



Short communication

A reliable sealing method for microbatteries



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H I G H L I G H T S

- A facile method for sealing mini-size or irregularly shaped batteries was developed.
- The first sealing barrier blocks liquid electrolytes.
- The second sealing barrier hermetically seals the cell.
- The sealing method is low-cost and widely applicable.

A R T I C L E I N F O

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As electronic devices continue to become smaller, their energy sources (i.e., batteries) also need to be smaller. Typically, energy densities of batteries decrease as the battery size decreases due to the relative increase of parasitic weight such as packaging materials. In addition, the sealing methods in conventional batteries are difficult to apply to microbatteries. In this work, we developed a facile sealing method for microbatteries. The method employs a dual-sealing concept: a first rubber barrier temporally confines the organic electrolytes and a second adhesive barrier forms a hermetic seal with the battery case. With this innovative sealing approach, excellent shelf life and operation life of the batteries have been demonstrated. A minimal amount of packing materials is employed resulting in high energy densities.

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1. Introduction

Batteries of various sizes and shapes have been used in a wide range of applications. Particularly, lithium (Li) batteries with organic electrolytes are the main power sources used in portable electronic devices and transportation applications. Both primary and secondary batteries require long shelf and service lives. Because of the volatile nature of organic electrolytes and the detrimental effect of moisture to battery performance, lithium batteries need to be tightly sealed to extend their calendar life and cycle life.

The energy density of batteries usually decreases with decreasing volume of the battery because the inactive materials (such as casing and sealing materials) occupy an increasing portion

of battery weight and volume in smaller batteries [1,2]. High energy densities ($\sim 250 \text{ Wh kg}^{-1}$, 650 WhL^{-1}) can be achieved for large size Li batteries with different shapes such as cylindrical or prismatic configurations [3]. Although thin-film batteries (with an electrode thickness of a few microns) have been developed for miniature device applications, the energy densities of these batteries are insufficient for many applications [4]. Another issue with two-dimensional, thin-film batteries are their large footprints and the more expensive preparation method required for their production (i.e., sputtering is used to deposit electrode materials for most thin-film batteries) [5]. With continuous miniaturization of electronic devices, the market demands low-cost microbatteries (a few millimeters in all dimensions) with high energy densities [2]. However, compared to conventional batteries, these smaller batteries are much more difficult to seal. In larger batteries, metal cases and multi-layer aluminum/polymer laminates have been used for sealing. However, for microbatteries, the lamination approach has become impractical because the seals required would be wider

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than the total size of the batteries. As a result, metal cases have become the dominant approach for packaging microbatteries.

In the case of implantable medical devices, precise laser welding often is used to seal the microbattery after electrolyte filling, but this process is expensive and too complex for batteries used in most of consumer electronics. Many low-cost sealing approaches have been tried for sealing microbatteries. For example, different kinds of sealing materials (e.g., epoxies, ultraviolet [UV] curable polymers, etc.) have been used in microbatteries and irregularly shaped batteries [6–8]. Direct application of adhesives usually yields unsatisfactory results because of incompatibilities between adhesives and organic electrolytes. Therefore, a low-cost, efficient, and more reliable sealing approach is highly desirable for these microbatteries.

Recently, it is reported that microbatteries (MB306, 3 mm in diameter and 6 mm in length, [9]) can be used to power an injectable acoustic microtransmitter for the Juvenile Salmon Acoustic Telemetry System [10]. The batteries are based on CF_x/Li chemistry, packaged in Al cases, and custom designed to deliver high gravimetric and volumetric energy densities. The MB306 batteries have worked very well in acoustic devices if they are fully-encapsulated in the device soon after the battery is prepared; however, they may lose capacity if stored for an extended time before being sealed inside a device. To further improve the longevity and reliability of these microbatteries, we developed a facile and effective dual-sealing approach that first provides a temporary barrier to liquid electrolytes and second provides a hermetic seal by bonding the casing material and appropriate adhesives. The details of this approach are described below.

2. Methods and experimental

Our dual-sealing method was applied to and evaluated on dry cells provided by EVE Energy Co., LTD. The cells employ CF_x/Li primary cell chemistry with a jelly-roll electrode design similar to our previously reported MB306 cells, which are 6 mm long and 3 mm in diameter. Two thin metallic leads provide external electrical connections. The cylindrical dry cells are packaged in aluminum cases with an open end (Fig. 1). The cases are 3 mm in diameter and 6.3 mm long before crimping.

