

Synthesis of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ Nano-powders using Glycine-Nitrate Process for Anode of High Temperature Electrolysis

Ho Sang Choi^{1*}, Si Ok Ryu², Hyun Jin Kim²,
Gab Jin Hwang³, Sang Kook Woo³

¹Department of Chemical Engineering, Kyungil University,
Gyeongsan-si, Korea, choihs@kiu.ac.kr

²School of Display & Chemical Engineering, Yeungnam University,
Gyeongsan-si, Korea, soryu@ynu.ac.kr

³Thermochemical Hydrogen Research Group, Korea Institute of Energy Research,
Daejeon, Korea, gjhwang@kier.re.kr, skwoo@kier.re.kr

ABSTRACT: Lanthanum, strontium and manganese (LSM), as an oxygen-electrode (anode) material for high temperature electrolysis system (HTES), were synthesized by a modified-glycine nitrate process (GNP). The synthesis of LSM was carried out at three different conditions and the starting materials and solvent were also varied in this study. The ratio of La:Sr:Mn was fixed to 8:2:10 in the preparation. The ratio of LSM and glycine in the starting condition was 1:1. Based on the result of TG-DSC thermal analysis, the prepared LSM formula was calcined at 800°C and then it was further sintered at 1200°C to remove the organic residues from the material. Perovskite phase was observed and the secondary phases of Mn_2O_4 and La_2O_3 were detected in XRD measurement of the sintered powder. The microscopic structure of the powder was investigated by Scanning Electron Microscope (SEM) and a size of each agglomerated powder was larger than around 200 nm. The powder was sonicated in distilled water for the degglomeration and then the particle size distribution was confirmed by TEM. The average particle size of the powder was about 10 nm. Surface areas obtained from Brunauer-Emmett-Teller surface area measurement (BET) at three different conditions were 2.9796m²/g, 0.5272m²/g and 1.8870m²/g.

Keywords: High Temperature Electrolysis System (HTES), Perovskite (ABO_3), Anion, Glycine-Nitrate Process (GNP)

1. INTRODUCTION

The structure of high temperature electrolysis system (HTES) for hydrogen production is similar to the one of solid oxide fuel cell (SOFC) in technical aspects [1, 2]. It is operated in the inverse direction

of solid oxide fuel cell (SOFC). That is, steam is supplied into the cathode and then electrolyzed into hydrogen gas and oxide ion by passing an electric current through it. A negatively charged oxide ion is transferred from the cathode through the electrolyte to oxygen electrode (anode).

Product hydrogen is formed at the cathode. The electrolyte should be dense so that the reactant and product gases are not penetrated it. It requires a very highly oxygen ion conductivity. Meanwhile, the electrode must have a porous structure that allows rapid mass transport of reactant and product gases and have a high electronic conductivity. Since HTES utilizes the electrolysis of water steam at high temperature, its theoretical electrolytic voltage, $V_{o,rev,800\text{ }^{\circ}\text{C}}=0.69\text{V}$, for HTES is much less than the voltage, $V_{o,rev,25^{\circ}\text{C}}=1.23\text{V}$, for the electrolysis of water at low temperature. As the result, the high temperature electrolysis is more efficient economically than the traditional room-temperature electrolysis. Importance of hydrogen production at high temperature becomes greater due to an advantage of the cost reduction as only third of energy being necessary for water electrolysis is replaced with the thermal energy [3, 4]. (La, Sr) MnO_3 powder used for an oxygen-electrode (anode) of HTE has an advantage of synthesis at high temperature. Since the contamination of powder by the impurities will exert a negative influence on the performance of the anode, however, its introduction should be prevented during the synthesis of (La, Sr) MnO_3 powders.

For the synthesis of the anode, there are several different methods such as solid-state reaction method, co-precipitation method, hydrothermal process, and sol-gel method [5-8]. In this study, a modified-glycine nitrate process (GNP) was used in the synthesis of (La, Sr) MnO_3 powder for an oxygen-electrode (anode) of HTE. The modified-GNP is a method to obtain the perovskite-type nano-sized powder directly from the solution containing the powder precursors without formation of any secondary phase [9-11]. In the modified-GNP, the self-initiated combustion reaction is caused by glycine acting as a fuel and nitrate group acting as an oxidant. It is known that glycine plays two important roles in the synthesis of powders. First, it

increases the solubility as forming the metallic anions and the metallic complexes. Second, glycine is oxidized by a nitrate ion acting as a fuel for the self-initiated combustion if a precipitation is inhibited during the evaporation of moisture. In addition, it acts not only as a solvent to dissolve metal oxides and metallic nitrates, which are the sources of the anions, but also as a source of oxidant inducing the self-initiated combustion [12-14]. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ composite for the anode material was synthesized by the modified-GNP and the effect of the variation of conditions on the synthesis was investigated in this study.

