

# A comparative study on the effect of electrolyte/additives on the performance of ICP383562 Li-ion polymer (soft-pack) cells

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## Abstract

Two electrolyte additives (i.e. vinylene carbonate and organic borates), previously reported by several researchers to show enhanced performance in laboratory-scale Li-ion cells, have been studied in our commercial ICP383562 Li-ion polymer (soft-pack) cells. The objective is to examine how these performance enhancements translate to a commercial product. The performance characteristics analysed in the comparative testing include rate capability, temperature performance, cycle life and abuse (overcharge) resistance. Results show that both additives demonstrate improved cycle life performance; in addition, organic borates also exhibit enhanced rate capability and low-temperature performance. This study also highlights that the choice of the basic electrolyte composition is essential to achieve a balanced cell performance.

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## 1. Introduction

In recent years a number of additives to the commonly used electrolyte for lithium-ion cells (i.e. organic carbonate mixture +  $\text{LiPF}_6$ ) have been reported to considerably improve capacity retention during cycle life. Low-temperature performance is also reported to be improved by adding even small amounts of suitable additives [1].

Vinylene carbonate (VC) is an example of an electrolyte additive that can considerably improve cycle life performance [2]. It is postulated that VC takes part in the formation of the SEI, creating an interface that is more conducive to long term cycling [3].

Other possible additives are those based on alkylborates. Electrolytes based on innovative Li-salts like Li bis(oxalato)borate have been reported to have very good ionic conductivity and wide electrochemical stability. Moreover, the weak coordinating power of the bis(oxalato)borate anion leads to high conductivity levels in organic carbonate solutions. Salts containing alkyl borate anions have recently been put forward as additives able to enhance long-term cycling behaviour [4]. High cycling efficiency and cycle-ability in  $\text{Li/LiMn}_2\text{O}_4$  and  $\text{Li/LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  cells have been shown for alkyl borate compounds used as additives to lithium battery electrolytes [5].

This paper reports the results of a comparative study designed to test a selection of these new electrolyte additives for lithium-ion cells, which have already shown promising performance on a laboratory scale, in our commercial ICP383562 Li-ion polymer (soft-pack) cells.

Our study compares the rate capability of the cells, their high-temperature and low-temperature performance and their cycle life. In addition, since safety and abuse testing is a vital factor in commercially viable cells; we also compare the overcharge abuse resistance of the ICP383562 cells.

## 2. Experimental

The electrochemical system we used for testing different electrolytes is our standard ICP383562 lithium-ion polymer (soft pack) battery. The cell dimensions and rated capacity are reported in Table 1. The basic chemistry of the system is  $\text{LiCoO}_2/\text{graphite}$ .

The batteries were assembled and activated in our factory in Bazzano, Italy. These operations were performed by means of production-scale equipment.

Five different electrolytes were selected for evaluation (see Table 2 for details). Electrolyte 1 is standard-type electrolyte commonly used in the Li-ion industry; electrolytes 2 and 3 are created by adding vinylene carbonate and organic borate to electrolyte 1. Electrolyte 4 uses the same additive as electrolyte 3, but with a different mixture of

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Table 1  
Cell dimensions and rated capacity

Cell code	Thickness (mm)	Width (mm)	Length (mm)	Mass (g)	Rated capacity (mAh)
ICP383562	3.65 ± 0.05	35.0 ± 0.1	62.0 ± 0.1	15.5 ± 0.1	650

Table 2  
Description of the electrolytes tested

Electrolyte no.	Composition
1	EC:DEC:DMC 1:1:1 (w/w/w), LiPF <sub>6</sub> 1 M
2	EC:DEC:DMC 1:1:1 (w/w/w), LiPF <sub>6</sub> 1 M + VC 1% (w/w)
3	EC:DEC:DMC 1:1:1 (w/w/w), LiPF <sub>6</sub> 1 M + organic borate 0.25% (w/w)
4	EC:DMC 1:1 (w/w/w), LiPF <sub>6</sub> 1 M + organic borate 0.25% (w/w)
5	EC:DEC 1:4 (w/w/w), LiPF <sub>6</sub> 1 M

organic solvents, while electrolyte 5 has no additives and consists of a different mixture and type of organic solvent.

