



# Electrochemical properties of carbon-composite NASICON-type iron sulfate $\text{Fe}_2(\text{SO}_4)_3$ as a cathode for lithium secondary batteries



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## HIGHLIGHTS

- ▶ Mixing  $\text{Fe}_2(\text{SO}_4)_3$  with carbon improved its conductivity, capacity and cyclability.
- ▶ We studied to mixing methods of a conventional (CCT) and polymer added (PMCT).
- ▶ The capacity of non-treated sample of  $55 \text{ mA h g}^{-1}$  was improved by CCT to  $117 \text{ mA h g}^{-1}$ .
- ▶ In PMCT, carbonized polymer built a better mixture and doubles its cyclability.
- ▶ Particle size and distribution are keys to improve its capacity and cyclability.

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## ABSTRACT

We studied the effect of carbon treatment on improving the electrochemical properties (capacity and cyclability) of NASICON-type iron sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) for the cathodes of lithium ion batteries (LIBs). An optimized ball milling technique that was applied to a mixture of as-synthesized iron sulfate and conductive carbon ketjen black EC-600JD (KB) resulted a high capacity of  $117 \text{ mA h g}^{-1}$ , which is close to its theoretical capacity of  $134 \text{ mA h g}^{-1}$ . Moreover, the cyclability of coin-type test cell was doubled to 58 cycles by adding a polymer followed by heat treatment to the mixture of conductive carbon and  $\text{Fe}_2(\text{SO}_4)_3$ . The smaller particle size and more uniform distribution in the mixture of conductive carbon and  $\text{Fe}_2(\text{SO}_4)_3$  particles accounted for the improved electrochemical properties after treatment, as confirmed by FE-SEM observations.

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## 1. Introduction

Of the several electrochemically active compound materials containing transition metals that have been considered for use as the next generation cathodes for lithium ion batteries (LIBs), interest in iron-based compounds has increased because of their abundance and low cost. Many researchers have been attempting to find a high-performance iron-based electrode material by studying, for example,  $\text{FeOCl}$ ,  $\text{FeOOH}$ ,  $\text{FePS}_3$ ,  $\text{FeS}$ , [1] and  $\text{FeF}_3$  [2]. However, their results have shown that these iron compounds have relatively poor cyclability and a low discharge voltage, making them unsuitable for cathode applications.

Interest in studying polyanion based electrodes began after Goodenough [3,4] and Delmas [4] introduced the concept of three-

dimensional lithium intercalation using a polyanion ( $(\text{XO}_4)^{n-}$ ) compound as an alternative to the closely packed oxygen atoms. This kind of polyanion was found to possess strong covalently bonded oxygen atoms [4,5] that offered better stability in terms of both shifting the temperature of oxygen release and heat generation to higher one. Since then, iron-based polyanion compounds such as  $\text{PO}_4^{3-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  have attracted the interest of many researchers [6]. However, due to the low potential of  $\text{Fe}^{2+/3+}$  in these iron-based polyanion compounds, layer-structure cathodes such as  $\text{LiCoO}_2$  were dominantly used for commercial LIBs.

On the other hand, in recent years several environmental and energy issues have triggered a shift in the use of LIBs from small-sized batteries for mobile applications to large-capacity batteries for both cycle usage (electric vehicles and smart grids) and back-up power usage. Although several safety measures have been employed with large cells, such as controlling the cut-off voltage using a battery management system and equipping the cell with

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a shutdown separator and valve tools, several issues still remain. In particular, safety concerns have been raised in relation to back-up applications, where the battery is kept in a stand-by condition, ready to meet a sudden demand. For this reason, a material that is stable at charge state (Li delithiation condition) is preferable. This is why iron phosphate ( $\text{LiFePO}_4$ ) with olivine is now applied as a cathode for large-capacity LIBs despite its lower energy density (capacity  $150 \text{ mA h g}^{-1}$ , discharge voltage 3.5 V) [5] compared with other commercially available cathodes.

Another polyanion iron compound consisting of iron sulfate  $\text{Fe}_2(\text{SO}_4)_3$  with a NASICON structure has been suggested as a prospective material for the cathodes of LIBs because it has a flat profile at a high voltage of 3.6 V vs. Li metal and is easy to synthesize [6,7]. There are two kinds of NASICON-type iron sulfates that differ in terms of their monoclinic and hexagonal phase frameworks. Nanjundaswamy et al. [7] reported that although both phases provide a similar flat electrochemical profile, greater capacity fading was observed for the material with the monoclinic framework. Thus, our study was focused on the hexagonal type. A thermal study suggested that iron sulfate decomposes at temperatures above  $600^\circ\text{C}$ , while a Co based layer type  $\text{LiCoO}_2$  cathode and a spinel type  $\text{LiMn}_2\text{O}_4$  cathode decomposes and releases oxygen at  $250^\circ\text{C}$ , indicating that iron sulfate exhibits excellent stability at high temperature [1]. This is advantageous in terms of preventing the undesired heat release that might occur as a result of oxygen loss, even in an overcharged condition. However, there are still several technical problems, including low conductivity and the unavailability of lithium in the compound, with regard to using an iron sulfate cathode.

