Performance Testing of Yardney MCMB-$LiNiCoAlO_2$ Lithium-Ion Cells Possessing Electrolytes with Improved Safety Characteristics

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Abstract:

Many future NASA missions aimed at exploring the Moon and Mars require high specific energy rechargeable batteries that possess enhanced safety characteristics. There is also a strong desire to develop Li-ion batteries with improved safety characteristics for terrestrial applications, most notably for HEV and PHEV automotive applications. In previous work focused upon evaluating various potential flame retardant additives[1], triphenyl phosphate (TPP)[2] was observed to have the most desirable attributes, including good life characteristics and resilience to high voltage operation. We have employed a number of approaches in the design of promising TPP-based electrolytes with improved safety, including: (a) varying the flame retardant additive (FRA) content (from 5 to 15%), (b) the use of fluorinated co-solvents, (c) the use of additives to improve compatibility, and (c) the use of ester co-solvents to decrease the viscosity and increase the conductivity. In recent work, we have demonstrated a number of these electrolyte formulations to be compatible with a number of chemistries, including: MCMB carbon-$LiNi_{0.8}Co_{0.2}O_2$, graphite-$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, Li-$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$, Li-$LiNiCoMnO_2$ and graphite-$LiNiCoMnO_2$.[3,4] In the current study, we have demonstrated the performance of a number of TPP-containing electrolytes in 7 Ah prototype MCMB-$LiNiCoO_2$ cells. We will describe the results of a number of performance tests, including: a) 100% DOD cycle life testing at various temperatures, b) discharge rate characterization as a function of temperature, c) charge rate characterization as a function of temperature, and d) impedance as a function of temperature. In addition to displaying good life characteristics, being comparable to baseline chemistries, a number of cells were observed to provide good performance over a wide temperature range.

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

Introduction

To improve the safety of Li-ion batteries, one approach is to reduce the flammability of the electrolyte, so that the potential for harm under abuse conditions is decreased. In contrast to aqueous-based battery chemistries, Li-ion cells typically contain non-aqueous carbonate-based solvents which are flammable. In order to reduce the flammability of these electrolytes, many have employed the use of flame retardant additives (FRAs), such as organic phosphates, phosphonates, phosphites, and phosphazenes.[5,6] Depending upon the FRA species, upon decomposition these compounds can serve to release CO_2, promote char formation to protect the condensed phase and/or inhibit flame propagation in the gas phase by reacting with radicals. In our earlier work, we evaluated the compatibility of a number of FRAs in carbonate-based electrolytes with traditionally employed Li-ion electrode chemistries (i.e., $LiNi_{0.8}Co_{0.20}O_2$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ -based systems). The FRAs studied include trimethyl phosphate, triethyl phosphate, triphenyl phosphate, tris(2,2,2-trifluoroethyl) phosphate, and bis(2,2,2-trifluoroethyl) methyl phosphonate (TFMPo), tris(2,2,2-trifluoroethyl) phosphite, triphenylphosphite, diethyl ethylphosphonate, and diethyl phenylphosphonate. In terms of cell performance, triphenyl phosphate (TPP) was deemed to be the most attractive FRA investigated, since it displayed minimal impact upon life characteristics and rate capability, as well as the capability to be utilized for high voltage systems.

In addition to utilizing flame retardant additives, the use of halogenated co-solvents in conjunction with FRAs was also explored to further reduce the flammability the electrolyte formulations. In particular, fluorinated esters[7] and fluorinated carbonates[8], that were previously demonstrated to have good compatibility with $LiNi_{0.8}Co_{0.20}O_2$ systems, were blended with cyclic and linear carbonates containing TPP in multi-component formulations. The use of electrolyte additives (i.e., solid electrolyte interphase (SEI) film forming agents, such as vinylene carbonate) was also studied as a means to improve the electrolyte compatibility. It should be noted that the safety of the electrolyte should be substantially improved with FRA concentrations as low as 5% based on literature reports[2], however, it is anticipated that 10-15% is the preferred range to impart the desired reduction in flammability.

