



Subscriber access provided by ECU Libraries

## Tailoring Electrolyte Additives with Synergistic Functional Moieties for Silicon Negative Electrode-Based Lithium Ion Batteries: A Case Study on Lactic Acid O-Carboxyanhydride

Roman Nölle, Jan-Patrick Schmiegel, Martin Winter, and Tobias Placke

Chem. Mater., Just Accepted Manuscript • DOI: 10.1021/acs.chemmater.9b03173 • Publication Date (Web): 03 Dec 2019 Downloaded from pubs.acs.org on December 7, 2019

### **Just Accepted**

Article

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Page 1 of 34

# Tailoring Electrolyte Additives with Synergistic Functional Moieties for Silicon Negative Electrode-Based Lithium Ion Batteries: A Case Study on Lactic Acid *O*-Carboxyanhydride

Roman Nölle<sup>1</sup>, Jan-Patrick Schmiegel<sup>1</sup>, Martin Winter<sup>1,2, \*\*</sup>, Tobias Placke<sup>1, \*</sup>

<sup>1</sup>University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstr. 46, 48149 Münster, Germany

<sup>2</sup> Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich GmbH,

Corrensstr. 46, 48149 Münster, Germany

### Abstract

Silicon (Si) has attracted much attention to be applied as negative electrode (N) material for lithium ion batteries (LIBs) with increased energy density. However, the huge volume changes during (de-)lithiation of the Si, accompanied with the breakdown of the initially formed solid electrolyte interphase (SEI), result in the gradual consumption of active lithium and electrolyte and, hence, a poor cycling performance of LIBs with Si-based N. The addition of various electrolyte additives was proven to be able to reduce the active lithium consumption by the formation of a more effective/flexible and, therefore, better protecting SEI on the Si. Within this study, we synthesize the new electrolyte additive lactic acid O-carboxyanhydride (lacOCA), which is designed to incorporate two different moieties within its structure, that both show to function as effective SEI additives. The addition of small amounts of 2 wt.% of lacOCA to the baseline electrolyte significantly improves the electrochemical performance of NMC-111 || Si full cells in terms of discharge capacity retention and Coulombic efficiency. The lacOCA also outperforms the comparable additives lactide (LAC) and diethyl dicarbonate (DEDC), which are chosen to individually represent the moieties incorporated within the lacOCA structure, proving the synergistic effect of the two different moieties, when in one molecule. *Ex-situ* investigations of the SEI by means of X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) reveal that the SEI formed by lacOCA is mainly composed of poly lactic acid (PLA) and lithium carbonate, which enables a significant reduced consumption of active lithium during charge/discharge cycling of the NMC-111 || Si full cells.

## **\*Corresponding author:**

Dr. Tobias Placke tobias.placke@uni-muenster.de

# \*\*Co-Corresponding author: Prof. Dr. Martin Winter martin.winter@uni-muenster.de m.winter@fz-juelich.de

# **TOC (Graphical Abstract)**



#### **1. Introduction**

The demand for lithium ion batteries (LIBs) has grown significantly over the last few years, mainly driven by the automotive sector related to the development towards electro mobility. Although millions of electric vehicles (EVs), including plug-in hybrid electric vehicles (PHEVs) and battery-electric vehicles (BEVs), are already in use worldwide, there is still a need for improvements mainly in terms of energy density (>500 Wh L<sup>-1</sup> at pack level) and cost (<125 US\$ kWh<sup>-1</sup> at pack level) for LIBs to enable an extensive mass-market penetration of EVs.<sup>1-3</sup> Despite optimizations regarding the battery cell and pack design (*e.g.* cell housing, inactive materials, etc.), the development and inclusion of advanced active materials possessing higher energy densities than present state-of-the-art active materials, is believed to be the only option to achieve the aforementioned values for energy density and costs for future LIBs.<sup>4-6</sup> Apart from carbon/graphite as standard negative electrode (N) material <sup>7</sup>, mainly alloying-type negative electrode materials, and in particular silicon (Si) are considered to be the most promising candidates to further increase the energy density of N.<sup>4, 8-10</sup> Although already small amounts of silicon (very often as SiO<sub>r</sub>) are added to the carbon-based N within some commercial LIBs <sup>1, 11, 12</sup>, the incorporation of higher amounts of Si, which would enable a strong boost in terms of energy density, is still hampered by the insufficient cycle life of such cells. This issue is essentially related to huge volume variations of Si upon (de-)lithiation, going along with structural instabilities of N.<sup>10, 13, 14</sup> Mainly the breakdown and in consequence the continuous (re-)formation<sup>15, 16</sup> of the solid electrolyte interphase (SEI)<sup>17, 18</sup> at the alloy surface consumes significant amounts of active lithium (Li) and electrolyte, consequently resulting in a poor cycling performance of LIBs incorporating Si-based N.<sup>19-23</sup> Various approaches to address those issues are reported in the literature, including nanostructuring of the Si<sup>24-28</sup>, using intermetallic<sup>29, 30</sup>, or carbon-based composite materials<sup>31, 32</sup>, the application of artificial protection layers<sup>33, 34</sup> or including pre-lithiation techniques<sup>35-37</sup> for compensating active Li losses.

A straightforward approach, *i.e.* simple to incorporate within actual LIB cell production processes, is the addition of small amounts of appropriate additives to the base electrolyte consisting of LiPF<sub>6</sub> and organic carbonate solvents<sup>38, 39</sup>, which has proven to drastically improve the performance of Si-based N related to the formation of a more stable SEI. Doubtlessly, fluoroethylene carbonate (FEC) is the commonly used electrolyte additive when studying Si-based N.<sup>40-42</sup> However, various different additives including vinylene carbonate (VC)<sup>43, 44</sup>, borate-based molecules<sup>45-47</sup>, isocyanates<sup>20</sup> or anhydrides<sup>48, 49</sup> have also been reported to beneficially effect the performance of Si negative electrodes. Furthermore, carbon dioxide

(CO<sub>2</sub>), already investigated with Li metal and graphite N more than 20 years  $ago^{50-52}$ , was recently reported to remarkably improve the performance of LIBs containing a Si-based N.<sup>53-55</sup> In a recent publication, Gasteiger and co-workers revealed that the addition/presence of CO<sub>2</sub> in the electrolyte resulted mainly in the formation of Li<sub>2</sub>CO<sub>3</sub> as SEI component, whereas they proposed different mechanism for the formation of Li<sub>2</sub>CO<sub>3</sub> by CO<sub>2</sub>.<sup>56</sup> Besides an electrochemical reduction, CO<sub>2</sub> can also act as reaction-type additive to scavenge reactive components/impurities of the electrolyte (*e.g.* water, alkoxides *etc.*) and, hence, reduces or inhibits electrolyte degradation, like alkyl carbonate trans-esterification or LiPF<sub>6</sub> hydrolysis.<sup>55-59</sup>

Although all these electrolyte additives are reported to have a beneficial effect, there is still a debate on the exact working principle of those additives and how they influence the Si electrodes. Studies on the additives FEC and VC revealed the formation of polymeric species incorporated within the SEI, which are believed to be more compatible with the huge volume variations of Si.<sup>20, 41, 42, 60-62</sup> In contrast to that, various publications revealed that the inorganic lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) is the main SEI component when CO<sub>2</sub> is used as electrolyte additive, which cannot not be considered to be flexible.<sup>52, 56</sup> Hence, one need to keep in mind that the SEI is not a simple one-component system, but rather a complex interphase containing various different compounds, including salt decomposition products (e.g. LiF, Li<sub>x</sub>PO<sub>v</sub>F<sub>z</sub> for LiPF<sub>6</sub>based electrolytes) and solvent (e.g. lithium ethylene dicarbonate (LEDC) for EC-based electrolytes) or additive (e.g. poly(VC) for VC- or FEC-based electrolytes) decomposition products.<sup>18, 63</sup> Most likely, not solely the molecular composition but also the formed (nanostructured) morphology may determine the properties of the SEI.<sup>64</sup> Furthermore, synergistic effects have been observed for electrolytes containing more than one additive, indicating that an appropriate interplay between different compounds and structures may be the key to an optimized SEI for Si-based N.55, 65, 66

Considering the gained insights into the composition/structure-property relationships of the SEI, cyclic diesters like lactide (LAC) might be suitable candidates as electrolyte additives for Si-based N, as they are commonly known to be able to undergo ring opening polymerization (ROP) to form poly(lactic acid) (PLA) (see **Scheme 1**). Despite those cyclic diesters, *O*-carboxyanhydrides (OCA) are also able to form polyesters by a catalyst (*e.g.* nucleophilic or metal-based) induced ROP, including the release of one equivalent carbon dioxide (CO<sub>2</sub>).<sup>67, 68</sup> The ROP of lactic acid *O*-carboxyanhydride (lacOCA) to PLA is exemplarily depicted in **Scheme 1**. Actually, Jeon *et al.* reported the use of various cyclic diesters (including LAC) as SEI-forming electrolyte additive for LiCoO<sub>2</sub> || graphite LIBs, attributing their effectiveness to

the formation of a polymeric SEI at the graphite N by ROP of the cyclic diesters.<sup>69</sup> However, to best of our knowledge there is no scientific report using OCA molecules as electrolyte additives for LIBs. Due to the additional release of CO<sub>2</sub> during the ROP and, therefore, the incorporation of two moieties within one molecule, this material class might be even more interesting for application as electrolyte additive for Si-based N, as the simultaneous formation of polymeric (*i.e.* PLA) and inorganic species (*i.e.* Li<sub>2</sub>CO<sub>3</sub>) may allow for synergistic effects on the properties of the formed SEI.



**Scheme 1**: Ring opening polymerization of lactide (LAC) to poly(lactic acid) (PLA) and lactic acid *O*-carboxyanhydride (lacOCA) to poly(lactic acid) (PLA) including release of carbon dioxide (CO<sub>2</sub>).

As revealed in several scientific reports, a drastic decay in capacity of full cells incorporating a Si-based N is essentially triggered by the continuous (re-)formation of the SEI due to its breakoff during the huge volume changes of the Si. These volume variations impede an effective protection of the electrode by the SEI, as fresh surface of the Si is exposed to the electrolyte at potentials below its electrochemical stability window in every cycle, leading to reductive decomposition of the electrolyte going along with the continuous consumption of the electrolyte as well as active Li. Since the amount of active Li is restricted to the capacity of used positive electrode (P) material (*i.e.*, NMC in this study), in contrast to active Li-excessed "half cells" (*i.e.*, using a Li metal electrode in large capacity excess<sup>70</sup>), the described continuous SEI formation immediately shows up in capacity decrease of Si-based full cells.<sup>21</sup> It was reported for different additives (e.g. FEC and VC) that the formation of a more effective and, therefore, better protecting SEI by the additives can significantly decrease the mentioned consumption of active Li in full cells.<sup>21, 71</sup> Therefore, we strongly recommend to perform investigation of electrolyte additives for LIBs directly in full cells, as results achieved in half cells or Li metal cells may not directly be transferred to full cells.<sup>23,72</sup> Thus, we recently reported on how to choose the appropriate cell setup according to the intended aim of the investigation, including studies of electrolytes and additives.<sup>70</sup>

Within this work, lacOCA was synthesized *via* carbonylation of lactic acid using triphosgene as carbonylating agent. The as-synthesized molecule was investigated as electrolyte additive within NMC-111 || Si full cells and thoroughly compared with the additives LAC and

diethyl dicarbonate (DEDC), while the latter one undergoes decomposition to DEC and CO<sub>2</sub><sup>54,</sup> <sup>73, 74</sup>, therefore is considered as CO<sub>2</sub>-releasing additive. The performance of the Si-based LIB full cells is significantly improved by the addition of only 2 wt.% of lacOCA to the baseline electrolyte and also outperformed the comparative additives LAC and DEDC, proving the synergistic effect of both moieties incorporated within one molecule. Post-cycling investigation of the Si N by means of X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) confirmed the formation of an SEI incorporating both PLA and Li<sub>2</sub>CO<sub>3</sub>, related to the reductive decomposition of the lacOCA additive.

