Low temperature electrolytes for lithium/silver vanadium oxide cells

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Abstract

Combinations of methyl formate (MF) and propylene carbonate (PC) using salt concentrations of 0 6 to 2 4 M, with lithium hexafluoroarsenate and lithium tetrafluoroborate in a five to one molar ratio, were investigated as electrolytes in lithium/silver vanadium oxide batteries The composition of the electrolyte affected cell performance at low temperature, self-discharge and abuse resistance as characterized by short circuit and crush testing The electrolyte that provided the best combination of good low temperature performance, low cell self-discharge and abuse resistance was 0 6 M salt in 10 90 PC/MF

Introduction

Lithium metal is an attractive anode material due to its high standard electrochemical potential and low equivalent weight. Lithium has been used with a number of cathode materials to provide batteries of high energy density Cathode materials used in lithium batteries fall into three major categories: solid, liquid and soluble. The choice of cathode material depends on the specific voltage and power requirements of an application. A solid cathode material that has been developed for use in implantable medical cells is silver vanadium oxide (SVO) [1–5]. Lithium/silver vanadium oxide cells have demonstrated high volumetric energy density, low self-discharge, high rate capability under pulse, and state of charge indication [6–8] Recently, this cathode material has also been developed for non-medical applications and has been recommended for use in emergency locator transmitters [9, 10]

Another cell component that can dramatically influence cell performance is the electrolyte. The electrolyte can limit the rate capability of a cell as well as the temperature range of operation Some applications demand rather challenging cell performance such as high rate discharge at low temperature It has been shown by several researchers that electrolytes consisting of mixed solvents offer beneficial performance [11–14] This is frequently a result of combining one solvent with high dielectric constant but high viscosity, such as ethylene carbonate or propylene carbonate, with a solvent of low viscosity such as dimethoxyethane or 2-methyltetrahydrofuran Even these mixtures

do not always provide the necessary cell performance at temperatures as low as − 40 °C High conductivity and low viscosity over a wide temperature range make methyl formate an attractive solvent for use in low temperature applications [15] Lithium hexafluoroarsenate in methyl formate forms one of the most conductive organic electrolyte systems known [16] However, this electrolyte does not provide sufficient stability for long life cells The cause of the instability was investigated and the problem was solved by the addition of lithium tetrafluoroborate and lithium metal [16–18] The use of this mixed salt system in methyl formate has been reported to provide adequate cell performance at low temperature in reserve cells [19] This paper reports the investigation and development of a mixed solvent electrolyte, utilizing the mixed salt of lithium hexafluoroarsenate and lithium tetrafluoroborate, for use with lithium cells suitable for high rate discharge at low temperature The electrolytes investigated consist of mixtures of methyl formate with propylene carbonate The total salt concentration was varied, but the molar ratio of five to one lithium hexafluoroarsenate to lithium tetrafluoroborate was not modified in order to maintain the stability of the electrolyte The solvent combination allows the conductivity and thus the rate capability of a cell to be adjusted by modification of the solvent ratios or the salt concentration of the electrolytes This allows design freedom in that the electrolyte can be tailored to meet specific cell performance requirements to provide the best combination of cell performance and cell safety

Experimental

Materials

   Materials used for electrolyte preparation
   Propylene carbonate (PC) was purchased from Burdick and Jackson, stored over 4A molecular sieves and passed through a column of dry alumina in an inert atmosphere glove box Anhydrous methyl formate (MF) 99 + % packaged under nitrogen, was purchased from Aldrich Chemical Company and used as received Lithium tetrafluoroborate was purchased from Morita Chemical Company and dried in a vacuum oven at 70 °C for 16 h Electrochemical grade lithium hexafluoroarsenate was purchased from the Lithium Corporation of America and used as received

