

Lithium Ion Batteries for Space Applications

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Abstract—Interplanetary missions require rechargeable batteries with unique performance characteristics: high specific energy, wide operating temperatures, demonstrated reliability, and safety. Li-ion batteries are fast becoming the most common energy storage solution for these missions, as they are able to meet the more demanding technical specifications without being excessively massive. At JPL, we have undertaken materials development studies on both cathodes and electrolytes with the goal of further enhancing battery specific energy, discharge and charge capability, and functional temperature range. Results of these studies are described below.

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1. INTRODUCTION

NASA has unique needs for the energy storage systems in their planetary exploration missions, ones that are highly dependant upon the environment being explored as well as the type of mission: orbital, atmospheric, surface or sub-surface exploration. Batteries are essential components of the spacecraft and provide the heartbeat either alone or in conjunction with a primary energy source, such as photovoltaic or a nuclear radioisotope-based electric generator. Solar arrays are usually preferred for inner and near planets or planetary objects, where sufficient solar intensity is available. For missions to the more distant planets, where there is little solar intensity, nuclear power sources may be adopted, as exemplified by NASA's premier missions in the 80s, Voyager to the outer planets and Galileo to Jupiter. The choice of power generation source influences the requirements for energy storage, which in turn dictates the selection of the battery system. For solar powered missions, rechargeable battery systems with good cycle life are desirable to provide power during eclipse periods, while the radioisotope powered missions require

high power densities for load leveling, combined with long calendar life.

Rechargeable batteries are commonly used to provide power: i) during launch and post-launch until the deployment of solar panels, ii) for firing pyros and firing rockets for attitude control, iii) during cruise anomalies or trajectory control maneuvers of the spacecraft, iv) to the spacecraft, its equipment and payload during Sun eclipse periods, v) for night time or eclipse-time experimentation, vi) for communication and data transmission, and vii) to keep the electronics within a specified temperature range. The unique requirements for space batteries include: 1) extreme reliability, robustness and safety, especially in human exploration missions 2) the ability to operate under extreme temperatures, which could be as low as -120°C for mars and as high as 475°C in the Venus atmosphere (though often the batteries are environmentally protected to some degree), 3) tolerance to high intensity radiations, for example, of ~ 4 MRad in Jupiter environments. In addition to these environment-related needs, the requirements of the batteries are also governed by spacecraft functionality, e.g., orbiters, landers and rovers and probes. The batteries in the planetary orbiters have the benefit of controlled thermal environment and hence, the performance driver is long cycle life, typically in the range of 30,000 charge-discharge cycles combined with a good wet life exceeding five years. The surface missions, on the other hand, need batteries that can operate in extreme environments, either temperature or radiation. Accordingly, good low temperature performance from the batteries is desired for Mars surface missions.

In addition to the above requirements, all missions benefit by having lightweight and compact energy storage. Batteries that display higher gravimetric and volumetric energy densities can manifest in reduced mass and volume for the power subsystem and thus increased payload and mission capabilities. Batteries with tolerance to extreme environment, can, on the other hand, be mission enabling, rather than just enhancing, and may facilitate increased scientific capabilities of the mission, such as with the recent successful planetary exploration of Mars.

Until recently (through the late 1990's), the energy storage needs for all the space missions were met using aqueous rechargeable battery systems, primarily Ni-Cd, Ni-H₂, and

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² IEEEAC paper#1561, Version 4, Updated 2006:12:29

Ag-Zn. In the last decade, however, a new viable aerospace battery materials system emerged: lithium-ion.

Table: 1 Comparison of performance characteristics of State of practice rechargeable battery systems.

System	Specific Energy, Wh/kg	Energy Density, Wh/L	Operating Temp. Range, °C	Calendar life, y	Cycle life (* @ partial Depth of discharge)
Silver-Zinc	100	200	-10 to +25	<1	<100
Nickel-Cadmium	35	100	-10 to 25	> 5	>30,000*
Nickel-Hydrogen	40	80	-10 to 30	5 to 10	>40,000*
Lithium-Ion	100	240	-30 to 40	4	1000

This occurred largely because of the revolutionary impact these batteries have had on the portable electronics market and the concurrent investment placed in this technology as a whole. There are significant advantages associated with the use of this new system, listed in Table-1. As may be seen, lithium-ion batteries offer significant advantages in terms of mass, volume and temperature range and were perceived as the appropriate next generation technology for NASA missions.

