



Short communication

A high performance ceramic-polymer separator for lithium batteries



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HIGHLIGHTS

- A new separator has been fabricated using Electron beam physical vapor deposition.
- Hybrid separator shows better ion conductivity.
- Hybrid separator shows reduced charge-transfer resistance.
- Hybrid separator exhibit reduced Li plating/deplating voltage polarization.

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ABSTRACT

A three-layered (ceramic-polymer-ceramic) hybrid separator was prepared by coating ceramic electrolyte [lithium aluminum germanium phosphate (LAGP)] over both sides of polyethylene (PE) polymer membrane using electron beam physical vapor deposition (EB-PVD) technique. Ionic conductivities of membranes were evaluated after soaking PE and LAGP/PE/LAGP membranes in a 1 Molar (1M) lithium hexafluoroarsenate (LiAsF₆) electrolyte in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) in volume ratio (1:1:1). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques were employed to evaluate morphology and structure of the separators before and after cycling performance tests to better understand structure-property correlation. As compared to regular PE separator, LAGP/PE/LAGP hybrid separator showed: (i) higher liquid electrolyte uptake, (ii) higher ionic conductivity, (iii) lower interfacial resistance with lithium and (iv) lower cell voltage polarization during lithium cycling at high current density of 1.3 mA cm⁻² at room temperature. The enhanced performance is attributed to higher liquid uptake, LAGP-assisted faster ion conduction and dendrite prevention. Optimization of density and thickness of LAGP layer on PE or other membranes through manipulation of PVD deposition parameters will enable practical applications of this novel hybrid separator in rechargeable lithium batteries with high energy, high power, longer cycle life, and higher safety level.

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1. Introduction

Lithium-ion batteries (LIBs) having high energy density, power density, long cycle life, as well as low memory effect, are widely used in various applications ranging from mobile electronics to automotive [1,2]. Even though LIBs have transformed the electronics industry, the energy density, power density, cycle life and

safety are inadequate for higher-energy applications, such as all electric vehicles batteries, aircraft batteries, or batteries that can power heavy machinery or extend the working hours of the current batteries [3].

LIBs consist of lithium transition metal oxide cathode and carbonaceous anode, whereas Li batteries (Li-S, Li-O₂, and advanced LIBs) use Li metal as common anode and S, O₂ or transition metal oxides as cathode separated by a membrane containing a non-aqueous liquid electrolyte or solid/gel electrolytes. Solid/gel electrolytes perform both as separator and electrolyte. Functioning of LIBs involves reversible lithium extraction from transition metal

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oxide host as the rechargeable cathode and into graphite as the anode host. Whereas functioning of Li batteries involves reversible extraction of lithium from lithium metal anode and into S, O₂ or transition metal oxide cathode. Micro-porous polyolefin separators, such as PE and polypropylene (PP) are commonly used in LIBs or Li batteries involving non-aqueous liquid electrolyte. Separator is a key component of LIBs or liquid-based Li batteries, and serves as a physical membrane that allows the transport of Li ions, but prevents direct contact between cathode and anodes.

Efforts have been made to improve separator performance (especially for liquid electrolyte-based LIBs) by solution coating of inorganics (Al₂O₃, MMT, SiO₂, etc.), along with binders on polymer separators (PE, PP, etc.) or by fabricating nanostructured polymer/copolymer-inorganic mix by various techniques, such as electrospinning or fabricating alumina- or alumina/phenolphthalein polyetherketone-based, porous ceramic membranes [4–11]. Liang et al. [12], developed electrospun fibrous composite of Li⁺ ion conducting inorganics (lithium lanthanum titanate oxide) with polyacrylonitrile (PAN) that showed higher liquid uptake, higher ion conductivity, higher electrochemical stability and overall improvement on cell performance. Solid electrolytes based on polymer, ceramic, and polymer-ceramic composites have proven to be promising as separators as well as electrolytes for batteries beyond LIB [13–15]. Polymer and gel electrolytes can be fabricated in thin film form but they are unable to stop dendrite growth completely. In addition to high Li⁺ ion conductivity, ceramic solid electrolytes, such as LAGP (5 mS/cm at 23 °C) [14] or lithium aluminum titanium phosphate (LATP) (3 mS/cm at 25 °C) [16] combines many favorable properties such as solid-state nature, broad electrochemical window (>5 V), negligible porosity and single ion conduction (high transference number, no dendrite formation, no crossover of electrode materials to opposite side of electrodes compartment, etc.) enabling high-energy battery chemistries and mitigating safety and packaging issues of conventional lithium batteries [15].

