

Synthesis and Characterization of Oxide Nanoparticles by Plasma Assisted Spray Pyrolysis

Takayuki Kodera, Hajime Horikawa, Takahiro Nakamura,
Kenichi Myoujin and Takashi Ogihara

University of Fukui, 9-1 Bunkyo 3, Fukui-shi, Fukui, 910-8507 Japan
Fax: 81-0776-27-8624, e-mail: ogihara@matse.fukui-u.ac.jp

Various oxide nano-sized powders were successfully prepared by ultrasonic spray pyrolysis using arc plasma under the air atmosphere. Particle size, morphology, crystal phase and crystallinity of as-prepared powders were characterized by SEM and XRD. They had spherical morphology with narrow size distribution.

Key words: spray pyrolysis, oxide, plasma, nanoparticles

1. INTRODUCTION

Now, nano-sized oxide particles are noted as starting materials in electronic device, catalyst, filler and energy material. To achieve the formation of nano-sized particles, various solution technique such as sol-gel and hydrothermal and gas phase reaction have been developed. Spray pyrolysis technique [1-3] is one of solution technique and has the following potential advantage : (1) as-prepared particles are spheres with a high surface area, (2) chemical homogeneity is enhanced relative to solid state reaction, (3) oxide powders can be directly prepared and take much shorter than that is required for solid state reaction and the sol-gel method. It is well-known that ultrasonic spray pyrolysis has been applied to preparation of submicrometer oxide precursor particles with narrow sized distribution.

However it was difficult to prepare nano-sized powders by spray pyrolysis using electrical furnace because the break down sized of droplets generated by ultrasonic is limited at less than 1000 °C. Okuyama et al [4,5] reported that oxide nanoparticles could be obtained by salt-assisted spray pyrolysis.

On the other hand, we have been offered novel nano-sized oxide powders preparation system [6] in which the mist of starting solution was pyrolyzed over

7000 °C by arc plasma under air atmosphere.

In this paper, single and multicomponent oxide powders such as MgO, BaTiO₃ and LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ were synthesized by spray pyrolysis using arc plasma and their particle characteristics were also investigated.

2. EXPERIMENTAL PROCEDURE

Magnesium nitrate was used as starting solution of MgO. Barium nitrate and titanium tetraisopropoxide were used as starting solution of BaTiO₃. Titanium tetraisopropoxide was dissolved in water by using nitric acid or citric acid because titanium tetraisopropoxide was easily hydrolyzed to form hydroxide in the water. Metal carboxyl acid and lithium nitrate were used as the starting solution of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂. These were dissolved in water at 25°C. The concentration of starting solution ranged from 0.1 to 0.5mol/L.

The schematic diagram of ultrasonic spray pyrolysis apparatus with arc plasma was shown in Fig.1. The apparatus consisted of mist box, drying furnace, plasma reactor and powder collector. The starting solution was misted at 2.4MHz by an ultrasonic nebulizer (Honda Electronics, HM-2412) in mist box and dried in drying furnace at 200°C. After drying, the mist was introduced into plasma reactor by air carrier gas. The flow rate

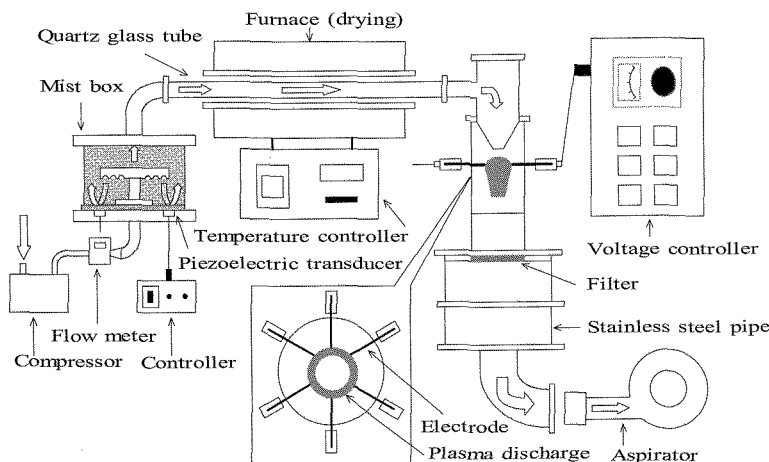


Fig.1. Schematic diagram of apparatus

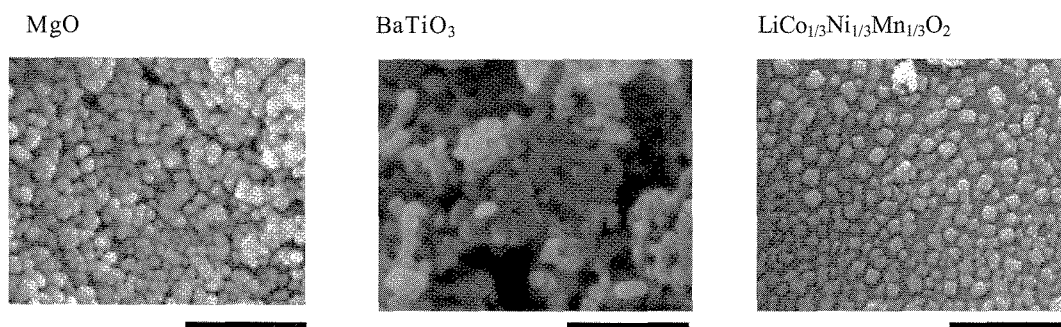


Fig.2 SEM photographs of as-prepared powders (bar=1 μ m)

