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The synthesis, spectroscopic and electrochemical characterization of \( \text{Li}[\text{N(SiMe}_3\text{)}_2\text{SO}_2\text{R}] \) (\( R^2 = \text{CF}_3, n\text{-C}_8\text{F}_8 \)) as well as their behavior as electrolyte additive in lithium ion batteries (LIBs) is reported. The lithium salts were obtained by deprotonation of the corresponding acids HN(SiMe\(_3\))\text{SO}_2\text{R}\) with \( n\text{-butyllithium} \) in \( n\text{-pentane} \). The electrochemical investigations suggested potential as additives for LIBs. Thus, NCM111/graphite cells \((\text{NCM}111 = \text{Li}[\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}]\text{O}_2)\) with LP57 as electrolyte \((\text{LP}_57 = 1.0 \text{ M LiPF}_6 \text{ in EC/EMC 3:7})\) were built to test the performance. Cells with Li[\text{N(SiMe}_3\text{)}_2\text{SO}_2\text{R}] as additives show coulombic efficiencies of over 99.6%, less capacity fading over 55 cycles and a significantly lower cell impedance built up.

1. Introduction

Lithium-ion batteries (LIBs) are indispensable in today's everyday lifetime and play roles in portable devices as well as for the demand of electric vehicles. Since the 1990s lithiated graphite as anode material, \( \text{Li}[(\text{Ni})_{x}\text{Co}_{y}\text{Mn}_{z}]\text{O}_2 \) (NCM; \( x + y + z = 1 \)) as cathode active material (CAM) and a mixture consisting of \( \text{LiPF}_6 \) and alkyl carbonates as electrolyte became state-of-the-art.[1–3] The CAMs based on Ni- or Mn-rich compounds arose as derivatives of LiCoO\(_2\) (LCO) used already in the first LIBs. Ni and Mn help to increase the capacity and improve the stability of the layered CAM.[4] Nevertheless, the limited thermal and chemical stability of the conducting salt \( \text{LiPF}_6 \) leads to problems due to the formation of \( \text{LiF} \) and \( \text{PF}_5 \) followed by the reaction with trace water yielding HF and \( \text{OPF}_3 \).[5] Electrolyte additives are able to improve the battery performance by formation of a solid electrolyte interphase (SEI) on the anode or a cathode electrolyte interphase (CEI) on the cathode side.[6–9] The SEI has been part of research for many decades and today vinylene carbonate (VC) and fluoroethylene carbonate (FEC) are the most mentioned above. Candidates are Lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI) and Lithium bis(fluorosulfonyl)imide (LiFSI) respectively asymmetric perfluoroalkylsulfonylimides, whether as pure conductive salt, as a combination (5) with lithium bis(oxalate)borate (LiBOB) or as additive in ionic liquid electrolytes.[10–12] Further, Lithium-cyclo-difluoromethane-1,1-bis(sulfonyl)imide (LIDMSI, 7), as a representative of these perfluoroalkylsulfonylimides, shows amongst other things the formation of a CEI and a decrease of resistance in LIBs with \( \text{LiPF}_6 \) based electrolytes (Scheme 1).[13,14] Thus, in this work the two asymmetric lithium-imides 1 and 2 were synthesized and investigated as electrolyte additives. They combine on one side a silyl group with potential \( \text{H}_2\text{O} \) and HF scavenger properties to improve cycling stability and on the other side a perfluoroalkyl-sulfonyl group for CEI formation and decreased resistance built up.

