Porous NASICON-Type \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \) Thin Film Deposited by RF Sputtering as Cathode Material for Li-Ion Microbatteries

Vinsensia Ade Sugiawati\(^1\), Florence Vacandio\(^1\)*, Marielle Eyraud\(^1\), Philippe Knauth\(^1\) and Thierry Djenizian\(^1,2\)*

Abstract
We report the electrochemical performance of porous NASICON-type \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \) thin films to be used as a cathode for Li-ion microbatteries. Crystalline porous NASICON-type \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \) layers were obtained by radio frequency sputtering with an annealing treatment. The thin films were characterized by XRD, SEM, and electrochemical techniques. The chronocoulometry experiments showed that a discharge capacity of 88 mAh g\(^{-1}\) (23 \( \mu \)Ah cm\(^{-2}\)) is attained for the first cycle at C/10 to reach 65 mAh g\(^{-1}\) (17 \( \mu \)Ah cm\(^{-2}\)) after 10 cycles with a good stability over 40 cycles.

Keywords: Radio frequency sputtering, Li-ion microbatteries, NASICON-type \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \), Cathode thin film

Background
Due to remarkable properties such as excellent cycle life, high thermal resistance, no memory effect, and low self-discharge, Li-ion batteries have attracted great attention in electrochemical energy storage [1–3]. More recently, the miniaturization of these power sources has been investigated to meet many applications in microelectronics such as real-time clocking (RTC), radio frequency identification (RFID), sensors, medical implants, memory backup power, solar cell, and smartcards [4–6]. One of the major challenges in the microbattery field is related to the manufacturing process and its compatibility with the integrated circuit technology. Particularly, metallic Li which is currently used as a negative electrode is not compatible with the reflow soldering process because of its low melting point (180.5 °C). Therefore, the rocking chair technology involving stable materials must be explored. Many researches focused on the development of new components with nanostructured materials and 3D designs [7–11].

As potential cathode materials, the NASICON-type compounds \( \text{A}_3\text{Fe}_2(\text{XO}_3)_3 \) (\( \text{A} = \text{Li, Na}; \text{X} = \text{P, As, S} \)) with 3D frameworks like \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \) have attracted considerable attention [12]. NASICON-type \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \) can generate 2.8 V vs. Li with an excellent capacity retention, and up to 2 mol of Li\(^+\) can be reversibly intercalated into \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \), delivering a capacity of 128 mAh g\(^{-1}\). NASICON has also a relatively high ionic conductivity resulting from the disorder of lithium ions in the structure, favorable redox properties, low cost, structural stability, and simple fabrication procedures [5, 6, 12]. Many methods have been reported to synthesize \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \) nanostructures such as hydrothermal [13, 14], gel combustion [15], solid state [16–19], solution with the use of citric acid [20], sol-gel [21], ultrasonic spray combustion [22], and ion exchange with molten salt [23, 24].

In this work, we report the fabrication of porous NASICON-type \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \) thin film electrodes by radio frequency sputtering. Sputtering techniques are widely employed in microelectronics for the successive deposition of thin films; they are the main process used to fabricate planar all-solid-state Li-ion microbatteries [25, 26]. To the best of our knowledge, this approach has never been applied to deposit \( \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 \). We show that this material tested as a cathode reveals a good electrochemical behavior for all-solid-state Li-ion microbatteries.
Methods

Preparation of Li$_3$Fe$_2$(PO$_4$)$_3$ Thin Films
Firstly, thin films of LiFePO$_4$ were deposited on titanium foil as substrate by radio frequency (RF) sputtering (PLASSYS). The target was LiFePO$_4$ (purity 99.9 %, Neyco). The process was carried out in a vacuum chamber with a base pressure before deposition of 10$^{-6}$ Torr. The sputtering gas was pure argon, and the working pressure was 10 mTorr with a gas flow of 21.5 sccm. A sputtering power of 150 W was applied to the target. The deposition time was 3 h. Secondly, the as-deposited thin films were annealed in air at 700 °C for 3 h with a heating rate of 10 °C min$^{-1}$ (furnace: NABERTHERM Controller B 180).

