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A thin-film solid-state microbattery

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Abstract

A functional thin-film microbattery has been developed at the Technology Laboratory of
Eveready Battery Company (EBC). The microbattery is constructed using cathode sputtering
for deposition of the contacts, TiS_2 cathode, and oxide–sulfide solid electrolyte; high vacuum
vapor deposition is used for a LiI layer and Li anode. The completed microbattery has
an overall thickness of approximately 10 μm and an open-circuit voltage near 2.5 V. On
the primary discharge the microbattery shows close to 100% cathode utilization (based on
a one electron change) to a 1.8 V cutoff at current densities ranging from 10 to
135 μA/cm^2. The microbattery is capable of supplying current pulses of two seconds duration
at current densities greater than 2 mA/cm^2. The microbattery also shows excellent secondary
performance. Cells routinely give over 1000 cycles of 100% cycling efficiency (discharge
capacity equal to the charge capacity) at greater than 70% cathode utilization on each
cycle.

Introduction

Thick-film solid-state batteries have been investigated for many years and have
been marketed commercially in the form of Li coin cells [1]. Improvements in the
microelectronics industry and the miniaturization of electronic devices have reduced
the current and power requirements of some devices to extremely low levels. These
developments have made possible the use of solid-state microbatteries to power such
devices. Thin-film solid-state microbatteries manufactured by the same techniques as
used in the microelectronics industry (cathode sputtering, vacuum evaporation, chemical
vapor deposition) have been reported by several research groups [2–4]. The thin-film
solid-state microbattery being developed at EBC is superior to other reported micro-
batteries in its ability to carry higher current density and its outstanding secondary
performance.

Experimental

The EBC microbattery was constructed by use of appropriate masks in the following
sequence: (i) d.c. magnetron sputtered chromium contacts; (ii) an RF magnetron

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sputtered TiS_2 cathode; (iii) an RF magnetron sputtered oxide–sulfide glass electrolyte; (iv) a vacuum evaporated film of LiI, and (v) a vacuum-evaporated Li anode. The microbattery configuration is shown in Fig. 1. The masks were simple line-of-sight masks machined from aluminum or Macor ceramic. The substrate for the microbatteries was either a glass microscope slide that held six microbatteries or alumina pieces that held one microbattery.

The sputtered layers were deposited using a Materials Research Corporation (MRC) 903 sputtering system. The sputtering gas was ultra-high purity argon from Linde. The chromium target was purchased from MRC and used with an MRC 900 cathode. The TiS_2 target and the solid-electrolyte target were made at EBC Technology. The electrolyte target composition was $6LiI–4Li_3PO_4–P_2S_5$. The targets were constructed from the powdered material that had been pressed into tiles of 6.45 cm^2. These tiles were mounted on special Vac-Tec cathodes that required only half the normal target area to be covered with target material (258 cm^2 versus 484 cm^2). All target preparation at EBC was done in a stainless-steel Vacuum/Atmospheres Dri-Lab. An MO-40 Dri-Train kept the argon atmosphere of the Dri-Lab below 1 ppm H_2O.

The vacuum evaporation system was built at EBC Technology and installed on a stainless-steel Vacuum/Atmospheres Dri-Lab such that the bell jar was inside the Dri-Lab. All other components of the system (turbomolecular pump, LN_2 trap, power supply, etc.) were outside the Dri-Lab. An MO-40 Dri-Train kept the argon atmosphere of the Dri-Lab below 1 ppm H_2O and 10 ppm O_2.

A stainless-steel glove box was built and installed over the load lock area of the MRC 903. Circulation through a canister of molecular sieves kept the argon atmosphere of the glove box below 5 ppm H_2O. This glove box was attached to the antechamber of the Dri-Lab containing the vacuum evaporation system. It was therefore possible to prepare substrates, change masks, sputter components, and vapor deposit components without removing the microbattery from a dry, inert atmosphere. The LiI (Aldrich), Li_3PO_4 (Pfaltz and Bauer), and P_2S_5 (Alfa) were dried before use. The TiS_2 (Degussa) and Li (Foote Mineral) were used as-received.

