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2/3 A-size rechargeable battery employing LiCoO_2 thin-film cathode

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Abstract

Lithium and thin-film lithium cobalt(III) oxide (LiCoO_2) were employed in a 2/3 A-size rechargeable battery as negative and positive electrodes. The cell capacity can reach 0.16 Ah/g. The lithium cobalt(III) oxide films were prepared by a spray-coating process. A series of sols were used as precursor for preparing the films. It was shown that different reaction conditions and precursors change the microstructure of the films and affect the electrochemical performance of the cells.

Keywords: Rechargeable lithium batteries; Thin-film cathodes; Cobalt oxide

1. Introduction

Rechargeable thin-film lithium batteries with solid polymer electrolytes have several important advantages. They can be readily fabricated in various shapes and sizes in order to provide high current capability and to maintain a high specific energy. With proper selection of the electrolyte, they may operate over a wide temperature range [1,2].

A decade ago, researchers in Japan and France reported the manufacturing of thin-film rechargeable batteries based on a lithium negative electrode, an amorphous inorganic lithium-ion conducting electrolyte, and a TiS_2 positive electrode. Cells made by the Japanese researchers had cycled 2000 times at a current density of $16 \mu\text{A}/\text{cm}^2$. Such promising results led to a great interest in the development of the thin-film batteries for many possible applications in electronic devices. However, up to date, there is still no commercial product in the market yet. The reason for the delay is likely due to the lack of a polymer electrolyte with sufficient long-term stability which can protect lithium from corrosion or passivation. The development of a new thin-film Li-TiS_2 battery has recently been reported by Eveready Battery Company. The battery adopted a new electrolyte, LIPON, developed in the Oak Ridge National Laboratory. Several cells have undergone more

than 10 000 charge/discharge cycles at current densities up to $100 \mu\text{A}/\text{cm}^2$.

We have been working on the development of a thin-film electrode battery with high current capability and high voltage for military applications. Preliminary efforts have been focused on the development of the high surface area thin positive electrodes and to evaluate the electrodes in 2/3 A-size cells.

2. Experimental

Lithium cobalt(III) oxide (LiCoO_2) thin-film electrodes were prepared by a modified spray-coating process [3,4]. A sol was used as precursor which was prepared by dissolving cobalt(II) nitrate hexahydrate (Merck Ltd.) and lithium nitrate (Merck Ltd.) in ethylene glycol (Merck Ltd.). The concentration of lithium and cobalt in the sol was 1.0 M. After the lithium and cobalt salts being dissolved in ethylene glycol, the sol was stirred for additional 3 h and stored in a sealed bottle with screw cap. A 0.05 cm thick aluminium foil was used as substrate. The substrate was pre-heated at 350°C on a hot plate. The sol was then sprayed on to the hot substrate using a commercial air brush. The substrate with the thin film was then placed in an oven at 600°C and heated under a flow of oxygen for 10 h. The weight of LiCoO_2 on the substrate was

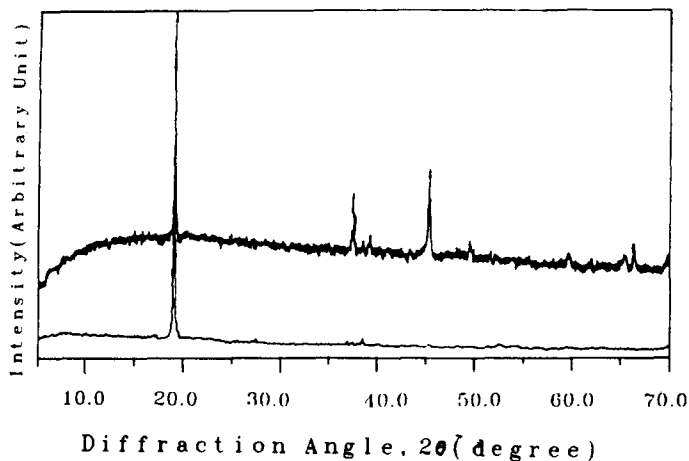


Fig. 1. X-ray powder diffraction pattern of the sol-gel method formed LiCoO_2 thin film electrode, by different substrates (a) aluminium, and (b) titanium.

about 3 mg/cm^2 . The X-ray powder diffraction pattern as shown in Fig. 1(a) indicates the formation of single-phase LiCoO_2 . By changing the substrates and spraying processes, films with preferred particle orientation were obtained (Fig. 1(b)).

