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A chemometric investigation of the effect of the process parameters on the performance of mixed Si/C electrodes

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Abstract

Silicon composite anodes are attractive candidates to replace present day carbonaceous anodes. In particular, silicon possess the highest theoretical capacity in an appropriate potential window, it is abundant and environmentally friendly. The present work consists of a systematic investigation of the influence of parameters during composite electrode fabrication. The following factors have been considered: SBR content, CMC content, slurry water content, drying temperature, and pressing force. A full factorial 2^5 experimental design was applied, considering two response variables: achieved cycle number at fixed capacity cycling test (y_1), and maximal observed coulombic efficiency (y_2). All statistically significant factors and their interactions have been identified.

Keywords: Silicon/graphite composites; Lithium-ion batteries; Alloying electrode; Factor experiment

1. Introduction

Recently, there has been a considerable interest in developing alternative anodes for lithium ion batteries. The driving force for these studies is based on the fact that the potential of the anode versus Li^+ should be close to 0 V. Hence the electrochemical reaction at the anode site should not necessarily be based on an intercalation type of reaction. Alloying of Li^+ with certain metals is very attractive, because the Li:M mole ratio in the Li_xM alloy at the end of charge might be much higher than in the case of intercalation hosts which generally cannot accommodate and release large amounts of Li^+ in order to maintain a stable crystal structure over the cycles. The most attractive candidates are therefore the light elements from groups III, IV and V of the periodic table. Because of its highest theoretical capacity, abundance and environmental friendliness silicon is considered as the most appropriate candidate to replace current carbonaceous anodes.

Unfortunately, electrodes that contain silicon as an active component show severe capacity loss due to the mechanical instability, which is a common problem for anodes that exhibit large volumetric variations. Cycle life of such composite silicon electrodes is known to depend on many process variables, including the amount of Si in the composition, binder properties, and electrode fabrication conditions. Due to the complexity of the relationship between these variables, the optimization and accurate prediction of the cycle life of such electrodes is difficult. The physically based approach is only possible in a limited number of cases where a physical understanding of the processes and model parameters (physical constants) are accurately known. For more complex situations, with many interrelated variables and where the relationships between model inputs and the output parameters are not clear, appropriate design of the experiment (DoE) may provide indispensable information on the importance of single factors as well as their interactions.

Astonishingly, most of the papers in the open literature are entirely focused in the material design approach, rather than the electrode preparation techniques [1–10]. However, the preparation technique might influence the performance of the final electrode so that even the same or similar active material–binder combination might provide very different results [11].

In this study, the influence of preparation conditions and binder amount on the performance of the mixed

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silicon–carbon electrodes is examined. It is shown that when using such a method most important parameters and their interactions influencing the performance of the electrodes can be identified.

2. Experimental

The active material used here was chosen to be simple on purpose. It was just a mixture of p-Si (1 μm particle grain size) and MCMB 6-28 (Osaka Gas Chemical, Japan) in a weight ratio of 1:1. The ingredients were mixed in a ball-mill (Fritsch, Germany) for 5 h at 250 min^{-1}. Balls:composite ratio was set to approx 10:1. A large batch (≈100 g) of this mixture was prepared and used in the experiments. This active material was bound onto a copper foil current collector by means of an aqueous styrene–butadiene copolymer binder (SBR, commercial designation BM-400B, ZEON Co., Japan). Sodium carboxy methyl cellulose (CMC, commercial designation HB-45, ZEON Co., Japan) was used as a thickening/setting agent. Advantages of this recently developed binder are that it possesses higher flexibility, stronger binding force and higher heat resistance than the widely adopted PVDF. Moreover, it is water soluble and therefore there is no need to work in a moisture-free atmosphere.

Electrode preparation was performed in the following way. Small batches of 2 g of the active material were mixed with calculated amount of CMC water solution with appropriate concentration and 40 wt.% SBR water suspension in order to maintain water content in the slurry 65 or 75 wt.%, respectively (− and + levels in this experimental design). It was found that such water content is appropriate to obtain slurry with sufficient viscosity to be coated onto the copper current collector. Slurry was coated by means of doctor blade and the electrode dried under a stream of fresh hot air at approx 90 and 170 °C (levels − and +), respectively. Afterwards, electrodes were punched, pressed under 0.5 and 5 t cm^{-2} (− and + levels) and cycled versus Li metal in 1 M LiPF$_6$ EC/DMC electrolyte.

