*Short Communication*

# LiPO$_2$F$_2$ as a LiPF$_6$ Stablizer Additive to Improve the high-temperature Performance of the NCM811/SiOx@C Battery

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Fluoroethylene Carbonate (FEC) is an indispensable additive to improve the cycle stability of silicon cathode, but the incompatibility between FEC and LiPF$_6$ seriously damages the high temperature performance of NCM811/SiOx@C. In this paper, the LiPO$_2$F$_2$, tris(trimethylsilyl) borate (TMSB) and tris(trimethylsilyl) phosphate (TMSP) were added as stabilizer to increase the compatibility between LiPF$_6$ and FEC at elevated temperatures. The visual experiments show that the traditional LiPF$_6$ stablizer additive, such as (TMSB) and (TMSP) additive, would accelerate the decomposition of LiPF$_6$ when FEC is present in the electrolyte solution. However, the introduction of LiPO$_2$F$_2$ additive can effectively inhibits the decomposition of LiPF$_6$, then obviously inhibits the side reactions and decrease the self-discharge of the NCM811/SiOx@C pouch cells under high temperature storage conditions. The high-temperature (45$^o$C) cycling performance of pouch cells with LiPO$_2$F$_2$ additive is 90.3% for 200 cycles and the swelling ratio is only 1.96% after storage at 55 $^o$C for 7days, which are all far superior to the contrast sample.

## 1. INTRODUCTION

In recent years, the demand for the energy density of lithium-ion power batteries has increased. According to the targets mentioned in the "Energy-Saving and New Energy Vehicle Industry Development Plan (2012-2020)" promulgated by China's State Council, the energy density of power battery module is projected reach to 300 Wh/kg by 2020. Currently, the active anode material of commercialized lithium ion battery is predominantly composed of graphite. The theoretical specific capacity of graphite is 372 mAh/g and the energy density is 100-120 Wh/kg[1], which is far from the

desired target value of 300 Wh/kg. In this context, silicon is a better choice for anode material as it has a lower probability of inducing surface Li precipitation during low-temperature and rapid charging processes due to its higher theoretical capacity (4212 mAh/g, $Li_{22}Si_5$)[2]. However, an interstitial solid solution is formed by embedding lithium into silicon, leading to a volume expansion ratio of up to 300% [3]. The significant volume effect causes the falling off of SEI film and self-cracking. The repair and reconstruction of SEI film consumes the active lithium continuously, eventually leading to the rapid reduction in capacity. It has been reported that fluoroethylene carbonate (FEC) can effectively alleviate the significant volume effect of silicon anode and significantly improve the cycling life[5]. Etacheri[4] studied the combination of FEC and SiNW (silicon nanowires) and found that after adding 10% FEC to the conventional electrolyte solution (1.0M $LiPF_6$ EC/DMC (1:1, wt.%), the retention rate in capacity of the SiNW/Li button battery after 30-week cycles at room temperature increased from 30% to 80%. Choi[5] reported an enhancement (68% to 89% increase in retention rate in 80-week capacity) in the ambient temperature cycling performance of silicon film/lithium half-battery when FEC was used as an additive. FEC can not only significantly improve the cycling performance of silicon-based anode, but also determine the cycling life of silicon-anode batteries[6].

Although FEC can significantly improve the room temperature cycling performance of battery with silicon-based anode, it has a deteriorating effect on the high-temperature performance. Dahn[7] examined the combination of Vinylene Carbonate (VC) and FEC with graphite anode by carrying out aging experiments. The irreversible capacity loss of the anode half-battery with FEC at 30°C was slightly lower than VC, indicating better film-forming properties of FEC over VC. However, at 60°C, the irreversible specific capacity loss with FEC is 60 mAh/g, which is much larger than that of the reference electrode and anode with VC. Similarly, Shin[8] investigated the combination of FEC and cathode $LiMn_2O_4$ (LMO) at room temperature and high temperature (55°C) through studies on the LMO/Li half-battery. At room temperature, the performance of cathode half-battery with FEC was similar to that of the blank control. The capacity stabilized at about 85% after a 50-week cycle. But at high temperature, the retention rate in capacity of the blank control was about 60% while the retention rate in the capacity of battery with FEC was less than 30%. It was hypothesized that the FEC in the electrolyte solution underwent an elimination reaction to form HF and VC at high temperature. The large amount of HF caused the excessive dissolution of metal ions at the cathode and damaged the anode SEI film [8, 9]. Choi et al.[10] proposed that the elimination reaction of FEC is caused by the catalytic role of $PF_5$, the high-temperature decomposition product of $LiPF_6$. In view of the extremely unstable $PF_5$, they replaced it with a strong Lewis acid tris(pentafluorophenyl)borane (TPFPB) to carry out simulations with FEC. After being stored at room temperature for 24 h, the color of the electrolyte solution was observed to vary from light yellow to dark black, and HF and VC were found in the decomposition product. The results confirm the hypothesis, although the researchers did not propose a solution.

