Thin-Film Lithium and Lithium-Ion Batteries

J. B. Bates, N. J. Dudney, B. Neudecker, A. Ueda, and C. D. Evans

Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6030
Thin-Film Lithium and Lithium-Ion Batteries

J. B. Bates, N. J. Dudney, B. Neudecker, A. Ueda, and C. D. Evans

Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6030

*Corresponding author e-mail address and fax number: joh@ornl.gov ; (423) 574-4143

Research over the last decade at Oak Ridge National Laboratory has led to the development of solid state thin-film lithium and lithium-ion batteries. The batteries, which are less than 15 micrometers thick, have important applications in a variety of consumer and medical products, and they are useful research tools in characterizing the properties of lithium intercalation compounds in thin-film form. The batteries consist of cathodes that are crystalline or nanocrystalline oxide-based lithium intercalation compounds such as LiCoO₂ and LiMn₂O₄, and anodes of lithium metal, inorganic compounds such as silicon-tin oxynitrides, Sn₃N₄ and Zn₃N₂, or metal films such as Cu in which the anode is formed by lithium plating on the initial charge. The electrolyte is a glassy lithium phosphorus oxynitride ("Lipon"). Cells with crystalline LiCoO₂ cathodes can deliver up to 30% of their maximum capacity between 4.2 V and 3 V at discharge currents of 10 mA/cm², and at more moderate discharge–charge rates, the capacity decreases by negligible amounts over thousands of cycles. Thin films of crystalline lithium manganese oxide with the general composition Li₁₊ₓMn₂₋ₙO₄ exhibit on the initial charge significant capacity at 5 V and, depending on the deposition process, at 4.6 V as well, as a consequence of the manganese deficiency-lithium excess. The 5 V plateau is believed to be due to oxidation Mn of ions to valence states higher than +4 accompanied by a rearrangement of the lattice. The gap between the discharge–charge curves of cells with as-deposited nanocrystalline Li₁₊ₓMn₂₋ₙO₄ cathodes is due to a true hysteresis as opposed to a kinetically hindered relaxation observed with the highly crystalline films. This behavior was confirmed by observing classic
scanning curves on charge and discharge at intermediate stages of insertion and extraction of Li$^+$ ions. Extended cycling of lithium cells with these cathodes at 25 and 100°C leads to grain growth and evolution of the charge-discharge profiles toward those characteristic of well crystallized films.

Key Words: Solid state thin-film battery, lithium battery, lithium-ion battery, LiCoO$_2$, LiMn$_2$O$_4$, hysteresis

1. Introduction

Research on thin-film solid state lithium batteries begun a decade ago at the Oak Ridge National Laboratory [1–4] has resulted in the development of practical thin-film rechargeable lithium and lithium-ion batteries, and several companies in the U.S. are now moving toward production of these devices for application in consumer and medical electronics. The long cycle and shelf life of these batteries results from the properties of the glassy lithium phosphorus oxynitride ("Lipon") electrolyte [5,6] which is stable in contact with metallic lithium at potentials from 0 to nearly 5.5 V and has an acceptable conductance in thin-film form. Responding to the need for thin-film batteries that can tolerate heating to 250°C–260°C so they can be integrated into circuits using the solder reflow process, we have synthesized several inorganic anode materials [7,8] that result in thin-film lithium-ion cells which are stable at these temperatures. Recently, we have investigated batteries with in-situ plated lithium anodes [9] which deliver the high energies of lithium cells while, prior to the initial plating, also are not affected by the solder reflow conditions. Thin-film batteries have been important tools in our studies of thin films of lithium intercalation compounds, allowing us to investigate the electrochemical properties of the pure phases free of binders [1–4,10–14] and to perform in-situ experiments such as x-ray
diffraction [11] and x-ray absorption [15] as a function of the lithium concentration in these materials.

The purpose of this paper is to summarize the results of recent studies of lithium, lithium-ion, and lithium free thin-film cells with crystalline LiCoO₂ cathodes and to briefly describe some of the interesting properties of nano- and microcrystalline films in the lithium manganese oxide system. Published results and work in progress on the structure and electrochemical properties of thin films of layered Li-Ni-Mn oxides [14,15] and amorphous [1,10] and crystalline V₂O₅ will not reviewed. The paper will conclude with a brief discussion of applications and the status of manufacturing scaleup.

