



# Flame-made Lithium Transition Metal Orthosilicates



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## ABSTRACT

$\text{Li}_2\text{MSiO}_4$  (M = Fe, Mn, Co) compounds have since their discovery gained increased attention as alternative, inexpensive and inherently safe positive electrodes for Li-ion batteries. To meet the required performance for an electrode, sophisticated, complex and time-consuming synthesis measures are required at present. Here, we present a time-efficient and scalable aerosol combustion method with subsequent annealing, leading to nanoscale and carbon-coated  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4$ . Using liquid-feed flame spray pyrolysis, we demonstrate synthesis of orthosilicate materials, with phase purities exceeding 95 wt. % according to Rietveld quantifications, in a relatively short time. The importance of the precursor concentration, in order to obtain loosely agglomerated nanoparticles, is discussed and the long-term performance is investigated. In the case of  $\text{Li}_2\text{FeSiO}_4$ , the optimised precursor concentration yielded particles of about 30 nm, which delivered an initial discharge capacity of up to  $150 \text{ mAhg}^{-1}$  at  $60^\circ\text{C}$  and C/20. Furthermore, over 50% of the capacity is retained at a high rate of 5C, and long-term cycling showed outstanding capacity retention of over 90% after 300 cycles at a moderate rate of C/2.  $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4$  on the other hand, was shown to suffer from a severe capacity fade, and upon prolonged cycling the redox activity can be attributed solely to Fe.

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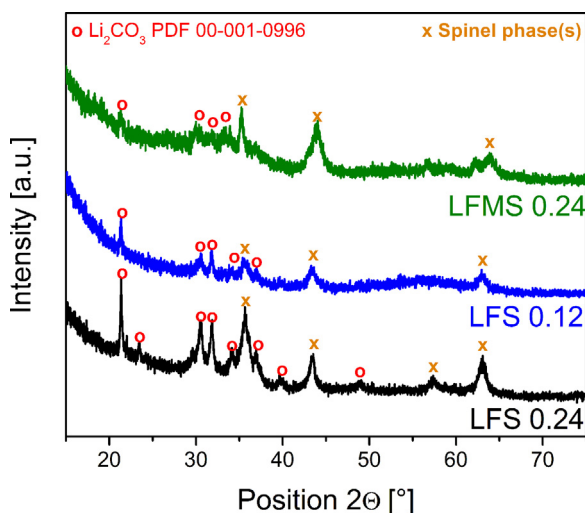
## 1. Introduction

As  $\text{LiFePO}_4$  is a well-established cathode material for Li-ion batteries, other polyanion materials, like  $\text{Li}_2\text{MSiO}_4$ , where M = Fe and Mn, have recently gained much interest as alternative cathode materials. They are interesting since they consist of cheap, abundant and environmentally benign elements. Strong Si-O bonds in the framework result in a good thermal stability and the transition metal to Li ratio of 1:2 could, in theory, allow the exchange of two Li per formula unit, giving rise to high theoretical capacities exceeding  $300 \text{ mAhg}^{-1}$  [1–3].  $\text{Li}_2\text{MSiO}_4$  compounds adopt  $\beta$  and  $\gamma$   $\text{Li}_3\text{PO}_4$  structures depending on the synthesis conditions and the transition metal cation [4,5]. One major shortcoming of the orthosilicates is the low conductivity values both with respect to electronic and ionic conductivity. These shortcomings can be overcome by the application of a conductive carbon coating and the synthesis of nanostructured materials to limit the mean diffusion length for Li ions [6,7]. A high porosity in the meso and macro range, and thus a high contact area for the electrolyte, was also shown to be significant [8–11]. The majority of reported syntheses are wet chemical methods, such as solvothermal [12–14], solution and sol-gel related processes [10,15–17], and

