Short communication

Synthesis by Spark Plasma Sintering: A new way to obtain electrode materials for lithium ion batteries

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ARTICLE INFO

ABSTRACT

In the search of high-performance materials for lithium ion batteries, Li_2CoPO_4F offers many advantages like high theoretical capacity and high operating potential. The synthesis of Li_2CoPO_4F has been reinvestigated considering a conventional solid state reaction and an unconventional way. Due to the long heat-treatments required by the conventional approach, a beginning of grains coalescence is observed. Limiting particles growth has been allowed by a shorter reaction done by SPS (Spark Plasma Sintering). By this method, the synthesis of Li_2CoPO_4F was greatly shortened (from 10 h to 9 min), which favours the getting of submicrometric particles. The comparison of the electrochemical properties of the Li_2CoPO_4F obtained by the different ways confirms the advantages of SPS synthesis in performance enhancement.

1. Introduction

Since the 90s, rechargeable Li-ion batteries are the most widely used for energy storage. However, today's most performing cells have almost reached their intrinsic limits while the demand in terms of performances is still increasing. To answer the expanding needs of the diversified applications (electric and hybrid vehicles, storage of sustainable energy, . . .), it is necessary to investigate new electrode materials to be used in lithium ion batteries. Conventional materials such as $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$ have been widely studied and optimized and no significative improvements are now expected. New research directions are then required to improve the energy densities of our future batteries. Amongst the most promising families, fluorophosphates like A_2MPO_4F compounds exhibit very high theoretical energy density, if we consider the exchange of more than one electron per mole of transition metal. Moreover, the presence of two different electronegative elements, phosphate groups and fluoride, would increase operating potential.

Recently, the good performances of Na_2FePO_4F in lithium ions batteries were demonstrated. The phase was obtained by either conventional solid state reaction, hydrothermal or ionothermal route [1,2]. While the Na phases are quite simple to obtain, the synthesis of Li_2MPO_4F remains difficult and requires either the ion exchange of the Na-counterparts or a lengthy solid state reaction. For example, the direct synthesis of Li_2MPO_4F has only been reported for M = Co [3] or Ni [4] as a long process at high temperatures. Li_2CoPO_4F is obtained by heat-treatment of a stoichiometric mixture of LiF and $LiCoPO_4$ at 780 °C during 78 h. In addition to time and energy consuming, these conditions lead to relatively large particles which induce kinetic limitations and may explain the poor electrochemical performances reported for Li_2CoPO_4F.

To promote the interest in the search for new materials it is then necessary to overpass these synthesis limitations. The aim is to propose a new chemistry route, which allows enhancing solid state reaction while decreasing reaction time and temperature with in addition the mastering of particle size.

Recent results by Galy et al. [5] suggest the Spark Plasma Sintering (SPS) technique favours fast chemical reactions. In this method, current pulses, internally heat material by Joule effect leading to fast heating rates and the application of an uniaxial pressure during the whole experiment allows maintaining contact between grains. Such technique permits then to shorten drastically the reaction time and limit the grains growth. Even though the involved

