

# Performance Characteristics of Lithium-Ion Technology Under Extreme Environmental Conditions

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## ABSTRACT

Lithium-ion technology has been demonstrated to have high specific energy, high energy density, and relatively long life. In addition, lithium-ion technology is especially attractive since it has the potential to operate over a very wide temperature range, which is particularly important for a number of applications. This potential derives from the fact that lithium-ion cells possess organic solvent-based electrolytes, in contrast to aqueous-based electrolytes, which can be tailored to provide high conductivity over a wide range of temperatures. Thus, in recent years, advances in electrolyte formulations have led to dramatic improvements in the capability of lithium-ion technology to operate at extreme temperatures, especially low temperatures. However, it still remains a challenge to demonstrate excellent low temperature capability throughout the life of a cell, especially after being subjected to high temperature cycling or exposure. In order to understand these performance limitations, a number of aerospace quality prototype cells, ranging in capacity from 1 to 45 AHr, have been tested over a wide range of temperatures (-70 to +75°C). In addition, many cells have been tested under conditions of alternating high and low temperatures to determine the impact that variable temperature cycling has upon cell health and performance. To further elaborate upon possible performance degradation mechanisms present, the results of a number of experimental three-electrode cells will be presented. In addition to enabling us to monitor the individual electrode potentials during cycling, these cells have provided a test vehicle in which electrochemical characterization of electrode can be performed.

## INTRODUCTION

In order to effectively explore the solar system, NASA has identified the need for primary and secondary batteries that can efficiently operate under extreme environmental conditions, including: (1) at ultra-low temperatures, (2) at extremely high temperatures (up to +550°C), (3) in high radiation environments, (4) and under high impact conditions.<sup>1</sup> For example, current projections of future missions aimed at the exploration of the moons of Jupiter, such as Europa and Titan, will require batteries that will power surface penetrating probes and atmospheric probes in environments that are as cold as -140°C. Missions planned to explore comets and asteroids are also expected to encounter similarly cold temperatures. In addition, future missions involving the exploration of Mars are expected to encounter environmental conditions as cold as -120°C. In contrast, future missions planned to explore Venus will require batteries that can operate at very high temperature, in excess of 450°C. Besides harsh temperature requirements imposed by many upcoming missions, many applications will require that the batteries possess good tolerance to high intensity gamma radiation, such as that encountered on Europa.

Although it may be difficult to develop technology to effectively operate under these extreme conditions, advances in both primary and secondary batteries are desired to alleviate some of the constraints imposed by the bulky thermal management designs. Due to its favorable characteristics, lithium-ion technology has been recognized as having great potential for meeting some of the low temperature performance requirements projected for some future missions (down to at least -60°C). In addition to NASA, the

Air Force and Army both desire secondary batteries that can operate over a wide temperature (-40 to +70°C).<sup>2,3,4</sup> Thus, our group has actively been involved in a testing and evaluation program to evaluate the potential and limitations of the technology, as well as, a research and development program to develop improved low temperature lithium-ion batteries. The primary focus of our develop efforts have focused upon developing improved low temperature electrolytes. In this paper, we would like to discuss our recent results obtained in performance characterization of lithium-ion cells under extreme environmental conditions, including: (1) at very low temperatures (< -40°C), (2) at high temperatures (> +40°C), (3) and under high intensity radiation.

### LOW TEMPERATURE DISCHARGE CHARACTERISTICS OF PROTOTYPE CELLS

For many applications, the energy storage device is only required to operate at very low temperatures in the discharge mode, with charging occurring at much milder temperatures. When cells are charged at room temperature, prototype cells have been shown to operate effectively down to -30 to -50°C using moderate rates, and even down to -70°C using very low rates. For example, 7-10 Ah cells developed by Lithion for use in NASA-JPL's Mars exploration applications display good performance down to -40°C using a C/10 discharge rate to 2.0V, as shown in Fig. 1, with 70% of the room temperature capacity being delivered at -40°C. The cell chemistry consists of mesocarbon microbeads (MCMB) carbon anodes, LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> cathode materials, and a low temperature electrolyte (1.0 M LiPF<sub>6</sub> EC+DMC+DEC (1:1:1)) developed at JPL.<sup>5,6</sup>

