Electrochemical Performance and Thermal Stability Studies of Two Lithium Sulfonyl Methide Salts in Lithium-Ion Battery Electrolytes

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In the last 25 years the demand for lithium-ion batteries has grown tremendously. As a consequence, fundamental research has been carried out regarding the improvement and understanding of technological and safety related aspects.1-8

Individual applications demand specifically tailored batteries in order to maximize the performance of the device which depicts a great challenge and opportunity for the scientific community to diversify the spectrum of compounds that can be utilized and to adapt the setup in a fast and efficient manner.9,10 In this respect, the electrolyte, as a multifunctional battery component, can consist of a wide array of compounds such as different solvents, conductive salts and numerous additives. The combination of various electrolyte compounds opens up the possibility to tailor the electrolyte and thus, to a significant extent, the battery cell performance.11-14

The current state-of-the-art electrolyte composition is comprised of the conductive salt lithium hexafluorophosphate (LiPF6) dissolved in a mixture of cyclic (e.g. ethylene carbonate and propylene carbonate)15-19 and linear carbonates (e.g. dimethyl-, diethyl- and ethyl-methyl carbonate).11,16-21 However, with increasing demands on the electrolyte regarding thermal and/or electrochemical stability, the limitations of such electrolyte mixtures are unraveled.12,21,27 Alternative electrolyte compositions that depict certain improvements compared to the state-of-the-art electrolyte are still required to fulfill the following properties: a sufficient ionic conductivity to transport the lithium ions, the ability to form an effective solid electrolyte interphase (SEI) on the graphitic anode22-37 which enables stable cycling in the low potential range as well as inertness toward aluminum to avoid anodic dissolution of the current collector on the cathode side.38,39 In addition to performance, more general aspects like low price and safety related aspects.1-8

Applications that require a battery to function partly or completely at temperatures above 55 °C, demand alternative salts. Such salts should ideally display no trade-off in performance on top of the superior thermal stability.

Different studies regarding lithium tetrafluoroborate (LiBF4),49 lithium bis(oxalato)borate (LiDFOB)50-52 and lithium difluoro-oxalato)borate (LiDFOB)53-54 are already well known. Furthermore, conductive salts possessing an imide group have been investigated and compared to LiPF6.55 One of the most investigated salts in this class is lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).36,39 However, LiTFSI in combination with carbonate based solvents is not inert to the aluminum current collector and is therefore not a viable alternative.48 A salt with a similar structure, although based on a methide group, has been reported (LiTFSM), however, the available information regarding this salt or even the methide group in general are limited.13,60-62 This manuscript offers a thorough investigation regarding the electrochemical and performance and thermal stability of conducting salts LiTFSM and LiPFSM (Table I) in comparison to the reference salt LiPF6 containing electrolyte.

The synthesis of both salts was carried out by the workgroup of Sartori and is described elsewhere.60,63,64

Experimental

Electrolyte, electrode and cell preparation.— The two investigated methide salts were dried under reduced pressure at 60 °C and other-wise used. All measurements were conducted in solutions of 1 M LiPF6 (Sigma Aldrich, battery grade), LiTFSM and LiPFSM (Workgroup of Sartori) in EC:DEC 1:1 (by wt) (BASF, battery grade). Regarding the measurement related to the anodic dissolution of the aluminum current collector, a 1 M solution of LiTFSI in the aforementioned solvent mixture was added as a second reference electrolyte to offer a salt that is known to show anodic dissolution. Three electrolyte type Swagelok® cell assembly for the linear sweep voltammetry (LSV), anodic dissolution and constant current cycling experiments was carried out under argon atmosphere in a glove box from MBraun with an atmospheric water and oxygen content below 0.1 ppm. The preparation for the ionic conductivity measurement as well as the preparation for the thermal aging experiments was performed under the same conditions.

