



Design of experiment methodology to improve the energy density of lithiated metal phosphates

Sebastien Martinet^{*}, Carole Bourbon, Mariana Amuntencei, Claude Chabrol, Daniel Tomasi, Marlène Rey, Sébastien Patoux

CEA-LITEN, Commissariat à l'Energie Atomique et aux Energies Alternatives, 17 Rue des Martyrs, F-38054 Grenoble Cedex 9, France

ARTICLE INFO

Article history:

Received 14 August 2013

Received in revised form 11 May 2014

Accepted 18 June 2014

Available online 25 July 2014

Keywords:

Lithium

Battery

Phosphate

Design of experiments

Diffusion

ABSTRACT

Phospho-olivines are highly promising cathode materials for lithium-ion batteries. To overcome the low discharge voltage of LiFePO_4 much attention has been paid to the partial substitution of iron by manganese and/or cobalt. In this work focused on lithiated mixed Fe–Mn–Co–B phosphates, we present the first study relative to the use of design of experiments for the optimization of battery active material composition. A good fit is obtained between experimental and adjusted values confirming the quality of the design. This methodology allows us to increase slightly the discharge capacity of $\text{LiFe}_{(1-x-y-z)}\text{Mn}_x\text{Co}_y\text{B}_z\text{PO}_4$ compounds. Additionally, cyclic voltammetry experiments indicate an improvement of lithium diffusion coefficient in $\text{LiFe}_{0.333}\text{Mn}_{0.667}\text{PO}_4$ for both iron and manganese redox couples by addition of boron.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

1.1. Lithiated metal phosphates as cathode materials for Li-ion batteries

Since the pioneering work of Goodenough et al. [1] in 1997, phospho-olivines and especially LiFePO_4 (LFP) have known major developments leading to their commercialization in Li-ion cells. LiFePO_4 is specifically interesting for its thermal stability allowing an improvement in the cell safety behavior. Besides this major advantage, this material suffers from a lower average voltage in discharge (a plateau at 3.45 V versus Li^+/Li in OCV leading to practical 3.2 V Li-ion cells) in comparison with conventional lithiated metal oxides that are integrated in 3.6 or 3.7 V Li-ion cells. This drawback directly contributes to lower the energy density of the LFP based Li-ion cells.

A possibility to overcome this major point consists in substituting iron by other transition metals such as manganese or cobalt. In the phospho-olivine materials, $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is electrochemically active at 4.1 V [1] and $\text{Co}^{3+}/\text{Co}^{2+}$ at around 4.7–4.8 V [2] versus Li^+/Li . Recently such solid solutions of $\text{LiFe}_{(1-x-y)}\text{Mn}_x\text{Co}_y\text{PO}_4$ have been paid much interest, especially the $\text{LiFe}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{PO}_4$ compound [3–7]. One issue relative to the increase of manganese content comes from the low electronic conductivity coupled with a slow Li ion diffusion of the LiMnPO_4 material (LMP) [8].

To solve this phosphate materials' specific drawback, many studies have been devoted to the doping solution [9–12], and some publications have also noticed the positive effect of boron addition [9,10]. Work on finding optimized compositions is necessary to reach the best performances of these iron substituted phosphate materials.

1.2. Short description of DOE methodology

Design of experiments methodology (DOE) is a homogeneous set of tools and algebro-statistical methods [13,14] that are aiming at establishing and analyzing relations between studied physical quantities (responses) as a function of its supposed variation sources (factors). This method is mainly used to reduce the experiment number in a context of lack of human or experimental resources.

There are 2 main approaches corresponding to 2 families of tools. The first one groups the screening designs used to identify qualitatively the most significant factors among those listed by the experimenter. The second set of tools corresponds to surface response designs when the experimenter wants to know how the response varies quantitatively. These two approaches are complementary and frequently a screening design is followed by a surface response design.

In both cases, studied responses are expressed as a function of input factors with a polynomial equation of n terms depending on the effects considered: linear effects, interactions between factors, quadratic terms, etc.

^{*} Corresponding author. Tel.: +33 4 38 78 57 11.

E-mail address: sebastien.martinet@cea.fr (S. Martinet).

In the case of a quadratic model of k factors with first order interactions, a response Y is expressed by the following expression:

$$Y = a_0 + a_1x_1 + a_2x_2 + \dots + a_kx_k + \sum_{j>i} a_{ij}x_ix_j + \sum_{i=1}^{i=k} a_{ii}x_i^2$$

including one constant term (a_0), k linear terms (a_1 to a_k) for each factor, $k(k-1)/2$ interactions (a_{ij}) and k quadratic terms (a_{ii}).

There are only few papers relative to DOE for battery development [15,16]. In the first one [15], an orthogonal design was used to optimize the binders of the negative electrode of a Ni-MH battery. In the second paper [16], the authors succeeded in statistically modeling a large scale aging experiment of Li-ion cells of 2 chemistries, LFP and NCA. While the full test plan would have 1024 trials corresponding to 5 levels for the 4 identified factors, the use of a D-Optimal design reduced the number of experiments down to 46.

To our knowledge, the work presented here is the first one related to the application of DOE to the optimization of battery active material composition.

