

# A Review of Temperature Effects on Varying Li-Ion Cell Chemistries for Electric Vehicle Applications

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## Introduction

The many advantages of modern electric vehicles (EVs) such as high efficiency and zero emissions are currently propelling the rise of EVs in today's transportation market. With a promise of a future in green travel and the introduction of new policies assisting the promotion of the EV market, it is no surprise that the market growth has continued to increase. An essential component of these electrical systems is the energy storage system, the most widely of which is adapted is the Lithium-ion (Li-ion) battery technology.

The reason behind the widespread utilization of Li-ion is because of the many advantages that this technology offers. These advantages include: high energy-to-weight and power-to-weight ratios (180 Wh/kg and 1500 W/kg, respectively), low self-discharge rate, and no memory effect (Capasso & Veneri, 2014; D. Linden, n.d.; Piao et al., 2015). Despite the many advantages offered by the Li-ion batteries, the performance of these batteries is severely impacted by temperature (Xiong et al., 2019). The suspected roots behind the poor performance of the Li-ion batteries at lower temperatures are (i) reduced ionic conductivity, (ii) formation and more rapid growth of the solid electrolyte interface (SEI) layer, (iii) slow Lithium-ion diffusion into graphite, (iv) high polarization of the graphite anode (which is linked to all the preceding factors)(Jaguemont et al., 2016; Zhang et al., 2002).

This paper reviews the effect that cold temperatures have on the different electrolytes that could potentially be used in Li-ion batteries. The effect of low temperature on conductivity, voltage, ageing, discharge capacity, self-discharge etc. for each different electrolyte material is described and trends regarding the electrolytes performance based on these factors at low temperatures are summarized.

## Background

The operating temperature and discharge rates have major impacts on the i) conductivity ii) energy iii) power and iv) cycle life of Li-ion cells. Moreover, the rate at which these cells are charged at various temperatures also has a crucial role in determining the cycle life. Understanding the general effects of the above factors (temperature, discharge rate, and charge rate) is critical in order to be able to understand and more easily grasp how the usage of different electrolyte and electrode materials can improve cell performance in colder environments.

Firstly, with decreasing temperature the Li-ion cells suffer losses in both operating voltage (power) and discharge capacity (energy)(Zhang et al., 2002). Secondly, as the rate of discharge decreases, the discharge capacity increases. Also, as the temperature is lowered, the discharge capacity is reduced (Jaguemont et al., 2016).

### *Factors effecting cycle life:*

Firstly, the change in rate of discharge does not have a great effect on charged capacity; on the other hand, a change in operating temperature does have an effect on charged capacity (Laforgue et al., 2020). Secondly, an increased charge rate negatively affects cycle life, with a higher charge rate yielding a lower cycle life. Furthermore, charging at lower temperatures causes more severe battery degradation compared to at ambient temperatures (Laforgue et al., 2020).

When it comes to the use of specific electrolytes it is generally carbon-based solvents that are used. The problem with these solvents is the poor cell performance at low temperatures. Due to relatively high freezing points of some

of the solvents used, the conductivity of the solution falls at lower temperatures. One way to get past this problem is to use ternary or quaternary solvents (Smart et al., 1999). In this paper the use of several additives is reviewed: Ethylene carbonate (EC), Dimethyl carbonate (DMC), Ethyl methyl carbonate (EMC), Diethyl carbonate (DEC), Polycarbonate (PC) and Butyl acrylate (BA).

## Results and discussion

### 3.1 BA and EC additives to EMC/DMC LiPF<sub>6</sub> electrolyte

The addition of BA and EC to a standard electrolyte containing DMC/EMC = 3:5 (W/W) using the Lithium salt 1mol/L LiPF<sub>6</sub> was explored by C. Zhu et al. They investigated the effects of these additives on cell performance at low temperatures, measuring several variables: conductivity, viscosity, discharge capacity, voltage and charging and discharging cycle performance (Zhu et al., 2020). While the effects of different concentrations of BA were examined, this paper will focus on the electrolytes containing BA0%, BA12%, BA0% + EC and BA16% + EC.

There is an increase in both ionic conductivity and viscosity as temperature increases for all four electrolytes; however, Fig. 1 (a) shows that the ionic conductivity of BA12% is greater than BA0% at all measured temperatures. Therefore, the inclusion of BA can improve the conductivity of the Lithium ions and of the electrolyte in general. The addition of BA also increases the viscosity of the electrolyte at temperatures above -20°C but preserves the viscosity at temperatures below -20°C (remains close to that of electrolyte without BA). Although the addition of BA does increase viscosity, it more importantly increases the ionic conductivity, improving the low temperature performance of the electrolyte. Furthermore, it should also be noted that BA has a very low melting point (-77.9°C). Hence, using it as an additive can significantly reduce the melting point of the mixed solvent such that the electrolyte is operational at temperatures below -40°C. The addition of EC further increases the ionic conductivity. As Fig. 1 (a) and Fig. 1 (b) show, BA16% + EC shows a higher ionic conductivity than all the other three electrolytes at all temperatures. This indicates that BA+EC should be used to further improve low temperature electrolyte performance.

