

Assessment of Various Low Temperature Electrolytes in Prototype Li-ion Cells Developed for ESMD Applications

M.C. Smart*, B.V. Ratnakumar, and L. D. Whitcanack

*Jet Propulsion Laboratory, California Institute of Technology
4800 Oak Grove Drive, Pasadena, CA 91109*

Due to their attractive properties and proven success, Li-ion batteries have become identified as the battery chemistry of choice for a number of future NASA missions. A number of these applications would be greatly benefited by improved performance of Li-ion technology over a wider operating temperature range, especially at low temperatures, such as future ESMD missions. In many cases, these technology improvements may be mission enabling, and at the very least mission enhancing. In addition to aerospace applications, the DoE has interest in developing advanced Li-ion batteries that can operate over a wide temperature range to enable terrestrial HEV applications. Thus, our focus at JPL in recent years has been to extend the operating temperature range of Li-ion batteries, especially at low temperatures. To accomplish this, the main focus of the research has been devoted to developing improved lithium-ion conducting electrolytes. In the present paper, we would like to present some of the results we have obtained with six different ethylene carbonate-based electrolytes optimized for low temperature. In addition to investigating the behavior in experimental cells initially, the performance of these promising low temperature electrolytes was demonstrated in large capacity, aerospace quality Li-ion prototype cells, manufactured by Yardney Technical Products and Saft America, Inc. These cells were subjected to a number of performance tests, including discharge rate characterization, charge rate characterization, cycle life performance at various temperatures, and power characterization tests.

I. Introduction

Although most current ESMD applications are anticipating requiring rechargeable batteries which operate over a relatively modest temperature range (i.e., 0 to 30°C), initial development work was focused on improving the operating temperature range of Li-ion batteries over a much wider temperature range (e.g., -60 to +60°C). For a number of future NASA applications, as well as many terrestrial applications, it would be very desirable to have efficient operation over such a large temperature range. Since the operating temperature range of Li-ion cells can be dramatically affected by the electrolyte type, significant research has been devoted to the development of advanced electrolytes for wide operating temperature Li-ion cells.¹ This performance goal continues to be a very challenging technical problem. To date, very good low temperature electrolytes tend to perform very poorly at higher temperatures, often due to the presence of low boiling, reactive components. For example, many low temperature electrolytes can contain large proportions of low boiling co-solvents, which tend to be more reactive than the traditional carbonate-based solvents, leading to increased cell impedance due to the formation of resistive surface films.² In addition, many of these systems can lead to cell venting episodes, due to the formation of excessive internal cell pressure. In contrast, electrolytes that perform very well at the higher temperatures tend to perform very poorly at lower temperatures. For example, cells containing electrolytes with a high proportion of cyclic carbonate, such as ethylene carbonate, have been demonstrated to perform better than cells with a lower proportion of EC.³ However, the low temperature performance is compromised, due to the high melting point of the solvent (and electrolyte) and the high viscosity, leading to low conductivity. Thus, most often the best compromise is the selection of an electrolyte that works well down to fairly low temperatures (i.e., -30 or -40°C), but still performs well when subjected to storage and/or cycling at higher temperatures. However, work is on-going to identify improved systems which further extend the range of operation.

With respect to NASA's ESMD program, the challenge of developing an electrolyte which will enable the operation of Li-ion cells over such a large temperature range is further exacerbated by the fact that there is also a desire to have increased safety and electrode couples that produce high energy density cells.⁴ The design of electrolytes with enhanced safety characteristics often involves approaches utilizing either low flammability

components (i.e., non-flammable co-solvents), the use additives (such as flame retardant additives), or the use of alternative lithium salts that are thermally more stable compared with the standard lithium hexafluorophosphate, LiPF₆. Unfortunately, most of these approaches tend to limit the temperature range of operation, especially at the lower temperatures due to increase impedance. In addition the safety characteristics, the fact that non-traditional electrode couples are desired to enable the realization of high energy density cells presents another technical challenge with respect to developing a wide operating temperature range electrolyte. This is due to the fact that these systems typically operate at high voltage, in excess of 4.3V, and oftentimes as high as 4.80V. Operating at such high potentials will likely be detrimental to many electrolyte components which are identified to aid the low temperature performance (i.e., low viscosity co-solvent).

To serve as a baseline for the electrolyte development of this program, the performance of 1.0 M LiPF₆ in EC+DMC+DEC (1:1:1 v/v) coupled with MCMB-LiNiCoO₂ is considered to be the benchmark for further improvements.⁵ This system has been utilized for a number of NASA missions, including the 2003 Mars Exploration Rover (MER) mission⁶, the Phoenix Mars Polar Lander, and the up-coming 2009 Mars Science Laboratory (MSL)⁷ mission. In parallel with more fundamental electrolyte development studies performed in experimental three electrode cells, a number of prototype cells manufactured by a number of battery vendors continue to be evaluated with various advanced electrolytes. An 8 Ah cell (nameplate capacity, actual capacity = 10Ah) manufactured by Yardney Technical Products for the MER program was selected to serve as baseline for prototype cell performance. Thus, there was an attempt to evaluate previously developed candidate electrolytes in a similar format (i.e., in prismatic cells of comparable size, 7-10 Ah, manufactured by Yardney Technical Products of similar chemistry). In addition to cells manufactured by Yardney, a number of electrolytes have been evaluated in cylindrical cells manufactured by Saft America, Inc. These aerospace quality cells typically range in capacity of 9-10 Ah (DD-size) and, thus, provide a good comparison to the electrolytes evaluated in the Yardney prismatic cells.

