Li-ion Battery Electrolytes
Designed For a Wide Temperature Range

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Abstract

In recent years, the applications for Li-ion batteries have expanded dramatically. Having displaced NiMH in the consumer electronics market and beginning to displace NiCd in the power tool market, Li-ion batteries are being actively developed for HEVs and the military/aerospace applications, where the required operational temperature range is significantly broader.

To date, the single technological bottleneck limiting the operation of the Li-ion battery over a wide temperature range is the electrolyte itself. In particular, Li-ion battery performance steeply declines as the operating temperature dips below -10°C. Additionally, battery characteristics rapidly deteriorate at temperatures above 60°C.

We report on the development of a new family of Li-ion battery electrolytes designed to operate over a wide temperature range. These electrolytes possess excellent transport properties along with high thermal stability. Li-ion cells incorporating new electrolyte formulations may now be discharged at rates as high as C/4 at -50°C. Further, such cells demonstrate long cycle life both at room temperature and at temperatures as high as 80°C.

In this paper we consider the operational temperature requirements for various applications and discuss the temperature limitations of state-of-the-art Li-ion battery electrolytes. We then present our results on the cycle life and charge/discharge characteristics of a new family of electrolytes over a wide temperature range. Finally, we consider potential compromises between Li-ion battery rate capability at low temperatures and high temperature cycle life.

Keywords: Li-ion; battery; electrolyte

Introduction and Background

The operational temperature range of a Li-ion battery is dictated by its specific application. At very low temperatures, NASA requires battery performance at a reasonable discharge rate from -60°C to -80°C. Alternatively, the drilling industry requires rechargeable battery solutions at temperatures well in excess of 100°C. It is widely believed that in order to reach these temperature extremes, task-formulated electrolytes tailored to specific operating temperature applications are required, *i.e.,* one class of electrolytes formulated strictly for low temperature applications and others formulated strictly for high temperature applications.

Beyond these two widely divergent market segments, the majority of Li-ion battery applications fit within a -50°C to 80°C window as depicted in Figure 1. This window includes consumer electronics and power tools (-20°C to 60°C), HEV (-30°C to 70°C) and military applications (-50°C to 80°C).

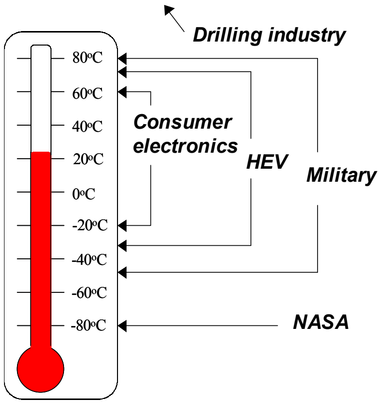

Figure 1. Temperature windows for various Li-ion battery markets.

Common Li-ion battery electrolytes are derived from solutions of $LiPF_6$ salt in a solvent blend of ethylene carbonate (EC) and various linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylmethyl carbonate (EMC).

Two of the above components are found in virtually every commercially available electrolyte formulation: EC, which is essential for good SEI formation, and $LiPF_6$, the supporting electrolyte of choice owing to its low cost, high conductivity, good SEI formation properties and ability to effectively passivate an Al foil current collector. These two electrolyte components also dictate the temperature limits of a Li-ion cell.

At low temperatures, EC leads to high electrolyte viscosity and poor Li^+ transport properties. At very low temperatures, electrolyte component phase separation may occur. At the same time, high concentrations of EC are beneficial for cell operation at elevated temperatures (1).

Additionally, the PF_6^- anion is unstable in electrolyte solutions at 60°C and above (2). Its reactions with carbonates and adventitious water result in a rapid degradation of the electrode materials and battery components.

Attempts to achieve a wide temperature range of operation have led Li-ion battery manufacturers to reduce the EC concentration by adding low viscosity linear carbonates and low melting esters such as methyl butyrate (MB) and ethyl butyrate (EB). This improves Li-ion cell performance at temperatures below -20°C and retains, to some extent, high temperature stability. We see a clear historical trend to decrease the amount of EC in electrolyte formulations in order to expend the thermal operating range of Li-ion cells. For example, in the beginning of the 1990's electrolyte formulations contained as much as 50% EC. By the end of the decade, a range of electrolyte compositions were introduced with 25% to 33% EC such as NASA JPL's (3) 1M $LiPF_6$/EC:DMC:DEC (1:1:1) or Covalent's (4) 1M $LiPF_6$/EC:EMC (1:3). More recently, JPL Gen III electrolyte (5) has further enhanced Li-ion low temperature performance with a formulation containing 17% EC: 1M $LiPF_6$/EC:DMC:DEC:EMC (1:1:1:3). Finally, last year JPL announced a low temperature formulation that contains only 10% EC, and incorporates an ester (6), *i.e.*, 1M $LiPF_6$/EC:EMC:MB (1:1:8). However, none of the above formulations provide suitably high discharge rates at low temperatures as required by the military and HEV markets let alone long cycle life at elevated temperatures.