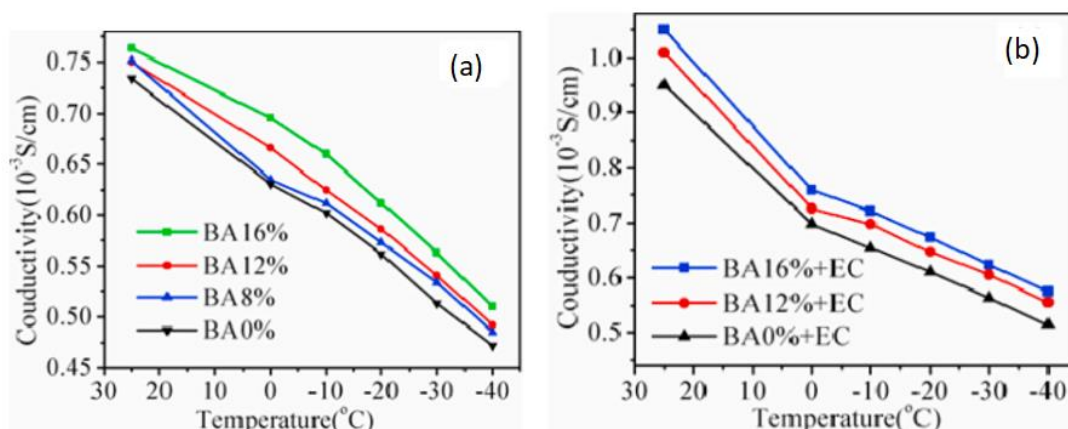
The addition of BA improves the specific capacity of the cell at low temperatures. Table 1. shows that at -10°C, the capacity of BA0% is actually greater than that of BA12%; However, from -20°C to -40°C, the capacity is greater for BA12%. It is also interesting to note that the BA12% electrolyte shows an increase in capacity of 116.7 to 124.2 mAh/g from -10°C to -20°C respectively, which is a pattern not shown by any of the other electrolytes being reviewed in this paper. Moreover, on addition of EC to the mixed solvent there is an obvious improvement in discharge performance of the cell. The BA16% + EC electrolyte shows the best performance with the highest capacity at all temperatures. Compared to BA0% + EC which has the second-best performance in the electrolytes discussed, BA16%+EC increases the capacity by 5.6%, 4.4%, 9.4%, and 17.3% at temperatures of -10°C, -20°C, -30°C, and -40°C, respectively. These results indicate that once again the BA16% + EC electrolyte possesses the best cell performance out of all the four electrolytes.

A similar trend in electrolyte performance is seen in the improvement of the voltage platform. Table 1. shows that at -10°C, -20°C, -30°C and -40°C the voltage values for the BA0% + EC electrolyte are 3.5%, 5.8%, 5% and 2.4% greater than that of the BA12% at the same temperatures respectively. These results indicate that an addition of EC to the electrolyte is required for improved low temperature voltage platform performance. Furthermore, the data also reveals that the voltage values for the BA16% + EC electrolyte at -10°C, -20°C, -30°C and -40°C are 0.73%, 1.73%, 2.9% and 3.2% greater than the BA0% + EC electrolyte respectively. These results suggest that higher concentrations of BA and an addition of EC are essential for optimal low temperature voltage performance.

The charging and discharging performance of batteries with different BA contents at room temperature and 0.2C were investigated. The initial discharge capacity and the discharge capacity after 50 cycles for BA0%, BA12%, and BA16% were measured. The results showed retention ratios of 89.6%, 88.4% and 83.8% respectively. This illustrates that although slightly degraded, the cycle performance of BA12% is close to that of BA0%. It is also worth noting that BA16% causes an obvious deterioration to the cell. Although not spoken about in this paper, BA16% demonstrates a better performance than BA12% in conductivity, voltage and discharge capacity; however, these results show that only the appropriate concentration of BA addition will positively affect low temperature

electrolyte performance while not severely reducing cycle performance. Fig. 2 shows that while the BA16% + EC mixed solvent shows higher capacity maintenance, it also displays lower capacity stability than the BA0% + EC. Additionally, it can be seen that the capacity maintenance of BA16% + EC and BA12% are similar.

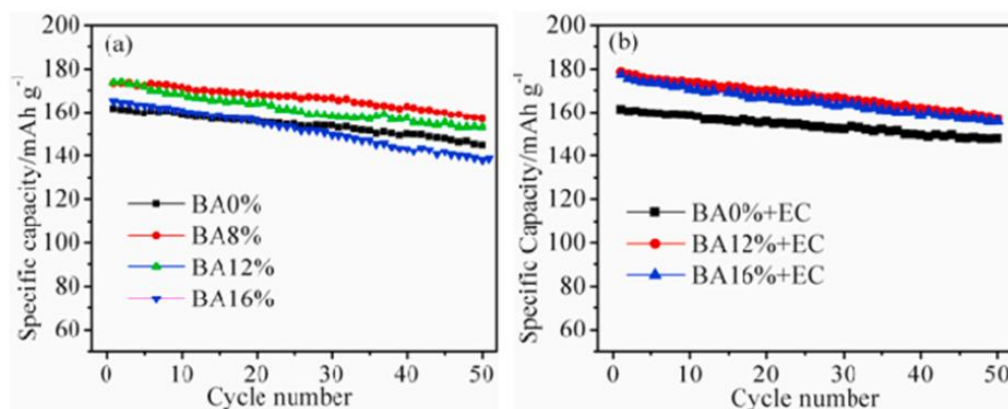
These results indicate that the additive BA16% + EC would make the best electrolyte compared to the other mixtures that were discussed. This is because it provides the best performance in conductivity, voltage and discharge capacities at all temperatures. Although it has poorer cyclic stability than BA0%, it still shows relatively high cycle maintenance (similar to that of BA12%) compared to the other three electrolytes.



**Fig. 1** (a) Shows the ionic conductivity values of the electrolytes with different compositions of BA at different temperatures; (b) shows ionic conductivity values of the electrolytes with different compositions of BA + EC at different temperatures (Zhu et al., 2020).

**Table 1.** Shows the capacity (mAh/g) and platform voltage (V) values of the electrolytes with different compositions at different temperatures (Zhu et al., 2020).

