



이학석사 학위논문

리튬이차전지의 양극소재로써 Fluorine 이 치환된 LiFeBO₃ 표면 카본 코팅의 효과

Effects of carbon coating on surface of F-substituted LiFeBO₃ as a cathode material for Li-ion battery

울산대학교 대학원

화학과

손유진

Effects of carbon coating on surface of F-substituted LiFeBO₃ as a cathode material for Li-ion

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이 논문을 이학석사학위 논문으로 제출함

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울산대학교 대학원

화 학 과

손유진

손유진의 석사학위 논문을 인준함

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English Abstract

Lithium iron borate (LiFeBO₃ or LFeB) is a potential candidate to use as a cathode material for next generation of Li-ion batteries due to its inexpensive and non-toxic characteristics. In addition, since BO₃ is a light polyion, it is theoretically a strong candidate with a large capacity of 220 mAh g⁻¹. The electrochemical performance of LFeB can be greatly improved along with the phase transition from monoclinic to vonsenite structure by substituting F anion at the oxygen sites of the LFeB. It should be noticed that the discharge capacity is greatly reduced due to structural instability occurring during cycling. Therefore, in this study, the surface of the fluorine-substituted LFeB is modified with carbon coating in order to increase the conductivity while ensuring the stability during the cycling processes.

In this study, the morphology and structure of synthesized materials were characterized through various analysis techniques such as X-ray diffraction (XRD), ⁷Li nuclear magnetic resonance (NMR), Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), and Transmission electron microscopes (TEM) to evaluate the effectiveness of carbon coating. In addition, the electrochemical performance of the synthesized material was measured using galvano static charge/discharge tests with a potential range of 1.0–4.5 V.

국문 초록

리튬 철붕산염(LiFeBO3 또는 LFeB)은 가격이 저렴하고 독성이 없는 특성 때문에 차세대 리튬이온 배터리의 양극재로 주목받는 물질이다. 여기서 BO3는 가벼운 Poly-anion 이기 때문에 이론적으로 220 mAh g⁻¹의 높은 이론 용량을 구현할 수 있다. 특히, 이전에 보고된 연구에 따르면 LFeB 의 산소 자리에 플루오린 음이온을 미량 치환함으로써 Monoclinic 에서 Vonsenite 구조로의 상전이를 통해 LFeB 의 전기화학적 성능을 크게 향상시킬 수 있다. 하지만, 충/방전 사이클링 중에 나타나는 구조적 불안정성으로 인해 방전 용량이 크게 감소하기 때문에 본 연구에서는 사이클링 과정 중 안정성을 확보하면서 전도성을 향상시키기 위해 플루오린이 치환된 LFeB(LFeBF)의 표면에 탄소를 코팅하고자 하였다.

본 연구에서는 X 선 회절(XRD), ⁷Li 핵자기공명(NMR) 분광법, 에너지 분산 X 선 분석(EDX), 투과 전자현미경(TEM) 등 다양한 분석 기법을 통해 탄소 코팅된 LFeBF(LFeBF/C)의 형태와 구조 등 특징에 대해 분석하였다. 또한 합성된 물질의 전기화학적 성능은 1.0-4.5V 의 전압 범위에서 galvano static charging/discharging 테스트를 사용하여 측정되었다.

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1. Introduction

1.1 Introduction to Lithium-ion batteries and cathode materials

1.1.1 The principle and compositions of Li-ion batteries

Lithium ion batteries (LIBs) is an energy storage device that mutually converts chemical energy into electrical energy through an electrochemical redox reaction using a potential difference depending on the intrinsic physical properties of internal chemicals (active material).² It consists of four main components such as anode, cathode, separator, and electrolyte. The anode and cathode materials are separated by a separator, and the electrolyte serves to transfer ions between the two electrodes.

Figure 1.1.1 shows a schematic diagram of typical LIB with the main components. Depending on types of the electrolyte, it is called a lithium ion battery (LIB) when the electrolyte is liquid, it is called a lithium polymer battery when the electrolyte is a polymer, and it is called an all solid state battery when the electrolyte is a solid. ³



Figure 1.1.1 Scheme of a typical Li-ion battery

The charge/discharge process of a LIB is carried out by the lithiation/delithiation reaction of Li⁺ ions. Li⁺ ion migrates from cathode to anode during the charging process. On the other hand, Li⁺ ion migrates from anode to cathode during the discharging process.⁴ The electrochemical reactions about charge/discharge process in LIB are as follows.

At the cathode:

$$xLi^{+} + xe^{-} + Li_{1-x}MO_2 \leftrightarrow LiMO_2$$
(1.1)

At the anode:

$$\operatorname{Li}_{x} \mathbb{C}_{6} \leftrightarrow \operatorname{xLi}^{+} + \operatorname{x}e^{-} + \mathbb{C}_{6}$$
(1.2)

Overall reaction:

$$LiMO_2 \leftrightarrow MO_2 + LiC_6 \tag{1.3}$$

The principle of electrochemical process in a LIB showed in Figure 1.1.2.



Figure 1.1.2 Scheme of the electrochemical process in a LIB.

Indicators that well represent battery performance include energy density (Wh/L), specific energy (Wh/kg), cycle life, and rate performance. It refers to Wh = Ah (amount of charge) x V (voltage) in Wh/L, which is a unit of energy density, and determines how small the capacity density can be made, and specific energy (Wh/kg) is a measure of how light a battery can be made. In addition, C-rate is used for performance measurements in batteries. C-rate is a current that flows when all capacities are released in one hour. For LIBs, the term rated capacity is used. The rate performance of a battery is an important factor in comparing the performance of the batteries.

In a typical LIB, the lithium transition metal oxide (LiMO₂) is mainly used as the cathode, and a lithium metal or a carbon-based material with a low standard reduction potential and can reversibly lithiation/delithiation Li⁺ ions is mainly used as the anode. The carbon-based material used as an anode material has a higher capacity and superior cycling properties than the cathode LiMO₂, and thus the LIB performance strongly depends on the properties of the cathode material.

1.1.2 Cathode materials for lithium ion battery

As the application of the LIBs expands from the existing small batteries to medium or large batteries, high-power, safety, and high-capacity anode materials are required. The performance of the LIBs is intimately related to the structural characteristics of the cathode material, and when the crystal structure of the cathode material is stable and the conductivity of the lithium ions is high, the capacity fade during charging/discharging is small and excellent electrochemical performance is exhibited.

