Performance of Wide Operating Temperature Range Electrolytes in Quallion Prototype Li-Ion Cells

M. C. Smart [a*], B. V. Ratnakumar [a], M. R. Tomcsi [b], M. Nagata [b],

V. Visco [b], and H. Tsukamoto [b]

[a]Jet Propulsion Laboratory, California Institute of Technology

4800 Oak Grove Drive, Pasadena, CA 91109–8099

[b]*Quallion LLC*

Sylmar Biomedical Park, 12744 San Fernando Rd., Sylmar, CA 91342

E-Mail: Marshall.C.Smart@jpl.nasa.gov

Abstract:

For a number of applications, there is a continued interest in the development of rechargeable lithium-based batteries that can effectively operate over a wide temperature range (i.e., -40 to +70ºC). These applications include powering future planetary rovers for NASA, enabling the next generation of automotive batteries for DOE, and supporting many DOD applications. Li-ion technology has been demonstrated to have good performance over a reasonably wide temperature range with many systems; however, there is still a desire to improve the low temperature rate capacity as well as the high temperature resilience. In the current study, we would like to present recent results obtained with prototype Li-Ion cells (manufactured by Quallion, LLC) which include various wide operating temperature range electrolytes developed by both JPL and Quallion. To demonstrate the viability of the technology, a number of performance tests were carried out, including: (a) discharge rate characterization over a wide temperature range (down to -60ºC) using various rates (up to 20C rates), (b) discharge rate characterization at low temperatures with low temperature charging, (c) variable temperature cycling over a wide temperature range (-40 to +70ºC), and (d) cycling at high temperature (50ºC). As will be discussed, impressive rate capability was observed at low temperatures with many systems, as well as good resilience to high temperature cycling. To augment the performance testing on the prototype cells, a number of experimental three electrodes cells were fabricated (including Li reference electrodes) to allow the determination of the lithium kinetics of the respective electrodes and interfacial properties as a function of temperatures.

Keywords: Lithium-ion cells; Wide operating temperature range electrolytes.

Introduction

A number of cell design aspects are known to influence the ability of Li-ion cells to operate over a wide temperature range, including the inherent properties of the electroactive materials, electrode design (i.e., loading, conductive diluent content, particle size, etc.), separator type, and electrolyte type. Of these, the electrolyte type plays a critical role in how well the cell will perform at the temperature extremes. For efficient low temperature operation the electrolyte must possess adequate conductivity and not be subject to salt precipitation phenomena (or solvent precipitation, such as ethylene carbonate) or the possibility of freezing. At high temperatures, the electrolyte components should not participate in decomposition reactions (either chemical or electrochemical in nature) ultimately leading to impedance growth due to the build of the surface films (i.e., the solid electrolyte interphase, SEI, layers). Furthermore, the nature of the electrolyte type dictates the properties of these SEI layers and how robust they are when subjected to operation under extreme temperatures, which defines the cycle life characteristics.

It is a significant technical challenge to develop an electrolyte system that can provide good performance over a wide temperature range *(*both charging and discharging from -40 to +70ºC*),* while still delivering excellent cycle life performance*.* To date, the most widely used electrolyte systems are based upon the use of lithium hexafluorophosphate ($LiPF_6$) dissolved in mixtures of cyclic and linear carbonates, including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). Optimization of all-carbonate solvent blends have enabled improved sub-zero performance, while still providing good cycle life and reasonable high temperature resilience. [2-5] However, there is a desire to further improve the rate capability at temperatures below -20°C, which the all carbonate-based blends are unable to provide.

In recent years, great progress has been made in improving the low temperature capability of Li-ion cells, most often through the addition of low viscosity, low melting co-solvent which improve the conductivity at the desired temperatures. For example, significant improvement in the performance below -20°C has been achieved with the use of ester co-solvents. [6-11] However, these improvements often are coupled with poorer high temperature resilience and cycle life, due to the increased reactivity of the co-solvents. Conversely, many electrolyte systems focused upon improving the high temperature performance (i.e., above +40°C) are often accompanied by poor low temperature performance, primarily due to the presence of large proportions of highly viscous solvents, such as ethylene carbonate. Thus, the development of electrolyte formulations that provide good performance at both extremes often balance these properties, often being optimized for the specific application.

