

# All-solid-state micro lithium-ion batteries fabricated by using dry polymer electrolyte with micro-phase separation structure

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## Abstract

Micro-batteries were fabricated by using BAB block copolymer as dry polymer electrolyte, which consisted of polyethylene oxide and polystyrene and had relatively high ionic conductivity at room temperature. The micro-batteries were fabricated by a sol-gel method combined with micro-injection system. Two types of micro-battery were fabricated. One consists of a single cell and another of 3-cells connected in series.  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  were used as active materials in positive and negative electrode, respectively. The micro-array batteries were operated at room temperature without any plasticizer in the polymer electrolyte. The operation voltages were 2.45 V and 7.40 V for a single cell and 3-cell array, respectively. The discharge capacities estimated from cyclic voltammetry measurements were 245 nA h for a single cell and 12.1 nA h for a 3-cell array, which corresponded to the energy densities of  $8.48 \mu\text{W h cm}^{-2}$  and  $4.54 \mu\text{W h cm}^{-2}$ , respectively.

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## 1. Introduction

Rechargeable lithium ion batteries have attracted much attention due to their high energy density and are applied to lightweight devices such as laptop computers, cellular phones, and personal digital assistants (PDAs). Many efforts have been devoted to fabricate micro-batteries for their application to micro-devices including micro-sensors, micro-mechanics, and micro-electronics. Several groups have developed planer thin-film batteries [1–7], which consists of a thin-film positive electrode, a solid electrolyte, and

a negative electrode (for example Li). The thin-film electrodes in those batteries are fabricated by the rf-sputtering [1,2,6,7], pulsed laser deposition (PLD) [4], and chemical vapor deposition methods [8,9]. Swider-Lyons et al. have developed a laser direct-write method for the patterning of conventional composite battery electrodes consisting of battery active materials, conductive agent, and binder [10]. Another method to fabricate thin film electrodes is a sol-gel method. We have fabricated thin-film electrodes by utilizing a sol-gel method [11–14]. In our previous study, we reported a novel technique for fabricating patterned-thin film electrodes by utilizing a sol-gel method combined with a micro-injection system [15–17]. In that technique, a precursor sol for an active material was used as “ink” and a glass capillary was used as a “pen”. By drawing with “ink” and a “pen”, we can fabricate any forms of electrode on a substrate.

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On the other hand,  $\text{Li}^+$  conducting solid materials are used as an electrolyte in micro-battery. Lithium–phosphorous oxynitride (LIPON), which is prepared by rf sputtering of  $\text{Li}_3\text{PO}_4$  as a target material under  $\text{N}_2$  atmosphere, is often used in thin film battery [1,2,5,7]. Thin film battery using dry polymer electrolyte was fabricated for the first time by Ogumi et al. [18]. The battery was composed of thin polymer electrolyte prepared by plasma polymerization,  $\text{TiS}_2$  thin film, and Li. Recently, Park et al. fabricated a thin film battery using  $\text{LiCoO}_2$ , Li, and a dry polymer electrolyte, which was prepared on  $\text{LiCoO}_2$  thin film by a spin coating method [19]. Dry polymer electrolytes do not contain any flammable organic liquids unlike gel polymer electrolytes. Thus the safety of the battery can be improved by using a dry polymer electrolyte. However, conductivity of a dry polymer is generally lower than that of a gel polymer electrolyte and an organic electrolyte. Therefore, most of the lithium polymer batteries reported so far were operated above  $60^\circ\text{C}$  due to low ionic conductivity of a dry polymer electrolyte [20–23].

We have prepared a block copolymer consisting of polyethylene oxide (PEO) and polystyrene (PSt) and investigated its electrochemical performance [23,24]. This polymer (denoted as MES polymer) showed high ionic conductivity at room temperature ( $>10^{-4}\text{ S cm}^{-1}$ ) without any organic additives (plasticizer) due to its micro-phase separation structure, in which PSt block provides a mechanical strength and PEO block allows fast ion conduction. By utilizing the dry MES polymer, we have fabricated all solid state lithium polymer batteries operating around room temperature [23].

In this study, using MES polymer, we fabricated two types of micro-battery by utilizing a sol–gel method combined with micro-injection technique. One consisted of a single cell. The other was an array of three single cells connected in series, which was fabricated to demonstrate the applicability of our technique to construct micro-battery systems. Both types of micro-batteries were fabricated on Au current collector prepared by photolithography.

