

Short communication

Gelled membranes for Li and Li-ion batteries prepared by electrospinning

D. Bansal, B. Meyer, M. Salomon*

MaxPower, Inc., 141 Christopher Lane, Harleysville, PA 19438, USA

Received 6 June 2007; received in revised form 20 July 2007; accepted 25 July 2007

Available online 7 August 2007

Abstract

Composite polymer gelled membranes have been prepared an electrospinning technique. Electrospinning of polymer fibers or electrospaying of particles is typically accomplished by applying a strong electric field (ca. $1\text{--}25\text{ kV cm}^{-1}$) to a polymer solution or slurry of solids in an appropriate solvent. The fibers are collected as a mat (membrane) on a grounded target such as Al, Cu, Ni, etc. Typical membranes (mats) consist of nanometer size fibers and have porosities of 65–85%. In the present paper, we describe the fabrication of electrospun membranes for use as gelled electrolytes in Li and Li-ion batteries. The electrospun polymer membranes used in this work are based on the polyimides (PIs) Matrimid and Ultem 1000. Pure PI membranes have been prepared, and blends of Matrimid and Ultem with PVdF-HFP and PAN have been studied in 250 mAh and 7 Ah Li-ion cells. Fully imidized polyimides such as Matrimid and Ultem 1000 do not form gels, and are used as a host matrix of high mechanical strength to immobilize the gelling constituents PVdF or PAN.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Li-ion; Gelled electrolytes; Electrospinning; Polyimides; Separators

1. Introduction

The majority of present day Li-based batteries employ thin ($\sim 25\text{ }\mu\text{m}$) microporous polyolefin separators (e.g. Celgard and Tonen amongst others) which constitute 25–30% of the overall cost of the manufacture of Li-ion batteries for HEV and EV application, and reduction of manufacturing cost by 50–75% has been identified as a key element for commercialization for HEVs and EVs [1]. In addition to the high cost of these microporous separators, wettability is another serious problem due to poor wetting capability of polyolefins and small pore sizes (~ 0.1 by $0.05\text{ }\mu\text{m}$) and small porosities ($\sim 35\text{--}45\%$) which result in difficulty of absorbing electrolyte solutions into microporous membranes. The net results are significant decreases in conductivities compared to pure liquid electrolyte solutions, and particularly for high temperature operation and storage, significant fade in capacity and power capability of a Li-ion battery due to degradation upon cycling because of electrolyte exudation from non-wetting pores and clogging of pores from particulate

matter, particularly at temperatures $\geq 60\text{ }^\circ\text{C}$ [1,2]. An alternate and much less expensive technology for the manufacture of battery separators is based on electrospinning which has recently been explored by a number of researchers (e.g. [3–7]) including ourselves [8]. Electrospinning and electrospaying of polymer fibers or particles to fabricate films is typically accomplished by applying a strong electric field (ca. $1\text{--}25\text{ kV cm}^{-1}$) to a polymer solution. By providing a small pressure at one end of a fluid reservoir and a small orifice at the other, a fine charged jet is generated. Depending upon the solvent evaporation rate, the charged jet forms dry submicron fibers or particles which are deposited onto an electrically grounded target. Compared to the technology for fabricating polyolefin separators, separators based on electrospinning technology are less labor intensive, and once setup will proceed unattended further reducing manufacturing costs relating to “touched labor.” Very recent applications of electrospinning separators for Li-ion systems have been successfully applied to prepare porous films composed of submicron fibers of such polymers as PVdF [3,5–7], PAN [4,8] while in [8] we introduced the use of polyimide based polymers to prepare new types of separators.

Polyimides (PIs) are synthesized by a reaction of an amic acid and a diamine at moderately high temperatures, $\geq 350\text{ }^\circ\text{C}$

* Corresponding author.

E-mail address: marksalomon@comcast.net (M. Salomon).

