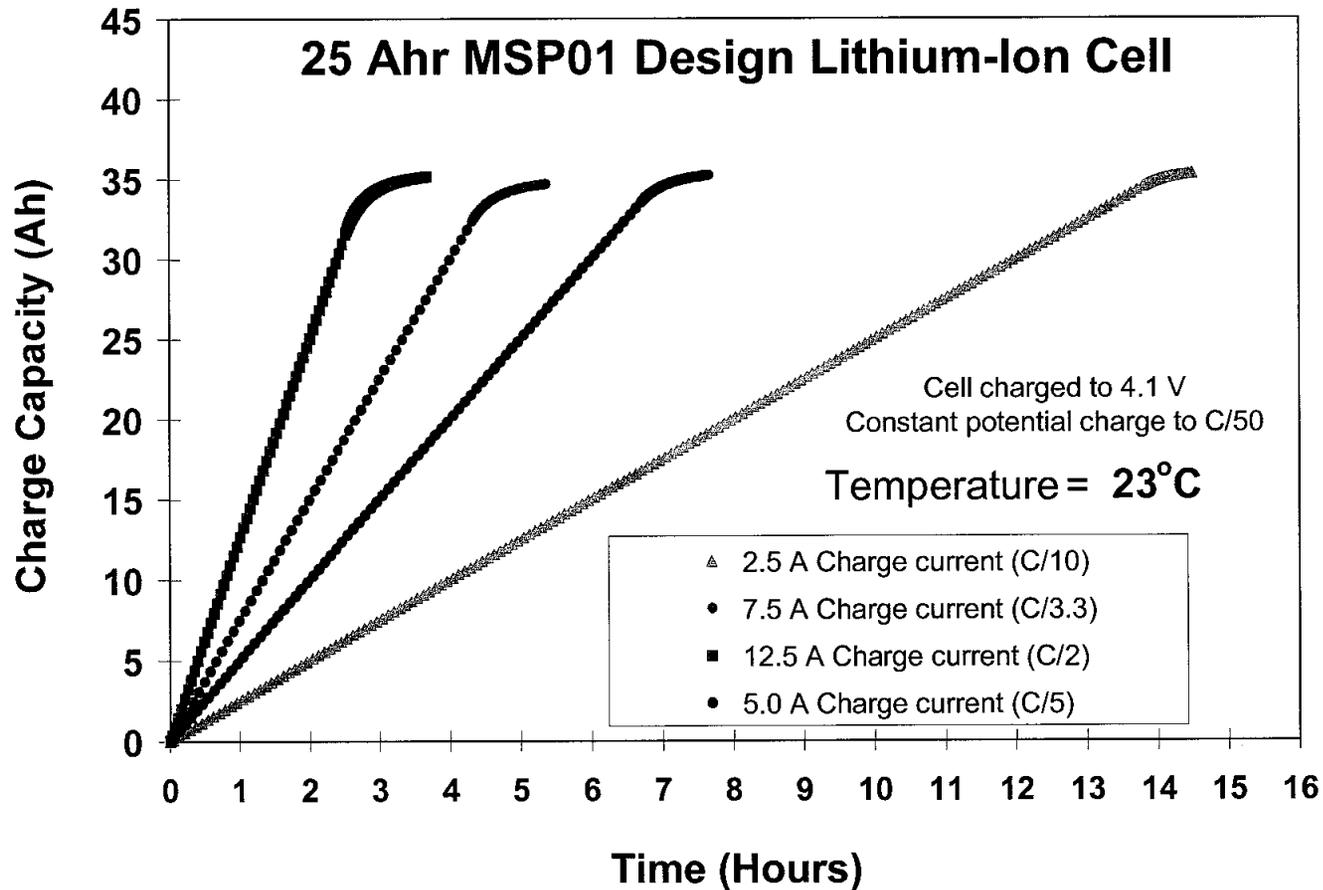


- Depending upon the chemistry employed (i.e., cathode and anode type) the voltage profile on charge and discharge can be distinctively different.



Lithium-Ion Cells for Mars Surveyor 2001 Lander

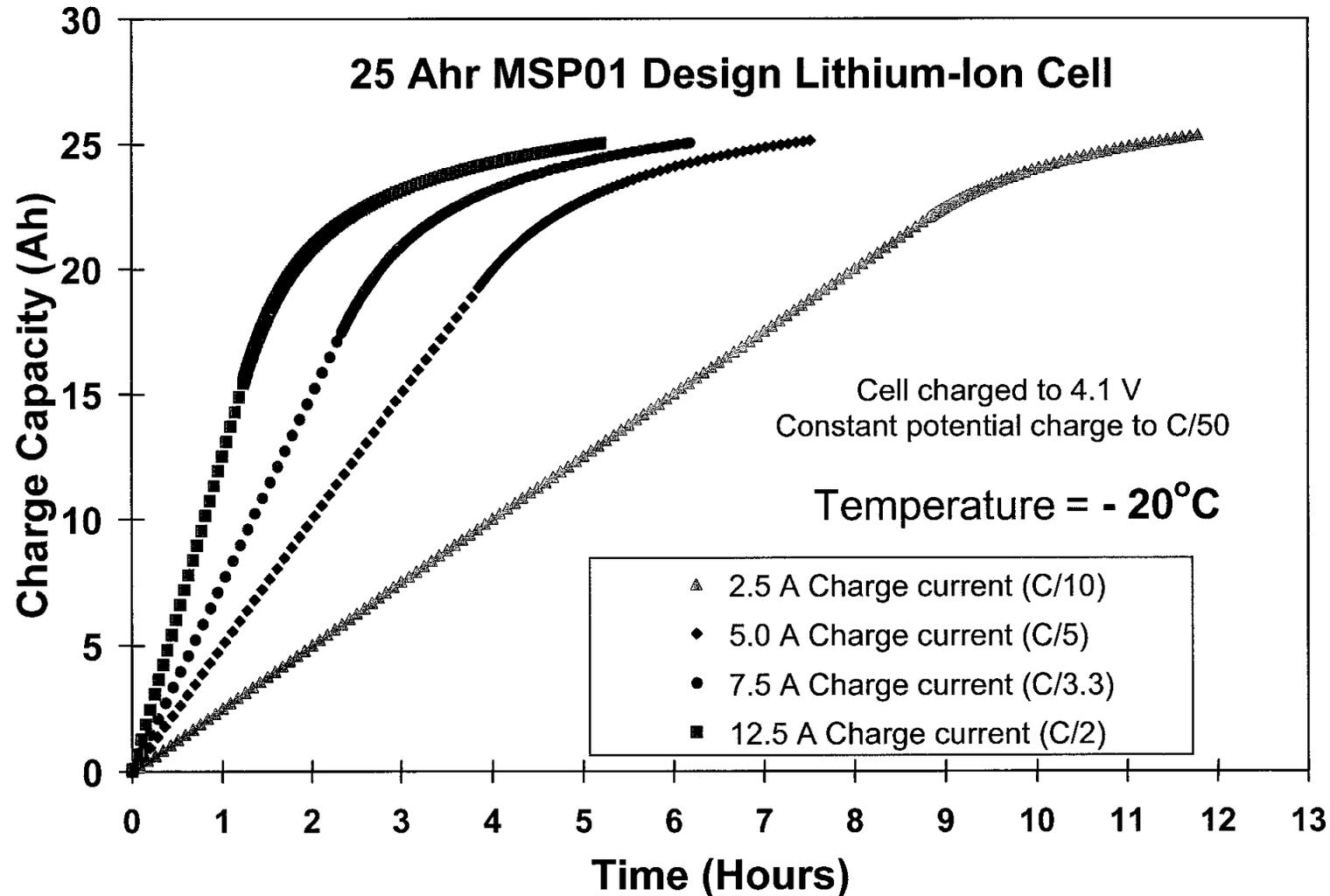
Room Temperature Charge Characteristics





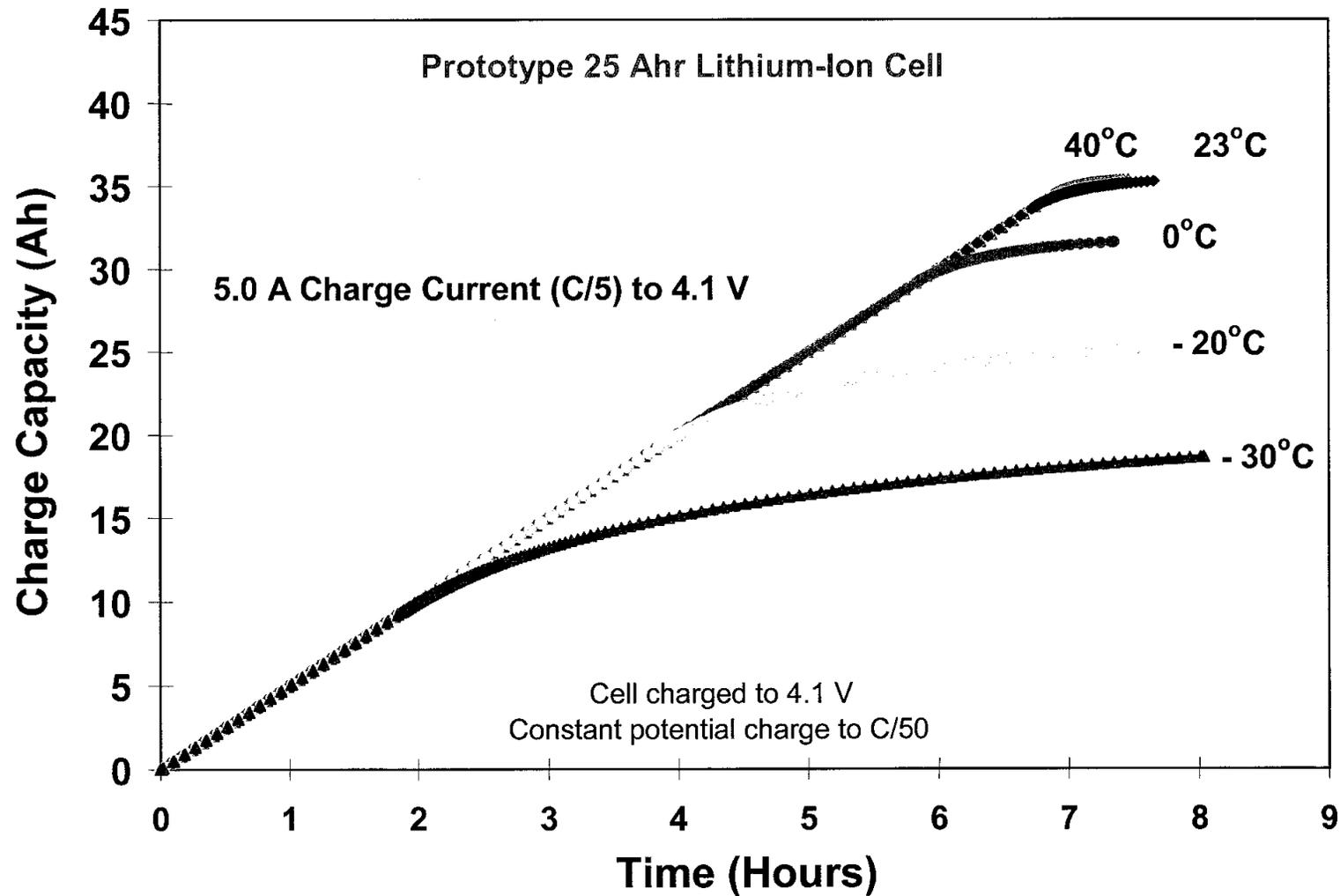
Lithium-Ion Cells for Mars Surveyor 2001 Lander

Low Temperature Charge Characteristics (-20°C)



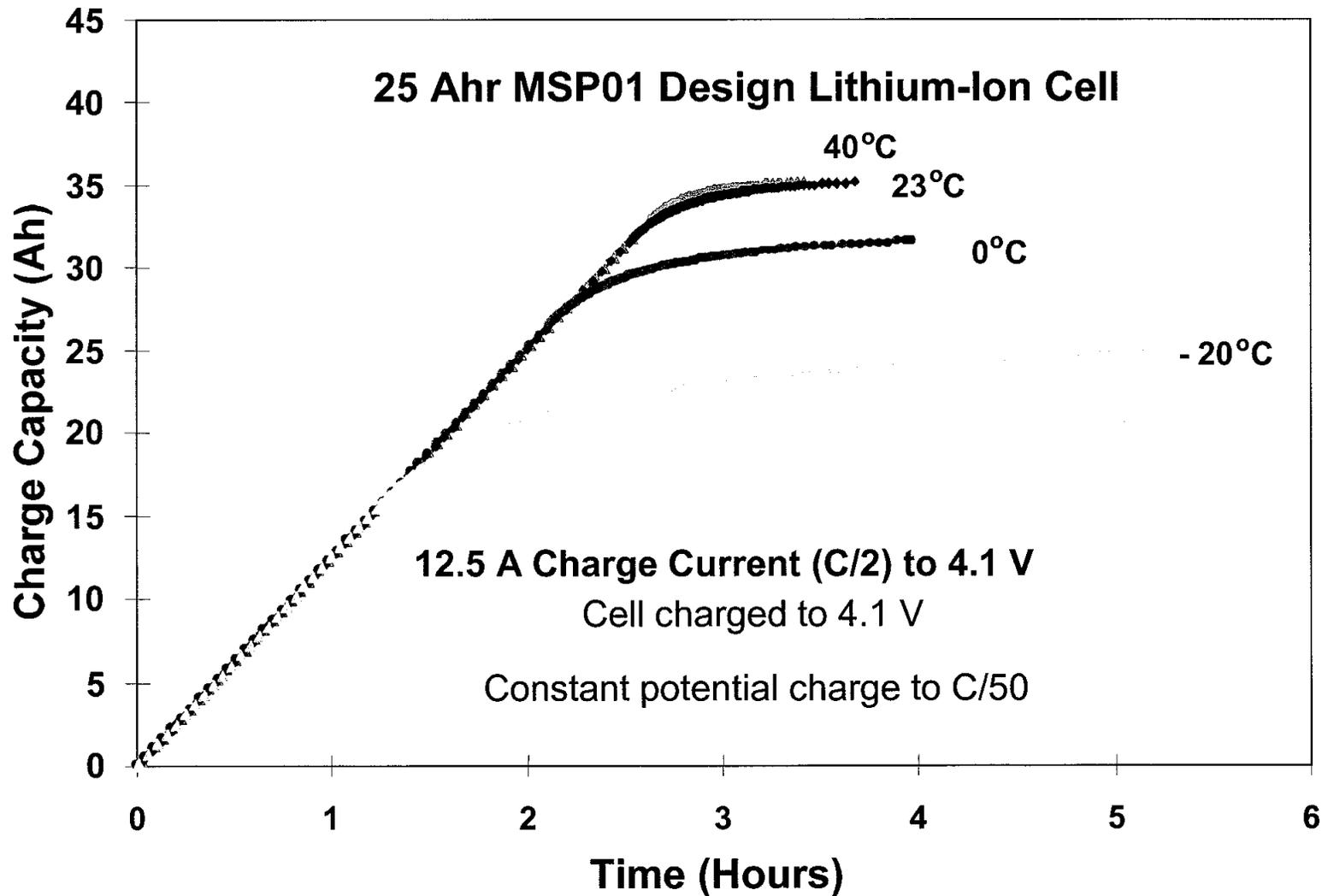


Lithium-Ion Cells for NASA and DoD Applications: Charge Capacity as a Function of Temperature





