Synthesis of $Li_xMn_2O_4$ for Recargable Battery with Various MnO_2 Structure Types

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1. Introduction

MnO_2 and realated managanese(IV) oxides are known to exit in a wide varity of structual forms. There are the materials β-MnO_2 (pyroluste) and ramsdellite, which are relatively pure MnO_2,; and other such as α-MnO_2, β-MnO_2, γ-MnO_2, etc., which contain signification amount of otherions as integral parts of the structure.
The structures can be described in terms of octahedra composed of oxygen atoms with managanese atoms in the center. The various structural forms are then built up by linking these octahedra together in various ways.
For most of the MnO_2 matrials, the structure can be described as consisting of parallel chains of edge-linked managanese oxygen octahedra, linked together in various ways. Thus pyrolusite (β-MnO_2) consiste of single chains connected by corner sharing to single chains.
α-MnO_2 (cryptomelane) and psilomelane. In these strutures there are parallel tunnels which are large enough to contain other species, such as potassium, sodium, barium, or lead, δ-MnO_2 has a layer structure, with sheets made from manganese-oxygen octahedra, separaed by alkali or other ions, and water. γ-MnO_2, the material most commonly used as a cathode material in dry-cell bateries, is considered to be a disordered intergrowth of the β-MnO_2 and ramsdellite structure, thus consisting of a random arrangement of single and double chains of MnO_6 octahedra.
There are some managanese(IV) containing compounds with structures based on a cubic closest packing(ccp) oxygen arrangement. Thus is proposed to have both lithium and managanese(IV) on octahedral sites in a ccp oxygen framework, while $LiMnO_4$ has the spinel structure, with lithium in tetrahedral sites and managanese(III) and managanese(IV) in octahedral sites of a ccp oxygen framework.
In this study, the spinel-type material $LiMn_2O_4$ with aqueous acid will be investigated the result in conversion of the $LiMn_2O_4$ to nearly pure MnO_2, while preserving the structural framework of the $LiMn_2O_4$. The cycling performance and the electrochemical properties of the spinel related structure will be studied as a function of MnO_2 forms in

Li/Li_xClO_4 PC-DME (1:1)/ $Li_xMn_2O_4$/cell. The effect of the chemical composition and the reaction temperature on electrochemical parameter of $Li_xMn_2O_4$ are studied by the phenomena of phase-transition, analysis of crystal lattice, fine structure, and thermal analysis.

