

Thin Film Micro-Batteries

by Nancy J. Dudney

Building a Battery by Vapor Deposition

Thin film batteries are built layer by layer by vapor deposition. The resulting battery is formed of parallel plates, much as an ordinary battery construction, just much thinner. The figure (Fig. 1) shows an example of a thin film battery layout where films are deposited symmetrically onto both sides of a supporting substrate. The full stack of films is only 10 to 15 μm thick, but including the support at least doubles the overall battery thickness. When the support is thin, the entire battery can be flexible. At least six companies have commercialized or are very close to commercializing such all-solid-state thin film batteries and market research¹ predicts a growing market and a variety of applications including sensors, RFID

tags, and smarter cards. In principle with a large deposition system, a thin film battery might cover a square meter, but in practice, most development is targeting individual cells with active areas less than 25 cm^2 . For very small battery areas, <1 mm^2 , microfabrication processes have been developed.² Typically the assembled batteries have capacities from 0.1 to 5 mAh.

The operation of a thin film battery is depicted in the schematic diagram (Fig. 2). Very simply, when the battery is allowed to discharge, a Li^+ ion migrates from the anode to the cathode film by diffusing through the solid electrolyte. When the anode and cathode reactions are reversible, as for an intercalation compound or alloy, the battery can be recharged by reversing the current. The difference in the electrochemical potential of the lithium determines the cell voltage.

Most of the thin films used in current commercial variations of this thin film battery are deposited in vacuum chambers by RF and DC magnetron sputtering and by thermal evaporation onto unheated substrates. In addition, many publications report exploring a variety of other physical and chemical vapor deposition processes, such as pulsed laser deposition, electron cyclotron resonance sputtering, and aerosol spray coating, for one or more components of the battery. The active materials used for the thin film cathodes and anodes are familiar intercalation compounds, but the microstructures and often the cycling properties of the thin films may be quite distinct from those of battery electrodes formed from powders. The thin film cathodes are dense and homogeneous with no added phases such as binders or electrolytes. When deposited at ambient temperatures, the films of cathodes, such as LiCoO_2 , V_2O_5 , LiMn_2O_4 , LiFePO_4 are amorphous or nanocrystalline. But even in this form, they often act as excellent cathodes with large specific capacities and good stability for hundreds to thousands of cycles.³ Annealing the cathode films at temperatures of 300° to 800°C may be used to induce crystallization and grain growth of the desired intercalation compound. Crystallizing the cathode film generally improves the Li chemical diffusivity in the electrode material, and hence the power delivered by the battery, by 1-2 orders of magnitude. The microstructure is also tailored by the deposition and heat treatment. Figure 3 shows a fracture edge of an annealed LiCoO_2 cathode film on an alumina substrate. The columnar microstructure, which is typical of a vapor deposited film, sinters at high temperatures leaving small fissures between the dense columns. Such crystalline films also may have a preferred crystallographic orientation. For LiCoO_2 films the crystallographic texture differs for films deposited by sputtering⁴ versus pulse laser ablation processes.⁵ To improve the manufacturability of the thin film batteries, it would be beneficial to eliminate or minimize the temperature or duration of the annealing step. Several efforts have led to low temperature fabrication of thin film batteries on polyimide substrates, but the battery capacity and rate are lower than those treated at high temperatures.^{6,7}

For the battery anode, many designs use a vapor-deposited metallic lithium film as both the anode and current collector. When used with a mechanically and chemically stable solid electrolyte, the lithium anodes give excellent charge-discharge

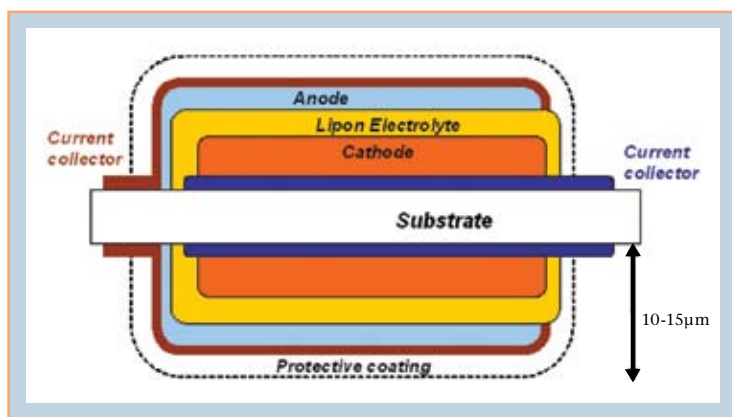


Fig. 1. Schematic cross section of a thin film battery fabricated by vapor deposition onto both sides of a substrate support.