Cathode materials are largely divided into three types: layered lithiated transition metal oxide (LiMO₂, M= Mn, Co, Fe, Ni, etc.), spinel, and poly-anion type compounds according to structural characteristics as shown in **Figure 1.1.3**.^{5,6} Comparison between those types of cathode materials are shown in the **Table 1.1**.



Figure 1.1.3 Crystal structures of the three lithium-insertion compounds in which the Li+ ions are mobile through the 2-D (layered), 3-D (spinel), and 1-D (olivine) frameworks. ⁶

LiCoO ₂		LiMnO ₄	LiFePO ₄	LiFeBO ₃			
Crystal structure	Layered structure	Spinel structure	Olivine structure	Monoclinic structure			
Theoretical capacity	145 mAh g ⁻¹	100 mAh g ⁻¹	170mAh g ⁻¹	220 mAh g ⁻¹			
Operating voltage	3.7 V	4.0 V	3.5 V	3.0 V			
Advantages	 easy to synthesis Large storage capacity and excellent cycling performances 	 High thermal stability. Volume change is small when lithiation/delithiation reaction 	High thermal stabilityGood cycle abilityEco-friendly	 High energy density Good Li⁺ ion diffusivity & rate performance Eco-friendly 			
Disadvantages	 Unstable structure Discharge of environmental pollutants. 	Unstable structure	Low conductivityLow energy density	• vulnerable to exposure to air.			

 Table 1.1.1. Comparison of the various kinds of cathode materials.

Among LiMO₂ (M = Co, Ni, Mn) cathode materials with layered structure, LiCoO₂ is the most commercialized electrode material for small batteries. ⁷ The LiCoO₂ has excellent charge, discharge, and high specific capacity, and is easy to synthesize but has a disadvantage in that the structure is unstable compared to other potential electrode materials that experience performance degradation during overcharging. ⁸ ⁹ Because of phase transition caused by the slow reaction rate and low electrode stability, a wider range of voltages will not be available. LiCoO₂ can only use half of its theoretical specific capacity because the CoO₂ layer of the LiCoO₂ crystal structure is separated into Li⁺ ions. When 50% or more (actual capacity: 137 mAh g⁻¹) of the ions is extracted, the structure collapses, and the electrochemically inactive state is changed instead of the electrochemically formed state. Since LiCoO₂ is expensive due to the presence of Co and has problems such as emitting environmental pollutants, research on a cathode material containing iron with high natural existence ratio has recently been conducted.

 LiM_2O_4 (M= Mn, Ni), a cathode material with spinel structure, is used in high power applications due to its high thermal stability. In the case of Mn-based spinel, such as $LiMn_2O_4$, octahedron MnO₆ has a strong edge-share and forms a continuous 3D cubic arrangement, thereby having high structural stability during the charging process. ¹⁰ However, this cathode material has the disadvantage of rapidly losing capacity and self-discharging, especially when the temperature is high.

Unlike these materials, poly-anion based cathode material is attracting attention as a cathode material to replace LiCoO₂, which has an existing layered structure, as it is inexpensive, has a high natural presence ratio of elements, can play a major role as an electrochemical energy storage medium, and is eco-friendly. Poly-anion based compounds are a kind of material in which tetrahedral structural units $(XO_4)^{n}$ (X= P, S, Mo, As, etc.) with strong covalent bonds are coordinated with the transition metal oxide polyhedron.⁷

 $LiMPO_4$ (M= Fe, Mn, Co, Ni) is a representative phosphate-type poly-anion based cathode material. The poly-anion based cathode materials exhibit a higher operating voltage than the oxide-based cathode materials due to the inductive effect.

However, since the valence electrons of the transition metal are isolated, they have low electrical conductivity. In the case of LiFePO₄, which is currently commercialized and used, it has structural stability due to strong covalent bonds between P-O. Lithium ions migrate one-dimensionally in parallel with the surface in which the PO₄ tetrahedral structure and the MO₆ octahedral structure are corner sharing. It is easy to synthesize because it is thermally stable at high temperatures, and the capacity fade is small even after repetitive cycling. In addition, since LiFePO₄ exhibits a high operating voltage of 3.5 V and excellent rate performances, this cathode material is attracting attention as a material for nextgeneration medium/large batteries. However, LiFePO₄ inherently has a low electrical conductivity of about 10⁻⁹ S cm⁻¹ and a low lithium ion diffusion coefficient (D= 10^{14} cm² s⁻¹). These problems can be improved by nanosizing the particle size to shorten the diffusion path of Li⁺ ion and carbon coating at the surface of LiFePO₄.⁶

For all known inorganic salt-types electrode materials, borates have much smaller molecular weights than those of phosphates, silicates, and sulphates which results in much higher capacities of borates than the other salts. For polyanion-type cathode materials, the most successful and famous one is LiFePO₄ with its theoretical capacity of only 170 mAh g⁻¹ which is lower than 200 mAh g⁻¹ for the simplest borate-type cathode LiFeBO₃. The basic structural units in borates are BO₃ triangle planar and BO₄ tetrahedron which can be connected to build various polyborate B_xO_y ions via sharing O-corner, edge, or plane. Compared with other polyanion-type inorganic salts, B element in borates have two types of coordination geometries with O atoms, while Si, P, and S are usually fourfold-coordinated with O atoms. Consequently, the quantity of available and potential borates is much larger than the others. With those features, the borates LiMBO₃ (M = Fe, Co, Mn, Zn) should have strong potentials as high energy density cathode materials for rechargeable batteries.

