The Evaluation of Triphenyl Phosphate as a Flame Retardant Additive to Improve the Safety of Lithium-Ion Battery Electrolytes

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With the intent of improving the safety characteristics of lithium-ion cells, electrolytes containing flame retardant additives have been investigated. A number of triphenyl phosphate-containing electrolytes were evaluated in both coin cells and experimental three electrode lithium-ion cells (containing reference electrodes). A number of chemistries were investigated, including MCMB carbon/$LiNi_{0.8}Co_{0.2}O_2$ (NCO), graphite/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), Li/$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$, Li/$LiNiMnCoO_2$ (NMC) and graphite/$LiNiMnCoO_2$ (NMC), to study the effect that different electrolyte compositions have upon performance. A wide range of TPP-containing electrolytes were demonstrated to have good compatibility with the C/NCO, C/NCA, and Li/NMC systems, however, poor performance was initially observed with the high voltage C/NMC system. This necessitated the development of improved electrolytes with stabilizing additives, leading to formulations containing lithium bis(oxalato)borate (LiBOB) that displayed substantially improved performance.

Introduction

There is continuing interest in developing lithium-ion batteries with improved safety. For a number of NASA's future applications under the Exploration Technology Development Program, there is a desire to have high specific energy rechargeable batteries that have improved safety. This is especially true for human rated applications, where the astronaut's safety is critical.

Since lithium-ion batteries have been identified as the technology of choice to meet the requirements of these missions, there has been an effort at NASA, as well as elsewhere, to identify approaches to improve the inherent safety of these devices. For example, the general battery industry and the Department of Energy, who are actively developing advanced lithium-ion technology for automotive applications, would greatly benefit from improvements in the safety of the devices, provided that there is minimal sacrifice in performance. Although there are a number of approaches to improve the safety of lithium-ion cells, we have focused upon modification of the electrolyte formulation to provide lower flammability. It is well know that under abuse conditions lithium-ion cells are prone to vent, catch on fire, or even explode, so reduced

flammability of the system is highly desirable. The flammability of the systems is primarily due to the cyclic and linear organic carbonates in the electrolyte system.

To reduce the flammability of the electrolyte, researchers have employed various strategies, including: (i) the use of low vapor pressure ionic liquids[1], (ii) the use of halogenated solvents (such as fluorinated carbonates)[2], and (iii) the use of flame retardant additives (FRAs). The last approach has been explored by a number of groups, with a number of potential additives showing good electrochemical capability and flame suppression, including triphenyl phosphate (TPP)[3], tris(2,2,2-trifluoroethyl) phosphate[4,5,6], and dimethyl methyl phosphonate (DMMP).[7,8]

After investigating the electrochemical characteristics of a number of flame retardant additives (shown in Figure 1) that were incorporated into multi-component electrolyte formulations, we have focused upon solutions that possess triphenyl phosphate, since it has displayed the best overall performance with a number of systems[9].

The TPP-containing electrolytes were evaluated in both coin cells and experimental three electrode lithium-ion cells (containing reference electrodes). A number of chemistries were investigated, including MCMB carbon/$LiNi_{0.8}Co_{0.2}O_2$ (NCO), graphite/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), Li/$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$, Li/$LiNiMnCoO_2$ (NMC), and graphite/$LiNiMnCoO_2$ (NMC), to study the effect that these additives have upon performance. During the course of this study, we have investigated the addition of fluorinated co-solvents, the optimization of the carbonate solvents, and the use of electrolyte additive to improve compatibility with the various systems. In the case of the three electrode cells, a number of electrochemical characterization techniques were performed to determine the effect that these additives have upon the SEI characteristics and the lithium intercalation/de-intercalation kinetics, including EIS, DC micropolarization, and Tafel polarization. One objective of the work was to determine the most compatible formulations for high voltage systems. It was generally noted that dramatically different trends were observed depending upon whether lithium metal or carbonaceous anodes materials were used when coupled with the high voltage cathodes.