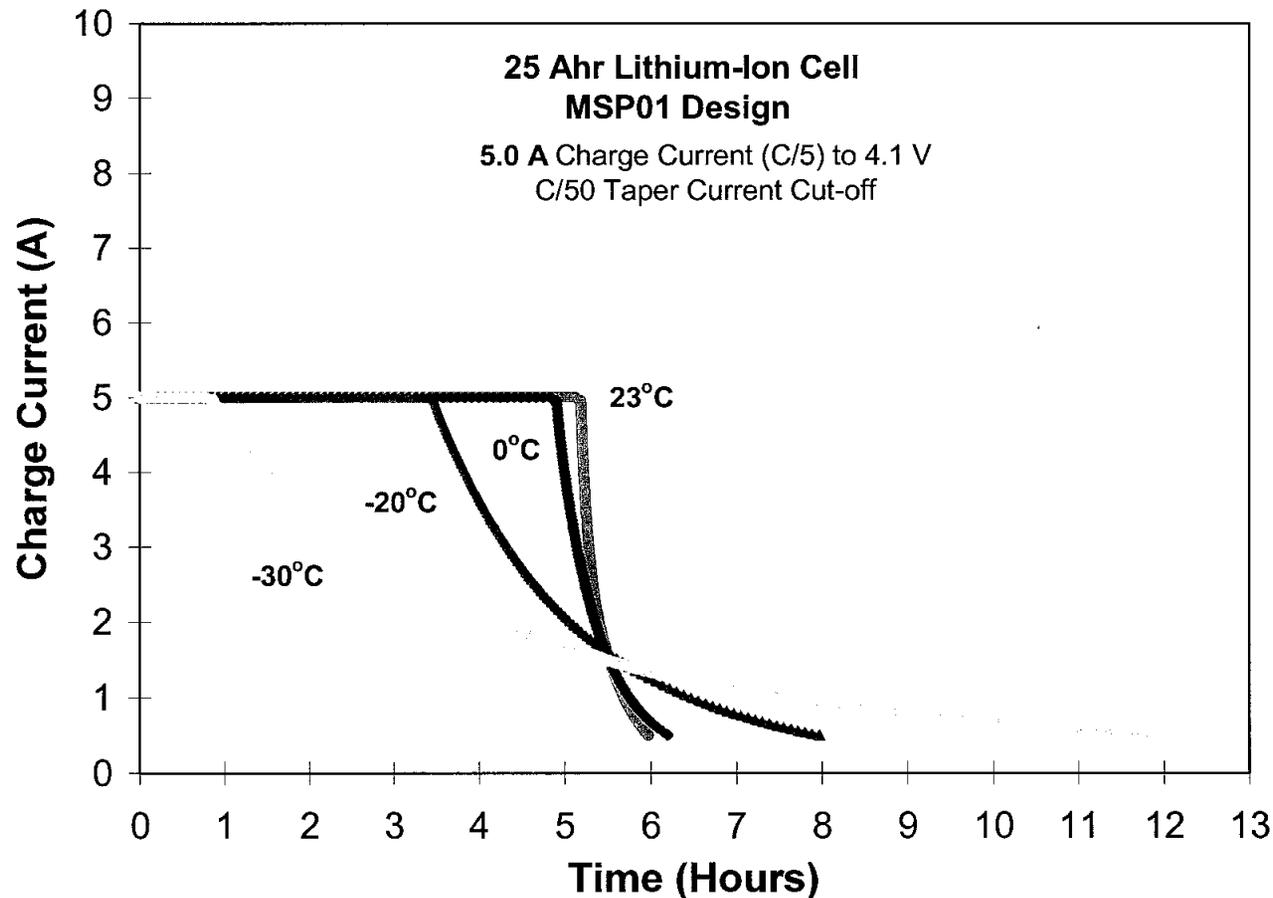
Lithium-Ion Cells for Mars Surveyor 2001 Lander Charge Characteristics as a Function of Temperature





Large Capacity Lithium-Ion Cells for Mars Lander Applications

Charge Characteristics as a Function of Temperature



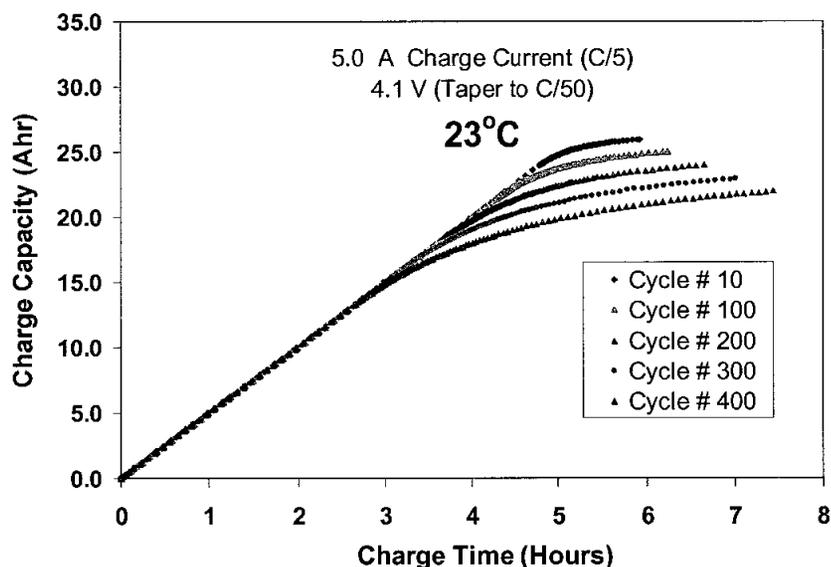
- At lower temperatures, significantly more capacity is obtained while the cell is in the taper mode (constant potential charging).



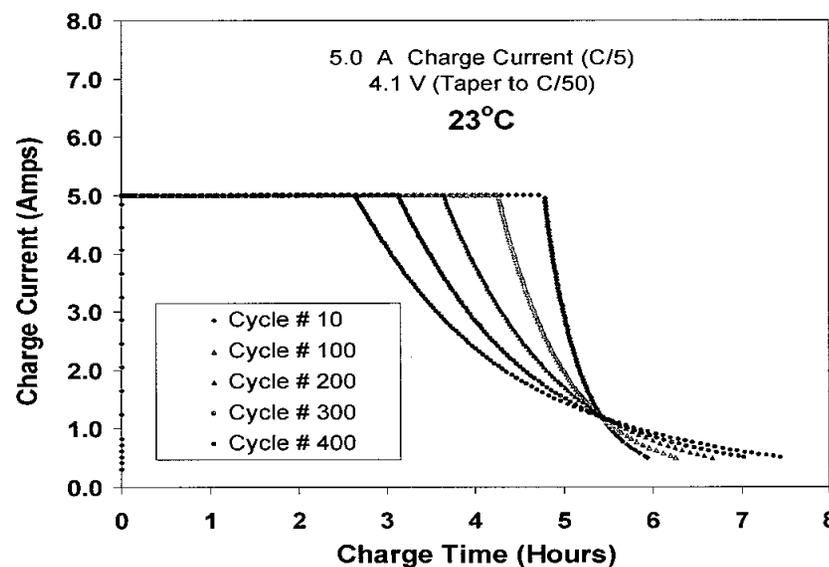
Large Capacity Lithium-Ion Cells for Mars Lander Applications

Effect of Cycle Life on Charge Characteristics

Charge Capacity



Charge Current

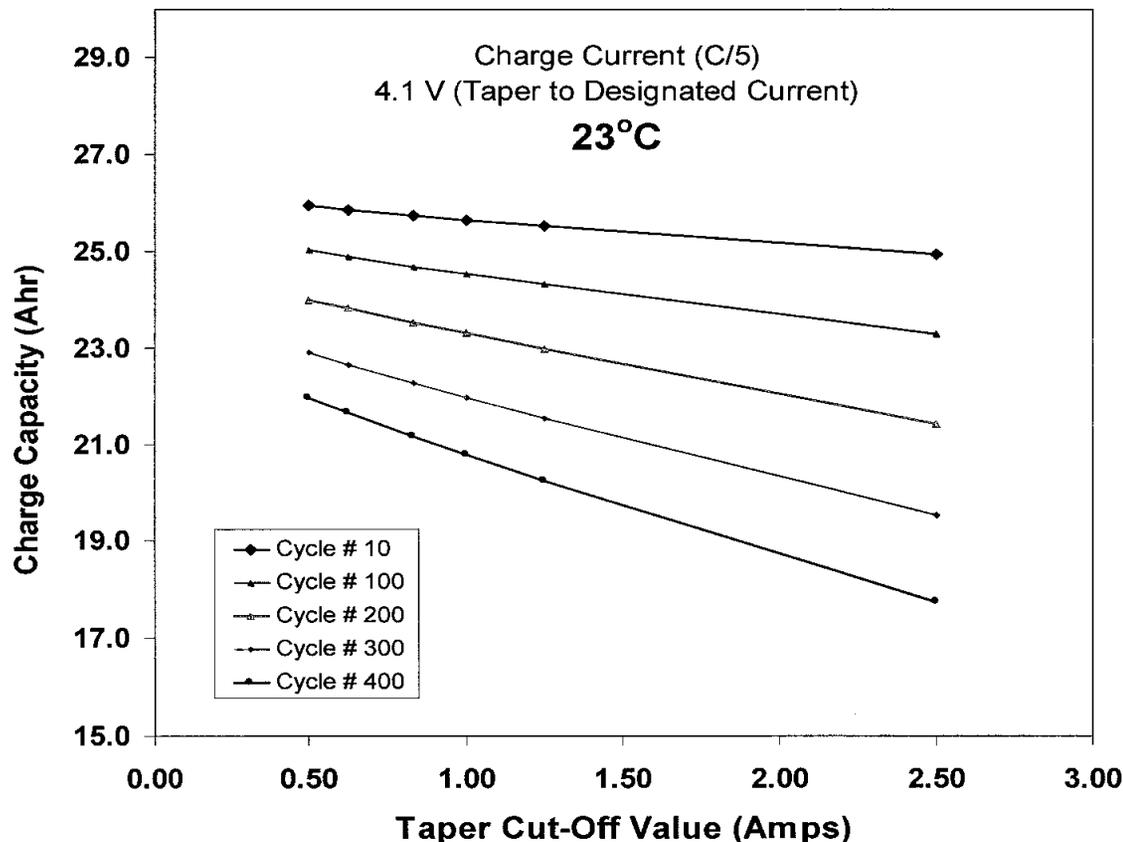


- Later in cell life, significantly more time is spent in the taper mode (constant potential charging) while being charged.
- Due to increased impedance, the overall charge time can increase (even though capacity has declined with cycling).



Large Capacity Lithium-Ion Cells for Future Mars Applications

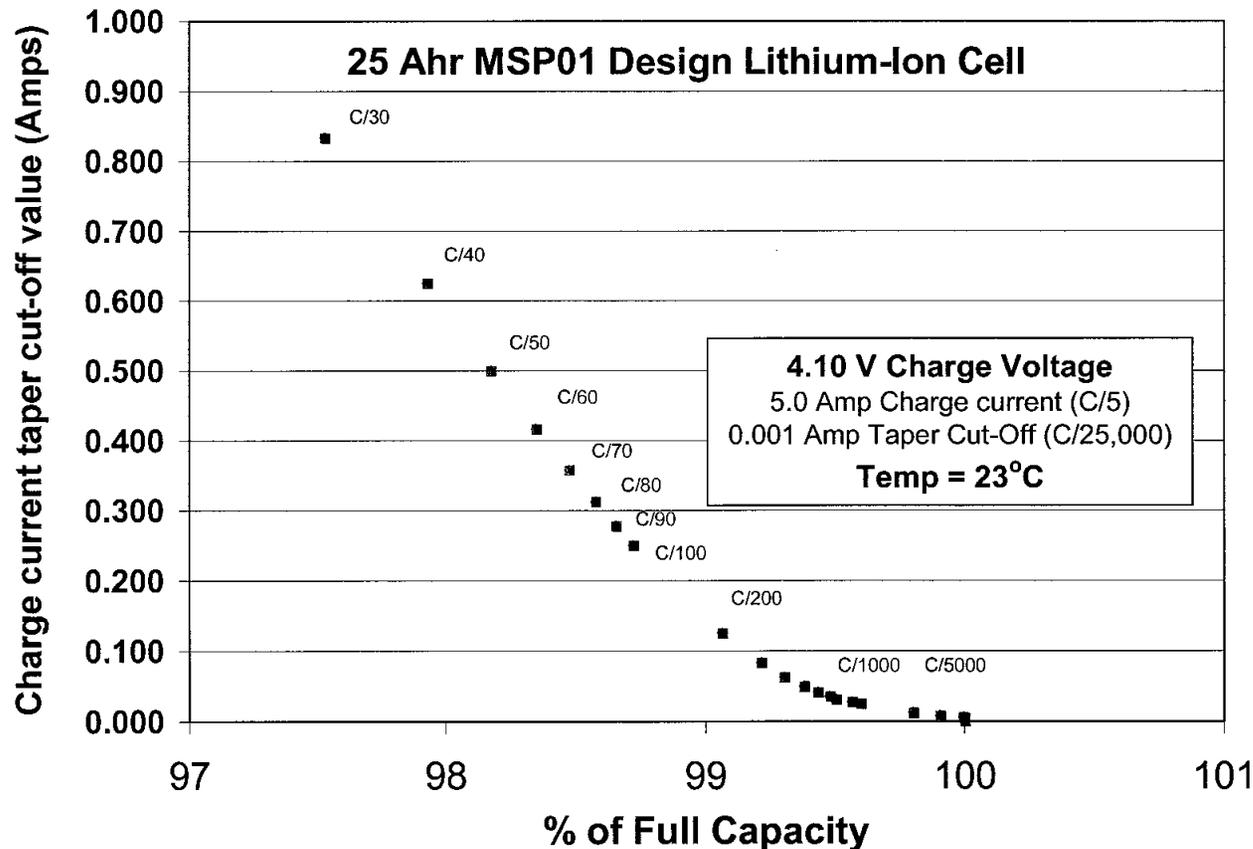
Effect of Cycle Life on Charge Characteristics



- Later in cell life, the impact of the selected taper current cut-off value upon charge capacity is more dramatic (due to increased cell impedance and poorer lithium intercalation/de-intercalation kinetics)



Large Capacity Lithium-Ion Cells for Future Mars Applications Effect of Taper Current on Charge Characteristics

