Preparation and Electrochemical properties of $LiMn_2O_4$ cathode of Lithium ion battery for Electric vehicles

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Abstract - Charge/discharge property of $LiMn_2O_4$ was investigated with $LiMn_2O_4$/Li cell for use of lithium ion battery in electric vehicle. $LiMn_2O_4$ calcined at 800℃ for 36hr show high charge/discharge capacity and excellent cycle stability than that of others. This is found to be in agreement with expectation in the X-ray diffraction analysis. In addition, the kind and volume of conductive agent involved in $LiMn_2O_4$ cathode is excellent at super-s-black and 20wt%, respectively.

1. Introduction

In recent years, interest on electric vehicles is increasing because of depletion of petroleum resources and environmental pollution. Electric vehicles can resolve problem of depletion of petroleum resources and environmental pollution. One of important element of electric vehicles is justly battery. Today, sources of electric vehicles have been used lead-acid batteries or Ni/Cd secondary batteries. However, lead-acid batteries or Ni/Cd secondary batteries represent property of low energy density and average voltage, and trigger off environmental pollution problem of Pb or Cd. So, anti-pollution power sources of high energy density for electric vehicles are needed. Pertinent batteries are certainly lithium secondary batteries. Lithium secondary batteries have properties of large operating range, high potential and energy density, low self-discharge and stable cycling. Recently, It is studied extensively that $LiCoO_2$[1,2], $LiNiO_2$[3,4], $LiCo_{1-x}Ni_xO_2$[5] and $LiMn_2O_4$[6] and so on as cathode active materials for lithium secondary batteries. Of these, $LiMn_2O_4$ have been using much than other material because Mn is low cost and plentiful sources. However, property of $LiMn_2O_4$ cathode changes by method of preparation of materials, kind and volume of conductive agent involved in $LiMn_2O_4$ cathode.

In this study, we report the results on variation of charge/discharge property by calcing time of $LiMn_2O_4$ cathode active material, and kind and volume of conductive agent involved in $LiMn_2O_4$ cathode.

2. Experimental

2.1. Preparation of $LiMn_2O_4$

Cathode active material $LiMn_2O_4$ prepared at this study was mixed $LiOH \cdot H_2O$ and MnO_2 at 5 hours in ethanol, and dried at vacuum during 100℃ 1hr, and then, calcined at 800℃ for 24, 36, 48, 60, 72hr. In addition, prepared $LiMn_2O_4$ powders were ground at Quartz bowl.

2.2. X-ray diffraction analysis of cathode active materials

Powder X-ray diffraction(XRD) data were collected

using Dmax/1200 X-ray diffraction analyzer of Rigaku Co. Scan range(=2θ) was 5° - 70°, and scan rate was 10°/min. X-ray is CuKα_1(1.5405Å) monochrorized with Ni-filter.

2.3. Preparation of electrode

Electrode preparation was mixed the cathode active material of 85～75wt%, super-s-black 10～20wt% and polyvinylidene fluoride(PVDF) 5wt% solved in N-methylpyrrolidone(NMP) solvent. Then, slurry was pasted on Al foil. Counter electrode was Li metal. $LiMn_2O_4$/Li cell was consised of $LiMn_2O_4$ electrode and Li counter electrode. Electrolyte was 1M $LiClO_4$/PC.

2.4. Chargc/discharge test

To analyze electrochemical property of $LiMn_2O_4$ cathode, $LiMn_2O_4$/Li cells were assembled in glove box. All the electrochemical test were carried out at room temperature. Cutoff voltage and constant current density were 4.3V ～ 3.0V and 0.1ma/cm^2, respectively.

3. Results and discussion

Fig. 1 shows X-ray diffraction pattern of $LiMn_2O_4$. All $LiMn_2O_4$ prepared in this study shown cubic phase. This was well agreed with standard X-ray diffraction peak site. Peaks shown X-ray diffraction analysis were corresponded to (111), (311), (222), (400), (331), (511), (440), (531) from left by standard cubic structure, which is basic on spinel structure, respectively.

Spinel structure is well formed this temperature. The cation mixing degree and the crystal regulation of $LiMn_2O_4$ are obtained by (111) peak/(311) peak ratio, and when this peak ratio is about 0.37, charge/discharge property will be good. In analysis of (111) and (311) peak ratio, the cathode active material calcined at 800℃ for 36hr is 0.37, and other things are 0.32 ～ 0.49.

By x-ray diffraction analysis, cathode active material

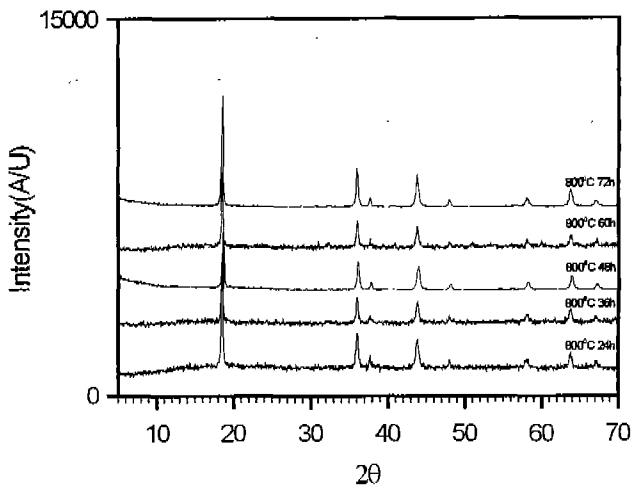

Fig. 1. X-ray diffraction pattern of $Limn_2O_4$.

calcined at 800℃ for 36hr is expected to have excellent property. Fig. 2 shows charge/discharge property of $LiMn_2O_4$ prepared by change of calcing time. Of $LiMn_2O_4$ prepared in this study, it calcined at 800℃ for 36hr, charge/discharge property was excellent than that of other materials. That is well agreed with result of X-ray diffraction analysis.