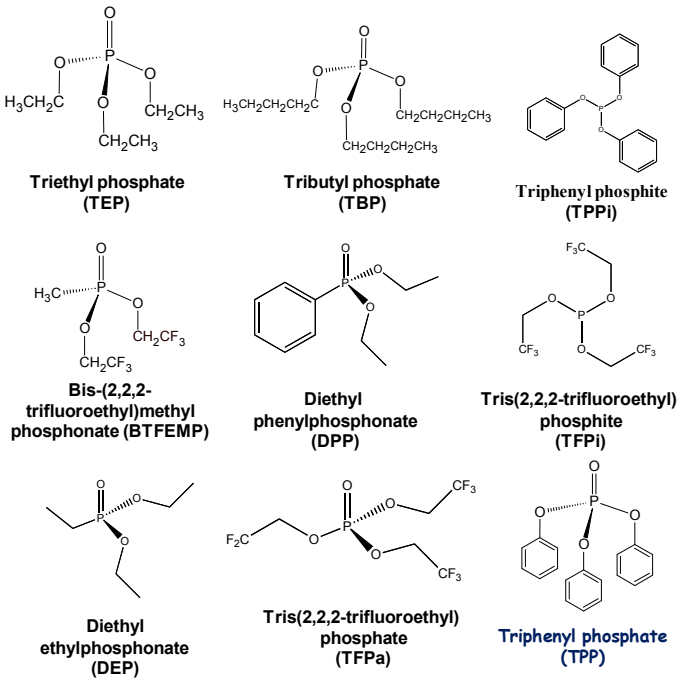

Figure 1. Chemical structures of various flame retardant additives (FRAs) investigated for use in lithium-ion battery electrolytes.

Experimental

For detailed electrical and electrochemical measurements, three-electrode, O-ring sealed, glass cells containing spiral rolls of MCMB (1028)-carbon anodes or MPG-111 graphite anodes, $LiNi_{0.80}Co_{0.2}O_2$ (NCO) or $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA) cathodes, and lithium reference electrodes separated by two layers of porous polypropylene (Tonen-Setella) were employed. The MCMB anode electrodes (~ 114 μm thickness) were coated with active material on both sides of the substrate and had an active material area of approximately 158.1 cm^2, corresponding to ~ 16 mg/cm^2. The NCO cathode electrodes (~ 114 μm thickness) were also double sided with an active material area of approximately 141.1 cm^2, corresponding to ~ 19 mg/cm^2. The $Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ and $LiNiMnCoO_2$ (NMC) electrodes were prepared by spray coating Al foil substrates with slurries of 80 wt% cathode powder, 10 wt% C black (Shawinigan), and 10 wt% PVDF binder (Sigma Aldrich, MW_{avg} = 534,000) in N-methyl-2-pyrrolidinone (NMP) (Sigma Aldrich). The electrode active mass loading was 5 – 6 mg/cm^2. Coin cell studies were performed with the $Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ and $LiNiMnCoO_2$ (NMC) electrodes by assembling them in stainless steel CR3032 coin cell hardware with Al clad stainless steel cases. The carbonate-based solutions, ethylene carbonate (EC) and ethyl methyl carbonate (EMC) containing $LiPF_6$ salt in the desired concentration, were purchased from Novolyte, Inc. and contained less than 50 ppm of water. The flame-retardant additives used in the study were generally purchased from Aldrich Chem. Co. and used as received.

Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat (273A) interfaced with an IBM PC, using Softcorr 352. A Solartron 1255 Frequency Response Analyzer was used with this potentiostat for impedance measurements, with M388 software. Charge-discharge measurements and cycling tests were performed with an Arbin battery cycler. The cycling tests were done at current densities of 0.25 mA/cm^2 (~ C/16 rate) and 0.50 mA/cm^2 (~ C/8 rate) for charge and discharge, respectively. The cells were charged to 4.10 V, followed by a tapered charge period at constant potential for three hours, and then discharged to 2.75 V following a 15 minute rest interval. For the low temperature discharge rate characterization of the experimental cells, after charging at room temperature, the cells were allowed to dwell at the desired temperature for at least 5 hours prior to discharging to 2.00 V.

For performance assessment, some candidate electrolytes were incorporated into 7Ah, prismatic Li-ion cells manufactured by Yardney Technical Products (Pawcatuck, CT). These cells consist of MCMB (1028)-carbon anodes, $LiNi_{0.80}Co_{0.2}O_2$ cathodes, and porous polypropylene separator material (Tonen-Setella). 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

As a result of the electrolyte development efforts performed previously[9], it was determined that triphenyl phosphate-containing electrolytes display the most attractive characteristics, in terms of the robustness and compatibility with a number of chemistries. Of the electrolyte investigated during these initial studies, the formulation consisting of 1.0M $LiPF_6$ in EC+EMC+TPP+VC (19.7:73.9:4.9:1.5 v/v %) displayed the best overall

performance. This conclusion was based upon: (i) good performance obtained in experimental MCMB/$LiNiCoO_2$ cells, (ii) good performance obtained in Li/$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ coin cells, (iii) excellent cycle life performance in prototype MCMB/$LiNiCoO_2$ cells (7 Ah), (iv) good rate capability and low temperature performance in prototype MCMB/$LiNiCoO_2$ cells (7 Ah), and (v) improved safety characteristics compared with a baseline formulation used by Saft America, Inc. (as determined by Saft and Thermal Hazard Solutions (THS) using ARC measurements).

