

Performance Demonstration of MCMB-LiNiCoO₂ Cells Containing Electrolytes Designed for Wide Operating Temperature Range

M. C. Smart¹, B. V. Ratnakumar¹, L. D. Whicanack¹, K. A. Smith¹,
S. Santee², F. J. Puglia², and R. Gitzendanner²

¹ Jet Propulsion Laboratory, California Institute of Technology,
Pasadena, California 91109-8099, USA

² Lithion Inc./Yardney Technical Products, Inc.
82 Mechanic Street, Pawcatuck, CT 06379

With the intent of improving the performance of Li-ion cells over a wide operating temperature range, we have investigated the use of co-solvents to improve the properties of electrolyte formulations. In the current study, we have focused upon evaluating promising electrolytes which have been incorporated into large capacity (7 Ah) prototype Li-ion cells, fabricated by Yardney Technical Products, Inc. The electrolytes selected for performance evaluation include the use of a number of esters as co-solvents, including methyl propionate (MP), ethyl propionate (EP), ethyl butyrate (EB), propyl butyrate (PB), and 2,2,2-trifluoroethyl butyrate (TFEB). The performance of the prototype cells containing the ester-based electrolytes was compared with an extensive data base generated on cells containing previously developed all carbonate-based electrolytes. A number of performance tests were performed, including determining (i) the discharge rate capacity over a wide range of temperatures, (ii) the charge characteristics, (iii) the cycle life characteristics under various conditions, and (iv) the impedance characteristics.

Introduction

Future NASA missions aimed at exploring Mars, the Moon and the outer planets require rechargeable batteries that can operate at low temperatures to satisfy the requirements of various applications, including: landers, rovers, and penetrators. Some future applications typically will require high specific energy batteries that can operate at very low temperatures (down to -60°C, or even below), while still providing adequate performance and stability at ambient temperatures. 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 over the electrode surface layers, and poor ionic diffusion in the electrode bulk.

In addition to focusing on the development of optimized 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. Toward this end, we have previously investigated the use of a number of esters, including methyl

formate (MF), methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP), and ethyl butyrate (EB), in multi-component electrolyte formulations.^{2,3} A number of other groups have also reported the beneficial use of ester co-solvents to improve the low temperature performance of Li-ion cells.⁴⁻⁷ Some of our recent studies have focused upon enabling operation at very low temperature (-40° to -80°C), which was accomplished by utilizing low ethylene carbonate content and high ester content.^{8,9}

In the current study, we have focused our attention on further optimizing the ester-based electrolyte formulations, with the intent of providing the best performance at temperatures ranging from -60° to +60°C, with an emphasis upon improving the rate capability and life at these temperatures. More specifically, we have systematically studied the addition of various esters to LiPF₆-based electrolytes which contain mixtures of aliphatic carbonates, primarily ethylene carbonate and ethyl methyl carbonate. The ester co-solvents investigated include, methyl propionate (MP), 1, ethyl propionate (EP), 2, ethyl butyrate (EB), 3, and propyl butyrate (PB), 4, as shown in Fig. 1. In addition to the use of non-halogenated esters, we have also investigated electrolytes which incorporate fluorinated esters, such as 2,2,2-trifluoroethyl butyrate (TFEB), 5, which has been demonstrated to have good characteristics in experimental Li-Ion cells.¹⁰

In our previous work¹¹, a number of experimental lithium-ion cells, consisting of MCMB carbon anodes and LiNi_{0.8}Co_{0.2}O₂ cathodes, were fabricated to study the effect that these co-solvents have upon performance. In the current study, we have focused upon evaluating promising electrolytes which have been incorporated into large capacity (7 Ah) prototype Li-ion cells, fabricated by Yardney Technical Products, Inc. The electrolytes selected for performance evaluation include the use of a number of esters as co-solvents, including MP, EP, EB, PB, and TFEB. The performance of the prototype cells containing the ester-based electrolytes was compared with an extensive data base generated on cells containing previously developed all carbonate-based electrolytes. A number of performance tests were performed, including determining (i) the discharge rate capacity over a wide range of temperatures, (ii) the charge characteristics, (iii) the cycle life characteristics under various conditions, and (iv) the impedance characteristics.