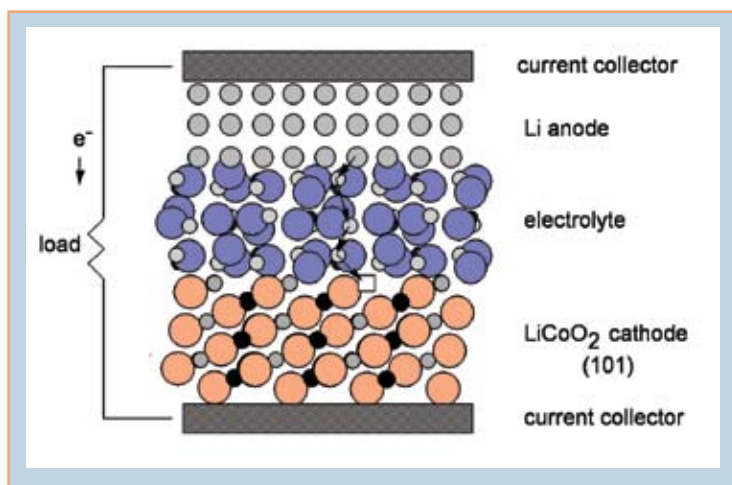


Fig. 2. Schematic illustration of a thin film battery. The arrows indicate the discharge reaction where a Li ion diffuses from the lithium metal anode to fill a vacancy in an intercalation compound that serves as the cathode. The compensating electron is conducted through the device.

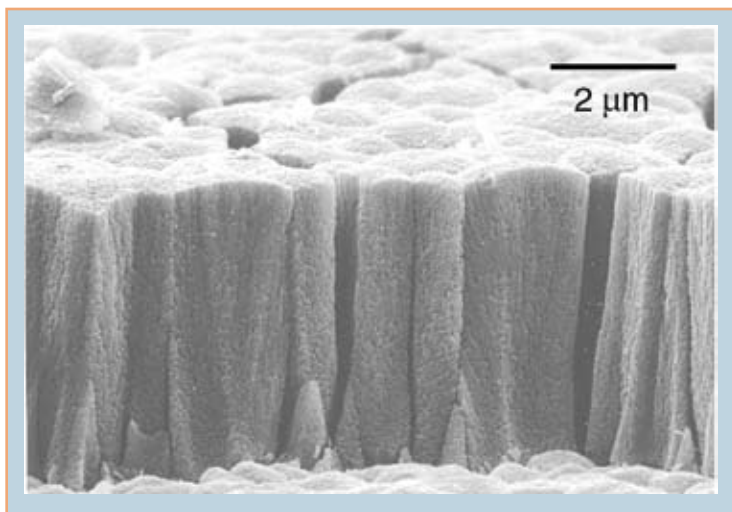


Fig. 3. Schematic cross section of a thin film battery fabricated by vapor deposition onto both sides of a substrate support.

cycling at high rates, and long battery life with no lithium dendrites. The chief drawback for metallic lithium anodes is the restricted maximum operating temperature to $<180^{\circ}\text{C}$, which avoids melting of the lithium. Alternatives that allow higher fabrication and operating temperatures include a Li-ion battery anode or a “Li-free” construction. For lithium-free batteries, the metallic lithium anode is omitted during the fabrication, but is subsequently plated at the anode current collector when the battery is charged for the first time.⁸ Lithium-ion anodes that have been proposed include single-phase and composite films based on reversible reactions of lithium with Sn, Si, Ge, and C. For the pure metals, only very thin films, ~ 50 nm, can tolerate the extreme volume changes associated with insertion and extraction of large amounts of lithium.^{9,10} Good cycling has been reported for various oxide, nitride and oxynitrides of Si, Sn, and Zn^{3,11} which likely form composite films upon cycling. Intercalation compounds, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$,¹² might also be used for thin film lithium-ion batteries.

