



Short communication

Characterization of two lithiation reactions starting with an amorphous FePO_4 precursor

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ABSTRACT

LiFePO_4 was prepared using two synthetic routes which involved the precipitation and lithiation of an amorphous FePO_4 precursor followed by a thermal treatment. Both hydrated and dehydrated FePO_4 were used. The XRD patterns confirm the amorphous nature of both the precipitated and the lithiated product, while a crystalline LiFePO_4 product is obtained after thermal treatment. Mössbauer spectroscopy was used to analyse the oxidation state of iron during various stages of the reaction. The Mössbauer data demonstrates a large amount of Fe^{3+} ions in the lithiated samples which suggest that the lithiation reaction does not go to completion. Therefore, the formation of LiFePO_4 may be in part associated with the thermal treatment and not the lithiation step.

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1. Introduction

Lithium ion batteries play an important role in various portable electronic devices. Numerous cathode materials have been proposed for these batteries, including lithium iron phosphate. LiFePO_4 can provide increased thermal stability, high theoretical capacity, low cost precursors and environmental friendliness over other commercial cathode materials. A variety of different synthetic routes have been developed for LiFePO_4 , including solid state reactions [1,2], microwave assisted methods [3], hydrothermal conditions [4,5] and many others [6–8]. Lithium can be extracted from LiFePO_4 and inserted into FePO_4 at a flat voltage potential of 3.5V versus lithium metal. However, a major disadvantage of pure LiFePO_4 can be attributed to its poor electronic conductivity which is on the order of $10^{-9} \text{ Sc}^{-1} \text{ m}^{-2}$ [9,10]. One of the strategies to overcome this problem is to use nanosize material. One of the methods to achieve these nanoscale dimensions is by precipitating amorphous nanosized FePO_4 which can later be lithiated and thermally treated to obtain crystalline LiFePO_4 with small particle size [11,12]. In this work, we present a detailed characterization of the reaction mechanism of two previously established synthesis routes that use amorphous FePO_4 (a- FePO_4) as a precursor. The a- FePO_4 is chemically lithiated and thermally treated to give rise to LiFePO_4 with high performance.

The first synthetic method (S1 in Fig. 1) involves the precipitation of an amorphous $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ material from a solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ [11]. Lithiation was performed using lithium acetate and ascorbic acid at a temperature of 60°C . The product from the lithiation reaction was then heated to obtain LiFePO_4 . The second synthesis (S2 in Fig. 1) involves the precipitation of an amorphous $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ from a solution of $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ [12]. The lithiation reaction was carried out using lithium iodide. The product was then heated to obtain crystalline LiFePO_4 . In this investigation we used both hydrated and dehydrated amorphous FePO_4 during the lithiation reaction to determine the effect of the presence of water on the purity and performance of the resultant product. The product of each step within the synthesis was fully characterized using XRD and Mössbauer spectroscopy. Electrochemical tests were performed to confirm the presence and performance of the synthesized LiFePO_4 .

2. Experimental methods

2.1. Preparation

An aqueous solution of 0.01 M of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ (Aldrich) was prepared in distilled H_2O . H_2O_2 (50% by weight, Aldrich) was added to the solution until a molar ratio of 1.1:2 for $\text{H}_2\text{O}_2:\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was obtained. This resulted in the formation of a yellowish precipitate that was later found to be amorphous iron phosphate (a- $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ denoted as FP1) through a combi-