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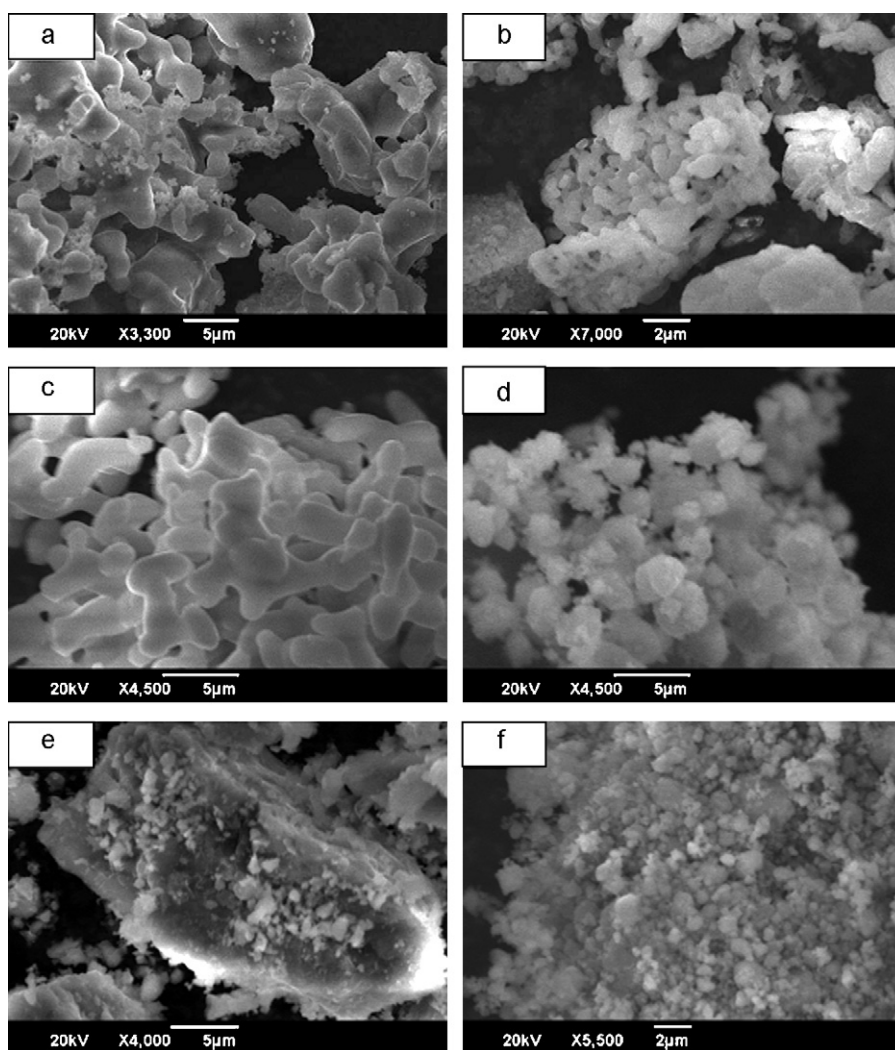
Fig. 1. Scanning electron micrograph of LiCoPO$_4$: conv-LiCoPO$_4$ (a), prec-LiCoPO$_4$ (b), Li$_2$CoPO$_4$F: conv-LCPF manually grinded (c), conv-LCPF ball milled (d), SPS-LCPF manually grinded (e), SPS-LCPF ball milled (f).

mechanisms are not clearly identified, our preliminary results encourage us to study the potentiality of such a technique for the fast synthesis of fluorophosphates.

The nature and properties of Li$_2$CoPO$_4$F samples obtained following conventional solid state routes and SPS derived ones will be described and compared with the scope to validate this process as a new efficient solid state chemical route.

2. Experimental

The different solid state synthesis were performed using Li$_2$CO$_3$ (99%, Alfa Aesar), Co$_3$O$_4$ (99.8%, Sigma Aldrich) (NH$_4$)$_2$HPO$_4$ (99%, Merck) and LiF (98.5%, Alfa Aesar) weighted in stoichiometric amounts. The powders were mixed in an agate mortar and heated in Pt crucibles under Ar flux.

For soft chemical routes, co-precipitation of NH$_4$CoPO$_4$·H$_2$O is obtained by dissolution of (CH$_3$COO)$_2$Co·4H$_2$O (99%, Merck) in solution (0.2 M) of (NH$_4$)$_2$HPO$_4$ in distilled water. Products obtained were filtered, washed with distilled water and dried at room temperature.

Spark plasma synthesis has been carried out using Dr. Sinter 2080 Syntex machine of the "Plate-forme Nationale de Frittage Flash-CNRS" (PNF2/CNRS). The samples are placed in carbon die (Carbone Lorraine 2333) of 8 mm or 15 mm inner diameter and treated in the SPS machine under vacuum.

