



Reaching the full capacity of the electrode material Li_3FeF_6 by decreasing the particle size to nanoscale

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ABSTRACT

An easy scalable reaction is used to prepare nanometric particles of the cryolite Li_3FeF_6 by precipitation below room temperature. Precipitation of Li_3FeF_6 in water:2-propanol ratio of 1:3 at 0 °C from a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $6\text{HF}_{(\text{aq})}$ and Li_2CO_3 , produces the smallest particles (ca. 20 nm). These particles are agglomerated building up spherical “raspberry-shaped” motifs having ca. 200 nm diameter. Interestingly, processing of as prepared Li_3FeF_6 using mechanical milling with carbon affects the size of agglomerates and its morphology, while the size of elemental nanometric particles is kept. Furthermore, mechanical milling has a beneficial effect on the electrochemical Li insertion and Li cells bearing Li_3FeF_6 as cathode deliver the theoretical full capacity (140 mAh g^{-1}). The improvement of electrochemical performances is related to the more intimate mixing of Li_3FeF_6 and carbon black in the electrode due to the breakage of the “raspberry-shaped” agglomerates upon ball milling. A different result is obtained when Li_3FeF_6 is prepared from pure aqueous solution without addition of alcohol. Isolated submicrometric prismatic particles having an average size of 300 nm are obtained. These release only a 70% of theoretical electrochemical capacity in Li cells after mechanical milling.

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1. Introduction

In the very next future electrical vehicles are going to reach the markets at a significant scale. If the scale of manufacturing was comparable to present vehicle industry, availability and prices of natural resources ores will be a serious limitation for the implementation of the new technology. A great demand of lithium battery materials and competitive prices can only be matched if non toxic and abundant metals are used to produce both negative and positive electrodes. It is then clear that Fe-based electrodes, as for example LiFePO_4 , will remain in the state-of-the art even in the large scale stage of the emerging EV technologies.

On the other hand, increase of energy of present batteries can only be achieved by using cathodes with higher redox potential. In this connection fluorides are an interesting alternative. Note that the high ionicity of the M–F bond produces a high redox potential of the respective transition metal [1]. Therefore, the operating voltage of batteries using fluorides as the cathode is expected to be higher than in homologous oxides for the same metal redox couple. In fact high specific energies have been already reported for several binary

metal fluorides [2]. On the other hand, some ternary fluorides have been investigated as cathodes for sodium batteries [3,4].

The high ionic nature of the M–F bond is clearly advantageous to produce high energy cathode materials, but one of the drawbacks is that most of them are insulators. This problem has been overcome at present for other cathode materials. Note that the commercialized LiFePO_4 electrode also suffers from poor electronic conductivity and slow kinetics of Li intercalation, which limit the electrochemical performances of Li cells under constant current conditions. Several authors have proved that some of the paths followed to overcome the limitations encountered for LiFePO_4 can be effectively applied with success to fluorides [3–6]. Therefore, it is obvious that fluorides, and in particular iron fluorides, may be extremely interesting candidates to cathodes.

Synthesis procedures are key factors to be investigated and optimized concerning production costs. Electrode materials are typically prepared by heating precursors (nitrates, oxides, carbonates, oxalates, etc.) containing the electroactive metals at high temperature. This mandatory step is needed to decompose the precursors at a minimum temperature depending on the nature of precursor. This already expensive step is just the beginning of the production as the material needs to be processed afterwards to fabricate an electrode with an optimum blend of active material, binder, black carbon, additives, etc.

In this connection, we have recently reported on the electrochemical lithium insertion properties of new potential positive

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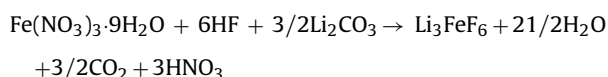
electrode materials in the Li-Fe-F system: the α - and β -polymorph of cryolite-like Li_3FeF_6 [7,8]. The main result of that work was that mechanical milling with carbon to enhance electronic conductivity of the composite and to reduce particle size of the fluoride to the nanoscale yielded quite similar electrochemical performances (capacity and capacity loss upon cycling) of both polymorphs when used as the cathode in Li batteries. However, α - Li_3FeF_6 was presented as an advantageous material, in as much as it can be prepared by precipitation from aqueous solution at 25 °C. Therefore, the synthesis procedure at room temperature may have a beneficial impact on the total cost of electrode production. Particles with sizes ranging from 250 to 400 nm (and larger but always submicrometric), were obtained following the reported precipitation route [7]. Though the synthesis procedure is easily scalable, an additional milling process with carbon is necessary after the precipitation step. Particle size was reduced to ca. 50 nm after milling α - Li_3FeF_6 with carbon for 12 h, and up to a 70% of theoretical quantity of lithium could be inserted accompanied by the partial reduction of Fe^{3+} to Fe^{2+} . A modified method to Li_3FeF_6 involving precipitation with ethanol has been recently described [9]. However, in that work no further details were given whether the synthesis conditions used by the authors produced nanocrystals suitable for lithium insertion without further need of reduction of particle size by long milling, coated with carbon, etc.

In this work we have studied the influence that the precipitation conditions have on both particle size and morphology of as-prepared α - Li_3FeF_6 . Water soluble alcohols with different polarities have been used to modify the solvent media. In particular three different variables of the precipitation conditions have been analysed; nature of alcohol, reaction temperature and $\text{H}_2\text{O}:\text{R}:\text{OH}$ ratio. The best results regarding electrochemical performances are achieved with 2-propanol and the corresponding results are herein presented. We further report on the influence that precipitation temperature and water:2-propanol ratio has on particle size, morphology and electrochemical performances of Li_3FeF_6 .

