Enhanced Physics-Based Models for State Estimation of Li-Ion Batteries

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INTRODUCTION: In this work the Doyle-Fuller-Newman (DFN) model, a physics-based pseudo-2D battery model relaying on porous electrode and concentrated solution theories [1, 2], is implemented in COMSOL Multiphysics. The main objectives are:

- Model parameters identification of a commercial lithium-ion battery including cross-validation.
- Validation of model simplifications capable to run on Battery Management Systems (BMSs) in real-time.

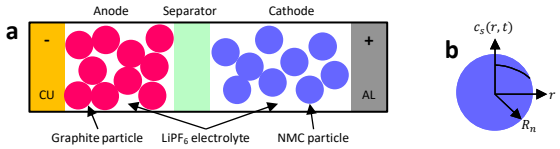

Figure 1. Pseudo-2D physics-based battery model **(a)** and detailed illustration of the spherical particle model **(b)**

Governing Equations: The model is solved stationary, in time and frequency-domain with COMSOL Multiphysics and the Batteries & Fuel Cells Module.

Charge conservation in the homogeneous solid	$\frac{\partial}{\partial x}\left(\sigma^{\text{eff}}\frac{\partial \Phi_s(x,t)}{\partial x}\right) - a_s F j(x,t) = 0$
Mass conservation in the homogeneous solid	$\frac{\partial c_s(x,r,t)}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_s(x,r,t)}{\partial r}\right)$
Mass conservation in the homogeneous electrolyte	$\varepsilon_e\frac{\partial c_e(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D_e^{\text{eff}}\frac{\partial c_e(x,t)}{\partial x}\right) + (1-t_+^0)a_s j(x,t)$
Charge conservation in the homogeneous electrolyte	$\frac{\partial}{\partial x}\left(\kappa^{\text{eff}}\frac{\partial \Phi_e(x,t)}{\partial x}\right) + \frac{\partial}{\partial x}\left(\kappa_D^{\text{eff}}\frac{\partial \ln(c_e(x,t))}{\partial x}\right) + a_s F j(x,t) = 0$ $\kappa^{\text{eff}} = \kappa\varepsilon_e^{\text{brug}}$ and $\kappa_D^{\text{eff}} = \frac{2RT}{F}\kappa^{\text{eff}}(t_+^0-1)\left(1+\frac{\partial \ln(f_\pm)}{\partial \ln(c_e(x,t))}\right)$
Lithium transfer between the solid and liquid phases (Butler-Volmer equation)	$j = k_0 c_e^{1-\alpha}(c_{s,\max}-c_{s,e})^{1-\alpha}c_{s,e}^{\alpha}\left(\exp\left(\frac{(1-\alpha)F}{RT}\eta\right) - \exp\left(-\frac{\alpha F}{RT}\eta\right)\right)$
Overpotential	$\eta = \Phi_s - \Phi_e - U_{\text{OCP}} - jFR_{\text{film}}$
Battery voltage	$v(t) = \Phi_s(0^+,t) - \Phi_s(0^-,t) - \frac{R_f}{A}i(t)$

Parameter Grouping and Sensitivity Analysis:
The influence of individual parameters on the model output is investigated for three groups:

- Geometric parameters → Li-ion battery geometry
- Thermodynamic parameters → equilibrium
- Kinetic parameters → dynamics

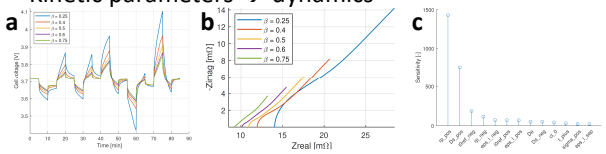

Figure 2. Time-domain voltage response during sensitivity analysis **(a)**, frequency-domain impedance during sensitivity analysis **(b)** and parameter ranking according to QR decomposition with column pivoting [3] **(c)**

Parameter Identification:

- Microstructure Analysis using optical microscope, Scanning Electron Microscope (SEM) and performing Energy dispersive X-ray spectroscopy (EDX).

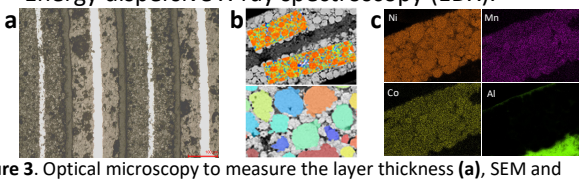

Figure 3. Optical microscopy to measure the layer thickness **(a)**, SEM and image processing to determine the porosity, active volume fraction and particle radius **(b)** and EDX to determine the coated electrode material composition **(c)**

- Open Circuit Voltage (OCV) model optimization (thermodynamic parameters).