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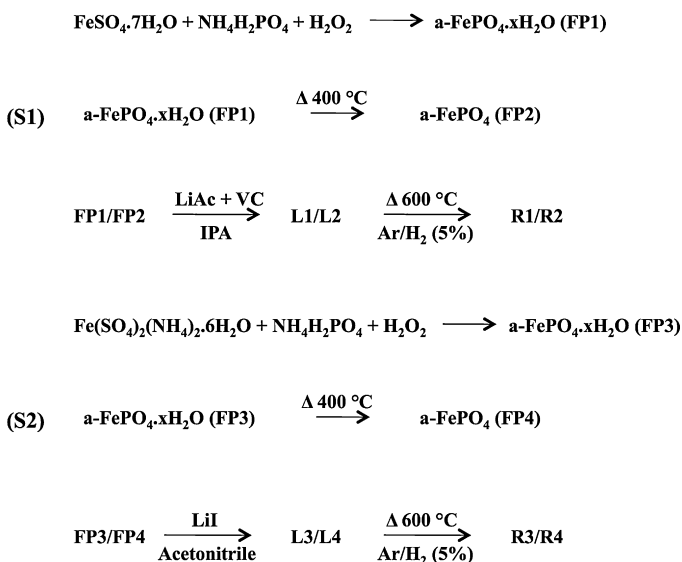


Fig. 1. Schemes 1 and 2 of the performed synthesis.

nation of XRD and spectroscopic methods. The sample was then centrifuged, washed with distilled water and dried in an oven at 60 °C. A dehydrated sample (FP2) was obtained by heating FP1 in air at 400 °C for 24 h. To synthesize LiFePO₄ from FP1 and FP2 a lithiation reaction was performed by adding FP1 or FP2 to a stirred solution of lithium acetate and ascorbic acid (VC) (molar ratio of Fe:Li:VC = 1:1.2:0.6) dissolved in iso-propyl alcohol (IPA) similarly to what is described in reference [11]. The sample was stirred for 5 h at 60 °C under an overpressure of dry nitrogen. The product (denoted as L1 and L2 respectively), was then centrifuged, washed with iso-propyl alcohol and dried in an oven at 60 °C under vacuum. The obtained powder was heated to 600 °C for 3 h under an Ar/H₂ (5%) atmosphere to obtain the crystallized product (R1 and R2 respectively). The reaction scheme for this preparation method (S1) is shown in Fig. 1.

The second reaction scheme (S2) is also described in Fig. 1 and consisted of mixing a 0.03 M equimolar aqueous solution of Fe(SO₄)₂(NH₄)₂·6H₂O and NH₄H₂PO₄ (Aldrich) together. The addition of 2 ml of 50 wt% H₂O₂ initiated the precipitation of a yellowish precipitate that was found to be amorphous iron phosphate (a-FePO₄·xH₂O denoted as FP3). The sample was centrifuged, washed with distilled water and dried at 60 °C. A dehydrated sample (denoted as FP4) was obtained via thermal treatment of FP3 at 400 °C under air for 24 h. The sample, FP3 or FP4, was then suspended in a 1 M solution of LiI in acetonitrile for 24 h (molar ratio of Li:Fe = 15:1). The reaction was performed in an argon filled glove box to avoid oxidation of LiI. The product was filtered, washed with

acetonitrile and dried at 60 °C under vacuum to obtain L3 and L4 respectively. A final thermal treatment to obtain a crystalline product was performed by heating the powder to 600 °C for 3 h under Ar/H₂ (5%) to obtain R3 and R4 respectively.

2.2. Characterization

The thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses were performed using a SDT600 from TA instruments. The heating rate was 5 °Cmin⁻¹ and the experiments were performed with a flowing He carrier gas. XRD analyses of the synthesized materials were performed on a Bruker D8 advance diffractometer using Cu Kα radiation. Mössbauer spectra were obtained using a 50 mCi ⁵⁷CoRh source mounted on a constant-acceleration spectrometer calibrated with α-Fe foil at room temperature. Samples weighing approximately 25–35 mg were mixed with boron nitride powder and spectra were collected at room temperature. A nonlinear least-squares minimization routine was used to fit the spectra to a sum of Lorentzian lines. Where significant disorder was present, the resulting line broadening was modeled using a Pseudo-Voigt lineshape. Isomer shifts are given relative to the centre of the α-Fe spectrum.

