



Investigation of lithium ion battery electrolytes containing flame retardants in combination with the film forming electrolyte additives vinylene carbonate, vinyl ethylene carbonate and fluoroethylene carbonate

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HIGHLIGHTS

- Enhanced thermal stability of the electrolyte by the safety additives.
- Electrochemical improvement of optimized electrolytes by film forming additives.
- Post mortem analysis of electrodes and electrolyte from cycled cells.
- Decomposition of the safety additives was hindered by film forming additives.

ARTICLE INFO

Keywords:

Film forming electrolyte additives
Flame retardant additives
Triphenyl phosphate
Vinylene carbonate
Vinyl ethylene carbonate
Fluoroethylene carbonate

ABSTRACT

In order to address the trade-off between the safety lithium ion battery (LIB) electrolytes and their electrochemical performance, synergetic effects of flame retardant additives (FRs) in combination with film forming additives (FFAs) are investigated. Triphenyl phosphate (TPP) and a silicon-containing additive (WA) are applied as FRs to improve the onset temperature of the thermal runaway of a LIB standard electrolyte (LP57: 1 M LiPF₆ in EC:EMC 3:7) about 15 K and 28 K, respectively. The application of the FRs in MCMB graphite/lithium metal and NMC111/lithium metal three-electrode cells induces insufficiencies in terms of charge/discharge cycling stability and rate capability.

It is investigated if the addition of FFAs can degrade the insufficiencies that are induced by the FRs. Vinylene carbonate, vinyl ethylene carbonate and fluoroethylene carbonate are added to a mixture of LP57 with 10% FR to enhance the cycling performance via improved interphase formation. Results reveal, that the rate capability of cells containing TPP or WA is especially improved by addition of 2% or 5% FEC, respectively.

Postmortem analyses of the electrodes by SEM and of the electrolyte by GC-MS are performed. Direct correlations between the cycling behavior during the C-rate study and the electrolyte decomposition products are drawn.

1. Introduction

Lithium ion batteries (LIBs) succeed in the market of portable consumer electronics for the last two decades. Nowadays, LIBs are used to power electric drive trains in hybrid electric and electric vehicles and are considered as key technology for grid scale storage [1–3]. The technology is promoted to face the depletion of fossil fuels, increasing carbon dioxide emissions and (urban) air pollution. However, to

enforce LIBs in large scale applications, improvements in terms of energy density, cycle-life and safety are indispensable [4–6]. Safety remains a serious concern for electro-mobility, especially since incidents of burning xEVs were reported [7]. These battery fires are mostly initialized by self-heated reactions under abuse conditions (induced e.g. by an internal short-circuit or overheating) [7]. Especially in case of insufficient heat dissipation, self-sustaining exothermic chemical reactions of the electrolyte and the electrode will accelerate and lead to

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smoke and fire development (thermal runaway). Several measures are taken to prevent or hamper the thermal runaway including safety vents [8] or positive temperature coefficient (PTC) elements [9] on cell level, as well as battery management systems (BMS) on module or battery level [10]. Unfortunately, safety features on cell level often only refer to a certain cell geometry and therefore, limit their potential application range. Nevertheless, to increase the intrinsic safety, the cell materials themselves have to be improved. Apart from approaches of increasing the thermal stability of electrode active materials, using ceramic electrode coatings and shutdown as well as ceramic separators [11–13], also the highly flammable electrolyte needs to be upgraded.

One of the most economic ways to improve properties of the LIB electrolyte in general is the addition of functional electrolyte additives to the electrolyte [14–17]. The incorporation of small amounts of additives to the existing electrolyte system holds the advantage of less additional expenses, because the established electrolyte production including plants and infrastructure can be maintained [18]. Zhang et al. divides different electrolyte additives in groups: (i) solid electrolyte interphase (SEI) forming improver [14,19], (ii) salt stabilizer [14,20], (iii) cathode protection agents [14,21,22], (iv) safety protection agents [14,23,24], (v) lithium deposit improver [14] and (vi) physical property improver [14].

The group of safety protection agents is represented by the flame retardant additives (FRs). FRs are frequently represented by organic phosphorous compounds like triphenyl phosphate (TPP) [25–27], triethyl phosphate (TEP) [28] and trimethyl phosphate (TMP) [29–31]. They interrupt the self-heating chain reactions of electrolyte decomposition products by scavenging the highly reactive free radicals. Thereby, they reduce the flammability of electrolytes. Furthermore, they are known to enhance the electrolyte's thermal stability [27,29]. Thus, thermal runaway onset temperature of the thermal runaway of the electrolyte is shifted to higher values by the reduction of heat release and self-heating.

However, due to their physical properties, including electrochemical instability and high viscosity, the application of such FRs in rising amounts may result in elevated impedances, advanced capacity fading and inferior rate capabilities. This trade-off between safety and electrochemical performance needs to be addressed. In the past it was shown, that specific insufficiencies of certain additives could be attenuated by addition of other additives [32], even synergetic effects of additive combinations were reported [33,34].

