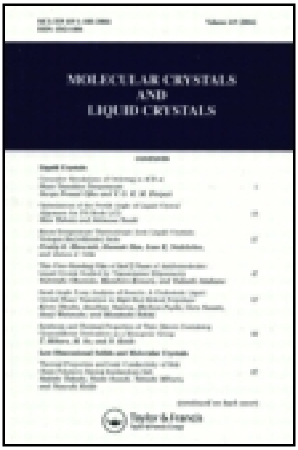

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Electrochemical Properties of Limn 2 O 4 Coated with Nano-Thickness Carbonand Fluorine

Masayuki Takashima [a] , Susumu Yonezawa [a] & Masaya Ozawa [a]

[a] Department of Materials Science & Engineering, Facultyof Engineering, Fukui University, 3-9-1 Bunkyo, Fukui, 910-8507, Japan

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ELECTROCHEMICAL PROPERTIES OF $LiMn_2O_4$ COATED WITH NANO-THICKNESS CARBON AND FLUORINE

Masayuki Takashima, Susumu Yonezawa, and Masaya Ozawa
Department of Materials Science & Engineering, Faculty of Engineering, Fukui University, 3-9-1 Bunkyo, Fukui 910-8507, Japan

Surface modification of $LiMn_2O_4$ by coating with nano-thickness carbon and fluorine were carried out by an arc discharge with carbon electrode (nC-$LiMn_2O_4$, n = number of times of arc discharge for 0.1 s) and a fluorination with NF_3 at 1.3 kPa for 1 hour at 100°C (F-$LiMn_2O_4$). Cyclic voltammograms revealed that the reversibility of the electrochemical process was improved by coating with nano-thickness carbon. The discharge capacities of nC-$LiMn_2O_4$ and F-$LiMn_2O_4$ were improved by 5 ~ 10%. 120C-$LiMn_2O_4$ exhibits the largest discharge capacity.

Keywords: nano-thickness carbon; surface modification; fluorination; lithium secondary battery; $LiMn_2O_4$ cathode; charge/discharge performance

1. INTRODUCTION

Since cathode active materials, LiMOx(M = Co, Mn, Ni), for lithium secondary battery are semiconductors with less electrical conductivity, carbon materials such as acetylene black (AB) are added to prepare an electrode with enough electrical conductivity [1,2]. The amount of AB in the battery has to be minimized to obtain a large electric capacity. One of methods to decrease the amount of AB is to coat on the surface of an active material with thin carbon layer having enough electrical conductivity. In addition, it is expected that coating of a carbon material on the active material contributes to the inhibition of the oxidative decomposition of the electrolyte solution [3].

It has been reported that the fluorination of $LiCoO_2$ surface improves its performance as a cathode active material in a previous paper [4]. The

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discharge capacity and the average discharge potential were enhanced by the surface fluorination. Some papers were also published about surface modification of a carbon material as an anode active material [5–9]. In this study, modification of $LiMn_2O_4$ surface was tried by coating of nano-thickness carbon material as well as by surface fluorination with NF_3. The influences of modification with nano-thickness carbon and fluorine on the electrochemical properties of $LiMn_2O_4$ were discussed.

