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Trimethylsiloxy based metal complexes as electrolyte additives for high voltage application in lithium ion cells

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TABSTRACT

Previous studies have shown that electrolyte additives based on metals and semimetals (LiBOB, Mg$(TFSI)_2$, $Al(TFSI)_3$) as well as additives containing trimethylsiloxyl (TMS) groups as ligands can have positive impact on the cycling performance of lithium ion battery cells due to solid electrolyte interphase (SEI) and/or cathode electrolyte interphase (CEI) film forming properties and/or scavenging properties towards acidic impurities. In this study, both active functionalities (metal core and trialkylsiloxy based ligands) were combined into one using Al, Ti and B as metal cores combined with TMS ligands ($M(TMS)_x$). All investigated additives $M(TMS)_x$ were able to improve the cycling performance regarding Coulombic efficiency, energy efficiency and capacity retention of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM111)/Li half-cells and NCM111/graphite full-cells at high potentials (>4.3 V vs. Li/Li$^+$). The formed CEI was studied by means of electrochemical impedance spectroscopy, scanning electron microscopy and X-ray photoelectron spectroscopy. The obtained results indicate that the investigated additives are either actively incorporated into the formed CEI layer (in case of Al, Ti as metal core) or interacting with decomposition products (in case of B as metal core) resulting in lower charge-transfer impedance and hence improved long-term cycling behavior.

1. Introduction

The development of lithium ion battery (LIB) cells with increased charging voltages (> 4.35 V) has become one of the most important strategies to enhance the LIB energy density [1–3]. The layered cathode material $LiNi_{1/3}Co_{1/3}Mn_{1/3}$ (NCM111) has attracted much attention for automotive applications [1,2]. By increasing the charging potential to 4.6 V vs. Li/Li$^+$, it is possible to increase the energy density of the NCM111 cathode based cells by 30%. However, the use of these materials at potentials $\geq$ 4.3 V vs. Li/Li$^+$ is still facing a series of challenges. One limitation is that the state-of-the-art organic carbonate based electrolytes get oxidized at potentials >4.5 V vs. Li/Li$^+$ [2,3]. As a consequence of this oxidation process protons are released, which initiate the disintegration of the cathode material [4]. While it has been found that the apparent capacity losses in the first initial cycle of NCM111 and other cathode materials are of kinetic nature and thus mostly recoverable[5], it is also clear from numerous reports that measures which reduce the reactivity at the cathode/electrolyte interface stabilize the layered transition metal oxide structure [6–8]. One approach is to artificially modify the cathode surface with metal oxide particles. In this regard, various inorganic oxides such as Al_2O_3, MgO, SiO_2 and TiO_2 were investigated as surface coating materials [9–11]. However, surface coatings are using complex production processes resulting in increased processing times and costs [12]. Hence, the utilization of electrolyte additives capable of *in situ* forming cathode electrolyte interphase (CEI) is considered as one of the most promising, economic and effective approaches. This concept accompanies the development of the LIB from the beginning on, since the pendant of the CEI, the solid electrolyte interphase (SEI), is technically essential for the anode side [2,13,14]. Today, specific SEI-forming electrolyte additives are used in order to modify the composition of the SEI [2,15–18]. Particular designed molecules are handpicked to decompose prior to the reduction of the main electrolyte components, i.e. $LiPF_6$ [19,20] and the organic carbonate solvents[15,21] in order to form a defined film of reduced thickness with improved ionic conductivity [2]. Only in

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recent time this approach is further applied to the cathode side to increase the performance at high potentials (>4.5 V vs. Li/Li^+). With an effective surface film the reactivity at the interface can be reduced stabilizing the layered transition metal oxide structure and thus reducing the Li^+/Ni^{2+} mixing effect. In addition, this formed surface layer can help to suppress further electrolyte decomposition and therefore decrease the disintegration of the cathode material. These film forming additives need to have a lower oxidative potential than the main electrolyte components in order to be able to form an effective cathode electrolyte interphase (CEI) before the main electrolyte components get oxidized [17]. A wide variety of electrolyte additives with different functions have been studied so far. Also salts like lithium bis(oxalato)borate (LiBOB) proposed by Xu et al. [22] can function as high voltage electrolyte additive in graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells showing enhanced cycling stability at 4.8 V vs. Li/Li^+. Murmann et al. [23] have shown that lithium-cyclo-difluoromethane-1,1-bis(sulfonyl)imide is an effective CEI additive for NCM operation at high potentials. Wagner et al. [7,24], using magnesium bis(trifluoromethanesulfonyl)imide ($Mg(TFSI)_2$) and aluminum tris(trifluoromethane)sulfonimide $Al(TFSI)_3$ as electrolyte additives, showed significant improvement in NCM111/Li half-cells at elevated potentials. It was shown that the metal cation and not the TFSI anion has the beneficial effect on cycling performance. Having this in mind, it becomes clear by calculating the weight percentage of the metal cation to the overall weight of the additive, that only 4.2% by weight of the additive relate to the positive effect in case of $Mg(TFSI)_2$ and 3.1% in the case of $Al(TFSI)_3$. Another detrimental effect on the lifetime of LIBs is caused by hydrogen fluoride (HF) promoted transition metal dissolution [4,8,25]. Much effort has been focused on additives capable of scavenging water and strong acids such as HF. Saidi et al. [26] first proposed trimethylsilyl (TMS) diethylamine as HF-scavenging additive for LIBs that effectively reduced the HF induced metal dissolution. Gallus et al. [27] have investigated in detail the mechanism of this additive and more oxidative stable TMS additives, whereas Qi et al. [28] could further prove a limited lifetime of these additives since the electrophilic TMS group not only reacts with HF and water from the electrolyte but also captures fluorophosphates and thus provokes the decomposition of the electrolyte salt $LiPF_6$.