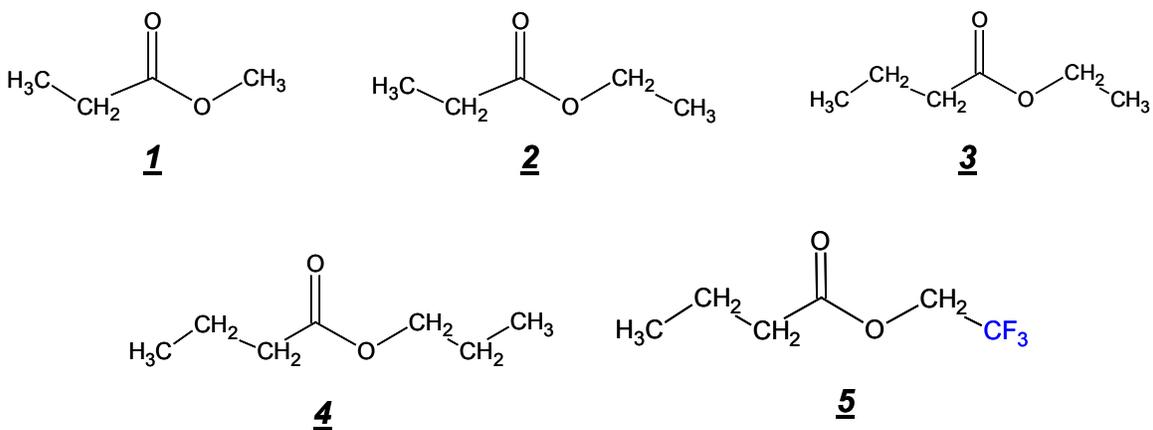


Figure 1. The chemical structures of co-solvents selected for incorporation into multi-component carbonate electrolyte solutions for investigation in 7 Ah MCMB-LiNiCoO₂ cells, which include methyl propionate (MP), 1, ethyl propionate (EP), 2, ethyl butyrate (EB), 3, propyl butyrate (PB), 4, and 2,2,2-trifluoroethyl butyrate (TFEB), 5.

Experimental

For performance assessment, candidate electrolytes were incorporated into 7Ah, prismatic Li-ion cells manufactured by Yardney Technical Products (Pawcatuct, CT). These cells consist of MCMB (1028)-carbon anodes, $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$ cathodes, and porous polypropylene separator material (Tonen-Setella). The electrolyte formulations were prepared using stock solutions procured from Ferro Corp. (now referred to as Novolyte Technologies, Inc.), consisting of 1.0M lithium hexafluorophosphate, LiPF_6 , dissolved in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) (50:50 vol %). To this stock solution, the candidate ester solvent was added in the desired concentration. The ester solvents were generally obtained from Aldrich Chemical Co. and were further distilled and/or stored over molecular sieves prior to use. The non-halogenated esters investigated include: methyl propionate (MP), 1, ethyl propionate (EP), 2, ethyl butyrate (EB), 3, propyl butyrate (PB), 4, and butyl butyrate (BB), 5, 2,2,2-Trifluoroethyl butyrate, 6, was synthesized at the University of Southern California using known methods of esterification and were purified using distillation under inert gas. The ester-based electrolytes evaluated in this study include: (a) 1.0 M LiPF_6 EC+EMC+MP (20:20:60 v/v %), (b) 1.0 M LiPF_6 EC+EMC+EP (20:20:60 v/v %), (c) 1.0 M LiPF_6 EC+EMC+EB (20:20:60 v/v %), (d) 1.0 M LiPF_6 EC+EMC+PB (20:20:60 v/v %) and (e) 1.0 M LiPF_6 EC+EMC+TFEB (20:20:60 v/v %). To serve as the baseline performance, previously developed all carbonate-based electrolytes were also investigated, including (a) 1.0 M LiPF_6 EC+DEC+DMC (1:1:1 v/v %), (b) 1.0 M LiPF_6 EC+DEC+DMC+EMC (1:1:1:3 v/v %), and (c) 1.0 M LiPF_6 EC+EMC (1:4 v/v %). In addition to these electrolytes, a formulation containing a flame retardant additive, namely triphenyl phosphate, was also investigated, consisting of 1.0M LiPF_6 EC+EMC+TPP (20:65:5 v/v%) + 1.5% vinylene carbonate (VC).

The cycling tests and charge-discharge measurements were performed with a Maccor battery cycler. To maintain the cells at the desired temperature, they were placed in Tenney environmental chambers (+/- 1°C).