2. Experimental methods

2.1. Preparation

The synthetic route used to obtain the α -polymorph of Li_3FeF_6 [7], follows a precipitation reaction in aqueous solution and is characterized by the chemical equation:



However, in the present work we have modified the precipitation conditions by using 2-propanol to precipitate the fluoride on the instant, and the results are compared with those obtained for the same compound precipitated by just concentrating the water solution.

The complete procedure can then be summarized as follows. The stoichiometric quantity of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in distilled water (typically 25 mL) was mixed with the stoichiometric quantity of an aqueous HF solution (40%). After adding Li_2CO_3 (stoichiometric amount) a transparent solution was obtained. This solution was then held at constant temperature (0 °C, 25 °C or 60 °C). The fluoride was precipitated by adding different quantities of 2-propanol (25 mL, 50 mL or 75 mL) to the ca. 25 mL solution containing the solved fluoride. Though precipitation of a white powder started immediately, the solution was stirred for 5 min to promote multiple nucleation. The obtained powder was centrifuged, washed twice with small portions of 2-propanol and finally dried at 60 °C overnight in a drying oven.

For reasons of comparison precipitation was also performed from aqueous solution, without adding 2-propanol, following the procedure previously described [7]. For that the aqueous solution was heated and concentrated at 60 °C, until precipitation of the fluoride was achieved. The solid was separated by centrifugation and the as obtained powder was dried at 80 °C.

2.2. Structural and chemical characterization

Preliminary structural characterization of powders was made by powder X-ray diffraction using a X'Pert PRO PANalytical diffractometer, operated at 45 kV and 40 mA, equipped with a hybrid monochromator, working with $\text{CuK}\alpha_1$ ($\lambda = 1.54056 \text{ \AA}$) radiation and a Bruker AXS' LynxEye detector. However, as the quality of X-ray patterns was strongly affected by X-ray fluorescence of iron, a more detailed structural characterization was done with a Philips X'PERT-PRO diffractometer, operated at 50 kV and 45 mA, using monochromatic $\text{MoK}\alpha_{1,2}$ ($\lambda = 0.71073 \text{ \AA}$). This apparatus was equipped with a graphite monochromator and a PW1964 scintillation point detector. The selected 2θ angular range was 4–50° with a 0.04°/10 s scan rate operated in continuous scan mode. Diffraction patterns were analyzed by the Rietveld method [10] using the FullProf program [11].

Morphological characterization has been carried out by means of Transmission Electron Microscopy (JEOL 2000FX) and Scanning Electron Microscopy (JEOL JSM-6335F and JEOL JSM-6400).

On the other hand, samples have been also characterized by thermal analysis to obtain information concerning stability of products and the effect that solvent can have on the Li insertion reaction. For this a TGA/DTA Netzsch STA 409 apparatus was used. Samples were heated at 10 K min^{-1} up to 600 °C under flowing nitrogen. XRD patterns were recorded after thermal treatment.

2.3. Mechanical milling

The as obtained products and conductive carbon were ground by using a planetary-type Pulverisette 7 ball mill (Fritsch GmbH, Germany) in order to obtain a carbon–metal fluoride nanocomposite (CMFNCs). The following conditions were used for different dry milling times ranging from 1 to 24 h in air: sample weight: 1 g; grinding media: 2 balls with 10 mm diameter each; milling media and chamber material: zirconium dioxide; volume of grinding chamber: 20 mL; mill speed: 500 rpm.

2.4. Fabrication of electrode and electrochemical characterization

Electrochemical reactions involving lithium insertion and deinsertion were performed in CR2032 coin cells. Lithium foil was used as the negative electrode, whereas the positive electrode was conformed as pellets by pressing the powdery samples (manually ground with carbon) obtained after precipitation or after mechanical milling. In all cases the electrode components were Li_3FeF_6 , carbon black and a binder (PTFE) in a 72:25:3 weight ratio. A 1 M LiPF_6 solution in EC:DMC (1:1) was used as the electrolyte (commercial battery electrolyte LP30). Cells were run using a MacPile II system. The electrochemical behaviour of Li_3FeF_6 composites were tested in galvanostatic mode, using a current density of 0.1 mA cm^{-2} .

3. Results and discussion

The morphology of α - Li_3FeF_6 obtained from water based solution is very different from that obtained with 2-propanol based solutions. Precipitation from aqueous solution at 60 °C yields prismatic crystals with a rather non homogeneous particle size distribution. Crystal sizes extend from ca. 250 nm to rather large

