Performance of Low Temperature Electrolytes in Experimental and Prototype Li-ion Cells

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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 ethylene carbonate-based electrolytes optimized for low temperature in experimental MCMB-$LiNi_xCo_{1-x}O_2$ cells. In addition to obtaining discharge and charge rate performance data at various temperatures, electrochemical measurements were performed on individual electrodes (made possible by the incorporation of Li reference electrodes), including EIS, linear polarization and Tafel polarization measurements. The combination of techniques enables the elucidation of various trends associated with electrolyte composition. In addition to investigating the behavior in experimental cells, the performance of many promising low temperature electrolytes was demonstrated in large capacity, aerospace quality Li-ion prototype cells. 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.

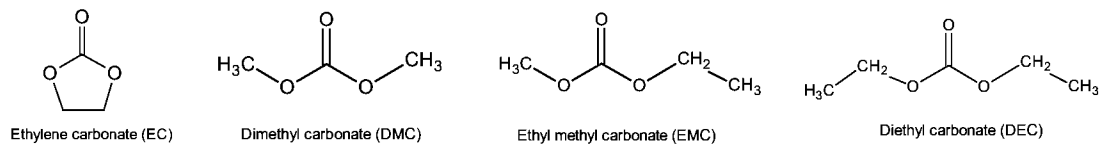
I. Introduction

Several factors can influence the low temperature performance of lithium-ion cells, including: lithium ion mobility in the electrolyte solution (electrolyte conductivity), cell design, electrode thickness, separator porosity and separator wetting properties. Of these parameters, the electrolyte properties are presumably the most dominant, in that sufficient conductivity is a necessary condition for good performance at low temperatures. In designing electrolytes with high conductivity at low temperatures, the solvents should possess a combination of several critical properties, such as: high dielectric constant, low viscosity, adequate coordination behavior, as well as appropriate liquid ranges and salt solubility in the medium. For Li-ion cells which possess graphitic-based anodes, ethylene carbonate (EC) is a desired electrolyte co-solvent, due to the fact that it leads to the formation of a protective surface film at the interface of the electrode, referred to as the solid electrolyte interface (SEI) layer. In addition to producing favorable surface films allowing facile Li^+ movement across the interface, EC also possesses a high dielectric constant (ε=89.6 at 40°C) enabling high electrolyte salt dissociation and solubility, leading to high conductivity of solutions. Furthermore, EC has a high boiling point (243°C), resulting in low vapor pressure solutions, and possesses good electrochemical stability. However, EC has some negative attributes when considered in the context of lithium battery electrolytes, namely it has a high melting point (36.4°C) and has high viscosity (η=1.90 cP at 40°C). Thus, in the design of lithium-ion battery electrolytes EC must be blended with other co-solvents in order to produce solutions that are highly conductive over a wide temperature range. Of the class of organic carbonate solvents, propylene carbonate (PC) is also an attractive solvent in terms of its physical properties, displaying a high dielectric constant (ε=64.9 at 25°C) and possessing a more desirable liquid range than EC (mp= -48.8°C, bp=242°C). However, the use of PC with graphitic anodes leads to a disintegration of the graphene structure, a process referred to as exfoliation, due to co-intercalation into the bulk of the electrodes leading to poor

cyclability. Thus, PC has not found extensive in Li-ion batteries, except when used with coke-based carbon anodes or used in conjunction with a good film forming solvent, such as EC. In general, the cyclic carbonates display properties of high polarity, due to the intramolecular strain of the structure, and high viscosity, in contrast to the linear acyclic carbonates that display lower polarity and lower viscosity.[1] Thus, to produce electrolytes with the desired properties required for efficient cell operation, especially over a wide operating temperature range, the cyclic carbonates, such as EC, have been blended with appropriate co-solvents to lower the melting point and viscosity of the medium.

The most versatile co-solvents employed with EC-based electrolytes have been the linear carbonates, such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC), the structures of which are shown in Fig. 1.

Figure 1. Structures of organic carbonates commonly used in Li-ion battery electrolytes.



The general trends of physical properties displayed by the linear carbonates include: decreasing melting point with increasing molecular weight (mp=4.6°, -53°, -74.3°C, for DMC, EMC, and DEC, respectively), increasing boiling point with increasing molecular weight (mp=91°, 110°, 126°C, for DMC, EMC, and DEC, respectively), and increasing viscosity with increasing molecular weight (mp=0.59cP at 20°C, 0.65cP at 25°C, 0.75cP at 25°C, for DMC, EMC, and DEC, respectively).[1] With regard to the electrochemical stability, especially with respect to the ability to form desirable SEI films in terms of the protective nature and ionic resistance, we have generally observed a trend of decreasing stability with increasing molecular weight (i.e., DMC > EMC > DEC).[2] In the early development of lithium-ion battery electrolytes, EC was successfully used in conjunction with one linear carbonate in binary solvent mixtures (i.e., EC+DMC and EC+DEC). However, in the optimization of low temperature electrolytes, multi-component ternary and quaternary solvent mixtures can be more advantageous, to allow the balancing of physical and electrochemical properties.