2. EXPERIMENTAL

Various metal oxides and metal nitrates were employed as the starting materials in the powder synthesis by the glycine-nitrate process (GNP). As presented in Table 1, La_2O_3 (Aldrich Chemicals, 99.9%), SrCO_3 (Aldrich Chemicals, 99.9+%), and MnO_2 (Aldrich Chemicals, $\geq 99\%$) were used in condition A, while $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{N}_2\text{O}_6\text{Sr}$, and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were used in conditions B and C as the oxidizing agents. Molar ratio of La : Sr : Mn was fixed to 8 : 2 : 10 in this study.

Table I: Starting Materials and Solvents for Glycine-Nitrate Process.

	Condition A	Condition B	Condition C
La	La(La ₂ O ₃)	La(NO ₃)	
Sr	Sr(SrCO ₃	N ₂ O ₆ Sr	
Mn	Mn(MnO ₂),	Mn(NO ₃) ₂ ·4H ₂ O	
Glycine	Glycine(Aminoacetic)		
Solvent	3 M Nitric acid solution		Distilled Water

In conditions A and B, the starting materials and glycine were dissolved in 100 ml of 3M nitric acid under constant

stirring and then H_2O_2 solution (30 wt%) was slowly added to the solution for dissolution of MnO_3 , which was insoluble in the nitric acid solution. The ratio of the starting materials acting as the oxidants to glycine acting as a fuel was 1:1 in the preparation [15]. In condition C, the distilled water was used as solvent instead of the nitric acid solution and the ratio of metal nitrates to glycine was also fixed to 1:1. A flow chart showing our experimental procedure is presented in Figure 1. The prepared solution was dried by air heated at 90°C in order to remove moisture from the dissolved material. Once the water in the solution was evaporated, the precursor was formed after passing through the stage of the opaque viscous liquid. After the auto-ignition and the initiation of a highly exothermic combustion reaction between glycine and oxidant, the precursor materials were converted into black powder. Based upon TG-DSC analysis, the resulting black powder of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ formula synthesized by GNP was calcined at 800°C for 2 hours and then it was further sintered at 1200°C for 4 hours to remove the organic residues from the powder.

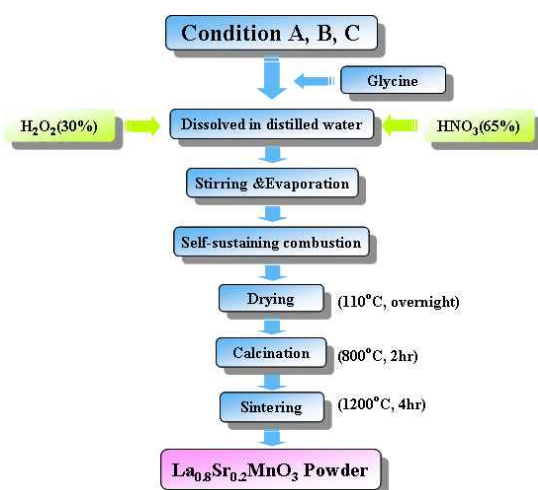


Figure 1: Flow chart of experimental procedure.

X-ray diffraction (XRD) analysis was performed using a Rigaku D/MAX-2500 to

identify the perovskite phases in the synthesized powders. The scans were carried out in the 2θ range ($20\sim 80^\circ$) with scanning speed of $5^\circ/\text{min}$ at 40kV and 100mA. The mass and heat changes of the samples were measured by Thermal Gravimetry and Differential Scanning Calorimetry (TG/DSC, Setaram, LABSIS TM). Temperatures were raised from room temperature up to 1300°C in the rate of $10^\circ\text{C}/\text{min}$ under Argon atmosphere and the weight changes were monitored during the process. The microscopic structure of the powder was investigated by Field Emission Scanning Electron Microscope (FE-SEM, HITACHI, S-4100). The detailed microstructure of the thermally treated $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ composite powder was observed by Transmission Electron Microscope (TEM, HITACHI, H-7600). Surface areas of the prepared powders were measured using Brunauer-Emmett-Teller surface area measurement (BET, Micromeritics, GEMINI 75).