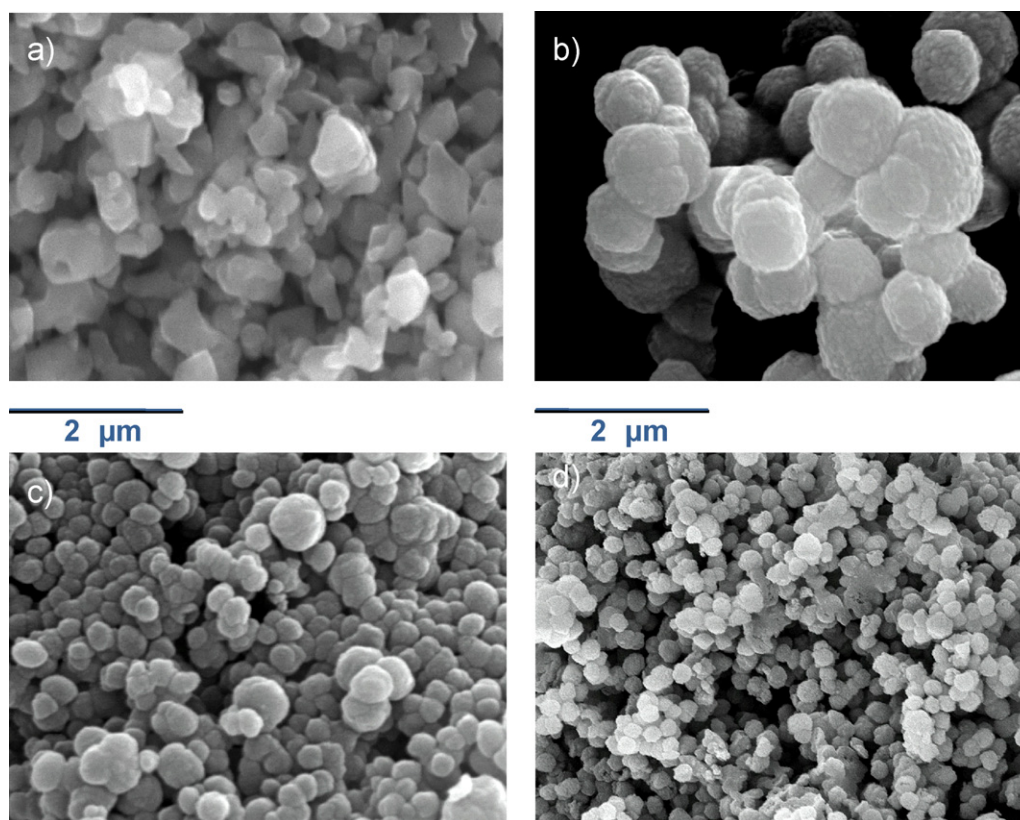


Fig. 1. SEM images of Li_3FeF_6 precipitated from water at 60 °C (a) and from a w:2p = 1:3 mixture at different temperatures: 60 °C (b), 25 °C (c) and 0 °C (d).

700 nm, as it can be seen in the SEM micrograph shown in Fig. 1a. The following comparison to nanocrystals obtained by precipitation using 2-propanol based solution (Fig. 1b–d) is very illustrative. The series of SEM micrographs shown in Fig. 1b–d correspond to crystals in which a water:2-propanol volume ratio (w:2p ratio hereafter) of 1:3 was used to precipitate the fluoride at different temperatures. The results obtained by precipitation at 60 °C show the effect of adding 2-propanol (Fig. 1b) to form a less polar precipitating media. While prismatic particles with sharp edges are obtained in aqueous solution (tallying with a 100:0 w:2p ratio), spherical particles are yielded when changing precipitation conditions to a 1:3 w:2p ratio. The size of these spherical particles is dependent on temperature, as it is clearly deduced from Fig. 1b–d, which correspond to precipitations at 60, 25 and 0 °C, respectively. These figures evidence that the lower the temperature, the smaller the size of the spherical particles. Note that at 60 °C these particles are as large as 1000 nm, while particles with homogeneous size of ca. 200 nm are obtained at 0 °C. It is then clear that the use of solutions based on water and 2-propanol instead of pure water and the concomitant change of precipitation media allows for the preparation of submicrometric particles. We have further used other either completely or only partially water soluble alcohols to investigate the influence they have on the precipitation reaction. As a conclusion the smallest spherical-like particles are obtained by using 2-propanol.

Besides temperature, the w:2p ratio has also an influence on the size of the spheres. The morphology and size of $\alpha\text{-Li}_3\text{FeF}_6$ particles obtained by precipitation at 25 °C in 1:1, 1:2 and 1:3 w:2p ratios are presented in Fig. 2. The solvent effect on particle size is evident by going from the first (Fig. 2a), where water is an abundant component of the solvent mixture, to the two latter (Fig. 2c), where 2-propanol is more abundant. It seems that formation of smaller

sized particles is favoured when using solvent mixtures having high content of alcohol.

In view of these findings we have focused on samples that have been prepared by precipitation in solution containing mainly 2-propanol and precipitated at 0 °C. Herein, we present the main results obtained by using a 1:3 (w:2p) solution as precipitating media and the comparison with previous results reported for $\alpha\text{-Li}_3\text{FeF}_6$ prepared by precipitation in water [7].

A more detailed microscopy analysis of the spheres obtained using the herein presented procedure reveals more interesting features. They seem to be composed of agglomeration of much smaller particles within the nanoscale (<100 nm), as it can be seen in Fig. 3. This micrograph corresponds to two images of the sample shown in Fig. 1d but obtained at larger magnification. The spherical particles have a peculiar morphology. Firstly, they are open on one side and they seem to be hollow as if some gas release was involved during formation. Secondly, the way in which the smallest constituent particle agglomerates gives rise to a raspberry-type shape.