The major objectives in further development of advanced electrolyte formulations were to (a) further decrease the flammability of the mixture (i.e., using high concentrations of the flame retardant additives and/or the use of fluorinated co-solvents) and (b) demonstrate the compatibility of the electrolytes with a high specific energy electrode couple (e.g., the MPG-111 graphite/Toda cathode system). In addition to focusing upon developing electrolytes compatible with the high voltage systems, effort was devoted to determining the compatibility of candidate electrolyte with a number of commonly used electrode chemistries, namely MCMB carbon/$LiNi_{0.8}Co_{0.2}O_2$ (NCO) and graphite/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). To expand the family of previously developed electrolytes, a number of additional electrolyte formulations containing triphenyl phosphate (TPP), were investigated and demonstrated in experimental cells. These electrolytes include: (i) formulations which incorporate greater concentrations of the flame retardant additive, (ii) the use di-2,2,2-trifluoroethyl carbonate (DTFEC) as a co-solvent, (iii) the use of 2,2,2-trifluoroethyl methyl carbonate (TFEMC), (iv) monofluoroethylene carbonate (FEC) as a co-solvent and/or a replacement for ethylene carbonate, and (v) vinylene carbonate as a "SEI promoting" electrolyte additive, to build on the favorable results previously obtained. The use of higher concentrations of the flame-retardant additive is known to reduce the flammability of the electrolyte solution, and thus a range of compositions were investigated (namely, from 5 to 20% by volume). The desired concentration of the flame-retardant additive is the greatest amount tolerable without adversely affecting the performance in terms of reversibility, ability to operate over a wide temperature range, and the discharge rate capability. The use of fluorinated carbonates, much in the same manner as the incorporation of fluorinated-ester-based solvents, was employed to reduce the inherent flammability of mixtures. Thus, electrolyte formulations which embody both approaches are anticipated to have much lower flammability, resulting in enhanced safety.

Performance in MCMB Carbon/$LiNiCoO_2$ (NCO) Cells.

A number of experimental lithium-ion cells, consisting of MCMB carbon anodes and $LiNi_{0.8}Co_{0.2}O_2$ cathodes, were fabricated to study the approaches described above. These cells serve to verify and demonstrate the reversibility, low temperature performance, and electrochemical aspects of each electrode as determined by a number of electrochemical characterization techniques. When the formation characteristics for a number of cells containing electrolytes with triphenyl phosphate (TPP) were compared, all of the cells displayed good reversibility at room temperature and minimal reactivity as determined by the high coulombic efficiencies and comparable irreversible capacity losses observed. For example, the FRA-containing electrolytes 1.0 M $LiPF_6$ in EC+EMC+DTFEC+TPP (20:50:20:10 v/v %) and 1.0 M $LiPF_6$ in FEC+EMC+TPP (20:70:10 v/v %) displayed higher coulombic efficiencies on the first cycle (85.9% and 85.6%, respectively) compared with all carbonate-based electrolytes (~ 83.5%).

Given that a higher concentration of triphenyl phosphate was utilized in many of the formulations, there was concern that the low temperature discharge performance may

be compromised due to the presence of a component which is expected to lower the ionic conductivity of the electrolyte. Thus, effort was devoted to fully characterizing the systems over a wide temperature range using a number of discharge rates. It should be noted that the electrode weights were comparable (i.e., < 5 % variation), and the cells delivered comparable room temperature capacities (365-406 mAh). As illustrated in Fig. 2, good performance was delivered from the cells containing 10% triphenyl phosphate and 2,2,2-trifluoroethyl methyl carbonate and/or mono-fluoroethylene carbonate when evaluated at a ~ C/8 discharge rate (50 mA) at 0 °C (a programmatically relevant discharge condition). In all cases, the cells were observed to deliver more capacity than the baseline system, with the cell containing the 1.0 M $LiPF_6$ in FEC+EMC+TFEMC+TPP (20:50:20:10 v/v %) electrolyte exhibiting the best performance. In addition to TPP-based electrolytes, investigation of a dimethyl methyl phosphate-based system developed by the University of Rhode Island and Yardney Technical Products was performed. Although this electrolyte (0.95 M $LiPF_6$ + 0.05 M LiBOB in EC+EMC+DMMP (30:55:15 wt %)) resulted in cells that exhibited good rate capability and cycle life performance, a decline in performance was observed resulting in loss of reversible capacity (ranging from 8 to 20% loss depending upon the test vehicle), which has been attributed to incompatibility with the anode, as discussed below.