Results and Discussion

Initial Conditioning Characteristics. As mentioned previously, a number of electrolytes containing ester-based co-solvent designed for operation over a wide temperature range were incorporated into 7 Ah (nameplate capacity) MCMB- $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$ cells manufactured by Yardney Technical Products. In addition, a number of all carbonate based electrolytes previously developed for good low temperature performance were also incorporated into similar cells to serve as a comparison. As illustrated in Table 1, when the initial conditioning characteristics are compared for a number of cells (17 total) containing various electrolyte types (6 total), consisting of both baseline all carbonate blends (3) and ester containing electrolytes (3), it is apparent that very comparable performance is obtained, with 8.0 Ah average capacity being delivered from the cells. This conditioning consisted of charging the cells using a C/5 rate (1.4A) to 4.10V, applying constant potential charging until the current decays to a C/100 rate (0.07A), and then discharging the cells using a C/5 rate (1.4A) to 2.75V. A noticeable difference among the cells is that the impedance is lowest for the cells containing the ester-based electrolytes, displaying the following trend (in increasing resistance): MP < EP < EB < all carbonate-based electrolytes. This suggests that the benefits of the higher ionic

conductivity of the ester containing electrolytes is not off set by any undesirable reactivity at the electrode interfaces which may lead to increased film and charge transfer resistance.

Table 1. The results of the initial conditioning cycling performed on 7Ah MCMB-LiNiCoO₂ cells containing various electrolytes at 20°C.

Cell Number	Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Initial Capacity (Ah)	Initial Watt-Hours	Initial Wh/kg	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (75% SOC)	Electrolyte Type
7-3-242	LW242	243.41	0.2434	3.564	8.0799	29.132	119.68	16.65	15.87	1.0 M LiPF ₆ in EC+DEC+DMC (1:1:1 v/v %)
7-3-275	LW275	243.68	0.2437	3.555	7.9548	28.714	117.84	18.49	16.17	1.0 M LiPF ₆ in EC+DEC+DMC (1:1:1 v/v %)
7-3-256	LW256	242.56	0.2426	3.566	7.8331	28.211	116.31	23.06	20.93	1.0 M LiPF ₆ in EC+DEC+DMC+EMC (1:1:1:3 v/v %)
7-3-258	LW258	242.01	0.2420	3.566	7.9002	28.519	117.84	18.66	16.57	1.0 M LiPF ₆ in EC+DEC+DMC+EMC (1:1:1:3 v/v %)
7-3-282	LW282	243.00	0.2430	3.554	7.9092	28.534	117.42	20.75	18.27	1.0 M LiPF ₆ in EC+DEC+DMC+EMC (1:1:1:3 v/v %)
7-3-266	LW266	241.20	0.2412	3.563	7.9038	28.524	118.26	20.01	17.70	1.0 M LiPF ₆ in EC+EMC (20:80 v/v %)
7-3-267	LW267	242.25	0.2423	3.565	7.9651	28.764	118.74	17.92	18.87	1.0 M LiPF ₆ in EC+EMC (20:80 v/v %)
7-3-268	LW268	241.74	0.2417	3.558	7.9632	28.744	118.91	18.57	16.48	1.0 M LiPF ₆ in EC+EMC (20:80 v/v %)
7-3-358	LW358	243.72	0.2437	3.565	8.0028	28.931	118.70	12.56	12.43	1.0 M LiPF ₆ in EC+EMC+MP (20:60:20 v/v %)
7-3-359	LW359	243.86	0.2439	3.566	7.9938	28.900	118.51	13.04	12.60	1.0 M LiPF ₆ in EC+EMC+MP (20:60:20 v/v %)
7-3-360	LW360	243.72	0.2437	3.561	7.9989	28.925	118.68	12.56	12.21	1.0 M LiPF ₆ in EC+EMC+MP (20:60:20 v/v %)
7-3-361	LW361	243.86	0.2439	3.566	8.0294	29.017	118.99	13.65	13.25	1.0 M LiPF ₆ in EC+EMC+EP (20:60:20 v/v %)
7-3-362	LW362	244.15	0.2442	3.565	8.0020	28.923	118.46	13.47	13.12	1.0 M LiPF ₆ in EC+EMC+EP (20:60:20 v/v %)
7-3-364	LW364	243.57	0.2436	3.565	8.0034	28.948	118.85	11.81	11.51	1.0 M LiPF ₆ in EC+EMC+EP (20:60:20 v/v %)
7-3-365	LW365	243.90	0.2439	3.567	8.0060	28.927	118.60	13.86	13.47	1.0 M LiPF ₆ in EC+EMC+EB (20:60:20 v/v %)
7-3-366	LW366	243.76	0.2438	3.566	8.0042	28.923	118.65	13.95	13.56	1.0 M LiPF ₆ in EC+EMC+EB (20:60:20 v/v %)
7-3-367	LW367	243.34	0.2433	3.568	8.0086	28.941	118.93	13.52	13.17	1.0 M LiPF ₆ in EC+EMC+EB (20:60:20 v/v %)
Average		243.16	0.24	3.56	7.97	28.80	118.43	16.03	15.07	

