Electrochemical Properties of Boron-Doped LiMn₂O₄ Nanoparticles Covered with Glass Material Prepared by High-Temperature Flame Spray Pyrolysis

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Lithium boron oxide (LBO) glass-modified LiMn₂O₄ nanoparticles are prepared by high-temperature flame spray pyrolysis. The mean sizes of the pure and 5 wt% glass-modified LiMn₂O₄ powders are 125 and 175 nm, respectively. In addition, their mean crystallite sizes are 62 and 82 nm, respectively. At a high operating temperature of 60°C and a current density of 1 C, the discharge capacity of the pure LiMn₂O₄ powders decreases from 143 to 93 mAh g⁻¹ after 100 cycles, with the capacity retention at 65% of the initial capacity. However, the discharge capacity of the 5 wt% glass-modified LiMn₂O₄ powders decreases from 123 to 106 mAh g⁻¹ after 100 cycles, with the capacity retention at 86% of the initial capacity. The LBO glass material covering the LiMn₂O₄ powders improves their electrochemical properties by decreasing their reactivity with acidic electrolytes. Moreover, the high crystallinity and stabilization effect of boron doping in the spinel structure improves the electrochemical properties of the LBO glass-modified LiMn₂O₄ powders.

Keywords: nanoparticles; flame spray pyrolysis; lithium manganate; glass material

1. INTRODUCTION

It is well known that the electrochemical performance of a cathode material is strongly affected by particle properties such as morphology, specific surface area, crystallinity, and composition [1–16]. The use of cathode powders comprising nanometer-sized particles has been investigated because these powders exhibit high charge/discharge rates due to their large electrode/electrolyte interface areas [12– 16]. However, nanometer-sized cathode powders suffer from high fading rates because of their large electrode/electrolyte interface areas and poor crystallinity [17–19]. The cycle properties as well as the initial charge/discharge capacities of the nanometer-sized cathode powders were strongly affected by their preparation processes and post-treatment conditions.

Electrochemical and physical properties of spinel LiMn₂O₄ nanoparticles prepared by various synthetic processes have been investigated [1–3,20–24]. Flame spray pyrolysis is known to be an efficient continuous process for the large-scale production of powders comprising nanosized particles [1–7]. Patey et al. produced crystalline LiMn₂O₄ nanoparticles on the order of 26 nm in a one-step flame spray pyrolysis process from a spray solution of Mn(III)-acetylacetonate and Li-acetylacetonate dissolved in a mixture of 2-ethylhexanoic acid and toluene. An optimized nanosized powder retained the highest galvanostatic discharge capacity of over 80 mAh g⁻¹ beyond 60 cycles at 50 C, proving to be a suitable positive material for high-power Li-ion batteries [1]. Zhang et al. prepared LiMn₂O₄ powders by low-temperature flame spray pyrolysis at about 1100°C from a spray solution of LiNO₃ and Mn(NO₃)₂·4H₂O dissolved in methanol. The geometric mean diameter of the annealed powder was 330 nm [2]. Yi et al. prepared LiMn₂O₄ nanoparticles by flame spray pyrolysis from an aqueous spray solution of the metal salts [3]. The initial discharge capacities of these powders changed from 91 to 112 mAh g⁻¹ when the quantity of excess lithium was increased from 0% to 30% of the stoichiometric amount.

To improve the electrochemical properties of the $LiMn_2O_4$ nanoparticles, surface modification by stable oxide materials has proven to be effective [25–29]. A lithium boron oxide (LBO) glass material has also been used as a coating material because of its high lithium ion conductivity, good wetting properties, and relatively low viscosity [30–34].

The direct surface modification of ceramic powders with other oxide materials during flame spray pyrolysis has been examined by various research groups [35–40]. However, this type of modification for nanometer-sized cathode particles has not been well studied in flame spray pyrolysis. In this investigation, LBO glass-modified LiMn₂O₄ nanoparticles were prepared by flame spray pyrolysis using an aqueous spray solution prepared from inexpensive metal salts. LBO glass material was applied as the source material of the boron dopant as well as the coating material of the LiMn₂O₄ nanoparticles. The electrochemical properties of the boron-doped LiMn₂O₄ nanoparticles covered with various amounts of glass material were investigated.

