



New flame-retardant composite separators based on metal hydroxides for lithium-ion batteries



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ABSTRACT

In order to improve the safety of lithium-ion batteries (LIBs), composite separators were developed using two typical metal hydroxides, aluminum hydroxide (Al(OH)₃) and magnesium hydroxide (Mg(OH)₂). The composite separators were prepared by adding ceramic coating layers comprising one of the chosen metal hydroxides and a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) binder to polyethylene (PE) separators. Both the metal hydroxide-composite separators exhibited promising fire-retardant properties, which resulted in a significant self-extinguishing time (SET) reduction and also helped to suppress any thermal dimensional changes in the PE separators that may occur at high temperatures. Due to the hydrophilic properties of metal hydroxides, unit cells employing the composite separators achieved significant improvements in rate capability that were closely associated with their improved wettability for liquid electrolytes. The electrochemical stability of the Mg(OH)₂-composite separators was verified to be comparable to that of PE separators; however, the Al(OH)₃-composite separators were electrochemically unstable over the same voltage range. This highlights the highly improved capacity retention of the developed unit cells that employ Mg(OH)₂-composite separators.

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1. Introduction

Ever since their debut in the early 1990s, lithium-ion batteries (LIBs) have dominated many fields of small-scale consumer electronics, and are now promising candidates for large-scale applications such as in electric vehicles (EVs) and energy storage systems (EESs) [1–5]. Along with the ever-increasing demand for high energy density, cathodes, anodes, and electrolytes have received significant interest, while the separators have received somewhat less interest. This is because separators are generally considered to be electrochemically inactive [6,7]. It must be noted, however, that large-scale LIBs will be much less viable if they are not sufficiently safe, because they could pose a threat to consumers' lives, causing problems for battery manufacturers.

Separators have been considered to be a critical component in securing battery safety [5–8]. Separators maintain the separation between the cathode and anode by acting as a physical barrier between these two components while providing a pathway for Li

ion migration [9]. Under abnormal conditions such as overcharging, high-temperature storage, mechanical rupture, and penetration, internal short-circuits between the cathode and anode can occur, leading to the so-called thermal runaway in LIBs, accompanied by explosions, smoke, and fire [8,9]. Commercialized separators, typically consisting of polyethylene (PE) and/or polypropylene (PP), have suffered from chronic drawbacks: low melting temperature and poor wettability with liquid electrolytes, making it difficult for them to be widely adopted in large-scale LIBs.

Composite separators are a widely used solution to these obstacles. Composite separators prepared by introducing surface coating layers containing ceramic compounds such as aluminum oxide (Al₂O₃), silica (SiO₂), tin oxide (TiO₂), and nickel oxide (NiO), and polymers such as polyethylene oxide (PEO), poly(vinylidene fluoride), and polydopamine have been studied [10–13]. In our previous study, we demonstrated the effectiveness of adding thermally resistant coating layers to PE separators, which significantly improved the thermal dimensional stability of the PE separators without impeding the cell performance [5,14].

Herein, as a further step toward achieving superior protection of LIBs against fire during thermal runaway, composite separators are prepared by adding ceramic metal hydroxides to the separators. As metal hydroxides are known to be one of the most used halogen-free flame retardants, it was anticipated that these

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hydroxides could enhance the thermal stability of LIBs. Metal hydroxides act as flame retardants by releasing water at high temperatures. Furthermore, metal hydroxides are deemed to be favorable for use in composite separators because of their higher decomposition temperatures than polyolefin-based separators, good mechanical and environmentally benign properties, and low price [15,16]. To the best of our knowledge, no report has been issued about the use of ceramic-based flame retardants in LIB separators. The typical metal hydroxides aluminum hydroxide (Al(OH)₃) and magnesium hydroxide (Mg(OH)₂) were selected for coating onto the PE separators to prepare novel composite separators. Furthermore, the effect of these composite coating layers on the thermal stability of the PE separators was evaluated. The influence of the composite separators on the electrochemical properties such as cycle life and rate capability of unit cells was also investigated.

2. Experimental

2.1. Materials

Lithium-cobalt oxide (LiCoO₂, KD-10, Umicore Korea, Korea), graphite (Showa Denko, Japan), polyvinylidene fluoride (PVDF; KF-1300, Kureha, Japan), conductive carbon (Super-P, Timcal, Switzerland), and Li metal foil (400 μm, Honjo Metal, Japan) were used. A mixture of 1.15 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate/ethyl methyl carbonate (EC/EMC=3:7 by volume) was purchased from PANAX ETEC (Korea) and used without further purification. *N*-methyl-2-pyrrolidone (NMP, Aldrich), acetone (purity: >99.9%, <0.005% water content, Aldrich), aluminum hydroxide (Al(OH)₃, Aldrich), magnesium hydroxide (Mg(OH)₂, Aldrich) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Kynar 2801, Arkema Co.) were purchased from Aldrich (Republic of Korea) and used without further purification and/or drying process. The specific properties of Al(OH)₃ and Mg(OH)₂ were listed in Table 1. Microporous polyethylene separators (PE, ND420, Asahi Kasei E-materials, Japan, porosity: 41%, thickness: 20 μm) were used as bare separators.