T/ $^{\circ}\text{C}$	Discharge	BA0%	BA12%	BA0% +EC	BA16% +EC
-10 $^{\circ}\text{C}$	Capacity/mAh/g Platform/V	121.96 3.292	116.67 3.565	160.14 3.690	169.12 3.717
-20 $^{\circ}\text{C}$	Capacity/mAh/g Platform/V	107.79 3.336	124.15 3.374	142.80 3.569	149.05 3.631
-30 $^{\circ}\text{C}$	Capacity/mAh/g Platform/V	95.65 3.129	110.95 3.279	126.32 3.444	138.15 3.544
-40 $^{\circ}\text{C}$	Capacity/mAh/g Platform/V	74.31 3.054	83.75 3.113	92.86 3.188	108.94 3.289



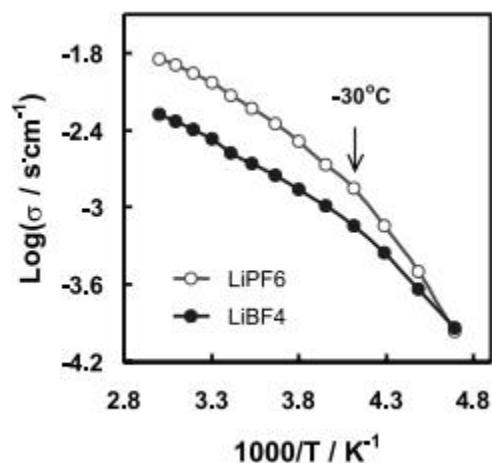
**Fig. 2** (a) Shows cycle performance of cells using electrolytes containing different proportions of BA; (b) shows cycle performance of cells using electrolytes containing different proportions of BA + EC (Zhu et al., 2020).

### 3.2 LiPF<sub>6</sub> dissolved in 1:1:3 PC/EC/EMC mixed solvent

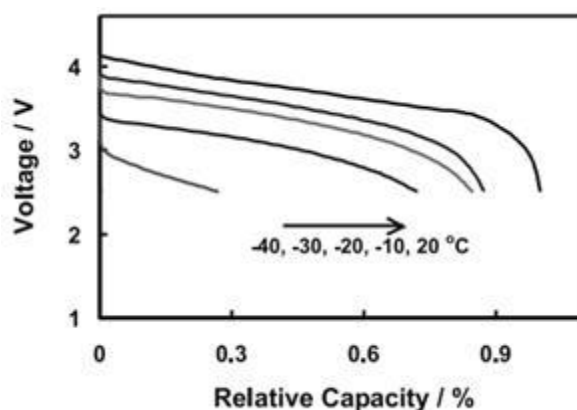
The utilization of 1M LiPF<sub>6</sub> dissolved in 1:1:3 PC/EC/EMC mixed solvent as a potential electrolyte was explored by Zhang et al. They investigated the performance of this electrolyte by obtaining data on several factors: melting point, ionic conductivity, voltage, and discharge capacity (Zhang et al., 2002). During the charge and discharge tests, each cell was first charged to 4.2V at 20°C and then discharged to 2.5V at a 0.5C rate over temperatures ranging from -40°C to 20°C.

The conductivity of the electrolyte was investigated, and the Arrhenius plot is shown in Fig. 3. The electrolyte shows the highest conductivity, about  $1.34 \times 10^{-2} \text{scm}^{-1}$ , at 60°C and conductivity decreases with a fall in temperature. At -30°C the conductivity is about  $1.2 \times 10^{-3} \text{scm}^{-1}$ , and at about -50°C the conductivity drops to  $3 \times 10^{-4} \text{scm}^{-1}$ . Furthermore, during the measurement of ionic conductivity at temperatures ranging from 60°C to -60°C, no freezing phenomenon was observed for the electrolyte.

Zhang et al. also examined the effect of temperature on discharge capacity for the LiPF<sub>6</sub> electrolyte. At 20°C the discharge capacity for the electrolyte is 1.13mAh/cm<sup>2</sup>. Fig. 4 shows the voltage capacity curve for the electrolyte where the value of relative capacity is defined as 1.0. It can be clearly seen that as temperature decreases, the cell suffers losses in both voltage (power) and capacity (energy). Between -30°C and 20°C the electrolyte is able to function without a very large loss in relative capacity. At -30°C, 72% of the relative capacity is retained. At temperatures below -30°C, there is a much greater loss in relative capacity. At -40°C, less than 30% of the relative capacity is retained. Furthermore, the LiPF<sub>6</sub> completely fails at -50°C. This indicates that although the electrolyte does not freeze at -60°C, it is only suitable to be used as an electrolyte in a Li-ion cell in temperatures above -30°C.



**Fig. 3** Arrhenius plots of the ionic conductivities for the  $\text{LiPF}_6$  and  $\text{LiBF}_4$  electrolytes dissolved in 1:1:3 PC/EC/EMC mixed solvent (Zhang et al., 2002).



**Fig. 4** Voltage–capacity plots of Li-ion cell at various temperatures, in which relative capacity is a ratio of the capacity at a specified temperature to the one obtained at 20°C for the  $\text{LiPF}_6$  electrolyte.

### 3.3 $\text{LiPF}_6$ dissolved in EC/DMC 30:70, EC/DEC 30:70 and EC/DMC/DEC 1:1:1

An investigation on the usage of binary and tertiary mixtures of Aliphatic carbonates (i.e., 1.0 M  $\text{LiPF}_6$  dissolved in 30:70 EC/DMC, 30:70 EC/DEC, and the equi-volume ternary mixture (EC/DMC/DEC)) was carried out by Smart et al. The authors compared the effect of temperature on several factors: electrolyte conductivity, rate capability, discharge capacity, and cycle performance. They also reviewed the self-discharge capacities for each of the electrolytes (Smart et al., 1999). For the charging and discharging tests, cells were first charged to a cut-off voltage of 4.1V, followed by tapered charging for an additional 3 hours and discharged at a constant current to 3V.

