ASSESSMENT OF MANUFACTURING LIMITS AND PROCESS-ABILITY FOR COMPOSITE STRUCTURES WITH EMBEDDED ENERGY DEVICES

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1 Introduction

Research has shown that the flight endurance of an electric propelled unmanned air vehicle (UAV) is significantly improved by reducing the weight of the aircraft more so than increasing the battery capacity [1]. Moreover the structure and the battery each contribute typically 20-40% to the total UAV mass [1]. The integration of battery and structure can theoretically reduce the total weight by reducing both the structure mass and the battery mass. The first is reduced by using the battery components as load bearing elements, while the second by eliminating fitting interfaces. In addition, rather that bulky, centralized batteries, the integration of multiple lightweight batteries into the structure enables distributed power supply and storage, thereby reducing the amount of wiring. Hence a composite structure with load bearing and energy storage capabilities would increase the system performance by saving weight and volume. However, system performance to date. improvements have been achieved and documented only for low mechanical stress demanding applications [2]. The batteries embedded into the structure have been designed to be active [2-5] in terms of load bearing capabilities, or passive [6]. While the first approach is the most promising in the long term because it utilizes the battery active components (i.e. cathode, anode, electrolyte, separators, current collectors) as structural members, the current battery technology based on lithium intercalation compounds is such that high specific energy and good mechanical properties cannot be contemporary achieved. The passive approach has led to greater battery performance because it requires the active components only to withstand the applied strain, and relies only on the battery substrate as load bearing element. The study presented hereinafter is part of a research project that follows the second approach and utilizes thin film, solid state, Li-ion batteries (TFB), Fig.1 and Fig.2, made by physical vapor deposition on a muscovite substrate. The battery lamina is subsequently integrated in a composite laminate, Fig.3. Objectives of the study include the assessment of TFB limits of process-ability in epoxy-based composite curing environment. Although thin film batteries (TFB) technology is still at an early development stage, among today's available battery types TFBs have the highest specific energy. All TFBs utilized in this research are made by Front Edge Technology (Baldwin Park, CA) under license from the Oak Ridge National Laboratory (ORNL). The cathode material is lithium cobalt oxide, the anode is Li-metal and the solid state electrolyte is LiPON. The active components are encased by two muscovite substrates bound by a polymer layer of Surlyn sealant, leading to a total TFB thickness of 150 µm, Fig.2. Critical temperature thresholds for the TFB materials are summarized in Tab.1. The TFB cell is a 1 in by 1 in square with nominal voltage of 4.2V, capacity of 1 mAh and specific energy higher than 300 Wh kg⁻¹.

2 Methodology

TFBs are subjected to pressure, temperature and resin environment representative of composite processing cycles. Battery capacity is monitored before and after testing through a survivability test which consists of five charge/discharge cycles: the first cycle is used to condition the battery; the last four provide the average discharge capacity. Moreover survivability test is repeated two months after processing to investigate the aging effects. TFB charge and discharge is performed at constant electrical load through an automated circuit, Fig.4, controlled by a personal computer via a LabView

program. Current and voltage readings are collected every three seconds. Discharging occurs under a constant resistive load of 3.8 k Ω , which gives a discharge current of about 1mA. The current can be considered constant over the entire discharge process, as shown in Fig.5, leading to a discharge rate of 1C. TFB is considered fully discharged when the voltage reaches 3 V. Immediately following a discharge, charging is performed at a constant voltage of 4.2. To measure the current a shunt resistance of 10 Ω is utilized. The battery is considered fully charged when the current drops below 50 µA. Batteries are subjected to a one hour isothermal hold at 250°F (121°C), 300°F (149°C), 350°F (177°C) and 390°F (199°C). At each temperature three batteries are tested, one at ambient pressure, one is placed under a 26 mm Hg vacuum and one is embedded in a pool of epoxy neat resin under a 26 mm Hg vacuum, Fig.6. Test is conducted under electrical load and voltage monitoring, Fig.7. Since the current level is small, in the order of 10 µA, TFB can be considered in a quiescent status. The resin temperature is monitored during thermal testing in order to record the actual temperature experienced by the TFB, Fig.8. In total 21 batteries have been tested at different charge levels. Pressure tests conducted through transverse mechanical compression are performed to confirm that TFB can withstand a cure pressure of 5 atm as previously shown by [7]. Finally, to confirm the findings of the processing tests, two TFBs are embedded in a glass fiber and carbon fiber epoxy composite laminate respectively. Laminates are made by press molding of prepreg materials (Fig.9).