Electrochemical evaluations on the synthesized LiFePO₄ were performed by combining LiFePO₄ (50% by weight) with a mixture of poly(ethylene oxide) (PEO) and KJ-Black carbon black (42% and 8% by weight respectively) following the procedure described previously [13]. This mixture was mixed with a mortar and pestle in acetonitrile to obtain a slurry. After well mixing, the slurry was deposited on a stainless steel current collector. The electrode was then left to dry overnight to evaporate the acetonitrile. The separator/electrolyte was prepared by mixing lithium bistrifluoromethanesulfonamide (LiTFSi) and POE (25% and 75% by weight respectively) in acetonitrile. The acetonitrile was slowly evaporated under dry air and the resultant polymeric film was cut into disks 13 mm in diameter. Standard 2032 coin-hardware (Hohsen) was used to test the electrochemical characteristics of these samples using lithium metal as both counter and reference electrode. Cells were assembled in argon filled glove box and the electrochemical evaluations were performed at 80 °C on a VMP electrochemical station (Biologic, France) with the EClab software. The cell was cycled galvanostatically with cut-off voltage of 2.0 and 4.0 V vs Li/Li⁺ at a current equal to a rate of C/10.

3. Results and discussion

All XRD patterns obtained during the investigation are summarized in Fig. 3. Clearly both the as-synthesized FePO₄·xH₂O (FP1 and FP3) materials and the dehydrated samples (FP2 and FP4) are amorphous. TGA-DSC data for FP1 and FP3 are presented in Fig. 2. The data demonstrate a continuous weight loss until 500 °C of approxi-

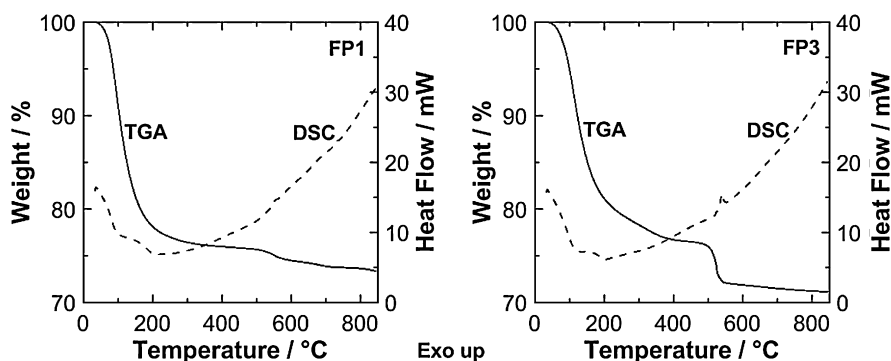


Fig. 2. TGA-DSC for the synthesized amorphous FePO₄ by scheme 1 (FP1) and by scheme 2 (FP3). The data were collected at a heating rate of 5 °Cmin⁻¹ under helium.