2. EXPERIMENTAL

The schematic diagram for the flame spray pyrolysis system used in this study was presented in a previous paper [3]. The flame spray pyrolysis system had a droplet generator, a flame nozzle, a quartz reactor, a powder collector, and a blower. A 1.7-MHz ultrasonic spray generator with six resonators was used to generate droplets, which were then carried into the high-temperature diffusion flame by oxygen (carrier gas). Droplets or powders evaporated, decomposed, and melted inside the diffusion flame. Propane (fuel) and oxygen (oxidizer) were used to produce the diffusion flame. The flame nozzle consisted of five concentric pipes. Droplets generated from the precursor solution were supplied to the diffusion flame through the central pipe by the carrier gas, with an appropriately varied

flow rate. The flow rate of the fuel gas was fixed at 5 L min⁻¹, and the flow rates of the oxidizer and carrier gases were fixed at 40 L min⁻¹ and 10 L min⁻¹, respectively.

An aqueous spray solution was prepared by dissolving lithium nitrate (LiNO₃, Junsei) and manganese nitrate hexahydrate [Mn(NO₃)₂.6H₂O, Junsei] in distilled water. The amount of lithium added to the spray solution was in excess of 20 wt% of the stoichiometric amount to facilitate the formation of LiMn₂O₄ powders. For the Li₂O–2B₂O₃ glass modifier, lithium nitrate (LiNO₃, Junsei) and boric acid (H₃BO₃, Aldrich) were added into the above Li and Mn spray solution. The amount of the LBO glass modifier was varied from 3 to 20 wt% of the LiMn₂O₄ powders. The precursor particles obtained by flame spray pyrolysis were post-treated at 650°C for 3 h in an air atmosphere.

The crystal structures of the prepared cathode powders were investigated using X-ray diffractometry (XRD, X'pert PRO MPD) with Cu K α radiation ($\lambda = 1.5418$ Å) at the Korea Basic Science Institute (Daegu). Morphological characteristics were investigated using scanning electron microscopy (SEM, JEOL JSM-6060) and high-resolution transmission electron microscopy (TEM, JEOL JEOL-2100F) at 200 kV. The XPS spectra of the powders were investigated using X-ray photoelectron spectroscopy (XPS, ESCALAB-210) with Al K α radiation (1486.6 eV). The binding energy was calibrated with reference to the C 1s level of carbon (284.5 eV). The elemental compositions of the powders were investigated using an inductively coupled plasma–optical emission spectrometer (ICP-OES, Thermo elemental, ICAP 6000). The surface areas of the powders were measured by the Brunauer–Emmett–Teller (BET) method using N₂ as the adsorbate gas.

The capacities and cycle properties of the powders were determined using a 2032-type coin cell. The cathode electrode was prepared from a mixture containing 20 mg LiMn₂O₄ and 12 mg TAB (TAB is a mixture of 9.6 mg teflonized acetylene black and 2.4 mg of a binder). Lithium metal and microporous polypropylene film were used as the anode electrode and separator, respectively. The electrolyte was 1 M LiPF₆ in a 1:1 mixture by volume of ethylene carbonate/dimethyl carbonate (EC/DMC). The charge/discharge characteristics of the samples were determined through cycling in the 3.2–4.5 V potential range at a constant current density of 1 C (120 mA g⁻¹). Cyclic voltammetry measurements were carried out at a scan rate of 0.07 mV s⁻¹. Electrochemical impedance spectra of the pure and LBO glass-modified LiMn₂O₄ powders in the fully charged state (4.5 V) were analyzed at 0.1 Hz to 100 KHz (VersaStat 4, Ametek).