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2. Results and Discussion

2.1. Syntheses and Characterization

Literature known[64] Li[N(SiMe₃)(SO₂CF₃)] 1 and novel Li[N(SiMe₃)(SO₂C₂F₆)] 2 were prepared by the reaction of the corresponding acids HN(SiMe₃)(SO₃R')(R' = CF₃, n-C₄F₉) with n-butyllithium in n-pentane in yields exceeding 99%. The compounds were investigated by multinuclear NMR spectroscopy (¹H, ²Li, ¹⁹F, ²⁹Si) and all expected signals (Electronic Supporting Information ESI: Figure S1 to S9) were detected and a purity of at least 99% was established. FT-IR (ESI: Figure S10, S11) confirmed the successful complete deprotonation of the starting material. Electrospray-ionization mass spectrometry (ESI: Figure S12, S13) showed in addition to the molecular ion peaks for 1 (m/z = 220) and 2 (m/z = 370), also one aggregate ion for 1 (m/z = 447, [LiN(SiMe₃)(SO₂CF₃)]²⁺), but two aggregate ions for 2 (m/z = 747 [Li₂A⁺], 1124 [Li₃A⁺], A = [N(SiMe₃)(SO₂C₂F₆)]⁻). The thermogravimetric analysis (Figure 1 and 2) proved thermal stability at least up to 280°C for both, 1 with a T onset of 297°C and 2 with a T onset of 312°C. We think due to the thermal stability and non-volatility of the solid additives, no negative impact on the flammability should be introduced to the investigated electrolyte, if compared to LP57 at least. Since additives 1 and 2 as a solid show no decomposition below 280°C and lithium ion complexation by the solvent of the electrolyte is to be expected, a reduction in flammability can even be assumed due to the further decreased solvent vapor pressure.

2.2. Conductivity

Compounds 1 and 2 in 3:7 EC/EMC (L57) exhibited overall a very low conductivity with a maximum at room temperature at 522 μS cm⁻¹ for the CF₃ derivat and 397 μS cm⁻¹ for the C₂F₆ derivat (Figure 3). It should be noted that 0.3 mol L⁻¹ is the highest concentration for both compounds to get a clear solution in L57.

These two facts indicate the high tendency of 1 and 2 towards ion pairing, as potentially induced by the structure of the anions. In the two additives used, there is only one sulfonyl group, which delocalizes the negative charge via a -M effect. In
comparison, LiNTf₂ (Li[N(SO₂CF₂)_2]) has two sulfonyl groups, which consequently delocalize the negative charge better over the entire anion. This leads to a high conductivity of 9 mScm⁻¹ [65].

Thus, the hyperconjugation induced by the SiMe₃-group does not compensate for the −M effect. Hence, any potential use as supporting electrolyte salt would be futile, and only additive testing was meaningful.

2.3. Electrochemical Testing

2.3.1. Cyclic voltammetry

The cyclic voltammograms of 0.1 M 1 and 0.1 M 2 in 1.0 M LiPF₆ in 3 : 7 (wt.%) EC/EMC (LP57) in the range of 0 to 5 V (0-3 V glassy carbon electrode, 3–5 V platinum electrode) vs Li/Li⁺ were recorded (Figure 4). For 1 it suggested a redox stability in the range of 1 to 4.5 V vs Li/Li⁺ and shows a rather slow drop for the anodic scan (4.5 to 5 V) from the 1st to the 5th cycle. For 2 the measured current drops both from 0 to 1 V and rather pronounced from 3.5 to 5 V from the 1st to the 5th cycle. This might indicate a passivation effect.

Compounds 1 and 2 were investigated as additives in NCM/graphite cells using galvanostatic cycling between 3.0 and 4.2 V at 25 °C. The electrolyte was composed of 0.25 wt.% 1 or 2 in LP57. The specific discharge capacities and coulombic efficiencies of cells with pure LP57 and with added 0.25 wt.% additive 1 or 2 as electrolyte show an almost equal curve progression over 55 cycles (Figure 5). The initial specific discharge capacity at a C-rate of C/20 is 152 mAh g⁻¹ for 1 and 150 mAh g⁻¹ for 2 and minimally lower than for pure LP57 (154 mAh g⁻¹). For a C-rate of C/2, the specific discharge capacity of cells with pure LP57 decreases over 50 cycles from 138 to 136 mAh g⁻¹, whereas with additive 1 it drops from 137 to 136 mAh g⁻¹ and with additive 2 it stays at 136 mAh g⁻¹. The loss of specific discharge capacity with respect to the 1st cycles after formation and 50 cycles at C/2 is 11.0% for the cells with pure LP57, but only 9.9% with 1 and only 9.3% for 2 as additives.