For the half-cell experiments the anodes were composed of 87 wt% T44 graphite powder (Imerys), 8 wt% carbon black Super C65 (Imerys) and 5 wt% polyvinylidene difluoride (PVdF) (Kynar 761)71 coated with 120 μm thickness on a copper foil current collector and...
the average active mass of the electrodes was 2.2 mg cm\(^{-2}\). The cathodes consisted of 85 wt% NCM (Toda), 8 wt% Super C65 (Imerys) and 7 wt% PVdF (Kynar 761) coated with 100 \(\mu\)m thickness on an aluminum foil current collector. The active mass of the NCM cathodes in the half-cells averaged 2.0 mg cm\(^{-2}\). In the constant current half-cell tests, lithium foil acted as counter (CE, 12 mm \(\Omega\)) and reference electrode (RE, 5 mm \(\Omega\)), whereas NCM and T44 graphite acted as working electrodes (WE, 12 mm \(\Omega\)), respectively.

Electrochemical measurements.— The conductivity measurements were performed with custom-made cells containing a two stainless steel electrode arrangement with a diameter of 4 mm for each electrode. For the conductivity measurements, a Solarton 1260A impedance gain phase analyzer was used in combination with a Solartron 1287A potentiostat. By setting the polarization parameters to 0 V vs. open circuit for the DC potential, an AC amplitude of 20 mV was applied. A frequency sweep was set from the initial frequency of 1 MHz to 10 kHz (logarithmic).

For the constant current measurements a MACCOR multichannel system (Series 4000) was used. The test procedure for the anode (T44 graphite) consisted of three sequences with an operating potential ranging from 1.5 V to 0.025 V vs. Li/Li\(^+\). The first sequence contained 3 formation cycles with a current-rate (C-rate) of C/5 followed by 20 cycles with C for both the discharge (intercalation in graphite half-cells/insertion in NCM-half-cells) and the charge (de-intercalation in graphite half-cells/de-insertion in NCM half-cells) step. To ensure a fully intercalated graphite electrode, a one hour constant potential step at 0.025 V vs. Li/Li\(^+\) was performed after the constant current step. In the second sequence, the discharge current step was kept at C/2 and followed by a constant potential step at 0.025 V vs. Li/Li\(^+\) to ensure a completely intercalated graphite electrode. The charge current step varied from C/5 over C/3, C/2, 1C, 2C, 3C, 5C to 10C in order to de-intercalate the graphite at different current-rates. In order to provide the cell with a recovery period, five cycles were added after the charge-rate test with a moderate current rate of C/5. A third sequence was added until 90 cycles were completed with a current-rate of 1C for the discharge and charge processes, respectively, again including a constant potential step at 0.025 V vs. Li/Li\(^+\) for one hour. The cycling experiments in the Li/NCM half-cells were conducted starting with three formation cycles with a C-rate of C/5 and were followed by 97 cycles with a C-rate of 1C for the charge and discharge steps. The potential ranged from 3.0 V to 4.3 V vs. Li/Li\(^+\) for the charge and discharge steps, respectively.

The LSV and anodic dissolution measurements were performed on a VSP Swagelok cell setup, respectively. For the LSV measurements, a polished platinum disk electrode (Cypres Systems 1 mm diameter) was used as WE and lithium metal as CE (12 mm \(\Omega\)) and RE (5 mm \(\Omega\)) with a scan rate of 1 mV s\(^{-1}\). The cell started at the open circuit potential which was increased to 6.5 V vs. Li/Li\(^+\). A current density of 0.05 mA cm\(^{-2}\) was chosen as a cutoff criterion.

AC electrochemical impedance spectroscopy (EIS) was performed after the 20th, 50th and 100th cycles at the open circuit potential (OCP) at a frequency range between 1 mHz and 1 MHz with a sinus amplitude of 5 mV using a Solartron 1260A impedance gain phase analyzer.

For the experiments related to anodic dissolution of Al, metallic lithium was used as counter and reference electrode whereas cleaned and pre-weighed aluminum foil (25 \(\mu\)m thickness, 12 mm diameter) acted as working electrode.\(^{38}\) For each salt, the mean value of three consecutive measurements was used. Starting from the open circuit potential, the cells were potentiodynamically forced to 4.5 V vs. Li/Li\(^+\) with a scan rate of approximately 0.5 mV s\(^{-1}\). Once 4.5 V vs. Li/Li\(^+\) was reached, the potential was kept constant for 24 h. The experimental procedure for the anodic dissolution experiment was taken from a previous publication.\(^{38}\)

Analytical measurements.— For the thermal aging investigations, the salts were dissolved in EC:DEC 1:1 (by wt) to yield the required molar solutions. The samples were stored in air tight glass chromatography (GC) vials. Furthermore, to avoid contamination and side reactions, special polyethylene (PEM)-GC vials were used instead of common GC glass vials. The vials were then stored in an oven (Binder) which was held constant at 60°C for a specific time. The reference vials were handled in the same way but stored at room temperature.

