



Laser Transferable Polymer-Ionic Liquid Separator/Electrolytes for Solid-State Rechargeable Lithium-Ion Microbatteries

Thomas E. Sutto,^{a,*} Michael Ollinger,^b Heungsoo Kim,^b Craig B. Arnold,^{c,*} and Alberto Piqué^{b,z}

^aNaval Surface Warfare Center-Dahlgren Division, Science and Technology Division, Dahlgren, Virginia 22448, USA

^bNaval Research Laboratory, Materials Science and Technology Division, Washington, DC 20375, USA

^cDepartment of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08540, USA

A laser-transferable polymer gel separator formulated from an imidazolium-based ionic liquid, poly(vinylidene fluoride) (PVDF)-HFP, and ceramic nanoparticles was prepared and electrochemically characterized by ac-impedance spectroscopy and in lithium-ion microbatteries. Size and weight percent effects of the nanoparticulates added to the laser-transferred separator indicate that nanoparticulates under 100 nm in size and in the 10 wt % range exhibited the highest ionic conductivity (1–3 mS/cm). Li-ion microbatteries prepared using this separator, a LiCoO₂ cathode, and a carbon anode maintained an average discharge voltage of up to 4.2 V with a reversible specific energy of 330 mWh/g.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.2142158] All rights reserved.

Manuscript received September 6, 2005. Available electronically December 14, 2005.

The miniaturization of sensor, actuation, and control devices has produced a fundamental need for integrated power sources that are commensurate in size with the systems of interest, yet do not compromise the functionality of the microdevice.^{1–3} A promising approach to this problem is the development of integrated and distributed lithium microbatteries that are directly incorporated into the microdevice package where needed.^{4,5} However, reducing the size of lithium power sources, both in terms of their area and thickness while maintaining their robust electrochemical properties, is a significant challenge.⁶ Employed here is a laser direct-write (LDW) printing process that is capable of depositing films without affecting their chemical or physical properties.⁷ The LDW process uses pulsed UV laser irradiation to transfer a small volume of ink (~10 pL) containing the desired materials and deposit it at precise, computer controllable locations on a substrate. Thus, application of the LDW technique to the fabrication of lithium microbatteries requires the development of ink-like mixtures of cathodic and anodic materials, as well as laser printable separator/electrolyte formulations in order to build these cells.^{8,9} Although alternate techniques for depositing cathodic and anodic material exist, the development of a simple solution that can be laser transferred onto a substrate to form a solid separator/electrolyte layer for a lithium ion power source is a significant step forward in the development of these microbatteries. Key to this development is the use of ionic liquids to create highly ionically conductive solid separators. Ionic liquids, because of their high thermal stability, hydrophobic tendencies, and electrochemical stability are ideal choices for use in lithium ion batteries as well as numerous other applications.^{10–14}

The ionic liquid chosen for this work, 1-*n*-butyl-2,3-dimethylimidazolium bis-trifluoromethanesulfonylimide, BMMI⁺ TFSI⁻, exhibits significantly enhanced electrochemical and thermal stability, compared to many other ionic liquids. The TFSI anion forms an air-stable, nonflammable, hydrophobic ionic liquid when coupled with the BMMI cation, and has been shown to be electrochemically stable in lithium ion batteries.^{15,16} It is shown in this work that by combining a solid polymer, a ceramic nanopowder, and BMMI⁺ TFSI⁻ that the resulting ceramic-solid polymer ionic liquid nanocomposite (c-SPIL) material can be laser-transferred to form the separator/electrolyte layer required for building lithium microbatteries. Furthermore, these c-SPIL separators exhibit improved

mechanical properties, high ionic conductivity, and the electrochemical stability required for successive charge/discharge cycling of these novel microbatteries.

Experimental

The ink used to deposit LiCoO₂ is composed of a solid mixture of 90 wt % of the lithiated metal oxide and 10 wt % 1–2- μ m-sized graphite particles suspended in a 5 wt % poly(vinylidene fluoride) (PVDF)-HFP/dibasic ester (DBE) solution. For the anode, the ink is composed of 90 wt % high surface area synthetic carbon (specific surface area ~600 cm²/gm and 10 wt % 1–2 μ m graphite particles suspended in a similar polymer/dibasic ester solution. The c-SPIL separator/electrolyte ink is composed of approximately 60 wt % 1.0 M Li/BMMITFSI (prepared as in Ref. 14), 30-wt % PVDF-HFP, and 10-wt % of TiO₂ nanopowder (~20 nm average particle size). Once laser transferred, each layer is thermally treated in air at 75 °C for 10–15 min in order to remove the DBE.