As a result of our early efforts to develop improved low temperature electrolytes, we identified a ternary EC-based carbonate electrolyte formulation that lead to improved performance over a wide range of temperature, namely 1.0 M $LiPF_6$ dissolved in EC+DMC+DEC (1:1:1 v/v %), outperforming the commonly used binary mixtures.[2] This electrolyte was originally developed with the intention of enabling efficient Li-ion battery operation of the Lander on Mars for the 2001 Mars Surveyor Project[3], which was cancelled due to programmatic reasons. However, prior to mission cancellation, the battery was fully space qualified and demonstrated to operate over a wide temperature range (-20° to +30°C for mission operation and –30° to +40°C for qualification) and display the requisite cycle and calendar life characteristics. This same chemistry was later adopted by the 2003 Mars Exploration Program for use in the Li-ion batteries on the Mars rovers[4], Spirit and Opportunity, which have been effectively operating since their landing in the summer of 2003, representing over four years of operation on the surface of Mars.[5,6] Other groups since have also developed all-carbonate based low temperature electrolytes that enable successful operation down to ~ -30°C, including $LiPF_6$ in EC+DMC+EMC (1:1:1)[7], EC+DMC+DEC (2:2:1)[8], EC+EMC (1:3 and 3:7)[9], EC+DMC+i-propyl carbonate (IPC)[10], and EC+DMC+methyl propyl carbonate (MPC)[10]. Given the desire for improved operation below –20°C for future planetary applications, coupled with the need for long life, our efforts focused upon further optimizing all carbonate based solvent blends to provide improved low temperature performance. The approach taken focused upon reducing the ethylene carbonate content in the electrolyte (i.e., < 25%) and optimizing the mixture of linear carbonates, with the intention of reducing the viscosity, and subsequently increasing the conductivity, at low temperatures (i.e., < -30°C). These efforts lead to the development of a number of electrolytes that have enabled operation down to –50°C, in some cases, including: (a) 1.0 M $LiPF_6$ in EC+DMC+DEC+EMC (1:1:1:1 v/v %), (b) 1.0 M $LiPF_6$ in EC+DMC+DEC+EMC (1:1:1:2 v/v %), (c) 1.0 M $LiPF_6$ in EC+DMC+DEC+EMC (1:1:1:3 v/v %), (d) 1.0 M $LiPF_6$ in EC+DMC+DEC+EMC (1:1:1:4 v/v %), and 1.0 M $LiPF_6$ in EC+DMC+EMC (15:15:70v/v %).[11] For very low temperature applications, we

demonstrated all carbonate based electrolytes with only 10% EC-content resulted in good performance down to temperatures as low –60°C, such as displayed by 1.0 M $LiPF_6$ in EC+ EMC (1:9 v/v %). [12] However, with such low EC-content the high temperature resilience is likely compromised to some extent. Other efforts have focused upon further investigating the effect of salt composition and solvent ratio in the EC+EMC system, including the formulation 1.0 M LiPF6 in EC+EMC (20:80 v/v %), which has displayed good performance in experimental and prototype cells.[13]

In addition to focusing on development of all-carbonate-based electrolyte formulations, we have actively been pursuing the use of other low melting, low viscosity co-solvents to further improve the low temperature conductivity and performance of lithium-ion cells. Although the use of esters as co-solvents have not proven to provide the requisite stability to result in Li-ion cells possessing long life characteristics for many applications (i.e., long cycle and calendar life, as well as providing good low temperature performance throughout the life of the cell), their physical properties, namely low melting points and low viscosities, are desirable for low temperature electrolytes. Using this approach, we have investigated the use of methyl formate (MF), methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP), and ethyl butyrate (EB) in multi-component electrolyte formulations. As a result of this earlier work, it was shown that the higher molecular weight esters (i.e., ethyl propionate and ethyl butyrate) resulted in both improved low temperature performance and good stability at ambient temperatures.[14] Excellent performance was obtained down to –40°C with electrolytes consisting of the following formulations: a) 1.0 M $LiPF_6$ EC+DEC+DMC+ethyl butyrate (EB) (1:1:1:1 v/v %) and b) 1.0 M $LiPF_6$ EC+DEC+DMC+ethyl proprionate (EP) (1:1:1:1 v/v %). In contrast, although electrolytes containing methyl acetate and ethyl acetate (low molecular esters) were shown to result in high conductivity at low temperatures and good cell performance at low temperature initially, their high reactivity toward the anode led to continued cell degradation and poor long term performance. Thus, our current work has focused upon developing low temperature electrolytes that contain high molecular weight ester co-solvents (which inherently possess greater stability) that have been incorporated into electrolyte formulation in large proportion to further extend the low temperature performance down to -70°C. Toward this end we have demonstrated improved performance with multi-component electrolytes of the following composition: 1.0 M $LiPF_6$ in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + **X** (1:1:8 v/v %) (where X = methyl butyrate (MB), ethyl butyrate (EB), methyl propionate (MP), and ethyl valerate (EV).[15]

