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Investigations on the electrochemical performance and thermal stability of two new lithium electrolyte salts in comparison to $LiPF_6$

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ABSTRACT

Electrolyte solutions, containing the lithium salts lithium-cyclo-difluoromethane-1,1-bis(sulfonyl)imide (abbreviated as LiDMSI) and lithium-cyclo-hexafluoropropane-1,1-bis(sulfonyl)imide (LiHPSI) dissolved in organic carbonate solvents, were electrochemically investigated on graphite and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) electrodes and compared to the electrolyte salt $LiPF_6$ with regard to conductivity, the electrochemical stability window, the anodic dissolution behavior vs. aluminum as well as the thermal stability behavior at 60 °C. XPS studies were carried out to investigate the influence of the salt on the composition and the thickness of the solid electrolyte interphase (SEI). Constant current cycling experiments proved the potential applicability of the investigated salts for lithium ion batteries.

1. Introduction

The technical and economic impact of lithium-ion batteries has grown enormously in the past two decades [1–6]. The fact that the interest in battery applications that operate over a wide temperature range has recently increased leads to a rising demand for new cell materials.

Currently, the standard electrolyte solution is comprised of the conducting salt lithium hexafluorophosphate ($LiPF_6$) dissolved in mixtures of cyclic carbonates (e.g. ethylene carbonate and propylene carbonate [7–10]) and linear carbonates (e.g. dimethyl-, diethyl- and ethyl-methyl carbonate) [11,13–19]. In addition to the temperature range, further electrolyte requirements include: a sufficient electrochemical stability window [20], decent ionic conductivities, the ability to form a stable solid electrolyte interphase (SEI) on the graphitic anode [21–30] and the specification to avoid aluminum dissolution of the current collector on the cathode side [31,32]. In addition to the performance, economical aspects need to be regarded, as well [17,18,33–35]. Among the investigated electrolyte salts, $LiPF_6$ comprises the overall best compromise regarding performance and costs so far.

Still, there are properties of $LiPF_6$ that hinder the utilization to the fullest extent.

There is the limited chemical stability toward protons (stemming e.g. from trace amounts of water in the system or from electrolyte solvent oxidation) that can cause the formation of HF, which detrimentally affects the battery performance as well as the safety [36–38]. In addition, the thermal stability of an $LiPF_6$ based electrolyte solution is only given up to 55 °C [14,36,39–41]. At higher temperatures, $LiPF_6$ decomposes and the resulting products react with solvent molecules which can yield highly toxic substances [42].

In order to offer stability at higher temperatures, alternative salts with a higher thermal stability are required which are still able to compete with $LiPF_6$ concerning the mentioned performance related properties. Studies have shown that lithium borate salts fulfill these requirements to a certain point. Lithium bis(oxalato)borate (LIBOB) [43,44], lithium difluoro-(oxalato)borate (LiDFOB) [45–47] and lithium tetrafluoroborate ($LiBF_4$) [48] all showed promising temperature stability and cycling performance though not being able to replace $LiPF_6$ up to this day.

Another class of salts which offers sufficient cycling results are molecules which contain an imide group. The most investigated and promising salt in this class is displayed by lithium bis(trifluoromethanesulfonyl)imide (LITFSI) [49–52]. Although

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LiTFSI surpasses some of the properties of $LiPF_6$, the major drawback, the aluminum current collector dissolution [31], has limited the commercial use as a conductive salt [53–56].

Yang et al. showed that the $TFSI^-$ anion reacts with the aluminum to form $Al[N(SO_2CF_3)_2]_3$, which is then dissolved in carbonate electrolytes [57].

Krause et al. showed that imide salts with only a minor deviating structure to $TFSI^-$ do not dissolve the aluminum current collector [50]. For example, a deviation in side chains like in the salt $LiN(SO_2CF_2CF_3)_2$ (LiBETI) results in a reduced Al dissolution behavior almost comparable to $LiPF_6$.

In a previous publication double lithium salts with a similar structure to LiTFSI have been examined [58]. In this work we investigated two possible alternatives as conductive salt that also contain the imide function named lithium-cyclo-difluoromethane-1,1-bis(sulfonyl)imide (abbreviated as LiDMSI) and lithium-cyclo-hexafluoropropane-1,1-bis(sulfonyl)imide (LiHPSI).

The synthesis of these salts has been described elsewhere [59].

Only synthesis and conductivity measurements [60] of LiHPSI have been reported so far. A thorough electrochemical investigation of the two salts on Li-ion electrode materials has not yet been published.

