

Characterization of a LiCoO₂ thick film by screen-printing for a lithium ion micro-battery

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Abstract

A thick film cathode has been fabricated by a screen-printing technique using LiCoO₂ paste to improve the discharge capacity in lithium ion micro-batteries. The LiCoO₂ thick film (about 6 μm) was obtained by screen-printing, but high discharge capacity and a suitable surface roughness of printed LiCoO₂ film cathodes could not be obtained by adding carbon black only to the LiCoO₂ paste. On the other hand, the printed cathode which was prepared using the mixture of carbon-coated LiCoO₂ powders and carbon black showed a typical discharge curve of a LiCoO₂ cathode with a high discharge capacity (179 μAh cm⁻²).

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1. Introduction

There is a growing interest in micro-batteries, which show good thermal stability, relatively low self discharge and high safety performance in emerging applications, such as smart card, RF-ID tag, remote sensor, semiconductor and military devices, etc. They have the advantages of variable shape and size according to the customer's specifications. Lithium cobalt oxide as the lithium intercalation material with a layered rock salt structure has a high operating potential of ~4.0 V and reversible capacity of 69 μAh cm⁻² μm⁻¹ over the range 0.5 ≤ x ≤ 1 in Li_xCoO₂, and has been known to be a suitable cathode material for lithium batteries [1–4].

In micro-batteries, RF magnetron sputtering, sol-gel process or laser ablation has been widely used to make LiCoO₂ thin films. Although the characteristics of LiCoO₂ thin films could be easily changed by the deposition conditions, it was necessary to grow the crystalline phase through the post-annealing process above 700 °C. Another limitation in formerly reported micro-batteries is the low discharge capacity, which depends on the thickness of the cathode film. Even though, a 4 μm LiCoO₂

film was reported by Dudney and Jang [5], problems of film stress control, high electrical resistivity and limiting high rate discharge still remain.

In this study, we propose a novel method to fabricate the LiCoO₂ thick film, which does not need a post-annealing process. This screen-printing method could increase the film thickness and control the shape more easily. Also, it is a simple and a relatively economical process [6]. When the printed LiCoO₂ film is formulated for high discharge capacity by screen-printing, the key issue is the surface control of the printed cathode film. If the cathode surface had a high roughness, electrical shorts might occur between the cathode and anode material. Thus, in this work, we focused on reducing the surface roughness of the printed cathode film by changing the composition of the paste and by modifying the active material. Also, we tried to reduce the electrical resistance and improve the cell performance by carbon-coating through the pyrolyzing of resorcinol.

2. Experimental

2.1. Preparation of pastes

The active material was LiCoO₂ powder, which has a 5.34 μm average particle size.

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The pastes were formulated from the mixture of LiCoO_2 powder (JES E Chem., Korea) as an active material, ethyl cellulose and terpineol (Fluka, Swiss) as a vehicle, and emphos PS-21A (Witco, USA) as a dispersant. The ratio of the paste composition was kept at 76:21:3, respectively. Carbon black (Degussa, Germany; average primary particle size, 30 nm) as a conducting agent was added in various amounts. The pastes were prepared and homogenized on a standard three-roller mill (EXAKT-35, EXAKT) after premixing and aging at 50°C for 10 min. Surface modification of LiCoO_2 powder was by pyrolysis of resorcinol. Then, LiCoO_2 powder was suspended in the resorcinol solution with equilibrium concentration and vigorous stirring time. The solution of resorcinol with a weight ratio of 5–50 wt.% resorcinol to LiCoO_2 powder was added. After stirring, the suspended powder was separated by a centrifugal separator and the resorcinol adsorbed powder was pyrolyzed at 550°C for 1 h in N_2 atmosphere. Completion of the carbon-coating was checked by carbon/sulfur analyzer (EMIA-320 V, Horiba), scanning electron microscopy (S4700, Hitachi) and transmission electron microscopy (Technig2, FEI).

2.2. Film preparation and half-cell testing of the printed electrode

The thick film was screen-printed onto a Pt current collector/ SiO_2/Si wafer using a stainless 500 mesh screen. The platinum current collector with an area of $1\text{ cm} \times 1\text{ cm}$ was deposited by dc magnetron sputtering and the thickness was 300 nm. The electrical resistance of printed films was measured by a four-point probe (CMT-SR2000N, Chang-Min Ltd.). The rheological behavior of the pastes was determined using a rheometer (DV II⁺, Brookfield) and the surface roughness of the printed film was measured using the contact surface roughness profile-meter (SE3500, Kosaka Laboratory Ltd.). The used electrolyte 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 polypropylene separator (PP, Ube). Each printed cathode film was discharged by applying the constant current in the potential range from 3.0 to 4.2 V (versus Li/Li^+) with various current rates.

