

Short communication

Impact of synthesis conditions on the structure and performance of $\text{Li}_2\text{FeSiO}_4$

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DEDICATION: Dedicated to Professor Bruno Scrosati on the occasion of his 70th birthday.

Abstract

Three different synthesis techniques (hydrothermal synthesis, modified Pechini synthesis and Pechini synthesis) were successfully used for preparation of $\text{Li}_2\text{FeSiO}_4$ samples. The obtained samples possess some differences in the morphology and in the particle size, as well as in the presence of in situ formed carbon. The best electrochemical performance has been obtained with the smallest particles embedded into carbon matrix. Such a $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite contains the highest amounts of impurities (Fe_2O_3 , SiO_2 and Li_2SiO_3) and only 68.8 at.% of iron is in the form of Fe^{II} as detected by Mössbauer spectroscopy, respectively. Despite the highest amount of impurities, the sample shows the highest reversible capacity (approximately 100 mAh g^{-1} based on whole silicate-derived material). With the proper structuring of $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites, utilisation of large part of capacity is also possible at current densities corresponding to $C/5$ and $C/2$ cycling rate. A lower amount of impurities was found in the samples that do not contain any in situ carbon after synthesis. Among them, the highest purity is possessed by the sample prepared at 900°C , as determined using Mössbauer spectroscopy. The results obtained by Mössbauer spectroscopy and XRD analysis indicate on the differences in the crystal structure between the thermally treated samples and the sample prepared by hydrothermal synthesis.

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1. Introduction

The need for large-scale batteries is a leading force for research and development of new materials with a potential use for Li-ion batteries. High capacity, safety, environmental acceptability and price are the key factors in a research and development that have to be considered when new materials are tested [1]. Introduction of polyanionic-based cathode materials by Goodenough's group [2] and, later on, extensive research by other groups [3–6] have launched a completely new range of cathode materials for Li-ion batteries. One of the most studied cathode materials in the last decade, LiFePO_4 , is currently considered as the most promising for batteries to be used in HEV. The main obstacle – the low intrinsic conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$ at RT) – has been successfully overcome by

appropriate nano-architecturing using carbon as a conductive phase [3–10]. Today, LiFePO_4 -based materials yielding more than 50% of the nominal capacity even at current densities significantly above 10 C are quite common [9,10].

The next obvious step towards exploration of safe and cheap, but low-conductivity materials are orthosilicates with a polyanionic framework [11–19]. In particular, two compounds and their mixtures (Li_2MSiO_4 ; $\text{M} = \text{Fe}, \text{Mn}$), all with an orthosilicate polyanionic framework, have been recently synthesized and characterized. Especially $\text{Li}_2\text{FeSiO}_4$ has shown a good electrochemical activity (ca. 84% of the theoretical capacity at $C/16$ and 60°C [12]), although its electronic conductivity is as low as $\sim 2 \times 10^{-12} \text{ S cm}^{-1}$ (insulator range) at 60°C [17]. The cycling stability is also quite good (<3% of degradation over 120 cycles [14]). The rate performance, however, is still poor and certainly has to be improved to a similar degree as in LiFePO_4 in order to become competitive for real applications. By analogy to LiFePO_4 , the strategy that should lead to such an improvement seems clear: decrease the particle size as much as possible, cover

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the particles with a carbon nanofilm and assure certain porosity within the composite for easy access of electrolyte. In practice, this strategy is usually realized by addition of a carbon precursor (citrate anion, ethylene glycol, etc.) that simultaneously acts as a complexation agent in formation of a homogeneous gel. During subsequent heat treatment, the precursor carbonizes and, simultaneously, releases some gases that impart sufficient porosity to the final composite [7,8]. The presence of carbon during heat treatment has another crucial role—it suppresses active particle growth [20,21].

