



# Lithium aluminate-based ceramic membranes as separators for lithium-ion batteries

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## Abstract

Lithium aluminate, (LiAlO<sub>2</sub>)-based porous ceramic membrane (PCM) was prepared with poly(vinylidene fluoride-hexafluoropropylene) as binder. Physical properties such as thermal stability, porosity and tortuosity of the pores were measured. Effective ionic conductivity and compatibility with lithium metal anode were also studied. The porous ceramic membrane was found to be dimensionally stable even at 135 °C. The cycling performance of 2032-type coin cell composed of Li/PCM/LiFePO<sub>4</sub> was analyzed at different C-rates. A stable cycling was achieved at 0.1-C rate, which qualifies the membrane for lithium-ion battery applications.

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## 1. Introduction

Lithium-ion batteries play an important role in today's society, based in a large measure on portable devices, due to their unique properties such as high single cell voltage, energy density and long cycle life [1]. These appealing properties identify this system as an excellent choice to power portable electronic devices such as laptop computers, cellular phones, etc. [2]. Lithium-ion batteries are generally based on a carbonaceous anode, and a lithium transition-metal oxide cathode separated by a polyolefine-based non-polar separator soaked in a non-aqueous liquid electrolyte [3]. The separator is an important passive component that prevents short-circuit between the positive and negative electrodes, while permitting rapid Li<sup>+</sup> ion migration between them for cycling. Membrane properties such as porosity, tortuosity, shrinkage, wettability and ionic conductivity influence the cycling performance of the batteries [3,4].

Although polyolefin membranes are widely used in commercially available lithium-ion batteries they have several disadvantages such as low porosity (about 40%), poor wettability and uni-directional mechanical integrity. Above all, it is thermally stable only up to 135 °C. In addition to this, the olefin membranes are prone to shrink at elevated temperatures, which trigger unexpected exothermic reactions in the cells, leading to short-circuit. Therefore, membranes with enhanced thermal stability and good wettability in organic liquid electrolytes are highly desirable to guarantee safe and reliable lithium-ion battery operation [5].

Syzdek et al. [6] introduced a novel polymer-in-ceramic membrane in which a polymer is introduced in a ceramic matrix. Such materials are found to have long-term stability in contact with the lithium metal anode. In order to increase the thermal stability of the membranes, Jeong and co-workers [7] coated Al<sub>2</sub>O<sub>3</sub> on both sides of a porous polyethylene membrane. The Al<sub>2</sub>O<sub>3</sub> was also coated with poly(vinylidene fluoride-co-hexafluoropropene) (PVdF-HFP) on both sides of the poly(ethylene) separator, and its cycling profile was analyzed [8]. Recently, Pereira et al. [9] reported the physical and electrochemical properties of montmorillonite (MMT)/P(VdF-TrFE) microporous membranes for different contents of

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MMT. The authors concluded that MMT/P(VdF-TrFE) porous membrane with 4% filler content is considered optimal for battery application in terms of electrochemical stability and mechanical properties. The same group also explored the possibility of employing NaY zeolite/P(VdF-TrFE) membranes [10,11]. Costa et al. [12] reviewed battery separators based on vinylidene fluoride (VDF) polymers and copolymers for lithium-ion battery applications. Generally, ceramic materials are brittle and prone to cracking. However, when a ceramic material is incorporated in an inter-penetrating and co-continuous polymer matrix, an appreciable increase in the strain value was noticed against stress behavior [7].

In the present study,  $\text{LiAlO}_2$  is employed as a host in order to introduce lithium-ion for conduction [13]. Generally, metal ions of the inorganic oxides are in a high oxidation state, and can, therefore, take part in a reduction reaction when in contact with the anode, especially in its fully lithiated state and also expected to exhibit higher anodic stability [14].  $\text{LiAlO}_2$  was found to have a good stability towards a lithium metal anode in poly(ethylene oxide)-based electrolytes by Borghini et al. [15]. Very recently, Huang made a comprehensive review of the technological importance of separators for lithium-ion batteries [16]. According to the author, membranes with abuse tolerance, thermal stability and low cost are essential for large-scale applications in HEV/EV.