3. RESULTS AND DISCUSSION

The morphologies of the cathode powders prepared by flame spray pyrolysis were strongly affected by the preparation conditions, such as flame temperature, types of precursor materials, and solvent. In this study, a high-temperature diffusion flame was formed from the propane fuel gas to vaporize the cathode material. The morphologies of the pure and LBO glass-modified LiMn_2O_4 powders directly prepared by flame spray pyrolysis are shown in Fig. 1. The prepared powders had nanometer sizes and non-aggregation characteristics, irrespective of the glass modifier. Complete evaporation of LiMn_2O_4 and lithium borate glass materials occurred inside the high-temperature diffusion flame. Consequently, nanometer-sized cathode powders were formed from the vapors by

nucleation and growth processes. No micron or submicron-sized particles obtained from incompletely evaporated intermediate powders were observed in the SEM image.



(b) 5 wt% glass

Figure 1. Morphologies of the pure and LBO glass-modified LiMn₂O₄ powders directly prepared by flame spray pyrolysis.

The nanometer-size cathode powders directly prepared by flame spray pyrolysis had poor crystallinity and were compositionally non-homogeneous because the powders were formed from

vapors in the gas phase over a short residence time (on the order of milliseconds). To exhibit good electrochemical properties, cathode powders should have high crystallinity and phase homogeneity.



(b) 5 wt% glass

Figure 2. SEM images of the post-treated pure and LBO glass-modified LiMn₂O₄ powders.

Therefore, the powders prepared by flame spray pyrolysis were post-treated at 650°C. Figs. 2 and 3 show the SEM and TEM images of post-treated pure and LBO glass-modified $LiMn_2O_4$ powders. The powders were nanometer-sized irrespective of the glass modifier content, even though

crystal growth in the powders occurred during the post-treatment process. The mean sizes of the powders with and without 5 wt% glass modifier were 175 and 125 nm, respectively. The use of the glass modifier slightly increased the mean size of the $LiMn_2O_4$ powders, as measured from the TEM images.



(b) 5 wt%



(c) 10 wt%

Figure 3. TEM images of the post-treated pure and LBO glass-modified LiMn₂O₄ powders.

High-resolution TEM images exhibited clear lattice fringes with a separation of 0.48 nm and a single crystalline structure, irrespective of the glass modifier. This value corresponds to the (111) plane of the cubic lattice of $LiMn_2O_4$ [41]. The compositions of the pure and LBO glass-modified $LiMn_2O_4$ powders analyzed by ICP are summarized in Table 1.

	Crystalline Size (nm)	Lattice Parameter (Å)	Specific Surface Area $(m^2 g^{-1})$	ICP data (Li:Mn)
0 wt%	62	8.245	10.8	1:2
3 wt%	76	8.236	7.4	-
5 wt%	82	8.232	6.1	1.01 : 2
10 wt%	77	8.225	9.1	1.06 : 2
20 wt%	77	8.201	7.3	-

The ratio of Li and Mn components of the pure powder without the glass modifier was similar to that of stoichiometric $LiMn_2O_4$. The LBO glass-modified $LiMn_2O_4$ powders had excess lithium component, present in the form of LBO glass.

Fig. 4 shows the XRD patterns of the post-treated pure and LBO glass-modified $LiMn_2O_4$ powders. The powders had pure cubic spinel $LiMn_2O_4$ crystal structures irrespective of the glass modifier. Impurity peaks that could originate from the boron and lithium components of the glass modifier were not observed in the XRD patterns. The mean crystallite size of the pure LiMn_2O_4

powder, calculated by Scherrer's equation from the half-width of the (111) XRD peak, was 62 nm (Table 1). However, the mean crystallite size of the 5 wt% LBO glass-modified $LiMn_2O_4$ powder was 82 nm.



Figure 4. XRD patterns of the post-treated pure and LBO glass-modified LiMn₂O₄ powders.