2. Exprimental procedure

1) Synthesis of $LiMn_2O_4$

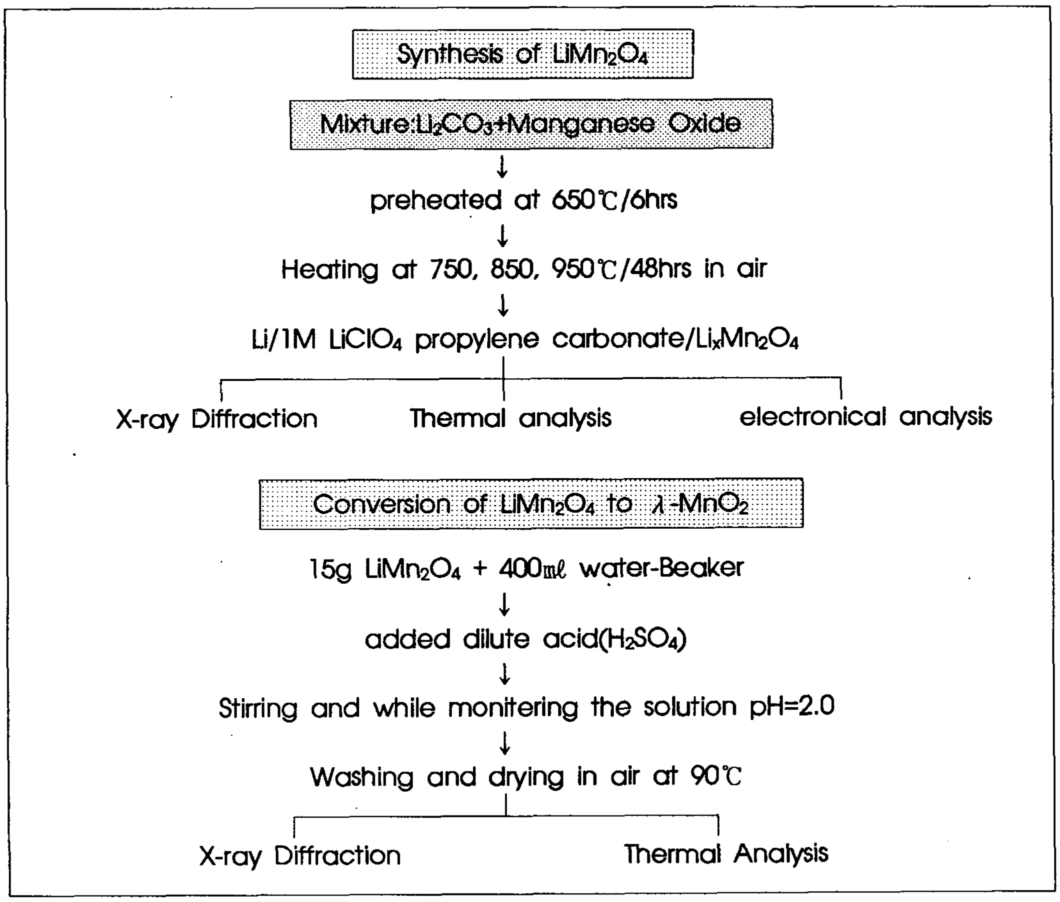

Fig. 1 : Schematic of experimental procedure for $Li_xMn_2O_4$ synthesis and conversion by λ-MnO_2.

① Chemical Analysis

- %Mn 와 manganese peroxidation → ferrous sulfate potassium permagnate
- Lithium concentration → atomic absorption specroscopy and XRF

② X-ray Diffraction

- X-ray powder diffraction analysis → Fe k_α, Cu k_α (with a graphite mono chiometer)
  Using a Stillation counter detector

- λ-MnO_2(Unit cell dimensions) → Debye- Scherrer Powder Camera
  (High- angle X-ray diffraction data)
  (Electronicchemistry of Manganese Dioxide in Lithium Nonaqueous Cell)

③ Thermal analysis : DTA/ TGA

2) Cathode and electroyte

① Cathode

- 90wt%- $LiMn_2O_4$
- 5wt%-Acetylene blanck
- 5wt%-Teflon organic Binder

② Electroyte

1M의 $LiClO_4$-propylene carbonate(PC) } 1 : 1 solution
1,2-dimethoxyethane(DME)

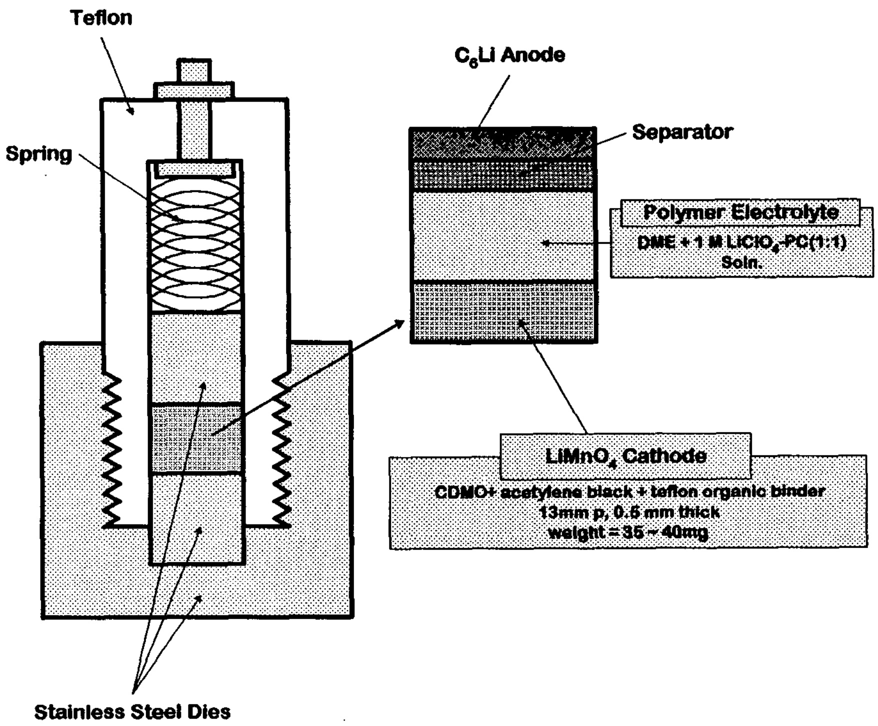

Fig. 2 : Working cell configuration

3. Results and Discussion

X-ray diffraction patterns indicated that the major phase in samples was β-MnO_2 in the temperature range of 25 ~ 450℃ and ε-MnO_2 between 550 and 850℃, respectively. In the case of γ-MnO_2 structure was seen at 950℃ (see Table 1). The measured lattice parameter of 8.226 ~8.239Å of the samples of $Li_xMn_2O_4$, ($0.2< \chi <1.2$) for the 750 and 850℃ is in good agreement with that reported for the stoichiometric spinel $LiMn_2O_4$ (1). In the samples prepared of $Li_xMn_2O_4$, ($1.4< \chi <2.0$) at 750℃ and 85 0℃ temperature was detected the tetragonal unit cell, with lattice constant a_o=5.75~6.129Å and c_o=9.145~9.489Å, respectively, as compared to a lattice constant of a_o=5.963Å and c_o=9.10Å for $Li_xMn_2O_4$, at 950℃(see Table 2).