It must be noted, however, that a significant portion of the capacity derived at these very low temperatures is obtained at voltages below 3.0V. For the purposes of characterization, we have routinely discharged the cells to low voltage (2.0-2.5V) to obtain the most capacity possible. It has been reported that at very low discharge potentials the anode substrate commonly used, e.g., copper foil, can dissolve into the electrolyte solution contributing to cell degradation. However, researchers have demonstrated that this effect is only significant when the anode potential is > +3 V vs. Li<sup>+</sup>/Li, which should not occur in full-cells unless the cell voltage is significantly below 1.0V.<sup>7,8</sup> In addition, this effect is not likely to be as significant at very low temperatures due to the overpotential present at each electrode (ohmic and charge transfer resistances).

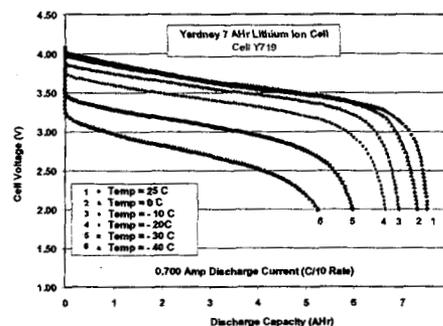


Fig. 1. Discharge capacity of a 7 Ah lithium-ion cell at various temperatures using a C/10 discharge rate (0.700 A) to a 2.0V cut-off.

As shown in Fig. 2, cells discharged under these conditions can deliver > 80 Wh/kg and > 64 wh/kg at -30 and -40°C, respectively.

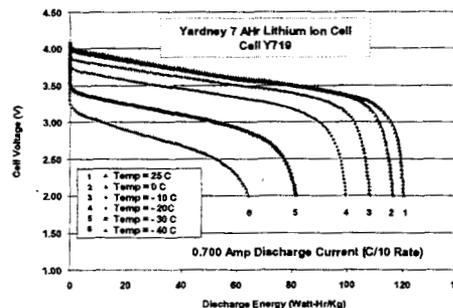


Fig. 2. Discharge energy of a 7 Ah lithium-ion cell at various temperatures using a C/10 discharge rate (0.700 A) to a 2.0V cut-off.

The performance of these cells drops off rapidly when attempting to discharge the cells at temperatures below -40°C, becoming very rate sensitive, and showing negligible capacity at -60°C with moderate rates (>C/15). The primary reason for the poor performance below -40°C in this system is due to the low conductivity of the electrolyte and/or the onset of electrolyte freezing. This is in part due to the large proportion of ethylene carbonate (33% by volume) present in the electrolyte formulation. Ethylene carbonate is an essential component in the electrolyte due to the fact that it possesses (a) a very high dielectric content providing good salt solvation characteristics and high ionic conductivity, (b) good electrode passivation characteristics leading to ionically conductive and protective surface films, especially on the carbon anode, and (c) good physical properties (e.g., high boiling point) which translate into greater cell stability at higher temperatures. However, since ethylene carbonate has a very high

melting point (+34°C) and high viscosity, it should not be used in large proportion when optimizing electrolyte formulations for low temperatures. Thus, current efforts at JPL<sup>9,10</sup> have focused upon investigating electrolytes with low ethylene carbonate-content to realize improved cell performance at temperatures below -40°C, with the recognition that some high temperature stability (> ~55°C) and ambient temperature rate capability may be compromised. Alternatively, propylene carbonate (PC) is often used in place of ethylene carbonate due to the fact that it has a much lower melting point (-55°C) and also possesses a very high dielectric constant, however, it cannot be used with graphitic carbon anodes readily due to an exfoliation process which occurs. In addition, electrolytes with a high proportion of PC display somewhat low conductivity at very low temperatures due to its high viscosity.