2. MISSIONS

The first major NASA mission that was intended to take advantage of lithium-ion batteries was the Mars lander under the 2001 Mars Surveyor Program (MSP01). Several modifications were made to develop aerospace-quality Li-ion batteries, under a NASA-DoD joint program. Significant among them was the development of a new electrolyte for enhancing low temperature performance of Li-ion batteries. The electrolyte utilized in the MSL 01 Lander contained the first-generation low temperature electrolyte, 1 M LiPF₆ in equi-proportion mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC), developed at JPL, which outperformed the binary electrolyte mixtures used thus far.¹ Considerable enhancement in low temperature performance was achieved, to about 70% of the room temperature value at -20°C, without compromising the cycle life or calendar life. The mission was cancelled by NASA due to

programmatic issues. Nonetheless, the batteries fabricated for this project have shown impressive performance in simulated Mars Orbiter or Mars lander applications, as shown in Figure 1.

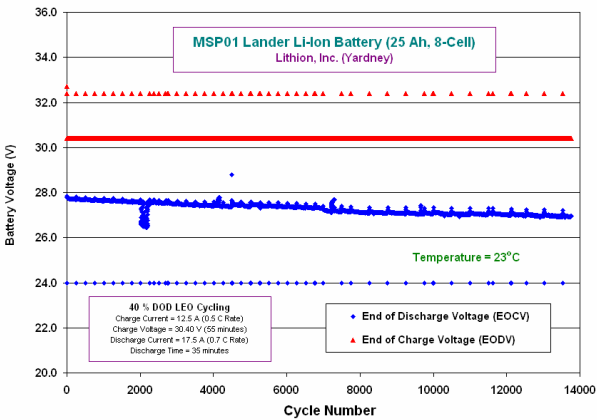


Figure.1: End of discharge and charge voltages of MSP 01 Lander Li-Ion battery during cycling at 40% depth of discharge (DOD) at 25°C, for an orbiter application.

As may be seen from Fig.1, the end of discharge voltage is decreased by about 1 V over ~ 14000 cycles. The capacity checks made after each 500 cycles showed less than 15% loss in the capacity, as a result of this cycling and long wet life of about five years. In a separate test, another MSP01 battery showed similarly impressive performance during Mars lander simulation cycling, losing less than 15% capacity over 500 sols.²

While the Li-ion batteries would have successfully powered the MSP 01 lander, if the mission had taken place as planned, the Mars Exploration Rovers mission were the first significant executed NASA mission to take advantage of the lithium-ion technology. In terms of chemistry, the batteries used on the Mars Exploration Rovers were identical to the MSP 01 Lander batteries, in terms of electrode active materials as well as electrolytes. The performance of these on both rovers, Spirit and Opportunity is as impressive as may be expected from the demonstrated durability of MSP01 lander batteries in laboratory tests. The rovers have completed 1000 sols on Mars, compared to the designed life of 90 sols, thus contributing to the astounding success of these rovers in exploration the Martian surface. Figs. 2 and 3 illustrate performance of the lithium ion battery assembly units on Spirit and Opportunity.³

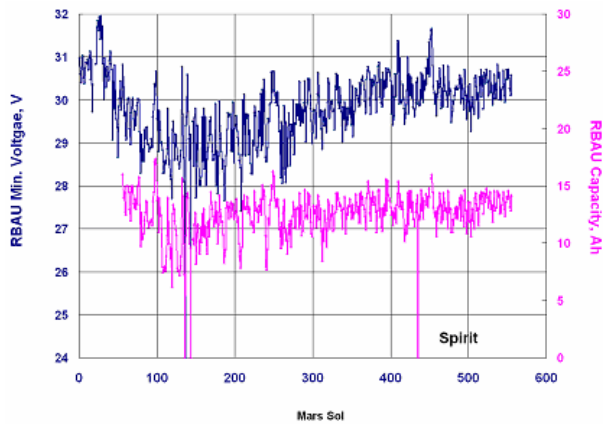


Figure 2. Performance of lithium-ion batteries on the Mars Exploration Rover, Spirit. The End of discharge voltage as well the delivered capacity are shown as a function of Sol.

