

# Laser printing of nanocomposite solid-state electrolyte membranes for Li micro-batteries

M. Ollinger<sup>a</sup>, H. Kim<sup>a</sup>, T. Sutto<sup>b</sup>, A. Piqué<sup>a,\*</sup>

<sup>a</sup>Materials Science & Technology Division, Naval Research Laboratory, Washington, DC 20375, USA

<sup>b</sup>Naval Surface Warfare Center, Dahlgren, VA 22448, USA

Received 1 August 2005; received in revised form 23 August 2005; accepted 24 October 2005

Available online 22 November 2005

## Abstract

The electrochemical and mechanical properties of nanocomposite solid-state electrolyte membranes deposited using a laser direct-write technique from a suspended solution comprised of an ionic liquid (1,2-dimethyl-3-*n*-butylimidazolium-bis-trifluoromethanesulfonylimide)–polymer (poly(vinylidene fluoride-co-hexafluoropropylene)) matrix with dispersed nano-particles (TiO<sub>2</sub>) are reported and discussed. These laser printed nanocomposite solid-state membranes are shown to exhibit the proper electrochemical behavior for ionic liquids while maintaining the strength and flexibility of the polymer matrix. This combination of physical properties and deposition technique makes these deposited nanocomposite membranes ideally suited for use as an electrolyte/separator in Li micro-batteries. Sample Li micro-batteries using these laser printed nanocomposite membranes have been fabricated and their charge/discharge behavior tested, demonstrating the feasibility of using these nanocomposite membranes in Li micro-battery applications.

Published by Elsevier B.V.

**Keywords:** Solid-state electrolyte; Polymer nanocomposite; Micro-battery; Laser direct-write

## 1. Introduction

In the last decade, we have seen a strong trend towards developing smaller and more autonomous microelectronic sensing and micro-electromechanical systems. However, as the size of devices has continued to shrink, the size of the corresponding power supplies has lagged behind. Therefore, in order to fully capitalize on the advantages of device miniaturization, one must correspondingly shrink the power sources. It has been generally agreed upon that Li-ion micro-batteries, with their high energy density and high cell voltage, will be the material system of choice to produce meso-scaled power sources for micro-devices. However, Li-ion batteries use a liquid electrolyte, which causes drawbacks in areas of packaging, cost, safety, and size when trying to develop a micro-battery. In order to overcome these limitations it is important to replace the liquid electrolyte with a solid-state polymer electrolyte. This would allow for easier packaging with less material. Also, these polymer electrolytes can be

made much thinner than the currently used permeable membranes. Using a solid-state polymer as an electrolyte also eliminates safety concerns since the volatility of the liquid electrolyte is no longer a concern. In this work, we present the development and optimization of an ionically conductive solid-state electrolyte membrane deposited by a laser forward transfer process.

When developing solid-state electrolytes for Li and Li-ion micro-batteries, they must possess certain properties in order for them to be useful in practical applications. They must be electrically insulating, ionically conducting, chemically and thermally stable, electrochemically stable over a wide voltage range (>4 V), flexible, and easily produced. To date, the majority of effort has been focused on three main classes of solid-state electrolytes: polymer [1,2], gel [3], and thin film [4]. For each of these solid-state electrolytes, functioning Li-ion batteries have been reported. However, a limitation of these solid-state electrolytes is their low ionic conductivities in comparison to traditionally used liquid electrolytes.

Another important factor to consider when developing a solid-state electrolyte for micro-batteries is how to produce it. When a micro-device is made, the power requirements and available footprint for a micro-battery will not be known until

\* Corresponding author. Tel.: +1 202 767 5653; fax: +1 202 767 1969.

E-mail address: [pique@nrl.navy.mil](mailto:pique@nrl.navy.mil) (A. Piqué).

after the micro-device is built. Therefore, in order to deposit the active materials, a technique will be needed that allows for flexible design. With this in mind, we have chosen to use a laser direct-write technique for the deposition of the solid-state electrolyte. In this paper, we will address these issues by presenting our work on the development of an ionic liquid based nanocomposite solid-state electrolyte membrane that can be laser printed for use in Li and Li-ion micro-battery systems.

