Short communication

Electrochemical performance of Al-doped LiMn$_2$O$_4$ prepared by different methods in solid-state reaction

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Abstract

Al-doped LiMn$_2$O$_4$ cathode materials synthesized by a newly developed wet-milling method and a dry process method using a conventional solid-state reaction were evaluated physicochemically and electrochemically. In the wet-milling method, a precursor was made from the raw materials atomized by a wet milling. A good cyclic performance was obtained for the LiMn$_2$O$_4$ samples prepared by the wet-milling method, achieved up to 99% of retention of capacity at 50 °C at the 30th cycle. The precursor obtained by the wet-milling method was well homogenous and highly reactive due to their finely ground particles, giving good crystallinity to LiMn$_2$O$_4$ products.
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Keywords: Cathode; LinMn$_2$O$_4$; Wet-milling method; Lithium ion battery

1. Introduction

LiMn$_2$O$_4$ is widely studied as a replaceable candidate for LiCoO$_2$ commonly used for a cathode material of lithium ion batteries because it has advantage in view of low cost, low toxicity and high safety [1–3]. However, for a pure LiMn$_2$O$_4$ cathode, the problem is how to suppress the reduction in capacity during charge/discharge cycling. The reduction in the capacity of LiMn$_2$O$_4$ is caused by dissolution of Mn into an electrolyte and the structural change due to the compositional change in Li component [4,5]. Since the structural change occurs by a Jahn–Teller ion of Mn^{3+}, it is effective for improvement of cyclic performance that Mn ions are substituted by other elements, such as Al, Fe, Co, Ni, and so on [6–8]. Conventional methods for the preparation of LiMn$_2$O$_4$ are in general solid-state reactions (dry process method). A precursor is prepared by mixing raw materials, MnO$_2$ and Li$_2$CO$_3$, in the dry process, and then LiMn$_2$O$_4$ is obtained by baking the mixture at high temperatures in air. In the case of substitution for Mn by other elements, since the concentration of the substituting element is usually a few percent for Mn, homogenous dispersion of the substituting element in crystal lattice is not so easy. Several solution synthetic methods, such as citric acid sol–gel method [9], Pechini method [10], emulsion-drying method [11], and spray pyrolysis method [6], have been investigated to obtain the precursor of doped LiMn$_2$O$_4$ with homogeneous composition. The preparation of the precursor powders using these sol–gel, Pechini, and emulsion-drying methods requires a severely controlled condition for doped element concentration, heating temperature, pH of starting solution, and solution stirring procedure. Moreover, a long drying time of the precursor powders is uneconomical. The spray pyrolysis technique, in which droplets of lithium and manganese nitrate solutions generated by an ultrasonic obviator are heated, gives a short heating time. This method, however, has a serious problem that the particles produced are frequently of hollow particle shapes [12]. In addition, a use of nitrate and organic compounds employed as starting materials in the above methods should be avoidable in view of environment pollution because of generation of harmful NO$_x$ and VOC on a heating process.

In this study, a new synthetic method, "wet-milling method", is proposed, and its advantage is proved. The spherical precursor particles with sufficient dispersion of substituting elements as co-precipitated particles can be prepared by the wet-milling