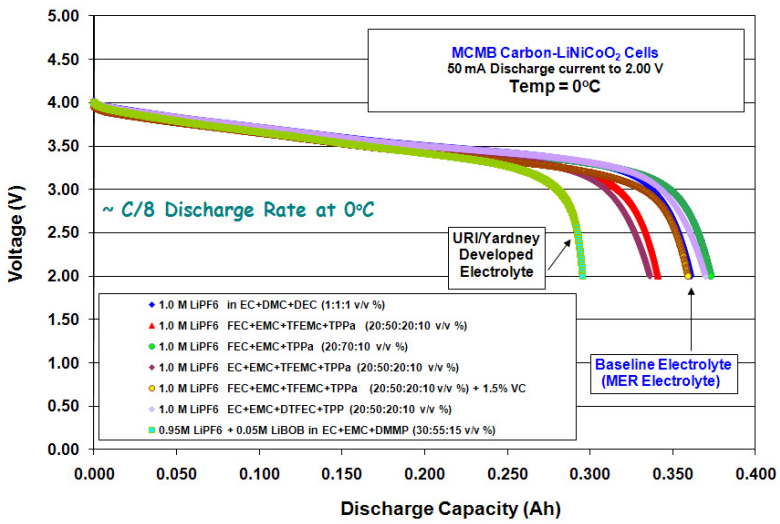

Figure 2. Discharge performance at MCMB-$LiNiCoO_2$ cells containing various FRA-containing electrolytes 0 °C using a ~ C/8 discharge rate to 2.0 V. Cells were charged at room temperature prior to discharge.

Upon completing the formation cycling of the cells, a number of electrochemical characterization measurements were performed to determine the lithium kinetics at both the anode and cathode, in an attempt to elucidate the trends observed in the electrical performance. When Tafel polarization measurements were performed, as illustrated in Figure 3, it was apparent that the lithium kinetics at the anode were dramatically impeded by the 0.95 M $LiPF_6$ + 0.05 M LiBOB in EC+EMC+DMMP (30:55:15 wt %)) electrolyte in contrast to cells containing the baseline electrolyte, as well as other cells containing the TPP-based electrolytes. Based upon in house data generated with electrolytes that contain LiBOB as an electrolyte additive, it is postulated that the source of the excessive reactivity is the DMMP, leading to undesirable SEI layers on the carbonaceous anodes. In contrast, the DMMP+LiBOB system appears to enhance the kinetics of the cathode (Fig. 3A).

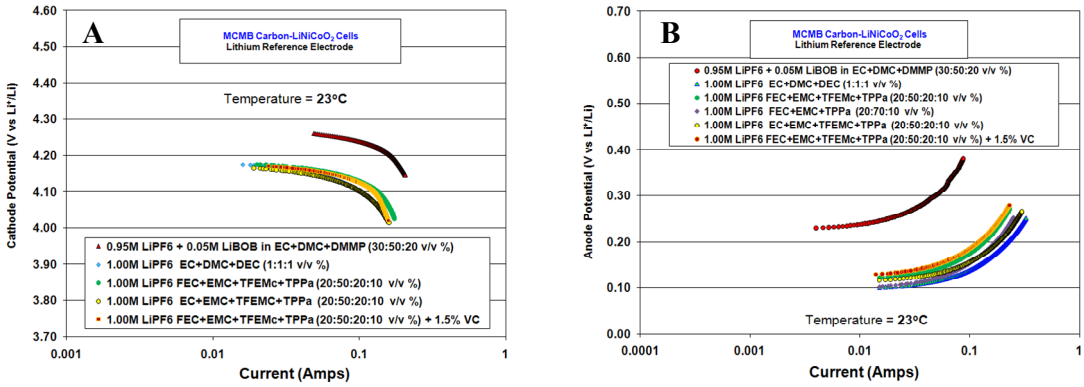

Figure 3. Tafel polarization measurements of both anodes and cathodes of MCMB-$LiNiCoO_2$ cells containing flame retardant additive-containing electrolytes.

To further assess the performance characteristics of candidate electrolyte formulations, a number of high capacity, hermetically sealed Li-ion cells were fabricated with one of the promising electrolyte solutions identified earlier, namely 1.0 M $LiPF_6$ in EC+EMC+TPP+VC (19.7/73.9/4.9/1.5 v/v %). After completing the initial characterization testing, a number of performance tests were performed on the cells, including evaluating: (a) the discharge rate performance at various temperatures, (b) the charge rate performance at various temperatures, and (c) determining the cycle life characteristics. As shown in Fig. 4, excellent 100% depth-of-discharge (DOD) cycle life performance was obtained compared with a cell containing a baseline all carbonate-based electrolyte (Fig. 4A) and good discharge rate capability was obtained at 20°C (Fig. 4B). Cells containing electrolytes with TPP also showed impressive low temperature discharge capability, albeit being modestly lower than that of cells containing analogous electrolytes without TPP.

