Electrochemical Studies of Spinel $LiMn_2O_4$ Films Prepared by Electrostatic Spray Deposition

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An uniform, dense film of spinel $LiMn_2O_4$ (thickness, about 0.5 μm) was prepared by the electrostatic spray deposition method onto a Pt film electrode on Si substrate kept at 400 °C. Electrochemical properties of the $LiMn_2O_4$ film in a solution of 1 M $LiClO_4$/propylene carbonate were studied by cyclic voltammetry and potential-step chronoamperometry. The oxidation and reduction of the film, which are accompanied by the extraction/insertion of lithium ions, proceeded almost quantitatively around 4 V vs. Li/Li^+ with excellent coulombic reversibility. The apparent chemical diffusion coefficient of Li^+ in $Li_{1-x}Mn_2O_4$ spinel phase varied on the order between 10^{-10} and 10^{-12} $cm^2\ s^{-1}$ as a function of electrode potentials with minima at the potentials corresponding to the voltammetric current peaks.

Progress in the miniaturization of electronic devices have reduced the current and power requirements to extremely low levels, making possible the use of thin-film microbatteries as power sources for some of these devices. Recently, encouraged by this practical importance, the fabrication of rechargeable lithium batteries of the film type has been studied exclusively.[1—3] To integrate such batteries into the electronics at the chip level, it is necessary to prepare thin-film components of the battery systems using processes compatible with the microelectronics fabrication technologies.

Another importance of the film-type electroactive materials is its simple geometric form which make the theoretical analysis of their electrochemical behaviors easier. The electrochemical properties of battery materials have been studied for composite electrodes consisting of powders of the material and an organic binder such as poly(vinylidene fluoride) (PVDF). The information obtained using such composite electrodes should be treated as that for a porous electrode. To eliminate uncertainties at the composite electrodes, the preparation and characterization of a fine film of battery materials should be an attractive approach.

Several kinds of deposition techniques, such as chemical vapor deposition and sputtering, have been used to prepare thin films of various lithium battery components. Recently, Schoonman et al.[4—6] have developed the electrostatic spray deposition (ESD) technique and used it to preparing thin films of lithium battery materials such as $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$. The ESD method uses a very fine aerosol of a precursor solution, which is electrohydrodynamically generated, to deposit a film on a heated electrode substrate. The method has many interesting features such as a simple and low-cost setup, low-temperature synthesis, and easy control of the composition and morphology of the films.

In this work, we prepared a thin film of spinel $LiMn_2O_4$, which is one of the most attractive cathode materials for lithium secondary batteries,[7—12] by the ESD method. Electrochemical behaviors of the obtained films were studied, including the measurement of the apparent chemical diffusion coefficient (D_{app}) of lithium ions in the manganese spinel phase.

Experimental

The ESD setup used here and its working principles have been described in the literature.[4—6] Briefly, a high DC voltage (in a range 0—20 kV) is applied between an electrically conductive substrate and a metal capillary nozzle, which is connected to a precursor solution. At a suitable flow rate, precursor solution is atomized at the orifice of the nozzle, generating the spray. The spray moves toward the heated substrate under the electrostatic force and, owing to the pyrolysis of precursors, a thin layer is formed on the substrate surface. An ethanol precursor solution of 25 mM $LiNO_3$ + 50 mM $Mn(NO_3)_2$ was pumped at 2 ml h^{-1} to a stainless steel nozzle (inner diam., 0.8 mm), which was placed 2 cm above the Pt electrode substrate heated, typically at 400 °C. The Pt electrode was prepared by sputtering Pt film (0.1 μm, thick) onto a thermally oxidized silicon wafer. The spraying nozzle was maintained at 12 kV against the electrode substrate. During the film deposition, the surface of the Pt electrode was masked to limit the exposed area to a circle 6 mm in diameter. The amount of deposit was estimated by weighing the electrode substrates before and after the deposition. The film morphology was studied using a scanning electron microscope (JSM-5310LV), while the crystalographic structure was studied using Cu $K\alpha$ radiation with an incident angle of 2° (Shimadzu XD-D1).

