Micro-patterning of $LiMn_2O_4$ Electrode Using Sol–Gel Process for Lithium Micro-batteries

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Micro-dot array of $LiMn_2O_4$ on Au substrate was prepared by sol–gel process combined with a micro-injection technology. The size of a dot of $LiMn_2O_4$ was 50 μm, and dot population density on the substrate was 5000 dots cm^{-2}. Electrochemical properties of micro-dots of $LiMn_2O_4$ in a PMMA-gel electrolyte were characterized as cathode for lithium micro-batteries. A micro-dot of $LiMn_2O_4$ exhibited a discharge capacity of 1.8 μC dot^{-1}, and the capacity fade was only 21% over 200 charge–discharge cycles.

Rechargeable lithium ion batteries have been used as power sources of cellular phones and laptop computers because of high energy density. Recently, microscale lithium-ion batteries have been studied by many researchers.[1–3] If micro-batteries are realized, it will be utilized in various application fields related to microsystems, such as microsensors, micromechanics, and microelectronics. In order to manufacture a micro-battery, novel technique for micro-patterning of electrodes should be developed. In this work, we developed a technique to prepare micro-patterns of ceramics on a substrate using sol–gel method combined with a micro-injection technology. Using this technique, micro-patterns of battery active materials can be prepared on conductive substrates. We have reported that $LiMn_2O_4$ thin film electrode can be prepared via a sol–gel process.[4] $LiMn_2O_4$ has a spinel-related structure with space group $Fd3m$, and Li^+ ion can be extracted/inserted from/into the crystallographic structure at 4 V vs Li/Li^+.[5] The volume change of $LiMn_2O_4$ during Li^+ ion insertion and extraction is very small,[6] and this material is a promising cathode for all solid-state lithium batteries. In the present paper, micro-dot array of $LiMn_2O_4$ was prepared on Au substrate by sol–gel process, and its electrochemical properties were investigated in a polymer-gel electrolyte.

$LiMn_2O_4$ was prepared via a PVP sol–gel process.[4] A precursor sol for $LiMn_2O_4$ was prepared from CH_3COOLi, $Mn(CH_3COO)_2 \cdot 4H_2O$, i-C_3H_7OH, CH_3COOH, H_2O, and poly(vinylpyrrolidone) (PVP, M_w: 55000). These starting materials were mixed in a molar ratio of 1:2:20:10:60:2 (VP monomer unit). By using a micro-injection system (InjectMan NI2, Eppendorf), micro-dots were drawn on Au substrates with a glass capillary (inner diameter: 0.5 μm) under an optical microscope observation (BX51W1, Olympus) as shown in the graphical abstract. The precursor sol was used as ink for the drawing. The injection pressure of the sol was set to be 1000 hPa. The sol was converted into gel in air at 60 °C. After the gelation, it was calcinated in air at 650–750 °C for 30 min. The surface morphologies of the dots were observed with a scanning electron microscope (JED-2100, JEOL), and crystallographic structures were characterized by micro-Raman spectroscopy (NRS-1000, Jasco) with 532 nm laser radiation (spot size: ca. 5 μm).

Electrochemical properties of micro-dots of $LiMn_2O_4$ were characterized with two-electrode system. The electrolyte was a gel sheet of poly(methyl methacrylate) (PMMA) containing $LiClO_4$. PMMA gel electrolyte was prepared by thermal polymerization.[7] Methyl methacrylate (MMA) monomer containing ethylene glycol dimethacrylate (EGMA) as cross-linking agent was polymerized in mixed solvents of ethylene carbonate and diethyl carbonate (1:1 in volume) containing 1 mol dm^{-3} $LiClO_4$ ($LiClO_4$-EC-DEC). Azobisisobutyronitrile (AIBN) was used as polymerization initiator. The mixed weight ratio of MMA, EGMA, AIBN, and $LiClO_4$-EC-DEC was 1:0.05:0.02:2.87. The polymerization was carried out in inert atmosphere at 80 °C for 1 h. The mechanical strength of PMMA gel was enough for the fabrication of a battery without separator. The thickness of the PMMA gel sheet was 300 μm, and the ionic conductivity of the gel electrolyte was ca. 1×10^{-3} S cm^{-1} at 25 °C. In order to fabricate an electrochemical cell, the PMMA gel sheet was put on the $LiMn_2O_4$ micro-dots, and then a counter electrode (a lithium metal foil) was put on the gel sheet. Electrochemical measurements were carried out using a potentiostat (Model 660B, ALS) in dry argon atmosphere at 25 °C.

Figure 1 shows optical microscope image of micro-dots of $LiMn_2O_4$ on Au substrate. Micro-pattern of $LiMn_2O_4$ could be drawn on a metal substrate by sol–gel process. The size of a dot was 50 μm in diameter, and the dot population density on the substrate was 5000 dots cm^{-2}. In the present study, only 10% of the gold substrate was covered by micro-dots. The thickness of a $LiMn_2O_4$ micro-dot was approximately 0.6 μm, however, the surface of the dot was not smooth observed by scanning electron microscope. The size of a dot is important for designing of a micro-battery. Optimization of viscosity of the precursor sol and modification of the substrate may be needed to control the dot size.

In order to characterize the crystallographic structure of

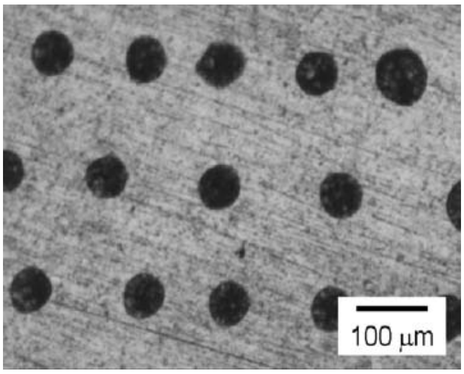

Figure 1. Optical microscope image of $LiMn_2O_4$ micro-dot array on Au substrate.