Since electrodes based on an alloying type of reaction are sensitive to the mode of testing, controlled capacity cycling test used in our previous studies is adopted here [12,13]. It was performed in the following manner: Li$^+$ insertion (current density ≈0.35 mA mg^{-1}) under constant current mode until reaching the required capacity of 700 mAh g^{-1}. In case voltage drops to 10 mV before reaching 700 mAh g^{-1}, current was decreased accordingly in order to keep cell voltage ≥10 mV. For most of the experimental points capacity of 700 mAh g^{-1} was reached well above 10 mV during the initial cycles. As cycling proceeded, voltage tended to drop down to 10 mV at the end of Li$^+$ insertion before reaching 700 mAh g^{-1}. Therefore most of the cycles were performed under constant current (CC) mode and only the last few Li$^+$ insertions were performed at potential kept at 10 mV. The last cycle of each test is the cycle when current approaches 0 mA at 10 mV without reaching 700 mAh g^{-1}.

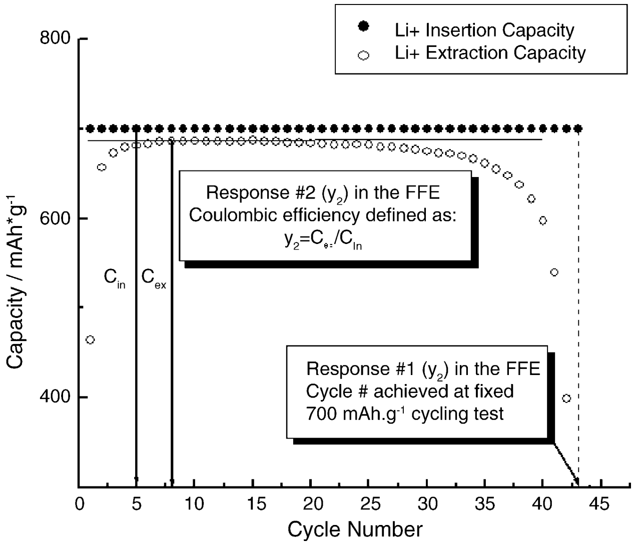

Fig. 1. Definition of the fixed capacity test and response factors used in the full factorial design. Note that the maximal values of the coulombic efficiency have been used since towards the end of the test efficiency decreases. Such an approach allows quantitative estimation of the significance of the parameters and their interactions. The level 700 mAh g^{-1} was chosen because at this level the responses are best resolved.

This number was obtained by averaging within three independent tests. It is regarded as the first response variable y_1 in this experimental design. The second response variable y_2 is the maximal coulombic efficiency observed during the test. These quantities and their definitions are shown in Fig. 1. As seen in the figure, coulombic efficiency increases, reaches maximum, and then drops suddenly at the end of the test. Advantage of such a test is that it allows not only working at strictly defined Li content in the initial cycles but also provides the necessary quantitative response variables needed to build a model for estimating the importance of process conditions and their interactions.

Generally speaking, the number of factors able to affect the properties of the final electrode is large: content of silicon in the composite, silicon particle grain size, electrode porosity, electrode thickness, binder elasticity, binder strength, electrode texture. The latter may depend also on the preparation conditions such as water content in the slurry, drying temperature, applied pressure.

It is not a priori known which of the factors may be significant. Obviously, CMC and SBR content directly control the strength and elasticity of the electrode film. However, it is not clear whether the process conditions such as slurry dry content and drying temperature influence the cycling performance of the electrode. Since the properties of the electrode film responsible for the cycling performance of the composite silicon-containing anode cannot be measured directly, the best way to retrieve information is to study the response of the electrode as a function of the selected input parameters. In this work input parameters were SBR and CMC content in the dry electrode, water content in the slurry, drying temperature and pressing force.

Preliminary experiment revealed that slurry obtained by this active material and SBR/CMC binder has an appropriate viscosity for coating onto the current collector when dry content lies in the range of 25–35 wt.%. Other parameters of interest were the drying temperature and the press force on the electrode. Slurry water content and drying temperature could possibly affect electrode texture while pressing force controls porosity and partly strength of the electrode film.