In the present work, we have demonstrated the performance of electrolytes developed[12] and further optimized at JPL containing methyl propionate (MP) and ethyl butyrate (EB) in prototype Li-ion cells. More specifically, we have investigated formulations consisting of $LiPF_6$ in EC+EMC+X (where X = MP or EB), which have been optimized to deliver improved rate capability at low temperatures, while still offering reasonable high temperature resilience and cycle life performance. In addition to these solutions, we have evaluated a number of wide operating temperature range electrolytes developed by Quallion, LLC (referred to as Quallion-A1, Quallion-A2, and Quallion-A3). These electrolytes were compared with the performance obtained with 1.0M $LiPF_6$ in EC+EMC (30:70 vol %), which is considered to be one of the baseline electrolyte solutions adopted by the DoE program. Thus, these six electrolyte formulations were incorporated into prototype 0.30Ah cells manufactured by Quallion, consisting of a cell design optimized for biomedical applications. Upon receipt of the cells, a number of performance tests were carried out on the cells, including: (a) initial characterization cycling at 20, 0, and -20°C, (b) discharge rate characterization over a wide temperature range (down to -60°C) using various rates (up to 20C rates), (c) discharge rate characterization at low temperatures with low temperature charging, (d) variable temperature cycling over a wide temperature range (-40 to +70°C), and (e) cycling at high temperature (50°C).

Characterization Cycling at 20, 0, and -20°C

After activation with the candidate electrolytes and formation of the cells at Quallion, all of the cells were subjected to conditioning/characterization cycling at three temperatures (20, 0, and –20°C) upon receipt. When the performance of the 0.30 Ah cells was evaluated at room temperature, good cell to cell reproducibility was observed for each electrolyte type evaluated. As summarized in Table 1, all of the wide operating temperature range electrolytes deliver comparable performance to the baseline electrolyte (i.e., EC+EMC). These initial tests consisted of charging the cells to 4.10V using a C/5 rate (and a C/100 taper current cut-off) and discharging the cells using a C/5 rate to 2.50V, based upon a nameplate capacity of 0.25 Ah. In addition, D.C. current-interrupt impedance measurements were performed as a function of state of charge. As illustrated in the table, somewhat lower impedance was observed at 20°C with the cells containing the MP-based electrolyte.

Cell ID	Initial Capacity (Ah)	Discharge Energy (Wh/kg)	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (80% SOC)	Calculated Impedance (mOhms) (60% SOC)	Electrolyte Type
NEC-02	0.303	109.42	106.81	108.64	106.20	EC+EMC
NEC-07	0.312	112.20	92.77	95.83	97.66	EC+EMC
NEC-09	0.307	110.24	103.76	107.42	107.42	EC+EMC
NEC-11	0.310	111.42	99.49	103.15	106.20	EC+EMC
NA1-18	0.310	110.64	123.29	128.18	128.79	Quallion A1
NA1-19	0.304	108.78	103.15	110.48	109.86	Quallion A1
NA1-20	0.305	109.10	107.42	111.09	113.53	Quallion A1
NA1-21	0.302	108.58	109.86	114.75	115.97	Quallion A1
NA2-33	0.300	108.96	108.64	114.14	114.14	Quallion A2
NA2-35	0.309	112.21	101.32	106.20	103.76	Quallion A2
NA3-42	0.315	115.09	138.55	133.06	133.67	Quallion A3
NA3-43	0.310	112.72	101.93	108.03	106.20	Quallion A3
NA3-44	0.305	111.54	102.54	106.81	106.81	Quallion A3
NA3-46	0.294	107.31	108.64	112.31	114.14	Quallion A3
NMP-07	0.293	106.73	98.27	101.32	98.88	JPL (EC+EMC+MP)
NMP-08	0.307	110.76	94.61	98.88	100.71	JPL (EC+EMC+MP)
NMP-09	0.297	108.11	95.22	98.27	97.66	JPL (EC+EMC+MP)
NMP-10	0.307	110.67	95.22	101.93	98.27	JPL (EC+EMC+MP)
NEB-19	0.286	104.33	105.59	108.03	104.98	JPL (EC+EMC+EB)
NEB-20	0.287	99.41	103.76	105.59	104.98	JPL (EC+EMC+EB)
NEB-22	0.304	109.38	101.93	106.20	106.20	JPL (EC+EMC+EB)
Average	0.303	109.41	104.89	108.59	108.38	

