

Electrolytes for Low Temperature Lithium-Ion Cells

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ABSTRACT

Lithium-ion rechargeable batteries have been demonstrated to have high energy density, high voltage, and excellent cycle life which make this technology more attractive than competing systems such as Ni-Cd and Ni-H₂. However, the SOA cells fail to meet certain requirements necessary for various future NASA missions, such as good low temperature performance. Under a program sponsored by the Mars Exploration Program we have developed an organic non-aqueous electrolyte which has been demonstrated to result in improved low temperature performance of lithium-ion cells. The electrolyte formulation which has resulted in excellent low temperature performance, as well as good cycle life performance at both ambient and low temperatures, consists of a 1.0M solution of a lithium salt, lithium hexafluorophosphate (LiPF₆), dissolved in a mixture of carbonates: ethylene carbonate + dimethyl carbonate + diethyl carbonate (1:1:1). Prototype cells with the improved electrolyte showed high capacity at low temperature (-20° to -40°C), high rate capabilities, and good cycle life at low temperature. These improvements were achieved through advances in materials development and cell design concepts.

INTRODUCTION

The Mars Exploration Program requires rechargeable batteries which can operate at low temperatures to satisfy the requirements of various applications which include landers, rovers, and penetrators. The applications require battery operation from -60° to 20°C. Furthermore, the batteries should be capable of delivering 300 cycles with high specific energy. The state-of-art lithium-ion system meets all of these requirements, except that it is lacking in adequate low temperature performance. The operating temperature ranges are confined to temperatures above -20°C and capacities below 0°C are generally poor. The poor performance observed is primarily due to the use of solvents, such as ethylene carbonate (EC) and dimethyl carbonate (DMC), in high proportions which produce highly viscous solutions and freeze at low temperatures

resulting in poor ionic (lithium ion) conductivity. To address these problems, we are examining numerous ways of improving the electrolyte solutions based on these solvents to enhance the low temperature performance of lithium-ion cells in order to meet the requirements of future Mars missions.

A number of factors can influence the low temperature performance of lithium-ion cells, including: lithium ion permittivity in the electrolyte solution (electrolyte conductivity), cell design, electrode thickness, separator porosity and separator wetting properties. Of these parameters, the electrolyte properties have the most dominant impact upon the low temperature performance, in that sufficient conductivity is a necessary condition for good performance at low temperatures. Conventional electrolytes employed in SOA lithium-ion cells generally consist of binary mixtures which contain high proportions of ethylene carbonate, propylene carbonate, or dimethyl carbonate (e.g., 1.0M LiPF₆ in EC + DMC (50:50) and 1.0M LiPF₆ in EC + DEC (50:50)). Although these electrolyte formulations can result in excellent film formation characteristics on graphitic-based carbon anodes and, hence, in excellent room temperature performance and cycle life, these solutions do not perform well at low temperature due to the fact that they become highly viscous and/or freeze resulting in poor conductivity.

For this reason, our approach in developing stable electrolytes which have improved low temperature performance has focused upon mixtures with small proportions of ethylene carbonate with suitable solvent additives to minimize the viscosity of the solution at low temperatures. Possible candidate solvent additives include formates, acetates, cyclic and aliphatic ethers, lactones, as well as other carbonates, such as diethyl carbonate (DEC).⁽¹⁾ In addition, it was identified that ternary and quaternary solvent systems are generally more desirable for low temperature lithium-ion applications, due to the fact that the electrolyte properties can be more easily tailored in multi-component systems (i.e., dielectric constant, viscosity, liquid range, coordination properties, and overall stability). The physical properties of a number of commonly used carbonate solvents used in lithium-ion cells is shown in Table 1. Other mixed solvent systems,

such as cyclic ether-based electrolytes, have been previously known to produce more highly conductive solutions at low temperatures compared with the single solvent systems due to a disordering effect in the lithium ion coordination behavior of the solvent medium.(1). Based on these approaches we have previously identified (2) a number of electrolytes which are highly conductive at low temperatures and successfully demonstrated their use in lithium-ion cells. Other groups have also reported improvements in the low temperature performance of lithium-ion cells based resulting from the development of electrolytes.(3,4)