Lipon, a Glassy Electrolyte

The thin film solid electrolyte invented at Oak Ridge National Laboratory in the early 1990s is the most widely used solid electrolyte for thin film batteries. The key insight by J. B. Bates was that addition of nitrogen to the glass structure might enhance the chemical and thermal stability of a lithium glass, as it does for sodium phosphate and sodium silicate glasses. The lithium phosphorus oxynitride electrolyte, which is now known as Lipon, is deposited by RF magnetron sputtering from a ceramic target of Li_3PO_4 using a nitrogen process gas to form the plasma.^{13,14} The films are amorphous and free of any columnar

microstructure or boundaries. Although the nitrogen partial pressure overwhelms that of the oxygen in the plasma, only a small amount of N replaces the oxygen in the composition, but this nitrogen has a profound effect on the ion conductivity and electrochemical stability. With a N/O ratio as small as 0.1, the ionic conductivity is 1 to 2 $\mu\text{S}/\text{cm}$, which is about 40-fold higher than glassy films of N-free Li_3PO_4 . More importantly, the ionic transport number of Lipon is one, the electrochemical window is enhanced to 5.5V versus Li/Li^+ , and Lipon is stable at both elevated temperatures and in contact with metallic lithium.¹⁵ The lithium ion conductivity, although 100X less than for many liquid electrolytes, is sufficient because just

1 μm -thick films are adequate for a pinhole-free barrier over most thin film electrodes. Further, the electronic resistivity of Lipon is very high, greater than $10^{14} \Omega\text{cm}$.

The ternary composition diagram (Fig 4) shows the composition range giving the highest lithium ion conductivity. The lithium content is slightly below that for the orthophosphate structure and spectroscopic studies indicate that much of the nitrogen substitutes for oxygen and forms links between two or three phosphate groups.¹⁴ The diagram also shows that the Lipon composition is well outside of the normal glass forming region. So far, synthesis of this material is limited to vapor deposition with an energetic source of nitrogen. When deposited by magnetron sputtering, film deposition rates can exceed 10 nm/m with good results. Higher Lipon deposition rates are reported for alternative processes such as plasma enhanced chemical vapor deposition¹⁶ and nitrogen ion beam assisted deposition.¹⁷

A variety of other inorganic and polymer electrolytes are being evaluated, but none have been as widely tested as the Lipon electrolyte in thin film rechargeable batteries. Inorganic glasses include binary and ternary mixes of lithium borate, phosphate, silicate, and vanadate, but most compositions do not appear to meet conductivity or stability standards. Glass-ceramics with higher ionic conductivities¹⁸ might be attractive as a self supporting electrolyte if fabricated as $<100 \mu\text{m}$ sheets. Promising polymer electrolytes are based on block copolymer compositions.¹⁹

