

# The Optimal Amount of Lithium Difluorophosphate as an Additive for Si-Dominant Anodes in an Application-Oriented Setup

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Fluoroethylene carbonate (FEC) and vinylene carbonate (VC) are considered the most effective electrolyte additives for improving the solid electrolyte interphase (SEI) of Si-containing anodes while lithium difluorophosphate (LiDFP) is known to improve the interphases of cathode materials and graphite. Here, we combine VC, FEC, and different amounts of LiDFP in a highlyconcentrated electrolyte to investigate the effect on Si-dominant anodes in detail. Cycle life tests, electrochemical impedance spectroscopy and rate tests with anode potential

## Introduction

Efforts have been expanded regarding the development of high-performance lithium-ion batteries (LIBs) in the last years, as the demand continues to grow, especially for the application in electric vehicles.<sup>[1,2]</sup> State-of-the-art LIBs mostly contain graphite anodes, which exhibit high capacity retention during long-term cycling.<sup>[2,3]</sup> However, the theoretical capacity of graphite is only 372 mAh g<sup>-1</sup>.<sup>[3]</sup> To further increase the gravimetric and volumetric capacity of future-generation LIBs, new anode materials are required.<sup>[1–4]</sup> Si is considered one of the

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© © 2023 The Authors. ChemSusChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes. monitoring were conducted in Si/NCM pouch cells. The results reveal that adding LiDFP to the electrolyte improves all performance criteria of the full cells, with a concentration of 1 wt% being the optimal value for most cases. Post-mortem analyses using scanning electron microscopy and x-ray photoelectron spectroscopy showed that a more beneficial SEI film was formed for higher LiDFP concentrations, which led to less decomposition of electrolyte components and a better-maintained anode microstructure.

most promising next-generation anode materials, as it provides a very high specific capacity of 3579 mAhg<sup>-1</sup> at room temperature, abundance and low operating potential.<sup>[4,5]</sup> However, Si materials suffer from a high volume expansion of more than 300% during lithiation, which causes material pulverization and loss of electrical contact to the current collector. The volume expansion causes cracking of the existing solid electrolyte interphase (SEI), exposing new particle surfaces to the electrolyte and thus forming new SEI during cycling. This accumulated SEI growth starts with a low first cycle efficiency and results in a low cycling stability.<sup>[4,6]</sup> To mitigate these problems, many efforts have been made to design the Si structure.<sup>[4,5]</sup> Recently, Maroni et al. presented a microsized Si material with nanopores, which is capable of stable cycling in full pouch cells (FPCs) with industrially relevant areal capacities.<sup>[6]</sup> The identical material was used in this study (supplied by E-magy B.V., Netherlands).

Despite the material design, a factor with a high influence on the electrochemical performance of Si anodes is the electrolyte. Small amounts (in the range of up to 10 wt.%) of chemical compounds mixed in the electrolyte are referred to as additives and can greatly affect cell performance.<sup>[7-9]</sup> During the first formation cycle, such additives are reduced on the anode surface and their reaction products contribute to the SEI formation.<sup>[7,8]</sup> The most effective additives for Si anodes have been proven to be vinylene carbonate (VC)<sup>[10,11]</sup> and fluoroethylene carbonate (FEC).<sup>[12,13]</sup> These additives have been widely studied and are known to improve the SEI composition for Sibased anodes by their reaction products and partially replacing those of the typically-used solvent ethylene carbonate (EC).<sup>[13]</sup> Another common additive is lithium difluorophosphate (LiDFP) which has been extensively studied on cathode materials and graphite.<sup>[14]</sup> In combination with VC, LiDFP is known to improve the rate capability of graphite because it forms an SEI with high ionic conductivity.<sup>[15]</sup> Regarding the effect of LiDFP on Si-based anodes, there are few studies that indicate a benefit in different electrochemical characteristics, such as first cycle coulombic efficiency, capacity retention, and rate capability.  $^{\scriptscriptstyle [16,17]}$  In this work, we investigated for the first time the effect of LiDFP additivities on Si-based anodes in an application-oriented setup. To achieve industrially-relevant conditions, we used a bi-layer pouch cell format, thin separators and high areal capacities (~3 mAh cm<sup>-2</sup>) for the electrodes. A highly-concentrated electrolyte optimized for Si anodes was used as a practical baseline, to which we added different concentrations of LiDFP (ranging from 0.5 wt% to 2 wt%, within the solubility limit). We conducted detailed electrochemical tests, including cycle life evaluations, rate tests and electrochemical impedance spectroscopy (EIS). For the latter two, we employed a reference electrode (RE) based on lithium iron phosphate (LFP), a design we have previously validated for EIS on graphite anodes.<sup>[18,19]</sup> In this work, the RE allowed us to monitor the Si anodes within the full cell configuration, enabling a precise examination of the influence of LiDFP on SEI formation. Our results show that all LiDFP concentrations enhance performance compared to the similar electrolyte without LiDFP, with a peak at the 1% concentration. A higher concentration of 2% exhibited slightly superior performance at low C-rates, but suffered at high rates. Post-mortem analyses, using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), proved that the thinnest and chemically most favorable SEI was formed at the 1% concentration.

