Structural and electrochemical study of cobalt doped LiMn$_2$O$_4$ spinels

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Abstract

Lithium transition-metal oxides Li(Mn$_{2-x}$CO$_x$)$_2$O$_4$ (0≤x≤0.5) have been synthesized by a solid state reaction. The phase transition in the spinel LiMn$_2$O$_4$ was investigated using powder synchrotron radiation diffraction. A transition from cubic (Fd$ar{3}$m) to orthorhombic (Fddd) was observed around $T$=220 K. Increasing the average valence of Mn, by doping with Co ion in the [Mn$_2$O$_4$] framework, reduces the concentration of the Mn$^{3+}$-ions, suppress as the Jahn-Teller distortion, and retains the cubic phase at low temperature. The capacity loss observed in the undoped Li/LiMn$_2$O$_4$ cell is about 25% after 20 cycles, whereas that for the x=0.1 and x=0.2 doped spinels it is about 0.5% and 1%, respectively. The cycle performance retention of the Li(Mn$_{2-x}$CO$_x$)$_2$O$_4$ (0.1≤x≤0.5) electrode is attributed to the chemical substitution of Co at the Mn sites in the spinel structure. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The basic electrochemistry of secondary battery materials involves only the transfer of Lithium ions between the two insertion electrodes. This ion transfer principle was proposed by Armand [1] who named them rocking chair batteries. Interest in lithium transition metal oxides as rechargeable cathodes in secondary lithium batteries has increased exponentially since Goodenough proposed LiCoO$_2$ for this application in 1980 [2]. Sony first commercialized lithium ion batteries in 1990, using a lithium carbon anode and a LiCoO$_2$ cathode [3]. The high cost of LiCoO$_2$ cathodes has prompted the design and synthesis of alternate insertion hosts. Lithium manganese oxides were found to be superior in terms of specific energy, low cost and environmental reasons. Unfortunately, these materials exhibit significant capacity fading during cycling. In addition to the instability of organic-based electrolyte, the unstable two phase mixture in the high-voltage region, the Jahn-Teller effect in deeply discharged LiMn$_2$O$_4$ electrodes and the non-homogeneous local structure of LiMn$_2$O$_4$ are believed to contribute to the capacity loss [4,5].

LiMn$_2$O$_4$ shows cubic Fd$ar{3}$m symmetry at room temperature and decreasing the temperature causes a structural transition around 280 K due to the Jahn-
Teller distortion of the Mn$^{3+}$O$_6$ octahedra. Oikawa et al. [6] showed that the reflections of the low temperature phase in its neutron and X-ray diffraction patterns were indexed not on the basis of a tetragonal unit cell but roughly on an orthorhombic one (space group: Fd$ar{3}$m) with lattice parameters $a=8.2797(2)$, $b=8.2444(3)$ and $c=8.1981(2)$ Å.

The Jahn-Teller effect is a tetragonal distortion induced by the instability of unequally filled $e_g$ orbitals in a strictly octahedral geometry. Several research groups have investigated the properties of manganese-substituted spinels, Li(Mn,M)$_2$O$_4$ (M=Ti, Ge, Fe, Co, Zn), with the goal of maintaining electrochemical capacity over a large number of cycles without sacrificing initial reversible capacity and also the performance at low or high temperatures [7,8].

Doping the Mn sites with a lower valent cation is a possibility because it reduces the Mn$^{3+}$ content and stabilizes the cubic structure in the face of Mn$^{3+}$ Jahn-Teller distortion [9,10]. Guohua et al. [9] have shown that the substitution by M ions at the Mn site, Li(Mn,M)$_2$O$_4$ (M=Cr, Co and Ni), increased the number of Jahn-Teller Mn$^{3+}$ ions. Considering both cycle life and capacity density, LiCo$_{1/6}$Mn$_{11/6}$O$_4$ showed good cycle performance with an energy density of 370 W h kg$^{-1}$ at the 300th cycle. The improvement in cycling performance is attributed to stabilization in the spinel structure by doped cations.

Here we report on the synthesis and analysis of Li(Mn$_{2-x}$Co$_x$)$_2$O$_4$ (0≤x≤0.5). We also present our studies on the phase transition as a function of temperature in LiMn$_2$O$_4$ and LiMn$_{1.9}$Co$_{0.1}$O$_4$.

