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**THIN-FILM RECHARGEABLE LITHIUM BATTERIES
FOR IMPLANTABLE DEVICES**

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Abstract

Thin films of LiCoO_2 have been synthesized in which the strongest x-ray reflection is either weak or missing, indicating a high degree of preferred orientation. Thin-film solid state batteries with these textured cathode films can deliver practical capacities at high current densities. For example, for one of the cells 70% of the maximum capacity between 4.2 V and 3 V ($\sim 0.2 \text{ mAh/cm}^2$) was delivered at a current of 2 mA/cm^2 . When cycled at rates of 0.1 mA/cm^2 , the capacity loss was 0.001 %/cycle or less. The reliability and performance of Li-LiCoO₂ thin-film batteries make them attractive for application in implantable devices such as neural stimulators, pacemakers, and defibrillators.

Introduction

Solid state rechargeable lithium batteries which are less than $15 \text{ }\mu\text{m}$ (micrometers) thick have been developed at the Oak Ridge National Laboratory. These batteries have high energy and power densities, can be cycled thousands of times, and they can be fabricated in arbitrary shapes and to any required size to meet the requirements of a specific application. When fabricated directly onto multichip packages, the batteries can save 100–1000 times the volume required by conventional lithium coin cells.

A schematic cross section of a thin-film battery is shown in Fig. 1. The active battery components are a lithium intercalation cathode, e.g. V_2O_5 , LiMn_2O_4 or LiCoO_2 , and a lithium metal anode which are separated by a lithium phosphorus oxynitride electrolyte (1). Graphs of voltage vs. discharge capacity for thin film cells with different types of crystalline and amorphous cathodes are shown in Fig. 2. Among the materials we have investigated, batteries with crystalline LiCoO_2 cathodes have the highest energy and power densities (2), making them attractive as compact rechargeable power sources for application in a variety electronic devices including neural stimulators, pacemakers, and defibrillators.

Crystalline LiCoO_2 has a layered structure in which lithium and cobalt ions are located in alternate planes that are separated by close-packed oxygen planes (3). In an earlier work (2), we

reported that thin-film rechargeable lithium batteries with crystalline LiCoO_2 cathodes could deliver of the order of $25 \mu\text{Ah per cm}^2$ of charge at rates up to $1000 \mu\text{A/cm}^2$ and could be cycled thousands of times with small capacity losses. The x-ray diffraction patterns of these films typically displayed a strong (003) reflection and weaker (101) and (104) reflections. Recently, we observed that diffraction patterns of annealed LiCoO_2 films that had been grown in different vacuum chambers using different LiCoO_2 targets displayed either a very weak or absent (003) reflection and a strong (104) or (101) reflection, indicating a high degree of preferred orientation or texturing. Batteries with these textured cathodes have significantly higher power and energy densities compared to those described earlier (2). In this paper, we discuss the effects of preferred orientation on the performance of thin-film lithium batteries.

Experimental Procedures

The LiCoO_2 films, 1 to 3 μm thick, were deposited over Pt current collectors on alumina substrates by rf magnetron sputtering of 2" diameter LiCoO_2 targets (2). The process gas was a 3/2 mixture of Ar/O_2 , the total pressure was 20 mTorr, and the target-to-substrate distance was 5 cm. Depositions were made in two vacuum chambers with different volumes and orientation of the sputter guns. Targets were prepared by cold pressing and sintering (1100°C in air) powders of LiCoO_2 obtained from Cerac (>99.5%) and Alfa Aesar (>98%). After deposition, the films were recrystallized by annealing in O_2 at 700°C for 2 h. X-ray diffraction measurements were made on the commercial powders and the annealed films over the 2-theta range from 10 to 70° . Thin-film cells with the annealed cathodes were fabricated using the deposition methods described previously (1), and their performance was evaluated by constant current cycling using a battery test system with high impedance channels.