(the imidization reaction). However, fully imidized polyimides are commercially available such as Matrimid and Ultem 1000, the latter being a *polyether* imide, and it is these two PIs which were used in the present study. The presence of ether oxygens lends to polymer flexibility. The structure of PIs is a layered one in which the electron accepting properties of the carbonyl groups of the polyimide and electron donating property of the nitrogen gives rise to charge transfer complexes formed between polymer chains forming a very stable “stack”. It is this property (charge transfer) which gives the PI unique mechanical strength and dimensional stability. In addition, because of the electron donor and acceptor groups of a PI, polar solvents such as EC, EMC and NMF are also strongly coordinated within the stacks which enhances the ability of PI-based battery separator to retain electrolyte solution at high temperatures ($>60^{\circ}\text{C}$ as discussed below). Another important property of PIs is that they do not form gels and thus serve as a perfect stable host for polymers which form gels, e.g. PAN and PVdF-HFP. Another important aspect of polyimides relates to safety. They are thermally stable to temperatures above 300°C , and ignition of PIs is difficult. However, if ignited, a surface char forms extinguishing the flame.

2. Experimental/materials and methods

The polymers used in this study are Matrimid (Ciba Geigy), Ultem-1000 (GE), PVdF-HFP (Kynar 2801) and PAN (Aldrich) were dried overnight in vacuum and not further treated. For the gelling (electrolyte) solution, we employed 1 mol dm^{-3} LiPF_6 in a 1:3 (v/v) mixture of EC:EMC. EC and were obtained from Ferro Corp. ($>99.9\%$ pure). Battery grade LiPF_6 obtained from Stella Chemifa Corp. was dried overnight under vacuum. After preparation in a standard dry box, the water content of this electrolyte solution was less than 20 ppm.

Membranes were prepared by adding the pure PI or the PI blended with PVdF-HFP or PAN to a common solvent such as NMP or DMC at $50\text{--}60^{\circ}\text{C}$ to insure complete dissolution. Normally, around 10 mass% polymer was used, and electrospinning carried out at room temperature and at $\sim 11\text{ kV}$ to the grounded target (Al in most cases) over a distance of 7–10 cm. The membranes produced had thicknesses of $13\text{--}60\ \mu\text{m}$ which is governed by the deposition time. For use in Li-ion cells, we used membranes which were $25\ \mu\text{m}$ thick. Films were dried at 60°C overnight in vacuum and characterized by Field Emission Scanning Electron Microscopy (FESEM) and Hg Porosimetry. To fabricate membranes of uniform thickness, we use a mini-conveyor line as shown in Fig. 1.

The line consists of a grounded conveyer (collector) which can be operated at variable speeds, and two syringes placed above the conveyer are mounted on a platform with a slider crank mechanism providing lateral motion perpendicular to the linear motion of the conveyer. With this mini-conveyor line, we have rapidly prepared very uniform free standing electrospun membranes up to 2 m in length and 15 cm in width. In addition to the preparation of free standing membranes, we also used this mini-conveyor coating line to directly coat anodes and cathodes. The coating of electrodes $\sim 77\text{ cm}^2$ in area is shown schemati-

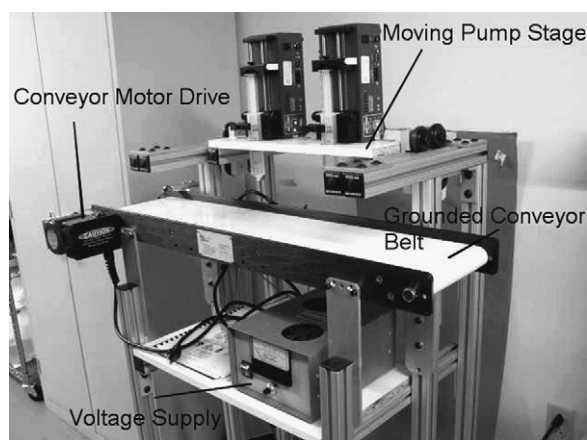


Fig. 1. The mini-conveyor electrospinning setup to fabricate stand-alone separator membranes.

cally in Fig. 2. The anodes and cathodes coated in this manner were used to build the 7 Ah Li-ion cells described below. The rate of production of free standing membranes or coated electrodes is dependent upon numerous factors such as distance from the syringe tip to the target, accelerating voltage, viscosity of the polymer solution, and speed of the conveyer line. Optimization of the rate of production for manufacturing is presently being investigated.