3. Results and discussion

3.1. LiCoO_2 pastes

While the LiCoO_2 thin film was deposited by conventional film technologies such as sputtering and sol-gel processes, the LiCoO_2 thick film was applied by screen-printing. To deposit the solid electrolyte by sputtering onto the printed thick film, the printed film needs to have a roughness controlled surface. The properties of the printed LiCoO_2 films with different carbon black contents are shown in Fig. 1a and b. The electrical resistance of the films was reduced to $120\text{ k}\Omega\text{ cm}^{-2}$ by addition of carbon black. Although the thickness of the printed LiCoO_2 film was not changed, the average (R_a) and maximum (R_{max}) surface roughness was increased from 0.54 to 1.00 and 6.2 to $18.7\ \mu\text{m}$ by increasing the carbon black amount, respectively. It is known that the surface roughness was affected by the paste dispersion, which could be represented by the paste viscosity [7]. Because the carbon black powder was very small in size but large in surface area, the viscosity of LiCoO_2 paste was increased from 6000 to 280,000 cps according to the amount of carbon black. Thus, it could be noted that the dramatic increase of surface roughness of printed LiCoO_2 film was due to increase in viscosity by the addition of carbon black.

Fig. 2 shows discharge profiles of printed LiCoO_2 film with various carbon black additions. Electrochemical measurements were carried out at a discharge rate of $80\ \mu\text{A cm}^{-2}$ ($\cong 0.3\text{ C}$) in the potential range 4.2 and 3.0 V (versus Li/Li^+). It was shown that the discharge capacity of the printed cathode was decreased as the amount of carbon black increased. However, the discharge capacity was drastically decreased, beyond our expectations for high capacity by decreasing the electrical resistance. It could be explained that the excess carbon black in LiCoO_2 thick film acts as a resistor to the transfer of Li ions, although it decreased the electrical resistance. Also, there was a large IR drop voltage of 0.08 V and a lower discharge capacity of about $46\ \mu\text{Ah cm}^{-2}$, which corresponds to 30 mAh g^{-1} , considering pure LiCoO_2 loading amounts in the paste. According to these results, it could be determined that the addition of carbon black is $<1.0\text{ wt.}\%$. At this composition, the maximum roughness and resistance

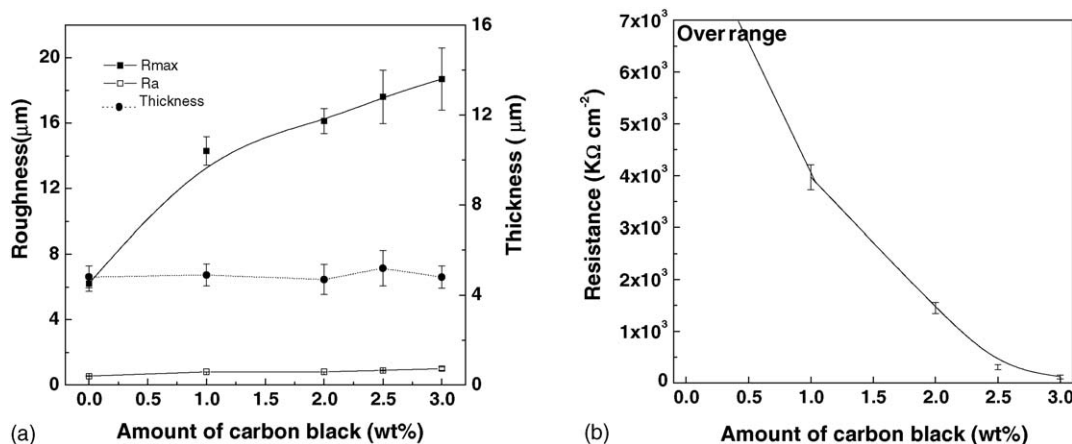


Fig. 1. Variations of (a) surface roughness, thickness and (b) resistance of printed LiCoO_2 films with the content of carbon black.

