Comparative study of electrochemical performance of commercial solid-state thin film Li microbatteries

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ABSTRACT

This work evaluates the behavior of three 4 V commercial all-solid-state lithium microbatteries, 80, 170 and 200 μm thick with the same announced capacity of 700 μA h. The electrochemical tests are based on galvanostatic experiments between 4.2 V and 3.6 V enabling to determine the real specific capacity achieved as a function of the C rate at room temperature and 60 °C. The results make differences visible between the three commercial thin film microbatteries. The thinnest battery exhibits the best properties with a high energy density of 42 mWh cm^{-3}, i.e. two fold the value offered by the other cells $\approx$ 200 μm thick, and an excellent cycle life at C rate over 1000 cycles with 100% of capacity retention and 100% of depth of discharge. This shows the maturity of the thin film battery technology now commercially available. The present contribution provides a punctual picture of the outstanding characteristics already offered by all solid-state Li microbatteries.

1. Introduction

Nowadays, lithium-ion (Li-ion) technology is well-known and lithium-ion batteries (LIB) are widely used in different equipment such as cell phones, laptop computers, portable power tools, hearing aids, etc. Conventional LIB consists of two electrodes isolated by a separator impregnated by a liquid electrolyte. The use of dissolved lithium salt in a mixture of organic solvents presents a major advantage toward an easier lithium ions transport to and from the cathode and anode. Unfortunately, it is responsible of serious safety problems. Indeed, in addition to the risk of leakage with the resulting effects on health and the environment, the formation of Li dendrites during the charge of the battery can lead to explosion. To solve the dendrites formation problem, one solution is to use negative electrode materials that work at higher potential like $Li_4Ti_5O_{12}$ or TiO_2. To avoid both leakage and dendrites formation, solid electrolytes have been developed, leading to solid-state battery.

In the same time, lifestyles and consumer customs have constantly evolved toward the reduction in the objects size and an increased portability. For these reasons, the development of batteries is inevitably focused on more miniaturization, autonomy, environmentally friendliness without forgetting the safety issues. Works of Kanehori et al., from Hitachi Corporation (Japan), are the first one reporting solid-state thin-film batteries (TFBs) with thickness of a few tens of micrometers [1]. A $Li_{3.6}Si_{0.6}P_{0.4}O_4$ thin film electrolyte obtained by RF sputtering was

sandwiched between TiS_2 deposited by chemical vapor deposition (CVD) at the cathode and metallic lithium at the anode. However, severe cycle life limitations have prohibited any commercial deployment. Thereafter, other corporations (NTT Applied Electronics Laboratories, Nippon Telegraph and Telephone Corporation, Japan [2,3], Eveready Battery Company, USA [4]) and research laboratories (ICMCB, France [5], Iwate University, Japan [6,7]) have pursued research on these thin-film solid-state batteries, and more particularly on the solid electrolyte. An ideal electrolyte should have good lithium ion conductivity with a transport number for Li^+ ion equals to 1 and it should be stable in contact with lithium metal at potentials from 0 to 5 V. In this context, other solid electrolytes have also attracted considerable attention. Among them, the lithium phosphorous oxynitride, named "LiPON", was found in the early 90s [8]. It is an amorphous and lithium ion conducting thin-film glass deposited by RF sputtering using a Li_3PO_4 target in N_2 plasma. Its chemical formula can be written as $xLi_2O{:}yP_2O_5{:}zPON$, where PON is phosphorous oxynitride, and depends on deposition experimental parameters. For example $Li_{3.1}PO_{3.8}N_{0.16}$, $Li_{3.3}PO_{3.8}N_{0.22}$ and $Li_{2.9}PO_{3.3}N_{0.46}$ compositions can be reached [8]. LiPON has been successfully incorporated into thin-film lithium battery and commercialized because of its very good stability with metallic lithium without formation of a passive resistive layer at the interface [9–12], which impairs the performance of the battery.

Despite optimistic growth prospects, the thin-film and printed batteries market has not come close to expected projections made 10 years

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ago [13]. Companies trend to fade away because thin film solid-state batteries cannot compete with conventional battery technologies in most applications, neither on performance (low energy density) nor on market stability. Indeed, the growth of this market is mainly restrained by the need for high initial investment and lack of standardization in the development of thin films batteries.

Despite this, n-tech Research analysts, who witness the evolutions of the society and examine the latest developments technologies from materials and design to manufacturing, believe that the worldwide market for thin-film and printed batteries will be, by 2022, 32 times larger than it was in 2015 [14]. It will grow, driven by smart cards, "smart" labels and packaging that will be able to track data like temperature in pharmaceuticals or perishable goods, the increasing trend of wearable devices and Internet of Things, consumer electronics.

Because Li-ion batteries are the key point technology for portable devices, EV, large scale energy storage systems to deal with the fluctuating power generation of renewable energy sources, a lot of works can be found on the evaluation of commercial Li-ion cells. Indeed various specific points such as the SEI formation [15], aging [16,17], mechanical abuse [18], working temperature [19], overdischarge [20], toxicity [21], etc. are addressed for commercial cylindrical 18650 type and pouch Li-ion cells. Comparison of commercial Li-ion battery cells provides also useful information [21–26].

Conversely, in spite of optimistic forecasts and given the total absence of commercialized thin-film solid-state battery comparative studies in literature, this paper aims at evaluating three commercial thin-film solid-state micro-batteries from different companies. Lithium-ion batteries with a capacity of 700 μA h have been selected. Several tests have been carried out on different cells of each model and results allow their comparison. Thus this work can be regarded as both a realistic examination and a punctual reference for this capacity model.