After evaluating the low temperature conductivity and assessing the relative stability of potential systems in experimental test cells, a number of electrolytes were selected for evaluation in lithium-ion AA-size prototype cells, which were fabricated by Wilson Greatbatch Ltd. according to JPL design and with electrolytes and electrode materials supplied by JPL. The electrolytes chosen for evaluation in the prototype cells included three ethylene carbonate-based solutions for use with graphite-type anodes: 1.0 M LiPF₆ EC + DMC (30:70), 1.0 M LiPF₆ EC + DEC (30:70), and 1.0 M LiPF₆ EC + DEC + DMC (1:1:1). Although a number of electrolyte solutions which consist of ternary and quaternary mixtures of carbonates with low viscosity additives were investigated and observed to have higher low temperature conductivity, the systems solely based on carbonate mixtures were evaluated at the prototype cell level due to the superior room temperature cycle life and stability. These approaches have led to the development of a novel ternary electrolyte system based on a mixtures of carbonate, i.e., 1.0 M LiPF₆ in EC + DMC + DEC (33.3 : 33.3 : 33.4) (vol %).(5) This electrolyte formulation has been demonstrated to have : (i) improved low temperature conductivity, (ii) improved low temperature discharge characteristics, (iii) excellent room temperature rate and cycle life capability, and (iv) good stability and self-discharge characteristics in experimental and prototype lithium-ion cells.

RESULTS AND DISCUSSION

Electrolyte Conductivity Studies

In designing electrolytes that are highly conductive at low temperatures it is necessary to consider a number of important parameters, such as the dielectric constant of the medium, viscosity, Lewis acid-base coordination behavior, as well as the appropriate liquid ranges and salt solubilities of the systems. For an electrolyte solution to be a viable candidate for lithium-ion cell applications, it must satisfy a number of requirements in addition to possessing the desired conductivity over the specified temperature range, such as (i) good electrochemical stability over a wide voltage window (0 to 4.5V), (ii) ability to form thin, stable passivating films at the carbonaceous anode electrode, and (iii) good thermal and chemical stability. The physical properties of a number of organic carbonate

solvents employed in lithium-ion technology are shown in Table 1.

	Viscosity η (cP, 25°C)	Dielectric Constant ε (25°C)	Donor Number D _N	M W	Melting Point	Boiling Point	Density
Ethylene carbonate (1,3-dioxolane 2-one)	1.85 (40°C)	39.6 (40°C)	16.4	88.08	38°C	243°	1.321
Propylene carbonate (1,2-propanediol cyclic carbonate)	2.53	64.4	15.1	102.09	-55°C	240°	1.189
Dimethyl carbonate (DMC)	0.585	3.12		90.08	3°C	90°	1.069
Diethyl carbonate (DEC)	0.748	2.82		118.13	-43°C	127°	0.975
Dipropyl carbonate				146.19		167°	0.944
Ethyl methyl carbonate (EMC)	0.65	2.4			-55°C		1.007

Table. 1. Physical properties of organic carbonate solvents commonly used in rechargeable lithium-ion cell technology.

High EC or DMC content in electrolyte solutions generally results in poor low temperature conductivity due to their high melting points and viscosities. The low temperature conductivity can, therefore, be improved by substituting these solvents with carbonates of lower melting points, such as PC or DEC, or by the addition of a third component which can serve as a low viscosity additive. For example, electrolytes composed of EC + DEC and EC + DEC + DMC both display higher conductivity at low temperatures due to the use of DEC which has a lower melting point and a lower viscosity, as shown in Table 2. It is evident that the electrolyte consisting of 1.0 M LiPF₆ in EC + DEC + DMC (1:1:1) displayed the highest conductivity of the EC-based electrolytes listed. The improved conductivity of the ternary system over the binary electrolytes at low temperatures is due to the synergistic effect of having EC (possesses good coordinating ability and high dielectric constant), DEC (lowers the melting point of the medium), and DMC (lowers the viscosity of the system) present in the proper proportions and the fact that the lithium coordination complexes formed in ternary solutions are more disordered allowing higher ionic mobility.

Electrolyte Concentration	Solvent System	Conductivity (mS/cm)					
		-60°	-40°	-20°	0°C	R.T.	
1.0 M LiPF ₆	EC + DMC		Fr.	1.9	7.1	12.2	
1.0 M LiPF ₆	EC + DEC (30:70)		Fr.	0.66	1.9	4.0	7.5
1.0 M LiPF ₆	EC + DEC + DMC (1:1:1)	0.02	1.01	2.9	5.6	9.7	

Table. 2. Specific conductivity of EC- based electrolytes from -60° to 25°C.