Results and Discussion

Structure of the LiCoO_2 films

The regions near the (003), (101), and (104) reflections of three representative LiCoO_2 films are shown in Fig. 3. The integrated intensities of the diffraction peaks were scaled to 100 for the

strongest reflection from each film, and their values are listed in Table I. The relative intensities observed with the powdered sample of LiCoO_2 (Table I) are in good agreement with the results reported previously for powdered samples of the high temperature form of LiCoO_2 (4) and also with the calculated diffraction pattern based on the cell parameters and atomic positions reported by Orman and Wiseman (3). The latter are the relative intensities expected for a random orientation of crystalline LiCoO_2 grains.

Scanning electron micrographs of fracture cross sections reveal that the films consist of columns of LiCoO_2 grains normal to the plane of the substrate. Provided a reflection is allowed by the crystal symmetry, diffraction can occur from only those crystal planes that are parallel to the surface of the substrate. The relative intensities of the three reflections shown in Fig. 3 are determined by their respective intrinsic intensities and by the fraction of the grains which are oriented such that their (003), (101), or (104) planes are parallel to the plane of the substrate. Comparing the relative intensities Table I with the values for the randomly oriented powdered sample, it is apparent that the three representative films exhibited significant texturing with different preferred orientation of the LiCoO_2 grains. The relative percentages of grains with one of the three preferred orientations were calculated by dividing the intensity observed for each of the three reflections of the films by the intensity of the corresponding reflections of the powdered sample and then normalizing the values for each film to 100%. The results are given in Table II. For example, dividing the intensities of film A by the corresponding powder intensities gives 1.0, 2.0, and 0.46, respectively, as the relative number of grains with their (003), (101), and (104) planes parallel to the substrate compared to the random powder distribution. Normalizing to 100% gives the percentages of the grains with each of the three particular orientations for film A (first row of Table II).

At the present time we do not understand the cause of the texturing of the LiCoO_2 films nor the origin of the differences in textures of films grown in different vacuum chambers and with different LiCoO_2 targets. It is known from other studies (5) that preferred orientation is due to the tendency to minimize the larger of the surface energy or the strain energy of a film. Both of

these energies differ from one crystallographic plane to another, and their relative values for the different planes generally do not have the same order. So if surface energy is dominant, a film will grow with one preferred orientation whereas if strain energy is dominant a film will grow with a different orientation. Surface energy is determined by the details of the crystal structure (coordination number and bond strengths) while the strain energy is determined by the stress in the film and the elastic properties of the material (5). The latter of course also depend on the details of the crystal structure. In general, the thinner the film the more likely that surface energy is dominant, while as the film becomes thicker the strain energy is larger (5). We speculate that for the relatively thicker films (1 to 3 μm) strain energy plays the more important role. From preliminary electron diffraction measurements on individual grains in as-deposited films (6), it appears that texturing is initiated during film growth.

Battery performance

Differences in the texturing of LiCoO_2 films result in differences in the resistance to lithium ion transport. From the schematic drawing in Fig. 1, Li^+ ions move perpendicular to the plane of the cathode films during charge and discharge. Since in the LiCoO_2 structure the Li^+ occupy alternate layers which are perpendicular to the c-axis, we expect a higher resistivity for films with a larger percentage of (003) oriented grains since Li^+ diffusion perpendicular to the (003) planes will be much slower than diffusion within (parallel) to these planes. The angles between the (003) and the (101) and (104) planes are 45° and 14° , respectively. Therefore we expect Li^+ diffusion perpendicular to either of these planes is faster than in a direction perpendicular to the (003) planes.

