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Gel polymer electrolyte lithium-ion cells with improved low temperature performance

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Abstract

For a number of NASA's future planetary and terrestrial applications, high energy density rechargeable lithium batteries that can operate at very low temperature are desired. In the pursuit of developing Li-ion batteries with improved low temperature performance, we have also focused on assessing the viability of using gel polymer systems, due to their desirable form factor and enhanced safety characteristics. In the present study we have evaluated three classes of promising liquid low-temperature electrolytes that have been impregnated into gel polymer electrolyte carbon-$LiMn_2O_4$-based Li-ion cells (manufactured by LG Chem. Inc.), consisting of: (a) binary EC + EMC mixtures with very low EC-content (10%), (b) quaternary carbonate mixtures with low EC-content (16–20%), and (c) ternary electrolytes with very low EC-content (10%) and high proportions of ester co-solvents (i.e., 80%). These electrolytes have been compared with a baseline formulation (i.e., 1.0 M $LiPF_6$ in EC + DEC + DMC (1:1:1%, v/v/v), where EC, ethylene carbonate, DEC, diethyl carbonate, and DMC, dimethyl carbonate). We have performed a number of characterization tests on these cells, including: determining the rate capacity as a function of temperature (with preceding charge at room temperature and also at low temperature), the cycle life performance (both 100% DOD and 30% DOD low earth orbit cycling), the pulse capability, and the impedance characteristics at different temperatures. We have obtained excellent performance at low temperatures with ester-based electrolytes, including the demonstration of >80% of the room temperature capacity at −60 °C using a *C*/20 discharge rate with cells containing 1.0 M $LiPF_6$ in EC + EMC + MB (1:1:8%, v/v/v) (MB, methyl butyrate) and 1.0 M $LiPF_6$ in EC + EMC + EB (1:1:8%, v/v/v) (EB, ethyl butyrate) electrolytes. In addition, cells containing the ester-based electrolytes were observed to support 5*C* pulses at −40 °C, while still maintaining a voltage >2.5 V at 100 and 80% state-of-charge (SOC).

Keywords: Gel polymer Li-ion cells; Low temperature Li-ion electrolytes

1. Introduction

Due to the attractive performance characteristics, lithium-ion batteries have been identified as the battery chemistry of choice for a number of NASA's future applications, including Mars and Lunar orbiters, rovers and landers [1]. Some future applications typically will require high specific energy batteries that can operate at very low temperatures (down to −80 °C). In addition to aerospace applications, JPL has interest in identifying energy storage devices that can operate at very low temperatures (<−50 °C) for terrestrial applications, including balloon experiments (i.e., PAUSE Aerobot) and remote Antarctic data collection facilities. Furthermore, NASA requires enhanced safety for a number of future human missions, for which gel polymer electrolyte-based pouch cell systems are inherently more suitable than traditional liquid electrolyte-based lithium-ion cell designs.

Currently, the state-of-art lithium-ion system has been demonstrated to operate over a wide range of temperatures (−40 to +40 °C); however, the performance is severely limited at temperatures below −40 °C. These limitations at very low temperatures are due to poor electrolyte conductivity, poor lithium intercalation kinetics at the SEI-covered electrode surfaces, and poor ionic diffusion in the electrode bulk. To address these limitations, we have focused our efforts upon the development of electrolyte solutions that possess high conductivity, good chemical and electrochemical stability, good electrode passivating characteristics (i.e., capable of producing protective and

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ionically conductive surface films), and a wide liquid range (low freezing point). In this paper, we would like to discuss our recent results relating to the investigation of various liquid electrolyte formulations that have been incorporated in prototype high-power and high-energy, gel polymer electrolyte lithium-ion cells fabricated by LG Chem. Inc. (and its US unit Compact Power, Inc.). Although it is generally anticipated that gel polymer electrolyte systems are less suited for enhanced low temperature operation compared with the traditional liquid-based Li-ion electrolyte systems, the excellent performance attributes of the high-power LG Chem. 7 Ah cells suggested good low temperature capability could also be achieved in gel polymers cells with optimization of the liquid component of the electrolyte. The electrolytes studied include multi-component all carbonate blends, formulations containing ester-based co-solvents, and solutions containing electrolyte "SEI promoting" additives. In previous work, we have demonstrated that multi-component electrolyte formulations, especially with low EC-content, have improved low temperature performance [2–4]. For further improvements, the use of aliphatic esters have been identified as promising co-solvents to improve electrolyte characteristics at low temperature and research in this area has been actively pursued at JPL [5,6] and by others [7–10] In our research, we have found that higher molecular weight ester tend to display improved stability electrochemically and are preferred over lower molecular weight esters (such as methyl acetate and ethyl acetate) for robust low temperature performance over the life of the cell, although the latter co-solvents can often yield excellent low temperature capability in the initial stages of cell life [6]. Thus, recent work has focused upon the development of formulations containing higher molecular weight co-solvents, such as methyl butyrate (MB), ethyl butyrate (EB), methyl propionate (MP), and ethyl propionate (EP), which display impressive liquidus temperature ranges and adequate stability [11,12]. The electrolytes evaluated for this study involve formulations which were previously investigated in experimental MCMB-$LiNi_xCo_{1-x}O_2$ three-electrode cells and electrochemically characterized by a number of techniques, the results of which will be communicated in another publication.

In the current study, we evaluated a number of different low temperature electrolytes, including all carbonate-based mixtures and ester-containing mixtures, which were developed and prepared at JPL and then impregnated into gel polymer Li-ion cells manufactured by LG Chem. Inc. The electrolytes studied include:

(1) 1.0 M $LiPF_6$ in EC + EMC (1:9%, v/v).
(2) 1.0 M $LiPF_6$ in EC + EMC + EB (1:1:8%, v/v/v).
(3) 1.0 M $LiPF_6$ in EC + EMC + MB (1:1:8%, v/v/v).
(4) 1.0 M $LiPF_6$ in EC + DEC + DMC + EMC (1:1:1:2%, v/v/v/v).
(5) 1.0 M $LiPF_6$ in EC + DEC + DMC + EMC (1:1:1:3%, v/v/v/v).
(6) 1.0 M $LiPF_6$ in EC + DEC + DMC (1:1:1%, v/v/v) (Baseline).

