

# Cathode performance and voltage estimation of metal trihalides

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## Abstract

Compounds with highly ionic metal-ligand bonds are attractive for use as high voltage cathodes. Therefore, we investigated metal trihalide cathodes, in particular trifluorides ( $\text{MF}_3$ ).  $\text{FeF}_3$  shows a mean discharge voltage and quasi open-circuit voltage (QOCV) of 3.0 and 3.4 V, respectively. X-ray analysis shows that the lithiation reaction proceeds in a topotactic manner.  $\text{TiF}_3$  and  $\text{VF}_3$  have mean discharge voltages of 2.5 and 2.2 V, respectively. These three compounds have the same layer structures and almost the same rechargeable capacity of  $80 \text{ mAh g}^{-1}$ .  $\text{MnF}_3$ , which has a monoclinic lattice, exhibits an initial voltage of 4.2 V, however, lithiation does not proceed due to a high overvoltage. These high voltages indicate the highly ionic nature of  $\text{MF}_3$  cathodes, and they correspond to values estimated using the standard electrode potentials of the 'naked' ions. © 1997 Elsevier Science S.A.

*Keywords.* Lithium batteries; High voltage cathode; Metal trihalides; Iron trifluoride; Voltage estimation; Standard electrode potential

## 1. Introduction

Numerous studies have been devoted to transition metal oxides and chalcogenides as the cathode materials for lithium batteries. Recently,  $\text{Fe}_2(\text{SO}_4)_3$  [1] and  $\text{Li}_x\text{FePO}_4$  ( $x < 1$ ) [2], which have oxyanions as the ligands, have been reported as reversible cathode materials. Important features of these cathodes are the high discharge voltages of 3.6 and 3.5 V for  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Li}_x\text{FePO}_4$ , respectively. These voltages are higher than that of any other known iron(III) oxide cathode, such as  $\text{Fe}_2\text{O}_3$  [3], and  $\text{LiFe}_5\text{O}_8$  [4]. This can be attributed to the highly ionic bonds between the central metal ions and the oxyanion ligands, in contrast to the covalent bonds in oxides. This implies a possibility of finding new high voltage (hence high energy) cathode materials among highly ionic compounds. On this basis, we report the cathode performance of transition metal compounds with halogen ligands in place of oxygen and oxyanions. We focus particularly on fluorides which are attractive because fluorine has the highest electronegativity and a small atomic weight. Although some dihalides, such as  $\text{CuF}_2$  and  $\text{CuCl}_2$ , were studied in the early days of lithium battery development [5], there have been few reports on metal trihalides [6]. We also discuss the ionic nature of the compounds and the voltage regions of the cathodes.

## 2. Experimental

Reagent grade  $\text{FeF}_3$ ,  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{TiF}_3$ ,  $\text{MnF}_3$  (Soekawa Chemicals),  $\text{VF}_3$  and  $\text{CoF}_3$  (Trichemical Laboratories) were dried in a vacuum at  $90^\circ\text{C}$  prior to use. The cathode mixture was prepared from cathode active material (70 wt.%), acetylene black (25 wt.%, Denki Kagaku) and polytetrafluoroethylene (5 wt.%, Daikin). The electrolyte was a 1 M  $\text{LiPF}_6$  solution in a 1:4 volume ratio mixture of ethylene carbonate and dimethyl carbonate. The anode was metallic lithium. A microporous polypropylene film (Celgard 3501, Celanese) was used as a separator. The cell elements were fabricated into coin-type cells which have been described previously [7]. We tested the cell performance at  $25^\circ\text{C}$  using cell cyclers equipped with a data acquisition system (Hokuto Denko). For the cycle tests, the voltage range was between 2.0 and 4.5 V with a constant-current density of  $0.2 \text{ mA cm}^{-2}$ . To measure the quasi open-circuit potential (QOCV), we carried out an intermittent discharging or charging at  $0.1 \text{ mA cm}^{-2}$  for 6 h, followed by a rest period of 44 h. To determine the structure of lithiated (lithium inserted) and delithiated (lithium extracted) compounds, the cathode samples were discharged and charged at a current density of  $0.1 \text{ mA cm}^{-2}$ , and after a relaxation period of one week, they were analyzed by X-ray diffraction (Rigaku RU-200, RAD-rX) with  $\text{Cu K}\alpha$

radiation. The chemical composition of the compounds were determined from the current passed and the cathode active mass.