2. Experimental

None of the thin film microbatteries were a prototype, they were all commercially available. The rated capacity announced by the manufacturer is 700 μA h. All three are micro-batteries whose thickness is less than millimeter (between 0.08 and 0.2 mm) and the surface < 9 cm². Their dimensions are reported in Table 1 as well as other cell specifications available on data sheets. For two of them, the electrochemical

Table 1
Characteristics of the three solid-state thin film microbatteries according to their data sheets.

Model of microbattery	A	B	C
Capacity	700 μA h	700 μA h	700 μA h
Nominal voltage	3.9 V	3.9 V	3.9 V
Max charging voltage	4.2 V	4.1 V	4.15 V
Discharge voltage	3.6 V	3.0 V	2.1 V if $i > 10$ mA 3.0 V if $i < 10$ mA
Storage temperature range	$> -40\,°C$ $< 60\,°C$	$> -50\,°C$ $< 70\,°C$	$> -40\,°C$ $< 50\,°C$
Operating temperature range	$> -40\,°C$ $< 60\,°C$	$> -20\,°C$ $< 120\,°C$	$> -40\,°C$ $< 85\,°C$
Electrochemical system	$LiCoO_2/LiPON/Li$	LiMO/Li conducting glassy inorganic thin film/Li	$LiCoO_2/LiPON/Li$
Dimensions	25.4 × 25.4 mm²	29 × 28 mm²	25.4 × 25.4 mm²
Thickness	200 μm	80 μm	170 μm
Mid-discharge voltage at 1 C	3.7 V	3.85 V	3.9 V
Volumetric energy density	21 mWh cm⁻³	42 mWh cm⁻³	25 mWh cm⁻³

system is well defined, based on lithium cobalt oxide ($LiCoO_2$) and metallic lithium (Li) as respectively cathodic and anodic materials. LIPON is the solid electrolyte. In the third model, the transition metal oxide is not explicitly given and the electrolyte is given as being a Li conducting glassy inorganic thin film.

The electrochemical characterization of these microbatteries consists to apply charge-discharge cycles using a multi-channel potentiostat from Bio-logic either at 20 °C or 60 °C, in thermostated rooms. The charge/discharge rate is calculated based on the 700 μA h announced capacity, consequently C/n rate matches a constant current of 700/n μA. During discharge measurements, a single galvanostatic step is applied while during the charge, the galvanostatic step (CCC for constant current charge) is followed by a polarization period under a constant applied potential (CVC for constant voltage charge). This warrants a systematic complete state of charge (SOC) before a new cycle starts, regardless of the currents previously applied. Note that in this study, tests are performed with a depth of discharge (DOD) and state of charge (SOC) of 100%, which represents the most severe conditions of use for a battery.

3. Results and discussion

First of all, one cell of each model has been cycled at the C/50 very slow rate. A constant cathodic current of 14 μA has been applied until a potential of 3.6 V was reached (full line) after which the opposite-sign current was applied in turn (dashed line). Corresponding chronopotentiograms are reported in Fig. 1. They all present a potential plateau around 3.9 V characteristic of delithiation/lithiation of lithium cobalt oxide $LiCoO_2$. The typical shape of the signal confirms no transition metal substitution has been made. Considering the very low used amount of $LiCoO_2$ in these commercial cells, substitution of cobalt probably does not appear to be a critical issue from an economic point of view.

For cells A and B, the available capacity is about 800 μA h, i.e. just over 100 μA h more than the expected capacity available for a 1 C rate. In the case of cell C discharge and charge curves are strictly identical and superimpose. This finding is indicative of an excellent rechargeability. For this battery, surprisingly the capacity is largely higher than that announced by the manufacturer (1200 μA h).

In order to assess to what types of applications these batteries can be used, higher C rates have been applied during the discharge and charge steps, by using a constant current. After 2 cycles registered at C/50, C/5, C and 10 C rates were successively applied for 10 cycles each. Whatever the C rate, when the galvanostatic sequence in charge ends, the cut-off voltage, 4.2 V (cells A and B) or 4.1 V (cell C), was held constant till the current drops to 25 μA. Using this protocol ensures the cell being completely charged to obtain the nominal capacity at the beginning of each discharge. Fig. 2 shows the discharge/charge profiles obtained during the second cycle at C/50 and during the fifth cycle of each series for the different increasing current values (C/5–C–10 C), as a representative one of all other cycles.

For the three cells, increasing C rate approximately entails the same consequences on the observed profiles. Rising from C/50 to C/5 has only low effect on the available capacity: it remains close to 800 μA h for cells A and B, slightly lower than 1200 μA h for cell C. At 1 C rate the achieved capacities are 700 μA h for cells A and B while 900 μA h are delivered by cell C. Considering this latter value, the real volumetric energy density is about 32 mWh cm⁻³. This corresponds to an available energy density 28% higher than the nominal one. Then cell C exhibits a characteristic behavior intermediate to that of cells A and B.

Concomitantly, an increasing hysteresis is observed, ranging from 25 mV to 100 mV at C/5 and from 100 mV to 500 mV at 1 C considering successively the cells C, B and A. Note the higher the hysteresis, the more the upper cut-off voltage is rapidly reached and the longer the potentiostatic step at the end of the charge. At 10 C, no capacity is achieved. The hysteresis becomes so important that no cycling is