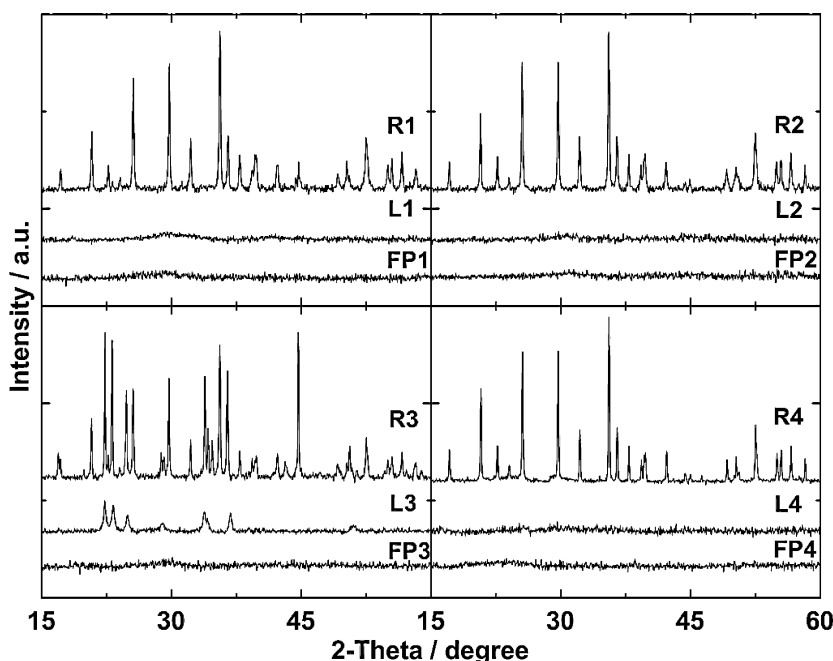


Fig. 3. XRD patterns of the precipitated FePO_4 (FP1 and FP3) which was dehydrated (FP2 and FP4) followed by a lithiation (L1 through L4) and a thermal treatment (R1 through R4). The symbols used to describe the various products obtained from the reaction schemes are described in Fig. 1.

mately 24% which can be associated with loss of water as reported previously [11,12]. The weight loss, at approximately 550°C can be associated with the decomposition of co-precipitated ferric sulphate as described previously in [14].

The goal of this study was to investigate the “so-called” amorphous intermediate sample (L1 to L4, in Fig. 3) described by the previous reports as amorphous LiFePO_4 [11,12]. The amorphous nature of the samples after the lithiation step by XRD is shown in Fig. 3 for samples L1 through to L4. Clearly, the amorphous nature of the samples is conserved through the various procedures except for L3 which contains a significant amount of a poorly crystallized Li_3PO_4 impurity. Following thermal treatment at 600°C under Ar/H_2 (5%), the products R1, R2 along with R4 demonstrate crystalline LiFePO_4 without any impurities. In the case of R3, a mixture of Li_3PO_4 and LiFePO_4 is obtained. Thus, both scheme 1 and 2 give rise to an amorphous precipitated product that contains roughly 24% water and the amorphous character is maintained during dehydration. After the “so-called” lithiation reactions from Refs. [11,12] (Fig. 1), the amorphous phase is maintained for the resulting precipitate. Heating this precipitate to elevated temperature in a reducing atmosphere results in the preparation of crystalline LiFePO_4 . Unfortunately, the XRD investigation does not provide us with any indication that we are passing through an amorphous LiFePO_4 phase. We require the use of different structure characterization tools to investigate these amorphous structures. Mössbauer spectroscopy is perfect for the investigation of the local environment for materials containing Mössbauer active metals such as iron. It has been used in the past to aid in the characterization of LiFePO_4 and is ideal for investigating amorphous structures as it depends solely on the local Fe environment [15–17]. It can clearly identify the oxidation state of the Fe atoms within the structure and is a great tool to fully characterize the two reaction schemes described in Fig. 1.

Fig. 4 provides the Mössbauer spectras for all the prepared samples and their hyperfine parameters are reported in Table 1. In the case of FP1, the sample demonstrates an isomer shift (IS) of 0.41 mm s^{-1} along with a quadrupole splitting (QS) of 0.68 mm s^{-1} which can be attributed to a purely Fe^{3+} species. This sample after the lithiation reaction, L1, consists of two overlapping doublets.

One doublet has an IS of 1.20 mm s^{-1} and a QS of 2.19 mm s^{-1} with an area of 25% comparing to the second doublet having an IS of 0.38 mm s^{-1} , QS of 0.83 mm s^{-1} which has an area of 75%. The former (IS = 1.20 mm s^{-1}) may be attributed to a Fe^{2+} species and the later (IS = 0.38 mm s^{-1}) to a Fe^{3+} species [17]. The product of the thermal treatment, R1, has two doublets. The first doublet has an area of 96% with an IS of 1.21 mm s^{-1} and a QS of 2.96 mm s^{-1} which corresponds to an octahedral Fe^{2+} species with high spin 3d electrons which is typically obtained for LiFePO_4 [17,18]. The second one has an IS of 0.35 mm s^{-1} and a QS of 0.78 mm s^{-1} with an area of 4%, which corresponds to a small amount of Fe^{3+} containing impu-

