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Synthesis and Electrochemical Properties of Al doped Lithium Manganate Powders by Spray Pyrolysis Using Carbonate Aqueous Solution

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Keywords: Lithium ion battery, Spray Pyrolysis, Lithium Manganate, Spinel, Aerosol

Abstract Al doped $LiMn_2O_4$ powders were prepared by spray pyrolysis using the aqueous solution of manganese carbonate. The aqueous solution, in which manganese carbonate was uniformly dispersed by a surfactant, was used as the starting solution. Al_2O_3 nanopowders, $Al(OH)_3$ and $Al(NO_3)_3 \cdot 9H_2O$ were used as the doping agent of Al. A scanning electron microscope photograph showed that Al doped $LiMn_2O_4$ powders had spherical morphology with broad particle size distribution. X-ray diffraction revealed that crystal phase of all samples were good agreement with spinel phase. The rechargeable capacity of Al doped $LiMn_2O_4$ cathode was about 110 mAh/g at 1 C regardless of doping agent. 75% of initial discharge capacity was maintained after 100 cycles.

Introduction

Lithium ion batteries are expected as the energy storage [1] for electric vehicles and hybrid electric vehicles, the load leveling of photovoltaic power generation or the wind power generation. Lithium ion batteries for these applications require cathode materials that combine low cost, high safety and cycle stability at the high rate rechargeable performance. Spinel type $LiMn_2O_4$ [2] is regarded as a promising cathode material for lithium ion batteries due to their advantages such as low cost, abundance resources, non-toxicity and thermally stable. It has been reported that spray pyrolysis is a versatile process that is used to synthesize homogeneous $LiMn_2O_4$ powders [3-5]. However, the toxic and corrosive gases such as NO_X, Cl_X and SO_X are often discharged during the particle formation because the reagent material such as metal nitrate, chloride and sulfide are used as starting solution.

It was known [6-8] that the cycle stability $LiMn_2O_4$ was faded due to Jahn-Teller effect in the rechargeable process and the dissolution of Mn ion at the elevated temperature. These problems have been solved by substituting the foreign metal ion [9] to 16d site of the octahedron in the cubic spinel. In this paper, we report the production technique of the Al doped $LiMn_2O_4$ powders without using the toxic starting material in order to solve this problem.

In this work, the starting solution in which manganese carbonate was uniformly dispersed in aqueous solution by using surfactants was prepared. We tried to prepare Al doped $LiMn_2O_4$ powders from aqueous solution of manganese carbonate by spray pyrolysis. The powder characteristics of them were investigated in detail. Furthermore, the electrochemical properties of Al doped $LiMn_2O_4$ cathodes were also estimated by rechargeable capacity and cycle performance.

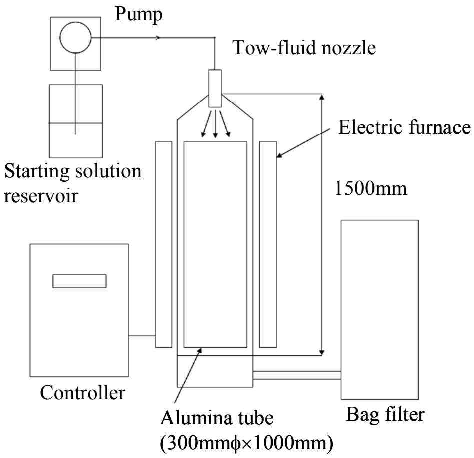

Fig.1 Schematic diagram of spray pyrolysis apparatus.

