NEW AMORPHOUS THIN-FILM LITHIUM ELECTROLYTE AND RECHARGEABLE MICROBATTERY

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Abstract

Sputtering of Li3PO4 in pure N2 results in the formation of an amorphous lithium electrolyte that is stable in contact with lithium and has electrical properties that are suitable for application in a thin-film cell. Thin-film rechargeable lithium cells have been fabricated and characterized using this electrolyte between a lithium anode and an amorphous vanadium oxide cathode. The open circuit voltage of the cell is 3.6 to 3.7 V, and it has a capacity of 130 µAh/cm² when discharged to 1.5 V. The ac impedance of the cells measured at different stages of discharge indicate a significant decrease in internal resistance at about the midpoint of the discharge.

Introduction

Research on the deposition and characterization of amorphous lithium electrolyte and vanadium oxide thin films in this Laboratory [1-3] has been directed toward the development of a thin-film rechargeable lithium battery suitable for circuit integration. There are potentially many uses for such a battery as a primary or standby power source for low current electronic devices. One of the possible applications envisioned is illustrated schematically in Fig. 1 which shows a thin-film cell that was deposited onto a DIP package with current leads extending to a CMOS-SRAM chip. A Li-VOx cell about 8 µm thick occupying an area of 1 cm² as illustrated has a capacity of 130 µAh and could supply a current of up to 100 µA at a voltage that ranges from about 3.7 V at full charge to about 1.5 V near the end of its discharge. Of course, the capacity and current density could be significantly increased if a larger battery were deposited over the unused area of the package.

Experimental Procedures

Schematic diagrams of the thin-film cell in cross section and plan view are shown in Fig. 2. The 0.5-µm-thick vanadium current collectors were deposited onto a 25 mm × 25 mm glass microscope slide by dc magnetron sputtering of V in Ar. The VOx film was then deposited over the larger current collector to a thickness of about 1 µm by dc magnetron sputtering of V in Ar + 14% O2. In most cases following this deposition, the substrate was transferred into a scanning electron microscope under high purity argon for examination of the microstructure of the cathode film. The structure of selected films was also investigated by grazing angle x-ray diffraction and by Raman scattering using a microprobe.

Results and Discussion

The electrolyte for a thin-film rechargeable lithium battery should ideally have a high lithium ion conductivity, a negligible electronic conductivity, and it must be chemically stable in contact with lithium. Films deposited by sputtering or evaporation of inorganic compounds onto substrates held at ambient temperatures are usually amorphous. This is advantageous because, for many lithium compounds, the lithium ion conductivity of the amorphous phase is orders of magnitude higher than that of the crystalline...
Table 1. Comparison of the compositions, conductivities, and activation energies of amorphous lithium phosphate, phosphosilicate, and phosphorus oxynitride electrolyte films

<table>
<thead>
<tr>
<th>Target Process Gas</th>
<th>Film Composition</th>
<th>(\sigma(25^\circ C) \times 10^8) (S/cm)</th>
<th>(E_a) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_3)PO(_4)</td>
<td>Li(<em>{2.7})PO(</em>{3.9})</td>
<td>7</td>
<td>0.68</td>
</tr>
<tr>
<td>Li(_3)PO(_4)</td>
<td>Li(<em>{4.8})Si(</em>{0.23})PO(_{5.2})</td>
<td>20</td>
<td>0.57</td>
</tr>
<tr>
<td>Li(_3)PO(_4)</td>
<td>Li(_3.3)P(_0.17)</td>
<td>240</td>
<td>0.56</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) Determined from a least squares fit of conductivity data to \(\sigma T = \sigma_0 \exp(-E_a/kT)\)

phase, and the conductance of the amorphous film is often adequate for use as an electrolyte. As many of these amorphous materials have acceptable low electronic conductivities, there is a wide choice of materials available for possible application in thin-film cells which meet the first two requirements. However, instability in contact with lithium eliminates many materials from consideration and has, until recently, posed a major problem in the development of a thin-film lithium cell.

During an extensive investigation of amorphous films in the Li\(_2\)O:SiO\(_2\):P\(_2\)O\(_5\) system [1-4] deposited by sputtering lithium silicates and lithium phosphates in Ar and Ar + O\(_2\) we prepared an electrolyte that is stable in contact with Li and that has suitable electrical properties by sputtering Li\(_3\)PO\(_4\) in pure N\(_2\). A comparison of the conductivities at 25°C for several compositions is given in Table 1. The lithium phosphosilicate listed had the highest conductivity of the films in the Li\(_2\)O:SiO\(_2\):P\(_2\)O\(_5\) system. Several of the more highly conductive lithium phosphosilicate films with different compositions were selected as the electrolyte for lithium cells. In each case, the lithium reacted with the electrolyte film. However, the lithium phosphorus oxynitride electrolyte was found to be stable in contact with Li although it contained only about 2 at% N. Moreover, as shown in Table 1, the conductivity is more than 30 times larger than that of the films deposited by sputtering Li\(_3\)PO\(_4\) in 40% O\(_2\) in Ar. The cause of this increase in \(\sigma\) is believed to be due to an increase in lithium ion mobility rather than an increase in the number of charge carriers brought about by a change in the structure of the electrolyte.