1.1.3. General properties of LiFeBO₃

LiFePO₄ is one of the promising cathode materials in electric vehicle (EV) applications due to its low-cost components and safety. However, due to its lower energy density than other competing materials like $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, studies on safe cathode materials that operate below about 4.1 V with high discharge capacities have been conducted. LiFeBO₃ is attracting attention as a material to replace LiFePO₄ because of its larger theoretical discharge capacity from high charge/mass ratio of lightest small triangle oxyanion unit (BO₃)³⁻.^{11, 12}

The **Figure 1.1.4** shows the crystal structure of LiFeBO₃. The crystal structure of the LiFeBO₃ is a monoclinic (space group of C2/c) structure, including a chain in which the tetrahedral LiO₄ is edge-sharing and a chain in which the trigonal bipyramidal FeO₅ structure is edge-sharing. The planar triangular $(BO_3)^{3-}$ is one-dimensionally connected to FeO₅ along the $[10\overline{1}]$ direction, so Li-ions can move one-dimensionally. Moreover, the planar triangular $(BO_3)^{3-}$ occupies a minimum volume which makes the density of LiFeBO₃ is 3.46 g cm⁻³, resulting in a large energy per volume compared to LiFePO₄. ¹³



Figure 1.1.4 Crystal structure of monoclinic LiFeBO₃ with space group of C2/c viewed along [001] direction to emphasize the pseudo-trigonal symmetry in the planar layers of BO₃ triangles, FeO₅ trigonal bipyramids, and LiO₅ trigonal bipyramids. ^{11, 12}

Undeniably, the syntheses of borates are more difficult than the others due to their low stabilities. Varieties of borate ions can be constructed by simple sharing of BO₃ planar triangle and BO₄ tetrahedron, which may result in difficult preparations of pure phases materials. LiFeBO₃ is also vulnerable to exposure to air. When moisture in the air is in contact with the surface of the LiFeBO₃ material, the performance of the electrode is significantly degraded and the essential properties of the cathode are lost. The main reason is that when the LiFeBO₃ is exposed to air, the ratio of Fe³⁺ increases rapidly by oxidation reaction, and at the same time lithium ions move to the particle surface to maintain the charge balance. Lithium ions on the surface react with charged species such as OH⁻, O²⁻, and CO_3^{2-} in the atmosphere and produce a reaction product of LiOH and LiCO₃. The **Figure 1.1.5** briefly shows the process that occurs when LiFeBO₃ is exposed to air. ¹



Figure 1.1.5 a. Schematic illustration of LiFeBO₃ degradation forming core-shell structure. Air/moisture attack converts Fe^{2+} to Fe^{3+} at the interface along with leaching of Li atoms from bulk to surface forming byproducts like Li₂CO₃.

b Series of pie charts showing relative content of Fe^{2+} (green) and Fe^{3+} (red) species as derived from Mössbauer analysis. The numbers in the center of each circle indicates the amount of Fe^{2+} species. A 1-year-long study has been conducted that shows almost 100 % Fe^{2+} to Fe^{3+} conversion.¹

1.1.4. Electrochemical improvement of cathode materials

Intensive researches on performance improvement are required to enable the application to EV, ESS, and etc of new types of electrode materials. Various strategies for improving the performance of the cathode material have been used, including dimension reduction (nano-sizing), composite formation, doping, morphology control, etc.^{1, 14} **Figure 1.1.6** shows these strategies, which are similar regardless of the type of material, crystal structure, or mechanism of operation.²



Figure 1.1.6 General strategies for performance enhancement and their rationale: (a) reducing dimensions of active materials, (b) formation of composites, (c) doping and functionalization, (d) tuning particle morphology, (e) formation of coatings or shells around active materials, (f) modification of electrolyte. 2

Cathode materials with high rate capability are characterized by rapid Li⁺ ions deintercalation and stable cycling and thus general optimization strategies include constructing short lithium diffusion pathways and providing high ionic conductive. Considering the particle scale, the liquid phase diffusion of Li⁺ ions within the electrolyte, the reactions at the electrode-electrolyte interfaces, and the transport of Li-ions within are involved and govern the electrochemical kinetics. Obviously, it is assumed that the particle size, size distribution, surface resistance, and equilibrium potential of the cathode material have a great influence on the electrochemical performance of the battery. For example, Xu et al. simulated the discharge process and studied the effect of LiFePO4. LiFePO4 material with PO4 particle size for speed performance reported that, when the particle size of cathode material is small, the difference in emission curve was relatively small at different rates, but when the particle size is large, the maximum capacity is greatly reduced at a high rate with power voltage.¹⁵ Indeed, the slow solid-state diffusion of Li⁺ ions through the micron length scale powders making up the electrodes caused the slow charging. Diffusion path lengths would be shorter and charging times could be faster when the electrodes were made out of nanoparticles rather than micronparticles.

The particle packing and polydispersity of electrode materials strongly determines the tap density of electrode materials and the energy density of the LIBs and thus the particle size distribution is another factor that should be considered. It was reported that a broad particle size distribution increased the energy density two times higher than monodispersesized particles based electrodes for low C-rates applications. ¹⁶ However, due to a relatively higher surface area per volume ratio of the monodisperse-sized particles based electrodes, the monodisperse-sized particles based electrodes delivered higher power density for high discharge rates. It was also reported that uniform particle size distribution of cathode particles could reduce the polarization and thus exhibited a better electrochemical performance than the cathode made from less uniform particle size. ¹⁷

Surface coating is an effective method to enhance the performance of cathode materials. The surface coating materials prevents the direct contact between active materials and electrolyte, stabilizes the surface structure of the cathode material, reduces side reactions between the electrode material and the electrolyte. Consquently, it is helpful to improve the cycle stability. Various surface modification compounds have been reported, including TiO₂,

 SiO_2 , ZrO_2 , and some lithium-ion conductors such as LiPON, LiAlO₂, Li₃PO₄, and Li₂ZrO₃ in order to improve the ionic conductivity of these coating materials. ¹⁸⁻²³

Bulk doping is another method to decrease the electrode resistance, simultaneously to improve the electronic conductivity, to reduce the tortuosity, and to shorten the diffusion distance of Li⁺ ions. Effects of anion substitution at poly-anion cathodes such as LiMPO₄ (M= Fe and Mn) to species such as F and I have been studied and reported in which electrochemical performance is greatly improved with phase transition, particularly, from monoclinic to vonsenite through F substitution at the oxygen sites of the LFB.²⁴ A small amount of fluorine substitution and surface coating improves conductivity, stabilize the structure, and have a positive effect on electrochemical performance. However, after the first charge/discharge cycle, the discharge capacity was significantly reduced. That motivated us to improve the stability of the LFB structure by carbon coating at the surface of F-doped LiFeBO₃ (LFeBF) while maintaining high discharge capacity.