3. RESULTS AND DISCUSSIONS

TG-DSC thermal analysis was carried out to measure the weight and heat changes of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powders synthesized by GNP at three different conditions. Figure 2 shows the TG/DTA curves of the synthesized powders prepared by GNP for $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powders. In the measurement, temperature was increased at a heating rate of $10^\circ\text{C}/\text{min}$ from 24°C to 1300°C under Argon atmosphere. The weight losses in the TG curve and the heat flow changes in DTA curve were observed in condition A in the range of $25\sim 100^\circ\text{C}$ as shown in Figure 2(a). The heat flow change was likely due to the dehydration. Weight loss and heat release in the range of $190\sim 350^\circ\text{C}$ were caused by the combustion of the residual glycine remained in the system after the synthesis. It was considered that a further weight loss and heat release

around at 600°C was due to the loss of organic residues by the oxidation and the loss of NO_3^- and CO_3^{2-} , respectively [16]. In Figure 2(b) for condition B, the weight loss was observed in the range of 25~100°C due to the dehydration and its curve was gradually descendent. The heat release around at 600°C was likely due to the loss of NO_3^- . It was considered that a further weight loss around at 600°C was due to the loss of organic residues by the oxidation. As shown in Figure 2(c) for condition C, the weight loss in the TG curve was less than the one in the conditions of A and B. It is indicated that the synthesis was carried out properly in the modified GNP. Weight loss and heat release at 300°C were caused by the combustion of the residual glycine remained in the system. Heat releases observed at 960°C in condition A, B, and C are likely caused by the formation of perovskite-type structures.

Figure 3 shows XRD patterns of the synthesized $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powders obtained in three different conditions. Figure 3(a) presents condition A, in which La_2O_3 , SrCO_3 , MnO_2 , and glycine were dissolved in 100 ml of 3M nitric acid. Figure 3(b) shows XRD pattern of condition B, in which $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{N}_2\text{O}_6\text{Sr}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and glycine were dissolved in 100 ml of 3M nitric acid. XRD pattern of condition C, in which the same powder precursors as in condition B and glycine were dissolved in the distilled water instead of nitric acid, was presented in Fig 3(c). The crystallinity of the resulting black powder of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ formula, which was calcined at 800°C and then further sintered at 1200°C on the basis of TG-DSC thermal analysis, was confirmed in Figure 3.

Strong crystallinity of perovskite phase was confirmed in the synthesized powder and formation of secondary phases such as La_2O_3 and Mn_2O_4 was also observed in Figure 3(a). The synthesized powder in condition B also shows the strong crystallinity of perovskite phase as shown in

Figure 3(b). No secondary phases but La_2O_3 were observed in condition B. As shown in Figure 3(c), the strong peaks identifying the crystallinity of perovskite phase were observed for the powder synthesized in condition C. Formation of secondary phases such as La_2O_3 and Mn_2O_4 was also observed in Figure 3(c) and, specially, the peak for La_2O_3 was stronger than the peaks in Figure 3(a) and (b). It was known that the formation of La_2O_3 was because of the hydration of metallic salts in the synthesis [16]. It was also reported that the secondary phase of La_2O_3 inhibited the powder growth and lowered the electric conductivity because La_2O_3 acts as an insulator [17].

