Korean J. Chem. Eng., **23**(5), 714-719 (2006)

Synthesis of manganese oxide particles in supercritical water

Joo-Heon Lee and Jae-Yong Ham*,†

Department of Environmental Engineering, *Department of Chemical Engineering,
Daegu University, 15 Naeriri, Jinryang, Gyoungsan, Gyoungbuk 712-714, Korea
(*Received 26 October 2005 • accepted 15 March 2006*)

Abstract−The synthesis of manganese oxide and $LiMn_2O_4$ particles in supercritical water has been investigated with a residence time of 10-40 seconds. It was suggested that the reaction temperature for SCW process should be relatively higher than the critical temperature of water, to synthesize the particles of uniform size and shape. It was observed that the selective synthesis of $LiMn_2O_4$ was mainly dependent of the amount of OH^- ion in the reactants. We concluded that the size, shape and structure of particles were strongly influenced by a change in the reaction temperature, reactant composition and OH^- ion amount, and thus enabling to synthesize a specific metal oxide particles. The reaction mechanisms for manganese oxides and $LiMn_2O_4$ have been proposed with the oxidation, hydrolysis and dehydration steps.

Key words: Supercritical Water, Manganese Oxide, Mechanism, Synthesis, Particles

INTRODUCTION

It seems needless to say that fine metal oxide particles perfectly controlled in the sub-micro and nano meter range of size are of interest from both research and industrial standpoints, because these particles can be applied to various areas such as coatings, catalysts, sensors, semiconductors, and electronic devices. The fine particles have been produced by various methods such as chemical vapor deposition, co-precipitation, sol-gel process, solid state transformation, hydrothermal synthesis, rapid expansion of a supercritical solution, and so on. However, it is still difficult to produce particles of uniform size, shape and structure, and some of these methods are not environment friendly [Cabaoas and Poliakoff, 2001].

Recently, considerable attention has been paid to the production of fine particles in supercritical water (SCW) [Adschiri et al., 1992, 2000; Cabaoas and Poliakoff, 2001; Hakuta et al., 1997, 1998, 1999; Rho and Park, 2002; Lee et al., 2003; Nam and Kim, 2004]. Various metal oxide particles such as Fe_2O_3, Fe_3O_4, $ZnFe_2O_4$, TiO_2, CeO_2 and $BaO{\cdot}6Fe_2O_3$, etc. have been successfully synthesized in the SCW process [Adschiri et al., 1992; Cabaoas and Poliakoff, 2001; Rho and Park, 2002; Lee et al., 2003; Hakuta et al., 1997, 1998; Nam and Kim, 2004]. And compared to conventional methods, the SCW process has some advantages: (i) Reaction time is less than 1 min. (ii) High crystalline particles are formed. (iii) A continuous production for fine particles is feasible. (iv) It is an environment friendly process because of no addition of solvents.

However, although the SCW process has been successfully used for the synthesis of some metal oxide particles, the mechanisms of the reactions involved have not yet been fully understood. The available information in the literature is focused on the formation of the metal oxide particles. Little information on the mechanism for the synthesis of fine particles in SCW is available.

Adschiri et al. [1992] first suggested that the decomposition of aqueous metal salts proceeded via hydrolysis and dehydration steps. The hydrolysis step is to form metal hydroxides from metal salts ($ML_x(aq)+xH_2O \rightarrow M(OH)_x(s)+xHL$). The dehydration step is to convert the metal hydroxides to metal oxides ($M(OH)_x(s) \rightarrow M(O)_{x/2}(s)+x/2H_2O$).

In the present work, the focus was to synthesize manganese oxide and $LiMn_2O_4$ particles in SCW. The manganese oxide particles have been used in the production of pigments, magnets, catalyst support, etc. The $LiMn_2O_4$ particles are the most promising cathode material for lithium rechargeable batteries, which are generally known