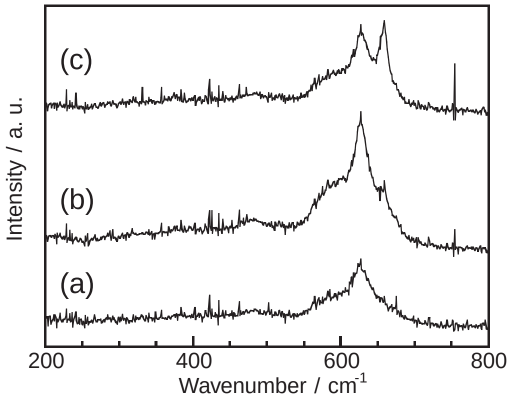

Figure 2. Raman spectra of $LiMn_2O_4$ micro-dots annealed at 650 (a), 700 (b), and 750 °C (c).

$LiMn_2O_4$ micro-dots, micro-Raman spectroscopy was carried out. Unfortunately, $LiMn_2O_4$ was not detected by X-ray diffraction measurement, because the dot population on the substrate was not enough to obtain good S/N ratio. Figure 2 shows Raman spectra of $LiMn_2O_4$ dots prepared at various temperatures. Raman spectra of $LiMn_2O_4$ dots consist of a series of broad bands between 450 and 700 cm^{-1}. The peaks at 620, 597, and 480 cm^{-1} are assigned to A_{1g}, $T_{2g}(3)$, $T_{2g}(2)$ modes, respectively, as predicted by group theory for a cubic compound.[8] The peak at 660 cm^{-1} observed for $LiMn_2O_4$ calicinated at 750 °C was attributed to Mn_3O_4.[9] Formation of Mn_3O_4 during the heat-treatment may be due to evaporation of lithium salts at high temperatures. Apparently, the Raman peaks of $LiMn_2O_4$ prepared at 700 °C were sharp compared with those of the sample prepared at 650 °C. This indicates the crystallinity of $LiMn_2O_4$ increases as the annealing temperature increases. The crystallinity of $LiMn_2O_4$ influence on its electrochemical properties, and high crystallinity is favorable to battery application.[10] Then, the optimized heat-treatment temperature was 700 °C for preparation of $LiMn_2O_4$ via PVP sol–gel process.

Figure 3 shows the cyclic voltammograms of the $LiMn_2O_4$ micro-dots on Au prepared at 700 °C. There were 1000 dots of $LiMn_2O_4$ on the gold substrate. Well-defined two reversible peaks are observed at 4.0 V and 4.1 V. This electrochemical behavior shows good agreement with that of $LiMn_2O_4$ thin film electrode.[4] These peaks correspond to the Li^+ ion insertion/extraction due to the redox of $Mn^{3+/4+}$ in the spinel structure.[5] The average current for a dot was nA level, and the discharge capacity of a $LiMn_2O_4$ dot was calculated from the integration of cathodic current as 1.8 μC. This capacity corresponded to 1.5 $nC\,\mu m^{-3}$ normalized by the volume of a dot, which was 70% of the theoretical capacity of $LiMn_2O_4$ (2.3 $nC\,\mu m^{-3}$). It was considered that the porosity of the prepared material decreased the specific capacity. Multi-scan cyclic voltammetry for $LiMn_2O_4$ was performed to examine the cycle stability of the electrode. Cyclic voltammogram changed depending on the cycle number as shown in Figure 3. As the cycle number increased, anodic peaks shifted to higher potentials and cathodic peaks did to lower potentials. However, the discharge capacity fade was only 21% over 200 cycles. This indicates that the kinetics of Li^+ ion extraction and insertion became sluggish as the cycle number increased. Probably, the charge transfer resistance between $LiMn_2O_4$ and PMMA-gel increased due to some kind of passivation film on $LiMn_2O_4$.[11] Organic solvents can be oxidized on $LiMn_2O_4$, and oxidation products form a passivation film. Surface modification of $LiMn_2O_4$ may be useful to stabilize the interface between $LiMn_2O_4$ and electrolyte.

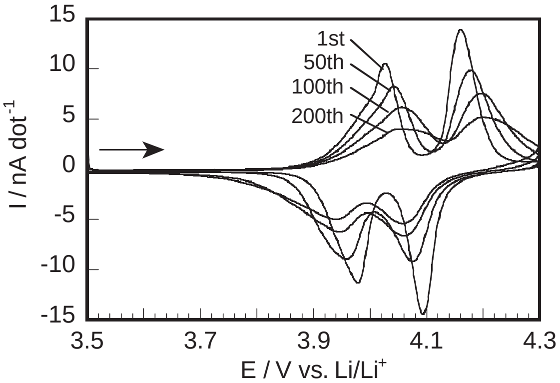

Figure 3. Cyclic voltammograms of $LiMn_2O_4$ micro-dot array on Au prepared at 700 °C. Electrolyte was PMMA gel containing $LiClO_4$-EC-DEC, and counter electrode was lithium metal foil. Scan rate was 1 $mV\,s^{-1}$. Current was divided by the number of dots on Au substrate.

As preliminary experiment, a micro-injection device was utilized in this work to draw a micro-pattern of $LiMn_2O_4$. Further efforts are under way to fabricate smaller patterns of electrodes for micro-batteries. The combination of micro-array electrode and polymer electrolyte will allow us to construct a micro-scale battery.

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