3. Method

Most of the papers that appear in the open literature consider conventional step-by-step procedures to improve the performance of the composite electrodes. Usually, only one factor at a time is considered, or more often only the composite *material design* itself is studied, but a little or nothing is said about the processing conditions and their influence on the cycling performance of the composite electrode as well as the properties of the *entire electrode layer*. However, the latter one plays a crucial role, particularly in improving the cycling performance of electrodes that undergo large volumetric variations during cycling, as evidenced by thin silicon layers directly deposited on a roughened copper current collector [14–17].

A conventional approach widely adopted in most of the studies consists in studying the influence of a given parameter whilst keeping constant the other variables. This may be misleading since it implies a partial exploration of the experimental field thus ignoring the possible interactions between the variables.

To overcome these problems, we use here a chemometric approach based upon screening experiments. The aim of this study is to identify the most important parameters as well as their interactions, which are responsible for the cycle performance of the composite silicon-based anodes. A full factorial 2^5 experiment (FFE) was designed using these parameters. Parameters and their values coded as −1 and +1 levels are shown in Table 1.

4. Results and discussion

Table 2 represents the full factorial experimental design including both responses and the actual run order.

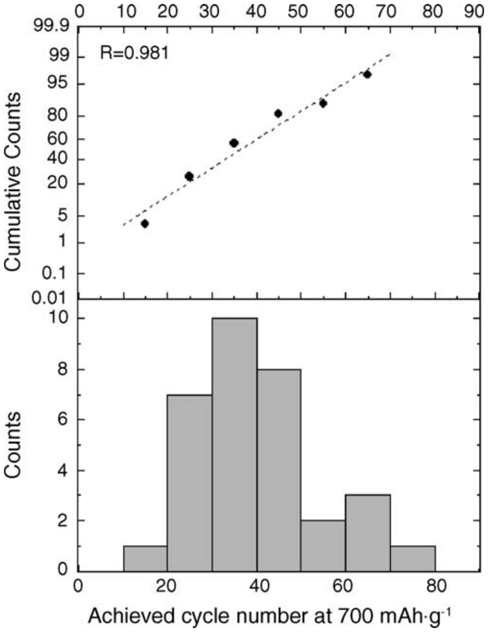

Fig. 2. Normal probability plot and histogram of the achieved cycle number (Response 1).

At first, the response variables should be plotted in several ways to see whether any trends or anomalies appear that would not be counted for by the standard linear response models. The first plot is a normal probability plot of the response variables. The straight dash line is the fitted normal distribution, and R is the correlation coefficient of the linear fit. The second plot is a histogram of response variables. These plots are shown in Figs. 2 and 3 for both responses. There is a slightly different 'structure' for both responses. The y_1 response is roughly separated into two different clumps, while y_2 is asymmetrically skewed around the value 97.59%. Clearly y_2 deviates more from the normal distribution. Fig. 4 shows the responses plotted versus run order. This plot indicates whether there might be a time sequence component affecting the response levels. This plot does not indicate any time dependency; therefore one may apply FFE calculations in order to find the relative contribution of the factors to the response variables.

Fig. 5 shows the responses sorted by factor columns. As expected several factors, most notably CMC, followed by

Table 1
Range of the parameters introduced in the design of the 2^5 complete factorial plan

	Physical meaning	Low (−)	High (+)
Parameter			
x_1	CMC content in the dry electrode (wt.%)	2.0	5.0
x_2	SBR content in the dry electrode (wt.%)	4.4	11.0
x_3	Water content in the slurry (wt.%)	65.0	75.0
x_4	Electrode drying temperature (°C)	≈90	≈170
x_5	Press force ($\mathrm{t\,cm^{-2}}$)	0.5	5.0
Responses			
y_1	Achieved cycle number at 700 $\mathrm{mAh\,g^{-1}}$	–	–
y_2	Coulombic efficiency	–	–

Table 2
Design of the 2^5 full factor experiment (FFE)