At room temperature (20°C) the DMC-based electrolytes have higher conductivity compared to DEC-based solutions. As shown in Fig. 5, the binary electrolyte containing DMC, which has a greater DMC concentration than the ternary solution, shows higher conductivity than the other electrolytes at temperatures above 0°C; however, at

temperatures below  $-20^{\circ}\text{C}$  the high conductivity drops drastically for the DMC-based binary solution and displays lower conductivity than the other electrolytes. On the other hand, solutions with high DEC concentration shows low conductivity above  $-20^{\circ}\text{C}$  with the DEC-based binary solution exhibiting the lowest conductivity out of the three solutions; nonetheless, at temperatures below  $-20^{\circ}\text{C}$  the DEC-based binary solution shows improved conductivity which is higher than the DMC-based binary solution. The ternary mixture makes the best of both worlds and manifests an overall better conductivity than both the DEC- and DMC-based solutions.

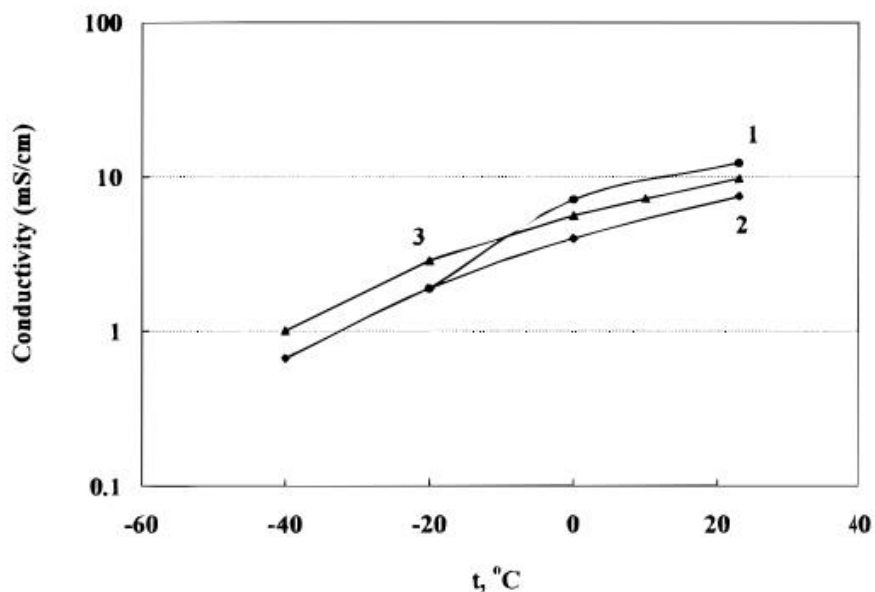
To predict the rate capabilities of the graphite anode using the three experimental electrolytes, current-voltage curves were generated. Each electrolyte was discharged at four different temperatures and the voltage delivered by the cell was recorded. As seen in Fig. 6, the ternary electrolyte showed higher voltages than the binary solutions at  $0^{\circ}\text{C}$  and is more noticeably seen at  $-20^{\circ}\text{C}$  and  $-40^{\circ}\text{C}$ . Moreover, it is also worthy to note that at  $0^{\circ}\text{C}$ , the DEC-based solution and the DMC-based solution deliver a similar voltage even though the DEC-based solution shows a lower conductivity at this temperature.

A comparison of the low temperature discharge performance of graphite-based cells was made. Fig. 7 shows that the ternary mixture provides the highest capacity at  $-20^{\circ}\text{C}$  with 85% of the room temperature capacity being realized while also delivering the highest voltages compared to the other electrolytes. In comparison, the cells with DMC and DEC yielded 15% and 67% of the room temperature capacity, respectively. This result in particular clearly confirms that other additives are required to be added to DMC-based cells in order for them to be better suited for low temperature performance. Fig. 8 shows the discharge capacities for the solvents at  $23^{\circ}\text{C}$ ,  $0^{\circ}\text{C}$  and  $-20^{\circ}\text{C}$ . The ternary solution maintains a discharge capacity above 400mAh at all temperatures while the DEC-based solution's capacity reduces below 400mAh at  $-20^{\circ}\text{C}$ . The DMC-based solution's capacity is maintained above 400mAh between  $0^{\circ}\text{C}$  and  $20^{\circ}\text{C}$ ; however, it drastically reduces to below 200mAh at  $-20^{\circ}\text{C}$ . Thus, these findings reiterate that additives must be added to improve low temperature performance of DMC-based electrolytes. They also verify that the ternary electrolyte shows the best performance in terms of discharge compared to the other electrolytes as it maintains a capacity above 400mAh at all temperatures.