Other researchers have also investigated some ester-based co-solvents and have recognized the potential for improved low temperature performance. For example, researchers at Matsushita[16] have investigated electrolyte of the following compositions: a) 1.5 M $LiPF_6$ in EC+DEC+MA (1:2:2), b) 1.5 M $LiPF_6$ in EC+DEC+MP (1:2:2), and c) 1.5 M $LiPF_6$ in EC+DEC+EP (1:2:2). Although promising performance was reported, the incorporation of a large proportion of diethyl carbonate (DEC) is not preferred due to the undesirable effects that this solvent has upon the surface films of carbon anodes. In addition, for very low temperature applications the ester proportion must be larger than 40%. More recently, researchers from Saft[17] have investigated electrolytes containing ethyl acetate (EA) and methyl butyrate (MB). More specifically, the group investigated the following electrolyte formulations: a) 1.0 M $LiPF_6$ in EC+DMC+MA , b) 1.0 M $LiPF_6$ in EC+DMC+MB, c) 1.0 M $LiPF_6$ in EC+PC+MB and d) 1.0 M $LiPF_6$ in EC+DMC+EA (solvent ratios not provided). The group reported good low temperature performance with the methyl butyrate-based electrolyte; however, they did not investigate the performance at temperatures below –40°C. Other researchers have also investigated the use of methyl acetate and ethyl acetate[18] in ternary mixtures with and without blending with toluene in an attempt to obtain improved performance to temperatures as low as –50°C. Work at Samsung[19] has involved the investigation of the performance of a number of electrolyte formulations at low temperatures, including the following: a) 1.0 M $LiPF_6$ in EC+EMC+EA (30:30:40), b) 1.0 M $LiPF_6$ in EC+DMC+MA (30:35:35), c) 1.0 M $LiPF_6$ in EC+DEC+EP (30:35:35), and d) 1.0 M $LiPF_6$ in EC+EMC+EP (30:30:40). Although good performance was demonstrated at –20°C, the group did not investigate the performance attributes at temperatures below –20°C. However, at very low temperatures (< -40°C) the high EC-content (30%) and low proportion of the ester-based component (30-40%) in these formulations are not anticipated to yield good performance.

As mentioned previously, although excellent low temperature performance can be obtained through the utilization of ester co-solvent in lithium-ion battery electrolytes, the all-carbonate based blends generally display superior stability and provide better life characteristics. Thus, most of the long-term performance testing performed on prototype cells in support of future applications has focused upon evaluating various all-carbonate blends. The focus of this paper is geared toward the results we have obtained with these cells, and some of the earlier work performed in experimental three-electrode cells, which preceded the incorporation of candidate electrolytes into large capacity prototype cells. It should be noted that in addition to approaches described above in the development of low temperature electrolytes, we have also investigated improving the low temperature performance by a number of other techniques, including the use of electrolyte additives to improve the SEI characteristics, the use of

fluorinated carbonate co-solvents, the use of fluorinated ester co-solvents, the optimization of salt content, and the use of electrolyte salt blends. However, full discussion of these approaches and the results are beyond the scope of this paper.

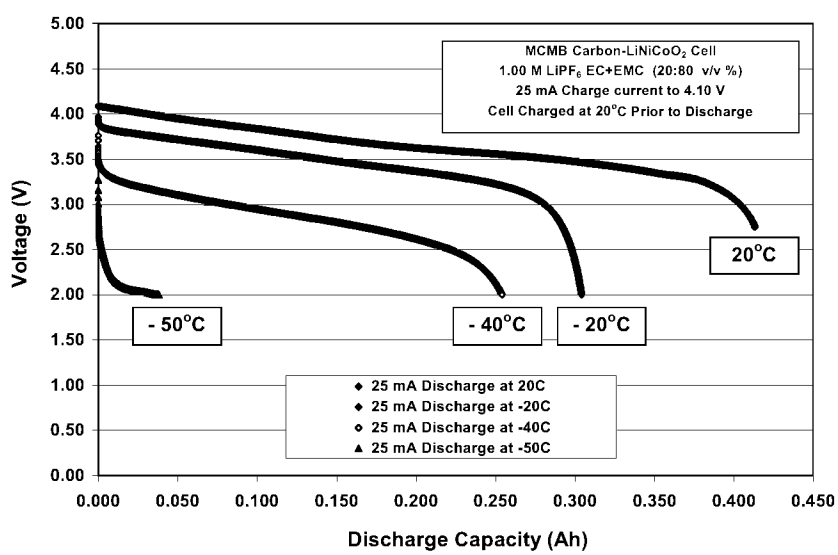
II. Results obtained in Experimental Li-Ion Cells

Experimental lithium-ion cells, consisting of MCMB carbon anodes and $LiNi_{0.8}Co_{0.2}O_2$ cathodes, were used to study various candidate low temperature electrolytes. These cells serve to verify and demonstrate the reversibility, low temperature performance, and electrochemical aspects of each electrode as determined from a number of electrochemical characterization techniques, including electrochemical impedance spectroscopy (EIS), dc micro-polarization and Tafel polarization measurements. After performing initial formation cycling on the cells (5 cycles), the experimental cells were generally subjected to electrochemical characterization at a number of temperatures (i.e., 25, 0, -20, -30, -40, -50, and –60°C) using the techniques described above. These results of these measurements are especially insightful in the determination of the rate limiting electrode, as well as aiding the comparative assessment of the relative reactivity of various electrolytes upon the kinetics and film polarization. Given the limited scope of the present paper, the details of these studies will not be described, however, the results are contained in the various references cited. The use of a reference electrode in these cells is especially beneficial to ascertain the low temperature characteristics of the cells, especially with respect to the possibility of lithium plating upon the anode under conditions of high rate charge at low temperatures.

