The Effects of Sulfur Doping on the Performance of O$_{1.7}$Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$O$_2$ Powder

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Abstract—Li$_3$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]O$_2$ and Li$_3$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]O$_2$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 transformed from layered to spinel structures with cycling. At the first cycle, Li$_3$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]O$_2$ and Li$_3$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]O$_2$S$_y$O$_{0.3}$S$_{0.3}$ and Li$_3$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]O$_2$S$_{0.1}$ delivered the discharge capacities of 238, 220, 224, and 226 mAh/g, respectively, with their capacity fading rates of 0.34, 0.21, 0.12, 0.2% cycle, respectively. The partial substitu tions of Ni and S for Mn and O in Li$_3$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]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 and for compact lightweight batteries with high energy and power capability, 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 Li$_{0.7}$Mn$_{1.2}$O$_{1.9}$S$_{0.3}$ prepared by substituting S for O in Li$_{0.7}$Mn$_{1.2}$O$_{1.9}$ showed an excellent cyclability, retaining 97% of the initial capacity at 50°C. Park et al. [2000] also reported that the retention rate of LiNiS$_{0.18}$O$_{1.82}$ electrode was greatly improved than that of undoped-LiNiO$_2$. From the above observation, it was experimentally demonstrated that the spinel LiMn$_2$O$_4$ and layered LiNiO$_2$ doped with S or F show a significant improvement of the capacity fading.

In this work, we synthesized Li$_3$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]O$_2$ and Li$_3$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]O$_2$S$_y$ (y=0.1, 0.2, 0.3) using a sol-gel method. We observed a serious capacity fading from layered Li$_3$[Li$_{0.7}$Mn$_{0.3}$]O$_2$ in our previous work [Park et al., 2002]. The partial substitution of Ni and S for Mn and O in Li$_3$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]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$_{0.5}$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]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$_3$CO$_2$Na, Aklith), lithium acetate (Li(CH$_3$COO)$_2$)·2H$_2$O, nickel acetate (Ni(CH$_3$COO)$_2$·4H$_2$O), and manganese acetate (Mn(CH$_3$COO)$_2$·4H$_2$O) were employed as starting materials for the synthesis of Na$_{0.5}$[Li$_{0.7}$Ni$_{0.3}$Mn$_{0.3}$]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 : 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 precipitated 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
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 h. After the calcination process, the powders were suddenly quenched in liquid N2. For the preparation of Na[Li1/12Ni9/12Mn1/12]O2 (y=0.1, 0.2, 0.3) precursors, the same processes were employed, except that the prepared viscous transparent gel precursors were mixed with a stoichiometric amount of sulfur powder to get oxychloride Na[Li1/12Ni9/12Mn1/12]O2S (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[Li1/12Ni9/12Mn1/12]O2 was carried out at 160°C for 3 h in a batch reactor equipped with a reflux condenser to prepare Li[Li1/12Ni9/12Mn1/12]O2. 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 h 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 CR2025 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 mm² stainless steel mesh used as the current collector at 300 kg/cm² and dried at 200°C for 5 h 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 LiPF6, 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/cm² in the voltage range of 2.0-4.6 V (vs. Li/Li+).

RESULTS AND DISCUSSION

1. Structural Characterization

![Fig. 1. XRD spectra for (a) Na[Li1/12Ni9/12Mn1/12]O2 (b) Na[Li1/12Ni9/12Mn1/12]O2S0.3 (c) Na[Li1/12Ni9/12Mn1/12]O2S0.2 and (d) Na[Li1/12Ni9/12Mn1/12]O2S0.1 powders synthesized at 700°C using adipic acid.](image1)

![Fig. 2. XRD spectra for (a) Li[Li1/12Ni9/12Mn1/12]O2 (b) Li[Li1/12Ni9/12Mn1/12]O2S0.3 (c) Li[Li1/12Ni9/12Mn1/12]O2S0.2 and (d) Li[Li1/12Ni9/12Mn1/12]O2S0.1 prepared by ion exchange of sodium manganese bronzes.](image2)
rhombohedral structure produces good electrochemical property when the intensity ratio of (003)/(104) peaks is higher than 1.2 [Ohtuka 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 \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \), \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \), \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \), and \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \) 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 \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \), \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \), \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \), and \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \) 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 LiMnO2 materials prepared at low temperature may show much better capacities with a good rate capability. For \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{y} (y = 0.1, 0.2, 0.3) \) 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 \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \) might have a catalytic activity in the crystallization of the material. A similar observation was taken from S-doped LiNO3, [Park et al., 2002] and LiMnO2 [Sun et al., 1998, 1999]. However, further experimental evidence is necessary to clarify the agglomeration of the particles at higher S contents.