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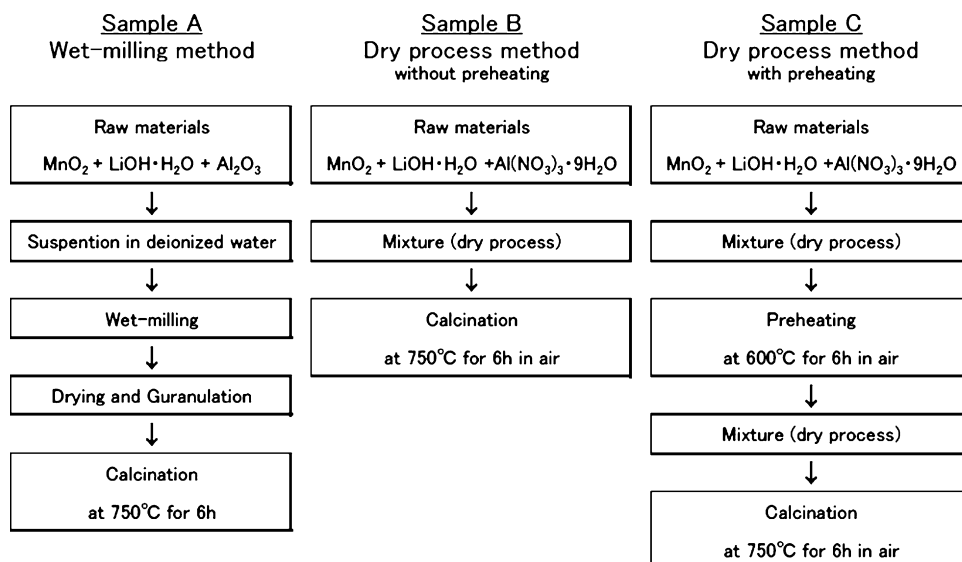*E-mail address:* msato@eng.niigata-u.ac.jp (M. Sato).

Raw materials	Raw materials	Raw materials
MnO_2 + $LiOH·H_2O$ + Al_2O_3	MnO_2 + $LiOH·H_2O$ + $Al(NO_3)_3·9H_2O$	MnO_2 + $LiOH·H_2O$ + $Al(NO_3)_3·9H_2O$

Sample A:
- Raw materials MnO_2 + $LiOH·H_2O$ + Al_2O_3 ↓
- Suspention in deionized water ↓
- Wet-milling ↓
- Drying and Guranulation ↓
- Calcination at 750°C for 6h

Sample B:
- Raw materials MnO_2 + $LiOH·H_2O$ + $Al(NO_3)_3·9H_2O$ ↓
- Mixture (dry process) ↓
- Calcination at 750°C for 6h in air

Sample C:
- Raw materials MnO_2 + $LiOH·H_2O$ + $Al(NO_3)_3·9H_2O$ ↓
- Mixture (dry process) ↓
- Preheating at 600°C for 6h in air ↓
- Mixture (dry process) ↓
- Calcination at 750°C for 6h in air

Fig. 1. Flowcharts for preparation of samples.

method without chemical reaction process. In this method, the precursor is easily obtained in the form of submicron particles after granulating a slurry solution of raw materials with a spray-drier. Because the precursor particles consist of fine grains of raw materials prepared from environmentally friendly metal oxides and metal hydroxides, the high reactive precursor with a homogeneous composition is also obtained. While submicron particles are scarcely obtained by the dry-milling processes using pulverizing machines such as a planetary ball mill [13] and a jet mill [14], the particles of the raw materials can be readily grained to submicron primary particles in the wet-milling method using a beads-mill [15]. The granulation of the slurry including solid particles by the spray-dryer is more facile than that of aqueous solution [16]. A use of oxides and hydroxides in the wet-milling method also becomes much advantageous. The wet-milling method is a clean process without production of toxic exhaust gas and liquid wastes because environmentally friendly metal oxides and metal hydroxides can be used as raw materials. In this study, this new method is applied to synthesize Al-doped $LiMn_2O_4$ cathode materials. Physical and electrochemical properties of the cathode materials prepared by two different methods, the wet milling and a dry process method, are evaluated.

2. Experimental

Three kinds of samples having the composition of $Li_{1.10}Mn_{1.90}Al_{0.10}O_4$ were prepared by three different synthetic methods. Flowcharts for preparation of the samples are given in Fig. 1. Sample A was synthesized by the wet-milling method. Stoichiometric amounts of MnO_2, $LiOH·H_2O$, and γ-Al_2O_3 were dispersed in a deionized water and milled to 0.5 μm in size with a beads-mill in the wet process. A schematic diagram of the beads-mill is shown in Fig. 2. The slurry thus obtained was dried and granulated to 15 μm in particle size by a spray-drier. The precursor was heated at 750 °C for 6 h in air. Samples B and

C were prepared by the dry process method. The precursor for this process was obtained by mixing stoichiometric amounts of MnO_2, $LiOH·H_2O$, and $Al(NO_3)_3$. Sample B was obtained by heating at 750 °C for 6 h. Sample C was preheated at 600 °C for 6 h. The preheated powder was ground and calcined at 750 °C for 6 h in air again.