Since the initial focus was to provide good performance over a wide range of temperatures, a significant portion of our efforts have been devoted to evaluating all carbonate-based electrolytes in prototype cells. A more comprehensive discussion regarding the factors governing the selection of candidate wide operating temperature electrolytes, as well as previous approaches is provided in our previous papers.⁸⁻¹³ The LiPF₆-based all carbonate blends have, thus far, proven to provide the best life characteristics, as well as the best resilience to high temperatures. With optimization of the cyclic and linear carbonate proportions good low temperature performance can be obtained without sacrificing the life characteristics. For further improvements in the low temperature performance (i.e., -40°C and below), the use of low viscosity, low melting co-solvents is especially effective, such as with the use of esters. Thus, embracing these approaches a number of formulations have been evaluated in the prototype cells described, including:

- 1) 1.0 M LiPF₆ in EC + DEC+ DMC (1:1:1 v/v %) (Baseline solution)
- 2) 1.0 M LiPF₆ in EC + DEC+ DMC + EMC (1:1:1:3 v/v %)
- 3) 1.0 M LiPF₆ in EC + EMC (1:4 v/v %)
- 4) 1.0 M LiPF₆ in EC + EMC + MP (1:3:1 v/v %)
- 5) 1.0 M LiPF₆ in EC + EMC + EP (1:4 v/v %)
- 6) 1.0 M LiPF₆ in EC + EMC + EB (1:4 v/v %)

Where EC=ethylene carbonate, DEC=diethyl carbonate, DMC=dimethyl carbonate, EMC=ethyl methyl carbonate, MP=methyl propionate, EP=ethyl propionate, and EB=ethyl butyrate. In addition to cells manufactured by Yardney and Saft, candidate low temperature electrolytes developed at JPL have also been evaluated in other prototype cells manufactured by other vendors, including: (i) Compact Power/LG Chem, (ii) A123 Systems, Inc., (iii) Quallion, LLC, (iv) MER Corp, and (v) MaxPower, Inc. However, due to the scope of this paper a detailed description of these results will not be provided.

II. Performance of All-Carbonate Based Electrolytes in Yardney and Saft Cells

A number of electrical performance tests were performed on the three all carbonate-based electrolytes listed above in both prismatic 7 Ah Yardney Technical Products cells and cylindrical 9 Ah Saft DD-size Li-ion cells. These tests include: (a) discharge characterization over a wide range of temperatures (-70 to +30°C), with charging at room temperature, (b) discharge rate characterization at various temperatures, with the charging being performed at the respective temperature of interest, (c) charge rate characterization over a wide range of temperatures (-40 to +30°C), (d) 100% DOD cycle life performance at various temperatures, including variable temperature cycling (e)

power characterization testing at various temperatures, (f) current-interrupt impedance measurements as a function of temperature, and (g) various mission specific testing, in some cases. The focus of this paper will be to describe the results of the discharge rate characterization as a function of temperature to establish the capability to provide operation over a wide temperature and to determine the relative specific energy densities of large capacity cells under various temperatures.

A. Initial Characterization Testing

Upon receipt of the prototype cells from the vendor, following the formation process, the cells were subjected to initial conditioning cycling at three different temperatures (i.e., 20, 0, and -20°C) to establish the initial capacity and impedance characteristics. At 20°C, the Yardney cells containing the all-carbonate based electrolytes displayed initial discharge capacities ranging from 7.83 to 8.07 Ah (7.94 average) when the cells were charged using C/5 charge and discharge rates over a voltage range of 2.75 to 4.10V (cells designated 7 Ah nameplate capacity and “LW series cells”). Under similar conditions, the Saft cells containing the same electrolytes displayed a range of capacities from 10.41 to 10.60 Ah (cells designated 9 Ah nameplate capacity and “NCS series cells”). When the specific energies of all of the cells were compared, as shown in Fig. 1, the cylindrical Saft cells displayed higher specific energies compared to the prismatic Yardney cells, with an average of 147.9 Wh/kg and 118.1 Wh/kg being observed, respectively. In terms of performance, the electrolyte type had little effect upon the capacity or energy displayed by the cells.

