

A facile route to thin-film solid state lithium microelectronic batteries

R.P. Raffaele^{a,*}, J.D. Harris^b, D. Hehemann^b, D. Scheiman^c, G. Rybicki^d, A.F. Hepp^{d,2}

^a Physics Department, College of Sciences, Rochester Institute of Technology, 85 Lomb Memorial Drive, Rochester, NY 14623-5603, USA

^b School of Technology, Kent State University, Kent, OH 44242, USA

^c Ohio Aerospace Institute, Brook Park, OH 44142, USA

^d NASA Glenn Research Center at Lewis Field, Cleveland, OH 44135, USA

Received 17 November 1999; accepted 28 December 1999

Abstract

We describe the synthesis and characterization of a thin-film solid state lithium rechargeable battery. This battery was designed for integration into a multi-chip module (MCM). The battery consists of a spin-on Ag_2WO_4 — polymer cathode, a lithium hexafluorophosphate — polymer-impregnated microporous nylon membrane electrolytic separator, and a lithium foil anode. Kapton™ was used as the substrate and encapsulating top layer of the battery. The battery had a total area of approximately 4.0 cm^2 thickness of 0.6 mm, and weighed 0.4 g. The battery had an open circuit voltage of 3.5 V and was able to deliver a current density of 0.05 mA/cm^2 for 1.5 h while maintaining a voltage above 2.0 V. The battery was cycled over 12,000 times between 3.5 and 2.0 V using a constant discharging current density of 0.1 mA/cm^2 and charging current density of 0.05 mA/cm^2 . The battery was designed for integration into a standard 96 pin Kovar/Glass Bead quad-flatpack programmable MCM ($1.42 \times 1.42 \times 0.16 \text{ in.}$). The charging and discharging characteristics of this battery are presented and discussed in terms of its intended application. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lithium; Secondary batteries; Polymers; Thin films; MCM

1. Introduction

The development of solid state thin-film lithium batteries has generated considerable interest for some time [1]. Lithium is an extremely attractive battery element due to its small atomic radius and extraordinarily large standard reduction potential (i.e., -3.0401 vs. a normal hydrogen electrode (NHE)) [2]. Batteries utilizing Li have the capability of providing high voltage and excellent capacity, resulting in large energy densities (e.g., factor of 2 greater than NiCd batteries) [3]. Large energy density lithium batteries that are safe, compact, light-weight, and rechargeable have a wide variety of possible applications. Examples of their current and projected applications include medical devices and sensors, backup power for SRAM and DRAM memory devices, electric vehicles, and various

telecommunication applications [4]. The space power industry is particularly interested in their use in integrated solar power supplies, satellite microelectronic “stay alive” power, and as a solution to solar array “shadowing” problems [5].

The open circuit voltage of a lithium battery is dependent on the cathode material. Currently, the most frequently used cathode materials rely on intercalation of lithium (e.g., TiO_2 , MnO_2 , V_3O_8 , CoO_2) [6]. These materials provide good cyclability, but suffer from sloping charge and discharge voltage profiles [7]. Other cathode materials such as CuWO_4 or Ag_2WO_4 (i.e., the material used in this work) rely on a displacement reaction [8]. These materials have been shown to have flat charge and discharge curves and in the case of the Ag_2WO_4 , good cyclability.

Significant advances in the use of polymer cathodes and electrolytes have fueled the development of solid state lithium batteries [9]. Polymer cathodes incorporate the metal oxides discussed above and the polymer electrolytes incorporate such lithium salts as LiAsF_6 , LiClO_4 , LiAlO_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and lithium hexafluorophosphate (LiPF_6) (i.e., the Li salt used in this work) [10]. Numerous polymers have been used in Li battery develop-

* Corresponding author. Tel.: +1-216-433-2057; fax: +1-216-433-6106.

E-mail addresses: ryne.raffaele@grc.nasa.gov (R.P. Raffaele), a.f.hepp@grc.nasa.gov (A.F. Hepp).

¹ On sabbatical from RIT.

² Also corresponding author.

ment efforts [11]. Some of the more promising polymers include poly(acrylonitrile), poly(vinyl chloride), poly(ethylene oxide), poly(vinyl pyrrolidone), poly(propylene oxide), and poly(ethylene glycol) diacrylate. The polymer electrolytes in these batteries serve two principle roles, they allow for the Li ion transport, and they provide electrical insulation between the anode and the cathode. Unfortunately, free standing polymer electrolytes have demonstrated poor cycling characteristics and lack of mechanical stability [12]. This problem has been addressed by the use of semi-permeable microporous membranes, similar to the membranes used in organic solvent based Li batteries [13]. In the case of a thin-film solid state battery, the membranes are impregnated with a polymer electrolyte. This has been shown to greatly improved the mechanical and electrical stability of these batteries.