The crystal structure of the samples was identified by an X-ray diffractometer (Rigaku, MultiFlex). The morphology of the sample powders was observed using a scanning electron microscope (JEOL, JSM-6100). The elementary mapping analysis of the sample particles was performed using an energy-dispersive X-ray (EDX) analyzer (JOEL, JED-2001). The specific surface area was measured by single point BET analysis (Yuasa Ionics, Multisorb 12).

Electrochemical performance was tested using a half-cell. The positive electrode was a pellet with 14 mm in diameter composed of 70 wt.% $LiMn_2O_4$, 25 wt.% acetylene black, and 5 wt.% PTFE. The negative electrode was a Li foil and the electrolyte was 1 M $LiClO_4$ dissolved in PC + DMC (1:1). The initial capacity was measured at a current density of 10 mA g^{-1} with a 3.0–4.3 V cut off voltage range at 30 °C, and the cycling test was performed at a current density of 50 mA g^{-1} with a 3.0–4.3 V cut off voltage range at 50 °C.
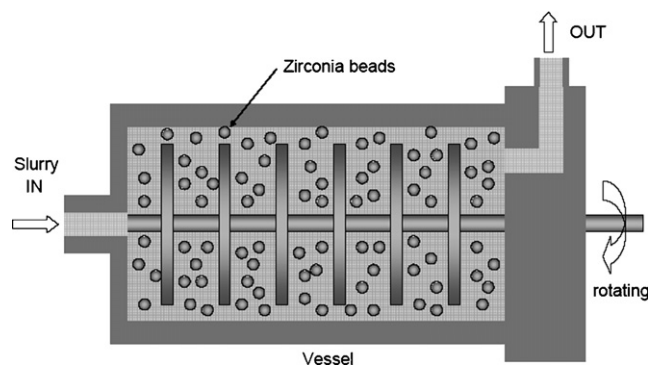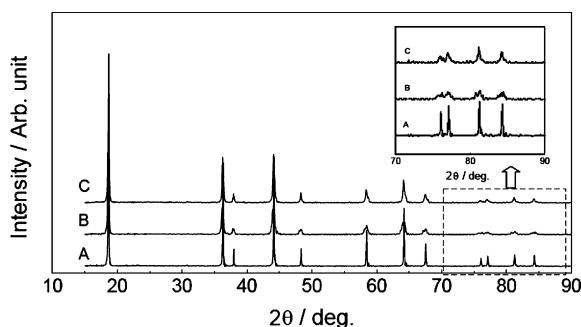

Fig. 2. Schematic diagram of beads-mill.

Fig. 3. XRD patterns of samples: (A) wet milling, (B) dry process (without preheating) and (C) dry process (with preheating).