Nature of Electrolyte Interaction with Graphite Anode Electrode

A number of cells were fabricated with EC-based electrolytes and evaluated in terms of the reversible and irreversible capacity upon cycling. As illustrated in Table 3, the cells containing electrolytes consisting of 1.0M LiPF₆ EC + DMC (30:70) display the lowest irreversible capacities of the series studied, whereas the cells with 1.0M LiPF₆ EC + DEC (30:70) displayed the highest irreversible capacities. This trend suggests that DMC has inherently greater stability compared with DEC when placed in contact with lithiated carbon. As expected, cells containing an electrolyte consisting of 1.0 M LiPF₆ in EC + DEC + DMC (1:1:1) displayed irreversible capacity values which are intermediary between the EC + DEC and EC + DMC-based cells. The data suggest that cells containing EC+DMC-based electrolytes display the least amount of electrolyte decomposition when in contact with graphite anodes under charging conditions and therefore possess superior surface films. In contrast, the cells containing the 1.0M LiPF₆ EC + DEC (30:70) electrolyte display properties indicative of greater electrolyte decomposition rates and/or the formation of surface films without the desirable passivating qualities. As expected, the cells containing an electrolyte consisting of 1.0 M LiPF₆ in EC + DEC + DMC (1:1:1) displayed behavior consistent with the fact that it is a mixture containing both DMC (less reactive) and DEC (more reactive).

Cell Number	Electrolyte Type (All contain 1.0 M LiPF ₆)	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)
108028	EC + DMC + DEC (1:1:1)	235.36	82.16
108029	EC + DMC + DEC (1:1:1)	217.97	72.30
108033	EC + DEC (30/70)	200.73	111.90
108034	EC + DEC (30/70)	215.31	139.49
108036	EC + DMC (30/70)	221.86	47.18
108037	EC + DMC (30/70)	261.57	48.91

Table 3. Reversible and irreversible capacities of lithium-ion cells containing EC-based electrolytes. The capacity values are expressed in terms of the active anode material (graphite) weight.

Determination of Cell Polarization Characteristics

In order to characterize the rate capability of various systems as a function of temperature, we

generated galvanostatic polarization curves. This technique can be used to determine the effect of discharge current upon the polarization behavior of the cell reactions (e.g., lithium intercalation and diffusion). The technique involved measuring the observed cell potentials when subjected to discharge current pulses, of 45 second duration, increasing from 10mA (~C/40 rate) to 400mA (~C rate). As shown in Fig. 1, at lower temperatures it becomes increasingly more difficult to sustain high cell voltages with high discharge rates as expected.

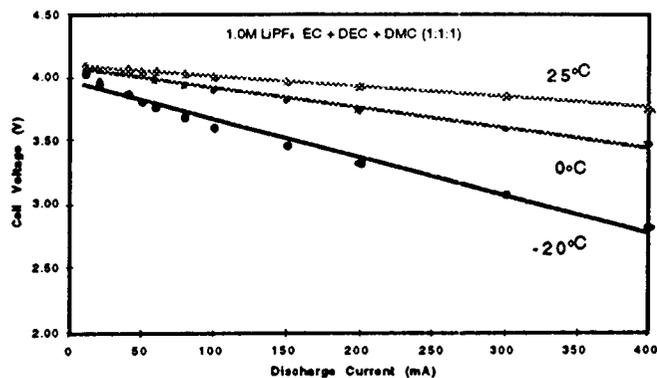


Fig. 1. Cell polarization characteristics of AA-size lithium-ion cell containing 1.0M LiPF₆ EC+DEC+DMC (1:1:1) electrolyte at different temperatures.

When the polarization plots are compared for various carbonate systems, the cells containing the 1.0 M LiPF₆ EC + DMC + DEC (1:1:1) electrolyte displayed the lowest cell overvoltages. This behavior becomes more dramatic at low temperatures, as shown in Figs. 2-4, with the least amount of polarization occurring in the cells containing the ternary electrolyte and displaying the following trend: EC+DMC+DEC > EC+DEC > EC+DMC. At 0°C, cells with the ternary electrolyte displayed ~ 85 mV less polarization at a discharge current of 400mA (~C rate discharge) than the other two electrolyte systems which showed comparable performance. However, at -20°C the cells with the ternary electrolyte displayed potentials greater than 450mV and 800mV at a discharge current of 400mA compared with cells containing EC+DEC and EC+DMC electrolytes, respectively.