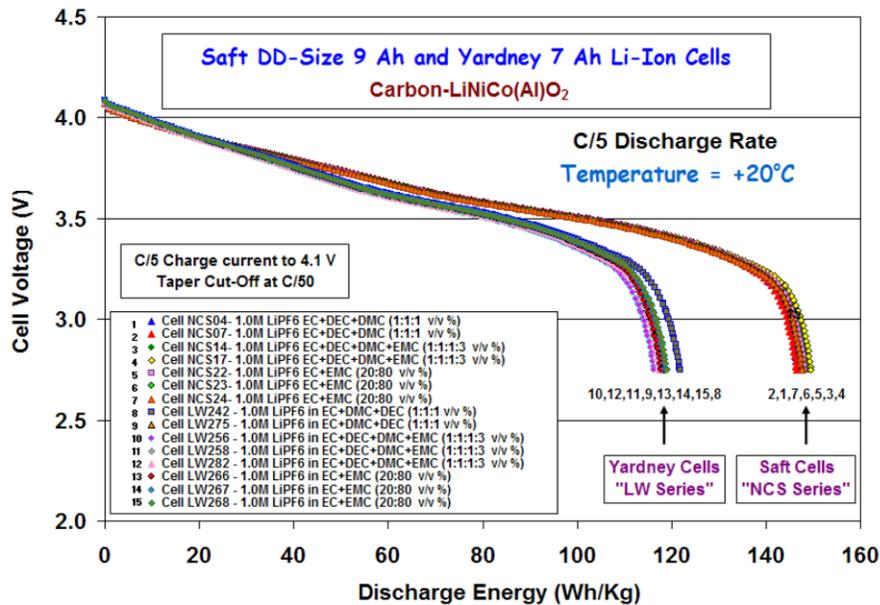


Figure 1. Initial specific energies of Saft and Yardney prototypes cells at 20°C, using C/5 charge and discharge rates over a voltage range 2.75 to 4.10V (C/50 taper current cut-off on charge).

Under similar conditions at 0°C, the Saft cells displayed average capacities of 9.53 Ah and 9.39 Ah, using a room temperature charge and charging at 0°C, respectively, corresponding to 131.5 Wh/kg in the latter case. Whereas, the Yardney cells displayed average capacities of 7.24 Ah and 7.17 Ah using a room temperature charge and charging at 0°C, respectively. When the cells were evaluated at -20°C (using a C/10 charge and C/5 discharge), the Saft cells displayed average capacities of 8.28 Ah and 7.75 Ah, depending upon whether the cells were charge at 20 or -20°C, whereas the Yardney cells delivered 6.68 Ah and 6.38 Ah, respectively. In addition to determining the capacity and energy values for the cells, DC current-interrupt impedance measurements were performed as a function of state-of-charge (e.g., 100, 80, 60, 40, and 20 % SOC), using C/2 discharge currents for a duration of 60 seconds (impedance value determined from open circuit voltage one hour after discharge). At 20°C, the Saft cells displayed an average

impedance of 20.76 mΩ at 100% SOC and 23.00 mΩ at 80% SOC. Although minor, trends were observed depending upon the electrolyte type, with the ternary baseline electrolyte (1.0 M LiPF₆ in EC+DEC+DMC) displaying the lowest impedance at 100% SOC, 19.75 mΩ, followed by the quaternary electrolyte (1.0 M LiPF₆ in EC+DEC+DMC+EMC) which had an average of 20.81 mΩ, and the binary electrolyte (1.0 M LiPF₆ in EC+ EMC), which displayed the highest average impedance of 21.41 mΩ. When the Yardney cells were evaluated, the cells containing the ternary electrolyte also displayed the lowest average impedance at 100% SOC, 17.57 mΩ, whereas the binary electrolyte containing cells were observed to have the next lowest impedance, 18.83 mΩ, followed by the quaternary electrolytes cells, 19.71 mΩ. This trend in impedance can be rationalized, in part, by the corresponding ionic conductivities, which are increase with increasing ethylene carbonate content at ambient temperatures. It should be noted that the impedance values determined by this method are significantly higher than those derived from using a traditional milliohmeter (1 kHz), due to the fact that the low current and long discharge duration conditions reflect greater charge transfer and mass transfer contributions.

B. Discharge Performance at Various Temperatures (Room Temperature Charging)

After performing initial characterization, the cells were subjected to discharge characterization over a range temperatures (-70° to +30°C) and a range of discharge rates (C/100 to C rates). For this testing all charging of the cells was performed at room temperature. In addition, all of the cells were discharged to 2.0V, which is much lower than some particular applications can tolerate, to derive the greatest amount of capacity. However, the cells were routinely discharged to such low voltages with the intent of obtaining a more comprehensive data base of performance, since the discharge capacities delivered at higher end-of-discharge voltages can easily be extracted from the data, and any pronounced capacity fade and/or failure mechanisms have not been observed under such conditions. The characterization of the discharge performance was performed at the lower temperatures first, while the cells were still “fresh” and not degraded by cycling. In total, approximately 70 cycles were performed on the cells throughout the discharge rate characterization testing. Selected discharge conditions are described below, which illustrate the effect of that the electrolyte type has upon performance, as well as cell design aspects.

When the cells were evaluated at -20°C using a C/2 discharge rate, as illustrated in Fig. 2, all of the Yardney cells displayed a greater proportion of the room temperature capacity (81.5 to 83.5%) compared to the Saft cells (65.8 to 73.9%) and the electrolyte type was only observed to have a minor effect on the discharge capacity. In contrast, the electrolyte type was observed to play more of a role in the performance of the Saft with the ternary