ranged from 1 to 10L/min. The mist was continuously pyrolyzed by arc plasma under an air atmosphere. The pyrolysis temperature was adjusted by voltage controller and ranged from 7000 to 10000°C. Oxide precursor nanoparticles were collected using a collision type filter in powder collector. However, many particles passed the mesh because the mesh size of filter was barely large than the particle size.

Crystal phase of as-prepared powders and calcined powders was identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using $\text{CuK}\alpha$ radiation. Particle size and morphology were determined by scanning electron microscope (SEM, Hitachi, S-2300). The average particle size was determined by randomly sampling 200 particles from SEM photographs. The particle surface was measured by DTA-TG. Specific surface area of as-prepared powders was measured by BET method using N_2 adsorption (SSA, Shimadzu, Tristar-3000). The chemical composition of as-prepared powders was determined by atomic adsorption spectrum analysis (AAS, Shimadzu, AAS-6800). Dielectric properties of BaTiO_3 ceramics were measured by LCR meter (Kokuyo Denki, KC-537) at 100 kHz. Lithium secondary battery was produced by $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (cathode) and Li sheet (anode). Electrochemical properties of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were measured by battery tester (Hosen BTS-2005). The charge/discharge capacity and cycle life were investigated.

3. RESULTS AND DISCUSSION

The production capacity of as-prepared powders was about 0.1g/h when the solution concentration was

0.1mol/L. The yield of as-prepared powders was about 10%. This resulted in low collecting performance of filter used in synthesis. Figure 2 shows typical SEM photographs of typical MgO , BaTiO_3 and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ nanoparticles, respectively. They had spherical morphology with narrow size distribution. The average size of as-prepared particles determined by SEM photographs was less than 100 nm in all samples. It was found that the particle size of as-prepared powders was smaller than those obtained by ultrasonic spray pyrolysis using electric furnace. However, the particle size was not changed although the starting solution concentration was increased up to 0.5mol/L.

On the other hand, the geometrical standard deviation of their average size ranged from 1.3 to 1.5 regardless of starting solution concentration. It was found that few wt% of water was contained in all as-prepared powders from DTA-TG analysis. About 10wt% of undecomposed nitrate was also contained in MgO nanopowders. SSA of as-prepared powders was 10 – 20 m^2/g . The chemical composition of as-prepared powders determined by AAS was good agreement with that of starting solution composition.

The crystal phase and crystallinity of as-prepared powders and calcined powders were identified by XRD. Figure 3 shows XRD patterns of as-prepared powders and calcined powders. XRD revealed that the crystallinity of as-prepared MgO , BaTiO_3 and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders was very low and the phase of barium carbonate was also observed in BaTiO_3 . The crystallinity of as-prepared powders was not improved although pyrolysis temperature was increased