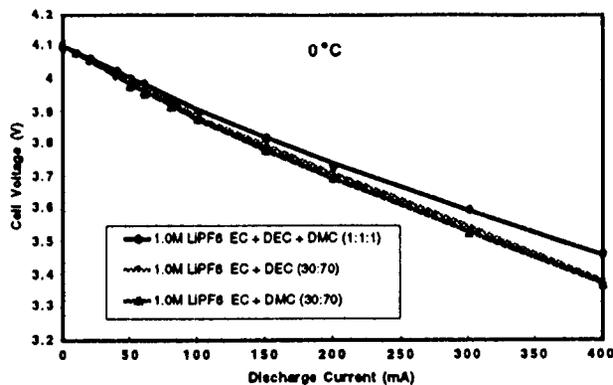


Fig. 2. Cell polarization characteristics of lithium-ion cells containing various EC-based electrolytes at low temperature (0°C).

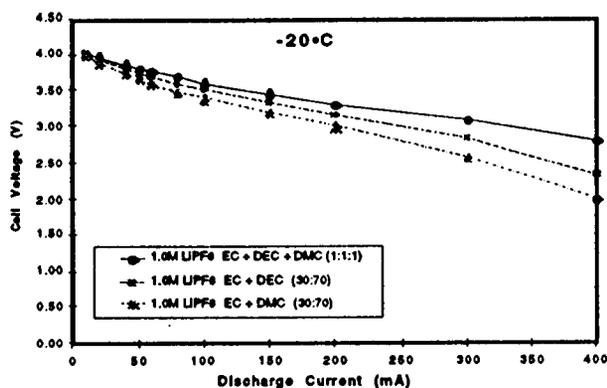


Fig. 3. Cell polarization characteristics of lithium-ion cells containing various EC-based electrolytes at low temperature (-20°C).

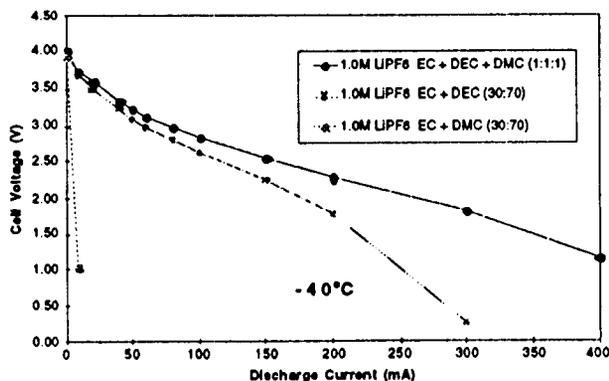


Fig. 4. Cell polarization characteristics of lithium-ion cells containing various EC-based electrolytes at low temperature (-40°C).

Discharge Capacity at Different Rates and Temperatures

In addition to determining the cell polarization characteristics, the discharge capacities of cells containing different electrolytes were measured as a function of temperature and discharge rates. When the low temperature discharge performance of the cells were compared at -20°C, the cells containing the electrolyte 1.0 M LiPF₆ EC+DEC+DMC (1:1:1) delivered the highest capacity when discharged at a -C/20 rate compared with cells containing the EC+DMC-based and EC+DEC-based electrolytes, as shown in Fig. 5. The capacity observed for the cell containing the ternary electrolyte at -20°C corresponds to over 85% of the room temperature capacity, whereas the EC+DEC-based and the EC+DMC-based cells delivered only 67% and 15% of the room temperature capacity, respectively. The cell containing the ternary electrolyte also displayed the highest discharge voltages, consistent with high conductivity and the performance observed for the cells at -20°C correlate well with the conductivity trend: EC + DEC + DMC > EC + DEC > EC + DMC. These results also correlate well with the trends observed from the polarization experiments discussed in the previous section. One significant aspect of these measurements is that both the charge and discharge were performed at low temperature. From the experimental results, it is evident that the incorporation of DEC into the solvent mixtures can greatly improve the low temperature performance compared to the SOA EC+DMC-based electrolyte systems.

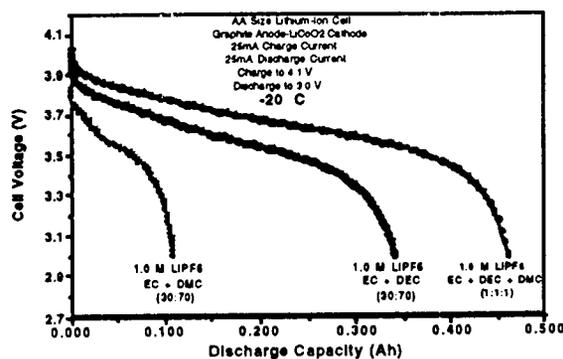


Fig. 5. Comparison of the discharge capacities of graphite-based JPL/WGL AA-size lithium-ion cells containing various EC-based electrolytes at -20°C.

