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The Effects of Sulfur Doping on the Performance of O_3-$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ Powder

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Abstract−$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) powders were synthesized by using a sol-gel method. As-prepared samples showed typical rhombohedral O3 layered structure. The shape of the initial discharge curve for the samples was almost equal to that of the layered structure. However, the electrode materials were transferred from layered to spinel structures with cycling. At the first cycle, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$ delivered the discharge capacities of 238, 230, 224, and 226 mAh/g, respectively, with their capacity fading rates of 0.34, 0.21, 0.12, 0.25%/cycle, respectively. The partial substitutions of Ni and S for Mn and O in $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ significantly enhanced the electrochemical properties of the lithium manganese oxide materials.

Key words: Sol-gel Method, Ni Doping, Rhombohedral Structure, S-doping, Nanodomain

INTRODUCTION

A growth in the number of portable electronic devices, such as cellular phones, laptop computers, etc. has led to an increasing demand for compact lightweight batteries with high energy and power capability. Lithium secondary batteries have satisfied this demand to a greater degree than other rechargeable battery systems [Dahn et al., 1990; Guyomard et al., 1994].

Recently, $LiMnO_2$ has been considered to be an attractive alternative cathode material in terms of nontoxicity, low cost, abundance and high theoretical capacity (288 mAh/g) [Jang et al., 1998; Chiang et al., 1999]. But, $LiMnO_2$ undergoes a rapid capacity fading due to a structural transition from layered to spinel during the intercalation/deintercalation of lithium ion. Several research groups stabilized the structure of $LiMnO_2$ powders with cation substitution technology. Partial substitution of Mn for $LiMnO_2$ with some transition metals such as Al [Ammundsen et al., 1996], Ni [Quine et al., 2000], Co [Armstrong et al., 1998, 1999], and Cr [Davidson et al., 1999] has been widely studied to improve the structural stability. Bruce et al. have reported the partial substitution of Co for Mn in the $LiMnO_2$ material [Bruce et al., 1999]. The substitution of around 10% Co (or Ni) forms a slightly Li-deficient $LiM_xMn_{1-x}O_2$ material with $R\bar{3}m$ lattice symmetry rather than the monoclinic distortion. Although the materials show the transition of the structure to a spinel structure with cycling, the resulting materials show an improved capacity, rate capability, and cycling stability, compared to non-substituted $LiMnO_2$.

Meanwhile, it was seen that the crystal structure of the material was stabilized by substituting anions (F, S) for O in $LiMn_2O_4$ [Park et al., 2000, 2001, 2002; Amatucci et al., 2001; Sun et al., 2002] and $LiNiO_2$ [Park et al., 2002]. Kubo et al. and Naghash et al. reported that the substitution of O in $LiNiO_2$ with by F resulted in the significant improvement of the $LiNiO_2$ cycleability [Naghash et al., 2001]. Amatucci et al. [2001] observed that the Al and F co-doped-$LiAl_xMn_{2-x}O_{4-z}F_z$ was very effective in stabilizing the crystal structure, leading to the improvement of electrochemical behavior with maintaining the manganese average oxidation state. A similar result was also reported by Sun et al. [2002]. They revealed that $LiAl_{0.18}Mn_{1.82}O_{3.97}S_{0.03}$ prepared by substituting S for O in $LiAl_{0.18}Mn_{1.82}O_4$ showed an excellent cycleability, retaining 97% of the initial capacity at 50 °C. Park et al. [2000] also reported that the retention rate of $LiNiS_yO_{2-y}$ electrode was greatly improved than that of undoped-$LiNiO_2$. From the above observation, it was experimentally demonstrated that the spinel $LiMn_2O_4$ and layered $LiNiO_2$ doped with S or F show a significant improvement of the capacity fading.

