Solid electrolyte interphase (SEI) is the layer produced on the surface of active materials during charge-discharge cycling of a battery. SEI affects electrochemical properties of active materials, such as capacity retention and rate performance, and a stable SEI is known to protect the active materials from electrolyte side reactions. A well-known example is the excellent cycling performance of graphite due to the thin SEI produced on the surface.\textsuperscript{1,2} SEI control for cathode materials is, therefore, important to improve the electrochemical performance of Li-secondary batteries. In particular, much interest has been given to the study of SEI formation on LiMn\textsubscript{2}O\textsubscript{4} particles, as its SEI is relatively unstable and ineffective in protecting the electrode surface from side reactions with a protic electrolyte, causing capacity fading due to Mn\textsuperscript{4+} ion dissolution.\textsuperscript{3-5} Although LiMn\textsubscript{2}O\textsubscript{4} has been considered as a promising cathode material for lithium ion secondary batteries due to its stability and high discharge voltage, as well as its non-toxicity and low cost, its capacity fading is known to be a part of the reason for its limited commercial application.

Many researchers have studied the effect of SEI on electrochemical properties; however, the transient nature of SEI formed during cycling, and their nanoscale dimension made detailed analyses difficult.\textsuperscript{6,7} Transmission electron microscopy (TEM) has been used for the observation of SEI,\textsuperscript{8,9} however, this has inherent shortcomings since SEI, which is composed of organic and inorganic materials (LiF, Li\textsubscript{2}CO\textsubscript{3}, R-CO\textsubscript{2}Li), can be decomposed at ultra-high vacuum conditions and by the high energy focused electron beam.\textsuperscript{10} Other techniques, such as spectroscopic ellipsometry\textsuperscript{11} and X-ray reflectivity analysis,\textsuperscript{12} were also used to analyze SEI. They found that the thickness of the SEI layer was less than 5 nm in the early stages of cycling.\textsuperscript{10-12} Atomic force microscopy (AFM) has been used to examine electrode surfaces, while most AFM research has been focused on the change in topography, particle morphology, and electrical conductivity of the electrode surface.\textsuperscript{13-15} Recently, Zhang et al. found that the SEI on a MnO anode surface is inhomogeneous with broad distributions of both the thickness and mechanical properties.\textsuperscript{16}

In this study, the SEI produced on the LiMn\textsubscript{2}O\textsubscript{4} particles in a cathode during cycling is studied using AFM. Particular attention was given to SEI evolution during cycling concerning the thickness and elastic modulus and the effects of SEI on the electrochemical properties of LiMn\textsubscript{2}O\textsubscript{4} are discussed.

**Experimental**

A LiMn\textsubscript{2}O\textsubscript{4} thin-film was prepared by a spin coating method to produce a binder-free electrode with a smooth surface for AFM analysis. Lithium acetate dihydrate (0.024 mol) with a stoichiometric composition was dissolved in 2-methoxyethanol (47 ml) and of ethanolamine (3 ml). The solution was coated on a stainless steel plate (1.86 cm\textsuperscript{2}) by spin coating (3000 rpm for 10 s), and the precursor coated substrate was heated at 350 °C for 10 min. The spin coating, followed by heating, was repeated 20 times. The final LiMn\textsubscript{2}O\textsubscript{4} thin-film electrode was obtained by annealing the precursor-coated substrate at 600 °C for 2 h in air.

For the battery cycling test, 2032 coin type cells were assembled using the LiMn\textsubscript{2}O\textsubscript{4} thin-film as a working electrode. Li metal, Celgard2500, and 1 M LiPF\textsubscript{6} dissolved solution of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (EC/DMC/EMC = 1:1:1 volume ratio) were used as a counter electrode, separator, and electrolyte, respectively. The separator was soaked in the electrolyte for 24 h before cell assembly. Cycling tests were performed with a VMP3 (Bio-Logic) with a current density of 50 μA/cm\textsuperscript{2} over a voltage range of 3.5–4.5 V. After the cycling tests, the electrodes were rinsed using DMC and dried at room temperature in an argon-filled glove box to remove residual LiPF\textsubscript{6} on the electrode surface before subsequent AFM analysis.\textsuperscript{3}

An AFM (XE-100, Park Systems) was used for SEI analysis before and after the cycling test. AFM measurements were carried out with a cantilever with a stiffness of 42 nN/nm. Topography was obtained in a non-contact mode to avoid SEI destruction by the AFM tip (tip radius ∼ 10 nm). Nano-indentation tests (indenting speed ∼ 50 nm/s) were performed with the same cantilever to examine the surface layer thickness in randomly selected locations on the electrode surface. Indentation experiments using the AFM were carried out in air within 20 min to minimize possible contamination or degradation.

The crystal structure and morphology of the LiMn\textsubscript{2}O\textsubscript{4} particles were examined by X-ray diffraction (XRD, D/MAX-Ⅱ A, Rigaku, using Cu Kα radiation) and scanning electron microscopy (SEM, FE-SEM, Hitachi, S-4300).