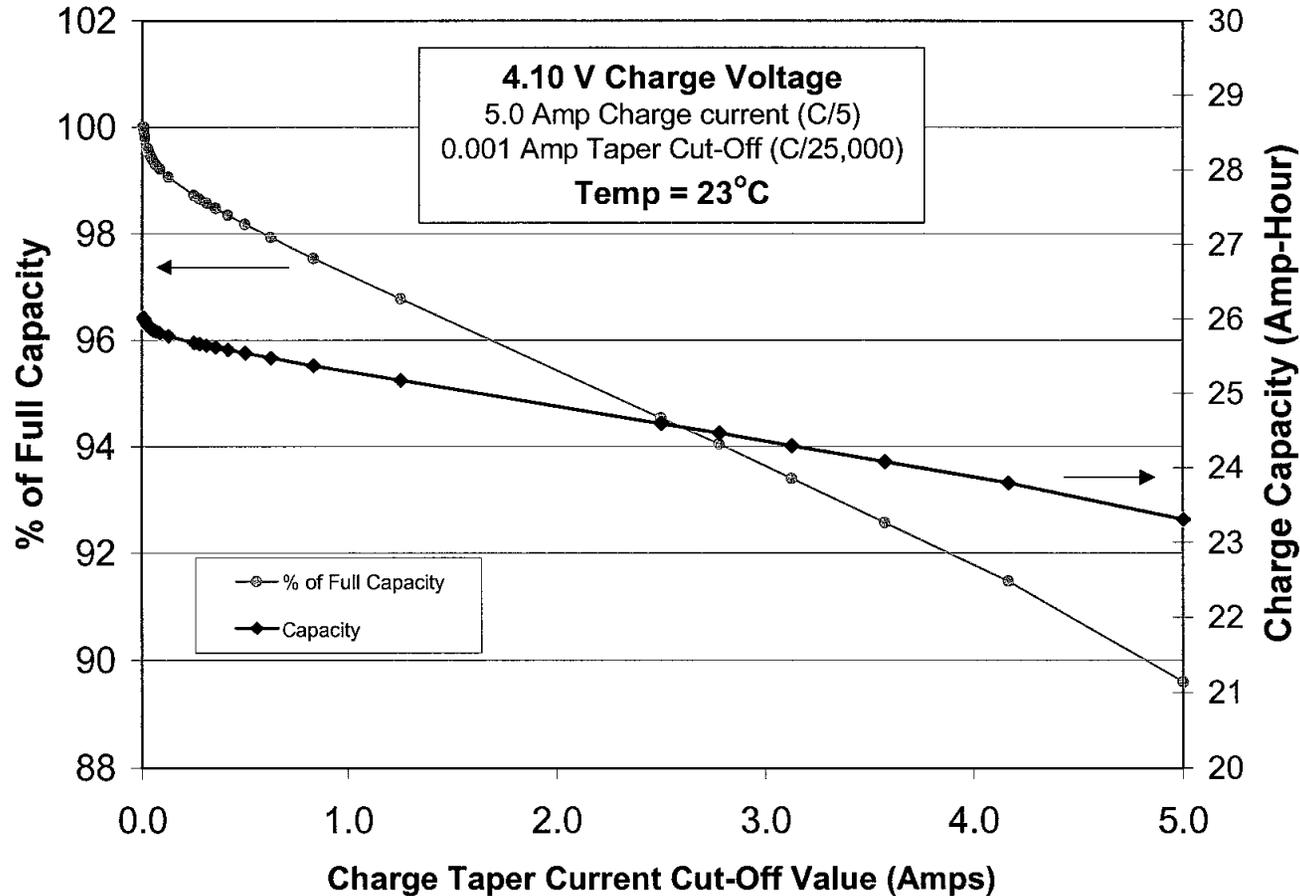


- With a fresh cell, the impact of the taper current cut-off value does not have a dramatic impact upon charge capacity (given that it is $<C/30$ and the constant current charge is of moderate rate ($<C/5$)).



Large Capacity Lithium-Ion Cells for Future Mars Applications

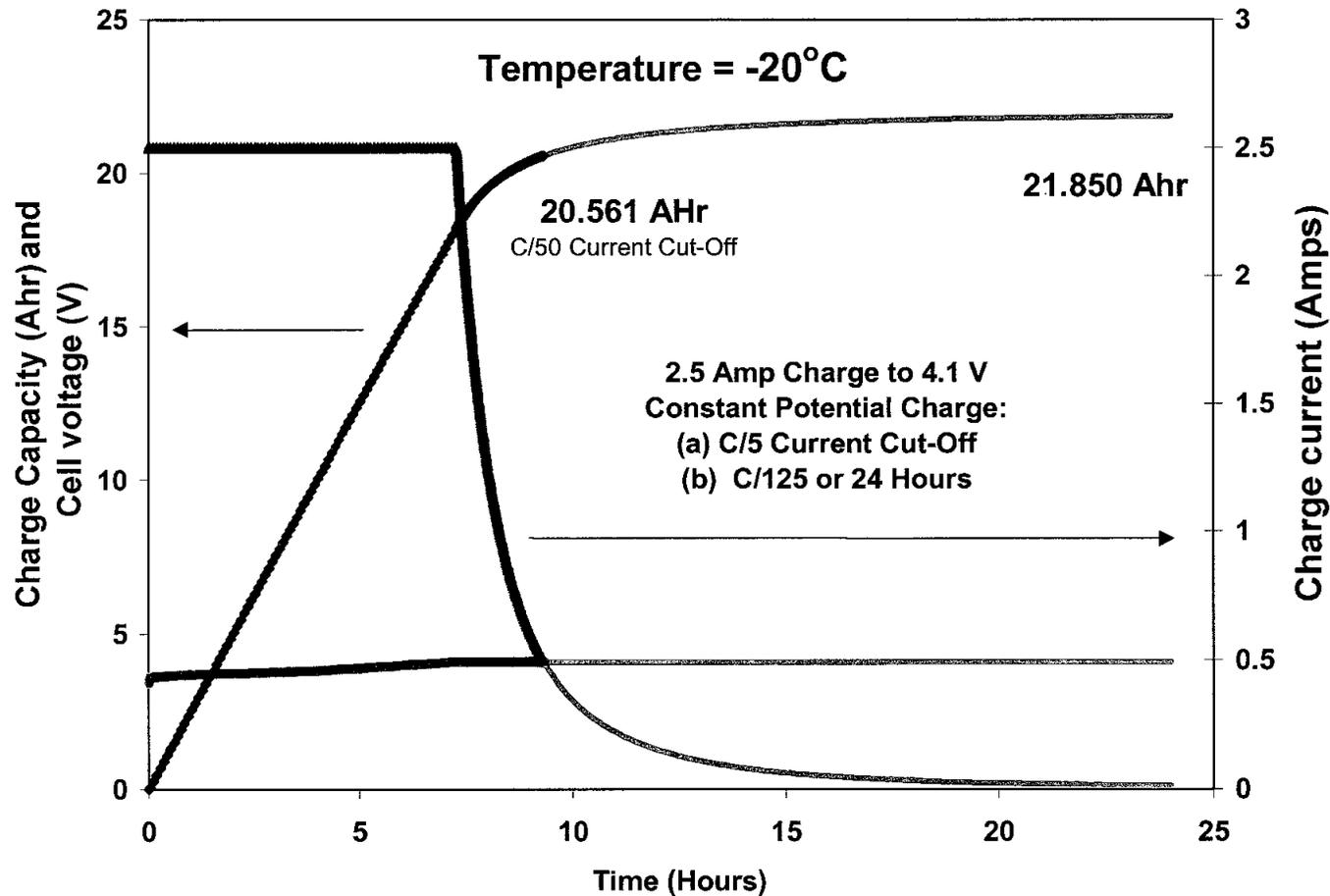
Effect of Taper Current on Charge Characteristics



- With a fresh cell, approximately 10% of the total capacity is obtained in the “taper mode” of the charge

Large Capacity Lithium-Ion Cells for Future Mars Applications

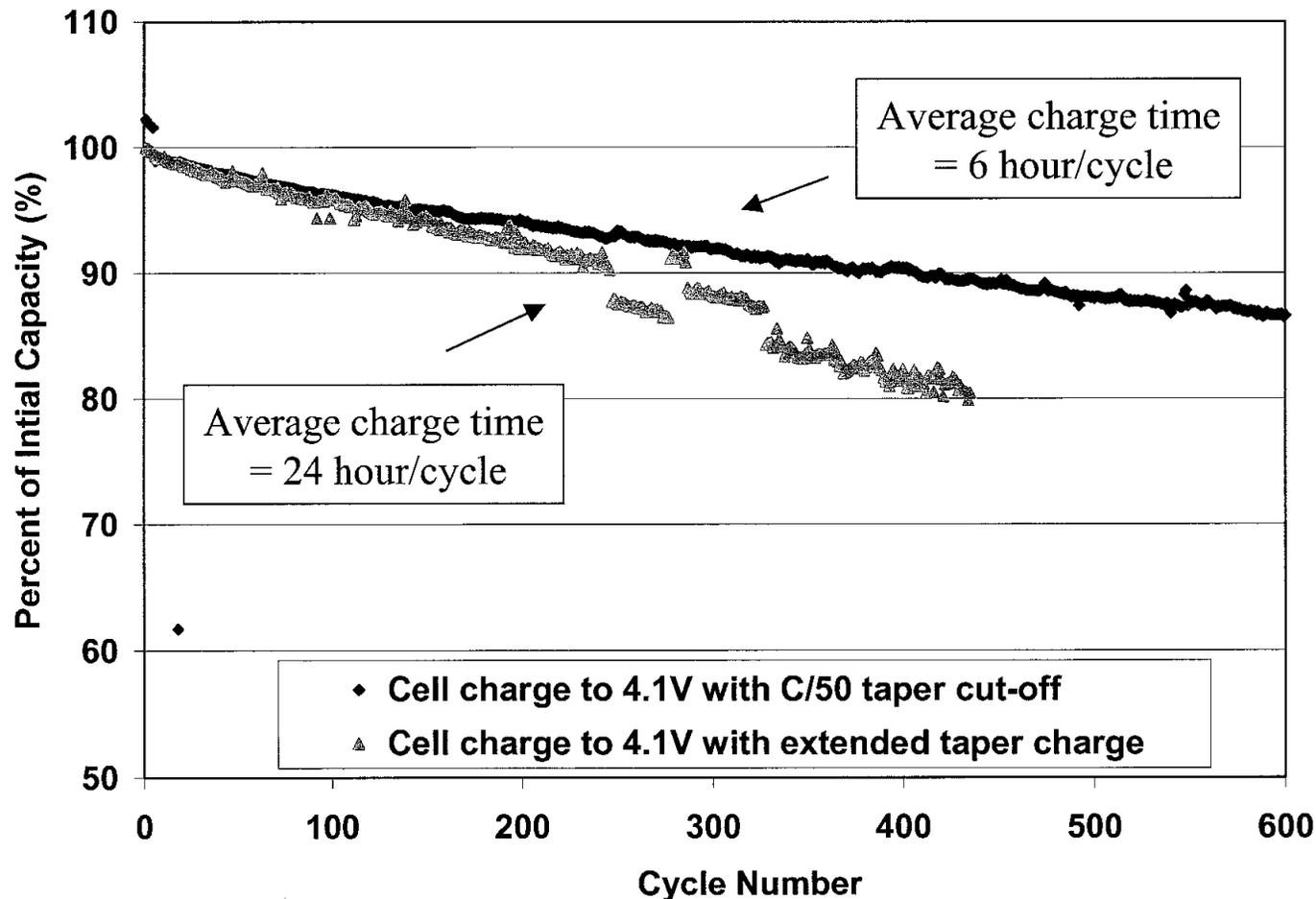
Effect of Taper Current on Charge Characteristics



- At low temperatures (-20°C), approximately 6% more capacity is obtained with an extended “taper mode”.

Large Capacity Lithium-Ion Cells for Future Mars Applications

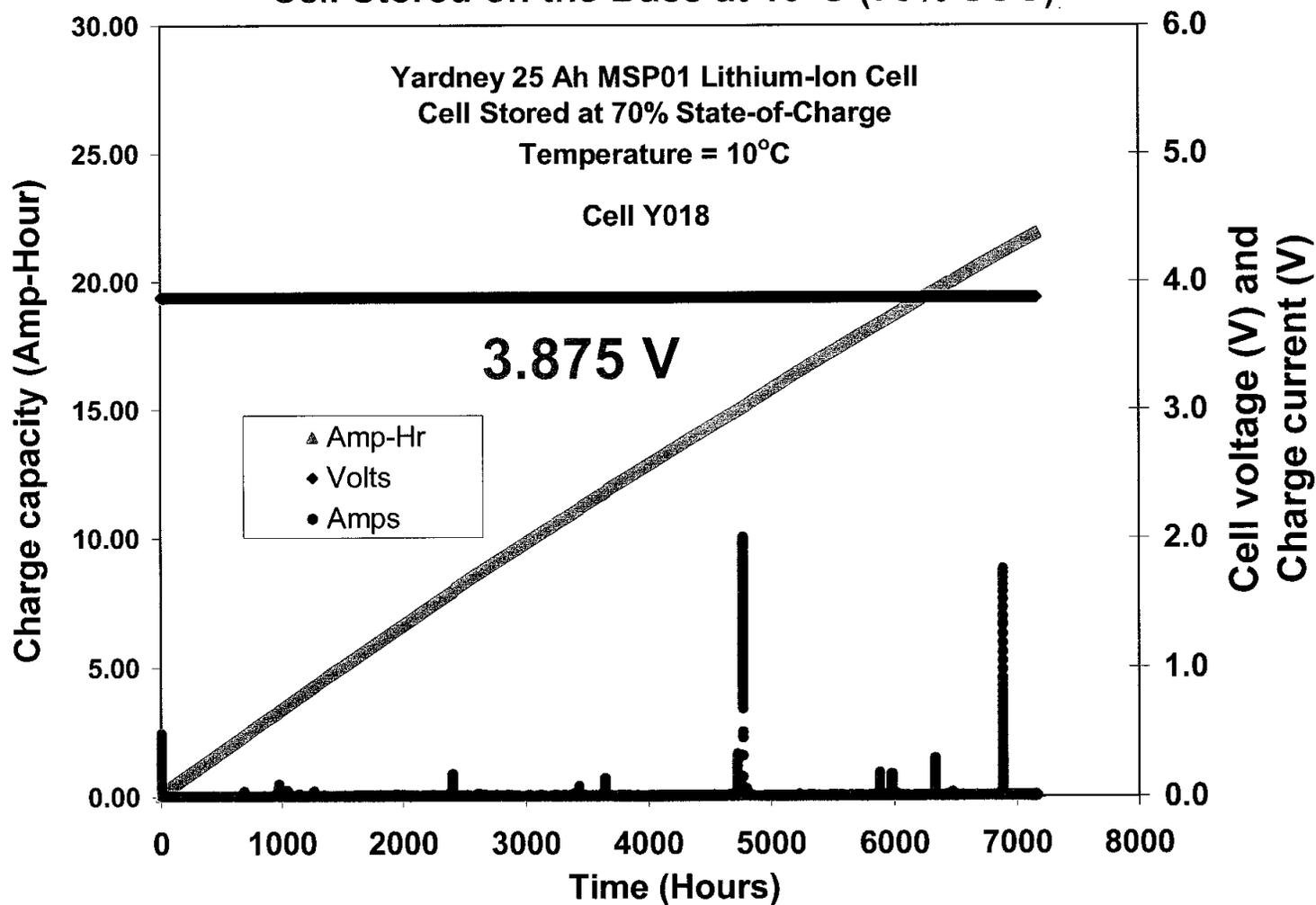
Effect of Taper Current on Charge Characteristics



- Extended taper charging appears to limit cycle life characteristics (similar to floating at high V).
- Capacity decline most likely due to enhanced impedance build-up and increased electrolyte oxidation