A. Discharge Performance at Low Temperatures

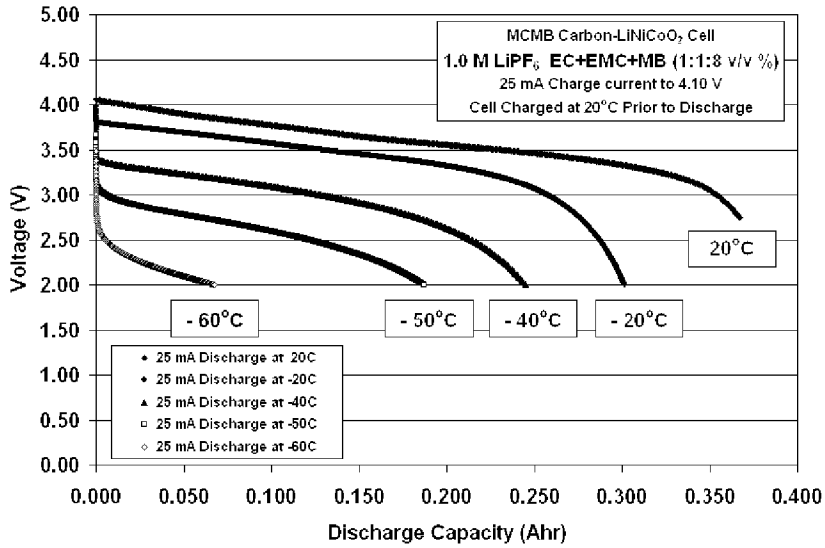
After compleing the electrochemical characterization described above, the experimental cells contining candidate low temperature electrolytes were typically charged under ambient conditions and discharged at various low temperatures (down to –60°C) using various discharge rates. As shown in Fig. 2, the discharge capacity of a cell contining an electrolyte consisting of 1.0 M $LiPF_6$ in EC+EMC (20:80 v/v/ %) is displayed as a function of

Fig. 2. Discharge capacity (Ah) at various temperatures of an experimental Li-ion cell with an all carbonate-based electrolyte using a 25 mA discharge current (~ C/16 rate).



temperature using a moderate discharge rate (~ C/16). As illustrated, the cell delivers reasonable capacity down to –40°C delivering ~ 61.5 % of the room temperature capacity, however, the performance is observed to significantly decline upon going to –50°C. In general, this type of performance is representative of most all-carbonate based electrolytes, in which the conductivity declines upon going to lower temperatures, resulting in poorer performance at the lower temperatures (< -40°C). However, it should be noted that this particular electrolyte that contains 20% EC

Fig. 3. Discharge capacity (Ah) at various temperatures of an experimental Li-ion cell with a low ethylene carbonate-content electrolyte containing an ester using a 25 mA discharge current (~ C/15 rate).



has been observed to perform considerably better at low temperatures (< -20oC) than all-carbonate formulations which contain a greater proportion of EC, such as 1.0 M $LiPF_6$ in EC+DEC+DMC (1:1:1 v/v %), which display lower conductivity due to increased viscosity. In contrast to the all carbonate blends, when an ester is used as a co-solvent in high proportion (i.e., 80%) in conjunction with very low EC-content (i.e., 10%), much better performance is obtained at the very low temperatures as displayed in Fig. 3. As illustrated for an experimental cell containing 1.0 M $LiPF_6$ in EC+EMC+methyl butyrate (MB) (1:1:8 v/v %), improved performance is observed with 66.7 % of the room temperature is obtained at –40°C using a comparable rate of ~ C/15, and over 50% of the room temperature; capacity is observed at –50oC. These results illustrate the general trend that improved low temperature performance can be obtained with the design of electrolyte containing a low proportion of ethylene carbonate and the incorporation of low viscosity, low melting esters, such as methyl butyrate. It should also be noted improved performance is generally observed when assessing various low temperature electrolytes in larger capacity prototype cells, however, the trends established in the smaller experimental cells track well to the larger format.

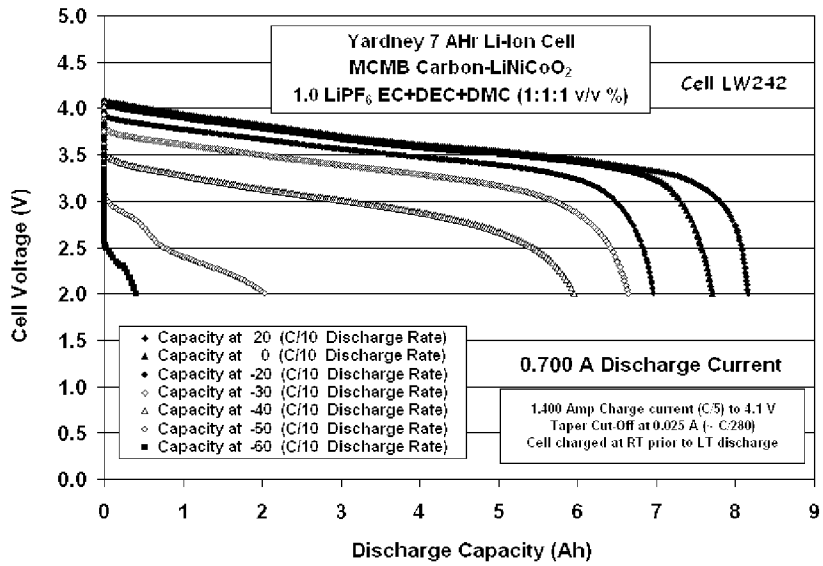
III. Results Obtained in Prototype Li-Ion Cells