### 3. Results and discussion

Fig. 1 shows a discharge–charge curve for  $\text{FeF}_3$ . The voltage gradually decreased during discharging from an initial value of 3.5 V, and the mean discharge voltage was about 3.0 V. During the first discharging, the capacity was about  $140 \text{ mAh g}^{-1}$ , and the following charge capacity was  $90 \text{ mAh g}^{-1}$ . After the first cycle, the  $\text{FeF}_3$  cathode showed a fairly good cycleability with a capacity of about  $80 \text{ mAh g}^{-1}$ .

The QOCVs of  $\text{FeF}_3$  are plotted in Fig. 2, together with a replot of the cycle behavior. Fairly high overvoltages are clearly seen and these are possibly due to low lithium-ion conductivity in  $\text{FeF}_3$ . Although the QOCVs during discharging and charging do not coincide completely, the mean value is about 3.4 V. This is a little lower than that of  $\text{Fe}_2(\text{SO}_4)_3$ , but is still very high for iron(III) cathodes. It can be attributed to the highly ionic character of the metal–ligand bonds in  $\text{FeF}_3$ .

We performed X-ray diffraction analysis to investigate structural changes in the cathode material during discharging and charging.  $\text{Li}_{0.15}\text{FeF}_3$  and  $\text{Li}_{0.50}\text{FeF}_3$  were sampled during the first discharging and they are denoted as (b) and (c), respectively. The delithiated compound was  $\text{Li}_{0.18}\text{FeF}_3$  denoted as (d), which was sampled during the first charging

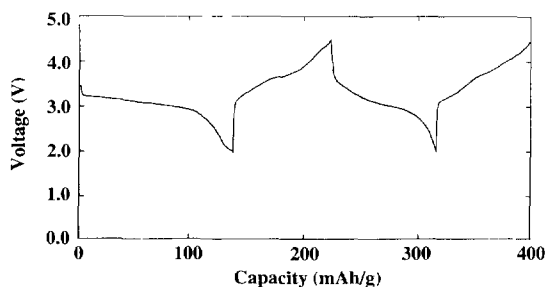


Fig. 1. Discharge–charge curve for  $\text{FeF}_3$  at  $0.2 \text{ mA cm}^{-2}$  between 2.0 and 4.5 V.

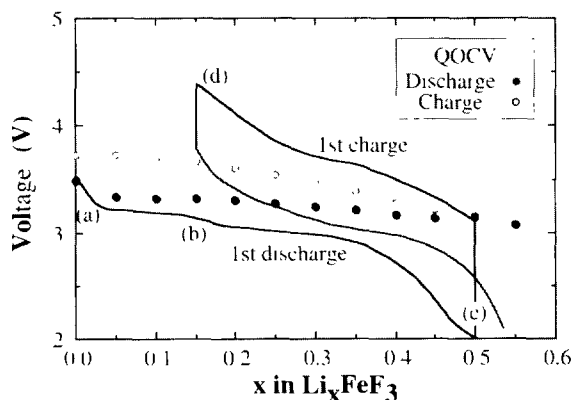


Fig. 2. Quasi open-circuit voltages and cycle curve of  $\text{FeF}_3$ ; (a)–(d) indicate the states where samples for X-ray analysis were taken.

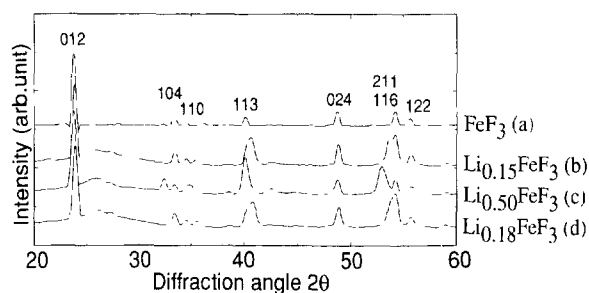


Fig. 3. X-ray diffraction patterns of  $\text{Li}_x\text{FeF}_3$ ; (a)–(d) correspond to the states shown in Fig. 2

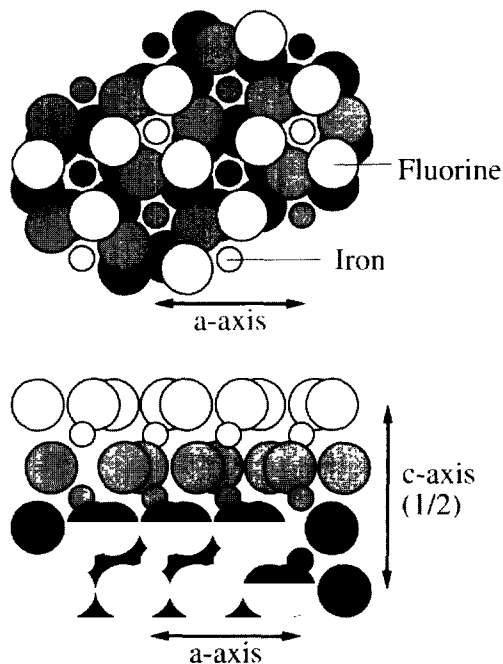


Fig. 4. Projections of hexagonal cells of  $\text{FeF}_3$ .