The intent of the study was to compare three classes of promising low temperature electrolyte with the baseline formulation (i.e., 1.0 M $LiPF_6$ in EC + DEC + DMC (1:1:1%, v/v/v)), consisting of: (a) binary EC + EMC mixtures with very low EC-content (10%), (b) quaternary carbonate mixtures with low EC-content (16–20%), and (c) electrolytes with low EC-content (10%) and high proportions of ester co-solvents (i.e., 80%). We have performed a number of characterization tests on the cells, including: determining the rate capacity as a function of temperature (both charge at room temperature and low temperature), the cycle life performance (both 100% DOD and 30% DOD LEO), the pulse capability, and the impedance characteristics at different temperatures.

2. Experimental

A number of 7 Ah prismatic, pouch design cells were fabricated by Compact Power, Inc. (LG Chem), consisting of $LiMn_2O_4$-based cathode material, graphite anode material, and a proprietary gel polymer electrolyte and delivered to JPL for performance characterization. As mentioned above, these cells possessed a number of different liquid electrolytes including two baseline electrolytes (a LG Chem formulation and a ternary EC-based electrolyte), optimized all carbonate-based blends with low EC-content, and ester-containing electrolytes developed at JPL. The carbonate-based solvents, ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) containing $LiPF_6$ salt in the desired concentration, were purchased form Mitsubishi Chemicals (battery grade) with less than 50 ppm of water. The ester solvents, methyl butyrate (MB) and ethyl butyrate (EB), were purchased from Aldrich and stored over Li metal chips and/or molecular sieves prior to use. The cells were evaluated in terms of: (i) the room temperature rate capability; (ii) cycle life performance at room temperature (30% DOD low-earth-orbit [LEO] test and 100% DOD test), (iii) the discharge characteristics at low temperature (with both charging at room temperature and at low temperatures), (iv) the impedance characteristics over a wide temperature range, and the (v) polarization behavior of the cells as a function of temperature. Charge-discharge measurements and cycling tests were performed with a Maccor battery cycler. A Tenney environmental chamber was used to maintain the desired temperature within ±1 °C for the cells (convectively cooled). Temperature measurements were performed using thermocouples attached to the cells.

3. Results and discussions

3.1. Cycle life performance

The first batch of cells fabricated and delivered to JPL, consisting of the LG Chem. baseline electrolyte formulation (January 2002) in a high-power cell design, were subjected to a number of generic performance characterization tests with the intent of evaluating their attributes over a wide range of conditions. As illustrated in Fig. 1, excellent cycle life performance was obtained when the cells were tested according to a standard

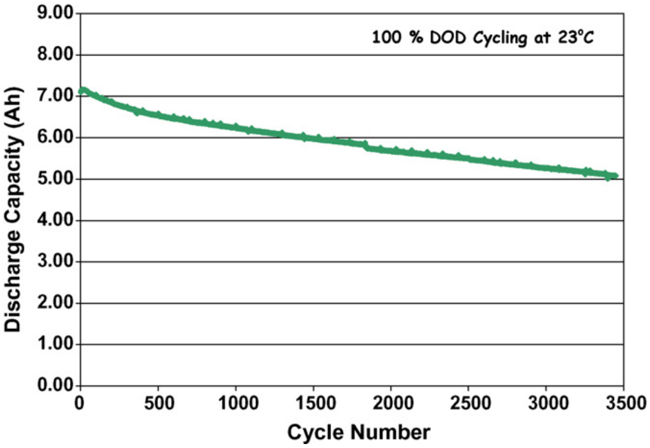

Fig. 1. Room temperature cycle life (100% DOD) performance of 7 Ah cells with the baseline electrolyte.

100% DOD test regime (*C*/5 charge to 4.1 V and *C*/5 discharge to 3.0 V) at room temperature. As shown, the cell has completed over 3450 cycles with minimal capacity fade (0.010% cycle^{-1}), corresponding to over 71.6% of the initial capacity (~88% at cycle #1000). During the course of this test, very stable performance continues to be observed with high columbic efficiency (>99%) and excellent watt-hour efficiency (98.1%) delivered after 3000 cycles completed (over 3.5 years of operation).

In addition to evaluating the performance under 100% DOD conditions, cells were also subjected to 30% DOD low-earth-orbit (LEO) cycle life testing to determine the viability of the technology to meet the requirements of planetary orbiter applications. This test consists of a 60-min charge period (0.4 C in-rush charge current to 4.0 V) and a 30-min discharge period (0.6*C* discharge rate). As illustrated in Fig. 2, excellent performance has been obtained to-date with over 21,500 cycles being delivered with minimal decay in the end of discharge voltage observed (~ 207 mV). Throughout this test, 100% DOD capacity checks have been performed, to determine the loss in capacity as a result of cycling. After completing 21,000 cycles, the cell delivered 5.17 Ah, or over 72% of the initial capacity, as shown in Fig. 3.

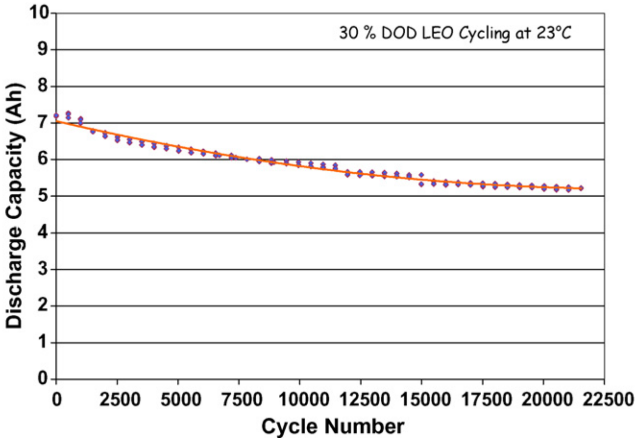

Fig. 3. Discharge capacity (100% DOD) determined during low-earth-orbit (LEO) cycle life (30% DOD) testing performed on a 7 Ah with baseline chemistry at 23 °C.

