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Author(s)	Aravindan, Vanchiappan; Umadevi, M.
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Synthesis and characterization of novel LiFeBO₃/C cathodes for lithium batteries

V. Aravindan^{a,*} and M. Umadevi^b

^a Energy Research Institute, Nanyang Technological University, Singapore 639798, Singapore

^b Department of Science and Humanities, SVS College of Engineering, Coimbatore-642109, India

Abstract

Carbon coated LiFeBO₃ has been successfully synthesized by solid state reaction method at 750°C under Ar atmosphere. Adipic acid was chosen for the source material for carbon during synthesis process. X-ray diffraction pattern confirms the formation of phase with monoclinic structure. Scanning electron microscopic study vindicates the particulate nature of the synthesized LiFeBO₃ with weak agglomeration. Electrochemical impedance spectroscopy parallels the enhanced conducting properties of carbon coated LiFeBO₃ rather pristine LiFeBO₃. The Li/carbon coated LiFeBO₃ and LiFeBO₃ cells presented the initial discharge capacities 93 and 47 mAh/g, respectively. After few cycles, the carbon coated LiFeBO₃ exhibited stable discharge behaviour (~53 mAh/g), whereas bare LiFeBO₃ is concerned poor electrochemical performance is resulted.

Keywords: LiFeBO₃; adipic acid; solid state synthesis; carbon coating; polyanion

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* Corresponding author: aravind_van@yahoo.com
Tel: +65 65162605; Fax: 65 6776126

1.0 Introduction

To the search of high performance rechargeable batteries for portable electronic devices, electrical vehicles and dispersed type energy systems has led to the development of lithium based rechargeable batteries with high safety. Major challenges lie in the areas of elevated-temperature performance, minimizing capacity fade during prolonged use, and replacement of the expensive and toxic LiCoO_2 cathode. The discovery of LiFePO_4 by Padhi *et al.* [1] in 1997 made the revolution in the polyanion based cathodes. Till now, several works are in progress based on olivine LiMPO_4 (M=Fe, Mn, Co and Ni) based compounds due to potentially low cost and environmentally friendly that could have the major impact in electrochemical energy storage systems. After the surface modification, especially coated with carbon, there is no obvious capacity fading was observed even after several hundred cycles for LiFePO_4 . Such stability is afforded by improved electronic conductivity, scaffold structure deriving from the strong covalent P–O bonding, which render into electrochemical, chemical as well thermal safety in a voltage domain where no protective passivation layer is needed [1-3].

Similarly, boron based i.e. LiMBO_3 (M=Fe, Mn, and Co) materials are recently attracted by the researchers [4-10]. The boron is light weight, less expensive, environmental friendly, relatively abundant and having slightly less electro-negativity than phosphorous. It is well known that boron can be coordinated by oxygen atoms to form a variety of atomic groups, which were considered to be the prevailing factor for physical properties. In addition, it has been exposed that polyanions facilitate low transition metal redox energies through the inductive effect, thus allowing some sort tuning of such energies. In spite of their appealing properties, Legagneur *et al.* [4] first demonstrated the possibility of using boron based cathodes in lithium batteries. However, these group materials also suffered due to their inherent conducting behavior similar to that of olivine framework materials. The appropriate synthesis condition, surface modification and desired particle size for

LiFePO₄ dramatically improved the cathodic performance [11], and a similar kind of improvement is expected here to enhance the performance of the boron based compounds. In this context, we have made an attempt to explore the possibility of using LiFeBO₃ *via* solid state reaction method with and without carbon treatment.

2.0 Experimental

The starting materials of LiOH.H₂O (Junsei, Japan), Fe(C₂O₄).2H₂O (Sigma-Aldrich, USA) and H₃BO₃ (Junsei, Japan) were used for the synthesis with high purity grades. An appropriate amount of adipic acid (0.1 mol. against total metal ion present in the compound) (Dae-Jung, Korea) was used as the chelating agent as well as carbon source material. Initially, the stoichiometric amounts of starting materials were fine grounded using mortar and precalcined at 250⁰C for 3 hours for decomposition of oxalates and hydroxides. Again, the intermediate product was fine ground using mortar and fired under Ar flow at 750⁰C for 15 hours to obtain the resultant material.

Powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) pattern was studied for structural analysis using CuK α radiation. Surface morphological studies were analyzed using a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Electrochemical impedance spectroscopic (EIS) analysis was carried out using Bio logic, USA electrochemical work station. The cycling performances were studied using CR2032 coin-type cell and the cathode was fabricated with 20 mg of exactly weighed active material, 3 mg of ketjen black and 3 mg of conductive binder (2 mg of Teflonized acetylene black (TAB) and 1 mg of graphite). The mixture was pressed on a 200 mm² stainless steel mesh which used as the current collector under a pressure of 300 kg/cm² and dried at 130 °C for 5 hours in a vacuum oven. The coin cell was made-up of a cathode and metallic lithium as anode, which was separated by a porous polypropylene film (Celgard 3401). The 1 M LiPF₆ in mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v, Techno Semichem Co., Ltd, Korea) was used as electrolyte. The cycling studies were carried out between 1.25-4.8 V at

ambient temperature with current density of C/20 (assumed 1 C = 220 mA g⁻¹).

3.0 Results and Discussion

Figure 1 represents the XRD patterns of pure and carbon treated LiFeBO₃. The reflections indicated that, synthesized materials exhibiting highly crystallized. However, very small amount of unknown impurities of present in the material and a similar kind of impurity was noticed by Dong *et al.* [7]. The structure of LiFeBO₃ is monoclinic, which is analogous to that of LiMnBO₃ [5]. Monoclinic structure of each unit cell contains four chemical formula units of LiFeBO₃ and all atoms occupy the 8f sites. Three dimensional framework of [FeBO₃]_n⁻ anion is drawn from FeO₅ trigonal bipyramids and BO₃ groups. The FeO₅ exhibits the distorted hexahedron linkage and the Fe atom occupies the central position of the said hexahedron. Further, FeO₅ hexahedrons are sharing their two edges with neighboring units of FeO₅ as a long chain. These chains are linked by BO₃ groups with corner sharing and whereas, the B atoms are not occupied in the central position of the triangle as that of Fe atoms. Each and every Li atoms are well surrounded by three nearby FeO₅ hexahedrons group long chains connected by BO₃ triangles. The observed XRD reflections are highly resembles the previously reported patterns [4, 5, 7]. This confirms the phase purity of the material prepared by adipic acid assisted solid state synthesis.

Figure 2 represents the surface morphological features of the LiFeBO₃ and LiFeBO₃/C materials respectively. The bare LiFeBO₃ images showed almost spherical morphology interlinked with nearest particles, in other words, weakly agglomerated with other particles. Whereas in the case of carbon coated LiFeBO₃, a thin layer like material has been covered on the surface of the particulates. This observed layer is none other than carbon; this may form the carbonization of the gelating agent (adipic acid) during high temperature synthesis. The present of carbon not only prevents the agglomeration of the particles during the synthesis process, it also provides the

improved electronic conductivity of the LiFeBO_3 .

Electrochemical Impedance Spectroscopy (EIS) is a versatile electrochemical tool to characterize intrinsic electrical properties of any material and its interface. The basis of EIS is the analysis of the impedance (resistance of alternating current) of the observed system in subject to the applied frequency and exciting signal. This analysis provides quantitative information about the conductance, the dielectric coefficient, the static properties of the interfaces of a system, and its dynamic change due to adsorption or charge-transfer-phenomena. The EIS uses alternating current with low amplitude signals. This provides a non-invasive observation of any sample without any or less influence on the electrochemical state. The EIS was performed to substantiate the effects of carbon coating on the electrical conductivity of the LiFeBO_3/C system. **Figure 3** illustrates the EIS of the LiFeBO_3 and LiFeBO_3/C cathodes synthesized via solid state method which is recorded in the fresh cell. The appearance of high-frequency semicircle is attributed to the formation of SEI film and/or contact resistance, the medium frequency region is assigned to the charge-transfer (CT) impedance on the electrode/electrolyte interface, and the inclined line (vertical tail) at approximately 45° angle to the real axis corresponds to the lithium diffusion kinetics towards the electrodes so called Warburg tail [12]. It is obviously seen that the diameter of the semicircle in the medium-frequency region for the LiFeBO_3/C electrode is extremely lower than LiFeBO_3 electrode, suggested that the lower CT impedance than the former. This confirms the electronic conductivity of LiFeBO_3/C is drastically improved after carbon coating.

