



# Polymer electrolyte membranes with exceptional conductivity anisotropy via holographic polymerization



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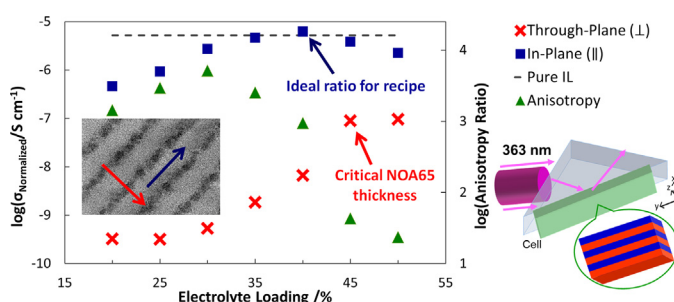
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## HIGHLIGHTS

- Holographic polymer electrolyte membranes have been fabricated.
- They are comprised of alternating nanolayers of ionic liquids and crosslinked resin.
- The membrane has an ionic conductivity anisotropy of ~5000.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Polymer electrolyte membranes using an ionic liquid as electrolyte with an ionic conductivity anisotropy of ~5000 have been fabricated using a holographic polymerization nanomanufacturing technique. The resultant structure is referred to as holographic polymer electrolyte membranes (hPEMs), which are comprised of alternating nanolayers of a room temperature ionic liquid and crosslinked polymer resin, confirmed under TEM imaging. These hPEMs also show no reduction in room temperature conductivity with respect to the loaded ionic liquid when characterized in the plane of ionic liquid nanolayers. At elevated temperatures with the optimal electrolyte volume loading, calculation shows that the free ion concentration is higher than the pure ionic liquid, suggesting that the photopolymer dual-functionalizes as a loadbearing scaffold and an ion-complexing agent, allowing for more ions to participate in charge transfer. These hPEMs provide a promising solution to decoupling mechanical enhancement and ion transport in polymer electrolyte membranes.

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## 1. Introduction

Polymer films with directional preference for ion transport are desirable for electrochemical, [1,2] purification, [3,4] sensor and stimuli-response, [5] and organic transistor [6] applications as the anisotropy can increase mass transport efficiency, permeability,

sensitivity and response times, and reduce gate leakage in the non-preferred direction. Anisotropic ion conducting films were first reported in 1995 in Nafion films after melt processing, where an anisotropy of 1.4 was reported. [7] Since then, applying external mechanical, [7–10] electrical [10] or magnetic fields, [11,12] solvent casting methods, [13] electrospraying block-co-polymers (BCPs), [14] liquid crystals polymer templating, [9,15–17] and tailoring crystalline polymer morphology have been demonstrated to increase ion flux anisotropy in polymer electrolyte films; however, there remains

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hurdles for each of these techniques to effectively direct ion transport, both from processing and device standpoints. Conductivity anisotropies of up to 10–12 can be achieved with single-step solution casting, [13] and higher anisotropies can be demonstrated via secondary processing techniques: 20 for mechanical stretching, [18] 75 for melt pressing diblock-copolymers, [10] and approaching 1000 for liquid crystalline BCPs aligned under an external 6 T magnetic field. [11] Of particular interest for this work is anisotropic conducting behavior in solid polymer electrolyte membranes (PEMs) for fuel cell and battery applications. PEMs with high conductivity and high mechanical integrity are critical for energy related applications including solid state batteries and fuel cells. For PEMs, since ion transportation is enabled by segmental motion of the host polymer matrix, modifying the membranes for enhanced mechanical properties often has a direct negative effect on the ionic transport properties. To address this structural/property tradeoff, films with highly ordered directionalized transport nanostructures have been employed to incorporate rigid load-bearing scaffolds which minimize any detrimental effects to the through-plane ionic conductivity. BCP PEMs with two distinct ion-conducting and load-bearing phases have shown great promise in addressing this property tradeoff. However, incorporating long-range order in these anisotropic films is difficult, as BCP grain boundaries typically introduce ion tortuosity. Correlation between BCP phase morphology and ionic conductivity is still a subject of intense study [19–21]. We report a new Holographic Polymerization (HP) system using Norland Optical Adhesive 65 (NOA65) as the photopolymerizable cross-linking resin, and an ionic liquid (IL) as the electrolyte, BrTHTDP, to convert a liquid electrolyte to a bulk solid free-standing film, decoupling mechanical enhancement and ion transport properties, resulting in films with anisotropic conductivity of ~5000.