The electrochemical measurements were done using 1 M $LiClO_4$/propylene carbonate (PC) solutions (1 M = 1 mol dm^{-3})

in a glove box (Miwa MDB-1B+MS-P15S) filled with dried Ar. The water content of the PC solution used was < 20 ppm. The electrode substrate was placed at a bottom hole of the electrochemical three-compartment glass cell with an O-ring (6 mm inner diam). Li foils were used as the reference and counter electrodes.

Results and Discussion

Figure 1 shows a cross-sectional SEM image of a $LiMn_2O_4$ film prepared by 30 min of deposition onto the Pt film electrode on a Si substrate maintained at 400 °C. The film is recognized to be uniform and dense, with the thickness of ca. 0.5 μm. As a control experiment, we prepared ESD films at 100 °C, followed by annealing at 400 °C in air for 1 h, which would be categorized as a typical sol–gel method. In this case, the films were found to be significantly porous (not shown), probably due to gas evolution during the decomposition and crystallization of the precursor. These results indicate that the ESD procedure accompanied by simultaneous synthetic decomposition of the precursor is the key to prepare an uniform film of $LiMn_2O_4$. Such simple morphology is desirable for the electrochemical characterizations because we can use established theories[13] without any corrections regarding a porous structure on the micrometer scale. It should be mentioned, however, that the porous form of electrode material is important because its high specific surface area often improves the kinetic performance of battery systems.[14—16]

We studied here the film prepared by ESD at 400 °C because of its compatibility with microelectronics fabrication technologies. Spinel $LiMn_2O_4$ has been routinely synthesized at temperatures in excess of 700 °C.[7—12] However, for a microbattery on a chip, processing temperatures must not exceed 600 °C for Si, and 400 °C for III–IV (GaAs, InP, ets) substrates.[1] Figure 2 shows the XRD spectra of the $LiMn_2O_4$ film prepared at 400 °C (a) and of that annealed at 700 °C using a furnace for 1 h (b). Both XRD spectra were well assigned to spinel $LiMn_2O_4$,[2,3] indicating the formation of a spinel phase even at 400 °C. The intensity of the (111) peak appeared around $2\theta = 20$ looks unusually strong, suggesting some crystallographic orientation within the ESD film, but the details are not clear at present.

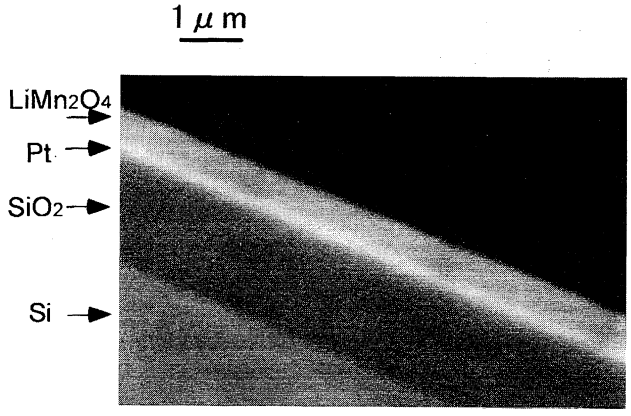

Fig. 1. Scanning electron micrographs showing a cross section of a $LiMn_2O_4$ film prepared by ESD method onto a $Pt/SiO_2/Si$ substrate maintained at 400 °C.