In this work, we synthesized $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) using a sol-gel method. We observed a serious capacity fading from layered $Li_{0.7}[Li_{1/6}Mn_{5/6}]O_2$ in our previous work [Park et al., 2002]. The partial substitution of Ni and S for Mn and O in $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ was studied to develop a high performance cathode material for lithium batteries. The effect of the cation and anion doping on the electrochemical performance of the layered lithium manganese oxide material was investigated by characterizing the structure and electrochemical properties of the prepared cathode materials.

EXPERIMENT

$Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ precursor was synthesized by using a sol-gel method as previously reported [Sun et al., 2002; Park et al., 2004]. Sodium acetate (CH_3CO_2Na, Aldrich), lithium acetate ($Li(CH_3COO)\cdot 2H_2O$), nickel acetate ($Ni(CH_3COO)_2\cdot 4H_2O$), and manganese acetate ($Mn(CH_3COO)\cdot 4H_2O$) were employed as starting materials for the synthesis of $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ powders. Stoichiometric amounts of the sodium, lithium, and nickel acetate salts were dissolved in DI water with a cationic ratio of Na : Li : Li : Mn=0.7 : 1/12 : 1/12 : 5/6. The dissolved solution was added drop by drop into continuously agitated aqueous adipic acid. The molar ratio of the chelating agent (adipic acid) to total metal ions was fixed at unity. The prepared solution was evaporated at 70-80 °C for 5 h until a transparent sol was obtained. As water evaporated further, the sol turned into a viscous transparent gel. The resulting gel precursors

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were heated with a ramping rate of 1 °C/min and decomposed at 450 °C for 10 h in air to eliminate organic components. Thus obtained powders were calcined at the temperature range of 700 °C in a flow of air for 10 hrs. After the calcination process, the powders were suddenly quenched in liquid N_2. For the preparation of $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) precursors, the some processes were employed, except that the prepared viscous transparent gel precursors were mixed with a stoichiometric amount of sulfur powders to get oxysulfide $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) compositions.

The prepared precursor powders (5 g) were introduced into a mixed solution of hexanol (150 ml) and lithium bromide (LiBr; 55 g). The ion exchange of Li for Na in $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ was carried out at 160 °C for 3 hrs in a batch reactor equipped with a reflux condenser to prepare $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$. After the reaction, the solution was filtered using an aspirator under vacuum and the remaining powders were washed with methyl alcohol. The washed powders were dried at 180 °C for 10 hrs in a vacuum oven.

The structure of the prepared powders was characterized by powder X-ray diffraction (XRD, D/Max-3A, Rigaku) measurements with a Cu-Kα radiation target. The electrochemical characterization was carried out using CR2032 coin-type cells. The test cells were assembled in the following method: the cathode was fabricated with an accurately weighed active material (20 mg) and conductive binder (13 mg). It was pressed on 25 mm^2 stainless steel mesh used as the current collector at 300 kg/cm^2 and dried at 200 °C for 5 hrs in an oven. This cell was composed of a cathode and a lithium metal anode (Cyprus Foote Mineral Co.) separated by a porous polypropylene film separator (Celgard 3401). The electrolyte used was a mixed solution of 1 M $LiPF_6$-ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 2 by volume). The cells were assembled in an argon-filled dry box and tested at room temperature. The cell was charged and discharged at a current density of 0.8 mA/cm^2 in the voltage range of 2.0-4.6 V (vs. Li/Li^+).