3 Results

Thermal testing at 250°F (121°C) of fully charged batteries always leads to capacity reduction. When TFBs are partially discharged to 3.9 V before being thermally tested, they withstand thermal testing up to 300°F without any detrimental effect on their electric performance. All the batteries tested at 350 °F are affected by partial or total capacity loss. TFB failures have been characterized based on optical microscopy and capacity retention, and three distinct types of failures have been recognized and analyzed, Fig.10(a-d),11. Type I failure, Fig.10(b,bb), is observed as a localized grey spot on the Li-anode with complete loss of grain boundaries. Front Edge attributed these observations as an electronic failure consisting of local breakdown of the electrolyte. The grey spot is always associated to bubbling of the overlaying Surlyn sealant layer at failure location. This failure occurs in batteries processed at ambient pressure or within the vacuum bag. The affected batteries are operational but with a reduced capacity. Type II failure produces a neutral grey discoloration, which contacts at least one edge of the active component, Fig.10(c,cc). The micrographs reveal dark patches intermixing with the pristine anode. It is believed that this failure is caused by the reaction of the Li-anode with reactants diffusing through the Surlyn sealant and entering into the battery. Lithium is highly reactive, in particular with oxygen, nitrogen and water, thereby requiring the TFB to be sealed. The appearance of Type II failure is always associated to total battery failure. This failure is observed after thermal processing of batteries embedded in neat resin, or in aged batteries previously processed at 350°F (177°C). The Type III failure shown in Fig.10(d,dd) has occurred for all the batteries tested at 390°F (177°C). The failure occurs above 350°F during temperature ramp-up, leading to sudden loss of voltage and battery failure. The failure is due to melting of lithium (M.P. 357°F (181°C)). The TFB becomes black at the anode side, occasionally showing gray spots which are probably Type I failure formed before the anode melting. TFB sealant bubbling and flowing has been noted even for TFBs tested at 250°F (121°C), Fig.12. However the functionality of those batteries, as tested for survivability after testing and after two months aging, is not affected. The batteries affected by Type I failure show Type II formations and total capacity loss after two months aging, Fig.13. Successful embedding tests with full capacity retention are performed by press molding at 270°F (132°C) and 75 psi (517 kPa), with a cure time of 2 hours, Fig.9. Thanks to a localized application of silicone conformal coating at TFB leads, it has not been necessary to pre-encase the battery for electrical insulation from carbon fibers, as shown in [6].

4 Conclusions

This study identified the limits of processing-ability of solid state thin film lithium batteries embedded into composite laminates. Cure temperature is the most influential parameter for battery survivability during composites manufacturing. Successful embedding tests, with full capacity retention, have

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been performed with carbon fiber/epoxy at 270° F (132°C) and 75 psi (517 kPa). With proper procedures it is possible to successfully cure the battery inside the laminate up to 300°F (149°C). If higher processing temperatures are reached, either locally, due to resin exothermic reaction, or by design, the battery's electrical performance will deteriorate. Failures are associated either to the TFB polymeric sealant failure, or to physical-chemical degradation of the electrolyte or the Li-anode. Ongoing research is focused on the mechanical and electrical characterization of laminates with embedded batteries under applied strain. Based on the findings of this study a prototype of energy selfsustained structure, which employs flexible solar arrays and TFBs to harvest and store energy, has been manufactured Fig.14.