3.2. High rate discharge and pulse capability at various temperatures

In the course of our studies, we placed emphasis upon evaluating the high rate and pulse discharge characteristics as a function of temperature. The main objective in performing pulse testing it to assess the technology's potential to meet future mission spacecraft power requirements during entry, descent and landing (EDL) procedures as well as for surface operations and communications, however, the performance was also assessed in the context of hybrid, electric vehicles and DOE's requirements. As

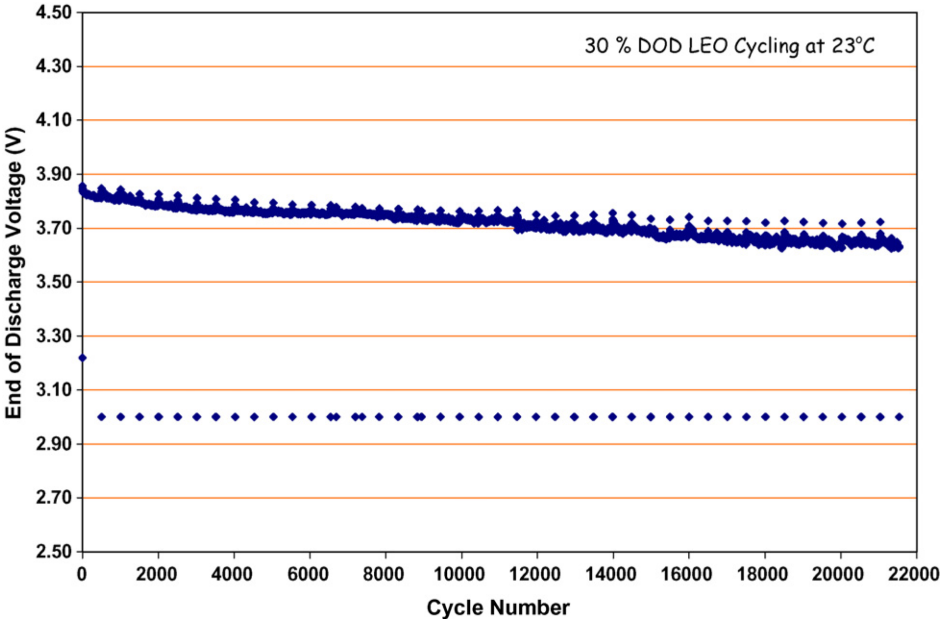

Fig. 2. End-of-discharge voltage (V) of a low-earth-orbit (LEO) cycle life (30% DOD) performance of 7 Ah with baseline chemistry at 23 °C.

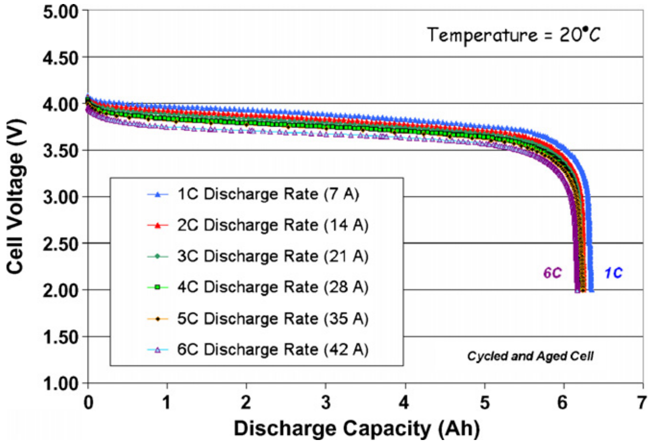

Fig. 4. Continuous high rate discharge characterization of a 7 Ah cell containing 1.0 M $LiPF_6$ EC + DEC + DMC + EMC (1:1:1:3%, v/v/v/v) electrolyte at 20 °C using C (7.00 A) to $6C$ (42 A) discharge rates.

illustrated in Fig. 4, good high rate capability was obtained with the cells containing the quaternary low temperature electrolyte at ambient temperatures, with nearly full capacity being delivered at a $6C$ rate (42 A). A notable aspect of these findings is that the results were obtained on an aged and cycled cell, and even better performance is anticipated with a fresh cell in which the impedance growth is minimized.

In addition to evaluating the performance of the cells under continuous discharge conditions, effort was focused upon determining the pulse discharge characteristics at various temperatures and state-of-charge. As illustrated in Fig. 5, good pulse rate capability was demonstrated at temperatures as low as −35 °C, in which $5C$ pulses (each 2 s in duration) are supported at various states-of-charge (100, 80, 60, and 50% SOC), with a cell containing the 1.0 M $LiPF_6$ in EC + DEC + DMC + EMC (1:1:1:3%, v/v/v/v) electrolyte. With the use of more aggressive ester-containing electrolytes, the operational temperature range can be extended to −40 °C, as illustrated in Fig. 6. As shown in the figure, a cell containing a 1.0 M $LiPF_6$ in EC + EMC + EB (1:1:8%, v/v/v) electrolyte supported the 35 A pulses at −40 °C, being above 2.5 V for the 100% SOC and 80% SOC condition. The data helps to illustrate the superiority of ester-based electrolytes containing low ethylene carbonate content at temperatures below −30 °C. This test helps to illustrate that the technology has great promise to support hybrid electric vehicle applications, specifically demonstrating the capability to provide adequate "cold-cranking" performance at low temperatures.

3.3. Discharge characteristics at low temperatures

Since many of NASA missions require good performance at low temperatures, emphasis was placed upon evaluating the discharge characteristics of the cells at low temperatures (−20 to −60 °C), using conditions of charging at both ambient and low temperatures. Extensive discharge characterization was performed (with both charges at room temperature and at low temperature) in an attempt to evaluate the performance of various low temperature electrolytes. As shown in Table 1, a number of cells containing different low temperature electrolyte variations were subjected to a number of discharge rates (C/400 to C/2) over a wide range of temperatures (+25 to −70 °C) in an attempt to map the performance characteristics and ascertain any electrolyte trends. During the course of the evaluation, the cells were routinely discharged to low potential (i.e., 2.0 V) at low temperature to extract the maximum capacity. It is recognized that discharging $LiMn_2O_4$-based systems to low voltage is associated with possible degradation of the $LiMn_2O_4$ cathode due to the occurrence of a Jahn-Teller distortion of the crystallographic structure and an increase in the concentration of $Mn^{3+}(d^4)$ ions which can undergo disproportionation to produce soluble manganese species (i.e., Mn^{2+}) [13,14]. Additionally, there is some concern that the anode potential becomes sufficiently positive