When the discharge capacities of the cells were evaluated over a range of temperatures (-40° to 23°C), the cells containing the 1.0M LiPF₆ EC+DEC+DMC (1:1:1) electrolyte displayed consistently superior performance at lower temperatures compared with cells containing EC+DEC-based and EC+DMC-based

electrolytes. When the cells were discharged at modest rates ($\sim C/20$), cells containing the ternary electrolyte were observed to deliver reasonable capacities ($\sim 60\%$ of the room temperature capacities) at temperatures even as low as -30°C , as shown in Fig. 6.

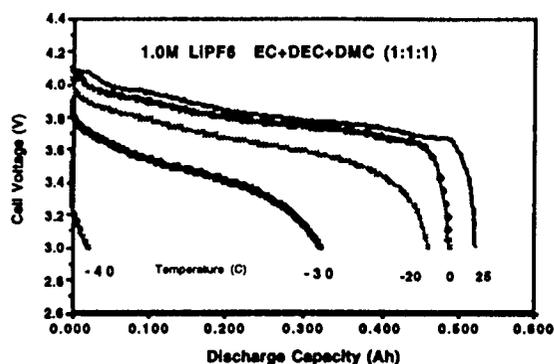


Fig. 6. Discharge capacity of JPL/WGL lithium-ion cell containing 1.0 M LiPF_6 EC + DMC + DEC (1:1:1) electrolyte as a function of temperature. Cell was charged at rate of 25mA ($\sim C/20$) to 4.1V and discharged at a rate of 25mA ($\sim C/20$) to 3.0V.

When the rate capability of the cells was tested at room temperature, there was little capacity loss observed for cells up to $C/2$ discharge rates, as illustrated in Fig. 7. However, at the higher rates there is a marginal decline in the cell voltage due to polarization effects.

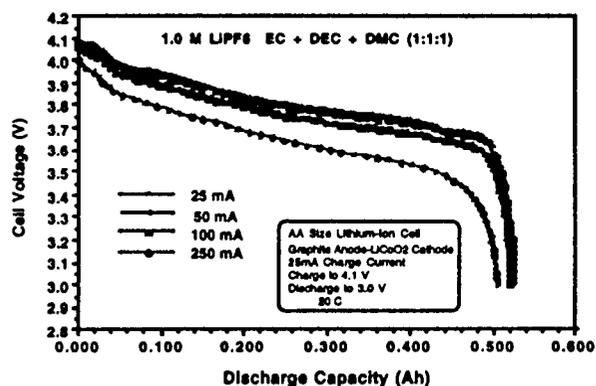


Fig. 7. Rate capability of JPL/WGL lithium-ion cell at room temperature containing 1.0 M LiPF_6 EC + DMC + DEC (1:1:1) electrolyte. Cell was charged at -20°C at a rate of 25mA ($\sim C/20$) to 4.1V and discharged at -20° at various rates to 3.0V.

When the rate capability of the cells was evaluated at lower temperatures, the observed capacities and discharge voltages are much lower at higher rate as expected. However, as illustrated in Fig. 8, a cell containing 1.0 M LiPF_6 EC + DEC + DMC (1:1:1) and discharged at a rate of $\sim C/5$ at -20°C was still capable of delivering 70% of the capacity displayed at a $C/20$ rate. It is important to note that in addition to the charge and discharge being performed at low temperature, all low temperature experiments were carried out in environmental chambers with forced convection. The possible benefit from internal heating which occurs upon discharge at higher rates at low temperatures may therefore be diminished. Higher capacities could be expected at lower temperatures and at higher rate if the cells are insulated or encased to utilize the effect of heating.

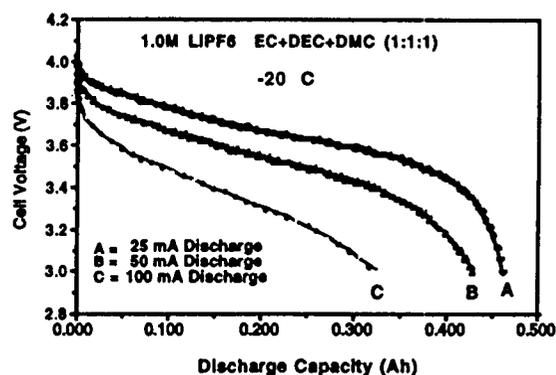


Fig. 8. Rate capability of JPL/WGL lithium-ion cell at -20°C containing 1.0 M LiPF_6 EC + DMC + DEC (1:1:1) electrolyte. Cell was charged at -20°C at a rate of 25mA ($\sim C/20$) to 4.1V and discharged at -20° at various rates to 3.0V.