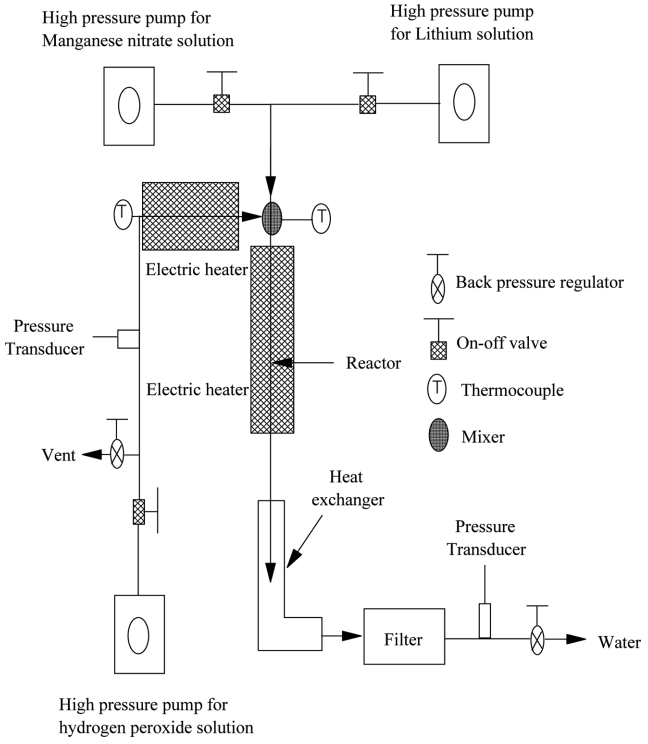


Fig. 1. A schematic flow diagram of experimental apparatus.

†To whom correspondence should be addressed.
E-mail: hjy6494@daegu.ac.kr

to be the highly efficient rechargeable batteries as a power source, specially, from the economic viewpoint [Wakihara et al., 1998].

The purpose of this study was to synthesize the fine manganese oxide and $LiMn_2O_4$ particles in the SCW, and specially to investigate their synthetic mechanisms.

EXPERIMENTAL

A schematic flow diagram of experimental apparatus for manganese oxide and $LiMn_2O_4$ particles is shown in Fig. 1. Hydrogen peroxide or pure water was delivered to high-pressure system by a high-pressure pump (Nihon Seimitsu Kagaku Co., Ltd., NP-AX-15) and it was heated to high temperature through a tubular preheater and became SCW. Another high-pressure pump (Nihon Seimitsu Kagaku Co., Ltd., NP-AX-15) was used to deliver manganese nitrate solution. The third high-pressure pump (Gilson, 305 pump) was used to deliver lithium solution to the system and it was mixed with the manganese nitrate solution in the first mixer. The solution from the first mixer was mixed with high temperature SCW in the second mixer. This mixing led to rapidly increasing the solution temperature, and the mixed stream was fed to the reactor (Hastelloy C-276 tube, 18 inch length, 0.245 inch I.D.) and fine particles were formed in the reactor. The high temperature/pressure reactor effluent including the formed particles was cooled down by a water-cooled double-pipe heat exchanger. The cooled slurry was then separated to water and particles in a filter (Millipore high pressure 316 SS filter holder). The separated water passed through a back-pressure regulator (Tescom, 54-2162-24-002). Three Inconel sheathed type-K thermocouples were installed respectively in the preheater, mixer and reactor. Two pressure transducers (type: AH-50, max: 500 kg/cm^2) were used to measure system pressure.

$Mn(NO_3)_2 \cdot 6H_2O$, KOH, LiOH, $LiNO_3$ were from Junsei Chemical Co., Ltd. (Japan) and the purity was higher than 97%. The concentration of manganese nitrate solution was 0.02-0.05 mol/liter and flow rate ranged from 2.0 to 6.0 ml/min. The hydrogen peroxide or pure water feed ranged from 4 to 12 ml/min. Residence time was 10-40 seconds. The size and shape of particles were evaluated by using Scanning electron microscope (SEM)/Transmission electron microscope (TEM) analyses and the structure of particles was analyzed by X-ray diffraction (XRD).