2. Experimental Procedures

A schematic drawing illustrating the layout of a thin film battery and a micrograph of a fracture cross section are shown in Fig. 1. For our laboratory cells, the substrate is typically a 2.54 cm × 1.27 cm × 0.1 cm thick polycrystalline alumina plate, but cells have been fabricated on silicon, metal foils, and plastics. For the latter two substrates, the batteries are quite flexible. The cathodes, which are deposited by rf magnetron sputtering of the parent compounds, are characterized using a variety of physical and chemical techniques prior to depositing the electrolyte. After depositing the lithium phosphorus oxynitride ("Lipon") electrolyte, the lithium anode is deposited by thermal evaporation to a thickness corresponding to three to four times overcapacity. The lithium-ion cells on the other hand typically are cathode heavy. Cells that are to be exposed to air in order to make in-sity x-ray diffraction measurements or that are to be subjected to extended cycling at high rates are covered with a protective coating consisting of a multilayer of parylene and titanium. Details about film deposition and characterization can be found in several references and on our web page [1–5,16].
3. Results and Discussion

3.1 Crystalline LiCoO$_2$: lithium, lithium-ion, and lithium free cells

Polycrystalline films of LiCoO$_2$ deposited by rf magnetron sputtering exhibited a strong preferred orientation or texturing after annealing at elevated temperatures [17–19]. For films thicker than about 1 $\mu$m, more than 90% of the grains were oriented with their (101) and (104) planes parallel to the substrate and less than 10% with their (003) planes parallel to the substrate. For example, the comparison of the x-ray diffraction pattern of a 4-$\mu$m-thick film with that of a powdered (random) sample (Fig. 2), shows that within the sensitivity of the measurement, none of the grains had their (003) planes oriented parallel to the substrate. As the film thickness decreased below 1 $\mu$m, the percentage of (003)-oriented grains increased until at a thickness of about 0.05 $\mu$m, 100% of the grains were (003) oriented [19]. These extremes in texturing were caused by the tendency to minimize volume strain energy for the thicker films and the surface energy for the very thin films [18]. The strain energy arises from the difference in thermal expansion between the LiCoO$_2$ film and the substrate on heating to the anneal temperature.

Examples of discharge curves of a Li-LiCoO$_2$ battery are shown in Fig. 3. At low currents, the discharge capacity corresponds to about 0.5 Li per CoO$_2$ or 137 mAh/g. The shift to lower potentials with increasing current is due to cell resistance. Although lithium ion diffusion should be much faster through cathodes with a high percentage of (101)- and (104)-oriented grains than through cathodes with predominately (003)-oriented grains [18,19], it was not possible to verify this expectation because the resistance of most cells was independent of cathode thickness up to 3 $\mu$m [19]. For cells with 1 cm$^2$ cathodes deposited below 70°C, the average resistance of about 110 $\Omega$ was due to the electrolyte and electrolyte-cathode interface. These cells could deliver significant fractions of their maximum capacity and energies at discharge rates of 5 mA/cm$^2$ or
higher as illustrated by the graphs in Fig. 4. The most important process variable in achieving low resistance cathode films is the deposition temperature. Deposition at temperatures above about 100°C leads to larger grains and increased void fraction. This reduces the contact area between the electrolyte and cathode as well as the contact area between the grains resulting in higher cell resistances.

The secondary performance of thin-film lithium batteries is illustrated in the graphs of capacity vs. cycle number in Fig. 5. The total capacity loss of the cell with the thinner cathode having a capacity of 65 μAh was less than 2% after more than 4000 cycles at discharge rates of 0.1 and 0.6 mA. The cell with the thicker cathode was discharged at rates from 0.1 mA to 1.5 mA. At 1 mA, the capacity loss per cycle was 0.02% and at 1.5 mA, 0.05% per cycle. The total capacity loss measured at 0.1 mA after more than 3800 cycles was smaller than the experimental error or less than 0.08%. Achieving a low capacity loss especially at high discharge rates requires that the lithium anode be covered with the protective parylene-titanium multilayer coating in order to prevent changes in the morphology of the anode evidently brought about by the combination of exposure of lithium to residual oxygen and the high rate of lithium plating and stripping.