Cycling profiles of $\text{Li}/\text{LiFeBO}_3$ or LiFeBO_3/C cells are given in **Figure 4a & b**. The **Figure 4a** shows typical charge-discharge traces of the $\text{Li}/\text{LiFeBO}_3\text{-C}$ cell cycled between 1.25-4.8 V at ambient temperature conditions with C/20 rate. **Figure 4b**, the cells delivered the initial discharge capacity 93 and 47 mAh/g against the charge capacity of 184 and 197 mAh/g for LiFeBO_3/C and LiFeBO_3 , respectively (not shown). The irreversible capacity loss may be ascribed to

the formation of solid electrolyte interface (SEI) towards the electrodes. After 30 cycles, discharge capacities 53 and 38 mAh/g is respectively observed for carbon coated and bare LiFeBO₃. Carbon coated LiFeBO₃ material exhibited the very stable discharge behavior (beyond 10th cycle) ~53 mAh/g until the 40th cycle, whereas uncoated material shows some irregular capacity profile. The carbon coating was performed during calcination process by the carbonization of chelating agent. The carbon coating is one of the effective approaches to improve the capacity of the material via enhanced conductivity. Coating provides the improved conductivity and connectivity between the active particles present in the electrode. The improved performance of carbon treated LiFeBO₃ may be ascribed to improved conductivity (confirmed by a.c. impedance studies) obtained from good contact between nearest neighbor particles i.e. active particles through such coating. Further, particle size, preparation of the sample and behaviors of the surfactants used are cannot be excluded [13]. Moreover, the source of carbon is also very important. Adipic acid is an excellent source material for carbon which was convincingly proven for LiFePO₄ system by Lee *et al.* [14]. Further, LiFeBO₃ contain one lithium ion per formula unit, thus, if one could completely extract the lithium and completely oxidization of Fe^{2+/3+}, the theoretical capacity would be 220 mAh/g. However, full capacity is rarely achieved owing to their limitations of structure and need for high electronic and ionic conductivity, composition of the materials etc. For example, the commercially available cells contain LiCoO₂ as cathode with the theoretical capacity of 274 mAh/g. However, only ~50% of (Li_{0.5}CoO₂) theoretical capacity (140 mAh/g) could be practically utilized, which originates from its structure and electrochemical behaviour [15].

4.0 Conclusion

A novel LiFeBO₃ cathode material was prepared by conventional solid state reaction method with and without carbon coating. The XRD reflections confirm the formation of electrodes at 750 °C

under Ar flow. Morphological features reveal the presence of carbon layer on the surface of the particulates. Electrochemical impedance spectroscopy corroborates the improved electronic conductivity of carbon coated LiFeBO₃. The Li/LiFeBO₃-C cell delivered an initial discharge capacity of 93 mAh/g and presented the stable discharge behaviour ~53 mAh/g upto 40th cycle, whereas irregular cycling profile was observed in the case of bare LiFeBO₃.

5.0 References

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Figure captions

- Figure 1** Powder X-ray diffractogram of (a) pure LiFeBO_3 and (b) carbon coated LiFeBO_3 synthesized at 750 °C
- Figure 2** Scanning electron microscopic images of (a) pure LiFeBO_3 and (b) carbon coated LiFeBO_3 cathodes
- Figure 3** Electrochemical impedance spectroscopy of LiFeBO_3 cathodes
- Figure 4** Electrochemical performance of LiFeBO_3 electrode (a) typical charge-discharge curves of carbon coated LiFeBO_3 (b) cycling profiles of pure and carbon coated LiFeBO_3 electrodes