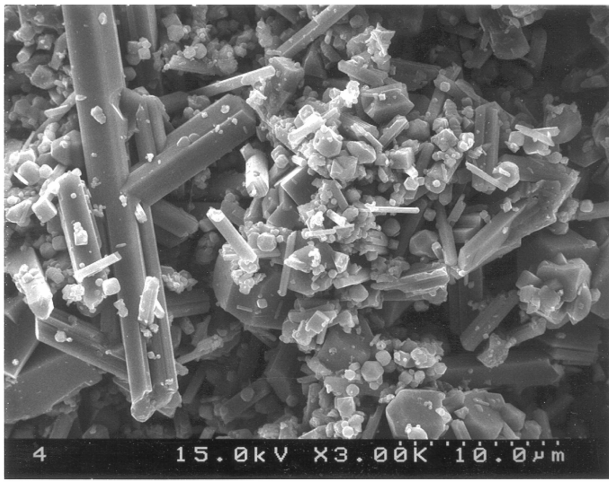
RESULTS AND DISCUSSION

1. Synthesis of Manganese Oxides

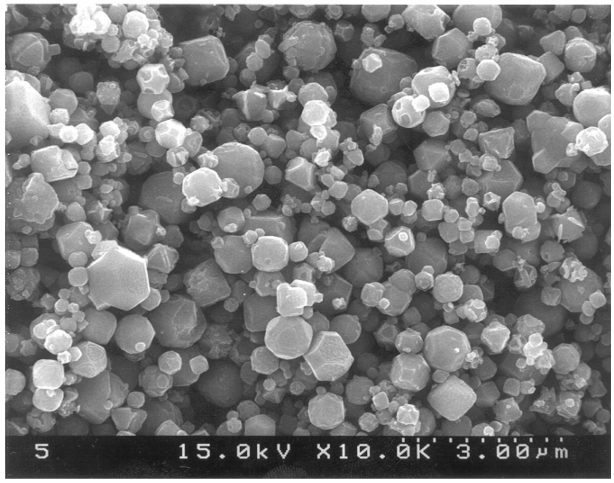
The manganese oxide particles were synthesized from $Mn(NO_3)_2 \cdot 6H_2O$ at the reaction temperatures of 380 °C to 430 °C. The experimental conditions and the structure of formed particles are represented in Table 1.

Table 1. Experimental conditions and synthesized particles

Temp. °C	Press. bar	$Mn(NO_3)_2$ mol/L	H_2O_2 Mol/L	Product
380	300	0.02	0	MnO_2, Mn_2O_3
380	300	0.05	0	MnO_2, Mn_2O_3
430	300	0.02	0	MnO_2, Mn_2O_3
430	300	0.05	0	MnO_2, Mn_2O_3



(a)



(b)

Fig. 2. SEM photographs of manganese oxides synthesized at 300 bar ($Mn(NO_3)_2$=0.02 mol/L).
(a) 380 °C, (b) 430 °C

SEM photos of the formed particles are represented in Fig. 2. It was observed that the shape and size of particles formed at 380 °C were so much different as shown in Fig. 2. It is generally known that the density of water changes rapidly near the critical temperature (374.3 °C). It is therefore hard to maintain a specific reaction condition in this region. This may result in various types of particles at 380 °C. However, the particles synthesized at 430 °C showed an almost spherical shape and their sizes were much smaller than those at 380 °C, as shown in Fig. 2. Their size distribution was also much narrower. This can be explained on the basis of the low solvent power of SCW. The higher temperature results in the lower solvent power. First step of the particle formation is the production of monomer by hydrolysis reaction and dehydration. When the water is supersaturated with monomers, nucleation takes place, followed by the crystal growth, which is basically the inclusion of monomers. However, since the hydrolysis rate is extremely high in SCW and the solvent power of SCW is quite low, very high degree of super-saturation is achieved instantly in SCW and thus enables to

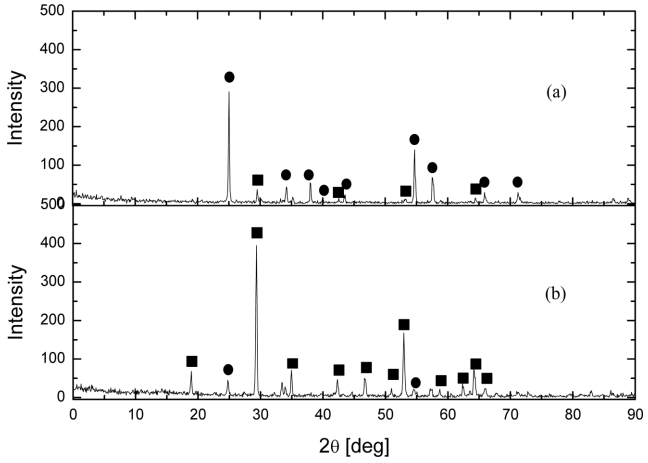


Fig. 3. XRD results for the manganese oxide particles synthesized at 300 bar ($Mn(NO_3)_2$=0.02 mol/L, ●: MnO_2, ■: Mn_2O_3). (a) 380 °C, (b) 430 °C