We manufactured and tested 20 samples for each different electrolyte. The quantity of electrolyte (in mass terms) was the same for all samples.

The cells were electrically formed (first charge) and aged according to our standard production procedure and were then tested according to the scheme reported in Table 3.

Cell testing was performed by using BT2000 series Arbin cyclers, while the impedance spectra were obtained using a Voltalab 10 PGZ100 potentiostat–galvanostat–electrochemical impedance analyzer system. Finally, we used a Tenney Junior environmental chamber for the discharge at different temperatures.

### 3. Results and discussion

#### 3.1. Rate capability test

In order to satisfy the demands of high-power applications such as GSM mobile phones, commercial Li-ion cells must deliver good performances at high current drains.

The room temperature (20 ± 5 °C) rate capability of the cells was evaluated via a constant current discharge at different current drains: i.e. 130 (C/5), 325 (C/2), 650 (1C) and 1300 mA (2C). The charge has been performed with a CCCV

Table 3  
Test scheme for cell performance evaluation

Test no.	Test name	Cells tested
1	Rate performance	1–22
2	Temperature performance	1–8
3	Cycle life	9–18
4	Overcharge	19–22

method, at a current of 650 mA, a 4.20 V charging voltage and a total charge time of 3 h, at room temperature. The resultant data are reported in Table 4 and in Fig. 1.

The most significant differences among the five electrolytes emerge during the discharge at the highest rate, 2C. Electrolyte 1–4 show satisfactory rate performances, delivering more than 90% of the rated capacity at a discharge rate of 2C. Among this group, electrolyte 3 is the one that gives the best performance (98% of RC at 2C rate).

The solvent mixture of electrolyte 5, on the other side, does not give satisfactory results in terms of rate capability.

#### 3.2. Temperature performance

Another important feature for commercial cells is their behaviour at extreme temperatures.

The performances of the cells at different temperatures was evaluated via a constant current discharge at a current drain of 650 mA (1C), at both low (0, –10 and –20 °C) and high (55 °C) temperatures. The charge has been performed with a CCCV method, at a current of 650 mA, a 4.20 V charging voltage and a total charge time of 3 h, at room temperature. Before starting the discharge, the cells were stored for 1 h at the temperature of the test. The results obtained are reported in Table 5 and in Fig. 2.

Electrolyte 3 demonstrates quite good low temperature performances, thanks to a good combination of solvent mixture/additive (organic borate). Vinylene carbonate (electrolyte 2), instead, leads to significantly poorer low-temperature performance than organic borate. The solvent mixtures of

Table 4  
Rate capability test results

Discharge capacity (mA)	Electrolyte 1 mAh (% of rated capacity)	Electrolyte 2 mAh (% of rated capacity)	Electrolyte 3 mAh (% of rated capacity)	Electrolyte 4 mAh (% of rated capacity)	Electrolyte 5 mAh (% of rated capacity)
130	671 ± 6 (103%)	662 ± 7 (102%)	671 ± 4 (103%)	667 ± 5 (103%)	620 ± 30 (96%)
325	666 ± 6 (103%)	658 ± 6 (101%)	668 ± 6 (103%)	663 ± 4 (102%)	620 ± 30 (95%)
650	658 ± 6 (101%)	652 ± 7 (100%)	663 ± 3 (102%)	656 ± 5 (101%)	590 ± 20 (91%)
1300	610 ± 20 (94%)	632 ± 9 (97%)	643 ± 6 (99%)	633 ± 12 (97%)	410 ± 60 (64%)

