# SURVEY OF LITHIUM - ION l1A1"l'ER% PERFORMANCE FOR POTENTIAL USE IN NASA MISSIONS

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## ABSTRACT

This paper presents the initial results of an exploratory effort undertaken at JPL to establish the baseline electrical performance and cycle life envelope for commercially available lithium-ion cells. Sample cells were obtained from three manufacturers for evaluation. Testing consists of evaluating the charge and discharge characteristics at different temperatures and rates. Cycle life performance is being determined with both 40% and 100% depth of discharge regimes without the benefit of individual cell bypass circuitry during charge. Energy densities in excess of 100 watt-hours pcr kilogram and very promising cycle life performance have actually been demonstrated in some cases, It is expected that this technology will be of value for future NASA missions if it can be scaled up to the 20 ampere-hour level and particularly if cycle life comparable to that of nickel-cadmiom or nickel-hydrogen can be demonstrated.

## INTRODUCTION

Reduction of the weight and volume requirements of the energy storage component of electronic devices has made a significant advancement with the appearance of the Lithium-Ion battery. Lithium-Ion batteries are replacing Nickel-Cadmium and Nickel-Metal Hydride batteries in consumer electronic devices such as cellular phones, portable computers and camcorders. More recently, this technology has received much attention in the Aerospace industry. Lithium-Ion batteries have the potential to provide twice the gravimetric energy density and up to 5 times the volumetric energy density of state of the art $NiH_2$ common pressure vessel (CPV) batteries. For example, the Mars Global Surveyor battery, based on the 2-cell CPV technology, actually real ized 36 Wh/Kg and 18 Wh/l. Near term goals for scaleable Lithium-Ion technology are modestly projected at 90 Wh/Kg and 140 Whit

The direction of the technology indicates that scaled up aerospace prototype cells will evolve from the currently available commercial technology. Th is technology is based upon use of lithiated, carbon anodes and lithiated, layered metal oxides immersed in an organic solvent electrolyte. Carbon anodes can intercalated lithium with a theoretical capacity of 372 mAh/g according to the following stoichiometry

$$xLi + 6C \rightarrow Li_xC_6.$$

Lithiated metal oxides serve as the source of lithium to form the $C/LiMO_2$ couple where M may be Cobalt, Nickel, some combination of the two, or in some cases, other layered materials. The lithium metal oxides have rechargeable capacities of approximately 137 mA h/g. The reversible react ion may be summarized as follows

$$LiMO_2 + 6C \longleftrightarrow Li_{(1-x)}MO_2 + LiC_6.$$

Electrolytes are usually made from lithium salts such as $LiPF_6$, $LiAsF_6$, $LiClO_4$, etc., dissolved in stable carbonate based solvents such as Ethylene Carbonate and Propylene Carbonate.

Most lithium-ion cells that are mass-produced today have capacities that do not exceed 1.5 anlpere-boors, In the transition from consumer to aerospace applications, it is expected that the chemistry of Lithium-Ion cells will be similar although cell capacity and packaging will tre modified. Hence, the electrical characteristics of commercially available Lithium-Ion cells will help identify battery control issues as they relate to the design of power subsystems for future spacecraft. ('characterization tests, typical of Nickel Cadmium and Nickel Hydrogen batteries, were performed on small Lithium-Ion cells that were readily available,

## EXPERIMENTAL

Sonic of the earliest cell samples were procured in 1993 and appeared to be a C size product from manufacturer S1, The cells weighed 41 grams with a volume of 16 $cm^3$ and had a 1.0 ampere-hour nameplate capacity. initial discharge characteristics show that tile actual C/2 capacity was 0.8 ampere-hours to a 3.00 volt/cell cut off. These cells yielded 78 Wh/Kg and 178 Wh/l. A set of three cells were series connected and subjected to a 40% depth of discharge cycle regime at 23 degrees Celsius. Each cycle consisted of a constant current discharge load at (),64 amperes for 30 minutes followed by a 60 minute current limited, constant voltage charge at 0.4A (C/2) to 12.3 volts. All battery packs discussed were not equipped with individual cell bypass circuitry therefore the individual cell voltages were distributed without restraint yet within the charge voltage limit. With this type of arrangement, the range of cell voltages at the end of charge, maximum minus minimum, is a useful tool for measurement of cell uniformity. Approximately 6000 cycles were realized and the range of cell voltages at end of charge was 0.050 volts at the end of life. The coulombic efficiency was stable across the cycle life of this battery pack at 0.99; however the energy efficiency began at ().92 and decreased to ().85 by the end of life.