The microbattery discharge and cycling data were acquired using a Hewlett-Packard 3852A data acquisition unit controlled by a Hewlett-Packard 319M computer. The constant current sources for the test system were made at EBC Technology. Because of the higher current values needed for the pulse data, a Keithly 224 programmable current source was used for these measurements. Complex impedance measurements were done using a Solartron 1170 frequency response analyzer and a Solartron 1186 electrochemical interface controlled by a Hewlett-Packard 9845B computer.
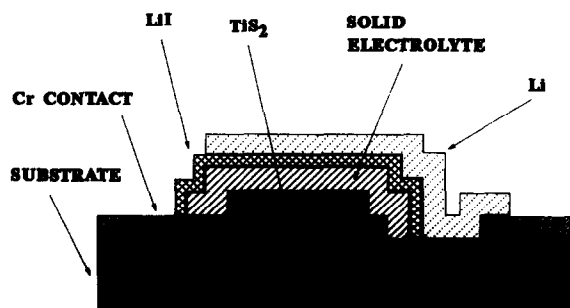

Fig. 1. Thin-film microbattery configuration. Total thickness about 10 μm.

Results and discussion

Contacts

Sputtered films of aluminum were originally used for the contacts of the EBC microbattery. However, the sputtered Al films were found to be too reactive to function as reliable contacts. They reacted with the sulfides contained in the other battery components and also formed Al_2O_3 crystals on their surface with the residual H_2O and O_2 in the Dri-Lab. These reactions increased the resistance of the Al contacts and also created a rough surface for deposition of the subsequent films of the microbattery.

Because of the potential problems that aluminum presented as a contact material for the microbattery, a chromium target was substituted. Contacts made from sputtered chromium do not have the problems associated with the aluminum contacts but care must still be exercised with the chromium contacts due to what appears to be a decreased adherence to the glass substrate and an increased film brittleness. However, if the substrate cleanliness and the sputtering conditions are properly controlled, sputtered chromium makes an adequate contact for the microbattery.

Cathode

The intercalation compound TiS_2 was chosen as the microbattery cathode for the following reasons: (i) Eveready's experience with it as a rechargeable cathode; (ii) its ready availability, and (iii) the relative ease with which it could be pressed into tiles for use in the construction of a sputtering target. Analysis of sputtered TiS_2 showed the films had good stoichiometry ($TiS_{2.09}$), with only a slight excess of sulfur.

The sputtered TiS_2 cathode is the limiting electrode of the microbattery. Its theoretical capacity was used to calculate the microbattery's discharge efficiency. Because the volume of the TiS_2 film was used to determine the cathode capacity, the density of sputtered TiS_2 film was gravimetrically determined. The density was found to be 1.47 g/cm^3, about 45% of the theoretical density of single crystal TiS_2. Scanning electron microscopy (SEM) pictures of the sputtered TiS_2 films (Fig. 2(a) and (b)) showed that they were similar in appearance to the chemical vapor deposition (CVD) TiS_2 film reported by Kanehori et al. [2]. The CVD TiS_2 has a reported density of 65% of theoretical. The major difference between the CVD TiS_2 films and the sputtered TiS_2 films is the small crystallite size of the sputtered films. Because of this small crystallite size, the sputtered films appeared amorphous to X-ray diffraction and therefore the orientation of the sputtered material could not be determined. To obtain the easiest Li insertion, one would prefer the TiS_2 to be oriented such that the c-axis was parallel with the substrate surface. However, as will be shown later in this paper, the sputtered thin films of TiS_2 will function at relatively high current densities. This indicates that the orientation of the TiS_2 crystallites is not a problem with the sputtered films.