### Table 1. Lattice parameters and discharge capacities for \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \) and \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \) (y = 0.1, 0.2, 0.3)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lattice parameters ( a (\text{Å}) )</th>
<th>( c (\text{Å}) )</th>
<th>Initial capacity ( \text{mAh/g} )</th>
<th>Capacity after 30 cycles ( \text{mAh/g} )</th>
<th>Capacity fading rate ( % / \text{cycle} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}<em>{0.7} \left[ \text{Li}</em>{1/12} \text{Ni}<em>{1/12} \text{Mn}</em>{5/6} \right] \text{O}_{2} )</td>
<td>2.91</td>
<td>2.99</td>
<td>238</td>
<td>214</td>
<td>0.34</td>
</tr>
<tr>
<td>( \text{Li}<em>{0.7} \left[ \text{Li}</em>{1/12} \text{Ni}<em>{1/12} \text{Mn}</em>{5/6} \right] \text{O}<em>{2} \text{S}</em>{1/12} )</td>
<td>2.89</td>
<td>14.95</td>
<td>230</td>
<td>216</td>
<td>0.21</td>
</tr>
<tr>
<td>( \text{Li}<em>{0.7} \left[ \text{Li}</em>{1/12} \text{Ni}<em>{1/12} \text{Mn}</em>{5/6} \right] \text{O}<em>{2} \text{S}</em>{1/12} )</td>
<td>2.90</td>
<td>14.93</td>
<td>224</td>
<td>216</td>
<td>0.12</td>
</tr>
<tr>
<td>( \text{Li}<em>{0.7} \left[ \text{Li}</em>{1/12} \text{Ni}<em>{1/12} \text{Mn}</em>{5/6} \right] \text{O}<em>{2} \text{S}</em>{1/12} )</td>
<td>2.88</td>
<td>14.96</td>
<td>226</td>
<td>209</td>
<td>0.25</td>
</tr>
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</table>

Figs. 4(a) and (b) show the electrochemical behaviors for \( \text{Li}_{1/12} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \) and \( \text{Li}_{1/12} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \), 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 structure. 

Fig. 3. SEM images for (a) \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \), (b) \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \), (c) \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \), and (d) \( \text{Li}_{0.7} \left[ \text{Li}_{1/12} \text{Ni}_{1/12} \text{Mn}_{5/6} \right] \text{O}_{2} \text{S}_{1/12} \) powders.

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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_{1/12}Ni_{5/6}Mn_{5/6}O_2 as the cycle number increases.

The capacity fading at 3 V region is smaller for Li_{1/12}Ni_{5/6}Mn_{5/6}O_2S_y (y=0.1, 0.2, 0.3) than for Li_{1/12}Ni_{5/6}Mn_{5/6}O_2. This means that the S-doping is proper to suppress the capacity fading of Li_{1/12}Ni_{5/6}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; Amatucci et al., 2001; Sun et al., 2002]. Sun et al. experimentally observed the increased discharge capacity and cycle life of the LiMnO_2 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_{1/12}Ni_{5/6}Mn_{5/6}O_2 were compared with those of Li_{1/12}Ni_{5/6}Mn_{5/6}O_2S_y (y=0.1, 0.2, 0.3). Fig. 4(b) shows the electrochemical behavior of Li_{1/12}Ni_{5/6}Mn_{5/6}O_2S_y. 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_{1/12}Ni_{5/6}Mn_{5/6}O_2S_y is very similar to that of Li_{1/12}Ni_{5/6}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 properties of Li_{1/12}Ni_{5/6}Mn_{5/6}O_2 and Li_{1/12}Ni_{5/6}Mn_{5/6}O_2S_y is not observed that the capacity fading of the S-doped Li_{1/12}Ni_{5/6}Mn_{5/6}O_2S_y is lower than that of the undoped Li_{1/12}Ni_{5/6}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 LiMnO_2 [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 doration between layers during the intercalation/deintercalation of the lithium ions in the layered framework. Goodenough [Goodenough et al., 1999] also reported that the electrochemical properties of LiTiS_x are superior to those of LiTiO_2. 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_{1/12}Ni_{5/6}Mn_{5/6}O_2 delivers an initial discharge capacity of 230 mAh/g with a high retention rate of 94% of the initial capacity after 50 cycles at a C/3 rate.