### **Results and Discussion**

## Capacity and first cycle coulombic efficiency evaluation in half-cell configuration

To study the influence of LiDFP on the first cycle coulombic efficiency, half-coin cells were built with the Si anode as the working electrode, and Li-metal as the counter electrode (see the experimental section for more details). The capacity was limited to 2000 mAhg<sup>-1</sup> to preserve the crystalline, nanoporous Si structure.<sup>[6]</sup> Figure 1 shows the first cycle coulombic efficiencies and discharge capacities obtained for the four different LiDFP contents in the electrolyte. Please note that the error bars for these and all following measurements originate from the natural deviations between identically constructed cells for each electrolyte. These deviations can arise due to factors such as minor differences in cell assembly or manufacturing tolerances. Similarly to the previously reported work by Li et al.,<sup>[17]</sup> we observed an increase in the first cycle efficiencies when the LiDFP concentration was increased from 0 to 1% (Figure 1a, 0% LiDFP: 84.8  $\pm$  0.3 %; 0.5 % LiDFP: 87.7  $\pm$  0.5 %; 1 % LiDFP: 88.7  $\pm$ 0.3%). This increase suggests that LiDFP helps to optimize the SEI formation in the first cycle, reducing side reactions with other electrolyte components. Interestingly, the first cycle coulombic efficiency is lower for the electrolyte containing 2% LiDFP ( $86.2\pm0.17\%$ ) is observed, indicating saturation of the beneficial effects on the SEI observed around 1% LiDFP. The contrary was observed by Li et al.<sup>[17]</sup> in half-coin cells using



**Figure 1.** (a) Evaluation of first cycle efficiencies at C/20 and (b) the discharge capacities of Li | Si at different LiDFP concentrations in half-cell configuration. The cells with 0% of LiDFP exhibit the lowest coulombic efficiencies and capacities in the first cycles, while those with 1% of LiDFP show the highest values.

electrodes containing Si nanoparticles. The complexity arises from the fact that our electrolyte is highly concentrated and contains other additives like VC and FEC. This suggests that solubility effects and interaction with the other additives could influence the trend. These effects are discussed in more detail in the following sections. The discharge capacities for the first 10 cycles are shown in Figure 1b. As the lithiation capacity is always limited to 2000 mAhg<sub>si</sub><sup>-1</sup>, the delithiation capacity is proportional to the coulombic efficiency of the corresponding cycle. In the first cycles, the delithiation capacities are higher as the LiDFP content increases up to 1%, while the values for 2%



are slightly below those for 0.5% LiDFP. The electrolyte without LiDFP exhibited the lowest capacities in the first 4 cycles. Thus, the trends are similar to the first cycle efficiencies and can be assigned to the same effects.

#### Cycle life evaluation in Si | NCM pouch cells

In the next step, the long-term cycling stability of Si | NCM in full-cell configuration using electrolytes with different LiDFP concentrations was evaluated. As shown in Figure 2a, no apparent capacity differences for the various additive concentrations are visible in the first cycles. Though the influence of LiDFP additives on the cycling stability becomes apparent after 60 cycles. The capacity retention increases from 63.9% at 0%