In order to address the high-temperature incompatibility between FEC and $LiPF_6$, the thermal decomposition of $LiPF_6$ needs to be inhibited. The thermal instability of $LiPF_6$ mainly results from the equilibrium existing at high temperature:

$LiPF_6 \leftrightarrow LiF + PF_5$
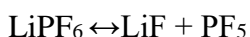
For ensuring that the electrolyte solution does not deteriorate by the decomposition products of $LiPF_6$, there are usually three approaches: 1) the addition of a catching agent for anion. Tasaki proposed

that an increased degree of dissociation of $LiPF_6$ in electrolyte solution can increase its thermal stability [11]. From theoretical calculations it was found that the addition of catching agent for anion can increase the distance between $Li^+$ and $PF_6^-$. This prevents the contact between $Li^+$ and F atoms and hinders the formation of LiF. Therefore, the "catcher" for anion can increase the thermal stability of $LiPF_6$ in electrolyte solution. The "catcher" for anions belongs to compounds capable of catching electrons and a common component is tris(trimethylsilyl) borate (TMSB). Boron being the central atom contains one empty 2p orbit that receives electrons, so it can be often used as stabilizer for $LiPF_6$ [12-14]; 2) The addition of catching agent for $PF_5$. Zhang proposed that the Lewis base can preferentially react with $PF_5$ in electrolyte solution and protect other effective components [15]. For instance, in tris(trimethylsilyl) phosphate (TMSP), the electron-donating capability of $-P=O$ and three strong electron-donating groups release the lone pair electrons of oxygen easily to make the TMSP a better catching agent for $PF_5$.

　　　　In this report, we aim to increase the compatibility between $LiPF_6$ and FEC, then improve the high-temperature performances of the NCM811/SiC battery in the presence of FEC. $LiPO_2F_2$ is the product of secondary hydrolysis of $LiPF_6$, may shifts the equilibrium in the direction of $LiPF_6$ formation [16]. Thereby, for the first time, we considered that addition of $LiPO_2F_2$ as a stabilizer to decrease the reaction between $LiPF_6$ and FEC at high temperatures, then enhancing the high-temperature performance of NCM811/SiOx@C based battery. Meanwhile, TMSB and TMSP were also studied together as comparative samples.

## 2. EXPERIMENTAL

### 2.1 Formulation of electrolyte solution

**Table 1.** the concrete compositions of electrolyte solutions

| Samples | Electrolyte content |
| --- | --- |
| STD | 1.0 M $LiPF_6$ EC/EMC/DEC (30:50:20) |
| FEC-STD | 1.0 M $LiPF_6$ EC/FEC/EMC/DEC (15:15:50:20) |
| TMSB | STD+0.5 wt.% TMSB |
| TMSP | STD+0.5 wt.% TMSP |
| $LiPO_2F_2$ | STD+0.5 wt.% $LiPO_2F_2$ |
| FEC-TMSB | STD-FEC+0.5 wt.% TMSB |
| FEC-TMSP | STD-FEC +0.5 wt. % TMSP |
| FEC-$LiPO_2F_2$ | STD-FEC +0.5 wt.% $LiPO_2F_2$ |

　　　　1.0 M $LiPF_6$ EC/EMC/DEC (30:50:20) as a standard (STD) electrolyte and 1.0 M $LiPF_6$ EC/FEC/EMC/DEC (15:15:50:20) (FEC-STD) electrolyte were purchased from Guangzhou Tinci high-performance and novel materials Co. Ltd (China) ($H_2O \leq 5.0$ ppm). The stabilizers additives for $LiPF_6$, such as TMSB, TMSP and $LiPO_2F_2$ (battery grade, $H_2O < 10$ppm), were purchased from Beijing Bailingwei Science and Technology Co. Ltd (China). The formulations of all electrolyte samples in the

paper were carried out in glove box filled with ultra-pure nitrogen ($H_2O$, $O_2$ <1 ppm). The concrete compositions of electrolyte solutions are shown in Table 1.

