Photo-Assisted Lithium Insertion to $Li_{1-x}Mn_2O_4$ Film Electrodes

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Photoelectrochemical properties of spinel $Li_{1-x}Mn_2O_4$ ($0 < x < 1$) thin film on ITO electrodes were studied in propylenecarbonate (PC) containing 1 M $LiClO_4$. Cathodic photocurrents were clearly observed, suggesting the occurrence of photo-assisted lithium insertion reaction at the $Li_{1-x}Mn_2O_4$ film electrode.

Electrochemical lithium-insertion / -extraction reactions for spinel $Li_{1-x}Mn_2O_4$ ($0<x<1$) have been studied extensively from the standpoint of developing cathode active materials for rechargeable lithium-ion batteries.[1] $Li_{1-x}Mn_2O_4$ spinel has Li^+ ions in tetrahedral (8a) sites which share faces with empty octahedral sites (16c), so that they form a three-dimensional network permitting diffusion of Li^+ ion through the structure. Being accompanied by such solid-state diffusion of Li^+, the electrochemical reaction proceeds reversibly at around 4 V vs. Li / Li^+ as follows

$$Li_{1-x}Mn(III)_{1-x}Mn(IV)_{1+x}O_4 + xLi^+ + xe^- \leftrightarrow LiMn(III)Mn(IV)\,O_4 \qquad (0<x<1) \qquad (1)$$

If the lithium insertion reaction can be driven by light energy, the construction of novel type of lithium battery may become feasible. Tributsch et al.[2] have studied the effects of light irradiation for several kinds of semiconducting insertion compounds, and showed the possibility of photo-induced insertion or extraction of guest atoms, such as H^+ or alkaline metal ions. We report here preliminary results showing the possible photo-insertion of Li^+ to $Li_{1-x}Mn_2O_4$, which is one of the most attractive battery materials as noted above.

$LiMn_2O_4$ thin films (ca. 0.2 μm thick) were deposited onto ITO electrodes by RF magnetron sputtering, and annealed at 600°C for 1 h to be crystallized as spinel.[3,4] The electrode surface area was 1 cm^2. Electrochemical measurements were carried out typically in 1 M $LiClO_4$ / PC solutions using Li foils as the reference and counter electrodes. Figure 1 shows variations of the open-circuit voltage (E_O) and the electrical conductivity of the $Li_{1-x}Mn_2O_4$ as a function of x.[5] E_O showed plateaus at around 3.9 V and 4.1 V vs. Li / Li^+, reflecting that the reaction (1) takes place through two stages.[1] The electronic conductivity of $Li_{1-x}Mn_2O_4$ was found to be almost constant (ca. 1×10^{-5} S / cm) regardless of the lithium content in the oxide film. Such a stable semiconducting property would be required for application to photo-rechargeable battery because the semiconductor-metal transition, which occurrs in $LiCoO_2$,[6] would reduce the photoelectrochemical activity of the electrodes.

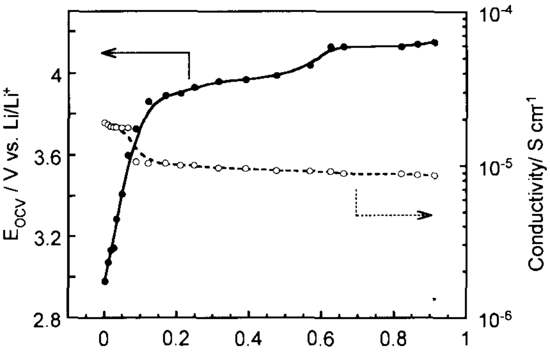

Figure 1. Variations of E_{OCV} and electrical conductivity of a sputtered $Li_{1-x}Mn_2O_4$ thin film as a function of x, measured in 1 M $LiClO_4$ / PC solution using a Li foil as a reference electrode.

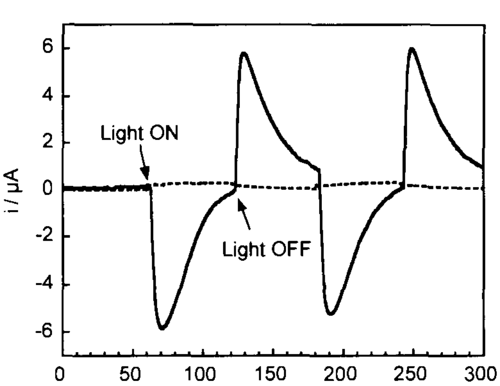

Figure 2. Current-responses of an ITO electrode coated with $Li_{0.5}Mn_2O_4$ thin film on light irradiation in 1 M $LiClO_4$ / PC (solid curve) and in 1 M TBAP / PC (dashed line) solutions. The electrode potential was held at 4.0 V vs. Li / Li^+. The surface area exposed to the electrolyte solution was 1 cm^2.

