Electrochemical modeling, validation and parameter identification under high current discharge conditions for a commercial Li-ion battery

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State of the art

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Physics Based

- Doyle and Newman [1,2] porous electrode, partial 2D model, widely accepted
- Used for many chemistries
- Parameters need **intra-cell data measurements**
  - Equilibrium potential, Kinetic constant, Diffusion Coef.

High current modeling and parameter identification

- up to 16 C, non-invasive experiments, SPM [3]
- up to 40A (26700 cells) with difficulties for low SOC, least-square 7 steps fitting [4]
- short circuits, non-isothermal [5,6], 15min simulation time

[1] M. Doyle, T. F. Fuller, and J. Newman, J. Electrochem. Soc., 140, 1526–1533 (1993).
[2] J. Newman and K. E. Thomas-Alyea, Electrochemical Systems Inc. Wiley-Interscience John Wiley \&. Sons, Editor, Electrochem. Soc. ,Series, (2004).
[3] A. P. Schmidt, M. Bitzer, Á. W. Imre, and L. Guzzella, J. Power Sources, 195, 5071–5080 (2010).
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[5] J. Mao, W. Tiedemann, and J. Newman, J. Power Sources, 271, 444–454 (2014).
[6] A. Rheinfeld et al., J. Electrochem. Soc., 165, A3427–A3448 (2018).

Scope of Work

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1) Physics based model validation for **high current discharge**

2) **Parameter identification** method in 3 steps based on **cell voltage** data

3) Experimental characterization

LG INR6 - 18650 -**1.5Ah** -LiNiCoMnO2 (**20 A max. current**)

25°C – thermal chamber

up to 40 C-rate (**60A**)

For more details:
L. Kostetzer, C. Nebl, M. Stich, A. Bund, and H.-G. Schweiger, Journal of The Electrochemical Society, 167, 140549 (2020) https://doi.org/10.1149/1945-7111/abc726.

Physics based electrochemical model

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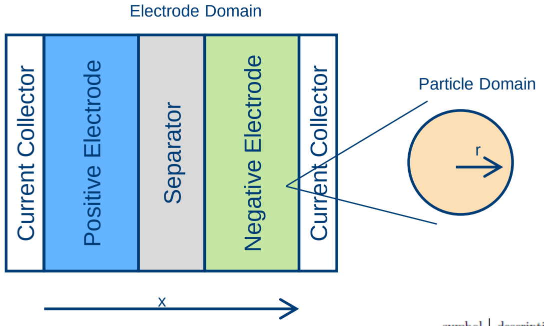
Model

Prof. Newman Model, porous electrode theory[1,2]

FVM, C code implementation



Parameters

Design / Thermodynamics (10)

symbol	description	unit	nominal value
L_p	positive electrode thickness	$[\mu m]$	183 [9]
L_s	separator thickness	$[\mu m]$	52 [9]
L_n	negative electrode thickness	$[\mu m]$	100 [9]
ε_p	volume fraction of electrolyte at the positive electrode	[ ]	0.444 [9]
ε_n	volume fraction of electrolyte at the positive electrode	[ ]	0.357 [9]
$\varepsilon_{f,p}$	volume fraction of filer at the positive electrode	[ ]	0.259 [9]
$\varepsilon_{f,n}$	volume fraction of filer at the positive electrode	[ ]	0.172 [9]
$brugg$	Bruggeman coefficient	[ ]	1.5 [9]
t_+	transfer number of Li ions	[ ]	0.363 [9]
A	electrode area	$[m^2]$	0.08 [27, 28]

Electrochemical / kinetics (11)

Lithiation limits (4)

Parameter Identification

symbol	description	unit	nominal value
$c_{t=0s}$	initial concentration at the electrolyte	$[mol\ m^{-3}]$	2000
κ	electrolyte electrical conductivity	$[S\ m^{-1}]$	0.6
D	electrolyte phase diffusion coefficient	$[m^2\ s^{-1}]$	7.5×10^{-11}
$D_{s,p}$	positive electrode solid phase diffusion coefficient	$[m^2\ s^{-1}]$	1.0×10^{-13}
$D_{s,n}$	negative electrode solid phase diffusion coefficient	$[m^2\ s^{-1}]$	3.9×10^{-14}
$k_{0,p}$	positive electrode electrochemical reaction rate constant	$[mol\ m^2\ s^{-1}\ (mol\ m^{-3})^{-1.5}]$	2.33×10^{-11}
$k_{0,n}$	negative electrode electrochemical reaction rate constant	$[mol\ m^2\ s^{-1}\ (mol\ m^{-3})^{-1.5}]$	2.33×10^{-11}
$R_{s,p}$	particle radius in positive electrode	$[\mu m]$	8.0
$R_{s,n}$	particle radius in negative electrode	$[\mu m]$	12.5
σ_p	positive electrode electrical conductivity	$[S\ m^{-1}]$	3.8
σ_n	negative electrode electrical conductivity	$[S\ m^{-1}]$ 14	100.0