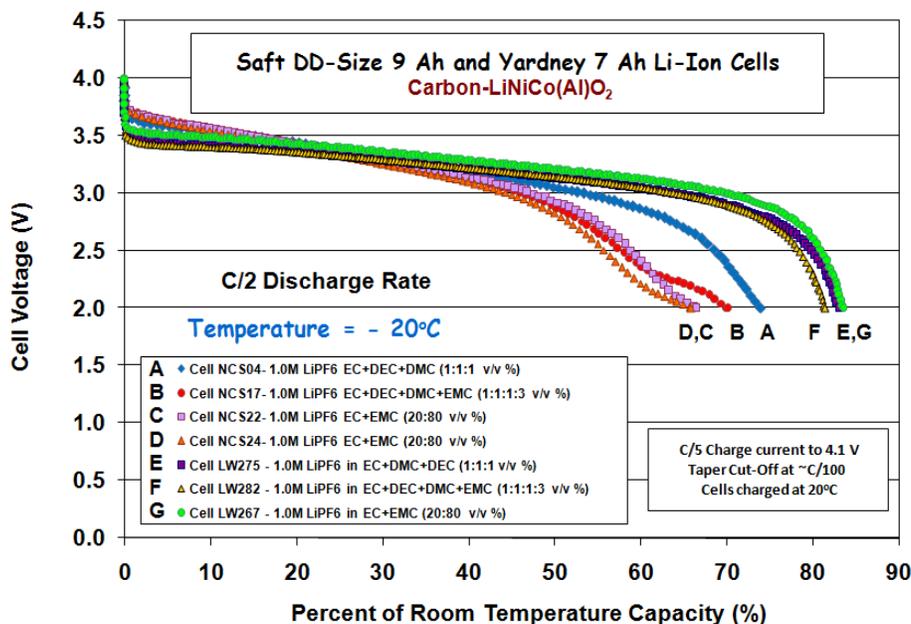


Figure 2. Percent of the room temperature capacity (Ah) delivered by Saft and Yardney prototype Li-ion cells at -20°C, using C/2 discharge rates to 2.0V (cells charged at room temperature).

baseline electrolyte displaying the best performance. Since the discharge energy is a more important metric for the comparison of differing cell designs and application trade off studies, the data was compared in the specific energy, as displayed in Figure 3. As shown, all of the cells displayed somewhat comparable performance ranging from 83.4 to 95.0 Wh/kg, due to the inherently higher specific energy of the Saft cells being offset by the better low temperature performance of the Yardney cells, with the Saft cells containing the ternary baseline electrolyte delivering the best performance (95.0 Wh/kg). It should be noted that even less differentiation between the electrolyte type was observed if the performance was compared using a 3.0V discharge voltage cut-off.

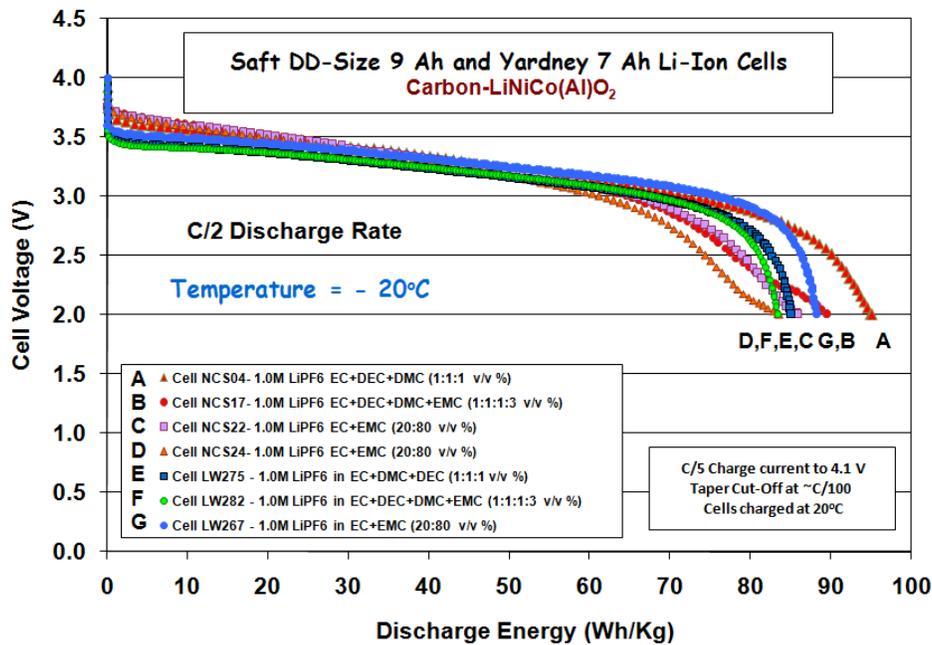


Figure 3. Discharge energy (Wh/kg) delivered by Saft and Yardney prototype Li-ion cells at -20°C, using C/2 discharge rates to 2.0V (cells charged at room temperature).

The impact of electrolyte type and cell design becomes more dramatic when the performance of cells is compared at lower temperature. For example, when the cells were discharged at -40°C using a C/10 discharge rate, as shown in Fig. 4, the Saft cells containing low ethylene content quaternary and binary low temperature electrolytes displayed much better performance (i.e., 90.7 Wh/kg and 88.7 Wh/kg, respectively) compared to the baseline formulation (i.e., 21.0 Wh/kg). The Yardney cells displayed a somewhat different trend with the binary solution showing the best performance (78.2 Wh/kg) followed by the quaternary electrolyte (72.2 Wh/kg) and the baseline ternary electrolyte (71.7 Wh/kg) displaying comparable performance. At moderate to lower rates at these temperatures the Saft cells containing the lower ethylene carbonate-based electrolytes (binary and quaternary solutions) delivered higher specific energies and had much higher operating voltages. However, at higher rates the Yardney cells were observed to provide much better performance, as illustrated in Fig. 5 in which the performance using a C/2 discharge rate at -40°C is displayed. As shown, Yardney cells containing the binary solution were capable of delivering 67.7 Wh/kg, followed by the cells containing the quaternary solution (62.2 Wh/kg) and the baseline ternary electrolyte (44.8 Wh/kg). In sharp contrast, the best performing Saft cells only delivered 17 to 18 Wh/kg (for both the binary and quaternary blends), and the baseline cells only displayed 9.5 Wh/kg. It should be noted that although only one cell per electrolyte type and cell design has been displayed in the figures discussed, multiple samples for each variation were tested and excellent reproducibility between cells was observed as illustrated by two of the Saft cells shown in Fig. 6 (cells NCS22 and NCS24).