Experimental procedure

Li(OH)·H_2O and $MnCO_3$ were used as starting materials. Al_2O_3 nanopowders (20 nm), $Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$ were used as the doping agent of Al. These were successfully dispersed in aqueous solution by using surfactant at room temperature. The molar ratio of Li, Al and Mn was set to 1.05 : 0.05 : 1.95 in the starting solution. The concentration of the solution was 0.25 mol/dm^3. 0.25 wt% of surfactant was added to the starting solution. Xanthan gum type surfactant (Roadpole, Rhodia Nicca) was used as surfactant. The pH of starting solution ranged from 7 to 9 using the pH adjustment agents such as CH_3COOH. Large spray pyrolysis apparatus (RH-2, Ohkawara Kakohki) was used in this work. Figure 1 shows the schematic diagram of it. This apparatus consisted of two-fluid nozzle, cylindrical type electric furnace with alumina tube (300 mmϕ × 1000 mm) and bag filter. The mist of starting solution was atomized with a two-fluid nozzle (nozzle diameter: 10 μm). The mists were introduced to an electric furnace by air carrier gas and then pyrolyzed at 800 °C. The flow rate of the carrier gas was 20 dm^3/min, and thus the residence time was about 60 s. As-prepared powders were continuously collected using the bag filters. Furthermore, they were calcined at 800 °C for 4 hr in the electric furnace under an air atmosphere. The particle size, morphology and microstructure of Al doped $LiMn_2O_4$ powders were determined by using scanning electron microscope (SEM, JSM-6390, JEOL). The average particle size of them was determined by randomly sampling 200 particles from SEM photographs. The crystal phase of Al doped $LiMn_2O_4$ powders were identified by powder X-ray diffraction using CuKα radiation (XRD, XRD-6100, Shimadzu). The specific surface area of Al doped $LiMn_2O_4$ powders were determined by BET method (BELSORP-mini, Bel Japan). Al doped $LiMn_2O_4$ cathode was prepared using 80 wt% of Al doped $LiMn_2O_4$ powders, 10 wt% of acetylene black and 10 wt% of fluorine resin. Metal lithium was used as an anode. The polypropylene sheet was used as a separator. 1mol/dm^3 $LiPF_6$ in ethylene carbonate / 1,2-dimethoxyethane (EC : DEC = 1 : 1) was used as the electrolyte. 2032 type coin cell was built up in globe box under an argon atmosphere. The rechargeable capacity and cycle life of Al doped $LiMn_2O_4$ cathode were measured with a battery tester (Hosen, BTS2004) at between 3.5V and 4.3V at 1 C.

Results and Discussion

Figure 2 shows XRD patterns of as-prepared and calcined Al doped $LiMn_2O_4$ powders. The crystal phase of as-prepared Al doped $LiMn_2O_4$ powders were agreement with spinel structure (Fd3m) regardless of doping agent. However, Mn_2O_3 phase was also observed in as-prepared powders. It was considered that $MnCO_3$ could not uniformly react with LiOH·H_2O in the mist during the pyrolysis. After the calcination, the peaks of Mn_2O_3 disappeared and the crystal phase of Al doped $LiMn_2O_4$ powders converted to the spinel structure with high crystallinity in all samples.

Figure 3 shows typical SEM photographs of as-prepared Al doped $LiMn_2O_4$ powders. They had a spherical and irregular morphology. The follow microstructure and fragment of particles were also observed in the large particles. They had also broad size distribution from 0.5 μm to 20 μm because the mist atomized by two-fluid nozzle had broad size distribution. SEM photograph suggested that

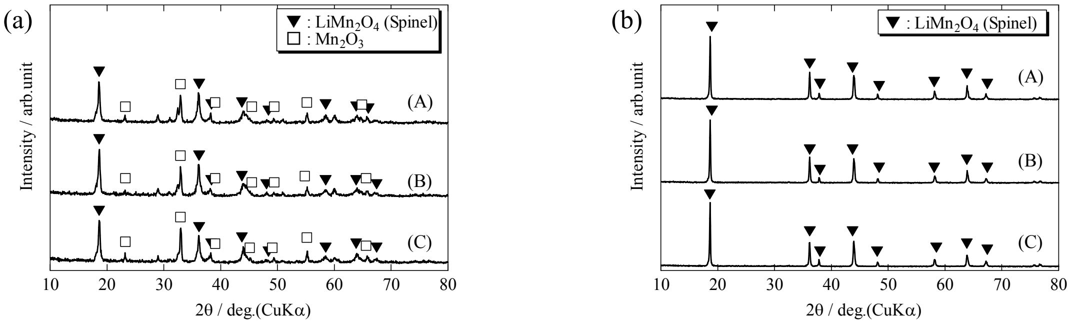

Fig. 2 XRD patterns of Al doped $LiMn_2O_4$ powders, (a) as-prepared, (b) 800 °C for 4 hr, (A) $Al(OH)_3$, (B) $Al(NO_3)_3$, (C) Al_2O_3.

they consisted of primary particles. Specific surface area of as-prepared Al doped $LiMn_2O_4$ powders derived from Al_2O_3 nanopowders, $Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$ was 18.7, 19.4 and 19.1 m^2/g, respectively. Figure 4 shows typical SEM photographs of Al doped $LiMn_2O_4$ powders calcined at 800 °C. After the calcination, the primary particles ranged from 100 nm to 200 nm were observed in all samples. The primary particles were sintered and then formation of the crystal habit such as a tetrahedron was also observed. Specific surface area of Al doped $LiMn_2O_4$ powders derived from Al_2O_3 nanopowders, $Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$ decreased to 4.1, 4.3 and 3.4 m^2/g, respectively. It was concluded that the microstructure was not influenced by the types of doping agent.

