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Development and performance of a rechargeable thin-film solid-state microbattery

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Abstract

A thin-film solid-state Li/TiS_2 microbattery has been developed at Eveready Battery Company (EBC). It is fabricated using sputtering for deposition of the metal contacts, TiS_2 cathode, and oxide/sulfide glassy electrolyte. High vacuum evaporation is used to deposit a LiI layer and Li anode. EBC Microbatteries range from 8 to 12 μm in thickness and have a capacity between 35 and 100 $\mu Ah/cm^2$, depending on the amount of anode and cathode deposited. The microbattery open-circuit voltage is approximately 2.5 V. EBC Microbatteries routinely go more than 1000 cycles between 1.4 and 2.8 V, with greater than 90% cathode utilization, at current densities as high as 300 $\mu A/cm^2$. Several EBC Microbatteries have gone over 10 000 cycles at 100 $\mu A/cm^2$ with greater than 90% cathode utilization on each cycle. The microbatteries will cycle at temperatures as low as -10 °C at a current density of 100 $\mu A/cm^2$, are capable of supplying pulse currents of several mA/cm^2, and have excellent long-term stability both on shelf and while cycling. Sets of five microbatteries have been assembled in either a series or parallel configuration and cycled more than 1000 times. EBC Microbatteries as large as 10 cm^2 have been fabricated and cycled over 1000 times at close to 100% cathode efficiency.

Keywords: Rechargeable lithium batteries; Thin-film batteries

1. Introduction

The miniaturization of electronic devices has, in many cases, resulted in extremely low current and power requirements. This has made possible the use of thin-film rechargeable microbatteries as power sources for these devices. Some of the advantages offered by thin-film microbatteries for these applications include: (i) they are manufactured by the same techniques as currently used in the microelectronics industry; (ii) the extreme thinness of the electrolyte layer allows the use of relatively poor ionic conductors such as glassy, solid-state electrolytes; (iii) the sequential vacuum deposition processes provide cleaner and more intimate interfaces between layers, and (iv) the microbattery can be constructed in almost any two-dimensional shape. The fabrication of a thin-film rechargeable microbattery has been investigated for many years [1–5]. However, no one has reported the development of a microbattery with properties suitable for use as a reliable, long-term, rechargeable power supply. We feel that the performance of the EBC Microbattery has accomplished these goals. The outstanding secondary performance with thousands of deep discharges, the capability of current density as high as several mA/cm^2, and the long-term stability both on shelf and during cycling make the EBC Microbattery superior to any other microbattery reported to date.

2. Experimental

The fabrication process and testing methods for the EBC Microbattery have been discussed elsewhere [6]. A recently developed protective coating used to isolate the EBC Microbattery from the environment is a proprietary polymer covered by a metallic layer [7]. The polymer coat is produced by vapor-phase deposition with polymerization of the conformal coating occurring at room temperature. The metallic coating is deposited by sputtering or vacuum evaporation. These layers may be repeated if required.

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3. Results and discussion

A cross section of the EBC Microbattery is shown in Fig. 1. The substrate for the microbattery is usually a glass microscope slide but any reasonably smooth surface can be used. For example, alumina, mylar, and paper have also been used as the substrate. The use of mylar and paper have shown that the EBC Microbattery has good flexibility in spite of its metallic and glass components. The sputter deposited TiS_2 cathode appears to be amorphous to X-ray analysis but scanning electron microscopy (SEM) shows it to consist of small crystallites. Photomicrographs of the edge and surface of a sputtered TiS_2 film appear very similar to that of the chemical vapor deposited (CVD) TiS_2 developed by Kanehori et al. [1] except for a smaller crystallite size in the sputtered film (0.3–0.4 μm versus 10–12 μm). The sputtered cathode film has good stoichiometry ($TiS_{2.09}$) and a density about 45% of theoretical (1.45 g/cm^3). A number of solid electrolyte compositions were investigated but for reasons such as high sulfide content, high internal stress, or low conductivity they were eliminated. The preferred electrolyte is sputter deposited from a target with the composition $6LiI–4Li_3PO_4–P_2S_5$. The conductivity of this glassy electrolyte as a thin film is 2×10^{-5} S/cm. The layer of LiI is necessary to prevent the Li anode from reacting with the electrolyte and forming a high resistance layer, probably Li_2S. The LiI layer is not used as the solid electrolyte because it is known to form 'color centers' that are electronically conductive if the stoichiometry of the material is modified. It is very possible that this could occur during deposition of the Li layer, therefore, the LiI is considered an ionically conductive protective layer. Complex impedance measurements on EBC Microbatteries show the total ionic conductivity (glassy electrolyte + LiI) to be 2×10^{-6} S/cm. This conductivity value correctly falls between the 10^{-7} S/cm conductivity of the LiI layer [8] and the 10^{-5} S/cm conductivity of the oxide/sulfide electrolyte layer.