[1] M. Doyle, T. F. Fuller, and J. Newman, J. Electrochem. Soc., 140, 1526–1533 (1993).
[2] J. Newman and K. E. Thomas-Alyea, Electrochemical Systems Inc. Wiley-Interscience John Wiley \&. Sons, Editor, Electrochem. Soc. ,Series, (2004).
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Equilibrium condition identification
Identification Step 1

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Electrode equilibrium potentials

NMC111 – $U_p(x)$ [1]

Graphite – $U_n(y)$ [2]

Problem→ Unknown Lithiation limits

Optimization – find practical limits

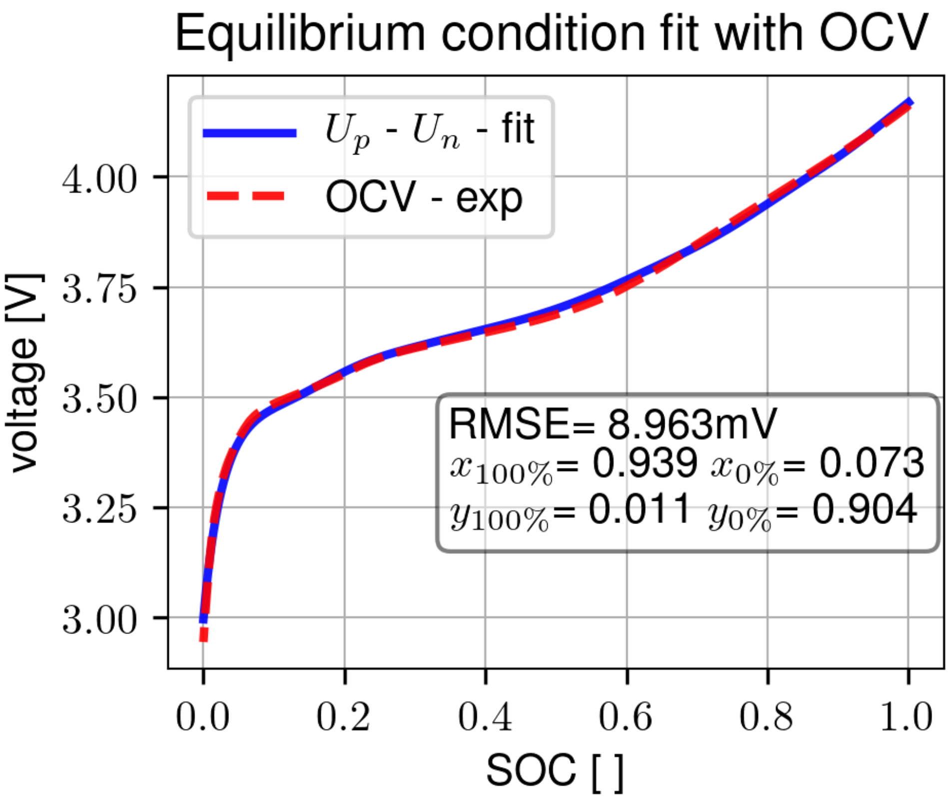
Cell Data: OCV

Find: $x_{100\%}, x_{0\%}, y_{100\%}, y_{0\%}$

$$\text{Obj. min } \left(OCV(SOC) - U_p(x) + U_n(y)\right)$$

$$x = x_{100\%} - (x_{100\%} - x_{0\%})SOC$$

$$y = (y_{100\%} - y_{0\%})SOC + y_{0\%}$$



[1] A. Rheinfeld, J. Sturm, A. Noel, J. Wilhelm, A. Kriston, A. Pfrang, and A. Jossen, J. Electrochem. Soc., 165, A3427{A3448 (2018).
[2] C. R. Birkl, E. McTurk, M. R. Roberts, P. G. Bruce, and D. A. Howey, J. Electrochem. Soc., 162, A2271{A2280 (2015).