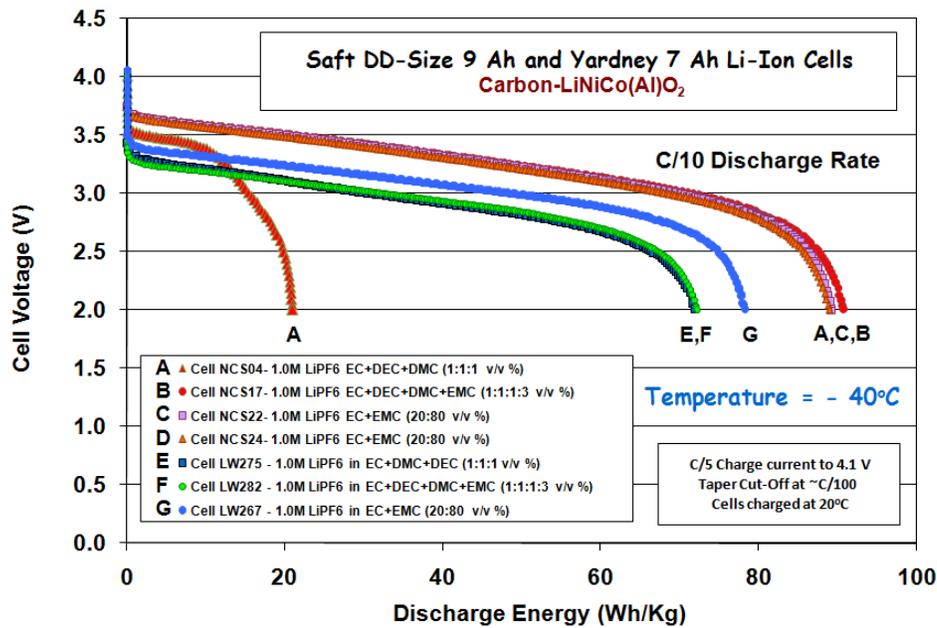


Figure 4. Discharge energy (Wh/kg) delivered by Saft and Yardney prototype Li-ion cells at - 40°C, using C/10 discharge rates to 2.0V (cells charged at room temperature).

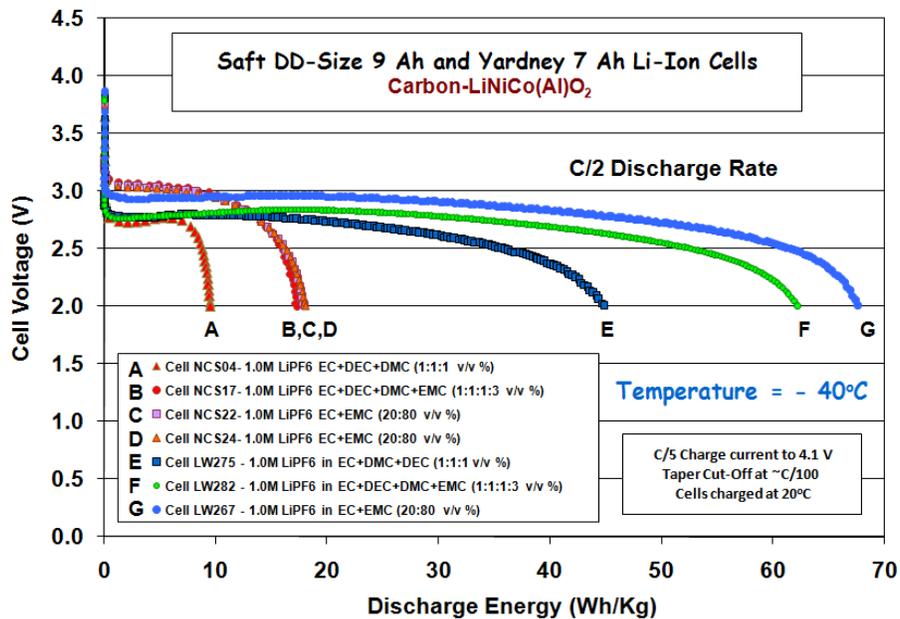


Figure 5. Discharge energy (Wh/kg) delivered by Saft and Yardney prototype Li-ion cells at - 40°C, using C/2 discharge rates to 2.0V (cells charged at room temperature).

Even greater differentiation between electrolyte type and cell design was observed when the cells were evaluated at even lower temperatures, as shown in Fig. 6 in which the discharge performance is shown at -40°C using a $C/10$ discharge rate. As shown, all of the Yardney cells displayed superior performance exhibiting the following trend in low temperature performance as a function of electrolyte type: binary solution (65.7 Wh/kg) > quaternary solution (59.0 Wh/kg) > baseline ternary solution (44.8 Wh/kg). Whereas, the Saft cells all displayed much lower specific energies and were observed to display a somewhat different trend as a function of electrolyte type: quaternary solution (32.9 Wh/kg) > binary solution (23.2 Wh/kg) > baseline ternary solution (5.9 Wh/kg). However, although the Yardney cells were capable of providing higher capacities and specific energies under these conditions, very little capacity was delivered above 3.0V, whereas the Saft cells were observed to have higher operating voltages during the initial portion of the discharge.