Aim of this work is to investigate electrolyte combinations including both, FRs and FFAs in order to generate synergetic effects and create electrolytes which are enhanced in safety and electrochemical performance. Vinylene carbonate (VC), vinyl ethylene carbonate (VEC) and fluoroethylene carbonate (FEC) are used as FFAs. These compounds are electrochemically reduced during the first cycle on the graphite surface [35,36]. Thereby, a surface layer on the anode is formed via electrochemically induced polymerization reactions [37–39]. In order to protect the FR from reductive decomposition, a FFA has to be used, that decomposes prior to the safety additive (TPP or WA).

The FFA should provide a SEI that reduces or prevents the reductive activity of the anode and prevents the decomposition of the safety additive on the graphite surface. VC is one of the most frequently used FFAs [40]. It is known for its effective SEI, which is formed during the first cycle before the main electrolyte solvents, consisting typically of ethylene carbonate (EC) and linear carbonates [41], decomposition occurs. VC improves the charge/discharge cycling capability and reduces the irreversible capacity loss of anodes [42]. The SEI formed by VEC containing electrolytes is believed to be stable during volume changes of the anode. Due to the achieved SEI flexibility, the reversibility of the lithium insertion and extraction can be enhanced [43]. It has already been investigated in combination with TPP and provides an enhanced rate capability [44]. Recently, FEC gained considerable attention. The additive provides good cycling performance and improves the capacity retention due to a lower SEI film resistance [45–48].

Herein, we report on the investigation of TPP and a silicon-containing phosphonate (WA) as FRs in LIB electrolytes, which were blended with a selection of FFAs to combine the enhanced safety performance (provided by the FRs) with an improved electrochemical performance (maintained by the FFAs).

2. Experimental

2.1. Electrolyte preparation

The electrolyte mixtures were prepared in an argon filled glovebox (H_2O and $\text{O}_2 < 0.1$ ppm). LP57 (1 M LiPF_6 ; EC/EMC (ethyl methyl carbonate), 3:7, by wt) from Merck was used as the reference electrolyte for all further mixtures. The additive containing electrolytes were mixed inside the glovebox by adding the weighted amount of additive into the weighted amount of LP57. TPP (purity 99 + %) was purchased by Acros Organics, the FR (WA) was provided by Wacker Chemie AG, VC (Battery grade) by UBE Industries, VEC (99.0%) by Sigma Aldrich and FEC (Battery grade) by Solvay. The investigated electrolyte mixtures are listed in Table SI 1.

2.2. Electrode preparation

The single side coated electrodes were purchased MCMB (meso-carbon microbeads) graphite electrodes with 100 g m^{-2} mass loading and 91.5 wt% MCMB graphite and NMC (lithium nickel manganese cobalt oxide) electrodes with 150 g m^{-2} mass loading and 93.0 wt% NMC111. The electrodes were punched into discs (diameter: 12 mm) and dried in a glass oven (B-585, Büchi) for 24 h under reduced pressure (1×10^{-3} mbar) at 120°C and stored in the Unilab glovebox by MBraun (H_2O and $\text{O}_2 < 0.1$ ppm) with argon atmosphere (99.998%, Westfalen Gas).

2.3. Thermal stability investigations

The accelerating rate calorimeter (ARC 254, Netzsch Gerätebau, Germany) was used to perform heat-wait-search-experiments (HWS), to identify onset temperatures of the thermal runaway (self-heating rate of 0.2 K min^{-1}) of different electrolyte mixtures. Bombs of stainless steel (Thermal Hazard Technology, UK) were filled with 2 mL electrolyte in the glovebox. The filled bomb was inserted into the reaction chamber located in the center of the accelerating rate calorimeter and connected to the sensor. Samples of LP57 and LP57 with 10% WA were initially heated (5 K min^{-1}) to 50°C , the sample with LP57 and 10% TPP to 100°C . The sample temperature was discreetly lifted up with temperature increments of 5 K (heat-mode) and stabilized (wait-mode) for 1 h. Afterwards the accelerating rate calorimeter monitored (search-mode) the bomb temperature for self-heating reactions (exothermic threshold of 0.02 K min^{-1}). By absence of self-heating reactions, the accelerating rate calorimeter will proceed with another HWS loop. If the exothermic threshold is exceeded due to self-heating reactions, the accelerating rate calorimeter switches to the adiabatic mode and follows the temperature of the sample to maintain adiabatic conditions until the exothermic limit of 400°C is reached or until the temperature increase stops. If the temperature increase stops, a new HWS loop was initiated which stops by reaching the limit temperature of 250°C . After the measurement ended by passing the exothermic limit of 400°C or reaching the temperature limit of 250°C , the sample was cooled down to 40°C .

2.4. Electrochemical investigations

All cycling experiments were performed in T-cells with a three-electrode set-up and MCMB or NMC electrodes as working electrodes, lithium as counter and reference electrode and six layers of Freudenberg FS 2190 separator. Varying electrolytes (see Table SI 1) were investigated in these cells. The cycling performance was

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