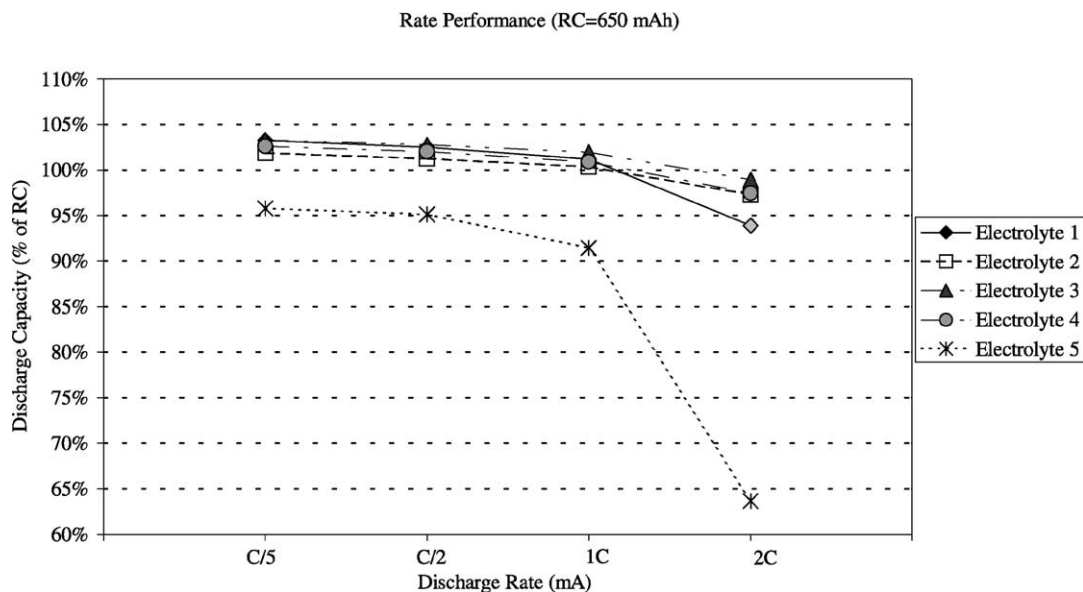


Fig. 1. Rate capability test results.

Table 5  
Temperature test results

Discharge capacity (°C)	Electrolyte 1 mAh (% of rated capacity)	Electrolyte 2 mAh (% of rated capacity)	Electrolyte 3 mAh (% of rated capacity)	Electrolyte 4 mAh (% of rated capacity)	Electrolyte 5 mAh (% of rated capacity)
0	598 ± 2 (92%)	572 ± 4 (88%)	613 ± 6 (94%)	557 ± 12 (86%)	370 ± 20 (57%)
-10	411 ± 7 (63%)	365 ± 9 (56%)	450 ± 20 (69%)	170 ± 30 (25%)	193 ± 14 (30%)
-20	158 ± 12 (24%)	117 ± 11 (19%)	190 ± 40 (29%)	46 ± 4 (7%)	56 ± 3 (9%)
55	668 ± 6 (103%)	673 ± 2 (104%)	678 ± 7 (105%)	680 ± 10 (105%)	619 ± 12 (95%)

electrolyte 4 and 5 are not suitable to low temperatures, the cells delivering an unsatisfactory capacity.

The results of this test confirm that the choice of the solvent mixture has a great impact on low temperature performance.

### 3.3. Cycle life

Cycle life valuation was carried out by repeatedly charging (method as above) and discharging (650 mA constant

