A Study on Li^+ Diffusion Behavior in $Li_4Ti_5O_{12}$ Thin Film Electrode Prepared Through PVP Sol-Gel Process

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$Li_4Ti_5O_{12}$ thin film electrode was prepared thorough sol-gel method with poly-(vinylpyrrolidone) (PVP). The thin film electrodes exhibited excellent electrochemical properties. Electrochemical impedance spectroscopy (EIS) was performed in order to estimate diffusion coefficients of Li^+ ion in the PVP sol-gel prepared thin films. The obtained diffusion coefficients of Li^+ ion in the $Li_4Ti_5O_{12}$ thin film electrode depended on electrode potential ranging from 10^{-9} cm^2 s^{-1} to 10^{-14} cm^2 s^{-1}.

Micro-scale Rechargeable lithium batteries have been studied for various micro-scale applications such as micro-sensor, micro-mechanics, microelectronics, and so on. In order to develop micro-scale rechargeable lithium batteries, micro-scale electrodes should be prepared. For example, thin film electrodes and dot electrodes are very important. By the way, lots of thin film preparation methods have been investigated. A sol-gel method is well known as one of promising thin film preparation methods, which has some advantages, such as low fabrication cost, relatively easy stoichiometric control, high deposition rate, and so on. In this study, $Li_4Ti_5O_{12}$ was successfully prepared and diffusion behavior of Li^+ ion in this thin film was studied by means of electrochemical impedance technique.

$Li_4Ti_5O_{12}$ thin film electrodes were prepared by a sol-gel method with PVP, according to following steps.
(1) A spin coating process of sol solution on Au substrate.
(2) The sol was dried to convert to a gel film.
(3) The gel film was heated at 600 ºC for 1 h.
The prepared thin film was about 0.4 μm thickness.

Electrochemical properties of the thin film electrodes were evaluated by using discharge and charge measurements and cyclic voltammogram (CV). Lithium metal was used as counter and reference. The electrolyte was a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (1 : 1 in volume) containing 1 mol dm^{-3} $LiClO_4$. EC+DEC/$LiClO_4$. Electrochemical impedance spectroscopy (EIS) technique was employed for the estimation of diffusion coefficients of Li^+ ion in $Li_4Ti_5O_{12}$ by using 5080 frequency response analyzer (NF electronic instruments) in the frequency range from 10^5 to 10^{-2} Hz. All electrochemical experiments were conducted in an argon-filled glove box at room temperature.

Fig. 1 shows CV of $Li_4Ti_5O_{12}$ thin film electrode prepared by PVP sol-gel method. Cathodic and anodic sharp redox peaks around at 1.55 V vs. Li/Li^+ indicates the PVP sol-gel prepared thin film has a typical electrochemical property of $Li_4Ti_5O_{12}$ active material.

Fig. 2 shows $|Z|$ vs. $\omega^{-1/2}$ plots at various potentials. The diffusion coefficients of Li^+ ion were estimated from the slopes of these curves.

Fig. 3 shows the diffusion coefficient of Li^+ ion in the PVP sol-gel prepared $Li_4Ti_5O_{12}$ thin film. At peak potentials (1.55 to 1.56 V vs. Li/Li^+), diffusion coefficients were 10^{-14} cm^2 s^{-1}. In other potential region, they were 10^{-9} to 10^{-12} cm^2 s^{-1}.

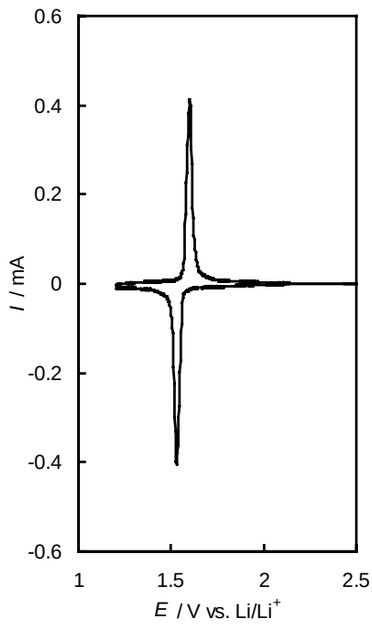

Fig. 1 Cyclic voltammogram of $Li_4Ti_5O_{12}$ thin film electrode prepared by sol-gel method with PVP.

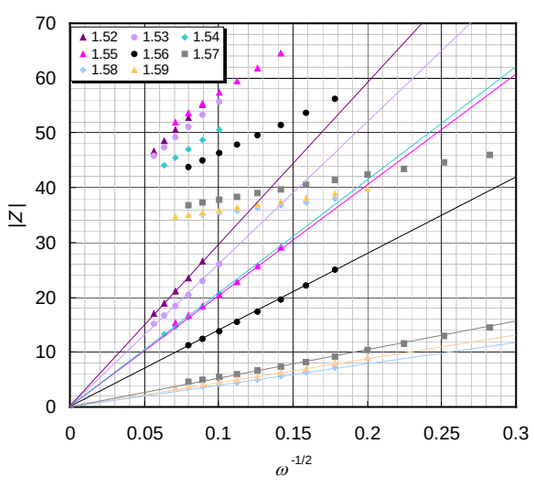

Fig. 2 $|Z|$ vs. $\omega^{-1/2}$ plots at various potentials.

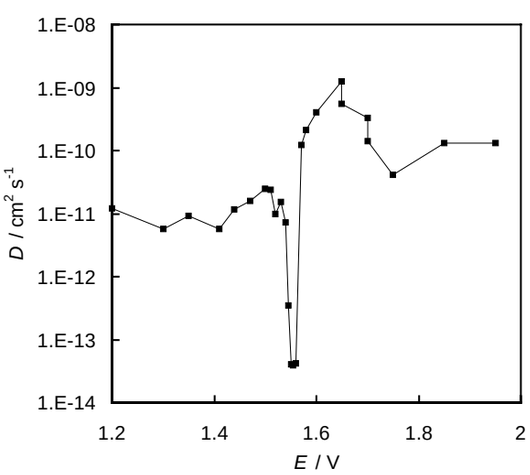

Fig. 3 Diffusion coefficients of Li^+ ion in $Li_4Ti_5O_{12}$ in a potential range from 1.2 V to 2 V vs. Li/Li^+.