

Thin Film Formation of LiCoO₂, LiMn₂O₄, and Li₄Ti₅O₁₂ For Rechargeable Lithium Batteries

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All solid-state rechargeable lithium batteries will be used in future electronic devices. In some case, batteries will be constructed on small tips. In order to realize such micro batteries, thin film technology is very important. In this study, we demonstrated the thin film formation of LiCoO₂, LiMn₂O₄, and Li₄Ti₅O₁₂ by using a sol-gel process. Thin film formation of these materials has been performed with dry processes, such as PVD and CVD methods. The obtained thin films exhibited and good electrochemical properties. However, a long reaction time and expensive equipments should be needed for these methods. On the other hand, a sol-gel process is one of soft-solution processes and suitable for easy and cheap preparation of thin films. In this study, this sol-gel process was selected for the thin film preparation technique of LiCoO₂, LiMn₂O₄, and Li₄Ti₅O₁₂ transition metal oxides as active materials of rechargeable lithium batteries.

In general, it is very difficult to obtain a thick film (a few μm) by using a sol-gel process, because of a formation of cracks in thin films. However, in this case, thick films are necessary to obtain a enough discharge capacity of micro batteries. Recently, Professor Kozuka proposed a new sol-gel process using poly(vinylpyrrolidone) (PVP). This process is very suitable for a preparation of thin films with a few μm thickness. In this study, this sol-gel process was adopted to prepare thin films of LiCoO₂, LiMn₂O₄, and Li₄Ti₅O₁₂ transition metal oxides.

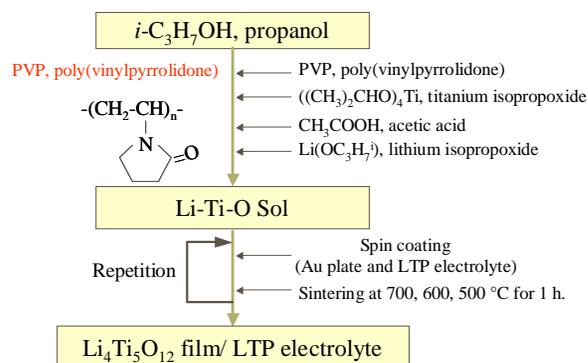
The sol-gel process was performed according to the scheme 1. Poly(vinylpyrrolidone) (PVP) with average molecular weight of 55000 were employed as a polymer binding with Li⁺ ions and metal cations. The addition of PVP polymer is helpful to form a uniform sol solution. Molar compositions of starting solution were Li(OC₃H₇)⁺ : ((CH₃)₂CHO)₄Ti : PVP : CH₃COOH : *i*-C₃H₇OH = 4 : 5 : 5 : 100 : 100. Here, the mole of vinylpyrrolidone represents an amount of PVP monomer unit. For LiCoO₂ and LiMn₂O₄ thin films, Co(CH₃COO)₂·H₂O or Mn(CH₃COO)₂·H₂O was used instead of ((CH₃)₂CHO)₄Ti. These sol solutions were coated on substrates with a spin-coating method (3000 rpm). The sol was dried under air atmosphere at room temperature for 5 min. Then the sol solution was coated, again. These procedures were repeated 10 times to obtain the thick gel films. The coated gel films were heated at 500~800 °C for 30 min~3 h to form the thick films of LiCoO₂, LiMn₂O₄, and Li₄Ti₅O₁₂ on the substrates.

The obtained thin films were analyzed with x-ray diffraction method to determine their crystal structure. The film prepared from Co-O-Li gel was assigned to layered LiCoO₂ and the films obtained from Mn-O-Li and Ti-O-Li gels were attributed to LiMn₂O₄ and Li₄Ti₅O₁₂ spinels. The thickness of these films was estimated from a scanning electron microscopic observation to be 0.5 μm. The surface of the films was smooth and the thickness was very uniform. Moreover, there were no cracks on the films. This means that the sol-gel process with PVP is suitable for a preparation of thick transition metal oxides as active material of rechargeable lithium batteries.

Three kinds of transition metal oxides were applied to

cathode and anode materials of rechargeable lithium batteries. Figure 1 shows the cyclic voltammogram of Li₄Ti₅O₁₂ at 10 mV min⁻¹ in a mixed solvent of ethylene carbonate and diethyl carbonate (1:1 in volume) containing 1.0 mol dm⁻³ LiClO₄. One pair of sharp redox peaks was observed at 1.55 V vs. Li/Li⁺. This voltammogram was in good agreement with that reported in our previous study in which Li₄Ti₅O₁₂ powder sample was used as active material. This voltammogram was not changed with cycle. From this result, it can be said that the Li₄Ti₅O₁₂ thin film works as highly reversible insertion anode material.

LiCoO₂ and LiMn₂O₄ thin films were also investigated with the cyclic voltammetry under the same conditions. Figures 2 and 3 show the obtained cyclic voltammograms. Several peaks observed in these voltammograms were also in good agreement with those of powder samples. Thus, the sole-gel process with PVP is an excellent method for the preparation of transition metal oxide films.



PVP: H.Kozuka and M.Kajimura, *Chem. Lett.*, 1029-1030 (1999)

Scheme 1 Sol-gel process with PVP for Li₄Ti₅O₁₂.

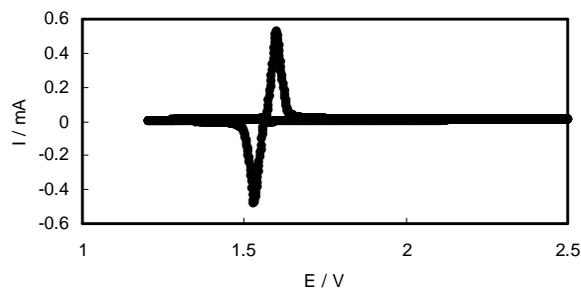


Figure 1 Cyclic voltammogram of Li₄Ti₅O₁₂ thin film.

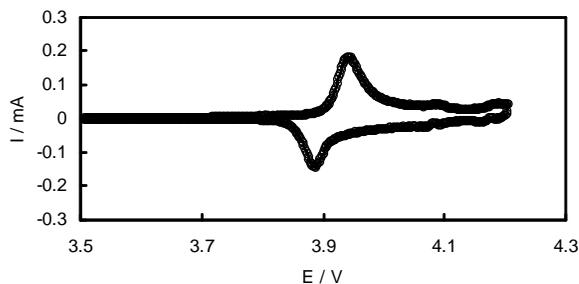


Figure 2 Cyclic voltammogram of LiCoO₂ thin film.

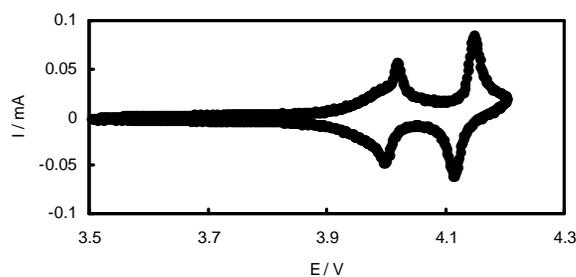


Figure 3 Cyclic voltammogram of LiMn₂O₄ thin film.