Some integrated circuits are fabricated using solder reflow (surface mount) assembly in which the IC is heated to 250–260°C for a short time causing all of the components to be soldered at once. Because of the low melting point of lithium, 180°C, lithium batteries fail when heated to these temperatures, and so we sought to replace the pure metallic anode with a high melting and less reactive inorganic compound. We have investigated several oxynitride [7] and nitride [8] compounds as possible anode materials. Low current discharge curves of LiCoO₂ lithium-ion cells with silicon tin oxynitride, tin nitride, and zinc nitride anodes are compared in
Fig. 6 with a discharge curve for a cell with a lithium metal anode. Silicon-tin oxynitride (SiTON) [7] with a typical composition SiSn$_{0.87}$O$_{1.20}$N$_{1.72}$ is deposited by sputtering SnSiO$_3$ in N$_2$ while tin and zinc nitride are deposited by sputtering of the base metals in N$_2$. On the initial charge, 40–50% of the lithium is irreversibly trapped in the anodes by the formation Li$_2$O and/or Li$_3$N. Because of the lower discharge potentials and smaller capacities per unit area and thickness of the cathode, the energy delivered by lithium-ion cells is lower that of the lithium batteries. For example, the energy of the Sn$_3$N$_4$ cell calculated from the curves in Fig. 6 is about 67% of that of the lithium anode cell. However, in optimized Sn$_3$N$_4$ cells in which lithium is plated on the anode during the charge step, the relative energy is increased to 83% [8]. More importantly, the lithium-ion cells are not affected by heat treatment at 250$^\circ$ for times much longer than required for solder reflow, and they can deliver more than 50% of their maximum capacity and energy at discharge rates up to 5 mA/cm$^2$ (Fig. 4). The secondary performance of lithium ion cells with Zn$_3$N$_2$ and Sn$_3$N$_4$ anodes [8] discharged at 0.1 and 1 mA/cm$^2$, respectively, is illustrated in Fig. 5. At 0.1 mA, the capacity of the Zn$_3$N$_2$ cell decreased by 27% over 1000 cycles while that of the Sn$_3$N$_4$ cell discharged at 1 mA decreased by 43% over 1000 cycles.

Recently, we have fabricated [9] cells that exhibit the performance of thin-film lithium batteries, yet can tolerate the solder reflow conditions. In these cells, a metal current collector such as Cu is deposited over the electrolyte in place of the anode. On the initial charge, lithium from the LiCoO$_2$ cathode is plated between the electrolyte and the Cu current collector as we have observed by viewing of a fracture cross section in a scanning electron microscope during charge and discharge. Cycling then involves repeated stripping and plating of lithium under the Cu. For cathodes of comparable thickness, the discharge curves of these “lithium free” lithium cells are identical to those for lithium anode cells such as those shown in Fig. 2. Before the
initial charge, the “lithium free” cells can be heated to solder reflow temperatures without degrading subsequent performance. The graphs of capacity and energy vs. current density for discharge between 4.2 V and 3.0 V shown in Fig. 4 demonstrate that, as for the lithium cell, over 50% of the maximum capacity and energy is delivered at a current density of 5 mA/cm$^2$. An example of cycle data for a lithium-free cell is shown in Fig. 5. At a discharge current of 1 mA/cm$^2$, the capacity decreased by 20% over 1000 cycles.

The problem remaining to be solved before lithium-ion and lithium free cells can be considered for applications is to reduce the percentage of cells that develop a leak on the initial charge, about 30 to 50% for both types. By comparison, the yield for cells with lithium anodes is over 90%.

3.2 Crystalline and nanocrystalline LiMn$_2$O$_4$

The Li-Mn-O system is significantly more complex than Li-Co-O system as a consequence of the large number of phases and the wide variations in stoichiometry possible within the spinel structure [20]. We have deposited thin films by e-beam evaporation of LiMn$_2$O$_4$ and by rf magnetron sputtering of LiMn$_2$O$_4$ in Ar + O$_2$ and Ar + N$_2$. Post deposition annealing of the nanocrystalline films in O$_2$ at temperatures from 400 - 900°C yields well crystallized films with the spinel structure. The films are manganese deficient-lithium rich with compositions described by Li$_{1+x}$Mn$_{2-y}$O$_4$, where the values of $x$ and $y$ depend on the deposition conditions. For example, for films sputter deposited in Ar + O$_2$, $y \sim 0.3$ and $0.2 < x < 1.2$.

Examples of low current discharge-charge curves for lithium cells with Li$_{1+x}$Mn$_{2-y}$O$_4$ cathodes sputter deposited in Ar + N$_2$ and Ar + O$_2$ and annealed in O$_2$ are shown in Fig. 7. Early in our investigations of lithium cells with e-beam deposited cathodes [21,22], we found significant capacity at 5 V on the initial charge ranging from about 0.2 to 0.5 Li per Mn$_2$O$_4$. The
total capacity above 3.8 V corresponded to about 1 Li per Mn$_2$O$_4$. In a few cases, a plateau also was seen at 4.6 V which is so flat as to suggest that a two phase reaction occurs at this potential. Following the initial charge, this plateau does not appear in subsequent cycles. The dashed line in Fig. 7b shows a cycle from 4.5 V–1.5 V–5.3 V after 10 cycles between 3 V and 5.3 V. The disappearance of the 4.6 V plateau was accompanied by an increase in the capacity at 4 V and at 3 V in the cubic-tetragonal two phase region. The 4.6 V plateau is a major feature in the initial charge curves of annealed films sputter deposited at low rates in Ar + O$_2$ (10:1) (Fig. 7), but it is not seen in films deposited at higher rates in either Ar + N$_2$ or leaner Ar + O$_2$ mixtures (e.g. 50:1). We have found that the cathodes of those cells which exhibit the 4.6 V plateau contain monoclinic Li$_2$MnO$_3$ in addition to the cubic LiMn$_2$O$_4$ phase. Recently Shao-Horn et al. [23] reported that Li$_2$MnO$_3$ decomposes to MnO$_2$ on acid delithiation. This suggests that in the thin-film cells, Li is extracted from Li$_2$MnO$_3$ during the initial charge causing decomposition and formation of MnO$_2$ and, possibly, Li$_2$O. On the subsequent discharge cycle, Li is inserted into the MnO$_2$ formed by this reaction, $x$ Li + 2MnO$_2$ = Li$_x$Mn$_2$O$_4$, increasing the capacity at 4 V and 3 V. However, there presently is no convincing evidence that Li$_2$MnO$_3$ is associated with the 4.6 V plateau. The capacity of the 5 V plateau also decreases on the discharge step following the initial charge (Fig. 7) and continues to decrease with subsequent cycles between 5.3 V and 3.8 V as shown in Fig. 8. As shown in this figure, however, the lost capacity is partially recovered on the charge cycle after discharge to potentials of 2 V or lower.