Mechanical grindings were carried out in Fritsch planetary micro-mill pulverisette 7, using tungsten carbide bowls (45 mL) and balls.
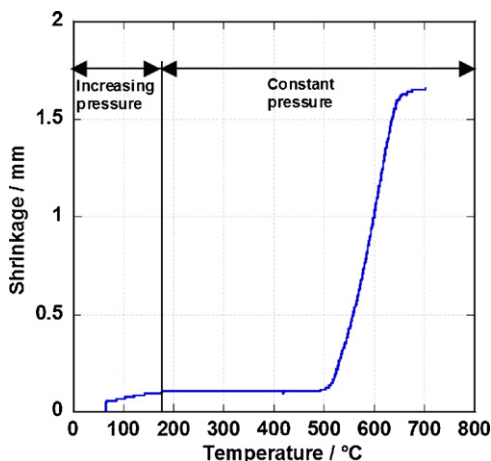
Fig. 2. Evolution of the distance between the punches (shrinkage) as a function of temperature during SPS synthesis.
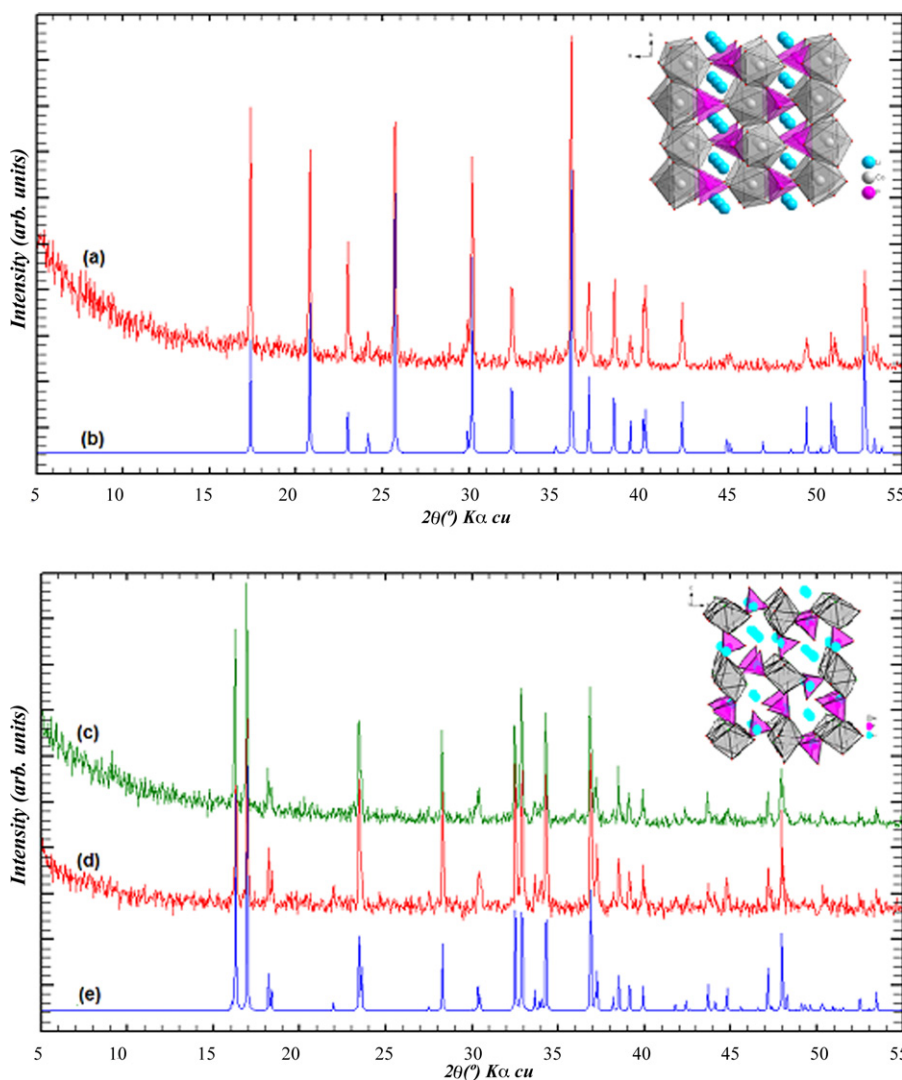
Fig. 3. X-ray patterns of LiCoPO$_4$, prec-LiCoPO$_4$ (a), calculated using JCPDS 32-552 (b), and Li$_2$CoPO$_4$F, SPS-LCPF (c), conv-LCPF (d), calculated using JCPDS 56-1493 (e).

The powders were characterized by X-ray diffraction (SEIFERT XRD 3000 X-ray diffractometer, using CuKα radiation) and scanning electron microscopy (JEOL JSM-6490).

A slurry of Li$_2$CoPO$_4$F cathode was prepared by mixing 80 wt.% Li$_2$CoPO$_4$F, 10 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride (PVdF) in N-methyl-2-pyrrolidene (NMP). The slurry was coated onto an Al foil and then dried at 55 °C for 15 h. The cathodes were cut into a disc of 14 mm in diameter, pressed (6.5 t cm^{-2}), and dried again for 48 h at 80 °C under vacuum. Coin-type cells were assembled in an argon-filled glove box by stacking the cathode, a Celgard^{TM} separator, containing a liquid electrolyte of 1 M LiPF$_6$ in EC/PC/DMC (1:1:3 in weight), and a lithium metal foil as anode. Measurements have been conducted at room temperature, between 2 V and 5.1 V or 5.5 V vs Li$^+$/Li, at C/10. Even if decomposition of conventional electrolytes begins over 5 V, these potentials are necessary to extract the greatest part of lithium and to compare its reinsertion.