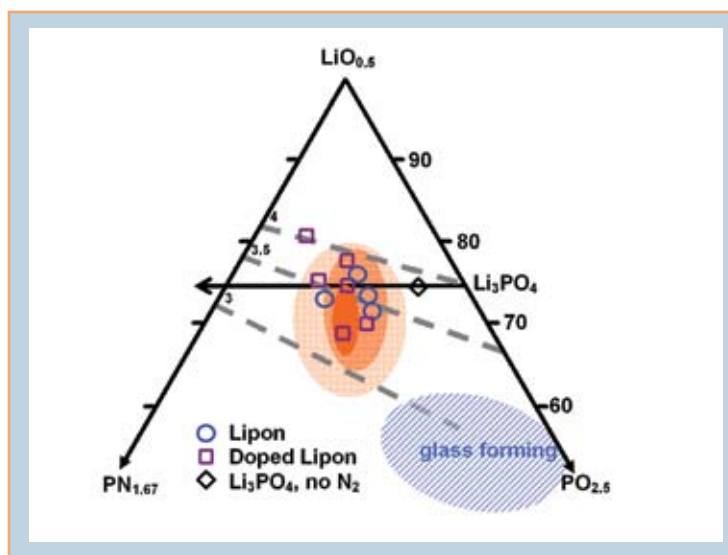


Fig. 4. Expanded region the $\text{LiO}_{0.5}\text{-PO}_{2.5}\text{-PN}_{1.67}$ composition diagram (mole percentages) showing results of thin electrolyte films obtained by magnetron sputtering. The orange shaded areas indicates the compositions giving increasing ionic conductivities exceeding 0.5, 1.0, and 2.0 $\mu\text{S}/\text{cm}$. Dashed lines indicate constant ratios of $(\text{N}+\text{O})/\text{P}$. The blue shading indicates the approximate compositions for glasses formed from a melt.

Cycle Life, Self Discharge, and Temperature Performance

Thin film batteries with several different cathode and anode materials have been cycled to hundreds and many thousands of deep cycles with little loss of capacity. This is attributed to: the stability of the Lipon electrolyte film, the ability of the thin film materials to accommodate the volume changes associated with the charge-discharge reactions, and the uniformity of the current and charge distribution in the thin film structure. With cycling, the batteries gradually become more resistive with aging rates that depend on the particular electrode materials, the thickness of the films, and the temperature and voltage range during operation of the battery.

As all-solid-state devices, thin film batteries can operate over a wider temperature range than most lithium-ion batteries. Results of reasonable cycling performance are reported for -40 and 150°C.^{16, 20} At low temperature, rates of battery charge and discharge are limited by the thermally activated diffusion and conduction processes, but no permanent damage to the battery occurs from freezing temperatures. When cycled at high temperatures, battery degradation increases and may be due to gradual microstructure or phase changes in the electrodes or at the interfaces. For example, aging for LiCoO₂ cathodes cycled above 75°C is associated with a trigonal to cubic transformation.²¹ There are no reactions reported where safety becomes a concern.

The self-discharge rates of most thin film batteries with a Lipon electrolyte are negligible. In fact, to obtain an accurate measure of the self discharge, the batteries must be physically disconnected and stored at open circuit because leakage currents through the testing equipment may exceed the internal self discharge rate of the battery. Thin film batteries as fabricated at ORNL can be expected to hold a full charge for years.³

Energy and Power

The energy and power delivered by thin film batteries are characterized by constant current discharge over a voltage range that gives a full depth of discharge at low currents. The Ragone plot (Fig. 5) of energy and average power shows results for typical thin film lithium batteries. These particular results are for batteries with a metallic lithium anode and a capacity limited by the mass of the cathode, but similar plots would be used to compare anode materials. Each curve

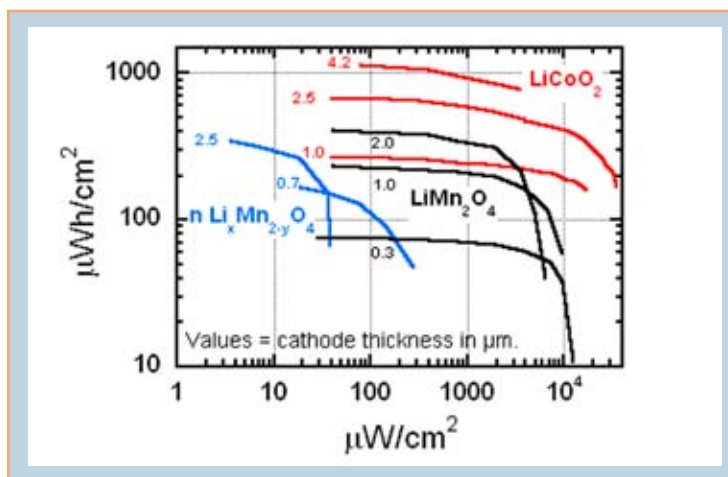


Fig. 5. Ragone plot for thin film lithium batteries comparing the energy and power delivered by constant current discharge. As indicated, the batteries have various crystalline and nanocrystalline (n) cathode materials with different film thicknesses. The energy and power are normalized by the active battery area.

