



## Water based processing of $\text{LiFePO}_4/\text{C}$ cathode material for Li-ion batteries utilizing freeze granulation

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### ABSTRACT

A water based solid state synthesis of  $\text{LiFePO}_4$  has been conducted by utilizing freeze granulation. Various processing conditions were tested and achieved powder properties were characterized by density, XRD, specific surface area, carbon content, conductivity and SEM. Freeze granulation, a novel method for precursor preparation was shown to be an effective method to provide high degree of homogeneity prior to calcination and high ultimate yield of pure  $\text{LiFePO}_4$ . Cathodes were manufactured by water based as well as NMP system based tape casting. A commercial  $\text{LiFePO}_4/\text{C}$  powder was also characterized and used to manufacture cathodes as comparison in this study. Charge cycling tests showed promising results with high capacity and long term stability, well in the range of what the commercial powder provided. Post-milling of calcined powder prior to paste preparation for tape casting tended, however, to retard the capacity owing to disturbed carbon distribution and loss of conductivity of the  $\text{LiFePO}_4/\text{C}$ . In comparison with the solvent system for cathode manufacturing, the water based system gave similar cell performance, illustrating the possibility to apply a more environmentally sustainable processing of Li-battery cells.

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### 1. Introduction

Production of electrical vehicles is foreseen to grow substantially in the near future with an accompanying request of up-scaled battery production. Therefore, it is strongly and urgently motivated to apply environmentally and economically sustainable concepts for the manufacture of battery cells including the entire chain from synthesis of the active electrode materials to the manufacture of electrodes and battery cells. With this motivation, our work was focused on the following topics; processing of low cost and high performance  $\text{LiFePO}_4$  applying freeze granulation as well as replacing organic solvents and fluorinated polymers with water and a more environmental friendly polymer for the cathode manufacture.

As active cathode material, Li-based compounds, especially  $\text{LiFePO}_4$ , have been in focus during recent time [1]. Primarily, there is a need to ensure reliable, cost efficient and environmentally sustainable synthesis routes of the  $\text{LiFePO}_4$  material prior to cathode production in order to establish realistic conditions for production scale-up. This should preferably include water processing of low cost precursors applying a cost effective synthesis

method prior to calcinations, still reaching a high yield of high performance cathode material. Secondly, a water-based manufacture of the cathode has to be established that meet all the environmental, economical and performance demands that will be raised in the near future.

There exist many different routes for synthesis of  $\text{LiFePO}_4$ , which regards the basic method, types of precursors as well as the medium used for the precursor preparation prior to reaction in the thermal treatment step (calcination). Schematically, the methods used can be divided into two main groups; solid state and solution chemical synthesis [1,2]. Moreover, there are a large variety of methods within each of these groups, especially within the latter. In general, the use of soluble reagents should provide greater homogeneity of the precursors as the mixing can be conducted on a molecular size-scale in contrast to what is the case in solid state syntheses. The synthesis process includes a drying step, normally done by evaporation, spray-drying or similar methods. Typically these conventional drying techniques lead to migration effects, separation of species, and loss of homogeneity in the dried precursor mix. Precipitation of dissolved salt mixes or sol-gel techniques prior to drying may reduce this effect but has to be carefully controlled and tends to make up-scaling complicated and expensive. The solid state synthesis routes, in general, offer simpler concepts for the  $\text{LiFePO}_4$  production that makes it easier to scale-up but normally suffer from a lesser degree of precursor homogeneity

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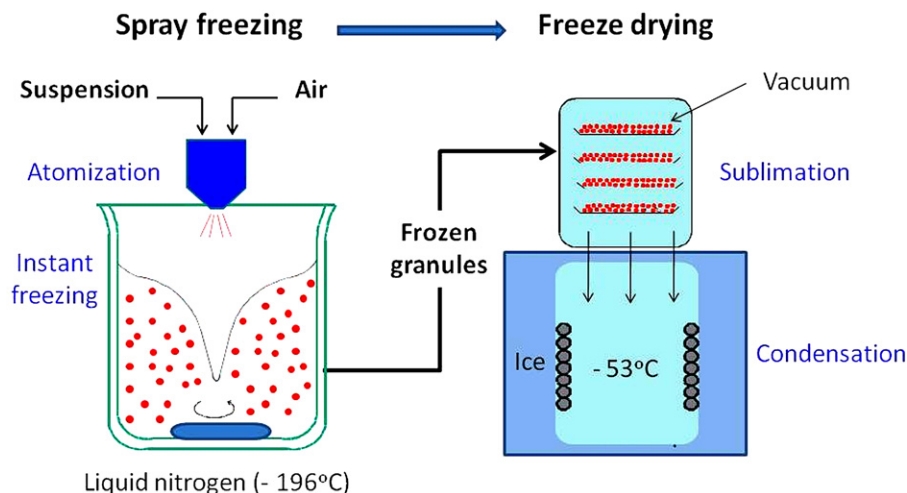


Fig. 1. Schematic illustration of the freeze granulation process.

and, hence, low ultimate purity and electrochemical performance. However, by developing the process of the solid precursor, for example by milling, and utilizing a drying technique that prevents migration, the yield of pure  $\text{LiFePO}_4$  can be substantially improved. Such a processing technique is Freeze Granulation. The Swedish Ceramic Institute (SCI) developed Spray Freeze Drying (SFD) or Spray Freezing into Liquid (SFL) for granulation of ceramic powders in the 1980s and since then this process was called Freeze Granulation (FG). It has been observed that FG provides granules with better homogeneity and superior sintering performance of ceramics after pressing than other granulation methods do [3]. The freeze granulation process is based on instant freezing of sprayed droplet (granules) of a powder suspension into stirred liquid nitrogen. This rapid freezing minimizes ice crystal growth that can disturb homogeneity that tends to occur during conventional freezing of larger volume units. In the subsequent freeze drying the frozen liquid is removed by sublimation. The granule size and density can be controlled by changing the powder concentration, adapt the atomizing airflow and suspension feed into the spray nozzle. Fig. 1 schematically shows the freeze granulation process.