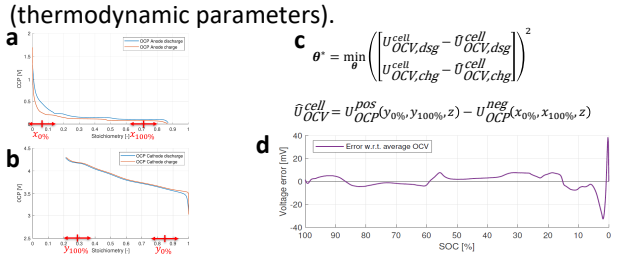

Figure 4. Anode Open Circuit Potential (OCP) **(a)** Cathode OCP **(b)** optimization function based on max and min lithium concentration **(c)** and thermodynamic model validation with average OCV measurements **(d)**

- Model optimization (kinetic parameters: D_e, D_s, κ, σ, …).

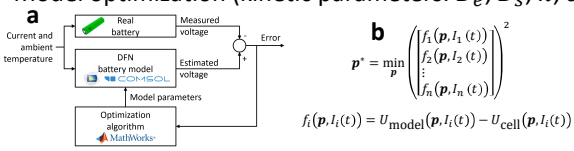

Figure 5. Model optimization with COMSOL LiveLink for Matlab **(a)** and the multi-objective optimization problem with shared model parameters **(b)**

Model Validation: Dynamic drive cycles scaled consecutively to 2C and 5C peak discharge current highlight an average model estimation error lower than 18mV.

Drive Cycle	C-rate [C]	SOC [%] 90	80	70	60	50	40	30	20	10
HWFET	2C	7.5	11.2	12.2	17.2	4.7	13.8	6.7	13.8	64.5
NYCC	2C	1.7	2.3	2.6	4.0	1.6	3.4	0.9	2.6	15.1
UDDS	2C	6.1	6.8	6.9	17.9	3.0	8.6	4.1	12.1	52.3
US06	2C	10.5	15.5	16.8	15.9	7.1	17.1	7.9	14.8	74.3
HWFET	5C	6.3	26.0	15.7	8.9	19.1	24.4	8.9	13.5	142.9
NYCC	5C	4.3	5.4	7.1	11.8	2.5	7.2	2.8	6.9	33.8
UDDS	5C	18.1	16.0	12.9	11.2	7.9	17.2	11.9	16.2	95.0
US06	5C	21.7	27.9	15.8	9.2	37.1	21.7	10.3	23.8	43.3

Table 1. RMSE estimation error in mV for the standardized dynamic drive cycles cross-validation

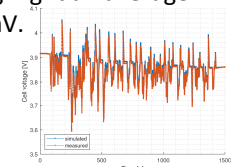

Figure 6. 5C UDDS drive cycle @70% SOC

Simulation Results:

- Simulation of non-measurable cell internal states.

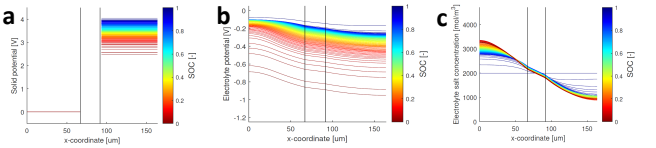

Figure 7. Simulation of solid phase potential **(a)**, liquid phase potential **(b)** and liquid phase salt concentration **(c)** for a complete 1C CC discharge cycle

- Reduced order model validation with the DFN model e.g. Single Particle Model (SPM) [4] represented in state-space.

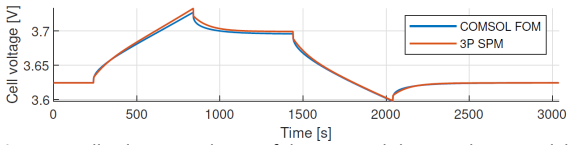

Figure 8. Cell voltage simulation of the SPM and the pseudo-2D model

CONCLUSIONS:

- Successful identification of physics-based battery model parameters for a commercial lithium-ion battery.
- Average model estimation RMSE over full SOC <18mV.
- Validation of simulated states on simplified physics-based battery models e.g. SPM in state-space intended for BMSs, enabling fast charging and extending the battery life.

REFERENCES:

1. Doyle et al., Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell, *JES*, 140(6), 1-36, (1993)
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3. Jin et al., Parameter Estimation of an Electrochemistry-based Lithium-ion Battery Model using a Two-Step Procedure and a Parameter Sensitivity Analysis, *IJER* , 42(7), 2417-2430, (2018)
4. Subramanian et al., Efficient Macro-Micro Scale Coupled Modeling of Batteries, *JES*, 152(10), A2002-A2008 (2005)