form the fine particles by rapid nucleation [Hakuta et al., 1997]. From these results, it is suggested that the reaction temperature for SCW process should be relatively higher than the critical temperature, to synthesize the particles of uniform size and shape.

Structure of the synthesized particles was analyzed by XRD and Fig. 3 represents the XRD patterns. As shown in Fig. 3, the peaks of manganese oxides from both conditions are quite sharp, which means that the formed particles have a high degree of crystallinity. It was also observed that the composition characteristic of particles at 430 °C was reverse to that at 380 °C. MnO_2 was a main product for the particles formed at 380 °C and a minor component was Mn_2O_3. Contrary to this, it was observed that Mn_2O_3 was a major product for the particles at 430 °C and MnO_2 was minor, as shown in Fig. 3. At temperatures above 527 °C, MnO_2 preferably begins to dissociate noticeably, giving Mn_2O_3 under ambient pressure [Holleman and Wiberg, 2001] so that the dissociation takes place slowly under the temperature of 527 °C. However, the reaction rates in SCW have been observed markedly faster than the reactions under the ambient pressure, because of the high pressure and specific properties of the SCW. This could be the reason for the observed reverse composition characteristic. At 380 °C, Mn_2O_3 may be oxidized to MnO_2, resulting that MnO_2 is a main product. But at 430 °C, the oxidation of Mn_2O_3 may be suppressed because of the relatively high temperature, thus enabling Mn_2O_3 to be a major product.

Adschiri et al. [1992] and Hakuta et al. [1997] reported that the conversion of metal salts to metal oxides in SCW proceeded via hydrolysis to the hydroxides, followed by dehydration to the oxides. Cabaoas and Poliakoff [2001] suggested that the higher self-dissociation constant and lower dielectric constant of water in SCW were the driving force inducing fast hydrolysis and dehydration. They also suggested that the mechanism for the formation of metal oxides in the SCW was composed of the oxidation step in addition to the hydrolysis and dehydration steps.

In this study, Mn^{3+} from Mn_2O_3 and Mn^{4+} from MnO_2 were found in products. However only the Mn^{2+} existed in reactants because $Mn(NO_3)_2$ was used as a Mn source. The Mn^{3+} and Mn^{4+} could be the result of Mn^{2+} oxidation step. It is therefore presumed that the synthesis of manganese oxides includes the oxidation as well as

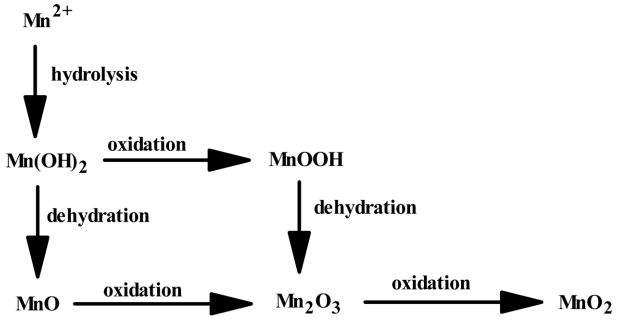


Fig. 4. A proposed mechanism for the synthesis of manganese oxides in SCW.

the hydrolysis and dehydration proposed by Adschiri et al. [1992] and Hakuta et al. [1997]. The proposed mechanism for the synthesis of manganese oxides is shown in Fig. 4.