3. Results and discussion

XRD patterns of three kinds of the samples are shown in Fig. 3. All diffraction lines were identified as a spinel phase, and no impurity was detected. The diffraction lines of Sample A synthesized by the wet-milling method were narrower than those of Samples B and C synthesized by the dry process method. The high angle diffraction lines of Samples B and C were splitted into two lines. This fact may indicate that Samples B and C are a mixture of compositionally different particles occurring due to insufficient homogeneity provided in the synthetic condition used in this study. The diffraction angles of $LiMn_2O_4$ usually shift depending on Li/Mn molar ratios [17]. The Li/Mn molar ratio of particles of Samples B and C may not be uniform. Hence, the sample with homogeneous composition is hardly obtained in the dry process method. The diffraction lines of Sample C without preheating were a little broader than those of Sample B with preheating and mixing. This indicates that the precursor with homogeneous composition can give a well-crystalline product. In the wet milling, the zirconia beads with a diameter size of 1mm was used for milling of the starting material slurry which was agitated by high speed (about 2000 rpm) rotating blades. The situation makes it possible for raw material particles much frequently to contact zirconia beads with high kinetic energy, giving highly efficient milling. From this point of view, the use of the slurry is also advantageous for homogeneous mixing. On the other hand, the solid-state raw materials are simply mixed just with a mortar and a pestle in the dry process method, and therefore, it is not easy to obtain a mixture with homogeneous composition. In order to directly observe homogeneous dispersion of substituting element of Al in the precursor particles prepared by the wet-milling method, the elementary mapping analysis was performed. As shown in Fig. 4(A), a secondary particle of the precursor is of aggregation consisting of fine primary particles (smaller than about 1 μm in size) of the raw materials. The homogeneous distribution of the raw material particles can be visible in the elementary mapping diagrams for Mn and Al (Fig. 4(B and C)). The reason for obtaining well-crystalline Al-doped $LiMn_2O_4$ powders should be originated from the precursors with homogeneous composition and high reactivity provided by the wet-milling method.

The first charge/discharge curves are shown in Fig. 5. All the samples showed almost the same behavior. A theoretical capac-

ity of ion-doped $LiMn_2O_4$ is in proportion to a concentration of Mn^{3+} [18]. The theoretical capacity, C_T, can be expressed as follows:

$$C_T = 26.8 \frac{p}{M} (Ah\,g^{-1}) \tag{1}$$

where p and M denote the number of Mn(III) and the molecular weight of ion-doped $LiMn_2O_4$, respectively. When Al and excess Li substitute Mn located in the 16d site, the chemical formula of $Li_{1.10}Mn_{1.90}Al_{0.10}O_4$ is expressed as follows:

$$[Li]_{8a}[Li_{0.10}Mn(III)_{0.60}Mn(IV)_{1.20}Al(III)_{0.10}]_{16d}O_4 \tag{2}$$
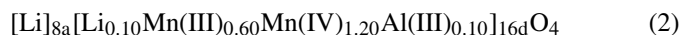
Thus, the theoretical capacity of $Li_{1.10}Mn_{1.90}Al_{0.10}O_4$ is calculated to be 93 mAh g^{-1} from Eq. (1). The measured initial capacities (92.9 mAh g^{-1} for Smaple A, 93.1 mAh g^{-1} for Smaple B and 92.6 mAh g^{-1} for Smaple C) correspond almost to the theoretical capacity, indicating that the produced $LiMn_2O_4$ samples have the nominal composition.

The cyclic performance at 50 °C is shown in Fig. 6. The retention of capacity of Samples A, B, and C at the 30th cycle were 99, 96, and 94%, respectively. Komaba et al. [19] reported the cyclic performance of the Al-doped spinel $Li_{1.05}Mn_{1.75}Al_{0.2}O_4$ cathode prepared from MnO_2, $LiNO_3$, and Al_2O_3 in a conventional solid-state reaction. The theoretical capacity of this composition sample is 101 mAh g^{-1}, fairly close to that of our sample with the formula, $Li_{1.10}Mn_{1.80}Al_{0.10}O_4$, with the theoretical capacity of 93 mAh g^{-1}. The retention of capacity of $Li_{1.05}Mn_{1.75}Al_{0.2}O_4$ prepared by the solid-state reaction at the 30th cycle was 70%, considerably lower than that of our three samples of $Li_{1.10}Mn_{1.80}Al_{0.10}O_4$ prepared both by the wet-milling method and the dry process method. The synthesis method used by Komaba et al. is approximately the same as our dry process method, and nevertheless, cyclic performance is considerably different. This difference may lie in the difference in sources of the raw materials. They chose Al_2O_3 powders for a source for Al while $Al(NO_3)_3$ powders were used in our samples prepared by the dry process method. The reactivity of Al_2O_3 (mp, 2050 °C) is much lower than that of $Al(NO_3)_3$ (mp, 70 °C). Consequently, $Al(NO_3)_3$ having such a low melting point may be suitable for homogeneous Al-doing on $LiMn_2O_4$ particularly for solid-state reactions. In spit of using Al_2O_3 in the wet-milling method, excellent performances were achieved for the cathode prepared by this method. This fact indicates the superiority of the wet-milling method even applied to low reactive raw materials. When the nitrate is used as a raw material, gener-
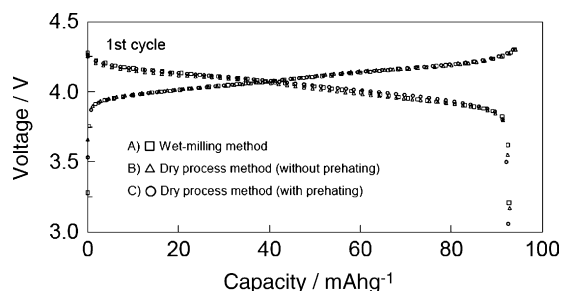