Despite all these beneficial effects of native carbon, there are strong indications that it also has one significant drawback: its presence during the synthesis, in certain cases, may lead to a significant amount of impurities in the final product. This disadvantage can be further amplified in delicate compounds that tend to occur in various polymorphs or in compounds with significant structural disorder. The Li_2MSiO_4 ($M = \text{Fe}, \text{Mn}$) family is a typical example of such delicate compounds.

In the present study, we try to evaluate the impact of the presence of carbon during the synthesis as well as after the completed synthesis with the respect to the morphology, impurity content, structure and, last but not least, the electrochemical performance of $\text{Li}_2\text{FeSiO}_4$. For this purpose, four samples were prepared using three different synthetic routes. Using a hydrothermal synthesis, we prepared a sample where no carbon appears during the whole synthesis procedure. A modified Pechini synthesis was used to prepare the next two samples. In both cases we started from a gel containing a reduced amount of carbon precursor (in the form of citric acid). One sample was prepared by heating the xerogel up to 700°C in the presence of CO/CO_2 and the other by heating up to 900°C in the same atmosphere. In both cases we expected that all carbon occurring from the precursor was (gradually) removed during the synthesis. We hoped that this could decrease the amount of impurities and/or had a beneficial effect on the structural ordering during formation of $\text{Li}_2\text{FeSiO}_4$. The fourth sample was supposed to represent the other extreme case: carbon was present during the whole synthesis procedure and remained also in significant amount in the final product. This sample was prepared using a standard Pechini procedure [23].

2. Experimental

As briefly mentioned in Introduction, four samples were prepared using three different techniques: a hydrothermal synthesis (HTS) [14], a modified Pechini synthesis (MPS) and a standard Pechini synthesis (PS) [23].

The starting precursors for $\text{Li}_2\text{FeSiO}_4$ prepared by hydrothermal synthesis (HTS- $\text{Li}_2\text{FeSiO}_4$) were 0.4 mol of lithium hydroxide (Aldrich), 0.1 mol of SiO_2 —Cabosil M5 (Riedel-de Haën) and 0.1 mol of Fe(II) chloride tetrahydrate (Aldrich). Fe(II) chloride solution was separately prepared under Ar and mixed with a dispersion of SiO_2 particles and LiOH. The slurry was sealed into a Teflon-lined stainless-steel autoclave and left for 14 days at 150°C . After the hydrothermal treatment had been completed, the resulting greyish-green powder was rinsed several times with a distilled water. Prior the use, the distilled water was boiled with a continuous flow of Ar through the

whole volume. The whole procedure was carried out in an Ar atmosphere.

$\text{Li}_2\text{FeSiO}_4$ prepared by modified Pechini synthesis was prepared by dispersing 0.15 mol of SiO_2 particles Cabosil M5 (Riedel-de Haën), 0.3 mol of LiNO_3 and 0.05 mol of citric acid in 100 ml of water. After 2 h of dispersing with use of ultrasound, 0.15 mol dissolved Fe(III)-nitrate (Aldrich) was added to the dispersion. For the preparation of $\text{Li}_2\text{FeSiO}_4$ by a standard Pechini synthesis we used a higher amount of complexation agents (0.15 mol of ethylene glycol (Riedel-de Haën) and 0.3 mol of citric acid) and Fe(III)-citrate (Aldrich). Both mixtures containing Li, Fe and SiO_2 in a molar ratio of 2:1:1 were stirred for 1 h and maintained during the night to enable formation of sol. The sol was dried at 80°C for at least 24 h. After thorough grinding with a mortar and pestle, the obtained xerogel was heat treated in a gas-tight quartz tube with a constant flow of CO/CO_2 (approximately 100 ml min^{-1} in volume ratio 1:1). The initial heating rate was $10^\circ\text{C min}^{-1}$. After reaching the pre-selected temperature, the samples were maintained at that temperature for 1 h and then left to cool slowly down to room temperature.