More recently, additional electrolytes were incorporated into Yardney 7 Ah cells, including the formulations containing propyl butyrate, 2,2,2-trifluoroethyl butyrate, and the triphenyl phosphate. Although these cells also consisted of similar MCMB and LiNi_{0.80}Co_{0.2}O₂ materials, differences in the cathode to anode active material ratios and the electrode loadings resulted in lower capacity for the cells (i.e., 6.9Ah compared with 8.0Ah), as shown in Table 2. As illustrated, good cell to cell reproducibility was also observed, similar to the previous batch of cells. With regard to the impedance characteristics displayed, the cells containing the electrolyte with propyl butyrate displayed the lowest impedance, whereas the cells containing the 2,2,2-trifluoroethyl

butyrate exhibited somewhat higher impedance. In part, this can be rationalized by the fact that fluorinated esters possess higher viscosity in contrast to their non-halogenated analogues, which results in lower ionic conductivity. This has been confirmed by performing conductivity measurements of comparable electrolytes with ethyl butyrate.

Table 2. The results of the initial conditioning cycling performed on 7Ah MCMB-LiNiCoO₂ cells containing electrolytes possessing propyl butyrate, 2,2,2-trifluoroethyl butyrate, and triphenyl phosphate at 20°C.

Cell Number	Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Initial Capacity (Ah)	Initial Watt Hours	Initial Wh/kg	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (75% SOC)	Calculated Impedance (mOhms) (50% SOC)	Electrolyte Type
7-3-463	LW463	239.8	0.2398	3.489	6.9579	25.305	105.52	13.73	13.08	13.52	1.0 M LiPF ₆ in EC+EMC+PB (20:60:20 v/v %)
7-3-464	LW464	239.6	0.2396	3.543	6.9045	25.102	104.77	14.91	14.17	14.82	1.0 M LiPF ₆ in EC+EMC+PB (20:60:20 v/v %)
7-3-468	LW468	240.6	0.2406	3.544	6.9250	25.154	104.55	15.91	14.82	15.69	1.0 M LiPF ₆ in EC+EMC+TFEB (20:60:20 v/v %)
7-3-469	LW469	240.5	0.2405	3.535	6.8894	25.025	104.06	16.17	15.17	15.83	1.0 M LiPF ₆ in EC+EMC+TFEB (20:60:20 v/v %)
7-3-473	LW473	241.2	0.2412	3.141	6.9080	25.073	103.95	16.00	14.91	16.22	1.0 M LiPF ₆ in EC+EMC+TPP+VC (19.7:73.9:4.9:1.5 v/v %)
7-3-474	LW474	240.5	0.2405	3.415	6.8947	25.027	104.06	15.69	14.82	15.83	1.0 M LiPF ₆ in EC+EMC+TPP+VC (19.7:73.9:4.9:1.5 v/v %)
Average		240.37	0.2404	3.444	6.913	25.114	104.48	15.4	14.5	15.3	

Discharge Characteristics at Low Temperature. Given that one of the major objectives of this work is to demonstrate improved performance over a wide operating temperature, and especially at low temperatures, significant effort was devoted to characterizing the discharge characteristics at low temperatures (down to -60°C) using a number of rates (ranging from C/100 to 3.0C). Due to concerns regarding the possibility of plating lithium when charging at low temperatures, the initial characterization was performed while charging at room temperature and then allowing the cells to equilibrate at the desired temperature for at least four hours prior to discharge. As shown in Fig. 2, excellent cell to cell reproducibility was obtained with this testing, as illustrated by the discharge behavior observed with a number of cells (3 cells per variation) containing ester-based electrolytes (i.e., MP, EP, and EB containing formulations) at -40°C using a C/10 rate. As illustrated, good performance can be obtained using these moderate rates at -40°C and discharging the cells down to low voltage (i.e., 2.0V), with approximately 80% of the room temperature capacity being delivered.