The batteries developed in this study were designed for integration in to a programmable multi-chip module (MCM). These devices currently serve a wide variety of roles an typical micro- and nano-satellites [14]. The electrical components used in these modules are continually improving and their current and voltage requirements are steadily decreasing. This improvement has made it feasible to power these modules with integrated Li batteries [15]. A typical 96 pin Kovar (ASTM F15) package can accommodate a 30×30 mm programmable substrate. The batteries that are to be integrated into a device of this type must have a slightly smaller area than the programmable substrate and have an overall thickness of less than 2 mm, due to the package size constraints. The batteries must be able to deliver at least $50 \mu\text{A}$ of current for 1.0 h or $1.0 \mu\text{A}$ for 60 s while maintaining a voltage of at least 2.0 V, to be viable for the intended micro- and nano-satellite applications. A satellite travelling in a low-earth orbit will make around 5700 orbits in a year. Therefore, batteries developed for this application should also be rechargeable, with a lifetime of approximately 11,000 cycles for a 2-year space mission.

As in the case of most batteries, the size will determine the ultimate capacity of the device. However, there is no fundamental limit on the dimensions, and the techniques used in the development of this battery are easily scalable, either larger or smaller. Also, the fact that it consists of thin films allows for the stacking of multiple cells in series, parallel, or combinations thereof to increase voltage, capacity, or voltage and capacity.

2. Experimental procedure

Two Sheets of Kapton™ were coated with approximately $1.0 \mu\text{m}$ of molybdenum using an e-beam evaporator. The battery cathode was based on the work of D. Passerini, S. Loutzky, and B. Scrosati [8], and consisted of (0.75 g) silver tungstate (Ag_2WO_4), (0.05 g) carbon black, and (0.20 g) polyvinylchloride (PVC), and 10 ml of tetra-

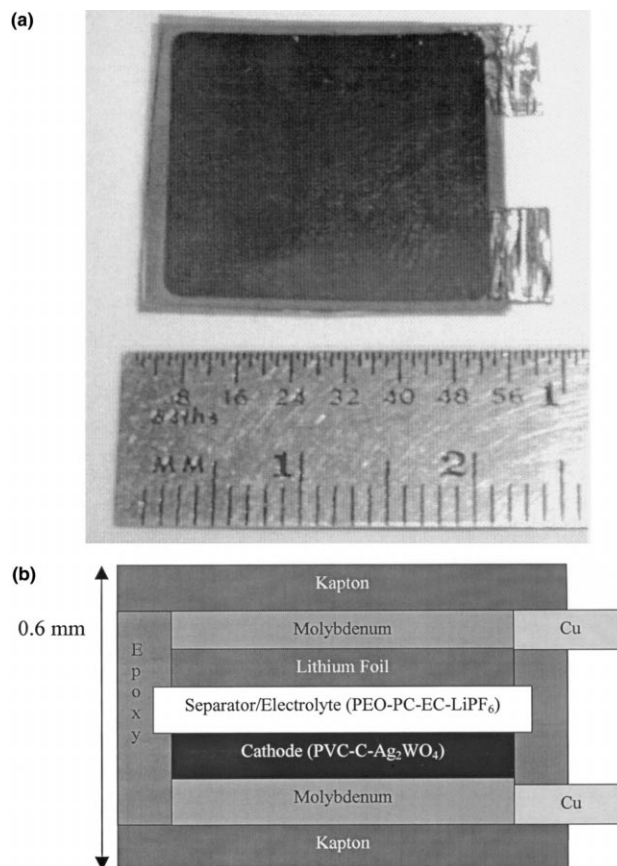


Fig. 1. (a) A photograph of the assembled battery; (b) a schematic of the individual battery components.

hydrofuran (THF). The cathode solution is stirred for 1 h and then ultrasonicated for 1 h. The thin film cathodes were deposited by spin coating at 4000 rpm onto the Mo coated Kapton™. The electrolyte/separator was prepared by soaking micropore nylon filters ($0.45 \mu\text{m}$ pore size) in a solution of (6.52 g) ethylene carbonate (EC), (1.38 ml) propylene carbonate (PC), (0.089 g) polyethylene oxide (PEO), (1.22 g) LiPF_6 , (10 ml) THF. The filter was soaked for 5 min in the solution, removed and allowed to dry for 20 min. The anode was prepared from lithium foil that was rolled to a nominal thickness of 0.3 mm. Electrical contact was made to the anode and cathode by attaching copper foil to the Mo coated Kapton. The edges of the battery were hermetically sealed using a thin bead of epoxy (see Fig. 1). Battery assembly was performed in argon-filled dry boxes. Series and parallel stacks of the cells were also fabricated using the double-sided Mo on Kapton films.