## *2.3 Thermal stability of electrolyte solution*

In order to determine the effects of additives on the thermal stability of electrolyte solution, 3 mL of the electrolyte solution (listed in Table 1) was extracted and placed in a thick glass tube (diameter of 10 mm, inner diameter of 2 mm). The top of tube was sealed and it was stored in an oil bath at 60 °C for 2-15 days. The variation in color of electrolyte solution was observed.

## *2.3 Liquid-injection, formation and fixing capacity for 5 Ah pouch cells*

93 wt.% NCM811 powders (Beijing Easpring Material Technology Co. Ltd), 3.4 wt.% acetylene black and 3.6 wt.% PVDF binder were coated uniformly on the Al foil as cathode. 92 wt.% $SiO_x$@C powders (S500, BTR Technology Co. Ltd), 3.4 wt.% acetylene black and 4.6 wt.% PVDF binder were coated uniformly on the Cu foil as anode. 5 Ah NCM811/$SiO_x$@C pouch cells were assembled with various electrolyte on battery assembly lines. The liquid-injection process for 5 Ah pouch cell was carried out in a glove box filled with ultra-pure nitrogen ($H_2O$, $O_2$ <1 ppm). The liquid amount injected was maintained at 4±0.1 g/Ah. After injection and encapsulation, the system was kept at room temperature for 12 h allowing the electrolyte solution to immerse the electrodes thoroughly. After the formation process at room temperature (charges to 3.4 V at 0.02 C then charges to 3.75 V at 0.08 C), the gas was removed and sealed again. The capacity was fixed at room temperature (charges to 4.25 V at 0.33 C, with a cutoff current of 0.05 C, then discharge to 2.5 V at the constant current of 0.33 C). With this, the formulation of battery core was completed.

## 3. RESULTS AND DISCUSSION

### *3.1 Thermal-aging test for the electrolyte solutions*

Fig.1 shows the photographs of the variations of four electrolyte solutions of STD and STD with 0.5 wt.% TMSB, TMSP, $LiPO_2F_2$ additive electrolyte after 15-day storage at 60 °C. It observes that the four electrolytes are all colorless transparent liquid. But when after storage at 60°C for 15 days, the color of STD electrolyte is changed remarkably from transparent to brownish black which indicates that the $LiPF_6$ salt in electrolyte has undergone a serious decomposition. Meanwhile, the color of STD electrolyte with 0.5 wt.% TMSB, TMSP or $LiPO_2F_2$ additives also gets more dark. From the appearance color comparison of STD, TMSB, TMSP and $LiPO_2F_2$ electrolytes before and after storage, when FEC isn't present in the electrolyte solution, all the additives (TMSB, TMSP, and $LiPO_2F_2$) can inhibit the decomposition of $LiPF_6$. Among the three electrolyte solutions, the inhibition effect of TMSB is more pronounced and $LiPO_2F_2$ is the most inefficient.
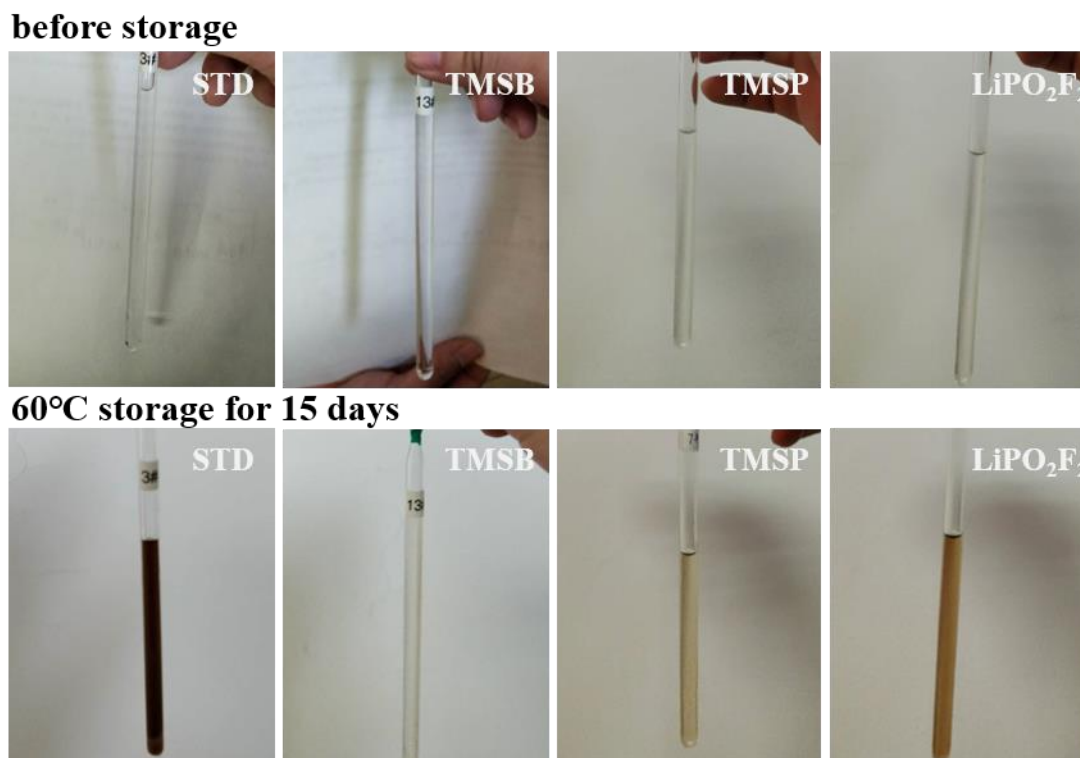
**Figure 1.** the variation of four electrolyte solutions in Table 1 (STD, TMSB, TMSP, LiPO$_2$F$_2$) before and after 15-day storage at 60°C

