Preparation of Li₄Ti₅O₁₂ Thin Film Electrode with PVP Sol-Gel for a Rechargeable Lithium Microbattery[†]

Young Ho RHO and Kiyoshi KANAMURA

Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University
1 1 Minami-Ohsawa, Hachiohji, Tokyo 192 0397

A Li₄Ti₅O₁₂ thin film electrode for rechargeable lithium microbatteries was prepared on Au substrate by a sol-gel method. A stable sol was successfully prepared by adding poly(vinylpyrrolidone) (PVP) into 2-propanol solvent, in which PVP prevented a crack formation. The sol was coated on Au substrates with a spin coater, and was converted to gel during the spin coating process. The gel was then heated to form Li₄Ti₅O₁₂ oxide. Optimized conditions for preparation of uniform film without any cracks were firstly a heating temperature of 600 , 3000 rpm, and secondly a sol with 5 mol   of PVP. An electrochemical cell was constructed with polymethylmethacrylate gel-polymer electrolyte, which was electrochemically evaluated using a cyclic voltammetry and a discharge and charge test. The discharge and charge curves were very flat around 1.55 V and the rechargeability increased up to 97.5   at 60th cycle. The Li ion diffusion coefficient at a potential of 1.57 V was estimated to be 6.5×10^{-10} cm² s⁻¹, indicating that the thin film exhibited a fast electrochemical response. From these results, it can be said that the Li₄Ti₅O₁₂ thin film with a fast electrochemical response is a prospect of an active electrode material, and that PVP sol-gel method is very useful for thin film preparation.

Introduction

Recently, many researchers have studied on rechargeable lithium micro-batteries.[1 8] The micro-scale batteries will be realized in all solid-state type, and utilized in various application fields related to microsystems, such as micro-sensor, micro-mechanics, microelectronics, and so on. In order to develop micro-scale lithium ion batteries with a high energy density, a fabrication technique for micro-scale anodes, cathodes, and electrolytes should be needed.

Various kinds of Li ion conductive materials and transition metal oxides have been prepared as electrolyte and electrode films for all solid-state rechargeable lithium batteries. As an anode active material for rechargeable lithium micro-batteries, a spinel Li₄Ti₅O₁₂ is a good candidate, because of its very flat discharge and charge curves and high cycleability.[9 17] In general, Li₄Ti₅O₁₂ has been synthesized by heating a mixture of Ti and Li sources at 800   for 24 h under air atmosphere. It exhibits a working potential of 1.55 V vs. Li Li   and its theoretical discharge capacity is 167

mA h g⁻¹.

By the way, various methods have been already developed for fabrication of thin film electrodes, such as chemical vapor deposition[18], r.f. magnetron sputtering[19], flash evaporation[20], pulsed laser ablation[21], spray coating[22], molten carbonate method[23], and so on. On the other hand, a sol-gel method[24], which is one of soft solution process, can be considered as a good candidate for fabrication of thin film electrodes with some advantages, such as low fabrication cost, low sintering temperature, relatively easy control of a stoichiometry, etc.

We have investigated on preparation of thin film electrodes and electrolytes by using a sol-gel method for rechargeable lithium micro-batteries.[16, 17, 25 29] Our efforts on preparation of Li₄Ti₅O₁₂, LiCoO₂ and LiMn₂O₄ thin film electrodes on Au substrate, and Li₀.₃₃La₀.₅₅TiO₃ thin film electrolyte on Pt substrate were successful by introducing poly(vinylpyrrolidone) (PVP) to a sol, which was very effective to prepare a crack-free thin film. Actually, our previous reports showed a smooth surface morphology and excellent electrochemical properties on Li₄Ti₅O₁₂, LiCoO₂ and LiMn₂O₄ thin film electrodes, and Li₀.₃₃La₀.₅₅TiO₃ thin film electrolyte.[16, 17, 25 29] In this study, Li₄Ti₅O₁₂ thin

E-mail: kanamura-kiyoshi@c.metro-u.ac.jp

film prepared by the PVP sol-gel method was applied to a lithium ion polymer battery with polymethyl-methacrylate gel-polymer electrolyte.

Experimental

Two kinds of sols were prepared according to a scheme illustrated in **Fig. 1** and our preliminary reports.[16, 17] In each sol, ethanol and 2-propanol with or without PVP were used as solvent. These sols were used for a preparation of a thin film electrode. The sols were coated on Au substrate with a spin coater for thin film preparation. The sols were converted to gel during the spin coating process. The gel films on Au substrate were heated to prepare $Li_4Ti_5O_{12}$ oxide. This procedure can be repeated to control film thickness.