#### 2. Experimental

### 2.1 Synthesis of lactic acid O-carboxyanhydride (lacOCA, 5-methyl-1,3-dioxolane-2,4-dione)

LacOCA was synthesized based on the methods reported by *Sun et al.*<sup>75</sup>, as depicted in **Scheme 2**. The synthesis of this air- and moisture-sensitive compound was performed under dry argon atmosphere using standard Schlenk techniques. THF (*Sigma Aldrich*, purity:  $\geq$ 99.9%), hexane (*Merck*, purity:  $\geq$ 99%) and diethyl ether (*Fisher Scientific*, purity:  $\geq$ 99%) were dried with the appropriate drying agent and stored under argon atmosphere, while all other chemicals were used as-received.

A flame-dried Schlenk flask was filled with a suspension of lactic acid lithium salt (0.90 g, 10 mmol, 1.0 eq., *Acros Organics*, purity: 99%) and activated charcoal (~30 mg) in 20 mL anhydrous THF. Triphosgene (3.56 g, 12 mmol, 1.2 eq., *Sigma Aldrich*, purity: 98%) was dissolved in 40 mL anhydrous THF and was slowly added to the cooled (0 °C) suspension by a dropping funnel. The reaction mixture was warmed up to room temperature and subsequently stirred for further 18 h. (**Caution:** Evolving gases were trapped with a wash-battle containing a mixture of ethanol, water and ammonia solution (25%). The solvent and any unreacted triphosgene or phosgene gas were removed under reduced pressure and trapped with liquid nitrogen. The latter solution was carefully neutralized with the ammonia solution.) The residue was washed with THF and filtrated using a filtration cannula in order to remove the activated charcoal. The solvent was removed under reduced pressure and subsequent recrystallization of the residue from dry diethyl ether and hexane at -25 °C afforded colorless, needlelike crystals.

Page 7 of 34

#### **Chemistry of Materials**



Scheme 2: Synthesis route of lactic acid O-carboxyanhydride (lacOCA) from lactic acid lithium salt and triphosgene.

NMR:  $\delta$ : <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 5.14 (q, 1H), 1.72 (d, 3H); <sup>13</sup>C (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 167.59, 148.03, 76.13, 16.48.

The analytical data is in accordance with the reported values.<sup>75</sup> The NMR spectra are depicted in the supporting information (see **Figure S1** and **Figure S2**). Furthermore, the amount of residual chloride ions was determined by ion chromatography and found to be  $\approx$ 34 ppm in the final electrolyte. The cycled Si electrodes were also analyzed *via* XPS, however, no chloride species were found, so that any significant impact of residual chloride impurities on the electrochemical performance and/or SEI formation can be excluded.

### 2.2 Electrochemical investigations

Pure Si thin film electrodes ( $\approx$ 750 nm,  $\approx$ 0.17 mg cm<sup>-2</sup>, for detailed description of preparation see ref.<sup>20</sup>) were paired with NMC-111 electrodes (Ø12 mm, 0.53 mAh cm<sup>-2</sup> for at cut-off potential of 4.3 V vs. Li|Li<sup>+</sup>, 90% active material content, Customcells Itzehoe) to NMC-111 || Si full cells with a N/P ratio of  $\approx 1.13$  (considering a capacity of 0.60 mAh cm<sup>-2</sup> for the Si electrodes, based on the active material content and a theoretical capacity of 3,579 mAh g<sup>-1</sup> for Si). Electrochemical investigations were carried out in three-electrode Swagelok-type T-cells assembled in an argon-filled glovebox (*MBraun*). High-purity Li metal foil (Albemarle Corporation, battery grade) was used for the reference electrode (Ø6 mm) and Celgard 2500 (polypropylene, one layer, Ø13 mm and Ø10 mm for reference) was applied as separator. An overall amount of 120 µL electrolyte was added to the cell. The "baseline" electrolyte contained 1 M LiPF<sub>6</sub> in EC/DEC 3:7 (w/w) (all components from BASF SE, battery grade) to which the investigated additives lacOCA (synthesized, 99.25 mol-% as determined via differential scanning calorimetry, see Figure S3), LAC (Alfa Aesar, 98+%) and diethyl dicarbonate (DEDC) (Alfa Aesar, 97%) were added in amounts of 2 wt.%. For further comparison to the lacOCA additive, the well-known additives vinylene carbonate (VC; BASF SE, battery grade) and fluoroethylene carbonate (FEC; BASF SE, battery grade) were also studied as "reference" electrolytes and each added in amounts of 2 wt.% to the baseline electrolyte. It should be noted, that a higher amount of electrolyte is used in these laboratory three-electrode T-cells in comparison to commercial cells. Therefore, the percentage of

electrolyte additive or the actual amount of additive molecules probably needs to be adjusted within commercial cell set-ups.

Charge/discharge cycling of the NMC-111 || Si cells was performed in a voltage range of 3.0 - 4.3 V at 20 °C on a *Maccor series 4000 battery tester*. The cycling protocol started by charging the cell up to 4.3 V with a current of 0.05C (1C = 150 mA g<sup>-1</sup>), followed by discharging down to 3.0 V at 0.1C. Two additional charge/discharge steps at 0.1C completed the formation process of the NMC-111 || Si full cells. Afterwards, the cells were cycled for 100 cycles at a constant charge/discharge current of 1C, additionally applying a constant voltage step at the charge and discharge cut-off voltage until the current dropped below 0.05C. The specific capacities shown in this report are related to the active material weight of the NMC-111 electrode. The presented data are average values of three cells for each electrolyte formulation, demonstrating reproducibility of the obtained results. Note, that the electrochemical results of the "baseline" and "reference" electrolytes shown in this manuscript (*i.e.*, baseline, baseline + 2 wt.% VC, baseline + 2 wt.% FEC) have already been reported in our previous publication.<sup>20</sup>

Linear sweep voltammetry measurements were performed at a *VMP3* (*Biologic Science Instruments*) with a scan-rate of 25  $\mu$ V s<sup>-1</sup> at 25 °C up to a potential of 6 V (*vs.* Li|Li<sup>+</sup>).

#### 2.3 Post-mortem investigations of Si negative electrodes

The Si thin film electrodes and NMC-111 electrodes were harvested from the cycled cells in an argon-filled glovebox and washed two times *via* dipping the cycled electrodes in 200  $\mu$ L DMC (*BASF*, battery grade) prior to surface analysis, in order to remove electrolyte residues and in particular LiPF<sub>6</sub> salt.

X-ray photoelectron spectroscopy (XPS) was performed to analyze the SEI formed on the Si thin film electrodes in different electrolyte solutions after 103 cycles. The samples were transferred to the XPS device (*Axis Ultra DLD, Kratos*) without exposure to ambient air in a sealed container. Monochromatic Al K $\alpha$  X-rays (hv = 1486.6 eV) with a 10 mA emission current and 12 kV accelerating voltage was applied. A charge neutralizer was used to compensate for charging of the samples. The measurement was performed at a 0° angle of emission and a pass energy of 20 eV. The fitting was carried out with CasaXPS. Calibration of the binding energy (BE) of the recorded spectra was performed by using the C 1s C-H/C-C peak (BE = 284.5 eV) as an internal reference. To guarantee reproducibility, three different measurement spots per sample were investigated.

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) of the cycled and washed Si electrodes was performed using a *Vertex 70* IR spectrometer from *Bruker* 

*Optics*. The measurements were conducted with 256 scans and a spectral resolution of 2 cm<sup>-1</sup> within a sample chamber, which was continuously purged with argon to minimize influences of ambient conditions.

#### 3. Results and discussion

### 3.1 Electrochemical performance of NMC-111 || Si cells

The effect of the synthesized lacOCA as SEI-forming electrolyte additive is investigated within NMC-111 || Si full cells. Amorphous, pure Si thin film electrodes, prepared *via* magnetron-sputtering, serve as negative electrode (N) within those full cells, as the absence of binder and conductive additives will enable a direct correlation of the SEI formed by the different electrolytes/additives on the performance of the Si-based N. The synthesized additive lacOCA was added in an amount of 2 wt.% to the baseline electrolyte, (*i.e.* 1M LiPF<sub>6</sub> in EC:DEC (3:7, by wt.)). Furthermore, lacOCA is compared to the electrolyte additive LAC, which was proven to form an polymeric SEI on a graphite-based N by reductive decomposition.<sup>69</sup> For a comparison to CO<sub>2</sub> as electrolyte additive, DEDC was additionally investigated as electrolyte additive, as it was revealed by Chevrier *et al.* that the addition of this CO<sub>2</sub>-liberating molecule to the electrolyte has the same effect on the performance of Si-based LIB cells like the addition of pure CO<sub>2</sub> to the cell *via* dry ice.<sup>54</sup>

To investigate the tendency of the different electrolytes and additives towards reductive decomposition, *i.e.* forming an SEI on the Si electrode, the differential capacity *vs.* the Si electrode potential plots of the NMC-111 || Si full cells during the first charge process for the four different electrolyte solutions are depicted in **Figure 1**. Since the lithiation of the used amorphous Si thin film electrodes starts below potentials of 0.3 V (*vs.* Li|Li<sup>+</sup>)<sup>20</sup>, any current flow at higher potentials can be attributed to parasitic reactions, *i.e.* the reductive decomposition of the electrolyte at the surface of the Si electrode. Note that the peak at an electrode potential of  $\approx 0.55$  V (*vs.* Li|Li<sup>+</sup>), observed for all four electrolyte solutions, is related to the formation of Li<sub>2</sub>O from the oxide surface layer on the Si electrodes.<sup>76</sup>



**Figure 1**: Differential capacity *vs.* electrode potential plots of Si negative electrodes within NMC-111 || Si full cells during the first charging process using different electrolytes, focussing the region of reductive electrolyte decomposition on the Si electrode. Additionally, the chemical structures of the investigated additives lactic acid *O*-carboxyanhydride (lacOCA), lactide (LAC) and diethyl dicarbonate (DEDC) are depicted.