The lattice parameters decreased with increasing amounts of the glass modifier in the prepared LiMn₂O₄ powders (Table 1). Doping of boron, with its small radius, in the spinel LiMn₂O₄ phase decreased the lattice parameters [42]. The XRD peaks also shifted to higher angles according to the doping concentration of boron in the powders, as shown in Fig. 4. Therefore, the boron doping concentration in the LiMn₂O₄ powders increased with increasing amounts of the glass modifier. The glass-modified LiMn₂O₄ powders had lower BET surface areas than the pure LiMn₂O₄ powders (Table 1). The LBO glass modifier, with its low melting temperature, also acted as a sintering agent to increase the mean particle size as well as decrease the BET surface areas of the LiMn₂O₄ powders. In the previous study, LBO glass-coated LiMn₂O₄ powders were prepared by spray pyrolysis from an aqueous spray solution of Li, Mn, and B components [34]. The precursor powders prepared at 900°C were post-treated at 650°C for 3 h. A decrease in the lattice constant of the LiMn₂O₄ powders as a result of the substitution by small-radius boron ions at manganese sites did not occur.

Fig. 5 shows the Mn 2p XPS spectra of the pure and LBO glass-modified $LiMn_2O_4$ powders prepared by flame spray pyrolysis. The Mn 2p XPS peaks shifted towards higher binding energy with increasing amounts of the LBO glass modifier. The Mn $2p_{3/2}$ binding energies for the pure and 20 wt% LBO glass-modified $LiMn_2O_4$ powders were 642.1 and 642.5 eV, respectively. The shifts of the Mn 2p

XPS peaks towards higher binding energies show the increase of the ratio of Mn^{+4} and Mn^{+3} ions in the $LiMn_2O_4$ powders. The relative ratios of Mn^{+3} and Mn^{+4} ions in the $LiMn_2O_4$ powders were calculated by least squares fitting analysis using two spectra of Mn_2O_3 and MnO_2 [43,44]. The average oxidation states of the Mn ions were calculated from the relative ratios of the Mn^{+3} and Mn^{+4} ions.



Figure 5. Mn 2p XPS spectra of the pure and LBO glass-modified LiMn₂O₄ powders

The average Mn ion oxidation states in the 0, 5, and 10 wt% LBO glass-modified $LiMn_2O_4$ powders were 3.50, 3.54, and 3.57. Boron dopant occupied the Mn^{3+} position in the lattices and decreased the Mn^{3+}/Mn^{4+} ratio in the LBO glass-modified $LiMn_2O_4$ powders. The lattice parameters of the LBO glass-modified $LiMn_2O_4$ were also decreased because the ionic radius of Mn^{4+} is smaller than that of Mn^{3+} [44–46]. A decrease in the Mn^{3+}/Mn^{4+} ratio increases structural stability during lithium intercalation and deintercalation reactions [46].

LBO glass-modified LiMn_2O_4 powders were prepared by low-temperature flame spray pyrolysis to examine boron doping in the LiMn_2O_4 powders during high-temperature flame spray pyrolysis. The temperature of the diffusion flame was lowered by decreasing the flow rates of the fuel and oxidizer gases. Fig. 6 shows the SEM images of the pure and LBO glass-modified LiMn_2O_4 powders prepared by low-temperature flame spray pyrolysis. The powders had spherical shapes and were several microns in size. Evaporation of the powders did not occur because of the low temperature of the diffusion flame and the short residence time of the powders inside the diffusion flame. Fig. 7 shows the XRD patterns of the LBO glass-modified LiMn_2O_4 powders post-treated at 650°C. The powders exhibited a pure cubic spinel LiMn_2O_4 phase, irrespective of the amount of the LBO glass



(b) 5 wt%

Figure 6. SEM images of the pure and LBO glass-modified LiMn₂O₄ powders prepared by low temperature flame spray pyrolysis.