In present work, ultrathin layer (\approx 130 nm) of superionic conducting ceramic (LAGP) has been deposited on both sides of PE separator by using EB PVD technique. The goal was to obtain thin film of single ion (Li⁺) conductor on mechanically-stable membranes that not only have the basic functions of battery separator, but also can conduct lithium ions and prevent Li dendrite growth, which can significantly improve the battery kinetics and cycle life. LAGP solid ceramic electrolytes that possesses high ion conductivity [14] was used as the single Li⁺ ion conducting ceramic to stop dendrite formation and growth during Li cycling. Results show that the coating of LAGP onto PE membrane can combine the advantageous properties of both components (PE and LAGP) and lead to a new hybrid separator that has high mechanical strength, large liquid electrolyte uptake, high ionic conductivity, good electrochemical stability, improved safety, reduced electrode–electrolyte interface resistance and low Li stripping/plating voltage polarization. As a result, the new LAGP/PE/LAGP hybrid membranes can provide ideal structures and properties for separating electrodes, supporting electrolytes, and transporting lithium ions. Lithium-ion cells using these membrane separators can achieve good battery performance, such as large capacity, good cycleability, high-rate capability, and enhanced safety.

2. Experimental details

2.1. Preparation of the hybrid membrane

LAGP target material for fabricating hybrid membrane was prepared following our earlier procedure [14]. First, LAGP glass with molar composition 19.75Li₂O·6.17Al₂O₃·37.04GeO₂·37.04P₂O₅ was

synthesized through solid–melt reaction at 1350 °C by using reagent-grade chemicals such as Li₂CO₃ (Alfa Aesar), Al₂O₃ (Aldrich), GeO₂ (Alfa Aesar), and NH₄H₂PO₄ (Acros Organics). Subsequently, LAGP glass was crystallized at 850 °C for 12 h, which is hereafter called LAGP ceramic for developing 3D ion conducting structure. The measured bulk ion conductivity of this LAGP composition was found to be \approx 5 mS cm⁻¹ at room temperature [14]. Even though, the ionic conductivity of LAGP is high, it cannot be used as an electrolyte with energy dense Li metal anode. This is because of the high level of chemical reactivity of LAGP, similar to other LiSICON ceramic electrolytes, when in direct contact with Li metal [17]. A possible solution to this chemical reactivity issue is to put a thin stable film at the Li/LAGP interface. For example, West et al. [18] suggested that a LiPON-coated LATP plate is chemically stable against Li metal. Kumar et al. [19] used lithium oxide/boron nitride based polymer-ceramics composite to stabilize Li/LAGP interface. In the present investigation liquid electrolyte (LiAsF₆ in EC:EMC:DMC) including 2 wt% vinylene carbonate (VC) has been used as interface layer between Li and LAGP to stabilize Li/LAGP interface. The use of VC for lithium metal anode suppresses the deleterious reaction between the deposited lithium (during lithium cycling) and the electrolyte [20].

A 130 nm-thick LAGP film was deposited on both sides of PE separator (Celgard, MTI Corp.) using EB-PVD. The EB-PVD system has a multi-hearth high power electron beam source capable of evaporating most metals and ceramics at a fast rate. In this process, electrolyte material (LAGP) was placed in a graphite crucible. The cleaned substrate (PE) was mounted on a metal plate. The chamber was evacuated to a base pressure of $<10^{-6}$ Torr. A deposition rate of 1.0–1.5 nm per/second was used to deposit \approx 130 nm LAGP film on one side of PE separator and then on the other side. The deposition parameters can be manipulated to obtain LAGP film of desired thickness, density/porosity. As prepared LAGP/PE/LAGP functional separator was used for the current investigation without further treatment. It is noteworthy to mention here that the flexibility of LAGP/PE/LAGP separator was similar to the PE separator. Separator in the form of a disc was punched out and used in the present investigation. Punching the separator may damage the edges and there may be risk of potential short circuit. Keeping this possibility in mind we have used larger size separator as compared to electrodes (Li or SS) in order to avoid short circuit risks that may arise from damaged separator edges. The diameter of separator and electrode used were 17 mm and 16 mm, respectively.

2.2. Characterization of hybrid membrane

Coin cells were fabricated to determine electrochemical impedance spectra of PE and hybrid separators using stainless steel (SS) electrodes (SS/separator-1 M LiAsF₆/EC-DMC-EMC/SS). In addition, coin cells were fabricated using pure lithium metal as electrodes to determine Li plating and stripping (Li/separator-1 M LiAsF₆/EC-DMC-EMC/Li). The liquid electrolyte used in the present investigation includes 2% vinylene carbonate (VC). Coin cells were assembled in a ultra-pure glove box (O₂, H₂O < 1 ppm) (Pure Lab^{HE} Innovative Technology, Industrial Way, Amesbury, MA 01913). Electrical and electrochemical performances of cells were evaluated using a Solartron SI 1287 electrochemical analyzer in conjunction with a SI 1260 Impedance/gain-phase analyzer. Electrochemical impedance spectroscopy (EIS) of the cells was conducted over a frequency range 0.1 Hz–10⁶ Hz. Li stripping-plating measurements on Li/Li symmetrical cells were performed in a galvanostatic mode with a constant current density 1.3 mAcm⁻². Surface morphologies of PE and hybrid separator were examined using SEM. The XRD patterns were collected between 2 θ = 15° to 80° on (Rigaku D/MAX) fitted with CuK α radiation source.

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