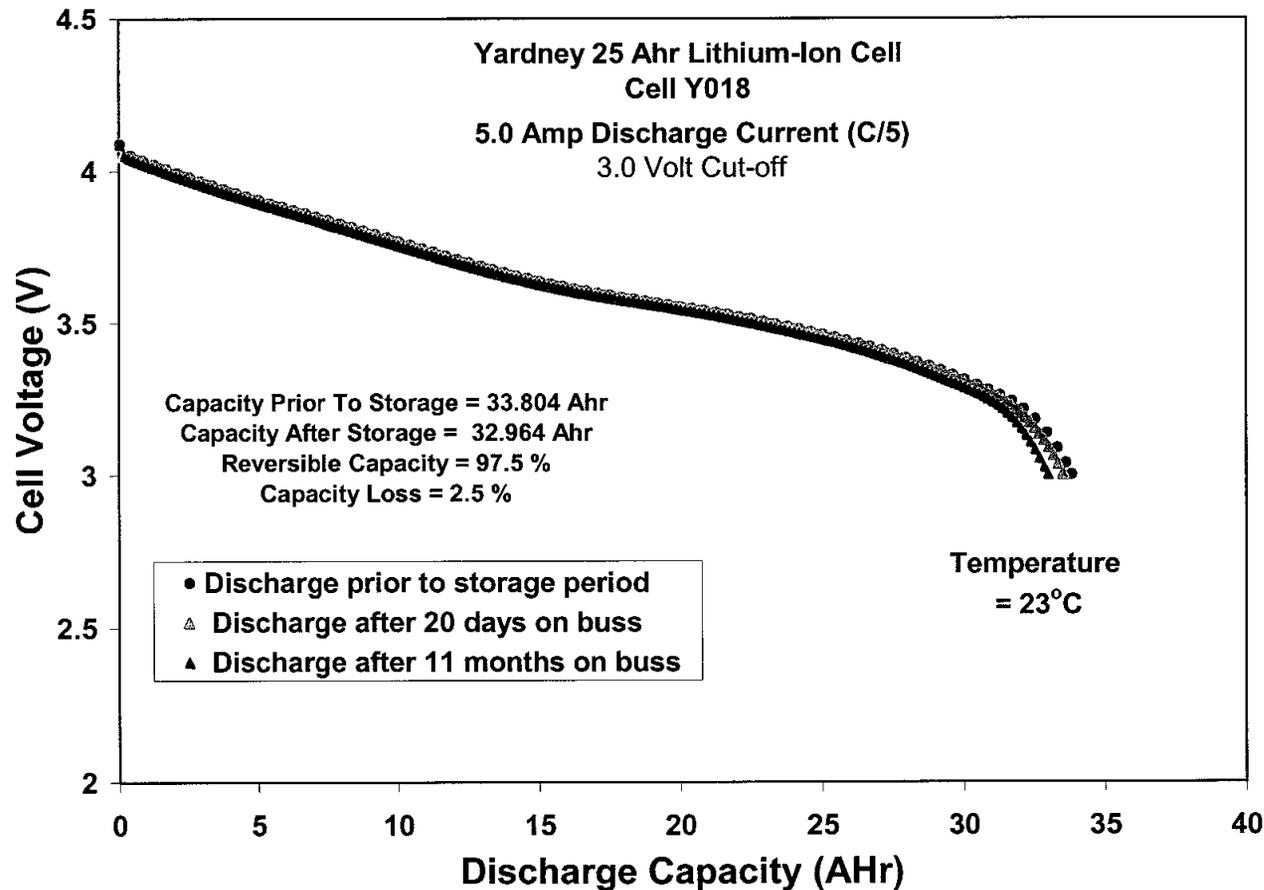
Lithium-Ion Cells for NASA and DoD Applications: Storage Characteristics of a 25 Ahr Cell- Results of 11 Month Storage Test Cell Stored on the Buss at 10°C (70% SOC)





Lithium-Ion Cells for NASA and DoD Applications:

Storage Characteristics of a 25 Ahr Cell- Results of 11 Month Storage Test Cell Stored on the Buss at 10°C (70% SOC)

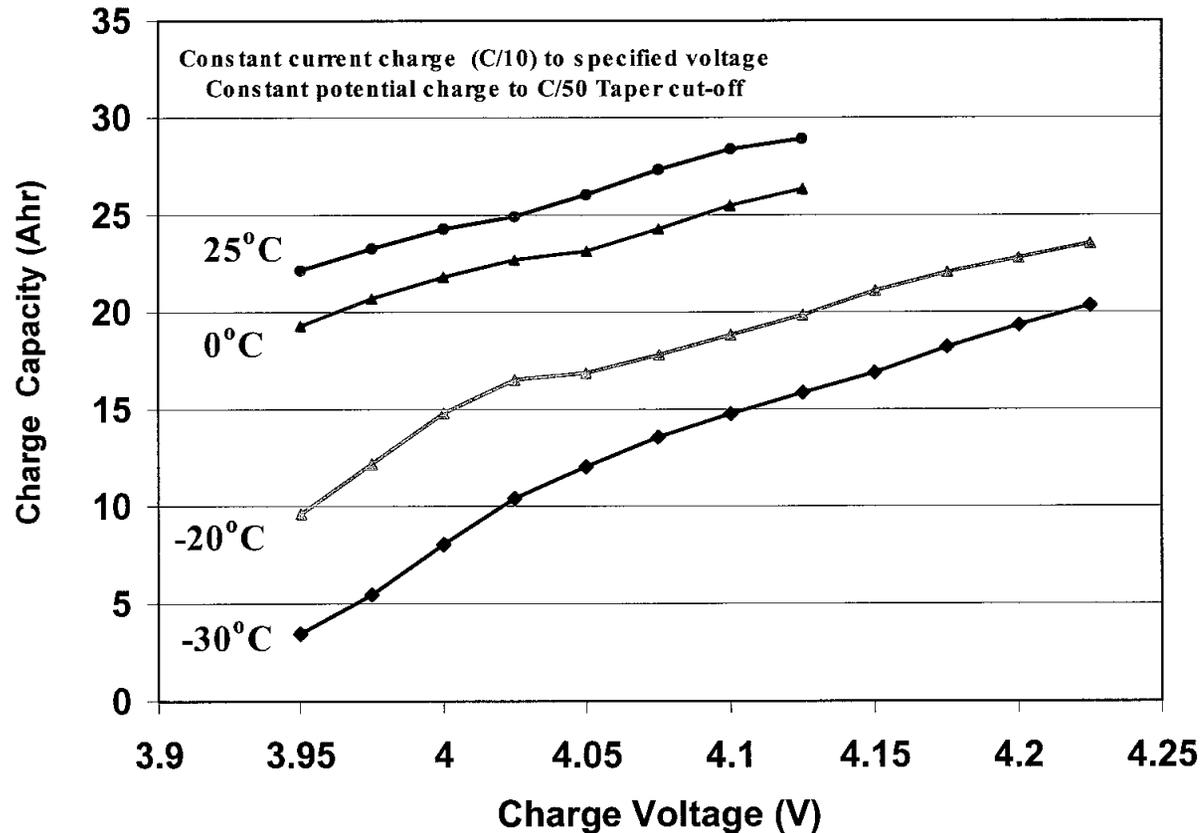


- Float charging (storage on the bus) results in minimal cell performance degradation if a moderately low voltage (low SOC) is selected.



Large Capacity Lithium-Ion Cells for Future Mars Applications

Effect of Charge Voltage on Charge Characteristics

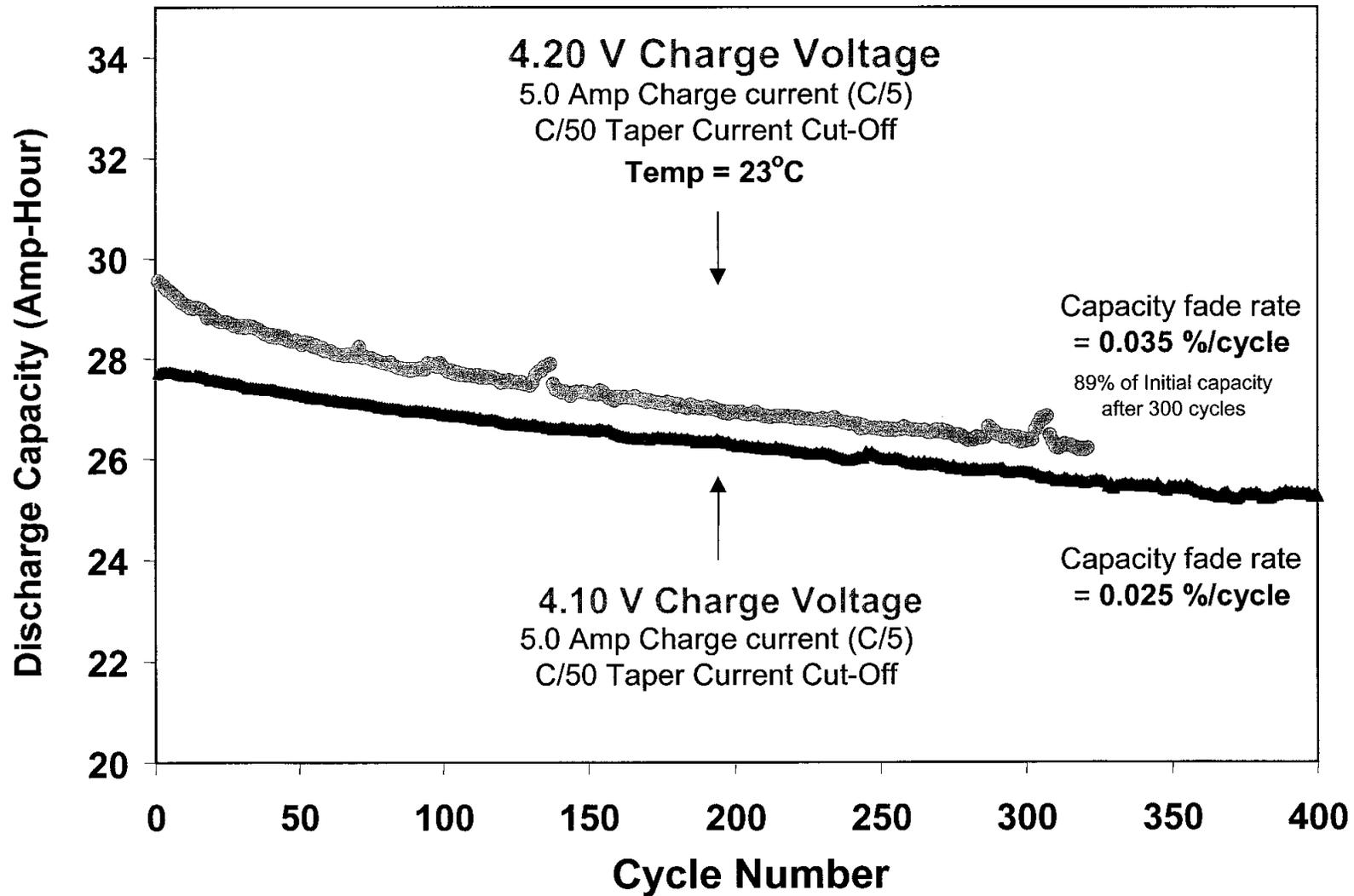


- Selected charge voltage has a more dramatic impact upon charge capacity at lower temperatures.
- Although charging to higher voltages yields higher capacity, it may also be accompanied by undesirable effects (i.e., electrolyte oxidation and/or lithium plating)



Large Capacity Lithium-Ion Cells for Future Mars Applications

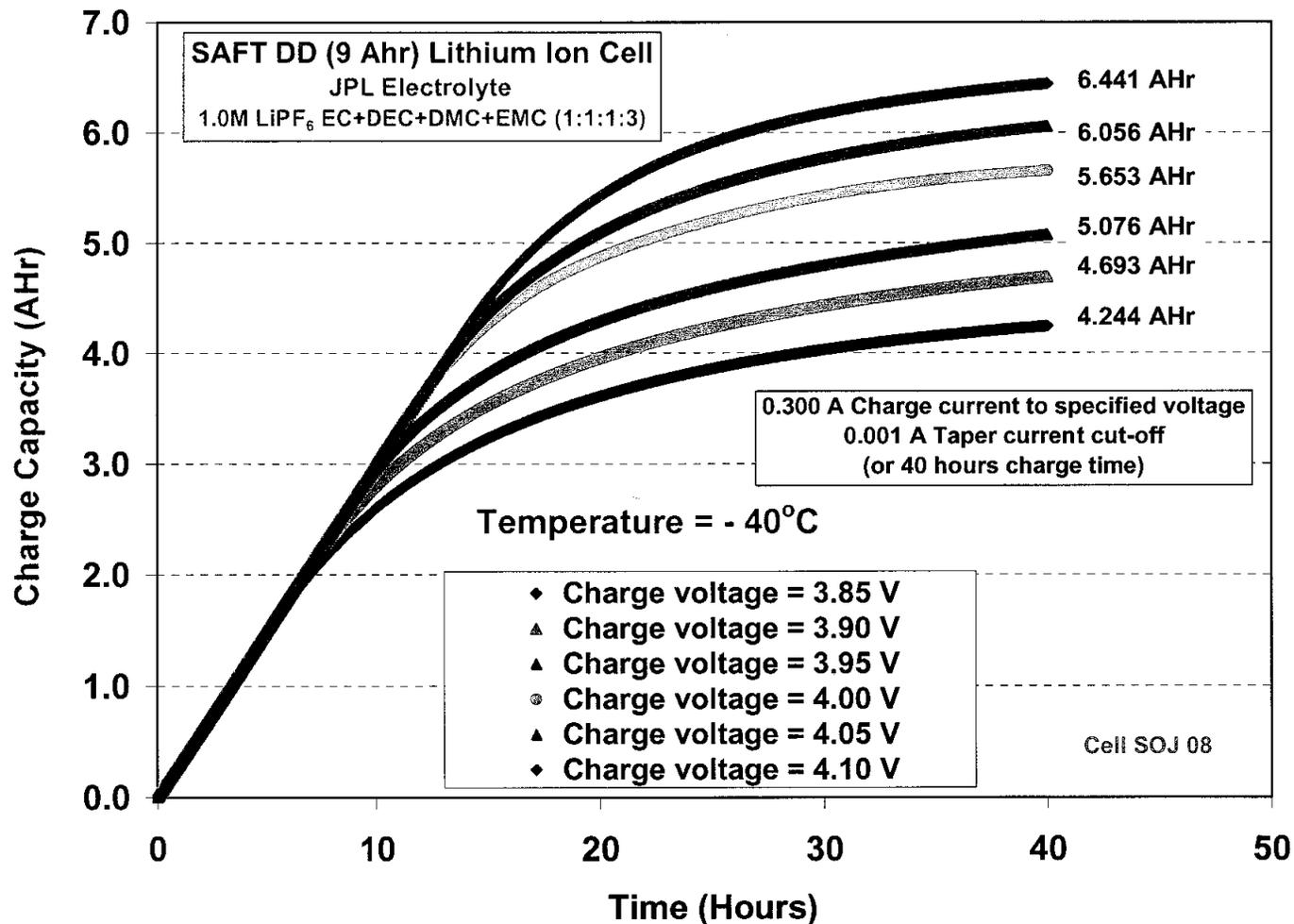
Effect of Charge Voltage on Cycle Life Characteristics



SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications

Cell Performance at Low Temperatures: JPL Electrolyte

Effect of Charge Voltage at - 40°C

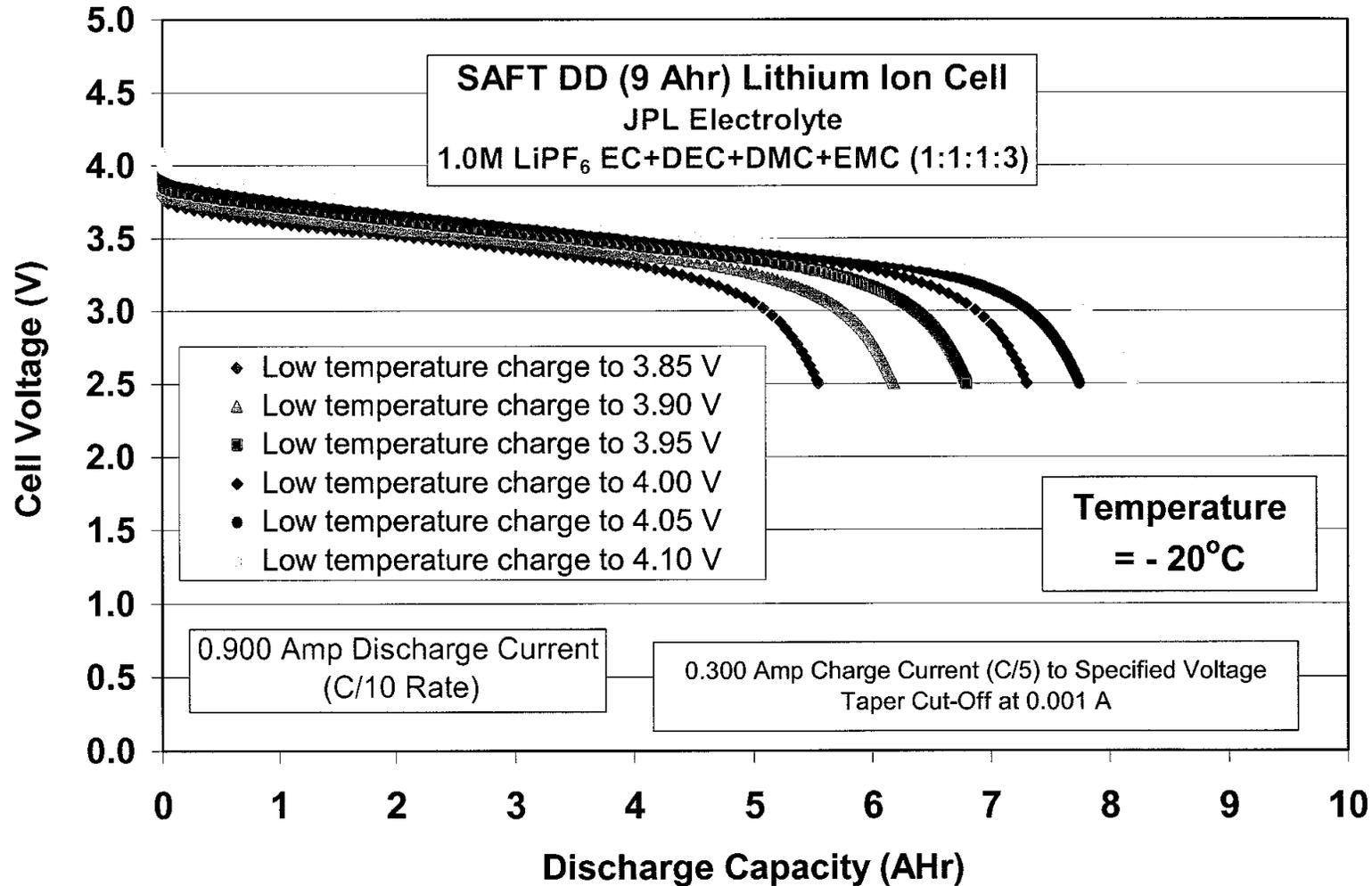




SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications

Cell Performance at Low Temperatures: JPL Electrolyte

Discharge Capacity (Ahr) – C/3 Rate (3.0 A)

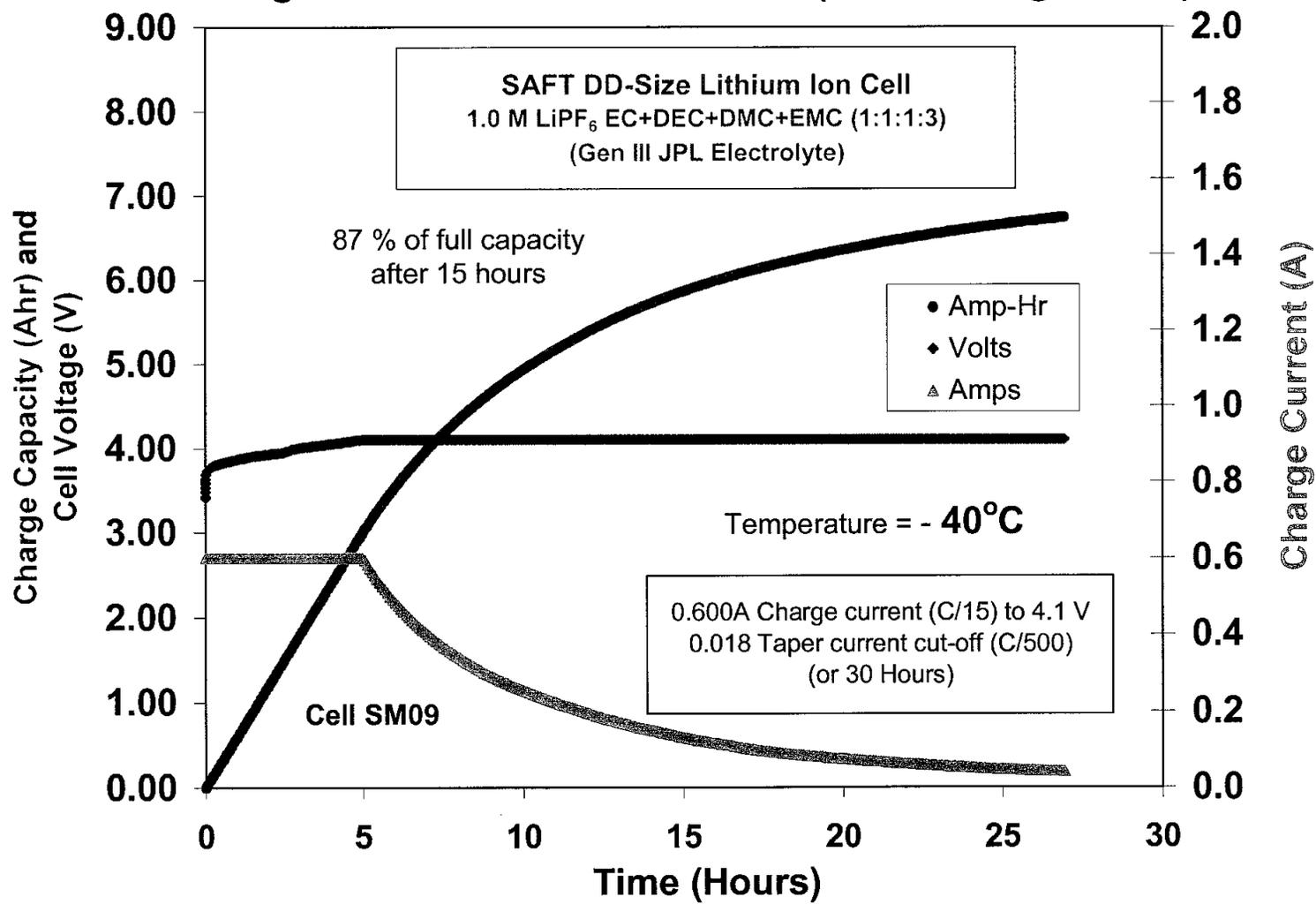




SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications

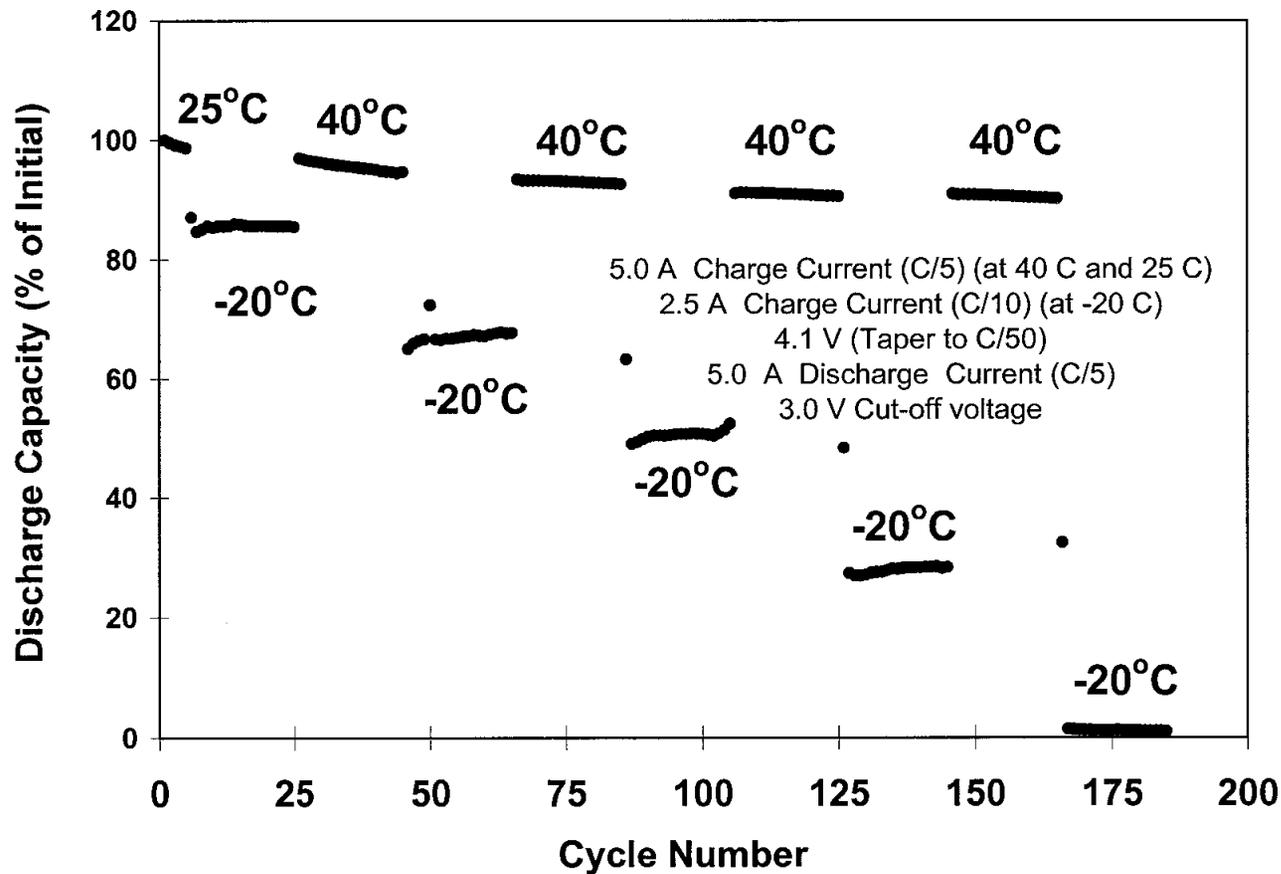
Performance with Improved Anode Material and JPL Electrolyte

Charge characteristics at -40°C (C/15 Charge Rate)



Large Capacity Lithium-Ion Cells for Future Mars Applications

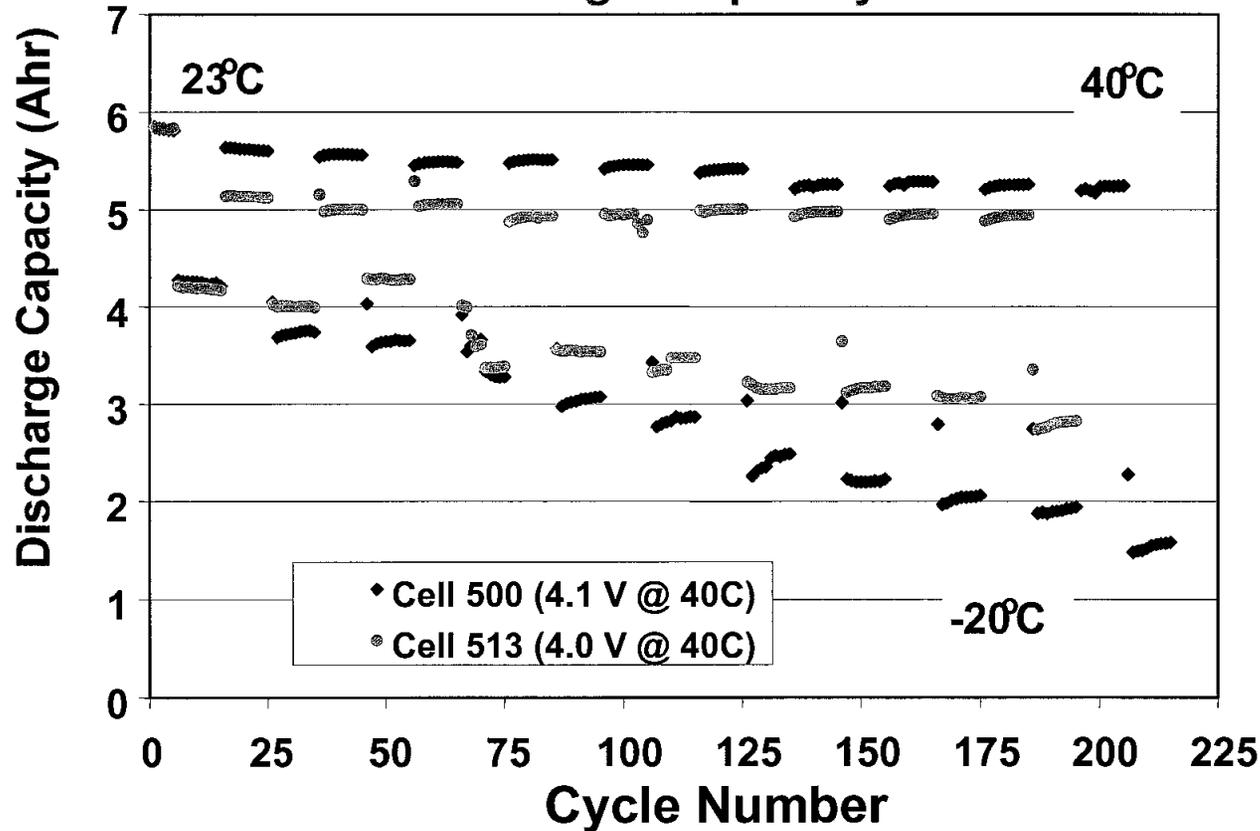
Cycle Life Performance at Varying Temperatures



- An increase in cell impedance and a decrease in low temperature performance capability was observed upon cycling between two temperature extremes.
- It was ascertained that the *charge voltage at high temperature* can influence trend.