combustion syntheses [11,18]. Unfortunately, most of these syntheses are not scalable, or are hard to control during up-scaling, and hence are not applicable for the preparation of large quantities of electrochemically active orthosilicates. We previously demonstrated liquid-feed flame spray pyrolysis (LF-FSP) as a novel alternative method to synthesise nanoscaled  $\text{Li}_2\text{MnSiO}_4$ , offering a high discharge capacity of up to  $190 \text{ mAhg}^{-1}$ , and excellent rate capability [19].  $\text{Li}_2\text{MnSiO}_4$ , however, suffers from severe capacity decay and amorphisation of the structure, caused by distortions and changes in the Mn coordination upon oxidation [19–22]. Contrarily,  $\text{Li}_2\text{FeSiO}_4$  was shown to be stable in the one electron reaction range and is thus an interesting candidate as low cost alternative cathode [7,23]. Mn substitution in  $\text{Li}_2\text{FeSiO}_4$  would be attractive, if the structure does not collapse, since Mn can give rise to two additional redox couples. Also, the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox reaction occurs at higher potentials vs.  $\text{Li}/\text{Li}^+$  compared to the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox reaction [24,25]. The combination could result in a higher specific energy, due to an increased capacity and higher voltage. Here, we communicate LF-FSP of an EtOH/p-Xylene based metal nitrate and tetraethyl orthosilicate solution, combined with a reducing heat-treatment and carbon coating, as a time-efficient and scalable method to synthesise  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4$  as a cathode material for Li-ion batteries.

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**Fig. 1.** Powder XRD patterns of as pyrolysed LFS 0.24 (black), LFS 0.12 (blue) and LFMS 0.24 (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 2. Experimental

### 2.1. Sample preparation

In this study, samples of the composition  $\text{Li}_2\text{FeSiO}_4$  (LFS) and  $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4$  (LFMS) were synthesised. The solutions for LF-FSP consisted of EtOH and p-Xylene in a volume ratio of 5:1 and a total volume of 125 mL. In the case of LFS, two different Fe precursor concentrations,  $0.24 \text{ mol L}^{-1}$  and  $0.12 \text{ mol L}^{-1}$ , were investigated. For the higher concentration,  $0.03 \text{ mol Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Sigma-Aldrich, >98%) was dissolved in the above mentioned amount of solvent under vigorous stirring at  $50^\circ\text{C}$ . Subsequently,  $0.06 \text{ mol LiNO}_3$  (Alfa Aesar, 99%) and  $0.03 \text{ mol}$  tetraethyl orthosilicate (TEOS) (VWR 99%) were added. The lower concentration solution was made with exactly half the amount of precursors. The samples are subsequently denoted as LFS 0.24 and LFS 0.12.

One solution of LFMS at high concentration was prepared. The LFMS 0.24 solution was prepared in the same manner as the higher concentrated LFS solution, and  $0.015 \text{ mol Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was substituted by  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Merck Ensure for analysis, >98%).

The LF-FSP process was performed on a NPS10 Tethis S.p.A., at a constant liquid and dispersion gas ( $\text{O}_2$ ) flow rate of  $5 \text{ mL min}^{-1}$ . The solutions were sprayed into a  $\text{CH}_4/\text{O}_2$  (flow rate:  $1.5/3 \text{ L min}^{-1}$ ) flame with a pressure drop (dispersion gas at the nozzle tip) of  $\sim 2 \text{ bar}$ . After the LF-FSP process, the powders were collected on a glass microfiber filter (Whatman GF6). As the carbon source, 30 wt. % corn-starch (Carl Roth GmbH & Co. KG for laboratory use) was mixed with the collected powders by wet ball milling for 10 h, using an equivalent volume of YSZ grinding media ( $\varnothing 5 \text{ mm}$ ) and EtOH as a dispersant. Heat treatments were carried out in a reducing atmosphere (2%  $\text{H}_2$  in Ar; flow rate  $10 \text{ L/h}$ ), at  $650^\circ\text{C}$  and 10 h dwell, to allow phase formation and carbon coating in a single step. The heating and cooling rates were  $200^\circ\text{C h}^{-1}$ .

