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Preparation of $LiMn_2O_4$ particles by glucose-assisted combustion method

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Lithium manganese oxide ($LiMn_2O_4$) powders with particle sizes in the range of 100–600 nm have been synthesized through glucose-assisted combustion synthesis. The presence of glucose increases the stability of the precursor solution, purity of the heat-treated powders, and decreasing on size of the synthesized particle. The formation of complex metal salts-glucose in the precursor solution and effect of the methods for preparing solid precursors on the final product were investigated.

Key-words : Spray drying, Metal oxide, Saccharide, Complex, Submicron, Powder

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1. Introduction

Combustion synthesis is a facile method for preparing metal oxides with advantages on high-purity products, low reaction temperature, short reaction time and one-step process.1) To date, metal oxide production via combustion synthesis has been reported widely. Various compounds such as tartaric acid,2) oxalic acid,3),4) urea,5) sucrose,6) L-alanine,7) glycine,8) citric acid,9)–14) hexamethylenetetramine,15) poly acrylic acid,16) and succinic acid17) have been utilized as fuel. Addition of the fuels controls the size of produced particles and increases conductivity due to the presence of carbon residue.

The procedure for preparing precursor material prior to combustion is an important factor to consider since it influences the morphology of the synthesized metal oxide particles. Solid-to-solid route where all solid precursors are mixed macroscopically by grinding suffer from inhomogeneous particle size distribution.18) In order to overcome the homogeneity problem, liquid-to-solid routes are used. The sol–gel also known as the Pechini method is a popular example of the liquid-to-solid route for producing fine particles.9) Complexing agents e.g. citric acid-glycol10),19) or glycine-nitrate compounds8) are utilized to tie the metal ion in a small size of homogenous clusters. However, this method requires additional chelating chemicals and pre-heat treatment to obtain dry precursor, increases production cost and time.

Glucose is a reducing saccharide, which can forms a complex with metal ions by deprotonation of its hydroxyl groups.20)–22) The use of glucose in combustion synthesis of $LiMn_2O_4$ in the last two decades has been reported in several papers. Fortunato et.al in 2001 reported the ultrasonic aerosol pyrolysis technique for producing spinel structure metal oxide with glucose.23) Kumar et.al in 2003 used glucose as mild reductant for synthesis of $LiMn_2O_4$ nanoparticles from electrolytic MnO_2 in an aqueous reduction method.24) Liang et.al in 2005 used one step low temperature route to produce $LiMn_2O_4$ also from electrolytic MnO_2.25) Zhou et.al, 2013, in the most recent work, reported a solid-state combustion method, where the glucose was ball-milled with solid precursors and calcined at 500°C for 1 h.18) However the advantages of glucose on forming metal ion complexes in aqueous solution and its effect on the morphology of produced particles are still unexplored.

In the present work, a spray drying method was utilized for preparing dry powders from the precursor metal salt solution prior to combustion. This method offers shorter preparation time26),27) compared to sol–gel method, leading to higher productivity. Fast-evaporation in the spray drier preserves the homogeneity of the precursor metal salt solution eliminating the need for additional chelating agents. For comparison purposes, the conventional solvent evaporation method was also employed to prepare $LiMn_2O_4$ particles. The effect of the presence of glucose in the precursor solution was also investigated.

2. Experimental

Precursors solutions were prepared from manganese acetate [$Mn(CH_3COO)_2.4H_2O$, 99%, Wako Chemicals, Tokyo] and lithium acetate ($CH_3COOLi.2H_2O$, 98%, Wako Chemicals, Tokyo), and D-Glucose ($C_6H_{12}O_6$, Kanto Chemicals, Tokyo) which were dissolved in ultra pure water. The solutions have a stoichiometric ratio of Li (0.02 moles) to Mn atoms (0.04 moles) and various concentrations of glucose. The dry precursors were obtained from the solution through two different pre-treatment methods, i.e. Method 1 and Method 2. In Method-1, the precursor solutions were stirred at room temperature (RT, 20°C) to obtain a clear solution. The solutions were subsequently introduced into a spray-drier (B-290, BÜCHI Labortechnik AG, Flawil) to obtain dry precursors. The drier utilized air with inlet and outlet temperatures that were set at 180 and 100°C, respectively. The produced dry mixed powders were collected in a cyclone separation system and were ready for heat treatment. In Method-2, the precursor solutions were heated at 70°C on a hot plate as they were continuously being stirred. The resulting gel-like slurry was transferred

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to a ceramic crucible and was ready for heat treatment.

