



A Flame-Retardant Composite Polymer Electrolyte for Lithium-Ion Polymer Batteries



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ABSTRACT

A new composite polymer electrolyte (CPE) containing a flame-retardant material, Mg(OH)₂, is fabricated via a two-step process: porous poly(vinylidene-co-hexafluoropropylene) films composited with different Mg(OH)₂ contents are first prepared via casting and extraction steps, and they are then impregnated with a liquid electrolyte. As the Mg(OH)₂ content in the CPEs increases, their flame-retardant properties are greatly improved compared to those of the bare polymer electrolyte. Moreover, the better wettability of Mg(OH)₂ toward a liquid electrolyte leads to higher ionic conductivities of CPEs, thereby resulting in a better rate capability in LiCoO₂/graphite lithium-ion polymer batteries (LiPBs). However, the Mg(OH)₂ content must be limited to less than 40 wt% to maintain the mechanical properties of the corresponding CPEs.

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1. Introduction

Unless the energy density level of the state-of-the-art lithium-ion batteries (LIBs) is raised significantly, it will difficult to encounter various electric vehicles (xEVs) on the road with any frequency or to use the cheap electricity stored in energy storage systems (ESSs) in the near future. [1–3] Thus, extensive efforts have been devoted to increasing the energy density of LIBs using new electrode and electrolyte materials and well-developed cell designs and production technologies. [4–6] However, unfortunately, a higher energy density of batteries always causes inevitable safety issues that are occasionally called abuse tolerances towards severe and abnormal testing conditions. [7] This is why mid- or large-format LIBs for xEVs cannot avoid the use of thermally stable separators that require additional ceramic particles or heat-resistive polymers, instead of the conventional cheap polyolefins. For example, when ceramic coated separators (CCSs) are used for LIB cells, they can survive even

in a hot box at 150 °C without any internal short-circuits due to the dimensional stability of CCSs. [8–10]

However, regardless of these improved safety of LIBs, there are few methods to delay or extinguish fires that occur on LIBs. One of the most representative methods is to introduce flame-retardant components such as phosphates into the liquid electrolyte that can act as fuels in the battery. [11,12] Moreover, Michael F. Rectenwald et al. reported phosphoryl-rich flame-retardant anions for new-type lithium salts towards safer LIBs. [13] However, because the flame-retardant level is exactly proportional to the flame-retardant content, it is difficult to reach a meaningful level without decreasing the electrochemical performance. To avoid these limitations, we proposed a new ceramic-coated separator by replacing the conventional ceramic particles such as alumina, Al₂O₃, with magnesium or aluminum hydroxides, Mg(OH)₂ or Al(OH)₃, that can produce water via thermal decomposition. In particular, the Mg(OH)₂-coated separators impregnated with the liquid electrolyte exhibited greatly improved the self-extinguishing property without reducing the electrochemical properties. [14] Then, we extended this concept to polymer electrolytes by fabricating a polymer/Mg(OH)₂ composite that can be an essential component for lithium-ion polymer batteries (LiPBs). In particular, a fully Mg(OH)₂-composited polymer electrolyte can not only enhance the flame retardancy by increasing Mg(OH)₂ content, but also impart

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Table 1
Coating slurry composition for each composite polymer film.

Components (10 g based)	Content of Mg(OH) ₂ in porous composite polymer films		
	0 wt%	20 wt%	40 wt%
Mg(OH) ₂	0.0 g	0.2 g	0.4 g
PVDF-HFP	1.0 g	0.8 g	0.6 g
DBP	1.0 g	1.0 g	1.0 g
Acetone	8.0 g	8.0 g	8.0 g

electrode/separator physical adhesion by adopting a polymer to be gelled with liquid electrolyte for large-format LIBs [15].

Herein, we report a new polymer electrolyte composited with a flame-retardant component, Mg(OH)₂. Porous composite polymer films with different poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) and Mg(OH)₂ ratios are prepared by casting the corresponding slurry on the glass substrate and removing the dibutyl phthalate (DBP), pore generation material, in the extraction bath. These films are then impregnated with the liquid electrolyte, thereby resulting in flame-retardant composite polymer electrolytes (CPEs). Their flame-retardant properties are evaluated by observing the firing behavior and appearance change of CPEs before and after the fire test. Then, their physical and electrochemical properties are investigated in detail.

2. Experimental

2.1. Materials

Lithium cobalt oxide (LiCoO₂, KD-10, Umicore, Korea), artificial graphite (SCMG-AR, Showa Denko, Japan), conductive carbon (Super P Li[®], Imerys, Belgium), and polyvinylidene fluoride (PVdF, Solef 6020, Solvay Chemicals, Belgium) were used for electrode fabrication. A mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) (3/7, v/v) containing 1.15 M lithium hexafluorophosphate (LiPF₆) (Enchem Co., Ltd., Korea) was used as the reference electrolyte without further purification. The water content in the liquid electrolyte was controlled to be less than 5 ppm. Dibutyl phthalate (DBP, 99%, Aldrich), N-methyl-2-pyrrolidone (NMP, Aldrich), acetone (99.9%, Aldrich), methyl alcohol (99.5%, Sanchun Co., Ltd.), Mg(OH)₂ (diameter: 500~700 nm, purity: ≥99.0%) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Kynar 2801, Arkema Co., Belgium) were purchased from Aldrich and used without further purification and/or drying process.

