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Improved cyclic stability by octahedral Co^{3+} substitution in spinel lithium manganese oxide thin-film cathode for rechargeable microbattery

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ABSTRACT

Co-doped lithium manganese oxide ($LiCo_xMn_{2-x}O_4$) cathodes were prepared as thin films via a sol-gel process to investigate the effects of the octahedral Co substitution on electrochemical properties. X-ray diffraction and scanning electron microscopy results showed that the polycrystalline films ($x \leq 0.3$) were composed of phase-pure grains with the sizes distributed mainly in 100–200 nm range. The cubic lattice parameters of the spinel $LiCo_xMn_{2-x}O_4$ samples decreased gradually with increasing Co composition. X-ray photoelectron spectroscopy data indicated that cobalt ions in $LiCo_xMn_{2-x}O_4$ exist as Co^{3+} mostly. The electrochemical investigations of $LiCo_xMn_{2-x}O_4$ cathodes include cyclic voltammetry, cycling performance, charge-discharge profile, and rate capability in the 3.5–4.3 V potential range. The $x = 0.05$ cathode exhibited initial discharge capacity close to that of $LiMn_2O_4$ cathode and less capacity fading than $LiMn_2O_4$ after extended charge-discharge cycles (>200). The $x = 0.1$ cathode exhibited a reduction in initial discharge capacity by ~10% but the capacity was retained up to ~300 cycles. The improved capacity retention of $LiCo_xMn_{2-x}O_4$ cathodes is attributable to the improved structural stability by octahedral Co^{3+} substitution for suppressing Mn^{3+}-related Jahn-Teller distortion and cathode dissolution into electrolyte.

1. Introduction

Spinel $LiMn_2O_4$-based cathodes of rechargeable batteries have been under attention recently due to the advantages in operational safety, environmental benignancy, and production cost over layered $LiCoO_2$-based ones that have been commercialized as power supplies for portable electronic products (e.g., mobile phones and lap-top computers). Recent research efforts have been focused on enhancement in charge capacity and output power for speedy automobiles, heavy machines and large-scale energy-storage systems. The electrical energy stored in a battery is determined by its charge capacity and potential difference between cathode and anode, and is mainly affected by the cathode in lithium batteries. Thus, efficient lithium batteries must have cathodes with large Li^+ capacities along with electrolytes having chemical stability for fast charging and discharging.

Spinel $LiMn_2O_4$ has theoretical capacity of 148 Ah/kg and effective potential ~4.1 V (vs. Li/Li^+) [1], being capable of supplying a maximal energy density of 607 Wh/kg. Also, $LiMn_2O_4$-based cathodes have been reported to be efficient for high power output due to 3-dimensional (3-D) Li-ion diffusion paths in the spinel lattice compared to layered $LiCoO_2$-based (2-D) and olivine $LiFePO_4$-based (1-D) ones [1]. In spinel $LiMn_2O_4$, Li^+ ions occupy tetrahedral 8a sites, while Mn^{3+} and Mn^{4+} ions occupy octahedral 16d sites. Each tetrahedral Li^+ ion has four empty octahedral 16c sites as neighbors. Thus, the spinel lattice offers a 3-D network of Li^+ diffusion paths (8a → 16c) during charging (Li^+ extraction) and discharging (Li^+ insertion) processes [1,2]. However, $LiMn_2O_4$-based cathodes are still faced with unresolved issues for improving battery efficiency. During extended charge-discharge (C-D) cycles, the Li^+ distribution in the cathode gets non-uniform to be liable to a disproportionate reaction ($2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$) that leads to Mn^{2+} dissolution in the electrolyte [3,4]. The resultant mass loss of cathode leads to rapid capacity fading [3–6] in $LiMn_2O_4$-based cathodes. Also, the lattice distortion associated with Jahn-Teller (J-T) effect due to octahedral high-spin Mn^{3+} ions has been pointed out as a major factor for weakening cycling stability of the cathode [5,6]. However, Mn^{3+} ions are essential for charging process through oxidation near 4 V in $LiMn_2O_4$-based cathodes. Also, the Mn^{3+} ions may contribute to the electrical conductivity of the

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cathode through polaronic hopping of electrons between octahedral Mn^{3+} and Mn^{4+} ions [7]. Thus, a solution for improving cathodic capability of $LiMn_2O_4$ may exist in manipulating the quantity, location and spin state of the Mn^{3+} ions.