Heat treatment for synthesis of $LiMn_2O_4$ particles was performed inside a programmable electric furnace. The temperature of the furnace was increased from RT to 500°C within 3 h under static air atmosphere condition. The post-heated samples were collected and ground to a fine powder by hand using pestle and mortar. Combustion of the precursor powders prepared by Method-1 was studied using thermogravimetric and differential thermal analysis (TG–DTA) instrument (TG8120, Rigaku, Tokyo). The precursor powders were heated under static air atmosphere from room temperature of 20 to 500°C at a heating rate of 168°C h^{-1} (similar to the heating profile applied in the electric furnace). The crystal structure of the produced metal oxide particles was studied by powder X-ray diffraction instrument (RINT2100VPC/N Rigaku, Tokyo) with a Cu Kα radiation. The instrument was operated at 2θ range of 10 to 70° and scan rate of 0.5° min^{-1}. Particle morphology and size distribution was investigated using field emission scanning electron microscope (JSM 6330FS, JEOL, Tokyo) and Dynamic Light Scattering (DLS) instrument (Zetasizer nano ZS, Malvern Instruments Ltd., Worcestershire) respectively. Raman scattering instrument (Nicholet Almega, Thermo Fisher Scientific Inc., Waltham) with laser wavelength of 532 nm was also used for chemical characterization.

3. Results and discussion

3.1 Effect of glucose on the stability of precursor solution

Glucose is known as a reducing monosaccharide because of its ability to form an aldehyde group in an open-chain form. This aldehyde group can be oxidized in a reduction–oxidation reaction. In an aqueous solution, the closed-chain form of D-glucose is thermodynamically more stable, although mutarotation temporarily provides the open-chain form.[28] The three adjacent hydroxyl groups in closed-chain form of glucose also can make a complex with metal ions either by axial-equatorial-axial or axial-axial-axial site, depending on the size of the ion.[29] Li^+ ions preferably attach to the former site while Mn^{2+} ions to the later ones.[30] The complex formation can increases solubility of the metal ions.

The experiments however, show a complex interaction among Li^+, Mn^{2+} ions, and glucose. The aqueous solutions containing both Mn-acetate and Li-acetate suffer from precipitation. A brown precipitate observed after the solution being left to stand for a while at room conditions was indexed as MnO(OH), based on X-ray diffraction analysis. In the presence of glucose, the solution became stable, where no detected precipitation even after 45 h (see inset Fig. 1). The interactions were studied further by adding glucose to individual solution of Mn^{2+} and Li^+ ions. Glucose was added at Glucose Molar Ratio (GMR) of 1 and stirred for 3 h prior to observation. The precipitation was detected in the Mn-acetate solution with glucose as in the Li–Mn-acetate solution without glucose, but not in solution of Li-acetate with glucose.

We analyzed the solution and precipitate using Raman and XRD, respectively, to confirm the ions interaction. The Raman spectrums are depicted in **Fig. 1**. The solution of glucose shows specific Raman peaks at 697, 1461, and 1777 cm^{-1} along with others peaks, which can be assigned to skeletal vibration of glucose, CH_2 vibration e.g. CH_2 twisting or bending,[31),32] and $\nu(C{=}O)$ stretching vibrations,[33] respectively. The fresh Li–Mn solution shows Raman specific peaks at 408, 808, 990, 1102, and 1158 cm^{-1}, which are not detected in the solution with glucose. In addition, the presence of glucose in the fresh Li–Mn solution leads to appearance of Raman peaks of glucose at 597, 859, and 1023 cm^{-1}. The C–C stretching vibration of aqueous CH_3COO^- were identified in both solutions from Raman band of 932 cm^{-1}.[34]