Interestingly, the size of the smallest constituent is ca. 20 nm which is small enough to avoid kinetics limitations due to lithium diffusion through many unit cells. Our previous results indicate that particles size has to be reduced below 50 nm and highly homogenized with carbon by ball milling to get an intercalated lithium amount corresponding to 100% of theoretical capacity [7]. The herein presented material is already composed by such required small particles, though the observed agglomeration may also inhibit intercalation in the same way a large single crystal does.

Having in mind that the intercalation rate and therefore, the performance as electrode material in a lithium battery are strongly dependant on particle size of active material, we have considered very relevant the study of the electrochemical behaviour. In this connection, we have tried to disaggregate the 20 nm particles from

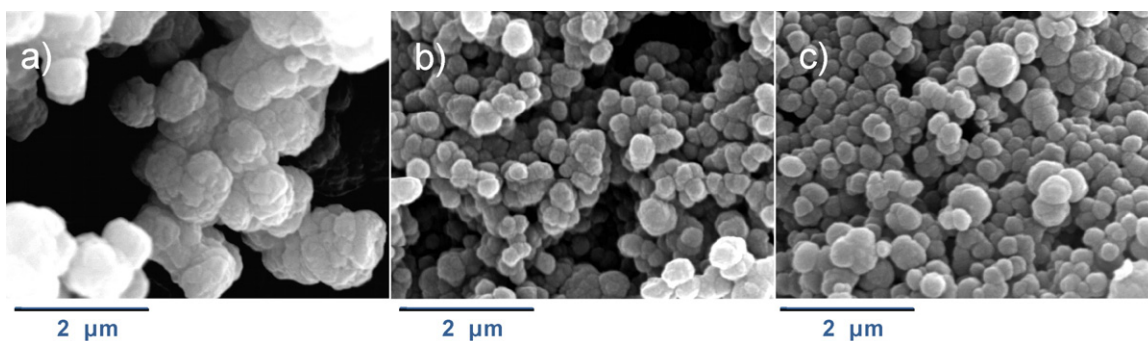


Fig. 2. SEM micrographs of Li_3FeF_6 precipitated at 25 °C using several w:2p solvent mixtures: 1:1 (a), 1:2 (b) and 1:3 (c).

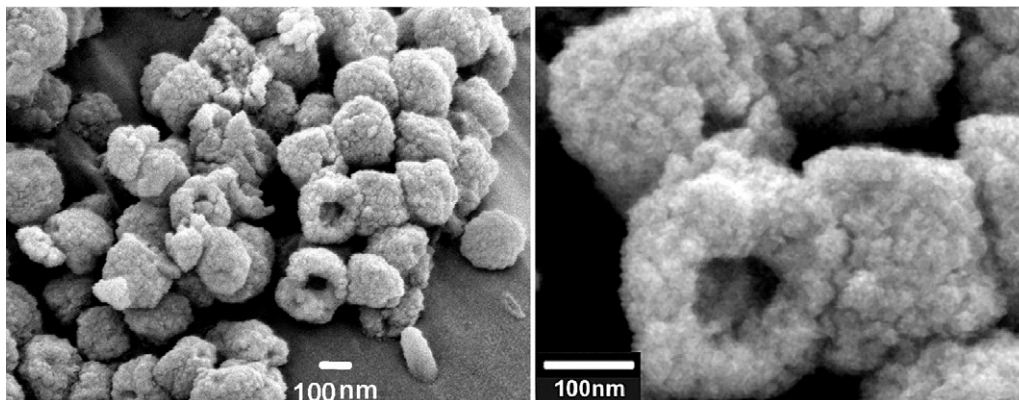


Fig. 3. High magnification SEM micrographs of a $\alpha\text{-Li}_3\text{FeF}_6$ sample precipitated from a w:2p = 1:3 mixture and at 0 °C. A lower magnification micrograph is shown in Fig. 1d.

the raspberry-like matrix by sonication during and after precipitation reaction, albeit neither of those trials was successful. Therefore, we are presenting the electrochemical behaviour of both as prepared and ball milled samples after a proper structural and thermal characterization.

Typical X-ray diffraction patterns of samples precipitated in water and in 2-propanol/water mixtures are presented in Fig. 4a and b, respectively. They are fully indexed with the cell reported for $\alpha\text{-Li}_3\text{FeF}_6$ ($a = 14.414(1)\text{Å}$; $b = 8.6685(7)\text{Å}$; $c = 10.0359(8)$; $\beta = 95.730(4)^\circ$; S.G. C2/c), though a significant difference can be seen regarding the width of peaks. For the former

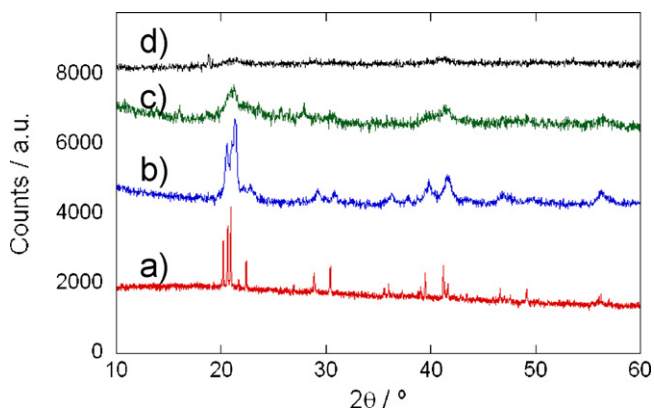


Fig. 4. X-ray diffraction patterns of monoclinic Li_3FeF_6 (S.G. C2/c) precipitated from aqueous solution (a); using 2-propanol at 0 °C in a 1:3 w:2p ratio (b); obtained by precipitation using 2-propanol and additionally dry-milled with carbon for 12 h (c); sample obtained by precipitation using 2-propanol and additionally dry-milled without carbon for 12 h (d).

pattern the larger crystalline size produces well defined and narrow peaks, while for the latter the lowering of particle size, and hence of the coherent diffraction domain, produces broader peaks that overlap in some cases forming wide bands. When the sample is milled with carbon, crystal size appears to further decrease (see Fig. 4c) in as much as peaks become less intense and broader. Interestingly, crystallinity is almost completely lost when the milling is made without carbon.