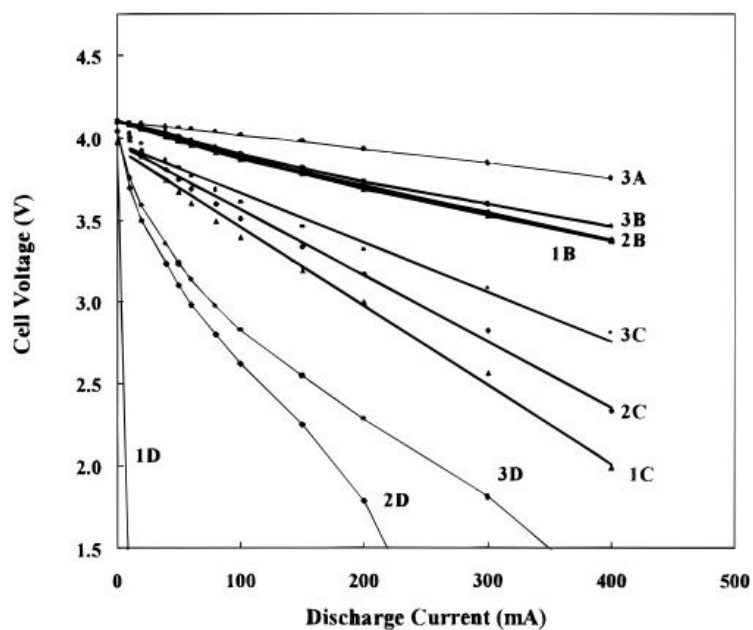
Cycle performance for all mixtures was tested at both room temperature and  $-20^{\circ}\text{C}$ . Testing at ambient conditions revealed that the ternary mixture has a capacity retention of over 85% after 600 cycles. The rate of capacity fade for the DEC-based solution is 0.06% per cycle and for the DMC-based electrolyte and the ternary electrolyte the rate of capacity fade is 0.04% per cycle at room temperature. At  $-20^{\circ}\text{C}$  the ternary mixture not only showed the highest discharge capacity but also had the lowest capacity fade rate of a mere 0.033% per cycle. The binary based electrolytes both showed inferior behaviour with lower discharge capacities as well as higher capacity fade rates.

Tests for self-discharge showed that the rate at which self-discharge occurs increases: 30:70 EC/DMC < 1:1:1 EC/DMC/ DEC < 30:70 EC/DEC. Self-discharge is an important factor for electrolytes as it affects capacity loss of batteries that are in storage. Hence, the DEC based electrolyte having the highest self-discharge rate means that it would lose capacity at the fastest rate when stored for long periods of time. The ternary electrolyte seems to show characteristics of both the DMC- and DEC based electrolytes as it has a self-discharge rate value between the two binary based solutions.

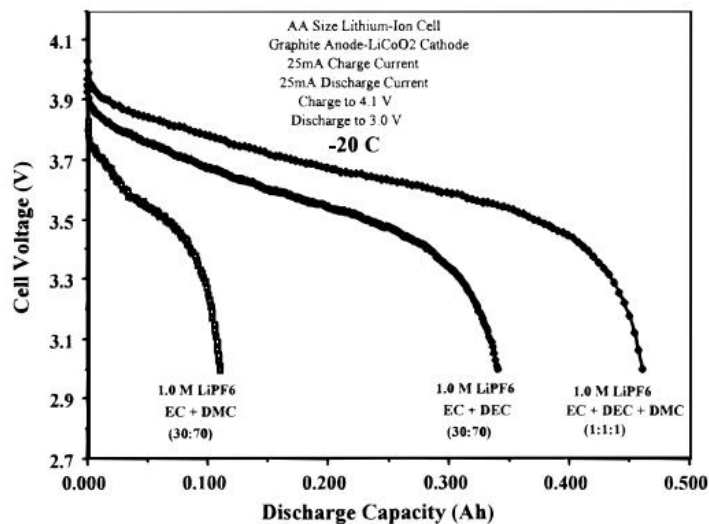
The results from this paper clearly demonstrate that the best performing electrolyte at room temperatures is the ternary electrolyte and is perhaps the most suitable out of the three electrolytes for application in EVs that require low temperature as well as room temperature performance. This is because the ternary electrolyte shows the best low temperature (lower than  $-10^{\circ}\text{C}$ ) performance in conductivity, voltage and discharge capacity. While it does have poorer conductivity at  $20^{\circ}\text{C}$  it still exhibits superior voltage and discharge capacity compared to the DMC-based electrolyte. These factors reiterate the conclusion that the ternary electrolyte is best for commercial usage.



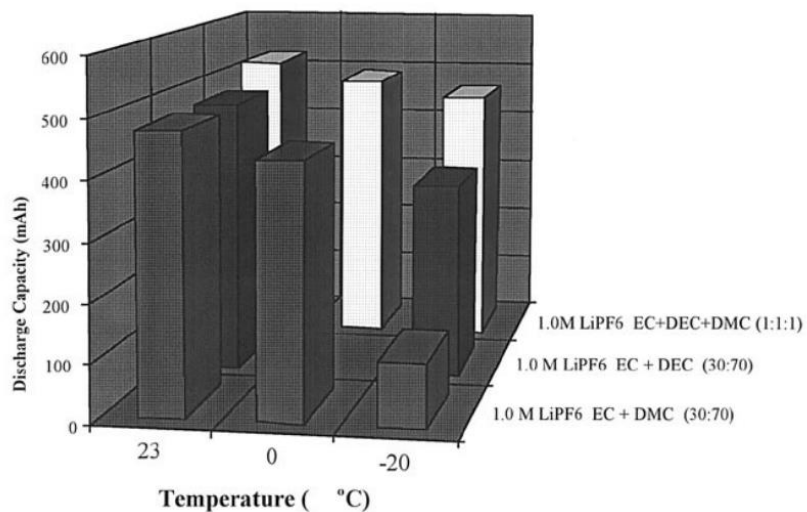
**Fig. 5** Shows the conductivity of the  $\text{LiPF}_6$  dissolved in (1) 30:70 EC/DMC, (2) 30:70 EC/DEC, and (3) 1:1:1 EC/DMC/DEC solvent mixtures at different temperatures (Smart et al., 1999).



**Fig. 6** Shows current-voltage curves with electrolytes based on (1) EC/DMC, (2) EC/DEC, and (3) EC/DMC/DEC solvent mixtures at (A) 25, (B) 0, (C) -20, and (D) -40°C respectively (Smart et al., 1999).



