



Performance evaluation of printed LiCoO₂ cathodes with PVDF-HFP gel electrolyte for lithium ion microbatteries

Moon-Soo Park^{a,b}, Sang-Hoon Hyun^{a,*}, Sang-Cheol Nam^c, Sung Back Cho^d

^a School of Advanced Materials Science and Engineering, College of Engineering, Yonsei University, Seoul 120-749, Republic of Korea

^b Samsung Electro-Mechanics Maetan-3-dong, YeongTong-gu, Suwon City, Gyeonggi Province 442-743, Republic of Korea

^c Nuricell Inc., 4F, GS Caltex New Energy Development Center, 453-2, Seongnae-dong, Gangdong-gu, Seoul 134-030, Republic of Korea

^d Advanced Technology Research Center, Agency for Defense Development, Daejeon 305-600, Republic of Korea

ARTICLE INFO

Article history:

Received 7 December 2007

Received in revised form 28 February 2008

Accepted 1 March 2008

Available online 13 March 2008

Keywords:

LiCoO₂ cathodes

Screen printing

Microbattery

PVDF-HFP

Gel electrolyte

ABSTRACT

In order to improve the discharge capacity in lithium ion microbatteries, a thick-film cathode was fabricated by a screen printing using LiCoO₂ pastes. The printed cathode showed a different discharge curves when the cell was tested using various (liquid, gel and solid-state) electrolytes. When a cell test was performed with organic liquid electrolyte, the maximum discharge capacity was 200 μAh cm⁻², which corresponded to approximately 133 mAh g⁻¹ when the loading weight of LiCoO₂ was calculated. An all-solid-state microbattery could be assembled using sputtered LiPON electrolyte, an evaporated Li anode, and printed LiCoO₂ cathode films without delamination or electrical problems. However, the highest discharge capacity showed a very small value (7 μAh cm⁻²). This problem could be improved using a poly(vinylidene fluoride-hexafluoro propylene) (PVDF-HFP) gel electrolyte, which enhanced the contact area and adhesion force between cathode and electrolyte. The discharge value of this cell was measured as approximately 164 μAh cm⁻² (≈110 mAh g⁻¹). As the PVDF-HFP electrolyte had a relatively soft contact property with higher ionic conductance, the cell performance was improved. In addition, the cell can be fabricated in a leakage-free process, which can resolve many safety problems. According to these results, there is a significant possibility that a film prepared using the aforementioned paste with screen printing and PVDF-HFP gel electrolyte is feasible for a microbattery.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Rechargeable lithium batteries have been utilized as efficient energy storage devices in many lightweight electronic appliances, cellular phones and laptop computers due to the high energy density of these batteries. As the general tendency of all advanced technologies is toward miniaturization, it is evident that the future development of batteries is in the direction of smaller dimensions with higher energy densities. There have been many attempts to create micro-scale lithium batteries. Li-ion microbatteries can vary in shape and size according to the specifications of the customer, which is an important advantage. LiCoO₂ as a lithium intercalation material with a layered rock-salt structure, a high operating potential of ~4.0 V and a theoretical capacity of 69 μAh cm⁻² over the range 0.5 ≤ x ≤ 1 in Li_xCoO₂ is a suitable cathode material. This material is now commercialized in lithium batteries [1–4]. With microbatteries, processes that include RF magnetron sputter-

ing, ion-beam directed assembly, a sol-gel process, laser printing technique or laser ablation are widely used to create LiCoO₂ thin films [5–8]. However, it is necessary expensive facilities or a post-annealing process above 700 °C to grow the crystalline phase of films. An additional restraint with earlier microbatteries is their low discharge capacity, which is determined by the thickness of the cathode film. Dudney and Jang [9] fabricated a thick LiCoO₂ film with a thickness of 4 μm. Nevertheless, there are a number of unsolved problems related to control of the film stress, high electrical resistivity, and limited high-rate discharge.

In this study, a novel method to fabricate a LiCoO₂ thick film that does not require a high-temperature post-annealing process is proposed. A screen printing method is used, which increases the thickness of the film and simplifies control of the pattern shape. In addition, it is a simple and relatively economical process [10]. When a printed LiCoO₂ film is formulated for high discharge capacity by means of screen printing, the key issues involved are the surface control of the printed cathode film and the contact area between the electrolyte and the printed cathode thick film.

A previous paper by the authors [11–13] showed the importance of the surface roughness of the printed cathode. In that paper,

* Corresponding author. Tel.: +82 2 365 5882; fax: +82 2 365 5882.

E-mail address: prohsh@yonsei.ac.kr (S.-H. Hyun).

methods that improved the electrical properties and microstructure of the printed cathode were discussed. However, a new problem related to the manufacture of microbatteries that use printed cathodes was discovered. As the contact area and adhesion force were insufficient, the discharge capacity showed very low value ($\approx 7 \mu\text{Ah cm}^{-2}$). Solid electrolytes are advantageous for battery construction. For example, they facilitate the production of miniaturized structures, they are safe, and they enable batteries to operate over a wide temperature range. On the other hand, their low ionic conductivity compared to liquid electrolytes has been a problem. Gel electrolytes are one type of solid electrolyte that can improve conductivity by dissolving a salt into a polar liquid in a polymer network while maintaining the mechanical stability. The main advantages of polymer electrolytes include their favorable mechanical properties, the ease with which thin films of desirable sizes can be fabricated, and the ability to form effective electrode–electrolyte contacts. Thus, in the present work, the focus is on an enhancement of the contact area and the adhesion force between the printed LiCoO_2 cathode and the electrolyte using PVDF–HFP gel electrolyte. PVDF–HFP is considered a highly promising material for the polymer electrolyte of a rechargeable lithium battery owing to its high solubility, low crystallinity, and its suitable glass transition temperature [14–18]. Moreover, it is a semi-crystalline polymer in which the amorphous domains can trap a greater amount of liquid electrolyte and wherein the crystalline regions contribute to the improvement of the mechanical integrity while the polymer is processed in free-standing films. Additionally, efforts have been made to reduce the electrical resistance and to improve the performance of the cell by changing the paste-fabrication method and using a different conducting agent. Finally, the possibility of a printed LiCoO_2 film as a cathode for a microbattery is suggested by fabricating a leakage-free microbattery with the structure of $\text{Li/PVDF-HFP gel/LiCoO}_2$.