**Results and Discussion**

The surface morphology and composition of the thin-film electrodes were analyzed before cycling tests and subsequent nano-indentation tests. Fig. 1 shows diffraction peaks obtained from the thin-film electrode produced on a steel substrate, indicating that the thin-film is LiMn\textsubscript{2}O\textsubscript{4} with a spinel structure. Some peaks corresponding to the Mn\textsubscript{2}O\textsubscript{3} impurity phase were also observed, which is known to be found, due to volatile lithium, in the case of LiMn\textsubscript{2}O\textsubscript{4} thin-film electrodes prepared by spin coating\textsuperscript{17} or pulsed laser deposition.\textsuperscript{18}

However, the voltage plateau of Mn\textsubscript{2}O\textsubscript{3} (lower than 3 V vs. Li\textsuperscript{+/Li}) is quite different with that of LiMn\textsubscript{2}O\textsubscript{4} thus the effect of Mn\textsubscript{2}O\textsubscript{3} on electrochemical properties of thin film electrode is not significant. AFM examination indicated that the thin-film was composed of nanosize particles less than ∼100 nm in diameter, and that the average
Figure 1. XRD results of (a) thin-film electrode and (b) stainless steel substrate.

Surface roughness ($R_s$) was approximately 4.5 nm, which is similar to the LiMn$_2$O$_4$ thin-film electrodes reported by other researchers (Fig. 2).\textsuperscript{20,21} Particles were not faceted, but rounded, suggesting that LiMn$_2$O$_4$ nanoparticles grew without maintaining the preferred low-energy crystal planes.

Figure 3 shows the electrochemical performance of the LiMn$_2$O$_4$ thin-film electrode up to 40 cycles at a current density of 50 $\mu$A/cm$^2$. A voltage plateau was found at approximately 4 V (an inset of Fig. 3), which is consistent to the voltage plateaus reported by other researchers.\textsuperscript{3,6,7} Coulombic efficiency at the initial cycle was relatively low (72%) and it rapidly increased at the 2nd cycle, and stabilized to 98–99% after the 20th cycle. On the other hand, the capacity retention decreased drastically to 88% during the early 10 cycles and it was maintained at approximately 81–84% after 20th cycle. These results suggest that the electrochemical property of the thin film electrode was stabilized after 20th cycle, while the Coulombic efficiency and capacity fading were significantly changed during early cycles.

In order to investigate the effect of the SEI on the electrochemical performance, the electrodes, after different cycle tests (1, 5, 10, 20, and 40 charge-discharge cycles), were retrieved from the cell for AFM analysis. Fig. 4 shows schematics of the indentation experiments performed on the SEI produced on the surface of the LiMn$_2$O$_4$ thin-film, and typical indenting force profiles as a function of penetration depth. The force-distance profiles showed different slopes, suggesting different mechanical properties of the surfaces, possibly due to soft SEI layers and hard LiMn$_2$O$_4$.

Before the contact with electrolyte, soft SEI was not found on the surface of the LiMn$_2$O$_4$ thin film: only a hard substrate was detected (Fig. 4b). On the other hand, a soft SEI was detected on the cycled LiMn$_2$O$_4$ electrode, indicating that the SEI layer was produced during the cycling tests. Fig. 4c shows an example of the soft SEI layer in thickness of 6.5 nm. In the latter case, the AFM tip penetrated into the soft SEI with a small force, while further indentation required a large indentation force, due to the relatively hard LiMn$_2$O$_4$.\textsuperscript{16}

The nano-indentation experiments were repeated 100 times on the LiMn$_2$O$_4$ surface and various types of force-distance profile were found (Fig. 5). The indentation was performed at randomly selected positions, while the distance between neighboring indenting points was maintained at approximately 120 nm. The figure indicated that the surface was often covered by multiple SEI layers with different stiffness. The topographical effect of the LiMn$_2$O$_4$ film appears small, in this case, because the average surface roughness ($R_s = 4.5$ nm) is smaller than the tip radius ($\sim 10$ nm), and the particle size ($\sim 50$ nm) is larger than the tip radius (Fig. 4a).