In order to fabricate a solid-state Li-ion microbattery, sequential layers corresponding to the cathode, c-SPIL separator, and anode are

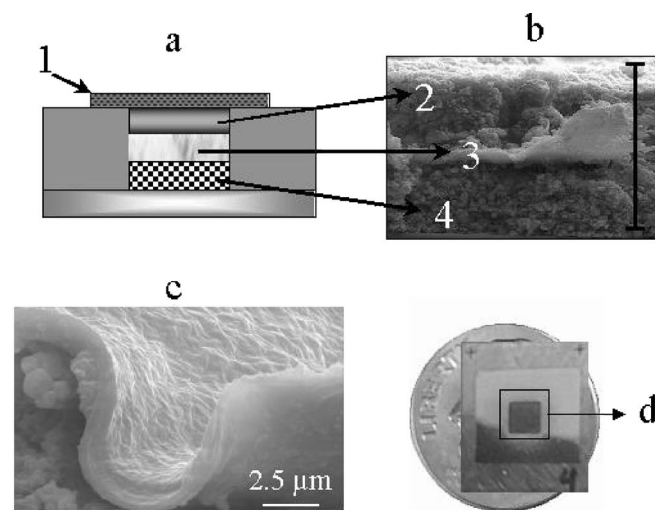


Figure 1. (a) Representative cross section and cutout schematic of an embedded microbattery made by LDW. (b) SEM cross section of the LDW microbattery. For both (a) and (b), 1 is the Pt metal sputter coat, 2 is the anode, 3 is the c-SPIL separator, and 4 is the cathode. (c) SEM image of the c-SPIL separator with the cathode and anode removed. (d) Actual LDW microbattery (black square indicates the active battery portion of the system).

* Electrochemical Society Active Member.

^z E-mail: pique@nrl.navy.mil

Table I. Dependency of the room temperature ionic conductivity on the size of ceramic particulates (barium titanium oxide) added.

Average BTO particle size	Ionic conductivity (mS/cm) at 22°C
1–2 μm	0.02588
600 nm	0.53093
60 nm	1.69011

deposited within a 3×3 mm laser micromachined pocket on a polyimide/aluminum flexible substrate as shown schematically in Fig. 1a. The exposed aluminum backing functions as a cathode current collector. Because the ionic liquid component of the c-SPIL separator is both nonvolatile and nonflammable, as opposed to the more common, volatile liquid/gel electrolytes, it is possible to vacuum-deposit Pt metal as the anode collector, while simultaneously encapsulating the cells. The resulting 9 mm^2 stacked structures exhibit a mass between 300–500 μg excluding the Pt layer. The fracture cross-sectional SEM micrograph of Fig. 1b shows an overall thickness of these cells of approximately $30 \mu\text{m}$, corresponding to a total volume of 270 nL (0.27 mm^3). Finally, the completed microbattery cells (Fig. 1d), are dried under a dynamic vacuum ($\sim 10^{-3}$ Torr) for two days at 75°C , and subsequently placed in an argon atmosphere dry box ($\text{ppm O}_2 < 0.10$ and $\text{ppm H}_2\text{O} < 0.5$ ppm) for electrochemical characterization. The microbatteries are cycled over 100 times between 4.65 and 3 V at charging and discharging currents of $110 \mu\text{A}/\text{cm}^2$.

Results and Discussion

The scanning electron microscope (SEM) images (Fig. 1b and c) show that the LDW transfer process deposits the c-SPIL ink to form a uniform, pinhole-free solid polymer layer. Because of the granular nature of the cathodic layer, the initial laser deposited c-SPIL separator is able to partially penetrate this material, allowing for enhanced surface area interactions between the electrolyte and the cathode. Ionic conductivity of the LDW c-SPIL nanocomposites is obtained through ac-impedance spectroscopy on $8 \text{ mm} \times 0.5 \text{ mm} \times \sim 1 \mu\text{m}$ thick laser transferred lines. Table I lists the ionic conductivity of the LDW separator for thin films composed of 30-wt % PVDF-HFP, 52-wt % 1 M Li/BMMITFSI, and 18-wt % of different size BTO particulates. The data clearly indicates that small particle size results in higher ionic conductivity. This size dependency is strong evidence that the larger particulates impede the migratory path of Li^+ through the separator, while the smaller particles enhance ion mobility by presenting the Li ion with a surface to migrate along. This is similar to the behavior seen in PEO-based nanocomposites.^{17,18} Table II lists the ionic conductivity for a series of laser-transferred separator films with decreasing amount of ionic liquid and increasing amounts of TiO_2 nanoparticulates, while Fig. 2 illustrates the temperature dependence of the ionic conductivity of these films as derived from ac-impedance measurements. The measured room temperature ionic conductivity of 2–3 mS/cm, is over 100 times greater than LiPON¹⁹ and over 10,000 times that of solid amorphous or crystalline polymers.^{20,21} The electrochemical behav-