For the baseline electrolyte no distinct peak, despite of the already mentioned one at  $\approx 0.55$  V (*vs.* Li|Li<sup>+</sup>), in the differential capacity plot can be observed, however at an electrode potential of  $\approx 1.1$  V (*vs.* Li|Li<sup>+</sup>) a start of parasitic current flow can be noted, which can be attributed to different reductive decomposition reactions of the electrolyte components like the solvents EC and DEC and also the conductive salt LiPF<sub>6</sub>.<sup>77</sup> When lacOCA is added to the baseline electrolyte, a distinct peak at 1.0 V (*vs.* Li|Li<sup>+</sup>) is observed, proving the reductive decomposition of the synthesized additive lacOCA at the Si electrode. When the additives LAC or DEDC are added to the baseline electrolyte, peaks at  $\approx 0.9$  V (*vs.* Li|Li<sup>+</sup>) are observed for both electrolytes, which is in good agreement to reports using these or similar additives.<sup>69, 73</sup> Hence, the additive lacOCA exhibits a tendency to be reductively decomposed at slightly higher potentials than the comparative additives LAC and DEDC, whereas for all three additives a decrease of current flow below electrode potentials of 0.6 V (*vs.* Li|Li<sup>+</sup>) is observed, indicating that the additive-derived SEI layer decreases parasitic reactions at lower potentials.

To analyze the oxidative stability of the various electrolyte solutions, linear sweep voltammetry measurements were performed on  $\text{LiMn}_2\text{O}_4$  electrodes<sup>78</sup>. As can be seen in **Figure S4**, all electrolytes display a sufficient stability (>5 V *vs.* Li|Li<sup>+</sup>) towards oxidative decomposition, with the VC-based electrolyte being oxidatively decomposed already at  $\approx$ 4.7 V (*vs.* Li|Li<sup>+</sup>). Hence, the developed additive lacOCA and also the investigated additives LAC and DEDC are not believed to undergo a significant oxidative decomposition at the P within the NMC-111 || Si full cells.

To investigate the impact of the synthesized lacOCA and the two additional additives LAC and DEDC on the cycling performance of Si-based LIBs, NMC-111 || Si full cells have been assembled and charged/discharged for 103 consecutive cycles. The specific discharge capacities as well as Coulombic efficiencies (CEs) *vs.* the cycle number of the cells containing the four different electrolytes are depicted in **Figure 2**, exact values thereof are provided in **Table 1** for selected cycles.



**Figure 2**: Specific discharge capacities (a) and Coulombic efficiencies (b) of NMC-111 || Si full cells cycled in the voltage range of 3.0 - 4.3 V at 20 °C with four different electrolyte solutions.

 Table 1: Specific discharge capacities and Coulombic efficiencies of selected cycles of NMC-111 || Si full cells for the four different electrolyte solutions.

Electrolyte	Discharge capacity (1 <sup>st</sup> cycle) / mAh g <sup>-1</sup>	Discharge capacity (103 <sup>rd</sup> cycle) / mAh g <sup>-1</sup>	Capacity retention (103 <sup>rd</sup> cycle) / %	Coulombic efficiency / %		
				1 <sup>st</sup>	5 <sup>th</sup>	103 <sup>rd</sup>
				cycle	cycle	cycle
Baseline	131 ± 3	$16 \pm 3$	$12.0 \pm 2.0$	$72.9 \pm$	98.7±	95.4 ±
				1.5	0.2	0.6
Baseline +	$136 \pm 3$	67 ± 2	49.4 ± 1.9	75.7±	99.2 ±	99.1 ±
2% lacOCA				1.9	0.1	0.1
Baseline +	126 ± 3	37 ± 5	29.4 ± 3.5	$68.2 \pm$	$98.3 \pm$	98.2 ±
2% LAC				1.8	0.4	0.4
Baseline +	129 ± 4	48 ± 5	$36.9 \pm 2.2$	$69.0 \pm$	98.6±	$97.9 \pm$
2% DEDC				2.1	0.2	0.4

The NMC-111 || Si full cells possess a discharge capacity of 131 mAh g<sup>-1</sup>, accompanied with a CE of 71.7% in first cycle, when applying the baseline electrolyte without any electrolyte additive. Upon continuous charge/discharge cycling, these cells show a strong decrease in discharge capacity, offering only a capacity of 15 mAh g<sup>-1</sup> in the 103<sup>rd</sup> cycle, associated with steadily declining CEs leading to a value of only 95.5% in the 103<sup>rd</sup> cycle. It has to be kept in mind, that pure Si electrodes are used for this study, therefore, the performance of these Sibased LIB cells cannot be directly compared to the cycling performance of Si/carbon-based negative electrodes. To check whether the SEI derived by the one of three different additives is capable of reducing the loss of active Li upon charge/discharge cycling, the NMC-111 || Si full cells are investigated with the baseline electrolyte comprising 2 wt.% of the additives. When lacOCA is added to the electrolyte, the discharge capacity as well as CE in the first cycle is increased to 136 mAh g<sup>-1</sup> and 75.7%, respectively. Furthermore, the capacity retention of the cells is significantly increased, namely 67 mAh g<sup>-1</sup> can be achieved during discharge in the 103<sup>rd</sup> cycle, corresponding to more than the fourfold of the cells with the baseline electrolyte. These huge improvements can also be observed in terms of the CE, which reaches a value higher than 99% in the 5<sup>th</sup> cycle, which is maintained until the last cycle. The addition of the two additional additives LAC and DEDC also results in an improvement of the full cells compared to the baseline electrolyte, as discharge capacities of 37 mAh g<sup>-1</sup> for LAC-based and 48 mAh g<sup>-1</sup> for DEDC-based electrolytes can be achieved after 103 cycles (**Table 1**). Whereas the addition of these two additives can enhance the performance related to discharge capacity

#### **Chemistry of Materials**

retention and CEs upon continuous charge/discharge cycling compared to the baseline electrolyte without an additive, both are not able to reach the performance of full cells containing lacOCA as electrolyte additive. As the structure of lacOCA was designed to combine both moieties, *i.e.* the liberation of CO<sub>2</sub> of DEDC and the ROP polymerization of LAC, within one molecule, we believe that this synergy is responsible for the effectiveness of the lacOCA additive. To verify this assumption, the additives DEDC (2 wt.%) and LAC (1 wt.%) are combined within one electrolyte (see Figure S5 and Table S1), enabling an increased discharge capacity of 60 mAh g<sup>-1</sup> in the 103<sup>rd</sup> cycle compared to the cells cycled with only one of the additives LAC or DEDC. However, the improvement achieved by the addition of lacOCA is not reached, what might be related to inclusion of both moieties within one molecule, rather than combining them separately. This is most likely also related to the different potentials at which the additives are reduced, with lacOCA exhibiting a higher reduction potential of  $\approx 1.0$  V (vs. Li|Li<sup>+</sup>) compared to the slightly lower potential of  $\approx 0.9$  V (vs. Li|Li<sup>+</sup>) for DEDC and LAC. Hence, the mechanism of SEI formation and, consequently the composition and morphology of the formed SEI might be different for lacOCA compared to the combination of LAC and DEDC which was intended to mimic the additive lacOCA. Nevertheless, it also has to be kept in mind that a further optimization of the electrolyte amount and additive amount in large-scale (e.g. pouch bag) cells is mandatory to verify this assumption. Recently, Lucht and co-workers revealed such a synergetic behavior for the salt lithium difluoro(oxalate)borate (LiDFOB), which in turn represents a combination of lithium bis(oxalato)borate (LiBOB) and lithium tetrafluoroborate (LiBF<sub>4</sub>). Despite an identical chemical composition by the combination of LiBOB and LiBF<sub>4</sub>, the LiDFOB-based electrolyte enabled significantly improved performance of the investigated Li metal electrodes formed on a copper current collector within LiFeO<sub>4</sub> || Cu cells, which was proven to be related to the nanostructured SEI formed by LiDFOB.<sup>64</sup> To assess the effectiveness of the lacOCA as additive for Si-based LIBs, a comparison to the standard additives FEC and VC is also performed (see Figure S6 and Table S1), in which the lacOCA-based outperforms the FEC-based electrolyte, identifying it as a highly interesting electrolyte additive for Si-based N. A more detailed comparison of the additives VC and FEC in the same cell setup can be found in our previous publication, in which the VC-based electrolyte showed an even better performance than the FEC-based electrolyte.<sup>20</sup> Note, that the type of active material (*i.e.* pure Si, Si/carbon composites *etc.*) and especially the cell setup (half-cell setup vs. full-cell setup) may have a significant influence on the results.<sup>70</sup>

In **Figure 3** the accumulated Coulombic inefficiencies (ACIEs) for the NMC-111 || Si full cells cycled with the four different electrolytes are depicted. As for full cells comprising a

Si-based N the Coulombic inefficiency is mainly attributed to SEI formation, the ACIE, which corresponds to the sum of the Coulombic inefficiencies over a number of cycles, can therefore be used as an indicator for the active Li loss related to SEI formation.<sup>19</sup> As already highlighted in **Table 1**, the cells containing the lacOCA additive exhibit the highest CE and, therefore, the lowest ACIE in the 1<sup>st</sup> cycle. Whereas for all electrolytes a steady increase of the ACIE can be observed, the slope for all additive containing cells is decreased compared to cells comprising the baseline electrolyte, with lacOCA showing the by far lowest slope. These findings are in good agreement with the results of the remaining discharge capacities (see **Figure 2** and **Table 1**) after 103 consecutive charge/discharge cycles, showing that the additives are able to decrease parasitic reactions, particularly the consumption of active Li by the formation of an SEI with improved protecting properties. As already observed in terms of capacity retention, the combination of both additives LAC and DEDC is not able to reach the low ACIE observed for lacOCA-based electrolyte (see **Figure S7**). A comparison to the prominent additives FEC and VC is also given, proving the promising results achieved for the lacOCA additive.



Figure 3: Accumulated Coulombic inefficiencies (ACIEs) of NMC-111 || Si full cells over 103 charge/discharge cycles for the four different electrolyte solutions.

