Electrochemical Characteristics of LiMnO₂ for Lithium Secondary Battery

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Well-defined orthorhombic $LiMnO_2$ and $LiCo_{0.1}Mn_{0.9}O_2$ were synthesized by a solid-state reaction and quenching process. X-ray diffraction (XRD) results revealed that the as-synthesized powders showed an orthorhombic phase of a space group with Pmnm. The $Li/LiMnO_2$ and $Li/LiCo_{0.1}Mn_{0.9}O_2$ cells were constituted and cycled galvanostatically in the voltage range of 2.0-4.3 V vs. Li/Li^+ at a current density of 0.5 mA cm^{-2} at room temperature and 50 ℃, respectively. The results demonstrated that the highest specific capacity of $Li/LiMnO_2$ cells at room temperature and 50 ℃ was 95 and 155 mAh g^{-1}, respectively. As for $Li/LiCo_{0.1}Mn_{0.9}O_2$ cells, the highest specific capacity at room temperature and 50 ℃ was 160 and 250 mAh g^{-1}, respectively. It could be seen that the performance of $Li/LiCo_{0.1}Mn_{0.9}O_2$ cells was better than that of $Li/LiMnO_2$ cells.

Keywords : Orthorhombic, LiMnO₂, Quenching, Cathode material

1. INTRODUCTION

Since the commercialization of rechargeable lithium-ion batteries by Sony Energy Tech[1]. 14 years ago, they have been widely utilized as the power sources in a wide range of applications, such as mobile phones, laptop computers, cameras, electrical vehicles, and hybrid electrical vehicles. In the rechargeable lithium-ion batteries, cathode material is the key component, and mainly devoted to the performance of the batteries. Among the known cathode materials, the layered $LiCoO_2$ and $LiNiO_2$, spinel $LiMn_2O_4$, and elemental sulfur have been studied extensively[2-9]. $LiCoO_2$ has been nowadays utilized for commercial lithium-ion batteries. However, novel cathode material must be developed not only in relation to battery performance, but also in relation to safety and cost.

Orthorhombic $LiMnO_2$ (hereafter referred to as *o*-$LiMnO_2$) has attracted the extensive attention due to its low cost, nontoxic nature, and a high theoretical specific capacity (285 mAh g^{-1}). Layered $LiMnO_2$ has a rock salt structure where lithium and manganese cations occupy alternating zigzag layers of octahedral sites in a distorted cubic close-packed oxygen array. The layered MnO_2 framework provides two-dimensional interstitial spaces which allow easy extraction of lithium ions[10-12]. It was known that $LiMnO_2$ structure with an ideal layered arrangement of the lithium and manganese ions could be prepared from Li^+ ion-exchange from α-$NaMnO_2$[13]. Orthorhombic $LiMnO_2$ was revealed by Johnston and Keikes[14], and the detailed structural information was reported by Hoppe et al.[15]. Electrochemical properties of *o*-$LiMnO_2$ are mainly dependent on the synthetic processes including high temperature solid-state reaction method[16-18], hydrothermal synthetic route[19], the precipitation method[20,21], and the sol-gel method [22,23].

In addition, partial substitution of Mn by Cr, Al, Mg, Ti, Mo and Co has been verified to stabilize the layered structure. Reasons for this could include: (1) doping cations prevent Mn ion migration during cycling, which would prevent cations redistributing, thus reducing the tendency of the layered structure converting to the more stable spinel[24]; and (2) doping cations dilute the Jahn-

Teller distortion due to partial substitution for the Mn ions[25]. Based on previous research, we synthesized $LiCo_{0.1}Mn_{0.9}O_2$ cathode material by a solid-state reaction and quenching process, $LiMnO_2$ was also prepared for the comparison.

In this study, The $Li/LiMnO_2$ and $Li/LiCo_{0.1}Mn_{0.9}O_2$ cells were fabricated and their electrochemical properties were analyzed using cyclic voltammetry (CV), ac impedance, and charge-discharge experiments.

2. EXPERIMENTAL

Orthorhombic $LiMnO_2$ and $LiCo_{0.1}Mn_{0.9}O_2$ were synthesized by a solid-state reaction and quenching process. Starting materials used for the synthesis of o-$LiMnO_2$ were $LiOH \cdot H_2O$ (Aldrich) and Mn_2O_3 (Aldrich), and that used for the synthesis of o-$LiCo_{0.1}Mn_{0.9}O_2$ were $LiOH \cdot H_2O$ (Aldrich), Mn_2O_3 (Aldrich), and Co_3O_4 (Aldrich). The starting materials were evenly mixed, and pressed into a pellet at a 3.5 ton pressure. After the calcinations at 1050 ℃ for 15 h under argon atmosphere, it was taken from the furnace and quickly quenched in liquid nitrogen.

