

## LITHIUM INSERTION INTO $\text{Fe}_2(\text{SO}_4)_3$ FRAMEWORKS

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### Summary

The two polymorphs of  $\text{Fe}_2(\text{SO}_4)_3$  consist of framework structures built up of tetrahedra sharing corners with octahedra and *vice versa*. One is rhombohedral, the other is monoclinic. Two moles of lithium insert rapidly into both structures at room temperature. However, lithium insertion into the rhombohedral phase is topotactic without any change of symmetry of the framework, whereas the monoclinic modification is converted to an orthorhombic  $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$  phase via a displacement transition; the existence of a two-phase region between  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$  results in a flat OCV of 3.6 V *versus* lithium, which is 600 mV higher than is found for  $\text{Li}_x\text{Fe}_2(\text{WO}_4)_3$  or  $\text{Li}_x\text{Fe}_2(\text{MoO}_4)_3$ . This difference is discussed in terms of the influence of the counter cation on the solid-state  $\text{Fe}^{3+/2+}$  redox couple.

### Introduction

Several oxides of general formula  $\text{A}_n\text{M}_2(\text{XO}_4)_3$  crystallize with  $\text{M}_2(\text{XO}_4)_3$  frameworks consisting of  $\text{XO}_4$  tetrahedra sharing all four corners with  $\text{MO}_6$  octahedra, and  $\text{MO}_6$  octahedra sharing their corners with  $\text{XO}_4$  tetrahedra. The character of the interstitial space of a framework depends upon the space-group symmetry of the framework. Conversely, the occupancy of the interstitial sites by A cations, and the size of the A cation, influence the symmetry of a framework. For example, the cubic garnet structure contains three dodecahedral sites per framework formula unit, and all are occupied, as in  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$  [1]. On the other hand, a change of the framework from cubic to rhombohedral ( $\text{R}\bar{3}\text{c}$ ) symmetry creates two distinguishable octahedral interstitial sites in the ratio 1:3 to give a total of four per framework formula unit (Fig. 1) [2, 3]. Moreover, these two types of interstitial sites are interconnected by six-sided interfaces and their occupancy is variable, so they exhibit interesting A-cation mobilities. In the NASICON system  $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$ , for example, the  $\text{Na}^+$ -ion occupancy varies over the complete range  $0 \leq x \leq 1$ , and an important  $\text{Na}^+$ -ion conductivity occurs over much of this range [3].

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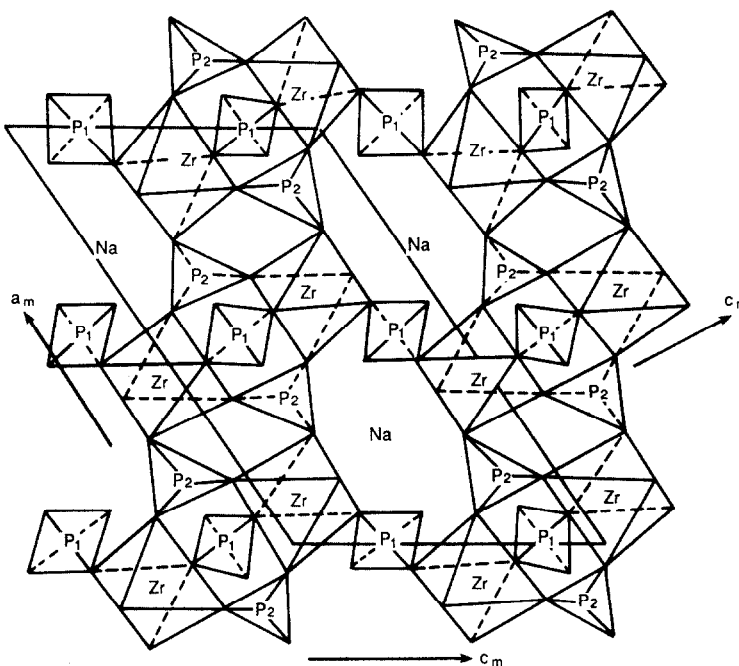


Fig. 1. Structure of rhombohedral  $\text{NaZr}_2(\text{PO}_4)_3$  showing framework built up by linking  $\text{PO}_4$  and  $\text{ZrO}_6$  groups (after ref. 2).