Evaluation of Candidate Electrolytes in Prototype MCMB-$LiNiCoAlO_2$ Cells

Based on findings from experimental coin and three-electrode cells, a number of promising candidate electrolytes containing TPP were identified for further evaluation in prototype cells. The selection of these electrolytes was intended to address a number of variables in electrolyte design, including (i) the impact of varying the TPP content (i.e., from 5% to 15%), (ii) the use of mono-fluoroethylene carbonate (FEC) in lieu of ethylene carbonate, (iii) the use of 2,2,2-trifluoroethyl methyl carbonate (TFEMC) as a co-solvent, and (iv) the use of SEI promoting electrolyte additives (i.e., vinylene carbonate). The electrolytes investigated include the following : (1) 1.0M $LiPF_6$ in EC+EMC+TPP (20:75:5 vol %) + 1.5% VC, (2) 1.0M $LiPF_6$ in EC+EMC+TPP (20:70:10 vol %), (3) 1.0M $LiPF_6$ in EC+EMC+TPP (20:65:15 vol %), (4) 1.0M $LiPF_6$ in FEC+EMC+TPP (20:70:10 vol %), and (5) 1.0M $LiPF_6$ in FEC+EMC +TFEMC+TPP (20:50:20:10 vol %) + 1.5% VC.

The electrolytes described above were incorporated into high capacity (7 Ah) prototype graphite/$LiNiCoAlO_2$ cells, manufactured by Yardney Technical Products, Inc. The intent of evaluating these cells was to (a) ascertain various trends related to the different non-flammable electrolyte approaches, and (b) demonstrate the life characteristics in a baseline chemistry and form factor. The testing of these cells included: (i) performing general characterization testing at 20°, 0°, and at -20°C (consisting of capacity and impedance characterization), (ii) discharge rate characterization over a wide temperature range (with room temperature charging), and (iii) performing cycle life testing (100% DOD and 30% DOD) at room temperature.

Upon performing the characterization testing at 20°C, it was observed that all of the cells delivered comparable capacity and discharge energy regardless of electrolyte type, suggesting that no significant impact upon performance was observed with the incorporation of higher TPP content (up to 15% TPP content). All of the cells delivered 125-130 Wh/kg under similar cycling conditions (i.e., C/5 charge to 4.10V and C/5 discharge to 2.75V). These results are very comparable to that obtained with a baseline formulation, 1.0M $LiPF_6$ in EC+DEC+DMC (1:1:1 vol %), that does not contain any flame retardant additives. When current-interrupt impedance measurements were performed at 20°C, as expected the cell containing the lowest TPP content displayed the lowest impedance, due to the higher ionic conductivity of the solution. Modestly higher impedance was observed when replacing EC with FEC, most likely due to increased viscosity of the electrolyte and somewhat poorer electrolyte salt dissociation, resulting in lower ionic conductivity. The most dramatic increase in impedance was observed with the cell contacting the TFEMC in conjunction with FEC, which can be attributed to lower electrolyte conductivity and most likely higher film and charge transfer resistance at the electrode interfaces, resulting in decreased lithium kinetics.

Discharge Rate Characterization Testing

Although the intended application of the development effort does not require operation at excessively low temperatures, discharge rate characterization of the cells was performed over a wide temperature range (-50 to +20°C) to assess the capability of the technology and determine the applicability for other applications (i.e., planetary rovers and landers). This testing consisted of charging the cells at room temperature and subsequently discharging the cells over a range of rates (C/100 to C/2) at the respective temperatures after soaking for at least eight hours to reach thermal equilibrium. In general, very good performance was obtained at low temperatures, which can be attributed to the low cyclic carbonate content in the electrolyte formulations leading to high ionic conductivity and low freezing points of the solutions. As shown in Fig. 1, good discharge rate capability was demonstrated with all of the cells containing electrolytes with high TPP concentration (i.e., either 10% or 15%). As expected, the better low temperature performance was observed with the cells containing electrolytes with lower TPP content (i.e., 1.0M $LiPF_6$ in EC+EMC+TPP (20:70:10 vol %), since they exhibit higher electrolyte conductivity at these temperatures.

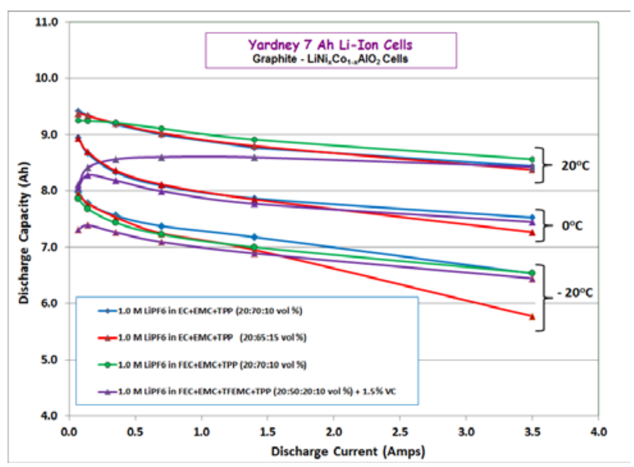

Figure 1. Discharge capacity (Ah) delivered at different discharge rates (C/100 to C/2) of Yardney 7 Ah Li-ion cells containing various electrolytes possessing triphenyl phosphate (TPP).