The appearance of the 4.6 V and 5 V plateaus is caused by the combination of the manganese deficiency and lithium excess of our sputter deposited films. Using a co-deposition process in which a second target of Mn was sputtered along with a LiMn$_2$O$_4$ target, additional Mn was added to the films with the result that capacity of the 5 V plateau was greatly diminished
(Fig. 9), and there was no capacity at 4.6 V. Typically we use a 0.03-μm-thick Mn layer under the Au or Pt current collector to improve adhesion of the cathode to the substrate. During the anneal in O₂ at high temperatures, Mn diffuses through the metal overlayer into the LiMn₂O₄ film, and, with oxygen supplied by the cover gas, compensates for some of the Mn deficiency. The inset in Fig. 9 shows that for a 0.05-μm-thick LiMn₂O₄ film, there is no capacity at either 4.6 V or 5 V as a result of the extra Mn from the current collector.

Several models have been proposed to account for the 5 V plateau. These are based on partially inverse spinel structures with some of the Mn 4+ ions located on the 8a sites and some of the Li+ ions on the 16d sites [21,22], structures with Li+ and Mn²⁺ ions on 16c sites in addition to the 8a and 16d sites [24], and the intergrowth of two spinel forms [25], one with the conventional structure, (Li)₈₈[Mn₂]₁₆dO₄, and one with the Li and Mn ions occupying the alternative tetrahedral and octahedral sites, respectively, (Li)₈₈[Mn₂]₁₆cO₄. From the results of chemical analyses for the Li and Mn content and Rutherford Backscattering Spectrometry that yielded the Mn/O ratios, the average composition our films sputter deposited in Ar + N₂ and annealed in O₂ at 700°C was Li₁.₄Mn₁.₈O₄, or, assuming only Mn⁴⁺ and Mn³⁺ ions are present, Li₁.₄Mn⁴⁺₄Mn³⁺₆. When the cells are charged at 4.5 V, Li⁺ ions are extracted the 8a sites as the Mn³⁺ ions are oxidized to Mn⁴⁺. Therefore, from the average composition, we expect a capacity at 4 V of 0.6 Li per Mn₂O₄, in close agreement with experiment based upon charge extracted and the mass of the cathodes estimated from the deposition rate and time. At the end of the 4.5 V charge, the average composition is Li₀.₃Mn⁴⁺₄Mn₄, and on charging to 5.3 V approximately 0.4 Li per Mn₂O₄ is extracted at 5 V. One possible explanation for the 5 V plateau is that further extraction of Li after complete oxidation of the Mn³⁺ results in the formation of holes in the O 2p valence band. However, because there is a one-to-one correlation between the shift to higher
energies of the Mn-K edge x-ray adsorption spectra [15] with the concentration of Li extracted on charging from 1.5 V to 5.3 V, it is more likely the 5 V plateau is due to oxidation of Mn$^{4+}$ ions, perhaps to Mn$^{5+}$. The rapid decrease in the 5 V plateau with cycling between 5.3 V and 3.8 V and the partial recovery of the capacity on discharging to potentials of 2 V or lower (Fig. 8) suggest that charging above 4.5 V induces a change in the lattice structure of the cathode which is partially reversed on discharge below 2 V. Recent in-situ x-ray diffraction measurements [11] are consistent with this speculation. At the present time, the data available are insufficient to distinguish among the defect models proposed for Li$_{1+x}$Mn$_{2-y}$O$_4$ films and the oxidation processes that occur on charging above 4.5 V. It is likely that refinement of neutron and x-ray diffraction measurements on bulk Li$_{1+x}$Mn$_{2-y}$O$_4$ cathodes as a function of the lithium concentration at potentials from 1 V to 5.3 V will be required in order to develop a credible model that is consistent with all of the data.