The sublimation in the freeze drying step prevents any liquid formation. As a result, many of the problems appearing when using other types of granulation methods (for example spray-drying), such as granule shrinkage, formation of cavities, strong inter-particle bonds and migration of additives and/or smaller particles to the granule surface, are avoided (see Fig. 2). Hence, the FG process provides granules with high degree of homogeneity that easily can be broken down in a subsequent processing step such as pressing or re-dispersing in a liquid. Normally, spherical granules with a size distribution in the range of 20–400  $\mu\text{m}$  are obtained by FG. Freeze granulation can be conducted with water as well as with organic solvents having a freezing point in the range of  $-20\text{ }^\circ\text{C}$ – $+10\text{ }^\circ\text{C}$ . Solvents with lower freezing point give rise to problems in the freeze drying process whereas those with a freezing point higher than  $+10\text{ }^\circ\text{C}$  can cause clogging of the spray nozzle.

In this study the purpose to use FG was to preserve the homogeneity of wet milled mixes of precursors until calcination took place in order to maximize the output of fine grained  $\text{LiFePO}_4$  with accurate phase composition. Wet milling prior to FG is supposed to

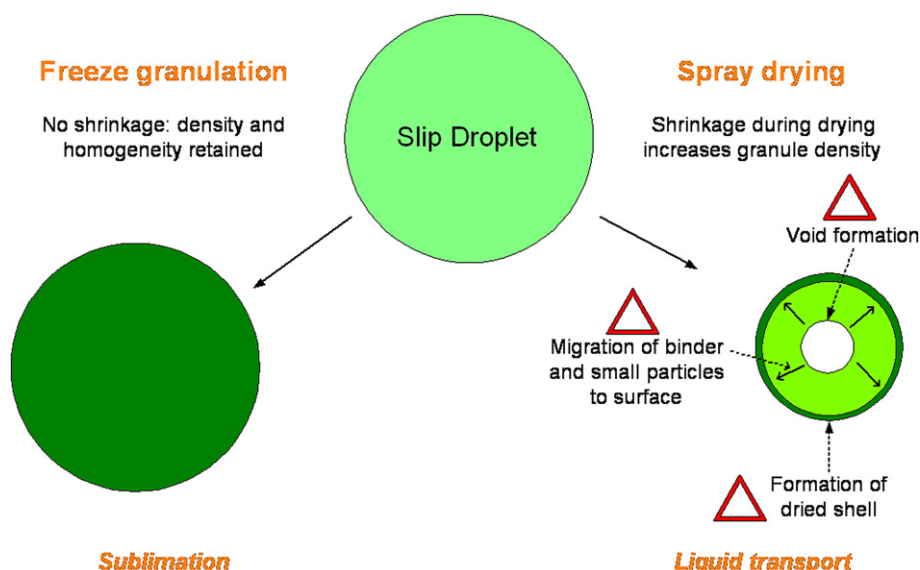


Fig. 2. Illustration of granule formation in freeze granulation vs spray-drying.

enhance the output by reducing the particle size of the precursor, promote the homogenization and support the reaction between the reactants. Additionally, since no shrinkage of the granules or strong bonds within the granules occurs with FG, a fairly loose structure of the fine primary particles also after calcination could be expected. However, paste preparation for casting of the cathode material may be conducted by less powerful mixing methods such as impeller stirring. To further enhance the separation of the primary particles in this step, a pre-milling of the calcined material and a new FG operation prior to paste preparation for cathode casting can optionally be applied.

Conclusively, the use of water based processing, milling, low cost precursors and FG, opens up a possibility to establish a reliable process for production of LiFePO<sub>4</sub> powder with high quality at a reasonable cost.

The next step, the electrode manufacturing, typically involves the use of polyvinylidene difluoride (PVdF) as binder, which requires the use of large amounts of flammable organic solvents, such as *N*-methyl-2-pyrrolidone (NMP), to obtain a stable suspension. NMP has been identified as environmentally harmful, toxic and reproductive damaging [4], thus introducing safety concerns in the manufacturing process. Besides the health/environmental aspects, NMP is an expensive solvent and the processing of toxic chemicals in large scale renders significant costs to meet national and international regulations that tend to be sharpened over time. Since ecotoxic chemicals are used to produce fluorinated polymers there are also environmental concerns about using PVdF as binder in the electrodes. In addition, PVdF is relatively costly and not easily disposable at the end of the battery life [5]. Therefore, when considering the overall electrode preparation process, the use of a safe and low cost material such as LiFePO<sub>4</sub> alone is insufficient for the development of greener batteries.

Zackrisson et al. [6] has made a life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles. In this study a battery made with NMP as solvent was compared with a battery made with water as processing medium. This study showed that also with respect to global warming it is environmentally preferable to use water as solvent instead of NMP in the slurry for casting cathodes and anodes of lithium-ion batteries. The battery made using NMP leads to emissions of about 4400 kg CO<sub>2</sub> equivalents, while the battery made using water leads to about 3400 kg CO<sub>2</sub>eq life cycle emissions. The difference occurs in the production phase and is mostly due to the fact that the battery with NMP uses PVdF as a binder.

According to a study by Muthu [7], the battery production costs would be significantly reduced if a water-based manufacturing process is used instead of a solvent-based one. In comparison with a traditional solvent-based process, it is reported that a water-based process will reduce capital investment costs by 10%, the waste management expenses by 85%, solvent costs by 65% and the cost of energy consumption by 10%. A facility with water-based process results in a radical reduction in volatile organic compound (VOC) emissions, lower energy consumption and a simplified process with environmental permits. Consequently, a water-based based manufacturing process is favourable in most aspects.

The transition from the non-aqueous to aqueous coating process has encountered difficulties related to slurry formulation, viscosity control and film processing. However, several works have reported a satisfactory switch from a non-aqueous to an aqueous processing for graphite-based anodes, in most cases by using a combination of carboxymethyl cellulose (CMC) and styrene-butadiene rubber latex (SBR) [8–16]. The number of publications on water-based production of cathode materials are limited, but the results

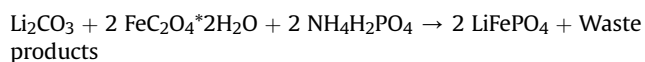
reported so far show that LiFePO<sub>4</sub> can be processed in aqueous slurries [5,17–20].

In the present work, water based solid state synthesis of LiFePO<sub>4</sub> has been conducted by utilizing ball milling and freeze granulation as pre-processing of the precursor including PVA as carbon source. Various processing conditions were tested and achieved powder properties were characterized by density, XRD, specific surface area, carbon content, conductivity and SEM. Further, cathodes were manufactured by tape casting with water based as well as NMP systems. A commercial LiFePO<sub>4</sub>/C produced by Linyi Gelon New Battery Materials Co (China) was also characterized and used as comparison in this study. Battery cells were assembled and the electrochemical performance were evaluated and compared by galvanostatic cycling.