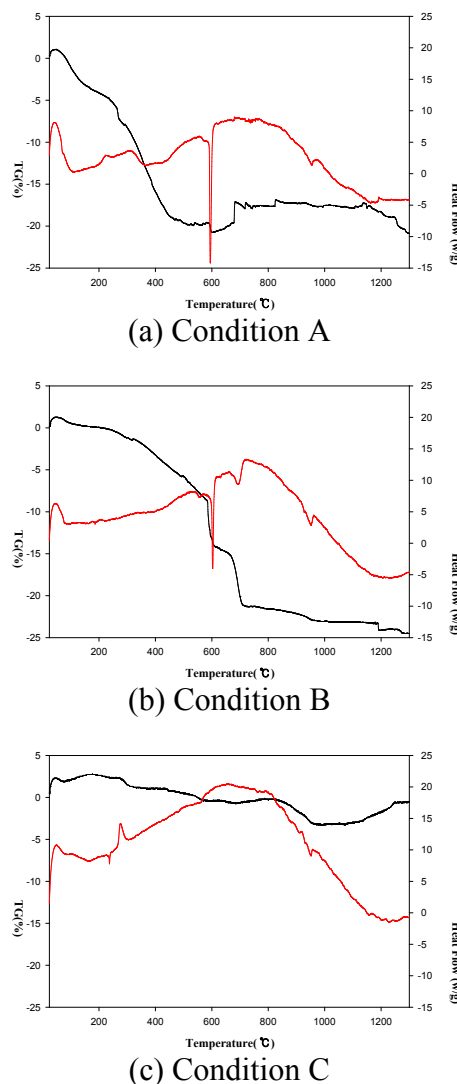


Figure 2: TG/DSC curves for the synthesized powders prepared using GNP method.

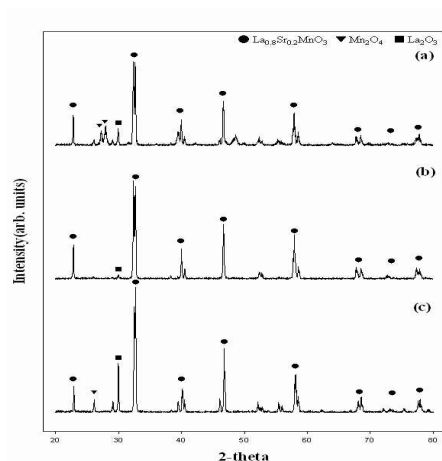
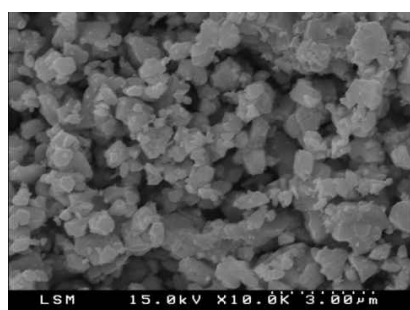
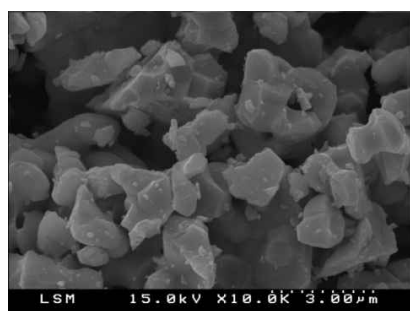


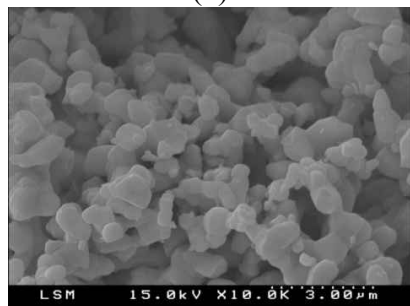
Figure 3: X-ray diffraction patterns of the synthesized $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powders in (a) Condition A, (b) Condition B, and (c) Condition C.



(a)



(b)



(c)

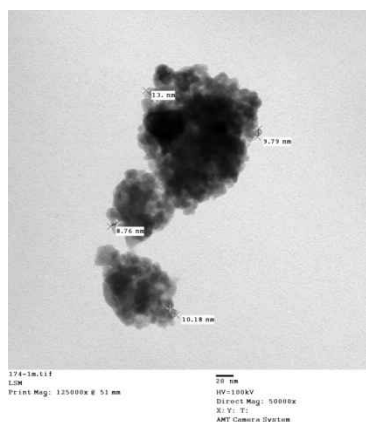
Figure 4: SEM micrographs of the powders synthesized by Glycine-Nitrate Process method in (a) Condition A, (b) Condition B, and (c) Condition C.