After promising low temperature electrolytes have been identified by performing characterization testing in experimental lithium-ion cells, larger prototype cells were obtained from a battery vendor for more rigorous evaluation. Over the years, we have collaborated with a number of vendors to obtain prototype cells that contain advanced low temperature electrolytes, including Yardney Technical Products, Saft America, Compact Power, MER Corp., WGL, A123, and Quallion. Thus, we have evaluated the performance of low temperature electrolytes in various cells sizes (0.50 Ah to 33 Ah), various chemistries (i.e., $LiNiCoO_2$ and $LiMn_2O_4$), and in various cell designs (prismatic, cylindrical, pouch cells, gel polymer electrolyte cells, etc.). Depending upon the number of test articles, we perform a number of performance characterization tests, including: 1) general characterization cycling at various temperatures (20, 0, and –20°C), 2) current-interrupt impedance measurements at various temperatures, 3) discharge rate characterization over a wide range of temperatures (+30 to –70°C), while charging the cells at room temperature, 4) discharge rate characterization with low temperature charge (+30 to –40°C), 5) charge rate characterization testing, 6) cycle life testing under various conditions and temperature, and 7) storage testing. The discussion below will mainly address the results that we have obtained with cells obtained from Yardney and Saft that contain various all-carbonate low temperature electrolyte, and focus will be placed upon the discharge rate performance over a wide range of temperatures.

Discharge Performance Over a Wide Range of Temperature

As mentioned previously, one of the electrical tests that we perform involves charging the cells at room temperature and discharging the cells over a wide range of temperatures (+30 to –70°C) using a wide range of discharge rates (C/100 to 3C rates). As shown in Fig. 4, the discharge capacity of Yardney 7 Ah cell containing a ternary electrolyte consisting of 1.0 M LiPF6 in EC+DMC+DEC (1:1:1 v/v) is displayed as a function of temperature using a C/10 discharge rate (7A).

Fig. 4. Discharge capacity (Ah) at various temperatures of a prototype Li-ion cell (7 Ah Yardney prismatic cell) containing 1.0 M $LiPF_6$ in EC+DEC+DMC (1:1:1 v/v %).



As illustrated, good performance is generally obtained down to –40°C, with 73.8% of the room temperature capacity being delivered. It should be noted that these characterization tests involve discharging the cells down to 2.0V, which is much lower than some particular applications can tolerate. 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. It is significant to note that the performance of the cell declines upon going to lower temperatures, with only 25.2% of the room temperature capacity being delivered at –50°C, and essentially no capacity being delivered at –60°C at a voltage above 2.5V. When the data is expressed in terms of the discharge energy (Wh/Kg), as shown in Fig. 5, the cell was observed to deliver 99.4, 90.0, 72.7, and 20.6 Wh/kg at –20°, -30°, -40°, and –50°C, respectively. These values compare with ~ 120 Wh/kg being delivered at 20°C. In Fig. 6, the discharge rate capability for the same cell containing the ternary electrolyte is displayed at –40°C. As shown in the figure, the cell performs well at rates of C/10 or below, with over 73% of the room temperature capacity being delivered.

When a cell containing an electrolyte possessing a lower EC-content was evaluated, namely 1.0M $LiPF^6$ in EC+EMC (20:80 v/v %), the discharge capacity delivered over the range of temperatures is improved, as illustrated in Fig. 7., with 86.8%, 82.9%, 77.7%, and 70.8% of the room temperature capacity being delivered at –20o, -30o, -40, and –50oC, respectively. In contrast to the ternary all-carbonate mixture, the performance obtained at –50oC is considerably improved, which can be attributed to the higher ionic conductivity resulting from the lower viscosity associated with lower EC-content. When the performance is expressed in the terms of the discharge energy delivered, the cell delivered 97.2, 88.0, 75.0, and 60.1 Wh/kg at –20°, -30°, -40°, and –50°C, respectively, as shown in Fig. 8.

Fig. 5. Discharge energy (Wh/Kg) at various temperatures of a prototype Li-ion cell (7 Ah Yardney prismatic cell) containing 1.0 M $LiPF_6$ in EC+DEC+DMC (1:1:1 v/v %).