Conductivities were measured in cells with stainless steel blocking electrodes by impedance spectroscopy using a Solartron 1286 electrochemical interface and 1253 HF frequency response analyzer. Selected gelled membranes were studied electrochemically in the following type of prismatic Li-ion cell.

| | | |
|----------------------------------|----------------------|---|
| MCMB 2528 (Cu current collector) | PI-based electrolyte | $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (Al current collector) |
|----------------------------------|----------------------|---|

Cathodes contained 90% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, 5% Super P and 5 mass% PVDF 761, and anodes contained 90% MCMB 2528, 3% Super P and 7 mass% PVDF 761. For the 250 mAh cells, the $25\ \mu\text{m}$ thick stand-alone separator was sandwiched between

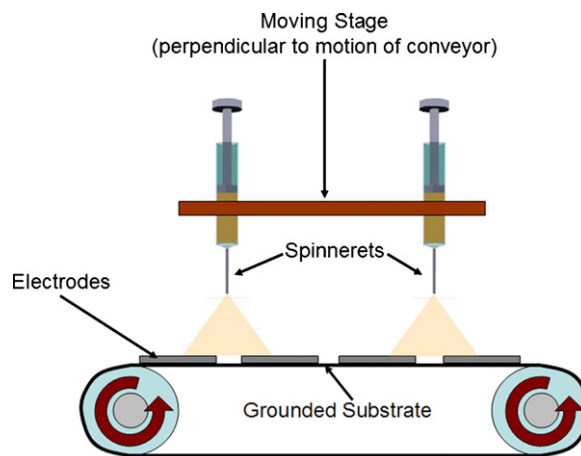


Fig. 2. Block diagram of the experimental setup of Fig. 1 showing (schematically) the coating of electrodes on the grounded substrate (the conveyor line).

Table 1
Composition of Ultem-PAN membranes

| Polyimide | Polyimide (mass%) | PAN (mass%) | PVdF (mass%) |
|------------|-------------------|-------------|--------------|
| Ultem 1000 | 80.0 | 20.0 | |
| Ultem 1000 | 50 | 50 | |
| Ultem 1000 | 33.3 | 66.7 | |
| Matrimid | 65.0 | | 35.0 |

anode and cathode, and sealed in polymer coated aluminum bags (“coffee bags”). For the 7 Ah Li-ion cells, electrodes were directly spray coated on both sides to a thickness of $\sim 13 \mu\text{m}$, and sealed in coffee bags. Thus the separation between each electrode was $\sim 26 \mu\text{m}$. Prior to completely sealing the coffee bags, the cells were activated with 1 mol dm^{-3} LiPF_6 in a 1:3 mixture (v/v) of EC:EMC (ethylene carbonate and ethylmethyl carbonate) and stored for several hours to allow for gel formation. Cells were charged at constant current corresponding to a rate of $C/10$ – 4.2 V followed by tapering at 4.2 V to $C/100$. The first three “formation cycles” were limited by both cell capacity and the voltage.

3. Results and discussion

Table 1 summarizes the compositions of electrospun membranes prepared in this study. Films with 33.3 mass% Ultem and 66.7 mass% PAN and 65 mass% Matrimid and 35 mass% PVdF showed superior strength and flexibility were therefore selected for conductivity and Li-ion cell studies. Typical densities for these electrospun membranes are $\sim 0.20 \text{ g cm}^{-3}$ for Ultem-based membranes and $\sim 0.40 \text{ g cm}^{-3}$ for Matrimid-based membranes. Based on these densities and using the following equation to calculate porosities,

$$P(\%) = 100 \left\{ 1 - \frac{\rho_{\text{app}}}{\rho_{\text{polymer}}} \right\}$$

the Ultem-based membranes have a porosity of $\sim 84\%$, and Matrimid-based membranes have a porosity of $\sim 67\%$. Fig. 3a and b show the FESEM images of the 33.3% Ultem membrane at 2000 and 30,000 magnification, respectively. From the latter