The SEM images of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powders synthesized by GNP after calcination and sintering at 800°C and 1200°C , respectively, are presented in Figure 4. The particle sizes and morphologies of the synthesized powders were varied with the conditions in the preparation of powders. The particle size of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powder prepared in condition A was uniformly distributed with its average size about 200 nm as shown in Figure 4(a). However, the particle sizes of the powders prepared in condition B and C were not uniformly distributed and the particles were agglomerated as presented in Figure 4(b) and (c). The average particle sizes of the powders prepared in condition B and C were about 500 nm and 300 nm, respectively. The powder synthesized in condition A had smaller size and more uniform distribution than the powders synthesized in condition B and C. The specific surface areas of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powders synthesized in three different conditions were measured by BET and it was presented in Table 2. It was well matched to the results of the SEM micrographs in Figure 4. In BET surface area measurement, the powder synthesized in condition A had the largest specific surface area, while the powder prepared in condition B had the smallest surface areas.

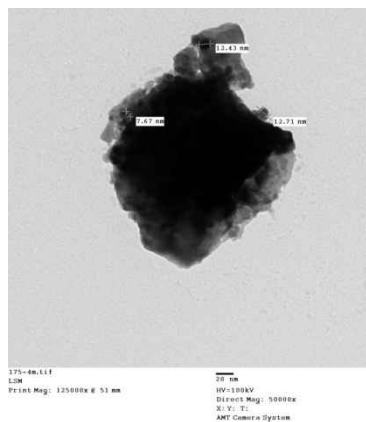
Table II: Specific Surface Areas of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$.

$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	BET(m^2/g)
Condition A	2.9796
Condition B	0.5272
Condition C	1.8870

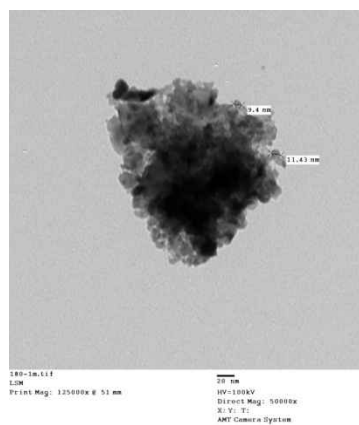
TEM observation was performed in order to evaluate the microstructure of the particles. For the TEM photographs, LSM composite powders were ground with a ball mill and then the powders were sonicated in the distilled water for 1 hour. Figure 5 shows the particle morphologies of the thermally treated $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powders, which were synthesized in conditions A, B, and C as presented in Table 1. The shapes of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ particles were not uniform for all conditions and the fine grains smaller than 10 nm were strongly agglomerated as shown in Figure 5. It was considered that the grains were agglomerated by a neck bond caused due to a release of high heat and an evolution of gases after the self-initiated combustion reaction.



(a)



(b)



(c)

Figure 5: TEM Photographs of the powders synthesized by Glycine-Nitrate Process method in (a) Condition A, (b) Condition B, and (c) Condition C.

4. CONCLUSION

$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ composite as the anode material for HTES was synthesized by the modified-GNP in this study. Metal oxides and metal nitrates were used as oxidants in the preparation of material. The synthesized LSM formula was calcined at 800°C and then it was further sintered at 1200 °C to remove the organic residues from the material. The perovskite-type phase was confirmed in the synthesized powder and the formation of secondary phases was also observed in XRD analysis. In condition A, La_2O_3 and Mn_2O_4 were formed as the secondary phases. No secondary phases but La_2O_3 were observed in condition B. Formation of La_2O_3 and Mn_2O_4 were also confirmed in condition C and, specially, the peak for La_2O_3 was stronger than the peaks in condition A and B. From TG-DSC thermal analysis, it was confirmed that the perovskite-type composite powders were formed around at 960 °C in all conditions. In the range of 750 °C~1200 °C, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powder having the excellent thermal stability was synthesized without a significant weight loss. Particle morphologies were determined by SEM

analysis. The synthesized $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powders had an average particle size of submicron. TEM observations confirmed the agglomerated particle structure composed of nanosized grains, of which mean size was around 10 nm. The specific surface areas of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ powders were measured by BET and it was well matched to the results of the SEM and TEM observations. In BET surface area measurement, the specific surface area became larger as the particle size was smaller. Since the synthesis of nanosized perovskite-type materials led to a significant reduction in the thickness of anode, it will be favorable for developing the tube-type stacks for HTES.

ACKNOWLEDGEMENT

This work was supported by a grant from 'The Hydrogen Energy R&D Center, one of the 21st Century Frontier Programs' and we are grateful for financial support to the Ministry of Science and Technology, S. Korea.

