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

著者	HIROSE Shoji, KODERA Takayuki, OGIHARA Takashi
journal or publication title	Key Engineering Materials
volume	485
page range	111-114
year	2011-07
URL	http://hdl.handle.net/10098/6823

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

Shoji Hirose, Takayuki Koderu, Takashi Ogihara

Graduate School of Material Science and Engineering, University of Fukui

3-9-1 Bunkyo, Fukui-shi, Fukui 910-8507 Japan

ogihara@matse.u-fukui.ac.jp

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, $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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)·H₂O and MnCO₃ were used as starting materials. Al₂O₃ nanopowders (20 nm), Al(NO₃)₃·9H₂O 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/dm³. 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 CH₃COOH. 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 dm³/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 LiMn₂O₄ 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 LiMn₂O₄ powders were identified by powder X-ray diffraction using CuKα radiation (XRD, XRD-6100, Shimadzu). The specific surface area of Al doped LiMn₂O₄ powders were determined by BET method (BELSORP-mini, Bel Japan). Al doped LiMn₂O₄ cathode was prepared using 80 wt% of Al doped LiMn₂O₄ 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/dm³ LiPF₆ 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 LiMn₂O₄ 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 LiMn₂O₄ powders. The crystal phase of as-prepared Al doped LiMn₂O₄ powders were agreement with spinel structure (Fd3m) regardless of doping agent. However, Mn₂O₃ phase was also observed in as-prepared powders. It was considered that MnCO₃ could not uniformly react with LiOH·H₂O in the mist during the pyrolysis. After the calcination, the peaks of Mn₂O₃ disappeared and the crystal phase of Al doped LiMn₂O₄ powders converted to the spinel structure with high crystallinity in all samples.

Figure 3 shows typical SEM photographs of as-prepared Al doped LiMn₂O₄ 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 LiMn₂O₄ powders, (a) as-prepared, (b) 800 °C for 4 hr, (A) Al(OH)₃, (B) Al(NO₃)₃, (C) Al₂O₃.

they consisted of primary particles. Specific surface area of as-prepared Al doped LiMn_2O_4 powders derived from Al_2O_3 nanopowders, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$ 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, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$ 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, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$ 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, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$ 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, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$ 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 doped LiMn_2O_4 derived from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ exhibited highest rechargeable capacity among the doping agent because $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was only dissolved in the starting solution. On the other hand, since $\text{Al}(\text{OH})_3$ and Al_2O_3 was not dissolved in the starting solution, the homogeneity of aluminum ion in LiMn_2O_4 particles was lower than that of LiMn_2O_4 particles derived from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. 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, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$ 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) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (c) $\text{Al}(\text{OH})_3$.

Fig. 4 SEM photograph of Al doped LiMn_2O_4 powders calcined at 800 °C.

(a) Al_2O_3 nanopowders, (b) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (c) $\text{Al}(\text{OH})_3$.

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.

Acknowledgement

This work was supported by Development of an Electric Energy Storage System for Grid-connection with New Energy Resources in New Energy and Industrial Technology Development Organization.

References

- [1] E. Karden, S. Ploumen, B. Fricke, T. Miller and K. Snyder : J. Power Sources 168 (2007), p. 2
- [2] Z. Pegeng, F. Huiqing, F. Yunfei, L. Zhuo and D. Yongli : Rare Metals 25 (2006), p. 100
- [3] T. Ogihara, N. Ogata, K. Katayama and Y. Azuma : Electrochemistry 68 (2000), p. 162
- [4] K. Myoujin, T. Ogihara, N. Ogata, N. Aoyagi, H. Aikiyo, T. Ookawa, S. Omura, M. Yanagimoto, M. Uede and T. Oohara : Adv. Powder Technol. 15 (2004), p. 397
- [5] I. Taniguchi, D. Song and M. Wakihara : J. Power Sources 109 (2002), p. 333
- [6] M.M. Thackeray : J. Electrochem. Soc. 142 (1995), p. 2558
- [7] A. Kock, E. Ferg, R.J. Gummow : J. Power Sources 70 (1998), p. 247
- [8] H. Kobayashia, H. Sakaebe, K. Komoto, H. Kageyama, M. Tabuchi, K. Tatsumia, T. Kohigashi, M. Yonemura, R. Kanno, T. Kamiyama : Solid State Ionics 156 (2003), p. 309
- [9] K.M. Shaju, G.V. Subba Rao, B.V.R. Chowdari : Solid State Ionics 148 (2002), p. 343

Electroceramics in Japan XIV

doi:10.4028/www.scientific.net/KEM.485

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

doi:10.4028/www.scientific.net/KEM.485.111