PROPERTIES OF LITHIUM–ALUMINUM–COBALT–MANGANESE OXIDE NANOCOMPOSITES FORMED BY CHEMICAL COPRECIPITATION

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Introduction

Kao and Wu have studied the preparation and properties of the lithium–manganese oxide ceramic matrix by various processes[1] and the lithium–manganese–vanadium oxide ceramic matrix composites by chemical coprecipitation[2].

Aluminum is very light metal and its electrode potential is high. Therefore it becomes a very important material in battery.

Kumagai et al. [3] have investigated the physical and electrochemical characterization of quaternary Li–Mn–V–O spinel as positive materials for rechargeable lithium batteries.

In this study, the particle size and electrical properties of the lithium–aluminum–cobalt–manganese oxide particle by chemical coprecipitation were determined.

Experimental

Fig. 1 Flow chart for experiment of $LiAl_xCo_yMn_{1-x-y}O_2$

$LiOH + xAl(NO_3)_3 + y\,Co(NO_3)_2 + (1-x-y)\,Mn(NO_3)_2 \rightarrow LiAl_xCo_yMn_{1-x-y}O_2$

where x = 2/3, 1/3.

The chemicals used were all of high purity. LiOH, $Al(NO_3)_3$, $Co(NO_3)_2$ and $Mn(NO_3)_2$ were used as the starting reagents of Li(I), Al(III), Co(II) and Mn(II), respectively.

The mole ratios of $LiAl_xCo_yMn_{1-x-y}O_2$ are 1:1/3:1/6:1/2, 1:1/3:1/3:1/3, 1:1/3:1/2:1/6, 1:2/3:1/9:2/9 and 1:2/3:2/9:1/9, respectively.

Result and Discussion

Lithium Aluminum Cobalt Manganese Oxide Nanocomposites

FTIR

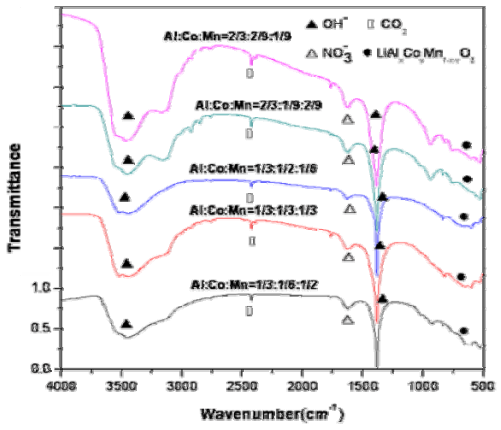

Fig. 2 FTIR spectra of

LiAlxCoyMn1−x−yO2 precursors dried at 150℃ for 24h

That there are peaks at 1210−1570 cm−1 and 2690−3750 cm−1 for OH− bending,

around 1570−1760 cm−1 for NO3−, and at 500−950 cm−1 for spinel [4].

TGA/DTA and XRD analyses of coprecipitated powder

There is a weight loss in the 273−473 K for the Li−Al−Co−Mn oxide particle in TGA/DTA, owing to the vaporization of the water in the precursor from absorption heat.

There is also a weight loss in 473−593 K, because nitrate reacted into nitrogen oxide.

In the vicinity of 593 K the OH− reacted into water and the vaporization of water from absorption heat.

There are clear peaks from the XRD pattern of the powder in coprecipitation of Li−Al−Co−Mn oxide particle at 423 K for 24 h. It is obvious that there is a crystal structure of LiAlxCoyMn1−x−yO2.

Heated to 1273 K, the product of LiAlxCoyMn1−x−yO2 is complete for the reaction.

Fig. 3 SEM of LiAlxCoyMn1−x−yO2

That there is a clear phenomenon of agglomeration from SEM . This phenomenon is attributed to van der Waals forces between molecules, the absorption of vapor and the defect for the surface of the grain or having no balance in electricity to produce aggregation and tendency of adsorptive outer substances [5,6]

Particle Size Distribution of LiAlxCoyMn1−x−yO2

The average particle sizes of LiAl2/3Co1/9 Mn2/9O2 and LiAl1/3Co1/2 Mn1/6O2 are 0.421 and 0.459 μm, respectively from their particle size distribution. Owing to the radius of cobalt is larger than that of aluminum , the average particle size of LiAl1/3Co1/2 Mn1/6O2 is larger than that of LiAl2/3Co1/9 Mn2/9O2.

XRD Analysis

It is obvious from Figure 4 that at 800^{0}C the structure of the lithium aluminum cobalt manganese oxide

appeared, and there was no change until 1000^{0}C. Some Mn_2O_3 existed at 800^{0}C and disappeared at 1000^{0}C. Therefore the optimal condition for preparing the lithium aluminum cobalt manganese oxide is at 1000^{0}C for 6 h.