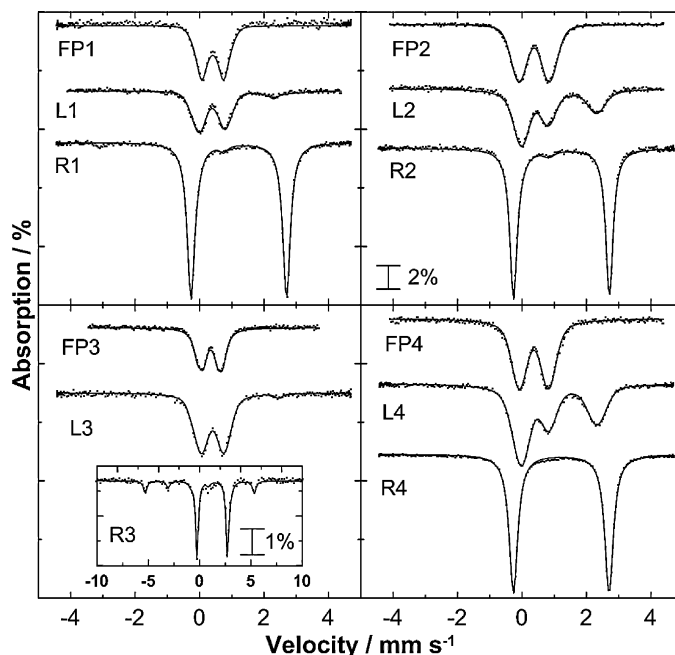


Fig. 4. Mössbauer spectra of all the synthesized samples from Fig. 1. For R3, the scanning parameters were modified in order to detect minor Fe impurities.

Table 1
Hyperfine parameters for the products at each step of S1 and S2.

Sample	IS (mm s ⁻¹)	QS (mm s ⁻¹)	I' (mm s ⁻¹)	Relative area (%)
FP1	0.41	0.68	0.16	100
L1	0.38	0.83	0.15	75
	1.20	2.19	0.15	25
R1	1.21	2.96	0.14	96
	0.35	0.78	0.14	4
FP2	0.38	0.94	0.38	100
L2	0.40	0.84	0.40	52
	1.15	2.31	0.40	48
R2	1.22	2.98	0.14	94
	0.39	0.89	0.14	6
FP3	0.41	0.73	0.40	100
L3	0.40	0.71	0.33	100
R3	1.23	2.97	0.19	72
	0.01 ^a	0.00	0.19	28
FP4	0.37	0.91	0.40	100
L4	1.14	2.37	0.60	56
	0.41	0.79	0.60	44
R4	1.22	2.97	0.16	100

^a Data corresponds to metallic iron with a magnetic hyperfine field of 33.0 T.

ity which is possibly amorphous since it is not clearly visible on the XRD pattern (Fig. 3). These data suggest that the lithiation step did not give rise to amorphous LiFePO₄ since the Mössbauer spectrum shows that the lithiation product has only a minor amount of Fe²⁺ ions. A thermal treatment step is necessary for the formation of LiFePO₄. This suggests that a lithium containing salt was present on the surface of the amorphous FePO₄ during heating which ultimately reacted to give crystalline LiFePO₄. A more detailed analysis of the Mössbauer spectra, shows very sharp peaks for the product R1, which suggests a well structured crystalline material, while FP1 and L1 contain broad/diffuse doublets that are characteristic of amorphous materials [19]. These results are supported by the XRD investigation shown in Fig. 3.