Fig.2 shows the photographs of the STD, FEC-STD, FEC-TMSB, FEC-TMSP, and FEC-LiPO$_2$F$_2$ electrolytes after storage at 60 °C for 1 and 3 days. In contrast, when 15 percent of FEC is added to the electrolyte solution, the thermal stability of electrolyte solution significantly deteriorated. This is evident from the brown color of the electrolyte solution containing 15 wt.% FEC (FEC-STD) after 3-day storage at 60 °C while the color of the electrolyte solution without FEC (STD) remained colorless and transparent, as shown in Fig. 2. Different from Fig. 1, after adding TMSB and TMSP to the electrolyte solution with FEC as a co-solvent, the electrolyte solution deteriorated more severely, exhibiting a black color. Additionally, the electrolyte solution became viscous and a large amount of insoluble solid LiF was observed at the bottom of the sealed tube. However, the FEC-LiPO$_2$F$_2$ electrolyte solution resulted in a lightest color, indicating that the introduction of LiPO$_2$F$_2$ additive can effectively inhibits the decomposition of LiPF$_6$ when the electrolyte solution containing 15 wt.% FEC.

Xianlin[9] observed that the fluorination of chloroethylene carbonate by a Lewis acid like SbF$_3$, resulted in the formation of a black viscous liquid and the target product FEC was not obtained; additionally, the product was completely carbonized under high temperature. Choi[10] used strong Lewis acid like tris(pentafluorophenyl) borane (TPFPB) to replace PF$_5$ to react with FEC for the simulations. After 24-hour storage at room temperature, the electrolyte solution was observed to transform from a light yellow to dark black color and the decomposition products contained HF and VC. The above facts indicate that FEC is unstable to Lewis acid and it can easily decompose to produce HF. At the same