In this work, we developed a new class of compounds combining the HF-scavenging properties with metal cores in order to combine both advantages of the aforementioned approaches. Metal compounds with Al and Ti as central atoms, namely tetrakis(trimethylsiloxy)titanium (TMST), lithium tetrakis(trimethylsiloxy)aluminate (LiTMSA) and tris(trimethylsiloxy)aluminum (TMSA) (Fig. 1), were synthesized and analyzed regarding their potential application as additives for lithium-ion cells operating at HV. The synthesized compounds were compared to the commercially available tris(trimethylsilyl)borate (TMSB) regarding their electrochemical performance. TMSB was already investigated by several research groups who found that TMSB is able to form a thin and compact surface film and can therefore improve the cycling performance of lithium ion batteries [3,29–31].

2. Experimental

2.1. Chemicals and preparation

Tris(trimethylsilyl)borate (TMSB) (98%) was purchased from abcr GmbH, Germany, and was purified by distillation. Aluminum chloride (99.99%), n-Butyllithium (1.6 M solution in hexane), Titanium isopropoxide (>97%) Trimethylsilylacetate (97%) and Trimethylsilanol (>98%) were purchased from sigma Aldrich, Germany and used as received. Battery grade electrolytes and electrolyte components, 1 M $LiPF_6$ in EC:DEC (3:7 by wt.) were provided by BASF and were used as received. All investigated electrolytes were prepared in an argon filled glovebox with a content of H_2O and O_2 below 0.5 ppm. The standard electrolyte (1 M $LiPF_6$ in EC:DEC (3:7 by wt), BASF, battery grade) was used and mixed with the desired amount of additive by weight (wt%). All electrolytes were directly prepared before use. The NCM111 based cathodes were obtained using a slurry of 85 wt% of NCM111 powder (Toda), 7 wt% of polyvinylidene difluoride (PVdF) (Kynar 761) binder, 8 wt% Super C65 carbon black (Imerys) in N-methyl pyrrolidone (NMP, Fluka Inc.), coated on an aluminum foil current collector. NCM111/Li half-cells were assembled in a three-electrode setup using a Swagelok® cell type and 1 layer of FS2226 separator (Freudenberg) in an argon-filled glove box. For the full-cell setup, coin cells containing NCM111 and graphite (both commercially available electrodes provided by Litarion) were used.

2.2. Synthesis and characterization of additives

All used solvents were pre-dried by a solvent purification system (from Innovative Technology) and all reactions were carried out under argon atmosphere. The NMR measurements were performed with an Advance III spectrometer (Bruker – Germany), working at 400 MHz (^1H).

Synthesis of tetrakis(trimethylsiloxy)titanium (TMST) – According to the method of Bradley et al. [32], trimethylsilylacetate (Me_3SiOAc) (9.88 g, 0.074 mol) in cyclohexane was added dropwise to a boiling solution of titanium isopropoxide (5.17 g, 0.0182 mol) in cyclohexane during 4 hours under vigorous stirring. The solution was stirred overnight under reflux condition (b.p. 56 °C). The azeotrope of cyclohexane-isopropyl acetate was collected by distillation (b.p. 63°/10 mbar). The product was purified by distillation and tetrakis(trimethylsiloxy)titanium ($Ti(OSiMe_3)_4$) was collected as a colorless liquid (yield: 6.15 g, 84.1%) ^1H-NMR ($CDCl_3$, ppm) δ 0.13(s), ^{13}C-NMR ($CDCl_3$, ppm) 1.80(s), ^{29}Si-NMR ($CDCl_3$, ppm) δ 13.24, CHN analysis: calc. C 35.62, H 8.97; meas. C 35.43, H 8.78, MS (g/mol): calc. 404.12 meas. 389.0.

Synthesis of lithium tetrakis(trimethylsiloxy)aluminate (LiTMSA) – According to Andrianov et al. [33], trimethylsilanol (7.41 g, 0.082 mol) was added dropwise to a mixture of *n*-butyllithium (56 mL) in toluene under cooling conditions (−80 °C) and argon atmosphere. The toluene was removed by distillation and the lithium trimethylsilanolate was collected as a white crystalline solid. A suspension of aluminumchloride ($AlCl_3$) (3.48 g, 0.026 mol) in toluene was added to the lithium silanolate

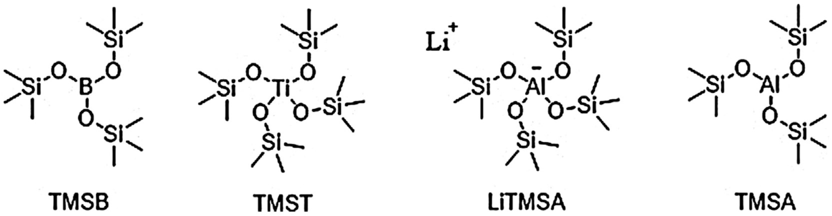

Fig. 1. Chemical structures of the commercially available additive TMSB and the synthesized additives TMST, LiTMSA and TMSA.