## 2. Experimental

### 2.1. Raw materials and suspension preparation

As precursor composition, lithium carbonate (13010, Sigma Aldrich), iron (II) oxalate dihydrate (307726, Sigma Aldrich) and ammonium phosphate monobasic (A1645) was chosen as a commonly used set of starting materials [21]. Stoichiometric relation between the reactants was used according to the reaction



Li<sub>2</sub>CO<sub>3</sub> and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O remain solid in water whereas NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> is completely dissolved. Li<sub>2</sub>CO<sub>3</sub> was initially ball milled 20 h in deionized water at a concentration of 30 vol% with addition of 0.3 wt% dispersant (Dolapix PC21, Zschimmer & Schwarz GmbH) based on powder. FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O and additional deionized water was added for another 24 h of ball milling at an ultimate powder concentration of 40 vol%. After completed milling the suspension was separated from the balls and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> aqueous solution (15 vol%) was added during stirring. The resulting suspension was stirred for 4 h and then divided into two parts. PVA (Mowiol 4-88, Kuraray Co, Ltd) as carbon source was added as aqueous solution (20%) in 5 or 7 wt% based on solid content, including the dissolved ammonium salt.

### 2.2. Freeze granulation

The precursor suspensions with PVA were sieved (250 μm) and freeze granulated utilizing a lab scale freeze granulator (LS-2, PowderPro AB, Sweden) applying a suspension feed of 1 L per hour and an atomizing air pressure of 30 kPa (0.3 bar). Produced frozen granules were freeze dried (Lyovac GT 2, SRK System Technik, Germany) where water was sublimated under controlled vacuum conditions. In a separate experiment the eutectic point of the media (the freezing point of the suspension) was investigated by continuously measuring the temperature and resistance during cooling the media [22]. The instant increase in suspension resistance indicated a eutectic or freezing point for the suspension of ca –16 °C. Therefore, the vacuum pressure in the drier was set to 5.7 Pa, which corresponds to a temperature of –26 °C, to insure sublimation of water from the frozen granules without any risk for melting. Dried granules were sieved (<355 μm) and stored for the calcination experiments.

### 2.3. Calcination

It has been reported that the crystallization temperature of amorphous LiFePO<sub>4</sub> is between 450 and 570 °C [1,23]. Moreover,

according to literature, PVA converts into aromatics and substituted olefins and further on to amorphous carbon at pyrolysis temperatures higher than 400 °C in inert or reducing atmosphere [24]. In many papers the LiFePO<sub>4</sub> materials that show the highest performance were calcined in the range of 600–800 °C [23,25–30]. In addition, the use of inert or even reducing atmosphere during calcination is necessary in order to prevent formation of undesirable Fe<sup>+3</sup> compounds and avoid oxidation of the carbon residues [25]. Thus, in this study it was decided to choose 700 °C as calcination temperature and evaluate the use of nitrogen or argon + 10% hydrogen as atmosphere applying a heating rate of 1 °C min<sup>-1</sup> and 10 h dwell time for calcination of the freeze dried precursor granules in a graphite resistance furnace (Pfeiffer Balzer, COV 373).

#### 2.4. Evaluation of calcined materials

Specific surface area of the as-calcined powder granules was measured according to the multi-point BET method (Gemini 2360, Micromeritics, US). Further, the powder density was measured with a helium pycnometer (AccuPyc 1330, Micromeritics, US). An automatic elemental analyzer (Heraeus Instruments GmbH, Germany) was used in order to determine the amount of carbon within the LiFePO<sub>4</sub>/C granules. The device uses a flow of pure oxygen at heating up to 800 °C to oxidize the carbon and measure the amount of carbon dioxide that passes through the filters and after calibration revealing the amount of residual carbon. The commercial LiFePO<sub>4</sub>/C (Linyi Gelon New Battery Materials Co) was similarly characterized for comparison.

The crystal structures of the prepared powder samples as well as the Gelon powder were examined by powder X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with chromium tube. Scanned data were collected over the 2θ range of 20–75° and the step size was 0.1° with a counting time of 10 s. The microstructure of the LiFePO<sub>4</sub>/C was investigated by field-emission scanning electron microscopy (Jeol, JSM-840A, SEM/EDX) by using secondary electron emission. Additionally, elemental map analysis was applied in order to investigate the homogeneity and distribution of the comprising elements (Fe, P and O) of LiFePO<sub>4</sub>/C.

Conductivity measurement of the produced LiFePO<sub>4</sub>/C materials was examined by preparing 12.6 mm tablets (ca 2 mm thickness) of the calcined granules. Two tablets of each material were hydraulic pressed at 88 MPa and subsequently cold isostatic pressed (C.I.P. 42260, Avure technologies) at 300 MPa. The top and bottom surfaces of the tablets were coated with a nano-silver paste (nanoTach, NBE Tech, LLC) to provide an adequate surface contact for the conductivity measurement. The resistances of the silver coated tablets were investigated through their thickness by measuring with a multimeter (FLUKE 23 Series II Multimeter). The conductivity was calculated by using the formula  $\sigma = L/(R \cdot A)$  in which  $\sigma$  is conductivity (S m<sup>-1</sup>),  $L$  is thickness (m),  $R$  is resistance (Ω) and  $A$  is cross-sectional area (m<sup>2</sup>). Tablets for conductivity measurement of the commercial Gelon powder could unfortunately not be produced owing to insufficient cohesion of the powder at pressing causing failure at pressure release.

#### 2.5. Electrode preparation and electrochemical evaluation

Cathodes were manufactured for electrochemical characterization. Selected LiFePO<sub>4</sub>/C, based on the powder characterisations, was wet ball milled to break down hard granules that possibly could be present after calcination. To facilitate proper dispersion of the active material in water or solvent when preparing paste for tape casting, the milled LiFePO<sub>4</sub>/C was freeze granulated once again. This was done to create weak granules, which easily could be

disintegrated at the paste preparation using impeller mixing of LiFePO<sub>4</sub>/C, polymeric binder and conductive additive.

