Graphite electrode thermal behavior and solid electrolyte interphase investigations: Role of state-of-the-art binders, carbonate additives and lithium bis(fluorosulfonyl)imide salt

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HIGHLIGHTS

- Lower and better distributed heat energy released with SBR/CMC binders.
- SBR is involved in the thermal processes.
- The polymeric nature of the VC-derived SEI is preferable for safer batteries.
- The 0.33 M LiFSI and 0.66 M LiPF$_6$ salt ratio hinders Al corrosion up to 4.3 V
- The 0.33 M LiFSI and 0.66 M LiPF$_6$ salt ratio improves the thermal behavior.

ARTICLE INFO

ABSTRACT

The risk of thermal runaway is, for Li-ion batteries, a critical issue for large-scale applications. This results in manufacturers and researchers placing great emphasis on minimizing the heat generation and thereby mitigating safety-related risks through the search for suitable materials or additives. To this end, an in-depth stepwise investigation has been undertaken to provide a better understanding of the exothermic processes that take place at the negative electrode/electrolyte interface as well as an increased visibility of the role of the state-of-the-art electrode binders, additives and lithium salt by means of the classical DSC technique.

A reliable experimental set up helped quantify the beneficial or harmful contribution of binder polymers to the exothermic behavior of the CMC/SBR containing graphite electrode film in contact with 1 M LiPF$_6$ in EC:DMC:EMC (1:1:1 v/v/v) electrolyte.

Further, the role of the VC, FEC and VEC electrolyte additives (2 wt%) in reinforcing the protective SEI layer towards thermally induced electrolyte reduction is discussed in the light of infrared spectroscopy and transmission electron microscopy analyzes results.

Moreover, after a preliminary corrosion study of LiPF$_6$/LiFSI mixtures, we showed that the 0.66/0.33 M composition can be used in commercial NMC-based LiBs with a positive effect on the thermal runaway.
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1. Introduction

The development of greener transportation is an alternative to mitigate environmental concerns and energy dependence on fossil fuels. Due to their high energy density and long cycle life, Li-ion batteries (LiBs) are the most attractive power source for electrical vehicles (EV) and hybrid electric vehicles (HEV). However, the use

of high energy LiBs imposes stringent safety requirements either to comply with international transport regulations or with regard to end use, though standardized safety tests are described in technical documents from various sources [1] (UL, ANSI, SEA, ISO, IEC and US ABC). These tests are widely performed at different scales (cell, battery, pack), and they are sometimes amended according to technical and scientific progress in order to ever more adequately reflect a battery failure process. Calorimetry techniques (DSC, ARC) are the techniques of choice for appraising thermal behaviors at component and cell levels respectively and coupling them with analytical methods [2–7] (FTIR, XRD, GC-MS, XPS …) can help identify the mechanisms involved during abusive use conditions.

The internal temperature rise can lead to thermal runaway triggered by several exothermic phenomena stemming from reduction/oxidation of the electrolyte as well as thermal decomposition of battery components (electrolyte [8–12], anode [3–5,7,13–20], cathode [21–24] and separator [25,26]) up to partial or complete oxidation of these components according to effective adverse effects of the thermal runaway process. As the first exothermic reaction takes place at the negative electrode/electrolyte interface, improving the understanding of the thermal behavior of this interface and more accurately assessing the safety gains (higher onset temperature of exothermic reactions, less related energy release) associated with an electrolyte or composite compound change is of utmost interest. Over the past two decades, a plethora of studies have been devoted to the elucidation of some of the cascade reactions involved in the thermal runaway complex phenomenon. The most important one relates to the SEI breakdown. Starting from 100 °C, the basic salts [27,28] (lithium carbonate Li_2CO_3, lithium alkyl carbonates $ROCO_2Li$, $(CH_2OCO_2Li)_2$) from the passivating layer (Solid Electrolyte Interphase -SEI- [29]) issuing from the carbonate solvents electrochemical reduction first react with gaseous PF_5 [17], coming from $LiPF_6$ salt thermal degradation [10,30–34]. These acid-base reactions promoted by the high volatility of linear carbonates in turn damage the SEI, hence facilitating the access of the electrolyte to the lithiated graphite. Such a consensual assumption offers a promising outlook to shift the SEI decomposition to higher temperature by changing its composition and limiting PF_5 formation.