All electrochemical experiments within this report are performed within a full cell setup,

#### **Chemistry of Materials**

meaning that the cell is operated via control of the cell voltage. However due to the incorporation of a reference electrode (Li|Li<sup>+</sup>) within the applied three-electrode configuration, the individual electrode potentials of the P (NMC-111) and N (Si), can be simultaneously monitored (NOT controlled!) upon cycling. As there is a distinct relation between the lithiation/de-lithiation degree and the electrode potential for both P and N<sup>70, 79</sup>, there should be a correlation between the development of the discharge capacities (i.e. capacity decrease related to the loss of active Li) and the electrode potentials of the NMC-111 || Si full cells during cycling. It was revealed that the loss of active Li, for example related to the SEI formation at N, can have a significant effect on the development of the electrode potentials within cellvoltage controlled full cells<sup>80</sup>, and this effect is particularly pronounced when a Si-based N is used.<sup>21</sup> The development of the individual electrode potentials (P: NMC-111 and N: Si) of the NMC-111 || Si full cells cycled with the baseline or lacOCA-based electrolyte is depicted in Figure 4, precise values for the electrode potentials at the end of charge/discharge are summarized in Table 2. Note, that any shift of electrode potentials of P or N at the end of charge/discharge are strictly interconnected, since the cut-off voltages are fixed and the cell voltage is defined as the difference of the electrode potentials of P and N.<sup>80</sup> In the first cycle, only small differences between both electrolytes can be observed. At the end of charge, both, P and N reach an electrode potential of  $\approx 4.4$  V (vs. Li|Li<sup>+</sup>) and  $\approx 0.1$  V (vs. Li|Li<sup>+</sup>), respectively, whereas at the end of discharge, P and N reach an electrode potential of  $\approx 3.7$  V (vs. Li|Li<sup>+</sup>) and  $\approx 0.7 \text{ V}$  (vs. Li|Li<sup>+</sup>), respectively. Upon continuous charge/discharge cycling of the full cells, the electrode potentials of P and N at the end of charge/discharge are gradually shifting towards higher values for both electrolytes, whereas these shifts are clearly increased for the baseline electrolyte. Related to the steady increase of the electrode potential of the N at the end of charge, also the P is forced to cycle at higher potentials, hence, to higher Li extraction ratios. Within the last cycles (>180 h) of the cell with baseline electrolyte, the P reaches values of higher than 4.6 V (vs. Li|Li<sup>+</sup>) with additional, abnormal spikes, indicating a strong overcharge of the NMC-111 going along with structural instabilities.<sup>81</sup> Furthermore, after the last discharge the N reaches a potential of  $\approx 1.3$  V (vs. Li|Li<sup>+</sup>), proving the complete de-lithiation of the Si, connected with a potential of  $\approx 4.3$  V (vs. Li|Li<sup>+</sup>) for P, demonstrating that the NMC-111 is re-lithiated to only a very low extent after 103 cycles in the baseline electrolyte. The observed strong shifts of the electrode potentials confirm that the continuous formation of the SEI on the Si gradually consumes active Li and subsequently result in poor performance of full cells. When lacOCA is added to the electrolyte, these shifts are strongly delayed to larger cycle numbers as can be seen for the electrode potentials after the last discharge cycle, namely  $\approx 0.8$  V (vs. Li|Li<sup>+</sup>) for N and  $\approx$ 3.8 V (*vs.* Li|Li<sup>+</sup>) for P. The addition of only small amounts of 2 wt.% of the additive thus can drastically reduce the consumption of active Li, most likely due to the formation of an SEI with improved protection behavior. A similar, but slightly reduced effect is observed for the comparative additives LAC and DEDC (see **Figure S8**).



**Figure 4**: Development of the individual electrode potentials of the NMC-111 positive electrode and the Si negative electrode upon 103 charge/discharge cycles of NMC-111 || Si full cells within baseline or lacOCA-based electrolyte in the voltage range of 3.0 - 4.3 V.

**Table 2:** Electrode potentials at the end of charge and end of discharge of the Si and NMC-111 electrodes during the  $1^{st}$  and  $103^{rd}$  cycle for NMC-111 || Si full cells cycled in the baseline or lacOCA-based electrolyte.

		Electrode potential / V vs. Li Li <sup>+</sup>					
Flootnolyto	Electrode	1 <sup>st</sup> charge	1 <sup>st</sup> discharge	103 <sup>rd</sup>	103 <sup>rd</sup>		
Electrolyte				charge	discharge		
Basalina	P (NMC-111)	4.40	3.67	4.53	4.27		
Daschilt	N (Si)	0.10	0.67	0.23	1.27		
Baseline + 2%	P (NMC-111)	4.37	3.67	4.46	3.78		
lacOCA	N (Si)	0.07	0.67	0.16	0.78		

Page 17 of 34

#### **Chemistry of Materials**

In addition to the individual electrode potentials, also the development of the difference between the average charge and discharge voltage ( $\Delta V$ ) of the full cells cycled with the different electrolytes is investigated, which displays the polarization of the cell and, hence, gives an indication on the cell impedance.<sup>82, 83</sup> As depicted in Figure 5,  $\Delta V$  is very similar for all electrolytes at the beginning of cycling, indicating that the different electrolyte additives have no significant impact on the overall impedance of the cell in the initial cycles. Whereas  $\Delta V$ increases over cycling for all different electrolytes, cells with the baseline electrolyte exhibit a stronger increase of  $\Delta V$  after  $\approx 60$  cycles compared to the additive-based cells, which all show the same increase over 103 cycles. Hence, all investigated additives are able to reduce the impedance increase of the NMC-111 || Si full cells during prolonged charge/discharge cycling. The polarization of the full cells is also investigated for the additives VC and FEC as can be seen in **Figure S9**. Whereas the cells cycled with the FEC-based electrolyte display a very similar increase of  $\Delta V$  compared to lacOCA, the VC-based cells show a slightly reduced polarization increase. Hence, the impact of (new) electrolyte additives on the polarization of Si-based full cells might be an aspect to be studied in more detail in following studies. In general, this effect is likely to a great extent related to the lower consumption of active Li for the additive-based cells, which results in lower de-lithiation degrees and, therefore, lower upper cut-off potentials of the NMC-111 positive electrodes. This again will lead to less parasitic reactions and structural instabilities at/of the NMC-111 P, respectively, which both are known to result in an impedance increase of the cell.<sup>84</sup> The phenomenon of the steady increase of  $\Delta V$ during cycling of full cells with a Si-containing N was recently also reported by Louli et al., which was not observed for full cells based on a graphitic negative electrode.<sup>85</sup> The values for  $\Delta V$  observed within our study are significantly higher compared to their ones, what is most likely related to completely different experimental conditions, including active materials, cell setup, cycling conditions etc. A study of Petibon et al. also revealed that  $\Delta V$  increased more rapidly for Si-based full cells after the applied electrolyte additive FEC was completely consumed, which also coincided with a more severe capacity loss of the cells.<sup>86</sup> These results underlines that electrolyte additives can have a severe impact on various parameters of LIB cells, including capacity retention but also cell polarization.





Figure 5: Development of the difference between average charge and discharge cell voltage ( $\Delta V$ ) over 103 charge/discharge cycles of the NMC-111 || Si full cells within the four different electrolytes.

### 3.2 SEI investigations by means of XPS and ATR-FTIR

*Ex situ* surface investigations of the cycled Si electrodes are performed to elucidate and confirm the beneficial impact of the addition of the electrolyte additives on the performance of the NMC-111 || Si full cells related to the SEI formation on the Si. ATR-FTIR spectra of the Si electrodes cycled in the four different electrolyte solutions and additional reference spectra of  $Li_2CO_3$  and PLA are presented in **Figure 6**. The Si electrode cycled within the baseline electrolyte shows strong absorptions at 1652, 1317 and 825 cm<sup>-1</sup>, which can be related to lithium alkyl carbonates, particularly lithium ethylene dicarbonate (LEDC)<sup>66, 87-89</sup>, and additional absorptions at 1480, 1413 and 860 cm<sup>-1</sup> related to  $Li_2CO_3$ , showing that the SEI in the baseline electrolyte is mainly formed by reductive decomposition of EC.<sup>88</sup> When lacOCA is added to the electrolyte, the cycled Si electrode clearly display characteristic absorptions related to C=O and C-O vibration bands at 1750 and 1082 cm<sup>-1</sup>, most likely arising from PLA as evidenced by the reference spectra. Absorptions at similar, slightly higher wave numbers have also been correlated to polycarbonates like poly(VC) formed by reductive decomposition of VC and also FEC.<sup>62, 90</sup> Additionally small peaks related to  $Li_2CO_3$  (1480, 1413 and 860 cm<sup>-1</sup>)

can be observed, proving the presence of both PLA and  $Li_2CO_3$  within SEI derived by lacOCA as supposed in **Scheme 1**. However, it should be noted that the observed  $Li_2CO_3$  (or at least a fraction of that) may also originate from reductive decomposition of EC, as EC reduction might not be fully prevented by the lacOCA additive. For Si electrodes cycled within the LAC-based electrolyte, also the absorptions at 1750 and 1082 cm<sup>-1</sup> corresponding to PLA can be observed, although with reduced intensities. Additional small absorptions related to LEDC (1652, 1317 and 825 cm<sup>-1</sup>) and also  $Li_2CO_3$  (1480, 1413 and 860 cm<sup>-1</sup>) can be observed, indicating that the LAC additive is not able to completely prevent the reductive decomposition of EC. When DEDC is added to the electrolyte, the spectra are strongly dominated by absorptions at 1480, 1413 and 860 cm<sup>-1</sup> indicating that the SEI is mainly composed of  $Li_2CO_3$ , which was already reported when  $CO_2$  is used as electrolyte additive.<sup>52, 56</sup>



**Figure 6**: ATR-FTIR spectra of the Si negative electrodes after charge/discharge cycling in NMC-111 || Si full cells in the four different electrolyte solutions for 103 cycles. Additionally, reference spectra of pure lithium carbonate ( $Li_2CO_3$ ) and poly(lactic acid) are depicted.

The cycled Si electrodes are also examined *via* XPS. The F 1s, O 1s and C 1s core spectra of the Si electrodes cycled in the four different electrolytes are provided in **Figure 7**.

The electrodes cycled in the baseline electrolyte display a strong peak in the F 1s spectra at 685 eV related to the presence of LiF <sup>42, 91</sup>, including a small shoulder at 687 eV, typically attributed to the presence of Li<sub>x</sub>PO<sub>y</sub>F<sub>z</sub> and/or Li<sub>x</sub>PF<sub>y</sub> <sup>22, 92</sup>, which are arising from decomposition of the conductive salt LiPF<sub>6</sub>. When lacOCA is added to the electrolyte these two peaks display a very low intensity, indicating that the addition of the additive significantly reduces the decomposition of the conductive salt to be incorporated within the SEI. In contrast, the electrodes cycled in the LAC- and DEDC-based electrolytes exhibit both peaks related to LiF and Li<sub>x</sub>PO<sub>y</sub>F<sub>z</sub> / Li<sub>x</sub>PF<sub>y</sub>, whereas the intensities of the latter are significantly higher and the former slightly lower compared to the baseline electrolyte, indicating that the ratio of Li<sub>x</sub>PO<sub>y</sub>F<sub>z</sub> / Li<sub>x</sub>PF<sub>6</sub> species to LiF within the SEI is increased by the addition of LAC or DEDC to the baseline electrolyte.