When the all carbonate blend low temperature electrolytes were compared with the ester-containing electrolytes using a somewhat higher discharge rate (C/5) at -40°C, as shown in Fig. 3, more differentiation of the performance can be observed as a function of the electrolyte type. As one would expect, the cells containing the electrolytes possessing the esters of the lowest viscosities yielded the best performance (i.e., the MP, EP, and EB containing cells), both in terms of the delivered capacity and the extent of polarization, owing to the higher ionic conductivity at low temperatures. Of the all carbonate blends, the best performance was observed with the 1.0M LiPF₆ in EC+EMC

(20:80 v/v%), followed by 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3 v/v %), and 1.0 M LiPF₆ EC+DEC+DMC (1:1:1 v/v %). This trend can be primarily attributed to the ethylene carbonate content of the blend, as well as preferable physical properties of EMC compared to DEC and DMC at lower temperatures. The cells containing the electrolytes with the other esters (PB and TFEB) and the TPP did not perform as well, which can in part be due to differences in cell design aspects mentioned previously and lower inherent conductivity of the solutions at low temperature.

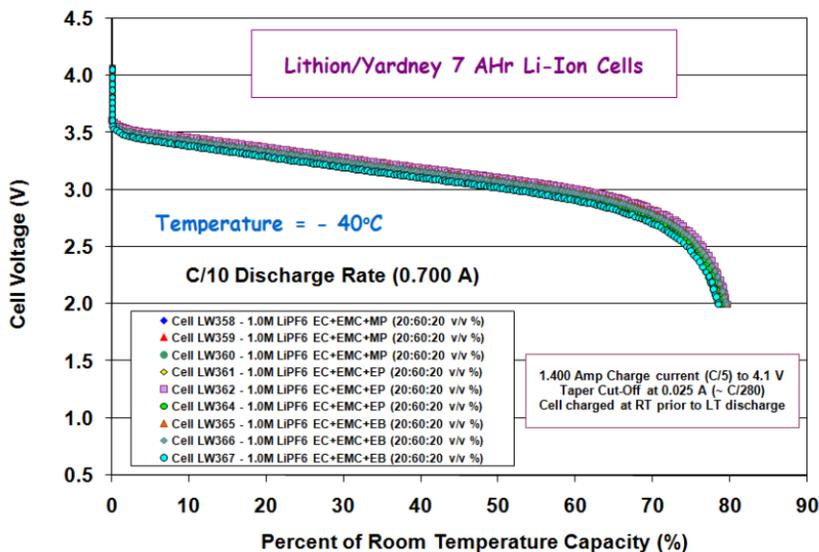


Figure 2. The discharge capacity (Ah) of cells containing ester-based electrolytes at -40°C using C/10 discharge rates (0.70A) (expressed in terms of the percentage of the room temperature capacity). Cells were charged at room temperature prior to discharge.

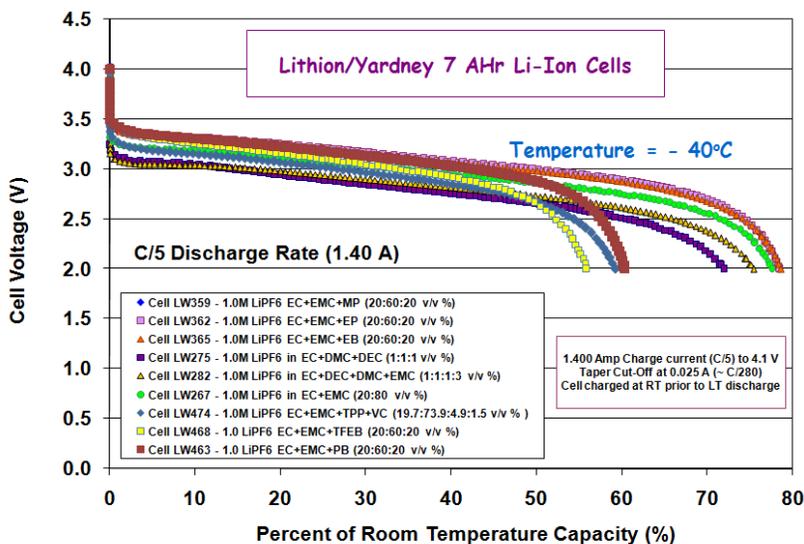


Figure 3. The discharge capacity (Ah) of cells containing ester-based electrolytes at -40°C using C/5 discharge rates (1.40A) (expressed in terms of the percentage of the room temperature capacity). Cells were charged at room temperature prior to discharge.