Crystal structure of the thin film was characterized with X-ray diffraction (XRD) method using multifunctional X-ray diffractometer (M 21 X-SRA, MAC Science Co., Ltd.). Cu *Ka* radiation was used as X-ray source. All films prepared in this study were confirmed as $Li_4Ti_5O_{12}$ oxide with a spinel structure. Surface morphologies were observed with scanning electron microscope (SEM, JED-2100, JEOL Co., Ltd.). Impedance spectroscopy was carried out in the frequency range from 50 kHz to 10 mHz with 5080 frequency response analyzer (NF electronic instruments).

The electrochemical cell was constructed with $Li_4Ti_5O_{12}$ cathode, lithium metal anode, and polymethylmethacrylate (PMMA) gel-polymer electrolyte. Charge and discharge tests were performed at a constant current using automatic discharge and charge equipment (HJR-110 mSM 6, HOKUTO DENKO Co.). Cut-off voltages were 1.2 V and 3.0 V vs. Li Li for discharge and charge processes, respectively. The cyclic voltammogram (CV) was recorded at a scan rates of 10 mV min^{-1} by using automatic polarization

system (HZ-3000, HOKUTO DENKO Co.). All electrochemical experiments were conducted in an argon-filled glove box at room temperature.

Result and Discussion

As well known, a sol-gel method is a simpler thin film technology compared with other thin film ones. However, in general, a relatively thick film without crack formation is hardly obtained by the sol-gel method. This crack formation has been understood via a mechanism shown in **Fig. 2** (a). Shrinkage of gel film occurs during a heat treatment process according to a formation of metalloxane polymer. When a gel film is prepared on a substrate, the same phenomenon also occurs. Since the gel film strongly adhered with a substrate, the shrinkage produces mechanical stress in the film. A mechanical stress due to a difference of thermal expansion between films and substrates is also produced during a heat treatment. Both stresses result in a crack formation in the film after a heat treatment. Hence, the stresses produced by two factors must be diminished. The shrinkage of gel film may be due to a dehydration-condensation reaction for hydroxyls of metalloxane polymer. If a structural relaxation in a gel film is enough fast, the stress can be minimized. Poly(vinylpyrrolidone) (PVP) can form hydrogen bonding with hydroxyls of metalloxane. According to Fig. 2 (b), an introduction of PVP to a sol can enhance a structural relaxation, while viscosity of a sol is increased. Both properties are good for a thicker film formation without any cracks.

In this study, two types of sols were applied to prepare a crack-free film. **Figure 3** shows the surface morphologies of thin films prepared by the sols made from ethanol and 2-propanol solvents, respectively. The sol prepared by ethanol solvent was not stable and a thin film was not uniformly deposited as seen in Fig. 3 (a). On the other hand, the sol prepared by 2-propanol solvent was more stable than that prepared by ethanol solvent and more uniform surface was obtained, as shown in Fig. 3 (b). However, the surface morphology was not enough uniform to use as electrode films of lithium batteries. In addition, large cracks were also observed. This crack prevents a use of the prepared thin films for lithium battery applications. Then, PVP was applied to 2-propanol solvent for preparing a uniform crack-free film. When PVP was added to a sol, its stability was dramatically increased. In fact, no precipitation of solid powder was observed during more than several months.

By using the PVP, preparation conditions for a uniform film without any cracks were optimized. **Figure**
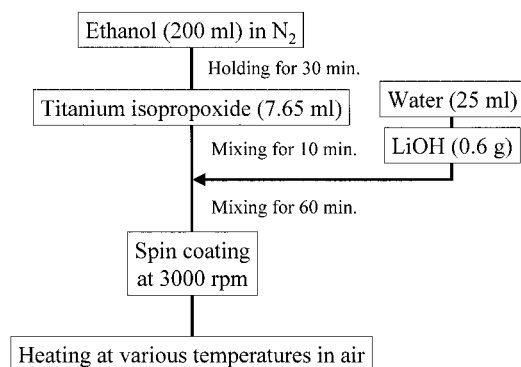