To prepare the microbattery, the electrode assembly (cathode/separator/anode) was inserted into the Al case as shown in Fig. 1(a). A thin (0.1 mm thick) neoprene rubber disk with a diameter equal

to the inner diameter of the Al case was then placed on the top of the cell assembly (Fig. 1(b)). Two metallic leads were passed through the rubber and provide electrical connection to the cell. The cell shown in Fig. 1(b) was then soaked in a liquid electrolyte (1 M LiPF₆ in ethylene carbonate/dimethyl carbonate, volume ratio 3:7) for at least half an hour. Partial vacuum was applied to the cell to ensure complete wetting of the electrode assembly. The amounts of electrolyte in the cells were obtained by weighing the cells before and after electrolyte impregnation. After the cell was wetted, it was first crimped with a custom-made die set as shown in Fig. 1(c). The cell was placed in a receptacle in the bottom piece of the die set; the top piece of the die set with a cone-shaped recess were pressed on the edge of the Al case so it bent inward at an angle of 45°. A moderately tight fit of the Al case in the receptacle was essential to prevent shifting or bending of the case along the radial direction. For the second crimping, another top piece of a die with a flat front and a small opening to accommodate the electrical leads was applied so the edge of the Al case folded completely onto the rubber disc (Fig. 1(d)). The cell assembly then was rinsed briefly with dimethyl carbonate and dried to remove any liquid electrolyte residues on the Al case. A small amount of Torr Seal epoxy was applied to cover the top surface of the cell (Fig. 1(e)). The epoxy was cured at room temperature. The thickness of the epoxy layer was less than 0.5 mm. The whole assembly process was carried out in a dry room with a dew point of $-50\text{ }^\circ\text{C}$.

Four identical cells were assembled using the approaches described above where Torr seal was used as the final sealant. Two of these cells (MB1 and MB2) were discharged immediately after assembly and two other cells (MB3 and MB4) were discharged after storing in ambient condition for 30 days. The mass of stored cells was measured on selected storage time using a precision weighing balance (Sartorius CPA225D) with an accuracy of 0.01 mg. A charge/discharge instrument (CH Model 6005D) was used to measure the open circuit voltage (OCV) and impedance spectra. Impedance measurements (over a frequency range of 100 KHz to 1 Hz with a voltage modulation of 5 mV) were performed on the MB3 and MB4 cells immediately after the epoxy was cured and after 30 days of storage. Prior to the impedance measurements, the cells were activated by discharging at 1 mA for 4 min (corresponding to 1% of the cell capacity) and allowed to equilibrate for at least 1 h. A Landt instrument (CT2001A) was used to discharge the cells to 1.5 V at a constant current of 1 mA. Scanning electron microscopy (SEM) (a JEOL 7001F Field Emission