RESULTS AND DISCUSSION

1. Structural Characterization

Figs. 1(a)-(d) show the XRD patterns of $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$, $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$ powders, respectively, synthesized at 700 °C by using adipic acid. The synthesized materials are considered to have a symmetric P3 structure partially mingled with the P2 phase. A main peak is observed at 2θ=16°, which results from Na phase. Two peaks appear at 2θ=36° and 46°, respectively. Other peaks developed at 2θ=54°, 58°, 66°, and 67°, which are not observed from the P2 structures, are also the characteristic XRD peaks of the P3 structure. The asterisks in the spectrum (a) are the characteristic peaks of the P2 structure. Therefore, it is considered that $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) are an intermediate material transforming from the P3 to the P2 structure. Similar results were observed by the previous experimental work [Park et al., 2002, 2004]. Paulsen et al. [2000] synthesized $Na_{0.89}[Ni_{9.44}Mn_{9.556}]O_2$ and reported that its structure is the P3 structure mingled with the P2 structure. The XRD spectra of S-doped samples (Fig. 1(b)-(d)) are similar to those of $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$. However, the peak at 2θ=62° for $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3), which is not observed from the undoped sample, is the characteristic XRD peak of the P2 structure. This means that the S-doped samples include the P2 structure more than the undoped sample. It seems that the S doping aids the formation of P2 structure at low temperature, although the mechanism is not clear at present.

Shown in Fig. 2(a)-(d) are the XRD patterns of $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$ powder prepared by ion exchange of $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3), respectively. As-prepared samples show the typical rhombohedral O3 layered structure. A perfect ion-exchange is accomplished for all the samples without the formation of impurities. The XRD patterns of the samples are similar to those of $Li(Mn_{1-y}Co_y)O_2$ synthesized by Bruce et al. [1999]. In the case of O3 structure, the main peaks must be observed at 2θ=8°, 36°, and 44° for (003), (101), and (104), respectively. It is also observed that the peak was split with (006) and (101) at 2θ=37°, and with (018) and (110) at 2θ=64° for the O3 structure. It was reported that $LiNiO_2$ having the O3

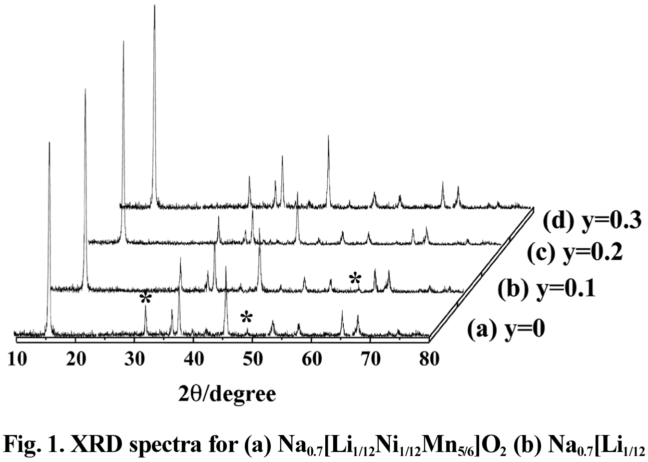

Fig. 1. XRD spectra for (a) $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ (b) $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, (c) $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and (d) $Na_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$ powders synthesized at 700 °C using adipic acid.

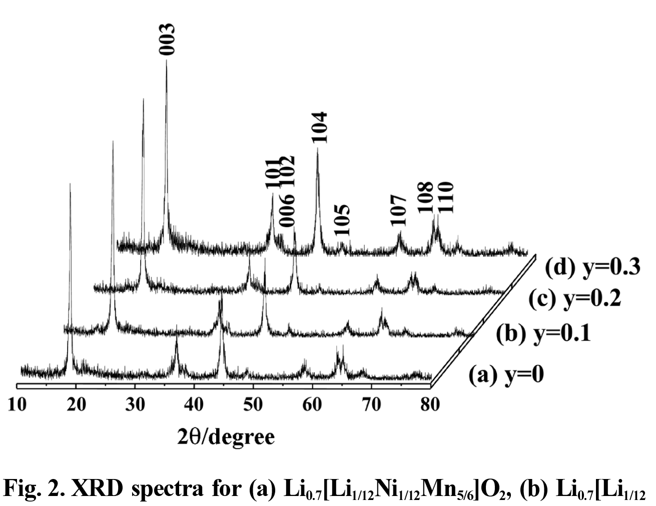

Fig. 2. XRD spectra for (a) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$, (b) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, (c) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and (d) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$ prepared by ion exchange of sodium manganese bronzes.

