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Rechargeable Thin-Film Lithium Batteries

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Abstract

Rechargeable thin-film batteries consisting of lithium metal anodes, an amorphous inorganic electrolyte, and cathodes of lithium intercalation compounds have recently been developed. The batteries, which are typically less than 6- μm thick, can be fabricated to any specified size, large or small, onto a variety of substrates including ceramics, semiconductors, and plastics. The cells that have been investigated include Li-TiS₂, Li-V₂O₅, and Li-Li_xMn₂O₄, with open circuit voltages at full charge of about 2.5, 3.6, and 4.2, respectively. The development of these batteries would not have been possible without the discovery of a new thin-film lithium electrolyte, lithium phosphorus oxynitride, that is stable in contact with metallic lithium at these potentials. Deposited by rf magnetron sputtering of Li₃PO₄ in N₂, this material has a typical composition of Li_{2.9}PO_{3.3}N_{0.46} and a conductivity at 25°C of 2 $\mu\text{S}/\text{cm}$. The maximum practical current density obtained from the thin-film cells is limited to about 100 $\mu\text{A}/\text{cm}^2$ due to a low diffusivity of Li⁺ ions in the cathodes.

NEARLY TEN YEARS AGO, groups in Japan [1] and France [2] reported the fabrication of thin-film rechargeable batteries based on a lithium anode, an amorphous inorganic lithium ion conducting electrolyte, and a TiS₂ cathode. The batteries had an open circuit voltage of about 2.5 V, and one of the Japanese cells was cycled 2000 times at current densities of up to 16 $\mu\text{A}/\text{cm}^2$. These promising results led to speculation about many possible applications for thin-film "microbatteries" in electronic devices, such as standby power for CMOS memory

chips in which the battery might be deposited onto the chip or the chip carrier. Although several U.S. patents resulted from the early Japanese work, no commercial applications have been reported, likely because of the lack of an electrolyte with sufficient long-term stability in lithium cells and the lack of a satisfactory protective coating.

One approach to the stability problem is to coat the electrolyte with a layer of LiI before depositing the lithium anode [3-5]. While this has allowed the fabrication of Li-TiS₂ cells with very long cycle lives and excellent shelf life [4,5], it introduces an extra layer into the battery. Recently, we reported [6,7] the synthesis of a new lithium electrolyte that is stable in contact with lithium at high-cell potentials, and thin-film rechargeable lithium batteries with several different kinds of cathodes having open circuit voltages (OCV) ranging from 4.2 to 2.5 V have been fabricated using this material [7,8]. Also, encouraging results have been obtained with a thin-film protective coating presently under investigation in our laboratory. In this paper, we present a short review of our work on rechargeable thin-film lithium batteries.

Cell Fabrication and Characterization

A cross-sectional drawing of a typical thin-film battery is shown in Fig. 1. The cathode illustrated is amorphous vanadium pentoxide (V₂O₅), but it could be any one of several lithium intercalation compounds that can be deposited in thin-film form such as titanium disulfide, TiS₂, or lithium manganese oxide, LiMn₂O₄. The steps for the fabrication of a Li-V₂O₅ cell illustrated in Fig. 2 include:

1. V current collectors—dc magnetron sputtering of V in Ar
2. V_2O_5 cathode—dc magnetron sputtering of V in Ar + 14% O_2
3. Li electrolyte—rf magnetron sputtering of Li_3PO_4 in N_2
4. Li anode—evaporation of Li (10^{-6} Torr)
5. Protective coating

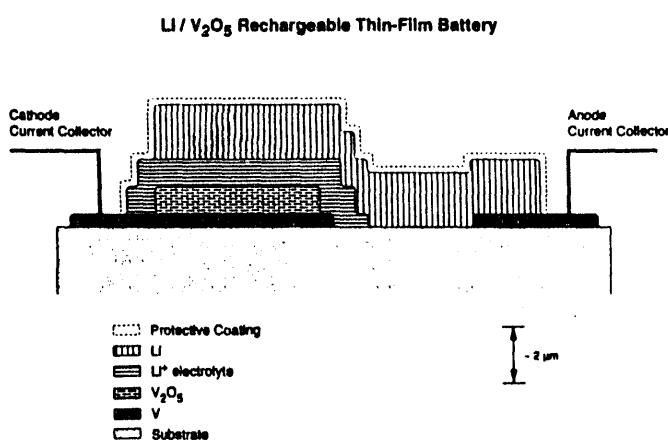


Fig. 1. Schematic cross section of a thin-film lithium battery.