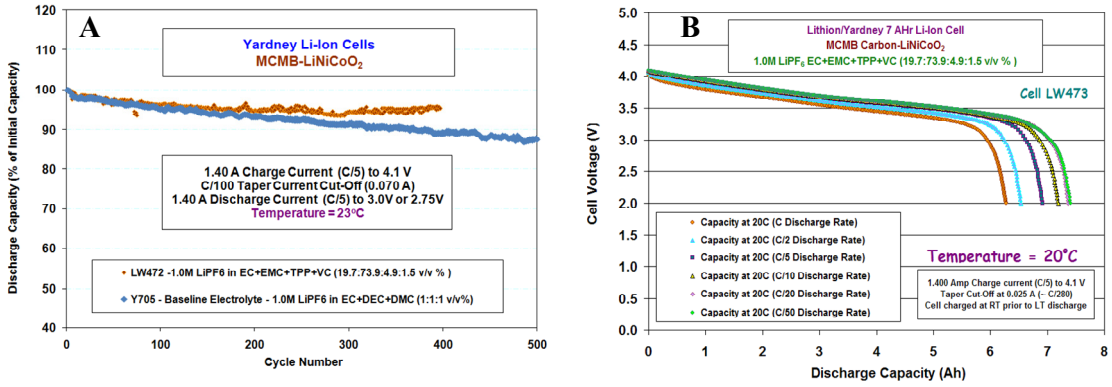

Figure 4. The 100% DOD cycle life performance of Yardney 7 Ah of cells containing a TPP-based electrolyte and a baseline control electrolyte (Fig. 4A) and the discharge rate capability of a 7 Ah cell containing 1.0 M $LiPF_6$ in EC+EMC+TPP+VC (19.7/73.9/4.9/1.5 v/v %).

Performance in Graphite/$LiNiCoAlO_2$ (NCA) Cells.

Effort was devoted to evaluating candidate FRA-containing electrolytes using a state-of-art chemistry, namely MPG-111 graphite anodes and $LiNiCoAlO_2$ cathodes. Electrodes of this chemistry were provided by Saft America and were fabricated into

experimental three-electrode cells in the jelly roll configuration (approximately 500 mAh cells). A number of electrolytes were evaluated, including (1) 1.0 M $LiPF_6$ in EC+EMC+TPP (20:70:10 v/v %), (2) 1.0 M $LiPF_6$ in EC+EMC+TPP (20:65:15 v/v %), (3) 1.0 M $LiPF_6$ in FEC+EMC+TPP (20:70:10 v/v %), (4) 1.0 M $LiPF_6$ + 0.15 M LiBOB in EC+EMC+TPP (20:70:10 v/v %), and (5) 1.0 M $LiPF_6$ in FEC+EMC+TPP (20:65:15 v/v %). The primary objective of these cells is to ascertain the impact of utilizing electrolytes that contain a higher proportion of TPP-content (i.e., 15% TPP) and the use of FEC in lieu of EC. Generally good performance was obtained throughout the formation cycling with all of the formulations, in that they provided high reversible capacity, low irreversible capacity, and high coulombic efficiency. After completing the formation and electrochemical characterization at various temperatures, the discharge rate capability of the cells was determined at 23, 0, and -20 °C, as shown in Table 1. The results of these tests correlate well with the findings observed with the MCMB-$LiNiCoO_2$ cells mentioned previously. For example, decreased rate capability and low temperature performance was observed upon increasing the FRA-content from 10% to 15%. When the cells were evaluated at low rate (50 mA discharge, or approximately C/10 discharge rate) at 0^oC, as shown in Fig. 5, the best performance was exhibited by the cell containing 1.0 M $LiPF_6$ + 0.15 M LiBOB in EC+EMC+TPP (20:70:10 v/v %), with comparable performance being displayed by the formulation with 10% TPP and without the addition of LiBOB.