In the O 1s spectra, the Si electrode cycled in the baseline electrolyte displays a peak centered at 531.4 eV (C=O) and an additional shoulder at 533.6 eV (C-O), which can be assigned to the presence of lithium alkyl carbonates, like LEDC, and Li<sub>2</sub>CO<sub>3</sub><sup>62, 93</sup>, which is also in good agreement with the results of the ATR-FTIR investigations (Figure 6). For the lacOCA, both peaks show an increased intensity and particularly the ratio of C-O to C=O bonds is increased. Considering pure PLA, the ratio of C-O to C=O should exactly account for 1:1<sup>94</sup>, however, the slightly increased contribution of C=O for the Si electrode cycled with lacOCA additive may be attributed to the existence of Li<sub>2</sub>CO<sub>3</sub> besides PLA as already revealed via ATR-FTIR. Besides that, also some additional species like alkyl carbonates, formed by a possible EC and/or DEC reduction, might also influence the ratio of C-O to C=O bonds. For the LAC-based electrolyte, the O 1s spectra displays a similar distribution as for the lacOCA sample with a decreased intensity of the peak at 533.6 eV (C-O), which might be related to the presence of significant amounts of LEDC and/or Li<sub>2</sub>CO<sub>3</sub>, related to EC/DEC reduction, besides PLA formed by the reduction of LAC. The Si electrode investigated with the DEDC additive shows a strong peak centered at 531.4 eV with only a small shoulder at 533.6 eV, indicating that the SEI formed in this electrolyte is dominated by Li<sub>2</sub>CO<sub>3</sub> accompanied with small amounts of lithium alkyl carbonates.93

In the C 1s spectrum for the baseline electrolyte, the main contribution is related to hydrocarbons (C-C/C-H) at a binding energy of 284.5 eV, including small additional peaks at 286.7 eV (C-O) and 289.9 eV (O-(C=O)-O / CO<sub>3</sub>). These findings are consistent with the presence of Li<sub>2</sub>CO<sub>3</sub> and high amounts of LEDC <sup>87, 93</sup>, as already observed in the O 1s and also ATR-FTIR spectra. When lacOCA is added to the electrolyte, the spectrum is dominated by peaks related to C-C/C-H bonds (284.5 eV), C-O bonds (286.7 eV) and C=O bonds/CO<sub>2</sub>

environments (289.0 eV). Furthermore, the intensities of the C-O and C=O peaks are very similar, matching the chemical structure of PLA (see **Scheme 1**), which was also reported in literature for PLA samples.<sup>94, 95</sup> Additionally, a small contribution at higher binding energies of 289.9 eV might be related to the presence of Li<sub>2</sub>CO<sub>3</sub> besides PLA. The Si electrode cycled in the LAC-based electrolyte displays a very similar spectra, with a slightly increased contribution of C-O environments, which could indicate higher amounts of lithium alkyl carbonates present in the SEI compared to lacOCA. For the DEDC-based sample, peaks at 284.5 (C-C/C-H), 286.7 (C-O) and 289.9 eV (O-(C=O)-O / CO<sub>3</sub>) are observed, consistent with the presence of high amounts of carbonates, *i.e.* Li<sub>2</sub>CO<sub>3</sub> and lithium alkyl carbonates like LEDC.

Similar results were also reported for the most commonly used additives for Si-based negative electrodes, VC and FEC. The formation of partially crosslinked polymeric species (like poly(VC)) within the SEI has been revealed to be the key for the effectiveness of those additives. <sup>61, 62, 96</sup>



Figure 7: XPS core spectra (F 1s, O 1s and C 1s) of the Si negative electrodes after cycling in NMC-111 || Si full cells in the four different electrolyte solutions for 103 cycles.

The relative atomic concentrations of the surface of the different electrodes are provided in **Figure 8**. Note that these ratios only provide information about the composition of the top surface of the Si electrodes (information depth of ~10 nm of XPS) and, therefore, about the elemental composition of the measured SEI but not absolute amounts of the whole width of the electrode or SEI. Consistent with the observations from the XPS core spectra, the addition of lacOCA to the baseline electrolyte strongly reduced the amount of fluorine species in the SEI layer formed at the Si electrode, demonstrating that the decomposition of LiPF<sub>6</sub> is diminished, what is likely related to a superior protection of the Si electrolyte by lacOCA reducing the decomposition of LiPF<sub>6</sub> at the Si N. At the same time, the relative amounts of carbon and oxygen are significantly increased, matching the findings of mainly PLA and additionally Li<sub>2</sub>CO<sub>3</sub> to be incorporated within the SEI formed by lacOCA. Furthermore, a lower amount of Li is found within the measured top layer of the SEI for the lacOCA-based electrolyte, which might indicate that the additive reduces the consumption of active Li via improved SEI formation. However, the relative concentration of Li measured via XPS cannot be directly related to the capacity loss (=loss of active Li) observed in the long-term cycling experiments of the NMC-111 || Si full cells, as only  $\approx 10$  nm of the SEI are investigated and statements on the thickness or the amount of the different SEI layers are not possible. As an example, the relative amounts of Li measured by XPS are very similar for the baseline and the DEDC-based electrolyte, although the DEDC additive significantly reduced the capacity fading of the full cells. Most likely, this is related to the formation of less SEI in cells comprising the additive, related to a better protection behavior of the SEI formed by the additive. Therefore, only the combination of various electrochemical investigations as described above and analytical methods (e.g. ATR-FTIR and XPS) allows for revealing the working principle of an electrolyte additive to improve the performance of LIBs.

Overall the data from ATR-FTIR and XPS reveal that the addition of the different electrolyte additives has a significant impact on SEI formation at the Si negative electrode, hence, could verified to be the reason for improving the electrochemical performance of the Sibased full cells. Moreover, the simultaneous formation of PLA and Li<sub>2</sub>CO<sub>3</sub> within the SEI for the lacOCA-based electrolyte could be proven, which underlines the synergistic effect of both species. Both species are likely formed by lacOCA, however, a contribution of reductive EC and/or DEC decomposition to the Li<sub>2</sub>CO<sub>3</sub> formation cannot be fully excluded. Further insights into the SEI formation mechanism at the Si electrodes might be achieved by cryo-SEM/TEM studies<sup>97</sup>, which however, is beyond the scope of this work.



Figure 8: Relative atomic concentrations of the surface of the Si electrodes after 103 charge/discharge cycles in NMC-111 || Si full cells within the four different electrolytes.

To analyze if the developed electrolyte additive lacOCA also influences the cathode electrolyte interphase (CEI) formation, the NMC-111 electrodes are investigated *via* XPS. The corresponding spectra can be seen in **Figure 9**. The pristine NMC-111 electrode displays a distinct peak at 688.2 eV in the F 1s spectra, which is related to the C-F bonds of the polyvinylidene difluoride (PVdF) binder used for the NMC-111 electrodes. After cycling in the baseline electrolyte, the intensity of this peak is reduced and further displays a shoulder to slightly lower binding energies, which can be related to a film covering the surface of the NMC-111 electrode, respectively. Furthermore, a strong peak related to LiF can be observed for the baseline electrolyte, whereas only a small shoulder is detected for the lacOCA-based electrolyte, showing that the addition of the additive significantly reduces the amount of LiF within the CEI layer. In the O 1s spectra, two distinct peaks at 529.4 eV and ≈532 eV can be observed for the pristine electrode, which can be attributed to metal oxides of the NMC (M-O) and residuals like Li<sub>2</sub>CO<sub>3</sub> or surface groups of the conductive carbon, respectively.<sup>66, 92</sup> After

cycling in the baseline electrolyte, the peak attributed to metal oxides is vanished, suggesting that the active material of the P is covered with a surface film. If lacOCA is added to the electrolyte, this peak is still visible with a slightly reduced intensity compared to the pristine electrode. This likely indicates that the formed CEI is thinner for the lacOCA-based electrolyte in comparison to the baseline electrolyte. The C 1s spectrum of the pristine NMC-111 electrode displays a main peak at 284.5 eV related to the conductive carbon of the composite electrode, and two additional peaks at 286.5 eV and 291.1 eV, which both can be attributed to the PVdF binder.<sup>92</sup> The electrode cycled in the baseline electrolyte does not show the peaks related to the binder, instead a significant shoulder related to C-O environments can be observed, referring to decomposition products of the electrolyte. For the lacOCA additive, the peaks attributed to PVdF still can be observed, however, also additional contributions of  $CO_2$  and  $CO_3$ environments are also present at the surface of the NMC-111 electrode. This points on the formation of a CEI layer mainly composed of organic species by the addition of lacOCA to the electrolyte. These observations are also supported by the P 2p spectra, in which a significant peak related to oxyfluorophosphate compounds at  $\approx 135$  eV can be seen for the baseline electrolyte, whereas only a very small shoulder at  $\approx 136.5$  eV related to residues of the conducting salt is observed for the electrode cycled in the lacOCA-based electrolyte. Overall, these results suggest that there is less electrolyte decomposition taking place at the NMC-111 P in the full cells containing the lacOCA additive. Hence, the formed CEI layer is likely to be thinner compared to the one formed in the baseline electrolyte. Furthermore, the latter is composed of both, inorganic and organic species, whereas the CEI formed in the lacOCA-based electrolyte mainly contains organic species. Considering the insights gained from Figure 4, namely the stronger potential shift of the NMC-111 electrode to higher values in the baseline electrolyte, the difference in the CEI may be also strongly related to the different upper cut-off potentials reached for the different electrolytes. Several publications have proven that higher cut-off potentials applied for NMC-based electrodes result in an increased electrolyte decomposition at the P. This phenomenon was mainly attributed to oxygen release from the NMC subsequently oxidizing the electrolyte, or the formation of highly reactive Ni<sup>4+</sup> at the surface of the NMC, which both are induced by high de-lithiation degrees (at high cut-off potentials) of the NMC active material.98-101 Hence, the reduced consumption of active Li within the NMC-111 || Si full cells by the addition of the lacOCA additive may also indirectly impact the CEI formation at the P, by lowering the effective cut-off potential of the NMC-111 electrode. To check if the lacOCA also directly impacts the formation and the composition of the CEI, the NMC-111 electrodes would need to be cycled at a fixed cut-off potential in a half

cell configuration for both electrolytes, what is, however, beyond the scope of this work.



Figure 9: XPS core spectra (F 1s, O 1s, C 1s and P 2p) of the NMC-111 positive electrodes, pristine and after cycling in NMC-111  $\parallel$  Si full cells in the baseline or lacOCA-based electrolyte for 103 cycles.

#### 4. Conclusion

Within this study, the specifically tailored molecule 5-methyl-1,3-dioxolane-2,4-dione (lacOCA) was successfully synthesized and investigated as electrolyte additive for Si-based electrodes within NMC-111 || Si full cells. The addition of only 2 wt.% of the additive to the carbonate-based baseline electrolyte significantly improved the electrochemical performance of the full cells in terms of capacity retention after 103 consecutive charge/discharge cycles and also in terms of Coulombic efficiency (CE) throughout the whole cycling. The synthesized additive lacOCA was compared to the two literature-known additives diethyl dicarbonate (DEDC) and lactide (LAC), as the lacOCA was designed to combine the beneficial effects on the SEI formation of both, *i.e.* the formation of  $Li_2CO_3$  by DEDC and of poly(lactic acid) (PLA) by LAC (see Scheme 1 and graphical abstract).

Both additives DEDC and LAC, used for comparison, helped to improve the performance of the full cells compared to the baseline electrolyte, but were not as effective as the synthesized molecule lacOCA. Trying to mimic the effect of the lacOCA *via* combination of DEDC and LAC within one electrolyte improved the performance of the cell compared to the single additives, however did not reach the improvements by the addition of lacOCA. These results suggest that the combination of two functional moieties within one molecule allows for better synergistic effects than the combination of two different molecules. This finding is confirmed by a recent literature report.<sup>64</sup> By the combination of different electrochemical and analytical investigations including XPS and ATR-FTIR surface analyses, the beneficial effect of the additive is suggested to be related to formation of a SEI layer composed mainly of reduction products of lacOCA (and possibly to some extent also of EC and/or DEC), namely

PLA and  $Li_2CO_3$ , which was able to significantly reduce the consumption of active Li upon charge/discharge cycling of the NMC-111 || Si full cells. The formation of an effective SEI layer by an electrolyte based on the lacOCA additive in comparison to an EC-based electrolyte without additive(s) is schematically depicted in **Figure 10**.



