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Figure 3. The charging mechanism of Li/Polyaniline battery.

capacity is almost not changed with cycling. After one or two cycles, the capacity becomes stable and constant. It is in good agreement with the results of voltammetric experiments. Discharge testing of the Li/polyaniline cells which are consisted of different molecular weight polyaniline was performed. As shown in Figure 2, discharge characteristics of the battery were greatly influenced by the molecular weight. In the cases where LMW-PANI and IMW-PANI are used, the discharge capacities are about 17 mAh/g and 34 mAh/g, respectively. The theoretical capacity of polyaniline salt is 95.2 mAh/g. Therefore, the efficiency of these batteries are 18% and 36%, respectively.

The original polyaniline film is a non-conducting material. Due to poor conductivity for this polyaniline film, we treated the polyaniline film with Li ionic salt solution. Then it is easily changed to the conducting material. In the case of the polyaniline film which is a non-conducting material or a conducting material treated with acid solution (HCl), the

cell current and the utilization of this polyaniline film were considerably lower. But the polyaniline film was gradually activated by doping with Li salt and the conductivity of cathode film is increased up to ~0.5 S/cm. When these films are used as a cathode in lithium secondary battery, undoped benzenoid ring is changed to doped form with proton during charge process. And the counter ion and Li ion in electrolyte move to electrode for electroneutralization. Discharge process is occurred to reverse direction. This is the charge and discharge mechanism and showed the charging mechanism in Figure 3.

In comparison with other lithium secondary batteries using inorganic intercalation compounds as cathode materials, there are advantages and disadvantages of the Li/polyaniline battery. The advantage is that capacity decay of this battery is very smaller than that of Li/inorganic compound battery. And the initial capacity decay for cycling proceeding is not found because of the electrolyte salt doping for cathode materials. The disadvantage is that the capacity of Li/polyaniline battery is smaller than that of Li/inorganic compound battery. But this problem can be improved by using other polymer (and/or copolymer) in the future. Therefore, it is possible to make the battery that have a good rechargeable and reversible characteristics.

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A Comparative Study on Electrochemical Properties for Manganese Oxide and Iron Substituted Manganese Oxides

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Lithium ions are intercalated/deintercalated in spinel $LiMn_2O_4$ during the electrochemical reaction. Normally in spinel $LiMn_2O_4$, Li ions are residing in tetrahedral (8a) sites, the Mn ions in octahedral (16d) sites, and O^{2-} ions in octahedral (32e) sites. These former ions form a cubic close-packed array. Tetrahedral (8a) sites share face with vacant octahedral sites (16c), so that they form three-dimensional vacant channels.[1] Li^+ ions can intercalate/deintercalate by these channels. Thackeray *et al.* first reported that lithium

ions can reversibly intercalate/deintercalate from $LiMn_2O_4$ by electrochemical reaction between 3 V and 4.1 V.[1,2] In $Li_xMn_2O_4$, structural transformation occurs during the electrochemical reaction. When $0 \le x \le 1$, $Li_xMn_2O_4$ remains a cubic spinel structure at near 4 V, whereas when $1 < x \le 2$, phase transition occurs from cubic symmetry to tetragonal symmetry at near 3 V.[3,4] Spinel $LiMn_2O_4$ shows different electrochemical properties depending on starting materials, annealing temperature, annealing time, cooling rate *etc.*[5,6]

Several research groups have investigated the substitution of other transition metals for Mn to make $LiM_yMn_{2-y}O_4$ (M=Al, Ti, Cr, Fe, Co, Ni, Zn, Ge, Ta $\cdots$).[7,8] The partial substitution of transition metal for Mn and nonstoichiometry in $LiMn_2O_4$ induce the suppression of Jahn-Teller distortion, which causes the rapid fading of capacity when $Li_xMn_2O_4$ electrodes are deeply discharged in the range of $1<x<2$ (around 3.5 V, $Mn^{III} > Mn^{IV}$). Capacity fading can be explained by the appearance of biphase and the distortion of local structure. Guohua *et al.* reported cycling performance improved by substitution of Co, Cr, Ni for Mn.[8] These transition metal substitutions are considered to stabilize the octahedral sites in spinel structure, so that cycling performance improved. Substituted spinel $LiM_yMn_{2-y}O_4$ shows different structures and electrochemical properties with transition metal species (M) and substitution content (y).

This work is intented to explain the reason for the capacity fading of the $LiMn_2O_4$ on cycling comparing it with the substituted spinel. In this paper, we report on the results of X-ray diffraction, phase transition during the electrochemical reaction , and the cyclic voltammetry of $LiFe_yMn_{2-y}O_4$ (y=0.0, 0.25, 0.5) in which Mn^{3+} ion was substituted for Fe^{3+} ion.

