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Solid-state thin-film rechargeable batteries

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Abstract

Thin-film solid-state rechargeable lithium batteries are ideal micropower sources for many applications requiring high energy and power densities, good capacity retention for thousands of discharge/charge cycles, and an extremely low self-discharge rate. Batteries fabricated using the crystalline $LiCoO_2$ cathode consistently provide the maximum power levels up to 30 mW/cm^2, long cycle life, negligible self-discharge and rapid charge rates. Similarly promising results have also been obtained with crystalline $LiMn_2O_4$ cathodes, although good reproducibility has not been achieved. These fully lithiated cathodes can be used with Li-free or Li-ion thin-film anodes to produce batteries that can withstand high temperature solder bonding processes.
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Keywords: Battery; Lithium; Thin films; Intercalation of lithium; Lipon electrolyte; $LiCoO_2$

1. Introduction

Thin-film rechargeable lithium batteries developed at Oak Ridge National Laboratory (ORNL) are fabricated by physical vapor phase deposition processes [1–4]. The battery is typically deposited onto an insulating substrate, most often a thin polycrystalline alumina, by successive film depositions of the metal current collectors, cathode, electrolyte, and anode, plus a multilayer protective coating of Ti and parylene-C permitting the battery to be exposed to the air for up to 1–3 months. A schematic cross-section is shown in Fig. 1. A variety of cathode and anode materials have been synthesized as thin films and evaluated within the complete thin-film battery. The most promising battery components and configurations will be mentioned in this report. In all cases, the battery electrolyte film is an amorphous lithium phosphorous oxynitride [5] sputter deposited to a thickness of 1 μm at rates of 100–200 Å/min. This electrolyte has become commonly known as Lipon and is now being used with good results by a number of research and development groups. The Lipon electrolyte has an acceptable lithium ionic conductivity (2×10^{-6} S/cm) and a good electrochemical stability with both metallic lithium and the transition metal cathodes at cell potentials up to 5.5 V versus Li. In addition, the electronic resistivity of the Lipon films is $>10^{14}$ Ω cm, which greatly minimizes the short circuit self-discharge of the battery. This report will provide key performance results for ORNL's thin-film batteries and highlight recent advances in their development.

2. Experimental

Fabrication of the thin-film batteries has been described in earlier publications and on our website [1,3,5]. The battery is built by a sequence of physical vapor deposition processes. Experimental cells are generally fabricated onto a ceramic alumina substrate. Metal current collectors are deposited by dc magnetron sputtering. The cathode films are deposited by rf magnetron sputtering of the parent compounds. These films were then annealed at temperatures of 300–800 °C to obtain a fully crystalline phase. The Lipon electrolyte is deposited as a 1 μm-thick film, fully covering the surface and edges of the cathode film, by rf magnetron sputtering of a Li_3PO_4 source in a nitrogen plasma. Metallic lithium anode films are deposited by thermal evaporation of the metal under vacuum. The capacity of the "lithium batteries" is limited

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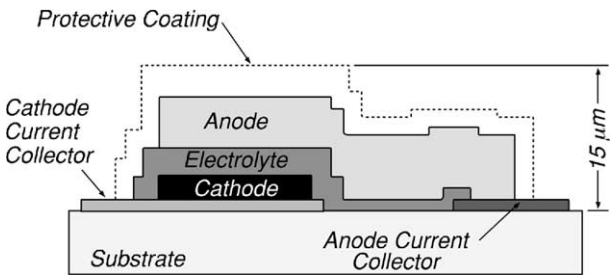

Fig. 1. Schematic cross-section of a thin-film lithium battery.

by the thickness of the cathode films, as the lithium film is several times thicker than that required to cycle the battery. The "lithium-ion" batteries, on the other hand, are limited by the thickness of the anode films which are also prepared by sputter deposition. The parylene-C coating is deposited by evaporation and polymerization under vacuum. When formed as a multilayer with interspersed titanium films, the parylene coating will protect the lithium metal from reaction with the air for periods of 1–3 months. Cycling for longer periods requires storing the batteries in a sealed container or glove box. Cycling was performed with a Maccor 4000 battery test system.

3. Results and discussion

Fig. 2 shows a low current discharge curve for batteries with several different cathode materials. In each case, the anode is a 3 μm-thick film of metallic lithium. The cell voltage indicates the electrochemical potential of the lithium in cathode materials. The capacities of crystalline, "*c*", $LiCoO_2$ and $LiMn_2O_4$ in the 3.9–4.2 V range correspond to extraction of 1 mol Li for every 2 mol of the transition metal:

$$LiCoO_2 \leftrightarrow Li_{0.5}CoO_2 + 0.5\,Li \quad \text{or}$$

$$LiMn_2O_4 \leftrightarrow Mn_2O_4 + Li.$$

The crystalline phases are formed by a post-deposition, high-temperature anneal of the cathode film. In contrast, for amorphous "*a*" cathodes, nanocrystalline "*n*," or submicron films of the crystalline phase, the capacity can be reversibly doubled by discharge to voltages below 3 V.