**Figure 10:** Schematic illustration of the SEI formation at the Si negative electrode by the EC-based baseline electrolyte (a) and the lacOCA-based electrolyte (b). The addition of the lacOCA additive to the baseline electrolyte results in the formation of a more effective SEI at the Si electrode, reducing the consumption of active lihium and electrolyte.

We anticipate that (new) electrolyte additives including two or more different functional moieties within their structure will boost the performance of LIB cells *via* synergistic effects of the different moieties. We have shown, that the beneficial effect of such additives can be well elucidated in LIB full cells based on Si/carbon negative electrodes. Furthermore, a comprehensive future study with respect to the optimization of the electrolyte amount and additive amount in large-scale (*e.g.* pouch bag) cells is mandatory to verify the practical usage of this novel additive, *e.g.* also with respect to gas formation during the formation cycles.<sup>102, 103</sup> Additionally, the incorporation of an additional functional moiety within the structure, *e.g.* a moiety including fluorine atom<sup>104</sup>, might be interesting to further investigate the aspect of

synergistic effects of electrolyte additives.

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at <a href="http://pubs.acs.org">http://pubs.acs.org</a>.

NMR spectra, differential scanning calorimetry, additional discharge capacity and Coulombic efficiency *vs.* cycle number plots, additional electrode potential *vs.* time plots,  $\Delta V$  plots.

### Acknowledgements

The authors wish to thank the German Federal Ministry for Economic Affairs and Energy (BMWi) for funding this work in the project "Go3" (03ETE002D). Dr. Vassilios Siozios is acknowledged for performing DSC measurements, Johannes Thienenkamp for the NMR measurements and Andre Bar for the graphical support.

## References

1. Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M., Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nat. Energy* **2018**, *3*, (4), 267-278.

2. Placke, T.; Kloepsch, R.; Dühnen, S.; Winter, M., Lithium ion, lithium metal, and alternative rechargeable battery technologies: the odyssey for high energy density. *J. Solid State Electrochem.* **2017**, *2*1, (7), 1939-1964.

3. Zeng, X.; Li, M.; Abd El-Hady, D.; Alshitari, W.; Al-Bogami, A. S.; Lu, J.; Amine, K., Commercialization of Lithium Battery Technologies for Electric Vehicles. *Adv. Energy Mat.* **2019**, 9, (27), 1900161-1900185.

4. Andre, D.; Hain, H.; Lamp, P.; Maglia, F.; Stiaszny, B., Future high-energy density anode materials from an automotive application perspective. *J. Mater. Chem. A* **2017**, *5*, (33), 17174-17198.

5. Winter, M.; Barnett, B.; Xu, K., Before Li Ion Batteries. *Chem. Rev.* **2018**, 118, (23), 11433-11456.

6. Wagner, R.; Preschitschek, N.; Passerini, S.; Leker, J.; Winter, M., Current research trends and prospects among the various materials and designs used in lithium-based batteries. *J. Appl. Electrochem.* **2013**, 43, (5), 481-496.

Winter, M.; Besenhard, J. O., Lithiated carbons. *Handb. Battery Mater.* 1998, 383-418.
 Chae, S.; Ko, M.; Kim, K.; Ahn, K.; Cho, J., Confronting Issues of the Practical Implementation of Si Anode in High-Energy Lithium-Ion Batteries. *Joule* 2017, 1, (1), 47-60.

9. Meister, P.; Jia, H.; Li, J.; Kloepsch, R.; Winter, M.; Placke, T., Best Practice: Performance and Cost Evaluation of Lithium Ion Battery Active Materials with Special Emphasis on Energy Efficiency. *Chem. Mater.* **2016**, 28, (20), 7203-7217.

10. Obrovac, M. N.; Chevrier, V. L., Alloy Negative Electrodes for Li-Ion Batteries. *Chem. Rev.* **2014**, 114, (23), 11444-11502.

11. Blomgren, G. E., The Development and Future of Lithium Ion Batteries. *J. Electrochem. Soc.* **2017**, 164, (1), A5019-A5025.

12. Hochgatterer, N. S.; Schweiger, M. R.; Koller, S.; Raimann, P. R.; Wohrle, T.; Wurm, C.; Winter, M., Silicon/graphite composite electrodes for high-capacity anodes: Influence of binder chemistry on cycling stability. *Electrochem. Solid-State Lett.* **2008**, 11, (5), A76-A80.

13. Winter, M.; Besenhard, J. O.; Albering, J. H.; Yang, J.; Wachtler, M., Lithium storage alloys as anode materials for lithium ion batteries. *Prog. Batteries Battery Mater.* **1998**, 17, 208-214.

14. Wetjen, M.; Pritzl, D.; Jung, R.; Solchenbach, S.; Ghadimi, R.; Gasteiger, H. A., Differentiating the Degradation Phenomena in Silicon-Graphite Electrodes for Lithium-Ion Batteries. *J. Electrochem. Soc.* **2017**, 164, (12), A2840-A2852.

15. Winter, M.; Appel, W. K.; Evers, B.; Hodal, T.; Möller, K. C.; Schneider, I.; Wachtler, M.; Wagner, M. R.; Wrodnigg, G. H.; Besenhard, J. O., Studies on the anode/electrolyte interface in lithium ion batteries. *Chemical Monthly* **2001**, 132, (4), 473-486.

16. Wachtler, M.; Besenhard, J. O.; Winter, M., Tin and tin-based intermetallics as new anode materials for lithium-ion cells. *J. Power Sources* **2001**, 94, (2), 189-193.

17. Peled, E., The Electrochemical-Behavior of Alkali and Alkaline-Earth Metals in Non-Aqueous Battery Systems - the Solid Electrolyte Interphase Model. *J. Electrochem. Soc.* **1979**, 126, (12), 2047-2051.

18. Winter, M., The Solid Electrolyte Interphase - The Most Important and the Least Understood Solid Electrolyte in Rechargeable Li Batteries. *Z. Phys. Chem.* **2009**, 223, (10-11), 1395-1406.

19. Holtstiege, F.; Wilken, A.; Winter, M.; Placke, T., Running out of lithium? A route to differentiate between capacity losses and active lithium losses in lithium-ion batteries. *Phys.* 

20.

21.

22.

2572.

23.

24.

25.

26.

Isocvanate as an Effective Electrolyte Additive for Improved Performance of Silicon-Based

D. P., Electrode Behavior RE-Visited: Monitoring Potential Windows, Capacity Loss, and

Impedance Changes in Li<sub>1.03</sub>(Ni<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>)<sub>0.97</sub>O<sub>2</sub>/Silicon-Graphite Full Cells. J. Electrochem.

C.; Bayle-Guillemaud, P.; Guyomard, D., Multiprobe Study of the Solid Electrolyte Interphase

on Silicon-Based Electrodes in Full-Cell Configuration. Chem. Mater. 2016, 28, (8), 2557-

Guyomard, D., Mechanism of Silicon Electrode Aging upon Cycling in Full Lithium-Ion

High Capacity and Long Cycle Life. *Electrochem. Solid-State Lett.* 2009, 12, (11), A215-A218.

Anodes for Lithium Battery Applications. *Electrochem. Solid-State Lett.* **2003**, 6, (5), A75-A79.

Lithium-Ion Full Cells. ACS Appl. Mater. Interfaces 2018, 10, (33), 28187-28198.

Nölle, R.; Achazi, A. J.; Kaghazchi, P.; Winter, M.; Placke, T., Pentafluorophenyl

Klett, M.; Gilbert, J. A.; Trask, S. E.; Polzin, B. J.; Jansen, A. N.; Dees, D. W.; Abraham,

Dupré, N.; Moreau, P.; De Vito, E.; Quazuguel, L.; Boniface, M.; Bordes, A.; Rudisch,

Delpuech, N.; Dupre, N.; Moreau, P.; Bridel, J.-S.; Gaubicher, J.; Lestriez, B.;

Szczech, J. R.; Jin, S., Nanostructured silicon for high capacity lithium battery anodes.

Mazouzi, D.; Lestriez, B.; Roue, L.; Guyomard, D., Silicon Composite Electrode with

Green, M.; Fielder, E.; Scrosati, B.; Wachtler, M.; Moreno, J. S., Structured Silicon

Ohara, S.; Suzuki, J.; Sekine, K.; Takamura, T., A thin film silicon anode for Li-ion

Reyes Jiménez, A.; Klöpsch, R.; Wagner, R.; Rodehorst, U. C.; Kolek, M.; Nölle, R.;

Ruttert, M.; Siozios, V.; Winter, M.; Placke, T., Synthesis and Comparative

Jia, H.; Stock, C.; Kloepsch, R.; He, X.; Badillo, J. P.; Fromm, O.; Vortmann, B.;

Ruttert, M.; Holtstiege, F.; Hüsker, J.; Börner, M.; Winter, M.; Placke, T.,

Yen, Y.-C.; Chao, S.-C.; Wu, H.-C.; Wu, N.-L., Study on Solid-Electrolyte-Interphase

Jin, Y.; Li, S.; Kushima, A.; Zheng, X.; Sun, Y.; Xie, J.; Sun, J.; Xue, W.; Zhou, G.;

Reves Jiménez, A.; Nölle, R.; Wagner, R.; Hüsker, J.; Kolek, M.; Schmuch, R.; Winter,

Holtstiege, F.; Bärmann, P.; Nölle, R.; Winter, M.; Placke, T., Pre-Lithiation Strategies

Investigation of Silicon Transition Metal Silicide Composite Anodes for Lithium Ion Batteries.

Winter, M.; Placke, T., Facile Synthesis and Lithium Storage Properties of a Porous

NiSi2/Si/Carbon Composite Anode Material for Lithium-Ion Batteries. ACS Appl. Mater.

Hydrothermal-derived carbon as a stabilizing matrix for improved cycling performance of

silicon-based anodes for lithium-ion full cells. Beilstein J. Nanotechnol. 2018, 9, (1), 2381-

of Si and C-Coated Si Electrodes in Lithium Cells. J. Electrochem. Soc. 2009, 156, (2), A95-

Wu, J.; Shi, F.; Zhang, R.; Zhu, Z.; So, K.; Cui, Y.; Li, J., Self-healing SEI enables full-cell

cycling of a silicon-majority anode with a coulombic efficiency exceeding 99.9%. Energy

M.; Placke, T., A step towards understanding the beneficial influence of a LIPON-based

artificial SEI on silicon thin film anodes in lithium-ion batteries. Nanoscale 2018, 10, (4), 2128-

for Rechargeable Energy Storage Technologies: Concepts, Promises and Challenges. Batteries 29

ACS Paragon Plus Environment

Chem. Chem. Phys. 2017, 19, (38), 25905-25918.

Batteries. ChemSusChem 2016, 9, (8), 841-848.

Z. Anorg. Allg. Chem. 2019, 645, (3), 248-256.

Interfaces 2015, 7, (3), 1508-1515.

Environ. Sci. 2017, 10, (2), 580-592.

Energy Environ. Sci. 2011, 4, (1), 56-72.

Soc. 2016, 163, (6), A875-A887.

- 37

26

34 35 36

38

39

40 41

42

43

44

45

46

47

48 49

50

51

52

53

54

55 56

57

58

59

60

29

33

30

31

Winter, M.; Placke, T., A Step toward High-Energy Silicon-Based Thin Film Lithium Ion

29.