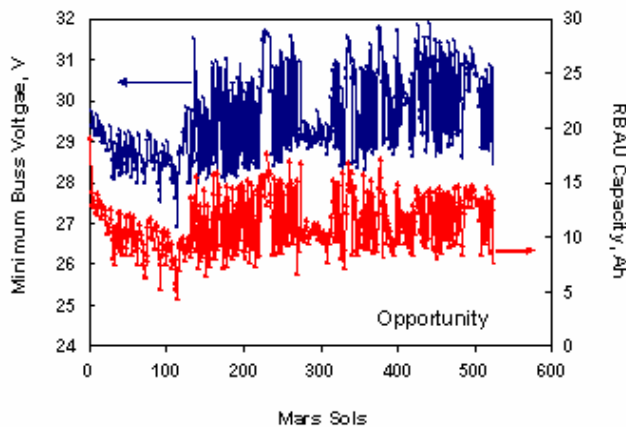


Fig. 3 Performance of lithium-ion batteries on the Mars Exploration Rover, Opportunity. The End of discharge voltage as well the delivered capacity are shown as a function of Sol.

As may be seen in figures 2 and 3, the end of discharge voltages during discharge at an average depth of discharge of 45%, are above 26 V and do not decay significantly over 600 sols. Further, the batteries displayed good tolerance to occasional deep discharge, some down to below 3 V, and as well to low temperatures approaching -30°C during winter. The mission-simulation tests being performed on ground on prototype batteries indicate that they still retain close to 90% of the initial capacity, and to a large extent, their low-temperature performance capability.⁴

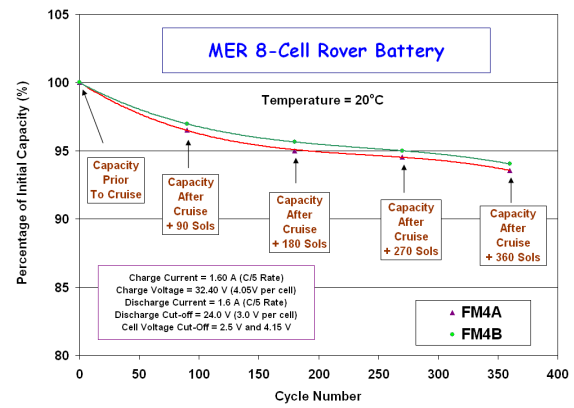


Fig. 4 Mission simulation ground testing of Mars Exploration Rover lithium-ion batteries.

These results are quite promising for future Mars missions, such as Phoenix Lander and Mars Science Laboratory.

3. RADIATION TOLERANCE OF LI-ION CELLS

Since lithium ion cells contain organic electrolytes and polymeric separators, their tolerance to high-intensity radiation environments, which is required for the exploration of Jupiter, is uncertain. We therefore carried out detailed experimental evaluation on cells from three different manufacturers, using ^{60}Co source. The cells were incrementally exposed to gamma radiation, both at high dosage rates of 30 rads/sec (corresponding to 1.5 Mrad over 14 hours) and a low level of 1.24 rad/sec (corresponding to 1.5 Mrad over two weeks). After each irradiation, the cell capacities were measured both at ambient and low temperatures. The fade rates were established from charge-discharge cycles, as illustrated in Fig. 5.⁵

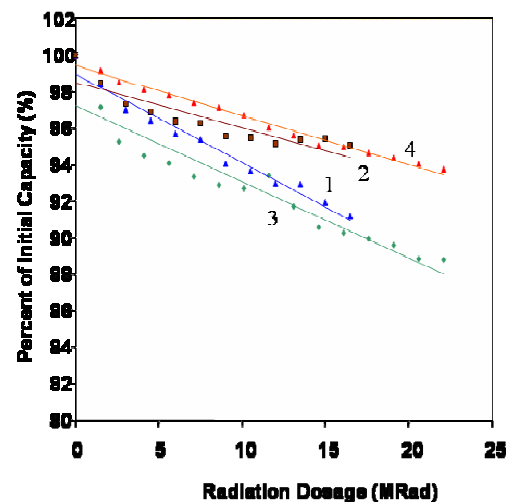


Fig. 5. Capacity retention of 1) Sony/AEA 18650, 2) Sony 18650 control cells, 3) Yardney 7 Ah, 4) SAFT 10 DD

lithium-ion cells during exposure to various cumulative levels of γ -radiation. The solid lines indicate predicted performance.