Cells based on TiS_2 and $LiMn_2O_4$ were fabricated in a similar manner using cathodes prepared by the methods described in the literature [4,5,9]. The $LiMn_2O_4$ cell was fabricated in the discharged state. For the sputter depositions, two inch magnetrons (Torus) were used. The commercial V target had a specified purity of 99.97%; the Li_3PO_4 target was prepared by pressing Li_3PO_4 powder (Johnson Mathey, 99.9%) into a 2"-diameter \times about 1/8"-thick disk and then sintering the disk in air at $900^\circ C$ for 4 hrs. The substrate was located 5 cm above the targets, and the total pressure during sputtering was 20 mTorr. The slowest steps in the fabrication were the deposition of the cathode and electrolyte films at rates of about $0.1 \mu m/hr$ using a powers of about 30 W (dc) and about 35 W (rf) applied to the V and Li_3PO_4 targets, respectively. Typically the cathode and electrolyte films were each about $1\text{-}\mu m$ thick. A variety of techniques have been used to characterize the physical and chemical properties of individual cathode and electrolyte films [10,11]. These include Rutherford backscattering spectrometry (RBS), proton induced gamma ray emission spectrometry (PIGE), x-ray diffraction,

scanning electron microscopy (SEM), x-ray microanalysis, x-ray photoelectron and Auger electron spectroscopies, and ac impedance.

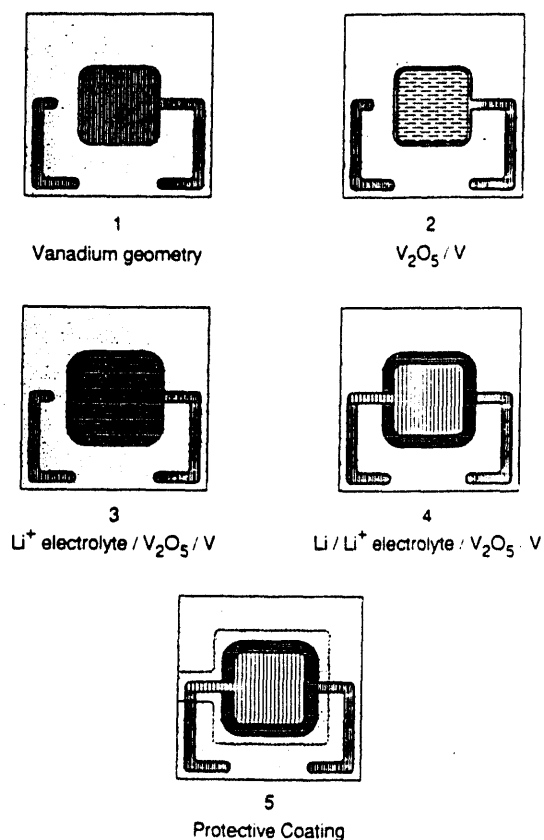


Fig. 2. Deposition sequence and typical geometry of a thin-film lithium battery.

The lithium films were deposited at a rate of about $10 \mu m/hr$ by evaporation of lithium metal contained in a Ti crucible. The substrate was located a few millimeters above a chimney placed on top of the crucible to minimize Li deposition on the chamber walls and fixtures. The Li films were typically 3- to $5\text{-}\mu m$ thick corresponding to three times to 10 times more lithium required for full discharge of the $1\text{-}\mu m$ thick cathode films. All of the operations with lithium were carried out in a recirculating glove box filled with Ar (99.999%) with the O_2 and H_2O content maintained at a few ppm. Prior to starting a series of lithium depositions, the box was purged with Ar to remove any residual N_2 . After deposition of the lithium film, the cells were transferred in Ar to a another deposition system where the protective coating was applied. The main function of the coating is to protect the lithium anode from air and water vapor, but it also protects nearby electronic components from contact with lithium.

