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Fabrication of Lithium-ion Microarray Battery by Electrophoresis

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Fabrication of microscale lithium batteries has been required for various applications. A microarray configuration which is composed of interdigitated two comb-type electrodes is an appropriate form for the microscale battery. By an electrophoresis deposition (EPD), LiCoO₂ was deposited only on the selected comb-type substrate successfully. The prepared LiCoO₂ electrode can intercalate and deintercalate Li ion, indicating that the electrode can be used for cathode of the lithium battery. The discharge capacity of the electrode was 5.3 μA h cm⁻² at 1 C and the capacity will be improved by optimization of the EPD condition.

Key Words: Electrophoresis Deposition, Lithium Ion Battery, Microbattery

1 Introduction

Since 1990, Li ion battery has attracted us due to their high energy density.¹ Many groups have paid much effort to fabricate lithium microscale batteries.²⁻⁵ It has been expected that the microscale batteries is useful for various application related to microsystems. So far, some microscale thin film batteries have been reported.⁶⁻⁹ They are usually composed of thin layers of a cathode, an anode and an electrolyte. This configuration allows them to provide high current density by fast lithium ion transport due to short Li ion diffusion path in the thin electrolyte.¹⁰ However, capacity was quite low due to small amount of active materials in the cathode and the anode. The microscale battery with microarray configuration¹¹ composed of interdigitated two comb-type electrodes, can achieve both high current density and capacity. So far, we reported that fabrication of the microarray battery by a sol-gel method combined with micro-injection system¹²,¹³ and electrophoresis deposition (EPD).¹⁴ By using the EPD, a composite electrode with Li₂Ti₅O₁₂, Ketjen Black and polyethylene oxide (PEO) which were used as an anode, an electronic conductive and a binding materials, respectively, can be deposited together on only one Au array electrode with only 10 μm wide and 5 μm gap and it was confirmed that the deposited electrode could charge and discharge, namely work as the negative electrode for the Li ion battery. As following step, the positive electrode deposited on the Au array electrode has been needed to fabricate the lithium micro battery.

In this study, we investigated a fabrication of LiCoO₂ cathode with the PEO binding material deposited on the Au array electrode by the EPD as a first step of deposition of the LiCoO₂ composite electrode. Small LiCoO₂ particles could be deposited on only one comb of the microarray electrodes with 10 μm wide successfully. A LiCoO₂ / gel electrolyte / Li metal cell was fabricated and its electrochemical properties were tested.

2 Experimental

The microarray pattern (BAS Inc., No.01164) was composed of two interdigitated comb-shape Au plates. The comb-shape Au plates with 10 μm wide and 2 cm long were interdigitated at 5 μm gap.¹⁰ LiCoO₂ small particles were prepared by a sol-gel method.¹⁰,¹² Pure LiCoO₂ was obtained by X-ray diffraction (XRD) pattern and its particle size was 600 nm that was estimated from scanning electron microscope (SEM) images. A suspension containing the LiCoO₂ for the EPD was prepared by mixing the LiCoO₂ (500 mg), PEO (24 mg, Nippon soda, MES-275, particle size 24 nm, Mw 235, purity 99%), and Acetone (50 ml, wako, purity 99.5%). The suspension was treated supersonically for 30 min prior to the EPD. The EPD process was carried out by using a three-electrode system (Fig. 1).¹⁰ In this EPD system, one working electrode and two counter electrodes are used and arrange-

![Fig. 1 Schematic illustration of three-electrode EPD system.](image-url)
ment of these electrodes for deposition of charged particles was optimized in order to control strengths of electric field generated in suspension. One of the comb-shape Au plates was used as the working electrode and another one acted as the counter electrode 1 during the EPD process. The working electrode in the EPD became a current collector after deposition of active materials. Total surface area of the working electrode was 0.023 cm². Distance between counter electrode 2 and working electrode was 1 mm. In preliminary experiment using LiMn₂O₄ suspension, the best EPD duration was 1 s and repeated 5 times. Therefore, the EPD duration was always set to 1 s and repeated 5 times in this study. SEM observation (JED-5310, JEOL Co.) was conducted to check location and morphology of the deposited LiCoO₂ on the microarray. To evaluate cathodic properties of the deposited material, LiCoO₂ / poly-methylmethacrylate (PMMA) gel electrolyte / Li metal half cell was fabricated. A cyclic voltammetry (CV) measurement and a charge / discharge test at various C rates were employed. The deposited amount of LiCoO₂ was too small to weigh. The C rate was estimated from a peak area in a cyclic voltammogram. Therefore, some particles which might not relate to the electrochemical reaction due to loose contact with the Au substrate, were excluded in the estimation.