Experimental

$LiMn_2O_4$ compound was prepared by solid state reaction of LiOH and manganese dioxide, in a $1:2$ molar ratio. To make $LiFe_yMn_{2-y}O_4$, Fe_2O_3 was used as iron source. The starting materials were calcined at 400 °C in air for 10 hrs after mixing. The samples were reground and annealed at 750 °C for 48 hrs with intermediate grinding. Samples were slowly cooled at a cooling rate of 1 °C/min. The phase identification and the evaluation of lattice parameters for the resulting samples were carried out by X-ray diffraction analysis using Cu-Kα radiation (MAC-Science Co. Ltd.). To investigate the electrochemical properties of the $LiFe_yMn_{2-y}O_4$ ($0 \le y \le 0.5$), an electrochemical cell was consisted of Li-$Fe_yMn_{2-y}O_4$ as positive electrode, Li metal as negative electrode, and 1M $LiPF_6$ which dissolved in a $2:1$ (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as electrolyte. The glass-filter was used as a separator. The cathode was mixture of 89% (wt.%) active material, 10% acetylene black, and 1% polytetrafluoroethylene (PTFE) binder. The cells were assembled in argon filled dry box. All the electrochemical tests were performed at room temperature and measured with a potentiostatic system and galvanostatic system (Mac-Pile system, Bio-Logic Co. Ltd.).

Results and Discussion

The X-ray diffraction patterns of the prepared samples could be indexed with the spinel having a space group Fd 3m. The lattice parameters of each sample are shown in Figure 1. As shown in the Figure 1, the lattice parameters slightly increased as iron is substituted in $LiFe_yMn_{2-y}O_4$. The radius of Fe^{3+} is similar to that of Mn^{3+}, so the lattice parameters of iron substituted manganese oxides are not varied significantly. The variation of lattice parameters is not observed in the range of y=0.0-0.25.

The electrochemical reaction of $Li/LiFe_yMn_{2-y}O_4$ is carried out in the voltage range of 3.5-4.3 V. Pistoia *et al.* reported that lithium ion can be deintercalated to $0<x<0.2$ in the first charge process of $Li/Li_xMn_2O_4$ cell, and can be intercalated up to x=0.8-0.9 in the first discharge process.[9] Figure 2 shows the variation of Li ion content(x) in the charge/discharge curve of $Li/LiFe_yMn_{2-y}O_4$ at constant current 265 $\mu A/cm^2$. In $LiMn_2O_4$ (y=0), 0.8 Li^+ ion was deintercalated in first charge and 0.6 Li^+ ion was intercalated in first discharge so 0.2 Li^+ ion is lost irreversibly. As shown in Figure 2, two voltage plateaus ranges in $LiMn_2O_4$ (y=0) were observed at 4.0 and 4.15 V, respectively. These results coincide with those of previous report.[9] The two plateaus indicate that biphase is formed during an electrochemical reaction. Xia *et al.* reported at average composition range of 0.1 $<x<0.45$ in $Li_xMn_2O_4$ for first charge biphase (cubic a_c= 8.154 Å and a_c=8.072 Å) exsists, and single phase reaction (cubic a_c=8.163 Å to 8.247 Å) occurs in the range of $0.45<x<1.0$.[10]

In $Li/LiFe_{0.25}Mn_{1.75}O_4$ cell, 0.6 Li^+ ion was reacted reversibly, therefore irreversible loss of lithium in first cycle is similar to that of $Li/LiMn_2O_4$ cell. The plateau observed at 4.15 V disappeared in y=0.25. In $Li/LiFe_{0.5}Mn_{1.5}O_4$ cell, the plateau is not shown in V vs. x curve. This means that the biphase region disappeared as the Fe content increases. Above results imply that cubic symmetry of the spinel host structure is maintained during charge/discharge cycle. The substituted Fe^{3+} restrains the unstable biphase coexisting, and does not induce Jahn-Teller distortion. The one electron
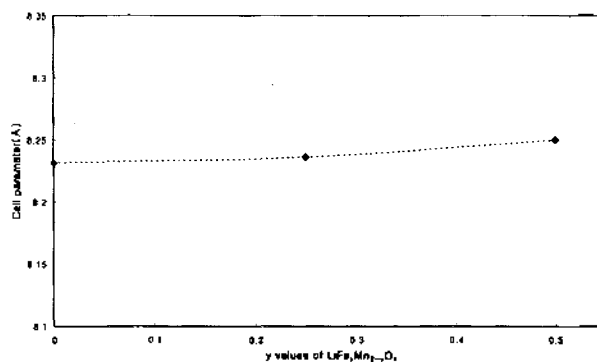

Figure 1. The variation of lattice parameters (Å) in $LiFe_yMn_{2-y}O_4$ (y=0.0, 0.25, 0.5).