Structural Characterization
Phases and crystallinity of thin films were examined by X-ray diffraction (XRD) with Cu K$_\alpha$ radiation (wavelength = 1.5405 Å) using a D5000 BRUKER-SIEMENS diffractometer. The morphology of the Li$_3$Fe$_2$(PO$_4$)$_3$ was investigated by scanning electron microscopy (SEM, Hitachi, S-570). Thickness measurement was performed by profilometry analysis using a DEKTAT XT (BRUKER) equipment. A portion of the sample is masked during deposition, and the thickness is given by the height of the step.

Electrochemical Measurements
The electrochemical tests of the half-cell were performed using Swagelok cell assembled in a glove box filled with purified argon in which moisture and oxygen content were less than 0.5 ppm. The half-cells consisted of metallic Li as counter electrode. Two circular sheets of Whatman glass microfiber soaked with lithium hexafluorophosphate in ethylene carbonate and diethylene carbonate (1 M LiPF$_6$ in (EC:DEC) 1:1 w/w) were used as separator. Cyclic voltammetry measurements were performed using a Versastat potentiostat (AMETEK) in the range of 1.25–5 V vs. Li/Li$^+$ with a scan rate of 1 mVs$^{-1}$. Galvanostatic cycles were performed with a VMP3 (Bio Logic) at 25 °C between 2 and 4 V vs. Li/Li$^+$. The different cycles of the charge/discharge rate were investigated at a kinetic rate of C/10 and C/5 considering that the theoretical capacity of Li$_3$Fe$_2$(PO$_4$)$_3$ is 128.25 mAhg$^{-1}$. Hence, the applied currents were 3.3 and 6.6 μA cm$^{-2}$, respectively. No additives or binder was used for all electrochemical tests.

Results and Discussion
Prior to battery assembly, the crystallinity of the thin films were examined by XRD. The XRD patterns of initial target and as-deposited sample are shown in Fig. 1. It can be seen that the target is well-crystallized and corresponds to the Olivine-type LiFePO$_4$ phase (JCPDS file no. 040-1499). Various deposition parameters (such as target power, substrate temperature, or argon pressure) were previously investigated, and in all cases, the as-deposited thin films were amorphous. As it can be seen in Fig. 1, the annealing treatment leads to the crystallization of NASICON-type Li$_3$Fe$_2$(PO$_4$)$_3$ phases (JCPDS file no. 047-0107), which is known to have better electrochemical properties [27]. Three small peaks are attributable to the Fe$_2$O$_3$ phase. The oxidation state of Fe in LiFePO$_4$ and Li$_3$Fe$_2$(PO$_4$)$_3$ are +II and +III, respectively. It can be noted that the annealing in air of amorphous LiFePO$_4$ not only leads to crystallization but also to the iron oxidation according to (Eq. 1) [28, 29]:

![Image](image_url)
12LiFePO₄ + 3O₂ = 4Li₃Fe₂(PO₄)₃ + 2Fe₂O₃ (1)

However, the conversion reaction of Fe₂O₃ with Li⁺ occurs at low potential which is not interesting for its use as a cathode [30, 31]. The morphology of the Li₃Fe₁₂(PO₄)₃ thin films before and after annealing was observed by SEM. From Fig. 2a, it is apparent that the as-deposited Li₃Fe₁₂(PO₄)₃ layer is homogeneous with a thickness of 850 nm according to the surface profilometry analysis given in Fig. 2b. After annealing, the film became rough and a sponge-like texture clearly appeared (Fig. 2c, d). Hence, the thermal treatment promoted the formation of a mesoporous material with a larger surface area than the as-deposited layer.

The electrochemical characterization of the porous Li₃Fe₁₂(PO₄)₃ thin film was carried out by cyclic voltammetry (CV). Figure 3 shows the cyclic voltammogram (CV) is obtained. In agreement with literature, the electrochemical reactivity of crystalline Li₃Fe₂(PO₄)₃ is confirmed by the presence of anodic and cathodic peaks [3, 32]. These two peak pairs can be attributed to the reversible insertion reactions of two Li⁺ according to Eqs. (2) and (3):

- First reduction (R1 2.68 V/Li) and oxidation peaks (O1 2.58 V/Li)
  \[ \text{Li}_4\text{Fe}_2(\text{PO}_4)_3 = \text{Li}^+ + \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 + e^- \] (2)

- Second reduction (R2 2.72 V/Li) and oxidation peaks (O2 2.85 V/Li)
  \[ \text{Li}_5\text{Fe}_2(\text{PO}_4)_3 = \text{Li}^+ + \text{Li}_4\text{Fe}_2(\text{PO}_4)_3 + e^- \] (3)

The presence of an additional reversible peak (O3 and R3 peaks) at around 2.4 V reveals that Li⁺ can also react with another phase. This active material is supposed to be LiFePO₄(OH) into which lithium intercalation occurs through the reduction of Fe³⁺ to Fe²⁺ [33–35].