time, as a halogenated hydrocarbon, FEC can easily undergo elimination reaction to form an alkene under the action of a base.
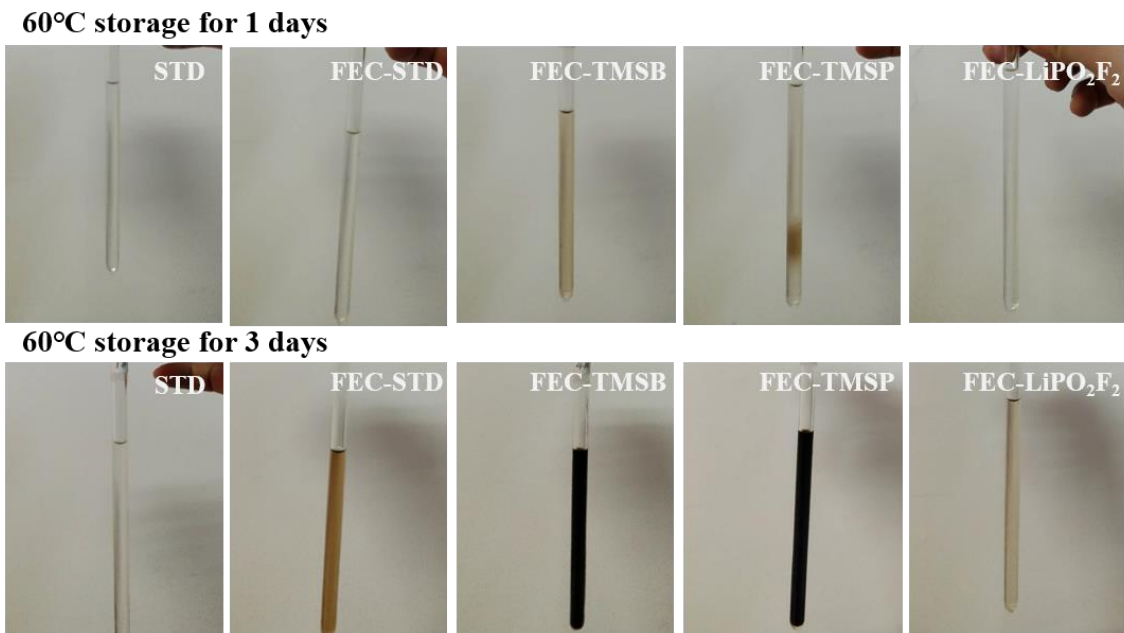


**Figure 2.** the variation of five electrolyte solutions in Table 1 (STD, FEC-STD, FEC-TMSB, FEC-TMSP and FEC-LiPO$_2$F$_2$) after storage at 60°C for 1 day and 3 days
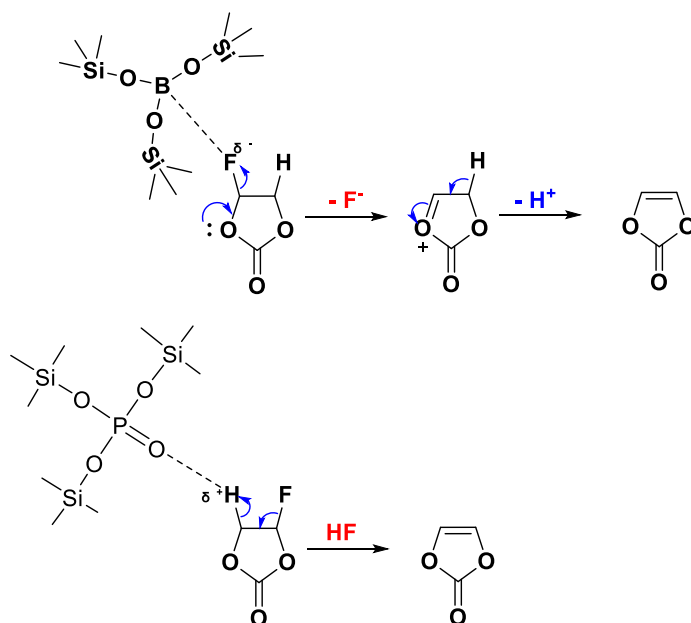


**Figure 3.** the mechanism for the reaction between TMSB/TMSP and FEC

Based on the above experimental facts and analysis, we propose high-temperature reaction mechanisms between TMSB/TMSP and FEC, as shown in Fig. 3. As for TMSB, the central boron atom with 2p empty orbits first complexes with the electronegative fluorine atom, then weakens the strength of C-F bond, which is ultimately equivalent to eliminating one HF from the molecule and generating

VC. For TMSP, the oxygen containing lone electron pair is complexed with a more acidic H atom, which eventually causes the elimination of HF from molecule and also generates VC[17,18]. The two additives eventually both lead to the decomposition of FEC and generate a large amount of HF. HF promotes the decomposition of $LiPF_6$, while $PF_5$ promotes the decomposition of FEC[20]. This eventually leads to the rapid deterioration and ineffectiveness of electrolyte solution and worsens the battery's high-temperature performance.