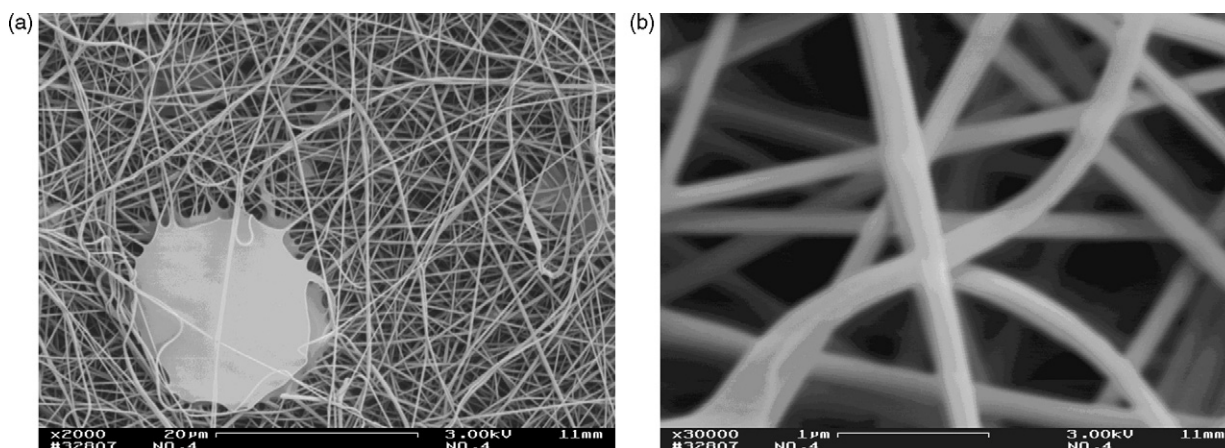


Fig. 3. FESEM images of the 33.3 mass% Ultem-based separator. Magnification is 2000 in (a) and 30,000 in (b).

Table 2
Hg porosimetry data for Ultem-based membranes

| PAN (mass%) | Total pore area ($\text{m}^2 \text{ g}^{-1}$) | Median pore diameter (μm) | Average pore diameter (μm) |
|-------------|---|--|---|
| 20 | 52.331 | 42.669 | 0.6807 |
| 50 | 2.652 | 39.9816 | 0.6388 |
| 66.7 | 21.116 | 15.627 | 1.0136 |

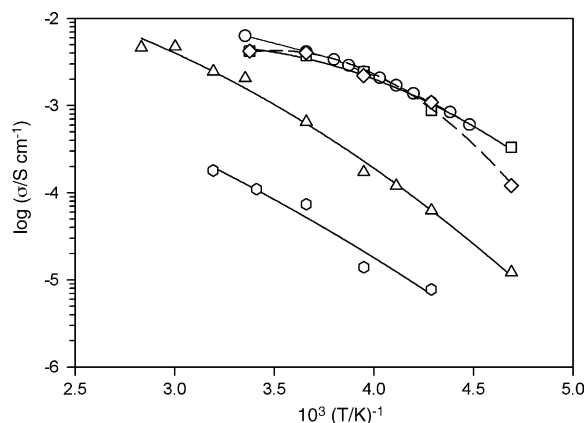


Fig. 4. Conductivities of electrospun membranes from -40 to $80 \text{ }^\circ\text{C}$. Compositions: Ultem-PAN gel is 66.7% PAN and Matrimid-PVdF gel is 75% PVdF.

figure, the fiber sizes in the non-woven membrane range from ~ 300 to $\sim 625 \text{ nm}$.