LiDFP to 65.8%, 72.1% and 69.6% after 100 cycles for the concentrations of 0.5%, 1% and 2% LiDFP, respectively (all related to the 1 C cycles). This finding provides further evidence for the positive impact of LiDFP on the SEI formation on Si, benefiting long-term cycling performance. The capacity retention is improved by ~13% from 0% to 1% of LiDFP, which is a lower benefit than results shown in previous studies.<sup>[16,17]</sup> However it is crucial to consider the key differences in our experimental setup. Unlike the previous studies, we use a more challenging full cell configuration and our baseline electrolyte is already optimized for Si anodes, which limits the additional benefit caused by LiDFP. Cells containing 2% LiDFP face accelerated degradation around the 80<sup>th</sup> cycle resulting in a decrease of 1 C cycle stability compared to cells with 1% LiDFP. However, if we consider the capacity retention related to the C/



**Figure 2.** Discharge Capacities (a), corresponding SOH after 100 cycles related to 1 C (b), and internal resistances (c) measured in FPCs with different LiDFP concentrations. An improvement in all metrics can be seen by addition of LiDFP. While the cells with 1% showed the highest capacity retention related to the 1 C cycles and the lowest resistance, those with 2% exhibited the highest capacity retention related to the C/3 cycles.

3 cycles, cells containing 1% LiDFP have lower values compared to the cells with 2% LiDFP (75.3% vs 78.9%, see final cycle in Figure 2a). Our hypothesis for this observation is that higher concentration of 2% LiDFP leads to a high electrolyte viscosity, increasing the Li-ion diffusion coefficient and thus decreasing the cell performance at high C-rates. The rate test results shown later in this work give further indication for this assumption.

As shown in Figure 2c, the direct current internal resistance (DCIR) exhibits a corresponding growth during cycling pointing towards the same degradation mechanism; the cells without LiDFP exhibit the highest DCIR, while the lowest was observed for the cells with 1% of LiDFP.This phenomenon is more pronounced for the last DCIR measurement after the 100th cycle, which suggests that LiDFP does not only form more beneficial interphases in the beginning, but these are also more stable throughout cycling, keeping the cell resistance lower. It is essential to note that the DCIR still exhibits significant growth for the LiDFP-containing cells during cycling, showing that they remain susceptible to the typical accumulated SEI growth of Si anodes. However, a clear improvement caused by LiDFP can be seen. Since the DCIR was measured at 1 C, their trend for the different LiDFP concentrations is in agreement with the obtained discharge capacities at this C rate (lower resistance relates to higher capacity retention).

## Morphological and chemical characterization of Si anodes cycled in full cells

To gain more insight into the microstructure of the anodes, post-mortem analyses were performed. After the cycle life tests were completed, representative cells for the different LiDFP concentrations were disassembled and the cycled Si anodes were investigated. Post-mortem SEM cross-section images were recorded (see Figure 3).

Figure 3c and d show the anodes obtained from the cells that contained 1% and 2% of LiDFP, respectively. These anodes have very plain surface and only narrow cracks throughout their structure. Thus, it can be stated that the microstructure of these anodes remained mostly intact during cycling, which contributes to their high capacity retention. In contrast, the anodes from the cells containing 0% and 0.5% LiDFP (Figure 3a, b) show much larger cracks and less homogenous surface with higher roughness. A partial delamination of the material close to the current collector is visible. Such delamination may also be the reason for the very rough surface of these post-mortem anodes. These observations match with the lower capacity retentions measured for the corresponding cells. Our hypothesis for the differences in the anode microstructure is that higher LiDFP concentrations contribute to a robust SEI, which is mechanically more stable towards to the volume expansion of the Si material. Thus, less accumulated SEI growth occurs on the Si surface, which helps to maintain the structure of the electrode. We further studied the cycled anodes by using XPS to obtain information about the elemental composition of the formed SEI. Figure 4 shows the elemental concentrations of



Figure 3. Cross-sectional SEM images of post-mortem Si anodes obtained from cells containing 0% (a), 0.5% (b), 1% (c) and 2% (d) of LiDFP in the electrolyte. The anodes from cells with low LiDFP content exhibit much larger cracks in their microstructure and a rougher surface originating from excessive SEI formation.

