

LiMnBO₃/C: A Potential Cathode Material for Lithium Batteries

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LiMnBO₃ was successfully synthesized by a solid-state reaction method both with and without a carbon coating. Adipic acid was used as source material for the carbon coating. LiMnBO₃ was composed of many small polycrystalline particles with a size of about 50 - 70 nm, which showed a very even particle morphology and highly ordered crystalline particulates. Whereas the carbon coated LiMnBO₃ was well covered by mat-like, fine material consisting of amorphous carbon derived from the carbonization of adipic acid during the synthetic process. Carbon coated cell exhibited improved and stable discharge capacity profile over the untreated. Two cells delivered an initial discharge capacity of 111 and 58 mAh/g for LiMnBO₃/C and LiMnBO₃, respectively. Carbon coating on the surface of the LiMnBO₃ drastically improved discharge capacity due to the improved electric conductivity in the LiMnBO₃ material.

Key Words: LiMnBO₃, Carbon coating, Nano materials, Adipic acid, Impedance spectroscopy

Introduction

As of late, an increasing interest is being devoted towards the development of cathode materials for lithium secondary batteries that bear a high capacity, are affordable, and are environmentally friendlier than existing, commercial, toxic LiCoO₂. Recently, growing interest has focused on polyanion framework structured compounds.¹ Generally, a polyanion containing a counteraction with a relatively high electronegativity functions as an electron withdrawing functional group where the electron-withdrawing density is obtained from the covalent bonds of the nearest-neighbor redox cations. This inductive effect lowers the redox potential of the metal used in the cathodes and substantially increases cell voltage effect and has been successfully explored for olivine framework structures, in particular, LiFePO₄.²⁻⁴ Further, LiFePO₄ possesses several benefits, including a flat discharge profile, the ability to sustain high current rates, low expense, natural abundance, thermal and chemical stability, and is eco-friendlier than Co.^{5,6}

Legagneur *et al.*⁷ first explored the possibility of using the boron-based compounds (LiMBO₃, M = Fe, Mn, & Co) as positive electrodes in lithium batteries. Since then, very few works have reported boron-based cathodes.⁷⁻¹⁰ The advantages of boron include being lightweight, high relative abundance in the earth's crust, environmental friendliness, and slightly less electronegativity than phosphorous. However, these compounds also suffer in terms of their inherent electronic conductivity similar to those of the olivine framework. The controlled particle size, carbon coating, and appropriate synthesis conditions for LiFePO₄ dramatically improve cathodic performance;⁶ a similar procedure is expected here to improve the boron-based cathodes. Very recently, Dong *et al.*^{8,9} reported upon the LiFeBO₃-based material with high discharge capacity values in different scenarios. Nevertheless, LiMnBO₃-based materials have yet to succeed lithium batteries.¹⁰ Given this current state, an attempt was made herein to synthesize LiMnBO₃ *via* a solid-state reaction method both with and without carbon coating. The results emphasize the

drastic improvement of capacity using adipic acid as a carbon source.

Experimental

High purity, analytical grade LiOH·H₂O (Junsei, Japan), MnCO₃ (Sigma-Aldrich, USA), and H₃BO₃ (Junsei, Japan) were used as the starting materials for the synthesis. C₆H₁₀O₄ (adipic acid, Dae-Jung, Korea) was used as a carbon source material (0.1 mol. against the total metal ion present in the compound). Stoichiometric amounts of the starting materials were fine-ground using a mortar and precalcined at 250 °C for 3 h for decomposition of carbonates and hydroxides. Then, the resultant material was again fine-ground using a mortar and heat-treated in the presence of Ar at 750 °C for 15 h to obtain the resulting material. Powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) was employed for structural analysis using Cu K α radiation. The carbon content of the synthesized LiMnBO₃ particles was determined using an elemental analyzer (CHN Flash EA series, CE Instruments, Italy). The surface morphological features were observed using a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Electrochemical impedance spectroscopy (EIS) was performed using a BioLogic (SP-150, Bio-Logic SAS, France) electrochemical workstation. The LiMnBO₃ electrodes served as working electrode and metallic lithium as counter and reference electrodes respectively between 3 MHz to 32 Hz at room temperature. The cycling performance was studied using a CR2032 coin-type cell and the cathode fabricated with 20 mg of precisely weighed active material, 3.0 mg of Ketjen black, and 3.0 mg of conductive binder (2.0 mg of Teflonized acetylene black (TAB) and 1.0 mg of graphite). This was pressed on a 200 mm² stainless steel mesh used as the current collector under a pressure of 300 kg/cm² and dried at 130 °C for 5 h in a vacuum oven. The coin cell was composed of a cathode with metallic lithium as the anode, separated by a porous polypropylene film (Celgard 3401). The 1.0 M LiPF₆, in a mixture of ethylene carbonate (EC)/dimethyl

carbonate (DMC) (1:1 v/v, Techno Semichem Co., Ltd, Korea), was used as an electrolyte. The cycling studies were carried out between 1.25 - 4.8 V at a C/20 rate under room temperature.

