



Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Phase transition-induced improvement in the capacity of fluorine-substituted LiFeBO_3 as a cathode material for lithium ion batteries

Khoirul Umam^{a,1}, Byung Cheol Sin^{b,1}, Laxman Singh^c, Chaewon Moon^a, Jaeun Choi^a, Inyoung Lee^a, Jaewoong Lim^d, Jaehoon Jung^{a,*}, Myoung Soo Lah^{d,*}, Youngil Lee^{a,*}

^a Department of Chemistry, University of Ulsan, Ulsan 44776, Republic of Korea

^b Fine Chemical and Material Technical Institute, Ulsan 44412, Republic of Korea

^c Department of Chemistry, RRS College (Patliputra University), Patnas 803302, Bihar, India

^d Department of Chemistry, Ulsan National Institute of Science and Technology, Ulsan 44919, Republic of Korea

ARTICLE INFO

Article history:

Received 15 September 2020

Revised 24 October 2020

Accepted 24 October 2020

Available online 12 November 2020

Keywords:

Fluorine-substituted LiFeBO_3

Vonsenite

Solid-state NMR

Density functional theory calculations

Cathode material for lithium ion battery

ABSTRACT

Among polyanion-type cathode materials used for large-scale lithium-ion batteries (LIBs), LiFeBO_3 (LFeB) has received attention due to its lowest weight framework with a larger theoretical capacity of 220 mAh g^{-1} compared with commercialized LiFePO_4 (170 mAh g^{-1}). The main drawback of LFeB, however, is its poor specific discharge capacity as a cathode material for LIBs. Herein, the fluorine-substituted LFeB at the oxygen site, $\text{LiFeBO}_{3-x}\text{F}_{2x}$ (LFeBF, $x = 0.05, 0.1, 0.2, 0.3$, and 0.5), has been prepared as a cathode material for LIBs via a solid-state reaction to improve the electrochemical behavior accompanied by phase transition. Morphological change as increasing x and well-distributed fluorine element of LFeBF have been observed using a scanning electron microscope combined with an energy dispersive X-ray spectrometer. X-ray diffraction, X-ray photoelectron spectroscopy, and solid-state ^7Li and ^{11}B nuclear magnetic resonance spectroscopy studies of LFeBF as well as increasing x show a dramatic phase transition from monoclinic to vonsenite-type structure. The plausible atomic arrangement has been also investigated using density functional theory. Furthermore, the fluorine substitution at the oxygen site of LFeB leads to a remarkable improvement in discharge capacity, the highest value ($361.15 \text{ mAh g}^{-1}$ for LFeBF ($x = 0.3$)) of which is about five times larger than that of LFeB (73.43 mAh g^{-1}) at 0.05 C rate, without any additional carbon source.

© 2020 Elsevier Ltd. All rights reserved.

1. Introduction

Lithium-ion batteries (LIBs) have been extensively employed as power sources in a wide range of applications due to their high energy density, high Coulombic efficiency, low self-discharge features, and chemical potential range that are all accessible by varying the electrode design. In the past decade, there has been a growing trend towards developing the next-generation LIBs with high charge capacity and power density for electric vehicles (EVs), hybrid electric vehicles (HEVs), energy storage systems (ESSs) [1], aerospace applications, and autonomous electric devices such as hybrid solar batteries [2]. However, the performance of LIBs for EV and ESS applications, such as high energy density, safety, re-

cycling, and cost efficiency, still needs to be significantly improved. Therefore, substantial efforts have been devoted to further develop the components of the LIB materials, in particular a cathode material with a high capacity, high voltage, and high-energy storage, to boost the performance of rechargeable LIBs [3,4].

In the past two decades, three types of cathode materials have been investigated intensively, including layered lithium transition metal oxides (LiNiO_2 [5], LiMnO_2 [6], LiCoO_2 [7], etc.), Mn-based spinels (LiMn_2O_4 , $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$, etc.) [8–10], and polyanion-type cathode materials [11]. Among them, the polyanion-type cathode materials exhibit a higher thermal stability than the conventional options using layered transition-metal oxides due to the strong covalently bonded oxygen atoms in the polyanion unit, which facilitate large-scale LIB applications by virtue of their improved safety [11]. As a new class of cathode materials for LIBs, polyanion compounds have attracted great interest, since the first report analyzing the electrochemical performance of LiFePO_4 by Padhi et al., [11,12] based on high cycle stability, high energy density, safety,

* Corresponding authors.

E-mail addresses: jjung2015@ulsan.ac.kr (J. Jung), mslah@unist.ac.kr (M.S. Lah), nmryil@ulsan.ac.kr (Y. Lee).

¹ These authors contributed equally to this work.