Different SEI thickness and stiffness observed in Fig. 5 indicate that the compositions of the layers are different (organic and
Figure 4. (a) Schematics of the AFM tip penetration onto the SEI. Penetration depth can be calculated from displacement of cantilever and displacement of z-scanner ($p = Z - \Delta d$, where $p$ is penetration depth and $Z$ is displacement of z-scanner, displacement of cantilever $\Delta d = d_0 - d' = k\Delta f$, where $k$: stiffness of cantilever). Force versus $Z$ distance curve obtained by nano-indentation can be transformed to force-penetration depth curve. Typical force-penetration depth curves obtained from (b) pristine electrode and (c) electrode after 40 cycles.

inorganic). Three different types of SEI layers such as a soft single layer, a stiff single layer, and a double layer with a stiff inner layer and a soft outer layer. The probability to find the SEI with double layers gradually increased, showing 3% from 1 cycled electrodes, 9% from 20 cycled electrodes, and 30% from 40 cycled electrodes. This result indicates that the soft SEI with organic components tends to produce on top of the stiff SEI layer with inorganic components and it is pronounced as the cycle continues. The nonuniform SEI chemical composition appears to be due to the random nature of the LiMn$_2$O$_4$ surface, such as the random grain orientation and surface roughness, which affect the reaction kinetics of the LiMn$_2$O$_4$ surface with an electrolyte. Similar results showing a non-uniform SEI have been reported by other researchers in the case of LiMn$_2$O$_4$, carbon, and MnO.

Based on Sneddon’s model, the elastic moduli of the fresh LiMn$_2$O$_4$ electrode were calculated assuming a conical tip.
Coulombic efficiency. The poor Coulomb efficiency found in the LiMn2O4 electrode was consistent with the studies that correlated SEI formation with electrochemical properties of the LiMn2O4 thin-film electrode. The SEI growth during the initial cycle is rapid (1.526 nm/cycle), suggesting that the low Coulombic efficiency during the initial cycling test can be attributed to rapid SEI growth on the LiMn2O4 surface. The change of the SEI thickness during cycling and its relation to the elastic modulus of LiMn2O4 reported by Sugiyama et al. was comparable to the elastic modulus of LiMn2O4 reported by Sugiyama et al. This is comparable to the elastic modulus of LiMn2O4 reported by Sugiyama et al. 

The SEI thickness, measured by the nano-indentation technique using an AFM, showed a broad distribution and its range increased with an increasing number of cycles. The histogram of SEI thickness as a function of cycle number, shown in Fig. 6, shows a broader SEI thickness distribution as the cycling tests continued, while the average thickness increased (an inset of Fig. 6), suggesting gradual SEI growth during cycling. The SEI thickness obtained in this study by indentation was thicker than the reported values measured by other techniques, such as ellipsometry and TEM, which reported that the SEI thickness was in the range of 2–5 nm, much smaller than the result in this study. The relatively thin SEI from TEM measurements probably appears because of SEI decomposition by the focused electron beam under high vacuum condition, while the ellipsometry technique seems to underestimate the thickness due to an assumption of an optically homogeneous and isotropic SEI.

A numerical summary of Fig. 3 and Fig. 6 is given in Table I. Very thin surface layer (∼1.3 nm) is detected from the electrode before cycle. It has been known that thin surface layer can be formed on electrode surface by contact with electrolyte. The growth of the SEI during the initial cycle is rapid (1.526 nm/cycle), suggesting that the low Coulombic efficiency during the initial cycling test can be attributed to rapid SEI growth on the LiMn2O4 surface. This is consistent with the studies that correlated SEI formation with Coulombic efficiency.

The poor Coulombic efficiency found in the early stages of the cycling test appears to be associated with the chemical reaction to produce a thin SEI, in which the ions required to run charge-discharge reactions are depleted at the interface, since they are consumed to produce the SEI.

The SEI growth rate during the first 20 cycles was 0.47 nm/cycle, which was about twice as fast as the growth rate measured during the second 20 cycles (0.19 nm/cycle). This suggests that the change of the average SEI thickness (or its growth rate) during cycling tests is rapidly reduced after 20th cycle, indicating that the SEI is thick enough to restrict electron tunneling across the layer. Considering the significant capacity fading during early cycles and stabilization of the capacity retention after 20th cycle (Fig. 3, Table I), these results suggest that a fully grown SEI, i.e. an SEI with sufficient thickness to diminish SEI growth rate, is required for protection of the electrode against Mn dissolution and corrosion of the cathode, indicating that, once the average SEI thickness grew sufficiently to protect side reactions, the passivated SEI is preserved.

Conclusions

The change of the SEI thickness during cycling and its relation with electrochemical properties of LiMn2O4 were studied by nano-indentation experiments using an AFM. The SEI produced on the LiMn2O4 surface after cycling tests showed broad distributions in terms of thickness and mechanical properties, which suggest considerable variation of the SEI composition. The SEI were often composed of double layers and the distribution of SEI thickness increased with cycling tests, which appeared to be a cause of inconsistency of SEI thickness reported by many researchers. The SEI growth was rapid during initial cycling and accompanied low Coulombic efficiency. The average thickness of the SEI increased until 20th cycle and accompanied significant capacity fading. On the other hands, the SEI growth rate was decreased and the capacity retention was stabilized after the 20th cycle, suggesting that the long-term stabilization of the
electrochemical properties was attributed to the thick SEI, which effectively protected the LiMn$_2$O$_4$ surface from the possible side reaction with electrolyte.

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