**Fig. 7** Shows the discharge curves of the  $\text{LiPF}_6$  dissolved in different mixed solvents at  $-20^\circ\text{C}$  using various electrolytes (Smart et al., 1999).



**Fig. 8** Shows the low temperature characteristics of  $\text{LiPF}_6$  electrolyte based on EC/DMC, EC/DEC, and EC/DMC/DEC solvent mixtures at a discharge rate of  $C/20$  and different temperatures (Smart et al., 1999).

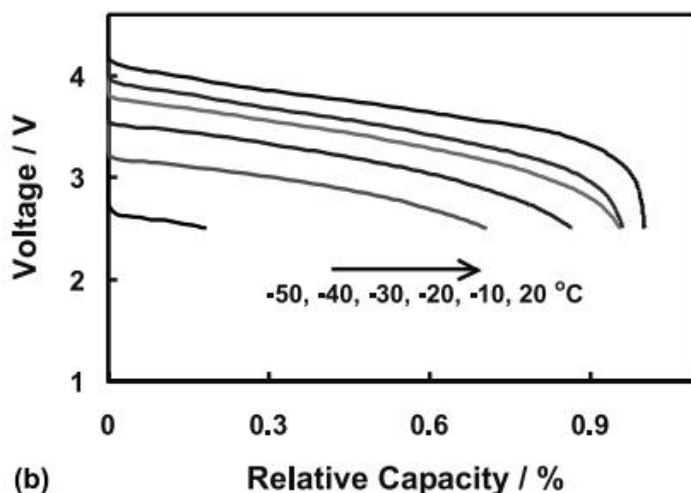
### 3.4 $\text{LiBF}_4$ dissolved in PC/EC/EMC

The utilization of 1M  $\text{LiBF}_4$  dissolved in 1:1:3 PC/EC/EMC mixed solvent as a potential electrolyte was explored by Zhang et al. The factors explored and the experimental method used during the charging and discharging tests are the same as in that in section 3.1 (Zhang et al., 2002).



The conductivity of the  $\text{LiBF}_4$  electrolyte was investigated and the Arrhenius plot is shown in Fig. 3. The electrolyte exhibits highest conductivity of about  $5.18 \times 10^{-3} \text{scm}^{-1}$  at  $60^\circ\text{C}$  and conductivity decreases with a fall in temperature. At  $-30^\circ\text{C}$ , the conductivity is about  $7.3 \times 10^{-4} \text{scm}^{-1}$ , and at  $-50^\circ\text{C}$  the conductivity falls to  $2.96 \times 10^{-4} \text{scm}^{-1}$ . Furthermore, during the measurement of ionic conductivity at temperatures ranging from  $60^\circ\text{C}$  to  $-60^\circ\text{C}$ , no freezing phenomenon was observed for the electrolyte. It is also worth noting that the  $\text{LiPF}_6$  electrolyte that is discussed in section 3.2, with the same ternary mixed solvent, does not freeze at  $-60^\circ\text{C}$ . This indicates that the 1:1:3 PC/EC/EMC mixed solvent is suitable for formation of an electrolyte that can operate at low temperatures.

The effect of temperature on discharge capacity for the  $\text{LiBF}_4$  electrolyte was also investigated. At  $20^\circ\text{C}$ , the discharge capacity for the electrolyte is  $1.05 \text{mAh/cm}^2$ . Fig. 9 shows the voltage capacity curve for the electrolyte. It can be seen from the figure that a decrease in temperature results in losses of voltage as well as capacity. Between  $-20^\circ\text{C}$  and  $20^\circ\text{C}$ , the relative capacity is above 90% and at  $-30^\circ\text{C}$  the relative capacity is 86%. However, at  $-50^\circ\text{C}$  the relative capacity undergoes a drastic decrease falling to 20%. These results indicate that this electrolyte mixture is suitable for low temperature performance as it possesses a high relative capacity even at low temperatures like  $-30^\circ\text{C}$ .



**Fig. 9** Voltage capacity plot of Li-ion cell (containing a  $\text{LiBF}_4$  electrolyte) at various temperatures (Zhang et al., 2002).

### 3.5 $\text{LiBF}_4$ dissolved in EC:DMC:DEC

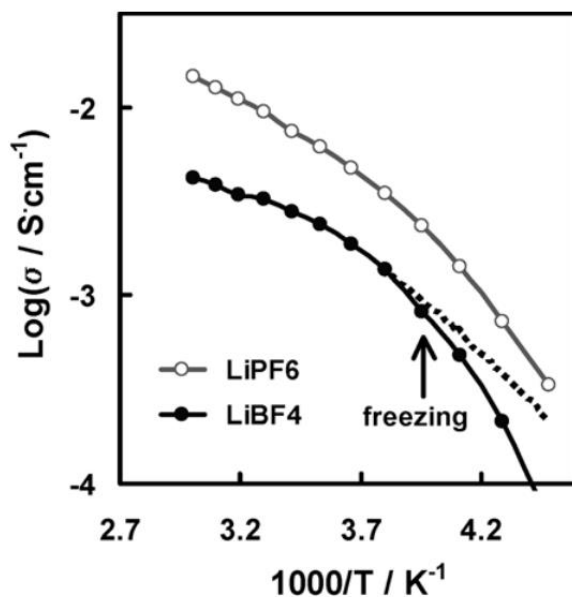
An exploration for the potential use of  $\text{LiBF}_4$  dissolved in 1:1:1 EC:DMC:DEC solution was carried out by Zhang and colleagues. They explored the effect of low temperatures on the conductivity, relative capacity, voltage, and cycle performance of the electrolyte solution (Zhang et al., 2003). In this investigation, all the charging processes were conducted at  $20^\circ\text{C}$  and  $0.5 \text{mA/cm}^2$  up until a charging potential of  $3.9 \text{V}$ . Additionally, the definition of “relative capacity” in the context of this paper being discussed is the ratio of discharge capacity at a certain temperature to the capacity assessed at  $20^\circ\text{C}$ .

