# Methodology to Assess the Impact of Electrochemical Model Parameters Based on Design of Experiments

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## Introduction

Electrochemical models could help in the development and redesign of existing Li-ion batteries as well as to develop more innovative concepts. These models can provide useful information related to the internal mechanisms occurring in these devices [1]. The aim of this work is to present a new tool for optimization of the internal parameters of the cells by means of the electrochemical models and design of experiments.

## Electrochemical battery model

A physics-based battery model implemented in COMSOL Multiphysics® simulation software and developed by G. Plett et. al. [1] is used for the analysis.

### Governing equations [2]

Charge conservation in the solid-phase

$$\frac{\partial}{\partial x}\left(\sigma_{eff}\frac{\partial}{\partial x}\phi_s(x,t)\right)-a_s F j(x,t)=0$$

Charge conservation in the liquid-phase

$$\frac{\partial}{\partial x}\left(\kappa_{eff}\frac{\partial}{\partial x}\phi_e(x,t)\right)+a_s F j(x,t)+\frac{\partial}{\partial x}\left(\kappa_{D,eff}\frac{\partial}{\partial x}\ln(c_e(x,t))\right)=0$$

Material balance of the electrolyte

$$\frac{\partial(\varepsilon_e c_e(x,t))}{\partial t}=\frac{\partial}{\partial x}(D_{e,eff}\frac{\partial}{\partial x}c_e(x,t))+a_s(1-t_+^0)j(x,t)$$

Material balance for the AM particles

$$\frac{\partial c_s(r,x,t)}{\partial t}=\frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_s(r,x,t)}{\partial r}\right)$$

Pore wall flux (Butler-Volmer kinetics)

$$j=\kappa_{0,norm}\left(\frac{c_e}{c_{e,0}}\right)^{1-\alpha}\left(\frac{c_{s,\max}-c_{s,e}}{c_{c,\max}}\right)^{1-\alpha}\left(\frac{c_{s,e}}{c_{s,\max}}\right)^{\alpha}\left\{\exp\left(\frac{(1-\alpha)F}{RT}\eta\right)-\exp\left(\frac{\alpha F}{RT}\eta\right)\right\}$$

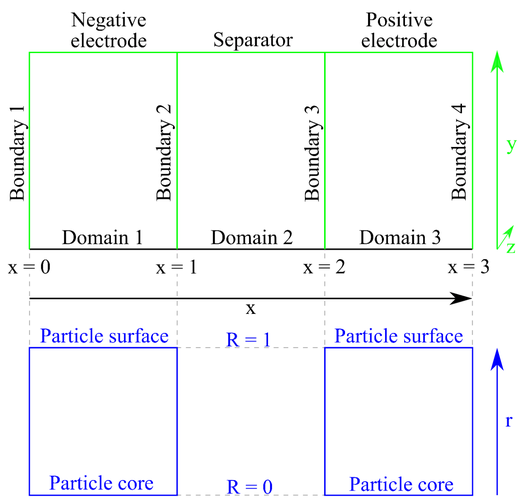


**Figure 1**. P2D model.

Analysed system: The Doyle cell [3] has been used for this work. This cell is composed of Carbon and Lithium Manganese Oxide (LMO) electrodes and $LiPF_6$ (EC:DMC) electrolyte.