After 18 h left in room condition, Raman peaks at 393 and 571 cm^{-1} appear in the Li–Mn solution without glucose, which are ascribed to Mn–O bond of MnO(OH).[35] The MnO(OH) compound detected in the precipitate by the XRD analysis support the conclusion. The water band of 1640 cm^{-1}[31] shift to 1635 cm^{-1}, probably from interaction of O–H bonding with the Mn^{2+} ions during solvation. In case of Li–Mn-glucose solution, the addition peaks at 1773 and 1904 cm^{-1} are detected after 18 h. The 1773 cm^{-1} peak is ascribed to shifting of $\nu(C{=}O)$ stretching vibration from aldehyde groups of glucose (1777 cm^{-1}), which may correlate with formation of complex.

A schematic diagram of the proposed interaction is depicted in **Fig. 2**. The Mn^{2+} ions can be oxidized to form insoluble brown manganese hydroxide, where the process increases in the

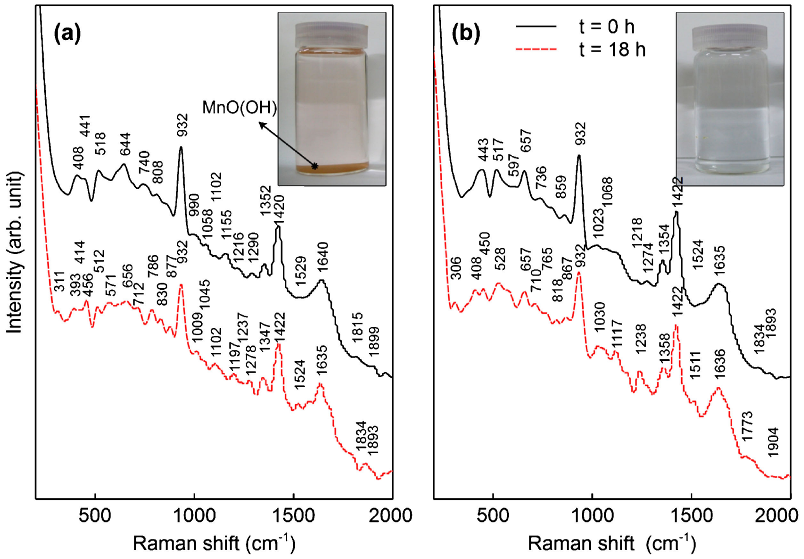

Fig. 1. Raman spectra of precursor solutions (a) without glucose (b) with glucose at GMR of 3. The inset figures are images of the solution after standing for 45 h at room conditions.

presence of an oxidant, e.g. air or glucose.[36] In the aqueous solution, the Mn^{2+} ions transforms into soluble $[Mn(H_2O)_6]^{2+}$ ions.[10] The addition of glucose increases the pH, leads to formation of less stable $[Mn(H_2O)_4(OH)_2]^+$ and H^+ ions as a counterbalance towards the changing pH. Further reaction results in the insoluble brown MnO(OH) compound. The Li^+ ions are supposed to stabilize the $[Mn(H_2O)_4(OH)_2]^+$ ions by forming a lithium-manganese aqua-complex, preventing precipitation from occurring.

3.2 Effect of glucose on decomposition mechanism

When glucose is heated, it slowly decomposes into a carboneous material in at least three stages.[37] The first stage starts from melting point of the glucose at 185°C and ended at 230°C. Formation of poly- and oligosaccharides was occurred as indicated by endothermic peak. This process also occurred in the other steps and was accompanied by release of water and carbon dioxide. The weight loss for 46% in the second stage indicates the decomposition of the poly- and oligosaccharides. The third stage of the decomposition which ended at 500°C produced an insoluble carboneous material. The Raman spectrum at wavenumber of 1355 (D-band) and 1575 cm^{-1} (G-band) confirmed the presence of carbon residue. It has been reported that carbon residue up to 2 wt% can increase conductivity and chemical capacity of the Li-ion batteries.[38]