Carbon treatment has been used as an effective method for obtaining better electrochemical performance from active materials, namely, longer cyclability and a larger capacity. In particular, the existence of conductive carbon between the particles of an active material is favorable in terms of the electrochemical reaction because it enhances the electron transport [8]. Moreover, the conductive carbon that is present on the surface of an active material also protects the active material from direct contact with the electrolyte [8], thus avoiding any undesired surface degradation that might lead to poor cyclability. We studied a method of improving the electrochemical properties (capacity and cyclability) of NASICON-type iron sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) by applying two kinds of carbon treatment; the conventional carbon treatment (CCT) and the polymer modified carbon treatment (PMCT). The former was carried out with a dry ball mill to obtain a homogeneous mixture of active material and conductive carbon, while the latter was carried out with the addition of a polymer as a carbon source into a mixture of conductive carbon and active material, followed by heat treatment.

## 2. Experimental

### 2.1. Synthesis and characterization of NASICON type $\text{Fe}_2(\text{SO}_4)_3$

$\text{Fe}_2(\text{SO}_4)_3$  with a hexagonal framework was synthesized by thermal decomposition of ferrous ammonium sulfate hexahydrate

$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Kanto Chemical Co., Inc.) in air at  $500^\circ\text{C}$  for 10 h, as reported elsewhere [6,7]. The resulting powder was vacuum treated for at least 12 h before being stored in a dry room with a constant dew point of  $-50^\circ\text{C}$ . The structure of the obtained powder was characterized with an X-ray diffractometer (Rigaku, RINT2000), using  $\text{CuK}\alpha$  radiation under a constant power of 30 kV and 100 mA. The structural phases of the synthesized powder were identified using the database of the International Center for Diffraction Data (ICDD). Moreover, to estimate the ratio of carbon to active material, the elemental composition was analyzed using the following three methods; inductively coupled plasma combined with atomic emission spectroscopy (ICP/AES, Shimadzu Instrument, ICPS-8000) for Fe and S analysis, a flame spectrophotometer (Varian Spectra, SpectrAA-55) for Li analysis, and an infrared combustion analyzer (Horiba, EMIA-800) for C analysis. The particle morphology was observed using a field emission scanning electron microscopy (JEOL JSM-890). The sample was prepared by spreading the particle in the double-side carbon tape.

### 2.2. Carbon treatment

#### 2.2.1. Conventional carbon treatment (CCT)

Generally, during electrode preparation, active material is mixed with a conductive carbon such as acetylene black (AB), in order to assist the electron transfer between the particles. When we employed a conventional mixing method to mix the conductive carbon AB and active material iron sulfate by grinding, the capacity was only  $55 \text{ mA h g}^{-1}$  (about 60% of its theoretical value). We assumed that this low capacity was because the active material iron sulfate and conductive carbon were insufficiently mixed. We studied two factors that were considered important in creating a uniform mixture of conductive carbon and active material iron sulfate, namely the type of conductive carbon and the mixing method.

First, we studied four types of conductive carbon; carbon nanotubes of C60 (CNT), maxsorb 3100 (Max), denka black (widely known in battery research as acetylene black (AB)), and ketjen black EC-600JD (KB), as given in Table 1. All the conductive carbons were pre-vacuumed for at least 12 h. The mixture of active material ( $\text{Fe}_2(\text{SO}_4)_3$  powder) to conductive carbon weight ratio was kept constant at 70:25. In the next step, we studied the effects of different mixing methods, namely grinding, mixing, and ball milling. The last evaluation involved in optimizing the ball mill conditions; i.e. rotation speed and mixing time.

After ball milling, the mixture of conductive carbon and the active material were sieved and stored in a dry room (dew point =  $-50^\circ\text{C}$ ). This mixture was then subjected to a vacuum for at least 12 h before binder was added in preparing pellet electrode for electrochemical evaluation.

#### 2.2.2. Polymer modified carbon treatment (PMCT)

In this study, additional polymer was mixed together with conductive carbon KB and active material of iron sulfate through ball mill. The mixture was then heat treated to carbonize the polymer. The ball mill condition was the optimized one described in

**Table 1**  
Conducting carbon and the 5th discharge capacity for iron sulfate  $\text{Fe}_2(\text{SO}_4)_3$  with CCT.

Category	Product name	Abbr.	SSA ( $\text{m}^2 \text{ g}^{-1}$ )	Average particle size ( $\mu\text{m}$ )	5th capacity ( $\text{mA h g}^{-1}$ )	Manufacturer
Carbon black	Ketjen black EC-600JD	KB	1270	0.03	117	Lion. Corp.
	Denka black	AB	68	0.03–0.04	104	Denki Kagaku Kogyo
Carbon nanotube	CNT-MTR	CNT	441	1.34	78	Material Technology Research (MTR), Ltd.
Alkaline activated carbon	Maxsorb 3100	Max.	3100	57	9	Kansai Coke and Chemicals

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