The granulated LiFePO<sub>4</sub>/C was thoroughly mixed with carbon black (Super P-Li, Timcal) and a modified styrene–butadiene rubber (SBR) copolymer (LHB-108P, LICO Technology) by using deionized water. For comparison cathodes were also manufactured with a conventional solvent-based system, i.e. with NMP (<99%, Alfa Aesar) as solvent and PVdF (Kynar 900 HSV, Arkema Inc.) as binder. The compositions are given in Table 1. Two water based pastes with the commercial LiFePO<sub>4</sub>/C powder from Linyi Gelon New Battery Materials were also prepared; one where the powder first had been wet ball milled and granulated before mixing with carbon black and SBR, like the LiFePO<sub>4</sub> synthesized in this work, and one where no pre-treatment had been done. The reason for the different paste compositions used was due to variations in wetting of the Al-foil and tape drying performance with the different powders. For example, milling and re-granulation of the calcined and the Gelon powder required higher amount of binder for proper wetting/adhesion to the aluminium foil as well as to avoid cracking at drying.

The obtained pastes were applied onto aluminium foil by tape casting with 80 μm blade gap. After drying, the electrodes were punched in the form of disks with a diameter of 1.5 cm, pressed with 20 MPa and finally dried at 120 °C (in air) for 15 h. The cathodes had a typical layer thickness of 30–40 μm containing 3–4 mg cm<sup>-2</sup> of active material. Two-electrode electrochemical cells were assembled in an argon-filled glove box (H<sub>2</sub>O and O<sub>2</sub> < 1 ppm). Lithium foil (Linyi Gelon New Battery Materials Co) and Celgard 2325 (Celgard, LLC) were used as an anode and a separator, respectively. The electrolyte was 1 M LiPF<sub>6</sub> in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) solution (LP 40 SelectiLyte from Merck). The electrochemical performance was evaluated by cycling under galvanostatic control at 0.1 and 1C rates over the potential range 2.7–4.2 V versus Li/Li<sup>+</sup> using a potentiostat/galvanostat (EG&G Model 173, Princeton Applied Research).

### 3. Results and discussion

#### 3.1. Processing aspects

During preparation of the precursor suspension, foaming occurred when the dissolved NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was added to the ball milled mix of Li<sub>2</sub>CO<sub>3</sub> and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. This indicates that the ball milling created reactive particle surfaces resulting in an immediate reaction in contact with the dissolved NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and a gas formation (most probably hydrogen) as by-product. The fact that dispersant was used in the milling operation could be expected to have supported milling efficiency as well as the following foaming reaction due to the situation of well dispersed powder particles. The reaction and foaming ceased out and the suspension became stable after about 1 h stirring and the freeze granulation was conducted without disturbances.

During suspension preparation for tape casting of the cathode material, the pre-milled and re-granulated powder was easily

**Table 1**  
Electrode composition and solid loading in the slurry.

LiFePO <sub>4</sub> powder	Solid loading in slurry (wt%)	Composition (wt%)			
		LiFePO <sub>4</sub>	CB	SBR	PVdF
Freeze granulated	55	85	9	6	–
Freeze granulated <sup>a</sup>	27	80	10	–	10
Gelon, re-granulated	55	87	5	8	–
Gelon, untreated	55	90	6	4	–

<sup>a</sup> With NMP solvent.

**Table 2**  
Properties of produced LiFePO<sub>4</sub>/C powders and the commercial Gelon version.

Sample	Calcination		PVA (wt%)	BET-area (m <sup>2</sup> g <sup>-1</sup> )	Carbon content (wt%)
	Temp. (°C)	Atmosphere			
N-7	700	N <sub>2</sub>	7	25.8	3.1
H-5	700	Ar + 10% H <sub>2</sub>	5	34.9	2.8
H-7	700	Ar + 10% H <sub>2</sub>	7	29.6	3.7
Gelon	–	–	–	35.9	4.3

dispersed in water by impeller stirring, a smooth paste was obtained and the casting worked out well. The system with NMP required significantly more dilution in order to achieve a castable suspension. A disadvantage of ball milling the calcined LiFePO<sub>4</sub>/C could be a negative influence of the carbon distribution and possible degradation of the LiFePO<sub>4</sub> phase composition by oxidation. It has been claimed that water or humidity exposure can have an ageing effect on LiFePO<sub>4</sub>, for example at long time storage without specific protection against ambient atmosphere [31]. In our case, energy in-put by the applied ball milling might also speed up such degradation.

### 3.2. Evaluation of calcined materials

Table 2 shows data from measurements of specific surface area, carbon content of as-calcined LiFePO<sub>4</sub>/C and the commercial Gelon powder version. As expected, the tendency was that higher PVA content in the precursor composition and more reducing calcination atmosphere favoured higher ultimate carbon content. The resulting surface area for the various powders was in the range of 25–35 m<sup>2</sup> g<sup>-1</sup>, indicating a nano-structured character of the powders. A high surface area is considered positive for the electrochemical performance of the material owing to a high degree of accessibility of the active cathode material in the application [30]. For the produced powders the surface area was on such a level that nano-structured properties can be expected and the accessibility aspect is enhanced. The commercial Gelon powder showed similar characteristics with only slightly higher surface area and carbon content compared to the synthesized powders.

Table 3 shows results from density and conductivity measurements for the powder calcined in Ar + 10% H<sub>2</sub>, before and after milling and re-granulation. The powder density was almost the same for H-7 (as-calcined) and H-7X (milled and re-granulated H-7) but the tablet density increased by the milling/re-granulation process. This better compaction performance was probably due to weaker bonding within the granules compared to the as-calcined powder. However, as the latter displayed higher conductivity than the milled/re-granulated version, despite of lower tablet density, a negative impact by the milling was indicated, an effect probably owing to disturbed carbon distribution and/or altered phase composition. For comparison, the density of the commercial Gelon powder was measured to 3.60 g cm<sup>-3</sup>, i.e. slightly lower than for the synthesized powders in this study. The reason for the poor pressing performance of this powder in terms of tablet failure at pressure release might be due to stronger particle clusters and a strong spring-back effect achieved. In comparison, the use of freeze

**Table 3**  
Density of powder and pressed tablets and measured conductivity.

Sample	Powder density (g cm <sup>-3</sup> )	Tablet density (g cm <sup>-3</sup> )	Conductivity (S m <sup>-1</sup> )
H-7	3.67	1.78	1.65
H-7X <sup>a</sup>	3.73	1.87	1.30

<sup>a</sup> Milled and re-granulated H7.

granulation prior to calcination and, even more, when calcined granules are milled and re-granulated prior to pressing, looser granules and better pressing performance is obviously achieved.