Certain applications have less demanding performance requirements and only require that the discharge be performed at low temperature with the charge step occurring under ambient conditions. Thus, a number of cycles were performed under conditions of room temperature charge and low temperature discharge, as shown in Fig. 9, to determine the effect upon the discharge capacity. When the performance is compared with that of charging and discharging at -20°C , more than a 10% improvement in the discharge capacity was observed when charged at room temperature.

When the discharge capacities of the prototype cells were evaluated at -30°C under the same rate conditions (Fig. 10), the cell containing 1.0 M LiPF_6 EC + DMC + DEC (1:1:1) out-performed all other systems dramatically.

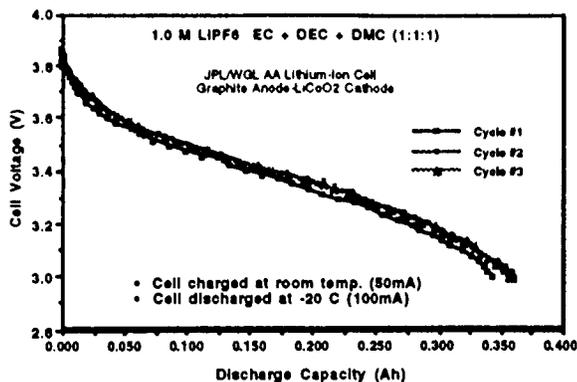


Fig. 9 Low temperature discharge capacity of JPL/WGL lithium-ion cell at -20°C containing 1.0 M LiPF_6 EC + DMC + DEC (1:1:1) electrolyte. Cell was charged at room temperature at a rate of 50mA ($\sim\text{C}/10$) to 4.1V and discharged at -20° at 100mA ($\sim\text{C}/5$) to 3.0V.

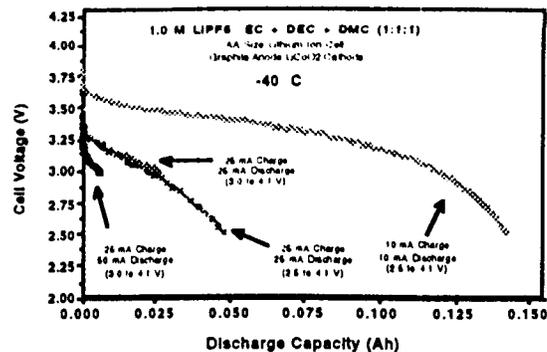


Fig. 11 Effect of discharge cut-off voltage and discharge current rate upon the capacity of lithium-ion cells containing 1.0 M LiPF_6 EC + DEC + DMC (1:1:1) electrolyte at -40°C

Evaluation of Performance for Future Mars Rover Applications

Certain NASA missions, such as the Mars Rover, have especially demanding requirements which include high rates of discharge ($>\text{C}/3$) at temperatures below -20°C . Thus, we have evaluated the performance of a number of prototype cells under conditions similar to those required by future Rovers, i.e., intermittent high rate discharge pulses to shallow depths of discharge ($\sim 25\%$), over a range of temperatures. Initially, we evaluated the performance of cells at room temperature discharged at a C rate to 20% DOD. As shown in Fig. 12, the ternary electrolyte displayed the highest voltages.

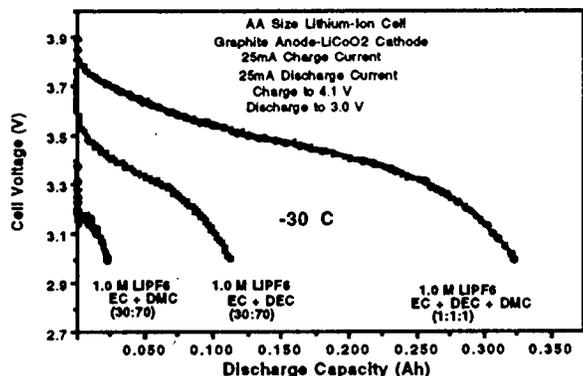


Fig. 10. Effect of electrolyte type upon discharge capacities of lithium-ion cells containing EC-based electrolytes at -30°C . Cells were charged (25 mA) and discharged (25 mA) at -30°C between 3.0 and 4.1 V.

The delivered discharge capacity can be increased greatly at low temperatures if low rates are used and the discharge cut-off voltage is lowered below 3.0V. As shown in Fig. 11, when the discharge cut-off voltage of a cell containing 1.0 M LiPF_6 EC + DMC + DEC (1:1:1) at -40°C is lowered to 2.5V and the discharge rate decreased from 25mA to 10mA (corresponding to a $\sim\text{C}/50$ rate) the discharge capacity increased by a factor of three to four, corresponding to more than one fourth of the room temperature capacity at -40°C . Although it has been suggested that continued discharge to low voltage may promote cell degradation mechanisms, the processes are likely to be less significant at lower temperatures.