Sensitivity analysis workflow
Identification Step 2

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dynardo optiSLang ⇔ P2D (C-code)

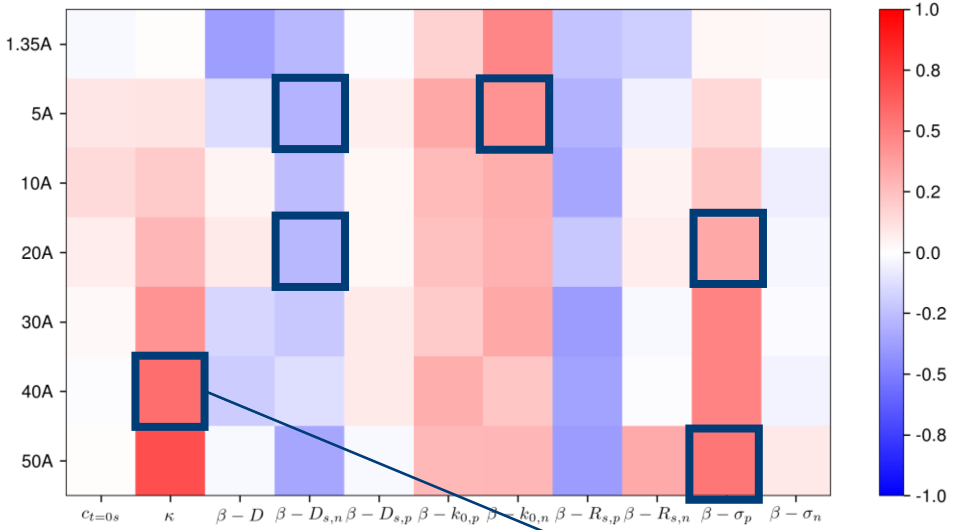
Latin Hyper Cube (5000 samples)

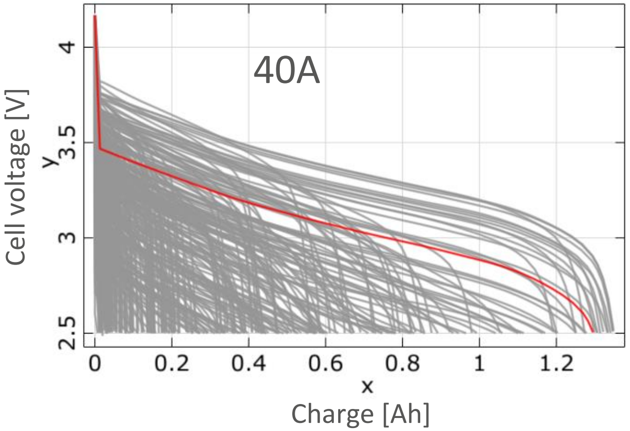
CC - sweep: [1.35, 5, 10, 20, 30, 40, 50] A

Coeff. Of Correlation

Voltage @ mid discharge

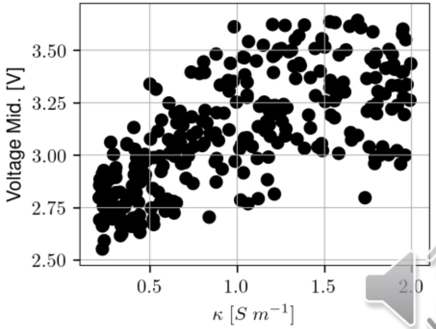
Coefficient of Correlation Matrix





Sorting most important parameter

- Low currents (<5A): $k_{0,n}, \mathrm{D_{s,n}}$ → NE limits
- Mid (10A, 20A) : $\mathrm{D_{s,n}}, \sigma_n$ → NE limits
- Very High(>40A): κ, σ_p → Ohmic Losses (electrode and electrolyte)



CoC= 0.689

Optimization results and verification

Identification Step 3

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Identification

10A + 30A for fitting

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i^* - y_i)^2}$$

Nature Inspired Optimization Algorithm

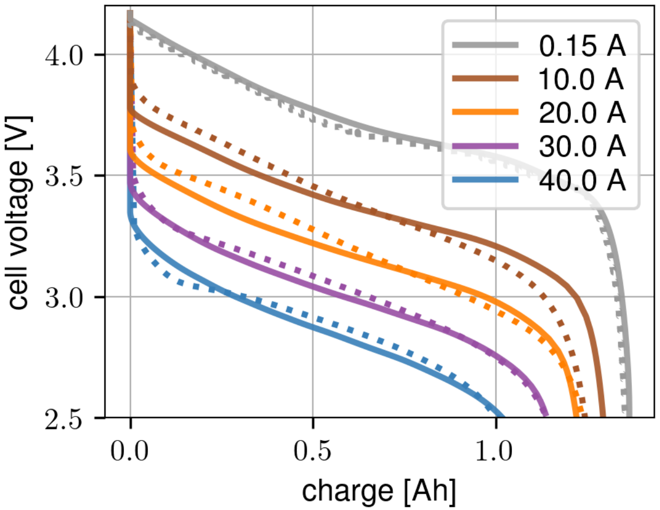
Verification

0.15, 20A, 40A + 50A

Extreme currents (>40A)

Same parameters did not work

Re-fit, shows that current dependent effects are present



Current [A]	Cell Voltage RMSE [mV]	Max. Cap. err. [%]
40	38	0.8
30	28	0.2
20	52	1.8
10	89	4.0
0.15	41	0.9