These observations indicate a slightly better long time cycling stability by using additive 1 and more so 2 at C/2 compared to pure LP57. The coulombic efficiency in the first cycle is with 87% for 1 and 86% for 2 a little bit lower than for pure LP57 (89%) and might indicate CEI formation. After the formation cycles, cells including additives 1, 2 or pure LP57 showed a similar progression of the coulombic efficiency at C/2 and ended all with a value of over 99.6%. The voltage profiles of the initial charge/discharge capacities of cells at C/20 with additives 1 and 2 as well as for pure LP57 show superimposable curve progressions (Figure 6a). The first cycle specific discharge capacity is with 152 mAh g⁻¹ for 1 and 150 mAh g⁻¹ for 2 lower by 1.9% and 3.2% compared to pure LP57 (155 mAh g⁻¹) (Figure 6b). By contrast, upon cycling at C/2 (Figure 6c), this capacity reduction with respect to cells with pure LP57 shrinks to only 0.7% for 1 and 1.4% for 2. The dQ/dV plot exhibits a slight shift to higher voltage for the first oxidation peak at 3.5 V (Figure 6c).

There is also a slight increase of the height of the peak in going from pure LP57 (605 mAh/gV) to 2 (646 mAh/gV) and 1 (647 mAh/gV). Both may speak for CEI formation. The voltage profiles after the 10th cycle at C/2 display for both additives 1 and 2 identical profiles compared to that of LP57 (Figure 6d). The dQ/dV plot shows completely equal curve progressions suggesting no interference of the additive with the cathode active material.

The impedance measurements showed for both additives 1 and 2 as well as pure LP57 two semicircles (Figure 7). The first semicircle related to the surface film exhibits as only difference the by 13% lower starting resistance in the presence of additive.
in the presence of 1 and 31 Ω with 2. Favorably, this led to nearly a halving of the CT-resistance by using only 0.25 wt % of additive 2. We think that the improved capacity fading and lower resistance could be due to the additives 1 and 2 acting as H₂O and HF scavengers, which thus induce less electrolyte decomposition and reduced impedance built up.

2.4. Surface Characterization of the NCM111 Electrodes after Cycling

Electrodes of cells after the 55th cycle measured at a C-rate of C/2 and cycled with pure LP57, 0.25 wt.% additive 1 and 2 as well as fresh NCM111 electrodes were investigated using ex-situ XPS surface analysis (Table 1; ESI: Figures S16 to S18). The concentration of surface carbon decreases compared to pure LP57 for both additives (1 and 2), with fresh NCM111 having the lowest carbon content. The fresh NCM111 shows a nitrogen content, which can be explained by N-methyl-2-pyrrolidone fused for the cathode tape preparation. Compared to this, cycled NCM111 with LP57 exhibits a lower nitrogen concentration due to deposits of electrolyte decomposition and the limited penetration depth of XPS. Both additives 1 and 2 show an increase of 0.7 % compared to LP57. The concentration of surface sulfur exhibits for the additives in comparison to LP57 a comparable increase like for nitrogen of 0.5 to 0.6 %. Oxygen again shows an increase of at least 1.4 %, which fits to the 1:1:2 chemical composition N–SO₄ of the additives 1 and 2. Due of the known amounts and proportions of nitrogen, sulfur and oxygen found on the CAM of the cells cycled with pure LP57 acting as a reference, the higher contents of these elements determined to reside on the CAMs being exposed to the additives have to come from the very reaction of additives 1 and 2 with the CAM in the course of the cycling. Thus, the surface compositions of the electrodes with additives 1 and 2 speak for formation of a protecting cathode electrolyte interface (CEI). Since all cycled electrodes exhibit a higher fluorine concentration than the fresh NCM111, but there is no clear trend observable, it is unclear whether the perfluoroalkyl groups are part of the CEI. The increase of the fluorine concentration among both additives may result from the longer perfluorooalkyl chain length, but does not explain the decreasing carbon concentration. The decrease of the fluorine concentration of 1 to LP57 may be an effect of less electrolyte decomposition combined by a thinner formed CEI. Thus, it appears a decomposition of the additives 1 and 2 has to take

Table 1. Relative atomic concentration of selected elements determined by ex-situ XPS surface analysis of electrodes of fresh NCM111, cycled with pure LP57 and cycled with 0.25 wt.% additive Li[N(SiMe₂)(SO₂CF₂)] 1 and Li[N(SiMe₃)(SO₂CF₂)] 2 after the 55th cycle at C/2.