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Component	Material	Temperature	Property
Sealant	Surlyn	208°F (98°C)	Melting point
Anode	Lithium	357°F (181°C)	Melting point
Electrolyte	Li ₃ PO ₄ (LiPON)	572°F (300°C)	Maximum operating temperature ¹⁾
Cathode	LiCO ₂	1292°F (700°C)	Annealing temperature ²⁾
Substrate	Muscovite	1292°F (700°C)	Calcination temperature
1) X. Yu et al. J.E	lectrochem. Soc. 147	(2), 517 (2000)	
2)J. B. Bates et a	I. J. Electrochem. Soo	c. 147, 59 (2000)	

Tab.1. Relevant temperature thresholds for TFB components.



Fig.1. Perspective photo of all solid state thin film Li-ion battery (TFB) with dimensions. Manufactured by FrontEdge Technology Inc.



Fig.2. TFB cross-sectional schematic.







Fig.4. Schematic of the circuit used to test a battery's survivability by monitoring charge and discharge cycles before and TFB processing.



Fig.5. Voltage and current profiles during the survivability test.



Fig.6. Simultaneous thermal treatment of batteries under ambient pressure, in a vacuum bag and embedded in a neat resin. (a) shows location of batteries before addition of (b) the vacuum bag



Fig.7. Voltage drop across R3 (108 k Ω) and thermocouple voltages are recorded by a LabView program via the data acquisition board (DAQ) during thermal testing.



Fig.8. (a) Typical temperature cycle for temperature test at 250°F (121°C). (b) Associated voltage profiles of the three TFBs shown in Fig.6. A drop in the voltage of the battery embedded within neat resin coincides with heat generation by the resin (exothermal reaction due to resin crosslinking).



Fig.9. Press molded laminates with embedded TFB. (a) Carbon fiber epoxy. (b) Glass fiber epoxy.

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Fig.10. TFB failures. (a) TFB as received;
(b)Type I – local breakdown of the electrolyte and bubbling of the sealant; partial capacity loss.
(c)Type II – contamination failure associated with sealant failure (reaction with N₂ and/or O₂); total capacity loss. (d)Type III – melting of Lithium (M.P. 357°F); total capacity loss.



Fig.11. Typical discharge voltage and current profiles associated to Type I failure.



Fig.12. (a) TFB specimen after thermal processing at 250 °F. TFB sealant bubbling (b) along the edge and over the active components and (c) over the leads.(d) TFB processed under vacuum bag shows the Surlyn squeezed out of between the muscovite substrate.



Fig.13. TFB thermally tested at 350° F showing (b) the formation of Type I failures immediately after testing, followed by Type II formations with two months of aging



Fig.14. Working prototype of energy self-sufficient CFRP stiffened panel with integrated TFBs and flexible solar array.

References

- J. P. Thomas and M. A. Qidway "Mechanical design and performance of composite multifunctional materials". *Acta Materialia*, Vol. 52, pp. 2155–2164, 2004.
- [2] J. P. Thomas and M. A. Qidway "The design and application of multifunctional structure-battery material systems". *Journal of the Minerals, Metals* and Materials Society, Vol. 57, No. 3, pp. 18-24, 2005.
- [3] P. Liu, E. Sherman, A. Jacobsen, "Design and fabrication of multifunctional structural batteries". *Journal of Power Sources*, Vol. 189, No. 1, pp 646-50, 2009.
- [4] J. F. Snyder, R. H. Carter, E. D. Wetzel, "Electrochemical and mechanical behavior in mechanically robust solid polymer electrolytes for use in multifunctional structural batteries". *Chem Mater*, Vol. 19, No. 3, pp 3793-3801, 2007.

- [5] J. F. Snyder, E. L. Wong, C. W. Hubbard, "Evaluation of commercially available carbon fibers, fabrics and papers for potential use in multifunctional energy storage applications". *J Electrochem*, Vol. 156, No. 3, pp 215-224, 2009.
- [6] T. Pereira, Z. Guo, S. Nieh, J. Arias and H. T. Hahn "Energy storage structural composites: a review". J Compos Mater, Vol. 43, No. 5, pp 549-560, 2009.
- [7] T. Pereira, R. Scaffaro, S. Nieh, J. Arias and H. T. Hahn "Performance of thin-film Lithium Energy cells under uniaxial pressure". *Advaced Engineerig Materials*, Vol. 10, No. 4, pp. 393–399 (2008).