THIN-FILM RECHARGEABLE LITHIUM BATTERIES

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ABSTRACT

Small thin-film rechargeable cells have been fabricated with a lithium phosphorus oxynitride electrolyte, Li metal anode, and Li$_{1-x}$Mn$_2$O$_4$ as the cathode film. The cathode films were fabricated by several different techniques resulting in both crystalline and amorphous films. These were compared by observing the cell discharge behavior. Estimates have been made for the scale-up of such a thin-film battery to meet the specifications for the electric vehicle application. The specific energy, energy density, and cycle life are expected to meet the USABC mid-term criteria. However, the areas of the thin-films needed to fabricate such a cell are very large. The required areas could be greatly reduced by operating the battery at temperatures near 100°C or by enhancing the lithium ion transport rate in the cathode material.

INTRODUCTION

Rechargeable lithium batteries offer significant advantages as advanced batteries for EV applications due to both the high reactivity and the low atomic mass of lithium. As shown in Table 1, the cells based on an electrochemical couple with lithium have much higher specific energy and energy densities than other cells.

A variety of different lithium batteries are currently at various stages of development. Many of these are based on a solid polymer (SPE) or organic liquid electrolyte. These electrolytes are thermodynamically unstable with metallic lithium and also at high cathode potentials. This instability restricts the cell potentials that can be utilized and may also limit the lifetime of the cells due to instabilities at the interfaces.

Research at Oak Ridge National Laboratory has lead to the development of all solid state thin-film rechargeable lithium cells for a variety of low power applications. The enabling breakthrough was the synthesis of a thin-film ceramic electrolyte, 'Lipon', that has an acceptable lithium conductivity and exceptional chemical and mechanical stability [1]. This electrolyte, which has a typical composition of Li$_3$PO$_3$N$_{0.22}$, has been coupled with several different lithium insertion materials as the cathode and a metallic lithium anode to form cells capable of being recharged 1000's of times with a shelf life in excess of a year. The resistance of these thin-film cells is largely determined by the lithium transport rate in the cathode material.

The purpose of this work was to develop a cell suitable for the EV application and evaluate whether it might meet the USABC advanced battery criteria when scaled to an automotive size. The major development needed to complete this assessment was a thin-film form of the LiMn$_2$O$_4$ cathode [3]. This insertion compound appears to be the most promising in terms of safety, cost and performance for the EV application.

Table 1. Comparison of Rechargeable Systems

<table>
<thead>
<tr>
<th>Battery type</th>
<th>Voltage (V)</th>
<th>Specific Energy (Wh/l)</th>
<th>Specific Energy (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin-film</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-V$_2$O$_5$</td>
<td>3.6–1.5</td>
<td>700</td>
<td>420</td>
</tr>
<tr>
<td>Li-Li$_2$Mn$_2$O$_4$</td>
<td>4.3–3.8</td>
<td>500</td>
<td>190</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-V$<em>6$O$</em>{13}$ (SPE)</td>
<td>2.5</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Al-air</td>
<td>1.6</td>
<td>360</td>
<td>250</td>
</tr>
<tr>
<td>Sodium-sulfur</td>
<td>2.1</td>
<td>120</td>
<td>160</td>
</tr>
<tr>
<td>Ni-metal hydride</td>
<td>1.35</td>
<td>150</td>
<td>55</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>1.35</td>
<td>80</td>
<td>38</td>
</tr>
<tr>
<td>Lead acid</td>
<td>2.10</td>
<td>80</td>
<td>35</td>
</tr>
</tbody>
</table>
CELL FABRICATION AND TESTING

The thin-film solid state cells fabricated in our laboratory have been prepared by sequential film depositions as illustrated in Fig. 1. A variety of ceramic, glass, and polymer materials have been used as the substrate material. Depending upon the subsequent processing temperatures, either Ni or Pt current collectors were deposited on the substrate. This was followed by deposition of the cathode film by one of several techniques discussed further below. The Lipon electrolyte film was grown by rf magnetron sputtering of Li3PO4 in a N2 process gas [1]. Finally, a lithium metal anode was deposited by thermal evaporation. The total cell thickness was typically ~5 μm, with an active area of ~1 cm2. To protect the lithium from reaction with the air, the cell was sealed in a bottle under Ar; in some cases, cells were sealed with a thin protective multilayer coating.

The LiMn2O4 cathode films have been grown by two different techniques. A number of films have been vapor deposited from an electron beam evaporated LiMn2O4 source. These films were subsequently annealed under various conditions at temperatures up to 800°C. Both the cathode capacity and lithium transport rate were found to be sensitive to the annealing conditions. The results presented here are for highly crystalline films with the desired LiMn2O4 spinel phase prepared by a 700–800°C anneal in O2. Films 0.3–4 μm thick have been grown by this technique.