When prototype cells containing a low temperature electrolyte possessing low ethylene carbonate-content and an optimized blend of linear aliphatic carbonates were evaluated, much better performance was obtained at temperatures below -40°C. For example, SAFT DD-size cells incorporating 1.0 M LiPF<sub>6</sub> EC+DEC+DMC+EMC (1:1:1:3) v/v<sup>10</sup>, an electrolyte developed recently at JPL, improved performance is observed as shown in Fig. 3. As illustrated, good performance is displayed down to -50°C using a C/10 discharge rate when the cells are charged at room temperature, with > 75% of the room temperature capacity being delivered at -50°C. In addition, the overpotential observed upon discharge observed is much lower than that observed with the previous system described, with > 75% of the capacity being delivered with an operating voltage > 3.0V at -40°C.

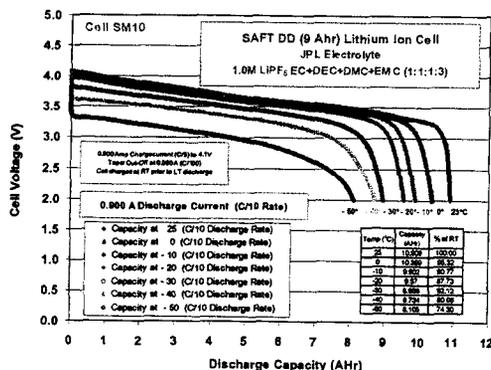


Fig. 3. Discharge energy of a SAFT DD-size lithium-ion cell at various temperatures using a C/10 discharge rate (0.900 A) to a 2.0V cut-off.

As shown in Fig. 4, when the discharge performance at low temperatures is expressed in terms of the specific energy, over 109 Wh/kg and 92 Wh/kg are delivered at -40 and -50°C, respectively, using a C/10 discharge rate (0.90 A). It should be noted that the cells were allowed to soak at the respective temperatures for 12 hours prior to discharge.

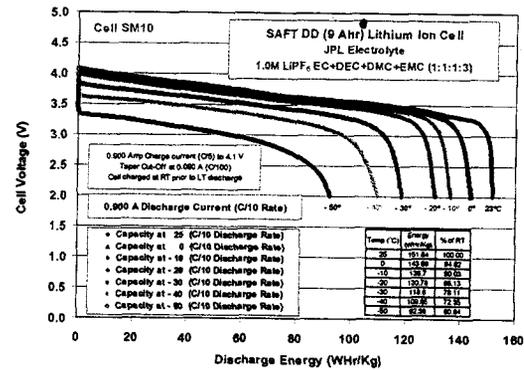


Fig. 4. Discharge energy of a SAFT DD-size lithium-ion cell at various temperatures using a C/10 discharge rate (0.900 A) to a 2.0V cut-off.

Good performance was also obtained with these cells at temperatures below -50°C, however, the sensitivity to the discharge rate becomes much more dramatic. As illustrated in Fig. 5, when a prototype cell was evaluated at -60°C, only 18 % of the room temperature capacity was realized using a C/5 discharge rate with no capacity being delivered with an operating voltage > 2.5V. However, using low rates (i.e., C/50 discharge rate) over 70% of the room temperature capacity was obtained at -60°C, corresponding to ~ 80 Wh/kg.

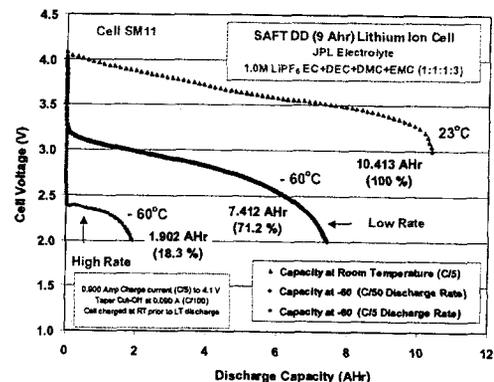


Fig. 5. Discharge energy of a SAFT DD-size lithium-ion cell at various temperatures using a C/10 discharge rate (0.900 A) to a 2.0V cut-off.

Using low rates, fair performance was also observed at  $-70^{\circ}\text{C}$ . As shown in Fig. 6, when low rates are used reasonable capacity levels were observed, with nearly 70% of the room temperature capacity being delivered at a C/150 rate. This data suggests that further advances can be made in improving the low temperature performance of lithium-ion cells, and an enhanced understanding of the factors which govern operation at such low temperatures (i.e., electrolyte conductivity, charge-transfer kinetics, bulk diffusion and mass transfer effects, and ohmic contributions) will facilitate attaining these objectives. Although good performance has been obtained when cells are charged at room temperature, the performance markedly declines when the cells are charged at low temperature ( $< -20^{\circ}\text{C}$ ), as discussed below.