1.2 Nuclear Magnetic Resonance (NMR) spectroscopy

1.2.1 Introduction to NMR spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a spectroscopy in which a particular nuclear spin can help to reveal the structure of a molecule by obtaining a spectrum according to the resonance of a radio wave (RF) in a strong magnetic field. NMR spectroscopy is generally used in the following cases; analyzing chemical structures using one-dimensional techniques or determining the structure of more complex molecules using two-dimensional techniques. The molecular structure can be analyzed through a spin that changes when a nucleus oriented parallel to a strong external magnetic field absorbs certain radio frequency (RF) radiation energy. When absorbed under certain conditions, the nuclei begin to resonate and other atoms in the molecule resonate at different frequencies. RF waves are low-energy electromagnetic waves with frequencies ranging from several kHz to several hundred GHz. The energy of RF wave radiation is insufficient to cause rotation, vibration, or electron excitation of atoms or molecules, but it's sufficient to affect atomic nuclear spins, so a detailed analysis of the molecular structure can be performed.²⁵

NMR may be divided into solution NMR and solid state NMR according to the state of the samples. Solution NMR is most basically used to study the structure of molecules in liquid state with a solvent substituted with deuterium. The solution NMR displays narrowspectrum lines because the anisotropic interaction of the nuclear spindle is averaged. In solution NMR, ¹H and ¹³C NMR are used the most. The ¹H and ¹³C solutions NMR play important roles in revealing the framework of the molecular structure. In addition, a correlation spectroscopy (COSY) technique is used to measure NMR two-dimensionally. ¹H-NMR is the most often used method for analyzing and determining organic compounds since ¹H atoms are included in most of the organic molecules. In ¹H NMR, ¹H has a different chemical shift depending on which atom and functional group it is attached to, so that it helps to obtain information for chemical structures.

The relative sensitivity of NMR is determined by the existence ratio of a certain element and its gyromagnetic ratio (γ). The higher the existence ratio and the self-rotation rate, the better the NMR signal can be obtained. The self-rotation rate is an inherent property

of the nucleus and cannot be changed. In the case of ¹H, the natural presence ratio is 99.98%, the gyromagnetic ratio is $26.75 \times 10^7 \text{ s}^{-1} \text{ T}^{-1}$. And the natural presence ratio of ¹³C is 1.108%, and the gyromagnetic ratio is $6.728 \times 10^7 \text{ s}^{-1} \text{ T}^{-1}$. Therefore, ¹H, which has a higher natural existence ratio and self-rotation rate may reveal a better signal than ¹³C. **Table 2.1** shows the natural existence ratio and gyromagnetic ratio of various elemental nuclide.

Nuclide	Natural abundance (%)	gyromagnetic ratio (γ, s ⁻¹ T ⁻¹)	v/MHz		
¹ H	99.985	26.75	400		
¹³ C	1.108	6.73	100.6		
¹⁵ N	0.37	-2.71	40.5		
¹⁹ F	100	25.18	376.5		
³¹ P	100	10.84	162.1		

Table 1.2.1 The natural abundance and gyromagnetic ratio (γ) of various nuclides.

Currently, NMRs such as 300, 400, 700, and 900 MHz NMR have been commercialized and used, and up to 1 GHz NMR has been developed. NMR techniques in time domains are very important for describing molecular dynamics in solutions, and solid-state NMR spectroscopy is being used to determine solid-phase molecular structures. Recently, research on materials has been actively conducted using solid-phase NMR. Due to these various uses of NMR, it is used in a wide range of scientific fields.

1.2.2 The principles of NMR spectroscopy

NMR is associated with the phenomenon in which the nuclei of atoms in a magnetic field absorb radio waves (radio frequency, RF). An atomic nucleus can change the direction of the spin axis by absorbing radio wave radiation in a magnetic field, and the nuclei of chemically different atoms with magnetic moments within a molecule each have their own resonance frequency. ²⁶

To measure NMR, the nuclide to be measured must be NMR active. The NMR phenomenon depends on the magnetism of the nucleus, where certain nucleons have their own spin angular momentum and produce different spin states within the magnetic field. The conditions of NMR active are as follows. The nuclear spin quantum number (I) should not be zero and have a magnetic moment (μ). When the atomic number and atomic weight are even, the number of nuclear spin quantum becomes zero due to no spin, making it impossible to measure NMR. Nuclear species, such as ¹²C and ¹⁶O, containing even numbers of both protons and neutrons, cannot perform NMR measurements because the nuclear spin quantum number (I) is zero and there is no magnetic moment. However, all elements in the periodic table have at least one isotope that can experience NMR, which is NMR active, when in a magnetic field. **Figure 1.2.1.** shows the nuclear spin quantum numbers of various elements.

1A												8A					
н	2A	Nuclear Spins for Main Elemental											4A	5A	6A	7A	He
3 Li	4 Be		Isotopes that Undergo NMR										6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3R	4B	58	68	7B		— 8 R —		18	28	13 Al	14 Si	15 P	16 S	17 CI	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 	54 Xe
55 Cs	56 Ba	57-71 Lanthanides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 TI	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	⁸⁸ Ra	89-103 Actinides	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 FI	115 Uup	116 LV	117 Uus	118 Uuo
	Lanthan	ides	57 La	58 Ce	⁵⁹ Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	
Nuclear Spin $1/2$ $3/2$ $7/2$ 5 No data for synthetic elements ≥ 103 1 $5/2$ $9/2$ 8											≥ 103						

Figure 1.2.1 Periodic table of nuclear spin for NMR. ²⁷

The arrangement of nuclear spins can be aligned in the same or opposite direction as the magnetic field. These two nuclear spin alignments have different energies, and this difference in energy is related to the Larmor frequency. For a ¹H nucleus, the energy levels become two because the nuclear spin quantum number is 1/2 (I = 1/2). A nucleus with a magnetic moment in the same direction as an external magnetic field B₀ is in a low energy state, and a nucleus with a magnetic moment in the opposite direction to the external magnetic field B₀ is in a high energy state. The most powerful and important interaction that enables nuclear resonance is the interaction between the nucleus and the external magnetic field, which is called the Zeeman effect as shown in **Figure 1.2.2**.²⁷ In the absence of a magnetic field, the nucleus is randomly oriented in some direction, but when the magnetic field B₀ is applied, the spin is oriented in the opposite direction as magnetic field B₀ are stable and show lower energy, while spins in other directions show higher energy.