Covalent's approach to the development of a wide temperature range Li-ion battery is to formulate an electrolyte with little or no EC making extensive use of electrolyte additives and alternative lithium salts to achieve a single, universal formulation that allows for high discharge rates at low temperatures (as low as -50°C) coupled with long cycle life at high temperatures (up to 80°C).

Experimental

All electrolyte materials were of the highest available purity. Solvents were further dried over molecular sieves and lithium salts were dried overnight on a high vacuum line prior to use. Electrolyte conductivities were measured in a Fisher Model 018010 conductivity cell with a GenRad Model 1656 Impedance Bridge. Linear sweep voltammetry and impedance measurements were accomplished with a VoltaLab PGZ 301 Electrochemical Measurements Unit. Li-ion cells were cycled on MACCOR Series 2000 Battery Tester, and Tenney Environmental chambers were used for temperature control.

In order to screen new electrolyte formulations we employed cathode limited 2325 crimped Li-ion coin cells ($Li_xC/Li_{1-x}CoO_2$) of approximately 5mA in capacity. Long-term cycling experiments were conducted in 1.4Ah wound cells employing graphite and lithium cobaltate as the active electrode materials.

Results and Discussion

A number of new electrolyte formulations were found to possess exceptionally high ionic conductivity over a wide temperature range as shown in Table 1. Even at temperatures as low as -50°C, these electrolyte formulations remained highly fluid with conductivities ranging from 2.0 mS/cm to 4.6 mS/cm.

Table 1. Specific conductance of various electrolyte formulations.

Formulation	**Conductivity (mS/cm) and physical appearance**		
	22°C	**–40°C**	**–50°C**
1M $LiPF_6$ / EC:EMC 1:3	8.8	0.8	0.5 *(glass)*
1M $LiPF_6$ / EC:DMC:DEC:EMC 1:1:1:3 (**JPL Gen III**)	10.0	1.3	0.7 *(viscous liquid)*
Covalent C	**17.6**	**6.4**	**4.6 *(liquid)***
Covalent D	**13.2**	**4.8**	**2.8 *(liquid)***
Covalent E	**12.1**	**3.6**	**2.0 *(liquid)***

However, ionic conductivity is not the only factor that accounts for good low temperature cell performance. Another key requirement is the ability of the electrolyte to form a stable SEI on the electrode materials. Further, a strong case has been made regarding low temperature Li-ion battery performance being controlled by slow Li^+ solvation/desolvation kinetics.

We have found that Li-ion cells filled with the new electrolytes "C", "D" and "E" demonstrate impressive performance on discharge at the C/4 rate at -40°C. In Figure 2 we compare our coin cell discharge curves to that of the JPL Gen III electrolyte.

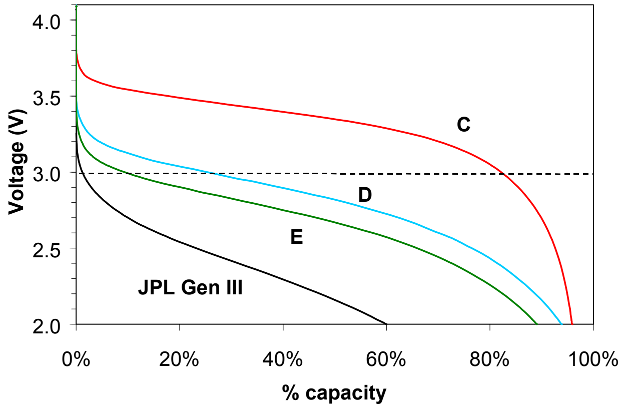

Figure 2. Discharge of various low temperature electrolytes in coin cells at -40°C; C/4 discharge rate.

Discharge of 1.4Ah cells yields even better results as seen in Figure 3, where all of the new electrolytes provide in excess of 90% of their capacity to a 2V cut-off potential at -40°C.