The photocurrent responses of $Li_{1-x}Mn_2O_4$ electrodes were measured at various electrode potentials (3.5 ~ 4.1 V vs. Li / Li^+) by using a 500 W Xenon lamp as the light source. Figure 2 shows a typical result taken at 4.0 V vs Li / Li^+ where the composition of the electrode material is roughly $Li_{0.5}Mn_2O_4$. A clear cathodic current was observed upon the irradiation and the same amount of anodic response appeared when the irradiation was terminated due to the potentiostatic condition. These responses were obtained repeatedly more than at least 10 times. Since no photocurrent flowed in the absence of Li^+ ion (1 M TBAP / PC, dashed curve in Figure 2),[7] it is of no doubt that the photocurrent observed in 1 M $LiClO_4$ / PC solution is due to Li^+-related reaction, probably the lithium insertion assisted by the photo-excited electron in the $Li_{0.5}Mn_2O_4$ electrodes. Upon the light-illumination, the electrode material itself is reduced ($Mn^{4+} \rightarrow Mn^{3+}$), being accompanied by insertion of Li^+ ions to maintain the electroneutrality. Therefore, although $Li_{1-x}Mn_2O_4$ spinel has been reported to be an n-type semiconductor,[8] the reaction studied here should be more complicated than the usual electrochemical reactions at a surface of semiconductor electrodes. The amount of inserted Li^+ was estimated by integrating the photocurrent, the result showing only ca. 8 % of the amount expected for the complete formation of $LiMn_2O_4$ over the film. Similar results were obtained also at the electrode potentials of 3.9 and 4.1 V vs. Li / Li^+, while no response was obtained at lower potentials than 3.8 V vs. Li / Li^+. Both the low reaction efficiency and the characteristic shape of the photocurrent responses would be partly caused by the slow diffusion process of Li^+ ions inside the solid-state phase of manganese oxide matrix. More essentially, the photovoltage developed in the $Li_{1-x}Mn_2O_4$ electrodes was found to be only +6 mV, the value being measured as a voltage developed between two $Li_{0.5}Mn_2O_4$ electrodes by illuminating one of the electrodes. The voltage of the illuminated electrode was measured against the masked electrode.

Figure 3 shows a photocurrent action spectrum measured at 4.0 V vs. Li / Li^+ using a monochromator (JASCO CT-25N), a light beam chopper (DL Instruments 220 + 220RG) and a lock-in amplifier (Stanford Research Systems SR830). A linear extrapolation of the main slope of the photocurrent yields E_G = 2.64 eV as a band-gap energy effective for the photo-insertion of Li^+. Absorption spectrum of $Li_{0.5}Mn_2O_4$ (dotted curve in Figure 3)[9] showed no clear correlation with the action spectrum, indicating that there are many other exciting states which can not contribute to the photo-insertion reaction.

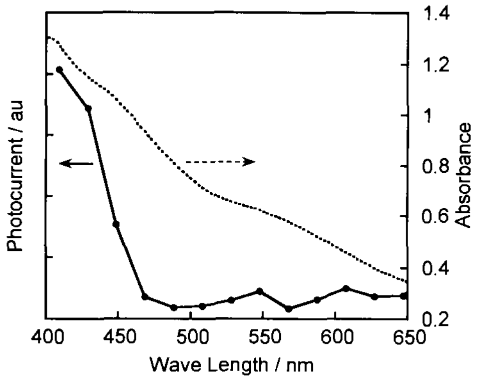

Figure 3. Photocurrent action spectrum of a $Li_{0.5}Mn_2O_4$ thin film electrode taken in 1 M $LiClO_4$ / PC (solid curve), and an absorption spectrum of the film in air (dashed curve).

While the results presented here are preliminary, we showed the possibility of photo-assisted lithium insertion to $Li_{1-x}Mn_2O_4$. Further investigations including the optimization of the thickness and morphology of the films would be needed to improve the reaction efficiency. Work along these lines are in progress.

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References and Notes

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3 S. Yamamura, H. Koshika, M. Nishizawa, T. Matsue, and I. Uchida, *J. Solid State Electrochem.*, in press.

4 The target for sputtering was prepared by sintering a mixture of polyethylene glycol (1 wt%) and $LiMn_2O_4$ powder prepared by the solid-state reaction of a stoichiometric mixture of $LiOH{\cdot}H_2O$ and MnO_2 at 800 ^{o}C in air for 24 h. Sputtering was carried out in 0.02 torr of a 4 : 1 Ar / O_2 mixture with 100 W RF power at the substrate temperature of 100 ^{o}C. The spinel structure of the annealed samples was examined by X-ray diffraction pattern referencing the JCPDS Powder Diffraction File, 35-782 (1985).

5 The values of x were calculated from the apparent volume of the film, the theoretical crystalline density of $LiMn_2O_4$, and the amount of injected charge. Conductivity of the film was measured in situ, using an interdigitated microarray electrode. See reference 7 for details.

6 M. Shibuya, T. Nishina, T. Matsue, and I. Uchida, *J. Electrochem. Soc.*, **143**, 3157 (1996).

7 A Li foil in 1 M $LiClO_4$ / PC was used as reference electrode, but it was connected to the measuring solution (1 M TBAP / PC) through double liquid junctions to prevent the contamination of Li^+ to the cell.

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9 The absorption spectra of $Li_{0.5}Mn_2O_4$ film-coated ITO electrode was measured in air using a multichannel photodetector (Otsuka MCPD) after drying the electrode substrates.