## 2. Experimental

For the deposition of the solid-state electrolyte membranes, a suspended solution was prepared that was subsequently deposited using a laser direct-write technique developed at the Naval Research Laboratory [5]. The solution was comprised of a 1 M lithium salt (lithium-bis-trifluoromethanesulfonylimide) dissolved in an ionic liquid (1,2-dimethyl-3-*n*-butylimidazolium-bis-trifluoromethanesulfonylimide—DMBITFSI), a polymer (poly(vinylidene fluoride-co-hexafluoropropylene)—PVdF-HFP), a solvent (dibasic ester—DBE), and ceramic nano-particles (25 nm nc-TiO<sub>2</sub>). The composition of the solution was 6.4 wt.% DMBITFSI, 3.6 wt.% PVdF-HFP, 1.1 wt.% nc-TiO<sub>2</sub>, and 88.9 wt.% DBE. The ionic liquid is responsible for the high ionic conductivity, the polymer gives the deposited suspension its solid structure, the nano-particles absorb the laser radiation and allow the material to be transferred, and the dibasic ester serves as the solvent allowing the mixing, in the form of a suspension or “ink” of the former three ingredients. Details of the laser printing process are provided elsewhere [6]. Briefly described, the suspension is spread onto a borosilicate glass slide using a wire coater. Then a frequency-tripled Nd:YVO<sub>4</sub> laser ( $\lambda = 355$  nm) with a 50  $\mu\text{m}^2$  spot size is used to irradiate the back side of the borosilicate glass slide and transfers the ink onto the awaiting substrate below ( $\sim 100$   $\mu\text{m}$  gap). Once transferred, the resulting ink layer is heated in a convection oven at 75 °C for 60 min and then placed in a vacuum oven and heated at 80 °C for 24 h in order to form a continuous pinhole-free, moisture-free ionically conductive membrane.

For the ionic conductivity experiments in this paper, the solid-state electrolyte membrane is laser transferred into an 8 mm long and 1 mm wide laser-machined trench. The substrate is insulating with conducting electrodes at either end of the 8 mm trench. Impedance spectroscopy (Gamry PC4-750 Impedance Analyzer) was then used to measure the impedance of the solid-state polymer electrolyte between the electrodes over the frequency range between 10 mHz and 100 kHz. Solution resistance was rationalized by equivalent circuit analysis of impedance data, using a single time constant resistor-constant phase element circuit analog. Chronopotentiometry measurements of the Li micro-batteries were made in a glove box with H<sub>2</sub>O and O<sub>2</sub> levels below 1 ppm using an Arbin battery tester.

## 3. Results and discussion

Ionic liquids are organic salts that are liquid at room temperature. These materials exhibit a unique set of properties that make them ideally suited for use in Li-ion micro-batteries.

Table 1  
Ionic conductivity values of electrolytes used in Li-ion batteries

Electrolyte	Ionic conductivity (mS/cm)
LiPF <sub>6</sub>	5–10
Ionic liquids	2–5
LiPON	0.01
PEO	0.01

These materials are very electrochemically [7] and thermally stable [8], ionically conductive [7], and non-volatile [9,10]. This combination of properties allows the ionic liquid based solid-state electrolyte membrane to remain stable at the high voltages used in Li-ion batteries ( $\sim 4.1$  V), have high ionic conductivity necessary for high charge and discharge rates, and alleviate safety concerns associated with liquid electrolytes. From this class of materials, we have chosen DMBITFSI because it possesses superior electrochemical and thermal stability compared to many other ionic liquids [11]. Table 1 compares the ionic conductivity values of DMBITFSI to a liquid electrolyte (LiPF<sub>6</sub>) typically used in Li-ion batteries [12] and to two solid-state electrolytes (poly-ethylene oxide (PEO) [13] and lithium phosphorus oxynitride (LiPON) [4]) used in the fabrication of Li-ion micro-batteries. From this table, one can see that the ionic conductivity of the pure ionic liquids is two orders of magnitude higher than the commonly used solid-state electrolytes of LiPON and PEO, respectively. Yet, the ionic conductivity of the typical liquid electrolyte is only two times higher than the pure ionic liquids. Based on these values, the attractiveness of using DMBITFSI in the development of a solid-state electrolyte membrane is clear.

The lithium salt (LiTFSI) was dissolved into DMBITFSI to introduce additional Li ions into the solid-state electrolyte membrane, which is necessary to improve the micro-battery performance. PVdF-HFP was selected as the host polymer because it has high anodal stability due to its strong electron-withdrawing functional group (–C–F) and its high dielectric constant that assists in the ionization of lithium salts, which increases the concentration of charge carriers [3]. The addition of nc-TiO<sub>2</sub> allows for the suspended solution or ink to be laser transferred, but in addition the TiO<sub>2</sub> nano-particles have also been shown to improve the ionic conductivity of other solid-state electrolytes [1,2].

### 3.1. Characterization of solid-state electrolyte membrane

While ionic liquids such as DMBITFSI have high ionic conductivities, it is important to determine whether they still maintain their high ionic conductivities even after being mixed with PVdF-HFP, LiTFSI, and nc-TiO<sub>2</sub> to form a nanocomposite solid-state electrolyte membrane. The ionic conductivity was obtained through ac-impedance spectroscopy measurements on the 8 mm  $\times$  1 mm  $\times$   $\sim 5$   $\mu\text{m}$  thick laser transferred lines. Fig. 1 shows the temperature dependence ac-impedance spectroscopy results of a laser printed solid-state electrolyte membrane. The room temperature ionic conductivity was measured to be 1.3 mS/cm, which is comparable to pure DMBITFSI. The

Download English Version:

<https://daneshyari.com/en/article/5366201>

Download Persian Version:

<https://daneshyari.com/article/5366201>

[Daneshyari.com](https://daneshyari.com)