After two weeks, the stored vials were transferred in the GC autosampler and the solution was directly injected into the GC system. After the separation on the polar column, the separated compounds were ionized with the electron ionization (EI) source and analyzed via their m/z ratio in the attached quadrupole mass spectrometer. The resulting graph represents a chromatogram of the separated compounds depending on the elution time from the column. Each peak was analyzed according to the matching mass spectra and the recorded spectra were analyzed with the help of the NIST database library (National Institutes of Standards library NIST08 LIBRARY JE) and assigned to the different compounds.

The GC-MS analyses were performed on a QP2010 GC-MS spectrometer with an AOC-5000 Liquid and HS Sampler and an Optic4PTV/C02 unit. In order to control the instrument, the GC-MS Solution Software 2.7 was used. All instrumental components were obtained from Shimadzu. Chromatographic separation was performed on a Stabilwax column (30 m \(\times\) 0.25 mm \(\times\) 0.25 \(\mu\)m) from Restek Corporation.

Results and Discussion

Table I shows that both methide salts do not reach the ionic conductivity of LiPF\(_6\). However, the obtained values of around 4.5 mS cm\(^{-1}\) are still at a sufficient level for application and due to the structural similarity of both salts, a small deviation in the ionic conductivity can be expected. The difference in the first cycle efficiencies is also only marginal for all three investigated electrolytes. Coulombic

| Structure | LiTFSM | LiPF\(_6\) |
|-----------|--------|---------|
| Conductivity/(mS cm\(^{-1}\)) (1 M) | 4.5 | 7.6 |
| 1\(^{st}\) cycle Coulombic efficiency Li/graphite half-cells(%) | 80.0 | 81.9 |
| Average Coulombic efficiency cycle 40-100 Li/graphite half-cells(%) | 99.9 | 99.9 |
| 1\(^{st}\) cycle Coulombic efficiency Li/NCM half-cells(%) | 81.7 | 85.2 |
| Average Coulombic efficiency cycle 5 - 100 Li/NCM half-cells(%) | 99.5 | 99.1 |
The complete electrochemical stability range is illustrated in Figure 1. With regard to the cathodic scan, there are no indications for an early reductive decomposition in any of the tested electrolytes. During the initial sweep from OCP toward low potentials, the only peak displayed at potentials below 0 V vs. Li/Li⁺ can be assigned to the lithium plating process accompanied by an alloy formation of platinum with lithium. The reverse scan reveals two additional peaks; the first one starting at about 0 V vs. Li/Li⁺ can be attributed to lithium stripping processes, while the second depicts the de-alloying process at a potential of about 0.5 V vs. Li/Li⁺.

With regard to the anodic stability window, the two investigated methide salts, compared to LiPF₆, illustrate a decomposition process starting at an earlier stage at a potential of ca. 4 V vs. Li/Li⁺ (observable in the insert of Figure 1). Due to the structural similarity of the two methide salts, the obtained value at the cutoff current density (0.05 mA cm⁻²) shows only a marginal difference. The obtained potential values for the anodic stability at the cutoff current density are 4.2-4.3 V vs. Li/Li⁺, however as the measurement was performed on a Pt electrode surface, the obtained stabilities cannot be directly transferred to real cathode material. This indicates acceptable electrolyte oxidative stability for 4 V battery cathode materials.

In order to evaluate the applicability of the methide salts with graphitic electrodes, the cycling behavior of the electrolytes was investigated in Li/graphite half-cell (Figures 2–5). Figure 2 illustrates inefficiencies of about 20% are typical for T44 graphite electrodes as it illustrates a great model-electrode in the lab scale.66
the first part of the cycling results with three formation cycles at a current rate of C/5 followed by additional 20 cycles with a current rate of 1C for the discharge and the charge process.