3. Results and discussion

In order to validate our approach, it was necessary to investigate the impact of the SPS synthesis in comparison with classical synthesis routes. Li$_2$CoPO$_4$F was then synthesized by a conventional solid state reaction and by SPS using the same starting materials (LiCoPO$_4$ and LiF). In order to obtain small particles, it was necessary to start with precursors as small as possible to favour the reactions and to limit the heat-treatments. The commercial LiF being with an average particles size of 1 μm, the LiCoPO$_4$ synthesis was reinvestigated to select the most appropriate for high reactivity.

LiCoPO$_4$ was firstly prepared by conventional ceramic route by heating stoichiometric mixture of Li$_2$CO$_3$, Co$_3$O$_4$ and (NH$_4$)$_2$HPO$_4$ at 800 °C for 24 h as already described [6]. The resulting powder was characterized using XRD, which confirms that single phase LiCoPO$_4$ (later called conv-LiCoPO$_4$) is obtained with an average particles size about 10 μm as confirmed by SEM observations (Fig. 1a) In order to minimize such particles size, a moderate temperature synthesis by precipitation followed by solid state reaction was realized as detailed elsewhere [7]. NH$_4$CoPO$_4$.H$_2$O precipitates from the add of (CH$_3$COO)$_2$Co·4H$_2$O, in a (NH$_4$)$_2$HPO$_4$ aqueous solution (ratio 1:2). After drying at room temperature, this compound was mixed with a stoichiometric amount of Li$_2$CO$_3$ at 630 °C during 10 h, to obtain LiCoPO$_4$ (later called prec-LiCoPO$_4$). The use of this precipitate led then to reduce the synthesis time and temperature of the LiCoPO$_4$ precursor from 24 h to 10 h and 800 °C to 630 °C, respectively. The XRD characterization confirms that the sample is
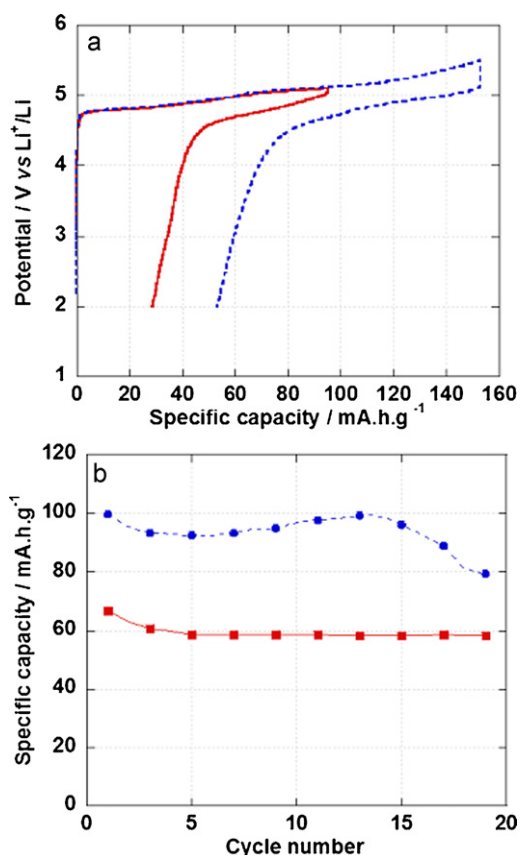
Fig. 4. Electrochemical first cycle (a) and capacity *vs* cycle number (b) of conv-LCPF, between 5.1 V (continuous line), or 5.5 V (dot line) and 2 V *vs* Li⁺/Li.
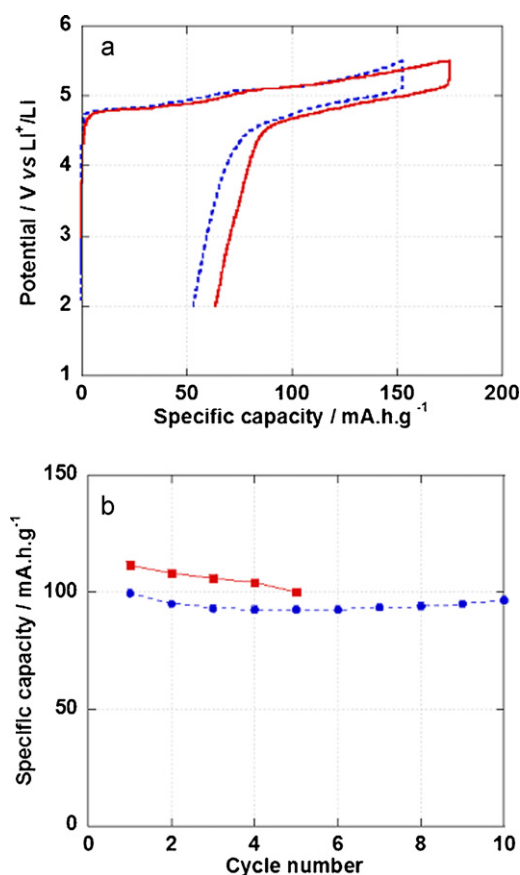