These data show that all the Li-Ion cells evaluated here displayed impressive and adequate tolerance to radiation levels as high as 18 Mrad and exhibit a loss of less than 10 % upon such high levels of radiation exposure. Furthermore, a portion of this loss can be attributed to the cycling or storage during this incremental radiation exposure. Further studies are underway to understand the effects of the radiation on individual cell components.

4. EXPLORATION SYSTEMS DIRECTORATE

Even though the infusion of lithium batteries into NASA's space missions may be regarded as successful in enhancing and/or enabling Mars missions, NASA's focus has shifted to new type of missions in the Exploration Systems Missions Directorate (ESMD), set up primarily to implement President Bush's vision to "Return to Moon, Mars and beyond". Unlike the previous planetary exploration missions, the ESMD mission have significant component of human exploration, with missions such as Crew Exploration Vehicle (to replace space shuttle), Cargo Launch Vehicle, Lunar stations / habitats, Pressurized Lunar Landers, Extra Vehicular Activities (EVA) etc. The energy storage requirements for such ESMD missions, as well as for the upcoming Space Science missions are becoming increasingly challenging in terms of reducing the mass and volume of energy storage device, enhancing its life and durability and improving its ability to withstand extreme environments.

A technology development project was thus awarded, under intramural technology programs, to JPL and its NASA and non-NASA collaborators to develop advanced lithium-ion batteries that would meet the energy storage demands of future ESMD missions. The participating organizations included three other NASA centers (GRC, JSC and MSFC), three universities (UT Austin, U.S.C and Caltech) and suitable industrial partners in the later years of the four-year project. Specific objectives of this project is to develop, among other energy storage systems, Li-ion batteries that would display enhanced energy densities and wider operating temperatures, compared to the state of art lithium ion technologies, as listed in Table-2. The projected improvements are expected to be realized through a development of advanced electrode materials and electrolyte solutions, which are demonstrated in prototype cells and batteries. These developments were to be achieved over a period of four years, with well-planned objectives for each year. Even though this project was re-defined based on the ESAS (Exploration Systems Architectural Studies) into the current space-rated Li-ion

batteries, it provided an excellent platform for the latter project. In addition, many of the materials development activities for Li-ion batteries have been retained in this transition. Some of the developments made in the cathode materials and electrolytes for advanced Li-ion cells and batteries are briefly described here.

Table-2 Performance goals for developing advanced Li-ion batteries for ESMD missions.

System	Phase	Technology Description	Technology Metrics	State of Art	Performance Goal	Test and Verification
Material Development	Phase-1	Cathode Sp. Capacity	mAh/g	160	200	Laboratory test cell
		Low temp. Electrolyte	$^{\circ}\text{C}$	-30	-40	
	Phase-2	Cathode Sp. Capacity	mAh/g	160	250	Laboratory test cell
		Low temp. Electrolyte	$^{\circ}\text{C}$	-30	-60	
Advanced Ion Cells	Li-Phase-2 Year 2	Specific energy	Wh/kg	140	200	EM cells (5-20 Ah)
		Energy Density	Wh/l	350	500	
		Temp. range	$^{\circ}\text{C}$	-30	-60	
Advanced Li-ion battery	Phase-2 Year 3	Specific energy	Wh/kg	100	160	EM batteries
		Energy Density	Wh/l	240	320	
		Temp. range	$^{\circ}\text{C}$	-20	-60	

High Specific Capacity Cathodes

The cathode materials typically used in Li-ion batteries consist of lithiated metal oxides, LiMO_2 , where M is cobalt, nickel, manganese or mixtures thereof. Their layered structure permits intercalation of Li^+ into the galleries of cathode, a reaction similar to that occurs at the graphitic anodes. Lithium cobalt oxide represents the first successful cathode material used in Li-ion batteries, with a specific capacity of 140 mAh/g (to a charge potential of 4.2 V vs Li), good reversibility and moderate thermal stability. The cathode material that is currently used in most of the aerospace battery industries is a mixture of Ni-Co oxide, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, with and without small Al additions. This material provides about 160 mAh/g, good cycle life and slightly improved thermal stability.