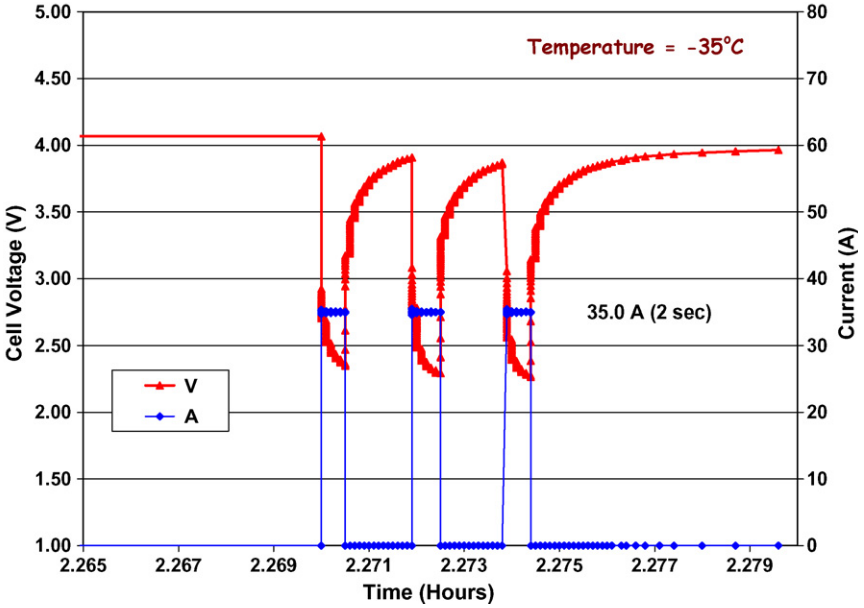

Fig. 5. High rate pulse discharge performance at −35 °C of a 7 Ah cell containing the 1.0 M $LiPF_6$ EC + DEC + DMC + EMC (1:1:1:3%, v/v/v/v) electrolyte.

Table 1

Temperature (°C)	Rate	Current (A)	1.0 M LiPF6 EC + EMC + MB (1:1:8%, v/v/v)		1.0 M LiPF6 (1:1:8%, EC + EMC + EB, v/v/v)		1.0 M LiPF6 EC + EMC (1:9%, v/v)		1.0 M LiPF6 EC + DEC + DMC + EMC (1:1:1:2%, v/v/v/v)		1.0 M LiPF6 EC + DEC + DMC (1:1:1%, v/v/v)	
			Capacity (Ah)	% of room temperature	Capacity (Ah)	% of room temperature	Capacity (Ah)	% of room temperature	Capacity (Ah)	% of room temperature	Capacity (Ah)	% of room temperature
25	*C*/5	1.400	6.2414	100.00	6.8248	100.00	7.0407	100	7.2043	100.00	6.9457	100.00
−20	*C*	7.000	5.4243	86.91			6.4728	91.93	6.7420	93.58	6.5237	93.92
	C/2	3.500	5.6403	90.37	6.4186	94.05	6.7259	95.53	6.8613	95.24	6.6481	95.72
	C/5	1.400	5.7247	91.72	6.4568	94.61	6.7826	96.33	6.9155	96.69	6.6935	96.37
	C/10	0.700	5.7591	92.27	6.4863	95.04	6.7963	96.53	6.9321	96.22	6.7051	96.54
	C/20	0.350	5.8354	93.49	6.5095	95.38	6.8222	96.90	6.636	96.63	6.7240	96.81
−40	*C*	7.000	5.2190	83.62			6.1753	87.71	6.4061	88.92	6.2012	89.28
	C/2	3.500	5.5965	89.67	6.4846	95.01	6.6697	94.73	6.7680	93.94	6.5385	94.14
	C/5	1.400	5.7694	92.44	6.4868	95.05	6.6779	94.85	6.7553	93.77	6.5302	94.02
	C/10	0.700	5.7305	91.81	6.5460	95.91	6.7495	95.86	6.8925	95.67	6.6623	95.92
	C/20	0.350	5.7840	92.67	6.5890	96.54	6.7802	96.30	6.9224	96.09	6.6636	95.94
	C/50	0.140			6.5944	96.62	6.7942	96.50	6.9315	96.21	6.6648	95.96
	C/100	0.070	5.8941	94.43	6.7786	99.32	6.9562	76.80	7.1013	98.57	6.8060	97.99
−50	*C*/2	3.500	5.3223	85.27	6.2761	91.96	6.5156	92.54	6.4899	90.08	0.2566	3.70
	C/5	1.400	5.2514	84.14	5.6844	83.29	5.7422	81.56	5.4397	75.51	4.9223	70.87
	C/10	0.700	5.5378	88.73	6.1578	90.23	6.3301	89.91	6.2036	86.11	5.9543	85.73
	C/20	0.350	5.7703	92.45	6.4543	94.57	6.6374	94.27	6.6857	92.80	6.4549	92.93
	C/50	0.140	5.9414	95.19	6.6743	97.80	6.8331	97.05	6.9836	96.94	6.7418	97.06
	C/100	0.070	6.0187	96.43	6.8250	100.00	6.9646	98.92	7.1174	98.79	6.8378	98.45
−60	*C*/2	3.500	5.3232	85.29	6.3245	92.67	6.4635	91.80	0.2700	3.75	0.0164	0.24
	C/5	1.400	3.3658	53.93	2.6442	38.74	1.4604	20.74	0.2059	2.86	0.0966	1.39
	C/10	0.700	4.3151	69.14	4.1638	61.01	3.7109	52.71	1.1646	16.17	0.4945	7.12
	C/20	0.350	5.2938	84.82	5.3550	78.46	5.1971	73.81	4.3983	61.05	1.8178	26.17
	C/50	0.140	5.7834	92.66	6.2789	92.00	6.3613	90.35	6.0935	84.98	4.9894	71.83
	C/100	0.070	6.1528	98.58	6.5854	96.49	6.7340	95.64	6.7543	93.75	6.1563	88.64
−70	*C*/20	0.350	2.0645	33.08	0.7782	11.40	0.4029	5.72	0.0005	1.39	0.0005	0.01
	C/50	0.140	4.3723	70.05	3.6773	53.88	3.882	37.76	0.5842	8.11	0.0122	0.18
	C/100	0.070	5.3431	85.61	5.3486	78.37	4.9245	69.94	3.5854	49.77	0.0957	1.38