Two distinct types of microstructure were observed for vanadium oxide films deposited by reactive sputtering of V. When deposited at a total flow rate of about 10 sccm of 14% O\(_2\) in Ar, the films were characterized by a high density of micron-sized fibrous clusters that were identified as crystalline V\(_2\)O\(_5\). These clusters can be seen in the upper micrograph of Fig. 3. When the flow rate was increased to about 20 sccm, the films were smooth on a submicron scale as shown by the lower micrograph, provided the V target was relatively new. These smooth V\(_2\)O\(_5\) films were amorphous, and their Raman spectra are consistent with \(x < 2.5\) [5]. Also as will be shown below, the cycling data for these cathode films are similar to those reported by West et al. [6] for crystalline V\(_2\)O\(_5\) films after they were converted to an amorphous form on insertion of more than 1.8 Li per V\(_2\)O\(_5\).

As the V target aged by extended sputtering, the microstructure of the films deposited with the higher flow rate gradually evolved to that of the films deposited at the lower flow rate; with continued use of the same target, the density of the fibrous clusters gradually increased as illustrated by the top micrograph in Fig. 3. This change was marked by a decrease in target voltage (at constant power) and a significant decrease in the deposition rate. For example, the rate for the film shown in the lower micrograph of Fig. 3 was 18 A/min whereas the rate for the film in the upper micrograph was 12 A/min using the same sputtering conditions. To regain the smooth amorphous form, a fresh V target (or target face) was required. Aita et al. [7] investigated the formation of crystalline and amorphous V\(_2\)O\(_5\) films by reactive r f diode sputtering of V as a function of O\(_2\) content and cathode voltage. For 14% O\(_2\) in Ar, the amorphous form was obtained only at the lowest cathode voltage used whereas the crystalline form was obtained at all higher voltages. These findings appear to be inconsistent with ours, but this can probably be explained by the differences in the sputtering processes between r f diode (Aita et al.) and dc magnetron (present work).
Cells fabricated with crystalline or amorphous V\textsubscript{2}O\textsubscript{5} cathodes had open circuit voltages of 3.6 to 3.7 V. However, compared with amorphous cathodes, the rates of discharge and charge that the cells with the crystalline cathodes could sustain without excessive polarization were significantly lower, usually less than 3 \mu A/cm\textsuperscript{2}. This is believed to be due to poor transport across the electrolyte-cathode interface and through the fibrous structure of the cathode. Micrographs of the interface published earlier [1] show that the electrolyte does not conformally coat the fibrous clusters of the crystalline cathodes but rather covers just their top portion, resulting in a relatively small contact area.

Cells with the smooth amorphous cathodes, on the other hand, were discharged at rates of up to 60 \mu A/cm\textsuperscript{2}. An example of a set of charge-discharge curves for one cycle is shown in Fig. 4. The total charge passed through this cell between 3.64 V and 1.5 V was about 575 mC. Based on the estimated mass of the cathode using the deposition rate and a film density of 3.35 g/cm\textsuperscript{3}, this corresponds to a composition of Li\textsubscript{2.7}V\textsubscript{2}O\textsubscript{5} at 1.5 V, in good agreement with the results of West et al. [6]. The capacity of the cell over this voltage range is 130 \mu Ah/cm\textsuperscript{2}, and, using the mass of the anode, cathode, and electrolyte, its energy density is 1.2 \times 10\uppercase{6} J/kg assuming a linear voltage drop with increasing x in Li\textsubscript{1-x}V\textsubscript{2}O\textsubscript{5}.

![Graph](image)

Fig. 4. Charge-discharge curves for Li-VO\textsubscript{x} cell. Discharge at 15 \mu A/cm\textsuperscript{2}; charge at 5 \mu A/cm\textsuperscript{2}.

At a rate of 15 \mu A/cm\textsuperscript{2}, the cell voltage dropped from 3.65 V to about 3.4 V at the beginning of the discharge due to an internal resistance of about 15K ohms, consistent with the measured impedance of a fully charged cell. As the cell voltage drops to about 2.7 V, the impedance measurements indicate that the cell resistance decreases to about 3200 ohms and remains near this value as the cell is discharged to 2.2 V. At the end of the discharge with the cell at about 1.5 V, the internal resistance appears to increase, but the measurement did not extend to low enough frequencies to extract an accurate value.

**Conclusions**

A stable rechargeable thin-film lithium battery has been successfully fabricated and tested using amorphous lithium phosphorus oxynitride as the electrolyte between a lithium anode and an amorphous vanadium oxide cathode. The open circuit voltage of about 3.7 V decreases to about 1.5 V as the cell is discharged to a state at which, based on some reasonable assumptions, the cathode has the composition Li\textsubscript{2.7}V\textsubscript{2}O\textsubscript{5}. Application of the battery awaits the development of a method to protect the lithium anode with a thin-film coating.

**References**


**Acknowledgement**