## 3.2 High-temperature storage

Figure 4(a) shows the electron microscope morphology of NCM811 materials. It can be seen that this NCM811 is a spherical structure with particle size of about 10-30um. Figure 4b is the charging and discharging curves of this material.  It observes that the initial discharging capacity of this materials at 0.1 C is 208.3mAh/g. After initial 3 cycles at 0.1C, we tested the cycling performance at 0.5 C, it is found that the initial discharge capacity is 190.2mAh/g， and after 200 cycles, this capacity decreased to 165.3mAh/g， the capacity retention is about 86.9%. These test results show that the NCM811 cathode material we choose is relatively stable.
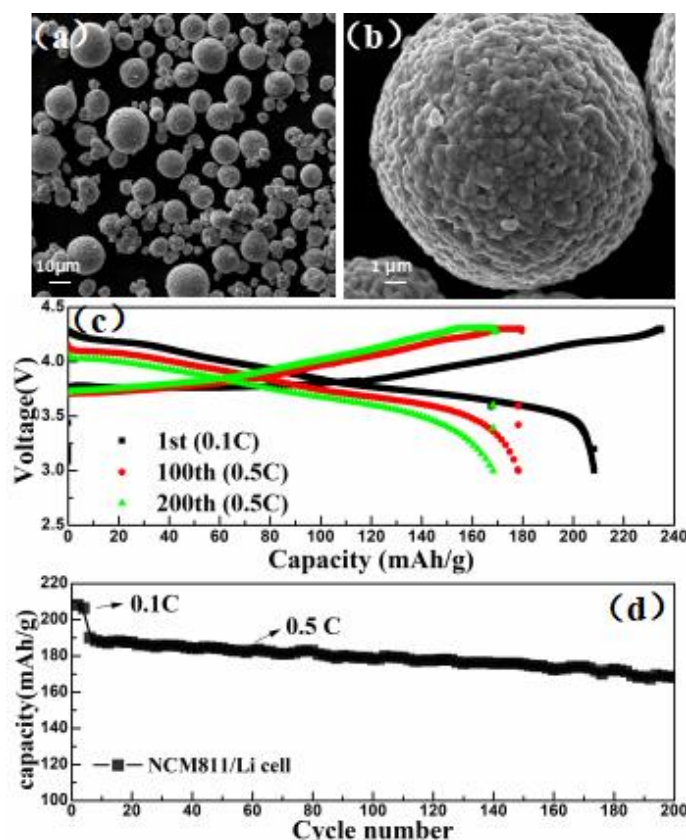


**Figure 4.** (a) the SEM image of the NCM811cathode materials, (b) the charge-discharge profile of NCM811/Li half cells, (c) cycling performance of the NCM811/Li half cells

In order to study the effect of additives on the high temperature storage performance, the NCM811/SiO$_x$@C pouch cells were place in a constant temperature oven and were stored for 7 days at

