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Electrical characterization of all-solid-state thin film batteries

G. Nagasubramanian*, D.H. Doughty

Sandia National Laboratories, 2521 Lithium Battery R&D 1515, Albuquerque, NM 97185-0613, USA

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Abstract

All-solid-state thin film micro-batteries comprised of a lithium anode, lithium phosphorus oxy-nitride (LiPON) solid electrolyte and Li_xCoO_2 cathode were evaluated at different temperatures from −50 to 80 °C for electrical behavior and impedance raise. The cell dimensions were ∼2 cm long, ∼1.5 cm wide and ∼15 μm thick. The rated capacity of the cells was about 400 μAh. The cells were cycled (charge/discharge) at room temperature over 100 times at a 0.25*C* rate. The charge and discharge cut-off voltages were 4.2 and 3.0 V, respectively. The cells did not show any capacity decay over 100 cycles. The measured capacity was 400 μAh. The coulombic efficiency was 1, which suggests that the cell reaction is free from any parasitic side reactions and the lithium intercalation and de-intercalation reaction is completely and totally reversible. These cells also have good high-rate performance at room temperature. For example, these cells discharged at a 2.5*C* rate delivered ∼90% of the capacity at a 0.25*C* rate. However, the delivered capacities even at a 0.25*C* rate at 80 and −50 °C were much lower than the room temperature capacity. Cells soaked at −50 °C were not damaged permanently as seen by the near normal behavior when returned to room temperature. However, cells heated to 80 °C were permanently damaged as seen by the lack of normal performance back at room temperature. Cell impedance was measured before and after cycling at different temperatures. The high-frequency resistance (generally ascribed to the electrolyte and other resistances in series with the electrolyte resistance) decreased with decreasing temperature. However, the interfacial resistance increased significantly with decreasing temperature. Further, the electrolyte resistance accounted for ∼2% of the total cell resistance. The cycled cells showed higher impedance than the uncycled cells.

Keywords: Solid-state batteries; Impedance; Coulombic efficiency; Discharge capacity

1. Introduction

There is an abiding interest in long-life power supplies, and this is particularly true for weapon systems. Applications exist where small/light high-reliability and long-life power sources are needed.

This program aims at integrating a new prototype beta-cell (which delivers continuous power) and a long-life battery to follow the dynamic power requirements of the application. For the energy storage part of the investigation, we are currently evaluating the electrical and electrochemical properties all-solid-state thin film cells.

The all-solid-state thin film battery technology has several attractive features including:

(1) the potential to make <10 μm thin batteries;
(2) possible integration of battery fabrication with that of the microelectronic devices.

Further, miniaturization and the advances in the microelectronic industry have reduced the power and current requirements of electronic devices. Therefore, thin film all-solid-state batteries are being considered to power small hand-held electronic devices such as smart cards and other CMOS-based integrated circuit applications. Although thin film micro-batteries have been studied for many years [1,2] only recently, with the development of LiPON (lithium phosphorus oxy-nitride) as a solid electrolyte [3,4] has there been a surge in research activity in this area. Bates et al., have demonstrated the performance characteristics of thin film cells comprising a Li anode, LiPON electrolyte and $LiCoO_2$ cathode. Since this is a relatively new technology very little published data on the cell performance and stability of the performance over time are available. Further, the performance characteristics above and below room temperature are unavailable.

* Corresponding author. Tel.: +1-505-844-16-84; fax: +1-505-844-69-72.
E-mail address: gnagasu@sandia.gov (G. Nagasubramanian).

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In this study we have evaluated the electrical and electrochemical characteristics of small thin film cells over a wide temperature range (−50–80 °C).

2. Experimental

Thin film cells purchased from vendors were used as received. An Arbin cycler was used for charging/discharging the cells. A model 283 EG&G potentiostat/galvanostat equipped with a model 1025 EG&G frequency analyzer and controlled with a Power Suite impedance software was used to perform impedance measurements.