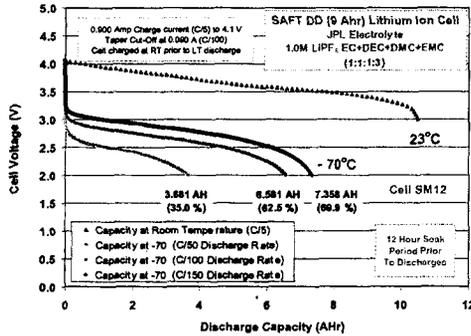


Fig. 6. Discharge capacity of a SAFT DD-size lithium-ion cell at different rates (C/50, C/100 and C/150) at  $-70^{\circ}\text{C}$  to a 2.0V cut-off.

### LOW TEMPERATURE CYCLING CHARACTERISTICS OF PROTOTYPE CELLS

In order to determine the viability of supporting missions subjected to prolonged cold temperature periods, we have performed 100 % DOD cycling tests at both  $-20$  and  $-40^{\circ}\text{C}$  (charge and discharge at low temperature). As illustrated in Fig. 6, when the cycle life performance of a number of prototype cells (varying in vendor, cell size, chemistry, and cell design) cycled under similar conditions (C/10 charge to 4.1V, and C/5 discharge to 3.0V) is compared at  $-20^{\circ}\text{C}$ , dramatic differences in the extent of capacity fade is observed, in contrast to the room temperature performance trends, suggesting that other cell degradation modes are present at low temperature. However, it should be noted that some systems are particularly stable and have demonstrated over 2000 cycles at  $-20^{\circ}\text{C}$ , and still yield over 60% of the initial room temperature capacity.

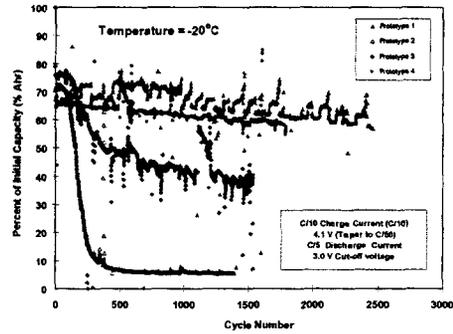


Fig. 6. Cycle life performance of various prototype cells at  $-20^{\circ}\text{C}$  (C/10 charge to 4.1V, C/5 discharge to 3.0V).

In addition to  $-20^{\circ}\text{C}$ , we have performed a number of 100% DOD cycling tests at  $-40^{\circ}\text{C}$  (continuous cycling) on various types and generations of cells ranging in sizes and have observed a similar wide variation in performance (albeit cycled under slightly different conditions in terms of rate), as shown in Fig. 7. From our studies and others, it is clear that the low temperature charge methodology and charge characteristics can greatly influence the cycle life performance at very low temperatures. Excessively high rates can result in lithium metal plating upon the carbon anode surface, rather than intended intercalation/insertion reaction, resulting in a reactive system. The exposed lithium metal can facilitate electrolyte reduction and gas generation and generally results in increased electrode impedance due to the build-up of resistive SEI films.

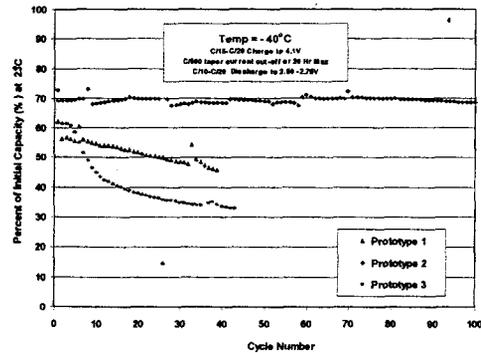


Fig. 7. Cycle life performance of various prototype cells at  $-40^{\circ}\text{C}$  (C/15-C/20 charge to 4.1V, C/10-C/20 discharge to 3.0V).