A few  $\text{M}_2(\text{XO}_4)_3$  frameworks are stable in the total absence of A-cations; these include the molybdates and tungstates of the smaller trivalent ions as well as sulfates of trivalent V, Cr and Fe [4 - 6]. These empty frameworks crystallize in two different structural types; one is the rhombohedral ( $R\bar{3}c$ ) framework of Fig. 1 and the other is an orthorhombic ( $Pnca$  or  $Pbcn$ ) structure that, on cooling, undergoes a ferroelastic transformation to the monoclinic ( $P2_1/a$ ) form of Fig. 2. The displacive phase transition commonly occurs above room temperature. All the sulfates adopt the rhombohedral structure; all the molybdates and tungstates adopt the monoclinic/orthorhombic structure. Only  $\text{Fe}_2(\text{SO}_4)_3$  is known to crystallize in both modifications, rhombohedral and monoclinic, at room temperature.

The availability of a framework that not only supports fast  $\text{Li}^+$ -ion and  $\text{Na}^+$ -ion conductivity, but also contains transition-metal ions having an accessible redox potential has invited exploration of these materials as candidate electrodes for secondary batteries [6 - 8]. Initial investigations have used lithium as the insertion species.

The monoclinic ( $P2_1/a$ ) frameworks  $\text{Fe}_2(\text{XO}_4)_3$  with  $\text{X} = \text{Mo}$  or  $\text{W}$  transform on lithiation to orthorhombic ( $Pbcn$ )  $\text{Li}_{2-\delta}\text{Fe}_2(\text{XO}_4)_3$  structures containing  $\text{Li}^+$  ions in distorted tetrahedral sites formed by the edges of two  $\text{FeO}_6$  octahedra [9]. The lithium may be inserted at room temperature either chemically or electrochemically, and a constant open-circuit voltage (OCV) versus lithium content,  $x$ , of an  $\text{Li}/\text{Li}_x\text{Fe}_2(\text{XO}_4)_3$  cell over most of the com-

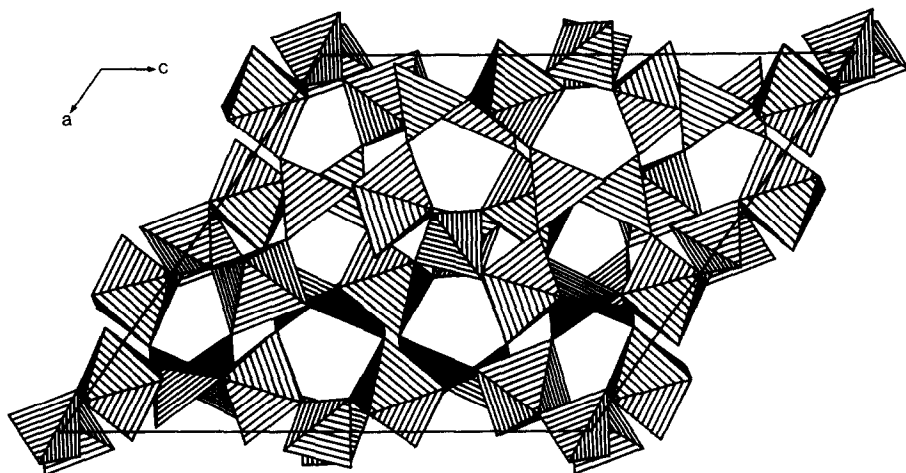


Fig. 2. Structure of monoclinic  $\text{Fe}_2(\text{XO}_4)_3$  ( $\text{X} = \text{Mo}, \text{W}$  or  $\text{S}$ ) drawn with STRUPLO program (ref. 12).

positional range  $0 \leq x \leq 2$  indicates that there is little solid solution between the two end members ( $\delta$  is a small fraction).

In this paper we present a comparison of the electrochemical data of  $\text{Li}_x\text{Fe}_2(\text{XO}_4)_3$  compounds having  $\text{X} = \text{Mo}$  versus  $\text{W}$  with those for the two modifications of  $\text{Li}_x\text{Fe}_2(\text{SO}_4)_3$ .