Figure 5 shows the first charge and discharge capacities of Al doped $LiMn_2O_4$ cathode at 25 °C and 50 °C. The rechargeable rate was 1 C. The voltage jump was observed at around 4 V in the charge and discharge curves. The discharge capacity of Al doped $LiMn_2O_4$ cathode obtained from Al_2O_3 nanopowders, $Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$ were 110, 110 and 108 mAh/g at 25 °C, respectively. The voltage jump of 4 V slightly disappeared in discharge curve of all samples. The discharge capacity of Al doped $LiMn_2O_4$ cathode obtained from Al_2O_3 nanopowders, $Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$ were 98, 113 and 93 mAh/g at 50 °C, respectively. Figure 6 shows relation between cycle number and discharge capacity of Al doped $LiMn_2O_4$ cathode at 25 °C and 50 °C. The discharge capacity of Al doped $LiMn_2O_4$ cathodes gradually decreased with increasing cycle number at 1 C. After 100 cycles at 25 °C, the discharge capacity of Al doped $LiMn_2O_4$ cathode obtained from Al_2O_3 nanopowders, $Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$ was 82, 79 and 76 mAh/g, respectively. The retention ratio of discharge capacity was 75, 72 and 70%, respectively. It was found that the rechargeable capacity of cathode was influenced by the dispersibility of doping agent in the starting solution. It was considered that Al dope $LiMn_2O_4$ derived from $Al(NO_3)_3 \cdot 9H_2O$ exhibited highest rechargeable capacity among the doping agent because $Al(NO_3)_3 \cdot 9H_2O$ was only dissolved in the starting solution. On the other hand, since $Al(OH)_3$ and Al_2O_3 was not dissolved in the starting solution, the homogeneity of aluminum ion in $LiMn_2O_4$ particles was lower that of $LiMn_2O_4$ particles derived from $Al(NO_3)_3 \cdot 9H_2O$. On the other hand, the discharge capacity was significantly reduced at 50 °C, The discharge capacity of Al doped $LiMn_2O_4$ cathode obtained from Al_2O_3 nanopowders, $Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$ were 38, 49 and 17 mAh/g after 100 cycles at 50 °C, respectively. This result suggested that the dissolution of Mn ion occurred in all samples even though aluminum ion was doped to $LiMn_2O_4$ particles. The retention ratio of discharge capacity was 39, 43 and 18 %, respectively.

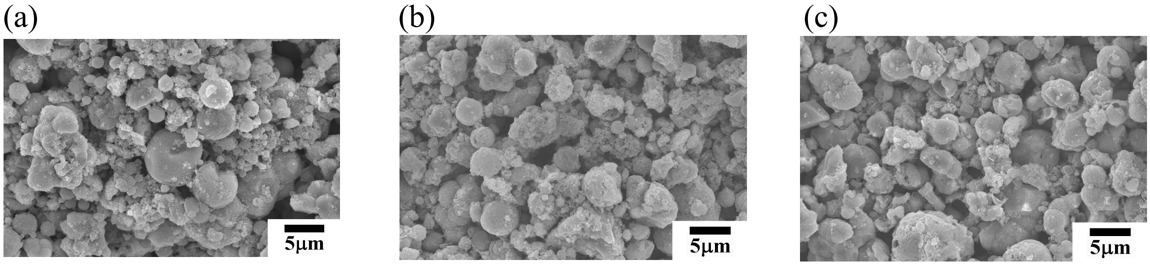

Fig. 3 SEM photograph of as-prepared Al doped $LiMn_2O_4$ powders.
(a) Al_2O_3 nanopowders, (b) $Al(NO_3)_3 \cdot 9H_2O$, (c) $Al(OH)_3$.