The $LiMn_2O_4$ powders prepared at a low temperature had lower mean crystallite sizes than those prepared at high temperature (Tables 1 and 2). The lattice parameters of the $LiMn_2O_4$ powders prepared at a low temperature increased slightly with increasing amounts of the glass modifier (Table 2). The ratio of Mn^{+3} and Mn^{+4} ions in the $LiMn_2O_4$ powders increased when the LBO glass modifier was applied.



Figure 7. XRD patterns of the pure and LBO glass-modified LiMn₂O₄ powders prepared by low temperature flame spray pyrolysis.

Table 2. Characteristics of pure and LBO glass-modified LiMn₂O₄ powders with micron sizes.

	Crystalline Size (nm)	Lattice Parameter (Å)
0 wt%	37	8.231
3 wt%	51	8.248
5 wt%	51	8.243
10 wt%	51	8.242
20 wt%	51	8.237

Therefore, stoichiometric $LiMn_2O_4$ powders (theoretical lattice parameter is 8.247 Å) were obtained even at a low post-treatment temperature of 650°C. The LBO glass modifier decreased the formation temperature of the stoichiometric $LiMn_2O_4$ powders in the flame spray pyrolysis. The decrease of the lattice parameters of the LBO glass-modified $LiMn_2O_4$ powders did not occur during low-temperature flame spray pyrolysis as a result of boron doping in the Mn site of $LiMn_2O_4$ powders. The LBO glass material, with its low melting point, improved crystal growth and promoted the formation of $LiMn_2O_4$ powders during low-temperature flame spray pyrolysis. Therefore, the doping of boron in the Mn sites of the $LiMn_2O_4$ powders, as observed in Figs. 4 and 5, was due to the high temperature of the diffusion flame.



Figure 8. Initial charge and discharge curves of the pure and LBO glass-modified $LiMn_2O_4$ powders at $60^{\circ}C$.

Fig. 8 shows the initial charge and discharge curves of the pure and LBO glass-modified $LiMn_2O_4$ nanopowders at 60°C. The operating cut-off voltages were 3.2 and 4.5 V at a current density of 1 C. The initial discharge capacities of $LiMn_2O_4$ powders with 0, 3, and 5 wt% glass material were 143, 133, and 123 mAh g⁻¹, respectively. The initial charge and discharge capacities decreased with increasing amounts of the glass modifier. Large amounts of inactive LBO glass material covering the $LiMn_2O_4$ powders decreased the initial charge and discharge capacities. The decrease of the Mn^{3+}/Mn^{4+} ratio also decreased the capacities of the LBO glass-modified $LiMn_2O_4$ powders. Two distinct voltage plateaus clearly appeared at approximately 4.1 V and 4 V on the charge and discharge curves of the pure $LiMn_2O_4$. However, the boundaries of the two voltage plateaus become less sharp in the charge and discharge curves of the LBO glass-modified $LiMn_2O_4$ powders, as shown by the circle in Fig. 8. Boron doping suppresses the formation of unstable phases and enhances the stability of the spinel structure [42]. The stronger bond of B–O (809 kJ mol⁻¹) compared to Mn–O (402 kJ mol⁻¹) enhanced the stability of the spinel structure [47].

65

108

100th

93

	0 wt%		3 wt%		5 wt%		10 wt%		20 wt%	
	Cap.	Ret.								
	$(mAh g^{-1})$	(%)								
1st	143	-	133	-	123	-	109	-	78	-
50th	120	84	118	89	113	92	100	92	74	95

86

97

89

72

106

81

Table 3. Capacities and capacity retentions of pure and LBO glass-modified LiMn2O4 powders withnanometer sizes.



Figure 9. Cycle properties of the pure and LBO glass-modified LiMn₂O₄ powders at 60°C.