Figure 1.2.2 The Zeeman energy splitting removes the degeneracy of the nuclear spin energy states, and the quadrupolar perturbation causes an inequality of the two energy-level transitions. ²⁸
When the nuclear spins are placed in the external magnetic field B_0 , each spins are aligned in the same or opposite direction as the magnetic field. The number of spins at low energy levels at room temperature is slightly higher than the number of spins at high energy levels. The NMR signal is detected from the transition from the α energy level state to the β energy level state, and the strength of the signal depends on the difference in density of the α energy level state from the β energy level state. This can be explained by Boltzmann distribution demonstrated in **Equation 2.1**. The Boltzmann equation represents the relationship between temperature and related energy as follows.

$$\frac{N_{\alpha}}{N_{\beta}} = e^{-\Delta E/kT}$$
(2.1)

$$\Delta E = hv = \frac{\gamma h}{2\pi} B_0$$
 (2.2)

Substituting the (2.2) into the (2.1), it can be summarized as follows.

$$\frac{N_{\alpha}}{N_{\beta}} = e^{-\left(\frac{\gamma h B_{0}}{2\pi kT}\right)}$$
(2.3)

in which,

 ΔE : Energy difference between the two energy levels,

K: Boltzmann constant (1.3805 × 10^{-23} J·K⁻¹),

T: temperature (in K),

 N_{α} : the number of spins at a low energy level,

 N_{β} : the number of spins at a high energy level,

h: Plank constant ($6.626 \times 10^{-34} \text{ J} \cdot \text{s}$),

v: frequency.

The NMR signal is generated by the difference in energy absorbed by the spin transmitted from a lower energy level to a higher energy level and emitted by the spin transition from a higher energy level to a lower energy level. That is, the larger the ΔE value, the lower the T (absolute temperature, K), and the larger the B₀, the greater the number of spins at the lower energy level, so the strength of the signal becomes stronger.²⁹

• T_1 (Spin-lattice relaxation) and T_2 (Spin-spin relaxation)

In NMR, the spin of the nucleus is aligned in the same or opposite direction as the external magnetic field along the z-axis. Since there are many atomic nuclei in the same direction as the magnetic field, the net magnetization vector exists parallel to the external magnetic field (B_0) in equilibrium. At that time, the nuclear spin of the z-axis can be inverted to the x-y plane by injecting a short pulse. After pulse injection, the spin system attempts to return to equilibrium, and the time it takes to do this is called relaxation time. The relaxation time is divided into T_1 (Spin-lattice relaxation time) and T_2 (Spin-spin relaxation time) indicating how fast the nucleus rotates on the z-axis. In equilibrium, the net magnetization vector is in the same direction as the external magnetic field (B_0) called equilibrium magnetization (M_0).

In general, the first relaxation process (vertical relaxation) called T_1 relaxation serves to restore the z component to its original value along the vertical (z) axis in an equilibrium state. For example, if a 90° pulse (saturated pulse) is applied in equilibrium, z-stimulation is saturated (reduced to zero) immediately after the pulse, but is initially recovered quickly along the z-axis with an equilibrium value and slows down as it approaches the equilibrium value (**Fig. 1.2.3**). In this case, the time taken for M_z to return to its original equilibrium from saturation is called T_1 (spin-lattice relaxation time) and can be expressed by the following equation. The shorter the T_1 time constant, the faster the relaxation process and equilibrium return. ³⁰



Figure 1.2.3 T_1 relaxation time. ³¹

When the net magnetization is in the x-y plane by pulse, it rotates about the z-axis at Lamar frequency and is called precession. Precession magnetization and net magnetization experience somewhat different magnetic fields in each spin, and finally rotate at different Larmor frequencies and deviate from phase. As a result, a larger phase deviation occurs over time. As a result, a larger phase deviation occurs over time. The time it takes for transverse magnetization M_{xy} to return to equilibrium is called T_2 (spin-spin relaxation time), as shown **Fig. 1.2.4**. ^{31, 32}



Figure 1.2.4 Transverse (T_2 and T_2^*) relaxation processes. ³¹

1.3. Introduction to Solid-state NMR

• Solid-state NMR

Solid-state NMR can identify the physical properties of the sample. Solid-state NMR shows a broad spectrum because the location of the atoms is fixed and the anisotropic interaction is not averaged. There are three factors that cause broadening of the solid-state NMR spectrum, as follow: dipole-diploe coupling, chemical shift anisotropic and orientation-dependent interactions. **Figure 1.2.5** shows the broadening effect according to sample type. The high-resolution NMR spectrum can provide the same type of information as can be used in the solution NMR spectrum. However, obtaining a high-resolution spectrum at solid-state NMR requires many special technologies/equipment, including magic angle spinning (MAS), cross polarization (CP), special 2D experiments, etc. ³³

For single crystal samples, changes in the resonant frequency are observed and analyzed according to the relative direction to the magnetic field. In addition, the presence of broad range of NMR lines, which are considered temporary obstacles, provides a lot of information about the chemistry, structure, and mechanics of solid state samples. ³⁴



Figure 1.2.5 Comparison of ¹³C NMR spectra in solution and solid-state. ³³

• Magic Angle Spinning (MAS) technique

Magic angle spinning (MAS) is a technique for obtaining high-resolution NMR data from solids. Unlike solution NMR, in solid-state NMR, interactions such as chemical shift anisotropy and dipolar coupling dominate, and thus the spectral line width of the solid nucleus is somewhat wide.³⁵ MAS techniques known since the 1950s are mainly used to overcome this problem in solid-state NMR. MAS techniques can reduce the following broadening factors.

i) Chemical shift anisotropy

Because of the anisotropy of the electronic environment, which varies depending on the direction, chemical shift anisotropy is caused by surrounding electrons that deform the local environment of the atomic nucleus. The equation is described in (2.4).

$$\Delta \omega = \omega_0 \delta(\frac{3}{2} + \eta)(3\cos^2\theta - 1)$$
(2.4)

ii) The dipolar coupling interaction

It is caused by a direct spatial bond between nuclei and is described in (2.5).

$$\Omega_{ji} = \frac{\alpha \gamma_{i\gamma_{j}}}{3\sqrt{2}r_{ij}^{3}} (1 - 3\cos^{2}\theta_{ij})$$
(2.5)

iii) The quadrupole interaction

The quadrupolar interaction caused by the interaction between the electric quadrupolar moment of the nucleus and the asymmetric electric field slope surrounding the nucleus occurs when the nuclear spin I is greater than $\frac{1}{2}$. The equation is expressed in (2.6).

$$H_{Q} = \frac{e^{2}qQ}{4I(2I-1)} \left(\frac{3\cos^{2}\theta - 1}{2}\right) [3m^{2} - I(I-1)]$$
(2.6)

Since these three interactions contain a term of $3\cos^2\theta - 1$, a sharp peak appears when the term is zero. Therefore, the sample must rotate at an angle of $\theta=54.74^{\circ}$ ($(3\cos^2\theta - 1) = 0$) relative to the magnetic field B₀.