3. Results and discussion

The spin-on cathode material was examined by scanning electron microscopy. An image of the as-deposited film is shown in Fig. 2. Energy dispersive spectroscopy

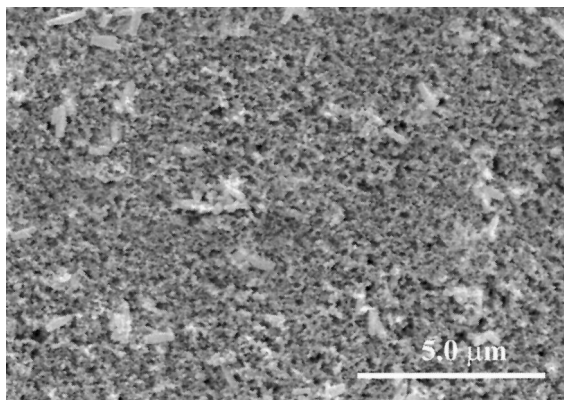
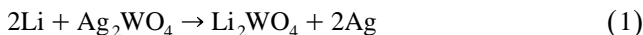


Fig. 2. SEM micrograph of the as-deposited PVC/Ag₂WO₄/carbon cathode film.

confirmed that the white crystallites in the image correspond to Ag₂WO₄ crystallites and the dark areas correspond to the carbon doped poly(vinylchloride) binder.

The assembled battery had a total thickness of 0.6 mm, an area of 4.0 cm², and weighed 0.4 g. The batteries exhibited an open-circuit voltage of approximately 3.5 V at room temperature, which is related to the discharge process (see Eq. (1)).



Monolithic stacks of two and three cells series combinations were also fabricated yielding voltages of 7.0 and 10.5 V, respectively. The heat generated by a single battery during a dead-short was monitored using a k-type thermocouple, however no measurable increase in temperature occurred. A typical charging/discharging cycle of a battery between 3.5 and 2.0 V is shown in Fig. 3. The battery was charged and discharged at a constant current density of 0.05 mA/cm².

Fig. 4 shows the discharge behavior for several discharge rates (i.e., 5.0, 1.0, 0.5, 0.1, 0.05 mA/cm²). The curves have a characteristic shape that is independent of the discharge current density. There exist plateaus that

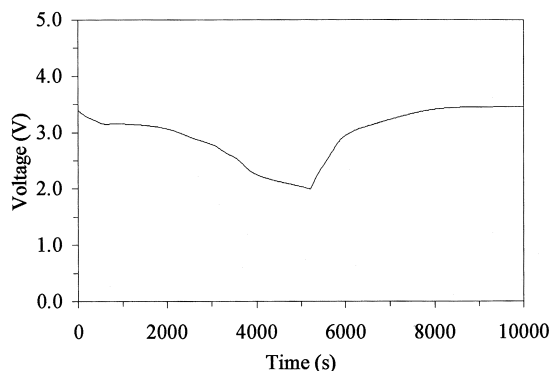


Fig. 3. Battery charging/discharging behavior at a constant current density of 0.05 mA/cm².

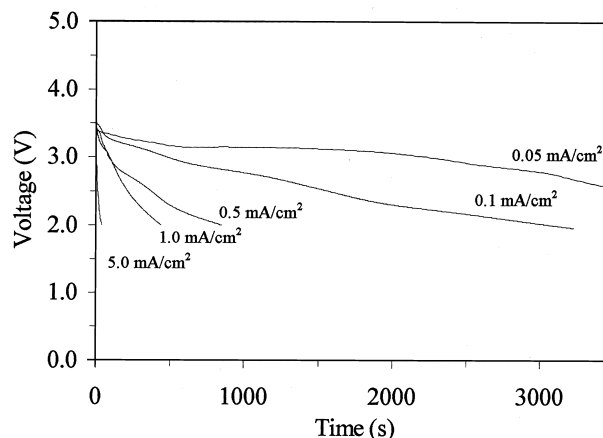


Fig. 4. Battery voltage vs. elapsed time at discharge rates of 5.0, 1.0, 0.5, 0.1, and 0.05 mA/cm².

occur near 3.0 and 2.0 V. These plateaus are attributed to the replacement reactions of Li for Ag in the Ag₂WO₄.