The evidence that lithium plating is indeed taking place can be indirectly suggested by observing the discharge profile after charging at low temperature. As shown in Fig. 8, when a prototype cell was charged at  $-40^{\circ}\text{C}$  the following discharge is characterized by a much higher discharge voltage initially compared to the discharge obtained with a room temperature charge. The higher discharge voltage observed is most likely due to presence of a lithium stripping reaction which is characterized by a lower overpotential compared to that of the lithium de-intercalation process at the anode. Analysis of this behavior has been investigated using experimental three-electrode cells containing lithium reference electrodes to enable the observation of electrode potential, as well as, to enable the electrochemical characterization of each electrode.<sup>11</sup>

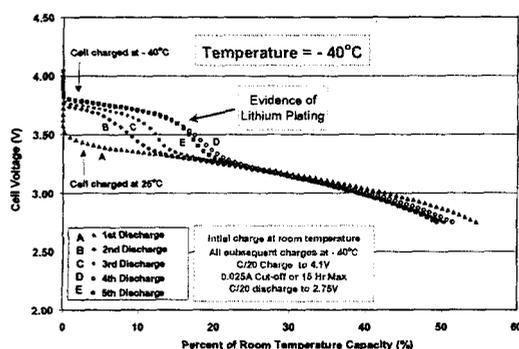


Fig. 8. Discharge profiles of a prototype cell cycling continuously at  $-40^{\circ}\text{C}$  (C/20 charge and discharge)

These studies have revealed that the relative electrode kinetics at low temperature can greatly influence the likelihood of lithium plating, and have shown that poor anode kinetics (or alternatively, excellent cathode kinetics) can contribute to the anode being preferentially (and undesirably) polarized upon charging at low temperature.

In contrast to the dramatic example of lithium plating described above, results obtained with SAFT DD-size lithium-ion cells containing the 1.0 M  $\text{LiPF}_6$  EC+DEC+DMC+EMC (1:1:1:3 v/v) electrolyte and an improved carbon anode material have yielded impressive cycle life performance at  $-40^{\circ}\text{C}$ , and have not displayed the behavior typical of lithium plating. As shown in Fig. 9, cell subjected to a 100% DOD cycle life test at  $-40^{\circ}\text{C}$  using moderate rates (C/15 charge and C/10 discharge) are observed to yield over 60-70% of the room temperature capacity for over 200 cycles, corresponding to 75-85 Wh/kg. As

expected, the cell charged to 4.0V at low temperature displays a less dramatic capacity decline with increasing cycles due to the effect of minimizing the possibility of the anode being driven negative during charge and the likelihood of lithium plating occurring.

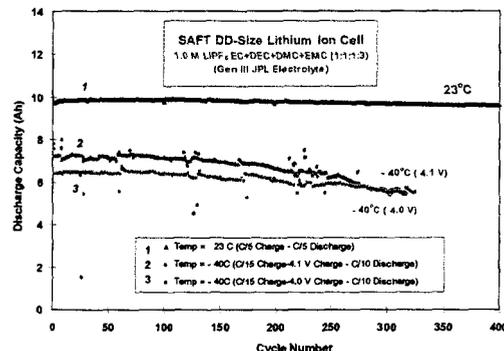


Fig. 9. Cycle life performance (100% DOD) of SAFT DD-size cells at different temperatures ( $23$  and  $-40^{\circ}\text{C}$ ).

From our studies, we have determined that poor performance is generally observed when cycling at low temperature when the lithium plating process is facilitated, such as when (1) high charge voltages are employed, (2) high charge rates are used, (3) short taper periods are used, (4) and when the anode is polarized to a much greater extent than that of the cathode at low temperature. These effects can often be exacerbated by the use of reactive electrolyte co-solvents, which are employed as a means to improve the low temperature electrolyte conductivity, which can decompose and form resistive, highly polarizing electrode surface films on carbon. It must be also be noted that although good cycling performance can be obtained with some systems at temperatures as low as  $-40^{\circ}\text{C}$ , these results generally involve long charging periods (15-24 hours) which may not be tolerable for many applications. Thus, these results emphasize the need to improve the low temperature charge characteristics and to develop stable, compatible highly conductive electrolytes which produce protective, ionically conductive surface films (SEI layers). In addition to further improvements in electrolyte and interfacial properties (kinetics at the SEI layer), identification of electrode materials with enhanced bulk diffusion characteristics at low temperature will become crucial for enhanced performance. The relative contribution of each factor to limiting the low temperature performance is highly dependent upon the system considered, conditions of operation, and temperature.