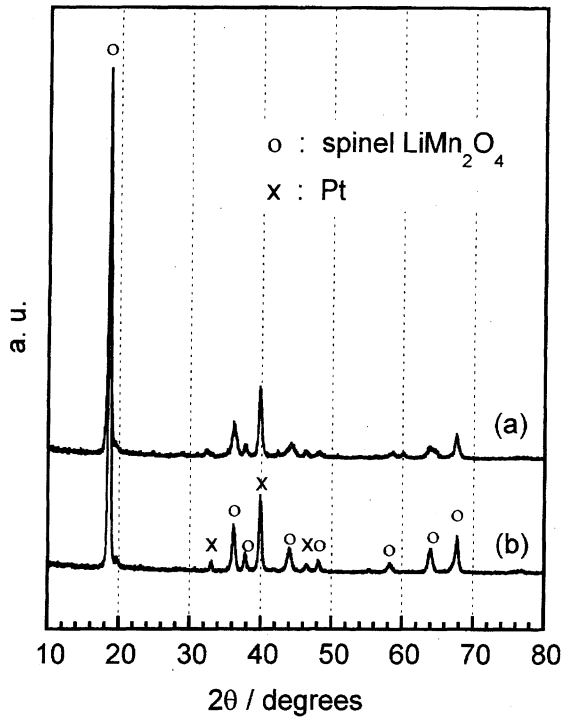

Fig. 2. X-Ray diffraction patterns for an as-prepared $LiMn_2O_4$ film (a) and for that post-annealed at 700 °C using a furnace for 1 h (b).

Figure 3 shows cyclic voltammograms (CVs) of a $LiMn_2O_4$ ESD film prepared at 400 °C, taken at the scan rate of 0.2 mV s^{-1}. Two couples of oxidation and reduction peaks appeared around 4.0 and 4.1 V vs. Li/Li^+, accompanied by extraction/insertion of lithium ions from/into the manganese spinel phase.[7—12] The coulombic reversibility was greater than 98%. The amount of charge consumed during the 1st

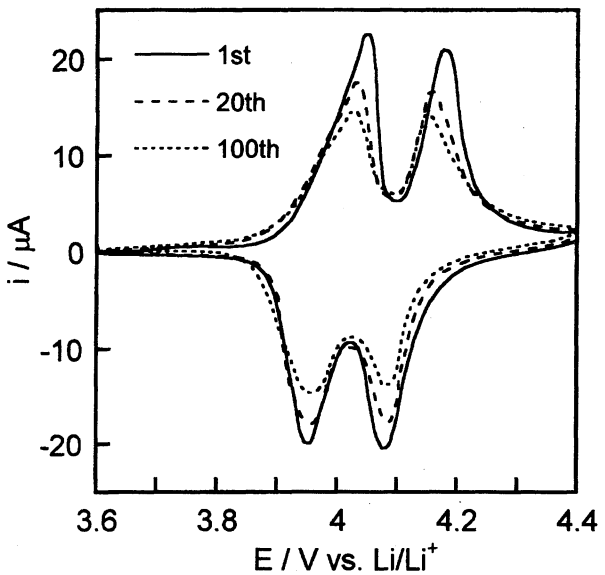

Fig. 3. CVs of a $LiMn_2O_4$ ESD film (37±2 μg) prepared at 400 °C, taken in 1 M $LiClO_4$/PC at the scan rate of 0.2 mV s^{-1}. Surface area and thickness of the film were ca. 0.28 cm^2 and 0.5 μm, respectively.

anodic scan up to 4.4 V was 2.05×10^{-2} C, the value corresponding to the specific capacity of 154±8 mA h g^{-1} as calculated using the weight of $LiMn_2O_4$ of 37±2 μg. This result is in agreement with the theoretical capacity of 148 mA h g^{-1} for the reaction given by

$$LiMn_2O_4 - Li^+ - e^- \Leftrightarrow Mn_2O_4 \quad (1)$$

It has been reported that the lithium extraction around 4.1 V results an irreversible structural change to some extent.[12] As shown in Fig. 3, even at the 100th scan, the electrode specific capacity retained more than 80% of the original capacity, ensuring the stability of this electrode for successive electrochemical measurements.