A lower-temperature fabrication of LiMn2O4 has been attempted by rf magnetron sputtering. Sputtering is potentially advantageous over evaporation techniques because the bombardment of the film with energetic ions may promote the crystallization, adhesion and densification of some materials. A number of parameters have been investigated to optimize the sputter deposition of the LiMn2O4 films, including the process gas composition and pressure, and the substrate temperature and bias. The results to date indicate that the amorphous films of LiMn2O4 are superior to those that exhibit a weak crystallinity. The data presented are for cathodes ≤1 μm thick grown at ambient substrate temperatures which do not exceed 120°C. This low fabrication temperature not only simplifies the processing, it also permits the sequential deposition of cells in a stack, since the process temperature remains below the melting temperature of lithium metal.

The as-fabricated Li/Lipon/LiMn2O4 cells had open circuit voltages of ~3 V indicating a near stoichiometric cathode composition. The cells were initially charged to 4.5 V by removing Li from the cathode, Li1–xMn2O4, and then cycled over the voltage range of interest at various constant current densities. Cell testing was usually performed at room temperature. The cells were also evaluated by ac impedance spectroscopy.

RESULTS

The low-current discharge curves shown in Fig. 2 illustrate the difference observed for cells with the e-beam evaporated and annealed cathodes (ev/800°C) versus cells with the low-temperature sputter deposited (sp/ambient) cathodes. Discharge of the annealed crystalline cathodes involves about half of the lithium and the insertion reaction occurs near 4 volts. Higher voltages, to 5.3 V, are needed to pull the remaining lithium from the cathode; preliminary results indicate that charging above 5 V causes irreversible changes in the cathode. For the cells with the amorphous cathodes, all the lithium can be reversibly cycled in and out of the cathode, although the reaction occurs at lower voltages. While the crystalline cathodes give a cell that can be cycled near 4 V, the amorphous cathodes must be discharged to ~3 V to realize the full capacity.

Sets of constant current discharge curves have been used to assess the polarization losses for the cells. Figure 3 shows discharge curves for the 4 μm thick ev/800°C cathode over the 4.5–3.8 V range. The polarization loss for 40 μA/cm2 was quite small, and 70% of the cathode capacity was utilized at 0.2 mA/cm2. This corresponded to a cell resistance of ~780 ohm. In comparison, Fig. 4 shows the discharge curves to 2.8 V for the cell with the 0.73 μm sp/ambient cathode. The polarization losses were much larger, greatly limiting the useful discharge current of the cell. The resistance for this cell is ~7000 ohm.

A number of LiMn2O4 cathodes are compared in Fig. 5 using a Ragone type of plot for cells discharged over the appropriate voltage ranges. Only the mass of the cathode film was considered in these calculations of the specific energy and power. The cathodes varied in thickness as well as in the particular deposition conditions used for their fabrication. Clearly cathodes that have been...
Fig. 2: Discharge curves for two batteries as a function of the lithium content in the cathodes. The compositions were calculated from the amount of charge, the cathode film thickness, and the cathode density, assumed to be 4.2 g/cm³. The discharge currents were 5 and 10 μA/cm². 

Fig. 3: Discharge curves of the ev/800°C cell of Fig. 2 at different current densities at 25°C. On the charge cycle, the voltage was held at 4.5 V until the current decreased to 1 μA.

Fig. 4: Discharge curves of the sp/ambient cell of Fig. 2 at different current densities at 25°C. On the charge cycle, the voltage was held at 4.5 V until the current decreased to 1 μA.

Fig. 5: Specific energy and power for selected cells with cathodes fabricated by either evaporation and high-temperature anneal (open symbols) or by sputter-deposition (solid symbols). The sputtered films were deposited at substrate temperatures of 120 and 230°C. The films deposited from the evaporation source were grown to different thicknesses and annealed in O₂ at 700–800°C.

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Annealed at high temperature give cells with the highest powers.

The cycle life of several cells has been evaluated by prolonged cycle testing. Typically the cells were discharged to a cutoff voltage of 3.8 or 3.0 V and then recharged and held at 4.5 V until the current decreased to 1 μA. Several hundred cycles were needed to determine the magnitude of the capacity loss. The majority of cells with either type of cathode were found to have <0.05% capacity loss per cycle and therefore meet the mid-term criteria for cycle life. Several of the annealed cathodes were cycled with <0.01% capacity loss per cycle.
These results for our small single-cell batteries have been used to estimate the power and energy that would be expected if the battery were to meet the EV requirements. Estimates have been made for a 200 V, 40 kWh battery, with 200 Ah capacity at a C/3 discharge rate. The results are summarized in Table 2.