The obtained samples were directly transferred into a glovebox, ground with 10 wt.% of added acetylene black and loosely pressed onto a circular Al foil with a diameter of 16 mm (2 cm^2). The active material mass was always between 5 and 6 mg. The electrochemical characteristics were measured in vacuum-sealed triplex foil (coffee bag foil) cells. The electrolyte used was a 0.8 M solution of LiBOB (Chemetall) in EC:DEC (1:1 ratio by volume) purchased from Aldrich. Solvents and salt were used as received. The working electrode and the counter electrode consisting of metallic lithium were separated with a glass wool separator. The electrochemical measurements were performed using a VMP3 potentiostat/galvanostat at a constant temperature of 60°C with a current density corresponding to $C/20$, if not stated otherwise.

Surfaces of samples were observed and analyzed with a field emission scanning electron microscope (FE-SEM, Supra 35 VP, Carl Zeiss, Germany) at an accelerating voltage of 1 kV. X-ray powder diffraction pattern of $\text{Li}_2\text{FeSiO}_4$ was collected on a Simens D-5000 diffractometer in reflection (Bragg–Brentano) mode using $\text{Cu K}\alpha$ radiation, monochromatized by a secondary graphite monochromator. The data were collected in the range between 15° and 70° in steps of 0.04° and the integration time of 8 s per step.

^{57}Fe Mössbauer experiments were performed at room temperature using a constant acceleration spectrometer. The source was ^{57}Co in a Rh matrix. Velocity calibration and isomer shifts (IS) are quoted relative to an absorber of metallic iron at room temperature. The experiments were performed in transmission geometry. Parameter fits were performed using a standard least-squares fitting routine with Lorentzian lines.

3. Results and discussion

The morphology of the four samples prepared using three different methods is displayed in Fig. 1. The sample prepared by hydrothermal synthesis (HTS sample) did not contain any carbon during the whole synthesis. The average particle size