Laboratory cells typically have an area of about 1 cm² and are about 6- μ m thick, and they are usually deposited on 1" square glass microscope slides. However, batteries could be fabricated to virtually any scale, large or small, as required for a particular application. Also the cells could be made in most any shape provided only that the electrolyte film completely separates the cathode and anode films. For cells based on V₂O₅ or TiS₂ cathodes, all of the films are deposited at ambient temperature, so batteries can be fabricated on virtually any substrate capable of supporting a thin film. For example, Li-V₂O₅ cells have been fabricated on alumina, glass, and 0.1-mm-thick polyester. Another promising cathode material, LiMn₂O₄ [9], requires a post deposition anneal at 400°C in order to obtain the crystalline spinel phase. Consequently, until a lower temperature deposition process can be found, the selection of substrates onto which Li-Li_xMn₂O₄ batteries can be fabricated is limited.

Cycling of the thin-film cells was carried out at constant current between specified voltage limits using two Keithley 617 electrometers operated under computer control. At the end of each half-cycle, the voltage was held constant until the current decreased to a specified fraction of the charge or discharge current, usually 10%. The impedance of the cells was measured at 25°C at frequencies from 0.01 Hz to 10 MHz using the methods described elsewhere [11]. These measurements were made at different cell potentials on both charge and discharge cycles. A dc bias equal to the OCV was applied to the cells during the impedance measurements, and the ac voltage was 50 mV or less. The OCV measured before and after the impedance measurements agreed within a few mV.

Results and Discussion

The good performance of the thin-film rechargeable lithium batteries discussed below is due primarily to the electrolyte, lithium phosphorus oxynitride, denoted by Lipon. This is a recently synthesized material [6,7] that has a lithium ion conductivity of about 2×10^{-6} S/cm at 25°C, a Li⁺ transport number of unity, and, most importantly, is stable in contact with metallic Li at high-cell voltages. Recent I-V measurements on V/Lipon/V thin-film structures indicate that the decomposition voltage is higher than 5 V. The composition of Lipon, as determined from RBS and PIGE measurements [7], is typically Li_{3.3}PO_{3.8}N_{0.22}, but the N content has been observed to vary from 2 to 6 at. %.

The vanadium oxide films were x-ray amorphous. Their O/V ratios determined from RBS and Auger measurements agreed well: O/V = 2.5 ± 0.1 . The density of the V₂O₅ films has not been accurately determined, but by comparing the film thickness measured with a profilometer with the mass of the deposited film determined with a quartz crystal oscillator, the average density of six films was 3 g/cm³. Kennedy et al. [12] reported that the density of V₂O₅ films grown by evaporation ranged from 2.42 g/cm³ to 2.69 g/cm³. We measured the electronic conductivity of a V₂O₅ film sandwiched between V contacts to be 1.5×10^{-7} S/cm at 25°C, compared to 10^{-6} S/cm for the evaporated thin films [12] and 6.5×10^{-6} S/cm reported [13] for bulk amorphous V₂O₅. The TiS₂ cathodes [5] were x-ray amorphous, presumably due to a small crystallite size, and the S/Ti ratio was 2.09. The composition and phase of the crystalline LiMn₂O₄ cathode was confirmed by x-ray diffraction.

Examples of discharge curves for Li-TiS₂, Li-V₂O₅, and Li-Li_xMn₂O₄ cells are shown in Fig. 3. The data are plotted as cell voltage vs. the quantity of charge passed per volume of cathode. The voltage decrease with discharge is characteristic of intercalation cathodes, and the magnitude of the voltage at any given point on the discharge curve depends on the cathode material and on the amount of lithium intercalated into its structure.

While the cells are normally cycled at room temperature, they are capable of operating at any temperature up to the melting point of Li at 180°C. A Li-V₂O₅ cell, for example, has been operated at -20°C and at 150°C.