Fig. 4. Elementary mapping analysis of precursor prepared by wet-milling method: (A) SEM images, (B) mapping for Mn and (C) mapping for Al.
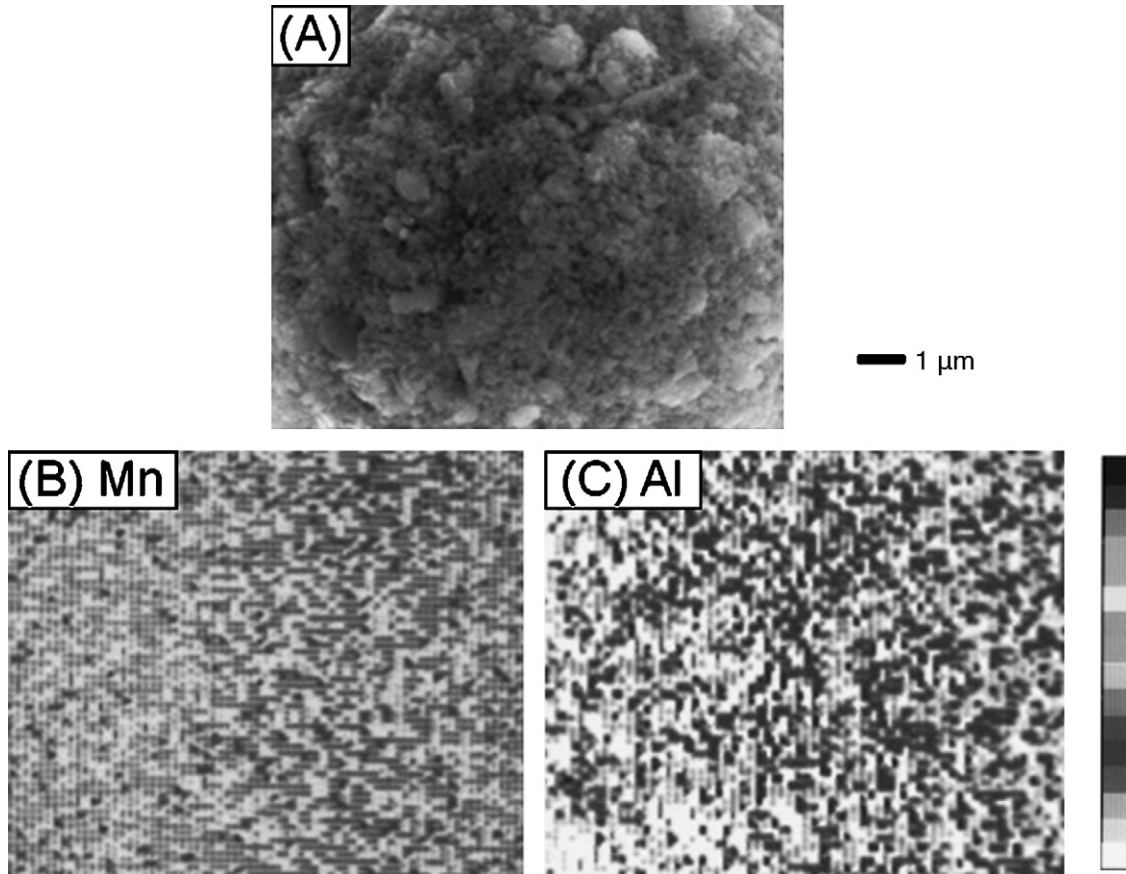
Fig. 5. Charge/discharge curves for first cycle at current of $10\,mA\,g^{-1}$ with 3.0–4.3 V cut off voltage at 30 °C.