Table 1. Lattice parameters and discharge capacities for $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3)

Samples	Lattice parameters		Initial capacity (mAh/g)	Capacity after 30 cycles (mAh/g)	Capacity fading rate (%/cycle)
	a (Å)	c (Å)			
$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$	2.91	2.99	238	214	0.34
$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$	2.89	14.95	230	216	0.21
$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$	2.90	14.93	224	216	0.12
$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$	2.88	14.96	226	209	0.25

rhombohedral structure produces good electrochemical property when the intensity ratio of (003)/(104) peaks is higher than 1.2 [Ohuzuku et al., 1993] and that of (006) and (101) peaks is lower than 1.0 [Nitta et al., 1995]. The clear splits of (006) and (101) peaks and (108) and (110) peaks also affect the electrochemical properties [Park et al., 2002; Sung et al., 1999]. For our prepared samples, the intensity ratio of (003)/(104) peaks of the as-prepared samples is higher than 1.2, and (006) and (102) peaks and (108) and (110) peaks were clearly split. It is believed that our prepared samples might show an improved electrochemical property. Lattice parameters, a and c, were measured by using the Rietveld method and are listed in Table 1. The c/a ratios of $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]$ $O_{1.7}S_{0.3}$ are 5.15, 5.17, 5.15, and 5.19, respectively. The c/a ratios of the prepared samples are higher than those of the spinel structure (the c/a ratio of the spinel structure: 4.9). This means that our prepared samples have the O3 structure without the spinel structure. According to the literature [Bruce et al., 1999; Armstrong et al., 1998, 1999], the c/a ratio of the layered is higher than that of the spinel structure (4.9).

Figs. 3(a)-(d) show the SEM images for $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and $Li_{0.7}[Li_{1/12}Ni_{1/12}\text{-}Mn_{5/6}]O_{1.7}S_{0.3}$ powders, respectively. The SEM pictures show that the samples are all the nanometer-sized powders. It is thought that the nanometer-sized particles afford the high surface area necessary for Li ion reaction and diffusion lengths. Therefore, the $LiMnO_2$ materials prepared at low temperature may show much better capacities with a good rate capability. For $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) powders, it is interesting to see the agglomeration of the particles at a higher S content of 0.3. It seems that the partial substituted S for O in $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ might have a catalytic activity in the crystallization of the material. A similar observation was taken from S-doped $LiNiO_2$ [Park et al., 2002] and $LiMn_2O_4$ [Sun et al., 1998, 1999]. However, further experimental evidence is necessary to clarify the agglomeration of the particles at higher S contents.

2. Electrochemical Characterization

Figs. 4(a) and (b) show the electrochemical behaviors for $Li/Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, respectively. The initial discharge curve shapes of the materials are very similar to those of the layered structure. However, it is seen that the structure of the materials begins to transfer from layered to spinel struc-