## 2. Experimental

### 2.1. Preparation of ceramic membrane

$\text{LiAlO}_2$  (Aldrich, USA) was sieved to remove larger aggregates and used as a host to make the porous ceramic membrane (PCM). The PVdF-HFP was dissolved in acetone with different weight ratios (10, 15 and 20%) and was stirred for 12 h.  $\text{LiAlO}_2$  was added to the polymer solution keeping the ceramic-to-polymer weight ratios at 85:15, 80:20 and 75:25. The resultant viscous slurry was spread over a glass plate in order to allow the solvent to evaporate and obtain a free-standing membrane. The thickness of the PCM was measured by a micrometer with a least count of 0.01 mm. These membranes were cut into a diameter of 10 mm and were subsequently hot-pressed in order to get a smooth surface on both sides of the membrane. The average thickness of the membrane was 70–80  $\mu\text{m}$ . Among the three samples prepared, the membrane with the ratio of 80:20 ( $\text{LiAlO}_2$ :PVdF-HFP) was found to be free standing and dimensionally stable. The membrane with this composition was stored in a glove box for further characterization. In the present study, PVdF-HFP was added as a binder and to entrap large amounts of polar non-aqueous liquid electrolyte due to its hydrophilic nature.

### 2.2. Characterization of PCM and lithium cell assembly

The morphology of the ceramic membrane was examined by scanning electron microscopy (SEM, Vega3, Tescan) under a vacuum condition ( $10^{-1}$  Pa) after coating gold on one side of the membrane. Thermal stability of the ceramic membrane was analysed by taking TG-traces in the range 20–700 °C under nitrogen atmosphere.

The effective ionic conductivity of the membrane, sandwiched between two stainless steel blocking electrodes (1.0 cm diameter) was measured using an electrochemical impedance analyser (IM6-Bio Analytical Systems) between frequency ranges 1 MHz to 50 mHz at various temperatures. In order to investigate the compatibility of the ceramic membrane with lithium metal anode, a symmetric non-blocking cell (Li/PCM/Li) was assembled and the time dependence of the impedance was analysed at 25 °C.

Evaluation of the membrane in lithium cells was carried out by galvanostatic charge/discharge cycling at ambient temperature (current regimes from 0.1C to 1C) with an Arbin BT-2000 battery cyler between 2.50 and 4.00 V vs.  $\text{Li}^+/\text{Li}$ . The composite cathode was prepared by blending  $\text{LiFePO}_4$  as active material with acetylene black and PVdF-HFP [17,18]. The PCM was soaked in a liquid electrolyte (1.0 M  $\text{LiPF}_6$  in a 1:1 v/v mixture of ethylene carbonate and diethyl carbonate (Ferro Corporation). All preparations were performed in an argon-filled MBraun glove box.  $\text{LiFePO}_4/\text{C}$  cathode material was synthesised in the form of nanostructured powder through a mild hydrothermal procedure as described earlier [17,18].

## 3. Results and discussion

### 3.1. Thermal analysis

Fig. 1(a) shows a photograph of the as-prepared porous ceramic membrane, which perfectly restored its original shape and size even after swelling with the non-aqueous liquid electrolyte solution for 15 min. Fig. 1(b)–(d) (SEM images) reveal the surface morphology of the ceramic membrane at three different magnifications. It can be seen that the ceramic particles are homogeneously held together by the polymeric binder, which is attributed to the high volumetric ratio of the binder with respect to the ceramic particles. The volume ratio of the polymer ensures that the surface groups on the ceramic particles can attach to suitable groups/ligands on the polymer chains. Extensive bonding of this kind can ensure homogeneity of the ceramic-polymer composites. A similar observation has been reported by Choi et al. [19], who coated nano- $\text{Al}_2\text{O}_3$  on both sides of a porous polyethylene membrane with and hydrophilic poly(lithium 4-styrenesulfonate) binder. This ceramic membrane did not show any pore structure with uniform pore diameter; however, large voids on its surface could facilitate trapping of non-aqueous liquid electrolyte.

The thermo-gravimetric behavior of the porous ceramic membrane composed of  $\text{LiAlO}_2$  and PVdF-HFP binder (80:20) is displayed in Fig. 2. A weight loss of approximately 2% is observed below 100 °C. It can be ascribed to two major contributions: (1) the presence of trapped acetone solvent (boiling point  $\sim 57$  °C) used for the preparation of the membranes and (2) the presence of moisture in the sample. In fact, the membrane seemed hygroscopic due to its porosity [20]. As the major component is high surface area  $\text{LiAlO}_2$ , it can trap traces of solvent and moisture into its ceramic cages. The weight loss above 200 °C is attributed to degradation of PVdF-HFP [21]. After complete thermal decomposition of the binder, no further weight loss was observed until 500 °C. This clearly suggests that the ceramic membrane is

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