ChemSusChem 2023, e202301153 (4 of 10)



**Figure 4.** Elemental concentrations of fluorine (a) and carbon (b) detected by XPS on the post-mortem anodes obtained from the cells with different LiDFP concentrations.

fluorine (F) and carbon (C) measured in the corresponding samples. The anodes obtained from cells with LiDFP show a significant increase in F concentration (Figure 4a), demonstrating that LiDFP contributes to an F-richer SEI. The highest F concentration was found in the anode from the cell containing 1% LiDFP, which also exhibited the best capacity retention related to 1 C. Figure 5a shows the corresponding F 1s spectra of Si anodes cycled in full cells using electrolytes with different LiDFP concentrations.

The higher F content originates from an increase in LiF in the SEI, which exhibits the highest proportion in the anode exposed to 1% of LiDFP. This finding is in line with previous studies, which reported an elevated amount of LiF in the SEI of Si anodes obtained from cells containing LiDFP.<sup>[16]</sup> Species containing phosphorous-F-bonds, such as Li<sub>x</sub>PF<sub>v</sub> and Li<sub>x</sub>PO<sub>v</sub>F<sub>z</sub> are known as decomposition and hydrolysis products of LiPF<sub>6</sub>. [15] Their amount is significantly lower in the SEI originating from 1% LiDFP compared to the other samples. This suggests that medium amounts of LiDFP in the electrolyte can help suppressing the decomposition of LiPF<sub>6</sub>. Additionally, higher LiDFP concentrations reduce the C content and thus the organic part in the SEI as shown in Figure 4b. Comparing the C 1s spectra (Figure 5b), revealed that reduced amounts of C=O and O-C=O species are observed in the samples with higher LiDFP content, which can be assigned to EC decomposition products, namely lithium alkyl carbonates.<sup>[20]</sup> Meanwhile, C-O species representing the polymerization products of VC<sup>[21]</sup>, exhibit roughly the same amounts in all samples. These findings indicate that LiDFP can help suppressing the decomposition of EC, while the reactions of the more beneficial SEI additive VC are only very slightly affected. In the Si 2p spectra, the peaks correlated to lithiated Si ( $Li_x$ Si) and SiO<sub>2</sub><sup>[10,22]</sup> are much lower in the anodes from cells containing LiDFP. The lowest intensities were measured in the anode exposed to 1% of LiDFP. These Si species can be assigned to Si material surface, which is visible in the XPS due to cracks in the SEI. Thus, this observation supports our hypothesis drawn from the SEM images that the SEI formed in the presence of LiDFP, especially by an amount of 1%, is more stable and consequently exhibits smaller and fewer cracks. In summary, the post-mortem analysis studies demonstrate that higher concentrations of LiDFP form chemically more favorable SEIs, suppressing the decomposition of LiPF<sub>6</sub> and EC, reducing cracks and better maintaining the microstructure of the anode. In our case, 1% of LiDFP seems to be the optimal amount, as the highest LiF content and the lowest amount of unfavorable decomposition products were obtained in the SEI composition.

#### Electrochemical impedance spectroscopy (EIS) measurements

Figure S1 shows the impedance spectra of the Si anodes measured at five states of charges (SoCs) with help of our owndesigned RE<sup>[18,19]</sup> in the FPCs. Especially at the SoCs of 0 and 25, a significant difference is visible in the mid-frequency semicircle between the cells with low amounts (0% and 0.5%) and higher amounts of LiDFP (1% and 2%). This semicircle can be assigned to the charge-transfer resistance  $(R_{ct})$  of the anode, mainly originated by the SEI.<sup>[23,24]</sup> An equivalent circuit model (ECM, shown in Figure 6c, which was simplified from literature models<sup>[24,25]</sup>, was used to quantify the  $R_{ct}$  values for the different additive concentrations at the five SoCs. The results are shown in Figure 6a, b. For all LiDFP concentrations,  $R_{ct}$  decreases with higher SoCs. This is a known phenomenon and can be assigned to a higher amount of lithium alkoxide (ROLi) molecules appearing in the SEI at higher SoCs, which facilitate Li-ion transport.  $^{\sc{[26]}}$  At all SoCs, the cells with 0 % and 0.5 % of LiDFP exhibit higher  $R_{\rm ct}$  values than their counterparts with 1% and 2% of LiDFP. For all.

conditions except SoC 0, we obtain similar  $R_{\rm ct}$  values for samples containing 1% and 2% of LiDFP Note that the charge rate to reach the corresponding SoCs was set to C/3, a rate at which 2% LiDFP exhibited the best capacity retention. This may explain their difference at SoC 0, where 2% LiDFP accounts for a lower  $R_{\rm ct}$ .