The resulting X-ray diffraction patterns are shown in Fig. 3 with the LiFePO<sub>4</sub> olivine pattern inserted as red bars. The diffraction patterns of the produced powder H-7, the post-treated H-7X and the commercial Gelon powder are very similar and all displayed a high degree of pure crystalline LiFePO<sub>4</sub>. No or very small contents of other phases could be detected. The intensity of the peaks was also similar for the three materials with only slightly lower intensity for the H-7 powder. Overall, the XRD results show that the reason for the lower conductivity of the post-treated H-7X is rather an effect of carbon re-distribution than a phase decomposition.

Fig. 4 shows SEM images of the LiFePO<sub>4</sub>/C granules processed with 7% PVA and calcined at 700 °C in 10% hydrogen, as-calcined H-7, milled/re-granulated H-7X and the commercial Gelon powder. In general produced granules are highly porous, consisting of a network of particles in the size range of a few hundred nanometres. The reducing condition at calcination and the resulting presence of carbon limits grain growth and should be responsible for the fine structured materials. From the SEM images it is difficult to detect any clear difference between as-calcined (a) and milled/re-granulated (c) powder. Both have minor quantities of iron rich grains (white) displayed in the cross-section images (b and d). On the other hand, the commercial Gelon powder (e and f) typically appears as a mix of porous particles with denser shells among smaller particles with more even density.

Elemental mapping of the LiFePO<sub>4</sub>/C powders regarding iron, oxygen and phosphorus are shown in Fig. 5. It is clear that all the elements are well distributed in the produced LiFePO<sub>4</sub>/C, a homogeneity that reflects the high yield of pure LiFePO<sub>4</sub> according to XRD, with a limited particle size and high surface area.

### 3.3. Electrochemical performance

The charge-discharge voltage profiles at current densities corresponding to a rate of 0.1C and 1C of a Li/LiFePO<sub>4</sub> cell containing a cathode with SBR as binder is shown in Fig. 6. The cell was cycled between 2.7 and 4.2 V, and the same cycling rates during charge and discharge were used. The flat voltage plateau over a wide voltage range at approximately 3.4 V is typical of a well-defined LiFePO<sub>4</sub> olivine structure indicating the two-phase redox reaction between LiFePO<sub>4</sub> and FePO<sub>4</sub> [32]. The obtained discharge capacity at the current rate 0.1C was 141 mA h g<sup>-1</sup>, which corresponds to 83% of the theoretical capacity (170 mA h g<sup>-1</sup>), a bit lower compared to the practical capacity of approximately 155 mA h g<sup>-1</sup> usually reported for LiFePO<sub>4</sub>-based cathodes at low C-rates [1]. The specific discharge capacity being inferior to the theoretical capacity might have several different reasons as the electrochemical insertion/extraction properties of LiFePO<sub>4</sub>/C are for example dependent on the powder morphology, particle size, impurity content, carbon source and electronic conductivity of the material. Phase-pure, highly crystalline, small particles with high surface area, uniform particle size distribution and a uniform carbon coating results in high specific capacity and stable cycle properties [1,33].

The purpose of coating the surfaces of the LiFePO<sub>4</sub> particles with a carbon source during synthesis was to enable good surface electronic conductivity so that the active material could be fully utilized. The structure of the formed carbon as well as the uniformity of the coating is important in achieving high performance. PVA has earlier been used as carbon source with good result by Yun et al. [25], but it has been reported that higher electronic conductivity and better performance is achieved by using organic precursors having carbon-ring structures, such as polystyrene and sugar [34]. Thus, changing the organic source and also the amount

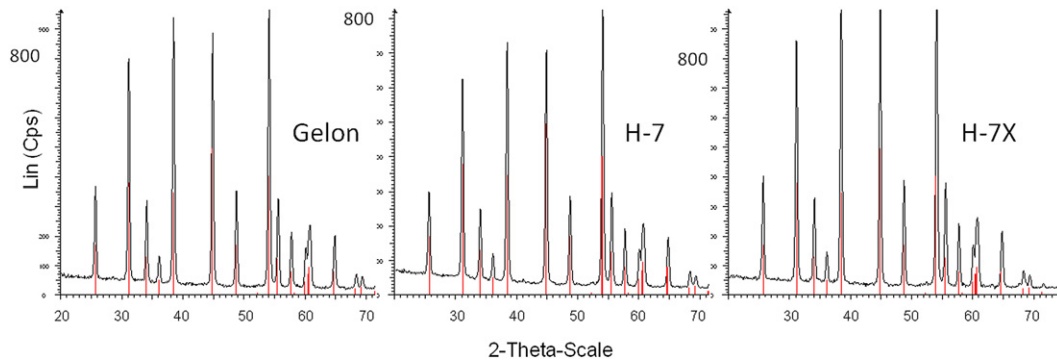


Fig. 3. X-ray diffraction patterns of produced and commercial LiFePO<sub>4</sub>/C powder respectively.

of carbon might increase the capacity obtained in this case. However, probably more important than the organic source is the effect of the process used at the preparation of the suspension. As indicated by the conductivity measurements (Table 3) the milling and re-granulation of the LiFePO<sub>4</sub>/C powder seems to negatively influence the homogeneity of the carbon coating and thus impair the electron diffusion possibilities. Accordingly, it should be possible to improve the capacity if this process step can be avoided. The conclusion that the milling/re-granulation process has affected the electrochemical performance is supported by test results where the commercial powder from Gelon has been processed with and without milling/re-granulation. As seen in Fig. 7, the discharge capacity decreased with approximately 9% from 154 mA h g<sup>-1</sup> to 140 mA h g<sup>-1</sup> when the milling/re-granulation step was introduced. The latter value is equivalent to the capacity of the LiFePO<sub>4</sub>/C powder produced in this work.