The manganese nitrate solution was rapidly heated to reaction temperature, and under supercritical condition it immediately hydrolyzed to $Mn(OH)_2$. The direct oxidation of Mn^{2+} to Mn^{3+} would not take place because the standard redox potential, E^o, was −1.6 V [Cotton et al., 1999]. However, although MnO was not detected in the products, the $Mn(OH)_2$ might be dehydrated further to the MnO that was not stable at temperatures above 250 °C [Holleman and Wiberg, 2001] and took up oxygen to become Mn_2O_3. Oxidation of $Mn(OH)_2$ to MnOOH could easily take place with small amounts of O_2 in the water and it would immediately dehydrate to Mn_2O_3 [Bailar et al., 1976; Cotton et al., 1999; Holleman and Wiberg, 2001]. The Mn_2O_3 could easily be oxidized to MnO_2. It is known that the $Mn(OH)_2$ in the basic media is very easily oxidized by air as shown by the potentials [Cotton et al., 1999]:

$$MnO_2 \cdot yH_2O \xrightarrow{-0.1\,V} Mn_2O_3 \cdot xH_2O \xrightarrow{-0.2\,V} Mn(OH)_2$$

However, the above discussion has been made without considering the effects of temperature, pressure and special properties of SCW on reaction rates and potentials. At this time, these parameters are unknown.

2. Synthesis of Lithium Manganese Oxide

We attempted to synthesize $LiMn_2O_4$ particles using $Mn(NO_3)_2 \cdot 6H_2O$, LiOH, KOH, $LiNO_3$ solutions. The experimental conditions and structure of formed particles are represented in Table 2.

Under constant reaction temperature and pressure, a change in reactant composition has led to the formation of particles with different structure such as $LiMn_2O_4$, Mn_2O_3 and MnO_2. As shown in Table 1, it was observed that the selective synthesis of $LiMn_2O_4$ was mainly dependent of the amounts of KOH and LiOH, not Li/Mn ratio or $LiNO_3$ amount. With a certain amount of OH^- ion, the $LiMn_2O_4$ began to be synthesized and it became a major product with increasing amount of OH^- ion. These results are similar to those of Rho and Park [2002] who reported that the formation of $BaO \cdot 6Fe_2O_3$ in SCW was dependent of alkali molar ratios in reactants. It is therefore suggested from this observation that the synthesis of $LiMn_2O_4$ is strongly influenced by the amount of OH^- ion in the reactants. The XRD patterns of the particles synthesized with the different composition of reactants are represented in Fig. 5. It was shown that the $LiMn_2O_4$ was formed with a relatively high concentration of LiOH (0.1 mol/L) and it was not detected in the products from a

Table 2. Summary of experimental conditions and results

Temp. °C	Press. bar	$Mn(NO_3)_2$ mol/L	LiOH mol/L	$LiNO_3$ mol/L	KOH mol/L	H_2O_2 mol/L	Li/Mn	Product
420	300	0.02	0.02	0.04	-	0.03	3	MnO_2, Mn_2O_3
400	300	0.025	0.025	0.075	-	0.03	4	MnO_2, Mn_2O_3
420	300	0.02	0.02	0.04	-	0	3	MnO_2, Mn_2O_3
420	300	0.02	0.06	-	-	0.03	3	$LiMn_2O_4$
420	300	0.025	0.05	-	-	0.03	2	MnO_2, Mn_2O_3, $LiMn_2O_4$
420	300	0.025	0.1	-	-	0.03	4	$LiMn_2O_4$
420	300	0.02	0.02	-	0.04	0.03	1	$LiMn_2O_4$
420	300	0.02	0.02	-	0.04	0	1	$LiMn_2O_4$
420	300	0.02	-	0.02	0.06	0.03	1	$LiMn_2O_4$
420	300	0.02	-	0.02	0.06	0	1	$LiMn_2O_4$
420	300	0.04	0.08	-	0.08	0.03	2	$LiMn_2O_4$
400	300	0.025	0.025		0.025	0.03	4	MnO_2, Mn_2O_3, $LiMn_2O_4$
400	300	0.025	-	0.1	-	0.03	4	MnO_2, Mn_2O_3