The obtained charge capacities for both lithium methide salt containing solutions are lower in the beginning of the cycling experiment than in the case of the LiPF₆ based electrolyte. While the cell with the LiPF₆ containing electrolyte shows a capacity of about 340 mAh g⁻¹ in the first three cycles and is reaching a steady capacity of approximately 350 mAh g⁻¹, the LiTFSM containing electrolyte follows with values of 320 mAh g⁻¹ while the electrolyte containing LiPFSM obtains capacities of about 280 mAh g⁻¹. However, the capacities are slowly increasing for both methide salts and reach values of about 350 mAh g⁻¹, which is a good value for the used graphite. One of the possible causes for this effect might be that in case of these electrolytes it takes more cycles to completely activate all particles of the graphite due to electrolyte wetting issues. Another reason could be that the SEI is not formed as fast as in the case of the LiPF₆ containing electrolyte. Nevertheless, it can be stated that except in the first cycles no difference in the obtained Coulombic efficiencies can be observed in the first part of the cycling.

Figure 3 displays the charge rate test results from cycles 24 to 36 starting from a current rate of C/5 over C/3, C/2, 1C, 2C, 3C, 5C up to 10C, whereas the discharge rate is fixed to C/2.

Having in mind that such high rates are rather stressful for the cell, five recovery cycles were applied adjacent to the rate test with a current rate of C/2 for charge and discharge. A constant potential step was not applied in the rate test to completely compare the influence of the different rates. With charge capacities of around 350 mAh g⁻¹ the starting values from C/5 to 1C can be considered similar for all three investigated electrolytes. Starting with 2C, a capacity fading is already observable for the LiPF₆ containing electrolyte and becomes more pronounced with increasing in current rates, dropping to 350 mAh g⁻¹ at 2C to about 347 mAh g⁻¹ at 3C to 316 mAh g⁻¹ at 5C and finally to 200 mAh g⁻¹ at 10C. The capacity of the LiTFSM containing electrolyte remains at the same level up to a current rate of 5C at which it drops to 350 mAh g⁻¹ and even further to 220 mAh g⁻¹ at 10C. The LiPF₆ electrolyte shows almost no capacity fade even at a current rate of 10C. Based on the aforementioned facts, it can be concluded that both lithium methide salts can be cycled up to a current rate of 3C with only minor losses in capacity, while higher current rates cause a considerable decrease in capacities.

The corresponding potential versus capacity plots of the three investigated salts at the charge rates of C/5, 1C as well as 10C are illustrated by Figure 4.

At the slowest charge rate of C/5, the potential profiles of all three salts show no noticeable difference. There is no disparity visible in the IR-drop values and differences in over-potentials are also not observable. At such slow charge rates all three electrolytes depict the same charge potentials in combination with T44 graphite. The changes are, however, evident at a charge rate of 1C, at which both methide salt based electrolytes show a slightly increased over-potential compared to the LiPF₆ salt based electrolyte. As a result, the charge potentials increase. However, the values for the over-potentials are so marginal that still the full capacity can be attained. A cycling at 1C is therefore viable for all three electrolytes. At a charge rate of 10C the drop after the reversal of potential in the tail end of the charge step (at 0.025 V vs. Li/Li⁺) is more intense for both methide salts. The typical charge profiles for the charge process are no longer observable and the cutoff potential is reached at lower capacities. The same refers to the LiPF₆ but is less pronounced. For the charge rate test, it can be concluded that at C/5 and 1C both methide salts can compete with the LiPF₆ based electrolyte in Li/graphite half-cells but at 10C the ionic conductivity as well as over-potentials due to different SEI impedance cause high capacity losses.

The remaining part of the cycling experiment is depicted in Figure 5, where the cells were cycled with a current rate of 1C for the charge and the discharge process from cycle number 40 to 100.

As the current rates do not vary throughout cycling, Figure 5 is plotted in a way that minor differences are visible. Therefore, the observed disparity in obtained capacities is less than 20 mAh g⁻¹, i.e. 5%. All three electrolytes show a stable cycling stability during 50 cycles. Besides the lower charge capacities, the only difference is observable in the Coulombic efficiencies, which are slightly higher for the LiPF₆ containing electrolyte but the values average over the displayed 50 cycles to over 99.9% for all three electrolytes. These results strongly confirm the applicability of both methide salts with graphic anodes, while the limited anodic stability prompts the question of the compatibility of the electrolytes with NCM cathodes. Figure 6 illustrates the cycling behavior of the three investigated salts in Li/NCM half-cells cycled with three formation cycles at C/5 and followed by standard cycles with 1C for the charge and discharge process, respectively.