As expected, the best low temperature performance was obtained with the cell containing electrolytes with lower TPP content, but good performance was also delivered with concentrations as high as 10%. For example, excellent performance was obtained at -40°C with ~ 95 Wh/kg being delivered at a C/20 discharge rate, as illustrated in Figure 2.

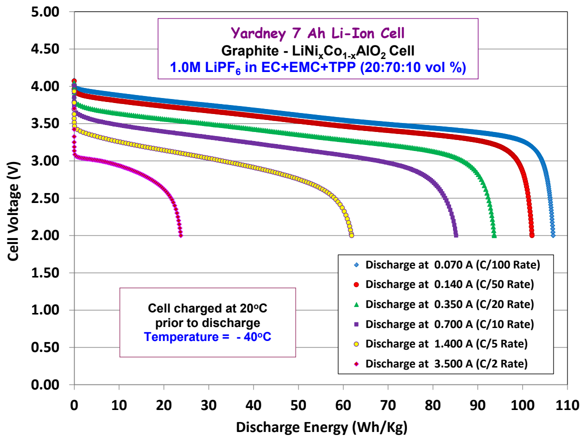

Figure 2. Discharge energy (Wh/kg) delivered at different discharge rates (C/100 to C/2) at -40°C of a Yardney 7 Ah Li-ion cells containing 1.0 M $LiPF_6$ in EC+EMC+TPP (20:70:10).

As anticipated, somewhat poorer performance was obtained at -40°C upon increasing the TPP content to 15% (i.e., 1.0M $LiPF_6$ in EC+EMC+TPP (20:65:15 vol %), as shown in Figure 3. However, when the performance of the cells was compared with the baseline formulation (i.e., 1.0M $LiPF_6$ in EC+DEC+DMC (1:1:1 vol %)) at low temperatures, cells containing 10% TPP have been observed to perform better than the baseline. For example, cells containing 1.0M $LiPF_6$ in EC+EMC+TPP (20:70:10 vol %) and 1.0M $LiPF_6$ in FEC+EMC+TPP (20: 70:10 vol %) were both observed to deliver greater capacity and higher operating voltage when discharged at a C/10 rate at -40°C, as illustrated in Figure 3. Upon increasing the TPP content to 15% there is a noticeable decrease in the delivered energy of the cells, which has been attributed to decreased electrolyte conductivity at these temperatures due to the increase in viscosity imparted by the TPP. In more recent studies, it has been shown that the use of low viscosity co-solvents can partially offset this increase in viscosity associated with high FRA concentration. It should be noted that although the current batch of cells containing the TPP-based electrolyte are similar to that of the baseline, some design differences exist. In general, it should be emphasized that this is a notable performance capability, since the cells provide reasonable operational capability at such low temperatures while providing improved safety characteristics.

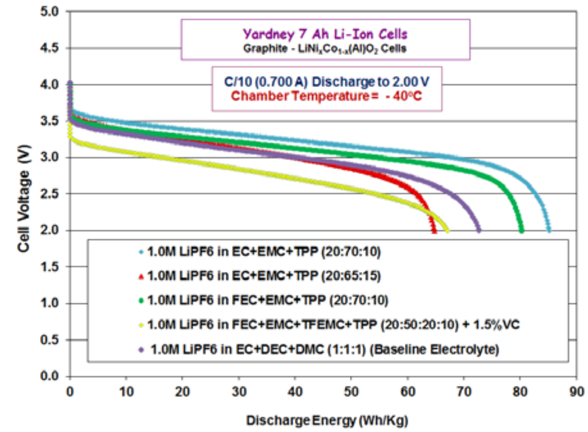

Figure 3. Discharge energy (Wh/kg) delivered at a C/10 rate at -40°C of Yardney 7 Ah Li-ion cells containing various electrolytes possessing triphenyl phosphate (TPP). The cells were charged at room temperature prior to discharge.