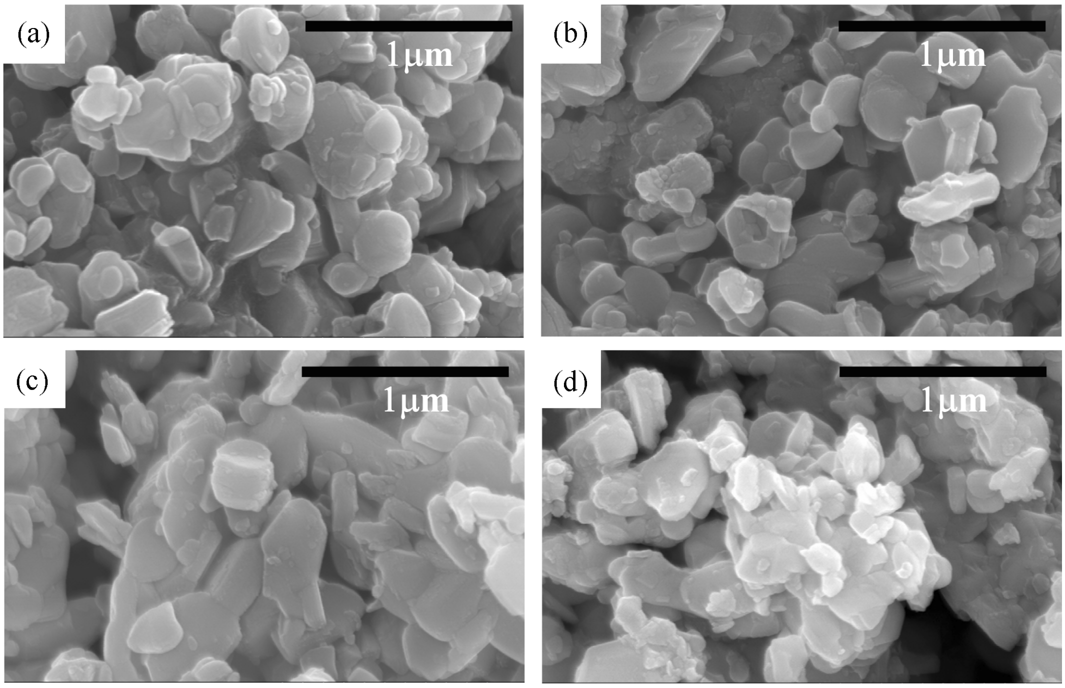

Fig. 3. SEM images for (a) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$, (b) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, (c) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and (d) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$ powders.

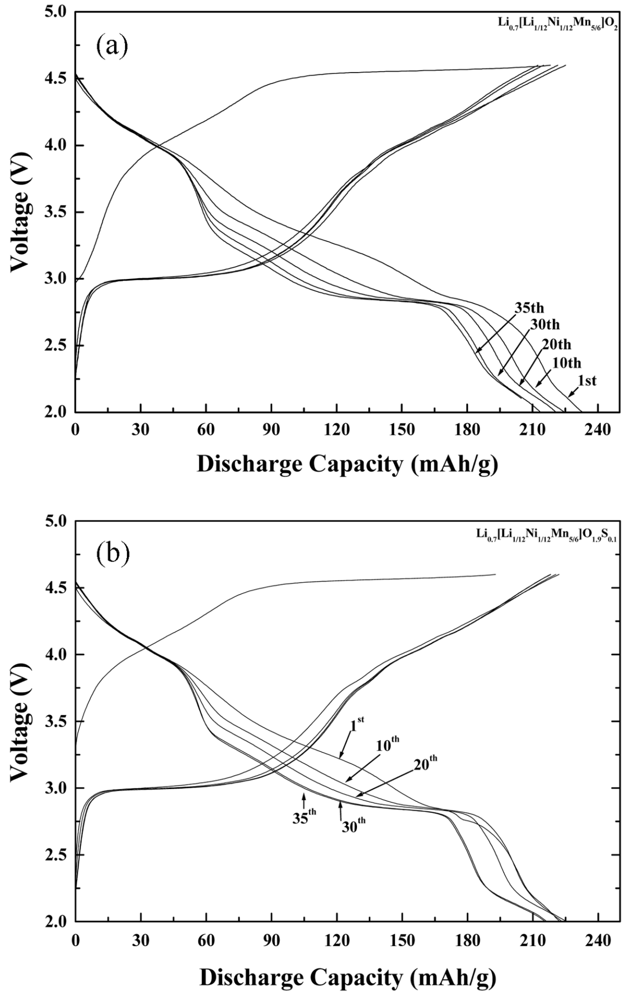

Fig. 4. Charge-discharge curves for (a) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$, (b) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$.