To improve the specific capacity, we have evaluated three generations of cathode materials, some of them from multiple sources, in addition to the baseline, $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$. These three generations may be categorized broadly as two types of layered compounds: Lithiated nickel-manganese-cobalt oxide ($\text{Ni}_x\text{Mn}_x\text{Co}_{1-x}\text{O}_2$) and excess-Li, Ni-Mn formulations, $\text{Li}(\text{Li},\text{Mn},\text{Ni})\text{O}_2$. The last type of compounds represent solid solutions between layered $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ (commonly designated as Li_2MnO_3) and LiMO_2 ($\text{M} = \text{Mn}_{0.5}\text{Ni}_{0.5}$) $\text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2$, and have been found to exhibit capacities as high as 250 mAh, on cycling them to 4.8 V.⁶

Table 3 lists the formulations and the sources of these cathode materials, which include our university and other collaborators.

Figure 6: Comparison of specific capacities and specific energies of advanced cathode materials.

Table 3: Advanced cathode materials for Li-ion batteries

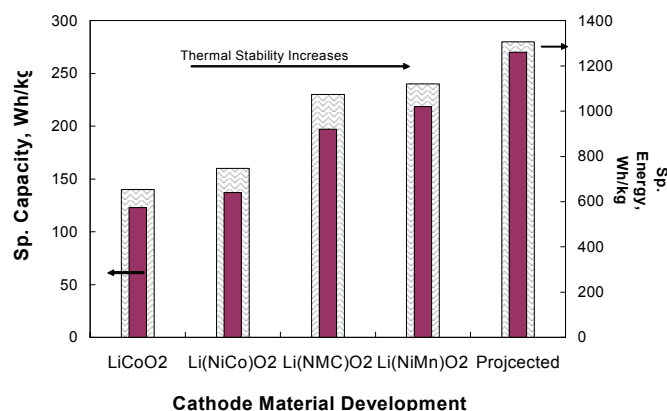
Material	Cathodes	
	Layered Mixed metal oxides	
	Composition	Source
State of Art SOA	$\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$	• Yardney electrodes • OMG powder
Gen 1	$\text{Li}(\text{Mn,Ni,Co,Li})\text{O}_2$	• Synthesized at JPL
Gen-2	$\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$	• UT Austin Powder • DoE and Enax electrodes • Max Power cells
Gen 3	$\text{Li}(\text{Mn,Ni,Co,Li})\text{O}_2$	• UT Austin Powder

The cathode materials have been evaluated in coin cells against Li anodes typically in the baseline or state of art electrolyte. The results of our evaluation of these three generations of cathode materials are listed in Table-4.

Table-4. Comparison of advanced cathode materials

Cathode	Composition	Performance Summary
SOA	Layered- $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$	• ~165 mAh/g when charged to 4.1 V. • Low irreversible capacity (< 30 mAh/g) & Good Cycle life
Generation 1	Layered $\text{Li}(\text{Mn,Ni,Co,Li})\text{O}_2$	• > 200 mAh/g when charged to 4.6 V. • High irrev. Cap. (> 30%); Rapid fade at high Voltage
Generation-2	Layered- $\text{Li}(\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33})\text{O}_2$	> 180 mAh/g reversible capacity > 30 mAh/g of Irrev. capacity and good cyclability
Generation 3	Layered $\text{Li}(\text{Mn,Ni,Co,Li})\text{O}_2$	> 240 mAh/g reversible capacity > 30 mAh/g of Irrev. capacity and good cyclability

As listed above, there is a substantial improvement, above 50%, in the specific capacity from the state of art materials (160 mAh/g) to the Generation 3 (and gen-1) materials. In addition to the improved capacities, these advanced cathodes also have higher voltages (4.5 V vs. 4.1), which contribute to higher specific energies, as illustrated in Fig. 6.