## EFFECT OF HIGH TEMPERATURE CYCLING AND EXPOSURE ON THE PERFORMANCE PROTOTYPE LITHIUM-ION CELLS

Most SOA lithium-ion cells can function effectively to temperatures as high as +40°C (operational and non-operational) with little impact on the long-term performance, including power capability and ability to operate at low temperatures. However, exposure and/or cycling at higher temperatures (> +40°C) can often lead to diminished low temperature capability, reduced rate capability, and decreased life. For example, when a prototype cell was cycled at +55°C (5 cycles) the low temperature capability was observed to be noticeably degraded, with ~20% less capacity being delivered, as shown in Fig. 10.

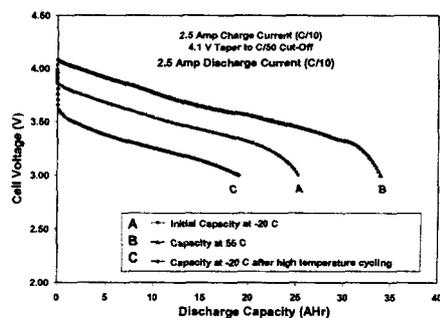


Fig. 10. Discharge capacity of a 33 Ah cell at -20°C before and after cycling at +55°C.

However, good results have been obtained with prototype cells continuously cycled at 55°C displaying, as shown in Fig. 11, with only a slightly higher capacity fade rate than that observed with a similar cell cycled at ambient temperature. This data illustrates that modestly high temperature tolerant cells are indeed available (cell not optimized for low temperature operation).

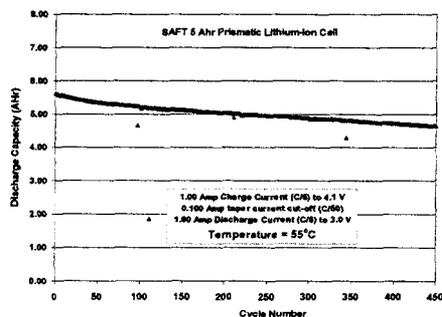


Fig. 11. Cycle life performance of a SAFT 5 Ahr prismatic cells cycled continuously at +55°C.

The aging phenomena taking place at higher temperatures is generally thought to involve increased rates of electrolyte oxidation and reduction, leading to increased electrode impedance. This behavior can be even more dramatic with systems incorporating low temperature electrolytes which contain reactive co-solvents. Our studies have shown that during the high temperature exposure, whether it involves cycling or storage, if the cell is maintained at lower voltages (lower state-of-charge) the cell degradation can be minimized. At very high temperatures (> 55°C), it has been reported that electrolyte thermal decomposition reactions can occur (i.e., LiPF<sub>6</sub>) leading to rapid performance degradation.<sup>12</sup> These issues emphasize the daunting challenge involved in developing a system that is capable of operating over a wide temperature range involving both low and high extremes (i.e., -60 to +70°C). The results obtained to-date suggest that one system alone may not adequately satisfy an application that requires both extreme low temperature operation (-40 to -60°C) and high temperature operation (+40 to +70°C).

## EFFECT OF HIGH INTENSITY RADIATION ON THE PERFORMANCE OF LITHIUM-ION CELLS

Since NASA intends to further explore Jupiter and its moons in the future, there is interest to determine the tolerance of spacecraft components, including primary and secondary batteries, to high intensity radiation. Thus, we have been actively involved in a testing program to determine the effects of gamma radiation upon the performance lithium-ion cells.<sup>13</sup> We have subjected a number of prototype cells, including cells from Lithion, Inc. (Yardney Technical Products), SAFT America, Inc., and SONY (AEA-Comdev), to gamma radiation emanating from a Co<sup>60</sup> source and have determined the impact upon the performance as a function of radiation dosage. The results obtained are very promising, in that prototype cells from all three manufacturers have shown minimal performance degradation after being subjected to radiation levels in excess of 18 Mrads. This result is significant due to the fact that initial projections for a mission to Europa involve radiation levels on the order of 8-10 Mrads of exposure. As shown in Fig. 12, SONY 18650 cells display minimal capacity loss (< 10%) after being subjected to 18 Mrad of radiation in 1.5 Mrad increments. Furthermore, it must be noted that the observed loss in capacity is in part due to calendar and cycling effects, rather than all attributable to radiation effects.