   Materials used for cell construction
   Lithium was obtained from Foote Mineral Company and was 99 8% pure The separator used in test cells (I) and prismatic cells (II) was a polypropylene laminate, Celgard 4560, from the Celgard division of Hoechst-Celanese and was 42 to 45% porous Silver vanadium oxide was prepared by thermal treatment of silver nitrate (Metz Metallurgical Corp) and vanadium pentoxide (Shieldalloy Corp) according to a previously reported procedure [20] Cathodes were prepared from a mix consisting of 94% silver vanadium oxide

(prepared in-house, see ref 6 for procedure), 2% Ketjenblack carbon (Akzo Chemical), 1% graphite (Fisher Scientific) and 3% Teflon 7A (Dupont Co) The average particle sizes of the materials used in preparation of the cathodes were 100 mμ for SVO, 0 03 mμ for carbon, 44 mμ for graphite and 35 mμ for Teflon 7A

Cell construction

Test cells (I) were used for rate capability studies Single cathode plates of 10 40 cm^2 surface area were constructed by compressing cathode mix onto a titanium mesh current collector. Each cathode contained 0 86 g of mix and was pressed at 2000 psi The final cathode thickness was 0 05 cm including the current collector which was 50% open and had a thickness of 0 01 cm The resultant cathodes had porosities of 20 to 22% The cathode was surrounded by a layer of polypropylene separator material A single anode strip, formed by pressing lithium onto both sides of a nickel screen, was folded around both sides of the cathode This electrode assembly was placed into a stainless steel can which was equipped with spacers to keep the electrode assembly snug The can was fitted with a lid containing a glass to metal seal and a fill hole After welding, the can was vacuum filled with electrolyte The test cells were electrolyte flooded and had electrolyte to cathode weight ratios of 9.2. Test cells were immersed in constant temperature baths to maintain the desired test temperature

Prismatic cells (II) of 90 cm^2 total cathode surface area were used for safety, microcalorimetry and performance testing Cathode construction was as described above except that the surface area of six cathodes was 12.0 cm^2, and 9 26 cm^2 for two cathodes The cathodes and anodes were surrounded by a layer of separator prior to assembly of the cell stack The eight cathodes were connected in parallel and a long anode strip was folded in between the cathode plates to form the cell stack. The cell stacks were inserted into cases made of 304L stainless steel and were fitted with lids containing glass to metal seals As a final step the cells were vacuum filled with electrolyte. The electrolyte to cathode weight ratio in these cells was 0 56. The external dimensions of the cells were $2.07 \times 1.35 \times 5.19$ cm.

Methods

All electrolyte preparation was conducted in an inert atmosphere glove box Solutions were prepared with solvent ratios of 10, 20, 40 and 50% by volume PC to 90, 80, 60 and 50% MF Electrolytes were prepared with salt concentrations of 2 4, 1 2 and 0 6 M with lithium hexafluoroarsenate and lithium tetrafluoroborate used in a five to one molar ratio

Conductivity measurements were performed using dip-type conductivity cells that had been standardized using potassium chloride solutions For the measurements, a conductivity cell was sealed to a test tube containing the electrolyte sample and the assembly was removed from the inert atmosphere box Conductivity readings were made using a YSI model 332 conductance meter at -40, -20, 0 and 20 °C. Temperature was maintained by a circulating constant temperature bath and was recorded to 0 1 °C

Low temperature rate capability of Li/SVO cells was determined by pulse discharging test cells at -40 °C in a circulating cold temperature bath The pulse regime comprised pulse trains with 30 s of rest after the application of each train The pulse trains consisted of four 10 s pulses with a 15 s rest after each pulse Pulse currents of 100, 50 and 10 mA were applied corresponding to current densities of 10, 5 and 1 mA/cm^2 The pulses were applied by a Kikisui constant current power source interfaced with a timer The data were recorded by a three-pen chart recorder