ation of harmful NO_x cannot be avoidable on calcinating at high temperatures.

Although the initial capacities of all the samples were almost the same (Fig. 5), their cyclic performances were remarkably different (Fig. 6). This difference seems to in the difference of the surface morphology of the products. The specific surface areas of the three samples are $0.67\,m^2\,g^{-1}$ for Sample A, $0.80\,m^2\,g^{-1}$ for Sample B and $1.00\,m^2\,g^{-1}$ for Sample C. The relationship between the retention of capacity and the specific surface area is shown in Fig. 7. Apparently, the cyclic performance was improved accompanied with decrease in specific

surface area. SEM images for the prepared products are shown in Fig. 8. Crystalline sizes of the Samples B and C were of several hundred nanometers whereas the particles of the Sample A grew to about $1\,\mu m$. Influence of specific surface area on cyclic performance was examined previously by Xia et al. [20]. They measured the cyclic performance for two kinds of the $Li_{1.1}Mn_2O_4$ samples with difference specific surface areas of 6.3 and $1.2\,m^2\,g^{-1}$. The reduction in capacity for the sample with $6.3\,m^2\,g^{-1}$ at the 100th cycle was lower by half than that of the sample with $1.2\,m^2\,g^{-1}$. Similar behavior is also obtained in this study. Thus, the remarkable suppression in fading capac-
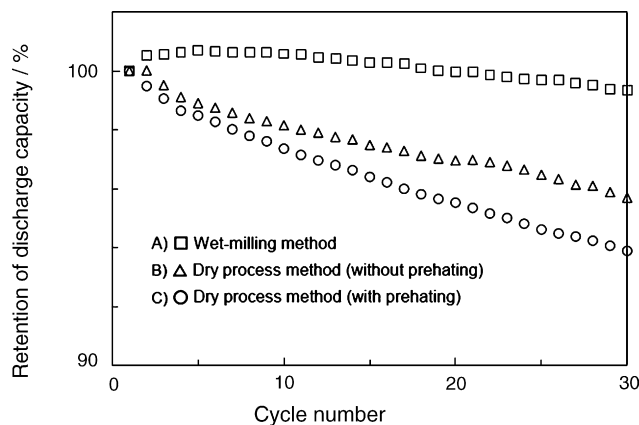

Fig. 6. Cyclic performance of samples at $50\,mA\,g^{-1}$ with 3.0–4.3 V at 50 °C.
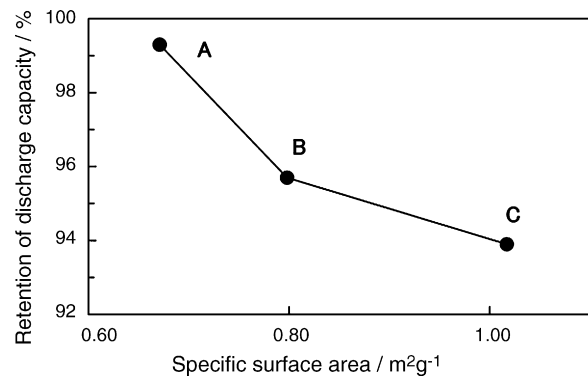