Electrolyte

The first electrolyte to be tried had the composition $5LiI-4Li_2S-1.95P_2S_5-0.05P_2O_5$. This electrolyte was chosen because it had been used successfully at Eveready to make thick-film solid-state Li coin cells. Thin films sputtered from this target had a conductivity of 2×10^{-5} S/cm. This is about an order of magnitude less than the 5×10^{-4} S/cm conductivity of bulk glass of the same composition [5]. Although microbatteries could be constructed with this electrolyte, the high sulfide content of this target presented a maintenance problem with the sputtering system. Therefore the use of this target was discontinued.
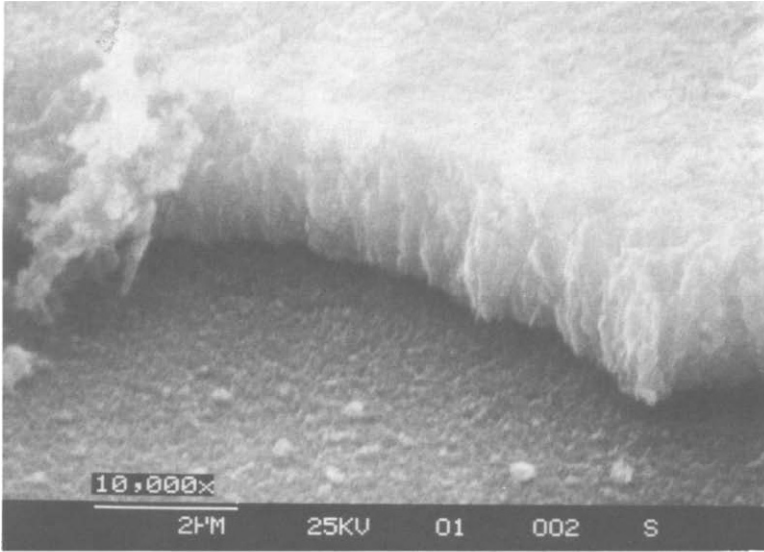
(a)
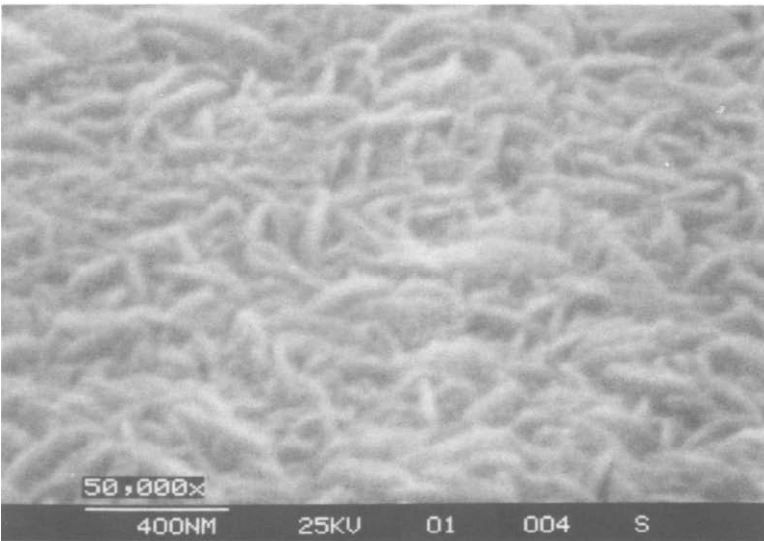
(b)

Fig. 2. (a) Edge of a sputtered TiS$_2$ film; (b) surface of a sputtered TiS$_2$ film.

A second target was constructed with a reduced sulfide level. This next target had the composition 4LiI–Li$_2$S–2Li$_3$PO$_4$–P$_2$S$_5$. A sputtered film of this electrolyte had a conductivity of 2×10^{-5} S/cm, equivalent to that of the higher sulfide containing electrolyte. However, many of the microbatteries constructed using this electrolyte were shorted. SEM photomicrographs showed that the sputtered films of this electrolyte had a tendency to crack.

The next target that was constructed had the composition $4LiI–Li_2S–3Li_2O–B_2O_3–P_2S_5$. Thin films of this electrolyte did not show any cracks in SEM photomicrographs, however, the conductivity of the sputtered film was reduced by an order of magnitude to 2×10^{-6} S/cm. Because of the thinness of the electrolyte layer in a microbattery (1–3 μm), a solid electrolyte with a conductivity of 10^{-6} S/cm would be acceptable. For example, a battery of 1 cm^2 area using this electrolyte would only add 50 Ω to the cell internal resistance (IR) for every μm of electrolyte thickness.