Solubility of SVO in the electrolytes under investigation was determined by combining samples of SVO cathode material and electrolyte solutions in vacuum sealed ampules After storage at 37 °C for 80 days, the ampules were opened and the contents were twice filtered through 0 2 μm PTFE syringe filters Silver and vanadium concentrations were determined in the electrolyte samples using a Perkin-Elmer model 3030 atomic absorption spectrophotometer

Storage characteristics of Li/SVO cells containing the electrolytes under investigation were determined by microcalorimetry and discharge testing of prismatic cells (II) The cells were first pre-discharged under constant resistance loads (2 49 kohms) to remove approximately 1% of the cells' theoretical discharge capacities After stabilization for a minimum of one week, heat dissipation of these cells at open circuit voltage was measured at 25 °C using a Tronac model 351RA microcalorimeter Fresh cells and cells stored for 390 days at room temperature were discharged by applying 900 mA pulse trains (current density of 10 mA/cm^2) every 30 s The pulse trains consisted of four 10 s pulses with 15 s of rest between each pulse After the cells fell below 1 0 V under pulse, discharge was continued under 500 ohm loads until the cell voltage reached 1 5 V The discharge testing was performed at room temperature

Safety characteristics of prismatic cells (II) were determined by short circuit and crush testing Cells subjected to short circuit testing were externally short circuited with a circuit resistance of less than 10 mohms, through four-gage cables, for a minimum of 4 h External case temperature, voltage and current were monitored throughout the test Cells subjected to crush testing were crushed using an Enerpac press with a 1/2" diameter phenolic ram until an internal short circuit was created as determined by a sharp drop in the open circuit voltage of the cell External case temperature and cell voltage were monitored throughout the test

Results and discussion

The conductivity of electrolyte solutions as a function of temperature between -40 and 40 °C is shown in Figs 1–4. The relationship of conductivity and temperature over the range investigated is linear The lines fitted to the data have linear correlation coefficients ranging from 0 986 to 1 00
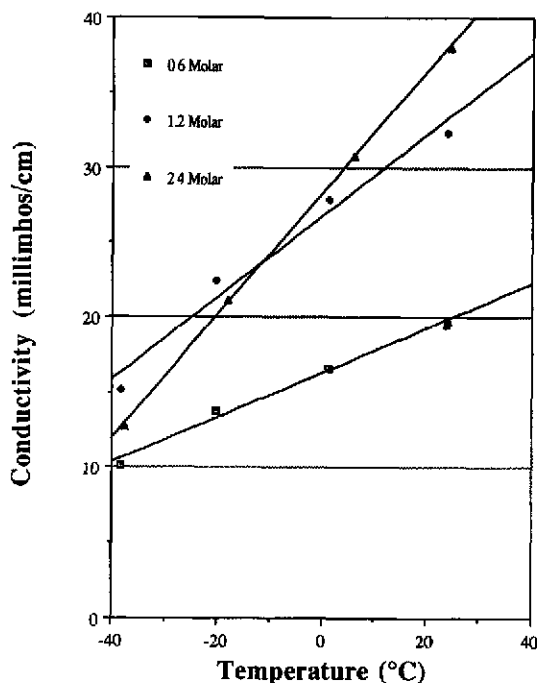
Fig 1 Conductivity as a function of temperature of 2 4, 1 2 and 0 6 M solutions of a five to one molar ratio of lithium hexafluoroarsenate and lithium tetrafluoroborate in 10 90 PC/MF by volume

Conductivities of the solutions at −40 0 °C are presented in Fig. 5. For the solutions with 90 and 80% MF content, the electrolytes with 1 2 M salt had the highest conductivity The electrolytes with higher PC content no longer showed maximum conductivity with the 1.2 M salt solution At 40% PC the 1 2 and 0.6 M solutions were about equal in conductivity whereas when the PC content was 50% the 0 6 M salt solution had the highest conductivity In all cases, the 2 4 M salt containing solutions had lower conductivity than the equivalent solutions with lower salt content