The battery capacity was examined as function of temperature. The battery capacity, measured with a discharge rate of 0.1 mA/cm², decreased from approximately 8.0 to 2.0 μA h under a temperature reduction from room temperature to −15°C. An order of magnitude decrease from the original capacity was measured when the temperature was reduced from room temperature to −20°C. However, the capacity was restored when the battery was allowed to return to room temperature.

A battery was cycled using a discharge rate of 0.1 mA/cm² and a charge rate of 0.05 mA/cm². The capacity slowly decreased over a range of 2000 cycles (see Fig. 5). The overall capacity decreased by about a factor of 2 over this range. The battery capacity continued to decrease with additional cycling to around 1/3 of the initial capacity after 6000 cycles, and 1/4 of initial capacity after 12,000 cycles. A battery was also cycled using a discharge rate of 0.5 mA/cm² and charge rate of 0.25 mA/cm². These conditions resulted in a decrease by a factor of 2 of the battery's capacity after 200 cycles.

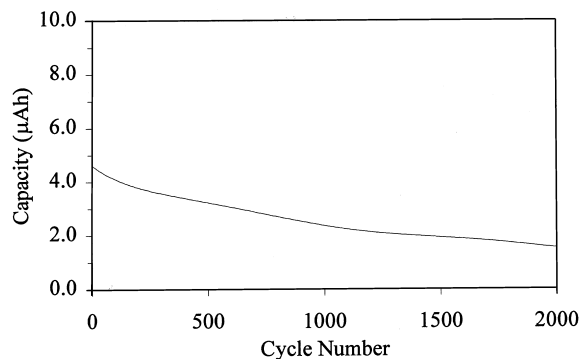


Fig. 5. Battery capacity vs. charging/discharging cycle between 3.5 and 2.0 V. Battery charging was done at 0.05 mA/cm² and discharging at 0.1 mA/cm².

4. Conclusions

We have produced robust thin-film solid state batteries that, while extremely small, are capable of delivering sufficient power for MCM designed for space applications. This battery has the ability to be discharged and recharged over thousands of cycles. It can also be cycled when charging and discharging at fairly rapid rates and at temperature as low as -20°C . The performance of this battery coupled with its simple and reliable manufacture method should provide suitable energy storage for a wide variety of electronic and power delivery systems.

Acknowledgements

The authors wish to thank Prashant Kumta of Carnegie Mellon University, Joe Gorse of Baldwin Wallace College, and Mike Seter of John Carroll University, and Harry Shaw of the NASA Goddard Space Flight Center for their advice, assistance, and encouragement pertaining to this work. The authors would also like to acknowledge the support of the NASA grants NCC3-710, NCC3-563, and the NASA Glenn Research Center Directors Discretionary Fund.

References

- [1] R.J. Jasinski, High Energy Batteries, Plenum, New York, 1967.
- [2] R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 1987, D-151.
- [3] J.P. Gabano (Ed.), Lithium Batteries, Academic Press, New York, 1983, 1.
- [4] B. Scrosati, Nature 373 (1995) 557.
- [5] A.B. Chmielewski, A. Das, C. Cassapakis, D. Allen, W.J. Schafer, J. Sercel, F. Deligiannis, M. Piszcor, P.A. Jones, D. Barnett, S. Rawal, T. Reddy, 31st Int. Energy Conv. Eng. Conf. 4 (1996) 2193.
- [6] R. Koksang, J. Barker, H. Shi, M.Y. Saidi, Solid State Ionics 84 (1996) 1.
- [7] J.B. Bates, N.J. Dudney, G.R. Gruzalski, C.F. Luck, R.A. Zuhr, A. Chudry, J.D. Robertson, J. Power Sources 43–44 (1993) 103.
- [8] S. Passerini, S. Loutzky, B. Scrosati, J. Electrochem. Soc. 141 (7) (1994) L80.
- [9] R. Koksang, I.I. Olsen, D. Shackle, Solid State Ionics 69 (1994) 320.
- [10] M.B. Armand, Solid State Ionics 9–10 (1983) 745.
- [11] K.M. Abraham, M. Alamgir, J. Electrochem. Soc. 137 (5) (1990) 1657.
- [12] T. Noda, S. Kato, Y. Yoshihisa, K. Takeuchi, K. Murata, J. Power Sources 43–44 (1993) 89.
- [13] K. Abraham, M. Alamgir, D. Hoffman, J. Electrochem. Soc. 142 (3) (1995) 683.
- [14] J. Banker, D. Alper, J. Plante, A. Garrison-Darrin, P.V. Panetta, H. Shaw, Adv. Packaging (1998) 35, March/April.
- [15] J.B. Bates, G.R. Gruzalski, N.J. Dudney, C.F. Luck, X.-H. Yu, S.D. Jones, Solid State Technol. (1993) 59, July.