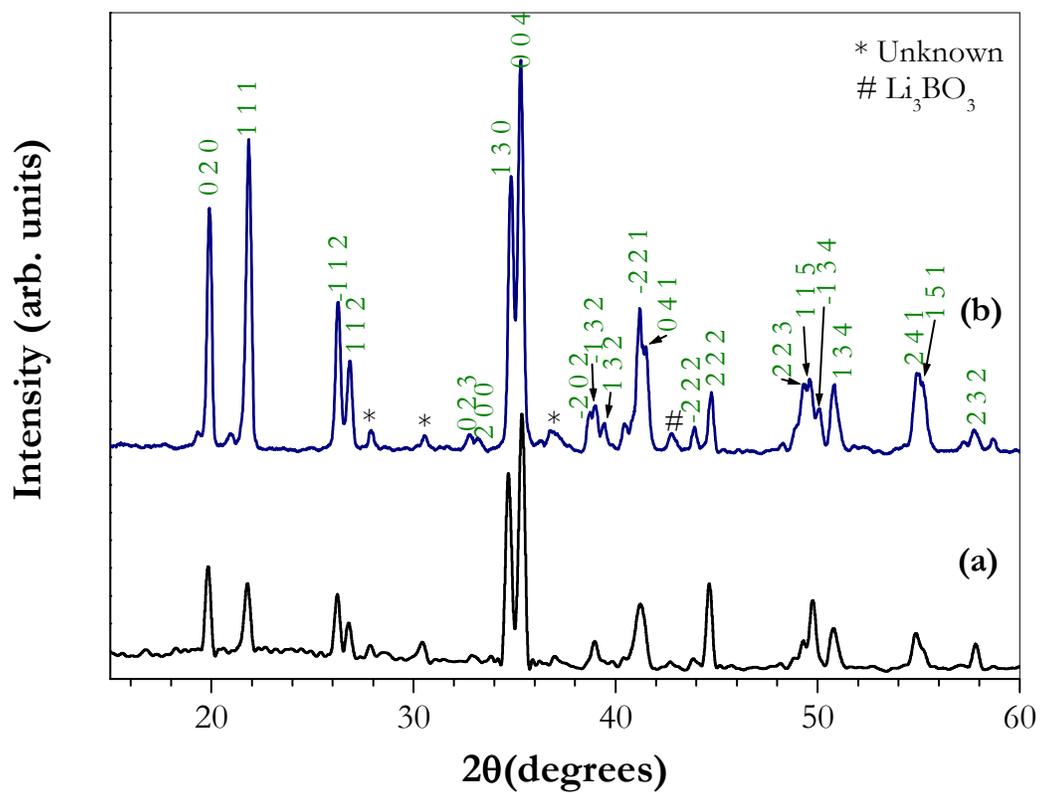


Figure 1

V. Aravindan & M. Umadevi

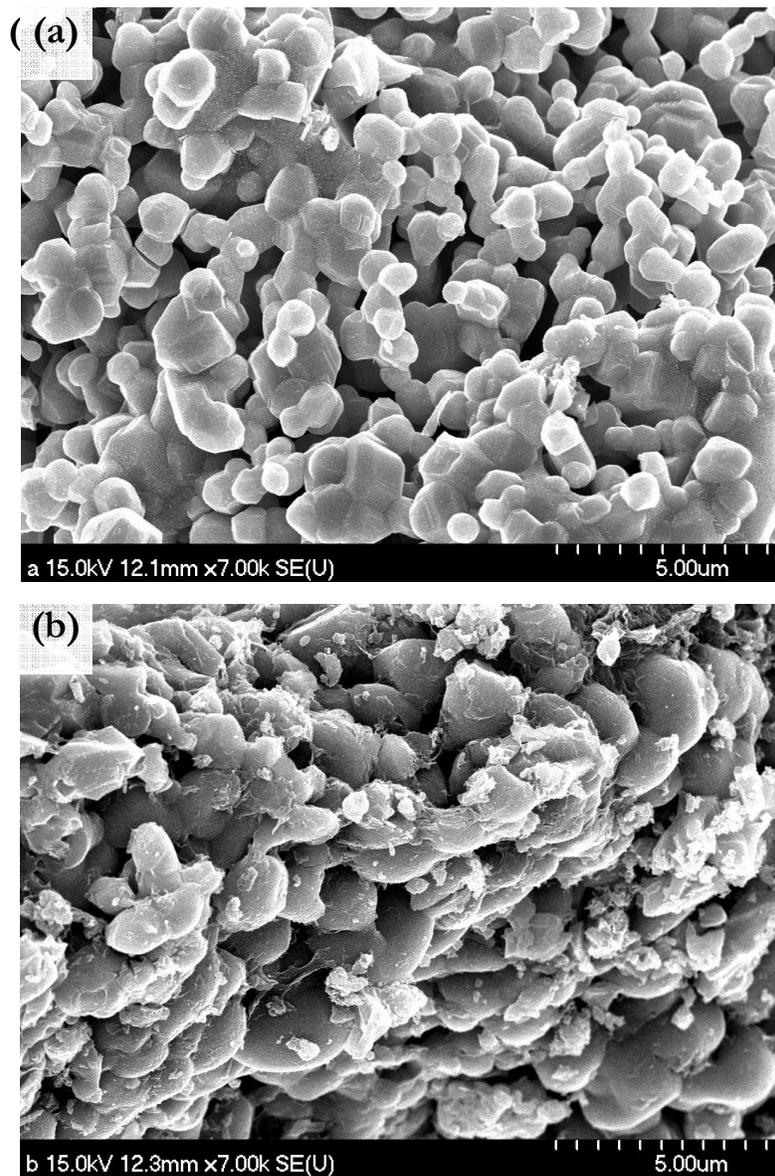