Table II. Dependency of the room temperature ionic conductivity on the wt % of ceramic nanoparticulates (titanium oxide) added

Weight percent			Ionic conductivity (mS/cm) at 22°C
1 M Li/BMMITFSI	TiO_2	PVDF-HFP	
65	5	30	1.94766
60	10	30	2.85208
52	18	30	3.11176
45	25	30	1.79964

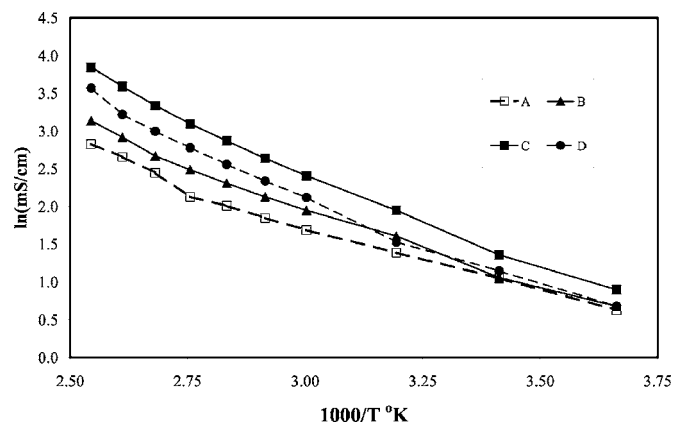


Figure 2. The temperature-dependent ionic conductivities of a LDW transferred c-SPIL separator/electrolyte with 30-wt % PVDF-HFP and varying concentrations of ionic liquid and TiO_2 nanoparticulates. (A) Composed of 65-wt % ionic liquid, 5-wt % TiO_2 ; (B) composed of 60-wt % ionic liquid, 10-wt % TiO_2 ; (C) composed of 52-wt % ionic liquid, 18-wt % TiO_2 ; (D) composed of 45-wt % ionic liquid, 25-wt % TiO_2 .

ior of the laser transferred c-SPIL separator is similar to that observed for simple drop cast films,^{11,13,14} with the advantage that the LDW process can be used to precisely control the deposition of the electrolyte/separator into predefined locations with the desired thickness. The TiO_2 nanopowder serves to partially absorb the incident laser radiation, and a stiffener to the nanocomposite, enhancing its mechanical strength in a manner similar to polyethylene oxide (PEO)-clay nanocomposites.¹⁷ Thus, the c-SPIL separators transferred by the LDW technique form uniform, nanocomposite layers on the order of 1 to $5 \mu\text{m}$ thickness with the high ionic conductivity and structural integrity necessary to serve as both the separator and electrolyte for a stacked, microbattery geometry.

Figure 3 illustrates the charge-discharge (C/3 Rate, $9.9 \mu\text{A}$ at $110 \mu\text{A}/\text{cm}^2$) of the Li-ion microbattery using the LiCoO_2 cathode and carbon anode. The energy density for this system is $1320 \mu\text{Wh}/\text{cm}^2$ (or $406 \mu\text{Wh}/\text{cm}^3$ based on volume) corresponding to a specific energy of $330 \text{ mWh}/\text{g}$ based on the battery mass. The cathodic capacity for this battery is near $100 \text{ mAh}/\text{g}$. Therefore, these LDW microbatteries exhibit energy densities and capacities similar to those observed for typical lithium ion batteries and current state of the art microbatteries.²²

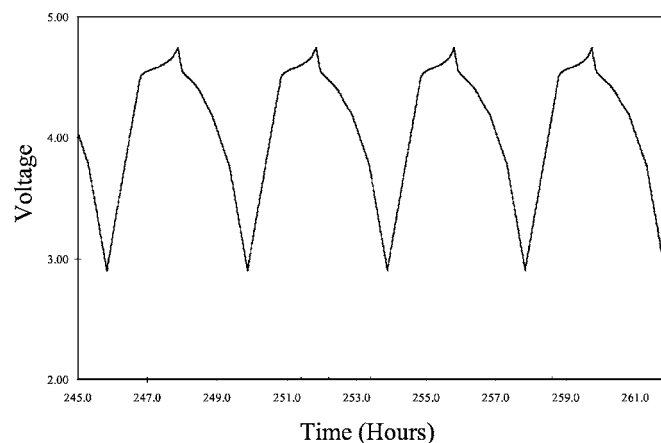


Figure 3. 50th to 53rd charge-discharge cycle of a LiCoO_2 -based microbattery made by LDW.