Shown in Fig. 5 are the discharge capacities for Li_{1/12}Ni_{5/6}Mn_{5/6}O_2 and Li_{1/12}Ni_{5/6}Mn_{5/6}O_2S_y (y=0.1, 0.2, 0.3) cells cycled.
between 2.0 and 4.6 V at room temperature. At the first cycle, Li$_{1-x}$Ni$_x$Mn$_2$O$_4$, Li$_{1-y}$Ni$_y$Mn$_2$O$_4$, S$_{0.0}$, and Li$_{1-y}$Ni$_2$Mn$_3$O$_4$S$_{0.2}$ deliver the discharge capacities of 238, 230, 224, and 226 m Ah g$^{-1}$, respectively, and maintain relatively higher discharge capacities of 214, 216, 216, and 209 m Ah g$^{-1}$ even after 30 cycles. The capacity fading rates are 0.34, 0.21, 0.12, and 0.25%/cycle for Li$_{1-x}$Ni$_x$Mn$_2$O$_4$, Li$_{1-y}$Ni$_y$Mn$_3$O$_4$, Li$_{1-y}$Ni$_2$Mn$_3$O$_4$, and Li$_{1-y}$Ni$_2$Mn$_3$O$_4$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$_{1-x}$Ni$_x$Mn$_2$O$_4$ cell was measured and depicted in Fig. 5(a). Li$_{1-x}$Ni$_x$Mn$_2$O$_4$ exhibits a serious capacity fading as reported in our previous work [Park et al., 2004]. The discharge capacity of Li$_{1-x}$Ni$_x$Mn$_2$O$_4$ is 261 m Ah g$^{-1}$ at the 1st cycle, but delivers 184 m Ah g$^{-1}$ after 30 cycles (the fading rate: 0.97%/cycle). From the comparison of the discharge capacities of Li$_{1-x}$Ni$_x$Mn$_2$O$_4$, Li$_{1-y}$Ni$_2$Mn$_3$O$_4$S$_{0.3}$, and Li$_{1-y}$Ni$_2$Mn$_3$O$_4$S$_{0.3}$, it can be concluded that the substitution of Ni for Mn or S for O in Li$_{1-x}$Ni$_x$Mn$_2$O$_4$ greatly suppresses the capacity fading, and especially, the S substitution is very effective to get a good cyclability 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$_{1-x}$Ni$_x$Mn$_2$O$_4$ and Li$_{1-y}$Ni$_2$Mn$_3$O$_4$S$_{0.3}$ ($y=0.1$, $0.2$, $0.3$) powders were synthesized by using a sol-gel method. As-prepared samples showed typical rhombohedral O3 layered structure. All the samples show the formation of nanometer-sized powders. Li$_{1-x}$Ni$_x$Mn$_2$O$_4$, Li$_{1-y}$Ni$_2$Mn$_3$O$_4$S$_{0.3}$, Li$_{1-y}$Ni$_2$Mn$_3$O$_4$S$_{0.2}$, and Li$_{1-y}$Ni$_2$Mn$_3$O$_4$S$_{0.3}$ delivered the initial discharge capacities of 238, 230, 224, and 226 m Ah g$^{-1}$ with their retention rates of 0.34, 0.21, 0.12, and 0.25%/cycle, respectively. The nanostructure of Li$_{1-x}$Ni$_x$Mn$_2$O$_4$ 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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