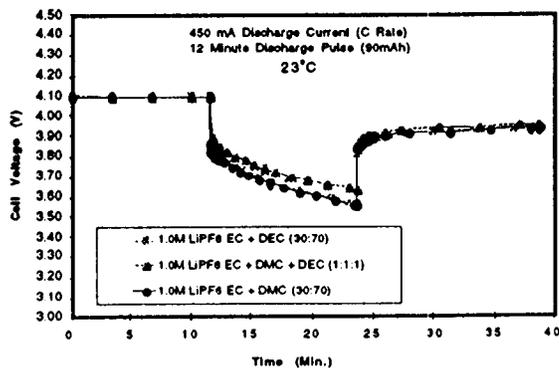


Fig. 12 High rate discharge (450 mA = $\sim\text{C}$ rate) characteristics of lithium-ion cells containing various EC-based electrolytes at room temperature.

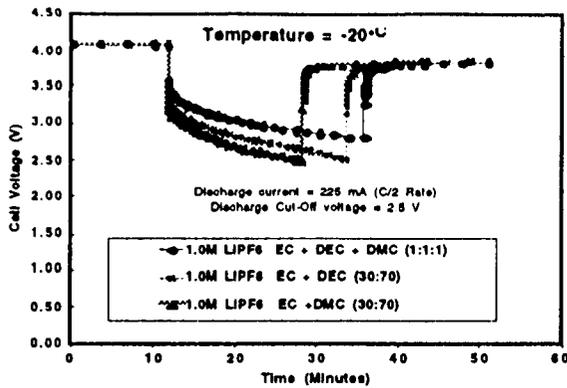


Fig. 13. High rate discharge (225 mA = ~C/2 rate) characteristics of lithium-ion cells containing various EC-based electrolytes at -20°C.

In addition to displaying the best performance at room temperature, when the cells were evaluated at lower temperatures the 1.0 M LiPF₆ EC + DMC + DEC (1:1:1) electrolyte was observed to dramatically outperform the other EC-based electrolytes. For example, cells containing the ternary electrolyte can be successfully discharged at a C/2 rate at -20°C, as shown in Fig. 13, while displaying an average voltage of 3V. However, it is evident that upon going to -30°C that much less capacity was delivered at the C/2 rate before the specified discharge cut-off voltage was reached, as shown in Fig. 14. In order to obtain the desired capacity (20-25% DOD) at -30°C, it was necessary to discharge the cells at lower rates, i.e., a discharge rate of C/5 as shown in Fig. 15.

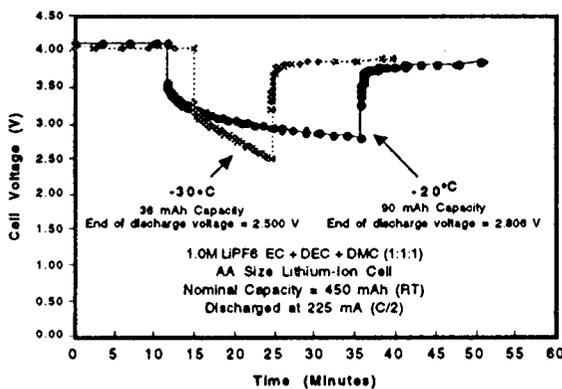


Fig. 14. High rate discharge (225 mA = ~C/2 rate) of lithium-ion cell containing 1.0M LiPF₆ EC+DEC+DMC (1:1:1) electrolyte at -20°C and at -30°C

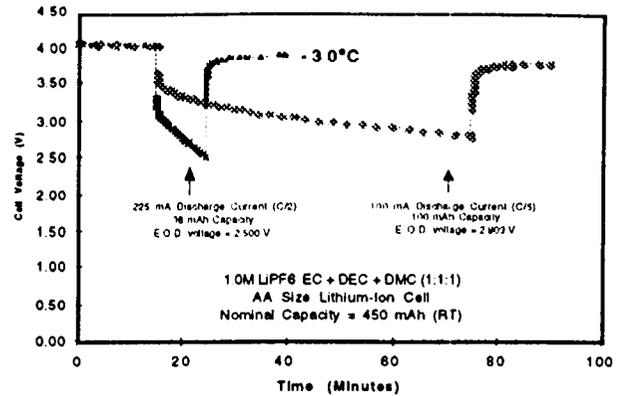


Fig. 15. High rate capability of lithium-ion cell containing 1.0M LiPF₆ EC+DEC+DMC (1:1:1) electrolyte at -30°C.