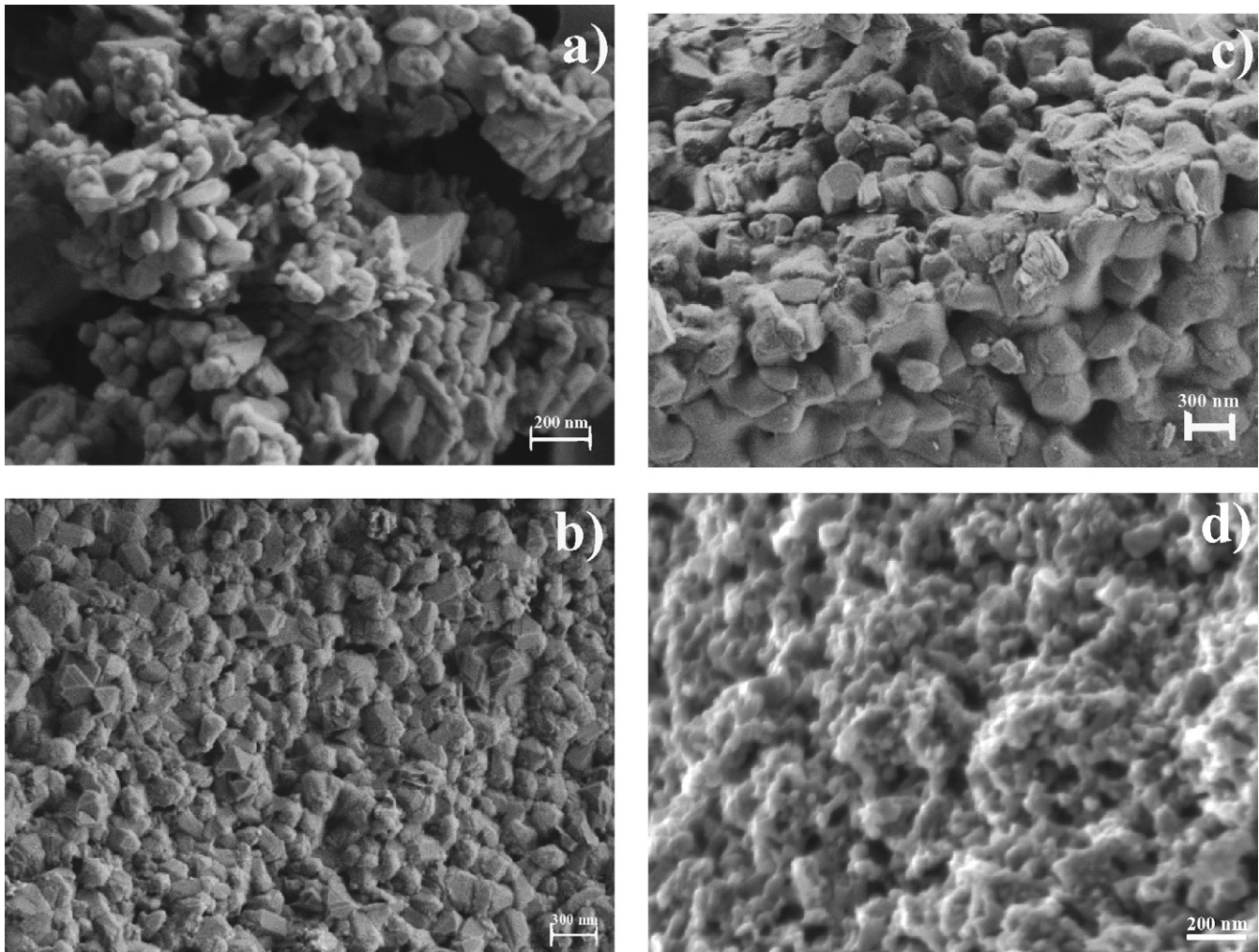


Fig. 1. SEM micrographs of $\text{Li}_2\text{FeSiO}_4$ samples corresponding to (a) hydrothermal sample (HTS), (b) modified Pechini synthesis sample fired at 700°C (MPS700), (c) modified Pechini synthesis sample fired at 900°C (MPS900) and (d) Pechini synthesis sample ($\text{PS-Li}_2\text{FeSiO}_4$).

is between 200 and 300 nm, but the size distribution is quite wide, so much larger (up to 500 nm) or smaller (down to 50 nm) individual particles can also be found (Fig. 1a). The sample obtained by modified Pechini synthesis followed by heating to 700°C (MPS700) contained some carbon during the synthesis but all carbon was removed during the heat treatment. This sample exhibits a much narrower particle size distribution so that the largest particles do not exceed 300 nm and there are very few particles with size on the order of 100 nm or smaller (Fig. 1b). However, a tendency toward agglomeration of individual particles is much more pronounced than in the case of HTS sample. The sample that was prepared by modified Pechini synthesis and heated to 900°C in CO/CO_2 (MPS900) contains significantly larger particles—about 400–500 nm in diameter (Fig. 1c). Some sintering of particles is also observed. The sample prepared by Pechini synthesis contained about 5.5 wt.% of native carbon after the completed synthesis. This is enough that particle growth during heating was considerably suppressed so the finite size of particles is in the range of merely 50 nm (Fig. 1d). The precise distribution of native carbon in this sample has not been determined. However, it can reasonably be assumed from a

range of our studies on olivines [6,7] and on TiO_2 [20,21] that in the PS sample basically a several-nanometre-thick native carbon film covers all particles.

In the next series of experiments we tried to determine the amount of impurities in the four samples. We focused predominantly on determination of the Fe^{III} impurities using the Mössbauer spectroscopy. In Table 1 the results for all samples are summarized. The corresponding fitted spectra are shown in Fig. 2. The amount of impurities in samples roughly follows the rule mentioned in Introduction: a higher content of carbon during synthesis generated a higher amount of impurities in the final product. Thus, PS sample has the highest amount of impurities, followed by sample MPS700 and MPS900. The origin of impurities in HTS sample most probably comes from the synthesis (FeCl_2 can be very easily oxidised by even small remainders of dissolved oxygen in the water) and it cannot be compared directly in terms of impurities to the other three samples. The difference in the nature of Fe^{III} impurities can be very easily deduced from the fitted Mössbauer parameters. Basically, Mössbauer spectra of the native-carbon-free samples (HTS, MPS700 and MPS900) can be very well fitted using two