Lithium-Ion Cells for NASA and DoD Applications: Rover Cell Design - Variable Temperature Cycling Discharge Capacity

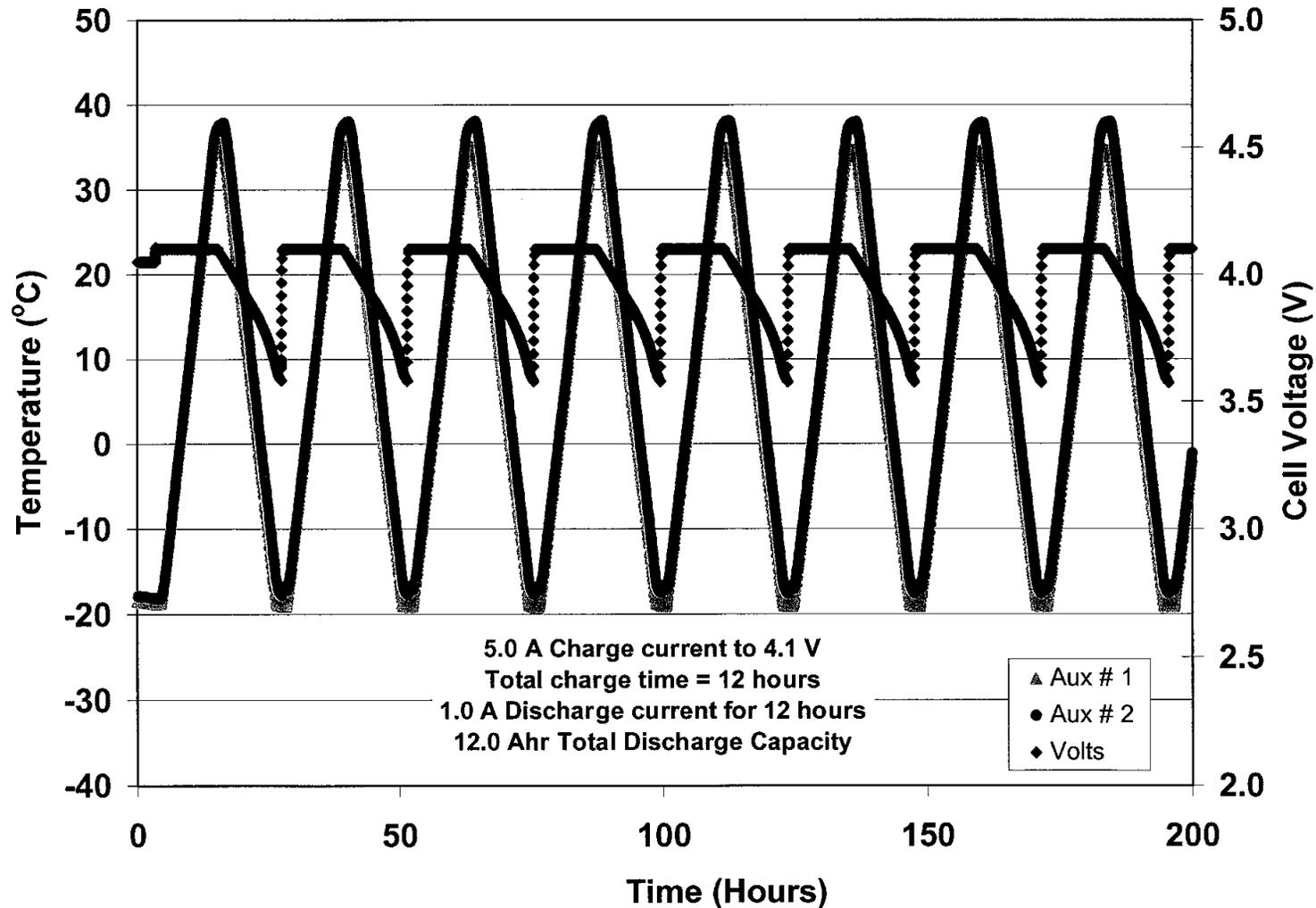


- Using lower charge voltages at high temperatures was observed to preserve the low temperature performance capability and extend life characteristics.



Lithium-Ion Cells for Mars Lander Applications

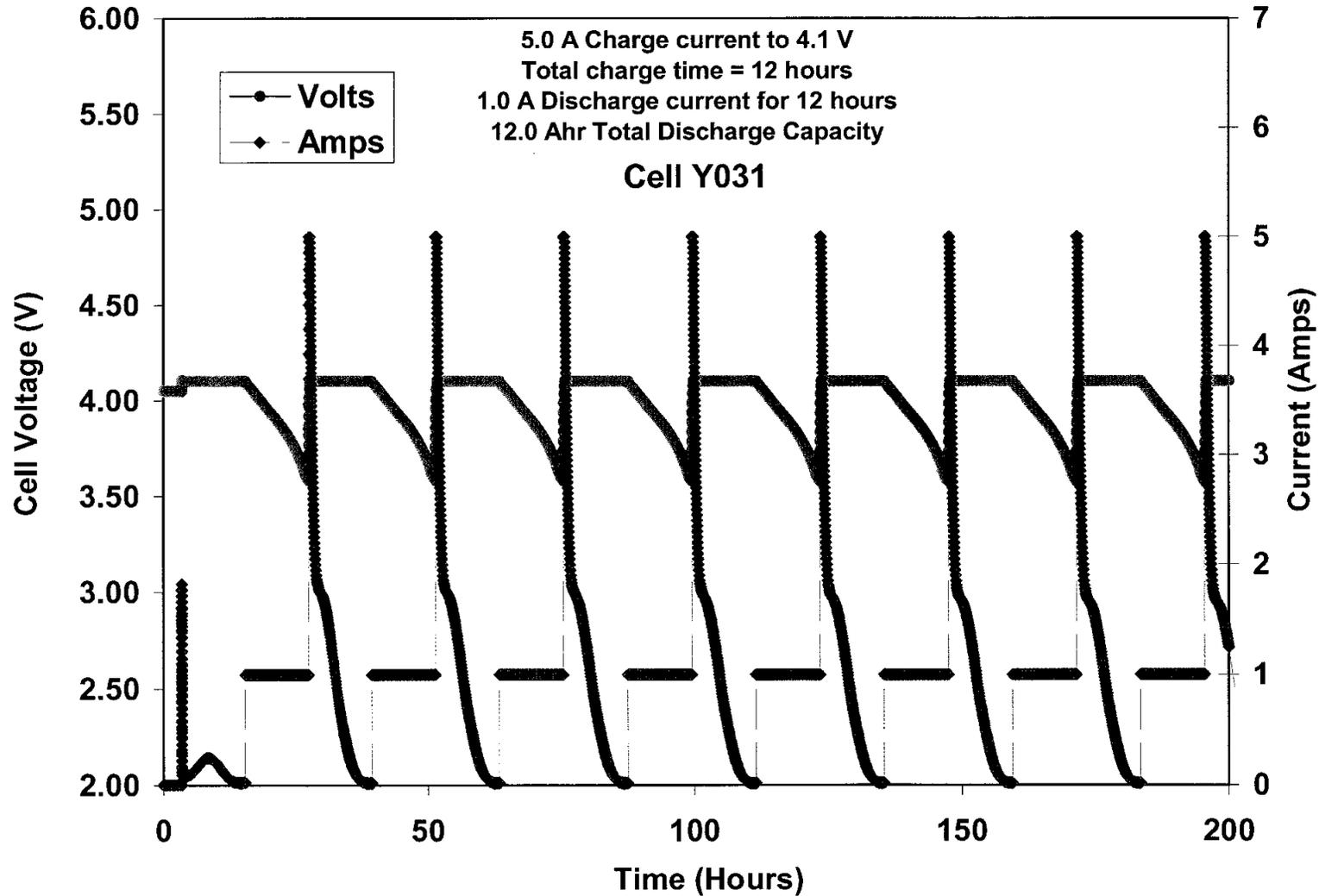
Mission Simulation Cycling (Temperature Range = - 20 to +40°C)





Lithium-Ion Cells for Mars Lander Applications

Mission Simulation Cycling



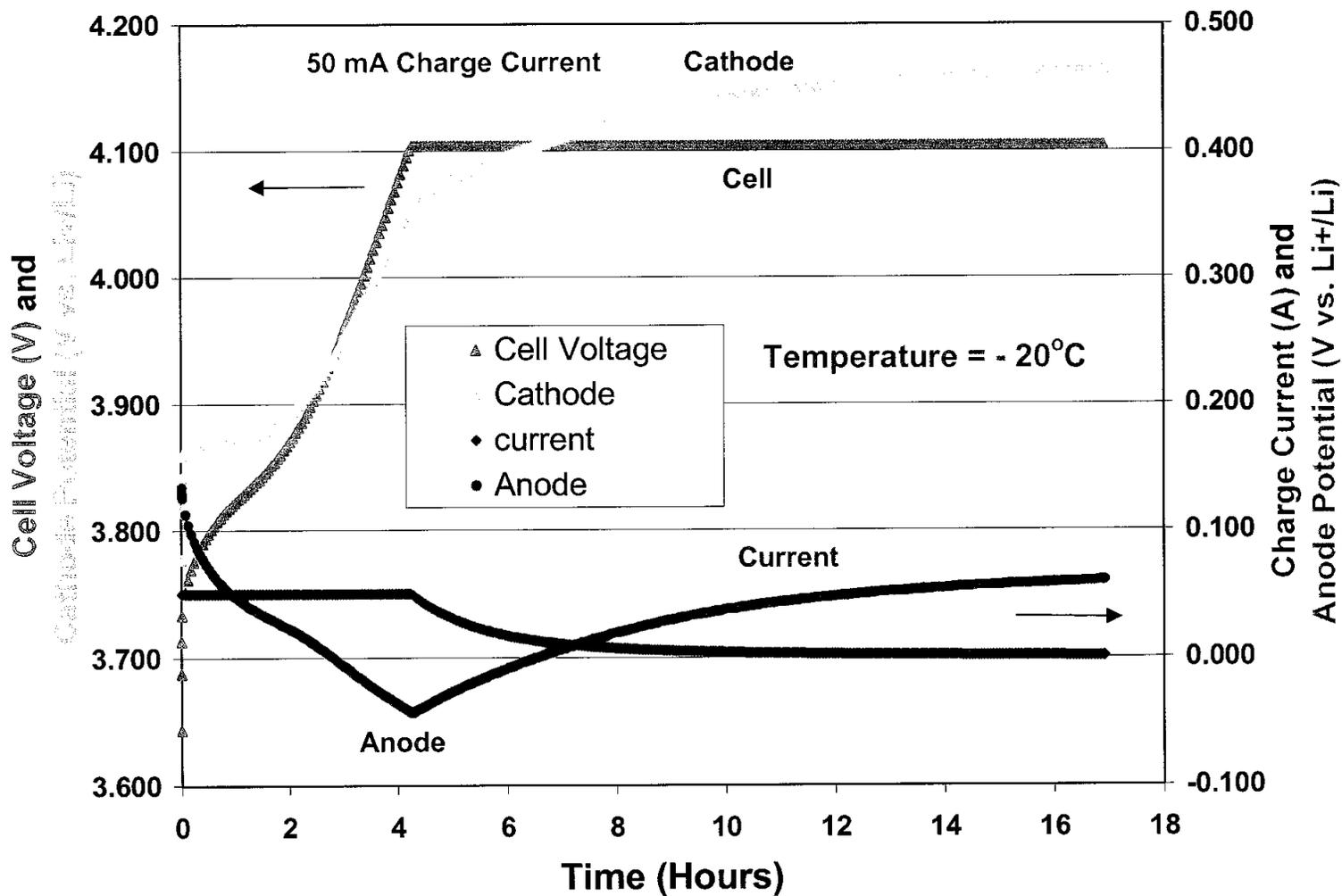


Charge Characteristics of Experimental Lithium Ion Cells (Three Electrode Cells)

- **Charge acceptance at various rates and temperatures**
 - Various chemistries, cell designs and sizes
 - Range of charge rates investigated (C/20 to C rate)
 - Range of Temperatures investigated (-40° to +40°C)
- **Effect of Charge Methodology Upon Cycle Life Performance**
 - Effect of charge voltage
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- **Effect of charge voltage upon cell performance**
 - V/T characterization



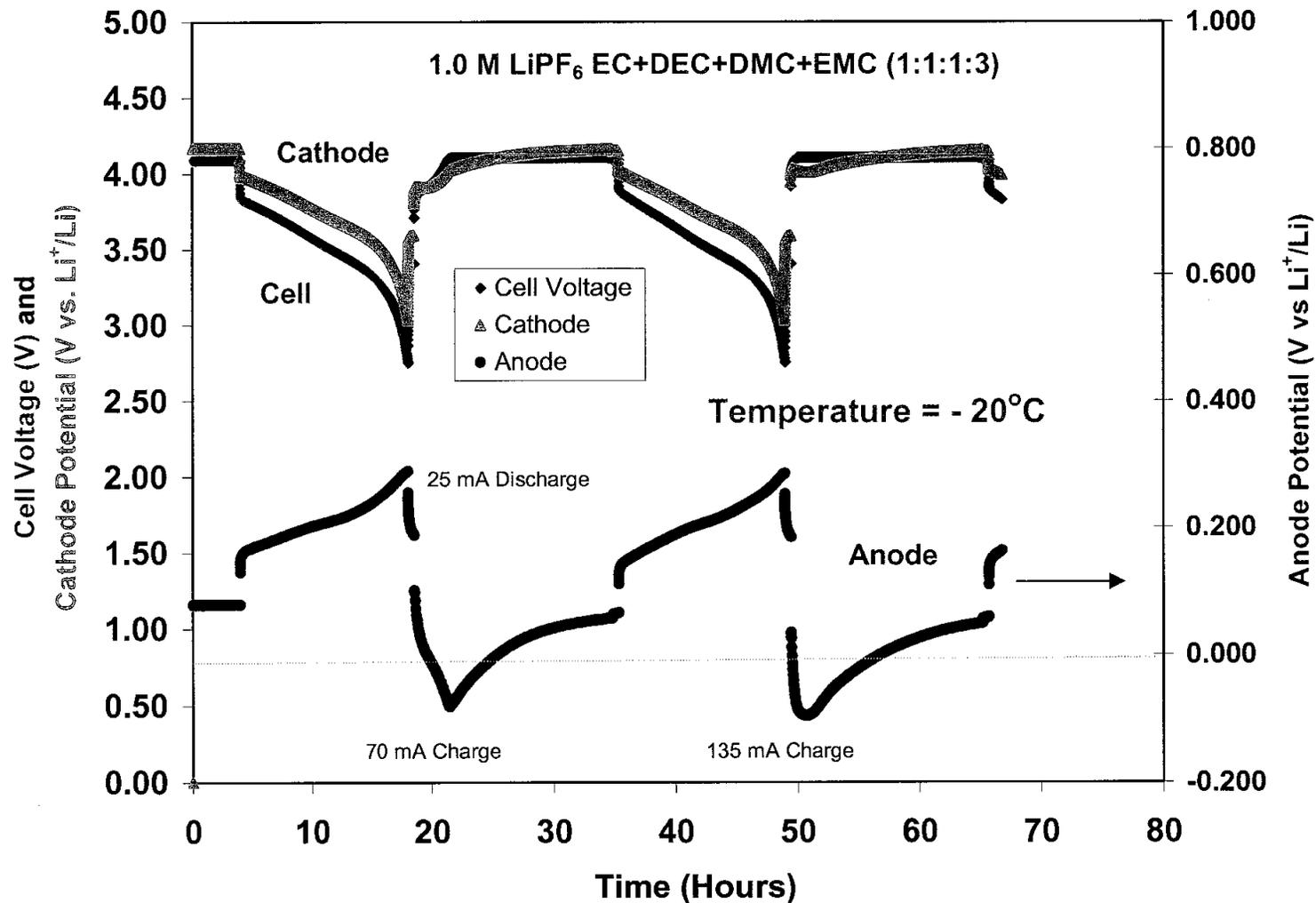
Charge Characteristics of Experimental Lithium Ion Cells Effect of Charging at Low Temperature (- 20°C)





