A rechargeable thin-film lithium battery that can be used as a miniature power supply for small devices has been recently developed. The battery consists of an amorphous vanadium pentoxide (aV_{2}O_{5}) cathode, an amorphous lithium phosphorus oxynitride (Lipon) electrolyte, and a lithium anode. A thin-film cover layer protects the battery from exposure to air and water vapor. The battery can deliver up to 60 \mu A/\text{cm}^{2} of current between 3.6 V and 1.5 V. Higher voltages can be achieved by fabricating two or more cells in series. A 1-cm^{2} cell with a 1 to 1.5-\mu m-thick cathode discharged from 3.6 to 1.5 V at 12 \mu A typically yields about 440 mC and delivers about 1 J. Using the combined mass of the cathode, electrolyte, and the anode (3x over capacity), the specific energy of the cell is 1.4 \times 10^{6} \text{ J/kg} and the energy density is 2.1 \times 10^{6} \text{ J/L}.

INTRODUCTION

Miniaturization of batteries has not kept pace with the reduction in size and power requirements of electronic devices. The size of conventional batteries is limited by bulk materials processing methods and by the battery container, which is typically a metal can. Nearly ten years ago, Kanehori and colleagues [1] in Japan reported the fabrication of thin-film rechargeable batteries based on a lithium anode, an amorphous lithium ion conducting electrolyte, and a TiS_{2} cathode. The cells had an open circuit voltage of about 2.5 V, and one of them was cycled 2000 times at a current density of 16 \mu A/cm^{2}. These promising results suggested many possible low current applications for thin-film batteries such as on-chip power supplies.

Although several patents resulted from the early Japanese work, no commercial applications have been reported, possibly because of the lack of an electrolyte with sufficient long-term stability in lithium cells and the lack of a satisfactory protective coating. Recent research in our Laboratory has led to solutions to these problems. A new lithium electrolyte that is stable at high cell potentials was recently discovered [2,3], and a protective coating has been developed. Using these developments, thin-film rechargeable lithium batteries with several different kinds of cathodes having open circuit voltages ranging from 4.4 to 2.8 V have been fabricated. In this article, we describe the fabrication and performance of these batteries so that their possible applications in MEMS devices can be evaluated.

FABRICATION AND PERFORMANCE

A cross-sectional drawing of a thin-film battery is shown in Fig. 1. The deposition sequence and techniques listed in Table 1 are described in detail elsewhere [2,3]. The cell includes a new amorphous lithium phosphorus oxynitride electrolyte and a recently developed proprietary coating, which serves to protect the lithium anode from air. While we have investigated most extensively cells with amorphous V_{2}O_{5} (aV_{2}O_{5}) cathodes, we have also fabricated thin-film batteries using other intercalation compounds including TiS_{2}, LiMn_{2}O_{4}, and LiCoO_{2} with open circuit voltages of 2.5 V, 4.2 V, and 4.4 V,

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Fig. 1. Schematic of the thin-film battery in cross section and in plan view. The cathode and electrolyte films are typically 1 µm thick while the lithium anode film is typically 2 to 5 µm thick.

Table 1. Steps in the Fabrication of a Thin-Film Li-aV2O5 Battery

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
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<tr>
<td>1.</td>
<td>V current collectors — dc magnetron sputtering of V in Ar</td>
</tr>
<tr>
<td>2.</td>
<td>a V2O5 cathode — dc magnetron sputtering of V in Ar + 14% O2</td>
</tr>
<tr>
<td>3.</td>
<td>Li electrolyte — rf magnetron sputtering of Li3PO4 in N2</td>
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<td>4.</td>
<td>Li anode — evaporation of Li (10^-6 Torr)</td>
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<tr>
<td>5.</td>
<td>Protective coating</td>
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respectively. While these cells typically have an area of 1 cm² and are about 5-μm thick, thin-film batteries could be fabricated to any scale, large or small, as required for a particular application. Because all of the films listed in Table 1 are deposited at ambient temperature, the Li-aV₂O₅ batteries can be fabricated onto virtually any substrate capable of supporting a thin film structure. Although typically fabricated on rigid substrates, we have deposited a battery on an 0.1-mm-thick polyester film, and it was possible to flex the battery without damaging it. Also, subject to the constraint that the anode and cathode must be isolated by the electrolyte, the batteries could be fabricated into any arbitrary shape.