30.

31.

2395.

A102.

32.

33.

34.

2137.

35.

(2), 303-306.

32

28

27

27. batteries having a very large specific capacity and long cycle life. J. Power Sources 2004, 136,

28.

Batteries. ACS Nano 2017, 11, (5), 4731-4744.

, 4, (1), 4-42.

36. Aravindan, V.; Lee, Y.-S.; Madhavi, S., Best Practices for Mitigating Irreversible Capacity Loss of Negative Electrodes in Li-Ion Batteries. *Adv. Energy Mat.* **2017**, 7, (17), 1602607.

37. Chevrier, V. L.; Liu, L.; Wohl, R.; Chandrasoma, A.; Vega, J. A.; Eberman, K. W.; Stegmaier, P.; Figgemeier, E., Design and Testing of Prelithiated Full Cells with High Silicon Content. *J. Electrochem. Soc.* **2018**, 165, (5), A1129-A1136.

38. Schmitz, R. W.; Murmann, P.; Schmitz, R.; Müller, R.; Krämer, L.; Kasnatscheew, J.; Isken, P.; Niehoff, P.; Nowak, S.; Röschenthaler, G.-V.; Ignatiev, N.; Sartori, P.; Passerini, S.; Kunze, M.; Lex-Balducci, A.; Schreiner, C.; Cekic-Laskovic, I.; Winter, M., Investigations on novel electrolytes, solvents and SEI additives for use in lithium-ion batteries: Systematic electrochemical characterization and detailed analysis by spectroscopic methods. *Prog. Solid State Chem.* **2014**, 42, (4), 65-84.

39. Cekic-Laskovic, I.; von Aspern, N.; Imholt, L.; Kaymaksiz, S.; Oldiges, K.; Rad, B. R.; Winter, M., Synergistic effect of blended components in nonaqueous electrolytes for lithium ion batteries. *Top. Curr. Chem.* **2017**, 375, (2), 37.

40. Choi, N.-S.; Yew, K. H.; Lee, K. Y.; Sung, M.; Kim, H.; Kim, S.-S., Effect of fluoroethylene carbonate additive on interfacial properties of silicon thin-film electrode. *J. Power Sources* **2006**, 161, (2), 1254-1259.

41. Shkrob, I. A.; Wishart, J. F.; Abraham, D. P., What Makes Fluoroethylene Carbonate Different? *J. Phys. Chem. C* **2015**, 119, (27), 14954-14964.

42. Etacheri, V.; Haik, O.; Goffer, Y.; Roberts, G. A.; Stefan, I. C.; Fasching, R.; Aurbach, D., Effect of Fluoroethylene Carbonate (FEC) on the Performance and Surface Chemistry of Si-Nanowire Li-Ion Battery Anodes. *Langmuir* **2012**, 28, (1), 965-976.

43. Chen, L.; Wang, K.; Xie, X.; Xie, J., Effect of vinylene carbonate (VC) as electrolyte additive on electrochemical performance of Si film anode for lithium ion batteries. *J. Power Sources* **2007**, 174, (2), 538-543.

44. Nguyen, C. C.; Lucht, B. L., Comparative Study of Fluoroethylene Carbonate and Vinylene Carbonate for Silicon Anodes in Lithium Ion Batteries. *J. Electrochem. Soc.* 2014, 161, (12), A1933-A1938.

45. Choi, N.-S.; Yew, K. H.; Kim, H.; Kim, S.-S.; Choi, W.-U., Surface layer formed on silicon thin-film electrode in lithium bis (oxalato) borate-based electrolyte. *J. Power Sources* **2007**, 172, (1), 404-409.

46. Dalavi, S.; Guduru, P.; Lucht, B. L., Performance Enhancing Electrolyte Additives for Lithium Ion Batteries with Silicon Anodes. *J. Electrochem. Soc.* **2012**, 159, (5), A642-A646.

47. Han, J.-G.; Lee, J. B.; Cha, A.; Lee, T. K.; Cho, W.; Chae, S.; Kang, S. J.; Kwak, S. K.; Cho, J.; Hong, S. Y., Unsymmetrical fluorinated malonatoborate as an amphoteric additive for high-energy-density lithium-ion batteries. *Energy Environ. Sci.* **2018**, 11, (6), 1552-1562.

48. Li, Y.; Xu, G.; Yao, Y.; Xue, L.; Zhang, S.; Lu, Y.; Toprakci, O.; Zhang, X., Improvement of cyclability of silicon-containing carbon nanofiber anodes for lithium-ion batteries by employing succinic anhydride as an electrolyte additive. *J. Solid State Electrochem.* **2013**, 17, (5), 1393-1399.

49. Han, G.-B.; Ryou, M.-H.; Cho, K. Y.; Lee, Y. M.; Park, J.-K., Effect of succinic anhydride as an electrolyte additive on electrochemical characteristics of silicon thin-film electrode. *J. Power Sources* **2010**, 195, (11), 3709-3714.

50. Plichta, E.; Slane, S.; Uchiyama, M.; Salomon, M.; Chua, D.; Ebner, W.; Lin, H., An Improved Li/Li<sub>x</sub>CoO<sub>2</sub> Rechargeable Cell. *J. Electrochem. Soc.* **1989**, 136, (7), 1865-1869.

51. Besenhard, J. O.; Wagner, M. W.; Winter, M.; Jannakoudakis, A. D.; Jannakoudakis, P. D.; Theodoridou, E., Inorganic Film-Forming Electrolyte Additives Improving the Cycling Behavior of Metallic Lithium Electrodes and the Self-Discharge of Carbon Lithium Electrodes. *J. Power Sources* **1993**, 44, (1-3), 413-420.

2 3 52. Chusid, O.; Ein Ely, E.; Aurbach, D.; Babai, M.; Carmeli, Y., Electrochemical and 4 spectroscopic studies of carbon electrodes in lithium battery electrolyte systems. J. Power 5 Sources 1993, 43, (1), 47-64. 6 Krause, L. J.; Chevrier, V. L.; Jensen, L. D.; Brandt, T., The Effect of Carbon Dioxide 53. 7 on the Cycle Life and Electrolyte Stability of Li-Ion Full Cells Containing Silicon Alloy. J. 8 Electrochem. Soc. 2017, 164, (12), A2527-A2533. 9 10 Chevrier, V. L.; Krause, L. J.; Jensen, L. D.; Huvnh, C.; Triemert, M.; Bowen, E. L.; 54. 11 Thorson, J., Design of Positive Electrodes for Li-Ion Full Cells with Silicon. J. Electrochem. 12 Soc. 2018, 165, (13), A2968-A2977. 13 Solchenbach, S.; Wetjen, M.; Pritzl, D.; Schwenke, K. U.; Gasteiger, H. A., Lithium 55. 14 Oxalate as Capacity and Cycle-Life Enhancer in LNMO/Graphite and LNMO/SiG Full Cells. 15 J. Electrochem. Soc. 2018, 165, (3), A512-A524. 16 Schwenke, K. U.; Solchenbach, S.; Demeaux, J.; Lucht, B. L.; Gasteiger, H. A., The 17 56. 18 Impact of CO<sub>2</sub> Evolved from VC and FEC during Formation of Graphite Anodes in Lithium-19 Ion Batteries. J. Electrochem. Soc. 2019, 166, (10), A2035-A2047. 20 57. Strehle, B.; Solchenbach, S.; Metzger, M.; Schwenke, K. U.; Gasteiger, H. A., The 21 Effect of CO<sub>2</sub> on Alkyl Carbonate Trans-Esterification during Formation of Graphite Electrodes 22 in Li-Ion Batteries. J. Electrochem. Soc. 2017, 164, (12), A2513-A2526. 23 58. Zhang, S. S., A review on electrolyte additives for lithium-ion batteries. J. Power 24 25 Sources 2006, 162, (2), 1379-1394. 26 59. Guéguen, A.; Streich, D.; He, M.; Mendez, M.; Chesneau, F. F.; Novák, P.; Berg, E. J., 27 Decomposition of LiPF<sub>6</sub> in high energy lithium-ion batteries studied with online 28 electrochemical mass spectrometry. J. Electrochem. Soc. 2016, 163, (6), A1095-A1100. 29 Jin, Y.; Kneusels, N.-J. H.; Marbella, L. E.; Castillo-Martínez, E.; Magusin, P. C. M. 60. 30 M.; Weatherup, R. S.; Jónsson, E.; Liu, T.; Paul, S.; Grey, C. P., Understanding Fluoroethylene 31 Carbonate and Vinylene Carbonate Based Electrolytes for Si Anodes in Lithium Ion Batteries 32 33 with NMR Spectroscopy. J. Am. Chem. Soc. 2018, 140, (31), 9854-9867. 34 Jin, Y.; Kneusels, N.-J. H.; Magusin, P. C. M. M.; Kim, G.; Castillo-Martínez, E.; 61. 35 Marbella, L. E.; Kerber, R. N.; Howe, D. J.; Paul, S.; Liu, T.; Grey, C. P., Identifying the 36 Structural Basis for the Increased Stability of the Solid Electrolyte Interphase Formed on 37 Silicon with the Additive Fluoroethylene Carbonate. J. Am. Chem. Soc. 2017, 139, (42), 14992-38 15004. 39 62. Michan, A. L.; Parimalam, B. S.; Leskes, M.; Kerber, R. N.; Yoon, T.; Grey, C. P.; 40 41 Lucht, B. L., Fluoroethylene Carbonate and Vinylene Carbonate Reduction: Understanding 42 Lithium-Ion Battery Electrolyte Additives and Solid Electrolyte Interphase Formation. Chem. 43 Mater. 2016, 28, (22), 8149-8159. 44 63. Xu, K., Electrolytes and Interphases in Li-Ion Batteries and Beyond. Chem. Rev. 2014, 45 114, (23), 11503-11618. 46 64. Jurng, S.; Brown, Z. L.; Kim, J.; Lucht, B. L., Effect of electrolyte on the nanostructure 47 of the solid electrolyte interphase (SEI) and performance of lithium metal anodes. Energy 48 49 Environ. Sci. 2018, 11, (9), 2600-2608. 50 Brown, Z. L.; Lucht, B. L., Synergistic Performance of Lithium Difluoro(oxalato)borate 65. 51 and Fluoroethylene Carbonate in Carbonate Electrolytes for Lithium Metal Anodes. J. 52 Electrochem. Soc. 2019, 166, (3), A5117-A5121. 53 Nguyen, C. C.; Lucht, B. L., Development of Electrolytes for Si-Graphite Composite 66. 54 Electrodes. J. Electrochem. Soc. 2018, 165, (10), A2154-A2161. 55 56 Cairns, S. A.; Schultheiss, A.; Shaver, M. P., A broad scope of aliphatic polyesters 67. 57 prepared by elimination of small molecules from sustainable 1,3-dioxolan-4-ones. Polym. 58 Chem. 2017, 8, (19), 2990-2996. 59 Martin Vaca, B.; Bourissou, D., O-Carboxyanhydrides: Useful Tools for the Preparation 68. 60 of Well-Defined Functionalized Polyesters. ACS Macro Lett. 2015, 4, (7), 792-798.