tures with the increase of the cycle number. The capacity fading is observed on the 3 voltage region for the Li/$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ cell. The discharge capacity fading was similarly observed by Bruce [Bruce et al., 1999]. They reported that the $LiMnO_2$ layered structure transits from layered to spinel structures with cycling. Although the capacity fading is observed, the Li/$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ cell shows a high initial discharge capacity due to the formation of nanodomains in the particle. The synthesis of the nanostructure particles affords the formation of the high surface area, necessary for the Li ion reaction and diffusion length. Ammudsen et al. [1996, 2001] reported that the materials prepared at low temperature might show much better capacity and rate capability. This is often due to the short diffusion length of Li ion in the materials, which typically have lower crystallinity and higher surface area. If the diffusion lengths are short, then the lithium ions may be easily inserted into and extracted from their sites or defects that would not be accessible in the crystalline materials, contributing to the large capacity. On the other hand, such the materials often have low volumetric densities, diminishing the energy density of the cathode. Furthermore, the large surface areas could speed up unwanted reactions at the interface between electrolyte and cathode, leading to a poor safety and cycling stability.

Our prepared samples produce the high discharge capacities at the initial cycle numbers with a relative low capacity fading. The discharge capacity at 3 V region slightly fades for $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ as the cycle number increases.

The capacity fading at 3 V region is smaller for $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) than for $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$. This means that the S-doping is proper to suppress the capacity fading of $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ electrode with maintaining high initial discharge capacity. Some researchers have also reported that the cycle life of the lithium ion batteries can be enhanced by substituting anion elements for O site [Park et al., 2000, 2001, 2002; Amatucci et al., 2001; Sun et al., 2002]. Sun et al. experimentally observed the increased discharge capacity and cycle life of the $LiMn_2O_4$ spinel structure by substituting S for O in the structure [Sun et al., 2002]. In the previous experiment work, we also found that the capacity fading could be suppressed by substituting S for O in $LiNiO_2$ [Park et al., 2002]. In this work, the electrochemical properties of the undoped $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ were compared with those of $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3). Fig. 4(b) shows the electrochemical behavior of $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$. The charge/discharge curve shape and the discharge capacity of all the S-doped samples were almost same, regardless of the amount of the S content. The electrochemical behavior of $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$ is very similar to that of $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$. The discharge curve shape at the initial cycle is almost equal to that of the layered structure. However, it is seen that the structure of the electrodes begins to transfer from layered to spinel structures with the increase of the cycle number. Although, an apparently different point in the electrochemical behaviors of $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$ is not observed that the capacity fading of the S doped $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$ is lower than that of the undoped $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$.

In the layered structure, cation mixing of Li and transition metal ion occurs due to the transport of transition metal ions from transition metal site into Li ion site during the charge process. This causes a deterioration of the electrochemical properties of the cathode materials. At present, we speculate that the capacity fading of the S-doped samples diminishes due to the formation of a more flexible structure by the S-doping. We observed a similar result from the S-doped $LiNiO_2$ [Park et al., 2002; Amatucci et al., 2001; Sun et al., 2002] and $LiMn_2O_4$ [Park et al., 2000, 2001; Naghash et al., 2001]. The partial substitution of oxygen with sulfur for the materials might create a more flexible structure because the electronegativity of sulfur is lower than that of oxygen. The formation of the flexible structure prevents the disintegration of the material structure by the elongation between layers during the intercalation/deintercalation of the lithium ions in the layered framework. Goodenough [Goodenough et al., 1959] also reported that the electrochemical properties of $Li_xTi_2S_4$ are superior to those of $Li_xTi_2O_4$. It is reasonable to assume that the relatively large size and polarizability of sulfur ion makes it easy for lithium ions to transport in the oxide structure, which reduces the structural strains of the materials formed in the process of Li ion insertion. The S-doped $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]$ $O_{1.9}S_{0.1}$ delivers an initial discharge capacity of 230 mAh/g with a high retention rate of 94% of the initial capacity after 30 cycles at a C/3 rate.