Typically, EBC Microbatteries have a total thickness around 10 μm and an OCV between 2.4 and 2.5 V. The primary discharge of the EBC Microbattery shows a classically shaped curve and close to 100% cathode utilization to a 1.8 V cutoff, based on the amount of TiS_2 present undergoing a 1 electron change, at current densities from 10 to 135 μA/cm^2. This is illustrated in Fig. 2. For these microbatteries this calculates to an energy density of 140 Wh/l and a power density up to 270 W/l. The energy density can be increased substantially by increasing the cathode thickness. For example, increasing the cathode thickness from 2 to 4 μm would result in an energy density of 230 Wh/l.

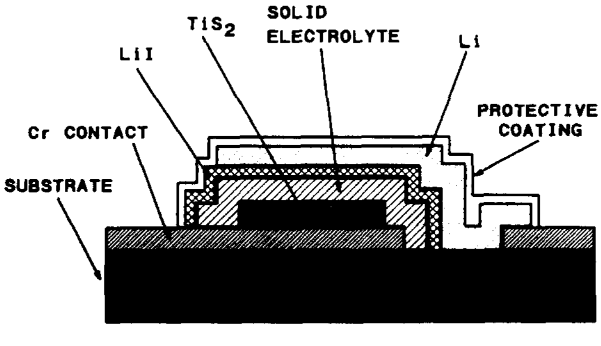

Fig. 1. Cross section of the EBC Microbattery.

The EBC Microbattery is capable of producing current densities as large as several mA/cm^2. Fig. 3 shows the closed-circuit voltage of a microbattery at the end of a 2 s current pulse up to a current density of 4 mA/cm^2. The 2 mA/cm^2 pulse would be equivalent to a power density of greater than 4000 W/l. Shorting the microbattery through a 0.1 Ω resistor produces a current density of approximately 12 mA/cm^2.

The EBC Microbattery shows outstanding secondary performance. Microbatteries achieve well over 1000 cycles with depths-of-discharge greater than 70% of 1 electron at current densities of up to 300 μA/cm^2 to the 1.8 V cutoff. A typical result is shown in Fig. 4. As can be seen, even after 6000 cycles at more than a 70% depth-of-discharge per cycle and a current density of 100 μA/cm^2, there has been little fade in the cell's capacity and very little change in the curve shape. It

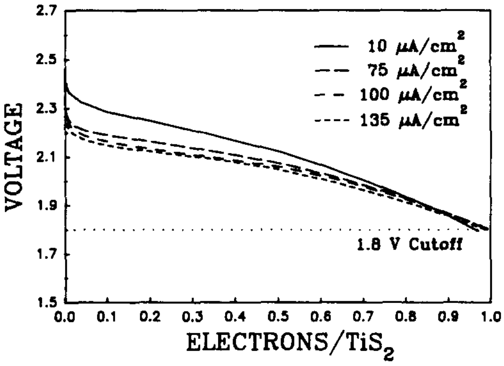

Fig. 2. Primary discharge of the EBC Microbattery at various current densities.

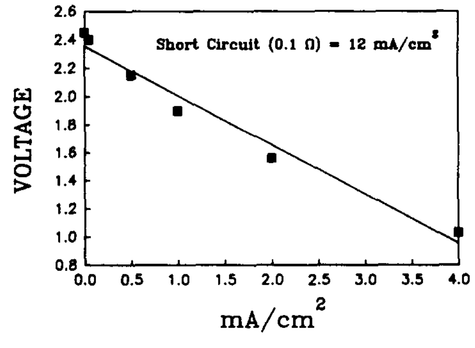

Fig. 3. Closed-circuit voltage of the EBC Microbattery after 2 s pulses of various current densities.

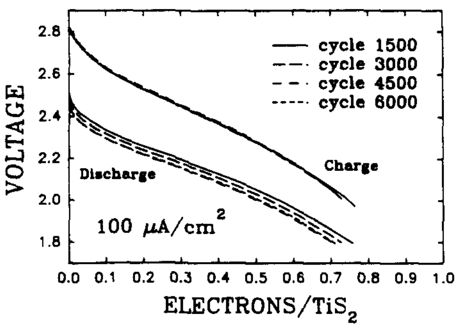

Fig. 4. Secondary performance of the EBC Microbattery to a 1.8 V cutoff.