Fig. 5. Electrochemical first cycle (a) of conv-LCPF (dot line) and SPS-LCPF (continuous line) between 2 V and 5.5 V *vs* Li⁺/Li, (b) discharge capacity *vs* cycle number of conv-LCPF and SPS-LCPF.

single phased and SEM analysis shows the particles size to be about 0.8 μm (Fig. 1b), which will favour the reactivity.

3.1. Conventional solid state process

The effect of the particle size reduction on the reaction kinetic is confirmed by the fact that single phase Li_2CoPO_4F is then obtained by a solid–solid reaction between prec-$LiCoPO_4$ and LiF at 700 °C for only 10 h instead of 78 h necessary when using conv-$LiCoPO_4$. Fig. 1c and d shows SEM micrographs of samples obtained after manual grinding (Fig. 1c) and after planetary ball milling during 1 h in a WC bowl (Fig. 1d). It shows that independently of the grinding method, the obtained powder present particles with an average size about 5 μm.

3.2. SPS based synthesis route

To prevent the particle growth, we then decided to carry out the Li_2CoPO_4F synthesis using the SPS technique. The shortness of the reaction due to the fast chemical diffusion, already observed in the case of $Cu_xV_2O_5$ synthesis [5], offers huge potentialities to limit the particles coalescence. The stoichiometric mixture of prec-$LiCoPO_4$ and commercial LiF was ground in an agate mortar and inserted into an 8 mm or 15 mm inner diameter carbon die. This last was introduced in the SPS chamber before being evacuated to a 6 Pa vacuum. The powder was placed under an increasing uniaxial pressure up to 25 MPa, which was reached in 1 min and kept constant during the rest of the reaction. Simultaneously, the temperature was raised via 3.3 ms DC electric pulses according to the following protocol: up to 500 °C with a heating rate of 100 °C⁻¹ min⁻¹, and from 500 °C to 700 °C in 4 min. Then the sample was cooled down fol-

lowing the inertia of the machine (roughly estimated to be close to 150 °C min⁻¹). Compaction/reaction of the powders was followed with a dilatometer to record the linear shrinkage of the sample as a function of temperature and/or time. Fig. 2 displays the shrinkage evolution upon the reaction between prec-$LiCoPO_4$ and LiF and it clearly shows an important displacement is observed between 500 °C and 700 °C.

Fig. 3 shows the XRD experimental pattern obtained with samples prepared by conventional solid–solid route (later called conv-LCPF) or by SPS (later called SPS-LCPF) compared to the pattern calculated using Li_2NiPO_4F structure [4]. This compound crystallises in the orthorhombic system, with space group Pnma. In both cases, pattern matching allows to confirm that single phase Li_2CoPO_4F is obtained. Refinement of cell parameters leads to $a = 10.453(1)$ Å, $b = 6.386(5)$ Å, $c = 10.874(8)$ Å, and $a = 10.449(4)$ Å, $b = 6.382(1)$ Å, $c = 10.872(5)$ Å for conv-LCPF and SPS-LCPF respectively, which are closed to the ones published by Okada et al. [3] ($a = 10.444$ Å, $b = 6.381$ Å, $c = 10.864$ Å). Using X-ray diffraction data, the shrinkage between 500 °C and 700 °C during SPS experiment was then associated to Li_2CoPO_4F formation and it confirms the Li_2CoPO_4F synthesis is complete in 9 min with a SPS heat-treatment up to 700 °C.

