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Evaluation and renovation of a mechanical activator for highly reactive precursors of electroceramics

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Abstract

To obtain precursors of a solid state reaction as reactive as possible, factors from the viewpoint of machine construction are examined. An example is given for successful synthesis of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ by using a multi-ring-type mechanical activator. With a renovation of the activator, the homogeneity and recovery of the products are increased. In order to delineate effects of renovation, samples and data from the area outside of electroceramics are also involved.

Keywords: Milling; Grain size; Reactivity; Spinels; Batteries

1. Introduction

While the downsizing and upgrading of electronic devices are proceeding tirelessly, additional requirements of environmentally benign processes make the process engineering of electroceramic materials more challenging. One of the most important items for this challenge is the ceramic processing at the incipient stage of solid state reactions before and during calcination. In this context, it is of utter importance to make the starting mixtures as reactive as possible.

The authors have paid, until now, substantial efforts to prepare highly reactive precursors by virtue of mechanochemical or soft-mechanochemical effects.[1–5] In view of the factors mentioned above, however, we have to improve overall efficiency of the pretreatment operation. This has to be done from the viewpoints of machine construction and operation optimization simultaneously.

Several years ago, we have established a multi-ring-type finest grinding machine. Details of the construction and operating mechanisms were given elsewhere.[6,7] An equipment without freely moving grinding media, unlike any kinds of ball mills or beads mills, has intrinsic benefits among others with a good predictability of scaling up. This was developed under the condition of wet-operation, although we obtained nanoparticles in dry operation as well.[8,9] We, therefore, subsequently developed a daughter machine for dry operation.[10] It turned out, however, that the machine still needs to be improved. Problems are mostly associated with insufficient homogeneity of the product and contamination.

We here demonstrate the effect of using a multi-ring-type mill on the preparation of complex oxide, $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. We discuss subsequently a renovation of the activator, to increase the homogeneity, degree of amorphization and recovery of the products. In order to delineate effects of renovation, samples and data from the area outside of electroceramics are also involved.

2. Experimental

2.1. Preparation of precursors for $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$

We prepared precursors for $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ by starting from $LiOH{\cdot}H_2O$ as a Li source, and $Ni(OH)_2$, CoOOH and Mn_2O_3, as transition metal sources. A stoichiometric mixture with a molar ratio Li:Ni:Co:Mn, 3:1:1:1 was mechanically activated by a multi-ring-type mechanical activator, Mechano-Micros® (M-MIC), Nara Machinery (see below for details), for 90 min. Rings and lining of the vessel were made of yttria-stabilized zirconia. Activated precursors were calcined at temperatures up to 1000 °C in air. Samples were characterized mainly by a field emission-scanning electron microscope (FE-SEM, S4700, Hitachi), a laser diffraction particle size

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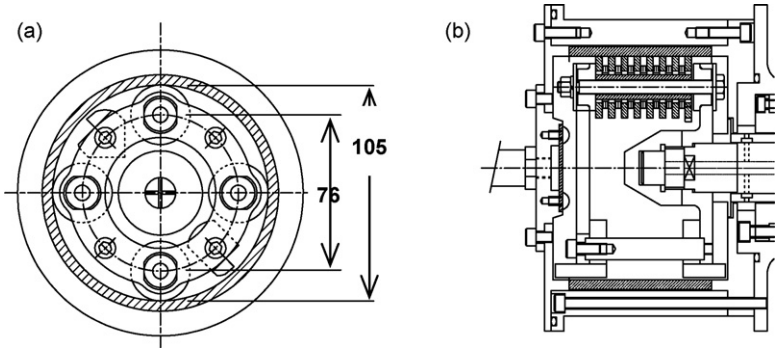

Fig. 1. Scheme of the structure of M-MIC: (a) the front and (b) the cross-sectional views.

analyser (LS, LS230, Beckman Coulter) and an X-ray diffractometer (XRD, RAD-C, Rint 2000, Rigaku).