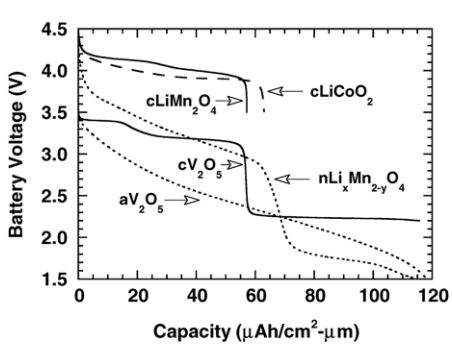

Fig. 2. Low current discharge curves for lithium batteries with different cathode films. The capacity is normalized by the volume of the cathode. The notation "*c*" refers to a crystalline cathode, while "*n*" is nanocrystalline and "*a*" denotes an amorphous structure.

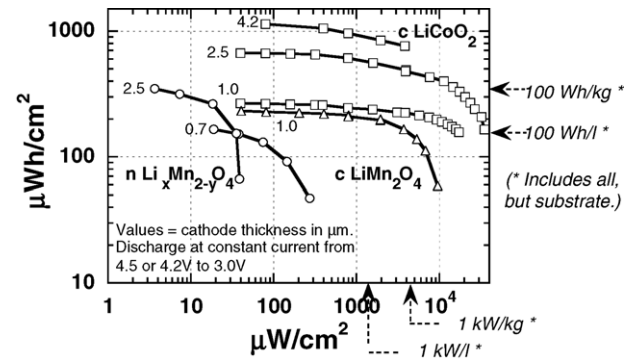

Fig. 3. Power and energy density determined from constant current discharge measurements for thin-film batteries with a Li anode and the indicated thin-film cathode: cLiCoO$_2$ (□), cLiMn$_2$O$_4$ (△), and nLi$_x$Mn$_{2-y}$O$_4$ (◯). The cathode thickness is given in μm. The batteries were discharged over 4.2–3.0, 4.5–3.0, and 4.5–2.5 V for the cLiCoO$_2$, cLiMn$_2$O$_4$, and nLi$_x$Mn$_{2-y}$O$_4$ cathodes, respectively.

Fig. 3 shows results for the power and energy densities that are obtained for thin-film batteries over a wide range of constant current discharge conditions. The values are normalized by the active area of the battery for ease in assessing the dimensions required for a particular application. The batteries all have a 3 μm-thick metallic lithium anode and the designated cathode. The cathode film thickness in micrometers is indicated beside each curve. This determines the capacity of the cell. Reference points giving the specific and volumetric energy and power densities are marked at the margins. These estimates include the volume and mass for all the active battery components, including the current collectors, electrodes and electrolyte, as well as a 7 μm-thick parylene and Ti protective coating. The substrate and the battery container have *not* been included and this obviously has a large impact on the battery specifications for the final product. Ideally, the thin-film batteries would be fully integrated and deposited directly onto the device or its package to avoid the excess weight and volume associated with an inactive substrate. In practice, commercial development efforts are focused on using thin flexible substrates of metals, plastics or silicon substrates. In any case, making the cathode and anode films as thick as possible, at least 1–5 μm, maximizes the energy and power densities achieved by the batteries. Unfortunately as the film thickness is increased, maintaining a strong bond between each of the films and the supporting substrate becomes increasingly difficult. This, more than the resistance of the films, dictates the maximum energy per unit area of the batteries.

Thin-film cLiCoO$_2$ cathodes discharged between 4.2 and 3.0 V give the best power densities [6,7]. This is due to the high diffusivity of lithium in the layered LiCoO$_2$ structure. Note that with a 4 μm-thick LiCoO$_2$ cathode, batteries can provide 1 mWh/cm^2 energy at a 1 mW/cm^2 power discharge.

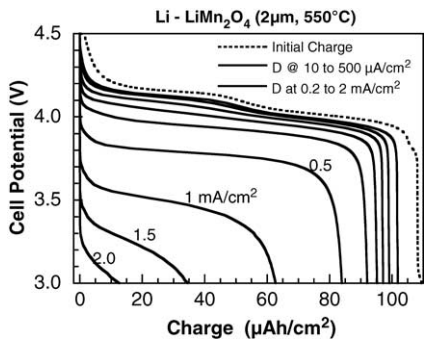

Fig. 4. Constant current discharge curves for a battery with a 2 μm-thick $LiMn_2O_4$ cathode. The cathode was crystallized at 550 °C. The currents ranged from 10 μA to 2 mA/cm^2.