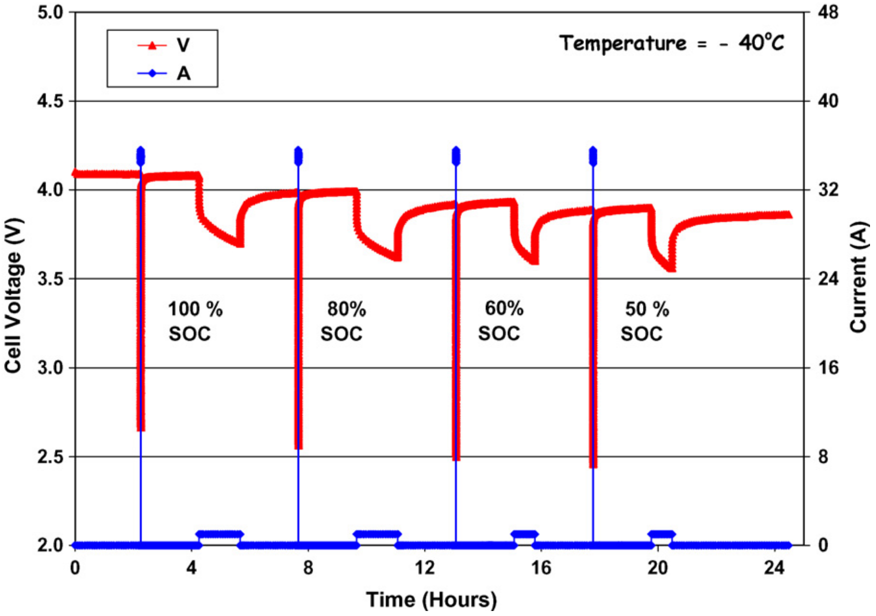

Fig. 6. High rate pulse discharge performance at −40 °C of a 7 Ah cell containing the 1.0 M $LiPF_6$ EC + EMC + MB (1:1:8%, v/v/v) electrolyte.

such that copper dissolution in the media is accelerated [15,16]. However, these processes are likely to occur at significant rates, due to polarization effects at low temperature the applied voltage does not the reflect the local electrochemical potential, which would be higher than observed. The copper dissolution process may not be an issue, since it has been shown to occur only at potentials 3.1 V versus Li^+/Li or higher, while the anode potential maximum typically recorded on such discharges is lower than 1.5 V versus Li^+/Li, even under these deep discharge conditions.

When the rate capability of the cell containing one of the JPL quaternary liquid electrolytes, 1.0 M LiPF6 in EC + DEC + DMC + EMC (1:1:1:3%, v/v/v/v) was evaluated at −20 °C (with both charge and discharge performed at low temperature), good performance was obtained with over 94% of the room temperature capacity delivered at a *C*/2 rate (6.636 Ah), as shown in Fig. 7. In order to obtain full state of charge prior to discharge, long charge periods were necessitated due to the low temperatures, a characteristic typically displayed by most lithium-ion cell chemistries and designs. Improving the charge acceptance characteristics, especially at low temperature, remains to be a focus of future interest. Excellent performance was also obtained at −30 °C, with over 76% of the room temperature capacity being delivered using a *C*/2 discharge rate (3.50 A), with the cell also being charged at low temperature.

For temperatures below −30 °C, the discharge characterization tests were performed utilizing a room temperature charge methodology, due to the slow charge kinetics and the possibility of lithium plating occurring on the anode, which can lead to premature cell degradation [17]. As illustrated in Fig. 8, when a cell containing the 1.0 M $LiPF_6$ in EC + DEC + DMC + EMC (1:1:1:3%, v/v/v/v) electrolyte was charged at room temperature and discharged at −40 °C, excellent capacity was delivered using a *C*/10 discharge rate with nearly full capacity (>99% of the room temperature value) being delivered when a low end-of-discharge voltage is used. In addition, over 94% of the room temperature capacity is delivered using a *C*/5 discharge rate, with a substantial portion of the capacity being delivered with an operating cell voltage of above 2.50 V.

When the discharge performance of the cells containing the different electrolytes was compared at −60 °C using a *C*/20 rate (with charging the cells at room temperature prior to discharge at low temperature), the cells containing the 1.0 M $LiPF_6$ EC + EMC + MB (1:1:8%, v/v/v) and 1.0 M $LiPF_6$ EC + EMC + EB (1:1:8%, v/v/v) electrolytes displayed the best performance with over 80% of the room temperature capacity being observed, as shown in Fig. 9. It should be noted that the EC + EMC solution performed nearly as well, illustrating that the improved low temperature performance is significantly

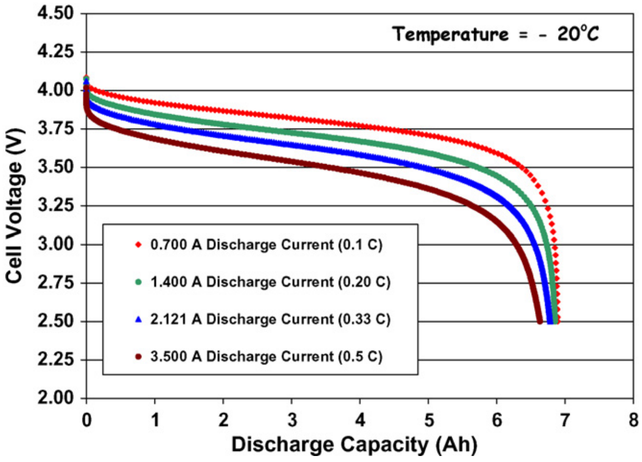

Fig. 7. Discharge rate characterization test of a 7 Ah cell containing 1.0 M $LiPF_6$ EC + DEC + DMC + EMC (1:1:1:3%, v/v/v/v) electrolyte at −20 °C. The charge consisted of using a *C*/10 (0.700 A) rate to 4.10 V with a 0.025 A cut-off (∼*C*/280) and a *C*10, *C*/5, *C*/3, and *C* discharge rates. Both charge and discharge were performed at −20 °C.

