Electrochimica Acta 184 (2015) 381–386

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Ultrafast, low temperature microwave-assisted solvothermal synthesis of nanostructured lithium iron phosphate optimized by a chemometric approach

N. Garino[a,**], A. Bedini[c,1], A. Chiappone[a], C. Gerbaldi[b,*]

[a] Center for Space Human Robotics @Polito, Istituto Italiano di Tecnologia, Corso Trento, 21, 10129 Torino, Italy
[b] GAME Lab, CHENERGY Group, Department of Applied Science and Technology—DISAT, Politecnico di Torino, C. so Duca degli Abruzzi 24, 10129 Torino, Italy
[c] Consultant in Chemistry and Chemometrics, Via Genova 152/26, 10127 Turin, Italy

ARTICLE INFO

Article history:
Received 13 July 2015
Received in revised form 3 October 2015
Accepted 9 October 2015
Available online 22 October 2015

Keywords:
lithium iron phosphate
microwave solvothermal synthesis
chemometric
design of experiment
cathode
lithium battery

ABSTRACT

Nanostructured $LiFePO_4$/C composites having ordered olivine structure are prepared by a newly elaborated low temperature microwave-assisted solvothermal synthesis in the presence of a cationic surfactant. The microwave-assisted approach is simple and cost effective: it significantly decreases reaction times compared to the conventional hydrothermal/solvothermal processes. A study on the influence of the synthesis parameters on both the morphology and the electrochemical behavior of the samples is performed by means of X-ray powder diffraction, N_2 physisorption at 77 K, scanning electron microscopy, cyclic voltammetry and constant current charge/discharge cycling. Moreover, a chemometric approach through design of experiments (DoE) is here successfully demonstrated for the first time for the optimization and fine tuning of the experimental conditions, including synthetic procedure and electrochemical characteristics of the materials. As a result, we show a nanostructured $LiFePO_4$/C with high rate capability and delivering a very stable cycling behavior for more than thousand cycles with excellent Coulombic efficiency and exceptional capacity retention at 1C.

1. Introduction

Secondary Li-ion batteries (LiBs) are extensively used in the market of portable electronics and are rapidly expanding their application as power sources for hybrid electric vehicles (HEV) and electric vehicle (EV) [1]. However, although serious barriers remain for their wider use in large-scale devices, such as the elevated toxicity of the LiB materials (i.e., Co-based cathode materials) and the production costs.

Lithium iron phosphate ($LiFePO_4$) having an olivine-type structure is largely investigated as the most promising cathode materials for the next generation of high performance LiBs powering electric transportation, because of its high theoretical capacity approaching 170 mAh g^{-1}, low toxicity and low cost due to the abundant raw materials [2]. Moreover, $LiFePO_4$ shows excellent cycling characteristics and remarkably stable thermal, chemical and structural features [3], thus great safety, due to the three-dimensional framework of the olivine structure that is stabilized by the strong covalent bonds between oxygen and phosphorous [4–9].

Various synthesis methods have been adopted to prepare olivine-type materials showing different structures, phases, sizes and electrochemical performances, mainly solid-state reactions [10] or wet methods [11–13]. Among them, hydrothermal methods have been widely investigated because they allow an easy control of both morphology and particle size [14–18].

In the perspective of a green chemical approach on electrode materials' synthesis, microwave-assisted processes are definitely greener, faster and cheaper than traditional methods currently used, resulting in a net reduction of time and energy consumption and a lowering of the environmental impact. The combined microwave-hydrothermal process is potentially advantageous for the study and synthesis of olivine cathode materials, mainly offering: an abatement of the reaction time from several hours down to 30 min or even less, an ultrafast heating rate into the liquid reaction medium and an efficient morphology control to produce particles having a narrow

* Corresponding author. fax: +39 011 090 4624.
** Corresponding author. fax: +39 011 090 3401.
E-mail addresses: nadia.garino@iit.it (N. Garino), claudio.gerbaldi@polito.it (C. Gerbaldi).
[1] As a freelance consultant chemist, Ph.D.

http://dx.doi.org/10.1016/j.electacta.2015.10.049
0013-4686/

size distribution [19–22]. In this respect, Murugan et al. [23] employed high temperature microwave synthesis to produce olivine-type $LiMPO_4$ (where M= Fe, Mn, Co), while Ji et al. [24] and Neef et al. [25] applied microwave-assisted synthesis for the development of $LiMnPO_4$ nanostructured cathodes.

In this work, homogeneously crystallized nanostructured $LiFePO_4$/C composite cathodes are successfully synthesized by microwave-assisted solvothermal synthesis exploiting an innovative approach at mild temperature of 80 °C. We prepared the samples in the presence of an organic cationic surfactant, already demonstrated to be fundamental as both dispersing and shape controlling agent, thus decreasing the grain size of the materials and increasing their specific surface areas [11]. The subsequent thermal treatment in inert atmosphere, decomposes the organic surfactant at the surface of the $LiFePO_4$ grains, resulting in improved electronic conductivity and enhanced electrochemical performances. In addition, the reaction conditions are optimized through a design of experiments (DoE) [26], to achieve the best performance as well as to understand how the synthesis parameters affect the properties and cycling ability of the resulting materials. To the best of our knowledge, this is the first example of thorough use of chemometric approach for optimizing the electrochemical performance of phospho-olivine cathodes. The best performing $LiFePO_4$/C composite shows superior characteristics in terms of rate capability at fast discharge regimes as high as 10C and cycling stability upon prolonged operation exceeding 1000 cycles. No comparable results are present now in the literature regarding a $LiFePO_4$/C composite obtained by means of low cost raw materials, as well as an experimental-design-driven simple, fast and cost-effective microwave-assisted synthesis at such mild conditions.