Conductivity depends on both viscosity and dielectric properties. Methyl formate has a viscosity of 0 328 cP at 25 °C whereas PC has a viscosity of 2.54 cP The dielectric constant of MF is 8 5 and that of PC is 64.4 If the low temperature conductivity was dominated by the dielectric constant then it would be expected that the conductivity should increase with increasing PC content This is not the case; the conductivity increases with MF content. This is in agreement with previous reports which state that the conductivity of electrolyte solutions with large anions such as hexafluoroarsenate are more influenced by viscosity than the dielectric properties of the solvent [21, 22] Therefore, in agreement with previous reports, the solutions with higher MF content show higher low temperature conductivity. Increased salt content also led to lower conductivity particularly at high PC content Solution
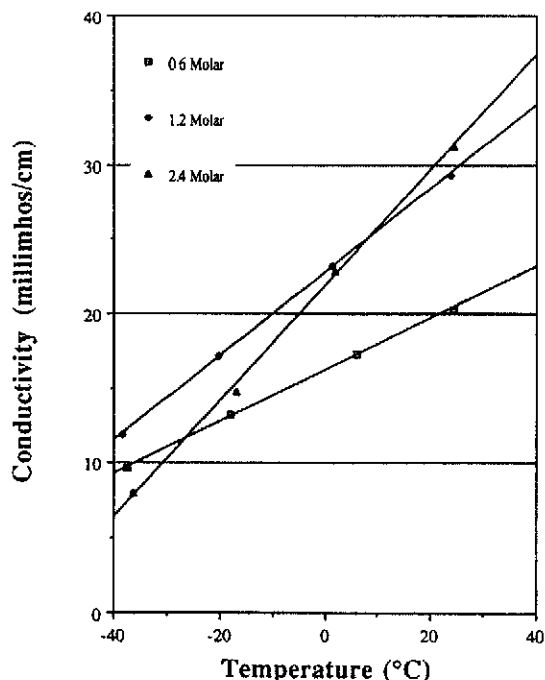
Fig 2 Conductivity as a function of temperature of 2 4, 1 2 and 0 6 M solutions of a five to one molar ratio of lithium hexafluoroarsenate and lithium tetrafluoroborate in 20 80 PC/MF by volume

viscosity is increased by higher salt concentration and it is this viscosity increase which is thought to lead to the decrease in conductivity Of the electrolytes tested, the four electrolyte solutions with the highest conductivities at −40 °C are 0 6, 1 2 and 2 4 M salt in 10 90 PC/MF and 1 2 M salt in 20 80 PC/MF These four electrolytes were studied further to determine their effect on cell performance

To determine the rate capability of Li/SVO cells at −40 °C, six test cells (I) were prepared with each of the four electrolytes with the highest −40 °C conductivity yielding a total of 24 cells for testing The cells were discharged at −40 °C using the pulse discharge mode with peak current densities of 10, 5 and 1 mA/cm² Two cells from each electrolyte group were tested under each current density and the average capacities delivered by these cells are presented in Table 1