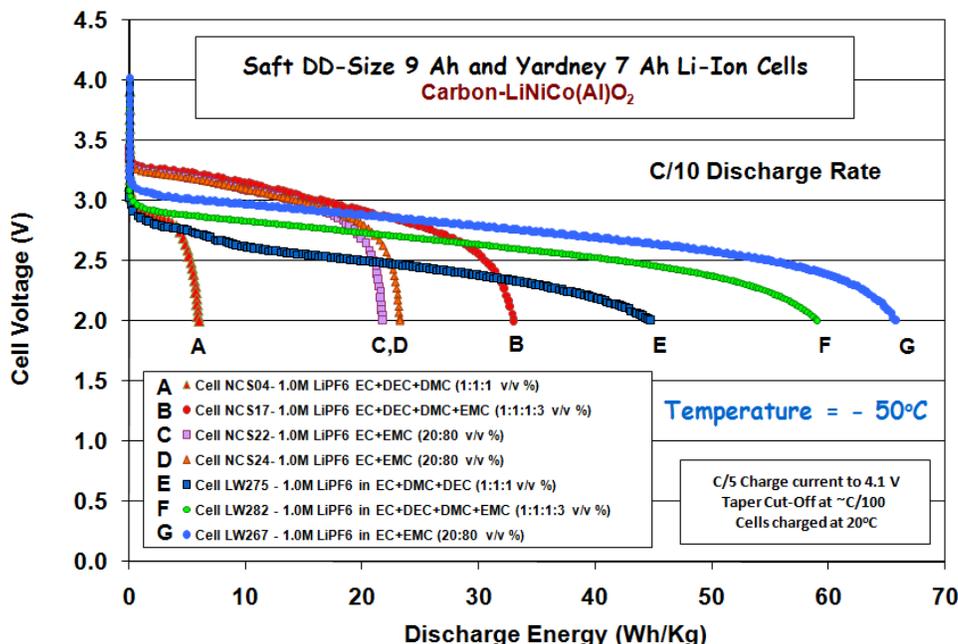


Figure 6. Discharge energy (Wh/kg) delivered by Saft and Yardney prototype Li-ion cells at -50°C , using $C/10$ discharge rates to 2.0V (cells charged at room temperature).

When the cells were evaluated at even lower temperatures (e.g., -40°C) using moderate rates ($C/20$), as shown in Fig. 7, the Yardney cells were again observed to deliver the most energy, with the cells containing the binary electrolyte providing the best performance (48.9 Wh/kg) followed by the quaternary electrolyte (38.6 Wh/kg), which both dramatically outperformed the baseline solution (5.2 Wh/kg). With regard to the Saft cells, both of the low ethylene carbonate-based low temperature electrolytes also outperformed the baseline solutions, however, the trend was reversed in that the quaternary solution displayed better performance than the binary solution (i.e., 13.8 Wh/kg and 7.9 Wh/kg, respectively). In similar fashion to the Yardney cells, the baseline Saft cells performed very poorly. In order to improve the performance at these very low temperatures further modification of the electrolyte type is needed. This can be achieved by decreasing the ethylene carbonate content further (i.e., < 15%) and/or adding low viscosity co-solvents which serve to increase the ionic conductivity at low temperatures. Using the latter approach we have developed a number of electrolyte formulations based upon the incorporation of ester co-solvents which have been observed to dramatically improve the low temperature performance below -40°C . Although large proportions of ester co-solvents (i.e., 40-80%) are desired for very low temperature operation, small quantities are still effective in improving the performance at these temperatures while not compromising the high temperature resilience or increasing the likelihood of pressure build-up with the cells. Using this approach, we have developed a number of formulation in which only 20% by volume of the low viscosity ester co-solvent has been added to the electrolyte with the expectation of improved performance below -40°C which still preserving the life characteristics at milder temperatures.