Fig. 1 Flowchart for a preparation of Li-Ti-O sol with a sol-gel method.
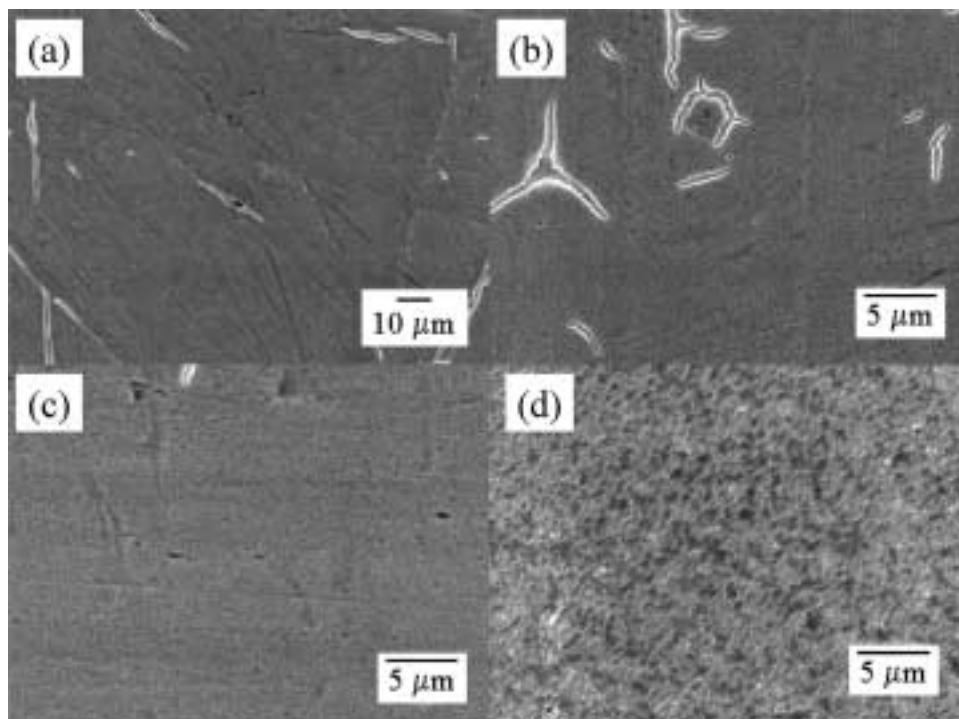
Fig. 2   (a) Scheme of crack formations in gel films during heat treatment and (b) structural relaxation mechanism on dehydration-condensation reaction for hydroxyls of metalloxane polymer by PVP.

Fig. 3   Scanning electron micrographs of Li₄Ti₅O₁₂ thin film prepared by the sol-gel method described in (a) Fig. 1 and (b) a previous report (without PVP).[16)]

4 shows SEM images of surface for the prepared films. All of surfaces were very smooth, but a few cracks were observed in Fig. 4 (a) and Fig. 4 (b). On the other hand, there were no cracks in both Fig. 4 (c) and Fig. 4 (d), but surface morphology of the film prepared at a heating temperature of 800   was slightly rough. As shown in Fig. 4 (a), a PVP content of 1 mol   was insufficient for suppressing a crack formation. Figure 4 (b) and Fig. 4 (c) show that a formation of cracks on a film depended on rotation speed during the spin coat-

ing process. For example, in case of a thin film prepared at a low rotation speed at 2,000 rpm, a few cracks were observed in the film surface, as shown in Fig. 4 (b). Because, a lower rotation speed results in a thicker film formation, leading to a crack formation. On the other hand, a compact thin film without any crack was prepared at 3000 rpm (Fig. 4 (c)). Therefore, it can be said that the optimized conditions for preparation of uniform film without any cracks are a heating temperature of 600   , 3000 rpm, and a sol

Fig. 4 Scanning electron micrographs of Li₄Ti₅O₁₂ thin film prepared by the sol-gel method under various condition, (a) at 3000 rpm and 700   with 1 mol   of PVP, (b) 2000 rpm and 600   with 5 mol   of PVP, (c) 3000 rpm and 600   with 5 mol   of PVP, and (d) 3000 rpm and 800   with 5 mol   of PVP.
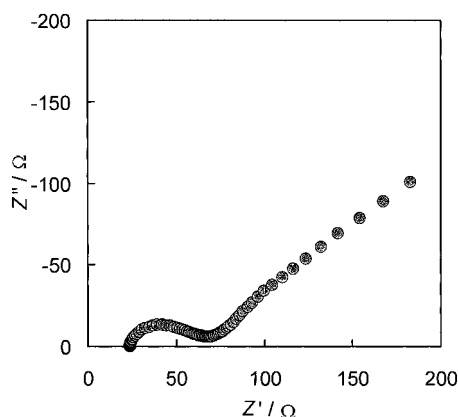

Fig. 5 Cole-Cole plot of the Li₄Ti₅O₁₂ thin film PMMA gel-polymer electrolyte lithium metal cell.

with 5 mol   of PVP. If a thicker crack-free film (e.g. 1 μm) is needed, it can be obtained by repeating the coating process.