The X-ray diffraction (XRD) patterns of prepared powders were investigated using a Rigaku diffractometer with Cu Kα radiation to identify their crystalline phases.

The cathodes were made from mixtures of the prepared powders, carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 75:20:5. The prepared powders and carbon black powders were first added to a solution of PVDF in N-methyl-2-pyrrolidinone (NMP) to make a slurry. The mixture was then coated on Al foil current collector. The resulting electrode film was pressed with a twin roller, cut into a rectangle (area= 2 cm²) and dried at 110 ℃ for 24 h under vacuum. The thickness of the pressed electrode film was about 42 μm. The test cells were assembled in an glove box filled with argon gas, and consisted of cathode, lithium foil as an anode and 1M $LiPF_6$ dissolved in a 50:50 vol.% mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as an electrolyte(SAMSUNG, CHEIL Industries Ltd.). The separator (Cellgard 2320) was between the cathode and lithium film, then fixed with slide-glasses on two sides, and finally immersed in the electrolyte. The cells were cycled galvanostatically in a potential range of 2.0-4.3 V with a current density of 0.5 mA cm⁻² at room temperature and 50 ℃ using a WBCS3000 (Wonatech) Battery Tester System, which were also used to measure cyclic voltammetry at a scan rate of 0.2 mV S⁻¹. Electrochemical impedance measurements were performed using an IM6 impedance system (Zahner Elektrik Company). The spectrum was potentiostatically measured by applying an ac voltage of 20 mV over the frequency range from 10 mHz to 1 MHz.
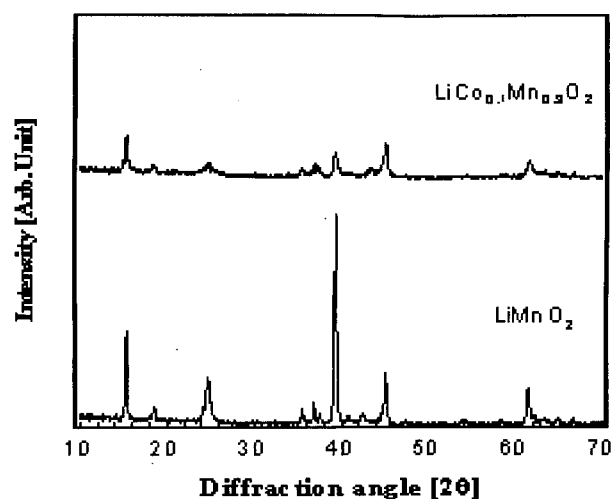

Fig. 1. XRD patterns of powders calcined at 1050 ℃.

3. RESULTS AND DISCUSSION

3.1 Crystal structure

XRD patterns of powders calcined at 1050 ℃ are shown in Fig. 1. All the powders have a single phase and all diffraction peaks can be indexed by an orthorhombic phase of a space group with Pmnm, which are the same as those listed in the JCPDS card. No impurity phase was discovered in the $LiMnO_2$ and $LiCo_{0.1}Mn_{0.9}O_2$ powders.
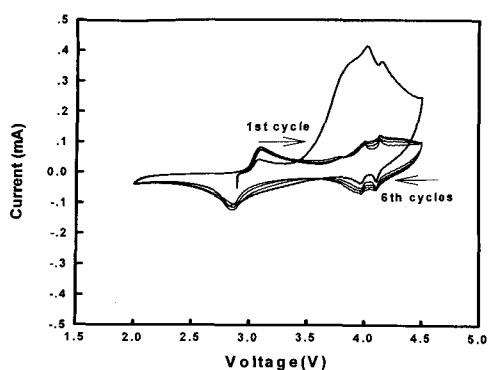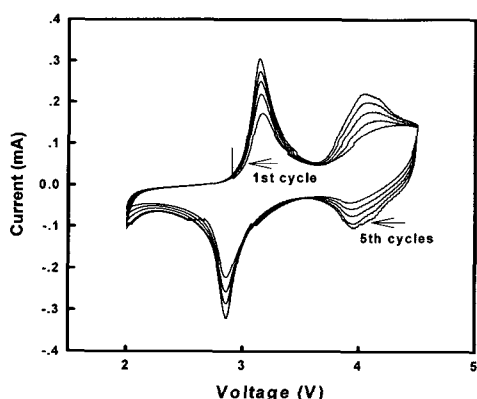
3.2 Cyclic voltammetry

Cyclic voltammograms of o-$LiMnO_2$ and o-$LiCo_{0.1}Mn_{0.9}O_2$ are shown in Fig. 2 and Fig. 3, respectively. As can be seen from Fig. 2, the oxidation peaks appear at 3.1, 4.0 and 4.12 V, the corresponding reduction peaks appear at 2.83, 3.95 and 4.1 V during the first cycle. After six cycles, the oxidation peaks decrease and shift to the higher potential, the corresponding reduction peaks also decrease and shift to the lower potential, this is due to the increase in the internal impedance of cathode material and polarization reaction.