55 °C under full charge condition (OCV, 4.25V). Fig. 5a shows the photograph of the NCM811/SiO$_x$@C pouch cells after the 7 days storage at 55°C. It is found that a noticeable gas expansion is observed in the pouch cells with FEC-STD, FEC-TMSB, FEC-TMSP electrolyte. In contrast, there is no obvious gas bubbling phenomenon in the cell with FEC-LiPO$_2$F$_2$ electrolyte. Meanwhile, we measured the variations in volume of the NCM811/SiO$_x$@C pouch cells after the 7 days storage at 55°C. The test results are shown in Fig. 5b. It observes that the swelling ratio of the cell with FEC-STD, FEC-TMSB, FEC-TMSP, FEC-LiPO$_2$F$_2$ electrolyte is 5.91%, 6.36%, 7.77% and 1.96%, respectively. Because gas is mainly produced by electrolyte decomposition, hence this results indicates that the TMSB and TMSP additive would accelerate the electrolyte decomposition when FEC is present in the electrolyte solution. However, the introduction of LiPO$_2$F$_2$ additive can effectively inhibits the decomposition of electrolyte solution when the electrolyte solution containing 15 wt.% FEC.
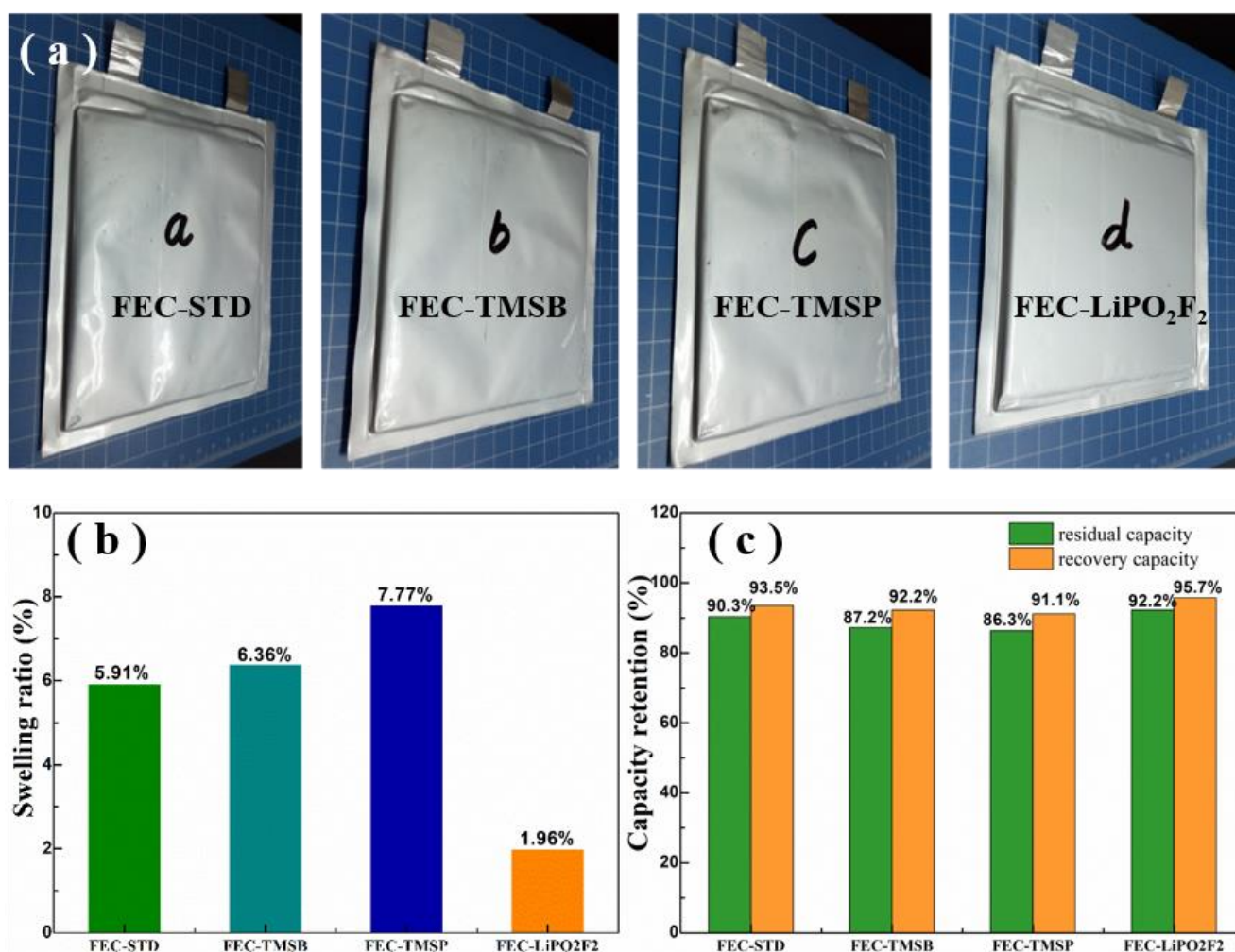


**Figure 5.** (a) the photograph of the NCM811/SiOx@C pouch cells after the 7 days storage at 55 °C, (b) the swelling ratio of the pouch cells after 7-day storage at 55°C, (c) The residual and recovery capacity of the pouch cells after 7-day storage at 55°C

After the 7 days storage at 55°C, the NCM811/SiO$_x$@C pouch cells were discharge to 3.0 V and the residual capacity retention were shown in Fig. 5c. It notes that the residual capacity retention of the cell with FEC-STD, FEC-TMSB, FEC-TMSP, FEC-LiPO$_2$F$_2$ electrolyte is 90.3%, 87.2%, 86.3% and 92.2%, respectively. Then, the NCM811/SiO$_x$@C pouch cells were charge to 4.25 V and discharge to 3.0 V, the recovery capacity retention can be obtained. As shown in Fig. 4c, the recovery capacity retention of the cell with FEC-STD, FEC-TMSB, FEC-TMSP, FEC-LiPO$_2$F$_2$ electrolyte is 93.5%, 92.2%, 91.1% and 95.7%, respectively. Accordingly, the irreversible capacity loss ratio is 6.5%, 7.8%, 8.9% and 4.3%, respectively. In general, the self-discharge of the battery mainly results from the side reaction between the anode and the electrolyte solution [19], so the battery with LiPO$_2$F$_2$ additive has the highest residual capacity and recovery capacity, indicating that LiPO$_2$F$_2$ additive can effectively inhibits the side reactions and decrease the self-discharge of the NCM811/SiO$_x$@C pouch cells under high temperature storage conditions.