Cycle Life Testing

In addition to characterizing the discharge rate performance at different temperatures, effort was focused upon evaluating the cycle life performance of the cells. This includes performing both (i) 100% depth of discharge (DOD) cycling, and (ii) 30% DOD low earth orbit (LEO) cycling. As illustrated in Fig. 4, when a number of cells were subjected to 100% DOD cycling testing at ambient temperature, excellent performance has been obtained thus far, with very modest capacity loss observed with all electrolyte formulations. This cycling consists of using C/5 charge and discharge rates over a voltage range of 2.75V to 4.10V.

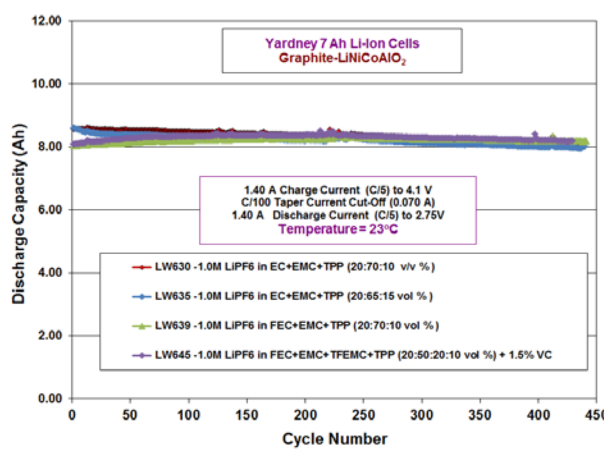

Figure 4. Cycle life performance (100% DOD) of Yardney 7 Ah Li-ion cells containing various electrolytes possessing triphenyl phosphate (TPP).

During the cycle life testing described above, current-interrupt impedance measurements were performed every 100 cycles to determine the influence of electrolyte type upon cell impedance growth as a function of life. As noted before, the lowest impedance was observed with the cell containing the lower TPP concentration and EC used instead of FEC as the cyclic carbonate. In terms of the impedance growth with cycling, the concentration of TPP and type of cyclic carbonate was not observed significantly change the impedance growth rate, suggesting that they are not participating in deleterious degradation mechanisms. Of the electrolyte studied, the cell containing the high proportion of fluorinated co-solvents (i.e., both FEC and TFEMC) displayed both high initial impedance and a higher growth rate, suggesting that the TFEMC may be degrading with time leading to more resistive interfacial electrode films.

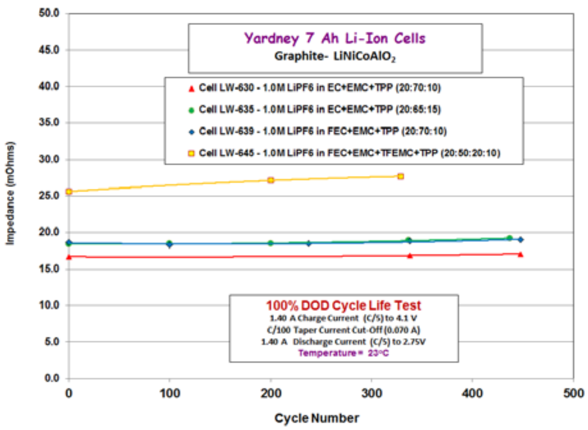

Figure 5. Cell impedance growth determined by current-interrupt measurements performed during 100% DOD life testing of Yardney 7 Ah Li-ion cells containing various electrolytes possessing triphenyl phosphate (TPP).

Conclusions

In this study, we have evaluated a number of high capacity Li-ion cells (manufactured by Yardney Technical Products) that contain electrolytes that possess enhanced safety characteristics (i.e., low flammability). In general, good discharge rate capability was observed over a wide temperature range (-50° to 20°C). At very low temperatures, cells containing electrolytes with lower TPP concentrations displayed the best performance. However, good performance was observed at temperatures as low as -40°C using TPP concentrations as high as 10%, outperforming all carbonate-based baseline solutions. Good cycle life performance has also been observed with all of the cells containing TPP-based electrolytes. When subjected to 100% DOD cycle life testing, very little capacity fade has been observed to-date, with over 400 cycles being completed. In summary, a number of Li-ion battery electrolytes possessing enhanced safety characteristics have been developed and demonstrated to perform well in prototype graphite/ $LiNiCoAlO_2$ cells, being capable of operating over a wide temperature range and delivering excellent cycle life. Future efforts will be focused upon evaluating these electrolytes with different chemistries, as well as verifying the anticipated safety improvements by performing abuse testing.

Acknowledgements

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