Since the X-ray scattering factors for manganese and oxygen are so much larger than for lithium, the diffraction pattern of $LiMn_2O_4$ is due mainly to the manganese and oxygen atoms. The great similarity of this pattern to that of the acid-treated $LiMn_2O_4$ thus implies that the latter material has the same arrangement of manganese and oxygen atoms as in the spinel, but with a slightly smaller unit cell (2). From the X-ray data and the analytical results, therefore, it appears that acid treatment of $LiMn_2O_4$ leads to formation of a manganese dioxide of unique structure, derived from the spinel structure of $LiMn_2O_4$ but with most of the lithium removed from the tetrahedral sites. This material has been given the designation of λ-MnO_2 (see Table 3). This type of structure related to spinel structure but with the tetrahedral sites vacant, is not adopted by any binary compound. From the conversion of of $LiMn_2O_4$ to λ-MnO_2, the lattice constant of 6.642Å and 6.071Å can be calculated for $Li_xMn_2O_4$, (x = 0.6~0.8) compared to a measured valve of 8.228Å and 8.229Å, respectively.

Differential thermal analysis (DTA) results for γ-MnO_2 and β-MnO_2 have been reported in the literature(3,4). In the case of β-MnO_2, an endothermic peak is seen in the temperature range of 100~400℃, corresponding to conversion of β-MnO_2 to ε-MnO_2 in the temperature range of 540~600℃, For conversion of ε-MnO_2 to the more stable form of γ-MnO_2 there is a broad endothermic region in the range of 940~950℃, Treatment of the spinel $Li_xMn_2O_4$ with aqueous acid was found to result in conversion of $Li_xMn_2O_4$ to nearly pure MnO_2, as evidenced by a reduction in the lattice constant of from 8.255 to 8.031Å. Thus has a structure related to spinel, but with most of the Li removed from the tetrahedral sites. At a composition range of $0.2 \leq x \leq 0.6$ in $Li_xMn_2O_4$ the reduction proceeded in a homogeneous phase, which was characterized by a constant voltage of 3.9~3.7V together with a lattice constant of 8.255Å.

4. Conclusion

Treatment of the spinel $Li_xMn_2O_4$ with aqueous acid was found to result in conversion of $Li_xMn_2O_4$ to nearly pure λ-MnO_2, as evidenced by a reduction in the lattice constant of from 8.255 to 8.031Å. A mechanism for the conversion of $Li_xMn_2O_4$ to λ-MnO_2 is proposed, which involves solid state diffusion of Li ion in the structure, in a manner analogues to the proton diffusion which occurs during the cathodic reduction of λ-MnO_2. At a composition range of $0.2 \leq x \leq 0.6$ in $Li_xMn_2O_4$ the reduction proceeded in a homogeneous phase, which was characterized by a constant voltage of 3.9~3.7V together with a lattice constant of 8.255Å.

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Table 1. Changes of structure of MnO_2 after heat treatment

Temp.(°C)	25	350	450	550	650	750	850	950
Structure of Type	β-MnO_2	β-MnO_2	β-MnO_2	ε-MnO_2	ε-MnO_2	ε-MnO_2	ε-MnO_2	γ-Mn_2O_3

Table 2. Evolution of the structure of the lattice as a function of X in $Li_xMn_2O_4$ at 750℃, 850℃ and 950℃ for 48hr.

Temperature	X	Structure Type	Lattice constant(Å)
750℃	0.2 ~ 0.4	Cubic	a = 8.226
	0.6 ~ 0.8	Cubic	a = 8.235
	1.0 ~ 1.2	Cubic	a = 8.239
	1.4 ~ 2.0	Tetragonal	a = 5.75 c = 9.145
850℃	0.2 ~ 0.4	Cubic	a = 8.226
	0.6 ~ 0.8	Cubic	a = 8.228
	1.0 ~ 1.2	Cubic	a = 8.239
	1.4 ~ 2.0	Tetragonal	a = 6.129 c = 9.489
950℃	0.2 ~ 0.4	Cubic	a = 8.224
	0.6 ~ 0.8	Cubic	a = 8.227
	1.0 ~ 1.2	Cubic	a = 8.230
	1.4 ~ 2.0	Tetragonal	a = 5.963 c = 9.10

Table 3 Evolution of the structure of the lattice as a fuction of X in $Li_xMn_2O_4$ at 750℃, 850℃ and 950℃ for 48h in untreatment and acid treatment