These improvements in the cathode materials are quite promising to result in a similar increase in the specific energies of Li-ion cells and batteries. There is, however, an operational difficulty associated with the high capacity cathode. The kinetics of the cathode chemistry are relatively slow, resulting in a reduction of the nominal obtainable power densities (i.e. the maximum useable discharge current). Alternately, at moderate to high power densities, the advantage of high capacity is diminished. This is being addressed in our on-going studies, by coating the cathode particles with suitable oxides, Al_2O_3 , Fe_2O_3 etc,

Low Temperature Electrolytes

The approach for developing low temperature electrolytes for Li-ion batteries involves: 1) Retaining the key film-forming solvent with high dielectric constant, which is either ethylene carbonate or propylene carbonate (for coke), 2) Reducing the EC (or PC) content, 3) adding co-solvents with low freezing point, low viscosity and good chemical and electrochemical stability and 4) use of mixed solvents. Using these approaches, we have developed several successful electrolytes over the last decade. For the developing electrolytes with wide operating temperatures under this program, we examined three generations of electrolytes, based on all-carbonate mixed solvents and with esters co-solvents. The three generations of electrolytes included 1) EC:DEC:DMC:EMC (1:1:1:3) – Gen 1, and 2) formulations based on EC: EMC (20:80)⁷ (generation 2 and 3), as listed in Table 5.

Table 5: Advanced Low Temperature Electrolytes

Material	Electrolytes	
	(Carbonate based mixed solvents)	
	Composition	Source
SOA	1.0 M LiPF ₆ in 1:1:1 EC+DMC+DEC	USC/JPL
Gen 1	1.0 M LiPF ₆ in 1:1:1:3 EC+DMC+DEC+EMC	USC/JPL
Gen-2	1.0 M LiPF ₆ in EC+EMC (20:80); 2) 1.2 LiPF ₆ in EC:EMC (20:80); and 1.2 LiPF ₆ in EC:EMC (30:70)	USC/JPL
Gen 3	1.0 M LiPF ₆ in 1:4 EC+EMC mixtures with ester co-solvents	USC/JPL

There is a considerable improvement in the low temperature performance from the SOA to the advanced electrolytes in terms of temperature range, as illustrated in Fig.7.

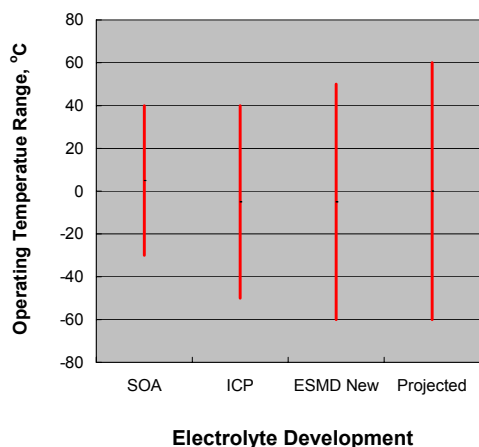


Figure 7: Comparison between state of art and several improvements made under ESMD programs for Li-ion battery operational temperature range.

The advanced electrolytes examined here performed well down to -60°C with about 50% yield at low to moderate discharge rates, as was demonstrated in laboratory test cells.

Subsequently some of these formulations have been further demonstrated in the prototype 7Ah prismatic and 10 Ah cylindrical cells from two representative aerospace battery manufacturers, i.e. Yardney or Lithion and SAFT America.

The 7 Ah cells made by Yardney also exhibit similar improvements in the low-temperature performance at -60°C (Fig. 8), consistent with our observations from laboratory cells.

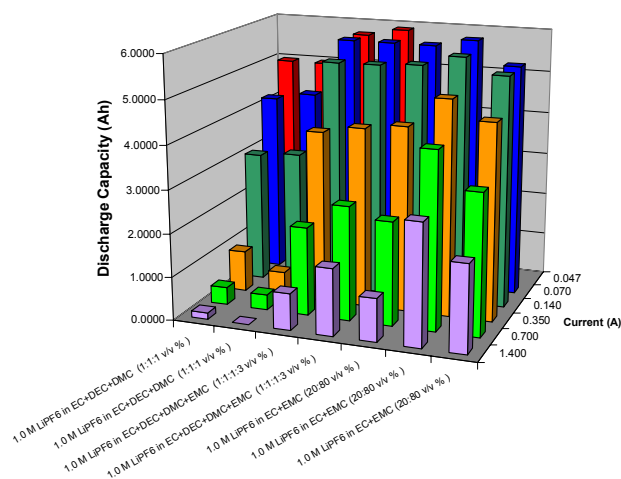


Figure 8: Performance of 7 Ah cells at -60°C with different low temperature electrolytes.