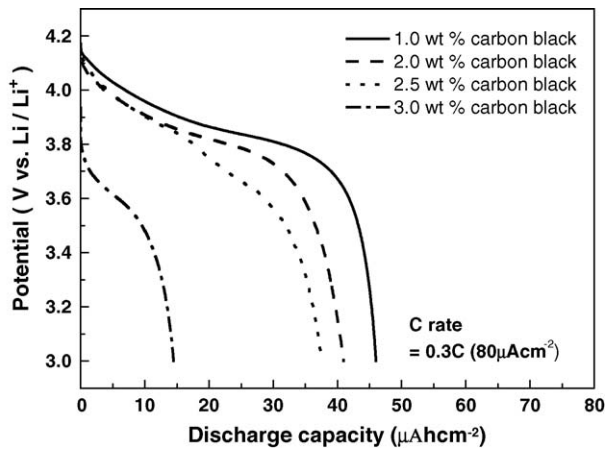


Fig. 2. Initial discharge curves of printed LiCoO₂ films depending on the content of carbon black at a rate of 80 $\mu\text{A cm}^{-2}$ between 3.0 and 4.2 V (vs. Li/Li⁺).

value were 14.3 μm and 3970 $\text{k}\Omega \text{cm}^{-2}$, respectively. This result shows that although the addition of carbon black considerably reduced the electrical resistance, the ideal discharge behavior and the small IR drop of the printed LiCoO₂ film could not be obtained via the simple addition of carbon black only. Also, the surface roughness was too high to make a Li ion micro-battery.

3.2. Effect of powder modification on paste electrode LiCoO₂ paste

Generally the surface roughness of the printed film is controlled by the size, shape and distribution of the active powder. It is important that the spherical shaped primary particles of the active powder are as small as possible. To reduce the surface roughness and the electrical resistance of the printed LiCoO₂ film, LiCoO₂ powders were modified by ball-milling and carbon-coating prior to paste formulation. Ball-milling of LiCoO₂ powders in ethanol for 24 h effectively reduced the maximum surface roughness of the LiCoO₂ paste. This is due to the reduction of the coagulation of LiCoO₂ powder. It reduced the

difference of the LiCoO₂ powder size and the repulsive force between the vehicle and LiCoO₂ powder. The optimized roughness R_a and R_{max} value was 0.49 and 5.38 μm , respectively, when the printed LiCoO₂ film was modified by controlling the LiCoO₂ powder size.

The specific amount of carbon-coating on the particle surface in water with adsorption time and equilibrium concentration are illustrated in Fig. 3a and b. As the adsorption time increased, carbon-coating was increased until the plateau was reached. The plateau started from 120 min. The adsorption isotherms appear to follow the Langmuir-typed behavior, suggesting that a monolayer coating of the resorcinol molecules has formed on the particle surface [8]. The amounts of coated carbon increased with equilibrium concentration, but the rate of increase was slow. The equilibrium concentration is defined by the concentration of carbon in the residual resorcinol solution after the adsorption equilibrium is obtained. The maximum adsorbed amount in our experimental condition is 1.1 wt.% (carbon per LiCoO₂), when the concentration at equilibrium is 150.96 g L^{-1} .

Figs. 4 and 5 show the SEM and TEM images of LiCoO₂ powder after ball-milling and carbon-coating. The average particle size of ball-milled LiCoO₂ decreased from 5.34 to 3.40 μm . After carbon-coating, we can see there are very small particles covered with LiCoO₂ powder. To confirm the carbon-coating we measured the interface of the LiCoO₂ particle by HRTEM. Apparently, the particles have a well-coated carbon layer on their surfaces. As a result of this, we note that the carbon could be applied by pyrolysis of resorcinol.

Using these carbon-coating powders, we fabricated the printed LiCoO₂ film, which has the properties shown in Fig. 6a and b. While the surface roughness was increased, the electrical resistance decreased with increasing carbon-coating.

This result shows that the properties of the printed LiCoO₂ film are dependent on the amount of carbon-coating. As can be seen in Fig. 5, the coated-carbon has a very small particle size and a large surface area, which makes the viscosity of the LiCoO₂ paste increase. Thus, it could be noted that the increase of surface roughness of the printed LiCoO₂ film is due to increasing