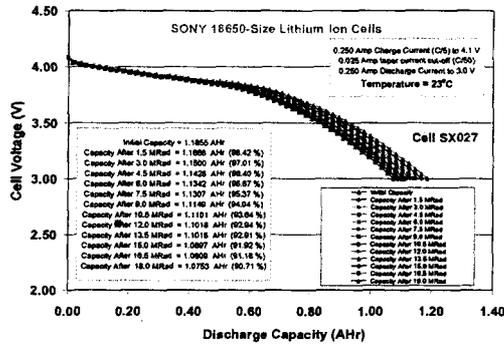


Fig. 12. Discharge capacity of a SONY 18650 cell measured after 1.5 Mrad increments of  $\text{Co}^{60}$  gamma radiation (C/5 charge and discharge).

In order to determine the relative contributions of radiation effects compared with calendar and cycling losses, an additional cell was tested to serve as a control measure and was subjected to identical testing conditions without being irradiated. As shown in Fig. 13, when an irradiated cell is compared with a control measure it is apparent that approximately half of the irreversible capacity loss observed can be attributed to cycling and storage losses, implying that ~ 5% of the capacity loss observed after 18 Mrad of exposure is due to radiation induced degradation. Results observed with Lithion and SAFT cells have yielded similar results and suggest that the technology has great promise in meeting the harsh requirements of mission in high radiation environments.

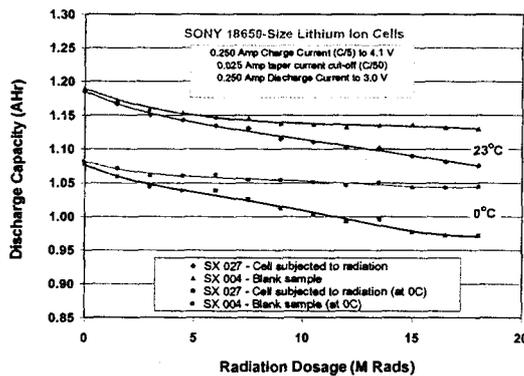


Fig. 13. Discharge capacity of SONY 18650 cells with and without being subjected to  $\text{Co}^{60}$  gamma radiation (C/5 charge and discharge) at 23°C and 0°C.

## CONCLUSIONS

In anticipation of future NASA missions which will require batteries that operate under extreme environmental conditions, we have actively been involved in the testing, evaluation, and development of lithium-ion batteries. Due to advances in electrolyte formulations, good low temperature discharge characteristics have been demonstrated down to temperature as low as  $-70^{\circ}\text{C}$  (provided low rates are used). Cells have been continuously cycled at low temperature ( $-20^{\circ}\text{C}$  and  $-40^{\circ}\text{C}$ ) and have been demonstrated to yield excellent performance in many cases. However, under certain conditions some prototype cells have displayed evidence of lithium plating upon charging at low temperature leading to performance degradation. We have also evaluated the impact of high temperature exposure and/or cycling upon the performance of lithium-ion cells, and have demonstrated that low temperature capability can often be compromised due to impedance build-up. In addition to evaluate the performance of lithium-ion cells under extreme temperature, we have also investigated the tolerance of lithium ion cells to high radiation environments. We have demonstrated that prototype cells display minimal capacity loss (< 5%) after being subjected to large doses of gamma radiation (18 Mrad).

## ACKNOWLEDGEMENTS

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, for the Code S Battery Program, DARPA-TRP program, and an internal Research and Development program (R&TD) under contract with the National Aeronautics and Space Administration (NASA).

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