Samples procured in 1995 from manufacturer S2 were configured in the now familiar 18650 packaging. These cells had a 1.2 ampere-hour nameplate capacity. The cells weighed 39 grams with a volume of 16 $cm^3$. Initial discharges indicated that the actual C/2 capacity was 1,2 ampere-hours to a 3.00 volt/cell cut off. These cells yielded 110 Wh/Kg and 268 Wh/l. A set of 7 cells were series connected. Ten cycles were applied for each of the following charge voltages 27.3, 28.0, 28.7. This corresponds to 3.900, 4,000, and 4.100 volts/cell. In all cases C/5 was used as the initial current, the charge was terminated when the current tapered to C/100. The ose of C'/IOf) as a charge cut oft' limit was a reliable and reproducible technique that assured a return ratio of 0,99 to 1.01 of the ampere-hours removed on the previous discharge regardless of temperature. C/2 was used as the discharge current and each discharge was terminated when the first cell reached 3.000 volts. This regime was repeated at -10, 0, 10, and 25 degrees Celsius. Figure 1 summarizes the sensitivity of capacity to both charge voltage and temperature.

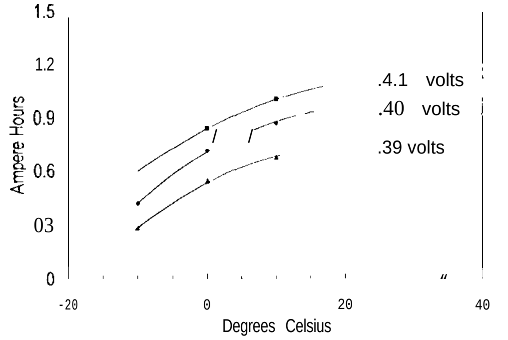


FIGURE 1- SENSITIVITY OF CAPACITY 10 TEMPERATURE AND CHARGE VOLTAGE

One cell was removed from this battery pack and the remaining set of six series connected cells were subjected to a 100% depth of discharge cycle regime at 23 degrees Celsius, Each cycle consisted of a cons! ant current discharge load at 0.6 amperes until the first cell reaches 3.000 volts followed by a current limited, constant voltage charge at 0.24A (C/5) to 24.6 volts for 8 hours or until a 1.01 charge to discharge ampere-hour ratio is achieved, Approximately 1000 cycles have been realized to date and the range of cell voltages at end of charge is on the order of 0,037 volts. The coulombic efficiency has been stable across the cycle life at 0.99 and the energy efficiency began at 0.90 and decreased to 0.83 thus far.

Another set of three cells from manufacturer S2 were series connected and subjected to a 40% depth of discharge cycle regime at 23 degrees Celsius. Each cycle consisted of a constant current discharge load at ().96 amperes for 30 minutes followed by a 60 minute current limited, constant voltage charge at 0.6A (C/2) to 12.3 volts. Approximately 3000 cycles were realized with this battery and the range of cell voltage sat end of charge was ().()45 volts by the end of life. Like the S1 battery, the coulombic efficiency was stable across the cycle life at 0.99; however the energy efficiency began at (),90 and decreased to 0.75 try the end of life. Temperature was measured on each cell case. Figure 2 shows a time versus average cell voltage and temperature for a single cycle late in the life of this battery. Figure 3 depicts the cycles versus end of discharge temperature trend. Figure 4 illustrates the overall effect of 3000 cycles upon discharge capacity at rates from C to C/20.

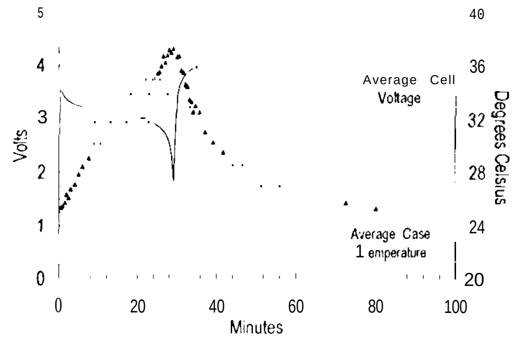


FIGURE 3 - A TYPIcAL TEMPERATURE EXCURSION I. ATE IN CYCLE LIFE

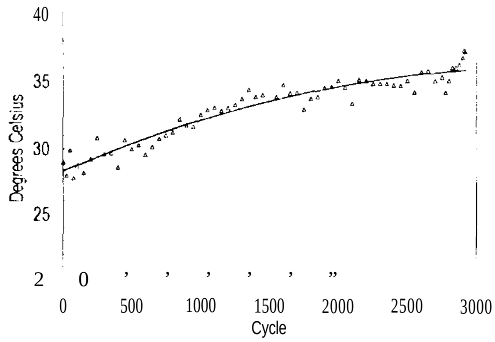


FIGURE 4 - CASE TEMPERATURE AT THE END OF DISCHARGE

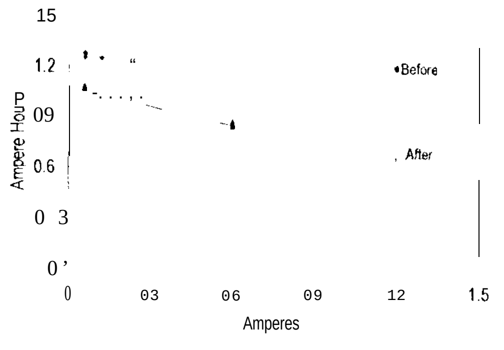


FIGURE 2- DISCHARGE PERFORMANCE BEFORE AND AFTER 3000 40% DOD CYCLES

Cell samples procured in 1996 from manufacturer S3 were configured in the 18650 packaging. These cells had a 1.2 ampere-hour nameplate capacity. The cells weighed