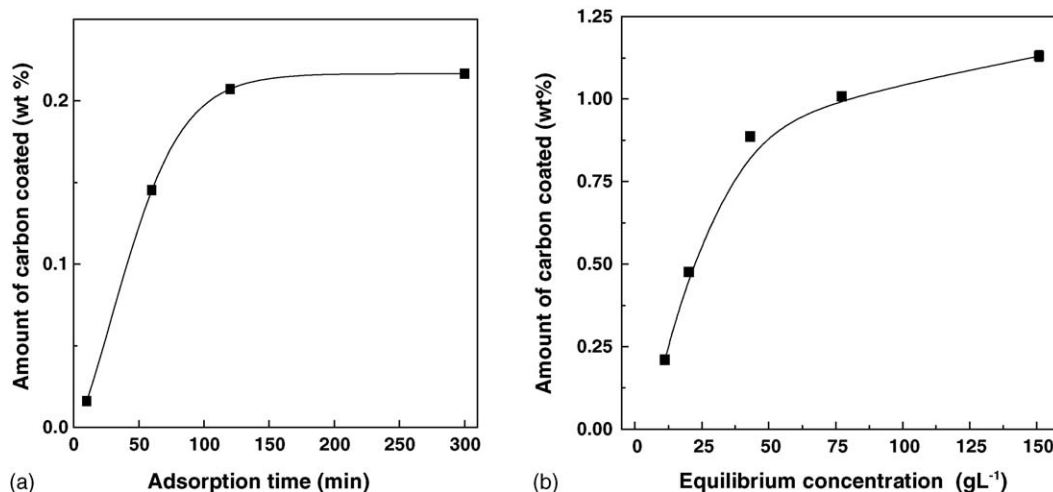


Fig. 3. Variations of the amount of carbon coated onto the LiCoO₂ powder with (a) the adsorption time and (b) the equilibrium concentration.

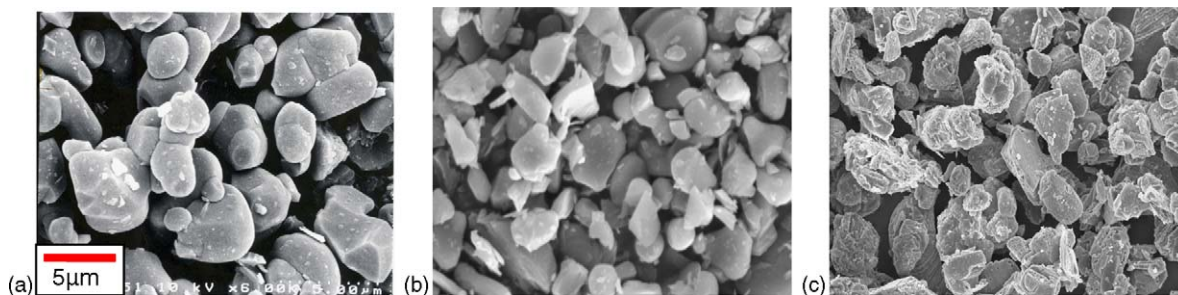


Fig. 4. Microstructures of modified LiCoO₂ powders: (a) as-received LiCoO₂ powders, (b) ball-milled LiCoO₂ powders and (c) carbon-coated LiCoO₂ powders.

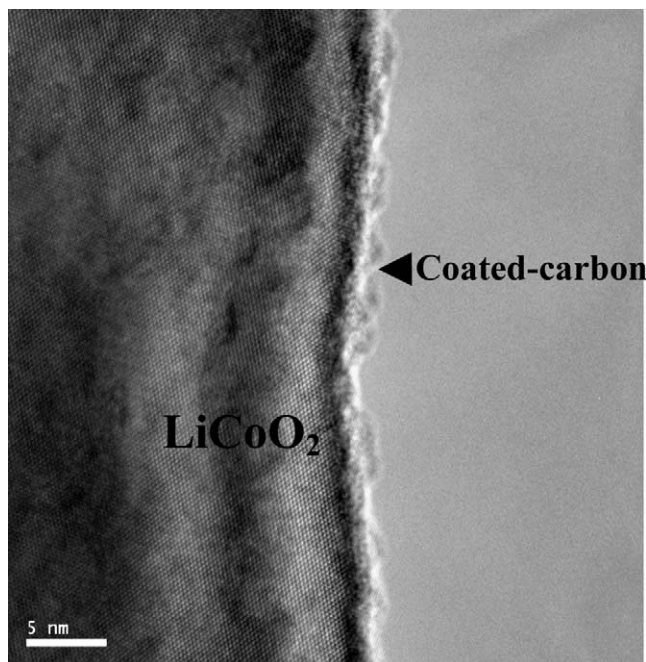


Fig. 5. TEM image of carbon-coated LiCoO₂ powder.

viscosity by carbon-coating. Also, carbon-coating reduced the electrical resistance.