Conclusion

In summary, this work clearly demonstrates that the use of the c-SPL separator combined with the LDW processing is an enabling technology for the fabrication of rechargeable lithium ion microbatteries. The ability to completely transfer and assemble electrochemically and thermally stable micropower sources into plastic substrates, such as polyimide, can be extended to more advanced applications in which the power source is directly incorporated and sealed within the substrates used by the microdevice. Notably, the LDW is not chemistry specific and through deposition of a liquid-phase polymer nanocomposite into a solid, ionically conductive micrometer thick solid separator, there exists the possibility for other types of microelectrochemical cells for incorporation into a wide variety of microdevices.

Acknowledgments

The authors gratefully acknowledge funding from the Air Force Office of Scientific Research and Office of Naval Research.

Naval Research Laboratory assisted in meeting the publication costs of this article.

References

1. M. Madou, *Fundamentals of Microfabrication*, CRC Press, Boca Raton, FL (1997).
2. J. W. Judy, *Smart Mater. Struct.*, **10**, 1115 (2001).
3. J. N. Harb, R. M. LaFollette, R. H. Selfridge, and L. L. Howell, *J. Power Sources*, **104**, 46 (2002).
4. P. B. Koneman, I. J. Busch-Vishniac, and K. L. Wood, *J. Microelectromech. Syst.*, **6**, 355 (1997).
5. M. Balkanski, *Sol. Energy Mater. Sol. Cells*, **62**, 21 (2000).
6. J.-M. Tarascon and M. Armand, *Nature (London)*, **414**, 359 (2001).
7. A. Piqué, D. B. Chrisey, R. C. Y. Auyeung, J. M. Fitz-Gerald, H. D. Wu, R. A. McGill, S. Lakeou, P. K. Wu, V. Nguyen, and M. Duignan, *Appl. Phys. A: Mater. Sci. Process.*, **A69**, 279 (1999).
8. A. Piqué, C. B. Arnold, H. Kim, M. Ollinger, and T. E. Sutto, *Appl. Phys. A: Mater. Sci. Process.*, **A79**, 783 (2004).
9. C. B. Arnold, R. C. Wartena, K. E. Swider-Lyons, and A. Piqué, *J. Electrochem. Soc.*, **150**, A571 (2003).
10. K. R. Seddon, *Nat. Mater.*, **2**, 363 (2003).
11. H. Nakagawa, S. Izuchi, K. Kuwana, T. Nukuda, and Y. Aihara, *J. Electrochem. Soc.*, **150**, A695 (2003).
12. Y. S. Fung and R. Q. Zhou, *J. Power Sources*, **81**, 891 (1999).
13. T. E. Sutto, P. C. Trulove, and H. C. De Long, *Z. Naturforsch., A: Phys. Sci.*, **57**, 839 (2002).
14. J. Gilman, W. Awad, T. E. Sutto, R. Davis, J. Shields, R. Harris, C. Davis, A. Morgan, J. Callahan, P. C. Trulove, and H. C. De Long, *Chem. Mater.*, **14**, 3776 (2002).
15. H. C. De Long, P. C. Trulove, and T. E. Sutto, in *Ionic Liquids as Green Solvents: Progress and Perspectives*, R. D. Rogers and K. R. Seddon, Editors, PV 02-41, The American Chemical Society, Inc., Washington, DC (2003).
16. T. E. Sutto, P. C. Trulove, and H. C. De Long, in *Molten Salts XII*, P. C. Trulove, H. C. De Long, G. R. Stafford, and S. Deki, Editors, PV 99-41, p. 32, The Electrochemical Society Proceedings Series, Pennington, NJ (2002).
17. M. M. E. Jacob, E. Hackett, and E. P. Giannelis, *J. Mater. Chem.*, **13**, 1 (2003).
18. J. Y. Song, C. L. Cheng, Y. Y. Wang, and C. C. Wan, *J. Electrochem. Soc.*, **149**, A1230 (2002).
19. X. Yu, J. B. Bates, G. E. Jellison, Jr., and F. X. Hart, *J. Electrochem. Soc.*, **144**, 524 (1997).
20. M. Alamgir and K. M. Abraham, in *Room Temperature Polymer Electrolytes. Lithium Batteries*, Vol. 5, G. Pistoia, Editor, Industrial Chemistry Library, p. 41, New York (1994).
21. Z. Gadjourova, Y. G. Andreev, D. P. Tunstall, and P. G. Bruce, *Nature (London)*, **412**, 520 (2001).
22. N. J. Dudney and Y.-I. Jang, *J. Power Sources*, **119**, 300 (2003).