

RECHARGEABLE THIN-FILM BATTERIES WITH LiMn₂O₄ AND LiCoO₂ CATHODES

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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 LiCoO₂ cathode consistently provide the maximum power levels up to 30 mW/cm², long cycle life, and rapid charge rates. Similarly promising results have also been obtained with crystalline LiMn₂O₄ 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.

INTRODUCTION

Thin film rechargeable lithium batteries at Oak Ridge National Laboratory (ORNL) are fabricated by physical vapor phase deposition processes (1-3). 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 metal/polymer protective coating permitting the battery to be exposed to the air for up to a month. 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 (4) 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 5.5V 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 the use of ORNL's thin film batteries as a micropower source and highlight recent advances in their development.

RESULTS AND DISCUSSION

Figure 1 shows recent results for the power and energy densities that are obtained with our thin film batteries. The values are normalized by the active area of the battery for ease in assessing the dimensions required to meet a particular micropower source application. These batteries all have a 3 μm thick metallic lithium anode and one of three

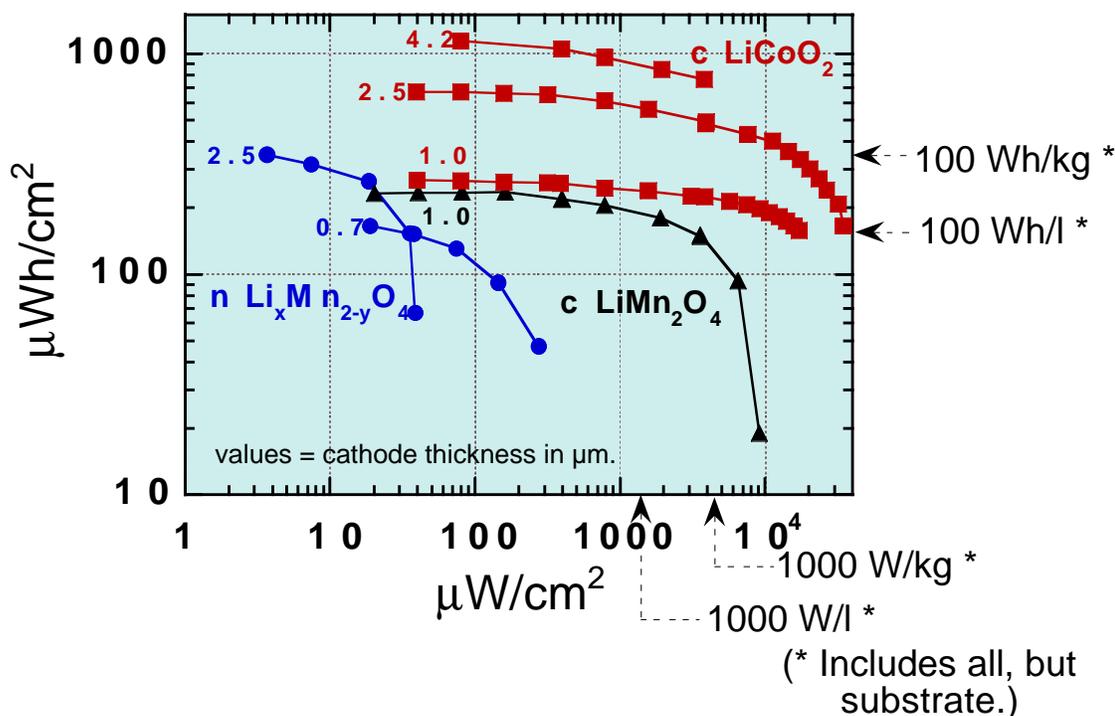


Figure 1: Power and energy density determined from constant current discharge measurements for thin film batteries with a Li anode and the indicated thin film cathode: cLiCoO₂ (□), cLiMn₂O₄ (Δ), and nLi_xMn_{2-y}O₄ (O). Annealed cathodes which were well crystallized are denoted with c, while n indicates an unannealed nanocrystalline cathode. The cathode thickness is given in μm. The batteries were discharged over 4.2–3.0, 4.5–3.0, and 4.5–2.5V for the cLiCoO₂, cLiMn₂O₄, and nLi_xMn_{2-y}O₄ cathodes respectively.