The problem with inhomogeneous carbon coating and hence lower electronic conductivity should be possible to solve by controlling the freeze granulation in terms of granule size distribution and to avoid milling after calcination. However, although the milling effect seems to be the main reason for the capacity being lower than anticipated, there are also other parameters which could be optimized to further improve the electrochemical performance. The calcination temperature is a very important synthesis parameter that influences the electrochemical properties. Too high temperature leads to the formation of larger particles with lower surface area, whereas too low temperature results in decreased capacity because of the lower crystallinity of the samples and presence of impure phases [1]. The calcination temperature used at the synthesis of LiFePO<sub>4</sub> in this report was 700 °C, but this temperature was not fully optimized. Although the X-ray diffraction and SEM images indicated high purity and small particle size, it

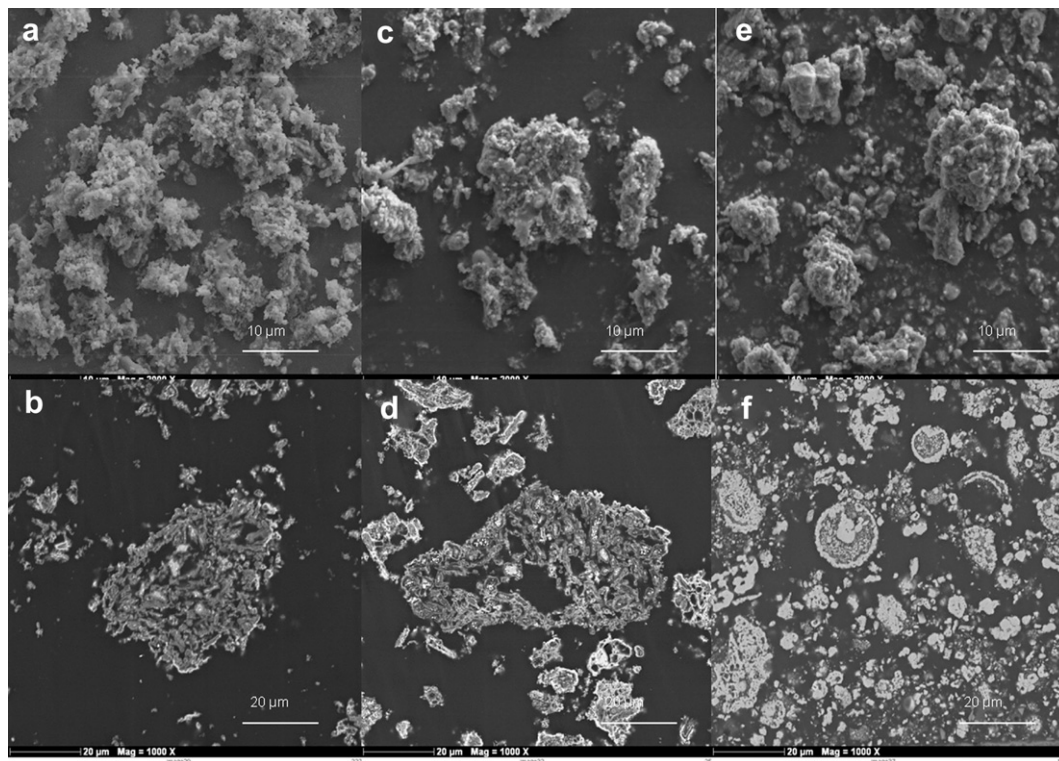


Fig. 4. SEM images of LiFePO<sub>4</sub>/C powder; a) As-calcined H-7, b) As-calcined H-7 cross-section, c) Milled/re-granulated H-7X, d) Milled/Re-granulated H-7X cross-section, e) Gelon, f) Gelon cross-section.

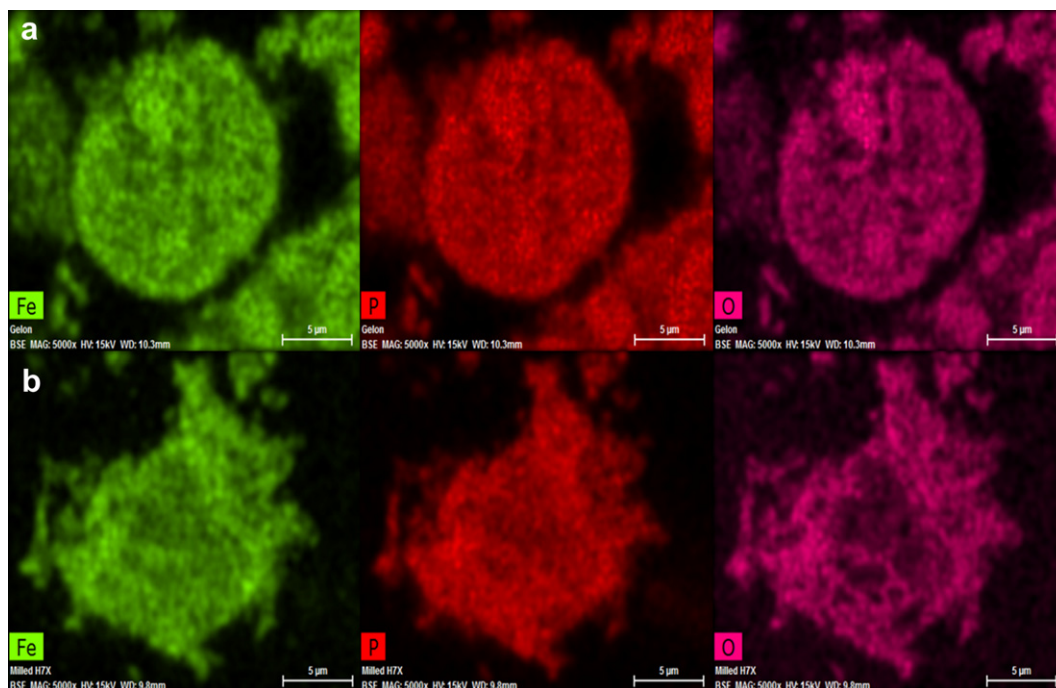


Fig. 5. Fe, P and O elemental mapping of LiFePO<sub>4</sub>/C a) Gelon powder and b) H-7X.

might be possible to further improve the results by changing the calcination temperature.

As seen in Fig. 6, the capacity decreased from 141 mA h g<sup>-1</sup> to 111 mA h g<sup>-1</sup> when the current rate was increased from 0.1C to 1C. Electrochemical performance at higher rates was not tested. Except low electronic conductivity due to the inhomogeneous carbon coating of the LiFePO<sub>4</sub>/C particles, high porosity can explain the large decrease in capacity as high porosity results in a low overall electronic conductivity of the electrode. The estimated porosity of the tested electrodes was 50%, which is quite high compared to porosity values generally observed [35]. When the cell was tested once again at the initial 0.1C rate after it had been tested at 1C for a few cycles, the same capacity was obtained as on the fresh cell. Accordingly, the capacity loss at the higher charge/discharge rate was related to the increase in internal resistance, and not to degradation of the material.