Figure 4 shows CVs of a $LiMn_2O_4$ film taken at various scan rates for the potential domain between 3.4 and 4.4 V vs. Li/Li^+. The weight of $LiMn_2O_4$ deposited was 37±2 μg and the film thickness was ca. 0.5 μm. On increasing the scan rate, the splitting fins of peaks became obscure, and the potentials of anodic and cathodic peaks are shifted positive and negative, respectively. These behaviors can be ascribed to the increased iR drop due to the film resistance. We have recently measured the in situ conductivity of spinel $LiMn_2O_4$ thin film by using an interdigitated microarray electrode,[17] and reported that its conductivity was almost constant in the range of 10^{-5} S cm over the course of lithium extraction/insertion. The inset is the plot of the amount of charge passed during the lithium extraction process against the reciprocal of scan rate (v^{-1}). At scan rates higher than 1 mV s^{-1}, the amount of charge decreased rapidly, indicating that the scan rates were too fast to complete the oxidation of the entire of $LiMn_2O_4$ film. The $LiMn_2O_4$ film seems to respond fully to the extraction of Li^+ ions at the rates lower than 0.5 mV s^{-1} where the amount of charge was almost constant. The amplitude of peak currents gave a liner relationship with the scan rate lower than 0.5 mV s^{-1}, while at higher scan rates it was in proportion to the square root of the scan rates. These results may be indicating that the electrochemical lithium insertion/extraction reaction is kinetically limited by diffusion of Li^+ within the solid phase,[13] although the apparent chemical diffusion coefficient of Li^+ changes as a function of electrode potential, as we discuss later. The kinetic response of the $LiMn_2O_4$ was thus changed by the thickness of the films. Figure 5 shows CVs of a thinner film (ca. 6 μg) of which thickness would be around 0.1 μm. The kinetic response is greatly improved at the thinner film, as judged from the sharp and symmetric shape of current peaks.

Potential steps of 10 mV were applied to the $LiMn_2O_4$ film electrode of ca. 0.5 μm thickness through the potential domains of interest (between 3.9 and 4.3 V vs. Li/Li^+). We used a long time period ($t \gg h^2/\pi^2 D_{app}$) corresponding to the finite diffusion case, in which a linear diffusion of lithium ions takes place in the bulk of the film of the thickness, h, with the apparent chemical diffusion coefficient (D_{app}). The current response within this time period can be expressed by Eq. 2:[18,19]

$$\ln(i) = \ln\left(\frac{2nFAD\Delta C}{h}\right) - \frac{\pi^2 D_{app}}{4h^2}t, \quad (2)$$

where h is the thickness of the film, A is the surface area of the film, and ΔC is the variation of lithium concentration in the film during the potential step. ΔC can be obtained from

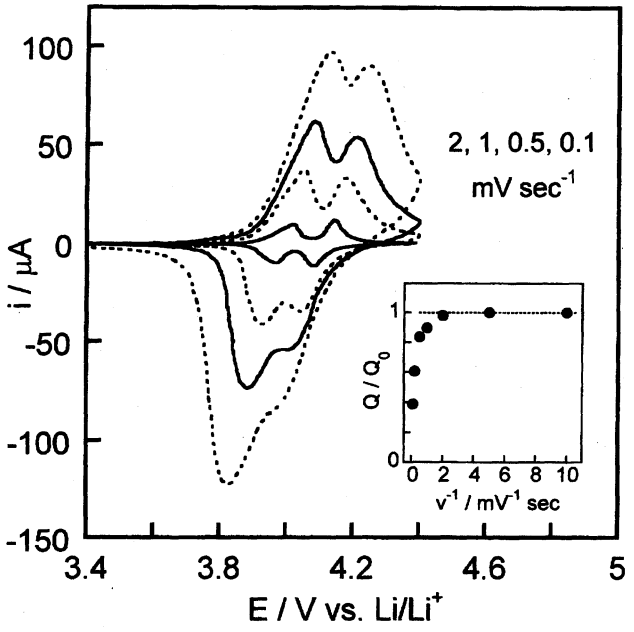

Fig. 4. CVs of a $LiMn_2O_4$ ESD film (37±2 μg) prepared at 400 °C, taken in 1 M $LiClO_4$/PC at various scan rates. Surface area and thickness of the film were ca. 0.28 cm^2 and 0.5 μm respectively. The inset is the plot of the amount of charge passed during anodic potential scans against the reciprocal of scan rate.