Table 1

Selected parameters from the Mössbauer data analyses (the center shift (CS), the quadrupole splitting (QS), the spectral intensity (*I*) for Li₂FeSiO₄; and Fe^{III}-based impurities

	Fe ^{II} (Li ₂ FeSiO ₄)			Fe ^{III} impurity			Fe ^{III} magnetic impurity		
	CS (mm s ⁻¹)	QS (mm s ⁻¹)	<i>I</i> (at.%)	CS (mm s ⁻¹)	QS (mm s ⁻¹)	<i>I</i> (at.%)	CS (mm s ⁻¹)	QS (mm s ⁻¹)	<i>I</i> (at.%)
HTS	0.980 (4)	2.651 (8)	80.8	0.352(3)	0.756(5)	19.2	/	/	/
MPS700	0.955 (4)	2.397 (8)	78.7	0.740(4)	0.583(6)	21.3	/	/	/
MPS900	0.957(4)	2.437(8)	84.1	0.746(4)	0.493(6)	15.9	/	/	/
PS	0.937 (1)	2.377 (2)	68.8	0.586(2)	0.434(8)	28.0	0.360(4)	-0.074(4)	3.2

quadrupole doublets, while the spectra pertaining to the PS sample could only be fitted if an additional sextet was used. Further pronounced difference between the thermally treated samples (MPS700, MPS900 and PS) and the HTS sample is in the fitted Mössbauer parameters for Fe^{II}. While thermally treated samples have the quadrupole splitting (QS) similar for Fe^{II} to the one found by Nyten et al. [12] in as-prepared samples, the HTS sample resembles the fit for Fe^{II} that the same authors observed after two full cycles. Nyten et al. ascribed this change in QS to an “intersite exchange” of Li and Fe during lithium extraction/insertion [12]. This difference can be explained by less disordered HTS sample, as it was prepared at lower temperature. An alternative explanation could be based on the fact that in the Li₂MSiO₄ family various polymorphs have been observed [22]. Thus, the HTS sample could contain a different polymorph, if compared to the other three samples. This assumption has been partly confirmed by XRD analysis where all three thermally treated samples can be fitted using *Pmn*21 space group [11,14], while HTS sample shows some differences in the XRD (Fig. 3). The major difference is the absence of the peak 2θ around 31.5° and the shift in the positions for at least two intense diffraction peaks (24.3–24.5° and 35.8–36.2°). Phases determined in samples MPS700 and MPS900 are Li₂FeSiO₄ Fe₂O₃ and Li₂SiO₃, respectively. Specifically, the amount of Li₂FeSiO₄ obtained from Rietveld analysis in MPS700 was 91.7 wt.% which is larger than the value observed for this sample using Mössbauer spectroscopy (Fig. 3b). Peaks are labelled

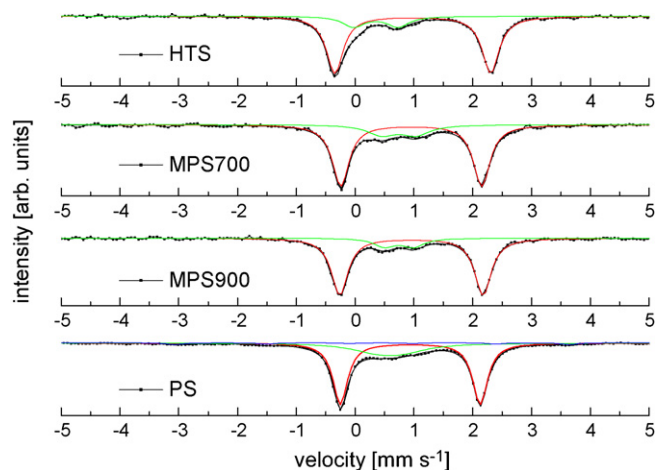


Fig. 2. Mössbauer spectra of Li₂FeSiO₄ samples (square symbols) and corresponding fits (lines). All spectra were measured in the transmission geometry.