This corresponds to a 0.2 mA/cm^2, or 0.6 C, continuous discharge rate. When discharged at higher rates, the available energy decreases due to the polarization of the cathode and the internal resistance of the electrolyte and its interfaces. In recent studies, $LiCoO_2$ batteries have been cycled to 4.4 V with good results [8,9]. This high-voltage stability is attributed to the ability of submicron grains to accommodate the volume changes associated with further Li extraction. Cycling to 4.4 V gives a 26% increase in the specific energy over that for a 4.2 V limit shown in Fig. 3. In addition, a study [10] of batteries with cLiCoO$_2$ cathodes of 5 nm to 4 μm thick indicates that the energy densities are ultimately limited by the rapidly decreasing Li ion diffusivity as the lithium content approaches compositions of $Li_{>0.96}CoO_2$ at cell voltages <3.8 V versus Li.

Batteries with a thin crystalline $LiMn_2O_4$ spinel cathode, cLiMn$_2$O$_4$ in Figs. 2 and 3, cycled between 4.5 and 3.0 V give energies comparable to that of cLiCoO$_2$ at low current discharge, but so far, have not matched the very high power performance achieved with the $LiCoO_2$ cathodes. An example of the discharge curves for a $LiMn_2O_4$–Li battery is given in Fig. 4. Unfortunately the $LiMn_2O_4$ batteries have not proven to be as reproducible as the $LiCoO_2$ batteries in terms of the cell resistivity and cycle stability. This is believed to be largely due to difficulties in optimizing and controlling the composition of the sputter deposited cathodes. Research is continuing to address these problems.

The third kind of battery included in Fig. 3 has an unannealed, nano-crystalline cathode film, nLi$_x$Mn$_{2-y}$O$_4$. The performance of these batteries has been reported in an earlier work [11]. The compositions of the as-deposited film are significantly Mn deficient, leading to a lithium substituted spinel structure when crystallized. Although the 4.5–2.5 V capacity of this cathode is comparable to the well-crystallized cathode, the Li^+ diffusivity is greatly reduced in the disordered material, thereby limiting the power that can be realized with this thin-film cathode. The bright side, however, is that this cathode can be used to fabricate thin-film batteries on low temperature substrates or temperature sensitive devices. Although the nLi$_x$Mn$_{2-y}$O$_4$ batteries cannot deliver a high power discharge, they have proven to be robust with long cycle lives, even when cycled at temperatures up to 100 °C.

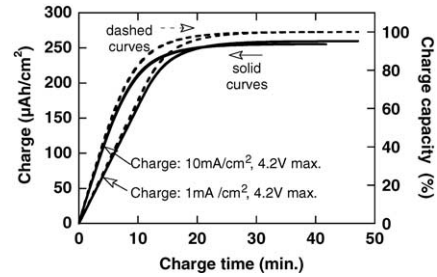

Fig. 5. Charge of a Li–$LiCoO_2$ thin-film battery to 4.2 V. The absolute and relative charge capacities are indicated by the solid and dashed curves, respectively.

For many applications, achieving a high charge rate for the battery is as important as the discharge power. Results in Fig. 5 show rapid charge of a Li–$LiCoO_2$ thin-film battery with a thick cathode. The maximum current was limited to either 1 or 10 mA/cm^2 and the battery potential was not allowed to exceed 4.2 V. The results show that a full charge was approached in just 20 min. To date, no deleterious effects have been attributed to such high maximum charge currents.

Several different experiments have been used to quantify the self-discharge of our thin-film batteries. The open circuit cell voltage has been monitored over prolonged periods for Li batteries with $LiCoO_2$ and $LiMn_2O_4$ cathodes ranging from 500 Å thick to more useful cathodes of 1–2 μm thickness. These batteries were stored at various states of charge under an inert atmosphere near 25 °C. Comparison of the battery potentials with low current discharge curves suggests a self-discharge rate of 1–3 μAh/cm^2/year. For a battery with a 2 μm-thick cathode, this corresponds to <2% self-discharge per year. If the self-discharge is attributed to the electronic conduction through the Lipon electrolyte film, the resistivity of Lipon must be >10^{14} Ω cm. A more rigorous test is shown in Fig. 6. Here the fully charged batteries were stored at room temperature under open circuit conditions for different periods of time before being suddenly discharged in a high current pulse (∼4 C-rate). The decrease in capacity reflects not only the self-discharge, but also any deleterious aging effects leading to an increase in cell resistance or a

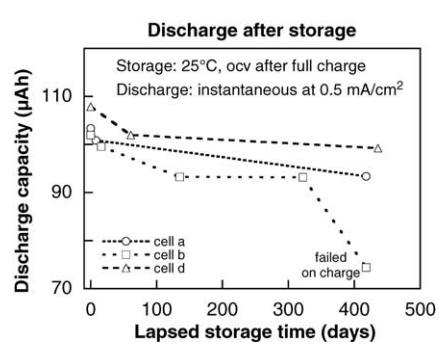

Fig. 6. Capacities recorded for three Li–$LiCoO_2$ thin-film batteries when rapidly discharged after prolonged storage in the fully charged state.