2. EXPERIMENTAL

An arc discharge with carbon electrode was performed for coating nano-thickness carbon on the surface of $LiMn_2O_4$ (Sanyu Electron Co., Ltd., model 701C). $LiMn_2O_4$ powder sample with the mean diameter of 5 µm was spread on the glass plate. Carbon was intermittently flashed by the arc discharge for 0.1 s under vacuum of around 1 Pa. After every 5 times flashing, the sample was taken out from the chamber and spread again after mixing. The samples coated with carbon by 30, 60 and 120 times flashing were designated to 30C-, 60C- and 120C-$LiMn_2O_4$, respectively. Since sample powder particles were cohered by coating, samples were ground for 1 hour with a ball-mill after coating. Particle size was homogenized to about 1 µm in diameter. $LiMn_2O_4$ and nC-$LiMn_2O_4$ (n = 30, 60 and 120) was treated with NF_3 (Central glass Co., Ltd.) by using the originally designed fluorination line at 1.3 kPa for 1 hour at 100℃. The surface fluorination was carried out before (nC-F-$LiMn_2O_4$) and after carbon coatings (F-nC-$LiMn_2O_4$). F-$LiMn_2O_4$ is NF_3-treated sample without carbon coating. Each treated-$LiMn_2O_4$ sample was characterized by using the atomic force microscope (AFM, SII SPI3700) and scanning electron microscope (SEM, Shimadzu EPMA C-1). Elemental analysis was carried out by using alumina powder having similar particle size as a substrate instead of $LiMn_2O_4$ because $LiMn_2O_4$ released oxygen by heating with carbon material. Three-electrodes test cell (Hokuto Denko Co., F-type cell) was used for the electrochemical measurements. The cathode mixture consisted of the treated $LiMn_2O_4$ sample, AB and polytetrafluroethylene (PTFE) in weight ratios of 5:4:1. The mixture was rolled spread to 0.1 mm thickness film and the film was cut into a disk with 13 mm^{ϕ}. And then, it was pressed onto a titanium mesh welded on the bottom of SUS304 container (20 $mm^{\phi} \times 3\,mm^{t}$). The cathode was fully dried by vacuuming ($\sim 10^{-1}$Pa) for 12 hrs at room temperature prior to use. The solution of propylene carbonate (PC) and dimethoxyethane (DME) mixed in the volume ratio of 1:1 containing 1.0 mol dm^{-3} $LiClO_4$ was used as an electrolyte solution. Li metal foil (0.2 mm^{t} Kyokuto Kinzoku Co. Ltd.) was used as the reference and counter electrodes. Cyclic voltammetry was performed at the sweep rate of 1 mV min^{-1} between 3.2 and 4.3 V (Hokuto Denko Co., HZ-3000 and HSV-100). Charge/discharge test was carried out at the currents of C/12 (discharge rate) and C/18 (charge rate) (Hokuto Denko Co., HJ101SM6). The temperature of the cathode was controlled at 25℃. Cut off potentials were 3.0 (discharge) and 4.5 V (charge).

3. RESULTS AND DISCUSSIONS

3.1. Characterization

To estimate the thickness of the carbon coated on the $LiMn_2O_4$ powder sample by AFM, a glass plate masked partly was used as a substrate for carbon coating. The thickness of the deposited carbon was measured to be 0.67 nm by one flash. Figure 1 shows the relationship between the number of times of flashing and the amount of carbon coated on the sample. The weight uptake due to deposited carbon was only 0.8 wt.% even after 120 flashes. Figure 2 shows SEM images of $LiMn_2O_4$, 240C-$LiMn_2O_4$ before and after grinding. The $LiMn_2O_4$ particles tended to aggregate together by carbon coating. The particle size was always regulated by grinding after coating. The BET surface areas of ground samples are around 8.0 $m^2 g^{-1}$. Electrical conductivity and density of each sample were summarized in Table 1. The coverage of carbon on the $LiMn_2O_4$ surface after grinding was estimated to be 3%. Figure 3 shows XP spectra of F1s level of $LiMn_2O_4$, F-$LiMn_2O_4$, 30C-F-$LiMn_2O_4$ and F-30C-$LiMn_2O_4$. The signal of F1s was detected in the case of F-$LiMn_2O_4$ and F-30C-$LiMn_2O_4$. The signal of F1s of F-30C-$LiMn_2O_4$ disappeared after keeping it in an argon at room temperature for 10 months while there was no change in case of F-$LiMn_2O_4$. NF_3 becomes reactive at around 230℃ due to dissociation into radicals of

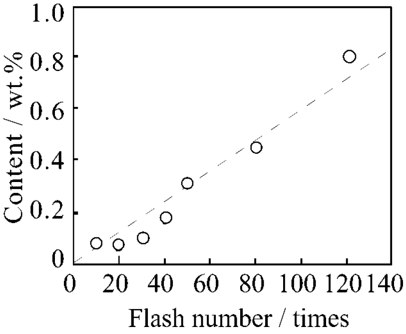

FIGURE 1 Carbon contents vs. flash number.

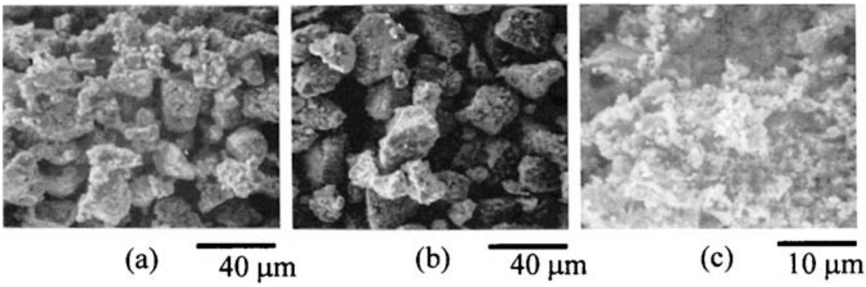

FIGURE 2 SEM images of (a) $LiMn_2O_4$, 240C-$LiMn_2O_4$ before (b) and after grinding (c).