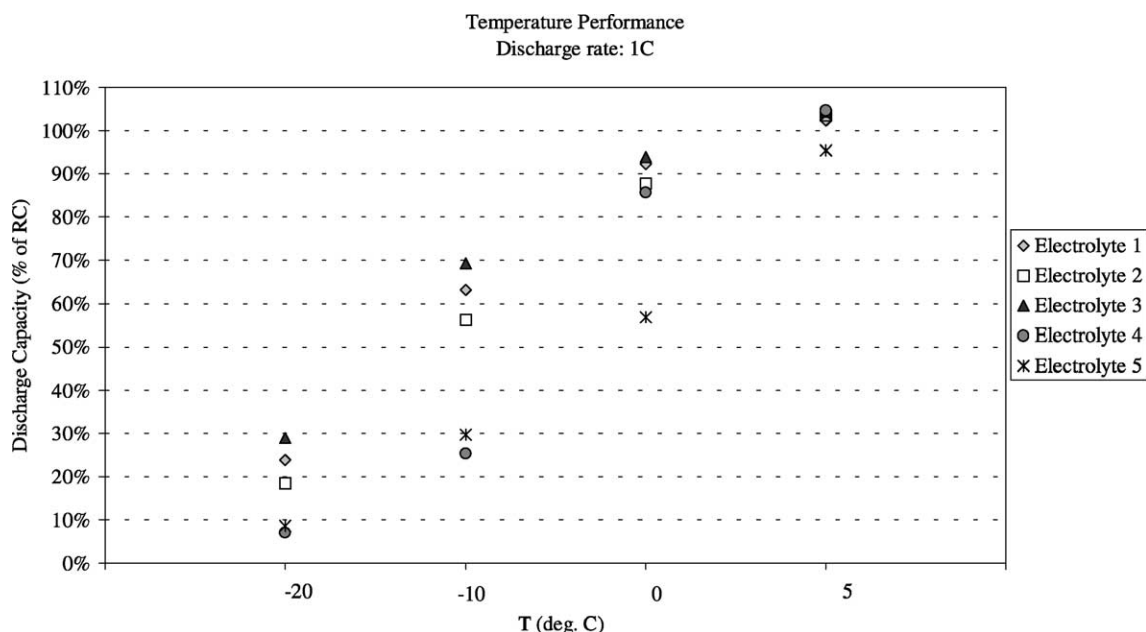


Fig. 2. Temperature test results.

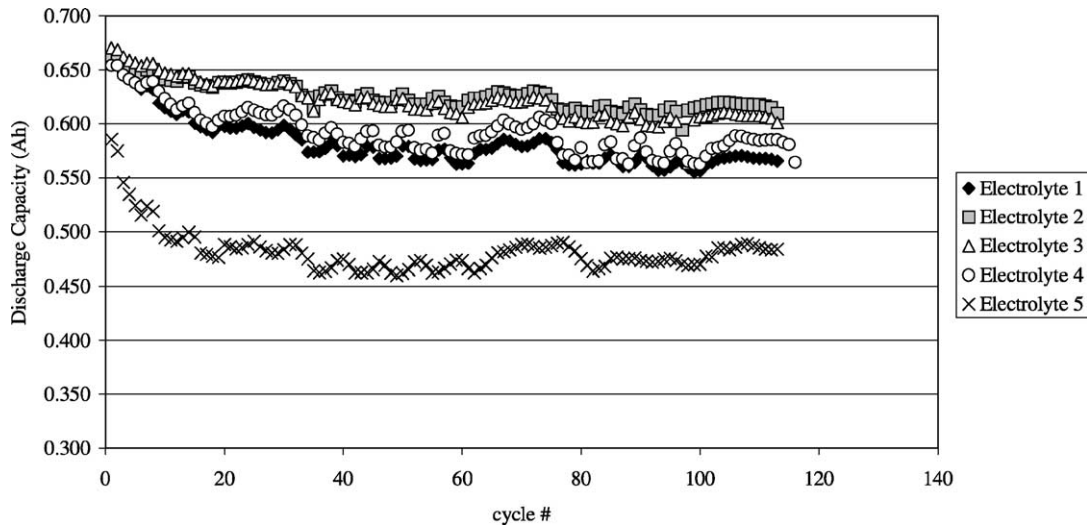


Fig. 3. Average discharge capacity values for each set of cells. Cycling at 1C rate.

current using a end-of-discharge voltage of 2.75 V) the cells. The discharge capacity was recorded for every cycle. The average discharge capacity values for each set of cells are reported in Fig. 3.

Looking at the capacity fade of ICP383562 batteries made with electrolyte 1–3, it is evident that both vinylene carbonate and the organic borate additives are effective in giving improved cycle life performance. Due to its different solvent mixture, electrolyte 4 does not show the same cycling performance of electrolyte 3, even though it also contains the organic borate additive. The right solvent mixture/additive combination is thus essential to achieve a good cycling behaviour.

The poor results showed by the cells made with electrolyte 5 confirm the key-role played by the selection of the solvent mixture in view of a good cycling behaviour.

In addition to the cycling data, impedance measurements were also performed on ICP383562 cells both before and after the long-term cycling (i.e. before the beginning of the test and after 100 cycles). Fig. 4 reports the impedance spectra of both electrolyte 1 and 3, before and after cycling. As expected, the data collected show an increase in the electrolyte resistance during cycling. The greatest contribution to

impedance increase comes from the second semicircle (attributed by recent literature to the growth of surface layer at the cathode [6]). Between the two electrolytes, electrolyte 1 shows a greater impedance increase than electrolyte 3, suggesting that the organic borate additive contributes to the formation on the electrodes surface of a passivation layer that is more stable on cycling.

