

# Laser Direct-Write of Polymer Nanocomposites

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Laser direct-write is shown as a viable technique for the deposition of solid-state polymer electrolytes for Li-ion micro-batteries. The quality of the solid-state polymer electrolyte was determined by the amount of solvent used in the transferred material. The addition of nano-particles (BaTiO<sub>3</sub> and TiO<sub>2</sub>) was shown to influence the ionic conductivity behavior of the solid-state polymer electrolyte.

**Keywords:** polymer nanocomposite, solid-state electrolyte, micro-battery, ionic liquid, lithium ion micro-batteries

## 1. Introduction

The practice of adding a second phase, whether inorganic or organic, to a polymer matrix to form a composite is common in modern plastics. However, in the last 15 years, efforts have shown that by adding nano-sized materials to a polymer matrix one can form polymer nanocomposites with better material properties than traditional polymer composites [1-3]. Due to their improved performance, they have been sought after for use in a wide range of applications such as fire retardant materials, permeation barriers, and solid-state electrolytes. In this paper, we will focus our effort on the development of a solid-state polymer electrolyte for Li-ion microbatteries that can be deposited using laser direct-write.

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 microbatteries, 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 polymer electrolyte deposited by laser direct-write (LDW).

## 2. Experimental

For the deposition of the solid-state polymer electrolyte, a suspended solution was prepared that was subsequently deposited using a patented laser direct-write technique developed at the Naval Research Laboratory [4]. The solution was comprised of an ionic liquid (1,2-dimethyl-3-n-butylimidazolium-bis-trifluoromethanesulfonylimide – DMBITFSI) with a dissolved lithium salt (lithium-bis-trifluoromethanesulfonylimide), a polymer (poly(vinylidene fluoride-co-hexafluoropropylene) – PvdF-HFP), a solvent (dibasic ester – DBE), and nano-particulates (TiO<sub>2</sub> or BaTiO<sub>3</sub>). 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. This suspension is then spread onto a borosilicate glass slide using a wire coater. Then a frequency-tripled Nd:YVO<sub>4</sub> laser ( $\lambda=355$  nm) is used to irradiate the back side of the borosilicate glass slide and transfer the ink onto the awaiting substrate below (~100  $\mu$ m gap). Once transferred, the resulting ink layer is heated in a convection oven at 75 °C for 60 minutes and then placed in a vacuum oven and heated at 80 °C for 24 hours in order to form a continuous, moisture-free ionically conductive membrane.

For the ionic conductivity experiments in this paper, the solid-state polymer electrolyte is laser transferred into a laser-machined trench, which is 8 mm long and 1 mm wide. 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 a frequency range between 100 kHz and 10 mHz. Solution resistance was rationalized by equivalent circuit analysis of impedance data, using a single time constant resistor-constant phase element circuit analog.

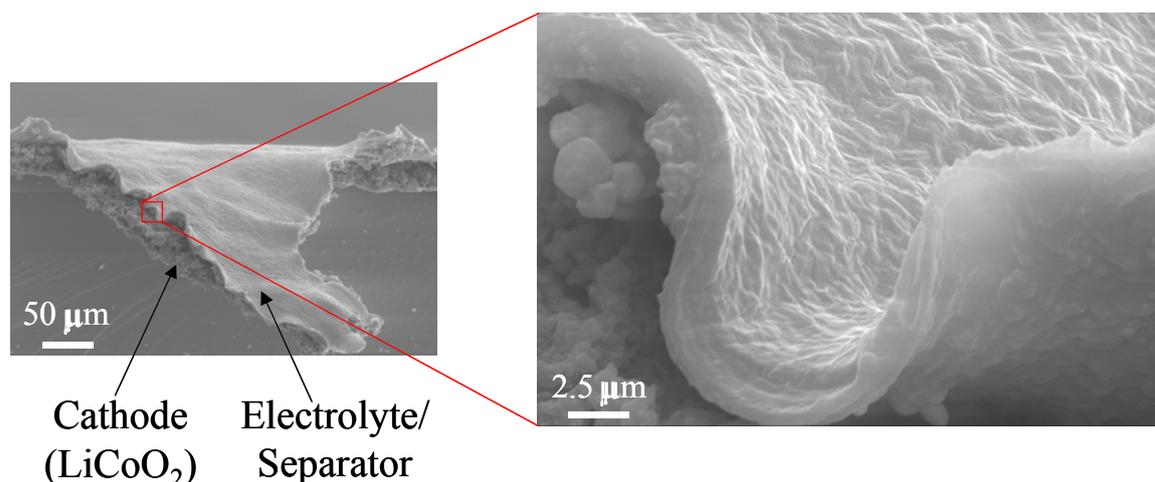


Fig. 1 SEM cross sectional micrograph of a LDW separator and cathode ( $\text{LiCoO}_2$ ) on a Si substrate.