different cathodes. The cathode film thickness is indicated beside each curve as this determines the capacity of the cell. The thin film crystalline (c) LiCoO₂ cathodes discharged between 4.2 and 3.0 V give the best performance (5). Note that with the 4 μm LiCoO₂ cathode, batteries have been fabricated which can provide 1 mWh/cm² energy at a 1mW/cm² power. This corresponds to a 0.2 mA/cm², or 0.6C, continuous discharge rate. When discharged at higher powers, the available energy decreases unless discharged in a pulsed mode. Batteries with a thin crystalline LiMn₂O₄ cathode cycled between 4.5 and 3.0 V give comparable energies, but so far have not matched the very high power performance achieved with the LiCoO₂ cathodes, nor have the LiMn₂O₄ batteries proven to be as reproducible as the LiCoO₂ in terms of the cell resistivity and high cycle stability. We believe this is largely due to difficulties in optimizing and controlling the composition of the sputter deposited cathodes. Research is continuing to try and address these properties. The third cathode in Figure 1 contrasts the performance achieved with an unannealed nano-crystalline LiMn₂O₄ cathode film (6) in contrast to the crystalline cathodes that have been annealed at high temperatures. The composition of the as-deposited film is significantly Mn deficient. Although the 4.5–2.5 V capacity of this cathode, with cycling of ~1 Li per Mn₂O₄, is comparable to the well crystallized cathode,

the Li^+ diffusivity is greatly reduced in the more disordered material. This cathode can be used to fabricate thin film batteries on low temperature substrates or devices and has proven to give robust batteries with long cycle lives even at temperatures to 100°C .

Conversions of the results in Figure 1 into the specific and volumetric energy and power densities are indicated at the margins. These calculations include all the active battery components, the current collectors, electrodes and electrolyte, as well as the $7\ \mu\text{m}$ 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. Double sided batteries have been fabricated by depositing films simultaneously onto both sides of thin metal ($25\ \mu\text{m}$ Ti) or thin alumina ($250\ \mu\text{m}$) sheets to minimize the volume and mass contributed by the substrate. In other cases the battery may be deposited directly onto the device or its packaging. Alternatively, making the cathode and anode films as thick as possible, at least 1–5 micrometers, also maximizes the energy and power densities. Maintaining a strong bond between each of the films and the supporting substrate becomes increasing difficult as the film thickness is increased.

For many applications, achieving a high charge rate for the battery is as important as the discharge power. Results in Figure 2 show rapid charge of a Li-LiCoO₂ thin film battery with a thick cathode. The maximum current was limited to either 1 or 10 mA/cm² and the battery potential was not allowed to exceed 4.2 V. The results show that close to a full charge was achieved in 20 minutes. To date, no deleterious effects have been attributed to such high initial charge currents.

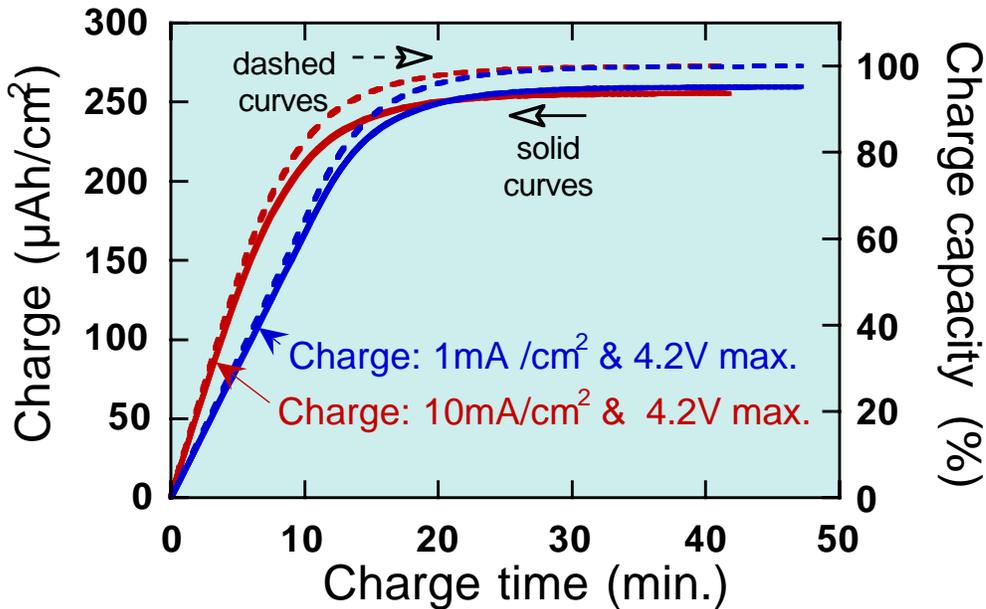


Figure 2: Charge of a Li-LiCoO₂ thin film battery to 4.2V. The absolute and relative charge are indicated by the solid and dashed curves, respectively.

Experiments to determine the shelf life of the thin film batteries are currently in the sixth month. The voltage is being monitored at different temperatures for a set of Li batteries with LiCoO_2 and LiMn_2O_4 cathodes ranging from 500Å thick to more useful cathodes of 1–2 μm thickness. Comparison of the battery potentials with earlier low current discharge curves suggest a self discharge rate of 1–3 Ah/cm²/yr at 25°C. 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 $> 10^{14}$ Ωcm. Definitive results for the shelf life study must await cycle testing of the batteries following the prolonged storage.