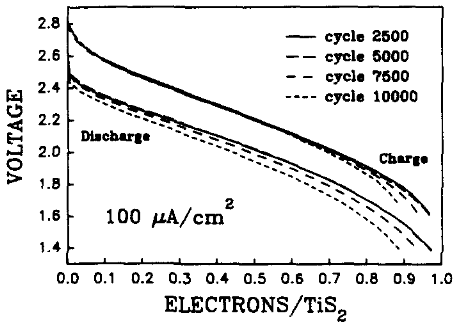

Fig. 5. Secondary performance of the EBC Microbattery to a 1.4 V cutoff.

was observed with the EBC Microbattery that discharges subsequent to the initial discharge were usually lower in depth-of-discharge. In intercalation systems it is commonly found that the first charge does not restore the same capacity to the cathode as was removed on the first discharge. It appears that some of the Li^+ becomes trapped in the cathode and is not removed during the charge. For the EBC Microbattery, after the first cycle the discharge efficiency is reduced to about 70–80% of its initial value to the 1.8 V cutoff. Though the cathode efficiency is reduced, cycles after the initial one are very reproducible and give essentially 100% cycling efficiency, meaning that all the capacity put in during the charge is removed on the subsequent discharge. No additional Li^+ becomes trapped after the first cycle.

It has been found that by changing the lower cutoff voltage from 1.8 to 1.4 V the discharge capacity can be brought up to approximately 100% cathode utilization with no detrimental effect on the microbattery's secondary performance. As an example, an EBC Microbattery was running at a current density of 40 $\mu A/cm^2$ and about 80% cathode utilization to the 1.8 V cutoff for the first 3000 cycles. The lower cutoff voltage was then changed to 1.4 V and the next 3500 cycles gave approximately 100% cathode utilization. Fig. 5 shows an EBC Microbattery that has gone 10 000 cycles at 100 $\mu A/cm^2$ and is still running at about 90% cathode utilization to a 1.4 V cutoff. These results show that the reduced cutoff voltage has no damaging effect on the secondary performance of the microbattery. Even at the high drain rates of 200 and 300 $\mu A/cm^2$, microbatteries have been cycled thousands of times at better than 90% cathode utilization between 1.4 and 2.8 V.

In other rechargeable Li systems, the charge current must be significantly lower than the discharge current to achieve reasonable cycle life. As shown by the cycling data presented above, the EBC Microbattery cycles well when the charge rate is equivalent to the discharge rate. It has also been found that the EBC Microbattery cycles well when the charge rate is significantly higher than the discharge rate. An example of this is shown in Fig. 6(a) and (b). This EBC Microbattery has gone 500 cycles at better than 90% cathode utilization at a discharge rate of 0.15*C* (5 $\mu A/cm^2$) and a charge rate of 5*C* (192 $\mu A/cm^2$). In another example, an EBC Microbattery has been cycled for over 21 months and more than 500 times at a discharge rate of 0.035*C* (1 $\mu A/cm^2$) and a charge rate of 3.5*C* (100 $\mu A/cm^2$). This type of result indicates that an EBC Microbattery could be designed to give days or even months of power at a low drain rate and then be fully recharged in a matter of minutes. This cycle could then be repeated hundreds or even thousands of times.

The EBC Microbattery can be cycled at the relatively high current density of 100 $\mu A/cm^2$ in the temperature range from −10 to 90 °C. The microbattery efficiency at various temperatures is shown in Fig. 7. This microbattery was originally taken from ambient to lower

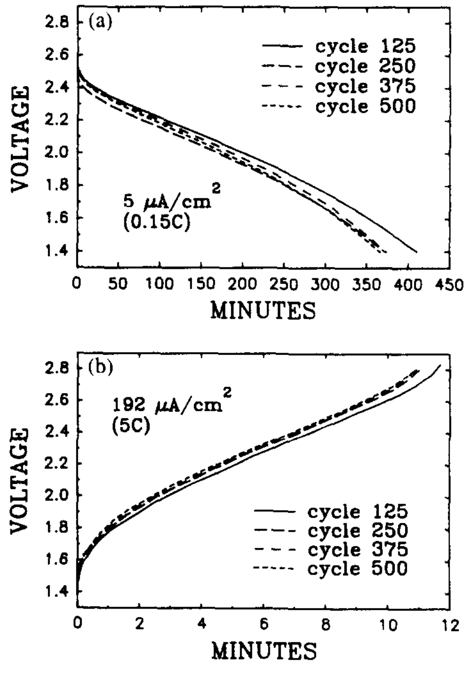

Fig. 6. (a) Low rate (0.15*C*) discharge half-cycle of the EBC Microbattery. (b) High rate (5*C*) charge half-cycle of the EBC Microbattery.

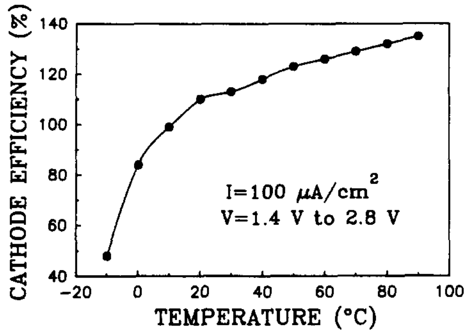

Fig. 7. Discharge efficiency of the EBC microbattery at various temperatures.