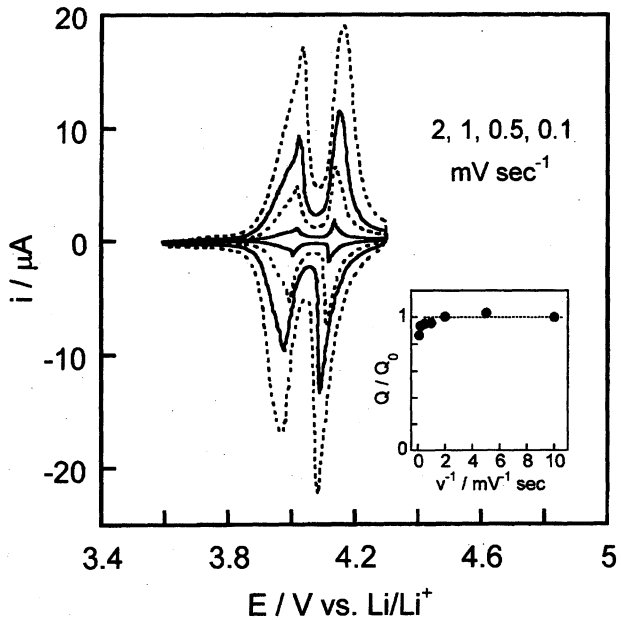

Fig. 5. CVs of a $LiMn_2O_4$ ESD film (ca. 6 μg) prepared at 400 °C, taken in 1 M Li ClO_4/PC at various scan rates. Surface area of the film was ca. 0.28 cm^2. The inset is the plot of the amount of charge passed during anodic potential scans against the reciprocal of scan rate.

the charge injected into the film until the current declined to nearly zero. It should be noted that Eq. 2 has been derived for a dense film, and it is the case for this study as judged from the SEM image shown in Fig. 1. As an example, Fig. 6 shows a typical current response obtained upon a potential step from 4.00 to 4.01 V vs. Li/Li^+, the potential corresponding to the first anodic peak on CV. According to Eq. 2, we can calculate D_{app} in different two ways: (i) from the linear slope of ln (i) vs. t, or (ii) from the intercept of ln (i) vs. t. The former way does not require the value of ΔC, a great advantage because the precise measurement of ΔC is often troublesome due to background currents such as a double layer charging current. As Aurbach et al. reported,[20] the time domain following Eq. 2 can be easily distinguished using a plot of $it^{1/2}$ vs. log (t). For the data shown in Fig. 6, the corresponding time domain was judged as $t \geqq 130$ s. In fact, a straight line can be fitted with the data in this time domain, as shown in Fig. 6(b). The apparent chemical diffusion coefficient (D_{app}) was then calculated to be 6.1×10^{-12} cm^2 s^{-1} for the lithium extraction process taking place with the electrode potential at ca. 4.0 V vs. Li/Li^+.

The D_{app} values were calculated for all of 10 mV potential steps conducted over the lithium extraction/insertion process. Figure 7 is the resulting plot of log (D_{app}) vs. E, showing that D_{app} varies the order between 10^{-10} and 10^{-12} cm^2 s^{-1}over the course of lithium extraction/insertion at $Li_{1-x}Mn_2O_4$. By comparing with the CV in Fig. 3, it was confirmed that