## Experimental

Monoclinic  $\text{Fe}_2(\text{SO}_4)_3$  was obtained [10] by refluxing  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  with concentrated sulfuric acid for about 4 h. The  $\text{SO}_2$  formed during the reaction was vented to a hood. The pale-pink precipitate formed was filtered, washed successively with sulfuric acid and acetone, and finally air-dried. Rhombohedral  $\text{Fe}_2(\text{SO}_4)_3$  was obtained by heating  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  at  $200^\circ\text{C}$  for 15 h [11]. Formation of the monoclinic and rhombohedral forms was confirmed by X-ray powder diffraction.

Chemical insertion of lithium into  $\text{Fe}_2(\text{SO}_4)_3$  frameworks was carried out by reaction with a calculated amount of *n*-butyllithium (Aldrich, 1.6 M solution) diluted with dry *n*-hexane. The reaction was carried out in a Schlenk flask under dry nitrogen at ambient temperature by continuously stirring with a magnetic stirrer for several days. The product was washed several times with *n*-hexane and dried under vacuum. The lithium content in the reaction product was estimated by atomic absorption spectroscopy.

Electrochemical insertion of lithium into  $\text{Fe}_2(\text{SO}_4)_3$  was studied with a cell  $\text{Li}/1 \text{ M LiBF}_4$  in propylene carbonate/ $\text{Li}_x\text{Fe}_2(\text{SO}_4)_3$  + graphite at a current density of  $15 \mu\text{A cm}^{-2}$ . Since ferric sulfate is a poor electronic conductor, 25% (by weight) graphite was mixed with the  $\text{Fe}_2(\text{SO}_4)_3$  to im-

prove the conductivity of the cathode. Cell voltages were allowed to equilibrate for from several hours to a few days in order to obtain a constant reading for open-circuit voltage.

## Results and discussion

Color changes indicate that both the modifications of  $\text{Fe}_2(\text{SO}_4)_3$  undergo rapid insertion of lithium from *n*-butyllithium. The color changes from pink at  $x = 0.0$  to brown at  $x = 2.0$ . X-ray diffraction of the reaction products indicated that the lithium insertion into the monoclinic  $\text{Fe}_2(\text{SO}_4)_3$  proceeds by a two-phase mechanism. Products with  $0 < x < 2.0$  showed diffraction peaks due to  $x = 0.0$  and  $x = 2.0$  phases. The two-phase character was also indicated by a constant open-circuit-voltage (OCV) for  $0 \leq x \leq 2.0$  (Fig. 3). The lithiated samples showed relatively broad diffraction patterns due to poor crystallinity; consequently calculation of precise lattice parameters was difficult.  $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$  appears to have an orthorhombic structure similar to that found in  $\text{Li}_2\text{Fe}_2(\text{XO}_4)_3$  ( $X = \text{Mo}$  or  $\text{W}$ ) [6].

By contrast, the open-circuit voltage for rhombohedral  $\text{Li}_x\text{Fe}_2(\text{SO}_4)_3$  decreases almost linearly with  $x$  over most of the compositional range  $0 \leq x \leq 2.0$  (Fig. 3). This indicates that the lithium insertion into the rhombohedral form proceeds by a single-phase mechanism. This conclusion was further supported by the X-ray diffraction of the lithiated products.

Reaction of  $\text{Fe}_2(\text{SO}_4)_3$  with a large excess of *n*-butyllithium causes breakage of the lattice, similar to that found in  $\text{Fe}_2(\text{XO}_4)_3$  ( $X = \text{Mo}$  or  $\text{W}$ ) [6]; for example, reaction with 8 moles of *n*-butyllithium gives amorphous phases, presumably iron metal and  $\text{Li}_2\text{SO}_4$ .