according to *Pmn*21 crystal structure and impurities are marked by asterisks. The obtained lattice parameters ($a = 6.2653(8) \text{ \AA}$, $b = 5.3437(1) \text{ \AA}$ and $c = 5.0139(3) \text{ \AA}$) for Li₂FeSiO₄ in MPS700 sample are in good agreement with previous reports [11]. Similar lattice parameters were obtained for MPS900, the sample which contains the highest amount of Li₂FeSiO₄ phase.

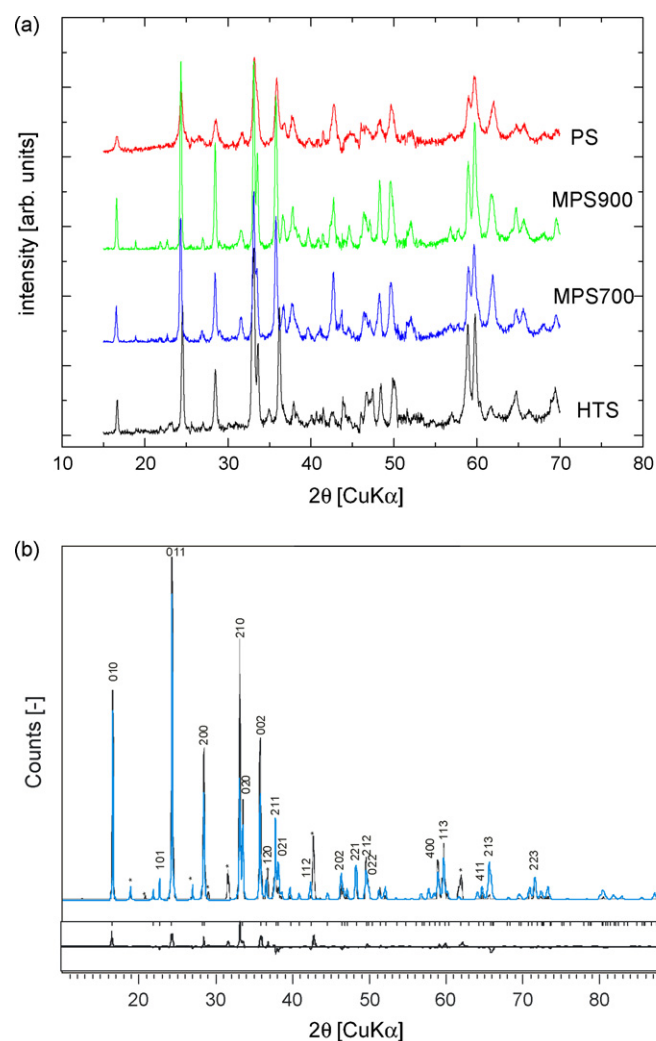


Fig. 3. (a) XRD patterns of four as-prepared Li₂FeSiO₄ samples (patterns were taken in the in situ XRD cell, reflections from the in situ cell are subtracted); (b) refinement of the room temperature XRD obtained from MPS700 sample (Li₂FeSiO₄ peaks are labelled with $[hkl]$ from *Pmn*21 space group and impurities are marked by asterisks).