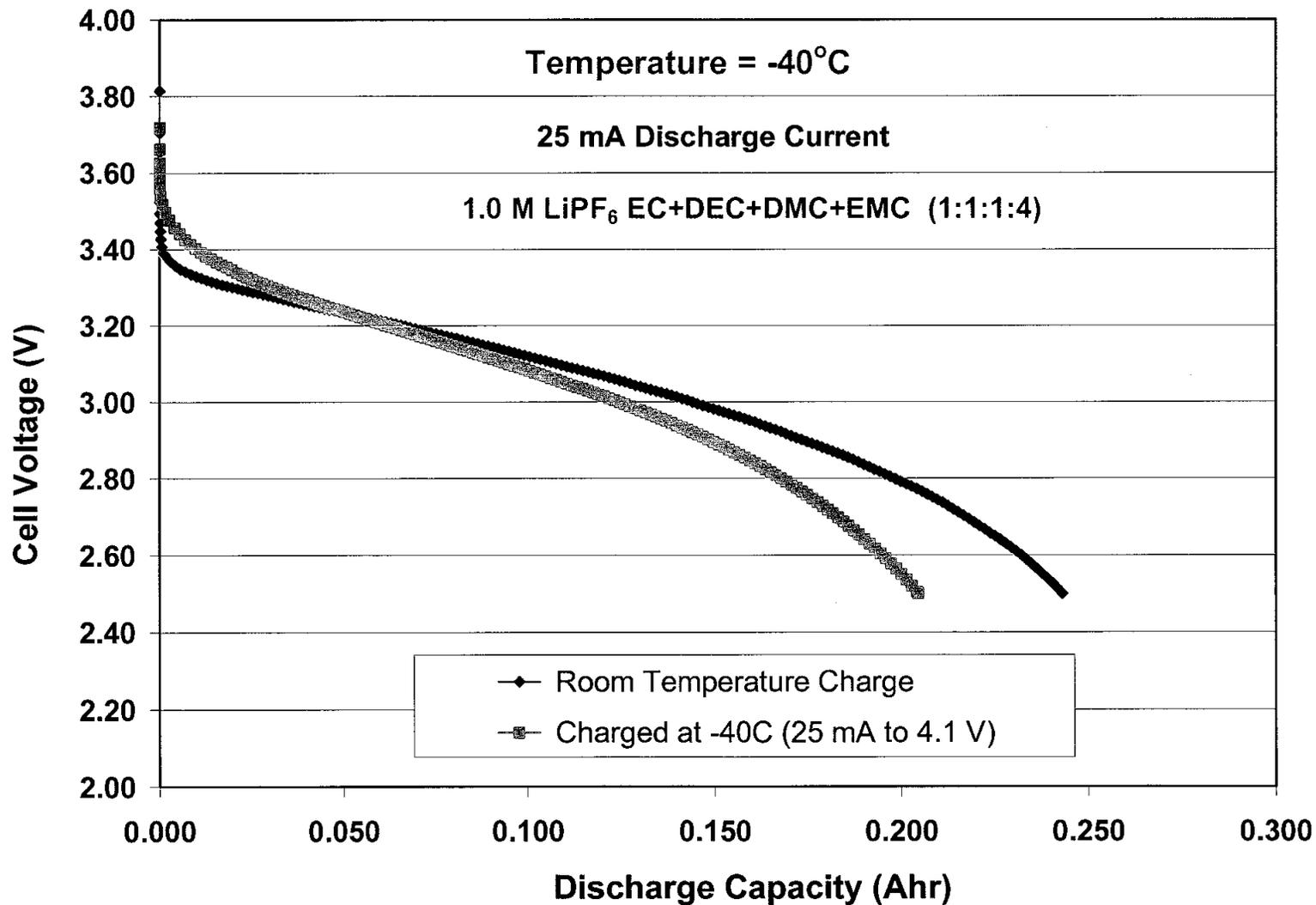
Low Temperature Performance of MCMB-LiNiCoO₂ Experimental Cells

Effect of Electrolyte Upon Low Temperature Performance

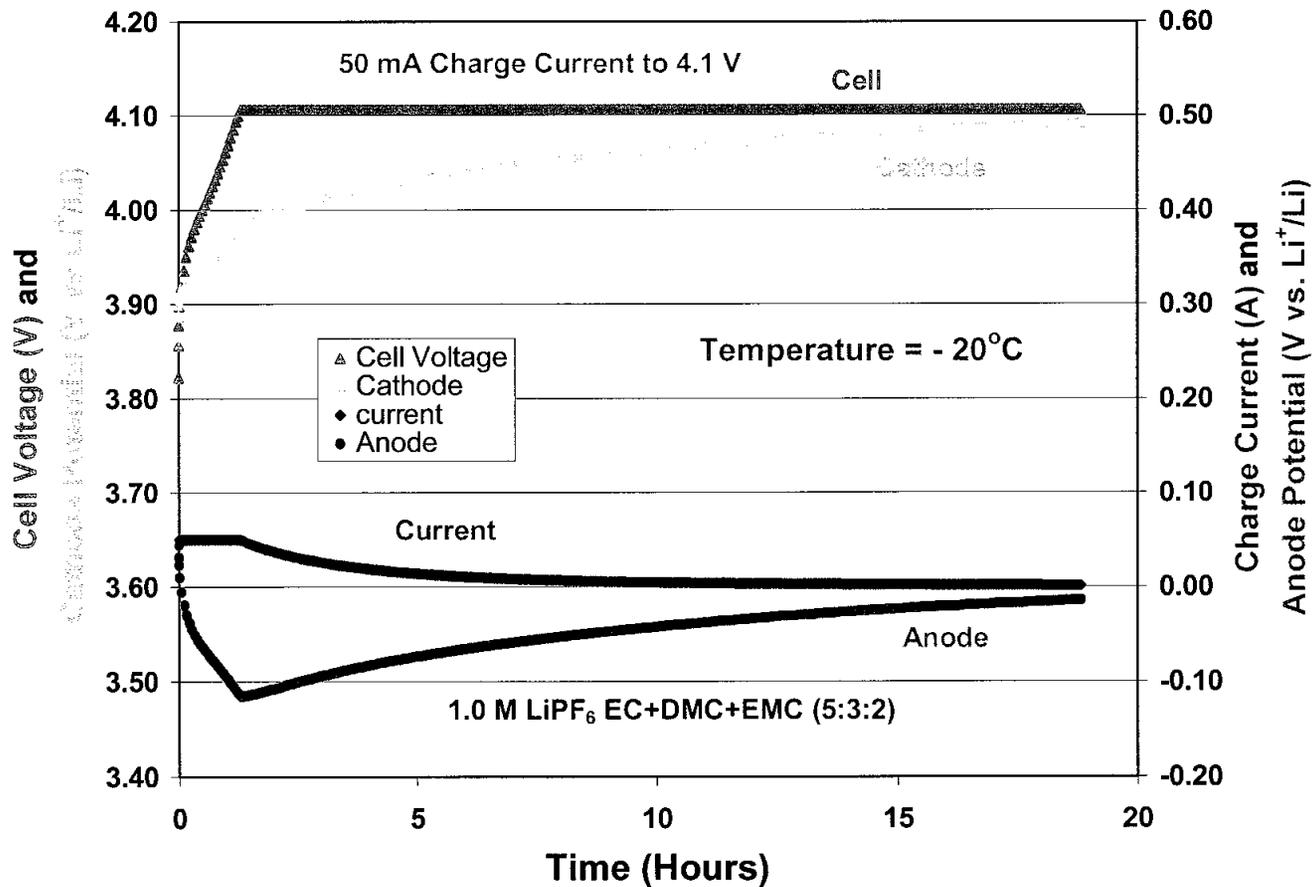




Charge Characteristics of Experimental Lithium Ion Cells Effect of Charging at Low Temperature (-40°C)



Charge Characteristics of Experimental Lithium Ion Cells Effect of Charging at Low Temperature (- 20°C)

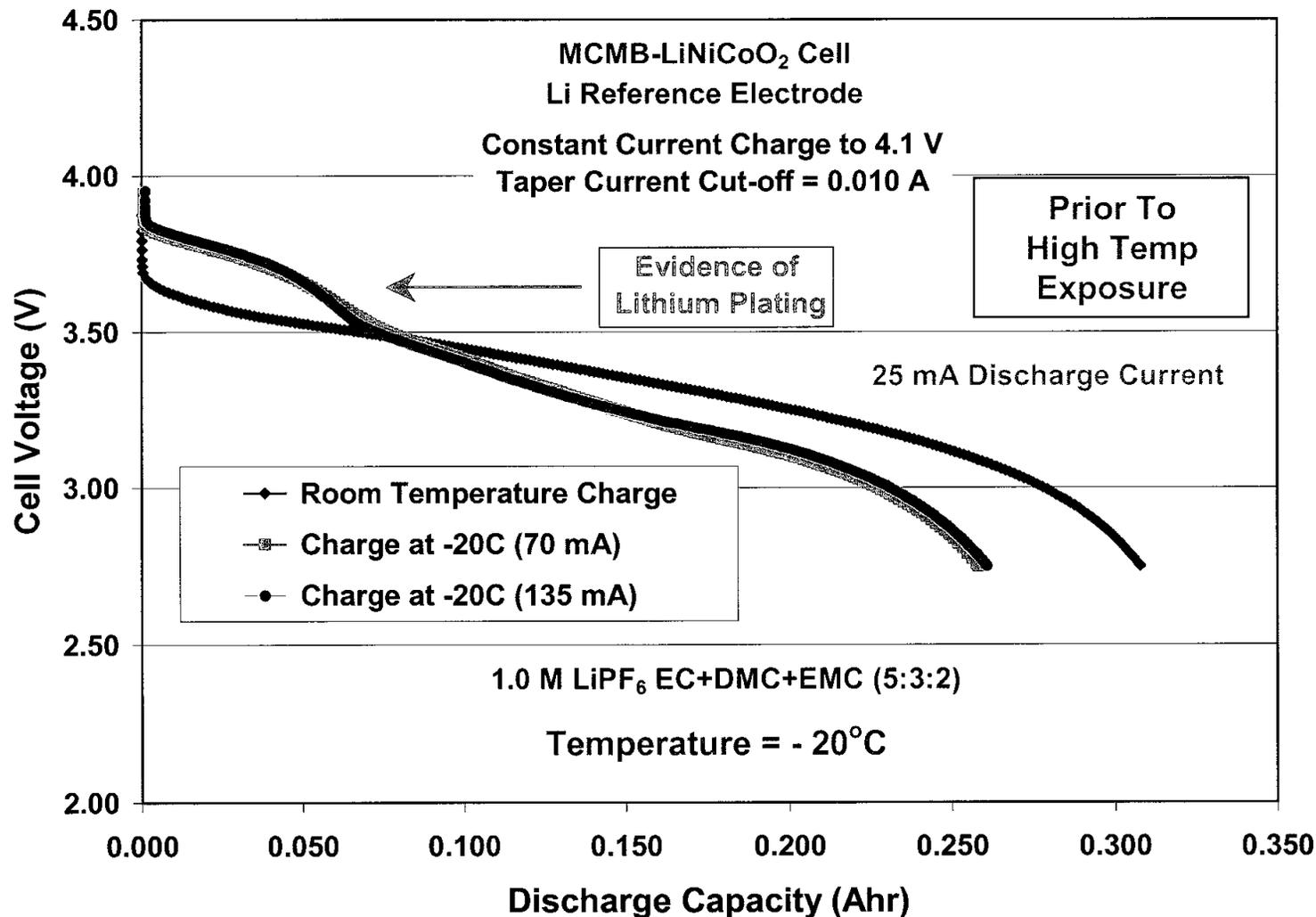


- In some cases, the anode can be excessively polarized in contrast to the cathode resulting in the possibility of lithium plating occurring.



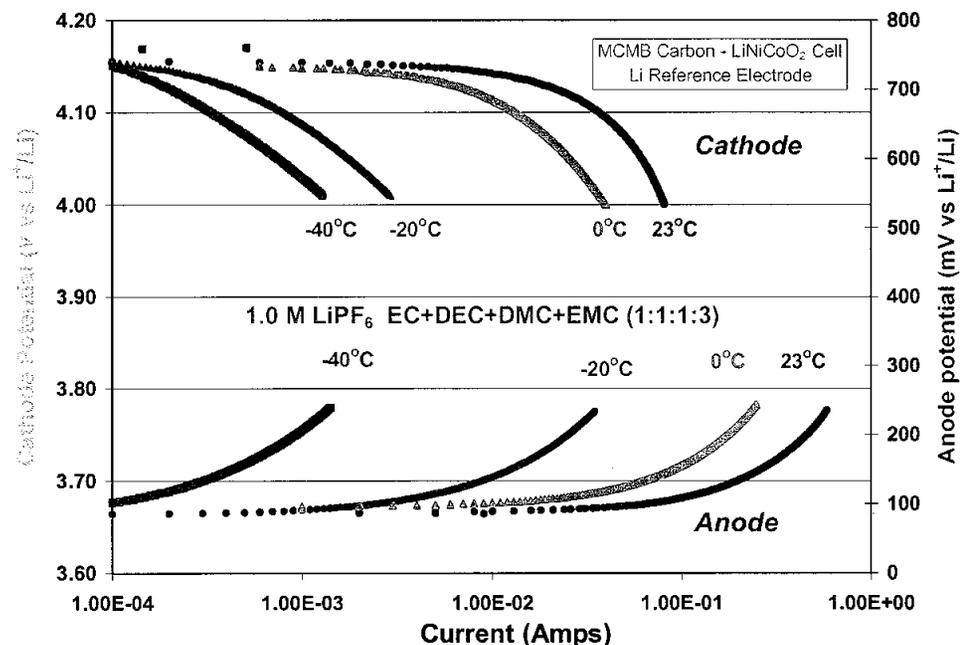
Effect of High Temperature Exposure on MCMB-LiNiCoO₂ Cells

Effect of Electrolyte Upon High Temperature Resilience



Tafel Polarization Measurements of MCMB and LiNiCoO₂ Electrodes Effect of Electrolyte upon Polarization at Different Temperatures

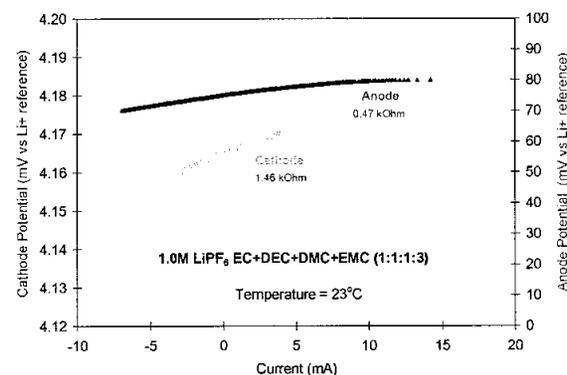
- Tafel polarization measurements allow further insight into the kinetics of lithium intercalation/de-intercalation on MCMB anodes and LiNiCoO₂ cathodes in these electrolytes.
- These measurements were made at scan rates slow enough (0.5 mV/s) to provide near-steady state conditions and yet with minimal changes in the state of charge of the electrode or its surface conditions.
- The cells were tested in near full state of charge and biased over a 150 mV range.
- Both anode and cathode polarization characteristics were measured at various different temperatures (23, 0, - 20 and – 40°C).



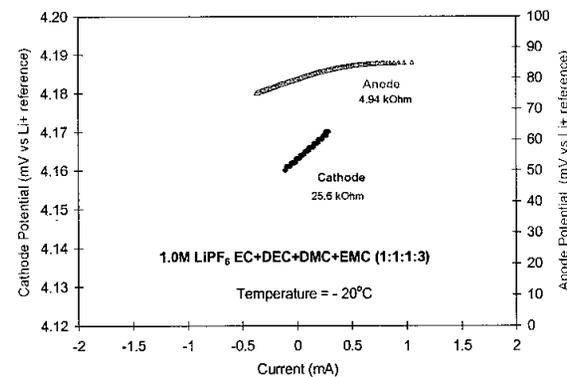
- > In most cases, the cathode displays poorer kinetics and is performance limiting.

Linear Micropolarization Measurements

Measurements at 23°C



Measurements at - 20°C



- * At low overpotentials ($\ll RT/\alpha nF$) the electrochemical rate equation can be linearized resulting in a linear current-potential relation.
- * The curves were obtained under potentiodynamic conditions conditions at scan rates of 0.02 mV/sec.
- * The polarization resistance, or the exchange current density, can be calculated from the slopes of the linear plots.
- * The electrodes were tested in near full state of charge and biased over a 10 mV range.
- * The resulting polarization resistance value is indicative of the facility of both the lithium intercalation and de-intercalation processes in the material (encompassing Li⁺ diffusion through the SEI layer as well as bulk diffusion in the carbon electrode).