For current pulse studies, a model 273A EG&G potentiostat in conjunction with a Tektronix oscilloscope (model TDS 754 C, Color 4-channel digitizing oscilloscope with InstatVu^{TM} Acquisition) was used. The cell temperatures during tests were controlled with a Tenney Jr. temperature chamber (bench top model, Union, New Jersey).

3. Results and discussion

The schematic of a thin film cell is given below in Fig. 1 The components of the cell are given in the figure itself. The typical thickness of the cell is ∼15 μm. A suite of electrochemical measurements was carried out on thin film cells to fully characterize the performance envelope of the cells.

3.1. Charge/discharge studies at room temperature

In Fig. 2 we show the first 40 charge/discharge cycles of the 100 cycles performed on a thin film cell. The cell was charged and discharged at 100 μA (∼0.25*C* rate) at room temperature. The discharge capacity measured from each discharge curve is 400 μAh. The shapes of the charge and discharge voltage profiles are symmetrical to each other, which implies that the electrochemical intercalation/deintercalation reaction of Li ions in the cathode is totally reversible. The coulombic efficiency is 1, which also implies that the insertion/de-insertion of Li ions in this system is free of parasitic side reactions.

In Fig. 3, we plot the cumulative discharge capacity (in mAh) versus cycle number. The plot is a straight line with a slope of unity, which means the cell does not lose capacity with cycling. The slope of the line gives the cell capacity in mAh, 0.404 mAh/cycle, which is very close to the rated cell capacity. This performance is typical of the several cells tested from two different vendors.

3.2. Rate capability

The cells were discharged at room temperature for different discharge current levels to evaluate the rate capability of the cells. Fig. 4 shows the discharge curves for different discharge currents ranging from 0.1 to 1 mA. The plots clearly show that these cells have good rate capability and even at a 2.5*C* rate (∼1 mA discharge current) the delivered capacity is ∼90% of the 0.25*C* rate capacity.

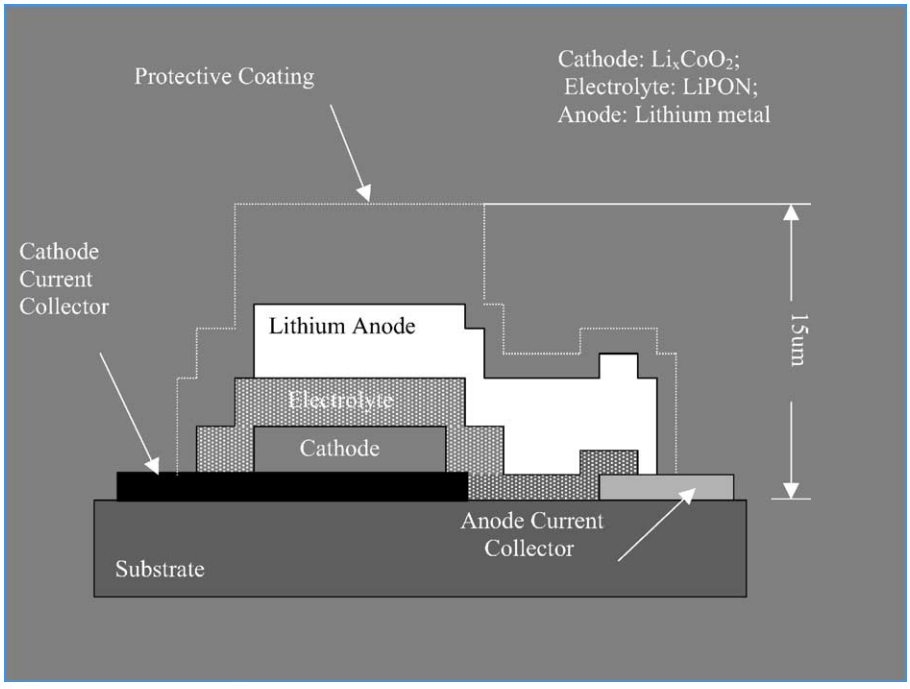

Fig. 1. Schematic of thin film micro-battery.