There have been numerous attempts for improving electrochemical performance of $LiMn_2O_4$-based cathodes by replacing some of Mn ions ($LiMn_{2-x}T_xO_4$) by foreign metal (T) ions where a number of elements were known to be effective such as Al [5,6], Cr [8,9], Co [10,11] and Ni [12,13]. Recently, improvements in discharge capacity and capacity retention capability were reported in Fe-doped $LiMn_2O_4$ cathodes with porous structure [14], although some of the Fe^{3+} ions are likely to occupy the tetrahedral sites in the spinel lattice [15], leading to a reduction in tetrahedral Li^+ density. In these works, however, the cathodes were fabricated by using powder-based composites that are coated by conductive particles and binder, which is likely to cause difficulty in analyzing the electrochemical characteristics of the active cathode material itself.

In this work, the effects of Co doping on structural and electrochemical properties of sol-gel-prepared $LiMn_2O_4$ thin-film cathodes were investigated. The advantage of studying thin-film cathodes lies in their purity that can facilitate the understanding of the intrinsic properties of the active materials and consequently the behavior of the powder-based electrodes. There have been a few reports on preparation and subsequent electrochemical investigations of pristine or metal-doped $LiMn_2O_4$ thin-film cathodes that were deposited on conducting substrates by magnetron sputtering [16], electrostatic spray deposition [17,18], pulsed laser deposition [19] and sol-gel [20–22] methods. The sol-gel method is known to have advantages of high film-deposition rate and easy control of the film morphology compared to other techniques.

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were performed for investigating the difference in crystal structure and ionic distribution between $LiCo_xMn_{2-x}O_4$ and pristine $LiMn_2O_4$ cathode. The electrochemical properties of the $LiCo_xMn_{2-x}O_4$ cathodes were investigated by measuring cyclic voltammetry (CV), C-D cycling performance and rate capability in comparison with those of $LiMn_2O_4$ cathode. The $LiCo_xMn_{2-x}O_4$ cathodes exhibited electrochemical properties with improved capacity retention and rate capability compared to pristine $LiMn_2O_4$ cathode.

2. Experimental

The present $LiCo_xMn_{2-x}O_4$ thin films were prepared by using a sol-gel method in which the precursor solution was prepared by dissolving manganese acetate tetrahydrate ($(CH_3COO)_2Mn{\cdot}4H_2O$), cobalt acetate tetrahydrate ($(CH_3COO)_2Co{\cdot}4H_2O$) and lithium acetate ($CH_3COOLi$) powders together in a mixed solutions of 2-methoxyethanol ($CH_3O(CH_2)_2OH$) and ethanolamine ($NH_2(CH_2)_2OH$) at 200 °C. Then, the sol was deposited on (111)-oriented Pt film that is used as a current collector. The Pt electrode deposited on multi-layered $Ti/SiO_2/Si$ substrates has thickness of ~150 nm.

The film deposition was performed by spin-coating the sol at 4000 rpm for 20 s followed by heating at 300 °C for 5 min. Once the gel formed, the deposition process was repeated several times to increase the film thickness. The gel was transformed into solid $LiCo_xMn_{2-x}O_4$ films by subsequent annealing treatments in air for 6 h at 700 °C. The structural properties of the films were characterized by XRD using Cu Kα radiation (wavelength = 0.15418 nm) in a grazing-incidence manner with fixed X-ray incidence angle of 4°. XPS measurements were performed using Al Kα radiation (photon energy = 1486.7 eV) in order to find preferred valence of Mn and Co ions in the spinel lattice.