![Fig. 2](image-url) (a) as-deposited Li₃Fe₁₂(PO₄)₃ with (b) profilometry analysis, low (c) and high magnification (d) SEM images of porous Li₃Fe₁₂(PO₄)₃ deposited by RF sputtering after annealing treatment
Compared with literature, it can be noticed that the peaks are quite broad. This phenomenon can be explained by the presence of pores. Indeed, the large surface area offered by the porous texture promotes the storage of charge at the surface according to a non-faradaic process. Hence, the contribution of the capacitive effect leads to the broadening of the peaks.

The galvanostatic charge/discharge profiles obtained at C/10 of the half-cell battery are shown in Fig. 4a. In agreement with the CV curve, the presence of three pseudo-plateaus confirms that Li\(^{+}\) ions react with Li\(_3\)Fe\(_2\)(PO\(_4\))\(_3\) and LiFePO\(_4\)(OH).

The capacity values obtained for the as-deposited sample (Fig. 4b) are very low in the range of 1–2 \(\mu\)Ah cm\(^{-2}\). But, a first discharge capacity of 88 mAh g\(^{-1}\) (23 \(\mu\)Ah cm\(^{-2}\)) is achieved at C/10 for the annealed sample. An average value of about 65 mAh g\(^{-1}\) (17 \(\mu\)Ah cm\(^{-2}\)) is delivered after 20 cycles. This capacity corresponds to more than 50 % of the theoretical capacity of Li\(_3\)Fe\(_2\)(PO\(_4\))\(_3\) (33 \(\mu\)Ah cm\(^{-2}\)). We can observe that capacity is slightly fading during the first cycles. The capacity lost may be caused by the different effects which are associated with side reactions due to the phase changes in the insertion electrode, dissolution of the active material, or the decomposition of the electrolyte. The capacity loss has been also discussed by Song et al. [36] who reported that capacity fading can be attributed to surface impurities (such as lithiated iron oxide which is also involved in the lithium insertion/extraction) leading to the irreversible reaction of Li\(^{+}\) with iron oxide and the formation of a solid electrolyte interface (SEI) at the surface of the electrode.

In order to study the operational stability of the NASICON-type Li\(_3\)Fe\(_2\)(PO\(_4\))\(_3\), the cycling life performance has been also studied at two different C-rates (Fig. 4b). From this graph, it can be seen that the capacity becomes stable after 10 cycles. At C/5, the battery capacity is about 50 mAh g\(^{-1}\) (13 \(\mu\)Ah cm\(^{-2}\)) and remains constant over 40 cycles. These results also show that the
porous geometry of the mesoporous electrode is beneficial for tolerating the volume expansion that generally occur during alloying/de-alloying reactions.

Conclusions
In this work, we report the fabrication of mesoporous NASICON-type Li$_3$Fe$_2$PO$_4$(OH)$_3$ thin film by radio frequency sputtering. The electrochemical studies suggest that after annealing, the crystallized layer is also composed of LiFePO$_4$(OH), which is able to react reversibly with Li$^+$. In the first cycle, the discharge capacity reaches about 88 mAh$^{-1}$ (23 μAh cm$^{-2}$) at C/10 and attains 65 mAh$^{-1}$ (17 μAh cm$^{-2}$) after 10 cycles. The electrochemical characteristics also reveal a good stability suggesting that this material can be used as a cathode for Li-ion microbatteries.

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Authors’ contributions
VAS did experimental works. ME and PK participated to the discussion. FV and TD supervised the research work.

Competing interests
The authors declare that they have no competing interests.

Author details
1 Aix-Marseille University, CNRS, MADIREL Laboratory, UMR 7246, 13397 Marseille, France. 2 Department of Flexible Electronics, Ecole National Supérieure des Mines de Saint-Etienne, Center of Microelectronics in Provence, 13 541 Gardanne, France.

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