REFERENCES

- [1] Minh NQ. High-Temperature Fuel Cells. Part II: The Solid Oxide Fuel Cell. Chemtech. 1991; 21: 120-26.
- [2] Minh NQ. Ceramic Fuel Cell. Journal of the American Ceramic Society. 1993; 76(3): 563-588.
- [3] Choi HS, Son HS, Hwang GJ, Bae KK. Microstructure Analysis with Preparation Condition of Electrolyte Membrane for High Temperature Electrolysis. Transactions of the Korean Hydrogen and new Energy Society. 2006; 17(2): 141-148.
- [4] Choi HS, Son HS, Sim KS, Hwang GJ. The thermal stabilization characteristics of electrolyte membrane in high temperature electrolysis (HTE). Transactions of the Korean Hydrogen and new Energy Society. 2005; 16(2): 150-158.
- [5] Taguchi H, Matsu-ura SI, Nagao M, Choso T, and Tabata K. Synthesis of $\text{LaMnO}_{3+\delta}$ by Firing Gels Using Citric Acid. Journal of Solid State Chemistry. 1997; 129(1): 60-65.
- [6] Zhang Q, Saito F. Mechanochemical Synthesis of LaMnO_3 from La_2O_3 and Mn_2O_3 Powders. Journal of Alloys and Compounds. 2000; 297: 99-103.
- [7] Kakihana M, Arima M, Yoshimura M, Ikeda N, Sugitani Y. Synthesis of High Surface Area $\text{LaMnO}_{3+\delta}$ by a Polymerizable Complex Method. Journal of Alloys and Compounds. 1999; 283: 102-105.
- [8] Shin WS, Park IS, Kim SJ, and Park S. Studies on the fabrication and Properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Cathode Contact Prepared by Glycine-Nitrate Process and Solid State Reaction Method for the High Efficient Solid Oxide Fuel Cells Applications. Bulletin of the Korean Institute of Electrical and Electronic Materials Engineers. 1997; 10(2): 141.
- [9] Chick LA, Pederson LR, Maupin GD. Glycine-Nitrate Combustion Synthesis of Oxide Ceramic Powders. Materials Letters. 1990; 10: 6-12.
- [10] Peng R, Xia C, Fu Q, Meng G, Peng D. Sintering and Electrical Properties of $(\text{CeO}_2)_{0.8}(\text{Sm}_2\text{O}_3)_{0.1}$ Powders Prepared by Glycine-Nitrate Process. Materials Letters. 2002; 56(6): 1043-1047.
- [11] Kim JD, Moon JW, Kim GD, Kim CE. Preparation of (La, Sr) MnO_3 Powder by Glycine-Nitrate Process Using Oxide as Starting Materials. Journal of the Korean Ceramic Society. 1997; 34(10): 1003-1008.
- [12] Lambert JB, Chick LA, Weber WJ. Synthesis, air sintering and properties of lanthanum and yttrium chromites and manganites. Solid State Ionics. 1992; 52: 235-42.
- [13] Kim GD, Park JA. Synthesis and sintering of BaTiO_3 Powder by the

- Glycine-Nitrate Process Using Metal Carbonate and Alkoxide. Journal of the Ceramic Society of Japan. 1999; 107: 691-696.
- [14] Koo BS, Yoon HS, Kim BH. Synthesis and Characterization of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ Cathode for Solid Oxide Fuel Cell by Glycine-Nitrate Process. Journal of the Korean Ceramic Society. 2001; 38(1): 45-51.
- [15] Choi HS, Kim HJ, Ryu SK, Hwang GJ. Preparation and Characterization of (La, Sr) MnO_3 Electrode for High Temperature Steam Electrolysis by Glycine-Nitrate Process. Transactions of the Korean Hydrogen and new Energy Society. 2007; 18(1): 46-51.
- [16] Lee MJ, Kim SK, Jee MJ, Choi BH, Park SS, Lee KH. Effect of Starting Materials on the Characteristics of $(\text{La}_{1-x}\text{Sr}_x)\text{Mn}_{1+y}\text{O}_{3-\delta}$ Powder Synthesized by GNP. Journal of the Korean Ceramic Society. 2007; 44(1): 52-57.
- [17] Lee HY. Study on the Electrochemical and Interfacial Properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Fe}_x\text{Co}_{1-x}\text{O}_3$ Cathode for SOFC. Ph. D. Thesis, Seoul National University, Seoul, 1997.