1.3. Application of DOE for multi-transition metal phosphate optimization

Our objective is to increase the energy density of LFP via the partial substitution with manganese and cobalt. In this study, we focused on manganese “rich” compounds and we used the following limits in the solid solution domain: between 0% and 33.3% for both iron and cobalt, between 28.4% and a maximum of 90% for manganese to avoid pure LMP that is known to have very bad electronic conductivity and diffusion coefficient of Li^+ [17]. Additionally we evaluated the possible doping effect of boron that is introduced or not at a maximum of 5%. The expected improvement of the average voltage is 12.5% i.e. a voltage of 3.88 V vs. Li^+/Li at the minimum for the highest content of iron and no presence of cobalt ($\text{LiFe}_{0.333}\text{Mn}_{0.67}\text{PO}_4$) to 25% i.e. 4.30 V at the maximum for the highest content of cobalt ($\text{LiMn}_{0.67}\text{Co}_{0.33}\text{PO}_4$). Even though cobalt strongly improves the voltage, we decided to limit its content due to the lack of stability that may be partially linked to electrolyte oxidation [18] occurring during charge up to 5 V. Finally, the studied materials follow the formula $\text{LiFe}_{(1-x-y-z)}\text{Mn}_x\text{Co}_y\text{B}_z\text{PO}_4$.

Here we are in a specific DOE as the main factors are linked all together: the sum of iron, manganese, cobalt and boron is always equal to 1. In that case, specific DOE called “mixture designs” are available

[13,14] in which the constant term a_0 of the response Y is suppressed as $x_1 + x_2 + x_3 + x_4 = 1$. To take into account our specific constraints, we selected an extreme vertices mixture design with MINITAB® software. The extreme vertices design accounts for factor limits and selects vertices and their averages (formed by factor limits) as design points. Additional limits in this type of design are usually in the form of range constraints, upper bounds, and lower bounds on the factor values. This resulted in the set of 21 trials indicated in Table 1. All the corresponding materials were synthesized with the experimental protocol defined in the next section, and the results are discussed in the following part.

2. Experimental

2.1. Material synthesis and electrode preparation

The active materials were prepared by a solid-state synthesis route based on ball milling selected precursors followed by heat treatment at medium temperature.

The following chemicals were used as received lithium phosphate Li_3PO_4 (Aldrich), manganese carbonate MnCO_3 (Aldrich 99.9%), hydrated iron phosphate $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich), hydrated cobalt phosphate $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Aldrich), cellulose microcrystalline powder (Aldrich), manganese (III) phosphate (Alpha Aesar 99%) and boron phosphate BPO_4 (Alpha Aesar). Stoichiometric amounts of each precursor, depending on the expected composition, were previously mixed. The raw materials were ball-milled (Vario-Planetary Mill PULVERISETTE 4) 400 rpm for 30 min. After ball-milling, a thermal treatment was performed on the mixture at 600–650 °C for 10 min under argon flow. The carbon content in sample was 3 wt.% determined by ATG measurement (SETARAM Setsys) and was the same for all compounds.

The synthesis conditions were adjusted during preliminary tests with several compositions at the limits of the studied domain: for instance without cobalt, without iron, with a high content of manganese or with boron. The scope of these trials was not to optimize the synthesis conditions for each material, but really to find the same synthesis condition set leading to a successful synthesis of the olivine phase. This is illustrated in Fig. 1 with the XRD pattern of $\text{LiFe}_{0.333}\text{Mn}_{0.284}\text{Co}_{0.333}\text{B}_{0.05}\text{PO}_4$. As an example, SEM images of this compound are given in Fig. 2a and b, showing primary particles in the range of 50 to 200 nm and secondary particles of several micrometers. The analyses performed on all the other 20 trials of the DOE gave similar results.

Table 1
Matrix of the 21 trials of the mixture design with the measured and estimated discharge capacity.

Trial no.	Ratio of each component in mixed lithiated metal phosphate (%)				Discharge capacity (mAh g ⁻¹)	
	Fe	Mn	Co	B	Experimental	Adjusted
1	33.3	61.7	0	5	98	88.5
2	24.06	64.78	7.41	3.75	106	105.5
3	33.3	66.7	0	0	76	89.6
4	33.3	33.4	33.3	0	99	91.5
5	7.41	64.78	24.06	3.75	102	97.9
6	0	61.7	33.3	5	69	61.6
7	24.06	67.28	7.41	1.25	114	108.4
8	24.06	48.13	24.06	3.75	93	107.8
9	0	66.7	33.3	0	74	77.1
10	12.41	78.93	7.41	1.25	104	95.1
11	0	90	10	0	62	63.3
12	7.41	67.28	24.06	1.25	91	104.4
13	5	90	0	5	14	30.5
14	14.82	67.86	14.82	2.5	115	112.4
15	9.91	78.93	7.41	3.75	91	91.1
16	0	90	5	5	51	45.2
17	33.3	28.4	33.3	5	99	101.7
18	7.41	78.93	12.41	1.25	101	101.7
19	7.41	78.93	9.91	3.75	97	94.7
20	10	90	0	0	44	36.2
21	24.06	50.63	24.06	1.25	112	107.8

Download English Version:

<https://daneshyari.com/en/article/1296517>

Download Persian Version:

<https://daneshyari.com/article/1296517>

[Daneshyari.com](https://daneshyari.com)