Table 1. The discharge rate characteristics of three electrode MPG-111/$LiNiCoAlO_2$ cells containing

			ST13		ST14		ST15		ST16		ST17	
Electrolyte Type →			1.00M $LiPF_6$ EC+EMC+TPP (20:70:10 vol %)		1.00M $LiPF_6$ EC+EMC+TPP (20:65:15 vol %)		1.00M $LiPF_6$ FEC+EMC+TPP (20:70:10 vol %)		1.0M $LiPF_6$ + 0.15M LiBOB EC+EMC+TPP (20:70:10 vol %)		1.0 M LiPF6 FEC+EMC+TPP (20:65:15 vol %)	
Temp.	Current (mA)	Rate	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)
23°C	7.50 mA	C/65	0.5134	100.00	0.4991	100.00	0.5302	100.00	0.5253	100.00	0.5415	100.00
	25 mA	C/20	0.4888	95.19	0.4783	95.83	0.4922	92.83	0.5104	97.18	0.5203	96.08
	50 mA	C/10	0.4589	89.37	0.4440	88.95	0.4537	85.57	0.4881	92.93	0.4498	83.07
	100 mA	C/5	0.4046	78.81	0.3722	74.58	0.3881	73.20	0.4300	81.86	0.2867	52.95
	150 mA	C/3.3	0.3805	74.12	0.3203	64.18	0.3643	68.70	0.4015	76.44	0.2273	41.98
0°C	25 mA	C/20	0.4060	79.08	0.3877	77.68	0.3944	74.37	0.4308	82.02	0.3512	64.85
	50 mA	C/10	0.4213	82.06	0.3800	76.14	0.4123	77.76	0.4430	84.34	0.4024	74.31
	100 mA	C/5	0.3647	71.04	0.2428	48.65	0.3563	67.20	0.3926	74.74	0.2101	38.79
	150 mA	C/3.3	0.2897	56.41	0.1132	22.69	0.3201	60.38	0.3414	65.00	0.0823	15.20
- 20°C	25 mA	C/20	0.3499	68.15	0.2838	56.87	0.3294	62.13	0.3362	64.01	0.2291	42.31
	50 mA	C/10	0.2750	53.57	0.0975	2.00	0.2844	53.64	0.2631	50.10	0.0752	13.88
	100 mA	C/5	0.1027	19.99	0.0338	6.76	0.1365	25.74	0.1233	23.48	0.0207	3.83
	150 mA	C/3.3	0.0551	10.73	0.0217	4.34	0.0474	8.94	0.0687	13.08	0.0133	2.46

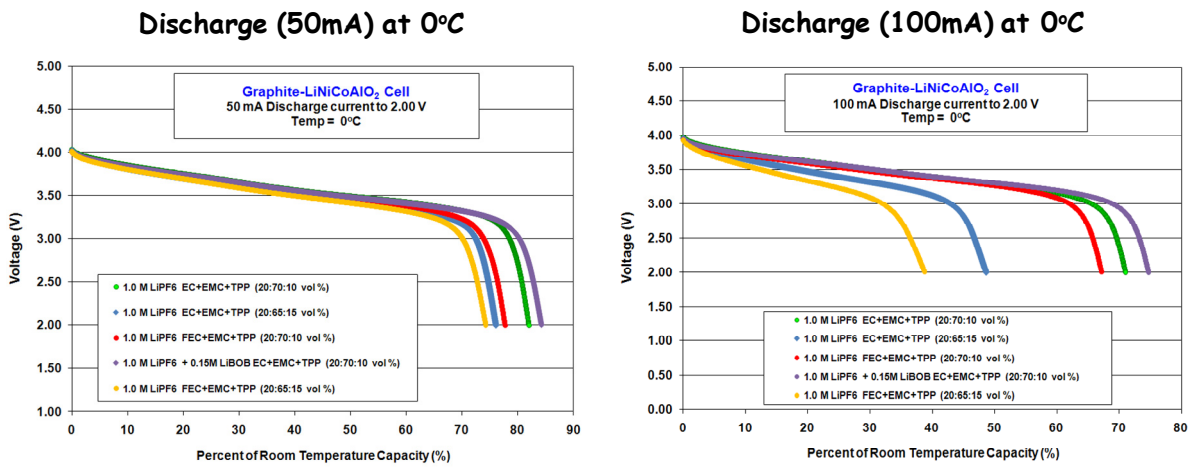

Figure 5. Discharge rate capability of MPG-111/$LiNiCoAlO_2$ cells at 0 °C containing various FRA-containing electrolytes. Cells charged at room temperature prior to discharge.

Performance in Lithium/ $Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ Cells.

