Preparation of $Li_{4/3}Ti_{5/3}O_4$ Thin Film Anode with High Electrochemical Response for Rechargeable Lithium Batteries by Sol–Gel Method

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A stoichiometric spinel $Li_{4/3}Ti_{5/3}O_4$ thin film was prepared by a sol–gel method with poly(vinylpyrrolidone) (PVP) as an anode of rechargeable lithium micro-batteries. The prepared film was evaluated electrochemically by cyclic voltammetry (CV). One-time-coated thin film had 0.4 μm of thickness and showed high electrochemical response until 50 mV s^{-1}. In this study, it was first reported that a thin film electrode with high electrochemical response was obtained by the sol–gel method with PVP.

Many researchers have been focusing on rechargeable lithium micro-batteries and their various applications.[1–6] For development of micro-batteries, inorganic solid electrolyte systems[7–10] and micro-scale thin film electrodes[4,11–15] are needed. Many researchers have prepared various kinds of transition metal thin films as cathode and anode materials for micro-scale rechargeable lithium batteries. Various chemical and physical vapor deposition processes have been applied to prepare $LiCoO_2$ and $LiMn_2O_4$ thin films.[11–16] These processes have provided good thin films with a high electrochemical properties as an insertion material.

A sol–gel process is also a good candidate for preparation of thin film electrodes. When thin film electrodes were prepared, a stoichiometry of the electrodes can be hardly controlled in case of the above methods. However, in the sol–gel method, it is easier to prepare stoichiometric thin film electrodes. Therefore, it is expected that sol–gel prepared thin film electrodes have better electrochemical properties, e.g., high electrochemical response.

A sol–gel process has been applied to a preparation of various kinds of thin films used in many devices.[17,18] However, many cracks have been sometimes formed in prepared films. In order to avoid the crack formation, some of researchers have studied on a sol–gel process using a polymer. Kozuka et al. have found that poly(vinylpyrrolidone) (PVP) is very useful for suppressing the crack formation in the film.[17] For example, they have successfully prepared a thick $BaTiO_3$ using the sol–gel process with PVP. In rechargeable lithium battery systems, electrodes having enough capacities are required, so that a preparation of a few μm of thick film is important. In this study, we adopted this excellent technique for the preparation of $Li_{4/3}Ti_{5/3}O_4$ thin film electrodes with high electrochemical response for rechargeable lithium batteries.

A stoichiometric spinel $Li_{4/3}Ti_{5/3}O_4$ is a good candidate as an anode active material for rechargeable lithium batteries, because of a very flat discharge and charge curves and a high cyclability.[19–22] $Li_{4/3}Ti_{5/3}O_4$ has been synthesized by a sintering at 800 °C for 24 hours under air atmosphere.[19–22] It exhibits a working potential of 1.55 V vs Li/Li^+ and its standard discharge capacity is 167 mA h g^{-1}.[19–22]

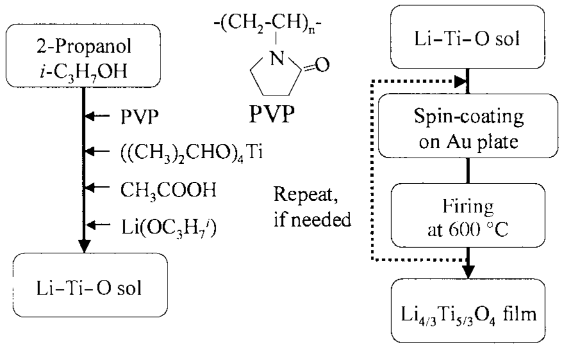

Figure 1. Flow-chart of preparation of $Li_{4/3}Ti_{5/3}O_4$ thin film electrodes from Li–Ti–O sols.

A molar ratio of each component of a Li–Ti–O sol was $Li(OC_3H_7^i)$: $((CH_3)_2CHO)_4Ti$: PVP (PVP monomer unit) : CH_3COOH : $i\text{-}C_3H_7OH$ = 4 : 5 : 5 : 100 : 100. The solution was prepared according to a scheme illustration in Figure 1. A molar ratio of PVP in this scheme is based on a mole number of PVP monomer unit. The prepared sol kept in a tightly sealed bottle was stable for a long period. In fact, no precipitation of solid powder was observed during more than one month. However, under high humidity, a white powder was precipitated, as a result of chemical reaction of alkoxides with water.

A spin coating method was used to prepare Li–Ti–O gel films on Au substrates. A rotation speed for the spin coating was 3000 rpm. The sol deposited on Au substrate was changed to a gel film through the spin coating process. The gel film was heated at a temperature of 600 °C for 1 h. These processes were repeated to obtain an enough thickness of the film, if needed. The thickness of the film obtained by each process was 0.4 μm. The crystal phases were identified by X-ray diffraction (XRD) analysis with Cu Kα and its surface morphology and thickness was observed by scanning electron micrographs (SEM). Three-electrode cell was assembled with lithium metal foil and wire as a reference and a counter electrode. A mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume) containing 1 mol dm^{-3} $LiClO_4$ was used as an electrolyte. A cyclic voltammetry (CV) was also employed to evaluate the prepared film electrochemically. The cyclic voltammogram was measured at various scan rates in potential region from 1.2 V to 2.5 V (HZ-3000 automatic polarization system, HOKUTO DENKO Co.). All electrochemical experiments were conducted in an argon-filled glove box at room temperature.