An example of a charge-discharge curve for a Li-aV₂O₅ cell is shown in Fig. 2. The data are plotted as cell voltage vs. the quantity of charge cycled through the cell following the first discharge. This charge corresponds to about 2.8 Li per V₂O₅ [4]. The decrease in voltage during discharge shown in Fig. 2 is typical of intercalation cathodes [5,6]. The magnitude of the voltage change at any given point on the discharge curve depends on the amount of lithium intercalated into the V₂O₅ structure. By limiting the discharge range, the voltage change could be minimized but at a sacrifice of capacity. Another characteristic of intercalation cathodes is the change in the resistance to lithium ion diffusion over the course of the discharge [5]. The resistance is highest at the beginning of the cycle near 3.6 V and decreases to its minimum near 1.7 V as the lithium content in the cathode increases. The resistance increases again at lower voltages.

Several properties of the thin film Li-aV₂O₅ battery are listed in Table 2. The capacities given per unit volume of cathode and the energy density are based on the density of crystalline V₂O₅. The density of the amorphous V₂O₅ films is not accurately known, but it is estimated to be as much as 25% lower than the crystal density. Since the capacity of a battery scales with the volume of the cathode for an excess of the anode, the data in Table 2 can be used to estimate the size of the battery required for a given application. A tradeoff occurs in the decision of whether to increase the thickness of a cathode or its area to achieve a higher capacity: a thicker cathode will increase cell resistance and lower maximum current densities, while a thinner cathode with a larger area will allow higher current densities but will occupy more of the substrate.

While rechargeability might not be an important characteristic for many applications, thin-film solid state batteries have unsurpassed cycle lives. After nearly 100 cycles, Li-aV₂O₅ cells show no significant
Table 2. Specifications for Rechargeable Thin-Film Li-aV$_2$O$_5$ batteries

<table>
<thead>
<tr>
<th></th>
<th>3.6 V to 1.5 V</th>
<th>440 mC/cm$^2$/$\mu$m</th>
<th>120 $\mu$Ah/cm$^2$/$\mu$m</th>
<th>2.1 J/l</th>
<th>1.4 J/kg</th>
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<tr>
<td>Operating voltage:</td>
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<tr>
<td>Capacity:$^a$</td>
<td></td>
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<tr>
<td>Energy density:$^b$</td>
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<tr>
<td>Specific energy:$^b$</td>
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</table>

$^a$For a discharge rate of 10 to 15 $\mu$A/cm$^2$.

$^b$Based on the combined mass of the lithium anode at three times overcapacity, the 1-$\mu$m-thick electrolyte film, and the cathode. The crystalline density of V$_2$O$_5$, 3.36 g/cm$^3$, was assumed.

Applications and Limitations

Rechargeable thin-film lithium batteries have several important advantages as power sources, including unsurpassed specific energy and energy density, number of charge-discharge cycles, and safety. They can also operate at any temperature below 25°C and as high as 150°C. Because they are fabricated using thin-film techniques, they can be made to any required shape and size, large or small, on virtually any type of substrate. To achieve higher voltages, multicell batteries could be fabricated in series in a stacked or side-by-side (array) configuration. For example, we recently fabricated a two-cell Li-aV$_2$O$_5$ battery that operates between 7 V and 3 V.

One limitation of thin-film solid state batteries is the low current density at which they must be operated, <100 $\mu$A/cm$^2$, without causing a significant internal voltage drop. In order to increase the current as well as the capacity without increasing the area occupied by the battery, stacks of cells could be connected in parallel.

Future Research

Work is under way to improve the current density of thin-film cathodes and to develop rechargeable thin-film batteries for a variety of applications. Several types of multicell batteries of both the stacked and array type are currently under investigation. The authors invite members of the MEMS community who are interested in miniature power supplies to explore collaborative research opportunities at ORNL.
ACKNOWLEDGEMENT

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REFERENCES

[4] During cycling, the composition of the cathode varies from about Li_0.16V_2O_5 to about Li_2.98V_2O_5.