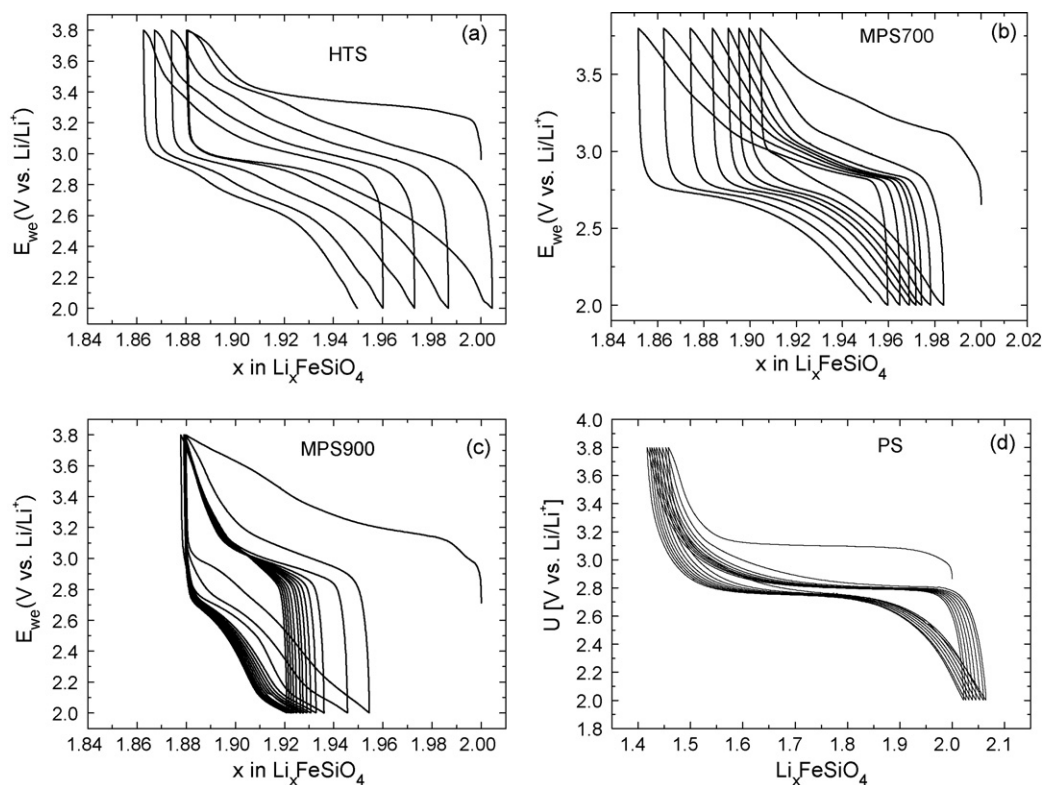


Fig. 4. Cycle performance of $\text{Li}_2\text{FeSiO}_4$ samples at $C/20$ rate: (a) hydrothermal sample (HTS), (b) modified Pechini synthesis sample fired at 700°C (MPS700), (c) modified Pechini synthesis sample fired at 900°C (MPS900) and (d) Pechini synthesis sample (PS- $\text{Li}_2\text{FeSiO}_4$).

PS sample contains some magnetic impurity with magnetic hyperfine field of 20.2 T (as observed by Mössbauer spectroscopy), which cannot be determined from XRD spectra. This might be due to small, loosely crystalline particles that also make some difficulties in the lattice parameter refinement. Detailed structural refinement (including also NMR spectroscopy) of all four samples will be a subject of our work in the near future.

It is well known that the electrochemical performance of olivines (e.g. LiFePO_4) is the best in samples with smallest particles and, additionally, where the particles are in intimate contact with a carbon film [3–11]. However, we showed above that in the case of $\text{Li}_2\text{FeSiO}_4$ the presence of carbon generates a high amount of impurities (about 30 at.% Fe). Therefore, it could be arguable if a standard carbon-based procedure is the optimal procedure also in this case. The comparison of electrochemical performance (Fig. 4) shows clearly that, indeed, the sample containing native carbon (PS sample) shows by far the best performance (Fig. 4d). Note that the reversible capacity is about 60% if we take into account the whole silicate-derived material (both the Fe^{II} and the Fe^{III} state including impurities without iron). However, if we recalculate the capacity by disregarding impurities, we find that the reversible capacity for PS sample is close to the theoretical value. The other three samples show a performance that can be explained mainly on the basis of their particle sizes and a lack of perfect contact with a conducting phase. Thus, the worst electrochemical performance is found for sample MPS900 with the largest average particle size.