### 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. These materials are very electrochemically [5] and thermally stable [6], ionically conductive [5], and non-volatile [7,8]. This combination of properties allows the ionic liquid based solid-state polymer electrolyte 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 these materials, we have chosen DMBITFSI because it possesses superior electrochemical and thermal stability compared to many other ionic liquids [9]. Table 1 compares ionic conductivity values of ionic liquids to a liquid electrolyte ( $\text{LiPF}_6$ ) typically used in Li-ion batteries [10] and to two solid-state electrolytes: poly-ethylene oxide (PEO) [11] and lithium phosphorus oxynitride ( $\text{LiPON}$ ) [12] 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 to four orders of magnitude higher than commonly used solid-state electrolytes such as  $\text{LiPON}$  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 ionic liquids is clear.

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

Electrolyte	Ionic Conductivity (mS/cm)
$\text{LiPF}_6$	5-10
Ionic Liquids	2-5
$\text{LiPON}$	0.01
PEO	0.0001

When adding a second phase of nano-particles to an existing polymer matrix, we chose  $\text{BaTiO}_3$  and  $\text{TiO}_2$  because they are readily available in various sizes, are relatively inert, are absorbing in the UV, and have different densities for future comparisons. These materials have also

been used in the development of previous polymer-nanocomposites for use as electrolytes [13,14].

#### 3.1 Viability of Solid-State Polymer Electrolyte as a Separator

When fabricating a solid-state micro-battery, the solid-state electrolyte in addition to being ionically conductive and electrically insulating, it must also act as a physical separator between the cathode and anode of the battery or a short will occur and the battery will fail. Therefore, the first step in this research was to verify that a high quality uniform and continuous separator membrane layer could be deposited via LDW. In Figure 1, a cross-sectional SEM micrograph is shown of a LDW deposited cathode and separator. Notice that when the sample was cleaved, that the solid-state polymer electrolyte (or separator) did not break uniformly. This is evidence that the deposited separator is flexible and has some mechanical strength. This is critical because during packaging, pressure is applied to seal the battery and we must ensure that the separator is mechanically strong enough to endure the pressure and flexible enough to be able to deform appropriately and not cause a short. From the higher magnification micrograph, we can see that the separator is also continuous and pinhole free. Also, notice that thickness of the separator is on the order of a few microns. This is vital when trying to minimize the size of the micro-batteries. Currently, in liquid electrolyte based Li-ion batteries, a permeable membrane such as Celgard is used with a minimum thickness between 25 to 50 microns.

#### 3.2 Effect of Viscosity on Separator Quality

In preparing the solution for our separator, one of the important parameters to control is how much solvent to add to the solution. By controlling the amount of solvent, while keeping the other components the same, it is possible to control the viscosity of the suspension. Figure 2 shows the effect viscosity has on the separator quality. As the percentage of solvent (DBE) decreases (going from 91% in (a) to 87% in (e)), one can see that the separator does not seep as far down into the porous cathode ( $\text{LiCoO}_2$ ). This is important because if the separator seeps too far into the

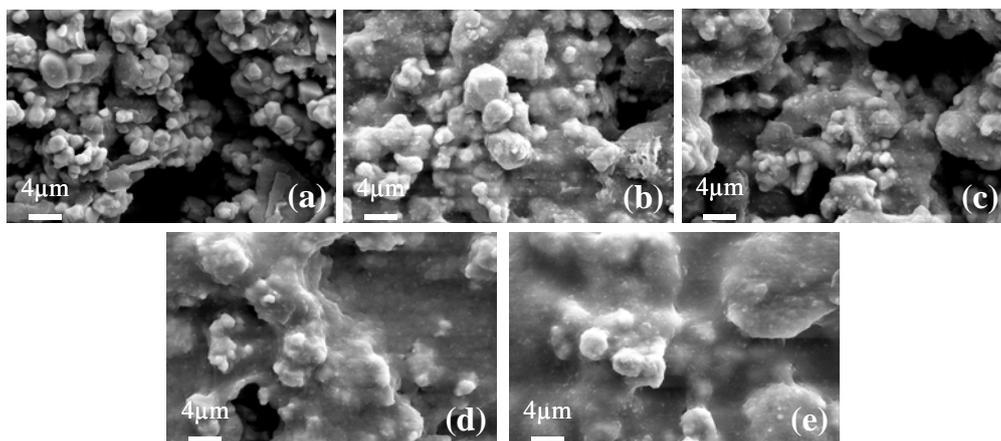


Fig. 2 SEM micrographs of separators transferred onto porous cathodes with various weight percentages (a. 91 wt.% DBE, b. 90 wt.% DBE, c. 89 wt.% DBE d. 88 wt.% DBE, e. 87 wt.% DBE) of solvent (DBE) showing effect of viscosity on separator quality.

porous cathode, we will not be able to deposit a separator that adequately isolates the cathode from the anode.

### 3.3 Effect of Particle Size on Ionic Conductivity of Separator

When fabricating a solid-state micro-battery, the ionic conductivity of the separator determines the rate at which we can discharge and charge the micro-battery. Therefore, it is critical to optimize the separator to have the highest ionic conductivity possible in order to draw the highest possible currents from the micro-battery.