Shown in Fig. 5 are the discharge capacities for Li/ $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) cells cycled

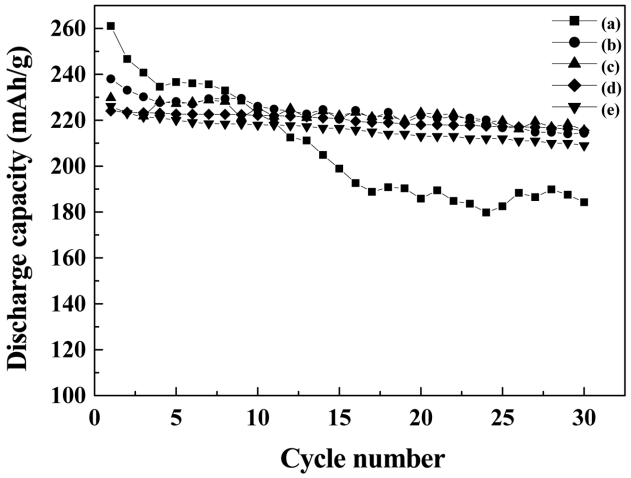

Fig. 5. Plots of specific discharge capacity versus cyclic number for (a) $Li_{0.7}[Li_{1/6}Mn_{5/6}]O_2$, (b) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$, (c) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, (d) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and (e) $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$ powders.

between 2.0 and 4.6 V at room temperature. At the first cycle, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]\ O_{1.7}S_{0.3}$ deliver the discharge capacities of 238, 230, 224, and 226 mAh/g, respectively, and maintain relatively higher discharge capacities of 214, 216, 216, and 209 mAh/g even after 30 cycles. The capacity fading rates are 0.34, 0.21, 0.12, and 0.25%/cycle for $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$, respectively. In order to clearly see the enhancement of the electrochemical properties due to Ni and S substitution, the discharge capacity of Li/$Li_{0.7}[Li_{1/6}Mn_{5/6}]O_2$ cell was measured and depicted in Fig. 5(a). $Li_{0.7}[Li_{1/6}Mn_{5/6}]O_2$ exhibits a serious capacity fading as reported in our previous work [Park et al., 2004]. The discharge capacity of $Li_{0.7}[Li_{1/6}Mn_{5/6}]O_2$ is 261 mAh/g at the 1st cycle, but delivers 184 mAh/g after 30 cycles (the fading rate: 0.98%/cycle). From the comparison of the discharge capacities of Li/$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and Li/$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) cells with Li/$Li_{0.7}[Li_{1/6}Mn_{5/6}]O_2$, it is concluded that the substitution of Ni for Mn or S for O in $Li_{0.7}[Li_{1/6}Mn_{5/6}]O$ greatly suppresses the capacity fading and, especially, the S substitution is very effective to get a good cycleability although the initial discharge capacity of S-doped sample is a little bit lower than the undoped samples. This means that sulfur plays an improvement role in repressing the capacity fading.

CONCLUSION

$Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$ and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{2-y}S_y$ (y=0.1, 0.2, 0.3) powders were synthesized by using a sol-gel method. As-prepared samples show typical rhombohedral O3 layered structure. All the samples show the formation of nanometer-sized powders. $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_2$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.9}S_{0.1}$, $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.8}S_{0.2}$, and $Li_{0.7}[Li_{1/12}Ni_{1/12}Mn_{5/6}]O_{1.7}S_{0.3}$ delivered the initial discharge capacities of 238, 230, 224, and 226 mAh/g with their retention rates of 0.34, 0.21, 0.12, and 0.25%/cycle, respectively. The nanostructure of the synthesized powders seems to result in the high initial discharge capacity as well as in the suppression of the discharge capacity fading by providing high surface area needed for Li ion reaction. The S-doped samples significantly diminished the discharge capacity fading. It was speculated that lower electronegativity of sulfur might form a more flexible structure, resulting in preventing the disintegration of the structure by the elongation between layers during intercalation/deintercalation of lithium ions during the charge-discharge cycles. It was seen that sulfur plays an important role in the excellent electrochemical behavior of the lithium manganese oxides.

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