A number of the formulations were investigated in $Li/Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ cells to determine their compatibility with high voltage, high capacity cathode materials. These types of materials are actively being developed for Li-ion systems that deliver high specific energy, owing to the high specific capacity of the materials (200-250 mAh/g) and high operating voltage, and are being pursued by NASA and DoE for automotive applications (i.e., plug-in hybrid electric vehicles, or PHEVs). $Li\text{-}Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ cells, containing an all-carbonate-based electrolyte that does not contain any flame retardant additives, delivered an average of 234 mAh/g in reversible capacity when cycled to 4.80V vs. Li+/Li using C/20 charge and discharge rates. When triphenyl phosphate (TPP) was incorporated into the electrolyte formulation, very little loss in reversible capacity was observed, with the cells displaying an average of 228 and 221 mAh/g with 5% TPP and 10% TPP, respectively. Slightly lower reversible capacity was observed upon incorporation of 10% TPP and 20% BTFEC (i.e., 216 mAh/g). Whereas, the use of triphenyl phosphite (TPPi), which delivered desirable performance in the MCMB-$LiNiCoO_2$ system, was accompanied by a sharp decline in the performance, resulting in much lower reversible capacity and an increase in irreversible capacity.

After completing the formation cycling of the cells, discharge rate characterization was performed at a number of rates (C/20, C/10, C/5 and C/2) and at different temperatures (20, 0, -10, and -20 °C). When cells containing electrolyte with TPP were evaluated, decreased performance was also observed, being more dramatic with increasing TPP concentration. For example, when cells containing 1.0 M LPF_6 in EC+EMC+TPP (20:65:15 v/v %) and 1.0 M $LiPF_6$ in FEC+EC+EMC+TPP (20:20:45:15 v/v %) decreased capacity and rate capability was obtained, as illustrated in Table 9. In general, the incorporation of FEC did not appear to improve the performance, nor was it observed to be especially detrimental. Although the use of vinylene carbonate has been observed to have a beneficial effect upon the cathode kinetics in some lower voltage systems, its incorporation appeared to have a detrimental effect with the high voltage system. When the discharge capacity was assessed at 0 °C with a C/10 rate, as illustrated in Fig. 6, the cells containing the DMMP+LiBOB electrolyte delivered the best performance of the solutions evaluated, far exceeding that of the TPP-containing

electrolyte. However, as elaborated upon below, this electrolyte performed very poorly when coupled with carbonaceous anodes.

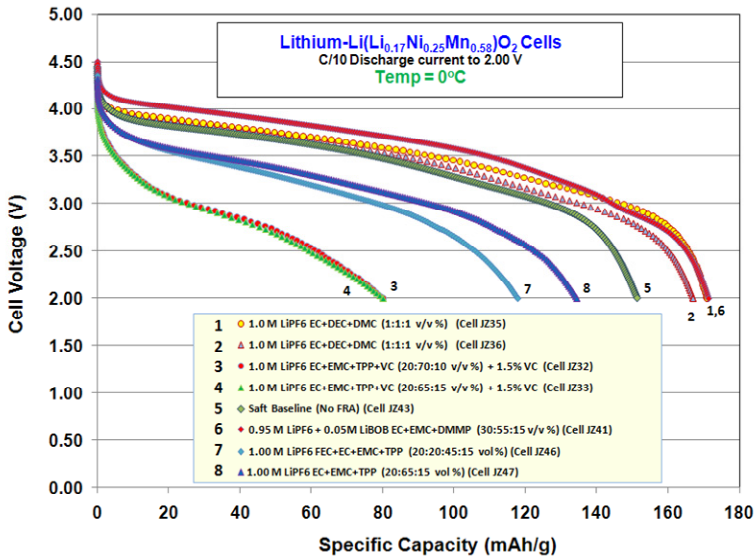

Figure 6. Discharge performance of Li/Li($Li_{0.17}Ni_{0.25}Mn_{0.58}$)$O_2$ Cells at 0 °C using a C/10 discharge rate to 2.0 V. Cells were charged at room temperature prior to discharge.

Performance in Graphite/$LiNiMnCoO_2$ (NMC) Cells.