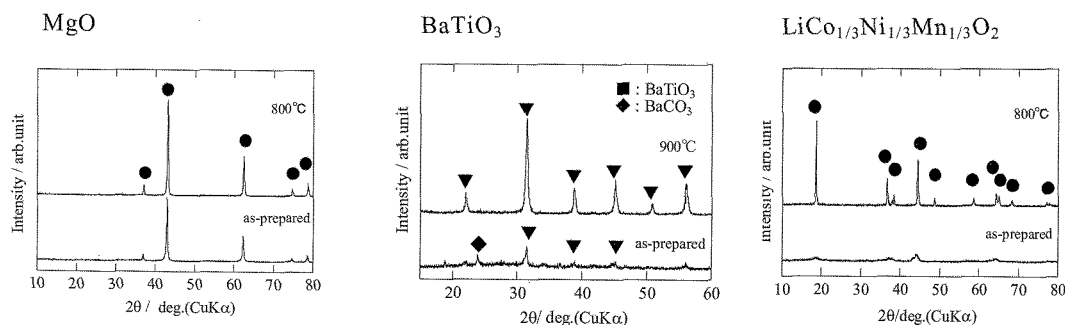


Fig.3. XRD patterns of as-prepared and calcined powders

from 7000 to 10000°C. This resulted in the very short residence time of mist in the plasma reactor. The residence time was few second in the plasma reactor. After the calcination at more than 800°C, the crystallinity of them became higher than that of as-prepared powders. The phase of barium carbonate also disappeared in BaTiO₃. Chemical analysis revealed that Ba/Ti ratio of as-prepared powders was agreement with starting solution component. 5% particle size of BaTiO₃ particles decreased by the calcination at more than 800°C and as-prepared particles were also nonaggregated. The sinterability of BaTiO₃ nanopowders was compared with commercial BaTiO₃ (KCM corporation, The average size of BaTiO₃ particles was 240nm.) powders. The relative density of BaTiO₃ nanopowders was 92% at 1200°C. That of commercial BaTiO₃ powders was 80%. It was found that BaTiO₃ powder obtained by aerosol plasma pyrolysis was sintered in lower temperature compare with commercial BaTiO₃ powders because the average size of BaTiO₃ particles obtained by aerosol plasma pyrolysis was very small. The dielectric constant and tanδ of BaTiO₃ ceramics obtained from nanopowders was about 2000 and 0.025 at 25°C, respectively.

Figure 4 shows the discharge properties of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ as a cathode for lithium secondary battery. The discharge curves of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ were measured from 2.5V to 4.1V at rate of indicated. As shown in Fig.4 (a), the s type of smooth line was plotted in the discharge curves. The discharge capacity of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ determined by discharge curves were 140 under the rate of 2C (current density of 2mA/cm²). These are higher than that of LiCoO₂ and LiMn₂O₄. The discharge capacity decreased to 90mAh/g under the rate of 10C.

The cycle performance for discharge of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ was also examined. Figure 5 shows the relation between discharge capacity and cycle number at 25°C. The discharge capacity gradually decreased with increasing cycle number. After 50 cycles, 90% of discharge capacity at first was maintained under the rate of 1C. 80% of it was also maintained under the rate of 10C.

The heat-resistance of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ was investigated by examined cycle performance at 80°C.

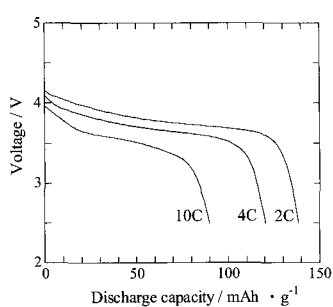


Fig. 4 Discharge curves at the rate of 2C to 10C

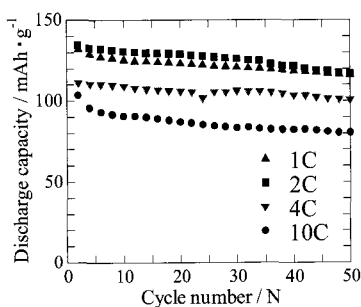


Fig. 5 Relation between discharge capacity and cycle number at room temperature

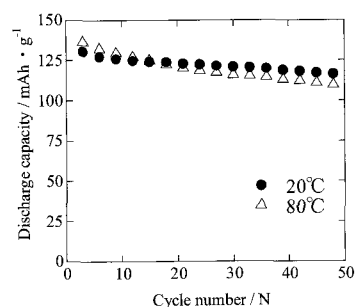


Fig. 6 Relation between discharge capacity and cycle number at 20°C and 80°C

Figure 6 shows the relation between discharge capacity and cycle number at 20°C and 80°C under the rate of 1C. The discharge capacity decreased with increasing cycle number. The cycle performance at 80°C was much the same as that at 20°C. It was found that the discharge of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ could be done at high temperature.

4. CONCLUSION

Various types of oxide nano-sized powders were successfully prepared by ultrasonic spray pyrolysis using arc plasma under the air atmosphere. As-prepared powders had uniform morphology with narrow size distribution. The chemical composition of BaTiO₃ and LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ nanopowders was good agreement with the starting solution composition. The crystallinity of as-prepared powders was low, but improved by calcined at more than 800°C.

The dielectric constant and tanδ of BaTiO₃ ceramics obtained from nanopowders was about 2000 and 0.025 at 25°C, respectively. The discharge capacity of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ was 140mAh/g and 90mAh/g under the rate of 2C and 10C, respectively. Discharge capacity of them decreased with increasing cycle number. The discharge of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ could be also done at 80°C.

References

- [1] G. L. Messing, S. C. Zhang and G. V. Javanthi, *J. Am. Ceram. Soc.*, 76, 2707-26 (1993).
- [2] H. Ishizawa, O. Sakurai, N. Mizutani and M. Kato, *Am. Ceram. Soc. Bull.*, 65, 1399-1402 (1986).
- [3] B. Dubois, D. Ruffier and P. Odier, *J. Am. Ceram. Soc.*, 72, 713-15 (1989).
- [4] B. Xia, I. W. Lenggoro and K. Okuyama, *J. Mater. Chem.*, 11, 2925-27 (2001).
- [5] Y. Ito and K. Okuyama, *J. Ceram. Soc. Jpn.*, 111, 815-20 (2003).
- [6] T. Kodera, H. Horikawa, T. Ogihara, N. Ogata, K. Nakane, S. Omura, M. Uede, K. Higeta and S. Hiyama, *Electroceramics in Japan*, 9, 135-138 (2006).

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