

# Additives in Localized High Concentration Electrolytes for Safe Lithium-Ion Batteries

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## Abstract

In this work, the effects of various additives in a localized high concentration electrolyte (LHCE) on the cycling performance of lithium (Li)-ion batteries were studied. The LHCEs utilize trimethyl phosphate as a flame-retarding solvent and 1H,1H,5H-octafluoropentyl 1,1,2,2-tetrafluoroethyl ether as a medium-high flash point diluent, for the purpose to reduce the electrolyte flammability and improve the battery safety, which are not possessed by the conventional electrolytes of LiPF<sub>6</sub> in organic carbonates due to their high flammability. The LHCEs have unique solvation structure which enables the use of flame-retardant solvents to greatly decrease the electrolyte flammability as well as enhance the battery cycling stability. However, the additives added in the LHCEs result in different battery performances. The organic carbonate additives largely reduce the initial capacities although the cell capacity can be partially recovered with cycling. The two phosphate salt additives behave better than the organic carbonate additives in terms of cell capacity and cycling stability. More cell performance evaluation will be conducted and the detailed characterization will be performed to investigate the root causes of different behaviors of additives in the LHCEs on battery performances.

## Introduction

With the recent drive for increased energy production from naturally intermittent green energy sources and the rise of electric vehicles, there has been a great demand for higher efficiency, more dense energy storage technologies. At the forefront of this research are lithium (Li)-ion batteries (LIBs), which have seen steady improvements since their commercialization in the 1990s.[1] However, with increased energy density has also come shortened cycle life and increased safety risks, both of which are associated with the use of state-of-the-art electrolytes.

The current industry standard electrolyte consists of LiPF<sub>6</sub> salt dissolved in cyclic carbonates, primarily ethylene carbonate (EC), and linear carbonates such as ethyl methyl carbonate (EMC) and diethyl carbonate (DEC), along with a variety of additives to increase performance. This

electrolyte has become ubiquitous for its ability to form an effective solid electrolyte interphase (SEI) that protects graphite (Gr) anodes from exfoliation, as well as its low viscosity, high electrochemical stability, and ionic conductivity that make it ideal for use in conventional LIB.[2-5] However, at the higher-voltage ( $\geq 4.4$  V) desired for greater energy density in industry, these electrolytes begin to fail. Their poor anodic stability and inability to form a sufficiently passivating cathode electrolyte interphase (CEI) leads to rapid electrolyte decomposition. Moreover, the chemical instability of lithium hexafluorophosphate (LiPF<sub>6</sub>) leads to spontaneous generation of hydrofluoric acid (HF), which contributes to aging issues such as transition metal dissolution. These factors lead to significantly decreased cycle life in high voltage, high energy density cells.[6, 7]

These electrolytes also face several safety issues. The linear carbonate solvents used have very low flash points. Such high flammability has led to several high-profile incidents in which LIBs have caught fire and explosions, resulting in seriously bodily harm and property damage.[8-11] The  $\text{LiPF}_6$  salt is also a liability, as it can decompose in cells, generating harmful HF and releasing large amounts of heat that can lead to thermal runaway.[12] These risks are exacerbated in high-voltage cells, which further motivates research into designing alternative electrolyte systems.

Many alternative electrolytes have been proposed to replace the conventional electrolytes in high voltage LIB electrolytes.[13-15] One of these solutions, localized high concentration electrolytes (LHCEs), has shown great promise in LIBs.[16, 17] They have shown excellent abilities of forming effective SEI and CEI, extended anodic stabilities toward positive materials operated at high upper cut-off voltage, and enhanced chemical stability because  $\text{LiPF}_6$  is substituted with a more chemically stable salt, Li bis(fluorosulfonyl)imide ( $\text{LiFSI}$ ). For these reasons, LHCEs facilitate long cycle life that surpasses conventional electrolytes in high energy density LIBs. In LHCEs, 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) is the most commonly adopted diluent. However, TTE suffers from a low flash point of 29 °C. To suppress the flammability of the LHCEs, a flame retarding solvent, trimethyl phosphate ( $\text{TMP}_a$ ) was employed to fabricate an LHCE with reduced flammability.[18] While the use of  $\text{TMP}_a$  significantly suppresses the flammability of the electrolyte,  $\text{TMP}_a$ /TTE-based LHCEs suffer from significant capacity loss in the SEI formation process, resulting in the decreased initial capacities of LIBs.[19] Therefore, these electrolytes require further development before they will be viable for industrial use.