## Applied methodology

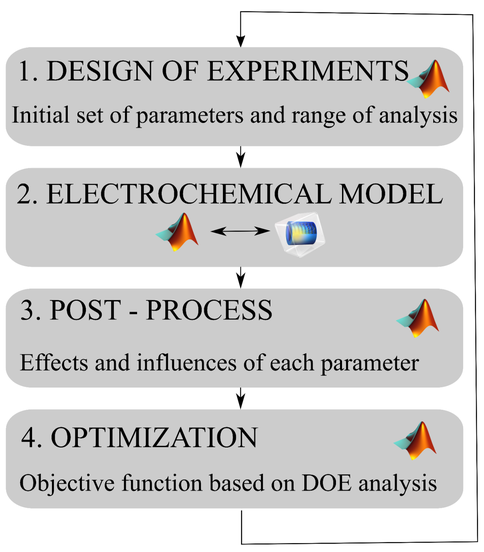


**Figure 2**. Methodology in four steps.

- A $2^9$ full factorial design has been used for main factor/interaction identification and a $3^8$ full factorial design for the implementation of the Response Surface Methodology (RSM).
- Models are solved using COMSOL Multiphysics® software linked with the LiveLink™ for MATLAB®. Parallel computing is used (20 workers).
- Half Probability plots, main effects, interaction effects linear regression models and RSM have been analysed for the energy density.
- Nelder-Mead simplex algorithm is used for the optimization of Energy and Power density.

## Results and discussion

### Two-level full factorial design [4]

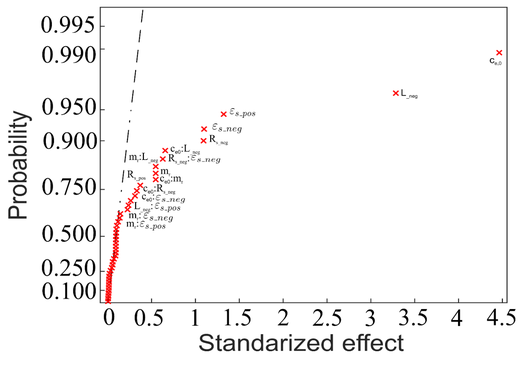


**Figure 3**. Half probability plot.

The electric conductivity of the negative electrode is not significant in this analysed range and responses. Therefore, in the three-level full factorial design that factor has been removed.