At 1 and 5 mA/cm² peak current densities, the test cells (I) with the 1 2 M salt in 20 80 PC/MF delivered the highest capacity At 10 mA/cm² the cells with 1 2 M salt in 10·90 PC/MF delivered the highest capacity. The electrolyte with the highest conductivity at −40 °C is 1 2 M salt in 10 90 PC/MF This electrolyte in two out of three cases did not lead to the highest delivered capacity under pulse test at −40 °C The electrolyte with the lowest conductivity at −40 °C is 0 6 M salt in 10 90 PC/MF This electrolyte did
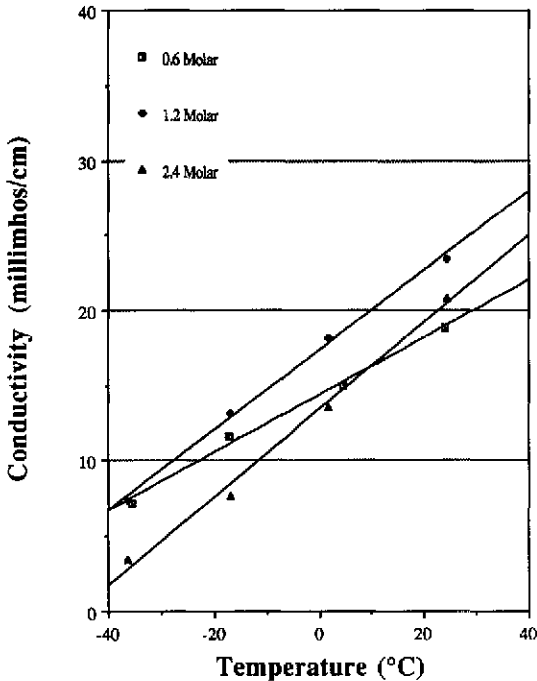
Fig 3 Conductivity as a function of temperature of 2 4, 1 2 and 0 6 M solutions of a five to one molar ratio of lithium hexafluoroarsenate and lithium tetrafluoroborate in 40 60 PC/MF by volume

not lead to the lowest delivered capacity in any of the three test conditions In general, there is not a direct correlation of electrolyte conductivity and cell performance This testing illustrates the complex relationship between electrolyte characteristics and cell performance and the need to conduct cell performance testing for electrolyte evaluation

A key characteristic along with cell performance is cell self-discharge In order to minimize self-discharge in a solid cathode cell, the cathode must be minimally soluble in the electrolyte. The solubility of SVO in PC/MF electrolyte solutions was determined by combining SVO cathode material with electrolyte in sealed ampules After 80 days storage at 37 °C, the concentrations of silver and vanadium in the electrolyte solutions were determined. The solubility data are presented in Table 2 The solubility of silver and vanadium increased with increased MF content in the electrolyte as the electrolyte with 10·90 PC/MF had more dissolved silver and vanadium than did the electrolyte with 50 50 PC/MF This predicts that the self-discharge rate of cells with higher MF content might be greater than that of cells with lower MF content due to the higher cathode solubility

Another method to determine cell self-discharge is to measure cell heat dissipation by microcalorimetry Two prismatic cells (II) from each electrolyte group were constructed and their heat dissipation was monitored at 25 °C
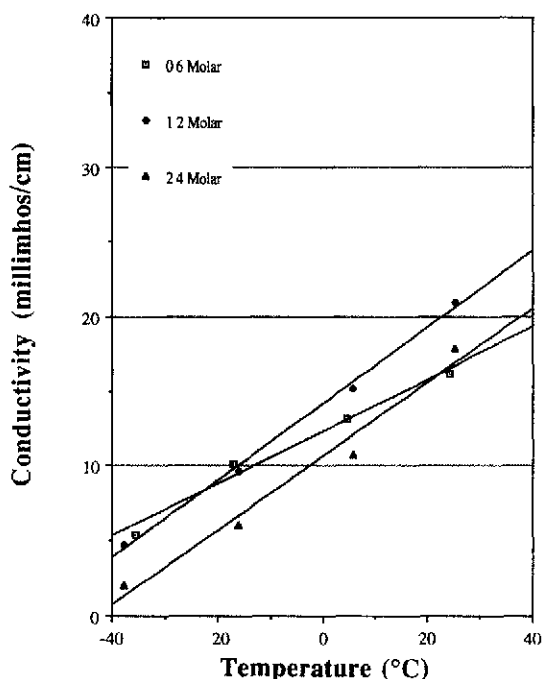
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Fig 4 Conductivity as a function of temperature of 2 4, 1 2 and 0 6 M solutions of a five to one molar ratio of lithium hexafluoroarsenate and lithium tetrafluoroborate in 50 50 PC/ MF by volume