represents a series of discharge curves for a battery with the designated cathode and cathode thickness. Cathodes that are X-ray amorphous have comparable energies, but less power than well crystallized cathodes. Thicker cathodes give proportionally higher energies, but often at the expense of the high power performance. The exception is for batteries with the highly conductive LiCoO₂ cathode films, where good performance with theoretical capacity utilization has been obtained for batteries made at ORNL with film thicknesses up to 4 μm. Intrinsic stresses in the films, as well as stresses due to electrochemical and thermal cycling, generally limit the cathode film thickness to several micrometers, but companies commercializing the thin film batteries report success in preparing LiCoO₂ cathodes well above 4 μm thick.²² Energy densities for a planar cell with thick cathodes may reach 2-3 mWh/cm².

Batteries with LiCoO₂ cathodes can be discharged at very high continuous and pulsed current densities. Similarly they can be rapidly charged at high currents. Charging at constant voltage is the simplest and fastest way to recharge a thin film battery. Batteries with a LiCoO₂ cathode can be charged at 4.2 or 4.5 V to >90% full capacity within a few minutes if the charging device can deliver a high current. At the other extreme, thin film batteries can be charged at trickle currents of <1 μA/cm², such as might be produced by an energy scavenging device.

For application of thin film batteries as energy storage for energy harvesting and scavenging devices, the energy efficiency is important. Energy dissipated in the battery charge and discharge is evident as a voltage gap between the charge and discharge curve of a battery cycle, such as shown in Fig. 6. For batteries with highly crystalline and reversible electrode materials such as

LiCoO₂ and LiMn₂O₄ cathodes with Li anodes, the battery cycling efficiency at low currents exceeds 96%. For batteries with amorphous cathodes, the energy efficiency is lower even for low current densities because of the hysteresis in the lithium insertion reaction for these materials.²³ Efficiencies may be only 80%.

For thin film batteries it is convenient to normalize values of energy and power by the active area of the battery because these values do not depend on the choice of substrate and protective packaging. If the substrate and packaging are negligible, the active battery components (*i.e.*, the current collectors plus electrode films and Lipon) sum to roughly 3 to 7 mg and 0.7 to 1.5 μl per cm² active area depending on the thicknesses of the active electrode films. A 1 mWh battery would be just 2.5 mg and less than 1 μl, so that specific energy and power approach 400 Wh/kg and 1 kWh/L. Under more realistic assumptions where a light-weight substrate and coating are included, the mass and volume of the battery is increased by 2- to 5-fold.

Protecting and Integrating the Battery with Devices

Supporting the battery on a thin lightweight substrate and protecting the lithium metal and lithium compounds from reaction with gases in the air have been perhaps the largest challenges in commercializing the thin film battery technology. A variety of proprietary packaging materials and battery layouts, such as an inverted stack,²⁴ are being used to ensure an effective, light-weight and inexpensive packaging. Thin film batteries have been fabricated on thin sheets of metal, polyimide, ceramics, silicon, and mica. For overlayer protection, limited success was achieved at ORNL with a conformal