38.8 grams with a volume of 16 cm³. Initial discharge characteristics show that the actual C/2 capacity was ().95 tinqrere-boors to a 3.00 volt/cell cot oft'. These cells yielded 90 Wh/Kg and 207 Wh/l. A set of four cells were series connected and subjected to a 40% depth of discharge cycle regime at 23 degrees Celsius. Each cycle consisted of a constant torrent discharge load at 0.69 amperes for 30 minutes followed by a 60 minute current limited, constant voltage charge at 0.43A (C/2) to 16.4 volts, Approximately 1700 cycles have been realized to date with this battery pack and the range of cell voltages at end of charge is 0.024 volts. The coulombic efficiency has been stable across the cycle life at 0.99; howevet the energy efficiency began at 0.90 and decreased to 0.80 thus far.

A second set of four cells from manufacturer S3 were series connected and subjected to a 100% depth of discharge cycle regime at 23 degrees Celsius. Each cycle consisted of a constant correot discharge load at 0.425 (C/2) amperes until the first cell reaches 3.000 volts followed by a current limited, constant voltage charge at 0.425A to 24.6 volts for 3 hours or until a 1.01 charge to discharge ampere-hour ratio is achieved. Approximately 450 cycles have been realized to date with this battery pack and the range of cell voltages at end of charge is 0,020 volts, The coulombic efficiency has been stable across the cycle life at 0.99; however the energy efficiency began at 0.89 and decreased to 0.83 thus far.

## SUMMARY

| Cell | Packaging | Amp-Hours | Wh/Kg | Wh/l |
|---|---|---|---|---|
| S1 | c | 0.80 | 78 | 178 |
| S2 | 18650 | 1,20 | 110 | 268 |
| S3 | 18650 | 095 | 90 | 207 |

TABLE 1- CELL PERFORMANCE BASELINE

| Cell Manufacturer | Depth of Discharge | Cycles to Date | Initial Energy Efficiency | Final Energy Efficiency |
|---|---|---|---|---|
| S1 | 40% | 6000 | 0 92 | 085 |
| S2 | 40% | 3000 | 090 | 075 |
| S3 ₍₁₎ | 40% | 1700 | 0 90 | 080 |
| S2 ₍₁₎ | 100% | 1000 | 0 90 | 083 |
| S3 ₍₁₎ | 100% | 450 | 0 90 | 083 |

(1) lest is in progress,

TABLE 2- CYCLE LIFE 10 DATE

The measured gravimetric energy density at the cell level is consistent with that expected; that is 90 Wh/Kg. The measured volumetric energy density at the cell level was greater than 200 Wh/l and was better than expected, State of the art commercial technology is sufficiently robust to support missions requiring a limited cycle life of at least one thousand cycles. The cycle life figures reported here were achieved without the benefit of individual cell charge control electronics, Liability exposure in consumer markets mandates rigid charge control at the cell level but it is not clear if aerospace applications need to bear the penalty of additional weight and complexity. When applying a current limited, constant voltage charge, the use of C/I(K) as a charge cot off' limit appears to be a reliable and reproducible technique for charge termi nation within the range of temperatures tested.

Throughout cycle life, a degradation in energy efficiency is accompanied by an increase in the operating temperature. These two factors suggest an increase in cell internal impedance; typically electrolyte degradation or breakdown of the layered electrode structure. If cycle life comparable to that of Ni-Cd or $NiH_2$ is to be realized then cell designers need to develop a better understanding of the underlying causes of this impedance. High external case temperatures on relatively small cells are a concern. In the near term, cell and battery designers need to consider thermal management; particularly so when contemplating scaling up from 1 to 20 anlpere-boor or larger cell sizes. Heat removal needs to be focused on the expected heat generated at the end, not the beginning, of life. On the other hand, given the sensitivity of capacity to temperature, designers might find a way to utilize these thermal characteristics for applications with very cold operating environments. Power system designers need to design to the end of life energy efficiency, This work is continuing and updates will be reported at a later date.

## REFERENCES

Armantrout, J., "Flattery System Prime's Perspective, " Space Power Workshop, Manhattan Beach, CA, April 23-25, 1996.

Surampudi, S., et. al., "Lithium Ion Battery Program Status," 1996 NASA Battery Workshop, November 28-30, 1996, NASA Conf. Pub. 3325, pp. 87-147,

Megahed, S., and Scrosati, Ft., "Lithium Inn Rechargeable Batteries, " J. Power Sources, 51 (1994) 79 104.

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