However, it was still felt that the sulfide content of the above electrolyte was causing equipment-maintenance problems. Therefore, an additional electrolyte sputtering target was constructed that further reduced the sulfide level. It had the composition $6LiI–4Li_3PO_4–P_2S_5$. SEM photomicrographs of sputtered films of this electrolyte did not show any cracking. The conductivity of these films was again found to be 2×10^{-5} S/cm. Impedance spectroscopy was used to determine the reactivity of the sputtered TiS_2 film with this sputtered electrolyte. These two layers did not seem to be reacting to any significant degree. It was therefore decided that this electrolyte would be used for the construction of the EBC microbattery because of its relatively good conductivity and its reduced sulfide level.

LiI layer

LiI is a Li ion conductor and could be used as the solid electrolyte. However, it has a relatively low conductivity of 1×10^{-7} S/cm [6]. Also, LiI forms electronically conductive 'color centers' if the stoichiometry of the compound is not correct [7]. Therefore, the LiI was used only as an intermediate layer over the oxide–sulfide electrolyte. This layer was necessary to prevent a passivating film from forming when the Li was vapor deposited directly onto the oxide–sulfide electrolyte.

Anode

Li films are vapor deposited rather than sputtered due to the low melting point of the Li metal. Vapor deposition of the Li film is relatively fast with Li being deposited on the substrate at a rate of 0.1 μm/s. The bottom of the vapor deposited Li film, as viewed through the glass microscope slide substrate, has a mirrored appearance. However, despite the facts that the H_2O and O_2 content of the Dri-Lab are kept very low by the Dri-Train and that Li foil is placed throughout the Dri-Lab to scavenge whatever reactive molecules it can, the top surface of the vapor deposited Li film quickly turns a dull gray. This rapid filming over of the exposed Li surface is the reason that the Li is the last layer of the microbattery to be deposited.

Microbattery

The thin-film microbatteries had a total thickness of 11 μm or less and displayed an OCV of between 2.4-2.5 V, close to the theoretical value of 2.49 for the Li/TiS_2 couple. Complex impedance measurements on these microbatteries result in classically shaped spectra that show the cell IR to be approximately 750 Ω and a charge-transfer resistance of about 9 kΩ (Fig. 3). The total electrolyte resistance calculated from the cell IR is 2×10^{-6} S/cm. As one would expect, this calculated conductivity is between the 10^{-7} S/cm conductivity of the LiI layer and the 10^{-5} S/cm conductivity of the oxide–sulfide electrolyte layer.

Microbatteries were galvanostatically pulsed to deterimine their maximum load capability and were found to be capable of carrying currents of greater than 2 mA/cm^2 in 2-s pulses (Fig. 4). This is equivalent to a pulse power density of greater than 4000 W/l. Because the pulses were done consecutively with only a few minutes
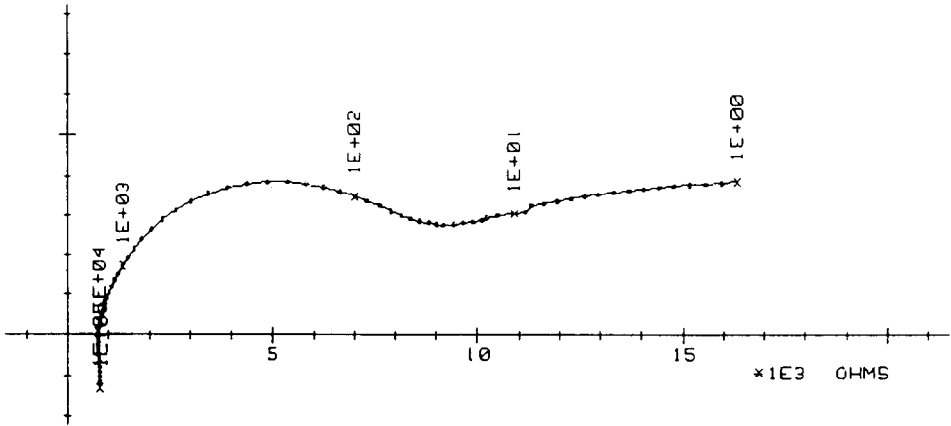
Fig. 3. Complex impedance spectrum of a thin-film microbattery.
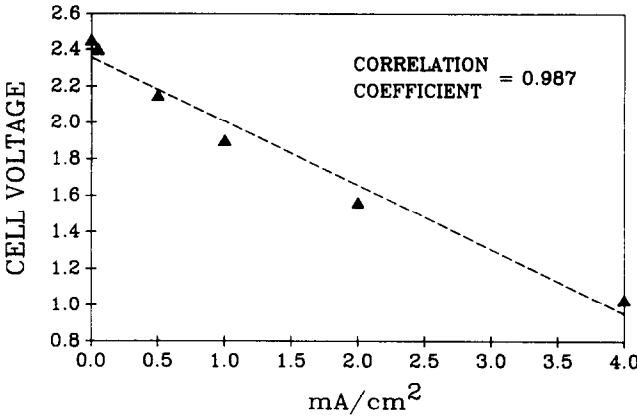