The effect of the presence of glucose on the decomposition mechanism of the individual metal salts was also studied. The interaction between glucose and the metal salts was clearly detected in the TG–DTA curve. In case of Li-acetate decomposition, two notable exothermic peaks at 153 and 390°C became undetectable in the presence of glucose. Initial decomposition temperature also decreased from 328 to 115°C. In the case of Mn-acetate, decrease of the initial decomposition temperature from 240 to 146°C was also detected. The two exothermic peaks at 283 and 320°C had changed to be only one peak (at 332°C) in presence of glucose. The two peaks observed in the absence of glucose were considered to be due to consecutive oxidation of Mn^{2+} to MnO and Mn_2O_3.[39] In the presence of glucose, excess heat released from combustion of glucose causes the two reactions to occur in one step. This was evidenced by the absence of MnO peak in the XRD spectra of oxide particles prepared with glucose addition.

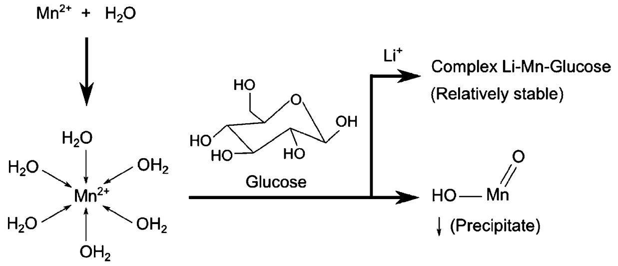

Fig. 2. Schematic diagram of proposed metal-glucose interaction.

The effects of glucose on combustion synthesis of $LiMn_2O_4$ powder are shown in **Fig. 3**. Powders obtained from spray-drying the precursor solution were heated in the TG–DTA apparatus. The difference observed on the TG profile due to the presence of glucose indicates changes in the decomposition mechanism. The two notable weight loss stages which began at 40 and 220°C respectively changed to be at least four stages in the presence of glucose. The first and second stages are considered be due to water evaporation and releasing of gases from glucose combustion (i.e. CO_2 and H_2O). The gradual weight loss in the third stage is indicated as polymerization and decomposition of glucose. The steep weight loss accompanied by an exothermic peak in the last stage is related to the formation of $LiMn_2O_4$.[40]

The exothermic peak position shifted from 291°C to around 360°C in the presence of glucose. Polymerization and decomposition of glucose which occurred prior to formation of the metal oxide are considered to be the reason for the exothermic peak shift. Two exothermic peaks (at 357 and 365°C) appeared when glucose concentration was increased to GMR of 4. The peaks may come from oxidation of Mn precursor because a similar peak was detected in the thermal decomposition of Mn-acetate powders. The presence of secondary phases in XRD spectra indicated that excess amounts of glucose reduces phase purity of the synthesized $LiMn_2O_4$ particles.

3.3 Effect of dry precursor preparation method on crystal structure of $LiMn_2O_4$

X-ray diffraction spectra of the synthesized particles shown in **Fig. 4** confirm the $LiMn_2O_4$ compound based on the ICDD PDF