Table 1. Summary of the results obtained upon characterizing the cells at 20°C.

When the cells were subjected to the initial characterization cycling at -20°C, comparable performance was obtained for all of the electrolyte formulations in terms of the capacity delivered, whether based upon charging at 20°C or at -20°C, as illustrated in Table 2. However, there was more variation in the measured impedance, with the Quallion electrolytes delivering somewhat higher impedance than the cells containing either the baseline electrolyte or the MP- and EB-based formulations.

Cell ID	Initial Capacity at 20°C (Ah)	Capacity at - 20°C (Ah) (Charge at 20°C)	Capacity at - 20°C (Ah) (Charge at -20°C)	Calculated Impedance (mOhms) (80% SOC)	Calculated Impedance (mOhms) (60% SOC)	Electrolyte Type
NEC-02	0.3026	0.2503	0.2421	659.80	646.37	EC+EMC
NEC-07	0.3121	0.2536	0.2385	732.43	737.32	EC+EMC
NEC-09	0.3070	0.2501	0.2382	760.51	761.12	EC+EMC
NEC-11	0.3102	0.2524	0.2411	740.98	744.03	EC+EMC
NA1-18	0.3099	0.2585	0.2433	1075.46	1093.16	Quallion A1
NA1-19	0.3040	0.2553	0.2312	1185.93	1214.01	Quallion A1
NA1-20	0.3047	0.2587	0.2367	1097.43	1119.40	Quallion A1
NA1-21	0.3025	0.2559	0.2323	1127.34	1152.36	Quallion A1
NA2-33	0.3000	0.2577	0.2392	931.41	946.67	Quallion A2
NA2-35	0.3093	0.2566	0.2379	959.49	1052.87	Quallion A2
NA3-42	0.3150	0.2653	0.2416	1224.99	1252.46	Quallion A3
NA3-43	0.3097	0.2592	0.2348	1140.76	1167.62	Quallion A3
NA3-44	0.3053	0.2564	0.2336	1152.36	1178.61	Quallion A3
NA3-46	0.2941	0.2498	0.2272	1074.24	1100.48	Quallion A3
NMP-07	0.2931	0.2476	0.2388	700.08	698.25	JPL (EC+EMC+MP)
NMP-08	0.3068	0.2560	0.2431	746.47	752.57	JPL (EC+EMC+MP)
NMP-09	0.2972	0.2493	0.2393	726.94	733.04	JPL (EC+EMC+MP)
NMP-10	0.3072	0.2580	0.2469	715.95	720.84	JPL (EC+EMC+MP)
NEB-19	0.2863	0.2374	0.2274	678.11	665.90	JPL (EC+EMC+EB)
NEB-20	0.2868	0.2364	0.2253	696.42	701.92	JPL (EC+EMC+EB)
NEB-22	0.3037	0.2495	0.2378	737.32	736.71	JPL (EC+EMC+EB)
Average	0.3032	0.2530	0.2370	898.31	913.13	

Table 2. Summary of the results obtained upon characterizing the cells at - 20°C.