### 3.4. Overcharge tests

Safety is a basic requirement for commercial Li-ion polymer (soft-pack) cells. They must be able to withstand abuse and other possible conditions that may occur due to a malfunction in for example the charger. A commonly performed abuse test is the overcharge of the cell; this is conceived to simulate a situation where a malfunction of the charger occurs and the battery is subject to a continuous galvanostatic current where the cell voltage is only limited by the power supply capability. The overcharge test is also seen as one of the most difficult tests to pass.

We performed this test by charging the cells with a constant current of 650 mA, with a voltage limit of 10 V, for 4 h. The test is passed if the cell does not explode nor catch fire.

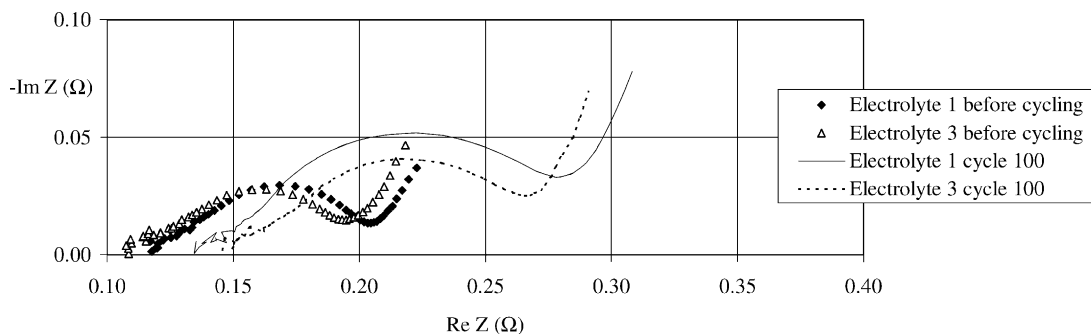


Fig. 4. Impedance spectra of cells with Electrolyte 1 and 3, taken both before cycling and after 100 cycles. Frequency range: 100 kHz–10 mHz. Cell voltage: 3.7 V.

Table 6  
Overcharge test

Electrolyte no.	Result
1	Passed
2	Passed
3	Passed
4	Passed
5	Failed

With respect to the safety of the cell, the electrolyte again plays a key role. All selected electrolytes, with the exception of electrolyte 5, demonstrated to be safe with respect to cell overcharge. Electrolyte 5, instead, led to the explosion of the cells during the test. The results are reported on [Table 6](#).

#### 4. Conclusions

Our study confirms that both vinylene carbonate and organic borates, when used as additives in standard organic electrolytes, lead to improved cycling behaviour in commercial ICP383562 cells. It is worth noting that the choice of

the appropriate solvent mixture is essential to achieve good cycle life performance. Our study also confirms that electrolyte additives can also reduce cell impedances, via higher ionic conductivity and lower resistance SEI layers, leading to increased capabilities under high current drains and a low temperatures.

Finally, we have confirmed that a key safety requirement, resistance to overcharge abuse, is not reduced when electrolyte additives are employed.

#### References

- [1] J.O. Besenhard, P. Castella, in: D. Tchoubar, I. Conard (Eds.), *Intercalation Compounds*, Trans. Tech. Publications, Zürich, 1992, p. 647.
- [2] US Patent 5,626,981.
- [3] O. Matsuoka, A. Hiwara, T. Omi, M. Toriida, T. Hayashi, C. Tanaka, Y. Saito, T. Ishida, H. Tan, S.S. Ono, S. Yamamoto, *J. Power Sources* 4712 (2002) 1–11.
- [4] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 146 (1999) 3655.
- [5] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 149 (3) (2002) A355–A359.
- [6] D. Zhang, B.S. Haran, A. Durairajan, R.E. White, Y. Podrazhansky, B.N. Popov, *J. Power Sources* 91 (2000) 122–129.