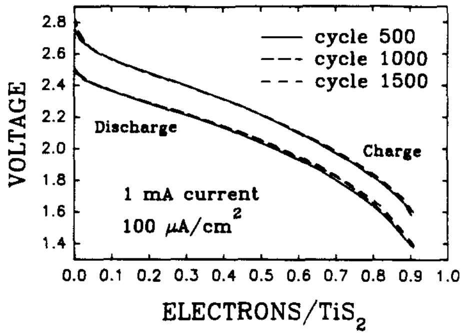

Fig. 8. Secondary performance of a large area (10 cm^2) EBC Microbattery.

temperatures. The cycle time is significantly shortened as the temperature is lowered (45% of the room temperature capacity at −10 °C). As would be expected for a solid-state battery, this reduced cycle time appears to be primarily the result of increased cell *IR*. At −20 °C the microbattery would no longer cycle at this current density. The microbattery was brought back up to room temperature where it showed no detrimental effect in its secondary performance from the low temperature excursion. The microbattery was then taken to higher temperatures and successfully cycled up to 90 °C. Temperatures higher than 90 °C were not investigated due to the temporary packaging available for the microbattery at the time, but there was no indication that the microbattery would not function up to the melting point of Li.

Possible applications for the EBC Microbattery require a higher voltage and/or more capacity than a single microbattery can supply. Therefore, groups of five EBC Microbatteries have been tested in both series and parallel configurations. (Five microbatteries were used because this is the amount fabricated per microscope slide.) The series configuration gives an OCV around 12.5 V and was cycled between 14 and 7 V. Five microbatteries in series were cycled for over 10 000 times at 100 μA/cm^2. The cathode efficiency of this set of microbatteries was only about 70% initially and faded to less than 50% after 10 000 cycles. The low efficiency is probably the result of one cell in the group being only marginally good and adding a disproportionate amount to the series *IR*. Another group of five microbatteries that was recently put on test in a series configuration has gone over 250 cycles at close to 100% efficiency. Five microbatteries in parallel have been cycling between 1.4 and 2.8 V for over 12 months and have gone more than 1000 cycles at close to 100% cathode efficiency. The total current through the parallel microbatteries is 100 μA which equates to a current density of 20 μA/cm^2 due to the larger cathode area involved with the parallel configuration.

The standard size of the EBC Microbatteries presently being tested is 1 cm^2. To demonstrate that it would be possible to scale up the size of the microbattery, a set of masks were made that increased the area of the microbattery to 10 cm^2. More than 1500 cycles between 1.4 and 2.8 V have been obtained with better than 90% cathode efficiency from a 10 cm^2 microbattery. This is shown in Fig. 8. The current density that this microbattery is being cycled at is 100 μA/cm^2. Because of the larger area of this microbattery, the total current is 1 mA. This indicates that the scale-up in area of the EBC Microbattery is not be a problem. We are now developing a set of masks that will demonstrate that potentially any two-dimensional shape can be used for an EBC Microbattery.

After storage at room temperature for an average of 3.2 years, EBC Microbatteries still show 93% voltage maintenance and pulse performance similar to when they were fresh. This small voltage loss indicates that the electronic conductivity of the glassy electrolyte/LiI combination must be very low. Assuming all the loss to be from self-discharge through these layers, the volume resistivity is estimated to be 10^{13} to 10^{14} Ω cm. At this rate of loss the microbatteries should be discharged to 1.8 V after 11.5 years on shelf. The components of the EBC Microbattery also appear to be very stable during cycling. More than 21 000 cycles have been obtained from an EBC Microbattery during 29 months of cycling between 1.4 and 2.8 V at 100 μA/cm^2 with about a 20% loss in cathode efficiency. Another EBC Microbattery has been continuously cycled at 40 μA/cm^2 for more than 39 months and 12 000 cycles with about a 15% loss in efficiency during this time.

Due to the recent development of the protective coating, none of the testing reported to date has been done on a microbattery that includes this feature. Further performance testing, shelf-life testing, and thermal cycling must now be done on EBC Microbatteries that include the protective coating.

4. Summary

The EBC Microbattery has been shown to be a thin-film solid-state system that demonstrates high cathode utilization, the capability of producing current densities in the mA/cm^2 range, outstanding secondary performance, and excellent long-term stability. In the near future it will be possible to incorporate the EBC Microbattery with many types of microdevices (microsensors, CMOS-SRAM, etc.) during their manufacture to provide a rechargeable, long-term power supply for the device.

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