2.2. Preparation of the ceramic-coated separators

The coating solution was prepared by mixing ceramic compounds (Al(OH)₃, Mg(OH)₂) and PVDF-HFP into acetone solvent, where weight ratio of ceramic/PVDF-HFP was fixed. Once 1 wt.% PVDF-HFP solution was prepared by dissolving PVDF-HFP in acetone after stirring 24 h at room temperature, and then proper amount of ceramic fillers (PVDF-HFP/ceramic=1/9 by weight) were dispersed by stirring for 24 h at room temperature, followed by 1 h ultra-sonication. PE separators were soaked in the as-prepared coating solution for 30 sec using a dip-coating process. Immersed PE separators were then dried in the hood for 12 h to evaporate acetone, followed by vacuum drying at 50 °C for 12 h. Coating thickness was controlled in 12 μm for Al(OH)₃ and 5 μm for Mg(OH)₂, respectively. The surface morphology of the composite separators was examined by field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan).

2.3. Thermal stability of the ceramic-coated separators

To evaluate thermal stability of metal hydroxides, thermal gravimetric analysis (TGA851, Mettler Toledo) was carried out at a heating rate of 10 °C min⁻¹ in air, from which decomposition temperature of metal hydroxides was determined.

To examine the thermal stability of separators, dimensional changes of separators cut into squares (3 cm × 3 cm) were monitored as keeping them at 140 °C for 30 min. Thermal shrinkage was calculated according to the following equation, where A_i and A_f indicate the area of the samples before and after the high temperature storage, especially:

$$\text{Thermal shrinkage ratio (\%)} = [A_f - A_i] / A_i \times 100 \quad (1)$$

2.4. Porosity of the ceramic-coated separators

The porosity of the bare separators was evaluated by a simple liquid absorption test according to ASTM D2873 [9,17]:

$$\text{Porosity (\%)} = V_{\text{occupied by hexadecane}} / (V_{\text{polymer}} + V_{\text{occupied by hexadecane}}) \times 100 \quad (2)$$

The porosity of the ceramic-coated layers was determined using Eq. (3) based on the true density of the composite substituents, where A is the area of the composite separators, t is the thickness of the ceramic-coating layers, w is the weight of the ceramic-coating layers. r_c and r_p are the ratio of the ceramic powder (90% in our case) and polymeric binder (10% in our case), respectively. d_c and d_p are the true density of the ceramic powder (Al(OH)₃ = 2.42 g cm⁻³, Mg(OH)₂ = 2.37 g cm⁻³) and polymeric binder (PVDF-HFP = 1.77 g cm⁻³).

porosity of ceramic coating layers

$$\begin{aligned} & \left(\frac{\text{volume of the ceramic coating layer}}{\text{volume of the ceramic composite}} \right) \\ &= \frac{\text{volume of the ceramic composite}}{\text{volume of the ceramic coating layer}} \\ &= \frac{(A \times t) - w(r_c \times d_c + r_p \times d_p)}{(A \times t)} \end{aligned}$$

2.5. Gurley number of the ceramic-coated separators

Gurley number of the separators was evaluated using a densometer (4110N, Thwing-Albert, USA) according to JIS P8117 [17]. The Gurley number is determined by measuring the elapsed time of a specific volume of air (100 mL) to pass through separators under a given pressure (here, 6.52psi) [17].

2.6. Electrolyte uptake of the ceramic-coated separators

The uptake of electrolyte solution was determined by measuring the weight changes of separators using Eq. (4) [2,13,17]:

$$\text{Uptake amount (wt.\%)} = [W_2 - W_1] / W_1 \times 100 \quad (4)$$

Here, W_1 and W_2 represent the weights of the samples before and after immersion in the electrolyte, respectively

Table 1
Specific physical properties of used inorganic powders.

	Particle size (nm)	Density (g cm ⁻³)	Specific surface area (m ² g ⁻¹)	Water content (wt.%)
Al(OH) ₃	~10	2.42	58.6	46
Mg(OH) ₂	500~700	2.34	6.9	30

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