Results and Discussion

Powder X-ray diffraction patterns of the LiMnBO_3 both with and without carbon-coated materials were presented in Fig. 1. The structure of the LiMnBO_3 was isotopic with the hexagonal form of LiCdBO_3 , which was built up from MnO_5 square pyramids, planar BO_3 groups, and LiO_4 in the tetrahedral sites. The MnO_5 pyramidal shared two opposite edges of its square base with two adjacent pyramids, thus forming chains along the *c*-axis. In the BO_3 planes, the B atoms were not located in the centre portion of the triangle.¹⁰ Planar polar groups were linked by edge-sharing and lithium ions occupied the tetrahedral sites of the LiO_4 in the three-dimensional polyanionic $[\text{MnBO}_3]_n^{n-}$ framework. Further, the LiO_4 tetrahedral sites shared two O and planer BO_3 groups and link to form a chain *via* corner sharing. Within this framework, Li atoms were occupying statistically tetrahedral sites sharing a face.^{7,9} Thus, the electronic conduction must occur *via* Mn-O-Mn bonding, unlike many polyanion structures, for example, NASICON, where the polyanions were completely isolated from each transition metal polyhedrons.¹⁰ The obtained XRD patterns of the LiMnBO_3 were in good agreement with the earlier report of Legagneur *et al.*⁷

The morphological features of the LiMnBO_3 and LiMnBO_3/C were analyzed by field emission scanning electron microscopy (SEM). LiMnBO_3 (Fig. 2a) was composed of many small polycrystalline particles with a size of about 50-70 nm, which showed a very even particle morphology and highly ordered crystalline particulates. Each particle was completely separated and located alone without any linkage. Whereas the LiMnBO_3/C was concerned (Fig. 2b), the surface of the LiMnBO_3 particles was well covered by mat-like, fine material consisting of carbon derived from the carbonization of adipic acid during the synthetic process. Moreover, this coating are also greatly interconnected with other particulates, yielding an increase in electronic conductivity of the LiMnBO_3 . The carbon content of LiMnBO_3/C material was 0.9 wt %.

Cycling performance of the Li/LiMnBO₃ or LiMnBO₃/C was presented in Fig. 3. Figure 3(a) represented the initial charge-discharge curves of the cells cycled between 1.25 - 4.8 V under ambient temperature at a C/20 rate. To improve the small discharge capacity in LiMnBO_3 in ref [10], it was conducted cycling test in wide voltage region in this study. These cells delivered an initial discharge capacity of 111 and 58 mAh/g against the charge capacity of 181 and 100 mAh/g for LiMnBO_3/C and LiMnBO_3 , respectively. The loss in capacity might be due to the formation of a solid electrolyte interface (SEI) on the electrodes. After 30 cycles, discharge capacities 89 and 69 mAh/g were maintained for carbon-coated and uncoated LiMnBO_3 . The LiMnBO_3 contained one lithium ion per formula unit, thus, if one could completely extract the lithium and completely oxidize Mn^{2+} to Mn^{3+} , the theoretical capacity would be 222 mAh/g. However, full capacity was rarely achieved owing to their limitations in structure and need for high electronic and ionic conductivity and composition of the materials.

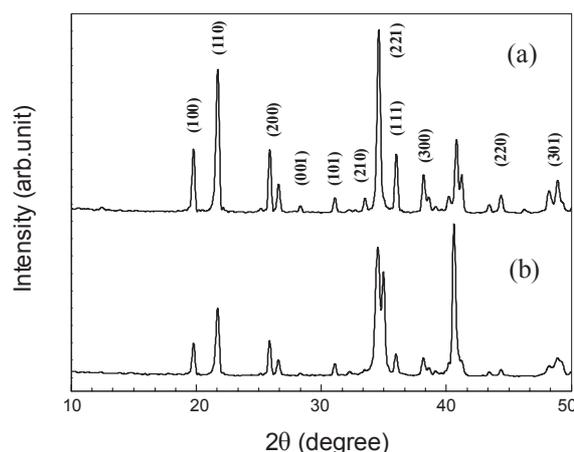


Figure 1. X-ray diffraction patterns of (a) LiMnBO_3 and (b) carbon coated LiMnBO_3 .

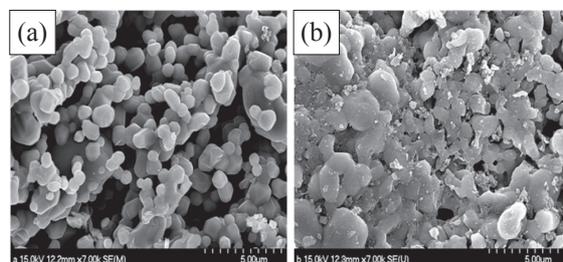


Figure 2. Scanning electron microscopy (SEM) images of (a) LiMnBO_3 and (b) carbon coated LiMnBO_3 .