$NF_2^\bullet$ and $F^\bullet$, but some fluorinating reaction is likely to take place on the surface of $LiMn_2O_4$ even at 100℃. The surface of a binary metal oxide containing lithium may be very active to NF_3 because oxides like Li_2O with high basicity are active to an acidic gas. Two kinds of fluorine were detected on $LiMn_2O_4$ surface treated with NF_3. One corresponds to Li-F type bond (685 eV) and another corresponds to Mn-F type bond (687 eV). Li-F type bond was dominant in this case. Although the C-F bond generated in case of F-30C-$LiMn_2O_4$ was weaker than that of F-$LiMn_2O_4$, F-30C-$LiMn_2O_4$ exhibits higher electrical conductivity than F-$LiMn_2O_4$ (Table 1). We obtained a result separately that the electrical conductivities of powder carbon materials such as graphite and AB was improved by treatment with NF_3 at room temperature. In other cases, the modification of the surface by carbon coating and/or fluorination lowered the electrical conductivity. The electrical conductivities in the nano-thickness carbon or on the fluorinated surface may be lower than that on $LiMn_2O_4$ surface. In case of 30C-F-$LiMn_2O_4$, fluorine seems to make a bond not with carbon but with $LiMn_2O_4$.

TABLE 1 Electrical Conductivity (σ) and Density

Sample name	σ ($10^{-3}\,S\,cm^{-1}$)	Density ($g\,cm^{-3}$)
$LiMn_2O_4$	2.16	4.2
30C-$LiMn_2O_4$	1.59	4.2
60C-$LiMn_2O_4$	1.31	–
120C-$LiMn_2O_4$	1.15	–
F-$LiMn_2O_4$	1.00	4.2
F-30C-$LiMn_2O_4$	2.88	4.2
30C-F-$LiMn_2O_4$	1.56	4.2

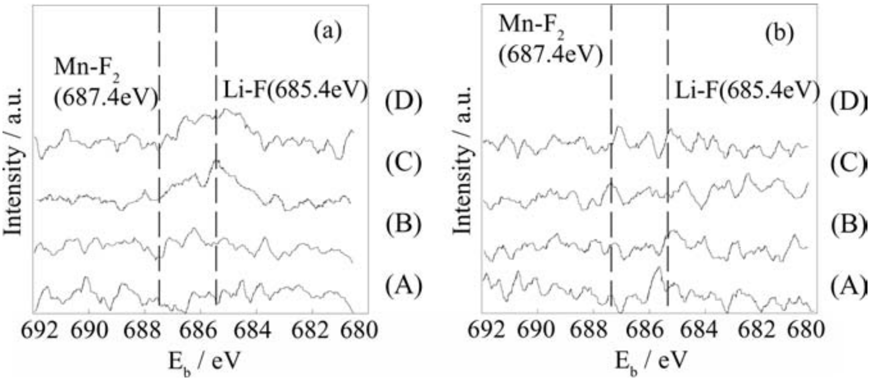

FIGURE 3 XP spectra of F1s level of $LiMn_2O_4$(A), 30C-F-$LiMn_2O_4$(B), F-30C-$LiMn_2O_4$(C) and F-$LiMn_2O_4$(D). (Before (a) and after (b) Ar ion etching for 30 min.)

3.2. Cyclic Voltammetry

As shown in Figure 4, two pairs of the redox peaks appeared on cyclic voltammograms for $LiMn_2O_4$. These peaks may result from phase transition due to the deformation of the MnO_6-octahedron [10]. The differences between anodic and cathodic peak potentials around 3.9 V, ΔE of 30C-$LiMn_2O_4$ (93 mV), F-$LiMn_2O_4$ (98 mV), F-30C-$LiMn_2O_4$ (86 mV) and 30C-F-$LiMn_2O_4$ (84 mV) were smaller than that of $LiMn_2O_4$ (126 mV). The cathode peak currents around 4.1 V of 30C-$LiMn_2O_4$ (24.0 mA g^{-1}) and F-$LiMn_2O_4$ (24.9 mA g^{-1}) were larger than that of $LiMn_2O_4$ (20.8 mA g^{-1}).