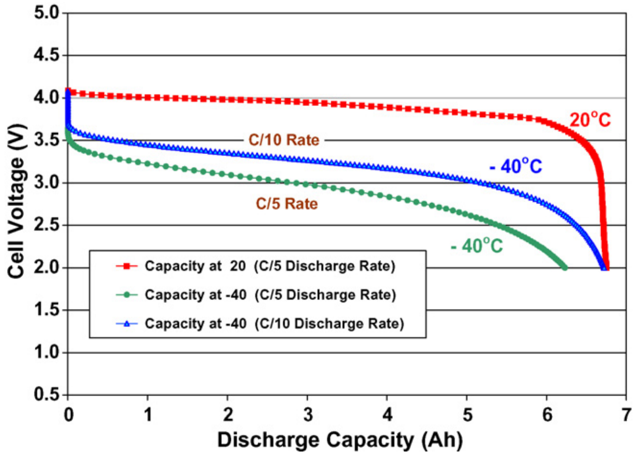

Fig. 8. Discharge capacity (Ah) of a 7 Ah cell containing 1.0 M $LiPF_6$ EC + DEC + DMC + EMC (1:1:1:3%, v/v/v/v) electrolyte at −40 °C using a *C*/5 (1.40 A) and *C*/10 (0.700 A) discharge rate to 2.0 V, compared to the performance obtained at 23 °C. (Cell charge at room temperature prior to discharge at low temperature.)

influenced by the EC-content, with solutions containing low proportions of EC (<15%) being preferred for operation at temperatures below −50 °C. In contrast, the cell containing the baseline ternary carbonate electrolyte delivered less than 30% of the room temperature capacity with low operating voltage. As shown in Fig. 10, good performance was obtained over a range of discharge rates (*C*/5 to *C*/100) at −60 °C with the cell containing the 1.0 M $LiPF_6$ EC + EMC + EB (1:1:8%, v/v/v) electrolyte. Interestingly, the cell was also observed to support a *C*/2 discharge rate at −60 °C, presumably due to a self-heating effect upon discharge. However, prior to this internal cell heating, the voltage was observed to dip to potentials as low as ∼1.8 V, being prohibitively low for a number of applications. Further improved performance at −60 °C was observed with the cell containing the 1.0 M $LiPF_6$ EC + EMC + MB (1:1:8%, v/v/v) electrolyte, as shown in Fig. 11.

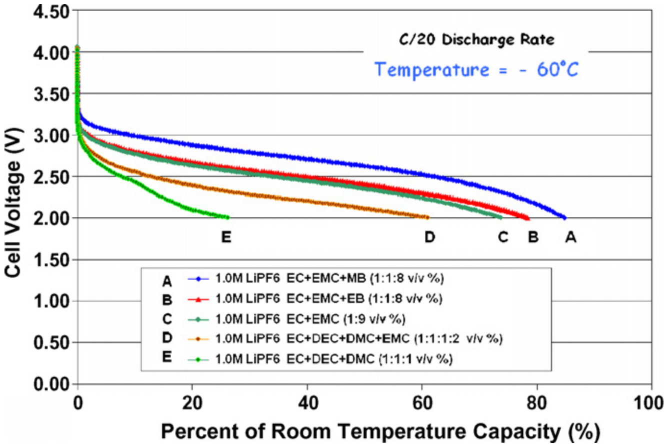

Fig. 9. Discharge capacity (Ah) of a 7 Ah cells containing various low temperature electrolytes at −60 °C using a *C*/20 (0.35 A) discharge rate to 2.0 V. (Cells charge at room temperature prior to discharge at low temperature using a *C*/5 charge rate to 4.1 V.)

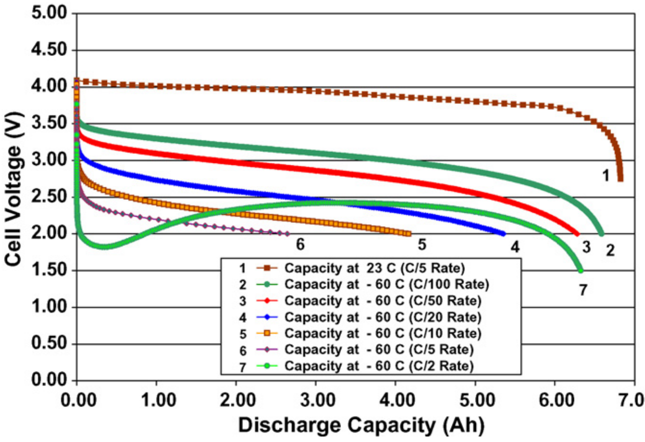

Fig. 10. Discharge capacity (Ah) of a 7 Ah cell containing 1.0 M $LiPF_6$ EC + EMC + EB (1:1:8%, v/v/v) electrolyte at −60 °C using a various rates ranging from *C*/100 (0.070 A) to *C*/2 (3.50 A) discharge rates, compared to the performance obtained at 23 °C. (Cell charge at room temperature prior to discharge at low temperature.)

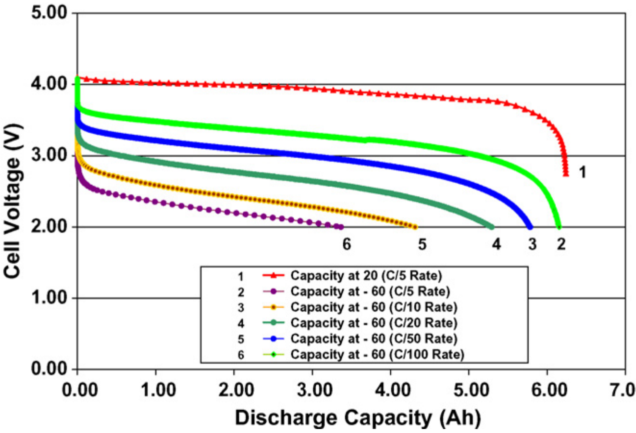

Fig. 11. Discharge capacity (Ah) of a 7 Ah cell containing 1.0 M $LiPF_6$ EC + EMC + MB (1:1:8%, v/v/v) electrolyte at −60 °C using a various rates ranging from *C*/100 (0.070 A) to *C*/2 (3.50 A) discharge rates, compared to the performance obtained at 23 °C. (Cell charge at room temperature prior to discharge at low temperature.)