The cycle properties of the pure and LBO glass-modified LiMn_2O_4 powders at 60°C are shown in Fig. 9. The discharge capacities at a constant current density of 1 C for 3.2–4.5 V are presented in Table 3. The discharge capacity of the pure LiMn_2O_4 powders decreased from 143 to 93 mAh g⁻¹ after 100 cycles, with capacity retention at 65% of the initial capacity. However, the discharge capacity of the 5 wt% glass-modified LiMn_2O_4 powders decreased from 123 to 106 mAh g⁻¹ after 100 cycles, with the capacity retention at 86% of the initial capacity. The cycle properties of the LiMn_2O_4 powders improved with increasing amounts of the glass modifier. The capacity retention of the 20 wt% glassmodified LiMn_2O_4 powders was 92% of the initial capacity after 100 cycles, even at a high operating temperature of 60°C and a high current density of 1 C.

Fig. 10 shows cyclic voltammograms of the first and third cycles for pure and 5 wt% LBO glass-modified LiMn_2O_4 powders; the voltammograms were recorded over the voltage range 3.2–4.5 V at a scan rate of 0.07 mV s⁻¹. The cyclic voltammogram of the pure LiMn_2O_4 powder showed shifts in the oxidation and reduction peaks upon cycling, indicative of a change in the surface structure and

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composition of the spinel electrode [37]. On the other hand, the cyclic voltammogram of the 5 wt% LBO glass-modified LiMn₂O₄ powder showed a small peak shift upon cycling. Fig. 11 shows the Nyquist plots of the electrochemical impedance spectra of the pure and 5 wt% LBO glass-modified LiMn₂O₄ powders in the fully charged state (4.5 V). After 1 cycle, the spectrum of the LBO glass-modified LiMn₂O₄ powder showed slightly larger impedance than the pure LiMn₂O₄ powder. After 30 cycles, the spectra of the pure and LBO glass-modified LiMn₂O₄ powder showed slightly larger impedance than the pure LiMn₂O₄ powder. After 30 cycles, the spectrum of the glass-modified LiMn₂O₄ powder displayed smaller impedances. On the other hand, the spectrum of the glass-modified LiMn₂O₄ powder displayed smaller impedance than the pure LiMn₂O₄ powder after 100 cycles. It has been reported that the reaction of pure LiMn₂O₄ powders and the electrolyte species generates a highly resistive LiF surface film [48]. The LBO glass material covering the LiMn₂O₄ powders increased the resistivity of the powders; however, it decreased the amount of resistive material formed on the surface of the active material. The LBO glass material coating improved the electrochemical properties of the powders by decreasing their reactivity with acidic electrolytes.



Figure 10. Cyclic voltammograms of the pure and 5 wt% LBO glass-modified LiMn₂O₄ powders of the first and third cycles.





Figure 11. Nyquist plots of the electrochemical impedance spectra of the pure and 5 wt% LBO glassmodified LiMn₂O₄ powders in the fully charged state (4.5 V).

Moreover, the high crystallinity and stabilization effect of boron doping in the spinel structure of the LBO glass-modified $LiMn_2O_4$ powders improved their electrochemical properties by increasing their stability in acidic electrolyte environments.

4. CONCLUSIONS

The direct surface modification of nanometer-sized LiMn₂O₄ cathode powders during flame spray pyrolysis was studied. The physical and electrochemical properties of LBO glass-modified

LiMn₂O₄ nanoparticles prepared by flame spray pyrolysis were investigated. The glass modifier acted as a sintering agent and slightly increased the mean size of the LiMn₂O₄ powders post-treated at 650°C. The results of XRD and XPS analyses showed that the boron doping concentration in the LiMn₂O₄ powders increased with increasing amounts of the glass modifier. The boron dopant occupied the position of Mn^{3+} in the lattices and decreased the Mn^{3+}/Mn^{4+} ratio in the LBO glass-modified LiMn₂O₄ powders. The initial charge and discharge capacities decreased with increasing amounts of the glass modifier. However, the LBO glass material covering the LiMn₂O₄ powders improved the electrochemical properties of the powders by decreasing the reactivity of the powders with acidic electrolytes. Moreover, the high crystallinity and stabilization effect of the boron dopant improved the electrochemical properties of the LiMn₂O₄ powders by increasing their stability in acidic electrolyte environments.

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