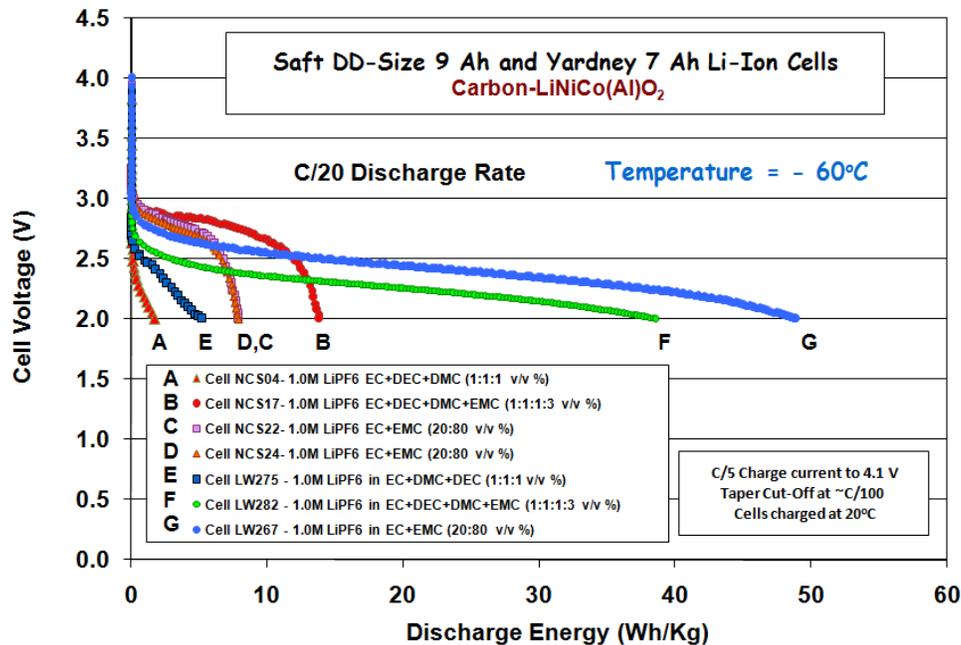


Figure 7. Discharge energy (Wh/kg) delivered by Saft and Yardney prototype Li-ion cells at -60°C , using C/20 discharge rates to 2.0V (cells charged at room temperature).

As shown in Fig. 8, when Yardney cells with electrolytes containing low viscosity ester co-solvents were compared with cells containing all carbonate-based electrolytes at -60°C using a C/20 discharge rate improved performance was observed.¹⁴ As illustrated, the addition of the ester co-solvents results in improved discharge energy being delivered, with the methyl propionate and ethyl propionate containing electrolyte displaying the best performance (both ~ 59 Wh/kg), followed by the ethyl butyrate containing electrolyte (~ 56 Wh/kg). In addition to providing higher discharge capacities and discharge energies, the ester containing electrolytes resulted in cells that displayed much higher operating discharge voltages under these conditions. This can be attributed primarily to the improved ionic conductivity resulting from the addition of these co-solvents, due to the greater ionic mobility as a result of lower viscosity. As mentioned previously, further improvement in the performance can be achieved by the use of even higher proportions of ester co-solvents. For example, we demonstrated further enhancement in the performance at -60°C using electrolytes such as 1.0M in LiPF_6 EC+EMC+MP (10:10:80 v/v %) and 1.0M in LiPF_6 EC+EMC+MB (10:10:80 v/v %) (where MB = methyl butyrate).¹² However, the performance at warmer temperatures ($> 30^{\circ}\text{C}$) is anticipated to be compromised and, thus, the use of these systems will likely be limited to applications in which there is adequate thermal control to ensure that they are not exposed to high temperatures for prolonged durations.

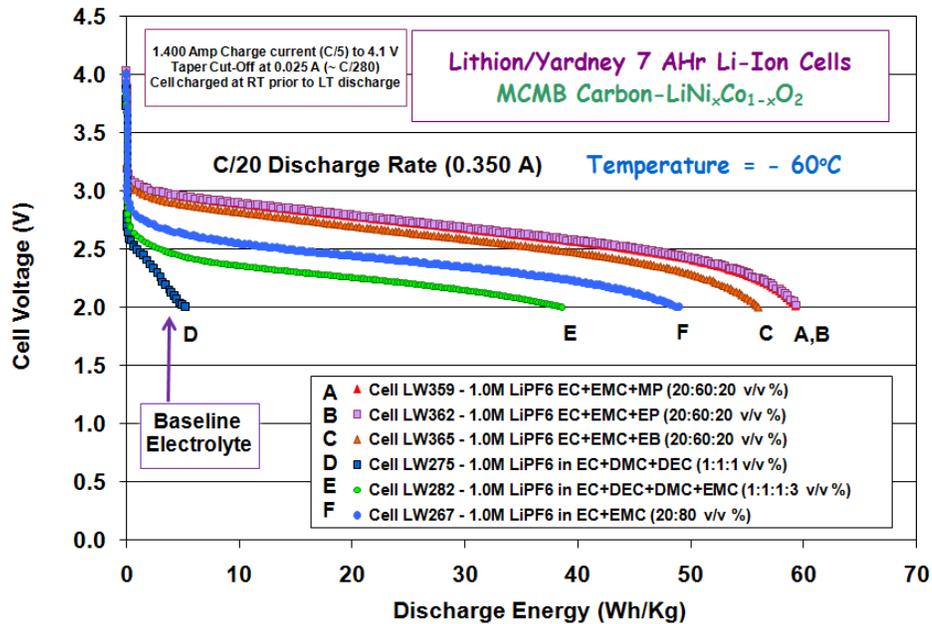


Figure 8. Discharge energy (Wh/kg) delivered by Yardney prototype Li-ion cells at -60°C , using C/20 discharge rates to 2.0V (cells charged at room temperature).

III. Conclusion

The performance of six different ethylene carbonate-based electrolytes previously developed and optimized for low temperature has been demonstrated in large capacity, aerospace quality Li-ion prototype cells, manufactured by Yardney Technical Products and Saft America, Inc. These cells were subjected to a number of performance tests, including discharge rate characterization, charge rate characterization, cycle life performance at various temperatures, and power characterization tests. A detailed discussion of the discharge characterization of the cells as a function of temperature has been provided, focusing upon the performance from -20 to -60°C . At moderate to low rates at -20 and -40°C , the Saft cells were observed to deliver higher discharge energy, owing to their inherently higher specific energy design. However, at higher rates and lower temperatures the Yardney cells displayed improved performance. Below -20°C the low ethylene carbonate based low temperature electrolytes resulted in cells with improved performance in both Saft and Yardney cells. Although both the binary and quaternary electrolytes outperformed the baseline ternary electrolyte below -20°C , different trends were displayed in the two types of prototype cells, with the binary electrolyte displaying better performance in the Yardney cells and the quaternary electrolyte showing the best performance in the Saft cells. In order to achieve improved performance at the very low temperatures (i.e., -60°C), the addition of low viscosity esters co-solvents has been demonstrated to dramatically improve the performance. Although not discussed in detail, excellent room temperature cycle life performance was obtained in a number of prototype cells incorporating these electrolytes.