Discharge Rate Characteristics (Charge at 20°C)

To evaluate the low temperature capability of the cells, a number of cells (two cells per electrolyte type) were subjected to discharge rate characterization over a wide range of temperatures (-70 to +20°C) using a number of rates (C/50 to 5C). The cells were fully charged at ambient temperature and allowed to soak at the desired temperature for at least 4 hours prior to discharge to 2.0V. As shown in Fig. 1, when the cells were discharged at a moderate rate (i.e., a C/10 rate) at -40°C, somewhat comparable performance was obtained with all of the electrolyte types resulting in similar discharge energy ranging from 74-82 Wh/kg being delivered. The best performance was observed with the cells containing the MP-based electrolyte and the Quallion-A1 electrolytes. A notable feature of the performance of all of the cells is that a significant amount of capacity is delivered with an operating voltage above 3.0V.

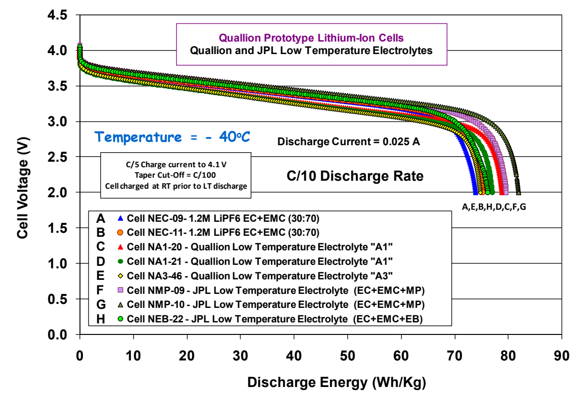

Figure 1. Discharge energy (Wh/Kg) of Quallion cells at -40°C containing various electrolytes. The cells were charged at room temperature and discharged using a C/10 rate.

Much more differentiation between the cells was observed upon subjecting the cells to more aggressive discharge rates at these temperatures. For example, when discharged at -40°C using a C rate discharge (0.25A) the cells possessing the wide operating temperature range electrolytes delivered much more energy than the baseline formulation, as illustrated in Fig. 2. Of the different electrolyte types, the cells containing the MP-based blend and the Quallion "A3" and "A1" solutions provided the best performance. The cell containing the EB-based solution delivered somewhat lower energy, presumably due to the lower conductivity of the electrolyte.

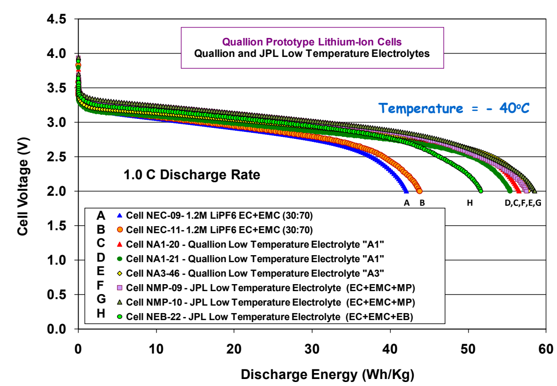

Figure 2. Discharge energy (Wh/Kg) of Quallion cells at -40°C containing various electrolytes. The cells were charged at room temperature and discharged using a C rate.

The cells were observed to support even more aggressive rates at -40°C, as illustrated in Fig. 3, in which the performance is displayed using a 5C discharge rate. The Quallion "A1" and "A3" solutions and the MP-based formulation all delivered comparable performance with approximately 50 Wh/kg being delivered. As shown, this represents roughly a five-fold improvement over the cells containing the baseline EC+EMC electrolyte.

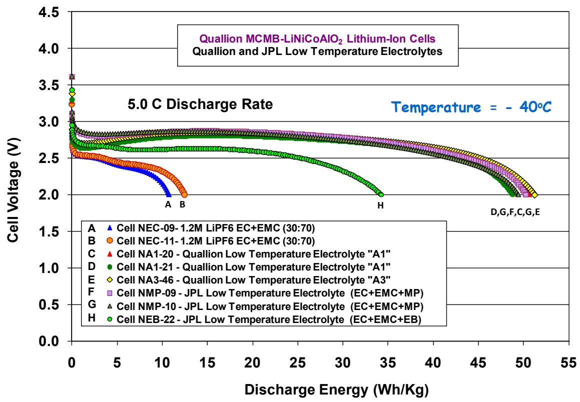

Figure 3. Discharge energy (Wh/Kg) of Quallion cells at -40°C containing various electrolytes. The cells were charged at room temperature and discharged using a 5C rate.