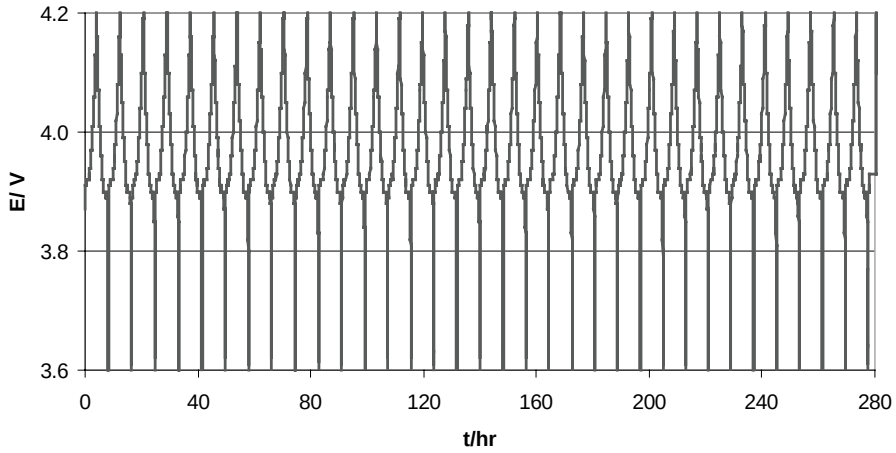

Fig. 2. Charge/discharge cycles for a thin film cell at room temperature.

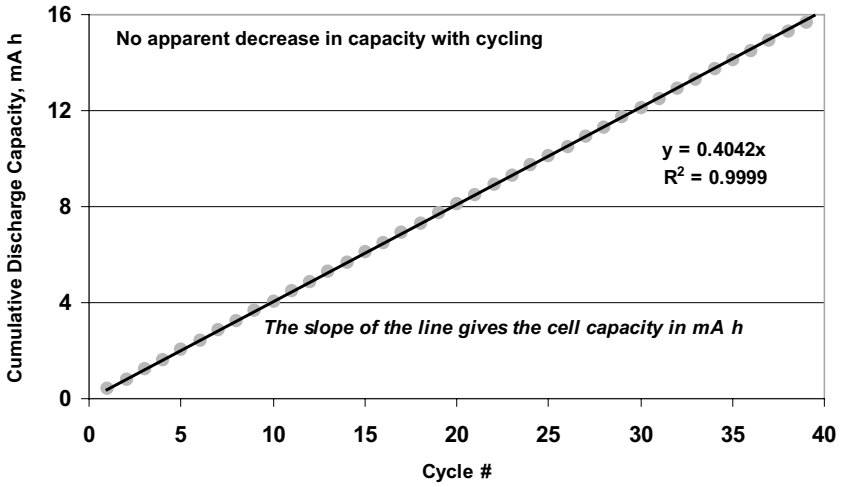

Fig. 3. Cumulative discharge capacity in mAh vs. cycle number.

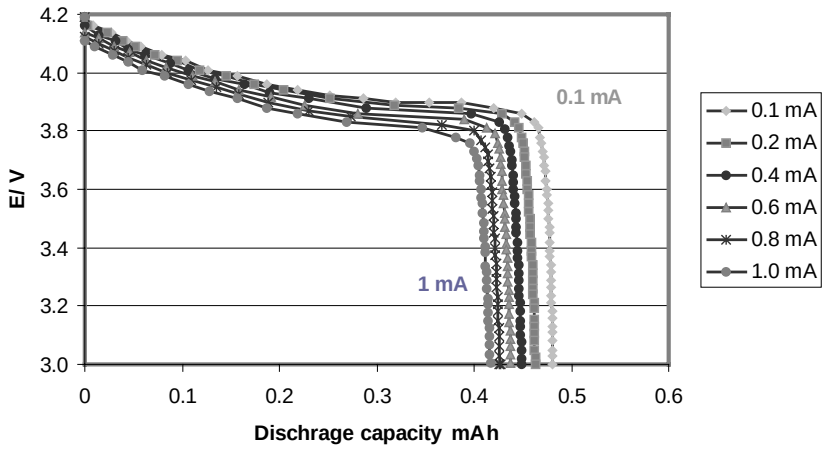

Fig. 4. Cell voltage vs. discharge capacity for different discharge currents. Values of discharge currents are given in the figure.