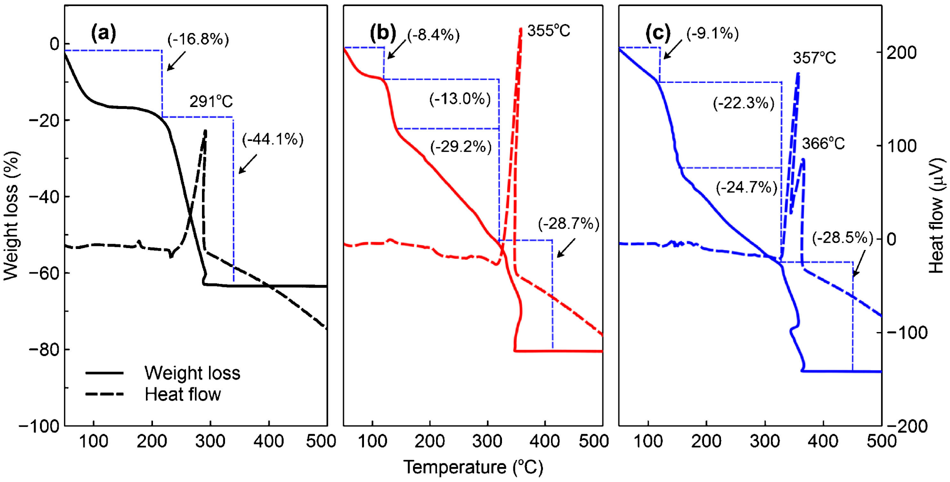

Fig. 3. TG–DTA curves of spray dried precursor powders (a) with no glucose (b) with glucose at GMR of 2 and (c) with glucose at GMR of 4. Temperature stated in the figures indicate peak temperature, values in parentheses indicate weight loss of each step.

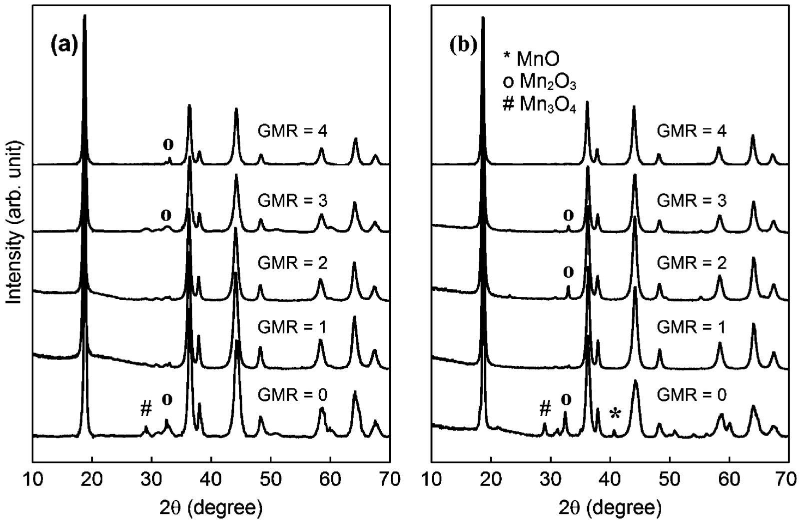

Fig. 4. X-ray diffraction patterns of synthesized samples prepared by (a) Method-1, spray drying preparation and (b) Method-2, conventional preparation.

Table 1. Crystal properties of synthesized $LiMn_2O_4$

GMR	Method-1		Method-2	
	Lattice distance, d_{004} (nm)	Crystallite size (nm)	Lattice distance, d_{004} (nm)	Crystallite size (nm)
0	0.471	29	0.473	36
1	0.475	30	0.474	33
2	0.475	29	0.476	25
3	0.471	24	0.475	28
4	0.472	33	0.476	32