Constant current discharge curves for a cell with a 2 μm thick film are shown in Fig. 4. The downward shift of the discharge curves with increasing current density is due to the internal resistance of the cell. Comparing similar curves for cells with each of the three types of cathodes of Table II, we find that batteries with B or C type cathodes have resistivities (resistance/cathode thickness) that are lower by as much as three times the resistivity of batteries with type A cathodes. Moreover, batteries with type B cathodes have resistivities lower by as much as 30%

compared to batteries with type C cathodes. Lower resistivities allows cells to be discharged at higher rates while delivering most of the available charge between 4.2 V and 3.0 V. This is illustrated by the graphs in Fig. 5 of the discharge capacity vs. current density obtained from the data in Fig. 4 and similar data for a cell with a 1.3 μm thick cathode. Both the 2 μm and 1.3 μm thick cathodes were type B. Even with the thicker cathode, the discharge capacity is above 50% of maximum at a current density of 3 mA/cm^2 . For comparison, data available over a limited range for a battery with a type A cathode also is shown. The much more rapid decrease in capacity with current is caused by the three times higher resistivity of the type A cathode.

Thin-film batteries with type B or C cathodes are also capable of delivering high pulse currents. This is illustrated in Fig. 6. The application in this case called for 2.3 mA/cm^2 pulses of 15 s duration separated by a rest period of 2 s. A minimum of five pulses was required on each cycle, i.e. before the battery is recharged. As illustrated, this particular cell could deliver eight of the required pulses before recharge.

The secondary performance of batteries with type B or C cathodes appears to be as good as those with type A cathodes (2) as illustrated in Fig. 7. For both cells, the capacity loss was about 0.001 %/cycle at discharge rates of 0.1 mA/cm^2 . This means, for example, that 95% of the original capacity remains after 5000 cycles.

Most of our battery tests have been conducted at 25°C, but we have observed the same performance and reliability at 37°C. This suggests possibilities for application in several types of implantable devices such as neural stimulators, pacemakers, and defibrillators where reliable batteries of the smallest possible size are desirable.

Conclusions

Thin films of LiCoO_2 deposited by rf magnetron sputtering and annealed at 700°C in O_2 exhibit three types of texturing with a varying distribution of grains having their (003), (101), and (104) planes parallel to the substrate. Thin-film batteries with type B or C cathodes have significantly higher power and energy densities compared to cells with type A cathodes. The type

of preferred orientation exhibited by the cathode films depends on the kind of LiCoO_2 target used and on the chamber in which the films were grown. We speculate that either the surface or stress energy is the leading factor in determining the type of texturing, and we expect that their relative importance depends on film thickness and on subtle differences in deposition parameters such as substrate bias, temperature, and flux of reflected neutral atoms.

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Table I. Relative integrated peak areas of (003), (101), and (104) reflections of LiCoO_2 thin films

Film	Intensity		
	(003)	(101)	(104)
A	100	72	29
B	13	100	46
C	--	15	100
Powder	100	30	63

No entry (--) indicates a very weak or missing reflection.

Table II. Relative percentage of grains with either their (003), (101), or (104) planes parallel to the substrate

Percentage			
Film	(003)	(101)	(104)
A	26	62	12
B	3	73	24
C	--	24	76

Figure Legends

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

Fig. 2. Low current discharge curves of thin-film lithium batteries with different crystalline and amorphous cathodes.

Fig. 3. X-ray diffraction from LiCoO₂ representative films in the region of the (003), (101), and (104) reflections. Peaks not identified are due to the alumina substrate and Pt current collector.

Fig. 4. Discharge curves at different current densities for a Li-LiCoO₂ cell with a type B cathode, 1 cm² × 1.3 μm thick.

Fig. 5. Discharge capacity per unit of active area vs. current density for two Li-LiCoO₂ cells with type B cathodes (solid squares) of different thicknesses and a cell with a type A cathode (open squares).

Fig. 6. Pulse testing of a Li-LiCoO₂ cell with a 2 μm thick type B cathode. The current pulses were 2.3 mA/cm² of 15 s duration followed by a 2 s rest.

Fig. 7. Cycle data for thin-film Li-LiCoO₂ batteries with type A and type C cathodes. The latest 610 cycles for the latter are shown.