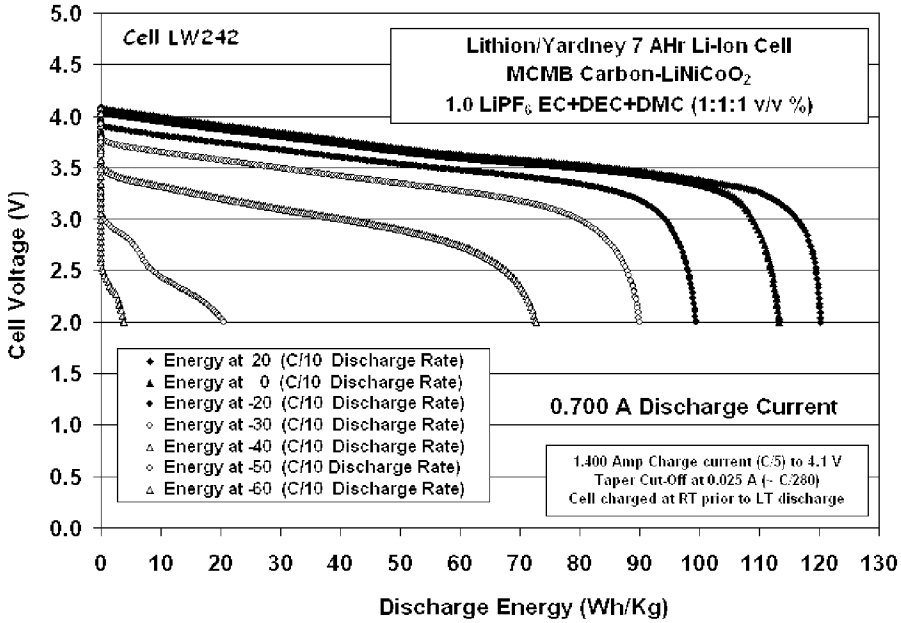


Fig. 6. Percent of room temperature capacity (Ah) delivered at –40°C of a prototype Li-ion cell (7 Ah Yardney prismatic cell) containing 1.0 M $LiPF_6$ in EC+DEC+DMC (1:1:1 v/v %).

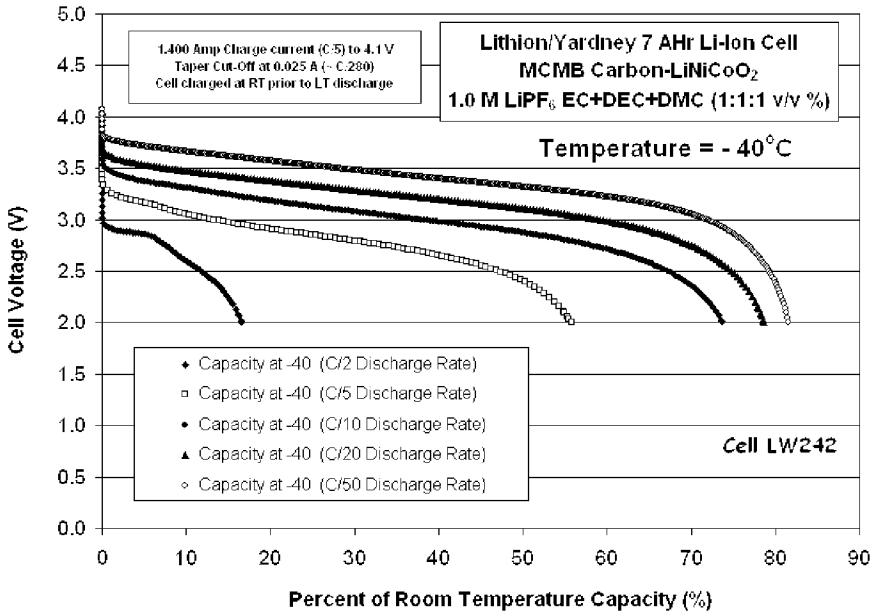


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Fig. 7. Discharge capacity (Ah) at various temperatures of a prototype Li-ion cell (7 Ah Yardney prismatic cell) containing 1.0 M $LiPF_6$ in EC+EMC (20:80 v/v %).

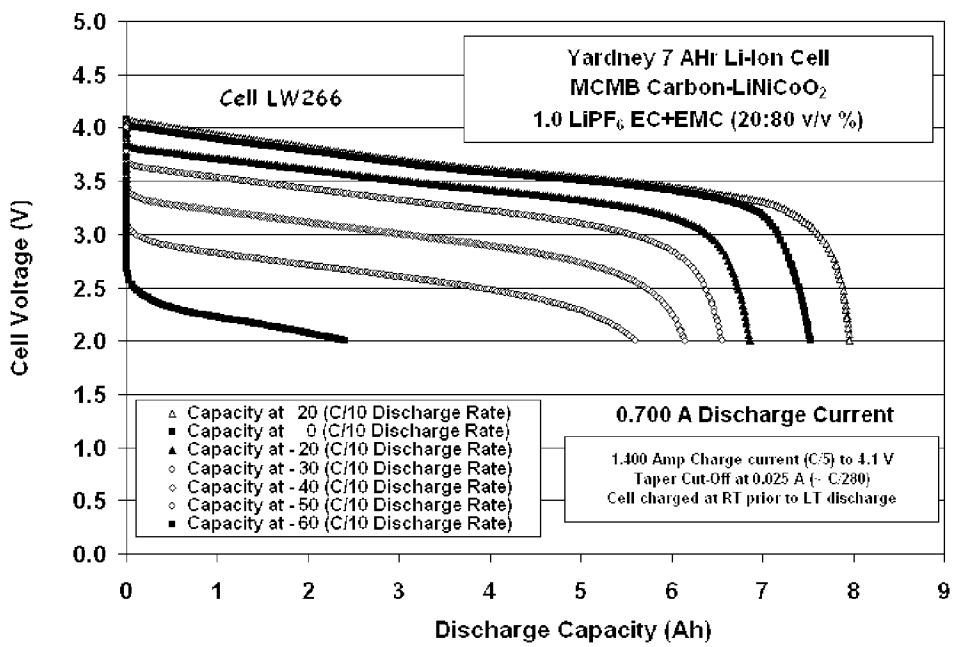


Fig. 8 Discharge energy (Wh/Kg) at various temperatures of a prototype Li-ion cell (7 Ah Yardney prismatic cell) containing 1.0 M $LiPF_6$ in EC+EMC (20:80 v/v %).