Similar trends were observed for the cells when they were evaluated at even lower temperatures, as illustrated in Fig. 4, in which the discharge behavior is shown using a C/5 rate at -50°C . The cells containing the methyl propionate and ethyl propionate-based electrolytes showed the best performance, both in terms of capacity (i.e., with nearly 75% of the room temperature capacity being delivered) and the extent of polarization observed. However, at these rates and such low temperatures, nearly all of the capacity (for all of the cells) is delivered at operating voltages of below 3.0V. It should also be noted that although the performance described corresponds to charging the cells at room temperature prior to discharge, rate characterization tests have also been performed on a number of cells in which the charge rate is varied and performed at low temperatures (i.e., up to C rate charge down to temperatures as low as -40°C). Under these conditions, no indirect evidence of lithium plating was observed (as ascertained by the presence of a lithium stripping plateau in the voltage profile on the subsequent discharge), although lower discharge capacity was obtained, as expected.

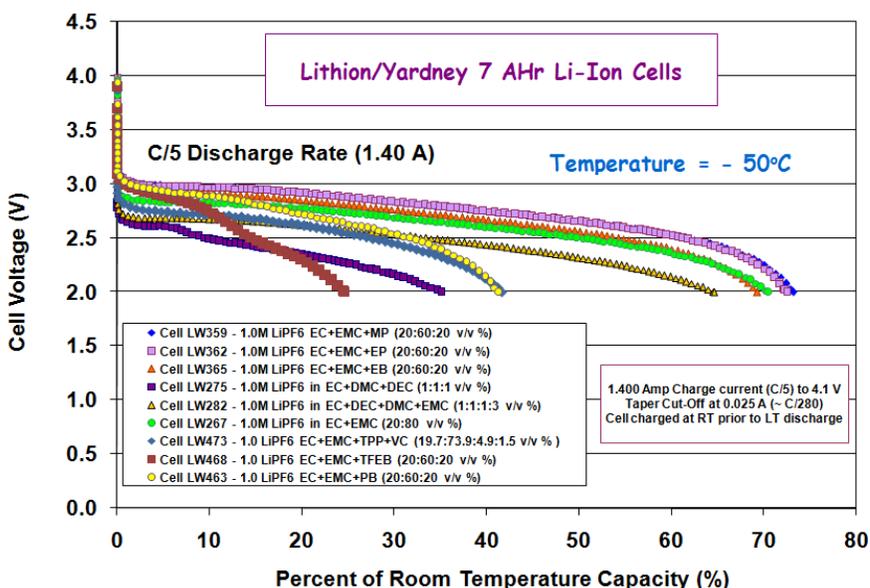


Figure 4. The discharge capacity (Ah) of cells containing various electrolytes at -50°C using C/10 discharge rates (0.70A) (expressed in terms of the percentage of the room temperature capacity). Cells were charged at room temperature prior to discharge.

Of the ester-based co-solvents investigated, the solutions containing methyl propionate yielded the best overall performance at low temperature, as illustrated in Fig. 5, in which the discharge behavior over a range of temperatures is displayed. Further enhancement of the low temperature performance, especially at high rates, has been achieved with further optimization of the ester content. However, a concern of using higher ester content is that the high temperature resilience may be compromised further.

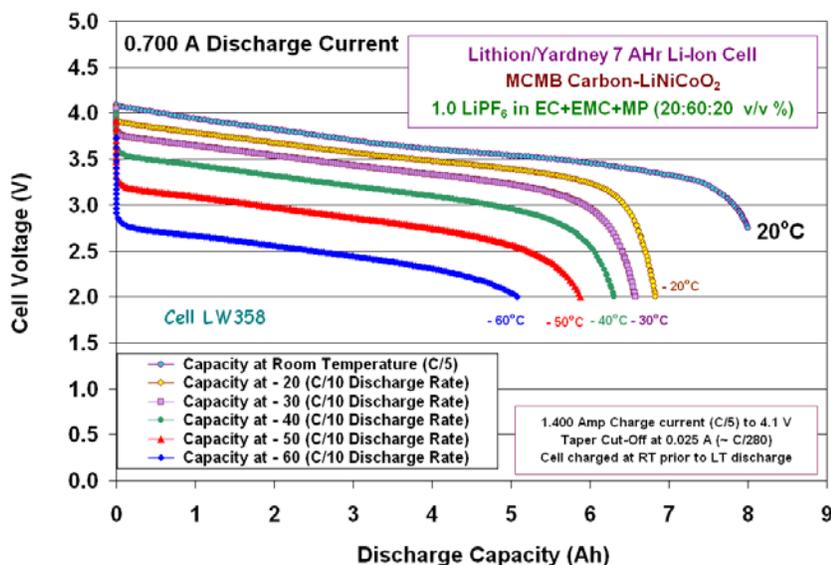


Figure 5. The discharge capacity (Ah) of a cell containing 1.0M LiPF₆ in EC+EMC+MP (20:20:60 v/v %) electrolyte over a wide range of temperatures using C/10 discharge rates (0.70A). The cell was charged at room temperature prior to discharge at low temperature.