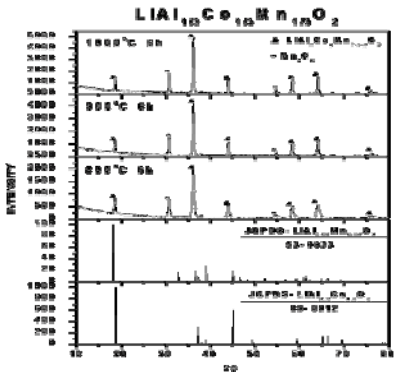

Fig. 4 XRD ofLiAl1/3Co1/3Mn1/302

Superconducting Quantum Interference Device (SQUID)

The magnetic susceptibility of the sintered lithium aluminum cobalt manganese oxide particle as a function of temperature by SQUID. The magnetic susceptibility decreases with increasing temperature. The magnetic intensity, I, with magnetic strength, H, is written as I = XH, where X is magnetic susceptibility.

And susceptibility is proportional to 1/T as C/T [7,8].

SQUID was used to measure 1/X vs. T. The results for the various sintered are paramagnetism.

Measurement of Resistivity for the Sintered Body in Air at Room Temperature

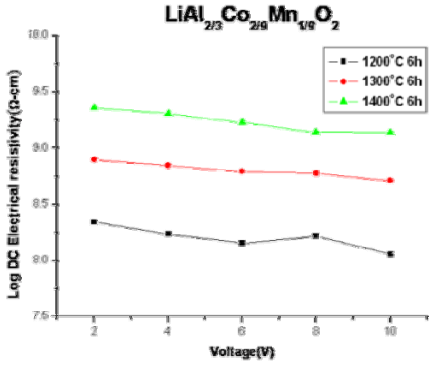

Fig. 5 DC electrical resistivity of LiAl2/3Co1/9 Mn2/902 bodies sintered at 1200,1300 and 1400C for 6h

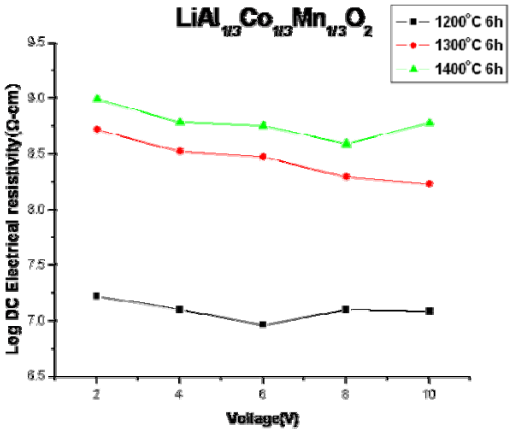

Fig. 6 DC electrical resistivity ofLiAl1/3Co1/3Mn1/302 bodies sintered at 1200, 1300 and 1400C for 6 h

Measurement of Dielectric Constant for the Sintered Body

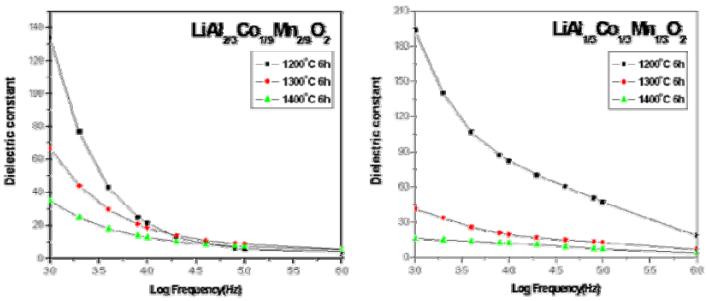

Fig.7 Dielectric constant of LiAlxCoyMn1−x−yO2

$\varepsilon_r = (t_a\ cp) / (\pi r^2 \varepsilon_o)$ [9], where t_a is the thickness of the sample, r is the measured radius of the holder, 2.5 x 10−3 m, ε_o is the dielectric constant in air, 8.854 x 10−12 F/m and cp is the measured capacitance.

That the dielectric constant decreases with increasing frequency. The dielectric constant decreases with increasing sintering temperature. And that the dielectric constant of high aluminum content is less than that of low aluminum content.

Charge and discharge curves of the lithium aluminum cobalt manganese oxide particles

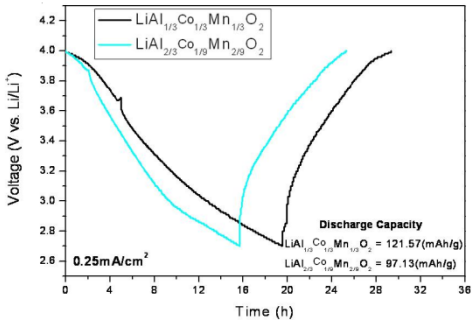

Fig. 8 Charge and discharge curves of the lithium aluminum cobalt manganese oxide

Conclusions

(1) The lithium−aluminum−cobalt−manganese oxide particles, the reactants act the coprecipitant to simplify the reaction procedure and obtain the fine powder at lower calcination temperature of 1273 K.

(2)The uniformities of the particles are better. XRD, SEM and FTIR were used to examine the effect of manganese.When the concentration of manganese ion increases, the absorption strength of the peak of spinel structure in the FTIR patterns decreases, due to the occupation of manganese in the aluminum position.

(3)The charge−discharge curve of the lithium−aluminum−cobalt−manganese oxide particle as a cathode material of the lithium ion battery was also determined.

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