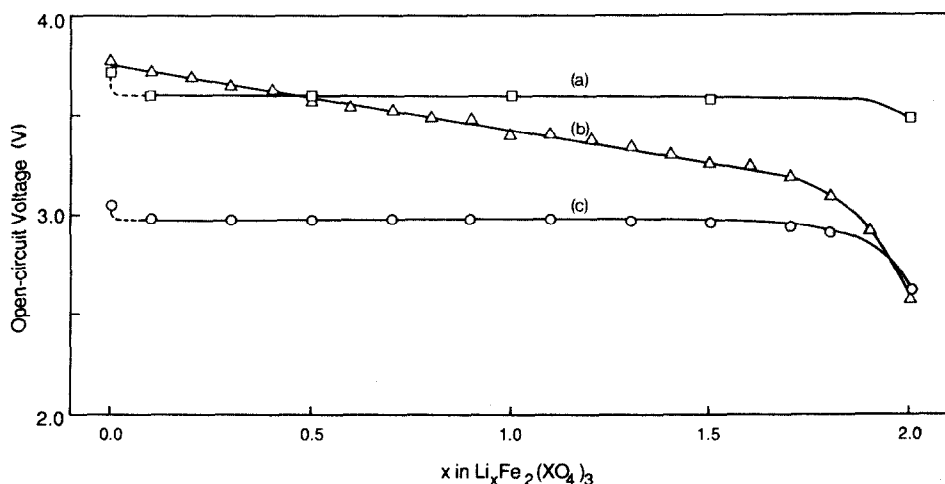


Fig. 3. Open-circuit voltage vs. lithium content in (a) monoclinic  $\text{Fe}_2(\text{SO}_4)_3$ ; (b) rhombohedral  $\text{Fe}_2(\text{SO}_4)_3$ ; (c) monoclinic  $\text{Fe}_2(\text{WO}_4)_3$ .

The plots of OCV *versus*  $x$  for both forms of  $\text{Fe}_2(\text{SO}_4)_3$  are also compared in Fig. 3 with that for  $\text{Fe}_2(\text{WO}_4)_3$ . Two features of these data deserve special emphasis: (i) both modifications of  $\text{Fe}_2(\text{SO}_4)_3$  have nearly the same OCV; (ii) the OCV for the monoclinic/orthorhombic  $\text{Li}_x\text{Fe}_2(\text{SO}_4)_3$  system is about 600 mV higher than that for the  $\text{Li}_x\text{Fe}_2(\text{WO}_4)_3$  system (and also the  $\text{Li}_x\text{Fe}_2(\text{MoO}_4)_3$  system, not shown). The first feature reveals that the OCV is not influenced significantly by symmetry changes of the framework. The second feature shows a remarkable sensitivity of the energy of the  $\text{Fe}^{3+/2+}$  redox couple to the character of the counter cation.

The 600 mV difference in the OCV of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Fe}_2(\text{WO}_4)_3$ , or  $\text{Fe}_2(\text{MoO}_4)_3$ , reflects a 0.6 eV difference in the position of the  $\text{Fe}^{3+/2+}$  redox couple since lithiation involves charge compensation of an inserted  $\text{Li}^+$  ion by reduction of an  $\text{Fe}^{3+}$  ion to  $\text{Fe}^{2+}$ . The difference in the position of the  $\text{Fe}^{3+/2+}$  redox couple in two isostructural compounds of identical formal valence and similar lattice parameters can only reflect a difference in the Fe-O  $\pi$ -bond covalent mixing since the minority-spin electron of a high-spin, octahedral-site  $\text{Fe}^{2+}:t_2^4e^2$  configuration occupies an antibonding  $t_2$  orbital that only mixes with the nearest-neighbor O-2p $_{\pi}$  orbitals. Covalent mixing introduces a quantum-mechanical repulsion between the bonding and antibonding orbitals, which raises the energy of the minority-spin  $t_2$  orbital and, hence, the energy of the  $\text{Fe}^{3+/2+}$  redox couple. The stronger the  $\pi$ -bond Fe-O covalence, the higher the energy of the  $\text{Fe}^{3+/2+}$  couple and, hence, the lower the OCV.

The counter cation, which shares a common oxygen nearest neighbor with Fe in an Fe-O-X linkage (X = Mo, W, or S), determines the strength of the Fe-O covalency via the inductive effect. The stronger the X-O bonding, the weaker is the Fe-O bonding and, hence, the larger the OCV. That the covalent bonding within an  $(\text{SO}_4)^{2-}$  complex should be stronger than that in a  $(\text{WO}_4)^{2-}$  or  $(\text{MoO}_4)^{2-}$  complex is not surprising; that the difference in the covalent-bond strength should be great enough to shift the  $\text{Fe}^{3+/2+}$  redox couple by 0.6 eV must be of interest to anyone concerned with tailoring the position of a solid-state redox potential via the choice of a counter cation of the solid.

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