<table>
<thead>
<tr>
<th>Element</th>
<th>C 1s</th>
<th>N 1s</th>
<th>O 1s</th>
<th>F 1s</th>
<th>S 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCM111 fresh</td>
<td>62.0</td>
<td>1.2</td>
<td>12.0</td>
<td>24.6</td>
<td>0.2</td>
</tr>
<tr>
<td>NCM111</td>
<td>57.2</td>
<td>0.4</td>
<td>11.6</td>
<td>30.5</td>
<td>0.3</td>
</tr>
<tr>
<td>with LP57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25 wt.% CF₃</td>
<td>55.8</td>
<td>1.1</td>
<td>13.8</td>
<td>28.4</td>
<td>0.8</td>
</tr>
<tr>
<td>0.25 wt.% CF₉</td>
<td>53.4</td>
<td>1.1</td>
<td>13.0</td>
<td>31.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>

1 (6.5 Ω) and 2 (6.5 Ω), if compared to pure LP57 (7.6 Ω). This finding indicates that both additives decrease the resistance of the electrolyte. Also the charge transfer resistance (CT-resistance), related to the second semicircle, with 1 and 2 as additive displays an explicitly lower resistance in comparison to pure LP57. The CT-resistance drops from 60 Ω for pure LP57 to 35 Ω

![Figure 6](image6.png)

Figure 6. a) Voltage profiles of the 1st cycle at a C-rate C/20 of cells with 0.25 wt.% additive Li[N(SiMe₂)(SO₂CF₂)] 1, 0.25 wt.% Li[N(SiMe₃)(SO₂CF₂)] 2 and pure LP57. b) Display detail of a). c) dQ/dV plot of cells after the 1st cycle at C/20 in the presence of 1, 2 as well as in pure LP57. d) Voltage profiles after the 10th cycle at a C-rate C/2 of cells with 0.25 wt.% additive Li[N(SiMe₂)(SO₂CF₂)] 1, 0.25 wt.% Li[N(SiMe₃)(SO₂CF₂)] 2 and with pure LP57. e) Display detail of d). f) dQ/dV plot of cells after the 10th cycle at C/2 in the presence of 1, 2 as well as in pure LP57.

![Figure 7](image7.png)

Figure 7. Nyquist plot of cells with 0.25 wt.% additive Li[N(SiMe₃)(SO₂CF₂)] 1, Li[N(SiMe₃)(SO₂CF₂)] 2 and in pure LP57 based on measurements at a constant potential of 0 V with an amplitude of 10 mV after the 55th cycle. The inset displays a zoom to the Z’ region between 6 and 9 Ω.
place and only nitrogen-sulfur-oxygen-structure elements in a stoichiometric ratio of 1:1:2 were incorporated in the CEI of the cathode material.

3. Conclusions

Known Li[N(SiMe$_3$)$_2$(SO$_2$F)$_2$] 1 and novel Li[N(SiMe$_3$)$_2$(SO$_2$CF$_2$)$_2$] 2 were synthesized, fully characterized by NMR, FT-IR, mass spectrometry and TGA and tested as electrolyte additives (0.25 wt.%) in NCM111/graphite LIB cells with LP57 as electrolyte. The electrochemical investigation displayed no effect on the coulombic efficiency after 55 cycles. Generally, both additives (1 and 2) show slightly lower initial discharge at C/20 of maximal 5 mAh/g compared to pure LP57 and only 2 mAh/g at C/2. By using the additives, the decrease of specific discharge capacity at C/2 over 50 cycles can be minimized. Compared to the first cycles, the capacity of cells with pure LP57 dropped by 11.0 %, while those with 1 only by 9.9 % and that with 2 by 9.3 %. Referring only to the C/2 cycles, only the cells with additive 2 showed virtually no capacity loss. Since the dQ/dV plots show a shift of the first oxidation peak at 3.5 V to higher voltage and XPS measurements of the cycled cells suggest N-, S- and O-uptake from the additives, apparently a favorable CEI formation did occur. Thus, initial EIS measurements and those after 55 cycles exhibit for both additives a greatly decreased resistance compared to the pure LP57 cells. Further, the charge transfer resistance can be nearly halved compared to pure LP57 using additives 1 or 2. All in all the chain length shows only a small effect on the electrochemical performance in cells. In conclusion, asymmetric imides as Li[N(SiMe$_3$)$_2$(SO$_2$R)$_2$] ([R = CF$_3$, n-C$_3$F$_7$]) are suitable electrolyte additives for LIBs to improve battery performance by decreasing the capacity fade and resistance, which may result from the potential H$_2$O and HF scavenger properties of the SiMe$_3$ group and the demonstrated generation of a CEI via the perfluoroalkylsulfonyl group.