2. Experimental

2.1. Cell preparation

The investigated salts were dried under reduced pressure at 60 °C. For all measurements 1 M solutions of $LiPF_6$ (Sigma Aldrich, battery grade), LiDMSI and LiHPSI (used as received) were prepared by dissolution in battery grade EC:DEC 1:1 (by wt%) (UBE). In order to provide a useful comparison of the two investigated salts concerning the literature known behavior of LiTFSI with regard to the anodic current collector dissolution, a 1 M solution of LiTFSI in the mentioned solvent mixture was applied for the purpose of this measurement only. The cell assembly for the constant current cycling experiments as well as the preparation for the conductivity, electrochemical stability window (ESW), aluminum anodic dissolution, cyclic voltammetry (CV) and thermal aging experiments were prepared under an argon atmosphere in a glove box from MBraun with an atmospheric water and oxygen content below 0.1 ppm. The anodes were composed of 87 wt% T44 graphite powder (Timcal), 8 wt% Super C65 (Timcal) and 5 wt% polyvinylidende difluoride (PVdF) (Kynar 761) [61] on copper foil current collectors. For the slurry preparation, Dimethylformamide (DMF) (Sigma–Aldrich, battery grade) was used. For the positive electrode $LiN_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) was used (Toda). The cathodes consisted of 85 wt% NMC, 8 wt% Super C65 (TIMCAL) and 7 wt% PVdF (Kynar 761) coated on aluminum foil current collectors. Dried *N*-methyl pyrrolidone (Fluka Inc.) served as solvent for the cathode slurry preparation. All electrochemical measurements were performed in three-electrode Swagelok® cell arrangements. The half-cell cycling tests were performed with lithium foil as counter (CE, 12 mm ∅) and reference electrode (RE, 5 mm ∅) and the graphite and NMC electrode as working electrodes (WE, 12 mm ∅), respectively. Whatman GfD fleece was used as a separator.

2.2. 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 Solartron 1260 A impedance gain phase analyzer was used in combination with a Solartron 1287 A 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 applied. The test procedure for the anodes (T44 graphite) consisted of three sequences with an operating potential range between 1.5 V and 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 1C for both the discharge and the charge 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 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 rates. With the intention to provide the cell with a recovery period, five cycles were added after the de-intercalation-rate test with a moderate current rate of C/5. The third sequence completed the 100 cycles with a current rate of 1C for the discharge and charge, which was again combined with a constant potential step at 0.025 V vs. Li/Li^+ for one hour. The cycling experiments were conducted on NMC, which required a different test procedure. The first three cycles functioned as formation cycles with a C-rate of C/5 and were followed by 50 cycles with a C-rate of 1C for the charge and discharge steps, respectively. The potential ranged from 3.0 V to 4.3 V vs. Li/Li^+ for the insertion and de-insertion steps, respectively.

The CV, ESW and anodic dissolution measurements were performed on a VSP potentiostat/galvanostat from BioLogic in the three electrode Swagelok® cell setup, respectively. For the CV measurements lithium metal was used as reference electrode (RE, 5 mm ∅) and counter electrode (CE, 12 mm ∅) and graphite electrodes (all with a similar weight) as working the electrode (WE, 12 mm ∅). The cell was run for three cycles within the potential range of 1.5 V to 0.025 V vs. Li/Li^+ with a potential sweep of $20\,\mu V\,s^{-1}$. For the anodic and cathodic stability window of the tested electrolyte salts in EC:DEC 1:1, a polished platinum disk electrode (Cypress Systems 1 mm diameter) was used as working electrode and lithium metal as CE (12 mm ∅) and RE (5 mm ∅). A potential sweep of $1\,mV\,s^{-1}$ was applied. The cell started at the open circuit potential which was increased to 6.1 V vs. Li/Li^+. A cut-off current density of $0.05\,mA\,cm^{-2}$ was chosen.

In the investigations regarding anodic dissolution of Al, metallic lithium was used as counter and reference electrode and a cleaned and pre-weighed aluminum foil (25 μm thickness, 12 mm diameter) acted as working electrode [31]. For each salt the mean values of three consecutive measurements were used. Starting from the open circuit potential, the cells were cycled to 4.5 V vs. Li/Li^+ with a rate of about $0.5\,mV\,s^{-1}$. Once 4.5 V vs. Li/Li^+ was reached, the potential was kept constant for 24 h. Afterwards, the aluminum electrode was taken out of the cell, cleaned, dried and weighed. The resulting weight (in grams) was compared to the value obtained before the cycling experiment in order to calculate the weight loss. The experimental procedure for the anodic dissolution experiment was taken from a previous publication [31].

2.3. Analytical measurements

For the thermal aging investigations, the salts were dissolved in EC:DEC 1:1 (by wt%) to yield the mentioned molar solutions. The samples were stored in air tight GC vials. Furthermore, to avoid contamination and side reactions, special PMP-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.