Fig. 7 shows the initial discharge curves of the printed LiCoO₂ films depending on the amount of carbon coated at a rate

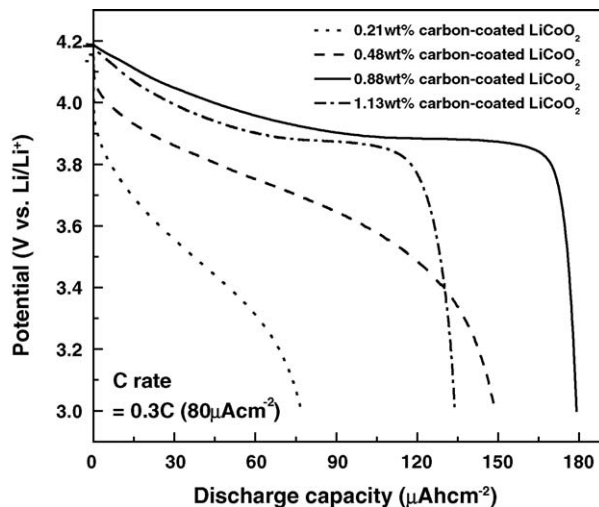


Fig. 7. Initial discharge curves of printed LiCoO₂ films depending on the amount of carbon coated at a rate of 80 μA cm⁻² between 3.0 and 4.2 V (vs. Li/Li⁺).

of 80 μA cm⁻² (≅0.3 C) between 4.2 and 3.0 V (versus Li/Li⁺). The discharge capacity was varied from 77 to 179 μAh cm⁻² dependent on the amount of carbon-coating. The maximum discharge capacity is 179 μAh cm⁻², which corresponds to about 147 mAh g⁻¹ when we calculated from the loading LiCoO₂ weight. This value closely corresponds to the original powder properties from JES E Chem. [9]. This increasing of discharge capacity was thought to be the surface reaction area increased

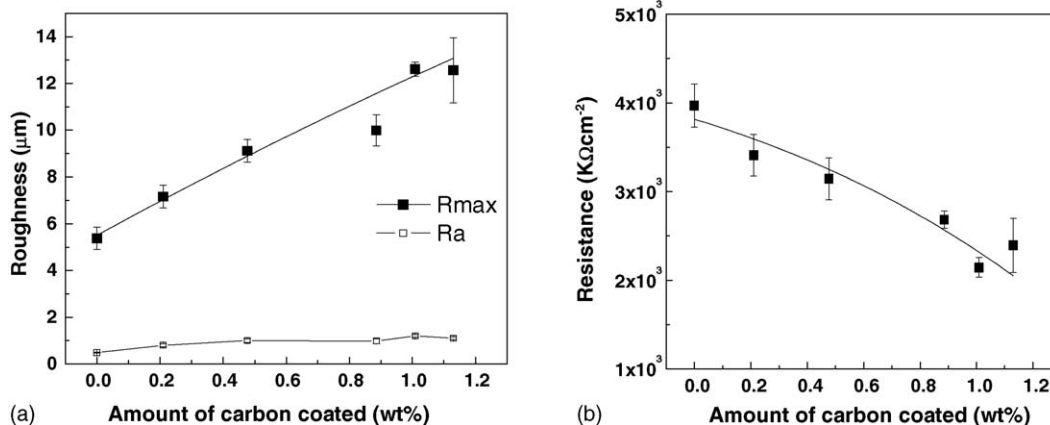


Fig. 6. Variations of (a) surface roughness and (b) resistance of printed LiCoO₂ films depending on the amount of carbon coated.

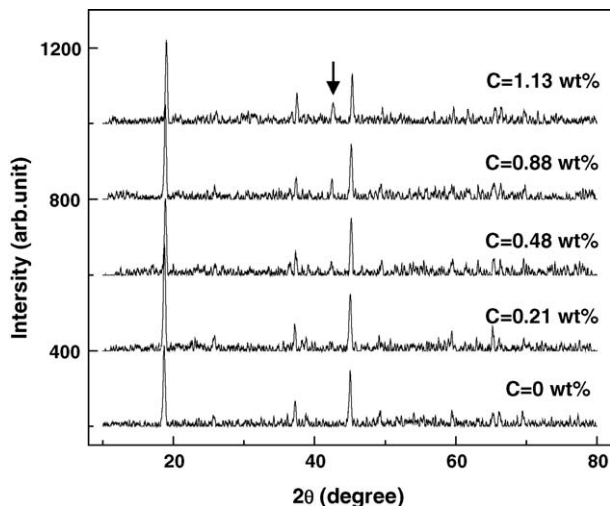


Fig. 8. XRD data of LiCoO₂ powders depending on the amount of carbon coated.