The thin-film electrodes were evaluated in 2/3 A-size cells with spiral-wound electrode design. Cells were made with an excess of electrolyte using 1 M LiPF_6 in PC/EC (propylene carbonate:ethylene carbonate = 1:1) solvent and a lithium negative electrode. Cell assembly was carried out in a dry room with less than 2% humidity. The cells were charged at 0.1 mA/cm^2 and discharged at 0.2 mA/cm^2 .

3. Result and discussions

A PARC M388 program with PAR 273 potentiostat and a Solartron 1255 frequency response analyser were used for impedance measurements. Fig. 2(a) shows the internal resistance of the electrolyte ($0.025 \Omega \text{ cm}$) and electrode ($300 \Omega \text{ cm}$) in the packed cell, before charge, that was measured by a.c. frequency sweep from 10^{-2} Hz to 10^4 Hz. The a.c. impedance was also monitored during charge and discharge. Fig. 2(b) and (c) shows the impedance change with different statuses of the cell; Fig. 2(d) displays the failed cell.

Fig. 3 illustrates the performance of the thin-film cell discharged to 3.0 V at 0.2 mA/cm^2 . A capacity utilization of 160 mAh/g of the sol-gel LiCoO_2 thin-film positive electrode was obtained. This utilization is higher than the value of 137 mAh/g obtained from the LiCoO_2 prepared by conventional sintering methods [5].

Fig. 4 shows the effect of the charging time on the discharge voltage profile. It appears that a fully charged state can be reached in a short time for the thin-film electrode. The thin-film electrode prepared by sol-gel

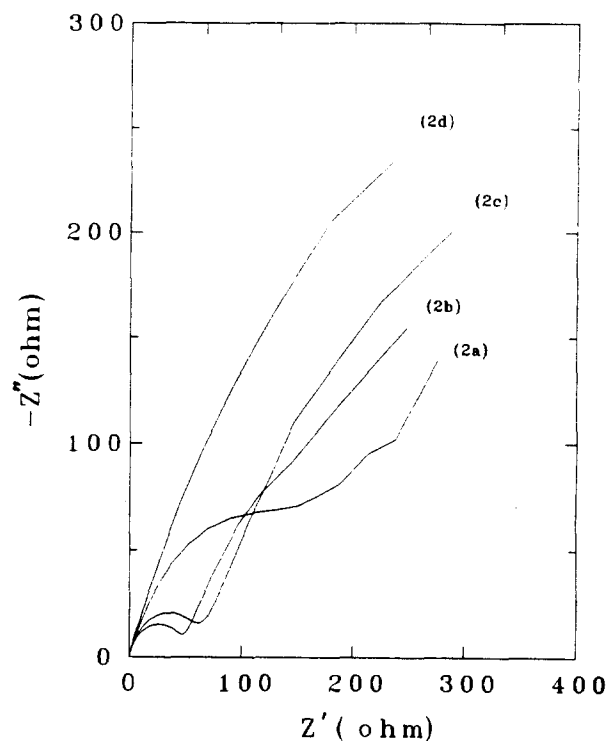


Fig. 2. Comparison of the impedance of LiCoO_2 cell at different statuses: (a) packed cell; (b) charge to 3.9 V after five cycles; (c) discharge to 3.0 V after six cycles, and (2d) failed cells.