2. Experimental

2.1. Preparation of pastes

LiCoO_2 powder with an average size of $5.34 \mu\text{m}$ was used as a cathode material. The pastes were formulated from a mixture of LiCoO_2 powder (J05A, JES E Chem.) as an active material, Emphos PS-21A (Witco) which contains a mixture of long-chain phosphate esters of ethoxylated C8–C12 (linear and branched) alcohols as a dispersant and various vehicle compositions, all of which were identical to those in a previous report by the authors [13]. Considering results of our previous paper [11–13]

and potential application for a microbattery, the paste composition as the ratio (wt.%) was determined as LiCoO_2 :vehicle:conductive agents:dispersant = 50–70:20–30:0–3:2–6. The pastes were prepared and homogenized on a standard three-roller mill (EXAKT-35, EXAKT) after pre-mixing and were then aged at 50°C for 10 min. Surface modification of the LiCoO_2 powder was pyrolyzed with resorcinol following the procedure outlined in the aforementioned earlier report by the authors [12].

2.2. Film preparation and cell testing of the printed electrode

A thick film was screen printed onto a platinum current collector/ SiO_2/Si wafer using a stainless 400-mesh screen. After the screen printing procedure, all samples were dried at 110°C for 10 min and cured at 190°C for 1 h. A Pt current collector with an area of $1 \text{ cm} \times 1 \text{ cm}$ was deposited by DC magnetron sputtering at a thickness of 300 nm. The electrical resistance of the printed films was measured using a four-point probe (CMT-SR2000N, Chang-min Ltd.). The surface roughness of the printed film was measured using a contact surface-roughness profile meter (SE3500, Kosaka Laboratory Ltd.). The electrolyte used was a solution of 1 M LiPF_6 in a 1:1 (v/v) mixture of ethylene carbonate (EC, Merck) and diethyl carbonate (DEC, Merck) with a poly-propylene separator (PP, Ube). Each printed cathode film was charged and discharged by applying a constant current in a potential range from 3.0 to 4.2 V (vs. Li/Li^+) at $20 \mu\text{A cm}^{-2}$. For the fabrication of complete thin-film batteries, LiPON solid electrolyte at a thickness of $1.5 \mu\text{m}$ was deposited onto a LiCoO_2 cathode film by RF magnetron sputtering. This experimental procedure was identical to that of a previous report by the authors [13]. A Li metal anode was deposited by thermal evaporation onto the LiPON film. The PVDF–HFP gel electrolyte was prepared by the solvent casting technique. The required amounts of PVDF–HFP were weighed and dissolved in DMC (Dimethyl Carbonate, Techno Semichem). After complete dissolution, the lithium salt LiPF_6 was added. The LiPF_6 concentration was fixed at 0.75 M LiPF_6 at $\text{EC/PC/DME} = 1/2/6$ (w/w). A homogeneous solution was obtained by stirring for 2 h at 85°C . The gel-type electrolyte was prepared by dipping the solutions using a poly-propylene separator (PP, Ube). The residual solvent was then allowed to evaporate slowly at room temperature. All fabrications and measurements were carried out in a dry room to protect the samples from moisture.

3. Results and discussion

LiCoO_2 thick films were replaced by screen printing while LiCoO_2 thin films were deposited using conventional film technolo-

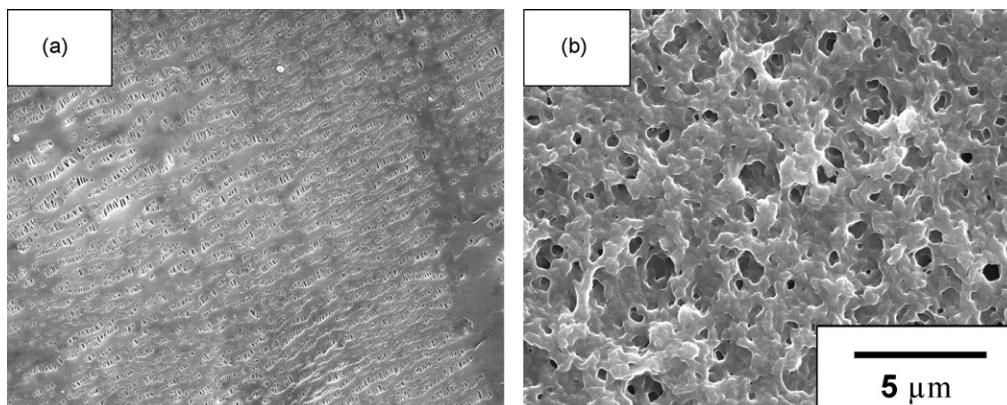


Fig. 1. Microstructures of the PVDF–HFP membrane prepared using a separator-dipping method: (a) before dipping—Bare separator films, (b) After dipping—PVDF–HFP films on separator films.

Download English Version:

<https://daneshyari.com/en/article/195528>

Download Persian Version:

<https://daneshyari.com/article/195528>

[Daneshyari.com](https://daneshyari.com)