The samples dried as indicated in the experimental section (60 °C overnight) have been analysed with thermogravimetry prior to its electrochemical characterization to know if the drying process was appropriate to eliminate any volatile physisorbed species. The lower curve in Fig. 5 (labelled as 1:2) corresponds to a sample obtained by precipitation at 0 °C after adding 50 mL 2-propanol to 25 mL aqueous solution, i.e. a w:2p ratio of 1:2. The upper curve (labelled as 1:0) corresponds to a sample obtained after concentrating 25 mL aqueous solution (w:2p ratio of 1:0) at 60 °C. Weight loss is negligible up to 80 °C for the 1:2 sample and up to 200 °C for the 1:0 sample. In general terms the weight loss of the 1:2 sample prepared by precipitation in 2-propanol:water mixtures, is always larger than that of the 1:0 sample (precipitated from water). The 1:2 sample shows a first weight loss in the range 80–150 °C, which is attributed to the release of solvent molecules. No weight loss is observed in the 1:0 sample in the same temperature range. The morphology and particle size of the former point to a larger surface where absorption of solvent molecules is favoured. Typical morphologies of 1:2 and 1:0 samples are presented as insets to Fig. 5. The relative large weight loss occurring above 150 °C in the 1:2 sample and above 200 °C in the 1:0 sample (involving 4–5% weight loss) is attributed to partial hydrolysis of the fluoride. An insufficient flushing with N_2 gas of the heating chamber of the TG apparatus or even the presence of some H_2O in this commercial gas can be responsible for this reaction [7].

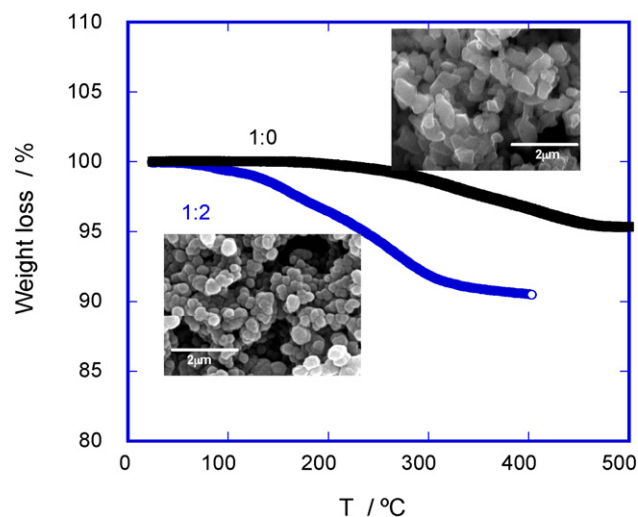


Fig. 5. Thermal behaviour of Li_3FeF_6 samples: (a) precipitated from water, $w:2p=1:0$ and (b) obtained from a $w:2p=1:2$ ratio. Insets show the respective morphology and size of particles at room temperature.

The electrochemical properties of $\alpha\text{-Li}_3\text{FeF}_6$ are interesting and deserve consideration because it is one of the scarce examples of electrode materials for lithium rechargeable batteries that can be prepared at room temperature [7]. However, up today full electrochemical capacity of Li_3FeF_6 has not been yet achieved. In fact, the fluoride material precipitated from aqueous solution has a very poor electrochemical behaviour that is significantly improved after proper processing by dry ball milling with carbon. Li_3FeF_6 was able to intercalate a high amount of lithium reaching ca. 70% of the theoretical capacity after 12 h of ball milling. For the sake of comparison data adapted from Ref. [7] are plotted in Fig. 6 together with the corresponding ones for a sample of $\alpha\text{-Li}_3\text{FeF}_6$ obtained using the conditions that we have found optimum ($w:2p=1:3$ ratio; 0°C) to yield fluoride particles with the smallest size (i.e. raspberry-shape agglomerates of ca. 200 nm formed by small particles of ca. 20 nm). The very significant difference regarding lithium intercalation in both as prepared materials can be depicted from Fig. 6a. While specific capacity is negligible for the sample precipitated in water ($w:2p$ ratio = 1:0, empty circles), up to a 40% of the theoretical capacity is released for the fluoride obtained by precipitation using a $w:2p$ ratio = 1:3 (full circles). Note that this same value of capacity is achieved in the sample precipitated from water only after 5 h dry ball milling with carbon (Fig. 6b). Ball milling of the 1:3 sample has a beneficial effect on both capacity and polarization, likely related to a more intimate mixture of carbon and active material obtained after this procedure. Thus, after 5 h ball milling more Li is inserted (0.5 $\text{Li}/\text{Li}_3\text{FeF}_6$), while increasing the operating voltage of the fluoride material at the same time (Fig. 6b). As quite outstanding finding the theoretical maximum electrochemical capacity for Li_3FeF_6 , 140 mAh g^{-1} , (1 Li per Li_3FeF_6) is reached after 12 h ball milling (labelled 1:3 in Fig. 6c).