This technique is called Magic Angle Spinning (MAS). **Figure 1.2.6** shows a schematic expression of the MAS experimental effect.



Figure 1.2.6 Representation of a MAS NMR probe head with an orientation of the stator at an angle (θ) of 54.7° between the axis of rotation and B₀. ³⁵

• Spin echo pulse sequence (Hahn echo)

Pulse sequence refers to a series of radio frequency (RF) pulses applied to a sample to obtain a desired NMR signal. ²⁹ The pulses mainly used in NMR are 90° pulse and 180° pulse. The 90° pulse maximizes the signal to the X-Y plane in which the NMR signal can detect net magnetization on the Z-axis. 180° pulse cannot detect a signal of NMR, but reverses the density of the spin. ³¹

There are two types of signals commonly encountered in spin-½ NMR experiments: the stimulated echo and the spin echo also known as Hahn echo (Hahn, 1950). Spin echo basically has two pulse systems, 90° and 180°. As opposed to FID, two RF pulses can be used continuously to generate spin echoes. **Figure 1.2.7** shows the spin echo pulse sequence. The NMR signal is measured according to initial excitation pulse attenuation.³⁶ The echo can be used to overcome the dead-time limit that is common when observing the resonance of the solid-state materials, which are shown in **Figure 1.2.8**.



Figure 1.2.7 Basic NMR pulse sequences: Hahn echo. ²⁷



Figure 1.2.8 The spin-echo: (a) Application of a 90° RF pulse at t = 0 tips the magnetization vector from its equilibrium state (green) into the x-y plane (dark blue); (b) In the x-y plane, spins at different locations lose phase coherence due to field inhomogeneity and begin to process at different frequencies, with faster spins shown in darker blue and slower spins in lighter blue. Application of a 180° RF pulse at t= τ rotates the magnetization about the y-axis; (c) The order of the spins is now reversed, with the slower spins 'ahead' of the faster spins; (d) this leads to the spins regaining coherence or 'refocusing' at a point in time t= 2τ . ²⁷

2. Experimental

2.1. Material synthesis

The solid-state reaction method was used to synthesize the cathode material LiFeBO_{2.7} $F_{0.6}$ /C (LFeBF/C). This method is simple and easy to apply to industries. Li₂CO₃ (Aldrich, 99.0%), FeC₂O₄·2H₂O (JUNSEI, 99.0%), and H₃BO₃ (Kanto chemical, 99.5%) were used as precursors of the basic substances LiFeBO₃. LiF (WAKO, 98.0%) was used as the source of F, sucrose (JUNSEI, 100%) was used as the source of C, and the stoichiometric ratio of Li was considered. For homogeneous mixing of the precursors, a planetary mill process was carried out at 300 rpm using 200 g of zirconia balls and acetone as a solvent.

The precursor of the dried fine powder was heat-treated in an electric furnace in a high purity Ar gas atmosphere. In order to synthesize a single phase and remove organic matter and moisture, the mixture was synthesized by calcination at 350 °C for 4 hours and sintering at 650 °C for 10 hours. The entire process of the experiment is shown in **Figure 2.1**.



Figure 2.1 Solid-state synthetic procedures of LiFeBO_{2.7}F_{0.6} (/C).

2.2. Characterization of cathode materials

The crystal structure and phase of the LFeBF/C were investigated by the powder Xray diffraction (XRD, Rigaku Ultima IV, Germany) with Cu K_a radiation radiation (λ = 1.5406 Å) at 50 kV and 40 mA over the 2 θ range between 10° and 80°. ⁷Li magic angle spinning (MAS) nuclear magnetic resonance (NMR, Bruker Avance III 300, Germany) measurements were carried out at room temperature with a 7.04 T magnet. The Hahn-echo pulse sequences for ⁷Li were used to observe the NMR signal, and the sample spinning rate was 25 kHz. Raman spectroscopic analysis was performed with a Confocal Raman Spectroscopic system (SR3031A, Ando Tech., Japan) utilizing a 785 nm incident radiation in the range from 600 to 2000 cm⁻¹. Fourier transfer infrared spectroscopy (FT-IR, Shimadzu IRAffinity-IS, Japan) was performed to confirm phase purity of the synthesized materials.

The morphology and elemental composition of the synthesized materials was investigated using field emission scanning electron microscope (FE-SEM, JEOL JSM6500F, Japan) combined with energy dispersive X-ray spectrometry (EDX, Oxford Instrument X-Max, UK) and field emission transmission electron microscope (FE-TEM, JEOL JEL2100F, Japan). The SEM samples were prepared using spread synthesized materials on the surface of carbon tape, and followed by Pt-coating using a Sputter Coater 108auto (Cressington, UK).

2.3. Electrochemical measurements of cathode materials

A 2016 type half-cell was prepared to evaluate the electrochemical performance of the synthesized cathode material. **Figure 2.2** shows the manufacturing process of the coin cell using cathode electrode (working electrode).

The electrodes were prepared by mixed active material (80 wt%), polyvinylidene fluoride (PVDF, Aldrich, Mw = 534,000,10 wt%), and carbon black (Super P, 10 wt%) with some amount of n-methyl-2-pyrolidinone (NMP) for ball milling.

The prepared slurry was brought into close contact with an aluminum foil substrate using a doctor blade and dried at 80 °C. After that, it was pressed using a roll press to ensure uniformity of the electrode thickness. And then, the 2016-coin cells were assembled in glove box filled Ar gas. The amount loaded on the cathode material was about 4 to 5 mg. A lithium metal foil having a thickness of 0.10 mm and a diameter of 15 mm was used as the anode (counter electrode). Porous polypropylene was used as a separator, and non-hydrophobic 1.0 M LiPF₆ in EC/DMC (ethylene carbonate/dimethyl carbonate) was used as an electrolyte.