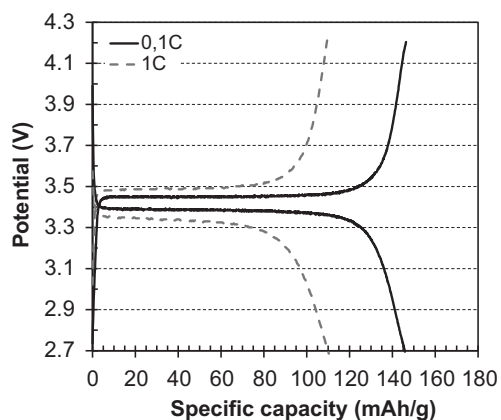


Fig. 6. The fifth charge and discharge curve of a cathode based on the freeze granulated LiFePO<sub>4</sub>/C powder H-7X (calcined at 700 °C in Ar/H<sub>2</sub>) with SBR as binder evaluated at various C-rates.

The purpose of this work was to use environmentally friendly processes not only at the synthesis of the LiFePO<sub>4</sub>/C powder, but also during subsequent electrode manufacturing. Thereby, the aqueous-based process was used at the electrode preparation. The aqueous-based electrode with SBR has also been compared to a conventional electrode material with PVdF as binder and cast with NMP solvent. The PVdF and CB concentration were not optimized, but corresponded to commonly used concentrations [19]. As seen in Fig. 8, the specific capacity of the PVdF-based electrode displays similar values as the electrode with SBR at both 0.1C and 1C rate. The capacity of the PVdF electrode at 0.1C is slightly higher than that with SBR, but at 1C the situation is the opposite. Accordingly, the SBR binder does not seem to negatively influence the electrochemical properties compared to the conventional binder system.

The behaviour of the electrodes containing SBR and those containing PVdF were also observed during long-term cycling tests

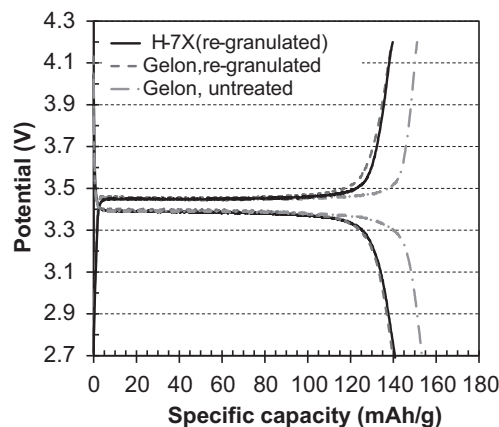
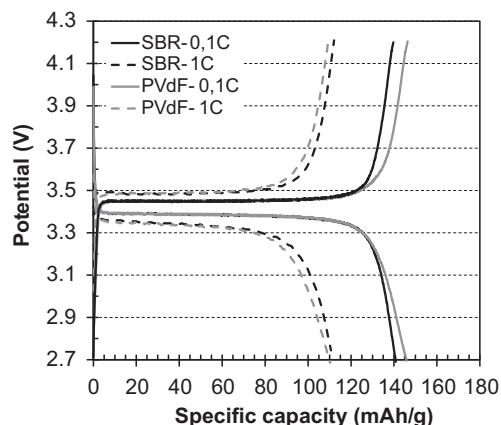
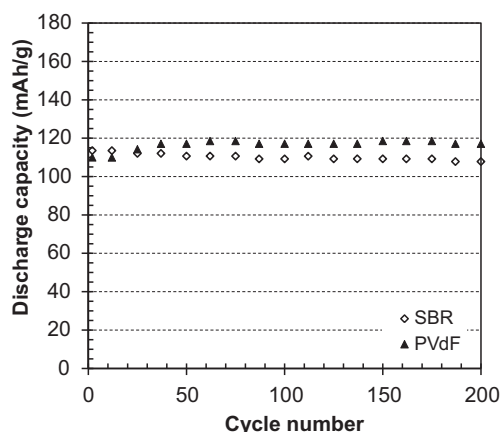


Fig. 7. Fifth cycle of cathodes based on SBR binder and the commercial LiFePO<sub>4</sub>/C from Gelon or the LiFePO<sub>4</sub>/C powder H-7X (calcined at 700 °C in Ar/H<sub>2</sub>) produced in this work. Charge/discharge rate was 0.1C. Cathodes with Gelon powder prepared with and without the milling/re-granulation process are also compared.



**Fig. 8.** The fifth charge and discharge curve of cathodes based on the freeze granulated LiFePO<sub>4</sub>/C powder H-7X (calcined at 700 °C in Ar/H<sub>2</sub>) with SBR and PVdF binders respectively at different discharge rates.



**Fig. 9.** Cycle life of cathodes based on the freeze granulated LiFePO<sub>4</sub>/C powder H-7X (calcined at 700 °C in Ar/H<sub>2</sub>) prepared with SBR and PVdF respectively evaluated at 1C rate.

with the results presented in Fig. 9. At a current density corresponding to 1C rate, the SBR-based electrode displayed an initial discharge capacity of approximately 114 mA h g<sup>-1</sup>. After 200 cycles, the capacity had decreased to 107 mA h g<sup>-1</sup>, which is 94% of its initial value. This corresponds to an average capacity fading of only 0.03% per cycle, which is considered good [1]. The initial discharge capacity of the PVdF-based electrode was 110 mA h g<sup>-1</sup>, but the discharge capacity gradually increased in subsequent cycles, reached a maximum at approximately 118 mA h g<sup>-1</sup> after 35 cycles, and then stabilized. The capacity was maintained constant after 200 cycles. These results clearly show that the LiFePO<sub>4</sub>/C powder synthesized by freeze granulation is able to exhibit very good capacity retention and can be considered as a promising electrode material. The PVdF-based electrode showed slightly better reversibility than the SBR-based one, but both displayed acceptable values.

#### 4. Conclusions

It has been shown that water based processing for both powder synthesis and cathode manufacture can be applied for Li-ion battery production with promising results. In this initial trial with solid-state synthesis of LiFePO<sub>4</sub>/C, utilization of freeze granulation for precursor preparation was shown to be an effective method to

provide a high degree of homogeneity prior to calcination and high ultimate yield of pure LiFePO<sub>4</sub>, most likely applicable for synthesis of other materials as well. Wet ball milling of the solid constituents of the precursor mix gave an immediate reaction when the dissolved part was added to the suspension, indicating an activation of the particle surfaces that may also contribute to the positive outcome. The high degree of homogeneity of the calcined material was confirmed by SEM and high LiFePO<sub>4</sub> purity was displayed by XRD, comparable to a commercially available LiFePO<sub>4</sub>/C powder. Cathode material were manufactured by water-based tape casting, using styrene butadiene rubber (SBR) as binder, and assembled into battery cells. Charge cycling showed promising results with high capacity and long term stability, in the range of what the commercial powder provided when exposed to similar processing. In comparison with the solvent system (NMP/PVdF) for cathode manufacturing, the water based system used in this study gave similar cell performance, illustrating the possibility to apply a more environmentally sustainable processing of Li-battery cells.