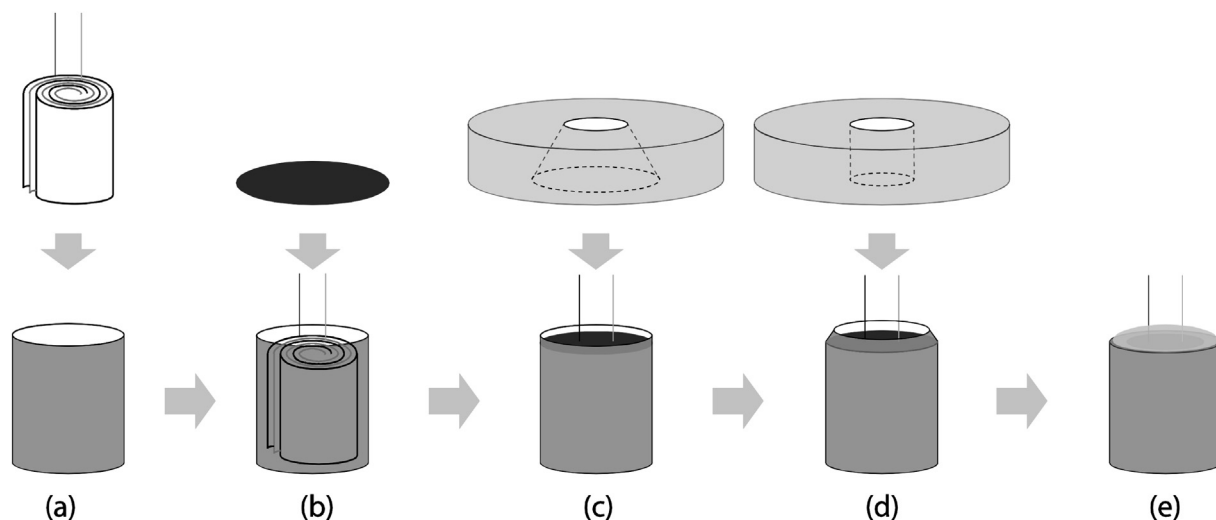


Fig. 1. Schematics of the CF_x/Li microbattery assembly using the dual-sealing method.

Gun SEM used in secondary electron mode with an accelerating voltage of 2 kV) was used to observe the binding on the interfacial region of Al/epoxy specimens.

3. Results and discussion

The main challenges of the sealing approach using epoxies/adhesives are that most adhesives are not stable with organic electrolytes used in Li batteries or are not impermeable to electrolyte vapor and moisture. These problems are exacerbated as the adhesive degrades over time when in direct contact with organic electrolytes. Most adhesives cannot cure properly in the presence of electrolytes so the seal between adhesives and battery cases is poor. Moreover, species released by the adhesive may be detrimental to the electrochemical performance of the cell. Therefore, minimizing the direct exposure of sealing adhesives to liquid electrolytes is a key to successfully achieving hermetic seals in microbatteries containing organic electrolytes.

In the design reported in this paper, the neoprene rubber disk (which exhibits an excellent stability in carbonate-based electrolytes) effectively prevents contact between the electrolyte and the adhesive. The high elasticity of the neoprene disc effectively closes gaps around the lead penetration. With the rubber barrier, no liquid electrolytes were visually observable at the upper surface of the disk. Although this is not a hermetic seal, it provides the conditions needed for the additional sealing materials to cure.

For the second sealing layer, an impermeable adhesive needs to be selected. Desirable properties of the adhesive include 1) good bonding with the Al case, 2) rapid curing, 3) very low permeability to electrolyte vapor and moisture, 4) good chemical compatibility with the electrolyte after curing, and 5) no release of harmful chemicals into liquid electrolytes. We investigated many different types of adhesives in this work. Batteries were assembled exactly the same way as presented in previous section except that different adhesives are used so that the electrolyte amount was essentially the same in all cells. Mass losses of these cells were monitored to detect the possible electrolyte leaks. At least two cells were tested for each type of adhesive, and the test results are summarized in Table 1.

Table 1 shows that Torr Seal epoxy yielded the most satisfactory results. As a reference, Torr Seal has been widely used in the vacuum industry as an excellent sealer to prevent leaks in vacuum systems. Fig. 2 shows mass changes of for the MB3 and MB4 cells over time. The total amount of electrolytes at the beginning of the test was ~17 mg. The mass for the MB3 and MB4 cells remained very stable over 30 days. This was in stark contrast with cells sealed with other adhesives, which continuously lost mass over time due to the evaporation of liquid electrolytes. Fig. 1(d) and (e) show that the sealing of the battery depends mainly on the bond between the Al case and the sealant material. Fig. 2 shows the mass loss of the samples (using Torr Seal) as a function of time when stored in

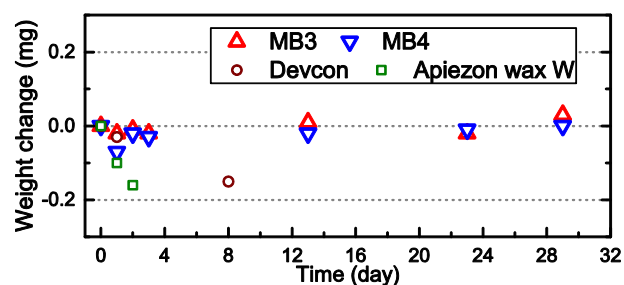


Fig. 2. Mass change of MB3 and MB4 cells over 30 days. The batteries are stored in ambient conditions.