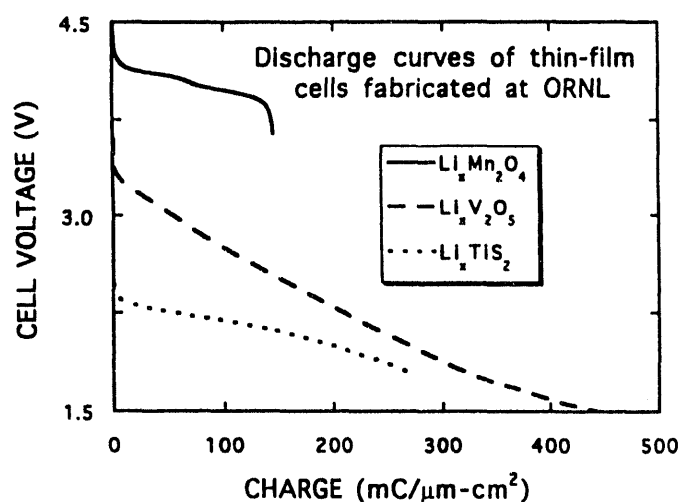
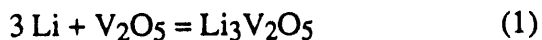
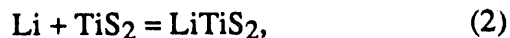


Fig. 3. Discharge curves for three types of thin-film batteries.

The Li-V₂O₅ and Li-TiS₂ cells are deposited in the fully charged state. The first deep discharge of these cells to 1.5 V and 1.8 V, respectively, is represented by



and



respectively. On the subsequent charge cycle, about 2.8 Li per V₂O₅ is extracted from the V₂O₅ cathode compared to the total mass of the film. This is illustrated in charge-discharge curves for a Li-V₂O₅ cell in Fig. 4 where it can be seen that the quantity of charge passed through the cell on the first discharge is larger than that of the following cycles. A similar effect is found for the Li-TiS₂ cells [5]. This initial large loss in capacity is not well understood, but it is typical of intercalation compounds. It has been suggested [14,15] that a discharge below about 2 Li per V₂O₅ induces an irreversible structural change in V₂O₅ forming domains with deep potential wells that trap some of the lithium ions. These ions then are not extracted on subsequent charge cycles. As illustrated in Fig. 5, after the first discharge, there is a slow but continuous decrease of about 0.4% per cycle in the amount of lithium inserted into and extracted from the cathode, possibly due to further irreversible structural changes.

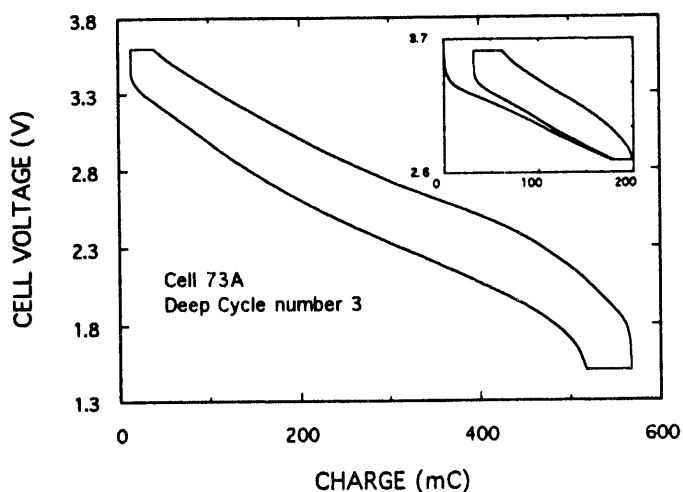


Fig. 4. Examples of the first discharge and first few cycles of a Li-V₂O₅ cell.

Examples of the charge-discharge curves for a Li-Li_xMn₂O₄ cell are shown in Fig. 6. The as-deposited cathode has a composition near LiMn₂O₄ [9], and the open circuit voltage of a cell can vary

between 3 and 3.9 V depending on the exact lithium content. The battery is first charged to 4.5 V. Assuming that one Li per Mn₂O₄ is extracted from the cathode during this initial charge [9], the subsequent discharge-charge cycles, restricted to the voltage range shown in Fig. 6, should be represented by