As may be seen from the above figure, the state of art electrolyte performs poorly at low temperatures under moderate rates of C/5 (i.e. rate that would result in a complete discharge after 5 hours at room temperature), displaying less than 5% of the room temperature capacity

while the low temperature electrolyte yields 20-40% room temperature capacity. These ongoing research studies are aimed at achieving high temperature resilience with these electrolytes, using suitable electrolyte additives that would minimize the degradation mechanisms, e.g., thermal decomposition of the salt.

5. CONCLUSIONS

Significant advances have been made in the cathode materials and electrolytes for Li-ion cells and batteries. Several new cathodes with high specific capacity approaching 250 mAh/g, coupled with high voltage and improved thermal stability have been identified. Likewise, several new electrolytes for enabling operations at -60°C have been demonstrated. These advances are expected to result in advanced lithium-ion cells and batteries with high specific energy and wide range of operating temperatures, as desired in future NASA missions.

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References

1. M. C. Smart, B. V. Ratnakumar, and S. Surampudi, Electrolytes for low-temperature lithium batteries based on ternary mixtures of aliphatic carbonates, *Journal of the Electrochemical Society*, 146 (2): 486-492 FEB 1999.
2. C. M. Reid, M. C. Smart, R. V. Bugga, M. A. Manzo, T. B. Miller, and R. Gitzendanner, "Performance and Comparison of Lithium-ion Batteries Under Low-Earth-Orbit Mission Profiles", 4th International Energy Conversion Engineering Conference (IECEC), San Diego, CA, June 26-29, 2006.
3. B.V. Ratnakumar, M.C. Smart, R. C. Ewell, L. D. Whitcanack, K. B. Chin, S. Surampudi, F. Pugliab, and R. Gitzendanner, "Telemetry Data of the Li-ion Batteries on JPL's 2003 Mars Exploration Rovers" 3rd International Energy Conversion Engineering Conference (IECEC), San Francisco, CA, Aug. 19, 2005.
4. M.C. Smart, B.V. Ratnakumar, R. C. Ewell, L. D. Whitcanack, K. B. Chin, S. Surampudi, F. Pugliab, and R. Gitzendanner, "Ground Testing of the Li-ion Batteries in Support of JPL's 2003 Mars Exploration Rover Mission" 3rd International Energy Conversion Engineering Conference (IECEC), San Francisco, CA, Aug. 19, 2005.

5. B. V. Ratnakumar, M. C. Smart, L. D. Whitcanack LD, et al., Behavior of Li-ion cells in high-intensity radiation environments II. Sony/AEA/ComDEV cells, *Journal of the Electrochemical Society* 152 (2): A357-A363 2005.
6. Y. Wu and A. Manthiram, "High Capacity, Surface Modified Layered $\text{Li}[\text{Li}_{(1-x)/3}\text{Mn}_{(2-x)/3}\text{Ni}_{x/3}\text{Co}_{x/3}]\text{O}_2$ Cathodes with Low Irreversible Capacity Loss," *Electrochemical and Solid State Letters*, 2006.
7. M. C. Smart, B. V. Ratanakumar, J. Whitacre and K. Amine, "Electrochemical performance and kinetics of $\text{LiCo}_{0.33}\text{Ni}_{0.33}\text{Mn}_{0.33}\text{O}_2$ electrodes in low temperature electrolytes", *J. Power Sources*, in press

Biography

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Kumar is currently a Principal Member of Technical Staff at JPL in the Electrochemical Technologies Group of the Power Systems Section (3463). He has been working on different primary and rechargeable battery systems for the last twenty five years. He has worked both in the development and mission insertion of Li-ion battery technology, and is the energy storage lead for both the Mars Exploration Rover and Mars Science Laboratory missions (among others).