2.2. Description of mechanochemical activator and its renovation

A scheme of M-MIC is given in Fig. 1. This is a daughter machine of the first multi-ring mill, MICROS® with a vertical rotating shaft.[6,7] The main part of M-MIC comprises a horizontally rotating main shaft with co-rotating four sub-shafts. A stack of thin toroidal disks or rings is mounted through each sub-shaft. Since the inner diameter of a ring is slightly larger than that of a sub-shaft, the periphery of the disk is forced to shift radially outward by the centrifugal force. All the powdery material inside is captured in the space between the ring and the inner wall of the vessel and subjected to compressive and shear stresses. The vessel and the main shaft are usually counter-rotating to enhance the shear stress exerted on the sample. The machine is operated under gas flow, either air, inert gases or reactive species, if necessary.

Renovation of M-MIC is now being carried out to rename to MIRALO®. As shown in Fig. 2, we reduced the number of sub-shafts from 4 to 2 to give more homogeneous shear stresses to the powdery specimen. In order to reduce the amount of the product attached to the inner wall of the vessel as well as rings and shafts, we tried to decrease the free-space in the vessel. The total number of the rings was reduced from 30 to 18. We also devised to install detachable scrapers at both ends of the rotor. Effect of renovation was evaluated in two different aspects, i.e. (1) by the change in the fractions of the products, i.e. free powders, samples attached to the machine and nonrecoverable loss, and (2) by the degree of amorphization.

3. Results and discussion

3.1. Synthesis of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$

As shown in Fig. 3, effects of mechanical activation on the precursor of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ are quite obvious. While the calcined product from the intact mixture contains Li_2MnO_3 and $LiCoO_2$ as second phases (profile a), the activated precursor results in a phase pure $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. Effects of precursor activation are clear on the particle size and morphology as well. As shown in Fig. 4, the grains are finer, more homogeneous and spherical by starting from the activated precursor.

3.2. Homogenization by mechanical activation

Now we discuss the change in the homogeneity during mechanical activation by M-MIC. Increase in the mean particle size of the precursor determined by LS was observed by mechanical activation, i.e. from 0.11 ± 0.16 to 0.28 ± 0.25 μm. Variation coefficients, i.e. standard deviation divided by the mean value of particle size of the precursor were reduced from 140 to 90 by the activation for 90 min. Likewise, those for the products were 220 (0.15 ± 3.2 μm) and 78 (1.9 ± 1.5 μm) by starting from the precursor without and with the mechanical activation, respectively.

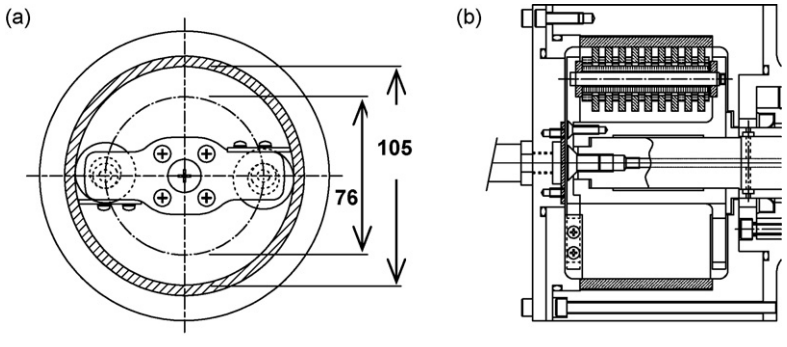

Fig. 2. Scheme of the structure of MIRALO: (a) the front and (b) the cross-sectional views.