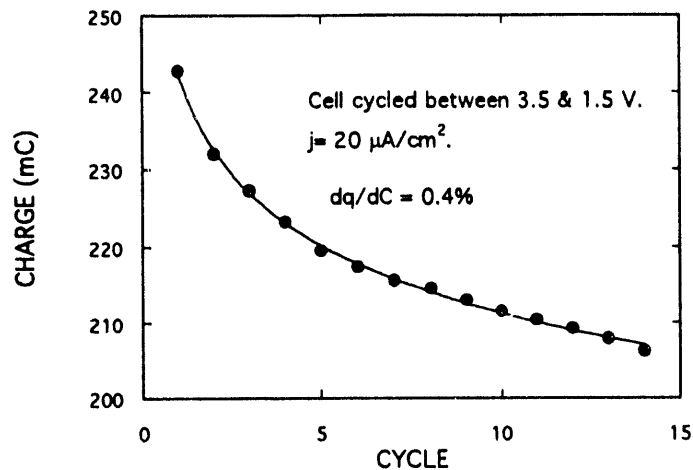
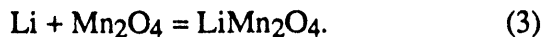


Fig. 5. Graph of the charge inserted into a V₂O₅ cathode as a function of the cycle number for cycling between 3.5 V and 1.5 V. The solid curve through the data is a fit of a power law fit in cycle number.

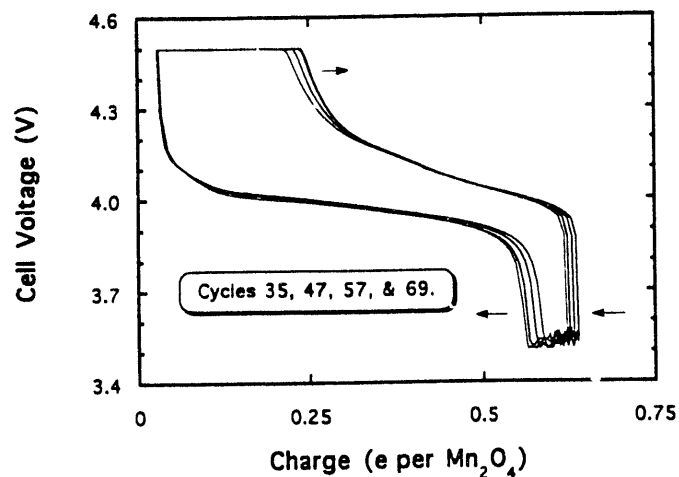


Fig. 6. Several charge-discharge curves for a Li-Li_xMn₂O₄ cell following the initial charge.

However, compared to the amount of cathode deposited, about 0.6 Li per Mn₂O₄ is cycled through the cell after the initial charge. Possibly the

assumed quantity of lithium initially extracted from the cathode was too large, but in any case it appears that a significant fraction of the as-deposited cathode becomes "electrochemically inactive" after the initial charge. This suggests an irreversible structural change occurs on the initial charge.

The charge-discharge curves are well-behaved provided the lower voltage limit does not fall below about 3.6 V. After the first charge, the amount of lithium that can be inserted into the cathode continues to decrease by about 0.1% on each successive cycle. This is shown by the data in Fig. 7, and it indicates that there is a continuous subtle change in the structure of the cathode with each cycle. If the discharge is extended beyond the cathode composition of LiMn_2O_4 (i.e., $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$), the cell potential drops abruptly to 3 V indicating the appearance of a second phase. When the discharge voltage was reduced to 3 V after completing 70 cycles of the $\text{Li-Li}_x\text{Mn}_2\text{O}_4$ cell, the films detached from the substrate possibly due to the nearly 6% increase in unit cell volume that occurs during the phase change [16].

Except for the small loss in cell capacity, all three of the thin-film lithium batteries show no degradation in performance after many charge-discharge cycles. Jones and colleagues at Eveready Battery Co. [5] have achieved more than 10,000 cycles with some of their Li-TiS_2 cells with little change in cell performance between the first and last cycle. We believe that this unique property of thin-film solid state cells is due to the rigid interfaces between the lithium anode and the