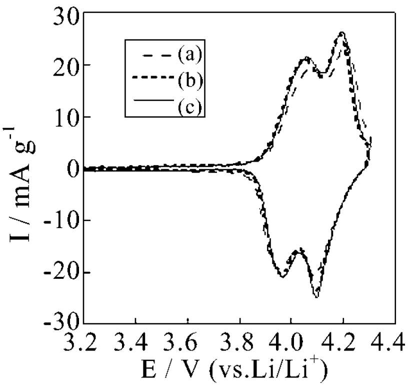

FIGURE 4 Cyclic voltammograms of $LiMn_2O_4$(a), 30C-$LiMn_2O_4$(b) and F-$LiMn_2O_4$(c).

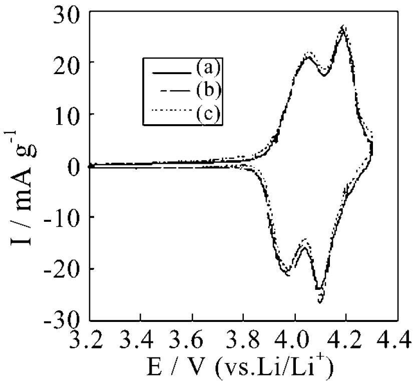

FIGURE 5 Cyclic voltammograms of 30C-$LiMn_2O_4$(a), F-30C-$LiMn_2O_4$(b) and 30C-F-$LiMn_2O_4$(c).

Both surface modifications with nano-thickness carbon and fluorine improve the performance of $LiMn_2O_4$ as a cathode active material. However, as far as the cyclic voltammograms showed, the additive effects of the surface modification layered with nano-thickness carbon and fluorine on the performance of the $LiMn_2O_4$ cathode was hardly expected.

3.3. Charge/discharge Measurement

As shown in Figure 6, the discharge capacity of nC-$LiMn_2O_4$ was enhanced 6 ~ 12% compared with $LiMn_2O_4$. However, there seems to be no significant difference in discharge capacities among carbon coated nC-$LiMn_2O_4$ samples. The discharge capacity was slightly improved by the surface

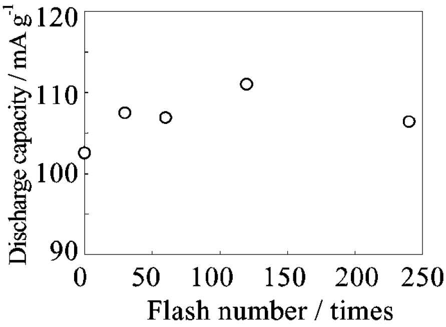

FIGURE 6 Relationship between the number of times of flashing and the discharge capacity.

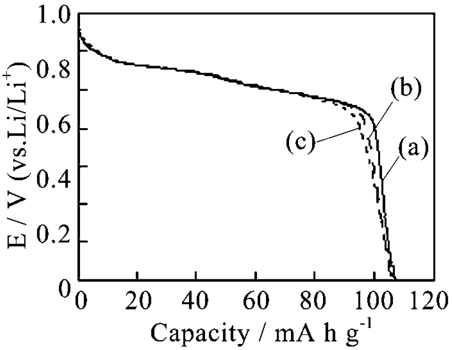

FIGURE 7 Discharge curves of F-$LiMn_2O_4$(a), 30C-F-$LiMn_2O_4$(b) and F-30C-$LiMn_2O_4$(c) at 1st cycle.

modification with nano-thickness carbon and fluorine as shown in Figure 7. The charge/discharge efficiency of $LiMn_2O_4$ was 98% while those of nC-$LiMn_2O_4$ were around 90%. The average discharge potentials were in the order of F-$LiMn_2O_4$ > 30C-$LiMn_2O_4$ > 30C-F-$LiMn_2O_4$ > F-30C-$LiMn_2O_4$ > $LiMn_2O_4$. Therefore, the layered-type surface modification like 30C-F-$LiMn_2O_4$ and F-30C-$LiMn_2O_4$ gives no positive effect on the charge/discharge performance. Considering the location of fluorine on the active materials, the nano-thickness carbon and the fluorine would be better to be placed separately on the surface of $LiMn_2O_4$ to improve electrochemical properties.

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