while on open circuit voltage For the cells on open circuit voltage, it can be assumed that all heat dissipated was due to self-discharge Dissipated heat, measured in watts, can be translated into self-discharge via the relationship $I = W/V$ where I is current, W is watts and V is voltage Table 3 shows the average heat dissipation measured for cells on storage for 390 days at 25 °C The capacity lost per year was calculated based on the average heat dissipation values The percent of total input capacity lost per year of storage for each cell group is also shown in Table 3 The cells with the higher salt content exhibit higher self-discharge as can be seen by comparing the three groups of cells with 10 90 PC/MF solvent. The annual predicted self-discharge is 3 10, 1 45 and 0 98% for the 2 4, 1 2 and 0 6 M salt concentrations By comparing the 1 2 M 10 90 PC/MF and the 20 80 PC/ MF containing cells it can be seen that there is no substantial difference in the heat dissipation of these cells

Heat dissipation in cells can be due to a variety of chemical reactions where not all of them lead to loss in cell capacity If the heat dissipation is due to the reaction of electrolyte with the lithium anode, then although there is some loss of anode capacity, this may not manifest itself as reduced cell capacity in a cathode limited cell until there is enough loss in anode capacity to become anode limited To further define the capacity retention
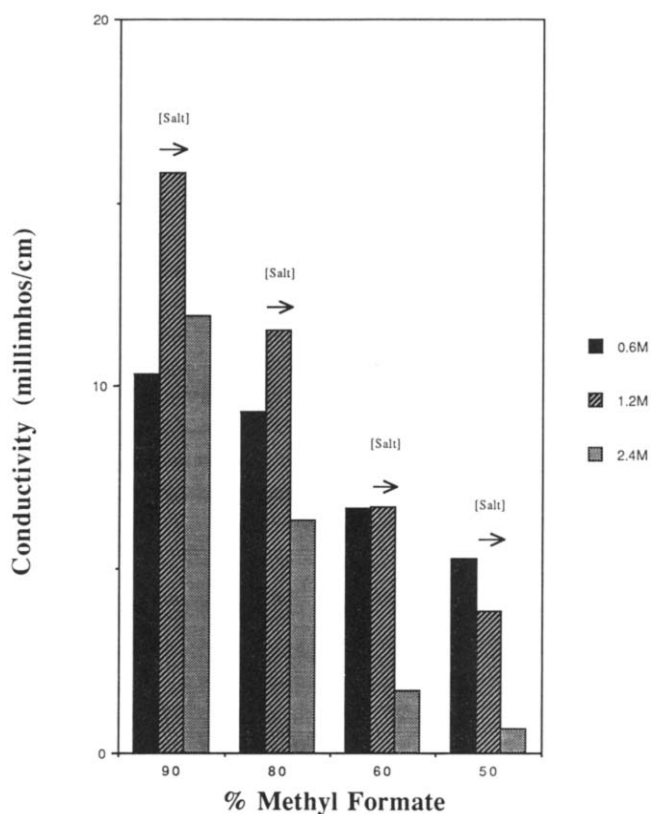
Fig 5 Conductivity at −40 °C as a function of methyl formate concentration in 2 4, 1 2 and 0 6 M PC/MF electrolyte solutions

TABLE 1

Delivered capacity and percent cathode utilization of test cells discharged at −40 °C

Electrolyte salt (PC/MF)	Conductivity[a] (millimhos/cm)	Delivered capacity (mA h) (% utilization) at discharge rate		
		10 mA (1 mA/cm²)[b]	50 mA (5 mA/cm²)[b]	100 mA (10 mA/cm²)[c]
2 4 M (10 90)	11 92	67 8 (29)	11 1 (4 7)	11 1 (4 7)
1 2 M (10 90)	15 80	71 7 (30)	23 6 (10)	31 4 (13)
0 6 M (10 90)	10 33	83 2 (35)	29 9 (13)	27 0 (11)
1 2 M (20 80)	11 51	109 (46)	40 3 (17)	15 9 (6 8)