Cycle Life Performance over a Wide Temperature Range

In addition to characterizing the discharge rate performance at different temperature (with both charging at room temperature and at low temperature), effort was focused upon evaluating the performance of the cells when cycled at high temperatures. One such test involves cycling the cells at alternating high and low temperatures (i.e., 20 cycles performed at -20°C, 20 cycles at 40°C, followed by cycling at -20°C, etc.) and to determine the life characteristics under these conditions and the extent to which the low temperature capability is preserved. Of the electrolytes investigated, the baseline EC+EMC solution displayed the greatest robustness cycling well over a temperature range of +40° to -30°C, with significant performance decline only observed after being subjected to cycling at 50°C. Of the wide operating temperature range electrolytes, the ethyl butyrate-based solution displayed the best overall performance. Although the Quallion-based electrolytes displayed good performance when continuously cycled at high temperatures, performance decline was observed when cycled at low temperatures, presumably due to the possibility of lithium plating upon charge.

Conclusions

In this study, we have evaluated a number of Li-ion electrolytes developed for operation over a wide temperature range in Quallion prototype cells. When the cells were discharge at low temperatures, both the JPL and Quallion developed electrolytes were observed to result in significant performance improvements at -40°C, being able to support rates at a high as 5C. Under these conditions, cell containing the electrolytes displayed a five-fold improvement in the discharge energy delivered, as well as significantly higher operating voltages. The cells were also observed to perform well when subjected to variable temperature cycling, retaining the low temperature capability after being subjected to cycling at 40°C. Current effort is being focused upon further improving the resilience to cycling at temperatures above 40°C.

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References

1. Xu, K., *Chem. Rev*., **104**, 4303-4417 (2004)
2. Smart, M. C., Ratnakumar, B. V. and S. Surampudi, *J. Electrochem.Soc*., **146**, 486 (1999).
3. Smart, M. C., Ratnakumar, B. V., Whitcanack, L. D., Chin, K. B., Surampudi, S., Croft, H., Tice, D., and R. Staniewicz, *J. Power Sources,* **119-121**, 349-358(2003).
4. Ein-Eli, Y., Thomas, S. R., Chadha, R., Blakley, T. J., and V. R. Koch, *J. Electrochem.Soc*., **144** (3), 823-829 (1997).
5. Plichta, E. J. and W. K. Behl, *J. Power Sources,* **88 (2)**, 192-196 (2000).
6. Smart,M. C., Ratnakumar, B. V., and S. Surampudi, *J. Electrochem. Soc*., **149 (4),** A361-A370 (2002).
7. Ohta, A., Koshina, H., Okuno, H., and H. Murai, *J. Power Sources*, **54 (1)**, 6-10 (1995).
8. Herreyre, S., Huchet, O., Barusseau, S., Perton, F., Bodet, J. M., and Ph. Biensan, *J. Power Sources*, **97-98**, 576 (2001).
9. Shiao, H. –C., Chua, D., Lin, H. –P., Slane, S., and M. Solomon, *J. Power Sources*, **87**, 167-173 (2000).
10. Sazhin, S. V., Khimchenko, M. Y., Tritenichenko, Y. N. and H. S. Lim, *J. Power Sources*, **87**, 112-117 (2000).
11. Jow, T. R., Xu, K., Ding, M. S., Zhang, S. S., Allen, J. L. and K. Amine, *J. Electrochem. Soc.*, **151**, A1702-A1706 (2004).
12. Smart, M. C., Ratnakumar, B. V., Whitcanack, L. D., Smith, K. A., Santee, S., Gitzendanner, and V. Yevoli, *ECS Trans.,* **11 (29)**, 91 (2008).