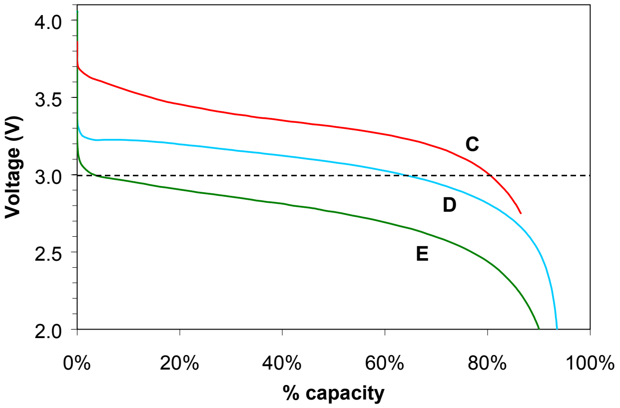

Figure 3. Discharge curves of Covalent electrolytes in 1.4Ah cells at -40°C; C/4 discharge rate.

In the field, Li-ion battery performance is further improved due to the self-heating phenomenon. Figure 4 presents the C/4 discharge curves at -40°C of a Li-ion cell filled with electrolyte "E". The only difference in the data is that in the first case the cell was placed in Tenney chamber with an active flow of cold air (solid curve), while the second case employs the same cell but discharged in a freezer in the absence of convection (dashed curve). In the latter case the battery heats up during discharge faster than it can be cooled, and thus delivers more capacity at a 500 mV higher average discharge voltage.

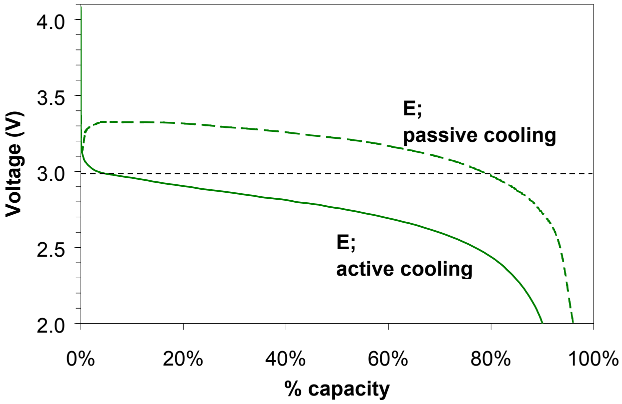

Figure 4. Self-heating phenomenon of a 1.4Ah Li-ion cell at C/4 discharge at -40°C.

The same self-heating phenomenon accounts for poor reproducibility of discharge results of the cells filled with "E" and "D" electrolyte formulations at high rates at -50°C (Figure 5). The observed delivered capacity turns out to depend on the position of the cell within the Tenney chamber.

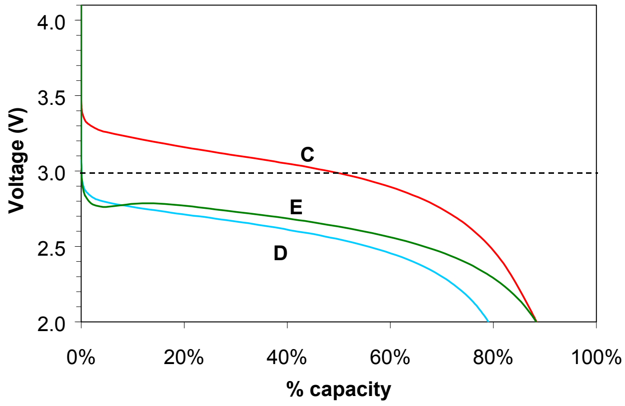

Figure 5. Discharge curves of Covalent electrolytes in 1.4Ah cells at -50°C; C/4 discharge rate.

It's important to note that even under such cold conditions the "C" electrolyte delivered 50% of cell capacity above a 3V cut-off at the C/4 rate. This represents an excellent solution to the problem of low temperature Li-ion battery performance. We have established, however, that the room temperature cycle life of cells incorporating the "C" electrolyte is poor when compared to that of commercially available batteries. We were able to significantly improve the room temperature performance by lowering the upper cut-off potential by 100 mV at a cost of ~12% of cell capacity (Figure 6).

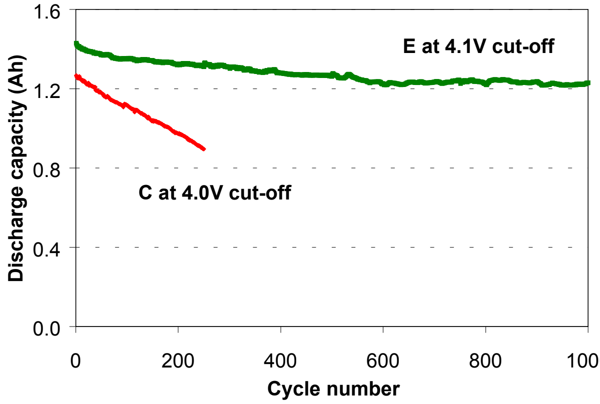

Figure 6. Cycle life of 1.4Ah Li-ion cells filled with electrolytes "C" and "E" at 22˚C; C/2 rate.