Point no.	Actual run no.	x_1	x_2	x_3	x_4	x_5	Achieved cycle no., y_1	Coulombic efficiency, y_2
1	22	−	−	−	−	−	25	95.81
2	31	−	−	−	−	+	31	96.96
3	25	−	−	−	+	−	17	94.34
4	12	−	−	−	+	+	26	97.44
5	1	−	−	+	−	−	25	96.18
6	5	−	−	+	−	+	33	97.45
7	30	−	−	+	+	−	29	96.74
8	16	−	−	+	+	+	34	98.24
9	23	−	+	−	−	−	40	97.79
10	9	−	+	−	−	+	31	96.79
11	15	−	+	−	+	−	44	98.02
12	18	−	+	−	+	+	28	97.14
13	19	−	+	+	−	−	40	97.49
14	7	−	+	+	−	+	29	97.72
15	28	−	+	+	+	−	36	98.38
16	17	−	+	+	+	+	30	97.64
17	24	+	−	−	−	−	52	98.07
18	11	+	−	−	−	+	40	97.57
19	29	+	−	−	+	−	25	98.45
20	10	+	−	−	+	+	39	98.57
21	4	+	−	+	−	−	40	97.70
22	8	+	−	+	−	+	38	97.57
23	3	+	−	+	+	−	39	98.21
24	21	+	−	+	+	+	35	98.39
25	26	+	+	−	−	−	62	97.97
26	6	+	+	−	−	+	52	97.49
27	35	+	+	−	+	−	65	98.06
28	13	+	+	−	+	+	49	97.87
29	14	+	+	+	−	−	62	99.27
30	2	+	+	+	−	+	48	97.48
31	32	+	+	+	+	−	75	98.43
32	27	+	+	+	+	+	48	97.73
33	33	0	0	0	0	0	40	97.60
34	34	0	0	0	0	0	37	97.03
35	20	0	0	0	0	0	42	98.10

Because the design is completely randomized, the actual run order is given in the second column.

SBR and possibly pressure appear to change the average response level. Pressure is more influential on the response y_1. Both x_3 (slurry water content) and x_4 (drying temperature) do not appear to affect considerably both response variables.

With all this data, it is possible to build the model. With the 2^5 full factorial design one might fit a model containing a mean term, all 5 main effect terms, all ten 2-factor and 3-factor terms, all five 4-factor interaction terms and the 5-factor interaction term (32 parameters), i.e.

$$\begin{aligned} y = y_0 &+ \sum_{i=1}^{5} a_i X_i + \sum_{i=1}^{5}\sum_{j=1}^{5}{}^{i\neq j} a_{ij} X_i X_j \\ &+ \sum_{i=1}^{5}\sum_{j=1}^{5}\sum_{k=1}^{5}{}^{i\neq j\neq k} a_{ijk} X_i X_j X_k \\ &+ \sum_{i=1}^{5}\sum_{j=1}^{5}\sum_{k=1}^{5}\sum_{l=1}^{5}{}^{i\neq j\neq k\neq l} a_{ijkl} X_i X_j X_k X_l \\ &+ a_{12345} X_1 X_2 X_3 X_4 X_5 \end{aligned} \tag{1}$$

However, it is usually assumed that all three and higher order interactions are non-significant. It is rare for such high-order interactions to be significant and it is very difficult to find their physical meaning.

Mathematically, the aim of the full factorial design is to find the numerical values of the coefficients a_i, a_{ij}, a_{ijk}, . . ., corresponding to the influence of the single, double and higher order effects. Calculation of the corresponding coefficients is performed by means of the following equations:

$$a_i = \frac{1}{N}\sum_{u=1}^{N} X_{iu}\bar{y}_u, \quad i = \overline{0, k} \tag{2}$$

to calculate the contributions of the single effects, and

$$a_{i,\ldots,m} = \frac{1}{N}\sum_{u=1}^{N} X_{iu}\cdots X_{mu}\bar{y}_u, \quad i = \overline{1, k}, \quad m > i \tag{3}$$

to calculate the contributions of the interactions [18].

All coefficients (a_i) in (1) are determined by the simultaneous variation of the variable parameters. For this kind of experimental design they are calculated with the same

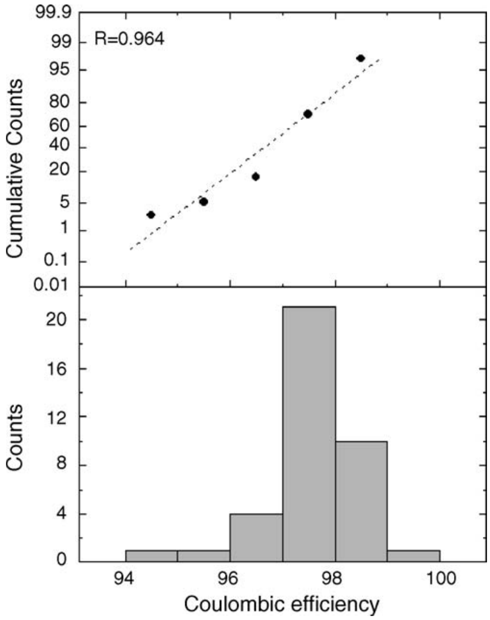

Fig. 3. Influence of the single factors on the responses. As expected, the most notable influence is due to CMC and SBR content. Other factors appear to be less significant. Particularly, pressure has opposite effects on both responses, although it almost does not influence the coulombic efficiency.