Figure 5 shows the Cole-Cole plot for the thin film prepared at 600   for 1 h. The cell was constructed with Li₄Ti₅O₁₂ thin film cathode, lithium metal anode,

and PMMA gel-polymer electrolyte. Electrochemical impedance was performed at open circuit potential of 1.57 V vs. Li Li . A semi-circle was observed in the high and intermediate frequency regions (50 kHz 0.7943 Hz), and a straight line in the low frequency region (0.7943 Hz 10 mHz). The diameter of semi-circle appeared at higher frequency region corresponds to a charge transfer resistance, which is estimated to be 45 Ω. The straight line corresponds to Warburg impedance due to a semi-infinite diffusion. From this region, a chemical diffusion coefficient of Li ion in Li₄Ti₅O₁₂ solid matrix can be obtained from a relation between impedance and angular frequency[30], according to equation.[1]

$$A \quad \frac{V_M (dE \quad dx)}{\sqrt{2} zFD^{1\ 2} a} \qquad (1)$$

where the slope A is in units of Ω s $^{1\ 2}$. Here, the chemical diffusion coefficient of Li ion was evaluated to be 6.5×10^{10} cm² s ^{1}. The parameters used for the calculation were summarized in **Table 1**.

Figure 6 shows the cyclic voltammogram of a Li₄Ti₅O₁₂ cell. PMMA gel-polymer electrolyte was also used as electrolyte. A couple of sharp redox peaks

Table 1 Parameters used for the calculation of Li ion diffusion coefficient.

Differential factor, dE/dx	Molar Volume, V_M mol cm^{-3}	Surface area, a cm^2	Pre-exponential factor, A Ωs$^{-1/2}$	Diffusion coefficient, D cm^{2}s^{-1}
1.43 at 1.57 V	45.74	0.785	24	6.5×10^{-10}

z: charge transfer number (1), F: Faraday constant (96500).
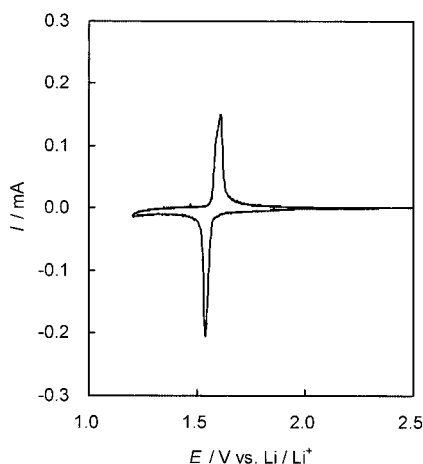
Fig. 6 Cyclic voltammogram of the Li$_4$Ti$_5$O$_{12}$ thin film PMMA gel-polymer electrolyte lithium metal cell at 10 mV min^{-1}.
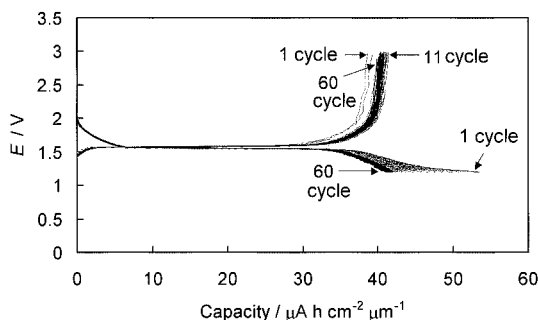
Fig. 7 Discharge and charge curves of the Li$_4$Ti$_5$O$_{12}$ thin film PMMA gel-polymer electrolyte Lithium metal cell at 20 mA cm^{-2} (0.4 C).

was observed at around 1.55 V vs. Li Li at a scan rate of 10 mV min^{-1}. This result was in good agreement with those of previous reports.[9,17]

Figure 7 shows discharge and charge curves of the Li$_4$Ti$_5$O$_{12}$ thin film PMMA gel-polymer electrolyte Lithium metal cell at a current density of 20 µA cm^{-2}, corresponding to 0.4 C rate, where the discharge and charge rate of 1 C means the current density required in order to reach the theoretical capacity for 1 h. During initial discharge processes, an irreversible capacity

was observed. This irreversible discharge capacity decreased with cycles. On the other hand, a charge capacity increased with cycles and a maximum charge capacity of 42 µA h cm^{-2} µm^{-1} was achieved at 11th cycle. Finally, the reversibility of redox reaction was increased up to 97.5 at 60th cycle. Both electrochemical experiments showed that Li$_4$Ti$_5$O$_{12}$ thin film has a fast electrochemical response, and indicated that a lithium ion polymer battery with good electrochemical properties can be fabricated by using the Li$_4$Ti$_5$O$_{12}$ thin film prepared by the PVP sol-gel method.

Conclusion

In summery, the sol-gel methods are very useful to prepare Li$_4$Ti$_5$O$_{12}$ electrode with a fast electrochemical response for rechargeable lithium batteries. Especially, the Li$_4$Ti$_5$O$_{12}$ thin film prepared by the PVP sol-gel method showed excellent electrochemical properties as anode of lithium ion polymer battery, such as high capacity and good reversibility during cycling. Therefore, it can be concluded that the PVP sol-gel method is a basic key technology for an establishment of rechargeable lithium microbatteries.

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