Although the anodic stability on a platinum working electrode amounted to just above 4 V vs. Li/Li⁺, the half-cell investigations depict very interesting results as the cycling for both methide salt containing electrolytes behaves differently compared to the cell containing the LiPF₆ salt. The first cycle Coulombic efficiencies vary from 85% for the electrolyte containing LiPF₆ to 82% for the LiTFSM and to 75% for the LiPFSM based electrolytes. Therefore, the irreversible processes for both methide salt containing cells are more pronounced in the first cycle. Taking the limited anodic stability into account, these results indicate a partial decomposition of the electrolyte which inhibits further decomposition when the potential increases further to the upper cutoff potential. Furthermore, both cells cycled with the methide salts do not depict capacity fading over the whole cycling duration, while the LiPF₆ cell depicts a discharge capacity fading of about 6 mAh g⁻¹. It is clearly observable that, although starting with high Coulombic efficiencies, the LiPF₆ based cell depicts decreasing values, while the behavior is the opposite for the methide salt containing cells. For the latter, the Coulombic efficiencies form a plateau at 99.8%. The illustrated behavior of the methide containing electrolytes to cycle without significant capacity fading and increasing Coulombic efficiencies underline the abovementioned suggestion that some kind of protective layer is formed that has been caused either by electrolyte decomposition or by NCM material surface changes. Despite the obtained limited stability to just above 4 V vs. Li/Li⁺, both methide salt containing electrolytes are very stable at the applied potential up to 4.3 V vs. Li/Li⁺. It can be suggested that the electrolytes are kinetically stable due to the surface layer induced by the methide salts. Such surface layer has been reported for a structurally similar sulfon fluoride salt as CEI forming additive at elevated potentials.

The differences in the Coulombic efficiencies were further compared by accumulating the inefficiency of the respective cycles and plotting it versus the cycle number as presented in Figure 7.

The abovementioned deviating behavior in the Coulombic efficiency can be underlined in this plot as the saturating slope of the two methide salt containing cells differs from the exponential curve of the LiPF₆ containing cell. This implies that the cycling in the half-cells containing the methide salts would be stable for an extended
time compared to the LiPF$_6$ containing cell. The insert in Figure 7 illustrates the cumulative Coulombic inefficiencies excluding the first three cycles. Here, the curves overlap even earlier, since the difference in the first three cycles is negated. While the LiPF$_6$ electrolyte yields average Coulombic efficiencies of 99.1%, the LiPFSM reach 99.4% and the LiTFSM even 99.5%.

These obtained average values, the higher inefficiencies in the first cycles and the lower anodic stability indicate that some kind of decomposition process takes place in the first cycles, which is beneficial for the later cycling. This can further be observed in the potential vs. capacity plot of three different cycles in Figure 8.

Here, the 1st, the 5th, and the 100th cycle are depicted and compared for all three investigated electrolytes. In the first cycle, the LiPF$_6$ based electrolyte shows a slightly lower over-potential for the charge step and, as expected, a higher Coulombic efficiency. However, in the profiles of the 5th and 100th cycle, the LiPF$_6$ containing electrolyte displays higher over-potentials for the charge as well as the discharge process and the complete curve is shifted to higher potentials. For all three electrolytes there is no significant difference observable in respect to the profiles of the 5th or the 100th cycle, underlining the cycling stability. In order to investigate the surface layer, AC impedance measurements were carried out of the cells after specific cycles and the data is depicted in Figure 9. It can clearly be observed that in case of the methide salt containing electrolyte, the impedance does not change significantly during cycling from the 20th to the 100th cycles. In contrast to this, the impedance of the LiPF$_6$ containing cell increases from the 20th to the 50th and the 100th cycle.