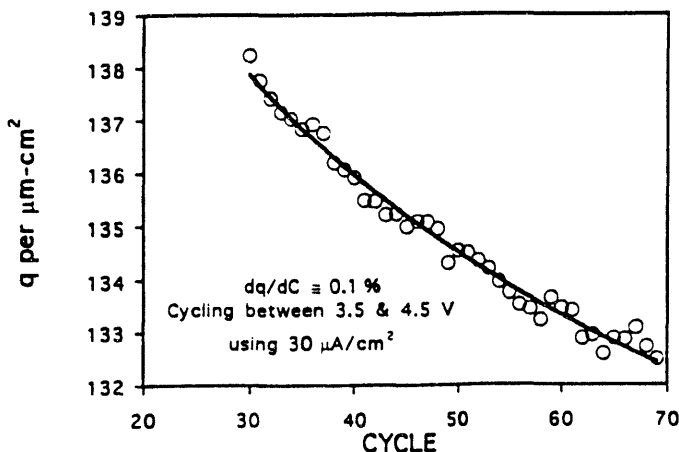


Fig. 7. The charge extracted from the $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode as a function of the cycle number.

electrolyte and between the electrolyte and the cathode. A Li-TiS_2 cell with a Lipon electrolyte was cycled over 4000 times before failing due to a short circuit. The cell was fractured in a glove box

and transferred to an SEM under high purity Ar. The micrograph of one of the fracture cross sections shown in Fig. 8 shows that the interface between the lithium anode and the electrolyte remained smooth. There is no evidence for the formation of lithium dendrites that occurs on cycling of lithium cells having organic liquid or polymer electrolytes. The shelf life of thin-film lithium batteries is also good. We observed no significant change in the open circuit voltage of a $\text{Li-V}_2\text{O}_5$ cell stored for more than 12 months.

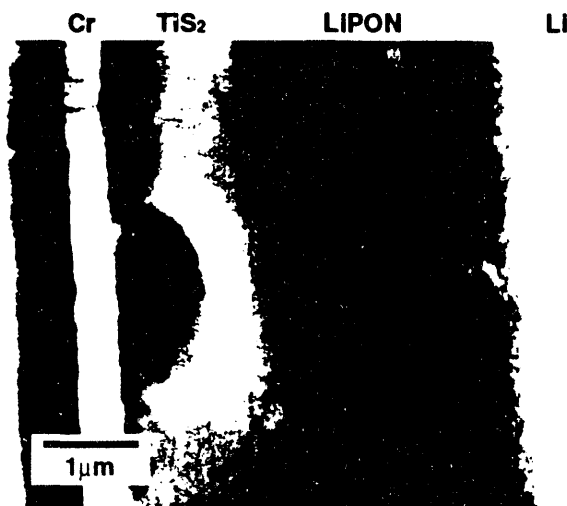


Fig. 8. SEM micrograph of a fracture cross section of a Li-TiS_2 cell after more than 4000 cycles.

The energy densities, specific energies, and capacities for the Li-TiS_2 , $\text{Li-V}_2\text{O}_5$, and $\text{Li-Li}_x\text{Mn}_2\text{O}_4$ thin-film batteries are listed in Table 1. The energy of the cells was determined from the integrals $\int V(q)dq$ over the respective discharge curves (Fig. 3) calculated between the voltages specified in the first column in the table. The mass and volume of the cells were based on 1- μm -thick cathode and electrolyte films plus an anode film thick enough to provide three times the maximum amount of Li required by the respective cathodes as specified in equations 1-3 above. For the cathodes, the crystalline densities were assumed, although the actual densities of the TiS_2 and V_2O_5 films are lower. This procedure was followed because the density of the LiMn_2O_4 film has not been determined. For the electrolyte film, the density of 2.4 g/cm^3 reported [17] for a bulk lithium phosphorus oxynitride glass was assumed. Since the capacity of a battery scales with the volume of the cathode for an excess of the anode, the data in Table 1 can be used to estimate the

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Table 1. Comparison of three types of rechargeable thin-film lithium batteries.

Cathode	Voltage (V)	Capacity	Energy Density ^a (Wh/l)	Specific Energy (Wh/kg)
		($\mu\text{Ah}/\text{cm}^2\text{-}\mu\text{m}$)		
TiS ₂	2.45–1.8	75	364	225
V ₂ O ₅	3.7–1.5	123	611	444
Li _x Mn ₂ O ₄	4.2–4.0	40	433	211

^a Based on the combined mass of the lithium anode at three times overcapacity, the electrolyte film 1- μm thick, and the cathode. Crystalline densities of the cathodes assumed to calculate the volume of the cells.

cathode size required for a given application. A tradeoff occurs in deciding whether to increase the thickness of a cathode or its area to achieve a required capacity: a thicker cathode will increase cell resistance and lower the maximum current, while a thinner cathode with larger area will allow higher currents but requires more lateral space.