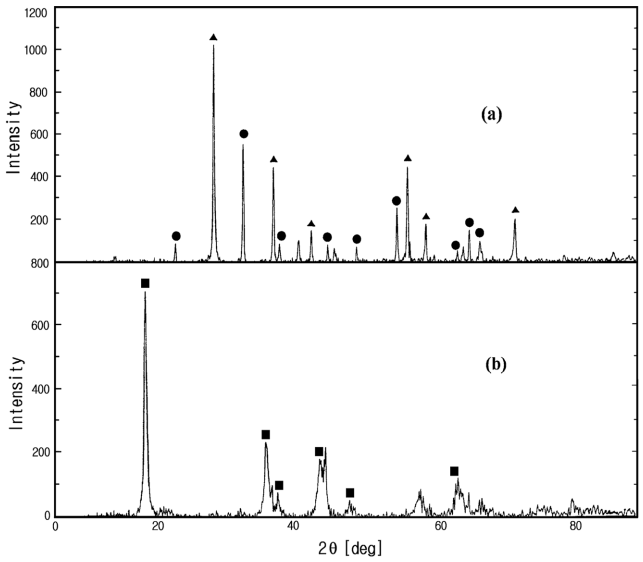


Fig. 5. XRD patterns for the manganese oxide particles synthesized from a 1 : 4 mixture of $Mn(NO_3)_2$ and $LiOH/LiNO_3$ at 400 °C and 300 bar (●: β-MnO_2, ▲: Mn_2O_3, ■: $LiMn_2O_4$).
(a) particles formed with LiOH (0.025 mol/L) and $LiNO_3$ (0.075 mol/L), Li/Mn=4. (b) particles formed with LiOH (0.1 mol/L), Li/Mn=4

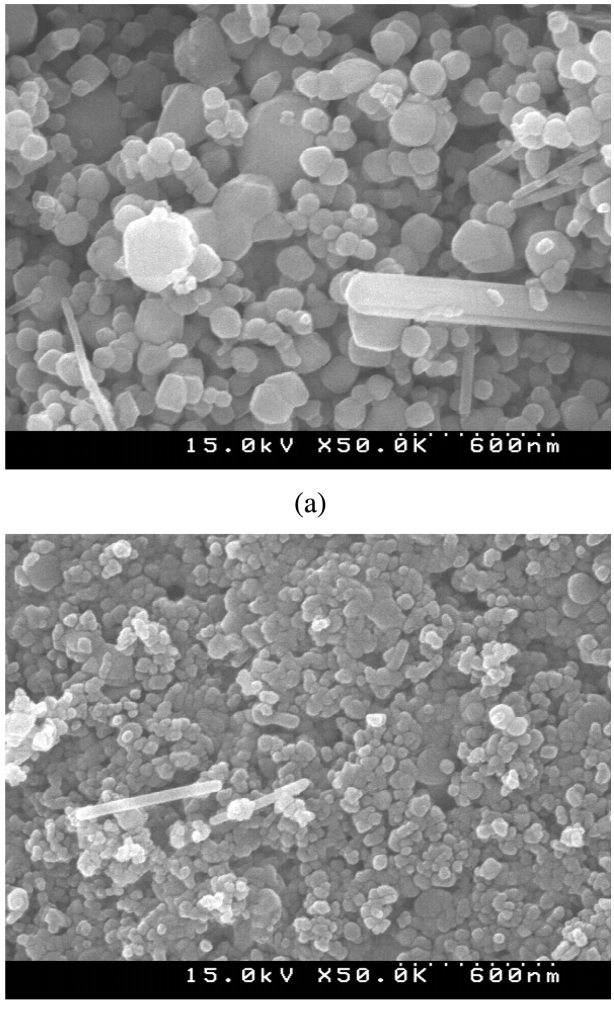


Fig. 6. SEM photographs of the synthesized particles from a 1 : 4 mixture of $Mn(NO_3)_2$ and $LiOH/LiNO_3$ at 400 °C and 300 bar.
(a) $LiNO_3$ (0.1 mol/L), synthesized particles: MnO_2 & Mn_2O_3.
(b) LiOH (0.1 mol/L), synthesized particles: $LiMn_2O_4$

$LiOH/LiNO_3$ mixture (LiOH=0.025 mol/L, $LiNO_3$=0.075 mol/L), so that it was synthesized with LiOH, not with $LiNO_3$. These results mean that the synthesis of $LiMn_2O_4$ is strongly influenced by the amount of OH^- ion in the reactants.