To resolve the issues of  $\text{TMP}_a$ /TTE-based LHCEs, an LHCE was developed using a mixture of tetramethyl sulfone (TMS) and  $\text{TMP}_a$  as the solvating solvent and 1H,1H,5H-octafluoropentyl 1,1,2,2-tetrafluoroethyl ether (OTE) as the diluent. TMS was introduced to increase the initial capacity and cycling performance while maintaining an adequately low flammability.[20] OTE was employed to substitute TTE as the new diluent because of its higher flash point of 60 °C. In this report, additives were introduced into an optimal LHCE based on  $\text{TMP}_a$ -TMS/OTE solvent mixture from the previous studies and their influences on the electrochemical performance of the  $\text{Gr}||\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}$  (NMC811) cells were studied. Two organic carbonate additives, EC and fluoroethylene carbonate (FEC) which have been shown to improve initial capacity and cycle life in previous LHCEs, were selected.[21, 22] Two salts,  $\text{LiPF}_6$  and Li difluorophosphate ( $\text{LiDFP}$ ), were also adopted as additives in the  $\text{TMP}_a$ -TMS/OTE LHCE.  $\text{LiDFP}$  was of particular interest, as it has been shown to facilitate the formation of stable CEI and SEI capable of improving the cycle life in high-voltage LIBs.[23, 24]

## Experimental

### Preparation of electrodes and electrolytes

The electrodes used in cell testing were received from the Cell Analysis, Modeling, and Prototyping (CAMP) facility at Argonne National Laboratory. Electrode sheets of NMC811 on an aluminum (Al) current collector with the areal loading of 1.5 mAh  $\text{cm}^{-2}$  and Gr on a copper (Cu) current collector with the areal loading of 1.8 mAh  $\text{cm}^{-2}$  were punched into circular electrodes of 12.7 mm and 15.0 mm diameters, respectively. The electrode disks were dried in a vacuum oven at 110 °C for 12 h before being moved to

an argon (Ar)-filled glovebox (MBraun) with O<sub>2</sub> and H<sub>2</sub>O concentrations maintained below 0.1 ppm.

The formulae for the electrolytes can be found in Table 1. The mol ratios of the electrolytes were not included due to intellectual property concerns. The solvents were stored in the Ar-filled glovebox and dried with preactivated molecular sieves. The electrolytes were prepared in two consecutive steps: 1) the salts were fully dissolved in the mixture of TMS, TMP<sub>a</sub>, and any liquid additives under magnetic stirring for 12 h to yield high concentration electrolytes (HCEs), and 2) the diluent OTE was added into HCEs to yield LHCEs. The electrolytes were mixed for another 12 h and stored in the glovebox until use. The conventional electrolyte (E-Baseline) was prepared by dissolving LiPF<sub>6</sub> in a mixture of EC:EMC (3:7 by wt.) at a concentration of 1.0 mol L<sup>-1</sup>, followed by the introduction of 2 wt.% vinylene carbonate (VC) as the additive.

Table 1. Electrolyte formulae studied in this work	
Electrolyte Code	Formulae
SEO-M1-F	LiFSI : TMP <sub>a</sub> : TMS : FEC : OTE
SEO-M1-E+F	LiFSI : TMP <sub>a</sub> : TMS : FEC : EC : OTE
SEO-M1-P	LiFSI : LiPF <sub>6</sub> : TMP <sub>a</sub> : TMS : OTE
SEO-M1-D	LiFSI : LiDfP : TMP <sub>a</sub> : TMS : OTE
SEO-M1-D+F	LiFSI : LiDfP : TMP <sub>a</sub> : TMS : OTE
SEO-M1-2D	LiFSI : LiDfP : TMP <sub>a</sub> : TMS : OTE

## Cell Preparation and Testing

Full Gr||NCM811 CR-2032 coin-cells were used in the evaluation of the LHCEs. Al-clad coin cell positive cases were used in tandem with a piece of Al foil in coin cell assembly to prevent the anodic corrosion of the cell casing by the LHCEs. Electrolyte was added in 25  $\mu$ L portions to the cathode and the anode for a total of 50  $\mu$ L electrolyte in each cell.