We note that the tensile strength of the PI-based membranes have not been optimized. It is known that the tensile strength of electrospun membranes can be increased either by hot pressing, e.g. at $70 \text{ }^\circ\text{C}$ [9] or by thermal treatment at $\sim 150 \text{ }^\circ\text{C}$ [10], but these procedures result in a decrease in pore volume and hence, in lower conductivities. The effects of hot pressing and thermal treatment are the focus of future studies Table 2.

Conductivities for selected membranes from -40 to $80 \text{ }^\circ\text{C}$ are shown in Fig. 4. For the pure Ultem membrane, the conductivities are essentially the same as those for the pure liquid electrolyte solution which is due to the high porosity of the membrane. For gelled electrolytes, conductivities decrease as expected.

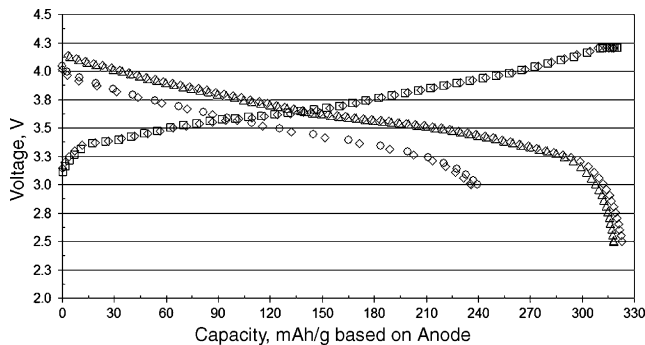


Fig. 5. Cell performance at room temperature before and after storage for 3 weeks: (□) charge before storage (4th cycle) and (◇) after storage (21st cycle) at C/10. (△) Discharge before storage (4th cycle) and (▽) after 3 week storage (21st cycle) at C/10. (○) Discharge before storage (12th cycle) and (◇) after 3 week storage (31st cycle) at the C rate.

Figs. 5 and 6 show the cycling performance of 250 mAh Li-ion cells using a gelled membrane based on a Ultem-PAN composition of 33.3 mass% Ultem and 66.7% PAN both before and after 3 weeks at room temperature (Fig. 5) and 50 °C (Fig. 6). Discharge after 3 weeks storage at 50 °C was carried out at room temperature. The cells were charged at the C/10 rate and discharged at various rates from C/10 to C. Essentially no capacity fade is observed after storage. Cells were cycled between 44 and 50 cycles with no significant loss in capacity before being removed from testing.

Fig. 7 shows the initial cycling performance of a 7 Ah Li-ion cell using the gelled membrane based on a Matrimid-PVdF composition of 65 mass% Matrimid and 35% PVdF. For these cells, both positive and negative electrodes were directly spray coated with the electrospun separator material to a thickness of 13 μm on both sides. Thus, the overall separation between anode and cathode was approximately 26 μm. The cells were sealed in polymer laminate ‘coffee bags’ and activated as previously described. The cells were cycled thirteen times and then removed from testing.

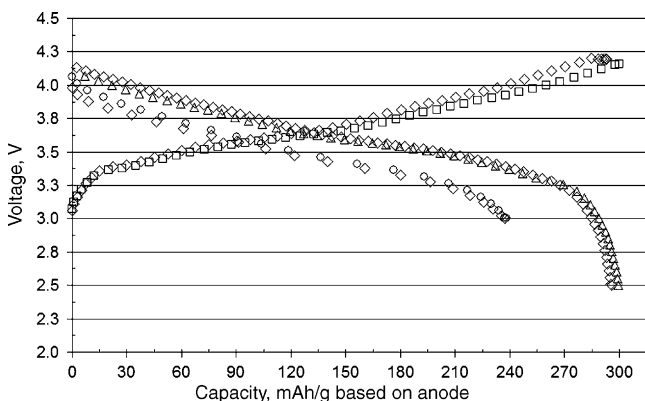


Fig. 6. Cell performance at room temperature before and after storage for 3 weeks at 50 °C: (□) charge before storage (18th cycle) and (◇) after storage (21st cycle) at C/10. (△) Discharge before storage (18h cycle) and (▽) after 3 week storage (21st cycle) at C/10. (○) Discharge before storage (13th cycle) and (◇) after 3 week storage (31st cycle) at the C rate.