Even though this value is a little bit lower than the state of the art reported for the LiFePO_4 olivine material (maximum capacity of 170 mAh g^{-1}), the low temperature synthesis of the herein reported material is an advantageous issue to take into account when large scale production is foreseen in order to sustain the future battery demand of automotive industry.

The herein presented electron microscopy study together with the data already reported in Ref. [7] will be used to explain the observed electrochemical behaviour. Assuming that the ball milling process provides a more intimate mixing of carbon and active materials in both 1:0 and 1:3 samples, then the particle size must be at the origin of the differences observed regarding capacities. We have

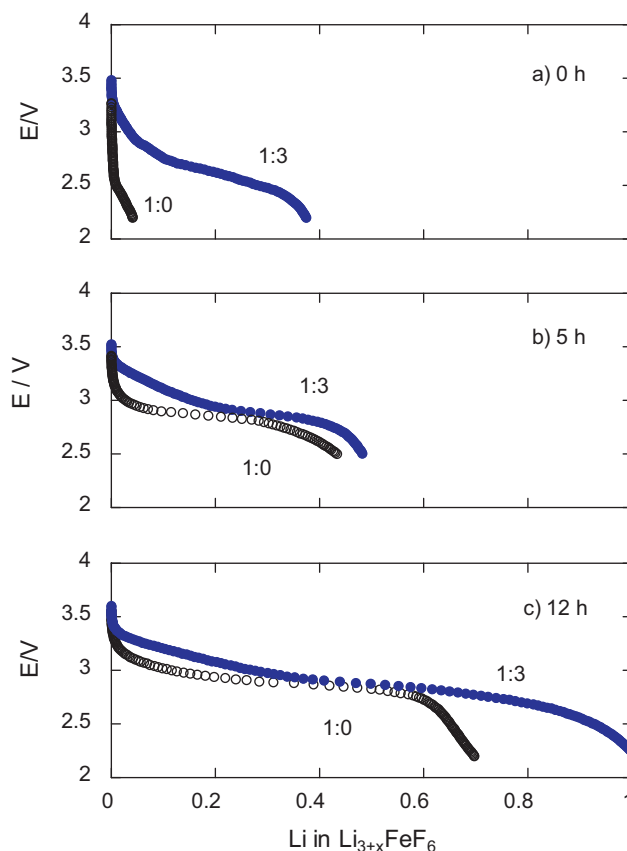


Fig. 6. First discharge curves of Li cells bearing $\alpha\text{-Li}_3\text{FeF}_6$ in the positive electrode material obtained by precipitation from aqueous solution (empty circles) and using a $w:2p=1:3$ ratio (full circles): as prepared materials milled manually with carbon (a) and after ball milling with carbon for 5 h (b) and 12 h (c).

recently shown [1] that 12 h ball milling of the 1:0 sample (precipitated in a $w:2p=1:0$ ratio) leads to a very significant decreasing of particle size, from initially 250–750 nm to ca. 50 nm.

To better understand the observed electrochemical behaviour of the 1:3 sample, we have investigated the effect that has the milling on both the agglomerates and their constituent particles. However, due to the (energy) limitation of the milling system used we only expected to modify the size of the agglomerates, since the elemental particles have already sizes in the order of 20 nm. Fig. 7 shows SEM images of as prepared (Fig. 7a) and 5 h and 12 h milled samples (Fig. 7b and c, respectively) taken at the same magnification ($40,000\times$). It can be seen that the effect of milling is the breakage of the spherical raspberry-like agglomerates, which were composed of smaller particles of ca. 20 nm. However, these agglomerates do not seem to become fully separated or dispersed by ball milling. Fragments of the spherical clusters are now formed, but also larger irregular shaped aggregates are detected producing finally a high inhomogeneity of the aggregate sizes (see Fig. 7b). On the other hand, when comparing the SEM micrographs corresponding to samples milled for 5 h and 12 h (Fig. 7b and c, respectively), it may seem that milling time does not change the scenario, at least under our experimental conditions. However, we found that ball milling for 12 h has a positive effect on electrochemical capacity (see Fig. 6) when compared to a 5 h milled sample. More detailed information on the origin of this improvement has been obtained by TEM. The TEM images depicted in Fig. 8 show: (a) a group of spherical raspberry-like 200 nm sized aggregates in as prepared Li_3FeF_6 ; (b) the result of breaking the agglomerates on one hand and the formation of larger agglomerates on the other with no evidences of isolated (disaggregated) 20 nm constituents after 5 h of milling;

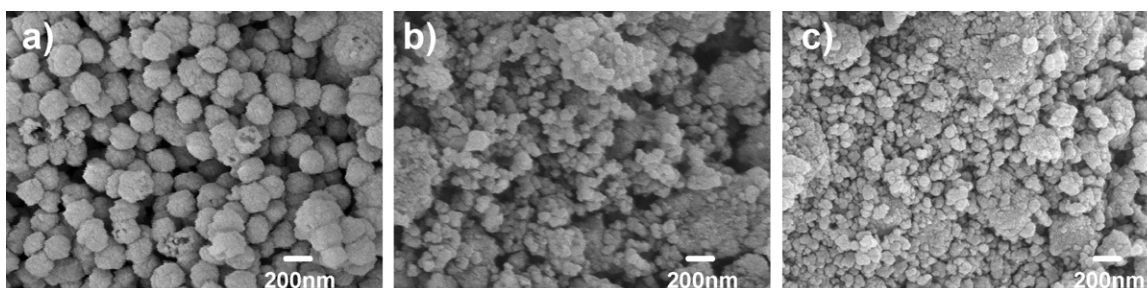


Fig. 7. SEM micrographs of Li_3FeF_6 prepared using a w:2p = 1:3 ratio. As prepared (a), after 5 h (b) and 12 h (c) ball milling with carbon.