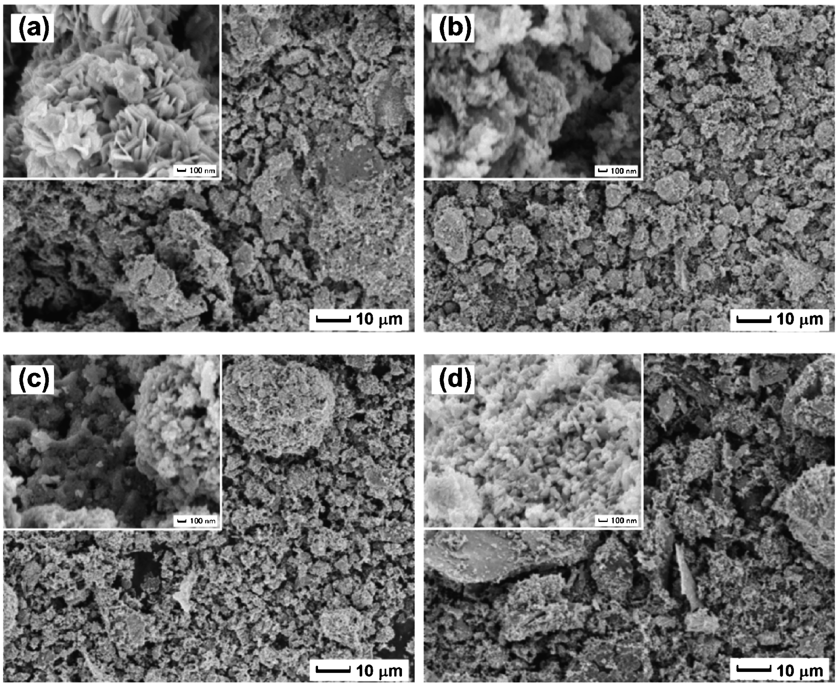

Fig. 5. SEM images of synthesized $LiMn_2O_4$ powders prepared by Method-1 (spray drying) with different glucose concentration (a) GMR of 0 (b) GMR of 1 (c) GMR of 2 and (d) GMR of 3.

No. 35-0782. Formation of secondary phases i.e. MnO, Mn_2O_3, and Mn_3O_4 were suppressed in presence of glucose in low concentration (up to GMR of 2 in Method-1 and 1 in Method-2). Those phases, however, appeared again with increasing on concentration of glucose. The Mn_2O_3 peak dominantly appeared, indicates enhanced oxidation reaction of Mn_3O_4 to the Mn_2O_3 in higher concentration of glucose.[41] The impurities can be eliminated in higher temperature and oxygen concentration. Therefore the balance between heat absorbed and released by glucose decomposition is required to achieve high-purity product.[18]

Crystallite size of the synthesized particles shown in **Table 1** was calculated by using the Scherrer equation. The lattice distance (d) is calculated for (400) crystal lattice. The crystallite size decreases slightly with increasing of glucose concentration. TG–DTA analyses show that the formation temperature of $LiMn_2O_4$ also increased with presence of glucose. That delay (means higher temperature) in the formation of $LiMn_2O_4$ is thought to be due to polymerization and decomposition products of glucose which may hinder the crystal growth. With increasing the glucose concentration (see Table 1), the produced heat of decomposition begins to overcomes the hindrance, resulting in increasing of the crystallite size.

3.4 Effect of glucose on particle morphology

The morphology of synthesized particles is observed by using SEM and shown in **Fig. 5** (Method-1) and **Fig. 6** (Method-2). The shape of $LiMn_2O_4$ crystallites is changing with addition of glucose. Flakes shape is clearly observed in the absence of glucose. With increasing of glucose concentration, the shape is dominated by a “spherical” one. The perceived “spherical” shape is actually the smaller size particles which appear due to a hindrance of crystallites growth in presence of glucose and decomposition residue. The size of crystallites however increases after certain concentration of glucose, as supported by the XRD analysis (see Table 1). The SEM images show that the size of particles produced by Method-1 is smaller (average size of about 50 nm) than that by Method-2 (average size of about 100 nm),