Fig. 4. Closed-circuit voltage of a thin-film microbattery after 2 s current pulses.

recovery time between each pulse, the linear fit to the data is not as good as it could be, however, an apparent cell IR can be determined form the slope of the fit. For this cell it was found to be about 1.75 kΩ, slightly more than 2 times the cell IR measured by impedance spectroscopy. However, due to the longer measurement time frame and the short recovery period allowed between each pulse, a higher polarization is expected with the pulse method.

The primary discharge of the EBC microbattery shows classically-shaped curves and close to 100% depth-of-discharge 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 $\mu A/cm^2$ (Fig. 5). For these microbatteries, this calculates to an energy density of 140 W h/l and power densities up to 270 W/l. The energy density can of course be increased substantially by increasing the cathode thickness. For example, increasing the cathode thickness to 4 μm would result in a microbattery with an energy density of 230 W h/l.
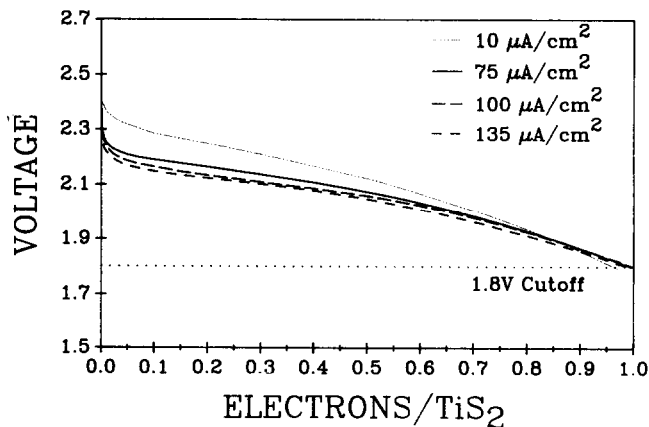
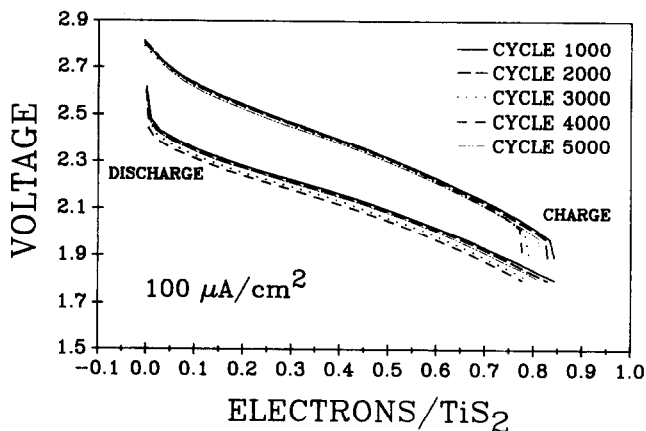Fig. 5. Primary discharges of thin-film microbatteries.

Fig. 6. Secondary performance of a thin-film microbattery.