## 2. Experimental

The patterned Au current collectors were fabricated by photolithography on a quartz glass ( $\text{SiO}_2$ ) substrate in Tohoku University. The  $\text{SiO}_2$  substrate was covered with a photoresist (S-1818, Shipley Corporation) with spin-coater at 4000 rpm for 20 s, and was baked at  $110^\circ\text{C}$  for 10 min. The photoresist was exposed to UV light through a photomask and developed. The Au pattern on Ti was fabricated by sputtering each thin layer (titanium and then gold) onto the photolithographic patterned substrate. The substrate was immersed in acetone and then the Au pattern was defined by lift-off of the resist polymer. In this study, two types of patterned-current collectors were fabricated. The current collectors shown in Figs. 1a and 2a were used for a single cell and an array of 3 single cells connected in

series, respectively. The current collector for a single cell consists of two sets of comb-type current collectors. Each current collector has 10 band-electrode elements of  $100\ \mu\text{m}$  width,  $2\ \text{mm}$  length, and  $0.1\ \mu\text{m}$  thickness, separated by  $50\ \mu\text{m}$  gap from adjacent elements with  $6.6 \times 10^{-2}\text{ cm}^2$  of cell area. The current collector for 3-cell array has 6 band-electrode elements of  $50\ \mu\text{m}$  width,  $2\ \text{mm}$  length,  $0.1\ \mu\text{m}$  thickness, and  $50\ \mu\text{m}$  gap with  $1.7 \times 10^{-2}\text{ cm}^2$  of cell area.

The substrate was cleaned in piranha, a 3:1 mixture of concentrated  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$ , for 15 min to remove impurities on the surface. The hydrophobic pretreatment of  $\text{SiO}_2$  and the hydrophilic pretreatment of Au were carried out to put precursor sol for active materials on Au electrode area selectively as will be mentioned below. First, for the hydrophobic pretreatment of  $\text{SiO}_2$ , the current collector was immersed in 10 mM *n*-octadecyltrichlorosilane/toluene solution for 5 h followed by a rinse with pure ethanol. Then, for the hydrophilic pretreatment of Au, it was immersed in 1 mM 3-mercapto-1-propanol/ethanol solution for 12 h.

The microarray electrodes of  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  were prepared on the Au current collectors using a sol–gel method in Tokyo Metropolitan University according to our previous reports [15–17]. The molar composition of the precursor of  $\text{LiMn}_2\text{O}_4$  was  $\text{CH}_3\text{COOLi}:\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}:\text{i-C}_3\text{H}_7\text{OH}:\text{CH}_3\text{COOH}:\text{H}_2\text{O}:\text{poly}(\text{vinylpyrrolidone})$  (PVP,  $M_w$ : 55000) = 1:2:20:10:60:2 [VP monomer unit]. The molar composition of the precursor of  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  was  $\text{CH}_3\text{COOLi}:[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}:\text{CH}_3\text{COOH}:\text{i-C}_3\text{H}_7\text{OH}:\text{PVP} = 4.5:5:60:100:2$  [VP monomer unit]. The precursor sol was put on the Au current collector using micro-injection system (InjectMan NI2, Eppendorf) under an optical microscope observation (BX51W1, Olympus). The detail of the experimental set up and conditions were described elsewhere [15,16]. In this system, a glass capillary (inner diameter:  $0.5\ \mu\text{m}$ ) was used as a pen and a precursor sol was used as ink. By utilizing this system, one can make it possible to do micro-patterning on the substrate. The injection pressure of the precursor sol was set to be 1000 hPa. The precursors were dried in air at  $60^\circ\text{C}$  and converted into gel films. The gel films were calcined at  $450^\circ\text{C}$  for 1 h and successively annealed at  $700^\circ\text{C}$  in air for 30 min. Thickness of the active materials was determined by atomic force microscope (NanoScope<sup>®</sup> IIIa).

The polymer electrolyte used in this study was PEO-based BAB block copolymer denoted as MES prepared in Nippon Soda Company Limited [23,24]. MES polymer and  $\text{LiClO}_4$  ( $[\text{Li}]/[\text{EO}] = 0.05$ ) were dissolved in the mixed solvent of tetrahydrofuran/acetone (1/1 in volume ratio). The mixture solution was cast on the substrate. Then the solvent was completely evaporated at  $110^\circ\text{C}$  overnight under high vacuum to prepare MES film without any plasticizers on the substrate.

Cyclic voltammogram (CV) was obtained at  $0.167\text{ mV s}^{-1}$  using a potentiostat/galvanostat (Model 660B, ALS) in dry argon atmosphere at room temperature.

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