Since both methide salt containing cells outperform the LiPF$_6$ electrolyte in Li/NCM half-cells at a working potential of 4.3 V vs. Li/Li$^+$, half-cell investigations were carried out at a potential of 4.6 V vs. Li/Li$^+$. However, at such high potential the measurements showed clear signs of faradaic reactions that either derived from electrolyte decomposition and/or anodic dissolution of the aluminum current collector. The possibility of Al dissolution was further investigated with the setup introduced by Kraemer et al. by stressing Al at a potential of 4.5 V vs. Li/Li$^+$ for 24 hours.

As expected, the LiPFSM based electrolyte containing LiPF$_6$ does not show any increase in the accumulated electric charge at 4.5 V vs. Li/Li$^+$, observable in Figure 10. On the other hand, the LiTFSI containing electrolyte shows an exponential growth from the start, which can be correlated to strong aluminum dissolution and is well-known in literature. The structures of the two investigated salts are so similar and a dissolution behavior has been reported for the LiTFSI, the same may be expected for the LiPFSM. Both salts indeed show a similar increase in electric charge over the time of the experiment, indicating anodic dissolution. However, since the shape of the curves differ from the LiTFSI containing cell, the electric charge is not as high in the case of the methide containing cells. Additionally, since both salts show a limited electrochemical anodic stability, electrolyte decomposition cannot be excluded.

Therefore with regard to the anodic dissolution behavior it can be stated that both methide salts show very similar properties while behaving differently to LiTFSI as well as to LiPF$_6$. The results indicate that both salts show anodic dissolution of the aluminum current collector but considerably less than LiTFSI. However, applications in 4 V batteries are a viable option for both methide salts.

Since the investigated methide salts illustrated overall competitive results compared to the reference salt LiPF$_6$, thermal aging experiments were conducted, as the thermal instability depicts one of the biggest drawbacks of LiPF$_6$ containing electrolytes. The experiments were performed via GC-MS analysis of thermally treated and untreated samples and are illustrated by Figure 11.

The peaks at a retention time of 5 min are corresponding to methanol, which is used as an eluent for the mass spectrometry measurement. The peak at minute 8 correlates to the masses of the DEC and the peak at minute 16 correlates to the masses of EC, both

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**Figure 7.** Accumulated Coulombic inefficiency of the three electrolytes in Li/NCM half-cells cycled from 3 V to 4.3 V vs. Li/Li$^+$. Insert: Accumulated Coulombic inefficiencies without the three formation cycles plotted versus the cycle number.

**Figure 8.** 1st, 5th and 100th cycle of the constant current cycling experiment of the Li/NCM half-cell depicted as a potential vs. capacity plots of the investigated electrolytes at 20 °C in the potential range from 3 to 4.3 V vs. Li/Li$^+$. The rate of the first cycles was C/5 and for the 5th and 100th cycle was 1C.
solvents in the used electrolyte. Decomposition products can be identified by comparison of the dotted lines (representing the electrolyte after temperature storage) with the straight lines (representing the electrolyte before storage). For the LiPF₆ containing electrolyte, smaller peaks have been assigned via the National Institutes of Standards library to 1,2-ethanediol, acetic acid and 2-fluorethanol. For both methide salt containing electrolytes no solvent decomposition products are observable in the abovementioned retention time window. It can be summarized that the investigated electrolytes containing 1 M of LiTFSI and LiPFSI respectively, have a superior thermal stability at 60°C, whereas LiPF₆ shows clear signs of thermal instability.