2. Experimental

Samples of the system Li(Mn$_{2-x}$Co$_x$)$_2$O$_4$ (0≤x≤0.5) were synthesized by a solid state reaction of Li$_2$CO$_3$, MnO$_2$ and Co$_3$O$_4$. Well ground mixtures of the starting materials were heated at 800 °C in air for 24 h, followed by two treatments each of 24 h at 800 °C with intermediate grindings. Powder X-ray diffraction analyses were carried out with a SCINTAG (X1) diffractometer (Cu Kα radiation, λ=1.5406 Å) at 40 keV and 30 mA. Data for Rietveld refinement were collected in the 2θ range 15–120° with a step size of 0.02° and a count time of 10 s per step. The GSAS program [11] was used for the Rietveld refinement in order to obtain the lattice parameter about the crystal structures (space group: Fd$ar{3}$m) of Li(Mn$_{2-x}$Co$_x$)$_2$O$_4$. A series of patterns was recorded with synchrotron radiation (λ=1.3271 Å) in a limited angular region at different temperatures. The Wiggler-A beamline of the Synchrotron Radiation Research Center (SRRC), Taiwan, has been designed for such experiments. A flat imaging plate (Fuji, 20×40 cm) was used as a 2D area detector, which collected diffraction data up to 80° in 2θ. The diffraction pattern was read out by using a MAC IPR420 off-line imaging plate scanner. The dynamic range is as high as 10⁸. In this study, the sample was cooled by an APD cryostat and the temperature was varied from 320 to 15 K.

The electrochemical characterization was performed using coin-type cells. The cathode was prepared by spreading a mixture of 85% LiMn$_2$O$_4$, 9% acetylene black used as conductive material and 6% PVDF (polyvinylidene fluoride) dissolved in 1-Methyl-2-Pyrolidinone (NMP) onto an aluminum foil. Cathode disks (1/2 in.) were punched from the sheet, with an average weight of 3 mg of active material. The cell consisted of a cathode and a lithium metal anode separated by a porous polyethylene film as a separator. The electrolyte used was 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in the volume ratio of 1 EC:2 DMC. The cell was assembled in an argon-filled dry box and tested at room temperature. The charge and discharge experiments were carried out using a Maccor battery cycling instrument. The cell was cycled at current density values between 0.3 and 3 mA cm$^{-2}$ in the 2.80–4.25 V range.

3. Results and discussion

The powder XRD patterns of Li(Mn$_{2-x}$Co$_x$)$_2$O$_4$ with x=0–0.5 are shown in Fig. 1. The Li(Mn$_{2-x}$Co$_x$)$_2$O$_4$ (0≤x≤0.5) samples are of single phase. Because the Co ion has a larger binding energy (1067 kJ mol$^{-1}$) in the CoO$_6$ octahedra than the Mn ion in the MnO$_6$ octahedra (946 kJ mol$^{-1}$) [9], so that we assume that the Co$^{3+}$ ions substitute the Mn sites homogeneously while retaining the Fd$ar{3}$m space group. The peaks in each XRD pattern can be indexed on the basis of a cubic unit cell. The perovskite cell
symmetry was identified by the observation of the reflections with the limiting condition on $hkl$: $h$, $k$, $l$ either all odd or all even, with the $F$ centering of the unit cell. The lattice constant $a$ and the cell volume $V$ decreased with the Co content as shown in the inset in Fig. 1, which is due to the smaller size of the substituting Co$^{3+}$ ion [0.545 Å for coordination number (C.N.)=6, in low crystal field] as compared to the larger Mn$^{3+}$ ions (0.645 Å for C.N.=6, in low crystal field) [12]. If Co$^{3+}$ substitutes into the Mn$^{4+}$ site (0.53 Å for C.N.=6, in low crystal field) [12], an increase in the lattice constant $a$ with increasing $x$ in Li(Mn$_{2-x}$Co$_x$)O$_4$ would be found. Therefore, based on our results, we confirm that the formula can thus be written as LiMn$_{1.4+}$Mn$_{1-x}$Co$_x$$_{3+}$O$_4$.

The low temperature structure of LiMn$_2$O$_4$ was investigated by powder synchrotron diffraction. The data were collected using an image plate from 300 to 15 K. Peak-broadening is clearly seen in the pattern at 220 K, especially for the peaks at high-angles. Fig. 2a
shows the diffraction patterns of LiMn$_2$O$_4$ in the 52–56$^\circ$ (2$\theta$) range at different temperatures from 300 to 25 K. With decreasing temperature, narrowing of the diffraction peaks is expected. However, the peaks become broader, as can be seen from the figure. The broad peak in doped compound are caused by structural disorder.

We have also investigated the Li(Mn$_{1.0}^{4+}$Mn$_{0.9}^{3+}$Co$_{0.1}^{3+}$)O$_4$ sample by powder synchrotron diffraction. The patterns show a cubic spinel structure from 300 down to 25 K without peak split or broadening, as shown in Fig. 2b. Fig. 2c shows the temperature variation of the full width at half maximum (FWHM) of the (440) reflection in LiMn$_2$O$_4$ and LiMn$_{1.9}$Co$_{0.1}$O$_4$. The FWHM of the latter composition is almost constant whereas it shows an increase in LiMn$_2$O$_4$ with decreasing temperature. In LiMn$_{1.9}$Co$_{0.1}$O$_4$, the Mn$^{3+}$ content decreases from 50% to 47%, and the change in the Mn$^{3+}$ distribution causes a change in the magnetic-ordering [13]. However, at low temperatures, the ordering of the distorted Mn$^{3+}$O$_6$ octahedra is quite small in LiMn$_{1.9}$Co$_{0.1}$O$_4$ as compared to the composition to LiMn$_2$O$_4$.