HP is a relatively simple and effective top-down technique to fabricate ordered nanostructures [22]. A photopolymerizable syrup, typically consisting of monomers, photoinitiator, and often inert materials, is exposed to two or more coherent laser beams whose interference creates a periodic standing wave pattern on a length scale dictated by the interference angle and the laser source. This results in spatially periodic polymer-rich and polymer-poor domain structures whose local morphology is driven by the complex interplay of reaction, phase separation, and transport dynamics. Simplistically, the photopolymerizable resin component diffuses into and reacts in the constructive interference volumes, and the non-reactive species is driven or transported into the local areas of destructive (dark) interference volumes. Typically a multifunctional monomer is polymerized via chain or step growth polymerization, enabled by a photoinitiator and coinitiator, combined with a reactive diluent to control polymerized network growth, and a non-reactive species. Materials that have been periodically patterned via HP include liquid crystals [22,23], nanoparticles, [24–27] homopolymers, [28,29] and BCPs [30,31]. Most recently, we showed that using polyethylene oxide (PEO) and a bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) electrolyte as the photo-inert material, fabrication of anisotropic PEMs for batteries could be obtained. [32] However, because a brick-and-mortar semi-continuous morphology was formed instead of continuous layers; an in-plane/through-plane conductivity ratio of approximately 35 was achieved. While already a 3-fold improvement over one-step thin film synthesis techniques, much available improvement exists by optimizing the morphology.

## 2. Experimental section

### 2.1. Materials

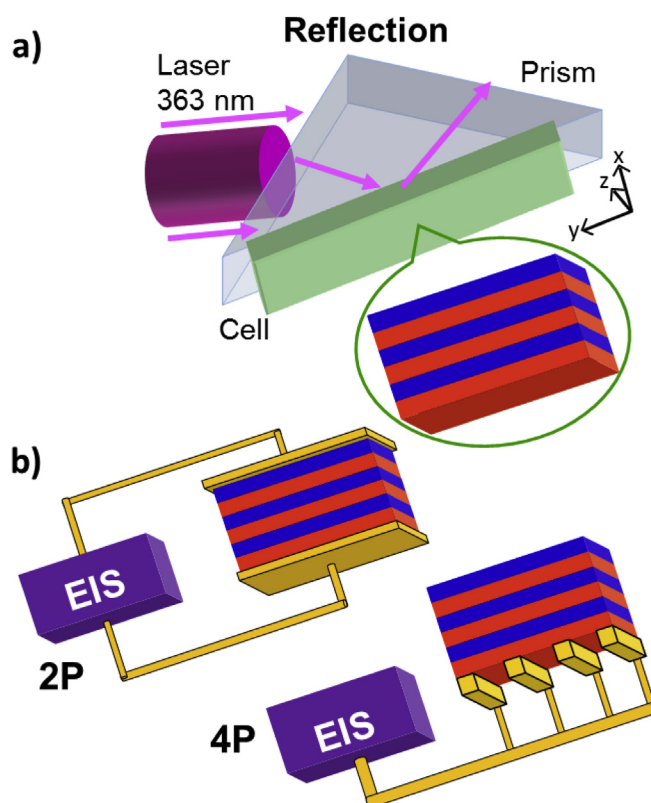
Trihexyltetradecylphosphonium bromide (BrTHTDP) ionic liquid (IL) was purchased from Aldrich; the crosslinkable monomer

system Norland Optical Adhesive 65 (NOA-65) was purchased from Norland Inc. A UV initiator, Darocure 4265 was graciously provided by CIBA-GEIGY Company. NOA-65 is proprietary information of Norland Products Inc, but is widely known to contain a tetrafunctional ene and a trifunctional thiol. The tetrafunctional ene in NOA-65 may contain two urethane groups per molecule.

### 2.2. Holographic polymerization

The output from a Coherent Ar-ion laser (model Sabre Innova 10R/2) with a laser wavelength of 363.8 nm and an output power of 240–270 mW was used for HP. The typical HP exposure time was 60 s. During the exposure, the laser beam enters the sample cell then reflects off of the glass/air surface of the sample wall and passes back through the cell (Fig. 1 shows the path of the laser beam). The overlap of the incoming and reflected beams result in a 1D interference pattern with the periodic intensity profile normal to the glass of the sample cell. In order to control the period of the grating, the prism and the cell assembly were placed on a rotation stage.

BrTHTDP, NOA65, Darocure 4265 and <0.01 w/w% 23  $\mu\text{m}$  glass bead spacers were mixed in a vortex for 5 min, followed by sandwiching between two glass slides; the spacers were included to control the thickness of the membrane. The glass sandwich cell containing the prepolymer syrup was placed on the hypotenuse of an isosceles 90° glass prism as shown in Fig. 1, adhered with a Cargille refractive index fluid, with  $n = 1.4900$  to match the prism for optical contact, via capillary force. The targeted PEMs have a lamellar structure with the lamellae parallel to the membrane



**Fig. 1.** (a) Schematic of optic setup for reflection hPEMs. (b) Schematic of the electrode configurations used to characterize the films' conductivity using a 4-line probe setup for in-plane conductivity (top) and a 2-point sandwich probe for through-plane conductivity (bottom). The blue and red layers represent NOA65-rich and IL-rich areas, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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