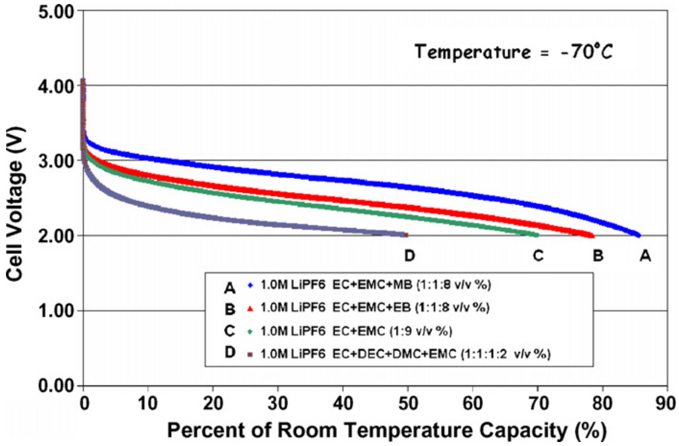

Fig. 12. Discharge capacity (Ah) of a 7 Ah cells containing various low temperature electrolytes at −70 °C using a *C*/100 (0.070 A) discharge rate to 2.0 V. (Cells charge at room temperature prior to discharge at low temperature using a *C*/5 charge rate to 4.1 V.)

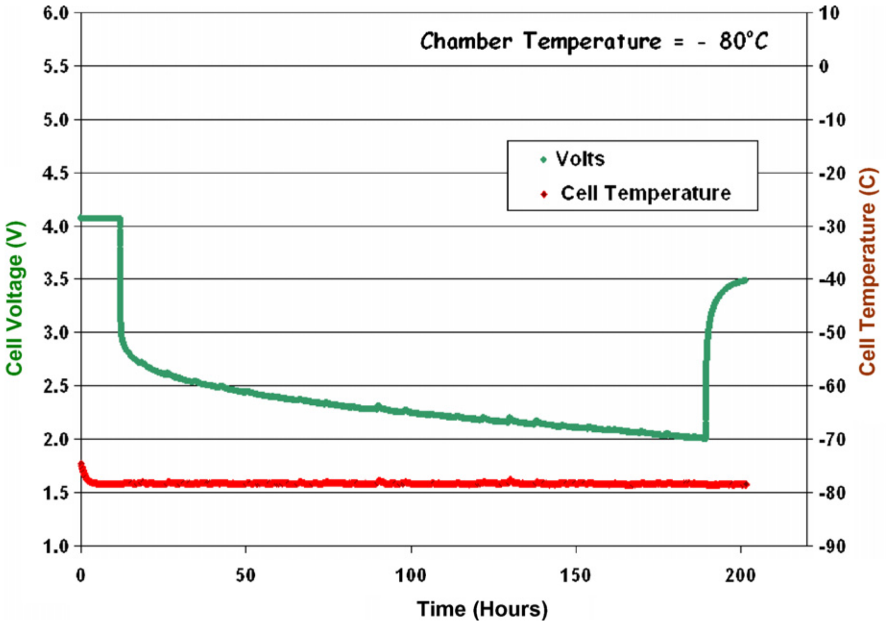

Fig. 13. Discharge performance of a 7 Ah cell containing 1.0 M $LiPF_6$ EC + EMC + MB (1:1:8%, v/v/v) electrolyte at −80 °C using a *C*/400 (17.5 mA) discharge rate to 2.0 V. (Cell charge at room temperature prior to discharge at low temperature using a *C*/5 charge rate to 4.1 V and allowed to soak at −80 °C for 12 h prior to discharge.)

This trend is maintained at −70 °C, where the cells containing the ester-based electrolytes continued to outperform the all carbonate blends, with the methyl butyrate-based system displaying the best performance with ∼85% of the room temperature capacity being delivered at low rate (i.e., *C*/100 or 0.070 A discharge current), as shown in Fig. 12. It should be noted that the baseline formulation, which contains a relatively high proportion of ethylene carbonate (33%), delivered negligible capacity under these conditions. These results illustrate the beneficial effect the ester co-solvents have upon the low temperature capability of the cells, mainly due to higher ionic conductivity of the solutions at these temperatures as a result of the lower viscosities and melting points. Cells containing the ester-based electrolytes were also observed to operate at temperatures as low as −80 °C, albeit at low discharge rates (*C*/400), as shown in Fig. 13. This finding may be significant for many applications which require a "survival" mode at very low temperatures without the available energy to power auxiliary heaters.

In addition to performing generic discharge characterization tests, a number of application specific tests at low temperature