Fig. 7. Relationship between specific surface area and retention of capacity at 30th cycle.
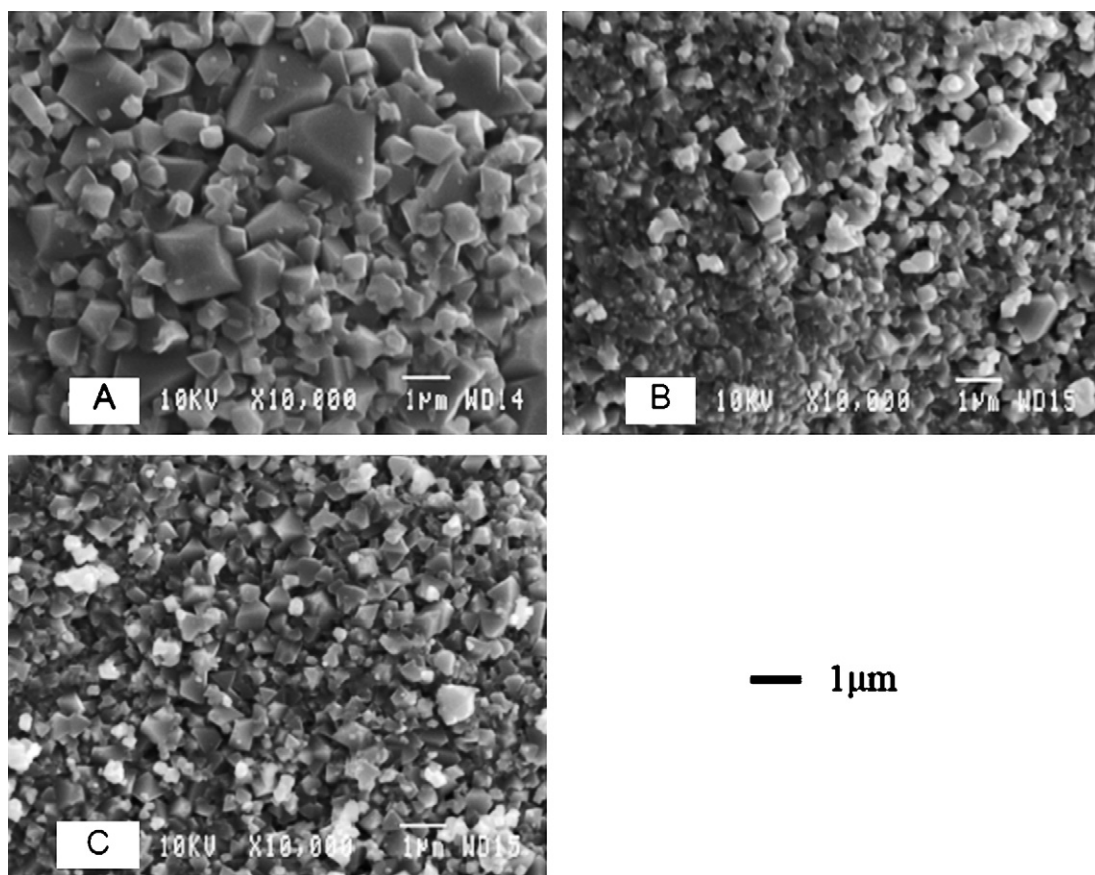
Fig. 8. SEM images of samples: (A) wet milling, (B) dry process (without preheating) and (C) dry process (with preheating).

ity found in Sample A with low surface area may come from low dissolution of Mn into the electrolyte. Although the burning temperature has to be raised to decrease the specific surface area, high heating temperature usually causes generation of oxygen defects frequently causing capacity fall [21,22]. It is, therefore, necessary for obtaining good electrochemically active $LiMn_2O_4$ samples with well-crystalline particles to heat the precursor at as low temperatures as possible. The wet-milling method can meet such demand.

Acknowledgement

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