In Fig. 3, the oxidation peaks appear at 3.1 and 3.8 V, the corresponding reduction peaks appear at 2.8 and 3.8 V during the first cycle. After five cycles, all the oxidation and reduction peaks decrease and hardly shift to the higher or lower potential, this is also due to the increase in the internal impedance of cathode material and polarization reaction. It is demonstrated that the oxidation/reduction reversibility of o- $LiCo_{0.1}Mn_{0.9}O_2$ is better than that of o-$LiMnO_2$.
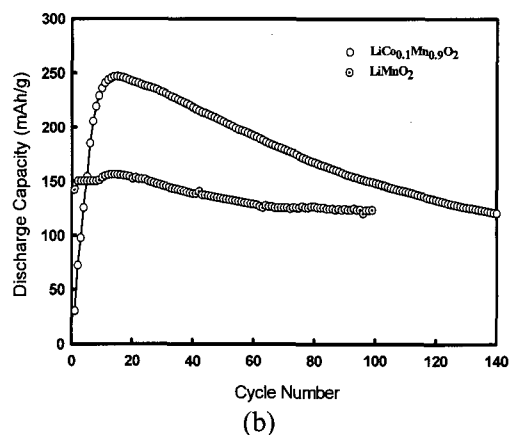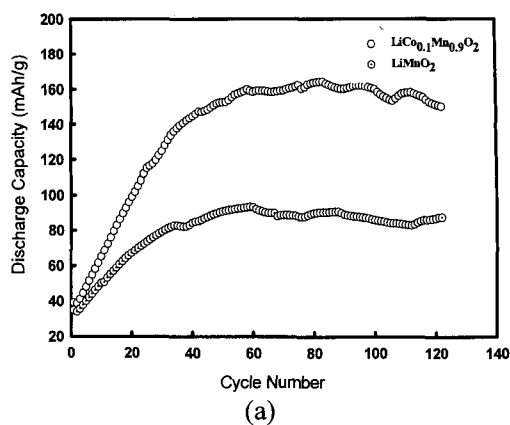
3.3 Charge/discharge properties

The cycle characteristics of $Li/LiMnO_2$ and $Li/LiCo_{0.1}$

Fig. 2. Cyclic voltammogram of o-LiMnO$_2$.

Fig. 3. Cyclic voltammogram of o-LiCo$_{0.1}$Mn$_{0.9}$O$_2$.

(a)

(b)

Fig. 4. The plots of specific discharge capacity vs. number of cycles for Li/LiMnO$_2$ and Li/ LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cells at (a) Room temperature and (b) 50 °C.

Mn$_{0.9}$O$_2$ cells at different temperatures are given in Fig. 4. At room temperature, the initial discharge capacity of Li/LiMnO$_2$ and Li/LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cells is 35 and 38 mAh g^{-1}, respectively. After 60 cycles, the highest discharge capacity increases to 95 and 160 mAh g^{-1}, respectively. Following the phase transition occurring at the first cycle, additional cycles up to 60 are necessary for the optimal capacity of materials. At 50 °C, the initial discharge capacity of Li/LiMnO$_2$ and Li/LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cells is 148 and 30 mAh g^{-1}, respectively. After 10 cycles, the discharge capacity of Li/LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cell increases to 250 mAh g^{-1}, and rapidly decrease upon cycling. As for Li/LiMnO$_2$ cell, the discharge capacity gradually decreases upon cycling. It is demonstrated that the lithium mobility and structural transformation at 50 °C is faster than that at room temperature.

The discharge curves of Li/LiMnO$_2$ and Li/ LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cells at room temperature are shown in Fig. 5. As can be seen from Fig. 5, voltage plateaus appear at around 4 and 2.9 V, which are indicative of Li intercalation on different sites, which are tetrahedral site over 4 V and octahedral site over 3 V in the cycled-induced spinel LiMn$_2$O$_4$[26]. It is obvious that the

voltage plateaus in Li/LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cell is longer than that in Li/LiMnO$_2$ cell, which means the discharge capacity of Li/ LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cell is bigger than that of Li/LiMnO$_2$ cell. It is consistent with the results of cyclic voltammograms of o-LiMnO$_2$ and o-LiCo$_{0.1}$Mn$_{0.9}$O$_2$, that is to say, charge/discharge properties of Li/LiCo$_{0.1}$ Mn$_{0.9}$O$_2$ cell is better than that of Li/LiMnO$_2$ cell.