To continue the study in the context of a potential high energy cell design, cells were fabricated using the Saft MPG-111 graphite anode material and a Toda high voltage $LiNiMnCoO_2$ cathode material. Initial results were very discouraging; in that many of the promising electrolytes identified using the different test vehicles previously discussed yielded very poor performance, as shown in Fig. 7. Although the Yardney/URI DMMP-based electrolyte displayed the best performance in the Li/Li($Li_{0.17}Ni_{0.25}Mn_{0.58}$)$O_2$ cells, it delivered poor performance with a 40% decrease in reversible capacity after 5 cycles. Since the performance of the previously developed FRA-containing electrolytes was unacceptably poor compared to the baseline formulation, additional (TPP-based) electrolytes which contained LiBOB as an additive were investigated. Dramatically better performance was observed, outperforming the TPP-based electrolytes that did not contain the LiBOB as well as the Yardney electrolyte. During the course of these studies, greater stability in the performance was observed when cycling to only 4.60V, and little benefit with respect to delivered capacity was observed with cycling to 4.80 V. Given that the TPP solutions perform well with the MPG-111/$LiNiCoAlO_2$ system, it is likely that the LiBOB has a beneficial effect upon the interfacial properties of the cathodes which prevents degradation of the flame retardant additive at high voltage. However, more research is needed to clearly ascertain the mechanism by which the LiBOB imparts beneficial properties (i.e., studies in three-electrode cells complemented by electrochemical characterization). As shown in Fig. 7, cells containing electrolytes with 10% TPP performed very comparably to the baseline solution, delivering ~ 230 mAh/g. Some trends emerged during the testing, including: (i) at moderate rates, all of the cells containing TPP+LiBOB displayed comparable performance with the baseline formulation, (ii) increasing LiBOB concentration appears to improve the higher rate capability, and (iii) the incorporation of VC into the electrolyte appears to have a slightly negative effect upon the performance. These results support the identification of 1.0 M $LiPF_6$ in

EC+EMC+TPP (20:70:10 vol %) + 0.15M LiBOB as an attractive electrolyte formulation with improved safety for high specific energy, high voltage systems.

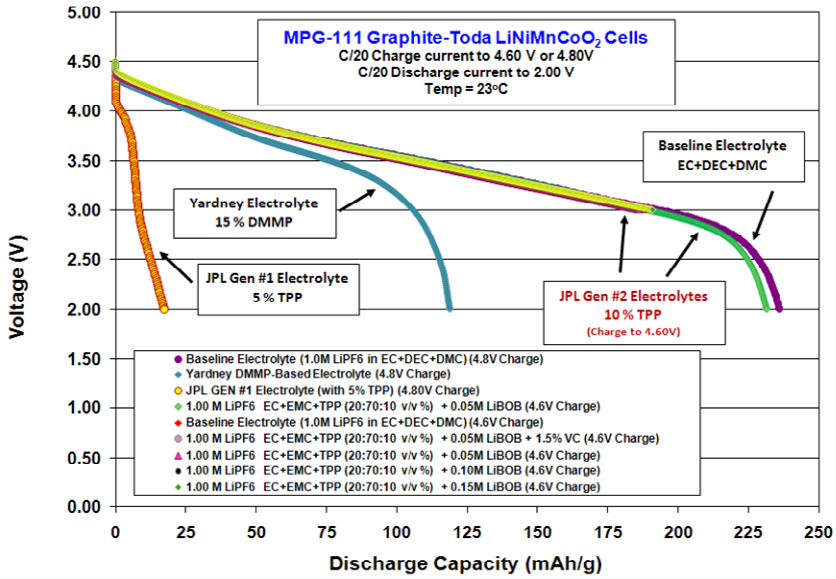

Figure 7. Discharge capacity (mAh/g) delivered on the 5th formation cycle of MPG-111/Toda ($LiNiMnCoO_2$) coin cells containing electrolytes with flame-retardant additives. Cells were charged using a C/20 rate to either 4.60 V or 4.80 V (with a C/100 taper current cut-off) and discharged to 2.0 V using a C/20 rate.

Summary and Conclusions

A number of triphenyl phosphate (TPP)-containing electrolytes were evaluated in both coin cells and experimental three electrode lithium-ion cells (containing reference electrodes). These electrolytes were evaluated with a number of electrode chemistries, including MCMB carbon/$LiNi_{0.8}Co_{0.2}O_2$ (NCO), graphite/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), Li/$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$, Li/$LiNiMnCoO_2$ (NMC) and graphite/$LiNiMnCoO_2$ (NMC), to study the effect that different electrolyte compositions have upon performance. In general, a wide range of TPP-containing electrolyte were demonstrated to be compatible with the commonly used low voltage NCO and NCA-based systems, including formulations that contain up to 15% FRA content and with the incorporation of fluorinated solvents. However, many of these formulations performed very poorly when investigated in the graphite/$LiNiMnCoO_2$ (NMC) system. Although the DMMP/LiBOB-based electrolyte solution was observed to perform well in the Li/$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ system, similarly poor performance was obtained with the graphite/$LiNiMnCoO_2$ (NMC) system. These results necessitated further development of TPP-containing electrolytes that incorporate stabilizing additives, which led to the identification of a number of formulations containing LiBOB that displayed substantially improved performance. Based upon results obtained in graphite/$LiNiMnCoO_2$ cells, as well as the lower voltage systems, 1.0 M $LiPF_6$ in EC+EMC+TPP (20:70:10 vol %) + 0.15M LiBOB was identified as an attractive electrolyte formulation with improved safety for high specific energy, high voltage systems

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