The capacity above 4.5 V in Li$_{1+x}$Mn$_{2-y}$O$_4$ films can be stabilized by doping with Ni$^{2+}$ ions [11]. We show in Fig. 10 the discharge curves for a film with Ni/Mn = 0.08 (± 0.02) prepared by sputtering a LiNi$_{0.1}$Mn$_{1.9}$O$_4$ target. There is a significant improvement in the capacity above 4.5 V compared to the undoped films (Fig. 7a), with the result that, for the same discharge current, the energy delivered by the cell is 20% higher than that supplied by a cell with an undoped LiMn$_2$O$_4$ film of equal thickness. On cycling between 5.3 V and 3.8 V, the total capacity decreased by less than 18% over 300 cycles (inset in Fig. 10). Although it has been reported that substitution [26–29] of Mn with Cr, Fe, Co, Ni, and Cu in bulk LiMn$_2$O$_4$ increased the capacity above 4.5 V, only Ni was found to enhance and stabilize the capacity above 4.5 V among the dopants introduced into the thin films which included Ti, V, Cr, Fe, Co, Ni, Cu, and
Zn. Substituting some of the Mn with Ti increased the capacity at 4 V at the expense of the capacity at 5 V.

The apparent hysteresis on cycling in the 3 V spinel-tetragonal two phase region (Figs. 7 and 11) is characteristic of all of our LiMn$_2$O$_4$ films [21,22,30]. Since the cell potential is a measure of the lithium activity in the cathode near the cathode-electrolyte interface, the sudden step in potential from 3 V to 2.5 V on discharge is caused by appearance of a new phase of Li$_{1+x}$Mn$_{2-y}$O$_4$ at the interface. If the current is stopped, the potential relaxes to 3 V with a relaxation time that increases from a few hours to more than 40 h from the beginning to the end of the 3 V region where the cathode is fully converted to the tetragonal phase (Fig. 11). On the charge half cycle, the sudden increase in potential from 3 V to ~3.8 V also is due to the formation of a third phase at the cathode-electrolyte interface, and the relaxation time increases in the same manner from the beginning to the end of the two-phase region where the cathode is fully converted to the spinel phase. Due to the simple geometry of the solid state cell, Li$^+$ diffuses from one interface to another in a linear fashion, and we believe that the cycling behavior in the 3 V region is due to nucleation at the cathode–electrolyte interface followed by phase boundary motion toward the cathode-current collector.

As-deposited Li$_{1+x}$Mn$_{2-y}$O$_4$ films are nanocrystalline, exhibiting weak, broad diffraction peaks in the 2-theta regions of the (111), (311), and (400) reflections [12]. Examples of charge-discharge curves of a lithium cell between 4.5 V and 1.5 V are shown in Fig. 12a. The sharp steps in the cell potential are reminiscent of the discharge-charge curves of the crystalline cathodes (Fig. 7). Analogous to the crystalline cathodes, the large potential gap between the discharge and charge curves near 80 $\mu$Ah is due largely to slow kinetics as can be seen by noting the much smaller gap between the OCV curves. However, unlike the crystalline cathodes, the
nanocrystalline films exhibit a true hysteresis [30] as opposed to slow relaxation kinetics as indicated by the large gap between the OCV charge and discharge curves above 3 V. The gap remains virtually unchanged at 100°C, and when the potential vs. relaxation time curves are extrapolated to infinite relaxation times, the maximum difference in potential between the extrapolated charge and discharge curves is about 1 V. Typical of a true hysteresis [31], scanning curves (Fig. 12b) show that the path between the charge and discharge curves on reversing the current depends on the starting point or cutoff voltage, and all points inside the hysteresis loop curves can be covered by a suitable choice of the starting point. We have observed similar behavior for as-deposited amorphous V$_2$O$_5$ cathodes and amorphous silicon tin oxynitride anodes. Hysteresis in solid state systems is understood to occur to some extent for all 1$^{st}$ order transitions at temperatures where the lattice mobility is small [32]. The effect is appreciable when the transformation requires a significant threshold driving force and occurs well away from equilibrium. This results in a dissipation of energy attributable to processes such as boundary motion, formation of dislocations, disordering, or plastic deformation. In order to describe real materials, it is often assumed that the material is composed of many independent “domains” giving a distribution of values for the transformation thresholds.

Lithium cells with nanocrystalline LiMn$_2$O$_4$ cathodes have undergone extended cycling at 25 and 100°C. As shown in Fig. 13a, the shape of the discharge curves gradually changed from the form characteristic of newly prepared cells to curves that closely resemble those for crystalline LiMn$_2$O$_4$. After many 100°C cycles, the discharge curves exhibit the characteristics of a well crystallized cathode including a plateau at 4 V. This evolution of the shape of the discharge-charge curve was accompanied by a narrowing of the x-ray diffraction peaks as
illustrated in Fig. 13b. These results suggest that extended cycling, especially at elevated temperatures, promotes the growth of the nanocrystalline grains.