Main effects and interaction effects for Energy Density

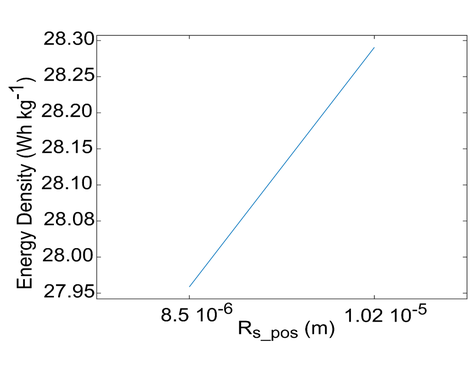


**Figure 4**. Main effect.

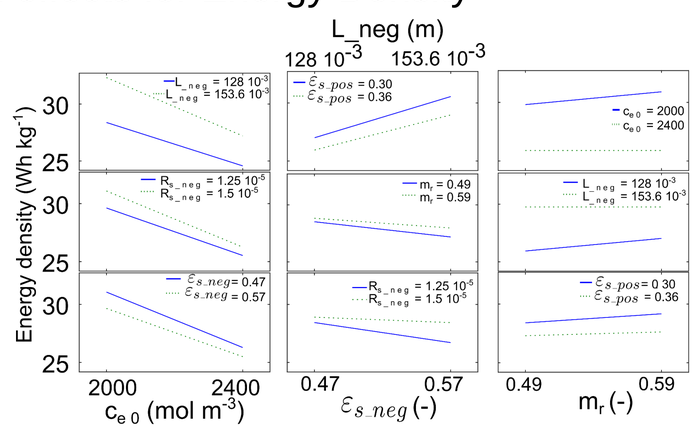


**Figure 5**. Interaction effects.

## Three-level full factorial design

| Parameter | Low level (-1) | Mean level (0) | High level (+1) |
|---|---|---|---|
| $L_{neg}$ (m) | 1.28 $10^{-4}$ | 1.41 $10^{-4}$ | 1.54 $10^{-4}$ |
| $m_r$(-) | 0.49 | 0.54 | 0.59 |
| $\varepsilon_{s\_neg}$ (-) | 0.471 | 0.518 | 0.57 |
| $\varepsilon_{s\_pos}$ (-) | 0.297 | 0.327 | 0.36 |
| $R_{s,neg}$ (m) | 12.5 $10^{-6}$ | 13.8 $10^{-6}$ | 15 $10^{-6}$ |
| $R_{s,pos}$ (m) | 8.5 $10^{-6}$ | 9.35 $10^{-6}$ | 10.2 $10^{-6}$ |
| $\sigma_{pos}$ (S $m^{-1}$) | 3.8 | 4.2 | 4.6 |
| $c_{e,0}$ (mol $m^3$) | 2000 | 2200 | 2400 |

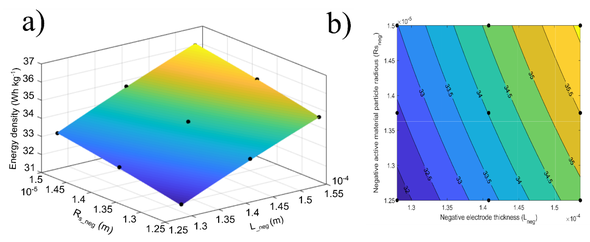


**Figure 6.** a) 3D surface plot and b) contour plot for the most significant interaction for Em.

Response surface methodology (RSM)

$$y=\beta_0+\sum_{i=1}^{k}\beta_i x_i+\sum\sum_{i<j}\beta_{ij}x_i x_j+\sum_{i=1}^{k}\beta_{ii}x_i^2+\varepsilon$$

Desirability function (maximization)

$$d_i[y_i(x)]=\begin{cases}0 & \text{if } y_i(x)<L_i\\ \left(\frac{y_i(x)-L_i}{U_i-L_i}\right)^r & \text{if } L_i\le y_i(x)\le U_i\\ 1 & \text{if } y_i(x)>U_i\end{cases}$$

Objective function

$$D(d_1[y_1(x)],d_2[y_2(x)],...,d_n[y_n(x)])=\left(\prod_{i=1}^{n}d_i[y_n(x)]\right)^{1/n}$$

Nelder-Mead simplex algorithm

**Optimized parameters**

| $L_{neg}$ | $m_r$ | $\varepsilon_{s\_neg}$ | $\varepsilon_{s\_pos}$ |
|---|---|---|---|
| 1.28 $10^{-4}$ | 0.51 | 0.47 | 0.32 |
| $R_{s,neg}$ | $R_{s,pos}$ | $\sigma_{pos}$ | $c_{e,0}$ |
| 1.26 $10^{-5}$ | 8.57 $10^{-6}$ | 3.84 | 2117 |

**Output responses**

| Response | Doyle cell | Optimized cell |
|---|---|---|
| $E_m$ | 32 | 31 |
| $P_m$ | 396 | 408 |

## Conclusions

This work presents a proof of concept of the methodology for the optimization of selected design parameters of batteries using design of experiments.

This tool can help in the design of new cells, as it provides highly valuable insights of the internal variables and characteristics of the cell (i.e. Energy density) as a function of design parameters.

## Future lines

- Extrapolate the methodology to wider ranges of analysis
- Test the tool using different cycling regimes (i.e. pulses) and other chemistries
- Reduce the computational time implementing the central composite design (CCD) or box-behkin design (BBD)

## References

1. G. Plett, *Battery Management Systems: Battery modeling*, Volume I. Artech House, 2015.
2. M. Doyle, T. F. Fuller, J. Newman, Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell, *J. Electrochem. Soc.,* **140** (6) 1526–1533 (1993).
3. M. Doyle J. Newman, Comparison of Modeling Predictions with Experimental Data from Plastic Lithium Ion Cells*, J. Electrochem. Soc*., **143** (6) 1890–1903 (1996).
4. 4. J. Antony, *Design of Experiments for Engineers and Scientists*. Butterworth Heinemann (2003).

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