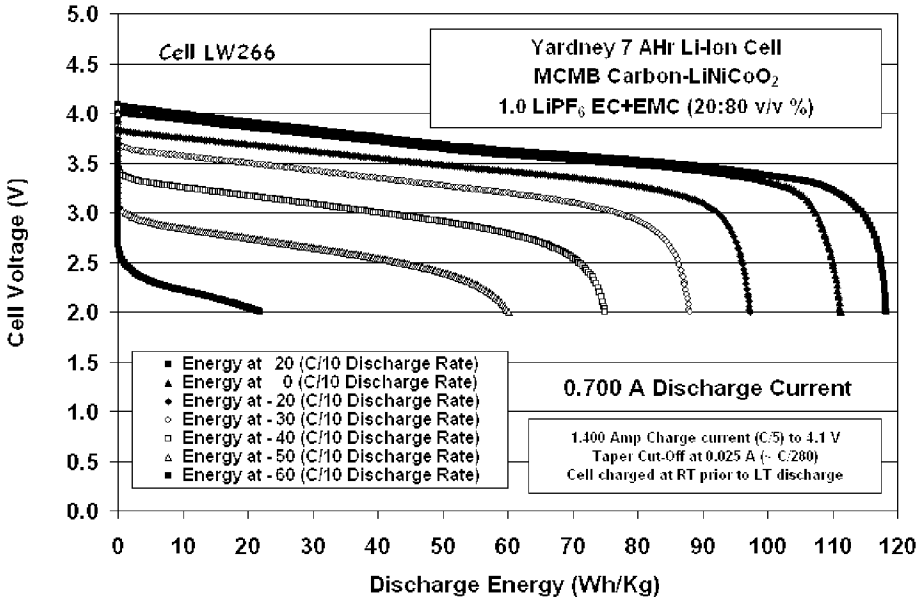


Fig. 9. Percent of room temperature capacity (Ah) delivered at –40°C of a prototype Li-ion cell (7 Ah Yardney prismatic cell) containing 1.0 M $LiPF_6$ in EC+DEC+DMC (1:1:1 v/v %).

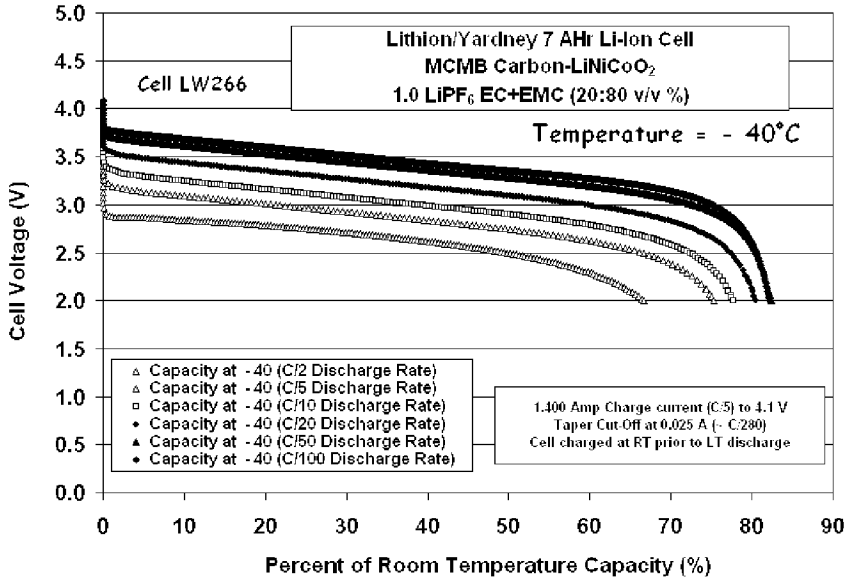
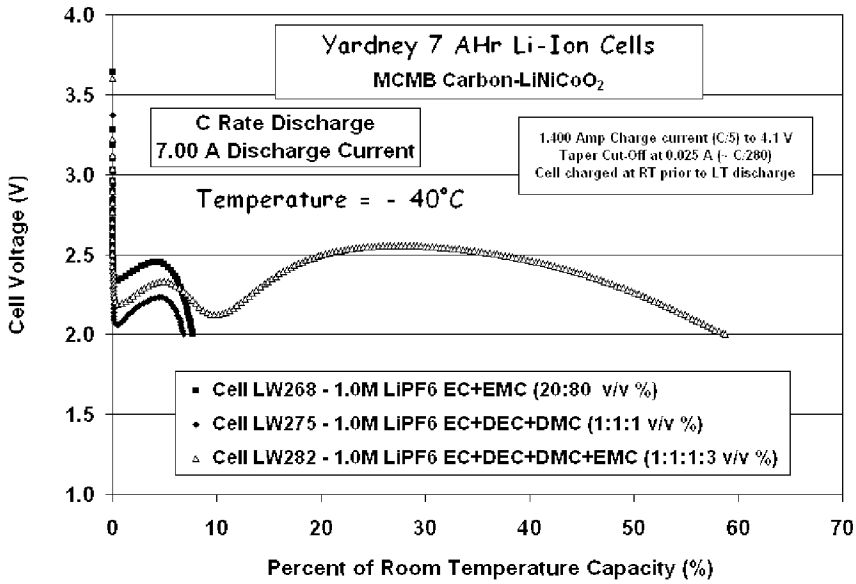


Fig. 10. Discharge capacity (Ah) at various temperatures of an experimental Li-ion cell with an all carbonate-based electrolyte using a 25 mA discharge current (~ C/16 rate).