69. Jeon, J.; Yoon, S.; Park, T.; Cho, J.-J.; Kang, S.; Han, Y.-K.; Lee, H., Tuning glycolide as an SEI-forming additive for thermally robust Li-ion batteries. *J. Mater. Chem.* **2012**, 22, (39), 21003-21008.

70. Nölle, R.; Beltrop, K.; Holtstiege, F.; Kasnatscheew, J.; Placke, T.; Winter, M., A reality check and tutorial on electrochemical characterization of battery cell materials: How to choose the appropriate cell setup. *Mater. Today* **2019**, doi: 10.1016/j.mattod.2019.07.002.

71. Trask, S. E.; Pupek, K. Z.; Gilbert, J. A.; Klett, M.; Polzin, B. J.; Jansen, A. N.; Abraham, D. P., Performance of Full Cells Containing Carbonate-Based LiFSI Electrolytes and Silicon-Graphite Negative Electrodes. *J. Electrochem. Soc.* **2015**, 163, (3), A345-A350.

72. Qian, Y.; Schultz, C.; Niehoff, P.; Schwieters, T.; Nowak, S.; Schappacher, F. M.; Winter, M., Investigations on the electrochemical decomposition of the electrolyte additive vinylene carbonate in Li metal half cells and lithium ion full cells. *J. Power Sources* **2016**, 332, 60-71.

73. Coowar, F.; Christie, A. M.; Bruce, P. G.; Vincent, C. A., Improving the performance of graphite anodes in rechargeable lithium batteries. *J. Power Sources* **1998**, 75, (1), 144-150.

74. Levi, M. D.; Markevich, E.; Wang, C.; Koltypin, M.; Aurbach, D., The effect of dimethyl pyrocarbonate on electroanalytical behavior and cycling of graphite electrodes. *J. Electrochem. Soc.* **2004**, 151, (6), A848-A856.

75. Sun, Y.; Jia, Z.; Chen, C.; Cong, Y.; Mao, X.; Wu, J., Alternating Sequence Controlled Copolymer Synthesis of α-Hydroxy Acids via Syndioselective Ring-Opening Polymerization of *O*-Carboxyanhydrides Using Zirconium/Hafnium Alkoxide Initiators. *J. Am. Chem. Soc.* **2017**, 139, (31), 10723-10732.

76. Omampuliyur, R. S.; Bhuiyan, M.; Han, Z.; Jing, Z.; Li, L.; Fitzgerald, E. A.; Thompson, C. V.; Choi, W. K., Nanostructured Thin Film Silicon Anodes for Li-Ion Microbatteries. *J. Nanosci. Nanotechnol.* **2015**, 15, (7), 4926-4933.

77. Xu, K., Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chem. Rev.* **2004,** 104, (10), 4303-4417.

78. Kasnatscheew, J.; Streipert, B.; Roser, S.; Wagner, R.; Cekic Laskovic, I.; Winter, M., Determining oxidative stability of battery electrolytes: validity of common electrochemical stability window (ESW) data and alternative strategies. *Phys. Chem. Chem. Phys.* **2017**, 19, (24), 16078-16086.

79. Kasnatscheew, J.; Placke, T.; Streipert, B.; Rothermel, S.; Wagner, R.; Meister, P.; Laskovic, I. C.; Winter, M., A tutorial into practical capacity and mass balancing of lithium ion batteries. *J. Electrochem. Soc.* **2017**, 164, (12), A2479-A2486.

80. Krueger, S.; Kloepsch, R.; Li, J.; Nowak, S.; Passerini, S.; Winter, M., How Do Reactions at the Anode/Electrolyte Interface Determine the Cathode Performance in Lithium-Ion Batteries? *J. Electrochem. Soc.* **2013**, 160, (4), A542-A548.

81. Manthiram, A.; Choi, J.; Choi, W., Factors limiting the electrochemical performance of oxide cathodes. *Solid State Ionics* **2006**, 177, (26-32), 2629-2634.

82. Burns, J.; Sinha, N.; Jain, G.; Ye, H.; VanElzen, C. M.; Lamanna, W.; Xiao, A.; Scott, E.; Choi, J.; Dahn, J., Impedance Reducing Additives and Their Effect on Cell Performance II. C<sub>3</sub>H<sub>9</sub>B<sub>3</sub>O<sub>6</sub>. *J. Electrochem. Soc.* **2012**, 159, (7), A1105-A1113.

83. Nelson, K.; d'Eon, G.; Wright, A.; Ma, L.; Xia, J.; Dahn, J., Studies of the effect of high voltage on the impedance and cycling performance of Li[Ni<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>]O<sub>2</sub>/graphite lithium-ion pouch cells. *J. Electrochem. Soc.* **2015**, 162, (6), A1046-A1054.

84. Xu, J.; Lin, F.; Doeff, M. M.; Tong, W., A review of Ni-based layered oxides for rechargeable Li-ion batteries. *J. Mater. Chem. A* **2017**, **5**, (3), 874-901.

85. Louli, A.; Ellis, L.; Dahn, J., Operando Pressure Measurements Reveal Solid Electrolyte Interphase Growth to Rank Li-Ion Cell Performance. *Joule* **2019**.

86. Petibon, R.; Chevrier, V. L.; Aiken, C. P.; Hall, D. S.; Hyatt, S. R.; Shunmugasundaram, R.; Dahn, J. R., Studies of the Capacity Fade Mechanisms of LiCoO<sub>2</sub>/Si-Alloy: Graphite Cells.

J. Electrochem. Soc. 2016, 163, (7), A1146-A1156.

87. Xu, K.; Zhuang, G. V.; Allen, J. L.; Lee, U.; Zhang, S. S.; Ross, P. N.; Jow, T. R., Syntheses and Characterization of Lithium Alkyl Mono- and Dicarbonates as Components of Surface Films in Li-Ion Batteries. *J. Phys. Chem. B* **2006**, 110, (15), 7708-7719.

88. Aurbach, D.; Gofer, Y.; Ben-Zion, M.; Aped, P., The behaviour of lithium electrodes in propylene and ethylene carbonate: Te major factors that influence Li cycling efficiency. *J. Electroanal. Chem.* **1992**, 339, (1), 451-471.

89. Aurbach, D.; Markovsky, B.; Shechter, A.; Ein-Eli, Y.; Cohen, H., A Comparative Study of Synthetic Graphite and Li Electrodes in Electrolyte Solutions Based on Ethylene Carbonate-Dimethyl Carbonate Mixtures. *J. Electrochem. Soc.* **1996**, 143, (12), 3809-3820.

90. Ota, H.; Sakata, Y.; Inoue, A.; Yamaguchi, S., Analysis of vinylene carbonate derived SEI layers on graphite anode. *J. Electrochem. Soc.* **2004**, 151, (10), A1659-A1669.

91. Niehoff, P.; Passerini, S.; Winter, M., Interface Investigations of a Commercial Lithium Ion Battery Graphite Anode Material by Sputter Depth Profile X-ray Photoelectron Spectroscopy. *Langmuir* **2013**, 29, (19), 5806-5816.

92. Niehoff, P.; Winter, M., Composition and Growth Behavior of the Surface and Electrolyte Decomposition Layer of/on a Commercial Lithium Ion Battery  $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  Cathode Determined by Sputter Depth Profile X-ray Photoelectron Spectroscopy. *Langmuir* **2013**, 29, (51), 15813-15821.

93. Dedryvere, R.; Gireaud, L.; Grugeon, S.; Laruelle, S.; Tarascon, J.-M.; Gonbeau, D., Characterization of Lithium Alkyl Carbonates by X-ray Photoelectron Spectroscopy: Experimental and Theoretical Study. *J. Phys. Chem. B* **2005**, 109, (33), 15868-15875.

94. Yeh, C.-H.; Chen, Y.-W.; Shie, M.-Y.; Fang, H.-Y., Poly(Dopamine)-Assisted Immobilization of Xu Duan on 3D Printed Poly(Lactic Acid) Scaffolds to Up-Regulate Osteogenic and Angiogenic Markers of Bone Marrow Stem Cells. *Materials* **2015**, 8, (7), 4299-4315.

95. Yu, X.; Xiong, Z.; Li, J.; Wu, Z.; Wang, Y.; Liu, F., Surface PEGylation on PLA membranes via micro-swelling and crosslinking for improved biocompatibility/hemocompatibility. *RSC Advances* **2015**, *5*, (130), 107949-107956.

96. Profatilova, I. A.; Stock, C.; Schmitz, A.; Passerini, S.; Winter, M., Enhanced thermal stability of a lithiated nano-silicon electrode by fluoroethylene carbonate and vinylene carbonate. *J. Power Sources* **2013**, 222, 140-149.

97. Li, Y.; Li, Y.; Pei, A.; Yan, K.; Sun, Y.; Wu, C.-L.; Joubert, L.-M.; Chin, R.; Koh, A. L.; Yu, Y., Atomic structure of sensitive battery materials and interfaces revealed by cryoelectron microscopy. *Science* **2017**, 358, (6362), 506-510.

98. Börner, M.; Horsthemke, F.; Kollmer, F.; Haseloff, S.; Friesen, A.; Niehoff, P.; Nowak, S.; Winter, M.; Schappacher, F. M., Degradation effects on the surface of commercial LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> electrodes. *J. Power Sources* **2016**, 335, 45-55.

99. Yu, Y.; Karayaylali, P.; Katayama, Y.; Giordano, L.; Gauthier, M.; Maglia, F.; Jung, R.; Lund, I.; Shao-Horn, Y., Coupled LiPF<sub>6</sub> Decomposition and Carbonate Dehydrogenation Enhanced by Highly Covalent Metal Oxides in High-Energy Li-Ion Batteries. *J. Phys. Chem. C* **2018**, 122, (48), 27368-27382.

100. Jung, R.; Metzger, M.; Maglia, F.; Stinner, C.; Gasteiger, H., Chemical vs. Electrochemical Electrolyte Oxidation on NMC111, NMC622, NMC811, LNMO, and Conductive Carbon. *J. Phys. Chem. Lett.* **2017**.

101. Schipper, F.; Erickson, E. M.; Erk, C.; Shin, J.-Y.; Chesneau, F. F.; Aurbach, D., Recent advances and remaining challenges for lithium ion battery cathodes I. Nickel-Rich, LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub>. *J. Electrochem. Soc.* **2017**, 164, (1), A6220-A6228.

102. Louli, A. J.; Li, J.; Trussler, S.; Fell, C. R.; Dahn, J. R., Volume, Pressure and Thickness Evolution of Li-Ion Pouch Cells with Silicon-Composite Negative Electrodes. *J. Electrochem. Soc.* **2017**, 164, (12), A2689-A2696.

103. Ellis, L.; Allen, J.; Thompson, L.; Harlow, J.; Stone, W.; Hill, I.; Dahn, J., Quantifying, understanding and evaluating the effects of gas consumption in lithium-ion cells. *J. Electrochem. Soc.* **2017**, 164, (14), A3518-A3528.

104. Wang, C.; Meng, Y. S.; Xu, K., Perspective—Fluorinating Interphases. *J. Electrochem. Soc.* **2019**, 166, (3), A5184-A5186.

ACS Paragon Plus Environment