	Untreatment		Acid Treatment	
X	Structure Type	Lattice Constant(Å)	Structure Type	Lattice Constant(Å)
0.2	Cubic	a=8.225	Cubic	a=8.021
0.4	Cubic	a=8.226	Cubic	a=7.867
0.6	Cubic	a=8.228	Cubic	a=6.642
0.8	Cubic	a=8.229	Cubic	a=6.071
1.0	Cubic	a=8.239	Cubic	a=8.0215
1.2	Cubic	a=8.2573	Cubic	a=8.0235
1.4~2.0	Tetragonal	a=5.963 c=9.10	Tetragonal	a=5.265 c=9.735

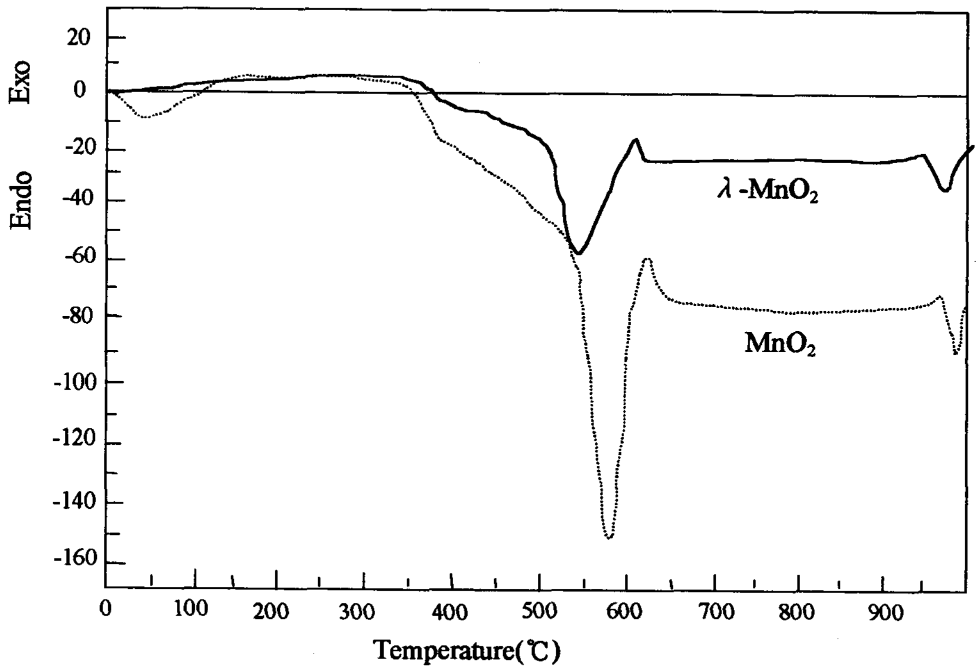

Fig. 3 DTA curves of the MnO_2 at 950℃ for 48hr and λ-MnO_2 resulting from pH 2 acid treatment of $Li_1Mn_2O_4$

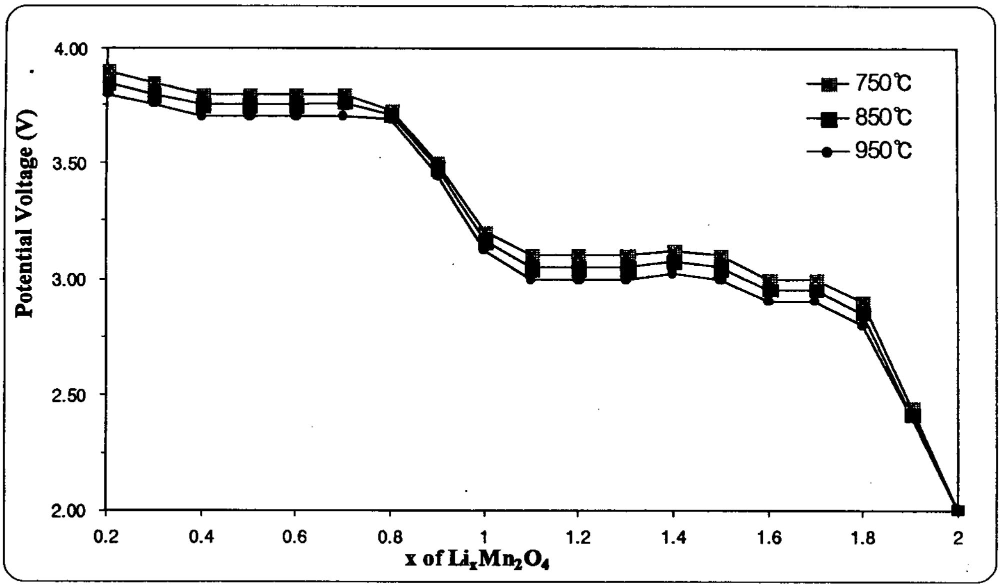

Fig. 4 Voltage curves of $Li_xMn_2O_4$ at 25℃
(a) 750℃ (b) 850℃ (c) 950℃