Cycle Life Performance.

When 100% DOD cycle life testing was performed on a number of cells at ambient temperature, good performance was obtained, as illustrated in Fig. 6. This cycling consist of charging with C/5 rates to 4.10V (C/50 taper cut-off) and discharging using C/5 rates to 2.75V. As shown in the figure, very comparable performance was obtained with all of the cells, with the delivering over 85% of the initial capacity after completing 500 cycles, being similar to that obtained with one of the all carbonate baseline solutions (i.e, 1.0M LiPF₆ in EC+DEC+DMC (1:1:1 v/v %)). There is slight difference in the slope of the capacity fade for the two groups of cells, suggesting that cell design features have more influence upon the performance than the effect of the electrolyte type.

Although good cycle life performance at ambient temperatures was generally anticipated, there were concerns that the high temperature resilience of these systems is compromised by the presence of the low viscosity, low boiling ester-based co-solvents. In addition, it is known that the low temperature capability of Li-ion cells is often compromised by exposure to high temperatures, due to the presence of degradation mechanisms which increase the cell impedance. To address these concerns and attempt to quantify the resilience to high temperature cycling, and the corresponding impact upon the low temperature capability, cycling tests were implemented in which 20 cycle increments were performed on a number of cells where the temperature was systematically varied over a wide operating temperature range (i.e., 20°, 40°, 20°, -20°, 20°, 40°, 20°, -20°C, etc.), as illustrated in Fig. 7. As shown, the capacity decline for the cells at 20° and 40°C is somewhat comparable to that obtained when continuously cycled 20°C. However, the low temperature capability declines dramatically with life, illustrating the deleterious effect of exposure to high temperatures. As shown, the cell

containing the methyl propionate containing electrolyte exhibits greater capacity fade than the all carbonate-based electrolytes, suggesting that the solvent participates in a degradation mechanism which leads to increased cell impedance and reduced lithium intercalation/de-intercalation kinetics. Future work is focused upon approaches by which the impedance growth and capacity loss sustained at high temperatures can be minimized with these ester-based systems.

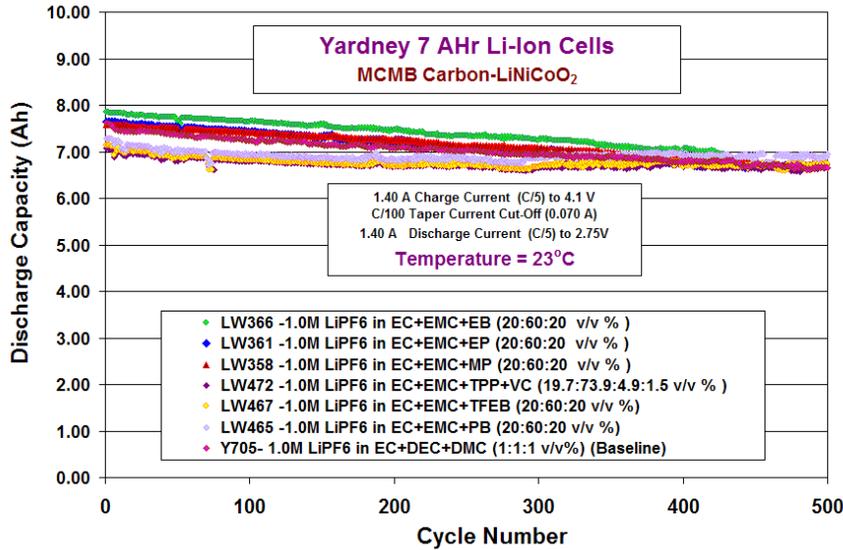


Figure 6. The cycle life performance (100% DOD) of 7Ah MCMB-LiNiCoO₂ cells containing various electrolytes at ~ 23°C.