[a]Conductivity at −40 °C
[b]Capacity reported to 2 0 V limit
[c]Capacity reported to 1 5 V limit, cell voltages did not reach 2 0 V

TABLE 2

Solubility of silver vanadium oxide in MF/PC electrolytes

Electrolyte salt (PC/MF ratio)	Vanadium (ppm)	Silver (ppm)
1 2 M (10 90)	27 4	681
1 2 M (50 50)	0 6	46

TABLE 3

Estimated self-discharge of Li/SVO cells with PC/MF electrolytes based on heat dissipation measurements

Electrolyte salt (PC/MF ratio)	Average μW during 372 days storage at 25 °C	Estimated capacity lost per year (A h)	Average capacity lost per year (%)
2 4 M (10 90)	37	0 10	3 10
1 2 M (10 90)	18	0 047	1 45
0 6 M (10 90)	12	0 032	0 98
1 2 M (20 80)	13	0 035	1 09

TABLE 4

Discharge capacities of fresh and aged cells

Electrolyte	Capacity delivered (A h)		Observed capacity loss (A h)	Predicted self-discharge (A h)
	Fresh cells	Aged cells (390 days)		
2 4 M (10 90)	3 42	3 41	0 01	0 107
1 2 M (10 90)	3 30	3 31	0	0 050
0 6 M (10 90)	3 23	3 27	0	0 034
1 2 M (20 80)	3 30	3 20	0 10	0 037

of cells built with MF/PC electrolytes, cells built with each group of electrolyte were stored for 390 days at room temperature These cells were discharged and the discharge performance was compared to that of fresh cells as shown in Table 4 For the cells with 0 6, 1 2 and 2 4 M salt and 90 10 MF PC electrolyte, there is no significant change in delivered capacity The cells with the 80 20 MF PC electrolyte showed a loss in capacity of about 0 1 A h The sample size for this experiment consisted of two cells from each group both fresh and stored Additional cells should be tested to gain statistical information on the distribution of delivered capacities in order to determine whether the apparent loss in capacity is due to self-discharge or variation in cell construction The cells with 1 2 M salt in both the 90 10 and 80 20 MF PC did display a loss in rate capability after storage as they had substantially

lower pulse voltages than did the other two groups of stored or fresh cells. This may be a result of anode passivation due to electrolyte decomposition at the lithium surface

Differences in cell performance and cell self-discharge were manifested by using different ratios of salt and solvents in the electrolyte. It was desired to determine the impact of these electrolyte variables on cell safety and abuse resistance. Prismatic cells (II) containing each of the four electrolytes were prepared for safety testing From each electrolyte group, two cells were short circuit tested and two were crushed The average results of the short circuit testing are presented in Table 5 The peak current of the cells containing 2.4 M salt in 10:90 PC/MF electrolyte was the highest at 21 A. The conductivity of this electrolyte is also the highest. The lowest peak current was seen with the 1.2 M salt in 20.80 PC/MF which does not have the lowest conductivity There is not a direct correlation of electrolyte conductivity and peak short circuit current. The highest peak temperature was recorded for the cells with 2 4 M salt in 10:90 PC/MF electrolyte although the temperature was not very different from cells with 1.2 M salt in either 10:90 or 20:80 PC/MF The cells with 0.6 M salt 10:90 PC/MF electrolyte had peak temperatures about 40 °C lower than the other cells tested. In addition, the time to peak temperature for the cells containing this electrolyte was about twice that for the other cells In order to examine the time and temperature characteristics further, the short circuit current versus time was plotted Figure 6 shows the data from one cell of each electrolyte group. The steady-state current during the first 200 s was highest for the cell with 2 4 M salt 10 90 PC/MF These cells also showed the fastest rise in temperature. Both cells with 1.2 M salt showed about the same current levels during the first 200 s and had about the same rate of temperature rise. The cell with 0.6 M salt showed lower current levels for about 550 s, but maintained a higher current longer. It took much longer to achieve the peak temperature of this cell The current profiles correlate closely with the peak temperatures, the rate of temperature rise and roughly with electrolyte conductivity.