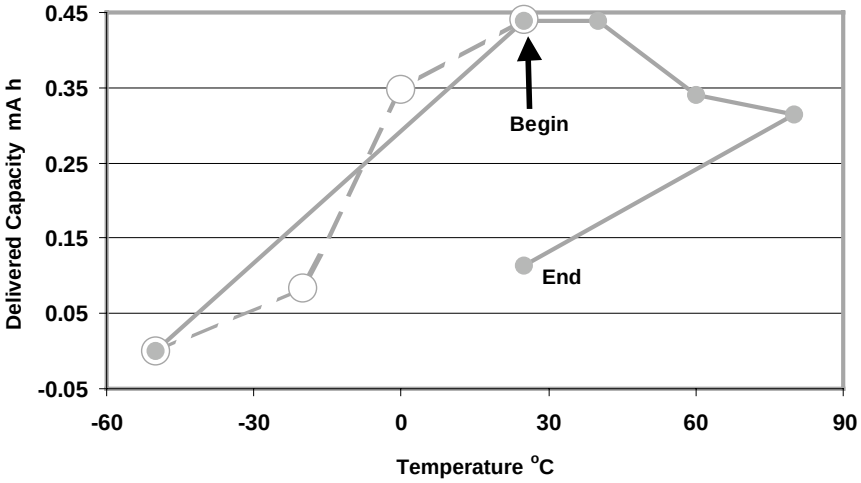

Fig. 5. Average discharge capacity vs. temperature.

3.3. Effect of temperature on delivered capacity

The capacity of the cells was measured between −50 and 80 °C and compared to the initial capacity measured at 25 °C. Then the capacity was measured at the temperatures in sequence as given below.

0ºC ⟶ -20ºC ⟶ -50ºC ⟶ 25ºC ⟶ 40ºC ⟶ 60ºC ⟶ 80ºC ⟶

The average discharge capacity is plotted versus temperature in Fig. 5. Each data point represents an average capacity of 6 cycles at the test temperature.

The plot indicates:

(1) the cells delivered progressively lower capacities at lower and higher temperatures (−50 and 80 °C) compared to 25 °C;
(2) the cells did not suffer any permanent damage at −50 °C since the cells delivered ∼400 μAh capacity when tested again at 25 °C; and
(3) at 80 °C the cells suffered permanent damage as seen by the much lower discharge capacity (∼113 mAh) at 25 °C. At this point it is not clear the cause for the permanent damage of the cells exposed to 80 °C. However, the decomposition of the partially charged cathode and/or the instability of the cathode–electrolyte interface at 80 °C may be responsible for the damage. It is also possible that the damage to the cell may have occurred even at 60 °C (as seen by a slightly lower capacity compared to at 25 °C) and the damage might have been exasperated at 80 °C. We performed impedance measurements on the fresh and damaged cells to compute the overall cell impedance. The delivered capacities obtained at the different temperatures are summarized in Table 1.

3.4. Electrochemica impedance studies

Impedance of the fresh and aged cells was measured at several different temperatures. NyQuist plots in Figs. 6 and 7 for the fresh and aged cells represent the impedances measured at different temperatures, respectively.

As expected, the cell impedance increased with decreasing temperature for both the fresh and aged cells. The high-frequency impedance at 25 °C increased from about 5 Ω for the fresh cell to about 60 Ω for the aged cell. Further, the low frequency impedance at −10 °C increased by ∼1200 Ω for the aged cell over the fresh cell.