Conclusions

In this manuscript two lithium sulfonyl methide salts were investigated for applications as conductive salts in lithium ion battery electrolytes. The salts consisted of LiTFSI and LiPFSI and were applied in 1 M concentration in an EC:DEC 1:1 (by wt) solvent system. The obtained electrolyte compositions were measured and compared to the reference electrolyte consisting of 1 M LiPF₆ in EC:DEC 1:1 (by wt) regarding the electrochemistry in Li/graphite as well as Li/NCM half-cells, the electrochemical stability window, the thermal behavior at 60°C as well as the anodic dissolution behavior of an Al current collector. In 1 M LiTFSI in EC:DEC 1:1 (by wt) compared to the LiPF₆ containing reference electrolyte, both methide salt electrolytes illustrate a thermal stability above 60°C. In a Li/graphite half-cell both methide salt containing electrolytes show results comparable to the LiPF₆ electrolyte at least up to a current rate of 3C. With regard to the electrochemistry in Li/NCM half-cells, both electrolytes containing the methide salts show even superior cycling compared to the LiPF₆ based electrolyte in form of almost no capacity fading as well as superior average Coulombic efficiencies. It is suggested that due to the limited anodic stability of the methide containing electrolytes some kind of decomposition takes place on the surface of the NCM which is reflected in the lower Coulombic efficiencies in the first three cycles. However, this apparent decomposition seems to be beneficial for long term cycling, as the Coulombic efficiencies increase. While a potential of 4.3 V vs. Li/Li⁺ seems to be an optimal value for the salts, increased potentials of e.g. 4.6 V vs. Li/Li⁺ cause the cell to malfunction due to a faradaic reactions of the electrolyte. Concluding, it can be stated that both methide salts but especially LiTFSI show very promising results when the cutoff potential does not surpass 4.3 V vs. Li/Li⁺.
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References