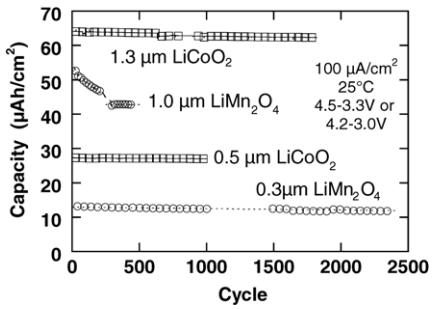

Fig. 7. Cycling results for four batteries with the indicated cathode films. All were discharged at a constant 100 μA/cm^2. Gaps in the data reflect cycles preformed at different currents or over a different voltage window.

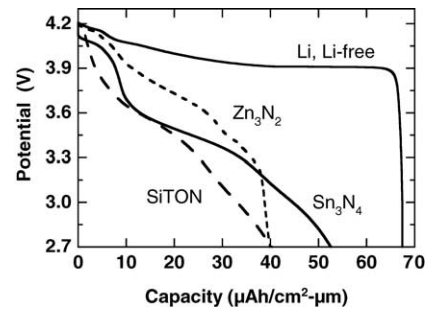

Fig. 8. Low current discharge curves for batteries with the indicated anode and a cLiCoO$_2$ cathode. "SiTON" = SiSn$_{0.9}$O$_{1.2}$N$_{1.7}$. The capacity is normalized for the dimensions of the cathode film (work by Neudecker et al. [13,14]).

loss of capacity. Although the sample population in this test was very small, the results indicate the excellent shelf life and negligible self-discharge that can be expected from these thin-film batteries.

Lithium–cLiCoO$_2$ thin-film batteries have been cycled many thousands of times with only small capacity losses, typically ∼0.2 nAh/cm^2/cycle at 25 °C [12]. Long-term cycling of Li–nLi$_x$Mn$_{2-y}$O$_4$ cells is likewise very stable for >1000 cycles [11]. As shown in Fig. 7, mixed results have been obtained for cells with cLiMn$_2$O$_4$ cathodes. Several have achieved thousands of cycles with <1 nAh/cm^2/cycle loss rates, while other batteries exhibit capacity fades of 30 nAh/cycle over at least part of the cycle life. These variations are only partially attributable to differences in the cathode film compositions. As shown in Fig. 7, unusual changes due to an interruption or change in the test can profoundly alter the capacity loss behavior.

In addition to the evaporated lithium anodes, Li-ion [13] and Li-free [14] thin-film cells have also been fabricated and tested at ORNL in recent years. The advantage of these anodes over the metallic lithium anode is that prior to the initial charge, the battery can be heated in air to 250 °C for purposes of device assembly. Presently, a major drawback is that the fabrication yield of these batteries is significantly lower than that for the Li anode cells. The reason for the higher frequency of leaky or shorted cells is unknown and is under investigation.

Fig. 8 shows low current discharge curves for batteries with several different thin-film Li-ion anodes compared to a Li or Li-free anode. In each case, the cathode is cLiCoO$_2$. For the Li-free cells, metallic lithium is electroplated at the electrolyte–current collector interface upon the initial charge. Discharge rates and initial capacities of the Li and Li-free cells are comparable, although the capacity loss upon extended cycling of the Li-free batteries is typically 10–20 nAh/cm^2/cycle, much larger than for the Li anode cells fabricated with an excess of lithium. Li-ion batteries with the tin and zinc nitride and oxynitride films have a reduced cell potential and capacity. These losses can be limited by using a subnitride anode film composition and a very thin anode film [13]. As for the Li-free battery, the capacity loss of the Li-ion cells during cycling is large compared to the batteries with a metal Li anode, although typical cells will retain more than half their capacity after 1000 cycles.

Prototype batteries have been fabricated for a number of applications including implantable medical devices, radio-frequency transmitters, backup power for CMOS memory devices, EKG and other sensors, and MEMS devices. The active battery areas for a single cell that have been deposited at ORNL range from 0.05 to 10 cm^2. Multiple cells can be readily connected in series or parallel arrangements to match a wide variety of battery requirements.

4. Conclusions

A family of thin-film rechargeable batteries is being developed at ORNL. The Li–cLiCoO$_2$ battery is the most mature having the highest capacity, energy and power densities. These cells have cycle and shelf lives of thousands of cycles and many years, respectively. Promising results have also been obtained for cells with LiMn$_2$O$_4$ cathodes and for both the Li-free and Li-ion anodes; although in each case additional research is required to understand and optimize the properties of the materials and interfaces.

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