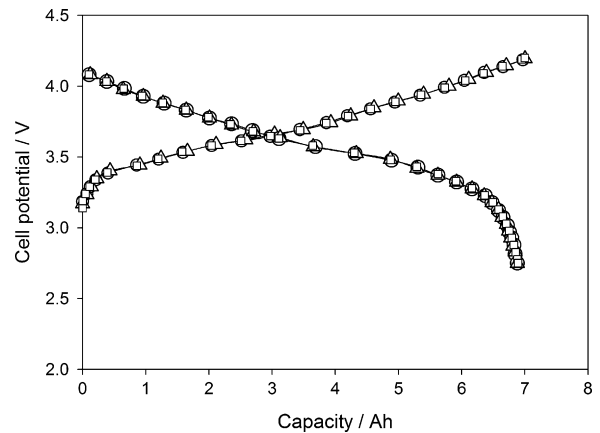


Fig. 7. First and third cycle performance of the 7 Ah Li-ion cell at room temperature using a gelled membrane based on a Matrimid-PVdF composition of 65 mass% Matrimid and 35% PVdF. The charge and discharge voltage window is 2.5–4.2 V. First cycle symbol (○), third cycle symbol (△), and thirteenth cycle symbol is (□).

4. Conclusions

An electrospinning setup was developed to fabricate thin and uniform non-woven separators. The polyimides Matrimid and Ultem-1000 were used to serve as host matrices for the gel capable polymers PVdF-HFP and PAN. Prior to gelling, these non-woven separators had porosities ranging from ~77 to 83%. Li-ion cells using these gelled separators exhibited excellent cycling performance with little or no loss in capacity before and after 3 weeks storage at room temperature and 50 °C.

Acknowledgments

This work was supported by the US Army under Contract Number W911QX-05-C-0001. The authors would like to thank Prof. John Xu and Mr Hui Ye of Rutgers University for the FESEM and Hg Porosimetry data.

References

- [1] US Department of Energy, “FY 2006 Progress Report for Energy Storage Research and Development.” This document is presently available on the internet at the following URL: <http://www1.eere.energy.gov/vehiclesandfuels/technologies/energy_storage/index.html>.
- [2] R. Kostecki, L. Norin, X. Song, F. McLarnon, J. Electrochem. Soc. 151 (2004) A522.
- [3] X. Li, G. Cheruvally, J.-K. Kim, J.-W. Choi, J.-H. Ahn, K.-W. Kim, H.-J. Ahn, J. Power Sources 167 (2007) 491.
- [4] T.H. Cho, T. Sakai, S. Tanase, K. Kimura, Y. Kondo, T. Terao, M. Tanaki, Electrochem. Solid State Lett. 10 (2007) A159.
- [5] K. Gao, X. Hu, C. Dai, T. Yi, Mater. Sci. Eng. B131 (2006) 100.
- [6] S.W. Lee, S.W. Choi, S.M. Jo, B.D. Chin, D.Y. Kim, K.Y. Lee, J. Power Sources 163 (2006) 41.
- [7] J.R. Kim, S.W. Choi, S.M. Jo, W.S. Lee, B.C. Kim, J. Electrochem. Soc. 152 (2005) A295.
- [8] B. Meyer, M. Salomon, D. Foster, Paper presented at the 209th Meeting of The Electrochemical Society, Denver, CO, May 7–12, 2006 (abstract 119).
- [9] S.W. Lee, S.W. Choi, S.M. Jo, B.D. Chin, D.Y. Kim, K.Y. Lee, J. Power Sources 163 (2006) 41.
- [10] K. Gao, X. Hu, C. Dai, T. Yi, Mater. Sci. Eng. B 131 (2006) 100.