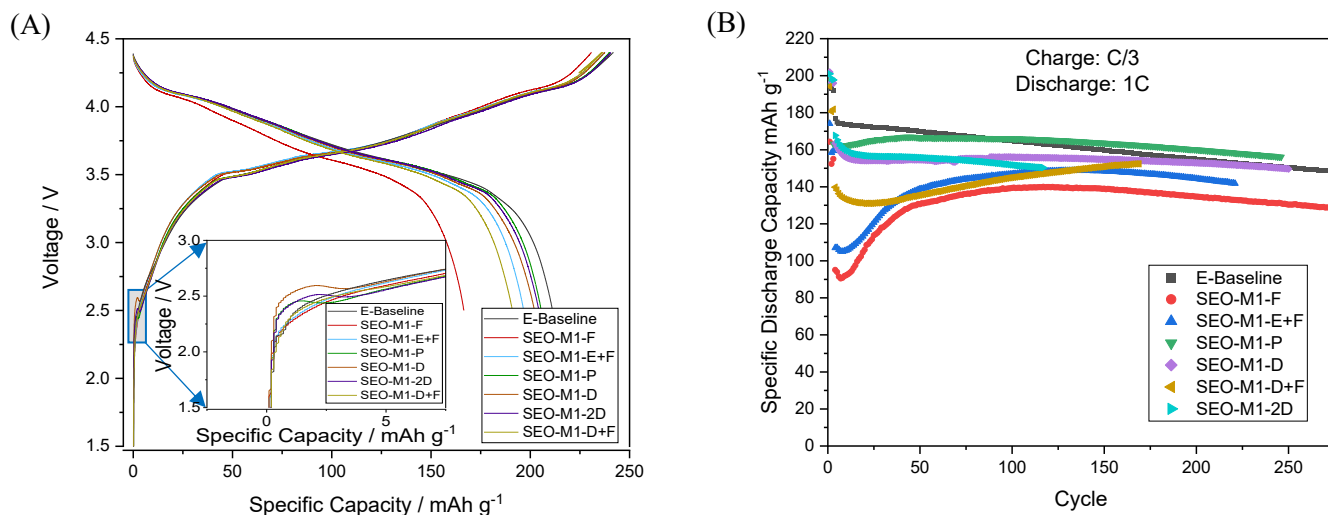
A Landt battery cycler was used to determine cycling performance. For long-term cycling at 25 °C, cells went through one cycle at C/20 followed by two cycles at

C/10 to ensure that a stable SEI was formed. Following the SEI formation cycles, the cells went through 500 cycles at C/3 charge and 1 C discharge. The cells were cycled in the voltage range of 2.5 to 4.4 V, where C = 1.5 mA cm<sup>-2</sup>.

## Results

Because of their unique solvation structure, LHCEs have been shown to effectively improve the anodic stability of electrolytes over conventional electrolytes. They also facilitate the activation of anions towards forming a stable SEI on Gr which can lead to improved cycling performance at high voltages.[25, 26] To test their cycling performance at high voltages, Gr||NMC811 cells were tested in long-term cycling with several LHCEs with an OTE diluent and various additives along with cells using a conventional E-baseline.

Figure 1A shows the charge-discharge voltage profiles of the Gr||NMC811 cells in their first formation cycle at C/20. The cells without FEC additive show clear voltage peaks in their first charge between 2.4 and 2.6 V. These peaks are associated with the decomposition of the solvation sheath on the Gr negative electrode to form the SEI. For the cells containing FEC, however, there is no such voltage peak. This indicates that the introduction of FEC changed the SEI formation behavior in LHCEs. There is a large difference in the first charge and discharge capacities of the cells. This difference was most pronounced in the FEC containing cells. Compared to the first cycle capacity difference of the electrolytes containing 1 wt.% LiPF<sub>6</sub> and LiDfP, 34.5 mAh g<sup>-1</sup> and 35.3 mAh g<sup>-1</sup>, respectively, the electrolyte with only FEC additive experienced a difference nearly twice as great of 64.3 mAh g<sup>-1</sup>. It can be concluded that after the introduction of FEC, SEI is formed at the cost of a higher capacity loss. For this reason, the cells containing FEC-additive electrolytes, including SEO-M1-



**Figure 1. Battery performance of LIBs using OTE-diluted LHCEs with electrolyte additives at 25 °C.** (A) The charge-discharge voltage profiles of the cells in their first formation cycle at C/20. (B) The long-term cycling discharge capacity performance.

D+F, exhibit inferior average specific discharge capacity in the first charge. According to the Gr intercalation compound model, SEI is predominantly formed by the cathodic decomposition of cation-solvation sheaths in the electrolyte. The introduction of electrolyte additives changes the composition of the cation solvation sheath and consequently the behavior of SEI formation.