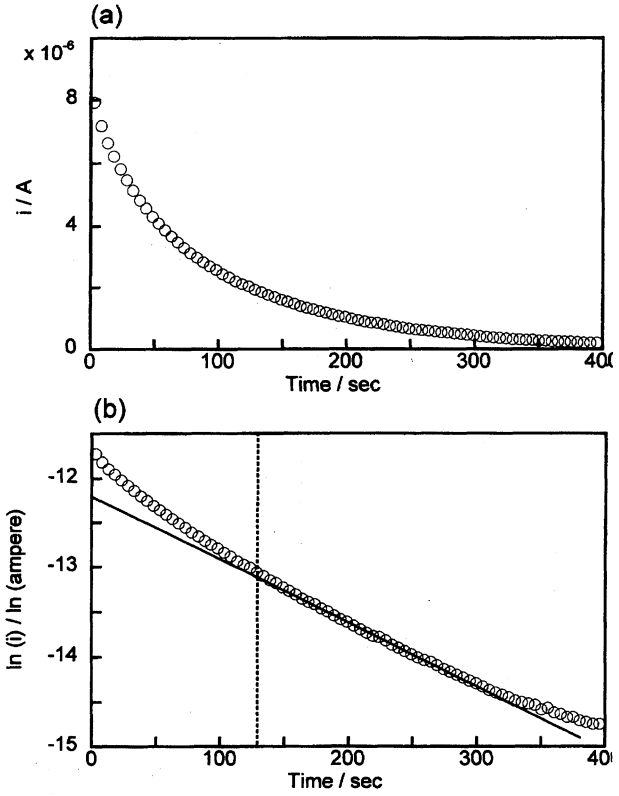

Fig. 6. The time courses of (a) i and (b) log (i) upon the potential step from 4.0 to 4.01 V vs. Li/Li^+. Other experimental conditions are the same as Fig. 4.

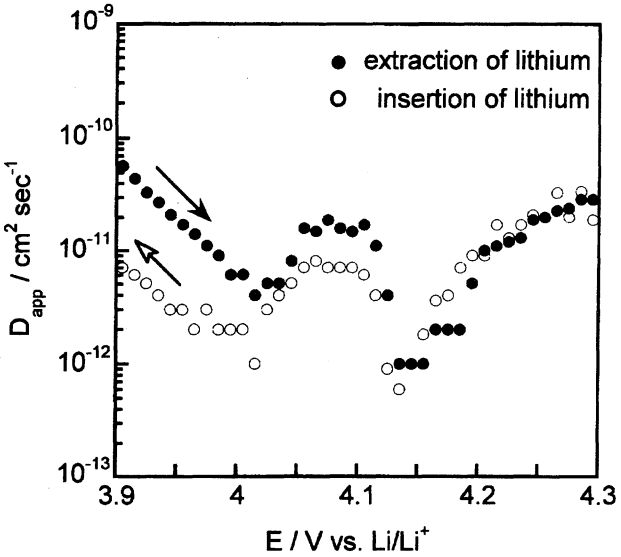

Fig. 7. Dependent of the apparent chemical diffusion coefficient (D_{app}) on the electrode potential at where the potential-step was applied. Width of a potential step; 10 mV.

the plot of log (D_{app}) shows minima correlating to the current peaks in the CV, as reported.[21] Recently, similar results have been observed for the intercalation/de-intercalation of lithium into graphite,[20,22,23] and has been explained successfully by taking into account the attractive interactions between the intercalated lithium ions during the growth of a new stage of lithium–graphite intercalation compound (LiGIC).[23] We are now attempting a theoretical understanding of the result observed here by considering coulombic interactions between the intercalated species. The D_{app} values obtained here were a few orders of magnitude lower than those in the literature.[11,21,24] This difference may be explained in terms of the different electrode preparation methods. In this work, binder-free, dense films were used as electrodes, while most of previous studies used composite electrodes consisting of the oxide powders, conductive agents, and organic binders such as PVDF. The great D_{app} values observed in the composite electrodes can be attributed to the nature of the porous electrodes; high surface area and increased ionic conductivity due to the impregnated electrolyte solution. Inside the porous composite body, the dispersed particles may act as single electrodes with μm sizes, nevertheless the D_{app} values are measured by using the overall thickness of the composite films. These may cause a significantly large D_{app} value.

Conclusion

We have prepared an uniform, dense film of spinel $LiMn_2O_4$ by the electrostatic spray deposition. Since the geometric form of the electrode material can be defined as an ideal film, we can reasonably treat its current responses using established theories of electrode kinetics. Furthermore, such the film electrode can give pure information about the materials, itself, without any dilution with additives such as organic binders.

One of the interesting feature of the ESD method is the

ease of controlling the composition of deposits. Recently, the use of other transition metal to dope the spinel manganese oxide ($LiM_yMn_{2-y}O_4$, M = Co, Cr, or Ni) has been studied extensively to improve the cyclability and to increase D_{app} of lithium ions.[24] We are planning investigate the electrochemical properties of these novel type of manganese spinel.

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