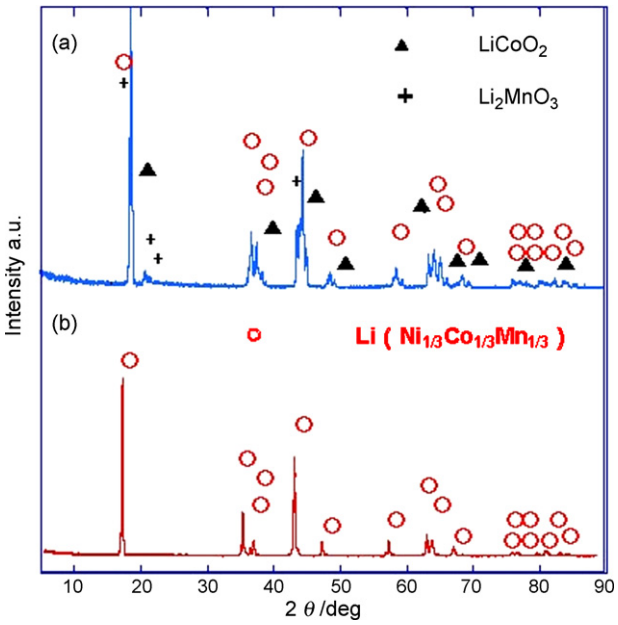

Fig. 3. XRD profiles of calcined products starting from precursors: (a) without and (b) with milling by M-MIC for 90 min in N_2 gas. Each precursor was calcined at 1000 °C for 1 h in air to synthesize $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$.

When we observe the local atomic concentration by an X-ray fluorescent microscope, homogenization of the local atomic concentration is also obvious. As shown in Table 1, the local composition becomes much closer to the theoretical one after mechanical activation on the samples before and after calcination. Reduction of the variation coefficient is also remarkable.

3.3. Improvement by machine renovation

While we are not ready to demonstrate the effect of machine renovation by the same $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ system, increase in the degree of amorphization, homogeneity and fractional recovery is given by the examples below.

(i) Effective recovery: it is practically very important to reduce the amount of the sample attached to the machine elements and/or vessel walls to increase the fraction of recovery. As shown in Fig. 5 for the precursor of $MgTiO_3$, the effective recovery as free powders was increased by 24%. Attachment to the vessel wall was reduced by 39%. The tendency was quite similar when we changed the test material from the mixture of $Mg(OH)_2$ and TiO_2 to an organic compound like indomethacin.

(ii) Degree of amorphization: change in the degree of amorphization of indomethacin with the activation (milling) time is shown in Fig. 6. Homogeneity of the sample was improved while keeping the degree of amorphization nearly the same. We also observed the local difference in the degree of amorphization. As shown in Fig. 7, the sample collected near the front lid was much less amorphous (profile c) and close to that of intact (profile a). After renovation, the local variation of the degree of amorphization became much smaller, as shown by profiles d and e. This is another indication of the increase in the homogeneity of the products by the renovation. Although the degree of amorphization slightly decreased after renovatation, under the present operating condition, simultaneous increase in the homogeneity to a significant extent outweighs the slight deamorphization.

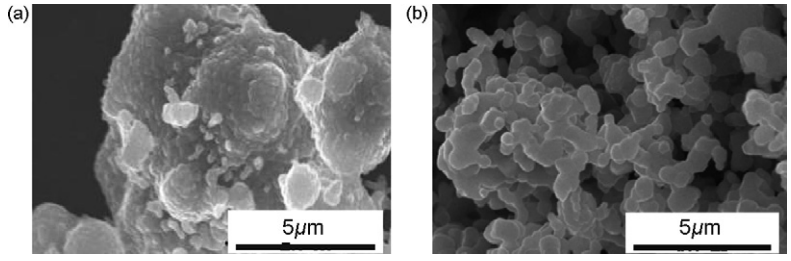

Fig. 4. SEM images of calcined products starting from precursors: (a) without and (b) with milling by M-MIC for 90 min in N_2 gas. Each precursors was calcined at 1000 °C for 1 h in air to synthesize $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$.

Table 1
Fluctuation of the metallic composition measured by X-ray microscope

	Intact (wt%)			Milled for 90 min (wt%)		
	Mn	Co	Ni	Mn	Co	Ni
Theoretical average	31.8	34.2	34.0	31.8	34.2	34.0
Before calcination						
Average	19.7	51.9	28.4	23.9	36.8	39.2
Standard deviation	7.3	23.0	17.0	3.1	5.2	4.1
Variation coefficient[a]	37	44	61	13	14	10
Calcinated at 1000 °C for 1 h						
Average	32.5	25.5	41.9	28.6	33.9	37.5
Standard deviation	6.3	13	10.5	1.8	2.2	1.1
Variation coefficient[a]	20	51	25	6.2	6.6	3.0

[a] Values of variation coefficients [–].