The tests for electrochemical cycling performance were performed using a Galvanostatic battery cycler (WonATech WBCS 3000, Korea) at room temperature. The coin cells for the rate test were cycled between 1.0 and 4.5 V vs. Li/Li⁺ using a constant current-constant voltage (CC-CV) protocol in charging mode. To observe the cycle performance, the discharge capacity was measured at various C-rate: 0.05, 0.1, 0.2, 0.5, 1 and 2 C. Reversibility was confirmed by measuring each 3 times at 0.05, 0.1, 0.2, 0.5, 1 and 2 C. Long cycle ability was measured 50 times at a 1 C rate to observe the discharge capacity.



Figure 2.2 Schematic representation of coin cell menufacturing process.

3. Results and Discussion

3.1. X-ray Diffraction (XRD)

3.1.1. X-ray diffraction patterns of synthesized active materials

Figure 3.1 shows the XRD patterns of synthesized LiFeBO_{2.7}F_{0.6} (LFeBF) and Carbon-coated LiFeBO_{2.7}F_{0.6}/C (LFeBF/C). Instead of two main characteristic peaks of conventional monoclinic LiFeBO₃ (LFeB), a single intense peak of the vonsenite around 35° corresponding to the (240) plane of its orthorhombic lattice was observed in both LFeBF and LFeBF/C. ^{24, 37} The XRD patterns of the LFeBF and LFeBF/C were well matched with the vonsenite structure, indicating the dominant features of vonsenite LFeBF over the conventional monoclinic LFeB. Currently, it has been experimentally and theoretically investigated and reported that substitution of fluorine atoms at the oxygen sites of the LFeB induced phase transition from monoclinic LFeB into vonsenite LFeBF and LFeBF/C, indicating that carbon was coated on the surface without changing the internal LFeBF structure. The diffraction peak of carbon was not clearly detected, implying the formation of amorphous carbon on the surface of the LFeBF.



Figure 3.1 The XRD patterns of (a) LFeBF/C and (b) LFeBF sintered at 650 $^\circ \text{C}$

3.1.2. X-ray diffraction patterns of air-exposed active materials

To evaluate the storage stability, both LFeBF and LFeBF/C samples were stored in air exposure for 2 months. XRD patterns of the LFeBF and LFeBF/C samples samples before and after storage are shown in **Figures 3.2**. The XRD pattern of LFeBF changed after storing for 2 months with appearance of peaks at 2theta = 11.2° and 21.8°. This phenomenon can be attributed to phase changing of LFeBF as recorded for LFeB with air corrosion.^{12, 38, 39} Carbon-coated sample (LFeBF/C) maintained its original crystal structure with no significant change after air exposure. The carbon-coated layer was strongly benefit to prevent LFeBF from moisture corrosion.



Figure 3.2 XRD patterns of (a) LFeBF and (b) LFeBF/C before and after storing for 2 months (air exposure at room temperature).

3.2. ⁷Li MAS NMR

Figure 3.3 shows the ⁷Li MAS spectrum measured at a spinning rate of 25 kHz for LFeBF, and LFeBF/C cathode materials as well as for pure LiFeBO₃ (LFB) as a reference. The ⁷Li MAS NMR was utilized to investigate the local environment of Li participating in electrochemical reactions in different cathode materials. The isotropic peaks of the ⁷Li spectra were indicated with a dashed line, and the spinning sideband manifolds were marked with asterisks (*). The peak intervals of the spinning sidebands were equal to the spinning rate.

As shown in **Figure 3.3**, a single isotropic peak of the LFB cathode material appeared at around -230 ppm and the isotropic peaks of both LFeBF and LFeBF/C cathode materials appeared at around 0 ppm, indicating a chemical shift of about -230 ppm between LFeBF, LFeBF/C and LFB materials. The shift to the downfield in the LFeBF and LFeBF/C cathode materials appeared due to a through-bond hyperfine interaction between paramagnetic Fe²⁺ and Li⁺ through interfering oxygen atoms in different structure geometries. As discussed previously, substitution of fluorine induced phase transition from monoclinic LFeB into vonsenite LFeBF. Therefore, Li ions were surrounded in an octahedral coordination geometry of vonsenite-type LFeBF in the LFeBF and LFeBF/C cathode materials instead of in a tetrahedra of the monoclinic-structured LFeB. The downfield shift in the NMR spectrum of LFeBF and LFeBF/C compared to LFB matched well with the XRD results which revealed the phase transition from monoclinine to vonsenite after fluorine substitution. ^{12 40 24}



Figure 3.3 ⁷Li MAS NMR spectra of (a) LFeBF/C, (b) LFeBF and (c) LFB at sample spinning rate of 25 kHz.

3.3. Field emission scanning electron microscopy and energy dispersive x-ray spectroscopy

The morphology of synthesized LFeBF/C was observed by field emission scanning electron microscopy (FE-SEM) measurement as shown in **Figure 3.4(a)**. The nano-sized LFeBF/C particles with rod-like and spherical morphologies were obtained. Since the substitution of fluorine induced phase transition from monoclinic into vonsenite, it also caused the morphology alteration into rod-like structures. The particle morphologies shown in **Figure 3.4** were well matched with observations from previous studies. ²⁴

Energy dispersive x-ray (EDX) spectra of LFeBF/C are shown in **Figure 3.4(b)** in order to confirm the presence of substituted elements. Obviously, all elements including Li, Fe, B, O, and substituted F were homogeneously distributed in the LFeBF/C particles. This investigation further confirmed the high purity of the LFeBF/C material synthesized by the solid state reaction technique.



Figure 3.4 (a) SEM image and (b) colored compositional image of LFeBF/C with purple color for B, cyan for Fe, green for O and yellow for F.

3.4. Transmission electron microscopy (TEM)

Figure 3.5 shows the TEM images of the LFeBF/C. In accordance with the previous SEM image, a mixture of rod-like and spherical particles were obtained. The lattice fringe of the LFeBF/C confirmed that highly crystalline products were synthesized. Magnification from the surface of the synthesized material revealed that the LFeBF/C particles were well wrapped by nano-carbon layers. The interconnected carbon between LFeBF particles were expected to improve the conductivity as well as to provide a rough surface to store and contact more electrolyte molecules. This carbon-coated layer was also expected to increase the structural stability against the mechanical stress inherent during the high current cycle process. ^{38,41} Last but not least, the formation of the carbon-coated layer would be extremely useful to prevent the LFeBF/C from moisture corrosion.