The top half of Table 2 gives estimates based on the cell measurements shown in Figs. 2–4 for the 4 μm-thick ev/800°C cathode and the 0.73 μm-thick sp/ambient cathode. For the ev/800°C cell, we assumed a discharge range per cell of 4.5–3.8 V, so the 200 V EV battery would require a series stack of ~50 cells. Alternatively, for the sp/ambient cathode cell, a larger stack of ~67 cells would be needed assuming each cell was discharged over 4.5–2.8 V. These cell stacks might be configured as cells deposited directly on top of each other with either an interconnect or an insulating film between the cells, or alternatively, the cell stack might consist of an overlapping chain of cells on a continuous thin substrate sheet. In each case the film serving as the interlayer or substrate was assumed to add 0.5 μm/cell or 4 g/m² to each cell. An additional 1 μm/cell and 2.5 g/m²/cell was added to accommodate the Lipon electrolyte, and 2 μm/cell and 1 g/m²/cell was included to account for the lithium anode in excess of the lithium incorporated with the LiMn₂O₄ cathode. This gave the total cell mass and volume used to calculate the tabulated values for the specific energy and energy density of the 40 kWh battery. These estimates for the battery did not include the battery casing and structural support frames nor the void space that would be needed between the modular cell stacks. Rough estimates suggested that their inclusion would reduce the tabulated specific energies and energy densities by a factor of 2–3. Even so, these values look promising compared to the published mid-term criteria of the advanced battery (135 Wh/l and 80 Wh/kg). The more sobering result of this exercise, however, is the tremendous area of films required to fabricate such a battery.

In the second half of Table 2, the lithium transport rate in the cathode films was assumed to be 100X higher than the room temperature rates that we have observed to date. If the lithium diffusion remains the rate controlling mechanism in the cathode, the concentration profiles in the cathode during the cell discharge will remain unchanged for constant values of the D/iL ratio, where D is the diffusivity, i the current density, and L the cathode thickness. The 100X enhanced diffusivity was incorporated in the estimates for the battery as a 10X increase in both the cathode thickness and the discharge current density. This greatly reduced the required area for the battery stacks and also increased the specific energy and the energy density sufficiently to meet even the long-term USABC battery criteria.

An increase of 100X in the room temperature diffusivity of lithium in the single phase cathode films is likely not achievable. Although work is continuing to optimize the LiMn₂O₄ cathode films, considerable effort has already been devoted to exploring the various film growth conditions. There is one report in the literature of a higher diffusivity for lithium in a bulk composite cathode of Li₄Mn₂O₄, ~10⁻⁹ cm²/s [4], but this remains unconfirmed as the diffusivity found for our pure crystalline films is only ~10⁻¹¹ cm²/s.

A more feasible approach is to operate the thin-film cells at an elevated temperatures. For a thermally activated lithium transport in LiMn₂O₄, an operating temperature of 80–115°C would be expected to give an estimated 100X enhanced diffusivity. One of our cells was successfully cycled at

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Thickness (μm)</th>
<th>Area of 200 V Battery Stack (m²)</th>
<th>Wh/kg</th>
<th>Wh/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ev/800°C</td>
<td>4</td>
<td>170</td>
<td>190</td>
<td>590</td>
</tr>
<tr>
<td>sp/ambient</td>
<td>1*</td>
<td>420</td>
<td>120</td>
<td>300</td>
</tr>
<tr>
<td>100X enhanced transport:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ev/800°C</td>
<td>40</td>
<td>17</td>
<td>270</td>
<td>970</td>
</tr>
<tr>
<td>sp/ambient</td>
<td>10</td>
<td>42</td>
<td>286</td>
<td>900</td>
</tr>
</tbody>
</table>

*Scaled from results for 0.73 μm cathode.
60°C. This appears to be a promising approach, but further cell testing at ~100°C is required to evaluate the operation and lifetime of the cells at these elevated temperatures.

An alternative strategy to achieving the needed enhanced transport in the cathode is to abandon the use of the homogeneous thin-film cathodes in favor of a thick film of LiMn$_2$O$_4$ in the form of a composite cathode material. Realizing an enhanced lithium transport in the composite cathode would depend on the formation of rapid diffusion paths for lithium in the composite. This approach poses a new set of materials and processing challenges and would inevitably sacrifice the specific capacity of the LiMn$_2$O$_4$ cathode to some degree. Even with a thick-film cathode, we anticipate that the Lipon film could still be utilized as the cell electrolyte to take advantage of the exceptional chemical stability and lifetime offered by this ceramic electrolyte.

CONCLUSIONS

Thin-film rechargeable lithium cells fabricated of LiMn$_2$O$_4$/Lipon/Li offer attractive specific energy and energy densities for EV application. The magnitude of the film areas required to scale up this cell and fabricate an EV battery however are staggering. This can be greatly reduced by further enhancement of the lithium ion transport in the cathode which might be accomplished by operating the cell at elevated temperatures. Alternatively, the investigation of thick film composites of LiMn$_2$O$_4$ may lead to a higher rate cathode that could be coupled with the thin-film Lipon electrolyte.

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