The long-term cycling performance of the cells is shown in Figure 1B. TMS-TMP<sub>a</sub>-based electrolytes with OTE diluent show excellent compatibility with Gr||NMC811 cells, as shown by their high coulombic efficiencies ( $\geq 99.5\%$ ) and stable long-term cycling. The cells containing SEO-M1-F are characterized by an initial decrease in capacity over the first 15 cycles followed by a gradual capacity increase that peaks around the 110<sup>th</sup> cycle. This effect is relatively substantial, with a 47% increase from 95 mAh g<sup>-1</sup> to 140 mAh g<sup>-1</sup>. This effect is still present with the addition of EC, which raises the initial capacity by about 10 mAh g<sup>-1</sup> and prolongs the increase by about 10 cycles for SEO-M1-EF. The mechanism behind such

“activation” process is not yet fully understood. For both FEC-containing electrolytes, after reaching peak capacity the Gr||NMC811 cells were very stable, maintaining about 97% and 96% of their peak capacity through cycle 200.

The addition of salt additives resulted in very stable and long cycle life. The cells containing LiPF<sub>6</sub> additive saw a small initial capacity increase peaking around cycle 50. Following their peak, they had very stable cycling, such that by 200 cycles that had 96% of their peak capacity as compared to 88% for the E-Baseline. This meant that, by cycle 120, cells containing SEO-M1-P had higher capacities than the baseline cells. The effect of LiDFP on the cells was an initial capacity decline followed by very stable cycling for both 1 and 2 wt.%. The cells with 1 wt.% LiDFP had a longer cycle life than those with 2 wt.%, having retained 94.4% of its initial capacity after 50 cycles versus 92.6% for SEO-M1-2D. One electrolyte, SEO-M1-D+F was tested with both FEC and LiDFP. This cell had similar characteristics to both the FEC and LiDFP only cells: it only displayed a slight capacity decline in the first cycles, much

like the other LiDFP-containing electrolytes, but also showed a distinct capacity increase through the 150<sup>th</sup> cycle. It also had a higher initial capacity than the FEC-only cells, starting around 140 mAh g<sup>-1</sup> after its formation cycles. For the TMS-TMP<sub>a</sub> based LHCEs, introducing salt-type additives shows more efficacy in improving the long-term cycling performance than the organic carbonate-type additives.

## Conclusion and Outlook

### Conclusion

An LHCE employing an OTE diluent and solvating solvent mixture of TMS and TMP<sub>a</sub> was successfully demonstrated to be compatible with Gr||NMC811 cells at voltages up to 4.4 V. Cells with Li salt and carbonate solvent as electrolyte additives displayed long, stable cycle lives. While they displayed lower initial capacities than the conventional electrolyte, their long cycle lives mean that, at 250 cycles, they had better cycling stability than the conventional electrolyte. Of particular interest are cells employing the two Li salt additives LiPF<sub>6</sub> and LiDFP, which displayed excellent stability with the capacity retention of 95.9% and 93.4% after 200 cycles, respectively. These additives are ideal candidates for further investigation due to their positive effects on cell performance.

### Outlook

While these electrolytes have displayed their abilities to improve high voltage cycling in Gr||NMC811 cells, more research and development must be done to fully understand their mechanisms and the effects they have on cells. First, longer cycling is required to determine their cycle lives and whether they outperform the baseline electrolyte through 500 cycles. LHCEs' rate capability has, to date, been relatively poor compared to conventional

electrolytes due to their low ionic conductivities. To elucidate the effect of OTE diluent on the rate capability, variable rate cycling up to 5C should be performed. LHCEs have been very effective in high temperature cycling,[27] so tests at higher temperatures up to 60 °C should be performed. It is beneficial to fully understand the physical and chemical properties of the electrolytes, so further characterization of their viscosity and ionic conductivity should be performed. Further, as solvation structure is vital for understanding LHCE characteristics and performance in cells, ab initio molecular dynamic simulations (AIMD) could be performed to garner a more developed understanding of the effects of the additives on electrolyte structure. While several electrolyte formulations were tested, more combinations of electrolyte additives could also yield different and potentially improved results. One such approach could include changing the main electrolyte salt from LiFSI to alternatives such as Li bis(trifluoromethanesulfonyl) imide (LiTFSI) or Li tetrafluoroborate (LiBF<sub>4</sub>) which have been demonstrated as potential substitutes for LiPF<sub>6</sub> with high thermal and electrochemical stability.[28, 29]

Aside from cell performance, the impact of the higher flash point OTE diluent and LiFSI salt on battery safety must also be determined. The self-extinguishing time of the electrolytes can demonstrate the effects of the flame-retardant TMP<sub>a</sub> on flammability of the electrolyte.[10] Furthermore, overheating, short circuit, and nail penetration tests should be used to determine the safety performance of electrolytes in full cells.[30]

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