Cycle Life Performance

The cycle life performance was assessed at room temperature, as well as, at -20°C. Although the primary focus of the Mars Exploration Program is to develop a rechargeable battery capable of operation at low temperature, room temperature cycling tests were deemed necessary to demonstrate the requisite stability during storage, launch, cruise or during daylight hours on Mars. The cycle life testing of a number of cells is currently in progress, with ~ 500 cycles completed at room temperature and > 300 cycles at -20°C, as shown in Fig. 16. Minimal capacity fade was observed for the cells containing the 1.0 M LiPF₆ EC+DMC+DEC (1:1:1) electrolyte at room temperature, corresponding to ~0.04%/cycle, with similar fade rate also being displayed at -20°C. The capacity delivered by these cells at -20°C corresponds to ~ 84% of the room temperature capacity and displayed >75 Wh/Kg at a C/10 rate. The cells containing 1.0 M LiPF₆ EC + DMC (30:70) and 1.0 M LiPF₆ EC + DEC (30:70) both showed inferior behavior with lower capacities and higher capacity fade rates.

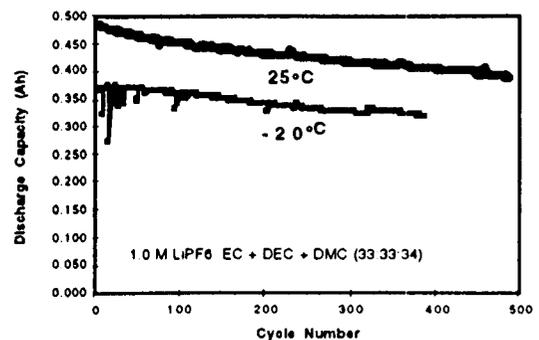


Fig.16. Cycle life performance of lithium-ion cells containing 1.0 M LiPF₆ EC+DMC+DEC (1:1:1)

electrolyte. The room temperature tests consisted of charging the cells at 50mA (~C/10) and discharging at 100mA (~C/5), and the cycling at -20°C consisted of charging the cells at 25mA (~C/20) and discharging at 50mA (~C/10).

Self Discharge Characteristics

After the prototype lithium-ion cells were placed in prolonged storage for approximately six months at 0°C in the fully charged state, they were placed on charge to determine how much capacity had been lost due to self-discharge mechanisms. As shown in Fig. 19, the graphite cells displayed the following trend expressed in greatest resistance to self-discharge: with 1.0 M LiPF₆ EC + DMC (30:70) > 1.0 M LiPF₆ EC + DMC + DEC (1:1:1) > with 1.0 M LiPF₆ EC + DEC (30:70) electrolyte. These results suggest that the DMC-based electrolytes solutions display more favorable film formation characteristics and/or degradative reactivity.

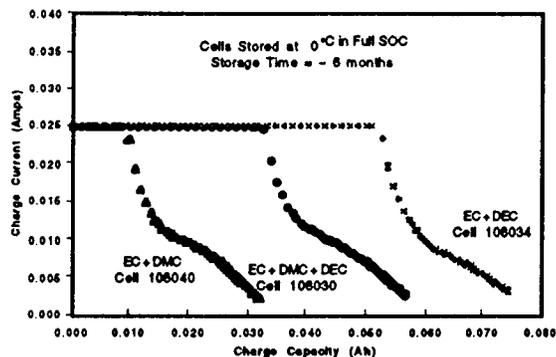


Fig. 20. Self-discharge characterization of lithium-ion cells: charge acceptance after prolonged storage.

CONCLUSION

Under a program sponsored by the Mars Exploration Program we have identified an organic non-aqueous electrolyte which has been demonstrated to result in improved low temperature performance of lithium-ion cells. The electrolyte formulation consists of a 1.0M solution of a lithium salt, lithium hexafluorophosphate (LiPF₆), dissolved in a mixture of carbonates: ethylene carbonate (EC) + dimethyl carbonate (DMC) + diethyl carbonate (DEC) (1:1:1). This electrolyte formulation has been demonstrated to have : (i) improved low temperature conductivity, (ii) improved low temperature discharge characteristics, (iii) excellent room temperature rate and cycle life capability, and (iv) good stability and self-discharge characteristics. The performance of this electrolyte has been demonstrated in prototype AA-size lithium ion cells.

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