*3.2 High-temperature cycle*

Fig. 6 shows the high-temperature (45 °C) cycling curve of the NCM811/SiO$_x$@C pouch cells (5 Ah) with the FEC-STD, FEC-TMSB, FEC-TMSP and FEC-LiPO$_2$F$_2$ electrolyte solutions (3.0-4.25V, 0.5C/0.5C). Among the four electrolyte solutions, FEC-STD is the reference solution and FEC as co-solvent replaces 15% of EC in order to ensure the long-term performance of silicon anode. It is observes that the initial capacity of the cell with FEC-STD electrolyte is 205.2 mAh/g, the remaining capacity is 168.8 mAh/g and the capacity retention rate is about 82.2% after 200 cycles. When 0.5wt% TMSB and TMSP additives added in the FEC-STD electrolyte, the initial capacity of the cell is decreased to 203.7 and 204.1 mAh/g, respectively. After 200 cycles, the remaining capacity is only 161.6 mAh/g (capacity rentetion ~79.3%) and 158.8 mAh/g (capacity rentetion ~77.8%). It indicates that the TMSB and TMSP additive, who was reported as electrolyte stabilizers for LiPF$_6$ [17, 18], did not work well when large amounts of FEC exist in electrolytes. This is consistent with the results of previous visualized experimental results. However, the initial capacity of the cell with FEC-LiPO$_2$F$_2$ electrolyte is 207.9 mAh/g, the remaining capacity is 187.7 mAh/g and the capacity retention rate is about 90. 3% after 200 cycles, which indicates that the LiPO$_2$F$_2$ additive can diminish the high-temperature incompatibility between LiPF$_6$ and FEC, but cannot completely eliminate it.
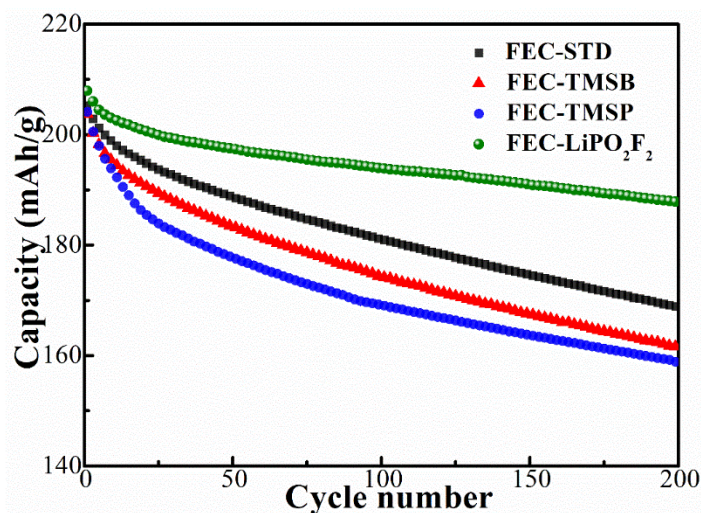
**Figure 6.** The high temperature (45 °C) cycling performance of the NCM811/SiO$_x$@C pouch cells (5 Ah) with the FEC-STD, FEC-TMSB, FEC-TMSP and FEC-LiPO$_2$F$_2$ electrolyte solutions (3.0-4.25V, 0.5C/0.5C)

## 4. CONCLUSIONS

In this paper, the LiPO$_2$F$_2$, TMSB and TMSP were added as stabilizer to increase the compatibility between LiPF$_6$ and FEC at high temperatures. The visual experiments show that the traditional LiPF$_6$ stablizer additive, such as TMSB and TMSP, are observed to reduce the thermal stability of the aforementioned electrolyte solution. This is due to the fact that the two additives can react with FEC at high temperature to form HF and VC, which worsens the high-temperature compatibility of LiPF$_6$ and FEC. However, the introduction of LiPO$_2$F$_2$ additive can effectively inhibits the decomposition of LiPF$_6$, then obviously inhibits the side reactions and decrease the self-discharge of the NCM811/SiOx@C pouch cells under high temperature storage conditions. The high-temperature (45°C) cycling performance of pouch cells with LiPO$_2$F$_2$ additive is 90.3% for 200 cycles and the swelling ratio is only 1.96% after storage at 55 °C for 7days, which are all far superior to the contrast sample.

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