3.3 Applications and Commercialization

The performance of thin-film solid state lithium and lithium-ion batteries makes them attractive for application in many consumer and medical products. Manufacturing scale-up is underway at several U.S. companies, and at presently estimated production costs, the products targeted first for commercial application include implantable medical devices, CMOS-based integrated circuits, and rf identification tags for inventory control and anti-theft protection. The batteries will be incorporated as separate components, or they will be integrated into devices by direct fabrication on IC packages or chips. We show in Fig. 14 photographs of a stand alone prototype “D”-shaped battery, a battery fabricated on a multichip module package, and a cell with a 1 cm² active area we use for our experiments. For high-power applications, it will be necessary to connect many thin-film cells in parallel. Recently, in collaboration with Dr. Leo Kwak of Teledyne Electronic Technologies, scaling of battery performance with increasing active area was demonstrated by connecting ten 7.5 cm² "D"-shaped Li-LiCoO₂ cells in parallel giving a battery with a total active area of 75 cm². The battery was required to supply on a single charge a minimum of five pulses of 2.5 mA/cm² amplitude, 8.5 s duration, followed by a 2 s rest with a minimum of 60 mJ/cm² of energy per pulse. For 75 cm², these requirements translate to a pulse amplitude of 187.5 mA and an energy of 4.5 J per pulse. As shown in Fig. 15, the battery supplied twelve pulses of the required amplitude and energy on a single charge. Single laboratory cells with 1 cm² active areas typically could supply 10 to 15 pulses of the required current and energy densities.
There are many other possible application of thin-film lithium and lithium-ion batteries in consumer products such as cellular telephones and notebook computers. The number and types of applications will be limited only by the cost of production.

Acknowledgements

The authors thank Mr. Chris Luck and Mr. Ivan Dunbar for fabricating many of the thin-film batteries discussed in this paper. Also, we gratefully acknowledge the support over many years by the U.S. Department of Energy’s Division of Materials Sciences, Division of Chemical Sciences, and Laboratory Technology Transfer Research Program under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

References

[1] J. B. Bates, N. J. Dudney, D. C. Lubben, G. R. Gruzalski, B. S. Kwak, X. Yu, and R. A. Zuhr, *J. Power Sources* 54, 58 (1995).

[2] N. J. Dudney, J. B. Bates, and D. Lubben, p. 113 in *Role of Ceramics in Advanced Electrochemical Systems*, American Ceramic Society, Westerville, Ohio, 1996.

[3] B. Wang, J. B. Bates, F. X. Hart, B. C. Sales, R. A. Zuhr, and J. D. Robertson, *J. Electrochem. Soc.* 143, 3203 (1996).

[4] J. B. Bates, N. J. Dudney, B. J. Neudecker, and B. Wang, “Thin-Film Lithium Batteries,” in *New Trends in Electrochemical Technology: Energy Storage Systems in Electronics*, ed. by T. Osaka and M. Data, Gordon and Breach (in press).

[5] J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury, and C. F. Luck, *J. Power Sources* 43–44, 103 (1993).

[6] X. Yu, J. B. Bates, G. E. Jellison, and B. C. Sales, *J. Electrochem. Soc.* 144, 524 (1997).

[7] B. J. Neudecker, R. A. Zuhr, and J. B. Bates, “Lithium Silicon Tin Oxynitride (Li₅SiTON): High Performance Anode in Thin-Film Lithium-Ion Batteries for Microelectronics,” *Journal of Power Sources* (in press).

[8] B. J. Neudecker, R. A. Zuhr, and J. B. Bates, Meeting abstracts for 196th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 17–22, 1999.
[9] B. J. Neudecker, N. J. Dudney, and J. B. Bates, “Lithium-Free Thin-Film Battery with In-Situ Plated Li Anode,” *Journal of the Electrochemical Society* (in press).

[10] B. S. Kwak, J. B. Bates, and F. X. Hart, p. 137 in *Thin-Film Solid Ionic Devices and Materials*, ed. by J. B. Bates, The Electrochemical Society, Pennington, New Jersey, 1996.

[11] A. Ueda, J. B. Bates, and R. A. Zuhr, *Proceedings of the Electrochemical Society*, Boston, Massachusetts, November 1–6, 1998 (in press).

[12] N. J. Dudney, J. B. Bates, R. A. Zuhr, S. Young, J. D. Robertson, H. P. Jun, and S. A. Hackney, “Nanocrystalline Li$_x$Mn$_{2-y}$O$_4$ Cathodes for Solid State Thin-Film Rechargeable Lithium Batteries,” *Journal of the Electrochemical Society* (in press).