Although it is clear from the data that the increase in interfacial impedance is much higher than the increase in ohmic resistance as the cell aged, it is unclear which of the two interfaces (anode/electrolyte or the cathode/electrolyte) is responsible for the impedance increase. Further, the ohmic resistance decreases with decreasing temperature. For example, a fresh cell exhibited ∼20 and 3 Ω at 40 and

Table 1
Delivered capacity at different test temperatures

Temperature (°C)	Capacity (mAh)
25	0.441
0	0.347
−20	0.0834
−50	0.000013
25 retested	0.438
40	0.438
60	0.341
80	0.314
25 retested	0.113

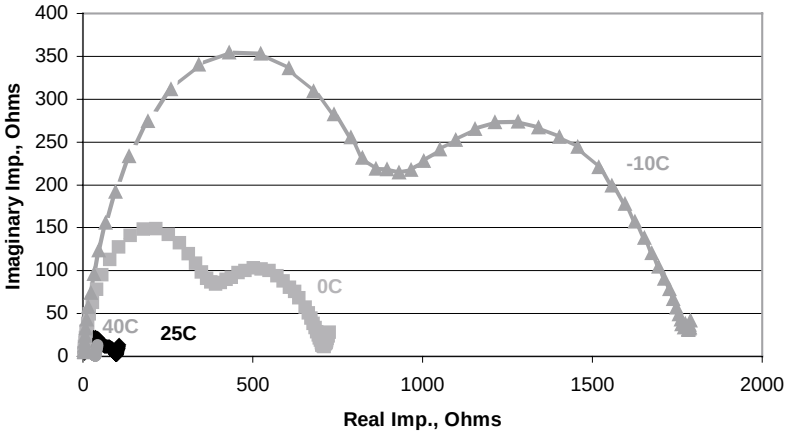

Fig. 6. NyQuist plot of impedance of a fresh cell at four different temperatures.

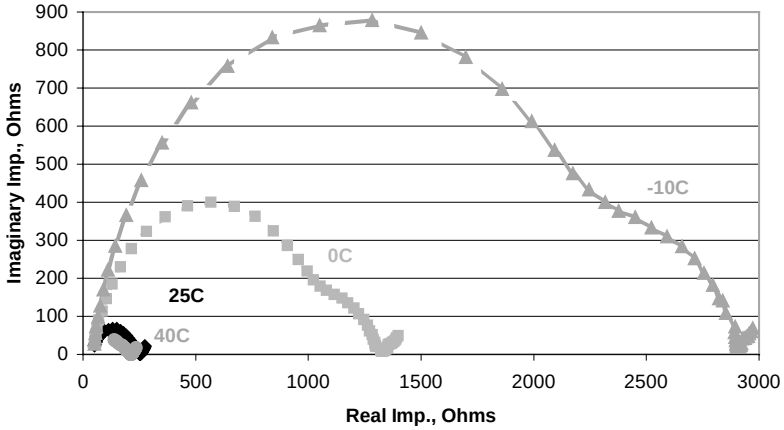

Fig. 7. NyQuist plot of impedance of an aged cell at four different temperatures.

−10 °C, respectively. Similar behavior was observed for the aged cells. This behavior is typical of metals. We interpret this result to mean that, since the electrolyte is very thin, the resistance of the metallic tabs and current collectors might dominate the ohmic part of the cell resistance. However, this speculation remains to be proven.

4. Conclusions

Thin film all-solid-state cells were studied for electrochemical and electrical properties in the temperature range −50 to 80 °C. The rated capacity agreed with the measured capacity of the cells at 25 °C, approximately 400 μAh. Compared to the capacity at 25 °C, the cells yielded progressively lower capacity at temperatures above and below 25 °C. The capacity recovered after the cells were chilled to −50 °C. However, the cells heated to 80 °C yielded only ∼110 μAh when retested at 25 °C. So it appears that the cells at –55 °C did not suffer any permanent damage to cell performance and the cells heated to 80 °C did suffer irreversible loss in capacity. It is also likely that even at 60 °C the cell may have suffered damage, which only got worse at 80 °C.

These cells have good rate capability; at a 2.5*C* rate (∼1 mA rate) these cells gave ∼90% of the 0.25*C* rate capacity. Both the ohmic and interfacial resistances are higher for the aged cells compared to the fresh cells. The ohmic resistance of the cells decreases with decreasing temperature, which is contrary to the expectation and may suggest significant contribution from the metallic current collectors and tabs. However the interfacial resistance increases with decreasing temperature, which could be due to kinetic limitations.

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