from  $\text{Li}_{0.50}\text{FeF}_3$ . These correspond to the states marked in Fig. 2. The X-ray patterns of these samples were the same compared with that of  $\text{FeF}_3$  denoted as (a), as shown in Fig. 3. Therefore, the basic  $\text{FeF}_3$  structure is maintained upon lithiation and delithiation. Neither lithium fluoride nor metallic iron was detected. This indicates that the lithiation reaction proceeds in a topotactic manner. The discharge mechanism is obviously different from that of many difluoride cathodes [5] or  $\text{BiF}_3$  [6], which dissolve in the electrolyte on discharging with structural decomposition. When  $\text{FeF}_3$  is reduced, the basic structure is maintained probably because the change of iron ion radius (i.e. ferric to ferrous) is not considerable. This is in contrast to the metal deposition when difluorides or  $\text{BiF}_3$  is reduced.

$\text{FeF}_3$  has a layer structure with a hexagonal unit cell, as shown in Fig. 4. Iron is in the center of an almost regular octahedron of fluorine. Only one third of the fluorine octahedrons are occupied by iron, and the empty octahedrons possibly accommodate the inserted lithium. The lattice parameters of samples (a)–(d) are shown in Fig. 5. During lithium insertion in (a) through (c), the  $a$ -axis and the  $c$ -axis

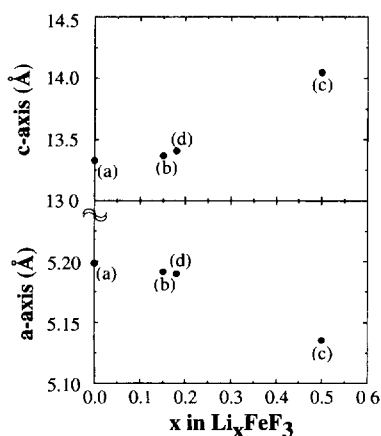


Fig. 5. Lattice parameters of  $\text{Li}_x\text{FeF}_3$ : (a)–(d) correspond to the states shown in Fig. 2.

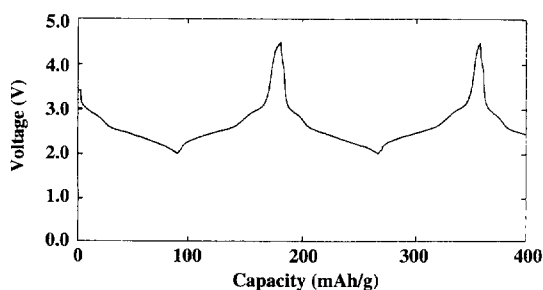


Fig. 6. Discharge/charge curve for  $\text{TiF}_3$  at  $0.2 \text{ mA cm}^{-2}$  between 2.0 and 4.5 V

in the hexagonal cell were found to decrease and increase, respectively. The total volume change was +3% for 0.5 lithium insertion into  $\text{FeF}_3$ . As the lattice parameters at (b) and (d) in Fig. 5 (and the X-ray patterns in Fig. 3) are almost the same, the structural changes seem to proceed in a reversible way.

We examined  $\text{FeCl}_3$  and  $\text{FeBr}_3$  whose structures are the same and are similar to  $\text{FeF}_3$ . However, they dissolved in the electrolyte, and we could not, therefore, observe the cathode performance. Ionic compounds, such as fluorides, are generally more soluble in a polar solvent than in covalent compounds, nevertheless,  $\text{FeF}_3$  can be cycled without dissolution. In the case of fluorides, short ligand-metal bonds may stabilize the solid state, and it results in the low solubility.

The cathode performance of  $\text{FeI}_3$  was not measured because it is unstable due to the strong reducing power of iodine versus ferric ions.

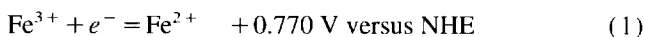
$\text{TiF}_3$  exhibited a mean voltage of 2.5 V and a fairly good rechargeability in the cycle test, as shown in Fig. 6.  $\text{VF}_3$  showed a mean voltage of 2.2 V with a considerable over-voltage. They both have the same structure as  $\text{FeF}_3$ . The three fluorides exhibited almost the same rechargeable capacity of  $80 \text{ mAh g}^{-1}$ . Accordingly, lithium is expected to be inserted at the same site in  $\text{Li}_x\text{MF}_3$  ( $M = \text{Fe}, \text{Ti}, \text{V}$ ), possibly the vacancy in the fluorine layer shown in Fig. 4.