Commercial electrolytes essentially consist in various binary or ternary mixtures of carbonate-based solvents (EC, PC, DMC, DEC, DMC) with $LiPF_6$ salt. Electrolyte additives (<10%) are added, in particular to improve the physical properties of the SEI during the formation of the LIBs and, consequently, to enhance their cyclability. The most popular additives enhancing SEI properties are i) vinylene carbonate (VC), ii) fluoroethylene carbonate (FEC) and iii) vinyl ethylene carbonate (VEC). On a safety point of view, the addition of VC leads to a higher onset temperature and a decrease of the total heat release upon heating of lithiated graphite [35]. FEC, which is widely used in the case of silicon electrodes, is reported to also improve the thermal stability of lithiated silicon/electrolyte interface [36]. On the other hand, unlike the case of VC and FEC, VEC does not lead to safety improvement of graphite-based complete cells as observed by Ma et al. using ARC measurements [37]. Hence, each additive leads to characteristic thermal behavior changes which are due to the different chemical/thermal properties of the SEI layer compounds of polymeric or organic and inorganic nature. These interesting results reported in literature stress the relevance of undertaking an in-depth comparative study on the role of each additive on the negative electrode/electrolyte interface thermal behavior through the determination of the SEI texture/composition by analytical methods.

As aforementioned, in terms of thermal runaway, $LiPF_6$ plays a crucial role due to the formation of the PF_5 Lewis acid. In fact, Ryou et al. [38] have proved the influence of the salt by demonstrating

the absence of reactivity between lithium alkyl carbonates and lithium bis(oxalate) borate (LiBOB) up to 150 °C in contrast to the exothermic reaction starting around 60 °C with $LiPF_6$. However, the limited solubility of LiBOB remains a critical drawback for considering this salt as a suitable alternative to $LiPF_6$ in commercial LiBs. Concerning the imide salts, our group has showed that acid-base reactions involving SEI components do not occur in the case of lithium bis(fluorosulfonyl)imide (LiFSI) salt but a sharp exothermic peak is observed with lithiated graphite powder at 200 °C due to FSI^- reduction [17].

Commercial negative electrodes consist of a film tape-cast on a copper foil, the film being composed of graphite (95–98%), conductive carbon (2–5%) and polymeric binders (2–5%). The role of binders on the thermal stability of graphite anodes has been studied by Park and al [7]. They showed that the heat energy release relative to the delithiation process is strongly diminished in the case of CMC/SBR or polyacrylic acid (PAA) binder, compared to PVDF binder. They assumed that this thermal stability improvement is due to the better coverage of the graphite particles, thanks to the strong interactions between functional groups of binder and graphite surface; the covering polymeric binder layer would have a lower lithium diffusivity than the SEI, slowing the thermally induced graphite delithiation. However, they only focused on the exothermic phenomena below 200 °C and did not take into account the reactivity of binders towards intercalated lithium as previously demonstrated in the case of PVDF [4].

Thanks to the numerous studies that have been devoted to the influence of binder, additive and salt components, it is clear that each of them plays a role on the thermal behavior of LiBs. However, identifying the contribution of each and comparing results with one another in a consistent way is quite difficult owing to differences in test samples (electrolyte and electrode composition …), techniques (DSC, C80, ARC …) and experimental protocols (sample preparation, heating ramp …) used in these studies.

To address these issues, we have carried out a comparative study where the same electrolyte (1 M $LiPF_6$ in EC:EMC:DMC (1:1:1 v/v/v)), and same negative electrode composite (graphite/Super P Carbon black/CMC/SBR 94/2/2/2 wt%) were used. Additionally, an optimized reliable experimental protocol was defined, allowing a high reproducibility of the DSC measurements. Using this configuration, our aim was to separate and trace back the origin of the contribution to exothermic reactions of CMC/SBR binder as well as the VEC, VC and FEC electrolyte additives, thanks to SEI characterization by means of FTIR and TEM. To complete this comparative study on critical components of LiBs under thermal abuse, the salt contribution was also studied through partial substitution of $LiPF_6$ by LiFSI, taking into account the aluminum corrosion issue [39].

2. Experimental

2.1. Materials

The reference electrolyte, purchased from Solvionic (France), is composed of 1 M $LiPF_6$ salt dissolved in a mixture of EC:DMC:EMC (1:1:1 v/v/v). Carbonate-based electrolyte test samples with salt mixtures of $LiPF_6$ (Aldrich, battery grade ≥ 99.99%) and LiFSI (Suzhou Fluolyte Co., purity > 99.9%) were prepared by adding the two salts in different molar ratios in EC:DMC:EMC (1:1:1 v/v/v, Solvionic) solvents mixture. Vinylene carbonate (VC), vinyl ethylene carbonate (VEC) and fluoroethylene carbonate (FEC) additives purchased from Sigma Aldrich (99% of purity) were added as 2 wt% level each to achieve final electrolytes composition for testing. The graphite powder electrode was composed of 90 wt% of natural graphite powder (d_{50}=19.4 μm, S.S.A. of 3 m^2/g, Hitachi) and 10 wt% of Super P carbon black (Timcal). The graphite film