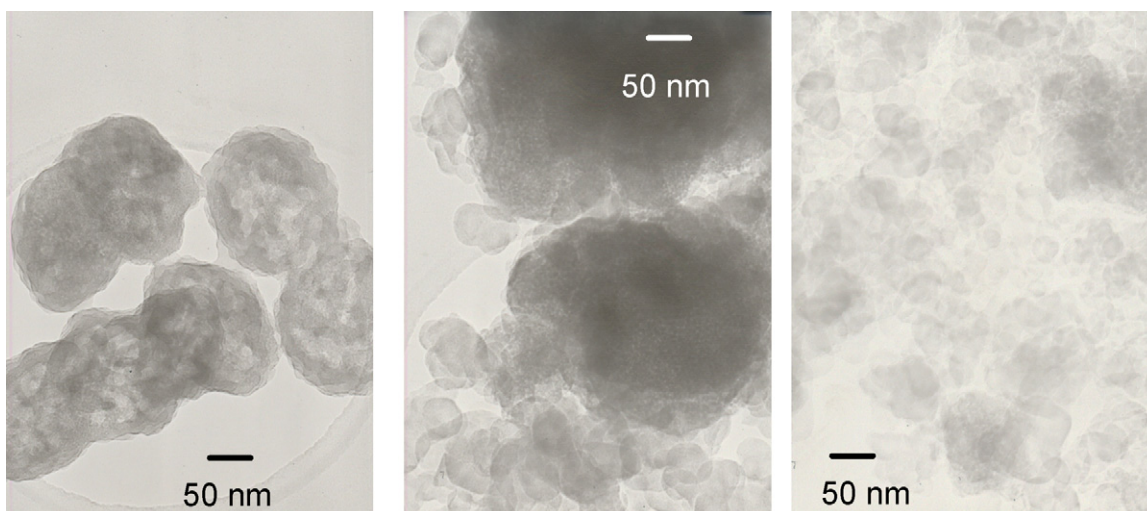


Fig. 8. TEM images of Li_3FeF_6 particles obtained from w:2p = 1:3 ratio at 0 °C: as prepared (a), after ball milling with carbon for 5 h (b) and 12 h (c).

(c) the same non homogeneous distribution is obtained after 12 h milling, but interestingly some small particles of ca. 20 nm are now seen disaggregated (likely the constituent of the raspberry-like agglomerates). These observations point to that the most important effect achieved by dry milling samples that have been prepared by precipitation from 2-propanol based solutions is just a better (or more intimate) mixing of carbon and active particles, since they already contain electroactive nanometric particles. We performed two Li cell discharge experiments to check this hypothesis. One Li cell bore a Li_3FeF_6 sample that was milled for 12 h without carbon and afterwards mixed manually with carbon (MC) as the positive electrode. The other one contained a sample that was ball milled with carbon (BC). The difference in capacity of cells loaded with the samples MC and BC observed in Fig. 9 is so huge that a close look to the microstructure of both is relevant. Interestingly the milling process without carbon has an unexpected effect. The raspberry-shaped agglomerates are destroyed and larger particles seem to be formed. The observed prismatic shapes seem to point to a kind of recrystallization that is probably due to the increase of temperature during the milling process. Then, the presence of carbon likely prevents the fluoride particles from growing by assisting in the dissipation of heat. Alternatively or in addition, the carbon added during ball milling may just simply prevent direct contact between fluoride particles inhibiting crystal growth. Note that in fact the electrochemical behaviour shown in curve MC is more similar to that of the sample precipitated in water (composed of large and prismatic particles shown in Fig. 1a) than to that typically developed by the raspberry-shaped agglomerates formed by 20 nm constituents.

The previously reported beneficial effect that milling has on $\alpha\text{-Li}_3\text{FeF}_6$ precipitated from water must then have a different

explanation [7]. In this case milling effectively produces a decrease of particle size from ca. 300 nm to 50 nm, which greatly enhances the lithium insertion in the fluoride.

Finally, it is interesting to show that the samples prepared by precipitation using water:2-propanol solutions also present a good cyclability. Fig. 10 shows the variation of capacity upon cycling for

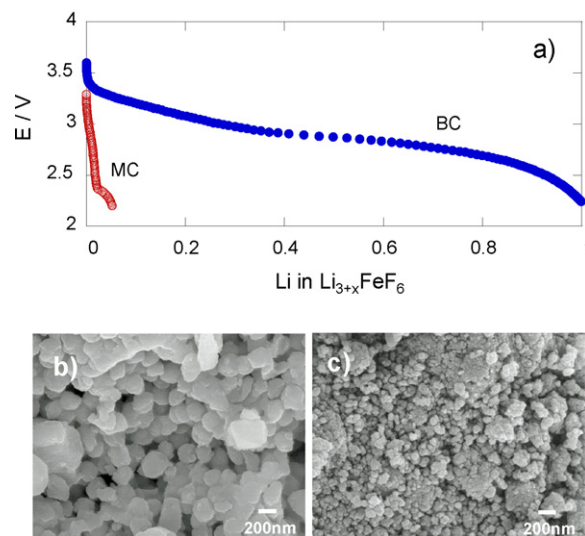


Fig. 9. (a) First discharge curves of Li cells having as positives Li_3FeF_6 milled for 12 h without carbon and mixed manually with carbon (MC) and milled for 12 h with carbon (BC); resulting morphology obtained after milling for (b) MC and (c) BC samples as viewed by SEM.