accuracy (same $\sigma(a_i)$). Since all coefficients have non-zero values, their statistical significance should be evaluated. A practical measure of their significance is obtained by comparing the coefficient value with their variance, i.e.:

$$\frac{|a_i|}{\sigma(a_i)} = c \tag{4}$$

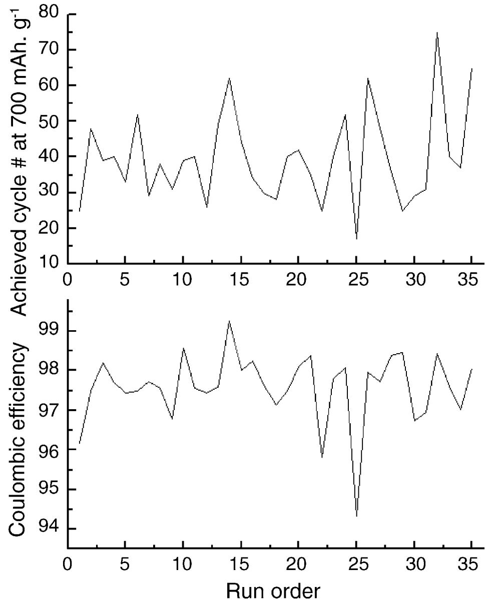

Fig. 4. Responses vs. run order as performed in the real experiment (Table 2). Absence of a trend for both responses vs. run order indicates the absence of a time-dependent systematic error.

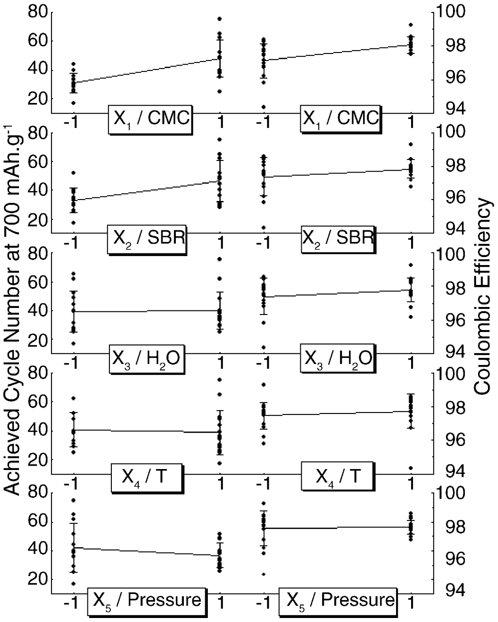

Fig. 5. Influence of the single factors on the responses. As expected, the most notable influence is due to CMC and SBR content. Other factors appear to be less significant. Particularly, pressure has opposite effects on both responses although pressure itself almost does not influence the coulombic efficiency.

Then c is compared with tabulated Student's test t-values. In case $c > t$, the parameter is considered significant, otherwise it is assumed non-significant.

Fig. 6 shows the values of the scaled parameters for both responses. All multiple interactions have been estimated by means of Eq. (3). However, all three and higher order interactions appeared to be non-significant. For the sake of clarity

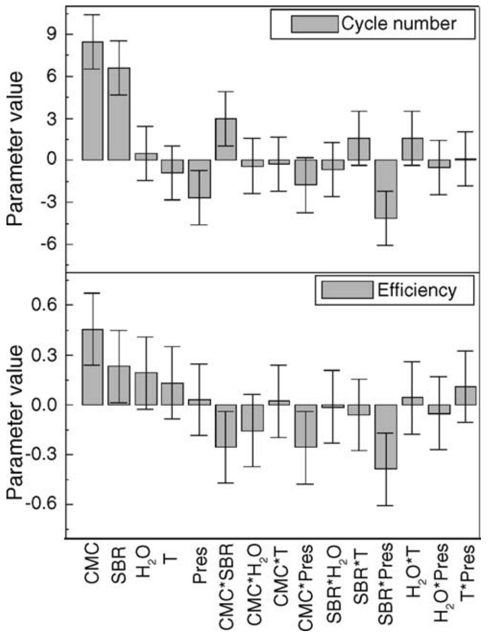

Fig. 6. Scaled single parameters and double interactions for both responses. Most of the significant parameters/interactions are the same for both responses as discussed in the text.