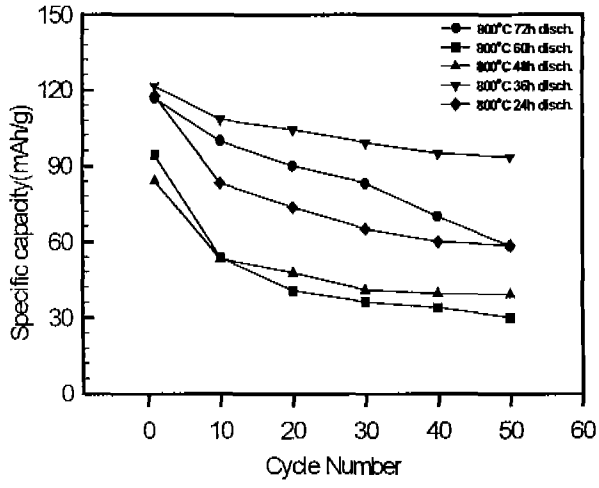

Fig. 2. Discharge capacity of $LiMn_2O_4$ prepared by calcing time change.

Discharge capacity of first cycle was 121mAh/g, and after 10 cycle, discharge capacity was stabilized about

110mAh/g. Fig. 3 shows charge/discharge properties by kind of conductive agent involved in $LiMn_2O_4$ cathode. Charge/discharge properties of $LiMn_2O_4$ cathode mixed with super-s-black as conductive agent

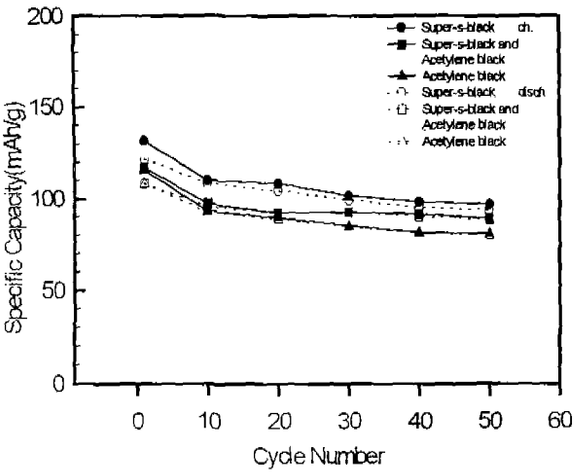

Fig. 3. Charge/discharge capacity by kind of conductive agent involved in $LiMn_2O_4$ cathode.

are better than that of $LiMn_2O_4$ cathode mixed with acetylene black or mixture of super-s-black and acetylene black. It is presumed because of interfacial reaction of organic electrolyte and conductive agent involved in $LiMn_2O_4$ cathode. That is, Mn dissolution breaks out at $LiMn_2O_4$. Fig. 4 shows charge/discharge property by volume of conductive agent involved in $LiMn_2O_4$ cathode. Charge/discharge property of $LiMn_2O_4$ cathode mixed conductive agent 20wt% present excellent than that of others which show low capacity and more capacity loss. Its charge/discharge capacity of first cycle is about 145mAh/g. That is very excellent capacity which is about 98% of theoretical capacity. After 10cycle, charge/discharge capacity is high and stable about 110 ~ 120mAh/g.

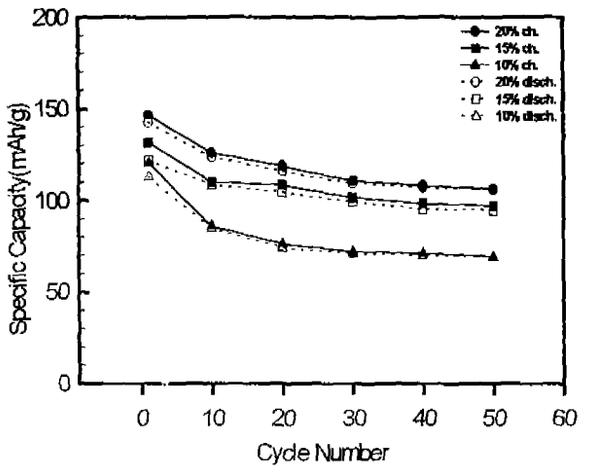

Fig. 4. Charge/discharge capacity of by volume of conductive agent involved in $LiMn_2O_4$ cathode.

4. Conclusion

This study investigated charge/discharge properties of $LiMn_2O_4$ with $LiMn_2O_4$/Li cell for use of lithium secondary battery as power source to electric vehicle. The results of charge/discharge properties of $LiMn_2O_4$/Li cell are presented the next.

1) In the result of the X-ray diffraction analysis, (111)/(311) peak ratio is changed by calcing time. (111)/(311) peak ratio is related with cation mixing degree of crystal structure.
2) In the result of the charge/discharge, $LiMn_2O_4$ prepared by calcing at 800℃ for 36hr shown excellent charge/discharge capacity. This has been found to be in good agreement with expectation in X-ray diffraction analysis.
3) Super-s-black as conductive agent involved in $LiMn_2O_4$ cathode shown excellent charge/discharge property than that of others.
4) The mixing volume of conductive agent involved in $LiMn_2O_4$ cathode is excellent at super-s-black 20wt%.
5) Because cathode active material calcined at 800℃ for 36hr shown high specific capacity and cycle stability, it is possible to prepare excellent

lithium ion batteries used that. So, this lithium ion battery will be possible as power source for electric vehicle.

Acknowledgement

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5. References

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