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Synergistic thermal stabilization of ceramic/co-polyimide coated polypropylene separators for lithium-ion batteries

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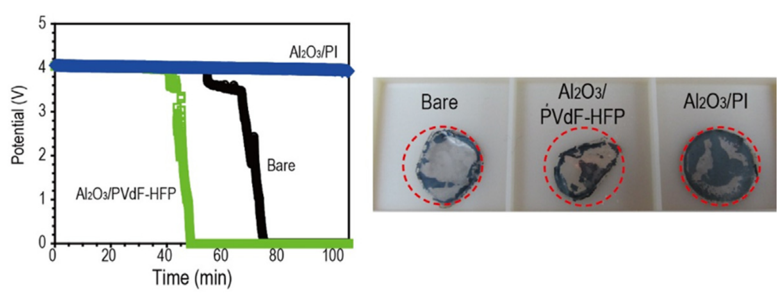
HIGHLIGHTS

- Co-polyimide (PI) is proposed as a polymeric binder for ceramic composite coatings.
- Al_2O_3/PI coatings synergistically enhance thermal stability of separators.
- Al_2O_3/PI coatings effectively improve the LIB safety by blocking short-circuits.

GRAPHICAL ABSTRACT



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ABSTRACT

To improve the safety of lithium-ion batteries (LIBs), co-polyimide (PI) P84 was introduced as a polymeric binder for Al_2O_3/polymer composite surface coatings on polypropylene (PP) separators. By monitoring the dimensional shrinkage of the PP separators at high temperatures, we verified a synergistic thermal stabilization effect between the Al_2O_3 ceramic and the PI polymeric binder. Although PI was thermally stable up to 300 °C, a coating consisting solely of PI did not impede the PP separator dimensional changes (−22% at 150 °C). On the other hand, the Al_2O_3/PI-coated PP separators efficiently impeded the thermal shrinkage (−10% at 150 °C). In contrast, an Al_2O_3/poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) combination lowered the thermal stability of the PP separators (−33% at 150 °C). As a result, the Al_2O_3/PI-coated PP separators remarkably suppressed the internal short-circuit of the unit half-cells associated with separator thermal shrinkage (100 min at 160 °C), whereas the PVdF-HFP retained only 40 min under identical conditions. The Al_2O_3/PI-coated PP separators achieved rate capabilities and cell performances similar to those of the bare PP separators.

1. Introduction

Because of their high energy density and the excellent cycle life, lithium-ion batteries (LIBs) have become one of the most promising power sources for new large-scale battery applications, such as for electric vehicles (EVs) and energy storage systems (ESSs) [1–5]. In order to fulfill consumer requirements for these new applications, new LIBs must reach a higher standard of safety, cycle retention, energy density, power capability, and price over those that have targeted small consumer electronics including laptops, cellular phones, and digital cameras. In particular, safety should be considered a top priority because LIBs can pose a threat to consumers' lives, thus threatening the very existence of battery

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manufacturers. Nevertheless, among the major LIB components, recent studies have mainly been devoted to the electrochemically active materials such as cathodes, anodes, and electrolytes, to achieve higher energy densities, while the importance of separators, which play a pivotal role in safety, have thus far been rarely examined [5,6].

Separators are physical barriers placed between the cathode and anode to protect against internal short-circuits, while simultaneously offering lithium ion pathways through their pores [7,8]. When LIBs are exposed to abnormal conditions such as overcharging, physical crushing, or penetration, an internal short-circuit is created between the cathode and anode, producing a large exothermic heat, which finally leads to thermal runaway (generating smoke, flame, and finally explosion). Although microporous polyolefin-based separators frequently based on polyethylene (PE) and polypropylene (PP) have been widely adopted in commercial LIBs, their inherent low melting points and poor surface wetting by the liquid electrolyte significantly impede both safety and power capability [7–10]. Consequently, they have been a limitation for making the first step towards large-scale LIB applications [9,11–14].

Among various approaches to overcome these obstacles, surface coatings based on organic polymers, occasionally combined with inorganic ceramic fillers such as SiO_2, Al_2O_3, TiO_2, and MgO, have attracted substantial attention because of their simplicity, effectiveness, and processing versatility [7,10,11,13,15–17]. In most cases, the inorganic ceramic compounds require a sufficient amount of polymeric binder to retain them on the separator surface under mechanical stress during assembly or operation. For example, poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) has been suggested as a promising polymeric binder. Various types of PVdF-HFP ceramic composites have been suggested, resulting in improved separator wetting ability and thermal shrinkage at high temperatures [18–22].