In total, the findings from the EIS measurements match well with the post-mortem analysis and the cycling performance of the LiDFP concentrations, confirming that the most favorable SEI was formed in cells with 1% and 2% of LiDFP. Major differences in cell performance start to surface at higher cycling rates underlying beneficial performance of moderate LiDFP content.

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Figure 5. High resolution XPS spectra of (a) F 1s, (b) C 1s and (c) Si 2p of Si anodes cycled in full cells with different concentrations of LiDFP in the electrolyte.

### **Rate Tests**

Figure 7 shows the rate capability of Si anodes in FPCs with different LiDFP concentrations. No significant differences can be observed in the capacities at charge rates until 4 C. When increasing the LiDFP concentration in the electrolyte from 0% to 1%, the cells exhibit slightly lower capacity retentions at 5 C (Cycle 17 related to cycle 1:  $57.1 \pm 0.2\%$  for 0% LiDFP,  $56.38 \pm 0.09\%$  for 0.5% LiDFP,  $54.6 \pm 1.2\%$  for 1% LiDFP). However, these differences are minor compared to the cells with 2% of LiDFP: They show clearly the lowest capacity retention in the findings from the cycle life test and supports our hypothesis drawn there: LiDFP is reaching its solubility limit in the 2% concentration and thus increasing the electrolyte viscosity. This

decreases the Li-ion diffusion coefficient and decreases the performance specifically at high charge rates<sup>[27]</sup>. The slightly lower capacity retentions at 5 C from the cells with 0.5% and 1% LiDFP can be assigned to the similar effect in less pronounced form. We monitored the anode voltages during the rate test with the help of our implemented RE. The complete capacity voltage curves are shown in Figure S2 (Supplementary Information). In these graphs, no significant differences can be observed in the bigger picture. However, as illustrated in Figure 8a, a closer look at the very beginning of the charge half-cycles shows interesting correlation between the voltages measured in this area and the LiDFP concentration. This phenomenon becomes more significant at higher charge rates. Such a voltage drop at the beginning of charge half-cycles can be observed in voltage profiles reported for electrolyte studies



**Figure 6.**  $R_{\rm ct}$  values of the Si anodes obtained from modeling the impedance spectra recorded from the cells with different LiDFP concentrations at SoCs of 0 (b) and 25–100 (a). For clarity, the  $R_{\rm ct}$  values obtained at SoC 0 were plotted separately. The fits were obtained using the anode ECM (c). The values confirm that higher LiDFP contents reduce the charge-transfer resistance of the anode.

in Si/Li half cells, although it is much less pronounced.<sup>[28]</sup> In contrast to our work, these studies applied lower C rates and did not explain this phenomenon specifically, so its origin remains unclear. In order to elucidate and quantify this potential drop, we extracted the minima of the Si voltage curves measured at different charge rates for the different LiDFP concentrations. The values are shown in Figure 8b. A clear trend is visible for all charge rates and the deviations are small, so the dip being a measurement artefact from our RE can be excluded. No significant differences can be observed in the measured anode voltage minima at moderate charge rates until 1 C. At all higher rates, the minima are the lowest for the cells without LiDFP, which is equivalent to their drop being the most

significant. For the cells containing LiDFP, the 1% concentration exhibits the highest minima or the least pronounced drop, followed by 2% and 0.5%.

Due to the clear electrolyte-dependency and the linear decrease of the voltage drop at higher C rates, we assign it to the internal cell resistance, which determines the voltage in the very beginning of the curves. Note that the trend visible in Figure 8b is identical with the one seen in the DCIR values shown in Figure 2c. Given this assumption and our results, we can state that the electrolyte containing 2% of LiDFP is less beneficial than 1% at higher charge rates due to the increased cell resistance, which originates not only from the SEI, but more from the electrolyte itself.

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Figure 7. Discharge Capacities obtained in FPCs during the rate tests. Charge rates are displayed. The cells containing 2% of LiDFP exhibited significantly lower capacity retention at 5 C than the other concentrations.