Nonetheless, we believe that "C" electrolyte remains a promising option when employed against lower voltage cathode materials such as $LiFePO_4$. In marked contrast, Li-ion cells filled with electrolyte "E" demonstrate excellent capacity retention over 1000 deep cycles at room temperature. These cells retained 85% of their initial capacity when cycled at the C/2 rate to 100% DOD.

Electrolyte “E” has also demonstrated good cycle life at 60°C and limited cycle life at 80°C in 2325 coin cells (Figure 7).

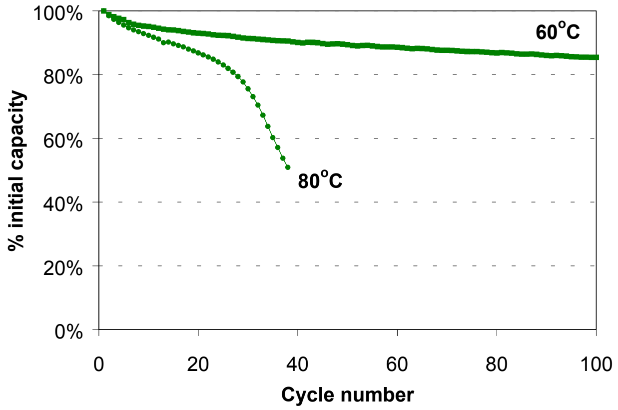

Figure 7. Cycle life of coin cells filled with electrolyte “E” at elevated temperatures; C/2.

Overall, the “E” electrolyte allows Li-ion cells to operate at high rates from -50°C to 60°C with occasional excursions to 80°C.

To achieve long cycle life at 80°C we modified the “E” electrolyte and have formulated several revised compositions that do in fact allow for adequate continuous cycle life at 80°C. Further designated as E2, E3 and E4 these electrolytes are able to withstand prolonged cycling at 80°C as shown in Figure 8 with an acceptable rate of fade.

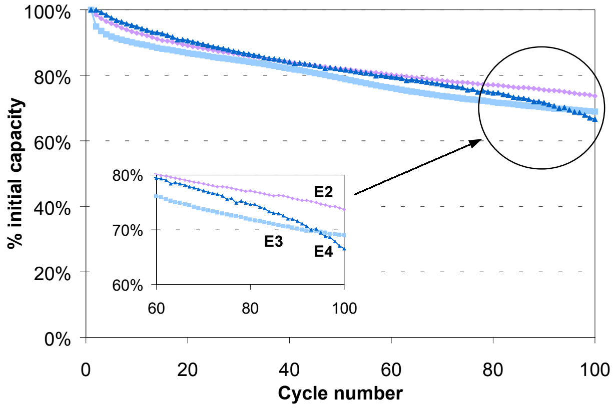

Figure 8. Cycle life (C/2) of coin cells filled with the E-family of electrolytes at 80°C; C/2.

Along with improved performance at 80°C, the new electrolyte formulations retain or exceed the low temperature discharge performance of the original “E” formulation. Discharge results in Li-ion coin cells are presented in Figure 9. Extensive testing of the “E” family of electrolytes in 1.4Ah wound cells in the temperature range from -50°C to 80°C will soon begin.

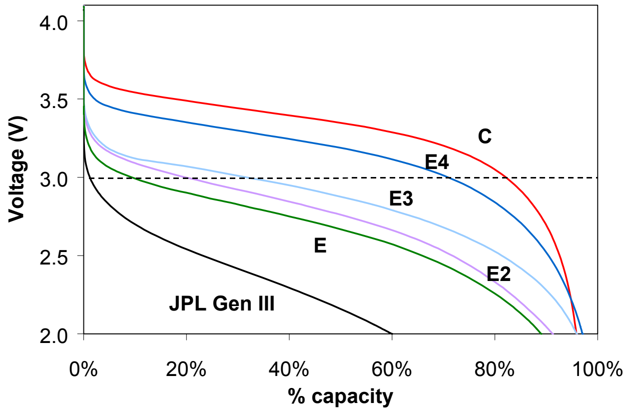

Figure 9. Discharge of various electrolytes in coin cells at -40°C; C/4 discharge rate.

Conclusions

A number of Li-ion battery electrolyte formulations that perform very well over a wide temperature range have been developed. In wound 1.4Ah Li-ion cells these electrolytes deliver 80% or more of their capacity at -50°C at the C/4 discharge rate. Several formulations can also be cycled continuously at 80°C with acceptable capacity fade. The “E” family of electrolytes represents a unique solution for those Li-ion battery applications that require performance over a wide temperature range

Acknowledgements

This work was accomplished under U. S. Air Force Contract No. FA8650-04-C-2489.

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