The results of the crush testing are presented in Table 6 Cell peak temperatures as a result of internal short circuits generated by crushing the

TABLE 5

Results of short circuit testing performed on Li/SVO test cells containing different PC/MF electrolytes

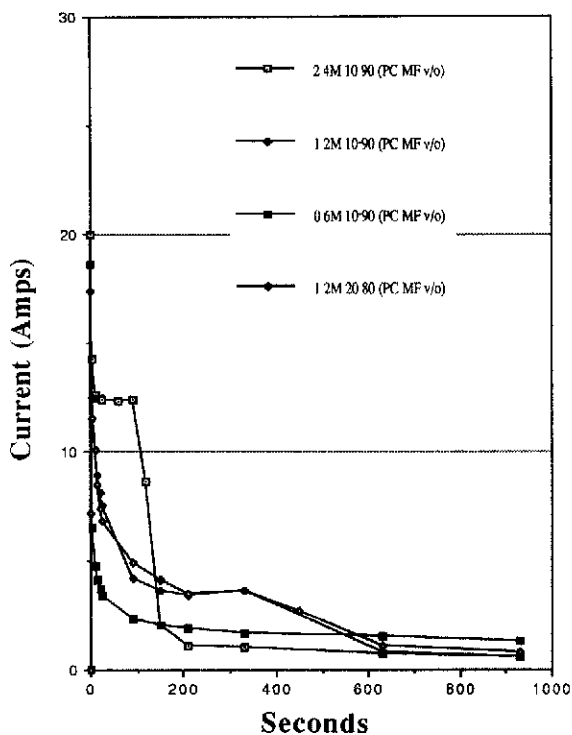| Electrolyte salt (PC/MF)	Conductivity[a] (millimhos/cm)	Peak current (A)	Peak temperature (°C)	Time to peak temperature (s)
2 4 M (10 90)	38 41	21 21	131 75	243
1 2 M (10 90)	33 49	17 50	128 50	479
0 6 M (10 90)	19 97	17 60	86 00	1083
1 2 M (20 80)	29 76	12 65	127 75	543

[a]Conductivity at 25 °C

Fig 6 Short circuit current vs time of full Li/SVO cells containing various PC/MF electrolytes as they were externally short circuited

TABLE 6

Results of crush testing performed on Li/SVO test cells containing different PC/MF electrolytes

Electrolyte salt (PC/MF)	Peak temperature (°C)
2 4 M (10 90)	117 5
1 2 M (10 90)	104 0
0 6 M (10 90)	46
1 2 M (20 80)	114

cells showed a similar trend to that seen in the external short circuit The cells with the highest peak temperature were those with 2 4 M salts in 10 90 PC/MF The next highest were the cells with the 1 2 M salt in 10·90 and 20 80 PC/MF electrolyte The cells that contained the 0 6 M salt in 10:90 PC/MF showed a much lower peak temperature Presumably the internal current that the cells can maintain during an internal short has the same rank order as that seen with the cells under external short

Conclusions

Combinations of methyl formate and propylene carbonate using salt concentrations of 0.6 to 2.4 M with lithium hexafluoroarsenate and lithium tetrafluoroborate in a five to one molar ratio were investigated as electrolytes in lithium/silver vanadium oxide batteries The composition of the electrolyte affected cell performance at low temperature, self-discharge and abuse resistance as characterized by short circuit and crush testing The electrolyte that provided the best combination of good low temperature performance, low cell self-discharge and abuse resistance was 0.6 M salt in 10·90 PC/MF

Acknowledgement

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