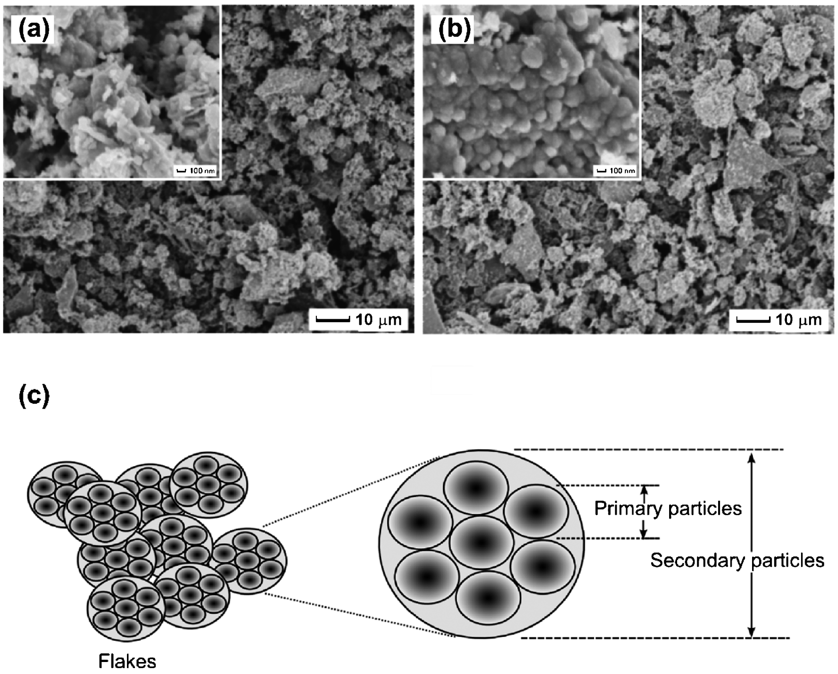

Fig. 6. SEM images of synthesized samples prepared by Method-2 (conventional evaporation) with different glucose concentration (a) GMR of 0.5 and (b) GMR of 1. Size of primary and secondary particles is illustrated in (c).

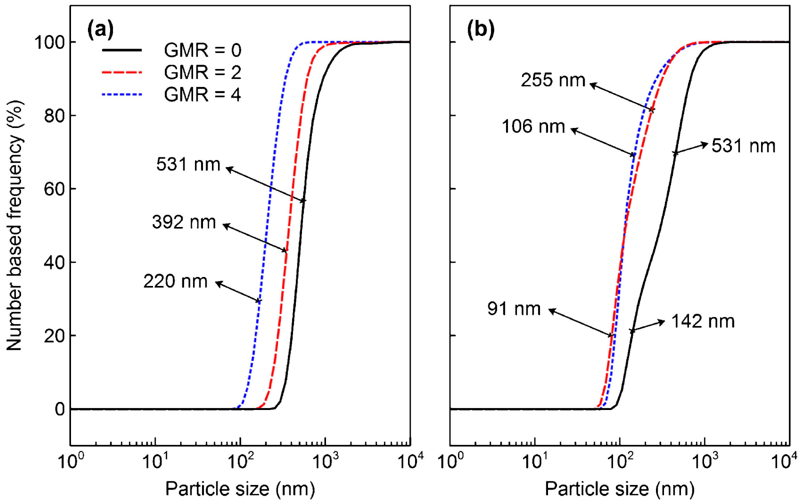

Fig. 7. Particle size distribution of synthesized samples after grinding, obtained from DLS analysis (a) Method-1 by spray drying preparation and (b) Method-2 by the conventional method with different glucose concentration. The values indicated by arrow show peaks of particle size distribution.

which is consistent with the XRD results.

The size distribution of the product was examined using DLS. The applied heat treatments causes an agglomeration on the product, thus grinding treatment is required prior to the analysis. A careful attention should be applied on the results because the DLS apparatus can only detect particles with maximum size of 6 µm. Therefore, the resulted distributions represent the part of products, in exclusion of the particles with size bigger than that size limitation.

The size distributions depicted in **Fig. 7** show effects of the glucose and preparation method. A shifting into smaller size is observed with increasing glucose concentration. Comparing the two preparation methods, homogeneity of the particles produced by the Method-1 is higher than those by the Method-2. In addition, the glucose increases homogeneity of the produced particles. As can be seen in the Fig. 7(b), the double-S curve distribution in absence of glucose (average size in 142 and 531 nm) and at GMR of 2 (average size in 91 and 255 nm) is not observed at GMR of 4. In contrary to the XRD and SEM results, the particles produced by the Method-1 have bigger size (220–531 nm) than that by the Method-2 (91–531 nm). The less-homogeneous distribution is supposed to be the cause of releasing smaller particles during the grinding treatment.[13)]

4. Conclusions

Sub-micro size of $LiMn_2O_4$ particles have been synthesized in the presence of glucose. The formation of metals-glucose complex increases the stability of precursor solution, resulting in increased homogeneity of product. The concentrations of glucose and the preparation methods of dry precursor are important factors determining purity and size of the product.

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