As shown in Fig. 10 the conductivity of the solution decreases as temperature reduces. It can be seen in the Arrhenius plot that at temperatures below  $-20^\circ\text{C}$  there is a significant drop observed in conductivity. For example, at about  $-10^\circ\text{C}$  the conductivity is roughly  $1.38 \times 10^{-3} \text{Scm}^{-1}$ , then at  $-20^\circ\text{C}$  the conductivity falls to roughly  $8.1 \times 10^{-4} \text{Scm}^{-1}$ , and finally at  $-30^\circ\text{C}$  there is a significant fall in conductivity as it falls to  $4.04 \times 10^{-4} \text{Scm}^{-1}$ . This exaggerated drop in conductivity is due to freezing of the liquid electrolyte. The freezing of the electrolyte was confirmed when the temperature was reduced to  $-40^\circ\text{C}$  where the  $\text{LiBF}_4$  electrolyte froze within 30 minutes.

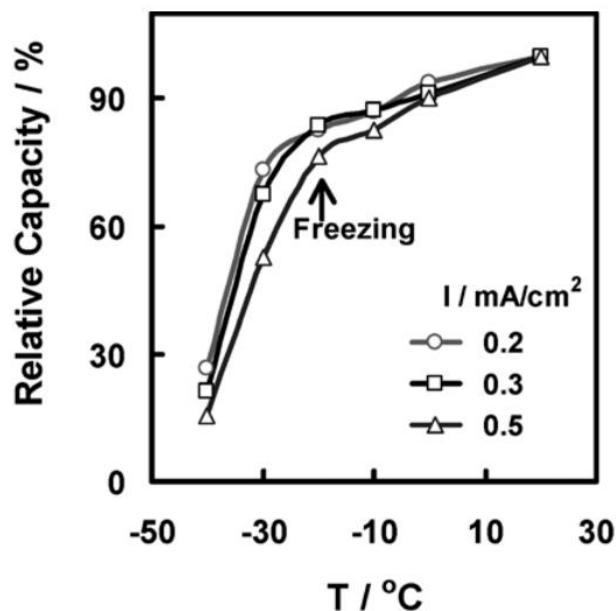
The effect of temperature on the relative capacity of Li-ion cells using the  $\text{LiBF}_4$  electrolyte was studied. From Fig. 11 we can see that as temperature decreases the relative capacity decreases as well. At temperatures of about  $10^\circ\text{C}$ ,  $0^\circ\text{C}$ ,  $-10^\circ\text{C}$ ,  $-20^\circ\text{C}$  and  $-30^\circ\text{C}$  the relative capacity values are roughly 95.3%, 90.5%, 87.0%, 84.5% and 69.1% respectively. Furthermore, we observe that there is a substantial drop in relative capacity at temperatures lower than  $-20^\circ\text{C}$  at all discharge rates which is shown in the drop in relative capacity between  $-20^\circ\text{C}$  and  $-30^\circ\text{C}$ . This drop in relative capacity can be attributed to the lower conductivity of the electrolyte due to its freezing. Although the cell shows the highest relative capacity at a discharge rate of  $0.2\text{mA}/\text{cm}^2$ , it is observed that the discharge rate has only a small impact on the relative capacity.

The effect of current density on the discharge voltage was investigated and a voltage capacity curve for the  $\text{LiBF}_4$  electrolyte at  $-20^\circ\text{C}$  was produced as shown in Fig. 12. Between  $0.3$  and  $0.5\text{mA}/\text{cm}^2$ , the current density has a negligible impact on the discharge voltage; however, when the current is increased to  $0.2\text{mA}/\text{cm}^2$  we can see that there is an increase in the discharge voltage delivered.

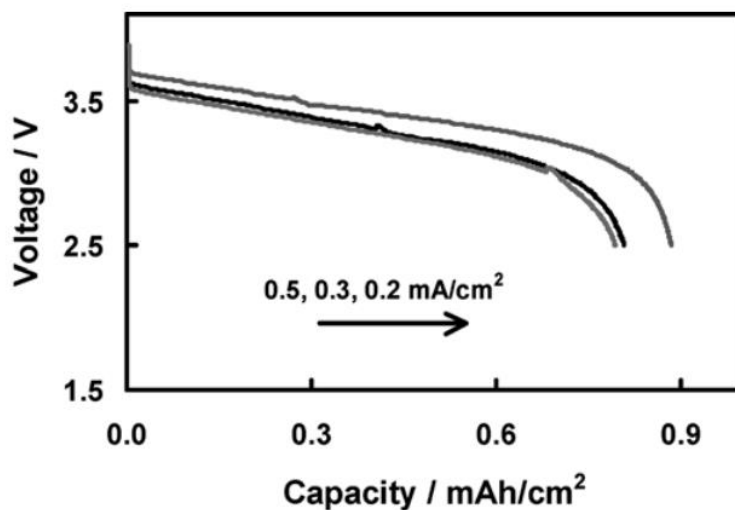
Finally, the cycle performance of the electrolyte was explored. Fig. 13 shows the capacity of the  $\text{LiBF}_4$  electrolyte before and after cycling at low temperatures. After around 10 cycles the “ratio vs 10<sup>th</sup> capacity” is roughly 0.988, then during low temperature cycling at the 16<sup>th</sup> cycle the ratio is approximately 0.9606 and then at the end of 30 cycles the ratio is roughly 0.966. The trend shows that as the cell undergoes increased cycling the ratio decreases; however, it is also observed that after the cell is brought back to room temperature cycling following low temperature cycling, the ratio increases slightly. Overall, the electrolyte shows good cycle stability with a capacity fade rate of around 0.0008% per cycle.