### 2.2. Physiochemical characterisation

The phase formation and phase purity was monitored by X-ray diffraction. All X-ray powder diffraction patterns were recorded on a Bruker D8 Advance Da-Vinci equipped with a LynxEye Xe detector, working in Bragg–Brentano ( $\theta/2\theta$ ) geometry. Patterns were recorded using  $\text{CuK}\alpha$  ( $1.54060 \text{ \AA}$ ) radiation. The scan range for the as pyrolysed powders was 15 to  $75 2\theta$  with a step-size of

0.013 and an integration time of 0.75 s. The final samples were recorded from 15 to  $140 2\theta$  with a step-size of 0.013 and an integration time of 1 s. Lattice parameter calculations and full pattern refinements for the quantification of secondary phases was performed with Topas (Bruker AXS Version 4.2). Fundamental parameters were applied to refine the peak shapes. The refinement of LFS in the space group  $P2_1/n$  was started with a model by Dahbi *et al.* [18]. The lattice parameters and the angle  $\beta$  were allowed to relax and subsequently the atomic positions were allowed to relax, starting with the heaviest atom. The refinements of the LFMS sample were done by combining this model with a previously reported model for  $\beta_{\text{II}} \text{Li}_2\text{MnSiO}_4$  [16,26].

The carbon content was estimated by thermogravimetric analysis (TGA) in synthetic air ( $30 \text{ mL min}^{-1}$ ) on a Netzsch STA 449C Jupiter thermo analyser. Samples were heated to  $850^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ . Surface area and pore size distribution data was acquired by nitrogen adsorption on a Micrometrics Tristar 3000, for which the samples were vacuum dried at  $110^\circ\text{C}$  for 24 h. Further morphological and structural investigations were carried out by field emission scanning electron microscopy (FE-SEM) on a Zeiss Supra 55 VP and (scanning) transmission electron microscopy ((S)TEM). ((S)TEM) coupled with electron energy loss spectroscopy (EELS) and X-ray energy dispersive spectroscopy (EDS) was performed on a double Cs corrected, coldFEG JEOL ARM200CF, operated at 200 kV and equipped with a Gatan Quantum ER for EELS and a large solid angle (98 srad) Centurio detector for EDS. EDS and EELS was performed with a 34 mrad convergence semi-angle and a 617 pA probe current. Sub-pixel scanning was applied to limit the effective exposure time to less than  $200 \mu\text{s}$  in every location of the map to avoid possible beam damage. Elemental mapping by EELS was performed with an energy dispersion of  $1 \text{ eV/channel}$  and a collection semi-angle of 66 mrad. Samples for microscopy were prepared by ultra-sonication of a powder EtOH suspension for 20 min prior to analysis. A droplet of the corresponding suspension was placed on a SEM sample holder or on a holey carbon coated Cu TEM grid respectively.

### 2.3. Electrochemical characterisation

The electrochemical properties were assessed by galvanostatic cycling experiments on a Maccor 4200. Applied voltage windows were 1.5–4.4 V for LFS samples and 1.5–4.7 V for LFMS samples. All samples were characterised at room temperature. Additionally, cells made with LFS 0.12 were characterised at  $60^\circ\text{C}$ .

The corresponding electrodes were prepared by a tape casting method. A slurry containing 75 wt. % active material, 15 wt. % conductive carbon (Super P Timcal) and 10 wt. % polyvinylidene fluoride (PVDF) (Kynar, reagent grade) as binder dispersed in N-Methyl-2-pyrrolidone (NMP) (Sigma Aldrich >99 %) was prepared using a shaker mill (20 min). This slurry was tape casted on Al foil as current collector and dried for 12 h at  $90^\circ\text{C}$  in vacuum. Circular cathodes ( $\varnothing 16 \text{ mm}$ ) with a solid load of about  $1.5 \text{ mg cm}^{-2}$  were cut from the casts. Using these cathodes, CR2016 coin cells were assembled in a glove box (dry Ar atmosphere). Circular Li discs acted as counter electrodes, separated by a Celgard 2400 PP film. The applied electrolyte was 1 M  $\text{LiPF}_6$  dissolved in a 1:1 volume ratio of ethylene carbonate/diethyl carbonate solution (Aldrich Battery grade). The measured capacities are reported with respect to the mass of the carbon coated composite. The charge rate, C, was defined as a current density of  $160 \text{ mA g}^{-1} = 1\text{C}$ . After galvanostatic cycling experiments, selected batteries were disassembled in a glove box, and XRD scans of the cathode were recorded to investigate the structural integrity. Scans were recorded from 15 to  $65 2\theta$  (step-size of 0.013, integration time

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