2.2. Preparation and morphological analysis of porous composite polymer films

A porous composite polymer film was prepared by casting the slurry consisting of PVDF-HFP, Mg(OH)₂, and the DBP, pore generation material, in acetone on a glass plate using a doctor blade with a clearance of 500 μm and immersing the corresponding cast films in methanol to remove DBP. Each slurry composition is summarized in Table 1. The films were then dried in the fume

Table 2
Dependence of composite polymer film properties on Mg(OH)₂ content.

	Content of Mg(OH) ₂ in porous composite polymer films		
	0 wt%	20 wt%	40 wt%
Thickness (μm)	25	25	25
Porosity (%)	3.7	13.4	25.3
Heat of Fusion (J g ⁻¹)	37.8	24.9	21.9
Uptake (%)	59.2	78.8	95.5
Ionic Conductivity (mS cm ⁻¹)	0.413	0.482	0.542

hood at room temperature to become free-standing. [16,17] Their surface and cross-sectional images were investigated by field emission scanning electron microscopy (FE-SEM, Hitachi, Japan). The porous composite polymer films were fractured in liquid nitrogen for cross-sectional SEM images. To confirm the dispersion state of PVdF-HFP and Mg(OH)₂, EDX mapping images of fluorine and magnesium in composite polymer films were investigated by energy-dispersive X-ray spectroscopy (EDX, AMETEK, USA).

2.3. Mechanical and thermal analysis of porous composite polymer films

To evaluate the mechanical strength of porous composite polymer films, their tensile stress and strain were measured using a micro materials tester (Instron, USA). Each specimen was trimmed to a 15 mm width and a 150 mm length and was then pulled at a rate of 50 mm min⁻¹. The thermal behavior of each sample was investigated using a differential scanning calorimeter (Q20, TA, USA) at temperatures ranging from room temperature to 400 °C at a rate of 20 °C min⁻¹.

2.4. Flame-retardant test of porous composite polymer films

To evaluate the flame-retardant characteristics of the porous composite polymer films, we ignited each film containing 0, 20, and 40 wt% Mg(OH)₂. Then, the changes in the appearance of the samples after the flame-retardant test were compared using a digital camera.

2.5. Electrochemical analyses of composite gel polymer electrolytes

Each porosity of composite polymer films having different Mg (OH)₂ contents was calculated by the following two equations [18]:

$$\text{Porosity}(\%) = \frac{V_{\text{film}} - V_{\text{film}}^*}{V_{\text{film}}} \times 100 \quad (1)$$

$$V_{\text{film}}^* = \frac{m_{\text{film}} \times X_{\text{PVDF-HFP}}}{\rho_{\text{PVDF-HFP}}} + \frac{m_{\text{film}} \times X_{\text{Mg(OH)}_2}}{\rho_{\text{Mg(OH)}_2}} \quad (2)$$

where V_{film} indicates an apparent volume calculated by multiplying three edge lengths of the film and V_{film}^* does a real volume occupied by polymer and Mg(OH)₂ particles. In particular, the V_{film}^* was calculated by the equation (2), in which m_{film} is the mass of film, $X_{\text{PVDF-HFP}}$ and $X_{\text{Mg(OH)}_2}$ are the composition of PVDF-HFP and Mg(OH)₂, and $\rho_{\text{PVDF-HFP}}$ and $\rho_{\text{Mg(OH)}_2}$ are the true density of PVDF-HFP and Mg(OH)₂ (PVDF-HFP: 1.78 g cm⁻³, Mg(OH)₂: 2.34 g cm⁻³).

To determine their uptake amount and ionic conductivities, the porous composite polymer films were impregnated with the liquid electrolyte, which was a mixture of 1.15 M LiPF₆ in ethylene carbonate/ethyl methyl carbonate (EC/EMC = 3/7, v/v, ENCHEM Co., Ltd., Korea), to obtain gel polymer electrolytes. The amount of the uptake of the liquid electrolyte by each polymer film was obtained by calculating the amount of the liquid electrolyte impregnated within the film.

$$\text{Uptake amount (wt}\%) = \frac{m - m_0}{m_0} \times 100 \quad (3)$$

where m_0 and m indicate the mass of the film before and after the liquid electrolyte absorption, respectively.

The gelled porous composite polymer films, referred to as gel polymer electrolytes, were sandwiched between two stainless-steel (SUS) electrodes and assembled into the 2032-type coin cells. Cell assembly was carried out in a glove box filled with argon gas. The bulk resistance (R_b) of each cell was obtained using an impedance analyzer (VSP, Bio-Logic, USA) for frequencies ranging from 1 MHz to

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