In order to assess the cycling performance of the $LiCo_xMn_{2-x}O_4$ films, CV and C-D studies were conducted by fabricating beaker-type electrochemical half-cells with the configuration of $Li/LiCo_xMn_{2-x}O_4$. The cells were assembled in an argon-filled glove-box using Li-metal foil as a counter-and-reference electrode. The $LiCo_xMn_{2-x}O_4$ films with active area of about 1.0 cm^2 were used as working cathodes. The electrolyte for Li^+ conduction consisted of 1 M $LiPF_6$ dissolved in 1:1 vol% mixture of ethylene carbonate ($C_2H_4O_2CO$) and diethyl carbonate ($(C_2H_5O)_2CO$). The cells were electrochemically cycled in the 3.5–4.3 V potential range with a constant current density of 0.1 mA cm^{-2}, equivalent to ~10C rate. At all the C-D cut-off steps, the cell potential was potentiostated until the current decreased to 0.02 mA cm^{-2}.

3. Results and discussion

In Fig. 1, representative scanning electron microscopy (SEM) top-view images showing the grain size and surface morphology of the $LiCo_xMn_{2-x}O_4$ cathodes are displayed. The $LiCo_xMn_{2-x}O_4$ cathodes are seen to have surface morphology similar to each other: the grains developed well-defined edges with sizes distributed mainly in the 100–200 nm range. The thicknesses of the $LiCo_xMn_{2-x}O_4$ films were ~200 nm measured from the side-views of the SEM images as shown in the insets of Fig. 1.

The XRD patterns of the polycrystalline $LiCo_xMn_{2-x}O_4$ films are displayed in comparison with that of a pristine $LiMn_2O_4$ film in Fig. 2. The Co-doped films are seen to maintain the same crystal structure of $LiMn_2O_4$ (JCPDS 88-1030) at all Co compositions: the observed diffraction patterns for $LiCo_xMn_{2-x}O_4$ are well indexed based on a cubic spinel phase (space group $Fd\overline{3}m$) and exhibit no trace of any secondary phase. However, the diffraction peaks shift to higher angles with increasing Co composition (x) as indicated by a dotted straight line near the (440) peak. The cubic lattice parameter (a_0) of the $LiCo_xMn_{2-x}O_4$ films estimated from the XRD peak positions by usings a least-squares method is 0.821, 0.820 and 0.815 nm for x = 0.05, 0.1 and 0.3, respectively. With $a_0 = 0.822$ nm for the $LiMn_2O_4$ film, the lattice parameter decreases in a linear manner with increasing Co content. The lattice parameter of the x = 0.3 sample is smaller by 0.9% than that of the $LiMn_2O_4$ sample. The XRD analysis implies that Co and Mn mix properly to form a solid-solution $LiCo_xMn_{2-x}O_4$. Also, the absence of (220) peak near $2\theta = 31^\circ$ in the XRD patterns of $LiCo_xMn_{2-x}O_4$ indicates that the transition-metal ions seldom exist in the tetrahedral sites of the spinel lattice [12].

In Fig. 3(a), Mn 2*p*-electron binding-energy spectra of the $LiCo_xMn_{2-x}O_4$ (x = 0.1 and 0.3) cathodes obtained from the XPS measurements are compared with that of the $LiMn_2O_4$ cathode. The electron binding energies were calibrated by using the C 1*s* peak (254.8 eV) as a reference. The Mn $2p_{3/2}$ peak for the $LiMn_2O_4$ cathode is seen to be well-resolved into two contributions, Mn^{3+} and Mn^{4+}, at about the electron binding energy (BE) of 641 and 642 eV, respectively [23], as marked by arrows in Fig. 3(a). As the Co composition (x) increases, the strength of the Mn^{3+} peak is seen to be gradually reduced compared to that of the Mn^{4+} peak. In Fig. 3(b), the Co 2*p* spectra for the $LiCo_xMn_{2-x}O_4$ (x = 0.1 and 0.3) cathodes exhibit sharp spin-orbit peaks with BE near 780 eV ($2p_{3/2}$) and 795 eV ($2p_{1/2}$). The Co 2*p* spectra also exhibit a discrete satellite peak near BE = 790 eV. The result suggests that the Co ions mostly have a valence of +3 [24–26] and explains the decrease of Mn^{3+} strength in Fig. 3(a). Also, the observed decrease of the lattice parameter by Co doping can be explained by Co^{3+} occupation of the octahedral 16d sites: the ionic radius of octahedral Co^{3+} ion (0.0545 nm for low-spin and 0.061 nm for high-spin) is smaller than that of octahedral Mn^{3+} ion (0.058 nm for low-spin and 0.0645 nm for high-spin) [27].