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# Phase transition-induced improvement in the capacity of fluorine-substituted $\text{LiFeBO}_3$ as a cathode material for lithium ion batteries

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## ABSTRACT

Among polyanion-type cathode materials used for large-scale lithium-ion batteries (LIBs),  $\text{LiFeBO}_3$  (LFeB) has received attention due to its lowest weight framework with a larger theoretical capacity of  $220 \text{ mAh g}^{-1}$  compared with commercialized  $\text{LiFePO}_4$  ( $170 \text{ mAh g}^{-1}$ ). 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  $^7\text{Li}$  and  $^{11}\text{B}$  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 ( $73.43 \text{ mAh g}^{-1}$ ) at  $0.05 \text{ C}$  rate, without any additional carbon source.

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## 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 ( $\text{LiNiO}_2$  [5],  $\text{LiMnO}_2$  [6],  $\text{LiCoO}_2$  [7], etc.), Mn-based spinels ( $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$ , 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  $\text{LiFePO}_4$  by Padhi et al., [11,12] based on high cycle stability, high energy density, safety,

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