Figure 2 shows scanning electron micrographs of (a) the surface and (b) the cross-section of the one time coated $Li_{4/3}Ti_{5/3}O_4$ films deposited on Au and quartz glass substrates, respectively, and fired at 600 °C. A uniform surface of the thin film was observed and any micro-cracks were not observed on an entire surface. From the cross sectional view for the prepared film, it can be seen that the thin film had a thickness of about 0.4 μm. This large film thickness indicates that the addition of the PVP is

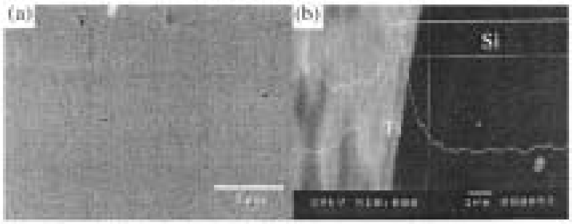

Figure 2. Scanning electron micrographs of (a) the surface of the $Li_{4/3}Ti_{5/3}O_4$ film on Au substrate and (b) the cross sectional view of $Li_{4/3}Ti_{5/3}O_4$ film on quartz glass (line profiles show EDX analysis line for Si and Ti).

very useful for sol–gel preparation of thick films without any cracks. In this way, the preparation of the film through the sol–gel method with the PVP is valid enough to accomplish the required thickness and the good contact of the film with the substrate (for example, ceramic electrolyte). This good contact may diminish a resistance problem due to the worse contact at interfaces between electrodes and electrolytes.

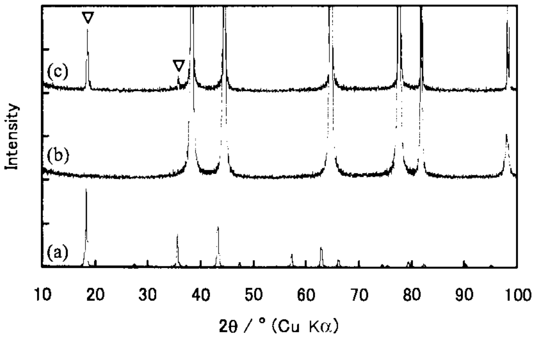

Figure 3. X-ray diffraction patterns of (a) a standard $Li_{4/3}Ti_{5/3}O_4$ powder, (b) Au plate, and (c) $Li_{4/3}Ti_{5/3}O_4$ thin film deposited on Au substrate.

Figure 3 shows the XRD patterns of the one time deposited $Li_{4/3}Ti_{5/3}O_4$ film on Au substrate, Au plate, and a standard $Li_{4/3}Ti_{5/3}O_4$ powder. From a comparison with these patterns, it can be said that all peaks observed in the X-ray diffraction pattern of the film prepared on Au substrate are attributed to Au and $Li_{4/3}Ti_{5/3}O_4$. This means that the film on Au substrate sintered at 600 °C for 1 h through the sol–gel process with the PVP is $Li_{4/3}Ti_{5/3}O_4$ with a spinel structure. However, the relative peak intensities were different from those for the powder sample. This may be due to an orientation of the thin film. The lowest temperature for the preparation of $Li_{4/3}Ti_{5/3}O_4$ was 550 °C. When all solid-state battery system is constructed by using such a sol–gel process, a low sintering temperature and a short sintering time are necessary to avoid undesirable interfacial reactions occurring between solid electrolytes and active materials. Therefore, the low sintering temperature and the short sintering time for our sol–gel process are very useful to construct all solid-state battries.

Electrochemical properties of the $Li_{4/3}Ti_{5/3}O_4$ film on Au substrate sintered at 600 °C were also evaluated by CV. Figure 4(a) shows the cyclic voltammogram of the one time deposited $Li_{4/3}Ti_{5/3}O_4$ thin film. The sharp redox peaks were observed around 1.55 V. This result was in good agreement with those of previous reports on $Li_{4/3}Ti_{5/3}O_4$ powder sample obtained by a solid-state reaction.[19–22] Figure 4(b) also shows cyclic voltammograms of the film at various scan rates ranging from 0.5 mV s^{-1} to 50 mV s^{-1}. The result shows that the higher the scan rate, the larger the peak current, and the CV curves are still sharp. This indicates that an electrochemical response of the film is very fast. Thus, it can be said that the $Li_{4/3}Ti_{5/3}O_4$ thin film prepared in this study can be used as anodes for micro-scale rechargeable lithium batteries.

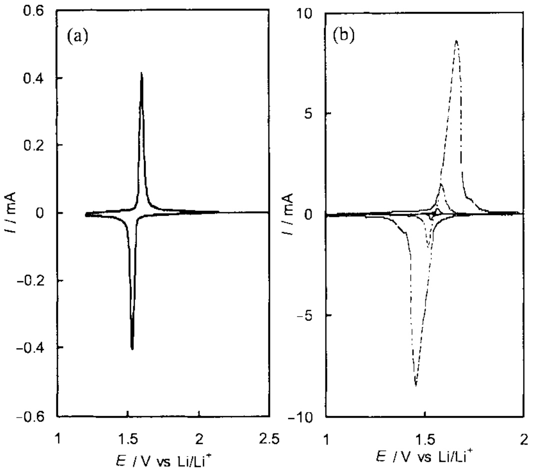

Figure 4. Cyclic voltammograms of $Li_{4/3}Ti_{5/3}O_4$ thin film deposited on Au substrate at a scan speed of (a) 10 mV m^{-1} and (b) 0.5 to 50 mV s^{-1}.

From the above results, it can be concluded that the sol–gel method with PVP is available for preparing $Li_{4/3}Ti_{5/3}O_4$ as anodes with high electrochemical response for rechargeable lithium batteries. This sol–gel process provides lower firing temperature (550 °C) and a very smooth surface and a uniform thickness of the film without any cracks. Therefore, this technique is very meaningful as a basic elemental technique for all solid-state micro-scale rechargeable lithium batteries.

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