Figure 8. Excerpt from the Si anode voltage profiles at 5 C for the different LiDFP concentrations (a) and voltage minima from all profiles plotted against the corresponding charge rate (b). The potential obtained from the LFP RE was corrected with  $U_{LFP vs Li/Li^+} = 3.428$  V. The "voltage drop" at the beginning is clearly electrolyte-dependent and correlates almost linearly with the applied charge rate.

## Conclusions

In this work, we investigated the effect of different LiDFP concentrations as an electrolyte additive on the SEI formation and cycling performance of Si-dominant anodes in an industryoriented setup. Concentrations of 0.5%, 1% and 2% of LiDFP were added to an electrolyte containing LiPF<sub>6</sub>, FEC and VC. For comparison, a similar electrolyte formulation without LiDFP was used. Electrodes were prepared out of a nanoporous Si material with industrially relevant areal capacities of ~3 mAh cm-2 and tested in Si | Li half cells and bi-layer Si | NCM, including cycle life tests and rate tests as well as EIS measurements with a reference electrode. All LiDFP concentrations exhibited increased cycle life and reduced cell impedance compared to the cells without additive. Of all concentrations, the cells containing 1% of LiDFP showed the best first cycle efficiency, capacity retention at 1 C and a reasonable rate capability. When increasing the LiDFP concentration to 2%, these values

ChemSusChem 2023, e202301153 (8 of 10)



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decreased significantly, which we assign to a slowed Li-ion diffusion caused by the high electrolyte viscosity, thus increasing the cell resistance. However, at C/3, the cells with 2% of LiDFP exhibited the best capacity retention. Post-mortem analyses conducted on the cycled anodes via XPS and SEM confirmed that 1% of LiDFP in the electrolyte led to the formation of the LiF-richest SEI with the lowest amount of unfavorable decomposition products and the least severe cracks, being responsible for a better-maintained microstructure of the Si anode. Our findings prove that LiDFP can provide benefits as an electrolyte additive for Si anode performance in full cells when applied in medium concentrations. 1% of LiDFP seems to be the optimal trade-off for most industrially relevant systems, as increasing the concentration further does not give significant benefits for most criteria, but significantly decreases the rate capability. However, for applications involving only lower C rates, 2% of LiDFP may be the concentration of choice.

## **Experimental Section**

#### **Electrode preparation**

For the electrode preparation Si, polyacrylic acid, graphite and C45 with a weight ratio of 80:10:5:5 were homogenously blended in water using a centrifugal mixer. The slurry was cast onto Cu foil using a doctor blade (BYK) and a casting speed of  $1 \text{ cm s}^{-1}$ . The casted electrodes were dried at 65 °Cat ambient pressure for 15 min and afterwards for another 45 min at 65 °C under vacuum. Target loadings of the electrodes were between 1.48 and 1.52 mg<sub>si</sub> cm<sup>-2</sup>.

#### Half-coin cell assembly and electrochemical testing

The anodes were tested using a CR2016 cell format. Five identical cells were prepared for each electrolyte, using 15 mm-diameter circular punches from the readily-prepared Si anode as the positive electrode. 16 mm-diameter circular punches of Li metal foil (China Energy Lithium) were used as the negative electrode, separated by 18 mm circular punches of ceramic-coated polyethylene separator (SKI, 21  $\mu$ m thick). A stainless steel spacer (16 mm diameter, 1.2 mm thick) was used to apply enough pressure to the electrodes. Each cell was filled with 100  $\mu\text{L}$  each of electrolyte, which contains 1.2 M LiPF<sub>6</sub>, EC, ethyl methyl carbonate, dimethyl carbonate, 1 wt.% VC, 7 wt.% FEC and the corresponding amount of LiDFP (0-2 wt.%). The cells were sealed by a hydraulic crimper and allowed to rest for 2 h. Subsequently, they were galvanostatically cycled using the CTS from Basytech at 25 °C between 0.01 and 1.5 V versus Li/Li<sup>+</sup> for one C/20 forming cycle, followed by one C/10 cycle, followed by 15 cycles at C/3. In order to preserve the nanoporous Si structure, 2000 mAhg<sub>si</sub><sup>-1</sup> was set as the nominal cell capacity<sup>[6]</sup>. Discharging was limited to this nominal capacity (even if the voltage limit was not reached there) and the before-mentioned C-rates also refer to