Figure 2

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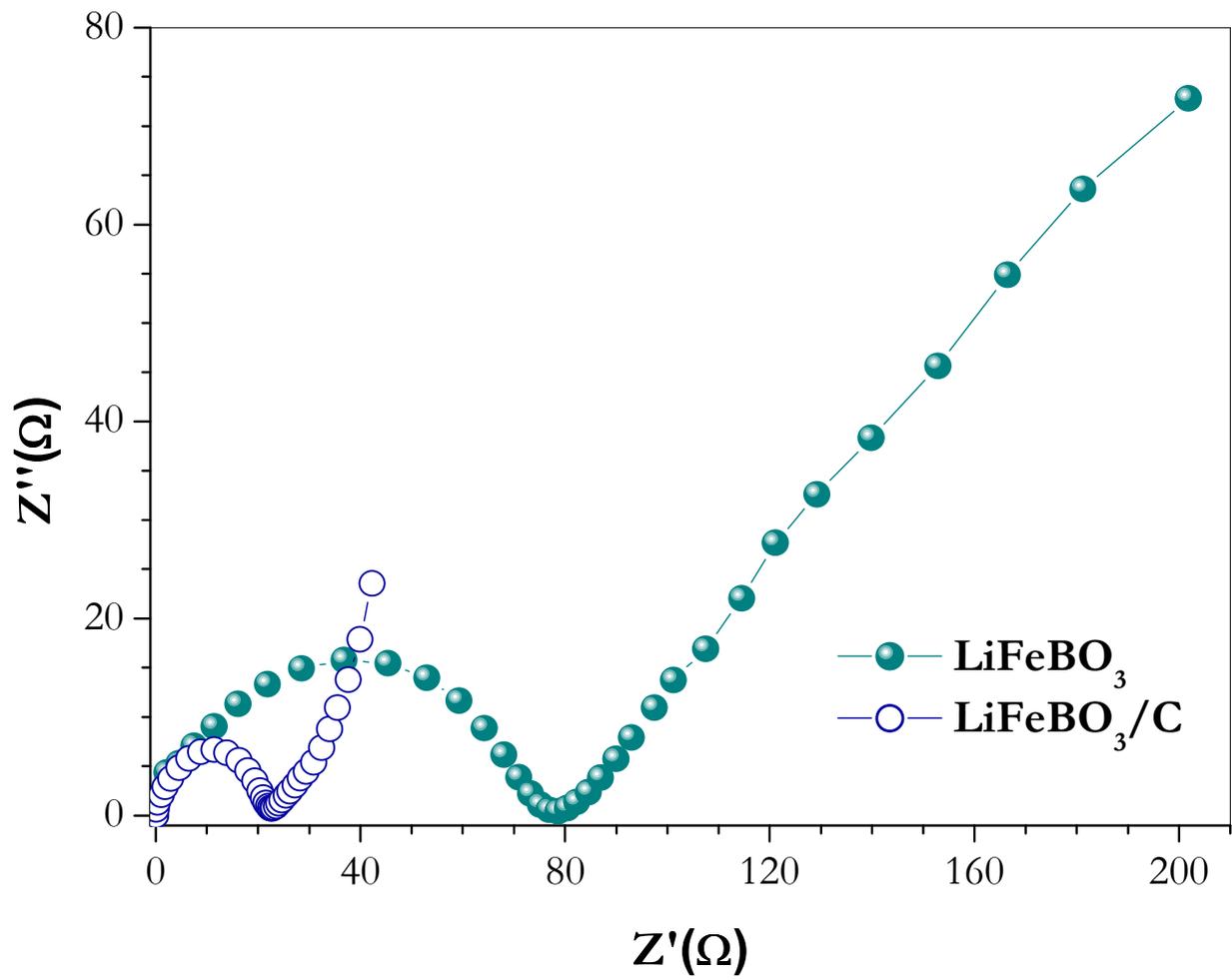