Lithium - cLiCoO₂ thin film batteries have been cycled many thousands of times with only small capacity losses, typically ~0.2 nAh/cm²/cycle at 25°C (7). Long term cycling of Li - nLi_xMn_{2-y}O₄ cells are likewise very stable for >1000 cycles (6). Mixed results have been found for cells with cLiMn₂O₄ cathodes. Several have achieved 1000's of cycles with < 1nAh/cm²/cycle loss rates, while other 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.

In addition to the evaporated lithium anodes, Li-ion (8) and Li-free (9) 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.

Figure 3 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 cLiCoO₂. 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, 10–20 nAh/cm²/cycle, is 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 (8). 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, radiofrequency 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 cm². Multiple cells can be readily connected in series or parallel arrangements to match a wide variety of battery requirements.

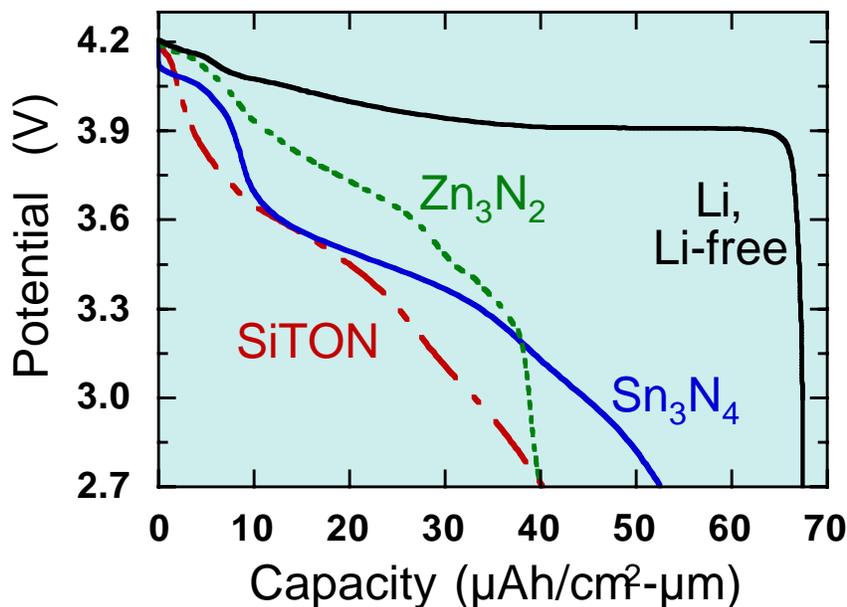


Figure 3: Low current discharge curves for batteries with the indicated anode and a cLiCoO₂ cathode. "SiTON" = SiSn_{0.9}O_{1.2}N_{1.7}. The capacity is normalized for the dimensions of the cathode film.

CONCLUSIONS

A family of thin film rechargeable batteries are being developed at ORNL. The Li - cLiCoO₂ 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 LiMn₂O₄ 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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REFERENCES

1. J. B. Bates, N. J. Dudney, B. J. Neudecker, A. Ueda and C.D. Evans, *Solid State Ionics*, in press.
2. N. J. Dudney and B. J. Neudecker, *Current Opinion in Solid State Materials Science*, in press.
3. <http://www.ssd.ornl.gov/Programs/BatteryWeb/index.htm>

4. X. Yu, J.B. Bates, G. E. Jellison, and F. X. Hart, *J. Electrochem. Soc.* **144**, 524 (1997).
5. J. B. Bates, N. J. Dudney, B. J. Neudecker, F. X. Hart, H.P. Jun, and S. A. Hackney, *J. Electrochem. Soc.* **147**, 59 (2000).
6. N. J. Dudney, J. B. Bates, R. A. Zuhr, S. Young, J. D. Robertson, H. P. Jun, and S. A. Hackney, *J. Electrochem. Soc.* **146**, 2455 (1999).
7. J. B. Bates, N. J. Dudney, B. J. Neudecker, and B. Wang, in *New Trends in Electrochemical Technology: Energy Storage System for Electronics*, T. Osaka and M. Datta, Editors, p. 453–485, Gordon and Breach (2000).
8. B. J. Neudecker and R. A. Zuhr, in *Intercalation Compounds for Battery Materials*, G.-A. Nazri, M. Thackeray, and T. Ohzuku, Editors, PV 99–24, p. 295, The Electrochemical Society Proceedings, Pennington, NJ (2000).
9. B. J. Neudecker, N. J. Dudney, and J. B. Bates, *J. Electrochem. Soc.* **147**, 517 (2000).

KEY WORDS

Thin film battery

Lithium battery

Lipon

LiCoO_2 thin film

LiMn_2O_4 thin film