From the chemical formula LiMn$_{1-x}^{4+}$Mn$_{1-x}^{3+}$Co$_x^{3+}$O$_4$ ($0 \leq x \leq 0.5$), the theoretical capacities based on a one-electron charge–discharge reaction were calculated to be in the range 148–96 mA h/g. The initial discharge capacity of Li/Li(Mn$_{2-x}$Co$_x$)$_2$O$_4$ decreased with increasing Co substitution. The values for $x=0$, 0.1, 0.2, 0.3, 0.4, 0.4 are 120, 105, 103, 95, 92 and 85 mA h/g, respectively. Since the deintercalation of Li$^+$ from the spinel structure must be electrically compensated by oxidation of Mn$^{3+}$ to Mn$^{4+}$, this suggests that even for substituted spinel phases, only the amount of Mn$^{3+}$ contributes to the charge–discharge capacity. So the initial capacity of Li(LiMn$_{2-x}$Co$_x$)$_2$O$_4$ ($0 \leq x \leq 0.5$) is limited by the initial amount of Mn$^{3+}$ in the 16$d$ sites. Typical charge–discharge behaviors of Li/LiMn$_2$O$_4$ (LiMn$_{1.4}^{4+}$Mn$_{1.3}^{3+}$Co$_{0.3}^{3+}$O$_4$) and Li/LiMn$_{4}^{4+}$Mn$_{0.8}^{3+}$Co$_{0.2}^{3+}$O$_4$ at a constant current rate of $c/5$ are shown in Fig. 3. The cells were first charged to their rest voltage of 4.25 V. The removal of approximately 0.7–0.8 Li$^+$ from the structure occurs in two steps. Two peaks corresponding to the reversible two step process for extracting Li from spinel LiMn$_2$O$_4$ have been observed at 4.00 and 4.12 V vs. Li/Li$^+$. A similar observation is found in the literature [14,15]. During the initial cycle, the capacity loss mainly occurs at the higher voltage plateau, which may be due to the unstable two-phase structure existing during Li ion insertion–extraction into/from the spinel structure. Fig. 3 also shows the first cycle charge–discharge curve vs. lithium composition $z$ for Li/LiMn$_{1.4}^{4+}$Mn$_{0.8}^{3+}$Co$_{0.2}^{3+}$O$_4$. In the composition near $z=0.6$, an anomaly in the charge curve was observed. Probably a lithium ordering–disordering process occurs during the lithium intercalation–deintercalation across $z=0.6$ which causes a phase trans-
formation. By increasing the substitution of Co$^{3+}$ in Mn $16d$ sites, there is a decrease in the unstable two-phase region [5,14–16] and the curve is smooth similar to that of the Li/LiMn$_2$O$_4$.

The discharge capacity of the Li(Mn$_{2-x}$Co$_x$)O$_4$ compositions is shown in Fig. 4. This was obtained with the spinel cathode at a current of $c$/5 density(0.6 mA cm$^{-2}$). It is apparent that the discharge capacity of the doped compositions ($x=0.1–0.2$) is more stable than that of the LiMn$_2$O$_4$ spinel phase, and the capacity fading was slightly suppressed by increasing the Co content from 0.1 and 0.2. For example, the capacity loss observed with the undoped LiMn$_2$O$_4$ is about 25% after 20 cycles, whereas that for $x=0.1$ and $x=0.2$ doped spinel materials is about 0.5% and 1%, respectively. For Li(Mn$_{1.0}$Mn$_{0.9}$Co$_{0.1}$)O$_4$, the capacity of the cell maintained 98% of the initial capacity at the 25th cycle which was nearly the same as Li(Mn$_{1.0}$Mn$_{0.8}$Co$_{0.2}$)O$_4$ (cut-off voltage 4.25–2.8 V, current density=0.6 mA cm$^{-2}$). Therefore, the spinel structure becomes more tolerant to repeated charge–discharge cycles due to the doping of Co, what may be attributed to the reduction of Mn valence giving rise to the suppression of the Jahn-Teller distortion by Co doping.

4. Conclusions

We have synthesized undoped and doped spinels with the nominal compositions Li(Mn$_{2-x}$Co$_x$)O$_4$ with $0 \leq x \leq 0.5$. Reduction of the concentration of the Mn$^{3+}$-ions results in the suppression of the Jahn-Teller distortion in LiMn$_{1.2}$Co$_{0.1}$O$_4$ and retains the cubic phase at low temperature. Chemical substitution of
Co$^{3+}$ for Mn$^{3+}$ in LiMn$_2$O$_4$ improves cathodic properties and the efficiency in maintaining electrochemical capacity over a large number of cycles without sacrificing initial reversible capacity and also its performance at temperature below room temperature.

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