$\text{MnF}_3$  exhibited a high open-circuit voltage (OCV) of 4.2 V. However, lithium insertion did not proceed because of a

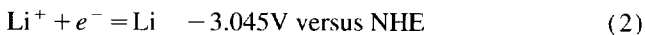
high over-voltage upon discharging.  $\text{MnF}_3$  has a layer structure similar to hexagonal  $\text{FeF}_3$ , however, it is distorted and the unit cell is monoclinic. This is attributed to the Jahn–Teller distortion of low spin Mn(III) whose electric state is  $(t_{2g})^3 (e_g)^1$ . Thus, the small interstitial space due to the distorted lattice may prevent the lithium insertion.

$\text{CoF}_3$  exhibited an initial OCV of 4.5 V. However, it decomposed the electrolyte which was accompanied by the evolution of gas, and the cathode performance was not observed. Because  $\text{CoF}_3$  has the same structure as  $\text{FeF}_3$ , this compound is expected to be rechargeable if we find a stable electrolyte.

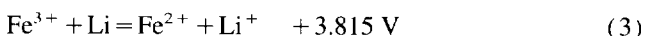
The high voltages of the trifluorides can be attributed to the highly ionic character of the metal–ligand bonds. If we ignore the ligand contribution to the metal electronic state, we can estimate the cathode redox potential using the standard electrode potentials. For example, the redox potential of ‘naked’ iron ion in strong acidic media, which is almost completely ionic, is known [8]



For lithium redox, the potential data is also known



Accordingly, we can estimate the lithium cell voltage with an ionic iron (III) cathode



This value is close to the voltages of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Li}_x\text{FePO}_4$  ( $x < 1$ ), therefore, iron(III) ions in these compounds are almost ionic as in strong acidic media.  $\text{FeF}_3$  has slightly lower voltage; nevertheless, it is still close to the estimated value.

Fig. 7 summarizes the initial OCVs and the mean discharge voltages to 2.0 V of the metal trifluorides discussed above. The values for the horizontal axis are voltages estimated using the differences between the standard electrode potentials of lithium and each ‘naked’ metal (III) ion. This figure shows that the actual voltage ranges of metal trifluorides correspond semi-quantitatively to the estimated voltages. Note that

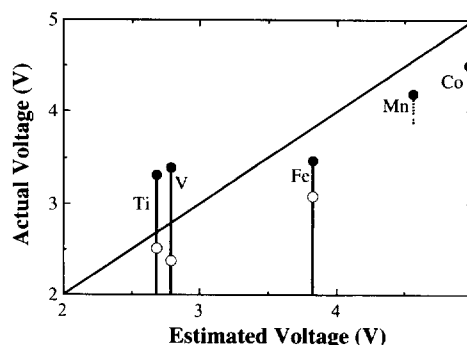


Fig. 7. Actual and estimated voltages of metal trifluorides  $\text{MF}_3$ . The metal elements M are shown in the figure. Black and white circles correspond to the initial and mean voltages upon discharging to 2.0 V, respectively

Co(III) in  $\text{CoF}_3$  and Mn(III) in  $\text{MnF}_3$  show voltages comparable to those of Co(IV) in  $\text{Li}_x\text{CoO}_2$  [9] and Mn(IV) in  $\text{Li}_x\text{Mn}_2\text{O}_4$  [10], respectively. This indicates that the oxygen ligand reduces the metal cation by about a single charge.

In this way, we can associate the voltage differences between cathodes having metal ions in the same environment with differences in the standard electrode potentials, even if they are not completely ionic. The method is very simple; nevertheless, it can be used as a criterion for estimating cathode voltages.

#### 4. Conclusions

$\text{FeF}_3$  shows a mean discharge voltage and a QOCV of 3.0 and 3.4 V, respectively. The lithiation reaction proceeds in a topotactic manner.  $\text{TiF}_3$  and  $\text{VF}_3$  exhibit a mean discharge voltage of 2.5 and 2.2 V, respectively. These three compounds have the same layer structures and almost the same rechargeable capacity of  $80 \text{ mAh g}^{-1}$ .  $\text{MnF}_3$  with a monoclinic lattice shows an initial voltage of 4.2 V, however, lithiation does not proceed due to a high overvoltage. These high voltages indicate the highly ionic nature of  $\text{MF}_3$  cathodes, and they correspond to the values estimated using the standard electrode potentials of the 'naked' ions.

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