Experimental Section

General methods and materials

All syntheses and measurements were done under Ar atmosphere using standard Schlenk techniques or inside a glovebox (GS Glovebox or M. Braun, O$_2$ and H$_2$O content < 1 ppm). Deuterated solvents were dried over CaH$_2$ and subsequently distilled. n-Pentane with a water content < 4 ppm was used. NMR measurements were performed on Bruker Avance II + WB 400 MHz and Avance III HD 200 MHz spectrometers and used for determination of purity. Chemical shifts were calibrated against the chemical shift of the residual solvent peak of CHD$_2$CN. A Bruker Alpha instrument with a Platinum ATR unit (diamond) was used for FT-IR measurements and evaluated with the OPUS 7.5 software (Bruker Optic GmbH). TGA was performed on a Netzsch STA 409 C/CD under nitrogen atmosphere with an empty Al$_2$O$_3$ crucible as reference. For mass spectrometry, an Advion expression L electron spray ionization mass spectrometer (ESI-MS, capillary temperature 250 °C, source voltage 30 V, source voltage dynamic 0 V, gas temperature 250 °C, ESI voltage 2500 V) was used. A Mettler Toledo SevenMulti conducting meter with a Mettler Toledo inLab710 4-pin platinum electrode was used for conductivity measurements. For cyclovoltammetric measurements, a Methrom potentiostat Autolab PGSTAT101 with glassy carbon electrode (surface area 0.0628 cm$^2$, 0–3 V) and a platinum electrode (surface area 0.0157 cm$^2$, 3–5 V) as working electrode as well as lithium foil (BASF) as reference and counter electrode was used with the NOVA 1.8 software.

Preparations

Li[N(SiMe$_3$)$_2$(SO$_2$F)$_2$]: Following the report by Chen et al, the synthesis proceeded from a mixture of HN(SiMe$_3$)(SO$_2$F)$_2$ (6.1 g, 27 mmol) and n-pentane (200 mL) at 263 K. To this mixture, n-butyl lithium (11 mL, 27 mmol, 2.5 M solution in n-hexane) was added dropwise. The suspension was stirred at 40 °C for three hours and 11.0 %, while those with

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LiF$_2$, in 3:7 (wt.%) EC/EMC (LP57, battery grade water content $\leq$ 50 ppm, BASF$^\text{®}$) were used. Additives used were added as weight percentage (0.25 wt.%) relating to the total mass of the electrolyte. All cells were prepared in duplicate.

**Electrochemical testing**

An Arbin BT2000 battery cycler was used for constant current charge/discharge cycling. Cycling performance of NCM/graphite cells was executed in the potential range between 3.00 and 4.20 V at 25 °C. The test procedure based on a formation cycling consisting of one step with a C-rate of C/20, two with C/10, two with C/5 followed by 50 cycles at C/2 starting at open circuit voltage (OCV). After 55 cycles, electrochemical impedance spectroscopy (EIS) analyses were executed three times at 25 °C for reproducibility on a Bio-Light potentiostat at 0% state of charge (SOC), with a perturbation of 10 mV, in a frequency range from 300 kHz to 10 mHz.

**Ex-situ surface analysis**

In a Glovebox, cells were disassembled, rinsed with EMC (3 × 500 μL) and dried overnight at elevated temperature. A thermos K-alpha system with monochromatized Al K $\alpha$ radiation (hv = 1486.6 eV) under ultra-high vacuum (8.1 $\times$ 10$^{-7}$ Pa) was used for X-ray photoelectron spectroscopy (XPS). A vacuum transfer vessel made of one step with a C-rate of C/20, two with C/10, two with C/5 of the Thermo Fisher$^\text{®}$ was used for transfer into the XPS chamber. Thermo’s Advantage software (Version 5.988) was used for the evaluation and the binding energy was calibrated using the C 1s peak at 284.8 eV of the orbital energy of a C–C bond of conductive carbon.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** additives · cathode electrolyte interphase · electrochemistry · lithium-ion battery · sulfur

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