ambient conditions. No significant mass loss was observed over a month. Fig. 3(a) and Fig. 3(b) show the interfacial regions of the Al/Torr Seal epoxy sample and the Al/Devcon 10-min epoxy sample. Observations on multiple locations show the similar gaps so the images are representative of the entire interfacial regions. The white line at the interface indicates steps (height difference) due to differences in the abrasion rate of dissimilar materials during polishing. Clearly, the cured Torr Seal epoxy bonded seamlessly with the Al substrates; the step was not quite obvious, suggesting a smooth transition from the epoxy layer to the Al. In comparison, a small gap and a sharp step were observed between the cured Devcon epoxy and the Al substrate. The epoxy cover connects with the Al case through an Al ring (i.e., the crimped edge of the Al case) to form a complete closure as shown in Fig. 1(d) and (e). Use of the neoprene rubber disk as the first barrier prevents direct exposure of the Torr Seal adhesive to liquid electrolytes so the seal can be fully cured. The excellent stability of the cells using Torr Seal epoxies demonstrates the merits of the dual-sealing concept.

Fig. 4(a) shows the OCV change of MB3 and MB4 cells over time. For both cells, the OCV increased slightly initially, which is consistent with the expected behavior of potential relaxation [11]. Interestingly, the OCV increased by about 20 mV on the fourth day and then stabilized. The stable OCV of the cells indicates that the internal electrochemical conditions of the cells were stable. The impedance spectra of the batteries (see Fig. 4(b)) consist of a depressed semicircle at high and intermediate frequencies and a tail at low frequencies, which is similar to the behavior of classical Randles cells. Therefore, the left intercept of the semicircle is assigned to the solution resistance, and the span of the semicircle reflects the contribution of the charge transfer resistance at both electrodes. For both cells, the semicircle grew slightly after being stored for 30 days, which may be the result of continuous passivation of the lithium anode. Values at the left intercept decreased for both cells, suggesting better wetting conditions after storage. If the cells lost electrolytes because of poor sealing, an increase in solution resistance would be expected. Impedance data clearly show that the seal was good for more than 30 days. Fig. 4(c) compares the

Table 1

Mass change of batteries sealed with different adhesives.

Adhesive name	Adhesive type	Mass change (mg/day)
ETPTA UV-curable	Acrylate polymer	-0.08 ^a
Devcon 10 min epoxy	Two component epoxy	-0.02
Apiezon wax W	Hydrocarbon	-0.1
Loctite 4311 UV-curable	Cyanoacrylate/UV	-0.08
Masterbond EP21TPND	Two component polysulfide	-0.18
Masterbond EP51FL	Two component epoxy	-0.02
Loctite E-20HP	Two component epoxy	0 in the first 5 days; -0.03 after 5 days
Torr Seal epoxy	Two component epoxy	No measurable mass loss in 30 days

^a The negative sign indicates battery mass loss.

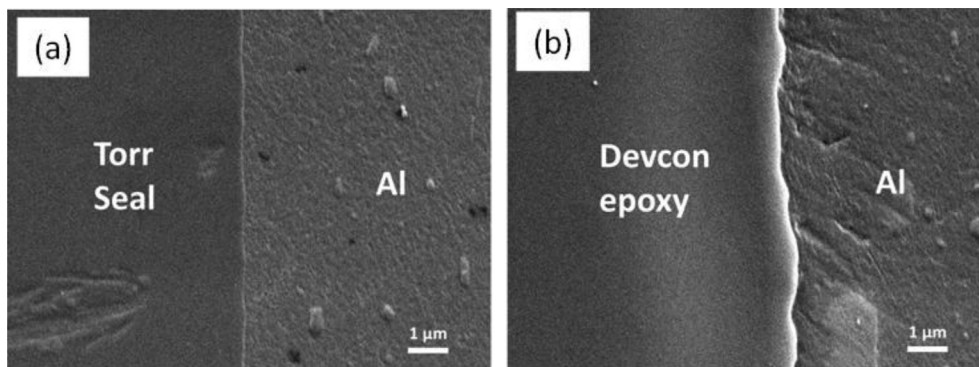


Fig. 3. Scanning electron microscopy images on the interfacial regions of Al/Torr Seal epoxy (a) and Al/Devcon epoxy (b).