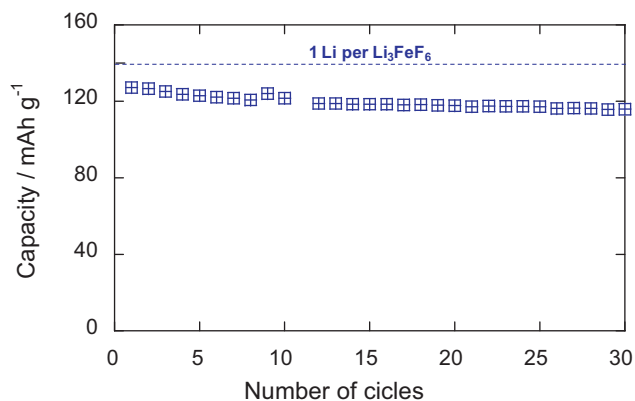


Fig. 10. Cycling of a Li coin cell bearing as the positive electrode Li_3FeF_6 precipitated in a w:2p = 1:3 ratio and milled with carbon for 12 h. The cycling was made at the rate of C/18.

a Li cell bearing Li_3FeF_6 precipitated in a w:2p = 1:3 ratio and milled with carbon for 12 h as the positive electrode. The cell was cycled at a C/18 rate (1 discharge in 18 h). As it can be seen the capacity remains ca. 120 mAh g^{-1} after 30 cycles.

Interestingly, we have found that the capacity of the first discharge and the first charge is directly related to all analysed parameters. Thus, the minimum irreversible capacity loss corresponds to the fluoride with the highest total discharge capacity, i.e. the sample precipitated in a w:2p = 1:3 ratio at 0°C and milled with carbon for 12 h, which is exemplified in Figs. 6c and 10. Therefore, note that either decrease of 2-propanol amount of the precipitation media, decrease of milling time or increase of temperature during precipitation have the same effect: increases of the capacity loss in the first cycle.

These promising results invite us to continue improving the synthetic and processing procedure of this interesting material. The ability to prepare 20 nm sized elemental $\alpha\text{-Li}_3\text{FeF}_6$ particles by precipitation in 2-propanol based solutions, which deliver the full electrochemical capacity, is an important finding and deserves special attention. From here on our investigation will address the nanocoating of nanometric $\alpha\text{-Li}_3\text{FeF}_6$ particles by chemical methods rather than pursuing a reduction of particle size below 20 nm by changing the synthetic procedure. In this way the time and energy consuming ball milling process would be avoided. However, our next improvement must also allow to prevent the nanoparticles from agglomeration during precipitation and to proceed with their nanocoating with carbon. Results of this new approach will be reported elsewhere.

4. Conclusions

The ternary fluoride $\alpha\text{-Li}_3\text{FeF}_6$, which is a newly reported intercalation electrode for lithium rechargeable batteries, is prepared from solution at mild temperature. In this work we have studied the influence that precipitation conditions have on the morphology and particle size of $\alpha\text{-Li}_3\text{FeF}_6$. Nanometric agglomerates of ca. 200 nm are obtained by precipitation from a water/2-propanol solution. The size of agglomerates depends on the water:2-propanol ratio

and the temperature at which precipitation is performed, yielding optimum results regarding particle size at 0°C . These agglomerates are formed by smaller constituents of ca. 20 nm.

Interestingly $\alpha\text{-Li}_3\text{FeF}_6$ is able to intercalate a considerable amount of lithium without being processed by ball milling with carbon. However, the capacity is very much improved if such a processing is followed. In this way, the full electrochemical capacity is reached, when determined experimental conditions are used. This is an outstanding progress to the previous reports, where only limited capacity was observed [7]. After exploring different synthesis variables we concluded that precipitation of Li_3FeF_6 from a solution prepared from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $6\text{HF}_{(\text{aq})}$, and Li_2CO_3 , using water:2-propanol ratio of 1:3 at 0°C produces the best electrochemical results. Interestingly, only the size of agglomerates and the morphology is seen to be affected after proper processing by mechanical milling with carbon, while the size of elemental nanometric particles is fairly kept. The effect of the milling process on some electrochemical characteristic is optimum, since the lithium cells develop full capacity (140 mAh g^{-1}). The improvement of electrochemical performances upon milling is related to a more intimate mixing of Li_3FeF_6 and carbon black in the electrode due to the breakage of the “raspberry-shaped” agglomerates. On the contrary, isolated submicrometric prismatic particles with an average size of 300 nm are obtained when Li_3FeF_6 is prepared from pure water solution. These particles only release a 70% of theoretical capacity after processing by extended dry ball milling with carbon. In this case, the reduction of particle size down to 50 nm likely does play a role in the increase of electrochemical Li insertion properties.

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