Figure 3

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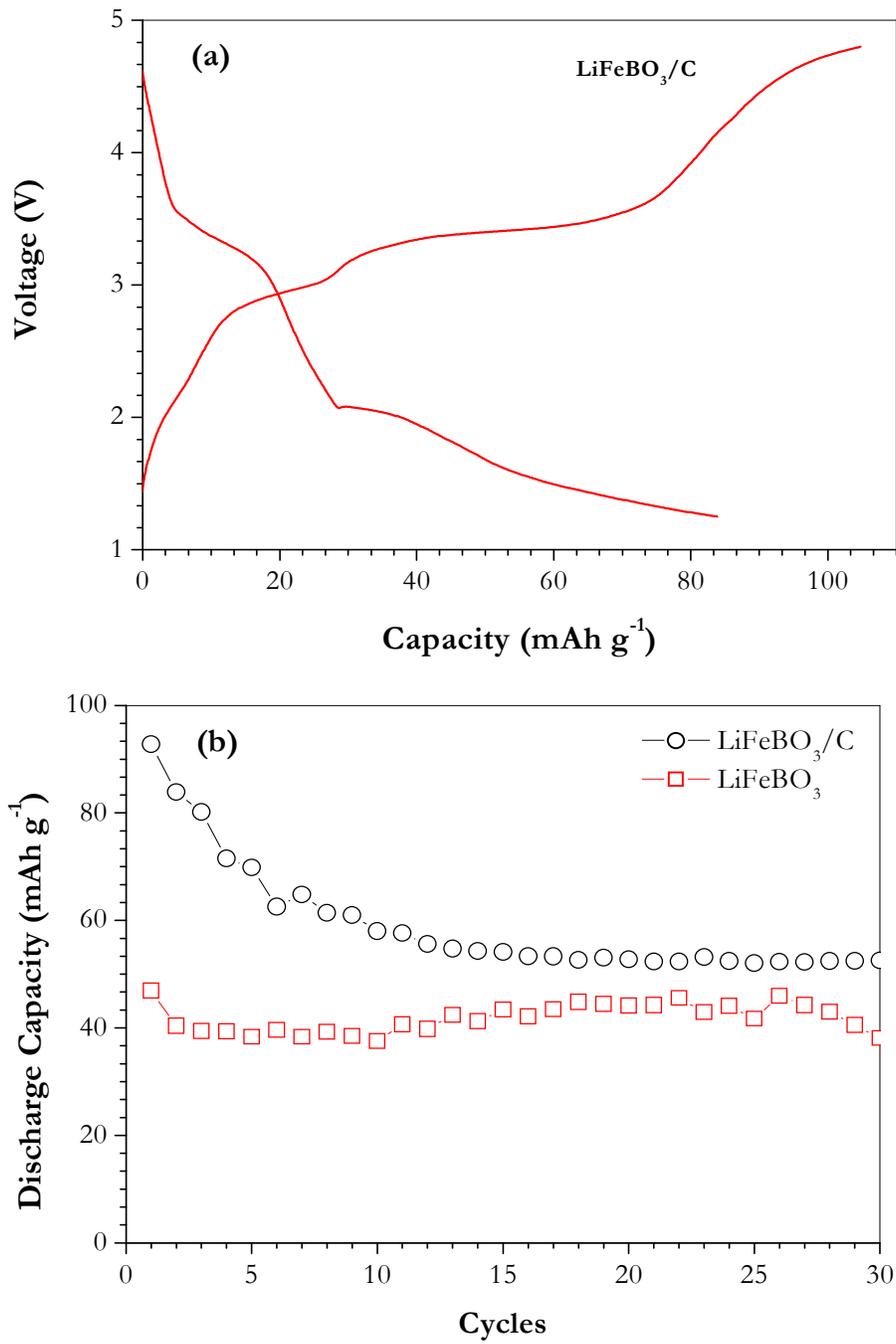


Figure 4

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