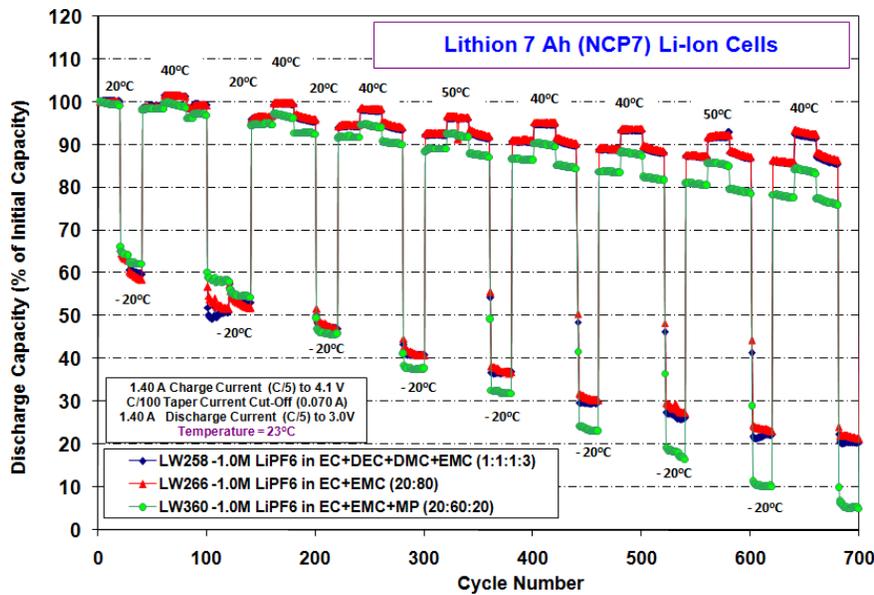


Figure 7. The cycle life performance (100% DOD) of 7Ah MCMB-LiNiCoO₂ cells containing various electrolytes at alternating temperatures (+50 to -20oC). Twenty cycles performed at each temperature.

Summary and Conclusions

We have demonstrated improved performance over a wide operating temperature range (-60°C to +50°C) with MCMB-Li_xNi_yCo_{1-y}O₂ cells containing electrolytes possessing ester co-solvents. The electrolytes selected for performance evaluation include the use of a number of esters, including methyl propionate (MP), ethyl propionate (EP), ethyl butyrate (EB), propyl butyrate (PB), and 2,2,2-trifluoroethyl butyrate (TFEB). Of the formulations investigated, the cells containing the 1.0M LiPF₆ in EC+EMC+MP (20:20:60 v/v %) electrolyte displayed the best performance at low temperatures. All of these solutions resulted in good cycle life performance (100%) when evaluated under ambient temperature. As anticipated, the low temperature capability of the cells was diminished upon being subjected to high temperature cycling, with the most dramatic decline being observed with the ester-containing electrolyte. Future effort is focused upon improving the high temperature resilience and preserving the low temperature capability throughout the life of the cell (i.e., with the use of electrolyte additives and/or the use of alternative electrode materials).

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References

1. R. A. Marsh, S. Vukson, S. Surampudi, B. V. Ratnakumar, M. C. Smart, M. Manzo, and P. J. Dalton, *J. Power Sources*, **97-98**, 25, (2001).
2. M. C. Smart, B. V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S. G. Greenbaum, A. Hightower, C. C. Ahn, and B. Fultz., *J. Electrochem. Soc.*, **146**, 3963 (1999).
3. M. C. Smart, B. V. Ratnakumar, and S. Surampudi, *J. Electrochem. Soc.*, **149 (4)**, A361-A370 (2002).
4. A. Ohta, H. Koshina, H. Okuno, and H. Murai, *J. Power Sources*, **54 (1)**, 6-10 (1995).
5. S. Herreyre, O. Huchet, S. Barusseau, F. Pertion, J. M. Bodet, Ph. Biensan, *J. Power Sources*, **97-98**, 576 (2001).
6. H. -C. Shiao, D. Chua, H. -P., Lin, S. Slane, and M. Solomon, *J. Power Sources*, **87**, 167-173 (2000).
7. S. V. Sazhin, M. Y. Khimchenko, Y. N. Trittenichenko, and H. S. Lim, *J. Power Sources*, **87**, 112-117 (2000).
8. M. C. Smart, B. V. Ratanakumar, K. B. Chin, and S. R. Narayanan, 206th Meeting of the Electrochemical Society, Oct. 3- Oct. 8, 2004.
9. M. C. Smart, B. V. Ratnakumar, A. Behar, L. D. Whitcanack, J. -S. Yu, and M. Alamgir, *J. Power Sources*, **165**, 535-543 (2007).
10. K.A. Smith, M.C. Smart, G.K.S Prakash, B.V. Ratnakumar, *ECS Trans.* **11**, (29) 91 (2008).
11. M.C. Smart, and B.V. Ratnakumar, L.D. Whitcanack, K.A. Smith, S. Santee, R. Gitzendanner, V. Yevoli, "Li-Ion Electrolytes Containing Ester Co-Solvents for Wide Operating Temperature Range", *ECS Trans.* **11**, (29) 99 (2008).