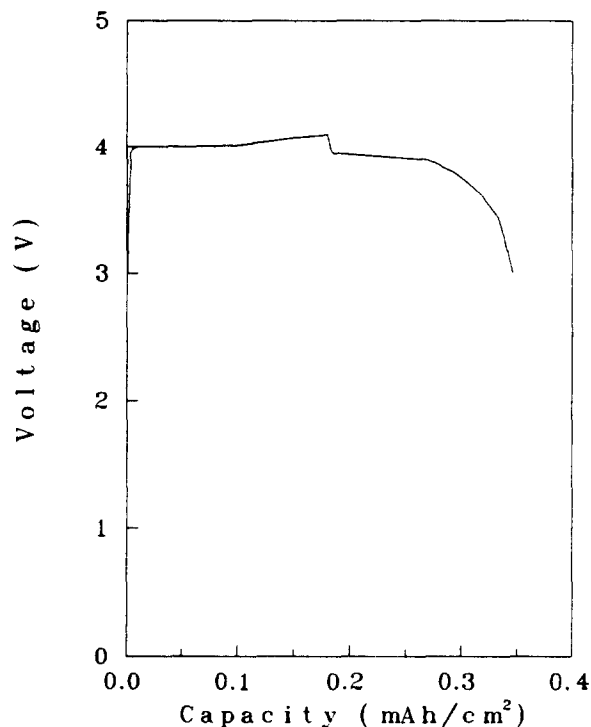


Fig. 3. Capacity vs. voltage of Li/LiCoO_2 thin-film cell; active cathode electrode: 6.28 m .

method has a fine crystallite, high surface area and a uniform porosity, which is believed to help improving the charge efficiency.

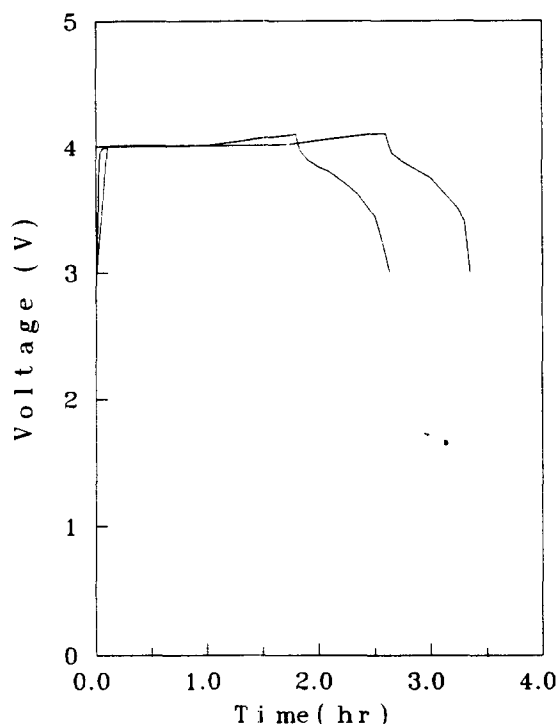


Fig. 4. Comparison of charge/discharge curves of Li/LiCoO₂ thin-film cell; charge = 0.1 mA/cm² to 4.1 V, and discharge = 0.2 mA/cm² to 3 V cutoff voltage.

The electrochemical performance of the thin-film electrode, including cycle life, charge/discharge behaviour at various current densities were evaluated. The crystalline plane and packing density of the thin film were also examined. In this study, the thin-film electrode prepared by sol-gel methods showed a better electrochemical performance than the electrode prepared by powder material. It also showed that the performance of the electrode depended strongly on the microstructure of the film, which changed with the starting precursors and the preparation processes.

4. Conclusions

It seems that the sol-gel method is a promising method to prepare cathode materials for rechargeable lithium batteries. These batteries can have a short charging time and high discharge current density. These improved properties are probable due to the proper microstructure of the thin-film electrode. Since the thickness of the thin-film electrode is much less than the electrode prepared by powder materials, the electrode area can be further increased in a standard battery can, thus may have the opportunity to obtain a higher total discharge current.

The failure of the thin-film cell is believed caused by the overcharge and discharge of the cell, since it is suggested that the fine LiCoO₂ crystals prepared by sol-gel method are sensitive to the current and voltage limit that may damage the electrode during charge/discharge processes.

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