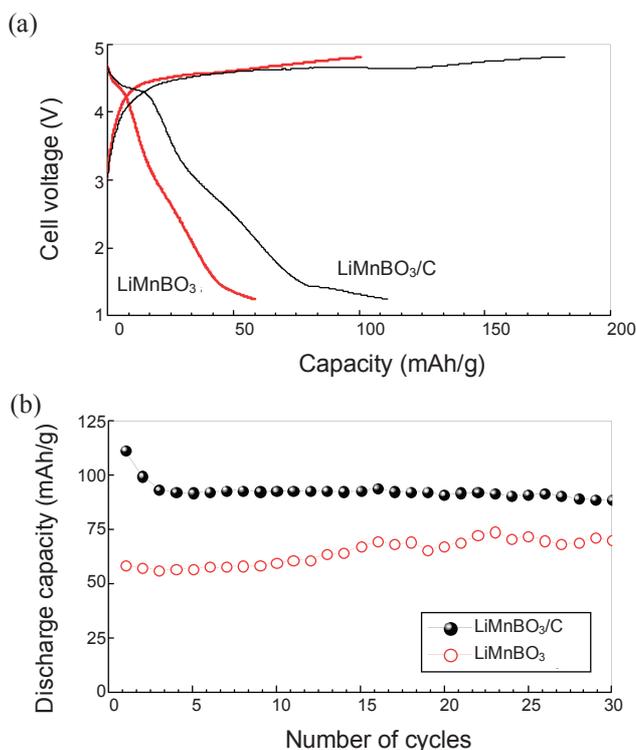


Figure 3. (a) Initial charge/discharge curves of Li/LiMnBO₃ and carbon coated LiMnBO_3 cells and (b) discharge capacity with number of cycles at room temperature.

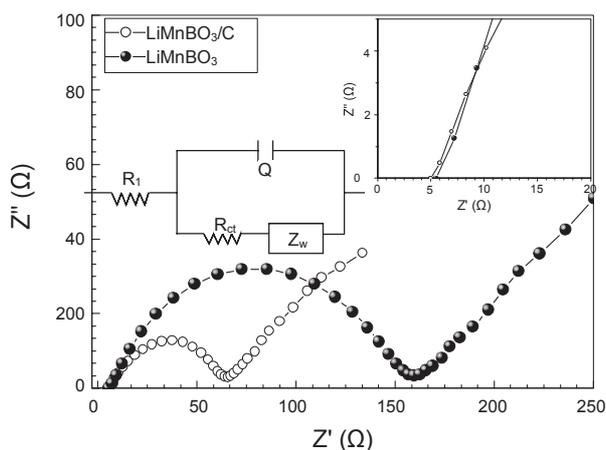


Figure 4. Electrochemical Impedance Spectroscopy (EIS) plots of LiMnBO₃ recorded at room temperature.

Carbon coating on the surface of the LiMnBO₃ drastically improved discharge capacity due to the improved conductivity derived from good contact between the nearest neighbor particles through such coating. It is well known that the capacity improvement in LiFePO₄ cell due to small particle size, forming a carbon coating layer using various carbon materials and surfactants.¹¹ In this study, we firstly have chosen adipic acid as carbon source material for the LiMnBO₃ system, which due to the appealing properties like, cost effective, environmental friendly, easily prepared at any laboratories. Furthermore, this was convincingly proven herein for the LiFePO₄ system.¹² Allen *et al.* has also tested several carbon sources for LiMnBO₃, but only a maximum discharge capacity of 20 mAh/g was achieved.¹⁰ Figure 3(b) displayed the discharge capacity profile with the number of cycles. The carbon-coated LiMnBO₃ material exhibited very stable discharge behavior, whereas uncoated material showed irregular capacity behavior. This may be ascribed to the uniform carbon coating derived from carbonization of a chelating agent such as adipic acid, leading to enhanced performance.

The effects of the carbon coating on the electrical conductivity of the LiMnBO₃/C, a.c. impedance measurements, were conducted. From the ac impedance spectrum, a typical equivalent circuit is depicted in Fig. 4 (inset), where R₁ is the ohmic resistance of the electrolyte, membrane and electrode, corresponding to the high frequency intercept of the semicircle with the horizontal axis, Q and R_{ct} represent constant phase element (CPE) and the charge-transfer resistance, respectively, corresponding to the semicircle, and Z_w is the Warburg impedance arising from the diffusion of Li⁺ ions in electrode, corresponding to the inclined straight line in low frequency. The high-

frequency semicircle was ascribed to the SEI film and/or contact resistance, the semicircle in the medium frequency region was assigned to the charge-transfer (CT) impedance on the electrode/electrolyte interface, and the inclined line at an approximate 45° angle to the real axis corresponds to the lithium diffusion kinetics towards the electrodes.¹³ It could be seen that the diameter of the semicircle in the medium-frequency region for the LiMnBO₃/C electrode was much smaller than the LiMnBO₃ electrode, revealing lower CT impedance and indicating that the electronic conductivity of the LiMnBO₃/C was dramatically improved after carbon coating, which significantly improved cycling performance of the cell.

Conclusion

To conclude, LiMnBO₃ cathodes, both with and without carbon coating, were successfully synthesized by a solid-state reaction method under an Ar flow. The LiMnBO₃/C exhibited stable and improved discharge capacities over the uncoated. This improved performance may be attributable to the coating of carbon on the surface of the particles by the carbonization of adipic acid.

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