Since the $LiMn_2O_4$ was only synthesized with an appropriate amount of OH^- ions, it was thought that they must have participated in the reaction steps and the formation of Mn_2O_3 must have been suppressed. According to the proposed mechanism in Fig. 4, the Mn_2O_3 is formed from MnO and MnOOH. The following mechanism was therefore proposed to illustrate the formation of $LiMn_2O_4$ in the SCW process:

$$4MnO+O_2 \rightarrow 2Mn_2O_3 \quad (1)$$

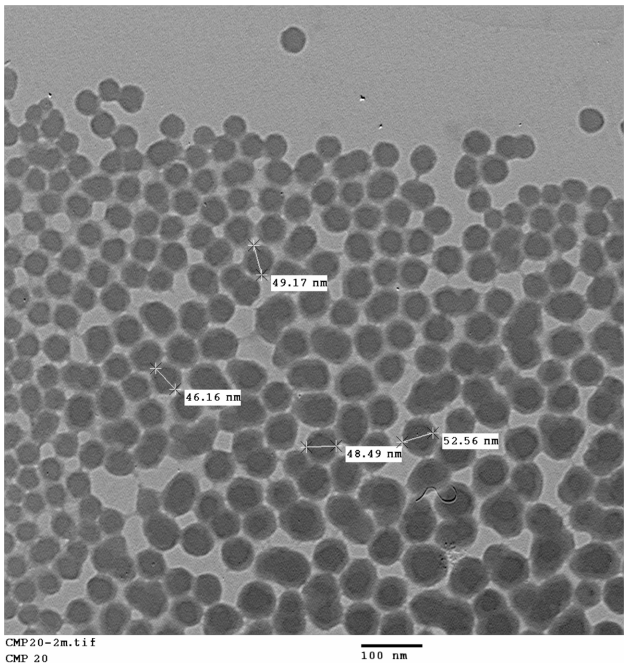


Fig. 7. TEM photograph of the synthesized $LiMn_2O_4$ particles at 400 °C and 300 bar.

$$2MnOOH \rightarrow Mn_2O_3 + H_2O \quad (2)$$

$$2MnOOH + Li^+ + 2OH^- \rightarrow LiMn_2O_4 + 2H_2O + e^- \quad (3)$$

Although the MnO and MnOOH were not detected in the products, they were assumed to be the intermediates. With a small amount of OH^- ions, reactions (1) and (2) will occur to form the Mn_2O_3 [Cotton et al., 1999; Holleman and Wiberg, 2001] as proposed in Fig. 4. And with an appropriate amount of OH^- ions, it is suggested that the reactions (1) and (2) may be suppressed and reaction (3) can take place to synthesize the $LiMn_2O_4$ because the OH^- ions participate in the reaction steps. However, at this time, the above mechanism cannot be verified yet because of little information on the parameters in SCW such as solubility, multi-phase thermodynamics, composition gradients and growth kinetics, etc.

The SEM photographs of particles synthesized with $LiNO_3$ and LiOH are represented in Fig. 6. Since $LiMn_2O_4$ particles were much smaller than Mn_2O_3 particles, the $LiMn_2O_4$ particles have been analyzed by TEM. The TEM photograph of $LiMn_2O_4$ particles is represented in Fig. 7. It was observed that the size of particles as well as the structure was different. It can be therefore concluded that the amount of OH^- ions significantly affect on the reaction pathways and thus enabling to change the size and structure of particles formed.

CONCLUSION

The synthesis of manganese oxide particles in SCW has been studied. The particles formed at 430 °C were smaller than those at 380 °C and their size distribution was also much narrower. Therefore the reaction temperature for synthesis in SCW should be relatively higher than the critical temperature, to synthesize the particles of uniform size and shape. MnO_2 was a main product for the particles formed at 380 °C and a minor component was Mn_2O_3, while Mn_2O_3 was a major product for the particles at 430 °C and MnO_2 was minor. This means that the structure of the formed particles is dependent on the reaction temperature. A reaction mechanism has been proposed with the oxidation, hydrolysis and dehydration steps.