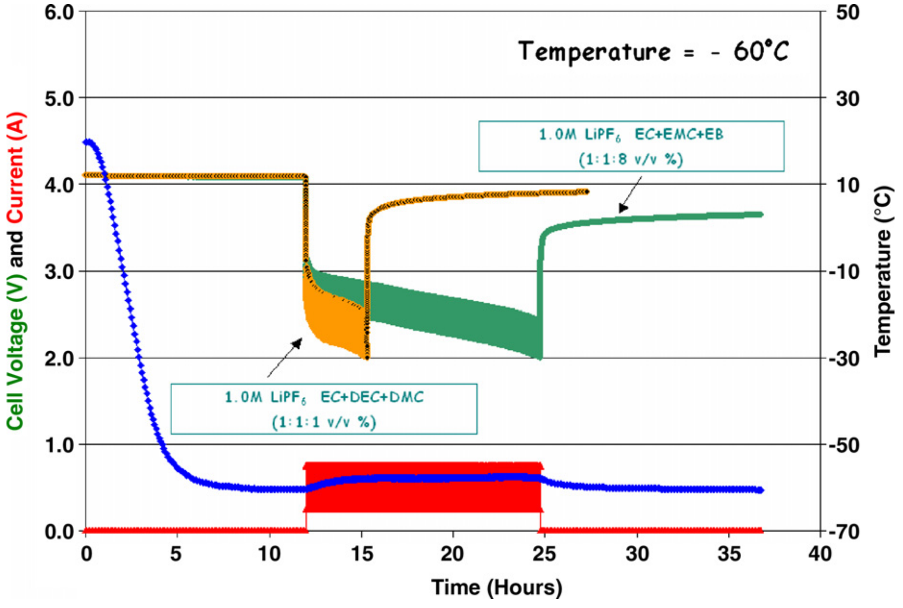

Fig. 14. Discharge profile of a 7 Ah cells containing 1.0 M $LiPF_6$ EC + EMC + MB (1:1:8%, v/v/v) and 1.0 M $LiPF_6$ EC + DEC + DMC (1:1:1%, v/v/v) electrolyte subjected to a duty cycle consisting of alternating 0.250 A for 2 min and 0.750 A for 0.50 min. (Cell charged at room temperature prior to discharge at low temperature using a *C*/5 charge rate to 4.1 V.)

were performed for both planetary and terrestrial applications. For example, some cells were subjected to Mars surface operation mission simulation testing, patterned after typical load profiles experienced by the Mars Exploration Rover mission. In addition, a number of cells were tested to determine their applicability for NASA/NSF terrestrial applications, including balloon experiments (i.e., PAUSE Aerobot) and remote Antarctic data collection facilities. For example, cells were subjected to a duty cycle consisting of alternating 0.250 A for 2 min and 0.750 A for 0.50 min at −60 °C, as illustrated in Fig. 14. As shown in the figure, the cell containing the 1.0 M $LiPF_6$ EC + EMC + MB (1:1:8%, v/v/v) electrolyte delivered superior performance compared to the baseline formulation, being capable of operating three times longer. The aim of this testing was to determine the general capability and the viability of replacing currently used chemistries (i.e., primary Li-SO_2 cells) with Li-ion cells containing low temperature electrolytes.

4. Conclusions

In this paper, we have evaluated high rate, gel-polymer lithium-ion prototype cells (fabricated by Compact Power, Inc.) to determine their viability for a number of NASA and DOD applications. We have demonstrated that the cells possess: (i) good cycle life performance (both at 100 and 30% DOD), (ii) excellent discharge characteristics at low temperature, and (iii) excellent pulse discharge behavior over a range of temperatures. With cells containing a low temperature quaternary electrolyte formulation, excellent performance was obtained at −40 °C using a *C*/10 discharge rate (room temperature charge), with nearly full capacity being delivered. Excellent high rate pulse discharge behavior was also observed over a wide range of temperatures, with 5*C* pulses being able to be supported at temperatures as low as −35 °C in the case with the quaternary carbonate-based electrolyte and −40 °C in the case of the ester-based electrolyte. The cells containing the 1.0 M $LiPF_6$ in EC + EMC + MB (1:1:8%, v/v/v) and 1.0 M $LiPF_6$ in EC + EMC + EB (1:1:8%, v/v/v) electrolytes displayed especially good performance at very low temperatures (−60 to −80 °C), with over 80% of the room temperature capacity being delivered at −60 °C using a *C*/20 discharge rate.

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References

[1] R.A. Marsh, S. Vukson, S. Surampudi, B.V. Ratnakumar, M.C. Smart, M. Manzo, P.J. Dalton, J. Power Sources 97–98 (2001) 25.
[2] M.C. Smart, B.V. Ratnakumar, S. Surampudi, J. Electrochem. Soc. 146 (1999) 486.
[3] M.C. Smart, B.V. Ratnakumar, L. Whitcanack, K. Chin, S. Surampudi, H. Croft, D. Tice, R. Staniewicz, J. Power Sources 119-12 (2003) 349–358.
[4] M.C. Smart, B.V. Ratnakumar, L.D. Whitcanack, K.B. Chin, S. Surampudi, M. Alamgir, J.-S. Yu, E.P. Plichta, 204th Electrochemical Society Meeting, Orlando, FL, October 10–13, 2003.
[5] M.C. Smart, B.V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S.G. Greenbaum, A. Hightower, C.C. Ahn, B. Fultz, J. Electrochem. Soc. 146 (1999) 3963.
[6] M.C. Smart, B.V. Ratnakumar, S. Surampudi, J. Electrochem. Soc. 149 (4) (2002) A361–A370.
[7] A. Ohta, H. Koshina, H. Okuno, H. Murai, J. Power Sources 54 (1) (1995) 6–10.
[8] S. Herreyre, O. Huchet, S. Barusseau, F. Perton, J.M. Bodet, Ph. Biensan, J. Power Sources 97–98 (2001) 576.
[9] H.-C. Shiao, D. Chua, H.-P. Lin, S. Slane, M. Solomon, J. Power Sources 87 (2000) 167–173.
[10] S.V. Sazhin, M.Y. Khimchenko, Y.N. Tritenichenko, H.S. Lim, J. Power Sources 87 (2000) 112–117.
[11] M.C. Smart, B.V. Ratanakumar, K.B. Chin, S.R. Narayanan, 206th Meeting of the Electrochemical Society, October 3–8, 2004.
[12] M.C. Smart, B.V. Ratnakumar, L.D. Whitcanack, J.-S. Yu, M. Alamgir, 207th Meeting of the Electrochemical Society, Quebec City, Canada, May 19, 2005.
[13] M.M. Thackeray, Prog. Solid State Chem. 25 (1997) 1–71.
[14] M.M. Thackeray, W.I.F. David, P.G. Bruce, J.B. Goodenough, Mater. Res. Bull 18 (1983) 461.
[15] M. Zhou, S. Kariuki, H.D. Dewald, F.R. Lemke, R.J. Staniewicz, E.J. Plichta, R.A. Marsh, J. Electrochem. Soc. 147 (2000) 2874.
[16] M.J. S Lain, "Three Electrode Cell Investigation of Lithium Ion Overdischarge" International Meeting on Lithium Batteries (IMLB 2006), Biarritz, France, June 18–23, 2006 (Abstract #451).
[17] M.C. Smart, B.V. Ratnakumar, L. Whitcanack, K. Chin, M. Rodriguez, S. Surampudi, IEEE Aerospace Electron. Syst. Mag. 17 (12) (2002) 16–20.