Figure 3.5 TEM images of of LFeBF/C with different magnifications, showing the formation of product particles covered by C layers.

3.5. Fourier Transform Infrared spectoscopy (FT-IR)

The phase purity of the prepared materials was investigated by FT-IR. All of the FT-IR spectrums went through baseline correction work. As indicated in **Figure 3.6**, changes in the binding structure due to fluorine substitution such as B-F bonding was confirmed. The FT-IR spectrum of the LFeBF/C composite exhibited the splitted vibrations at around 594, 687 and 1250 cm⁻¹, corresponding to the active bands of trigonal $[BO_3]^{3-.39}$ By FT-IR analysis, it would be confirmed that carbon was coated on the particle surface without affecting the internal structure.



Figure 3.6 FT-IR spectrums of (a) H₃BO₃, (b) LFB, (c) LFeBF and (d) LFeBF/C.

3.6 Raman spectroscopyaterials

Raman spectroscopy is a useful analysis method for characterizing structure of a carbon layer.⁴² To confirm the presence of amorphous carbon protecting the surface, a Raman spectrum was obtained. As shown in **Figure 3.7**, the presence of amorphous carbon was confirmed.



Figure 3.7 Raman spectra of the LFeBF/C

3.7. Electrochemical properties of cathode materials

Coin cells were assembled to evaluate the electrochemical performance of the synthesized cathode material, and measured using the Galvano static charge/discharge test in a potential range of 1.0 to 4.5V.

The electrochemical rate performances of LFeBF and LFeBF/C are shown in **Figure 3.8** during charge and discharge process depending on various C-rate from 0.05 to 2 C-rate. It was clearly observed that LFeBF and LFeBF/C increased discharge capacity at all C-rates in comparison with the conventional LFeB. The LFB, LFeBF and LFeBF/C showed initial discharge capacities of 73.4, 361.1 and 367.0 mAh g⁻¹ at 0.05 C-rate, respectively. In the case of the LFeBF material, the discharge capacity exceeded the theoretical capacity of LFB (220 mAh g⁻¹) at C-rate of 0.05, but the discharge capacity rapidly decreased to 254.67 mAh g⁻¹ in the secondary cycle performance which was consistent with previously reported research results. ²⁴ The carbon-coated LFeBF (LFeBF/C) exhibited a high discharge capacity of about 159 mAh g⁻¹ even at a high discharge rate of 2 C-rate. It should be emphasized that the LFeBF/C material showed the highest discharge capacity at all C-rates in comparison with the performances of the LFeBF and LFeBF materials.



Figure 3.8 Rate performances of LFB, LFeBF and LFeBF/C

The long cycle capabilities of LFB, LFeBF, and LFeBF/C are shown in Fig. 3.9, which were carried out in the voltage range of 1.0-4.5 V at 1 C-rate. Data for discharge capacity and capacity retention rates at 1 C-rate in the first, second, and 50th cycles of the LFB, LFeBF, and LFeBF/C materials were extracted and shown in Table 3.1. The specific capacity of the LFeBF and LFeBF/C at the first cycle were 291.55 mAh g⁻¹ and 231.70 mAh g⁻¹, respectively, and reached 162.32 mAh g⁻¹ and 197.53 mAh g⁻¹ after 50 cycles, respectively, indicating that both fluorine substitution and carbon coating strongly increased the specific capacity and the cylic stability. The fluctuations of specific capacity of the LFeBF and LFeBF/C materials might be related to the instability due to fluorine substitution at the borate unit as mentioned above. The phase transition from monoclinic to vosenite by fluorine substitution might help to make the lattice robust with strong metal-oxygen bonds, increase the Li-O distance and polarity which induce the Li ion diffusion. Consequently, the fluorine substitution could be a key factor to suppress transition-metal ion dissolution and improve the long-term cycle life. In addition, the carbon-coated layer and conductive carbon network could improve the conductivity of the LFeBF/C-based cathode material, which was also benefit to the electrochemical performances.

Cathode material	1 st cycle	2 nd cycle	50 th cycle	Capacity retention rates
LiFeBO₃ (LFeB)	57.27 mAh g ⁻¹	54.08 mAh g ⁻¹	80.56 mAh g ⁻¹	-
LFeBF	291.55 mAh g ⁻¹	190.46 mAh g ⁻¹	162.32 mAh g ⁻¹	0.5567
LFeBF/C	231.70 mAh g ⁻¹	252.232 mAh g ⁻¹	197.53 mAh g ⁻¹	0.8525

Table 3.1 The discharge capacity and capacity retention rates at 1C in the first, second, and 50th cycles of the prepared materials.


Figure 3.9 The long cycle ability at 1 C-rate of LFB, LFeBF and LFeBF/C

4. Conclusion

Carbon was successfully coated on the surface of the fluorine-substituted LFB using a solid-state reaction method. Various analysis techniques such as XRD, ⁷Li MAS NMR, SEM/EDX, TEM, Raman, FT-IR were used for structural and component characterization of the synthesized material. The XRD patterns and NMR spectra confirmed that fluorine successfully substituted oxygen sites in the monoclinic LFeB materials and induced a phase transition from monoclinic to vonsenite. EDX element mapping confirmed the homogeneous distribution of all elements including Li, Fe, B, O, and substituted F in the LFeBF/C particles. TEM image, Raman spectra of the synthesized material confirmed that the amorphous carbon layer was well coated on the surface of the LFeBF. XRD results also confirmed that degradation occurring on the surface of the cathode material during air exposure can be suppressed through surface carbon coating. The carbon coating layer did not affect the internal structure of the LFeBF.

The electrochemical characteristics measured within the range of 1.0-4.5 V for LFeBF/C showed the largest discharge capacity and great stability at all C-rates. The initial discharge capacity (231.7 mAh g⁻¹) of LFeBF/C at rate of 0.05C exceeded the theoretical capacity (220 mAh g⁻¹) of pristine LFB, and LFeBF/C at a high charge/discharge rate of 1C showed a high capacity retention rate of about 85%.

The LFeBF/C material, which stably exhibited high reversible capacity, would be a promising cathode material to be applied to the globally expanding lithium secondary battery market such as EV and ESS. Element substitution and carbon coating should be considered as effective approaches to improve the stability and the long-term cycle life of the cathode materials.

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