The synthesis of $LiMn_2O_4$ particles in SCW has been studied. Under the constant reaction temperature and pressure, a change in reactant composition has led to the formation of particles with different structure such as $LiMn_2O_4$, Mn_2O_3 and MnO_2. The selective synthesis of $LiMn_2O_4$ was mainly dependent on the amounts of OH^- ion in the reactants, not Li/Mn ratio or $LiNO_3$ amount. A reaction mechanism has also been proposed to illustrate the formation of $LiMn_2O_4$ in the SCW process. We therefore concluded that the amount of OH^- ions significantly affected the reaction pathways and thus enabling to change the size and structure of particles formed.

Consequently, it can be concluded that it is possible to synthesize specific metal oxide particles by changing reaction parameters such as the reaction temperature, reactant composition, and amount of OH^- ions.

ACKNOWLEDGMENT

This research has been supported by 2003 Daegu University Research Grant.

REFERENCES

Adschiri, T., Kanazawa, K. and Arai, K., "Rapid and continuous hydrothermal crystallization of metal oxide particles in supercritical water," *J. Am. Ceram. Soc.*, **75**, 1019 (1992).

Adschiri, T., Hakuta, Y. and Arai, K., "Hydrothermal synthesis of metal oxide fine articles at supercritical conditions," *Ind. Eng. Chem. Res.*, **39**, 4901 (2000).

Bailar, J. C., Emeleus, H. J., Nyholm, S. R. and Trotman-Dickenson, A. F., *Comprehensive inorganic chemistry*, vol. 3, Pergamon Press, New York (1976).

Cabaoas, A. and Poliakoff, M., "The continuous hydrothermal synthesis of nano-particulate ferrites in near critical and supercritical water," *J. Mater. Chem.*, **11**, 1408 (2001).

Cotton, F. A., Wilkinson, G., Murillo, C. A. and Bochmann, M., *Advanced inorganic chemistry*, 6th Edition, John Wiley & Sons, Inc., New York (1999).

Hakuta, Y., Terayama, H., Onai, S., Adschiri, T. and Arai, K., "Hydrothermal synthesis of CeO_2 fine particles in supercritical water," Proc. 4th Int. Symp. on 'Supercritical Fluids,' Sendai, Japan, May, 255-258 (1997).

Hakuta, Y., Adschiri, T., Suzuki, T., Chida, T., Senio, K. and Arai, K., "Flow method for rapidly producing barium hexaferrite particles in supercritical water," *J. Am. Ceram. Soc.*, **81**, 2461 (1998).

Hakuta, Y., Senio, K., Ura, H., Adschiri, T., Takizawa, H. and Arai, K., "Production of phosphor (YAG : Tb) fine particles by hydrothermal synthesis in supercritical water," *J. Mater. Chem.*, **9**, 2671 (1999).

Hakuta, Y., Yamamoto, Y., Okada, K.-I., Adschiri, T., Arai, K., Kanamura, K., Goto, A., Hamagami, J. and Umegaki, T., "Production of spinel $LiMn_2O_4$ fine crystals via hydrothermal synthesis in supercritical water," Proc. 40th Symp.in Japan on 'Battery,' Kyoto, Japan, November, 251-252 (1999).

Holleman, A. F. and Wiberg, E., *Inorganic chemistry*, 34th Edn, Aca-

demic Press, San Diego (2001).
Lee, J.-H., Kim, M.-H., Choo, K.-H. and Ham, J.-Y., "Synthesis of TiO_2 particles in water from subcritical to supercritical conditions," *J. Korean Ind. Eng. Chem*., **14**, 847 (2003).
Nam, S.-C. and Kim, G-J., "Characterization of barium hexaferrite produced by varying the reaction parameters at the mixing-points in a supercritical water crystallization process," *Korean J. Chem. Eng*., **21**, 582 (2004).
Rho, S.-W. and Park, S.-D., "Influence of stoichiometry and alkalinity on barium hexaferrite formation via the supercritical water crystallization method," *Korean J. Chem Eng.*, **19**, 120 (2002).
Wakihara, M., Li, G. and Ikuta, H., *Cathode active materials with a three-dimensional spinel framework*, Lithium Ion Batteries, Wakihara, M. and Yamamoto, O., eds., Wiley-Vch (1998).