Our work was motivated by an unlikely observation. The ceramic/polymer composite coating has been a versatile and popular method to improve separator thermal stability [7,23]. However, when the Al_2O_3/PVdF-HFP composite-coated PP separators were exposed to 150 °C for 30 min, the surface coated-separators shrank to a greater degree than the bare PP separators, as shown in Fig. 1 (the black dashed lines indicate the original size of the separators). As ceramic compounds are generally stable up to high temperatures, usually over 200 °C, this finding gave us the idea that ceramic/polymer composites can also play a crucial role in determining LIB safety. Despite the importance of polymeric binders, only a few detailed investigations on polymeric binder materials have been reported. Therefore, we herein consider the effect of polymeric binders on the thermal properties of separators. We previously suggested the use of thermally stable polyimide (PI)-based polymers, such as P84, as a coating layer for PE-based separators [11]. Furthermore, in a bid to explore the effect of P84 as a polymeric binder for ceramic/polymer composite separator coatings, various types of separators with different coatings were investigated for their dimensional stability at high temperatures, wetting abilities, rate capabilities, and cell performances.

2. Experimental

2.1. Materials

P84 co-polyimide (HP Polymer GmbH, M_w = 150,000), poly(-vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, Kynar Flex®2801, Arkema Inc.) and aluminum oxide (Al_2O_3, AES-11, Sumitomo Chemical Co.) were used as received without further purification. The chemical structure of P84 co-polyimide was shown in our previous work [11]. *N,N*-dimethyl-formamide (DMF), dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were purchased from Aldrich and used without further purification. $LiMn_2O_4$ (Kyushu Ceramics), polyvinylidene fluoride (PVdF, KF-1300, Kureha), conductive carbon (Super-P, Timcal), and Li metal foil (450 μm, Honjo Metal) were used. An ethylene carbonate/diethyl carbonate (EC/DEC = 1/1, v/v) mixture containing 1 M lithium hexafluorophosphate ($LiPF_6$) was used as a reference liquid electrolyte (PANAX ETEC Co.). Polypropylene (PP) separators were supplied from SKC Co. Ltd. (the prototype PP separators based on a dry process associated with biaxial stretching, thickness: 20 μm, porosity: 59%).

2.2. Preparation of surface-coated separators

DMF-based coating solution containing 3 wt.% of P84 was prepared for P84-coated PP separators. DMAc-based coating solution containing Al_2O_3/P84 (90/10 by weight), and acetone-based coating solution containing Al_2O_3/PVdF-HFP (97/3, 95/5, 93/7, and 90/10 by weight) were prepared for Al_2O_3/P84 coated separators and Al_2O_3/PVdF-HFP separators, respectively.

Various types of coating layers were formed onto PP separators via simple dip-coating process, followed by drying in the fume hood for 1 h at room temperature. The coated PP separators were dried in the vacuum oven for 24 h at 40 °C to completely evaporate the solvent prior to use.

2.3. Characterization of coated separators

The surface morphologies of bare and coated PP separators with different coating layers were investigated by field-emission scanning electron microscope (FE-SEM, S4800, Hitachi). The air permeability (Gurley number) of separators was determined using a densometer (4110N, Thwing-Albert). The electrolyte wettability of separators was determined using two different methods: electrolyte immersion-height test and electrolyte drop test [24]. Electrolyte immersion-height test was evaluated by measuring the

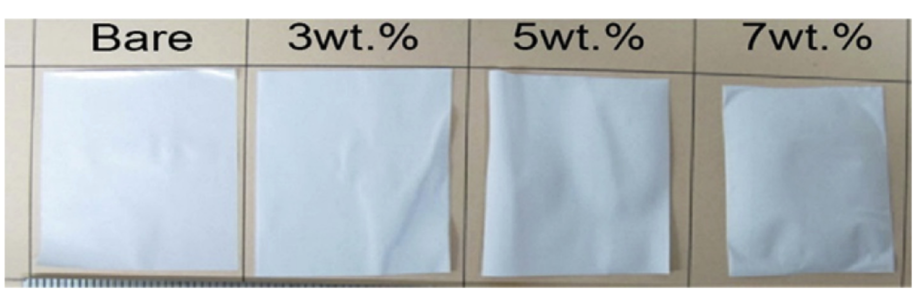

Fig. 1. Digital camera images of bare and Al_2O_3/PVdF-HFP composite-coated ceramic coated PP separators (3, 5, 7 wt.%) after heat treatment at 150 °C for 0.5 h.