Presently, the current density of rechargeable thin-film batteries with 1- μm -thick cathodes is limited to about 100 $\mu\text{A}/\text{cm}^2$ without an excessive voltage drop due to internal resistance. From impedance data for each of the three types of cells investigated, the diffusion of Li⁺ ions from the electrolyte into the cathode is the major source of this resistance over most of the charge-discharge range. A graph of this diffusion resistance (R_d) as a function of cell voltage for two Li-V₂O₅ cells is shown in Fig. 9. As the data indicate, R_d can differ by several orders of magnitude for different cells at high charge states. The decrease in R_d with decreasing cell voltage shows that the rate limiting step in the transfer of Li⁺ from the electrolyte to the cathode is the insertion of Li⁺ ions into the V₂O₅ structure: the diffusivity of Li⁺ in V₂O₅ increases as the Li⁺ content increases (cell voltage decreases). The electronic resistivity is also expected to decrease in a similar manner, but we know from the ac and dc measurements on the cathode alone that the electronic conductivity in V₂O₅ is much higher than the ionic conductivity. From analysis of the impedance data, the diffusion coefficient of Li⁺ in V₂O₅ at 25°C ranges from 4×10^{-15} cm²/s to 3×10^{-12} cm²/s depending on the particular cell and the state of charge. These are effective diffusion coefficients which include the effects of ion mobility, thermodynamic enhancement factors, film microstructure and composition.

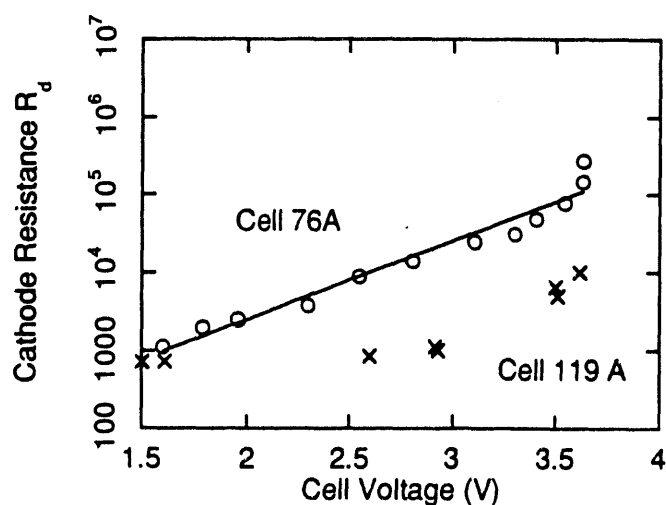


Fig. 9. Graphs of the resistance R_d due to Li⁺ ion diffusion into the cathode as a function of cell voltage for two Li-V₂O₅ cells.

Multicell thin-film batteries can be fabricated to obtain higher currents and capacities or higher voltages. By continuing the deposition sequence in Fig. 2, a two-cell Li-V₂O₅ battery with a 7.4 V to 3 V operating range was recently fabricated. The anode current collector of the bottom cell was separated from the cathode current collector of the top cell by a thin layer of the protective coating, and it was extended outside of the coating to allow the cells to be connected in series or parallel, or to allow them to be operated independently. Where space is not critical, a battery constructed of an array of thin-film cells deposited simultaneously is another means of achieving higher capacities and currents or higher voltage.

Conclusions

Rechargeable thin-film lithium batteries have high specific energies and energy densities, the ability to undergo thousands of charge-discharge cycles, and they can be fabricated into a variety of sizes and shapes on virtually any type of substrate. Because of the all solid state construction, thin-film batteries can operate over a wide temperature range limited at the upper end by the melting point of Li. The current density and the useful power produced by thin film batteries is limited by electrolyte-cathode interface resistance.

Acknowledgments

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