- > Polarization resistance is observed to be higher for the cathode with most systems.
- > Good tool to investigate kinetics at different temperatures as a function of electrolyte type

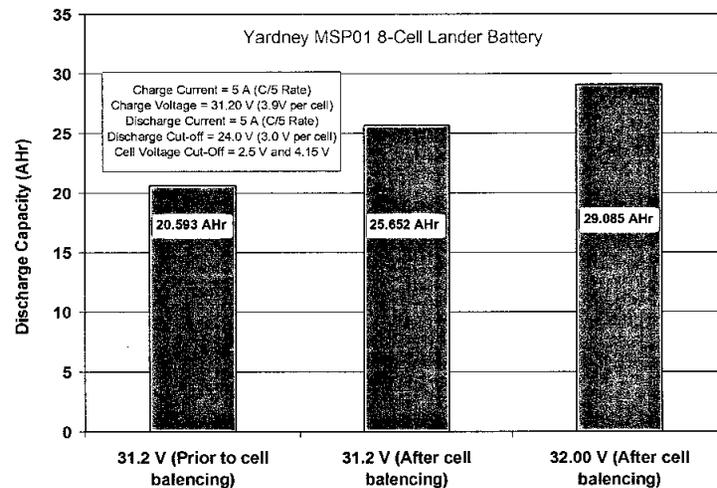


Charge Characteristics of Prototype Lithium Ion Batteries

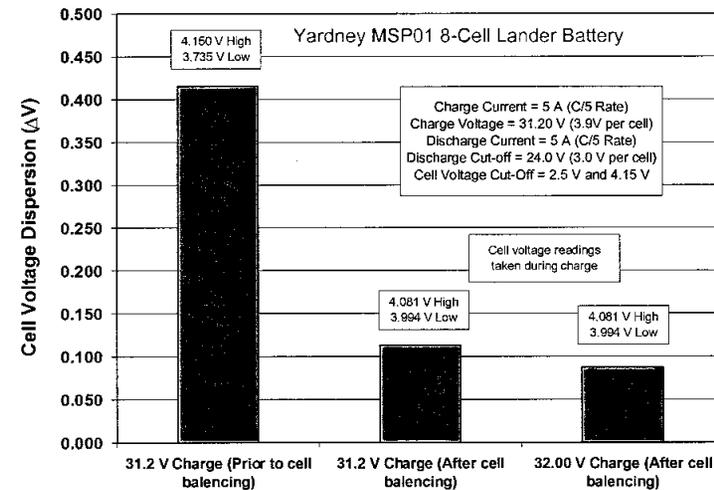
- **MSP01 Yardney 8-Cell Lander ATLO battery testing**
- Lander battery is being testing according to a Mars mission simulation profile
- Test plan reflects needs and requirements of '09 Smart Lander
- Test plan includes initial characterization, cruise period, EDL profile, and surface operation profile.
- **Charge Control**
 - 25 Ahr 8-cell battery (24-34.4 V)
 - Battery voltage controlled charging
 - Constant current and constant potential charging
 - Individual cell monitoring
 - Battery protection limits
 - Individual cell voltage exceeded (> 4.2 V)
 - Temperature limits exceeded ($> 50^{\circ}\text{C}$ for any input)
 - Charge/discharge capacity limit (> 35 Ahr)
 - Step time (> 10 hours)
 - Battery cell balancing methodology (TBD)
(i.e., resistively discharging cells to specified voltage)



Lithium Ion Technology Demonstration for 07 Smart Lander Application 2001 MSP01 Lander Battery Testing



Discharge Capacity (Ahr)



Cell Voltage Dispersion (ΔV)

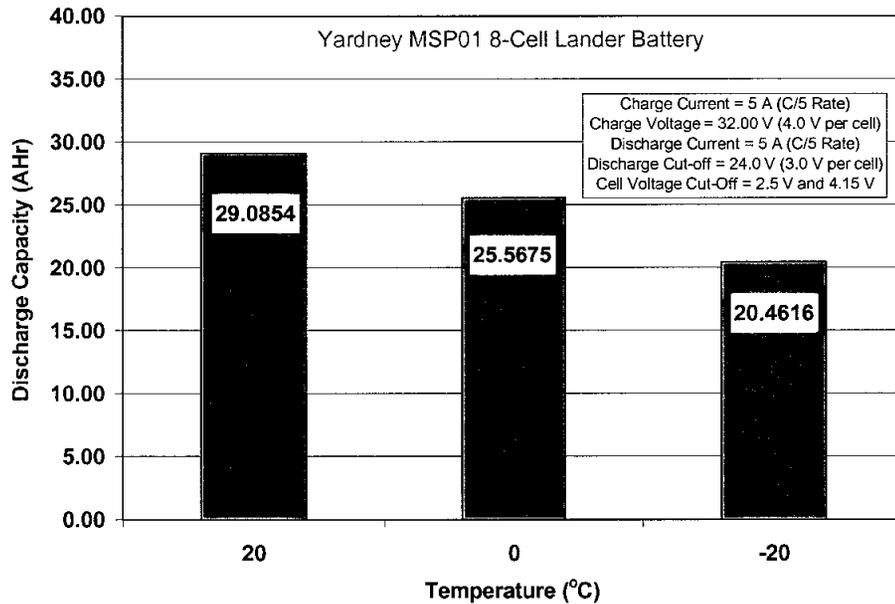
- Effect of cell balancing upon performance evaluated
- 25% more capacity delivered after cell balancing
- Much tighter grouping of cells observed (small cell voltage dispersion)



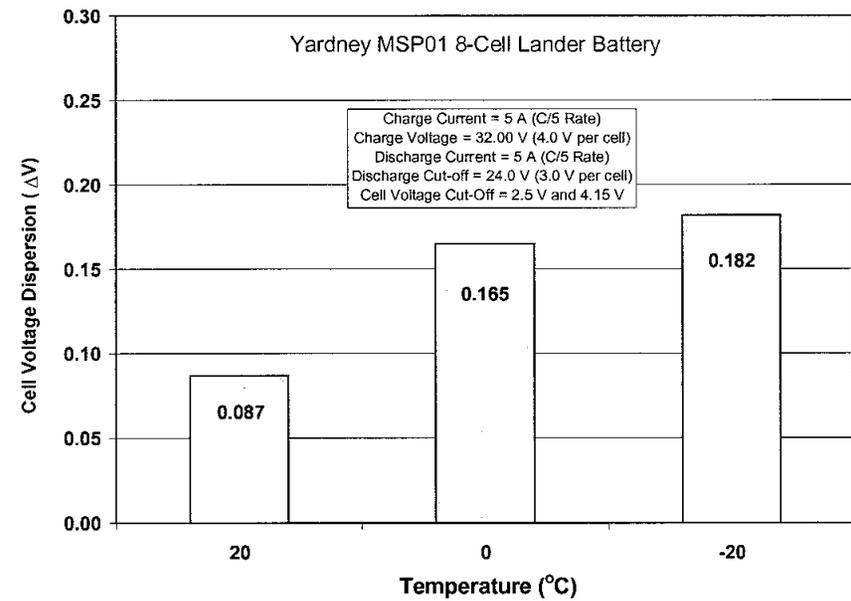
Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Initial Characterization/Conditioning at Different Temperatures

32 V Charge - Discharge Capacity (Ahr) at Various Temperatures



Discharge Capacity (Ahr)



Cell Voltage Dispersion (ΔV)

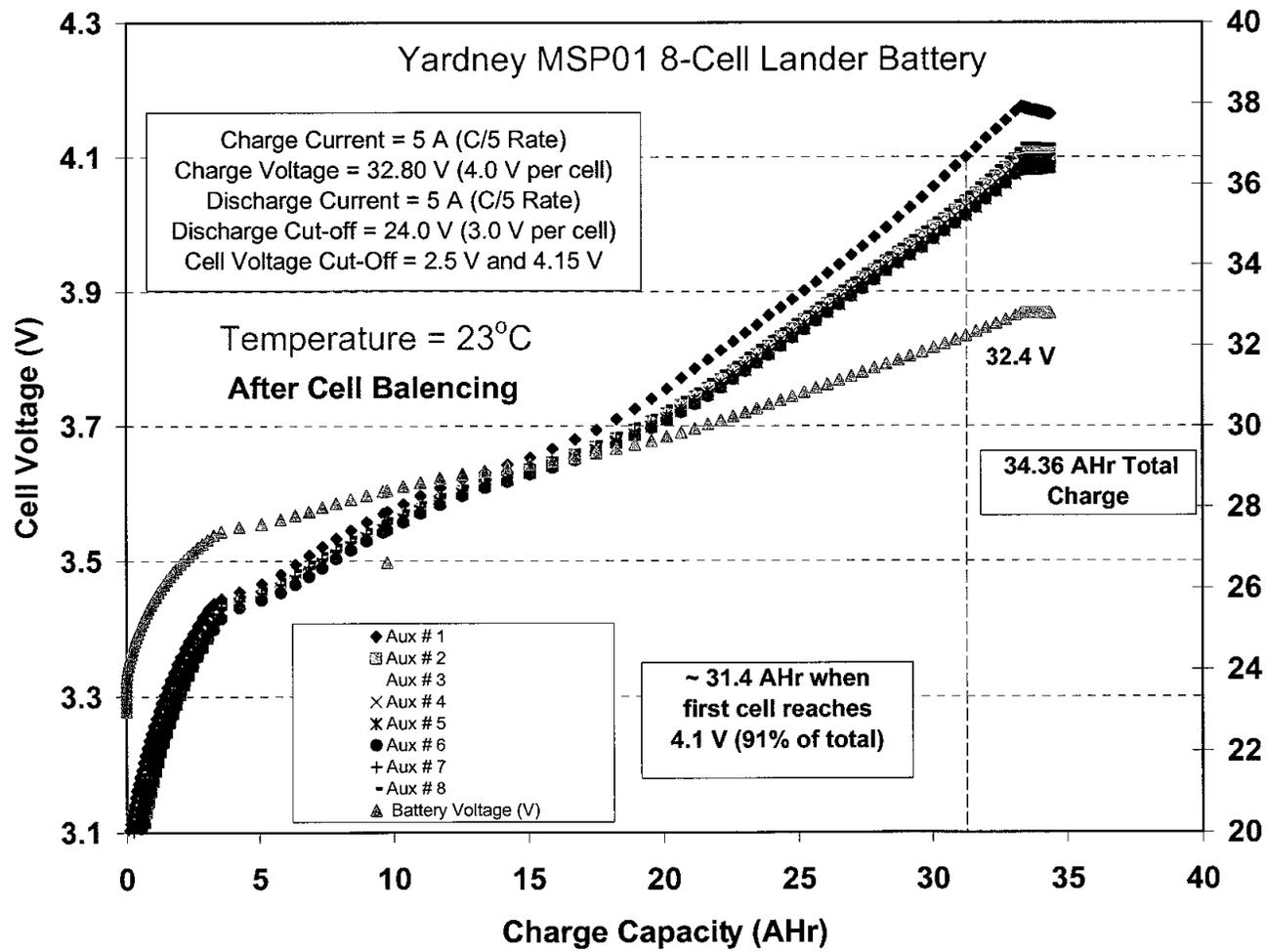
- Battery capacity at different temperatures determined
- Capacity determined after cell balancing
- Greater cell voltage dispersion observed at lower temperature



Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

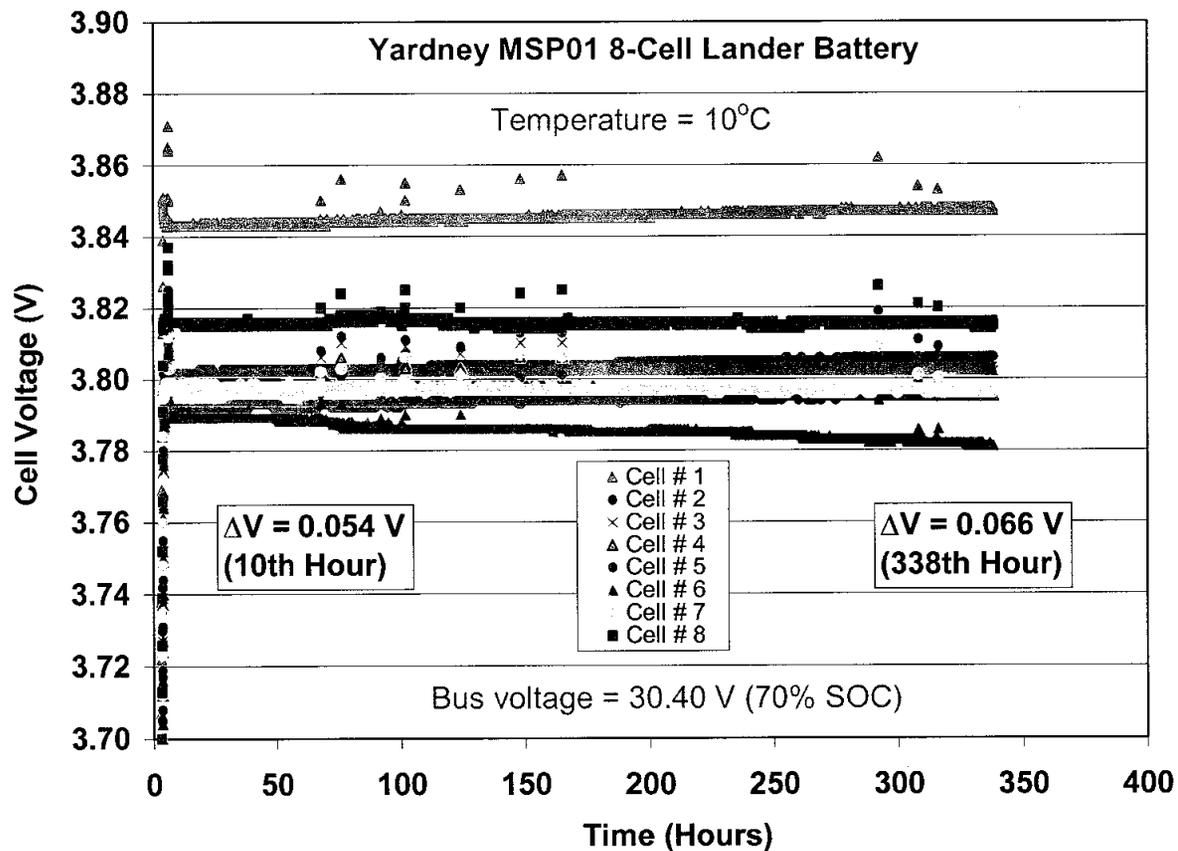
Initial Characterization/Conditioning at 20°C

32.8 V Charge (After Cell Balancing-Second Time)



Lithium Ion Technology Demonstration for 07 Smart Lander Application

2001 MSP01 Lander Battery Testing-Cruise Period Test



- Cells balanced prior to storage test
- Cell dispersion potential issue depending upon charge methodology



Summary and Conclusions

- The charge characteristics of a number of aerospace quality lithium-ion cells has been investigated.
- The effect of charge voltage upon performance has been determined, especially at lower temperatures, and has been observed to result in higher capacities.
- The effect of charge taper current cut-off methodology upon performance has been determined with the following observations being made: (1) lower taper current values at low temperature can result in significantly more capacity, (2) the impact of taper current value selection becomes more significant later in cell life, and (3) extended taper charging can limit life characteristics.
- The possibility of lithium plating occurring at low temperatures (and/or with high charge voltages) has been investigated in experimental three electrode cells. It was observed that high charge voltages, high charge currents and undesirable electrode kinetics can lead to conditions where lithium plating on the anode can occur.
- The charge characteristics of an 8-cell lithium ion battery has been investigated (without individual cell charging) with emphasis upon determining the extent of cell voltage dispersion.



Acknowledgments

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