In the case of the reaction involving dehydrated FePO₄, FP2, we obtain a doublet with a measured IS and QS of 0.38 and 0.94 mm s⁻¹ respectively. This suggests a presence of purely Fe³⁺ species. The product of the lithiation step, L2, contains Fe³⁺ species with IS of 0.40 and QS of 0.84 mm s⁻¹ and a large amount of Fe²⁺ species with an IS of 1.15 and QS of 2.31 mm s⁻¹. The relative area of the Fe³⁺ is 52% while the Fe²⁺ is 48%. These results indicate that for S1, the dehydrated species can be lithiated (reduction of Fe³⁺ to Fe²⁺) to a larger extent than the hydrated species (Fe²⁺ increases from 25% to 48% after dehydration) but, in both cases, the reaction does not go to completion. There is still a significant amount of Fe³⁺ remaining in the product. When the product of the lithiation reaction, L2, is thermally treated at 600 °C, crystalline LiFePO₄, R2, is obtained. The Mössbauer spectra of R2 demonstrates Fe²⁺ species with IS and QS of 1.22 and 2.98 mm s⁻¹ respectively with an area of 94% and a Fe³⁺ impurity species with IS and QS of 0.39 and 0.89 respectively with an area of 6%. As mentioned previously, the thermal treatment is necessary for the complete formation of LiFePO₄ and the formation of LiFePO₄ is not complete simply after the lithiation reaction. An unreacted lithium salt may be present on the surface of a-FePO₄ after the incomplete lithiation reaction along with some organic material. Once the material is heated to 600 °C, LiFePO₄ is formed via a solid state reaction between the lithium salt, carbon material and a-FePO₄. Thus, although we are able to obtain some reduction and the production of some Fe²⁺ species that are amorphous in L1 and L2, the reaction is not complete and the product is not pure amorphous LiFePO₄. The lack of Mössbauer data (or other methods to investigate electronic states) in previous work causes much doubt in our minds that a pure amorphous LiFePO₄ is indeed produced.

The a-FePO₄·xH₂O (FP3) that was synthesized with the second synthesis route (S2) demonstrates an IS of 0.41 mm s⁻¹ and a QS of

0.73 mm s⁻¹ which corresponds to an Fe³⁺ species with an area of 100%. Following the lithiation reaction, (L3) the sample has only one doublet with IS of 0.40 mm s⁻¹ and QS of 0.71 mm s⁻¹ suggesting a purely Fe³⁺ species. Once the thermal treatment is performed on L3, R3 is obtained. The data suggest the presence of a Fe²⁺ species with an area of 72% along with IS of 1.23 mm s⁻¹ and a QS of 2.97 mm s⁻¹ which is in the normal range for LiFePO₄. The remaining 28% of the spectral area is in the form of a magnetic sextet and reflects the presence of metallic iron which is confirmed with XRD by the presence of an intense peak at approximately 45° [20].

The dehydrated FePO₄ from the second synthesis route (FP4) has an IS of 0.37 mm s⁻¹ and a QS of 0.91 mm s⁻¹ with a relative area of a 100% suggesting a pure Fe³⁺ species. Once the lithiation reaction is performed with Lil in acetonitrile, the obtained sample (L4) has two doublets. The first doublet has an IS of 0.41 mm s⁻¹ and a QS of 0.79 mm s⁻¹ and the second one has an IS of 1.14 mm s⁻¹ and a QS of 2.37 mm s⁻¹ with relative area of 44% and 56% respectively. This former doublet can be attributed to a Fe³⁺ species and the later to a Fe²⁺ species. When the thermal treatment is performed at 600 °C under Ar/H₂, R4 is obtained which contains only a Fe²⁺ species with IS and QS of 1.22 mm s⁻¹ and 2.97 mm s⁻¹. The hyperfine parameters of R4 are typical of those obtained for LiFePO₄ which is in agreement with the XRD patterns (Fig. 3). Clearly for Lil in acetonitrile, the lithiation of a-FePO₄ is improved in the case of the dehydrated sample as compared to the hydrated sample. The dehydrated samples (L2 and L4) are lithiated (reduced) to a larger extent, possibly due to an easier accessibility of the active site by the reductant as opposed to the hydrated samples (L1 and L3) which contain a fair amount of structural water. Nevertheless, full lithiation is not achieved. A pure Fe²⁺ species is only obtained after thermal treatment suggesting that pure amorphous LiFePO₄ is not obtained.