By ceramic route, Li_2CoPO_4F particles size is homogenous about 5 μm, with a beginning of grains coalescence which is not reduced significantly after mechanical grinding. SEM experiments carried out on samples obtained by SPS show the presence of 20 μm grains, which apparently contradict the expected size mastering of short reaction time. However, 1 h ball milling appears enough to completely break the grains leading to submicronic particles (average 0.8 μm) (Fig. 1f). This indicates clearly that previously observed

grains correspond to agglomerated particles easily separated by mechanical grinding. Then, as expected the use of SPS technique instead of conventional ceramic route allows drastical shortening of the reaction time from 78 h to 9 min, which prevents the particle growth and allows obtaining in short time homogeneous, single phased material with submicronic particles size.

3.3. Electrochemical tests

To validate the SPS synthesis process, compounds obtained using the two synthesis ways were electrochemically compared. First characterizations were performed on conv-LCPF to evaluate cycling properties of this compound between 2 V and 5.1 V *vs* Li$^+$/Li (Fig. 4). In this potential windows, conv-LCPF exhibits a high oxidation potential at 4.8 V *vs* Li$^+$/Li, and a good cyclability during 20 cycles, with a reversibility of 60 mAh g^{-1}. The unusual end of the charge curve and the extraction of 0.65 Li per formula unit at 5.1 V confirm the charge is incomplete at this cut-off potential. In order to extract a more important amount of lithium, electrochemical tests between 2 V and 5.5 V *vs* Li$^+$/Li were carried out, even if today's electrolytes are not adapted to potentials above 5 V *vs* Li$^+$/Li. By changing the cut-off potential, discharge capacities were greatly improved up to 100 mAh g^{-1}. However, a more important irreversibility is observed, as well as fluctuations on capacity values depending of the cycle number. These phenomena are partially assigned to the electrolyte oxidation at the active material surface.

For comparison, SPS-LCPF has been characterized in the same condition between 2 V and 5.5 V *vs* Li$^+$/Li to estimate its electrochemical properties. After a manual grinding, a charged SPS-LCPF exhibits a smaller lithium reinsertion upon discharge corresponding to a capacity about 60 mAh g^{-1} (not shown), which confirms agglomerated Li$_2$CoPO$_4$F exhibits kinetic limitations. After ball-milling treatment, leading to submicronic particles of Li$_2$CoPO$_4$F, a capacity in charge of 170 mAh g^{-1} and 110 mAh g^{-1} in discharge are obtained, which is comparable with the one of the conv-LCPF (Fig. 5). A great part of the observed irreversibility is associated to the important specific area of this material, which favours the electrolyte oxidation.

After charging to 5.5 V *vs* Li$^+$/Li, SPS-LCPF delivers a maximum capacity of 110 mAh g^{-1} upon the following discharge. These values are greatly higher than the ones previously published by Okada et al. [3], which can be explained by our smaller particles size. Recently, Khasanova et al. [8] have proposed an irreversible structural rearrangement, appearing during cycling between 3 V and 5.1 V *vs* Li$^+$/Li, with an increase of cell parame-ters which can enhance lithium conductivity but do not explain the fading of cycling performances. To understand phenomenon occurring above 5.1 V, it will be necessary to minimize the electrolyte degradation at the electrode/electrolyte interfaces considering a coating approach, which has confirmed to be efficient in the case of LiCoO$_2$ in contact with sulphide solid electrolyte [9].

4. Conclusion

Despite the expected reactivity with the electrolyte at high potential, our results confirm the possibility to obtained electrode materials by Spark Plasma Sintering in few minutes, which show comparable electrochemical properties than the same materials obtained after hours by classical solid state routes. This clearly demonstrates the SPS approach can replace conventional ceramic routes leading to a drastic decrease of reaction time (from 78 h to 9 min for Li$_2$CoPO$_4$F), which is decisive when small particles size materials are desired. The extension to other chemical systems is currently under development with the scope to propose the definition of a fast synthesis method. Synthesis by SPS offers huge potentialities to solid state chemists and materials scientists regarding the (re-)investigations of compounds known to be difficult to synthesise like in the case of fluorophosphates. Moreover, an easy up-scaling of the materials amount is expected by increasing the dies diameter and by an adjustment of the SPS parameters (temperature, pressure, time, heating rates, . . .) to overpass the temperature gradient, which appears when using large dies.

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