IV. Conclusion

A general overview of the low temperature electrolyte development efforts at JPL has been provided, describing the approach and classes of formulations developed. In the course of these studies, a number of low temperature lithium-ion electrolytes have been investigated in experimental and prototype lithium-ion cells, consisting of MCMB anodes and $LiNiCoO_2$ cathodes. In the current paper, the results of discharge characterization tests which have been performed on prototype cells over a wide temperature range (+30 to –70°C) using various rates (C/100 to 3C rates) has been described. A number of all-carbonate-based electrolytes have been demonstrated to perform well down to temperatures as low as –50°C. Although not described in length, these all carbonate-based electrolytes also result in Li-ion cells with excellent life characteristics and cyclability. A number of aerospace quality prototype cells containing these electrolytes have been continuously cycled for over 5 years.

Acknowledgments

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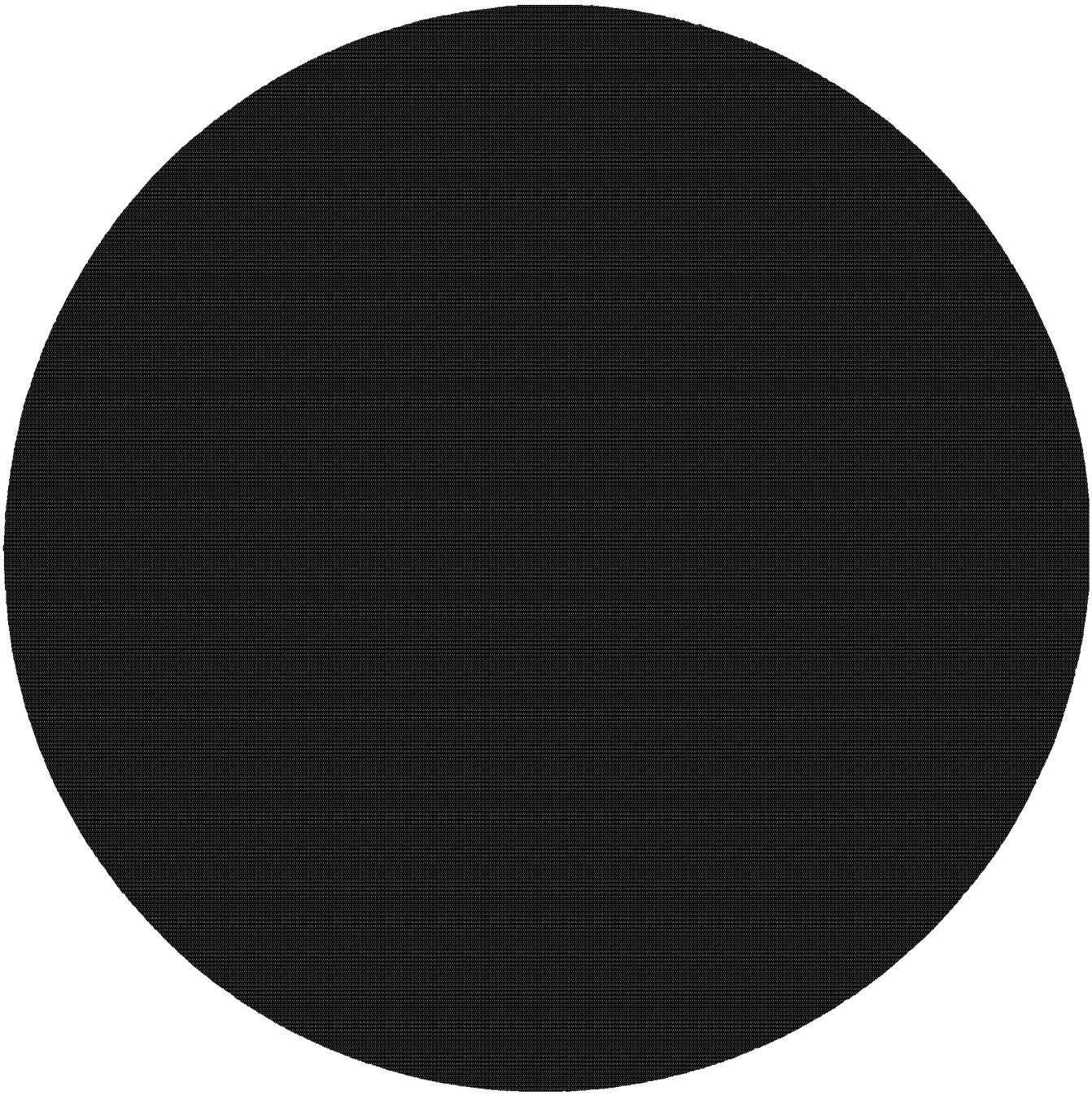
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