In this set of experiments, the influence of particle size on the ionic conductivity was studied. Three different sizes (1-2  $\mu\text{m}$  from Superior Micropowders, 350-600 nm from Cerac and 70-80 nm from Cabot) of barium titanate oxide (BTO) were used. The weight percentages of BTO were kept constant in each solid-state electrolyte. The resultant ionic conductivities for these three samples are shown in Figure 3. From this figure, one can see that as we decrease the BTO particle size, the ionic conductivity goes up. This result agrees with earlier reports by other groups [13,14]. As we decrease the particle size for a given weight percent, the number of particles dispersed in the solid-state electrolyte increases. This increases the number of local disordered or amorphous regions within the solid-state electrolyte and allows the lithium ions to have a less impeded path as they travel from one electrode to the other in the battery. Also, the increase in surface or grain-boundary area when using smaller particles helps increase the ionic conductivity of the separator.

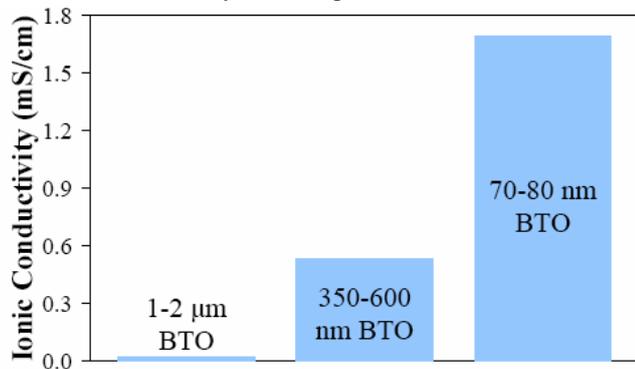


Fig. 3 Effect of nano-particle size of  $\text{BaTiO}_3$  in separator on the ionic conductivity.

### 3.4 Effect of Solids Loading on Ionic Conductivity of Separator

In this set of experiments, the influence of weight percent of nano-particles in the solid-state electrolyte was investigated. For this investigation, 25 nm  $\text{TiO}_2$  (P25 Degussa) nanopowders were mixed with the solid-state electrolyte at four weight percentages (5 wt%, 10wt%, 18 wt%, and 25 wt%). The resultant ionic conductivities are shown in Figure 4. This figure shows that as we increase the amount of nano-particles present in the solid-state electrolyte, the ionic conductivity initially increases before reaching a maximum around 18 wt% of  $\text{TiO}_2$  and then decreases. The results show that as we add more nano-particles to the solid-state electrolyte we are adding more and more localized amorphous regions to the solid-state electrolyte until we finally add too many nano-particles and they are no longer beneficial to the ion-polymer conduction and begin to impede the ionic mobility. However, a more detailed set of experiments needs to be conducted around the 18 wt% range to determine whether the maximum ionic conductivity occurred between 10 wt% and 18 wt % or between 18 wt% and 25 wt%.

It should be noted that a solid-state electrolyte with high ionic conductivity does not imply that it will be useful in practical terms. In order for a solid-state electrolyte to be effective, it must also have a wide electrochemical window and be electrochemically stable with the cathode and anode. As previously mentioned, ionic liquids meet these requirements [5-8] and have already been shown as a

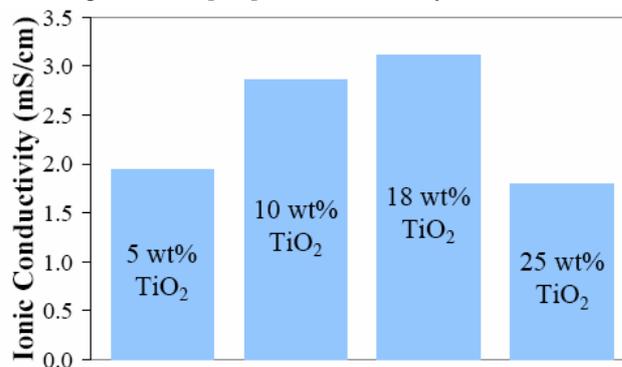


Fig. 4 Effect of solids loading on ionic conductivity of separator.

good candidate for use in Li-ion battery systems [15-16].

#### 4. Conclusions

It has been shown that laser direct-write is a viable technique for the deposition of solid-state polymer electrolytes. These deposited films are continuous, flexible, and pinhole free, which are crucial properties in the fabrication of solid-state polymer electrolytes (separators) for Li-ion micro-batteries. It was also shown that by controlling the viscosity of the precursor electrolyte, we are able to control the quality of the deposited solid-state polymer electrolyte.

The size and concentration of nano-particulates was shown to affect the ionic conductivity of the solid-state polymer electrolyte. As the size of BTO particles was reduced, the ionic conductivity of the solid-state polymer electrolyte increased. It was also shown that as we increase the concentration of TiO<sub>2</sub> in the separator, we increase the ionic conductivity up to a saturation concentration where the ionic conductivity goes down due to restriction of Li ion movement due to over saturation of nano-particles.

#### 5. Acknowledgements

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