by ball-milling and electrical conductance increased by carbon-coating. There are many resistive factors such as vehicle and dispersant in our printed LiCoO₂ films. It is possible that the performance of these thick film materials is limited not by Li⁺ intercalation kinetics but rather by electrical conductivity. Therefore, the electrical conductivity plays a dominant role in limiting the electrochemical performance in a lithium ion intercalation cell [10–12]. However, carbon-coating printed LiCoO₂ films showed different cell performance by simply adding carbon black. It was thought that additional carbon black could not reduce the electrical resistance which is related to Li ion transfer but a carbon-coating could help Li ion transfer. When the carbon-coating amount is 0.88 wt.%, LiCoO₂ cathode had the highest first discharge value of 179 μAh cm⁻² and showed typical LiCoO₂ discharge properties. This result is a very high capacity compared with the reported capacity of 69 μAh cm⁻² [1–4]. As expected, we did not use any thermal treatment and the discharge capacity was improved greatly by increasing the cathode thickness. By the way, when the amount of coated-carbon was 1.13 wt.%, the discharge capacity was decreased to 134 μAh cm⁻². The XRD patterns of carbon-coated LiCoO₂ powder with various coating amount are shown in Fig. 8. The patterns remain basically unchanged after carbon-coating; however, we could see that the new peak was increased depending on the carbon-coating amount, which came from the (1 0 0) peak of graphite. This suggests that carbon-coating has modified only the surface of the active material without changing the crystal structure of the bulk active material. The results in Figs. 6 and 7, shows that it is possible that the improvement of cell performance by enhancing the electrical conductance has some limit. Thus, the available carbon-coating helps the electrical performance, but excess carbon-coating prevents Li ion intercalation. Fig. 9 shows the rate capability of 0.88 wt.% carbon-coating printed LiCoO₂ films. The IR drop is very small with increasing current rate until 240 μA cm⁻². Thus, it appears that films prepared by the paste and screen-printing methods described can be used as the cathode for micro-batteries.

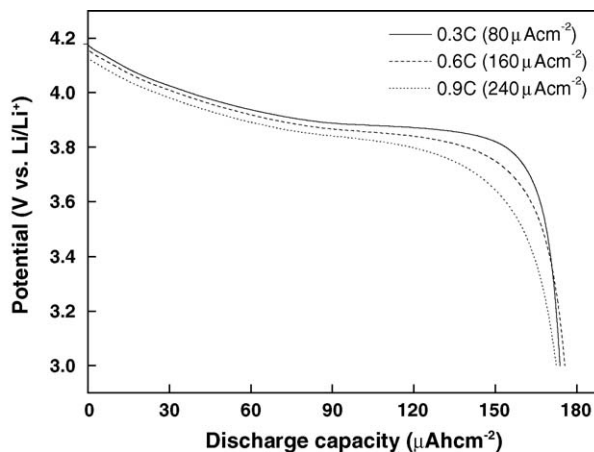


Fig. 9. Rate capability of printed LiCoO₂ films containing 0.88 wt.% carbon coated.

4. Conclusions

A thick film cathode has been fabricated by a screen-printing technique using LiCoO₂ paste to improve the discharge capacity in lithium ion micro-batteries. The LiCoO₂ thick film (about 6 μm) was obtained by screen-printing, but a high discharge capacity and suitable surface roughness of the printed LiCoO₂ film cathodes could not be obtained by simply adding carbon black to the LiCoO₂ paste. On the other hand, printed cathodes which were prepared using a mixture of carbon-coated LiCoO₂ powders and carbon black showed a typical discharge curve of LiCoO₂ cathode but with a high discharge capacity (179 μAh cm⁻²). The average and maximum values of surface roughness of printed LiCoO₂ films were effectively reduced from 0.8 to 0.49 and from 14.3 to 5.38 μm, respectively by controlling the LiCoO₂ powder size.

The results of this study indicate that screen-printed cathodes using a suitable LiCoO₂ paste are possible candidates for the thick film cathodes of micro-batteries.

Acknowledgement

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