Table 3
Significant factors and their interactions for both response parameters

y_1: achieved cycle number at 700 mAh g^{-1}		y_2: coulombic efficiency	
Factor	Value ($\sigma = 7.48$)	Factor	Value ($\sigma = 17.53$)
CMC content	8.4688	CMC content	0.4594
SBR content	6.5938	SBR content	0.2369
Press	−2.6563	CMC × SBR	−0.2513
CMC × SBR	2.9688	CMC × Press	−0.2538
SBR × Press	−4.1563	SBR × Press	−0.3825

only single factors and double interactions are shown. Scaling is visually represented in the form of error bars whose numerical values are set as *ct*, where *c* is the constant defined by (4). In case the parameter value is higher than the scaling factor it is considered as significant. All parameters whose values lie within the scaling bars are non-significant. Significant factors for both responses are summarized in Table 3.

Despite all of the numerous works dealing with silicon-based composites, the authors do not estimate the relative weight of the factors responsible for the improved cycle life. It is usually assumed that a decrease in the silicon particle grain size leads to a better capacity retention due to improved electrical contact and better distribution of the active silicon phase within the supporting matrix. However, this effect is not evaluated numerically. The results shown in Table 3 are a means of such evaluation.

As expected, SBR and CMC content are the most influential parameters for both responses. It is also notable that basically the same effects have statistical significance for both responses; these are CMC, SBR, CMC × SBR and SBR × Press. The only difference is that Press itself is statistically significant for y_1, while CMC × Press appear to be significant for y_2 instead. The most notable interaction is SBR × Press. It has a pronounced negative effect on both responses. An important question here is whether omission of triple and higher order effects limits the predictive power of this model. Practically, this can be estimated by plotting observed versus predicted values for both responses omitting the higher order effects. Such a plot is given in Fig. 7. Experimental point numbers (column 1 in Table 2) are also presented in the plot. It is seen that omission of higher interactions is more pronounced for y_2 (worse correlation in the observed/predicted plot). Since the aim in this study is to identify the important effects rather than to build a precise response model, such accuracy is sufficient for answering the objectives of the study.

First, it is obvious that both slurry water content (x_3) and drying temperature (x_4) do not influence considerably the performance of the electrodes. This means that there is no or there is a little difference in the electrode texture and electrode film mechanical properties caused by these two parameters. Therefore future work aiming at improving electrode texture should be based on a different approach rather than simple variation of the fabrication properties.

Pressure has an interesting influence on both responses. Pressure itself or interactions of pressure and either CMC or SBR have a pronounced negative effect on both responses. The strongest negative effect is due to SBR × Press. This result is in contrast with our previous data obtained with mixed Si/graphite composite and PVDF-binder. Unfortunately, previous investigations with PVDF were performed by means of simple variation of the parameters and therefore there is no direct way to compare the data. Nevertheless, previous results suggested that the stronger the press force the stronger the electrode film and the better the cycle life of the composite electrode. Hence the same parameter may have different influence depending on the type of the binder. A possible physical explanation is that the ‘breathing’ electrode needs some void spaces for successive expansions and contractions that happen during cycling. Therefore the