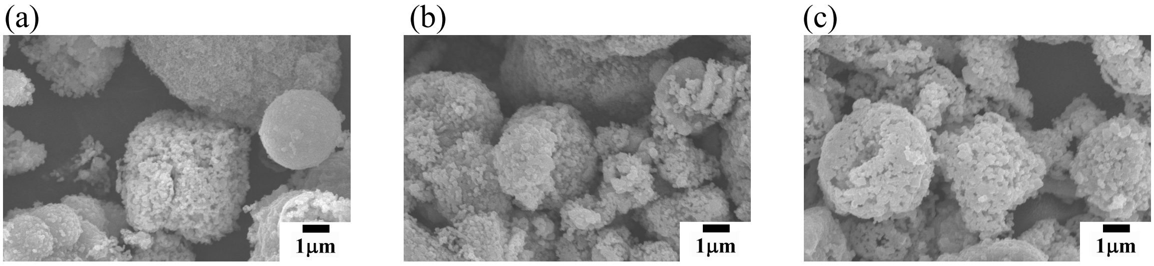

Fig. 4 SEM photograph of Al doped $LiMn_2O_4$ powders calcined at 800 °C.
(a) Al_2O_3 nanopowders, (b) $Al(NO_3)_3 \cdot 9H_2O$, (c) $Al(OH)_3$.

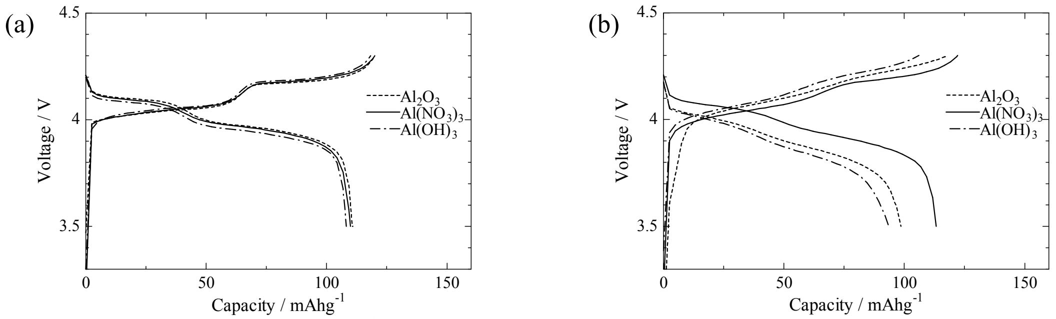

Fig. 5 First charge and discharge capacities of Al doped $LiMn_2O_4$ cathode, (a) 25 °C, (b) 50 °C.

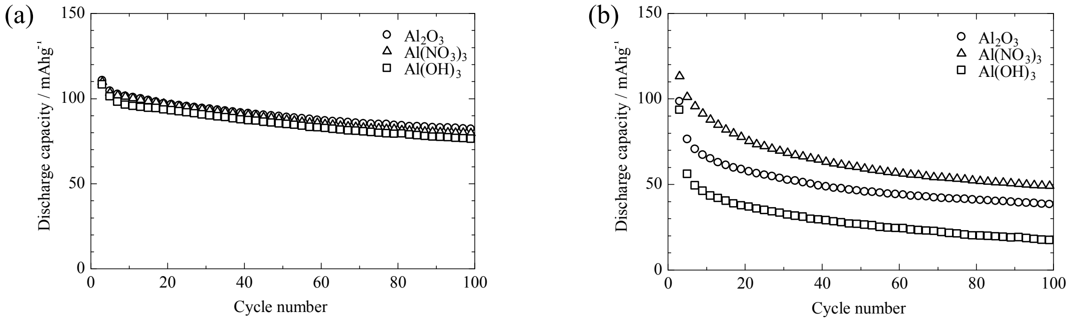

Fig. 6 Relation between cycle number and discharge capacity of Al doped $LiMn_2O_4$ cathode, (a) 25 °C, (b)50 °C.

Conclusion

Al doped $LiMn_2O_4$ powders were prepared by spray pyrolysis using an aqueous solution of manganese carbonate. Al doped $LiMn_2O_4$ powders had spherical and irregular morphology and consisted of the primary particles. The crystal phase of them was good agreement with spinel phase. The discharge capacity of Al doped $LiMn_2O_4$ cathode obtained from Al_2O_3 nanopowders was 110 mAh/g. 75% of initial discharge capacity was maintained after 100 cycles. The discharge capacity of Al doped $LiMn_2O_4$ cathode obtained from Al_2O_3 nanopowders was 82 mAh/g at 50 °C. 39% of initial discharge capacity was maintained after 100 cycles.

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