A detailed analysis of the Mössbauer data for the lithiated samples (L1 through L4) provides information on the various coordination for Fe in the samples. The data for all Fe²⁺ species in the lithiated samples have IS values higher than 1.14 mm s⁻¹. Typically, values of IS below 1 mm s⁻¹ signify a tetrahedral coordination around the Fe atom and IS values above 1 mm s⁻¹ signify an octahedral coordination [17]. This suggests that the Fe²⁺ present in the lithiated samples are in an octahedral bonding environment. It is important to note that, even with an octahedral coordination, it cannot be confirmed that the material is an olivine structure due to the amorphous nature of the lithiated intermediates.

The electrochemical performance of the crystalline LiFePO₄ samples (R1–R4) are displayed in Fig. 5. In the case of R1, the ini-

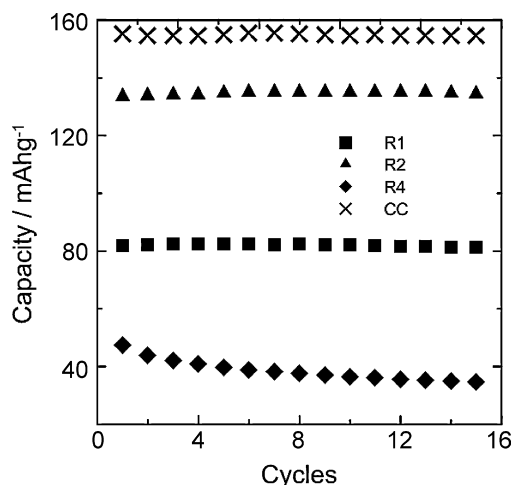


Fig. 5. Electrochemical performance of the synthesized LiFePO₄ material described in the text and Fig. 1, where CC represents carbon coated LiFePO₄.

tial discharge capacity is 82 mAh g⁻¹. No capacity fade is observed during the experiment. For R2, the first discharge capacity is 128 mAh g⁻¹ and similarly to R1, the capacity is stable. The performance is poor when compared to the theoretical capacity of LiFePO₄ (170 mAh g⁻¹). The low capacity is due to the low carbon content and inefficient carbon coating for these samples. The samples typically contain just 1% carbon which is significantly lower than that required for optimal electrochemical performance [21]. When either R1 or R2 is carbon coated (CC on Fig. 5) by dissolving 10% B-lactose in a solution of R1 or R2, followed by drying and thermal treatment at 700 °C under N₂, the samples display a significant improvement in performance yielding up to 92% of the theoretical capacity. In the case of R3, values below 10 mAh g⁻¹ were observed (not displayed in Fig. 5) due to high levels of impurities, mainly Li₃PO₄. For R4, the low capacity obtained is due to the extended annealing time at elevated temperature which results in increased particle size and can be associated with a decrease in performance.

4. Conclusions

Two different synthetic routes to prepare LiFePO₄ which involved the precipitation, chemical lithiation and thermal treatment of an amorphous FePO₄ sample were reproduced. The product of each step of the synthesis was characterized using XRD and Mössbauer spectroscopy. We have observed that for both synthetic routes, a dehydrated FePO₄ precursor can be lithiated in solution to a greater extent than a hydrated FePO₄ precursor. Nevertheless, the iron species after chemical lithiation are composed of both Fe³⁺ and

Fe²⁺ indicating that the lithiation step does not reach completion. Since the initial lithiation reaction is incomplete, a thermal treatment step, which was described in the literature as only associated with crystallization, is essential for the formation of and reduction to LiFePO₄. This reaction relies on lithium ions or salts present on the surface of the amorphous FePO₄ after lithiation. This is confirmed by Mössbauer data before (where the majority of Fe is Fe³⁺) and following the heating step (most of the Fe ions are Fe²⁺ in nature) where the hyperfine parameters are typical of an olivine LiFePO₄ material. This is confirmed via XRD that demonstrates the clear presence of crystalline LiFePO₄ after thermal treatment that was also found to be electrochemically active. The authors would like to stress the importance of Mössbauer spectroscopy in evaluating the reaction mechanism of these reactions and note its critical importance in investigating the characteristic of the amorphous precursors.

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