Acknowledgments

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA) in support of the Exploration Systems Mission Directorate (ESMD).

References

- ¹ Xu, K., “Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries”, *Chem. Rev.*, **104**, 4303-4417 (2004).
- ² Smart, M. C., Ratnakumar, B. V. and Surampudi, S., Wang, Y., Zhang, X., Greenbaum, S. G., Hightower, A., Ahn, C. and Fultz, B., “Irreversible Capacities of Graphite in Low Temperature Electrolytes for Lithium-Ion Batteries”, *J. Electrochem. Soc.*, **146**, 3963 (1999).
- ³ Smart, M. C., Ratnakumar, B. V., Whitacre, J. F., Whitcanack, L. D., Chin, K. B., Rodriguez, M. D., Zhao, D., Greenbaum, S. G., and Surampudi, S., “The effect of electrolyte type upon the high temperature resilience of lithium-ion cells”, *J. Electrochem. Soc.*, **152 (6)**, A1096-A1104 (2005).
- ⁴ Ratnakumar, B. V., Smart, M. C., West W. C., and Whitacre, J. F., “Development of Advanced Li-Ion Materials for Aerospace Applications”, 10th Electrochemical Power Sources R&D Symposium, Williamsburg, VA, Aug. 20-23, 2007.
- ⁵ Smart, M. C., Ratnakumar, B. V. and Surampudi, S., “Electrolytes for Low Temperature Lithium-ion Batteries Based on Mixtures of Aliphatic Carbonates”, *J. Electrochem. Soc.*, **146 (2)**, 1999, pp. 486-492.
- ⁶ (a) Ratnakumar, B. V., Smart, M. C., Kindler, A. Frank, H., Ewell, R., and Surampudi, S., “Lithium Batteries for Aerospace Applications: 2003 Mars Exploration Rover”, *J. Power Sources*, **119-121**, 2003, pp. 906-910. (b) Smart, M. C., Ratnakumar, B. V., Ewell, R. C., Whitcanack, L. D., Chin, K. B., Surampudi, S., Puglia, F., and Gitzendanner, R., “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.
- ⁷ Smart, M. C., Ratnakumar, B. V., Whitcanack, L. D., Dewell, E. A., Jones, L. E., Salvo, C. G., Puglia, F., Gitzendanner, R., “Performance Testing of Yardney Li-ion Cells and Batteries in Support of JPL’s 2009 Mars Science Laboratory Mission”, 6th International Energy Conversion Engineering Conference (IECEC), Cleveland, OH, July 28-30, 2008.
- ⁸ Smart, M. C., Ratnakumar, B. V., Whitcanack, L. D., Chin, K. B. Surampudi, S., Croft, H., Tice D., and Staniewicz, R., “Improved Low Temperature Performance of Lithium Ion Cells with Quaternary Carbonate-Based Electrolytes”, *J. Power Sources*, **119-121**, 349-358 (2003).
- ⁹ Smart, M. C., Ratnakumar, B. V., Behar, A., Whitcanack, L., D., Yu, J. –S., Alamgir, M., “Gel polymer electrolyte lithium-ion with improved low temperature performance”, *J. Power Sources*, **165**, 535-543 (2007).
- ¹⁰ Smart, M. C., Whitacre, J. F., Ratnakumar, B. V., and Amine, K., “Electrochemical performance and kinetics of $\text{Li}_{1+x}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cathodes and graphite anodes in low-temperature electrolytes”, *J. Power Sources*, **168/2**, 501-508 (2007).
- ¹¹ Smart, M. C., Ratnakumar, B. V. and Surampudi, S., “Use of Organic Esters as Co-Solvents in Electrolytes for Lithium Ion Batteries with Improved Low Temperature Performance”, *J. Electrochem. Soc.*, **149 (4)**, A361, (2002).
- ¹² Smart, M. C., Ratnakumar, B. V. Chin, K. B. and Narayanan, S. R., “Ester-based electrolytes that enable lithium-ion cell operation at very low temperatures (-40 to -70°C)”, 206th Meeting of the Electrochemical Society, Oct. 3- Oct. 8, 2004.
- ¹³ Smart, M. C., Ratnakumar, B. V., Whitcanack, L., D., “Performance of Low Temperature Electrolytes in Experimental and Prototype Li-ion Cells”, 5th International Energy Conversion Engineering Conference (IECEC), St. Louis, MI, June 27-29, 2007.
- ¹⁴ Smart, M. C., Ratnakumar, B. V. Whitcanack, L., D., Smith, K. A., Santee, S., Gitzendanner, R. and Yevoli, V., “Li-Ion Electrolytes Containing Ester Co-Solvents for Wide Operating Temperature Range”, 212th Meeting of the Electrochemical Society, Washington, DC, October 7-12, 2007.