3 Results and Discussion

In order to find a suitable EPD condition for the LiCoO₂ deposition, various sets of the strengths of the electric field 1 and 2 were tested. When the electric field 1 and 2 were 25 and 1667 V cm⁻¹, respectively, any deposition particles were not observed because the electric fields would be too weak. Then, the electric field was strengthened to 50 and 3333 V cm⁻¹, respectively. The deposition was observed. However, only edge of the working electrode was covered with the particles. In this case, the EPD was thought to be dominated by electric field 2 between the counter electrode 1 and the working electrode. The current is like to flow the shortest way. Thus, the current flows mainly between sides of the working electrode and the counter electrode 1 and the particles deposited on the edge of the electrode. The electric field 2 was 66 times stronger than the electric field 1. This difference should be decreased. Thus, the electric field 1 and 2 were fixed to same value. When both electric fields were 100 V cm⁻¹, the LiCoO₂ particles were deposited on the gap of the combs as well as on the working electrode. Figure 2 shows SEM images of surface of the working electrode after the EPD when both electric fields were 50 V cm⁻¹. The LiCoO₂ cathode material could be deposited on only one comb of the microarray electrode. However, as shown in higher magnification image (Fig. 2b), many spaces among the deposited particles could be observed, indicating that only small amounts of the LiCoO₂ particles were deposited. Larger amounts of the LiCoO₂ particle may be
deposited by optimization of the EPD duration.

The cyclic voltammogram (CV) of the LiCoO$_2$ / PMMA gel electrolyte / Li metal half cell was measured at 10 mV min$^{-1}$ (Fig. 3). In anode scan, three clear peaks were observed at 3.93, 4.07, and 4.18 V vs. Li / Li$^+$ corresponding to many structure changes of the LiCoO$_2$. In cathode scan, three clear peaks at 4.17, 4.07, and 3.89 V vs. Li / Li$^+$ were appeared as well. There is no doubt that the LiCoO$_2$ particles deposited on the working electrode by the EPD method are intercalated and deintercalated by Li ion since the redox couples were observed clearly.

Discharge curves of the LiCoO$_2$ / PMMA gel electrolyte / Li metal half cell measured at various C rates were shown in Fig. 4. The LiCoO$_2$ electrode was charged up to 4.1 V at 1 C prior to each discharge measurement. A discharge plateau around 3.94 V vs. Li / Li$^+$ was observed and the discharge capacity of the electrode at 1 C was 5.3 µA h cm$^{-2}$. Additionally, the electrode could keep its discharge capacity at even high C rate, 5.2 µA h cm$^{-2}$ at 10 C.

By using the EPD with the three-electrode configuration, the small particles of the LiCoO$_2$ can be deposited on a pair to the microarray electrodes. It is confirmed that the deposited LiCoO$_2$ particles can work as the positive electrode for the Li ion battery in the CV and the charge / discharge measurements. These results clearly show that it is possible to fabricate the microarray cathode by the EPD method. However, many spaces were observed among the deposited particles, indicating that amount of the deposited particle was relatively small. The discharge capacity would increase if large amounts of the LiCoO$_2$ were deposited. Optimization of the EPD process, which can deposit large amounts of the cathode material, is required. Moreover, no conductive material was contained in the suspension. This material should be needed for thick electrode to improve electronic conductivity. Thus, optimization of the EPD condition using the suspension with the conductive materials is also required. Both optimizations are going on now and they will be reported in due course.

4 Conclusion

By using the EPD, LiCoO$_2$ can be deposited on only one comb-type Au working electrode with 10 µm width. The deposited LiCoO$_2$ particles showed clear peaks with respect to Li intercalation / deintercalation in the CV, indicating that the electrode can be used for the Li ion battery. However, only small amounts of the LiCoO$_2$ can be deposited in our EPD condition. Due to deposition of large amounts of the LiCoO$_2$, it is expected that performance of the cathode will be improved. In order to fabricate the microbattery with the microarray configuration, further study on optimization of the EPD process is required.

References