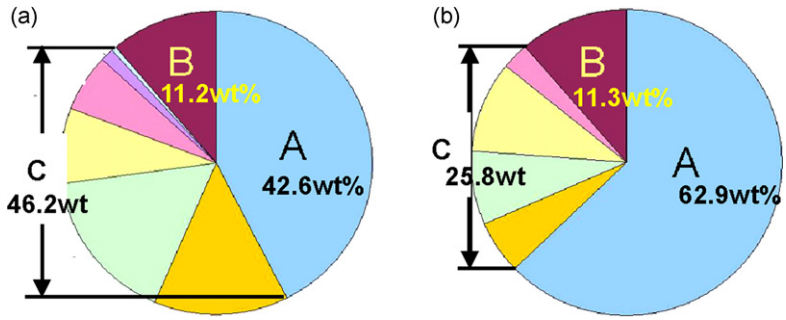

Fig. 5. Breakdown of product ($Mg(OH)_2$ and TiO_2), treated by: (a) M-MIC and (b) MIRALO. Area 'A' indicates the primary recovery, 'B' is the loss and 'C' is the adhesion on the different areas of the vessel wall.

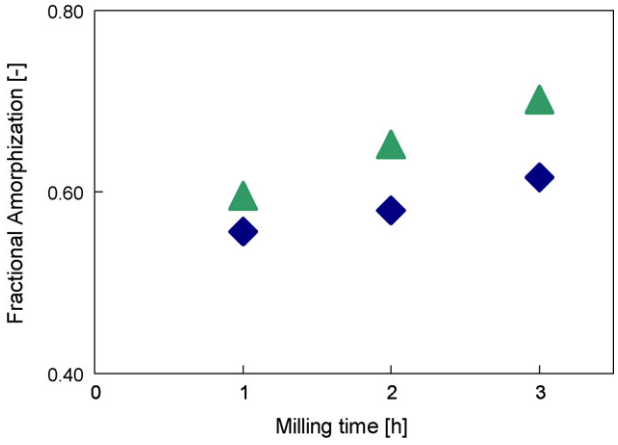

Fig. 6. Change of maximum peak intensities of indomethacin, before and after milling. Triangular marks indicate the data from M-MIC, and diamond marks, from MIRALO.

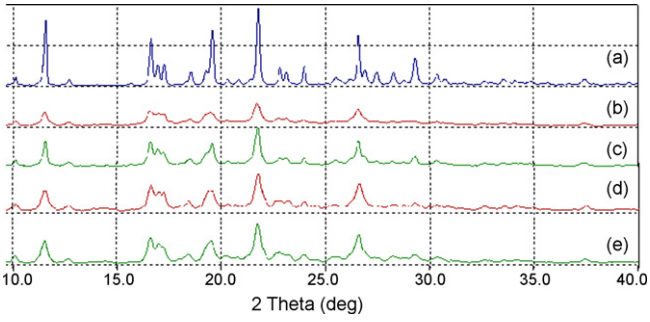

Fig. 7. XRD profiles of indomethacin: (a) intact, (b–c) milled by M-MIC and (d–e) by MIRALO. (b and d) Primary recoveries and (c and e) adhesion on the vessel wall. Milling time: 180 min.

4. Concluding remarks

By mechanically activating the mixture of $LiOH{\cdot}H_2O$, $Ni(OH)_2$, CoOOH and Mn_2O_3, with a multi-ring mill, phase pure $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ was obtained, mainly due to preliminary incipient reaction, homogenization and simultaneous size reduction during activation operation. Homogenization and recovery were improved by renovation of the machine to reduce the dead space of the machine.

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