Since no fine-tuning of precursor composition, calcinations process or cathode paste composition was conducted in this study, potential for improvements can be foreseen. For example, the post-treatment of the calcined powder in terms of milling and re-granulation appeared to be negative for carbon distribution and the powder conductivity and may, therefore, be avoided. Further, optimizing the carbon source and content, processing adaptations of synthesized powder as well as the use of alternative polymer types for the water-based tape casting are other actions to reach even better performance.

#### References

- [1] G. Cheruvally, Lithium Iron Phosphate: A Promising Cathode-Active Material for Lithium Secondary Batteries, Trans Tech Publications, Stafa-Zuerich, Switzerland, 2008.
- [2] D. Jugovi, D. Uskokovi, J. Power Sources 190 (2009) 538–544.
- [3] K. Rundgren, O. Lyckfeldt, M. Sjöstedt, Ceram. Ind. (April 2003) 40–44.
- [4] Scientific Committee on Consumer Safety of the European Commission, Report SCCS/1413/11, 22 March 2011.
- [5] S.F. Lux, F. Schappacher, A. Balducci, S. Passerini, M. Winter, J. Electrochem. Soc. 157 (2010) A320–A325.
- [6] M. Zackrisson, L. Avellan, J. Orlenius, J. Cleaner Prod. 18 (15) (2010) 1519–1529.
- [7] J. Muthu, J. Battaglini, Battery Power Products Technology 13 (6) (2009) 12–13.
- [8] J. Li, R. Lewis, J. Dahn, Electrochem. Solid-State Lett. 10 (2) (2007) A17–A20.
- [9] J.-H. Lee, S. Lee, U. Paik, Y.-M. Choi, J. Power Sources 147 (1,2) (2005) 249–255.
- [10] J.-H. Lee, U. Paik, V.A. Hackley, Y.-M. Choi, J. Electrochem. Soc. 152 (2005) A1763.
- [11] J.-H. Lee, Y.-M. Choi, U. Paik, J.-G. Park, J. Electroceram. 17 (2) (2006) 657–660.
- [12] H. Buqa, M. Holzapfel, F. Krumeich, C. Veit, P. Novák, J. Power Sources 161 (1) (2006) 617–622.
- [13] J.-H. Lee, U. Paik, V.A. Hackley, Y.-M. Choi, J. Power Sources 161 (1) (2006) 612–616.
- [14] S. Zhang, K. Xu, T. Jow, J. Power Sources 138 (1,2) (2004) 226–231.
- [15] M.R. Schweiger, S. Koller, P.R. Raimann, T. Wöhrle, C. Wurm, M. Winter, Electrochem. Solid-State Lett. 11 (5) (2008) A76–A80.
- [16] M. Gaberscek, R. Dominko, F.W. Poulsen, M. Mogensen, S. Pejovnik, J. Jamnik, Electrochim. Acta 48 (7) (2003) 883–889.
- [17] J.-H. Lee, J.-S. Kim, Y.C. Kim, D.S. Zang, U. Paik, Ultramicroscopy 108 (10) (2008) 1256–1259.
- [18] A. Guerfi, M. Kaneko, M. Petitclerc, M. Mori, K. Zaghib, J. Power Sources 163 (2) (2007) 1047–1052.
- [19] W. Porcher, B. Lestriez, S. Jouanneau, D. Guyomard, J. Electrochem. Soc. 156 (3) (2009) A133–A144.
- [20] W. Porcher, B. Lestriez, S. Jouanneau, D. Guyomard, J. Power Sources 195 (9) (2010) 2835–2843.
- [21] C. Parada, C. García Giron, L.E. Fuentes, E. Gonzalo, Phys. Procedia 8 (2010) 33–38.
- [22] N. Trsic-Milanovic, A. Kodzic, J. Baras, C. Dimitrijevic-Brankovic, J. Serb. Chem. Soc. 66 (7) (2001) 435–441.
- [23] L.N. Wang, X.C. Zhana, Z.G. Zhang, K.L. Zhang, J. Alloys Compd. 456 (1,2) (2008) 461–465.
- [24] J.W. Gilman, D.L. VanderHart, T. Kashiwagi (ACS Symposium Series 599), in: G.L. Nelson (Ed.), Fire and Polymers II: Materials and Test for Hazard Prevention, American Chemical Society, Washington, D.C., USA, 1995, p. 161.



- [25] N.J. Yun, H.W. Ha, K. Jeong, H.Y. Park, K. Kim, J. Power Sources 160 (2006) 1361–1368.
- [26] S. Luo, Z. Tang, J. Lu, Z. Zhang, Ceram. Int. 34 (2008) 1349–1351.
- [27] F. Gao, Z. Tang, J. Xue, Electrochim. Acta 53 (2007) 1939–1944.
- [28] A. Xinping, L. HaP, L. Xiaoyaff, L. Qinlin, L. Bingdong, Y. Hanxi, Wuhan Univ. J. Nat. Sci. 11 (3) (2006) 687–690.
- [29] S. Franger, F. Le Cras, C. Bourbon, H. Rouault, J. Power Sources 119–121 (2003) 252–257.
- [30] Y. Xia, M. Yoshio, H. Noguchi, Electrochim. Acta 52 (2006) 240–245.
- [31] K. Zaghib, M. Dontigny, P. Charest, J. Labrecque, A. Guerfi, M. Kopeck, A. Mauger, F. Gendron, C. Julien, J. Power Sources 185 (2) (2008) 698–710.
- [32] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (4) (1997) 1188–1194.
- [33] O. Toprakci, H.A.K. Toprakci, L. Ji, X. Zhang, KONA Powder Part. J. 28 (2010) 50–73.
- [34] W.-J. Zhang, J. Power Sources 196 (2011) 2962–2970.
- [35] B. Lestriez, C.R. Chim. 13 (2010) 1341–1350.