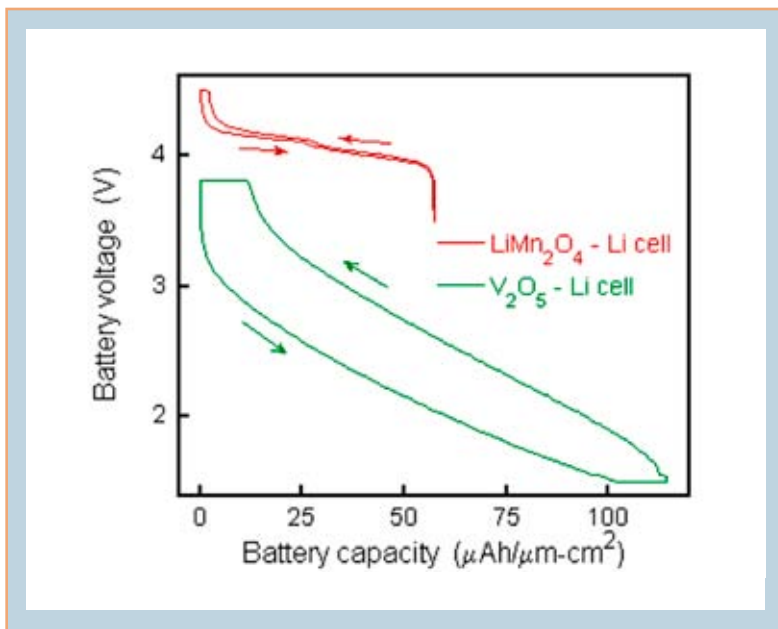


Fig. 6. Charge–discharge curves for a battery cycle measured with a low current density. The open loop for a battery with a V_2O_5 cathode is typical of batteries with an amorphous cathode, while batteries with crystalline cathodes nearly overlap.

coating of Parylene-C²⁵ alternating with sputtered metal or oxide films. Tests indicate that failure of the parylene protection initiates with flaws in the films. In applications where batteries are subject to mechanical abuse, thin film coatings are obviously insufficient and more robust materials are used for packaging and protection.

For near term applications, the complete thin film battery will be added to the device by soldering or lamination. When solder reflow bonding is needed, thin film batteries with Li-ion or Li-free anodes can be used. In the fully discharged state, these batteries can survive repeated solder reflow bonding procedures at 265°C without degradation of properties.²⁶ Ultimately however, the most efficient use of thin film batteries is in a fully integrated device. When physically integrated, the materials needed to support and protect the thin film battery should serve a dual purpose as an active or protective component of the device. Examples include thin film batteries deposited onto the back of a ceramic integrated circuit chip carrier and thin film batteries deposited on a substrate shared with thin film solar cells. Full integration of the battery and device requires coordination and compatibility of the fabrication processing which favors an all solid-state battery.

Ideally the battery and device should be functionally integrated as well. This minimizes power conditioning electronics that add complexity and mass to the device and reduce the overall energy efficiency. For thin film batteries, control of the voltage range is essential, while the current for pulse charge can vary widely. Although

more robust than batteries with liquid electrolytes, the thin film batteries may suffer irreversible damage from voltage excursions leading to prolonged overcharge or over-discharge conditions. With proper choice and balance of electrodes, some thin film lithium-ion batteries will survive full short circuit discharge.²⁷ Coordination at an early stage of the device design allows both device and battery to be tailored for maximum efficiency and voltage control.

Reducing the Footprint

For many small devices it may be inconvenient or impossible to accommodate a large planar battery area required to meet the energy or power requirements of the device. Stacking multiple cells to limit the footprint is a solution being developed commercially. With relatively thick electrodes, a stack consisting of a small number of thin film batteries connected in parallel can readily match projections of 5 mWh/cm² and 3.5 mAh/cm² proposed for more complex 3-dimensional battery structures.^{10,28} Another solution is to use higher surface area substrates, including fibers²⁹ and sheets with shallow machined ridges and dimples to provide more active area per footprint. These approaches preserve the uniform charge and current distribution of the planar battery architecture. For microbattery packages of millimeter-scale dimensions, efficient connection of many tiny cells in parallel will be needed. Future advances may lead to techniques to stack batteries directly by vapor deposition which will eliminate the volume and mass associated with multiple support layers.

Outlook

Research on thin film batteries has led to many hundreds of publications in the last five years. Applications for thin film batteries include: RFID tags, wireless sensors, medical devices, memory backup power, batteries for extreme high and low temperatures, and energy storage for solar cells and other harvesting devices. Manufacturing challenges, especially reduction of cost, are being addressed by current development efforts. Advanced processing will lead to high film deposition rates, reduced processing temperatures, and high yields. Exploration for new thin film materials, particularly those that can be used as thick anode and cathode films, will improve energy and power densities. In addition, research on materials for effective packaging and electrical connections for multi-cell battery assembly will be critical to enable many applications of thin film batteries. ■

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About the Author

NANCY J. DUDNEY is a senior staff scientist in the Materials Science and Technology Division at Oak Ridge National Laboratory. The focus in her research has been ion transport and mixed electronic/ionic conduction in materials for electrochemical applications with emphasis on thin film materials, lithium intercalation reactions, solid electrolytes, and most recently materials for heterogeneous catalysts. She joined ORNL as a Wigner Fellow after receiving a PhD in ceramic materials from the Massachusetts Institute of Technology and a BS in chemistry from the College of William and Mary. She may be reached at dudneynj@ornl.gov.