#### Full Pouch Cell Assembly and Cycle Life Tests

Double-sided cathodes with a loading of  $\sim$ 3.0 mAh cm<sup>-2</sup> and a formulation of 94.5% commercial NMC811, 1 wt.% C65 Carbon, 1 wt.% multi-walled carbon nanotubes, and 3.5 wt.% polyvinylidene fluoride were used as the positive electrodes. One cathode per cell was placed in between two Si anodes, separated by the identical separator used for the half-coin cell setup. The capacity of the Si

anodes in FPCs was also limited to 2000 mAhg<sup>-1</sup>, steered by the negative to positive electrode ratio of the cells. Three identical cells were prepared for each electrolyte. The coated electrode area was 11.34 cm<sup>2</sup> for the Si anodes and 10 cm<sup>2</sup> for the NMC811 cathodes. After filling with 0.5 mL of the identical electrolyte used in the half coin cells, the pouch cells were pressed between acrylic glass plates using 3 foldback clamps and allowed to rest for 2 h. For formation, the cells were galvanostatically cycled at 25 °C between 2.8 and 4.2 V for two C/10, two C/5, and three C/3 cycles, subsequently. For the long-term cycling evaluation, 1 C cycles were applied after the formation protocol until a state of health (SOH) of 80% was reached. After each charge step at constant current (CC), a constant voltage phase was applied with a cutoff current equal to 10% of the preceding CC. At the beginning of the cycling program and after every 50 cycles, a C/3 checkup cycle was applied. These checkup cycles included the evaluation of the current state of health (SOH) of the cell and a pulse test to determine the direct current internal resistance (DCIR). The pulse was applied for 5 s with a current rate of 1 C in discharging direction.

#### Full pouch cell assembly with re and rate tests

The cells were assembled in a similar way as the FPCs without RE, but two layers of a polyethylene separator (Entek, 9 mm thick) were applied between the anode and cathode. The LFP-based REs were prepared based on our previously published laser process, yielding in a micro-perforated electrode.<sup>[19]</sup> The readily prepared REs were placed in between two separator layers at the upper cell side and positioned horizontally in the middle of the cathode. For formation, the cells containing REs were galvanostatically cycled at 25 °C between 2.8 and 4.2 V for one C/10 cycle, followed by charging to 30% SoC. Subsequently, the RE was conditioned by applying two C/10 cycles, followed by a charge to 50% SoC.<sup>[19]</sup> The reference voltage between the anode and the RE was monitored for all following cycles. After rewiring, the cell was discharged to 2.8 V. Afterward, the formation program was completed by applying one C/10, two C/5, and three C/3 cycles. After the EIS measurements, rate tests were performed by varying the charge rates for two C/3, three 1 C, three 2 C, three 3 C, three 4 C, three 5 C, and two C/3 cycles (discharge rates were C/3 for all).

#### **Electrochemical Impedance Spectroscopy**

Between the formation protocol and the charge rate test, EIS was measured at 25 °C on a Biologic VMP 3e system. At first, the cells were discharged with a rate of C/3 to 2.8 V (referred to as SoC 0%) and allowed to rest for 30 min. Potential-controlled impedance spectra were recorded from 100 kHz to 50 mHz with an amplitude of 15 mV. Between recording the spectra, the cells were charged with C/3 in SoC 25 steps (related to the capacity of the last C/3 cycle of the formation) with a subsequent pause of 30 min. After the spectrum at 100% SoC was recorded, the cells were discharged to 30% SoC with C/3 again.

#### Post-mortem analysis

Information about preparing the post-mortem samples and the applied methods can be found in the Supporting Information.

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ChemSusChem 2023, e202301153 (9 of 10)

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## Conflict of Interests

There are no conflicts to declare.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: lithium difluorophosphate · electrolyte additive · Si anodes · lithium-ion battery · reference electrode

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## **RESEARCH ARTICLE**

Lithium difluorophosphate (LiPO<sub>2</sub>F<sub>2</sub>, LiDFP) was applied as a co-additive in application-oriented Si/NCM pouch cells in four different concentrations and detailed electrochemical and post-mortem analyses were performed. 1% of LiDFP exhibited the best performance for most criteria. However, 2% of LiDFP was better at some conditions, especially when applying low C rates.



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1 – 11

The Optimal Amount of Lithium Difluorophosphate as an Additive for Si-Dominant Anodes in an Application-Oriented Setup Special Collection