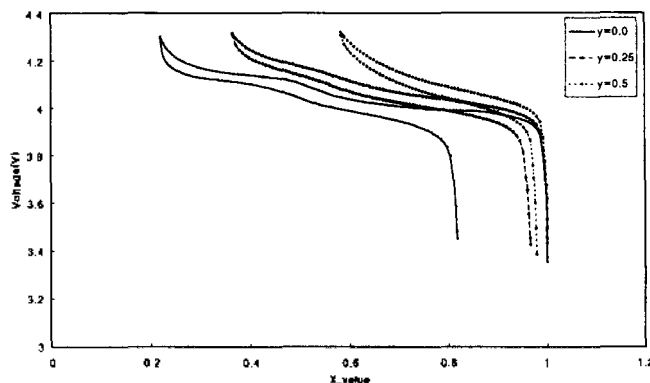**Figure 2.** The variation of Li ion content in the first charge and discharge curves of $Li/LiFe_yMn_{2-y}O_4$ (y=0.0, 0.25, 0.5) cell.

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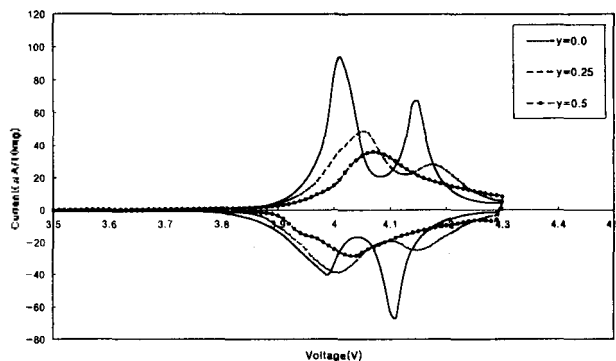*Bull. Korean Chem. Soc.* **1998**, Vol. 19, No. 2 265

Figure 3. Cyclic voltammogram of Li/LiFe$_x$Mn$_{2-y}$O$_4$ (*y*=0.0, 0.25, 0.5) cell.

of Mn^{3+} (t_{2g}^3 e_g^1) in the e_g orbital is repulsing 2O^{2-} ions along the *z*-axis and then Jahn-Teller distortion occurs in spinel LiMn$_2$O$_4$. If high spin (t_{2g}^3 e_g^2) of Fe^{3+} which does not induce Jahn-Teller distortion is substituted for Mn^{3+}, total Jahn-Teller distortion of the host structure may be reduced. Therefore, the cubic structure will be stabilized by Fe^{3+} substitution.

The phase transition of cathode material due to lithium intercalation/deintercalation was investigated by cyclic voltammetry. The cyclic voltammogram is acquired 10 mV/h scan rate in the voltage range of 3.5-4.3 V. The cyclic voltammogram for Li/LiFe$_y$Mn$_{2-y}$O$_4$ is given in Figure 3. In LiMn$_2$O$_4$, the oxidation peaks are located near 4.0 and 4.15 V, respectively. The electrochemical peaks become much broader and put together as Fe content increases. The

results of CV curve are shown for both oxidation and reduction process in Li/LiMn$_2$O$_4$ cell biphase gradually becomes single phase as Fe is substituted for Mn. Therefore, the substitution of Fe in LiMn$_2$O$_4$ may enhance the cycling performance of lithium manganese oxides.

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Electrochemical Performance of Chromium Substituted Spinel Lithium Manganese Oxides

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Spinel LiMn$_2$O$_4$ is the most attractive cathode material for the rechargeable lithium batteries due to good performances such as high specific energy and high voltage (~4 V) and its economical and environmental advantages compared to other cathode materials. When lithium content is 0≤*x*≤1 in Li//Li$_x$Mn$_2$O$_4$ cells, the cells discharge at ~4 V for lithium, whereas when 1<*x*≤2, the cells discharge at ~3 V.[1-3] LiMn$_2$O$_4$ which is prepared at 300-400 °C shows a good performance at 3 V than at 4 V.[4] At 700-900 °C, it shows better at 4 V than at 3 V.[5,6] But the capacity of LiMn$_2$O$_4$ is decreased more rapidly as the charge/discharge cycles are repeated in Li$_x$Mn$_2$O$_4$(0≤*x*≤1) than that of LiCoO$_2$, which is competitive cathode material.[7]

Tarascon *et al.* reported that the cations of valence 2 or 3 substituted LiM$_y$Mn$_{2-y}$O$_4$ reduced the capacity of the cells at 4.1 V, but did not affect their cycling performance.[8] Another researcher reported that the cobalt-doped LiCo$_x$Mn$_{2-x}$O$_4$ improved cycling behavior.[9]

For a long time, it was impossible to charge LiMn$_2$O$_4$ at high voltage (~4.4 V) due to oxidation of electrolytes. However, recent discovery of a high voltage oxidation-resistant electrolyte, ethylene carbonate(EC)-propylene carbonate (PC)-dimethyl carbonate(DMC)-lithium hexafluoro phosphate (LiPF$_6$) opened a way to study high voltage performance.[10,11] This work report the performance of Cr substituted spinel manganese oxide in a range of 3.4-5.2 V.