The reversible capacities of samples HTS and MPS700 are comparable, and so are the average sizes of the respective particles (in the order 200–300 nm)

Although the capacities of the three carbon-free samples are quite small, a closer examination and comparison of all charge/discharge curves reveals interesting differences in their shapes and potential values. First, let us point out at the specific shift of potential curve to lower potentials after the first discharge (insertion), as already observed and commented by

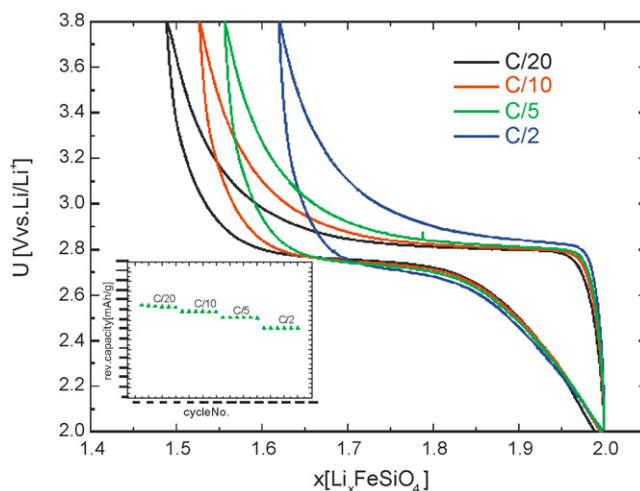


Fig. 5. Cycle performance of PS- $\text{Li}_2\text{FeSiO}_4$ sample at different C -rates. Capacity was measured on the basis of complete mass of electrode.

Nyten et al. [11–13]. For example, in sample MPS700 already the first insertion potential is at about 2.76 V (Fig. 5b) versus Li, however, this shift of potential in sample MPS900 is slightly slower and it gradually approaches this typical value (Fig. 5c). In HTS sample the behaviour is even more complex—the two limiting insertion values coexist in the insertion curves until about fifth cycle (Fig. 5a). It remains unclear whether these unusual potential shifts are due to compositional/structural differences or simply due to different kinetics of samples.

The sample with the highest reversible capacity (sample PS) was further electrochemically tested with respect to its rate performance (Fig. 5). Note again that the full silicate-derived mass is considered and not only the active Fe^{II} phase. The capacity retention at increasingly higher rates is quite good: at C/2 the reversible capacity is still about 75% of that obtained at C/20. This is quite good, although in olivines the capacity retention is even better when using similar coating techniques. We believe there is still room for improvement—at least the particle size can probably be further minimized by optimization of gel composition and firing parameters. The problem that remains to be solved is the purity of the final product and the potential impact of the structure on the electrochemical behaviour of Li₂FeSiO₄.

4. Conclusion

The carbon coating technique based on the carbonization of suitable organic precursor (citrate anion and ethylene glycol) has proven efficient for improvement of the rate performance of Li₂FeSiO₄, similarly as in the case of olivines. The presence of carbon suppresses active particle growth so that their final size in the present study was about 50 nm. However, unlike in the case of olivines, the same carbon that, during firing, suppresses the particle growth also increases the amount of impurities in the final product in much higher content than for olivines. The effect of particle size and the effect of carbon coating is even more pronounced in the case of Li₂FeSiO₄, when comparing electrochemical behaviour with LiFePO₄. Furthermore careful structural and electrochemical analysis suggest some differences not only in the structure, but also in the electrochemical behaviour if samples from different synthesis techniques were used. Based on the present findings, one of the future focuses in the field of Li₂FeSiO₄ could be the search for techniques that yield to specific structural polymorph with particles <50 nm in diameter in good contact with an electro-conducting phase.

Acknowledgements

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