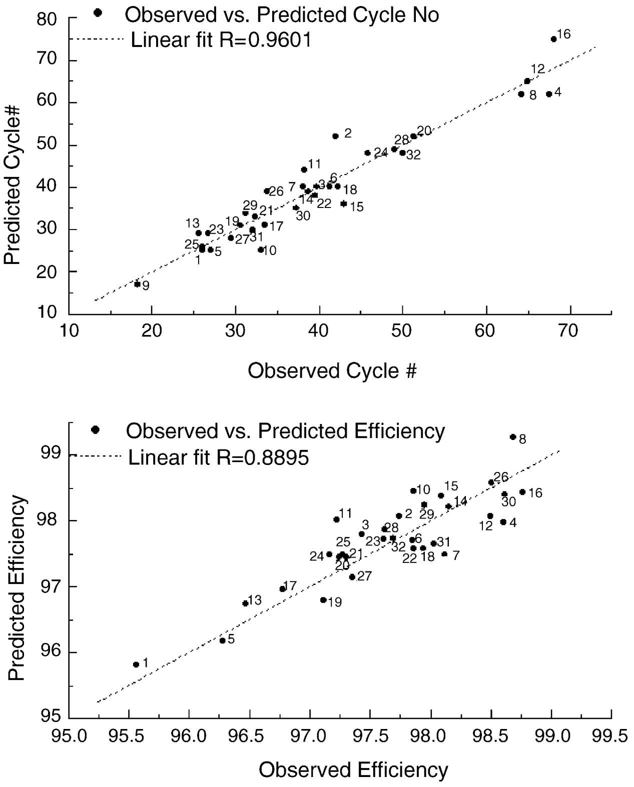

Fig. 7. Observed vs. predicted plots for both responses. Only single effects and double interactions are taken into account. Although the result is somewhat scattered, the accuracy is sufficient for finding the most important parameters and their interactions.

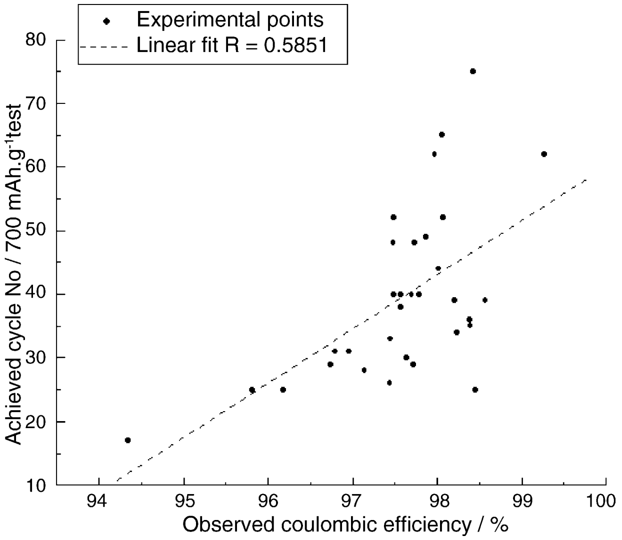

Fig. 8. Correlation between both responses in the full factorial design. Although the data are somewhat correlated, deviation from linearity suggests there is a complex relationship between observed coulombic efficiency and cycle life of the composite electrode.

porous structure is more favorable particularly when using an elastomeric binder such as SBR. This conclusion is further supported by the fact that all significant interactions that contain pressing power (SBR × Press and CMC × Press) are negative (Fig. 6).

Finally, it is notable there is a correlation, although it is not a straight relationship between both response variables shown in Fig. 8. There is a clear trend between both responses, i.e. the higher the observed coulombic efficiency, the longer the cycle life. However, the low value of the correlation coefficient between both variables suggests there is a more complex interaction rather than a straightforward dependency. The interaction CMC × SBR having opposite effects on both responses may explain the poor correlation between both responses. From Table 3 it is clear that CMC × SBR has a favorable influence on the cycle life probably due to the increased strength of the electrode film. However, the same interaction has a negative influence on the coulombic efficiency. This is an indication that the simultaneous increase in the amount of both SBR and CMC most probably worsens the conditions for SEI-formation by covering the surface of the active material with a barrier, impermeable for Li^+ diffusion.

5. Conclusions

Advantage of the factorial experimental design is that the significant parameters and their interactions can be reliably recognized. This is particularly important in the case of alloying composite electrodes, where the influence of the process parameters on the cycling performance of the composite electrodes is not obvious. Such a statistical approach allows us to consider the system under study as a 'black box' and therefore exclude any prejudice.

The most important conclusion from this experiment is that the electrode porosity plays a very important role in improving both the cycle life and the coulombic efficiency of the composite silicon containing anodes. Therefore additional efforts should be put on creating appropriate electrode structures that are stable over the cycles despite the large volumetric variations of the active silicon phase.

In this work only the 'obvious' process parameters have been considered. Since their number is not large, a full factorial design was applied in order to distinguish possible multiple interactions. However, one may assume that there are many other parameters that are not so 'obvious'. In the latter case economical experimental designs requiring fewer experimental points are more appropriate.

Acknowledgments

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