[13] B. J. Neudecker, R. A. Zuhr, B. S. Kwak, J. B. Bates, and J. D. Robertson, *J. Electrochem Soc.* **145**, 4148 (1998).

[14] B. J. Neudecker, R. A. Zuhr, J. D. Robertson, and J. B. Bates, *J. Electrochem. Soc.* **145**, 4160 (1998).

[15] M. Croft, D. Sills, J. B. Bates, P. Ansari, and A. Alaya, “A Mn-K Edge XAS Study of Thin-Film Li$_x$Mn$_2$O$_4$ Batteries,” *Physical Review B* (in press).

[16] [www.ssd.ornl.gov/BatteryWeb/](http://www.ssd.ornl.gov/BatteryWeb/)

[17] J. B. Bates and N. J. Dudney, *J. ASAIO* **43**, M644 (1997).

[18] F. X. Hart and J. B. Bates, *J. Appl. Phys.* **83**, 7560 (1998).

[19] J. B. Bates, N. J. Dudney, B. J. Neudecker, F. X. Hart, H. P. Jun, and S. A. Hackney, “Preferred Orientation of Polycrystalline LiCoO$_2$ Films,” *Journal of the Electrochemical Society* (in press).

[20] M. M. Thackeray, A. de Kock, M. H. Rossouw, D. Liles, R. Bittihn, and D. Hoge, *J. Electrochem. Soc.* **139**, 363 (1993).

[21] J. B. Bates, D. Lubben, N. J. Dudney, and F. X. Hart, *J. Electrochem. Soc.* **142**, L149 (1995).

[22] J. B. Bates, D. Lubben, N. J. Dudney, R. A. Zuhr, and F. X. Hart, p. 215 in *Thin Film Solid Ionic Devices and Materials*, ed. by J. B. Bates, The Electrochemical Society, Pennington, New Jersey (1996).

[23] Y. Shao-Horn, Y. Ein-Eli, A. D. Robertson, W. F. Averill, S. A. Hackney, and W. F. Howard, Jr., *J. Electrochem. Soc.* **145**, 16 (1998).
[24] M. M. Thackeray, M. F. Mansueto, and J. B. Bates, *J. Power Sources* **68**, 153 (1997).

[25] M. M. Thackeray, *J. Electrochem. Soc.* **144**, L100 (1997).

[26] T. Ohzuku, M. Iwanaga, S. Takeda, and S. Kitano, Abstract No. 121, 194th Meeting of the Electrochemical Society, Boston, Massachusetts, November 1–6, 1998.

[27] H. Kawai, M. Nagata, H. Tukamoto, and A. R. West, *Electrochem. and Solid-State Letters* **1**, 212 (1998).

[28] S. Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Bao, and J. R. Dahn, *J. Electrochem. Soc.* **144**, 205 (1997).

[29] Y. Ein-Eli, W. F. Howard, Jr., S. H. Lu, S. Mukerjee, J. McBreen, J. T. Vaughey, and M. M. Thackeray, *J. Electrochem. Soc.* **145**, 1238 (1998).

[30] N. J. Dudney, J. B. Bates, C. D. Evans, F. X. Hart, “Hysteresis in Thin-Film Rechargeable Lithium Batteries,” *Processing and Characterization of Electrochemical Materials and Devices*, Ceramic Transactions, American Ceramic Society (in press).

[31] D. H. Everett, W. I. Whitton, and F. W. Smith, *Trans. Faraday Soc.* **48**, 749 (1952) and **50**, 187 (1954).

[32] T. B. Flanagan, C.-N. Park, and W. A. Oates, *Prog. Solid St. Chem.* **23**, 291 (1995).
Figure Captions

1. Top: schematic cross section illustrating the layout of a thin-film battery. Bottom: Photograph of the fracture cross section of a thin-film lithium battery with a nanocrystalline as-deposited LiMn$_2$O$_4$ cathode fabricated on an alumina substrate. The apparent cracks in the Lipon electrolyte film and and pullouts from the cathode and substrate were caused by fracturing.

2. X-ray diffraction patterns of a 4 μm thick LiCoO$_2$ film and a commercial powdered sample. Peaks marked with * are due to the alumina substrate. The absence of the (003) reflection and the strong intensity of the (101) reflection from the film indicate a high degree of preferred orientation. The grains of the powdered sample are presumed to be randomly oriented.

3. Discharge of a lithium cell with a 1 cm$^2$ x 2.5 μm thick crystalline LiCoO$_2$ cathode.

4. Capacity and energy vs. discharge current for cells with crystalline 1 cm$^2$ crystalline LiCoO$_2$ cathodes. Lithium and lithium free cells discharged between 4.2 V and 3 V; lithium-ion cell discharged between 4.2 and 2.7 V. Cathode thickness: 2.5 μm, 3.2 μm, and 0.9 μm, respectively for the lithium, lithium-free, and Sn$_3$N$_4$ cells.