References

1. NanoMarkets Report, Thin-Film and Printed Batteries Market, White Paper, March 2008, www.nanomarkets.net.
2. W. C. West, J. F. Whitacre, V. White, and B.V. Ratnakumar, *J. Micromech. Microeng.*, **12**, 58 (2002).
3. N. J. Dudney, *Mat. Sci. Eng. B*, **116**, 245 (2005).
4. 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)

Dudney

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5. P. J. Bouwman, B. A. Boukamp, H. J. M. Bouwmeester, and P. H. L. Notten, *J. Electrochem. Soc.*, **149**, A699 (2002).
6. M. Hayashi, M. Takahashi, and Y. Sakurai, *J. Power Sources*, **174**, 990 (2007).
7. J. F. Whitacre, W. C. West, E. Brandon, and B. V. Ratnakumar, *J. Electrochem. Soc.*, **148**, A1078 (2001).
8. B. J. Neudecker, N. J. Dudney, and J. B. Bates, *J. Electrochem. Soc.*, **147**, 517 (2000).
9. B. Laforge, L. Levan-Jodin, R. Salot, and A. Billard, *J. Electrochem. Soc.*, **155**, A181 (2008).
10. P. H. L. Notten, F. Roozeboom, R. A. H. Niessen, and L. Baggetto, *Adv. Mat.*, **19**, 4564 (2007).
11. B. J. Neudecker, R. A. Zuhr, and J. B. Bates, *J. Power Sources*, **81-82**, 27 (1999).
12. C.-L. Wang, Y. C. Liao, F. C. Hsu, N. H. Tai, and M. K. Wua, *J. Electrochem. Soc.*, **152**, A653 (2005).
13. J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury, C. F. Luck, and J. D. Robertson, *Solid State Ionics*, **53-56**, 647 (1992).
14. J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury, C. F. Luck, and J. D. Robertson, *J. Power Sources*, **43-44**, 103 (1993).
15. X. Yu, J. B. Bates, G. E. Jellison, Jr., and F. X. Hart, *J. Electrochem. Soc.*, **144**, 524 (1997).
16. <http://www.excellatron.com/high.htm>.
17. F. Vereda, R. B. Goldner, T. E. Haas, and P. Zerigian, *Electrochem. Solid-State Lett.*, **5**, A239 (2002).
18. <http://www.ohara-inc.co.jp/en/product/special/lic-gc.html>.
19. P. E. Trapa, Y. Y. Won, S. C. Mui, E. A. Olivetti, B. Y. Huang, D. R. Sadoway, A. M. Mayes, and S. Dallek, *J. Electrochem. Soc.*, **152**, A1 (2005).
20. <http://www.frontedgetechnology.com/tech.htm>.
21. C. N. Li, J. M. Yang, V. Krasnov, J. Arias, and K. W. Nieh, *Electrochem. Solid-State Lett.*, **11**, A81 (2008).
22. Personal communication.
23. N. J. Dudney, J. B. Bates, and C. D. Evans, in *Ceramics Transactions*, **109**, 341 (2000) 341.
24. S. H. Lee, P. Liu, and C. E. Tracy, *Electrochem. Solid-State Lett.*, **6**, A275 (2003).
25. http://www.vp-scientific.com/parylene_properties.htm.
26. <http://www.oakridgemicro.com/tech/reflowtests.pdf>.
27. <http://www.oakridgemicro.com/tech/shortcircuittest.pdf>.
28. D. Golodnitsky, M. Nathan, V. Yufit, E. Strauss, K. Freedman, L. Burstein, A. Gladkikh, and E. Peled, *Solid State Ionics*, **177**, 2811 (2006).
29. http://www.itnes.com/technologies/lithium_ion.html.

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