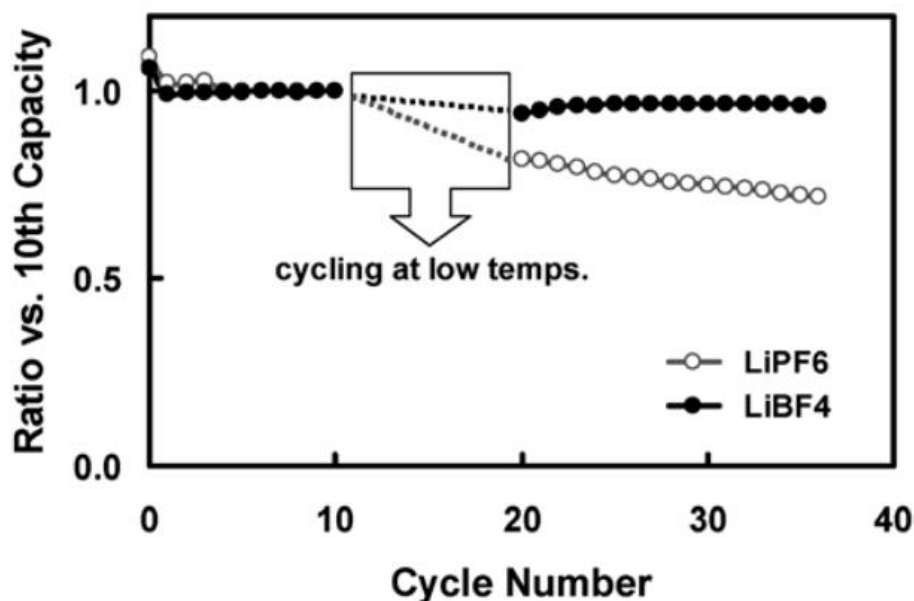
**Fig. 10** Shows Arrhenius plots of ionic conductivities for the electrolytes composed of  $\text{LiBF}_4$  and  $\text{LiPF}_6$  dissolved in a 1:1:1 EC/DMC/DEC mixture (Zhang et al., 2003).



**Fig. 11** The effect of temperature on the relative capacity of the Li-ion cells using either 1 M  $\text{LiPF}_6$  or 1 M  $\text{LiBF}_4$  salt dissolved in a 1:1:1 EC/DMC/DEC mixture is illustrated (Zhang et al., 2003).



**Fig. 12** Illustrates the influence of current density on discharge voltage of the Li-ion cells using 1 M  $\text{LiBF}_4$  in a 1:1:1 EC/DMC/DEC electrolyte, in which the cell was charged at 20°C and discharged at -20°C with a constant current density of 0.5 mA/cm² (Zhang et al., 2003).



**Fig. 13** Change in the discharge capacities of the Li-ion cells using LiPF<sub>6</sub> and LiBF<sub>4</sub>, respectively, before and after the cycling test at low temperatures. The data was obtained by cycling the cells at 0.5 mA/cm<sup>2</sup> at 20°C between 2.5 V and 3.9V (Zhang et al., 2003).

## Conclusion

In this review, electrolytes containing LiPF<sub>6</sub> and LiBF<sub>4</sub> dissolved in various co-solvents were explored, and their performances based on several factors were measured.

The use of LiBF<sub>4</sub> as an electrolytic salt presented mixed results. When dissolved in 1:1:1 EC:DMC:DEC, the electrolyte showed high freezing temperatures which would limit its use in EV applications; however, when dissolved in 1:1:3 PC/EC/EMC, the electrolyte displayed good capacity at low temperatures and had a low freezing point. More research should be conducted to explore the low-temperature performance of the respective electrolytes on voltage and cycle performance preferably with larger-scaled batteries that would be suitable for EV use. Although presented with limited data, these results indicate that LiBF<sub>4</sub> could be a potential candidate for application in EVs if the freezing point of the salt-containing solution is lowered -similarly to the way it was done in the PC/EC/EMC solution.

Through the review of electrolytes containing the LiPF<sub>6</sub> salt, it can be justified that this salt, when dissolved in some co-solvent, is more viable for application in EVs as it possesses lower freezing points. The use of binary electrolytes is unsuitable for low-temperature performance due to high freezing temperatures, ergo ternary/quaternary solutions are a better approach for low-temperature application. The use of LiPF<sub>6</sub> as an electrolyte is plausible even though it shows severe capacity loss below -30°C; however, information about its cycle performance is unknown and should be explored. The final two electrolyte solutions, LiPF<sub>6</sub> dissolved in 1:1:1 EC/DMC/DEC and LiPF<sub>6</sub> dissolved in 3:5 DMC/EMC containing BA16%+EC, the best performing BA-based electrolyte, are the best-performing electrolytes and seem to be the most suitable for EV application. These electrolytes are superior due to enhanced voltage, discharge capacity, and cycle performance (for the BA solution).

## Limitations

There are two limitations to this research:

- i) The electrolytes reviewed in this paper were studied under conditions that do not replicate those that would be found in EVs. While all the electrolytes were tested in Lithium-ion cells, the cells used in the study were not at the same scale and the conditions, such as discharge rate, charging rate, etc. were not exactly the same as those that would be found inside an EV. This paper assumes that the general trends followed by the electrolytes could also to the conditions found in EVs.
- ii) The data values that are referred to in some parts of this paper are non-exact and were extracted from the graphs using an external tool: WebPlotDigitizer.

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