1. B. Scrosati, K. M. Abraham, W. van Schalkwijk, and J. Hassoun, Lithium Batteries: Advanced Technologies and Applications, Wiley (2013).
2. J. B. Goodenough and J. O. Besenhard, J. Power Sources, 196, 6688 (2011).
3. V. Etacheri, R. Marom, R. Elazari, G. Salitra, and D. Aurbach, Energy Environ Sci., 4, 3243 (2011).
4. R. Wagner, N. Prestchitschek, S. Passerini, J. Leker, and M. Winter, J Appl Electrochem., 43, 481 (2013).
5. M. Buonomenna and J. Bae, Nanoscience & Nanotechnology-Africa, 3, 36 (2013).
6. P. G. Balakrishnan, R. Ramesh, and T. P. Kumar, J Power Sources, 155, 401 (2006).
7. M. Winter and R. J. Brodol, Chem Rev, 104, 4245 (2004).
8. J. A. Goodenough, Accounts Chem Res., 46, 1053 (2013).
9. A. Kraysberg, Y. Krayshtein, A. Ein Eli, and A. Kraysberg, Adv Energy Mater, 2, 922 (2012).
10. R. Marom, S. F. Amalraj, N. Leifer, D. Jacob, and D. Aurbach, J Mater Chem, 21, 9938 (2011).
11. K. Xu, Chem Rev, 104, 4303 (2004).
12. S. S. Zhang, J Power Sources, 162, 1379 (2006).
13. V. Aravindan, J. Ganaraj, S. Madhavi, and H. K. Liu, Chem-Eur J, 17, 14326 (2011).
14. D. Aurbach, Y. Talyosef, B. Markovsky, E. Markevich, E. Zinigrad, L. Asraf, R. Marom, R. Elazari, G. Salitra, and D. Aurbach, Chem Rev, 119, 129 (1999).
15. J. P. Olivier and M. Winter, J Electrochem Soc, 144, 1208 (1997).
16. E. Feled, D. Golodnitsky, and G. Ardel, J Electrochem Soc, 145, L27 (1998).
17. J. P. Olivier and M. Winter, J Power Sources, 97–98, 151 (2001).
18. E. Kramer, S. Passerini, and M. Winter, ECS Electrochemistry Letters, 1, C9 (2012).
19. E. Kramer, T. Schedlbauer, B. Hoffmann, L. Terborg, S. Nowak, H. J. Gores, S. Passerini, and M. Winter, J Electrochem Soc, 160, A356 (2013).
20. G. H. Wrodnigg, J. O. Besenhard, and M. Winter, J Power Sources, 97–8, 592 (2001).
21. R. M. Wagner, T. Hodal, W. K. Appel, M. Winter, and J. O. Besenhard, J Power Sources, 97–8, 595 (2001).
22. L. Terborg, S. Nowak, S. Passerini, M. Winter, U. Kastl, P. R. Haddad, and P. N. Nesterenko, Anal Chem Acta, 714, 121 (2012).
23. F. S. Lue, I. T. Lucas, E. Pollak, S. Passerini, M. Winter, and R. Kostekci, Electrochem Commun, 14, 47 (2012).
24. J. Vetter, P. Novak, M. R. Wagner, C. Veit, K. C. Moller, J. O. Besenhard, M. Winter, Wollfahrt-Mehrens, C. Vogler, and A. Hammouche, J Power Sources, 147, 269 (2005).
25. T. Kawanuma, A. Kimura, M. Esgahshira, S. Okada, and J. I. Yamaki, J Power Sources, 104, 260 (2002).
26. E. S. Sloop, J. K. Pugh, S. Wang, J. B. Kerr, and K. Kinosita, Electrochem Solid St, 4, A42 (2001).
27. T. Kawanuma, S. Okada, and J. Yamaki, J Power Sources, 156, 547 (2006).
28. A. Hammann, N. Raymond, and M. Armand, Nature, 424, 635 (2003).
29. S. S. Zhang, K. Xu, and T. R. Jow, J Electrochem Soc, 149, A586 (2002).
30. U. L. U. Wietelmann and M. Wegner, United States Pat. US 6506306 (2003), in.
31. M. Winter, S. S. Zhang, T. R. Jow, W. Xu, and C. A. Angell, Electrochem Solid St, 5, A26 (2002).
32. S. S. Zhang, Electrochem Commun, 8, 1423 (2006).
33. S. Zugmann, D. Moosbauer, M. Amereiler, C. Schreiner, F. Wudy, R. Schmitz, R. Schmitz, P. Isken, C. Dippel, R. Muller, M. Kunze, A. Lex-Balducci, M. Winter, and H. J. Gores, J Power Sources, 196, 1417 (2011).
34. H. J. Gores, S. Zugmann, D. Moosbauer, M. Amereiler, C. Schreiner, F. Wudy, R. Schmitz, R. Schmitz, P. Isken, C. Dippel, R. Muller, M. Kunze, A. Lex-Balducci, M. Winter, and M. Winter, J Power Sources, 196, 1417 (2011).
35. P. Murrmann, P. Niehoff, R. Schmitz, S. Nowak, H. Gores, N. Ignatiev, P. Sartori, M. Winter, and R. Schmitz, Electrochem Acta, 114, 658 (2013).
36. M. B. Armand and C. E. Kaldin, in United States Pat. US 4505997 (1985).
37. L. J. Krause, W. Lamanna, J. Summerfield, M. Engle, G. Korba, R. Loch, and R. Atanasoski, J Power Sources, 68, 320 (1997).
38. M. Winter, Doctoral thesis, Westfälische Wilhelms-Universität, in (1995).
39. M. Winter, G. H. Wrodnigg, J. O. Besenhard, W. Biberacher, and P. Novak, J Electrochem Soc, 147, 2427 (2000).
40. L. A. Dominie, V. R. Koch, and T. J. Blakley, Electrochim Acta, 37, 1511 (1992).
41. H. Yang, K. Kwon, T. M. Devine, and J. W. Evans, J Electrochem Soc, 147, 4399 (2000).
42. P. Murrmann, R. Schmitz, S. Nowak, H. Gores, N. Ignatiev, P. Sartori, S. Passerini, M. Winter, and R. W. Schmitz, J Electrochem Soc, 160, A535 (2013).
43. L. Turowsky and K. Seppel, Inorg Chem, 27, 2135 (1988).
44. L. A. Dominie, Wo 9202966, (1992), in.
45. M. Wachtler, M. R. Wagner, M. Schmied, M. Winter, and J. O. Besenhard, J Electroanal Chem, 510, 12 (2001).
46. R. Schmitz, R. Schmitz, R. Muller, O. Kazakova, N. Kalinovich, G. V. Roschenthalr, M. Winter, S. Passerini, and A. Lex-Balducci, J Power Sources, 205, 408 (2012).
47. K. Xu, S. P. Ding, and T. R. Jow, J Electrochem Soc, 146, 4172 (1999).
48. P. Murrmann, B. Streepert, R. Kloebsch, N. Ignatiev, P. Sartori, M. Winter, and I. Cekic-Laskovic, Phys Chem Chem Phys, 17, 9352 (2015).
49. K. Kanamura, T. Okagawa, and Z. Takehara, J Power Sources, 117, 59 (1995).
50. M. Dabbi, P. Ghamour, F. Tran-Van, D. Lemordant, and M. Amour, J Power Sources, 196, 9743 (2014).