5. Discharge capacity vs. cycle number for lithium, lithium-free, and lithium-ion cells with LiCoO$_2$ cathodes of different thickness cycled at different currents ●. Lithium cells and ■ lithium-free cells cycled between 4.2 V and 3 V; lithium-ion cells with ◆ Sn$_3$N$_4$ and ▲ Zn$_3$N$_2$ anodes cycled between 4.2 V and 2.7 V. The cycle performance of cells with silicon-tin oxynitride anodes is similar to that of the Sn$_3$N$_4$ cells. The dotted horizontal lines drawn through the data for the lithium cells emphasize the negligible capacity loss. Cycles in the gaps marked by "X" in the data for the Li cell given in the top panel were obtained at 0.2, 0.4, and 0.8 mA and are not shown for clarity.

6. Comparison of low current discharge curves of lithium-ion and lithium or lithium-free cells with crystalline LiCoO$_2$ cathodes. Capacity in μAh per unit of area in cm$^2$ and thickness in μm of the cathode.

7. Low current cycles of Li-Li$_{1+x}$Mn$_{2-y}$O$_4$ cells with cathodes sputter deposited in (a) Ar + N$_2$ and (b) Ar + O$_2$ and annealed in O$_2$ at 700°C for 2 h. Cycling sequence: (i) discharge from 4.5 V to 1.5 V, (ii) charge from 1.5 V and 5.3 V, and
(iii) discharge from 5.3 V to 3.8 V. Dashed line in (b) is a discharge-charge cycle 4.5 V - 1.5 V - 5.3 V following 10 cycles between 5.3 V and 3 V.

8. Charge capacity above 4.5 V of a Li-Li$_{1+x}$Mn$_{2-y}$O$_4$ cell with cycling in different potential windows.

9. Charge-discharge between 3.5 V and 5.3 V of a lithium cell with a cathode deposited by co-sputtering LiMn$_2$O$_4$ and Mn in Ar + O$_2$ and annealing in O$_2$ at 800°C for 2h. Inset: charge-discharge of a lithium cell with a 0.05 µm thick cathode deposited over a Au/Mn current collector by sputtering LiMn$_2$O$_4$ in Ar + N$_2$ and annealing in O$_2$ at 700°C for 2 h.

10. (a): discharge-charge cycle of a Li-Li$_{1+x}$Mn$_{2-y}$O$_4$ cell between 4.5 V and 1.0 V. OCV data upon discharge (open circles) and charge (open squares) are the potentials reached after relaxing until dV/dt < 5 mV/h following each 0.5 µAh of insertion or extraction of Li. (b): potential vs. time to reach the condition dV/dt < 5 mV/h after each insertion of 0.5 µAh of Li. Inset shows the longest relaxation at the end of the two-phase region.

11. Top: discharge-charge cycle of a Li-LiMn$_2$O$_4$ cell between 4.5 V and 1.0 V. OCV data given by open circles (discharge) and squares (charge) are the potentials reached after relaxing until dV/dt < 5 mV/h following each 0.5 µAh of insertion or extraction of Li. Bottom: potential vs. time to reach the condition dV/dt < 5 mV/h after each insertion of 0.5 µAh of Li. Inset shows the longest relaxation at the end of the two-phase region.

12. (a) Low current discharge-charge (solid line) and OCV data (open circles) for a lithium cell with an as-deposited nanocrystalline (n) Li$_{1+x}$Mn$_{2-y}$O$_4$ cathode. (b) Scanning curves for a Li-nLi$_{1+x}$Mn$_{2-y}$O$_4$ cell.

13. (a): 20 µA/cm$^2$ discharge curves for a Li-nLi$_{1+x}$Mn$_{2-y}$O$_4$ cell after selected cycles at 25 and 100°C; (b): in-situ x-ray diffraction from this cell after cycles 300 and 4650.

14. Photographs of some of the prototype Li-LiCoO$_2$ thin-film batteries fabricated at ORNL. (a) "D" cell with a 7.5 cm$^2$ active area. (b) Battery with a 6.5 cm$^2$ active area fabricated on the backside of a multichip module package to power the circuit fabricated on the front side of the package shown in (c). Connection of the battery to the circuit was made by depositing the current collectors over gold coated through holes. (d) A typical experimental cell with a 1 cm$^2$ active area.

15. Current pulses and total energy delivered by each pulse (solid points) for a Li-LiCoO$_2$ battery consisting of ten cells, each with a 7.5 cm$^2$ active area, connected in
parallel. The 187.5 mA pulses were 8.5 s in duration and repeated every 2 s until the potential decreased below 2.5 V.