3.4 Impedance properties

The impedance spectra of Li/LiMnO$_2$ cell as a function of charge/discharge cycling at room temperature are shown in Fig. 6. It is noted that the ac impedance response of Li/LiMnO$_2$ cell forms a broad semicircle over the frequency range of 1 M $-$10 mHz, and a line to the real axis in the lowest frequency range. The resistance of electrolyte is 2.6 Ω. The cell resistance is 110 Ω at the first cycle and 50 Ω after 55 cycles, respectively. It is obvious that the cell resistance decreases upon the cycling, and consistent with the results of Fig. 4 and Fig. 5, that is to say, the discharge capacity of cell increase upon cycling and reaches to the maximum after 60 cycles.
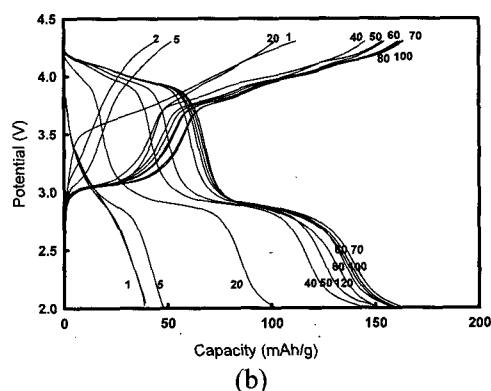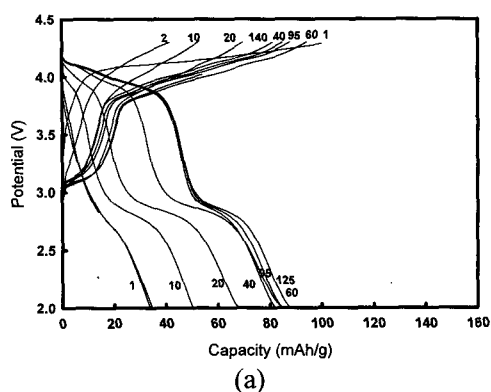
(a)

(b)

Fig. 5. Discharge curves of (a) Li/LiMnO$_2$ and (b) Li/LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cells at room temperature.
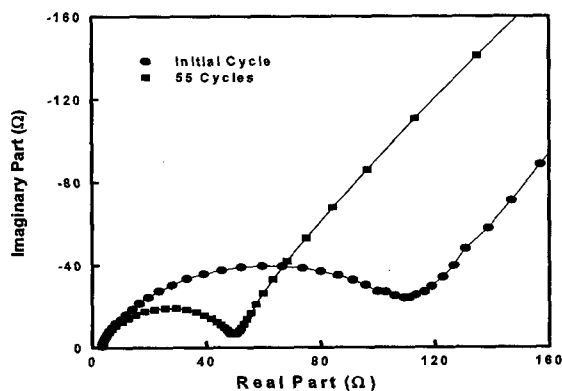

Fig. 6. Impedance spectra of Li/LiMnO$_2$ cell as a function of charge/discharge cycling at room temperature.

The impedance spectra of Li/ LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cell as a function of charge/discharge cycling at different temperatures are shown in Fig. 7. The resistance of electrolyte is 2.3 Ω. At room temperature, the resistance of cell is 110 Ω at the first cycle. At 50 $^\circ$C, The cell resistance is 30 Ω at the first cycle and 48 Ω after 48 cycles, respectively. It is obvious that the cell resistance
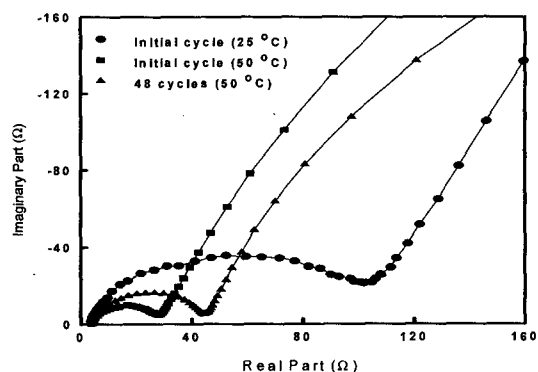

Fig. 7. Impedance spectra of Li/LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cell as a function of charge/discharge cycling at different temperatures.

decreases upon the increase in temperature, and consistent with the results of Fig. 4, that is to say, the lithium mobility and structural transformation at 50 $^\circ$C is faster than that at room temperature.

4. CONCLUSION

Well-defined orthorhombic LiMnO$_2$ and LiCo$_{0.1}$Mn$_{0.9}$O$_2$ were synthesized by a solid-state reaction and quenching process. Li/LiMnO$_2$ cell shows the highest specific capacity at room temperature and 50 $^\circ$C is 95 and 155 mAh g^{-1}, respectively. Li/ LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cell shows the highest specific capacity at room temperature and 50 $^\circ$C is 160 and 250 mAh g^{-1}, respectively. The performance of Li/LiCo$_{0.1}$Mn$_{0.9}$O$_2$ cells is better than that of Li/LiMnO$_2$ cells.

ACKNOWLEDGMENTS

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