The EBC microbattery also shows outstanding secondary performance. Micro-batteries have on the average achieved over 1000 cycles with depths-of-discharge greater than 70% of 1 electron at current densities of up to 150 $\mu A/cm^2$. A typical result is shown in Fig. 6. As can be seen, even after 5000 cycles at over 80% depth-of-discharge per cycle, the discharge/charge curves show little shape change. It should be noted that discharges subsequent to the initial discharge of a microbattery are usually lower in depth-of-discharge. It appears that the charge does not remove a full electron from the cathode. However, after the first cycle, the cycling efficiency is approximately 100% (the charge capacity and discharge capacity are equal). This is illustrated in Fig. 7.

To increase the discharge efficiency of the microbattery, a cutoff voltage lower than 1.8 V can be used without detrimental effects. For example, Fig. 8 shows a microbattery that was running about 70% efficiency to the 1.8 V cutoff for the first 500 cycles. Its cutoff voltage was then changed to 1.4 V and the cell now has gone several thousand cycles at 100% cathode utilization.
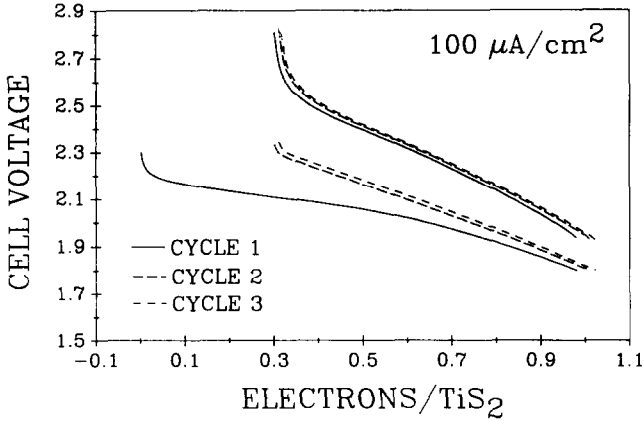
Fig. 7. Comparison between initial and subsequent discharges of a thin-film microbattery.
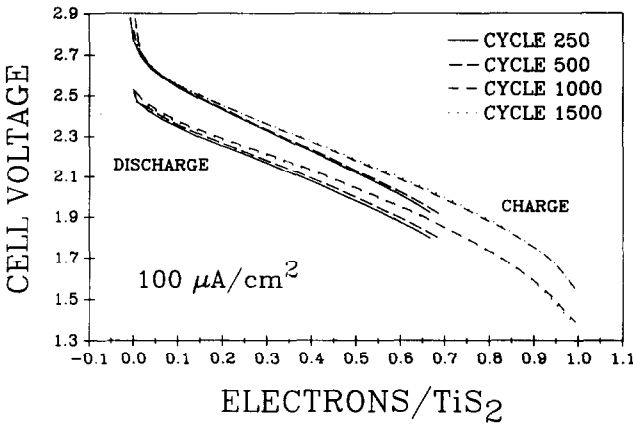

Fig. 8. Secondary performance of a thin-film microbattery that has had the lower voltage limit changed from 1.8 to 1.4 V.

Early data from microbatteries stored at room temperature had indicated that there could be a self-discharge occurring that would limit the shelf life of a microbattery, in the worst case, to about 2 years. However, several microbatteries have now been stored at room temperature for 22 months and, on the average, have maintained 98% of their initial voltage. Also, after about 14 months storage, these microbatteries were pulsed at 50 μA/cm^2 and the voltage drop showed only a slight increase from their original pulse behavior. These longer term data indicate that the EBC microbattery should have closer to a 20-year shelf life than a 2-year shelf life. Accelerated stability testing of the EBC microbattery at elevated temperature as well as thermal stress testing must yet be performed.

Summary

The miniaturization of electronic devices has reduced power requirements to extremely low levels. This has made possible the use of solid-state microbatteries to power such devices. In the future it may be possible that a microbattery of the type being developed at Eveready could be incorporated with many types of microdevices (sensors, CMOS-SRAM, etc.) during their manufacture to supply power for the device.

Acknowledgements

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