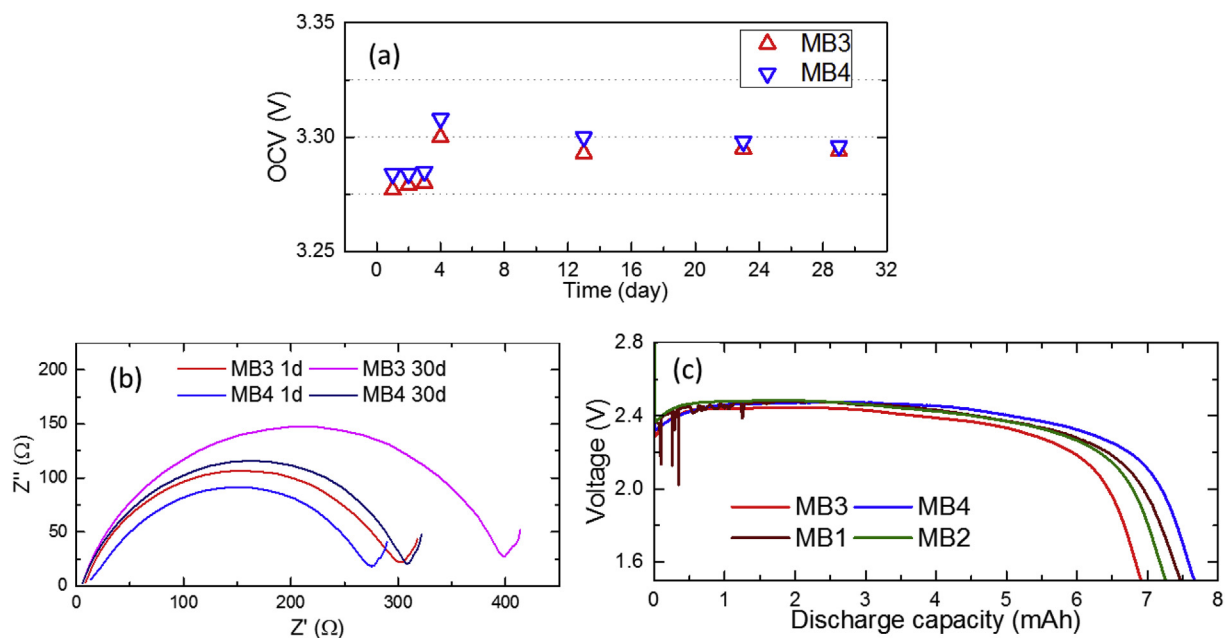


Fig. 4. (a) OCV vs. storage time of MB3 and MB4 cells. (b) Nyquist plots of MB3 and MB4 cells measured on the first day and last day. (c) Discharge curves of all cells at 1 mA constant current. MB1 and MB2 were discharged on day 1 day; MB3 and MB4 were discharged on day 30.

discharge curves of cells discharged on day 1 (MB1 and MB2) and on day 30 (MB3 and MB4). The voltage profiles and average discharge capacities are very similar for both fresh cells and stored cells. The variations in voltage profiles and capacities are reasonable considering the difficulty in precise control of manually prepared cells. Some voltage fluctuations were observed for the MB1 cell, possibly caused by poor electrical connections inside the cell.

Microbatteries (MB306) investigated in this work exhibit a discharge energy density of $\sim 430 \text{ Wh L}^{-1}$ and 240 Wh kg^{-1} at a discharge rate of $C/7$. Compared to the smallest Panasonic lithium coin cells (CR1025 (Li/MnO₂)), our microbatteries are only one-fifth the volume, but exhibit twice the gravimetric energy density and similar volumetric energy density. Our sealing method requires no heat, pressure, or precise laser welding so the production cost is low. The ease of implementation also renders wide applicability, facile downsizing, and tunability for specific applications.

4. Conclusions

We developed a facile, dual-sealing method for producing lithium batteries. This method is particularly suitable for sealing

small batteries. The feasibility of this method is demonstrated in MB306-type microbatteries that are only 6 mm long and 3 mm in diameter. Cells sealed with this method showed no mass loss and no degradation in the electrochemical performance over 30 days as demonstrated from a combination of mass change, OCV, impedance, and constant-current discharge tests. The cells deliver high volumetric and gravimetric energy densities, thereby highlighting the economic advantage of the sealing method. It is expected that the sealing concept will be useful not only in primary lithium batteries but also secondary lithium batteries and other types of electrochemical devices.

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