2. Experimental

2.1. Synthesis

$FeSO_4 \cdot 7H_2O$ (purity 99%), H_3PO_4 (purity > 85%), LiOH (purity > 98%) and cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, CTAB) were purchased from Aldrich. The carbon-coated lithium iron phosphate samples were prepared by microwave-assisted synthesis adapting the mild solvothermal procedure in the presence of a cationic surfactant previously demonstrated by Di Lupo et al. [15]. The precursor mixtures were prepared by dissolving proper stoichiometric amounts of reactants in doubly distilled water. The mixture was vigorously stirred for 1 min after adjusting the pH at about 7.5 and, then, quickly transferred in a 270 mL Teflon reactor, having pressure and temperature probe, connected with the microwave furnace (Milestone START-Synth, Milestone Inc Shelton, Connecticut). The reaction conditions and compositions are established in Table 1 and Table 2. The reactor was then cooled to ambient temperature and the resulting precipitate washed with 350 mL of doubly distilled water, filtered and dried overnight at 60 °C. The dried powders were introduced into a horizontal quartz tube equipped with a sintered glass filter (DISA Raffaele e F.lli s.a.s., Milano, Italy); the heated length and diameter of the quartz reactor were 300 and 35 mm, respectively. The quartz tube was positioned inside a tubular furnace (Carbolite, UK) with a temperature control of ±1 °C and heat-treated at 580 °C (heating rate of 2.0 °C min^{-1}) for 12 h in order to obtain the desired crystalline phase along with the carbonization of the organic surfactant forming a homogeneous film coating the active material grains [27]. The flow rate of the nitrogen carrier gas was fixed at 40 sccm.

Table 1
Factor levels for the microwave-assisted solvothermal synthesis. 26-3III Fr. F. design.

Exp. no.	x1	x2	x3	x4	x5	x6
1	0	0	0	0	0	0
2	1	-1	1	-1	1	-1
3	-1	1	1	-1	-1	1
4	0	0	0	0	0	0
5	-1	1	-1	-1	1	-1
6	-1	-1	-1	1	1	1
7	1	1	1	1	1	1
8	1	1	-1	1	-1	-1
9	-1	-1	1	1	-1	-1
10	1	-1	-1	-1	-1	1

Table 2
Factor levels and codes used for the microwave-assisted solvothermal synthesis optimization.

Factor	Code	Low (-1)	High (+1)	Centre (0)
Reaction time (min)	x1	20	40	30
Reaction temperature (°C)	x2	80	120	100
Reagent concentration (mol L^{-1})	x3	0.30	0.15	0.23
Surfactant concentration (mol L^{-1})	x4	0.30	0.15	0.23
Warming ramp (°C min^{-1})	x5	5.0	20.0	12.5
Quantity of EtOH (mol L^{-1})	x6	2.64	5.25	3.95

2.2. The role of design of experiments in materials' optimization

The use of statistical methods for experimental design makes it possible to vary several factors using a minimum number of experimental runs [28]. This approach has several advantages over the “one factor at a time” approach. The key advantages are: fewer experimental runs, increased precision, possibility of estimation of the interaction effects and wider inductive basis. Thus, the use of statistical methods of experimental design is an effective approach to identify the most significant factors regarding the complexity of both the synthetic procedure and the final performance of the synthesized material.

In this case of study, microwave-assisted solvothermal synthesis of $LiFePO_4$ must take into account many reaction variables and, to the best of our knowledge, so far no evidence is reported in the scientific literature about a clear contribution of each reaction parameter to the final electrochemical performance of the synthetized material. Thus, in order to establish the relative influences of the reaction variables, we initially planned different syntheses according to a Design of Experiments (DoE), ad hoc patterned as a three level Fractional Factorial design with six factors, including a replicate point for each synthesis to evaluate the entity of the experimental error, here labelled as 2^{6-3}_{III} Fr. F. design. This design had a Resolution III, meaning that only main effects can be estimated, as three of six factors are confounded with the interaction terms according to the common rules applied for these designs and described elsewhere [29]. This resulted in 10 different experiments being performed over some months' period of work.

The following reaction variables represented the explored factors: reaction time, reaction temperature, reagent concentration, surfactant concentration, warming ramp of the reactor and added quantity of ethyl alcohol. These factors were modified as described in Table 1 and their levels are listed in Table 2 (i.e., the experimental domain for the screening step). Experiments were executed in random order, not to introduce unwanted systematic effects. The experiments were evaluated through the regression

Table 3
Factor levels for the optimized microwave-solvothermal synthesis.

Exp. no.	x1	x2	x3	x4	x5	x6
13	0	-1	1	-1	1	0