

# Electrochemical Modeling of a single Li-Ion cell

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# Overview

- Modeling approaches
  - Equivalent circuit model
  - Electrochemical model
  
- Mathematical Model of the electrochemical system
  
- Numerical realization
  - Method
  - Discretization in space
  - Discretization in time
  
- Simulation Results
  
- Problems

# Equivalent Circuit Model I

## ■ Pros and Cons

- + small set of parameters
- + straight-forward implementation
- + effects can be allocated to a frequency band
- limited to one operating point
- many measurements required for coupling of these points
- only the current input/voltage output characteristic can be monitored/displayed

## Equivalent Circuit Model II

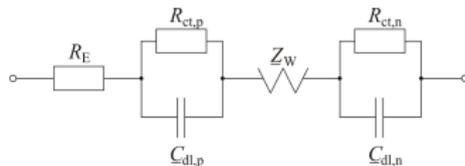


Abbildung 1: Simple RC-model with additional impedance  $Z_W$  for low frequencies.

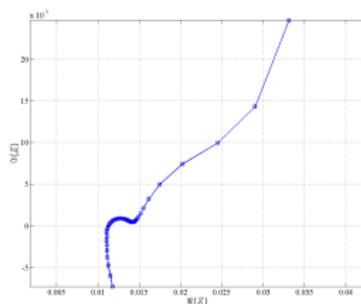


Abbildung 2: Nyquist plot of a Li-Ion battery showing a characteristic half circle and a  $45^\circ$  straight line.

# Electrochemical Reactions I

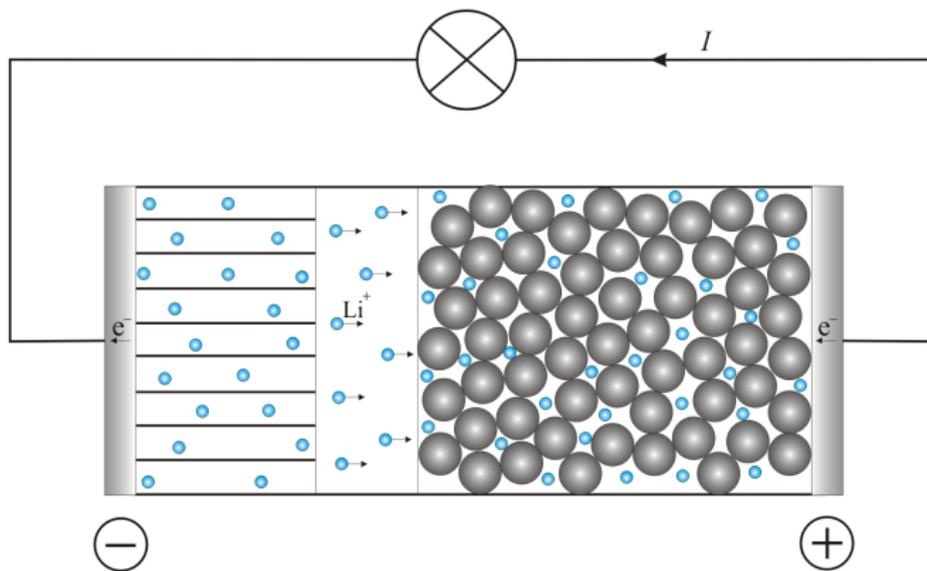
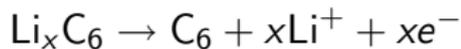


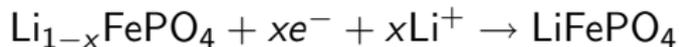
Abbildung 3: Electrochemical reaction during discharge of the cell.

## Electrochemical Reactions II

- Reaction in the Negative during discharge:



- Reaction in the Positive during discharge:



## Mathematical Formulation I

- Charge balance in the solid phase:

$$-\nabla(\sigma\nabla\Phi_s) = -j \quad (1)$$

- Charge balance in the fluid phase:

$$-\nabla(\kappa(c_e)\nabla\Phi_e) + \nabla\left(\frac{2\kappa(c_e)RT}{F}\nabla\ln c_e\right) = j \quad (2)$$

- Butler–Volmer equation (charge transfer):

$$i_0 = ak\sqrt{c_e(c_{S,\max} - c_{S,\text{surf}})c_{S,\text{surf}}} \quad (3)$$

$$j = i_0 \left( e^{\frac{\alpha F}{RT}(\Phi_s - \Phi_e - U_{OCV})} - e^{-\frac{(1-\alpha)F}{RT}(\Phi_s - \Phi_e - U_{OCV})} \right) \quad (4)$$

## Mathematical Formulation II

- Concentration in the solid phase:

$$\frac{\partial c_s}{\partial t} = D_s \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial c_s}{\partial r} \right] \quad (5)$$

- Concentration in the fluid phase:

$$\frac{\partial(\varepsilon c_e)}{\partial t} = \nabla(D \nabla c_e) + \frac{1 - t_+}{F} j \quad (6)$$

Taking the porosity of the electrodes into account often the Bruggemann–relations:

$\sigma^{\text{eff}} = \sigma \varepsilon_s^{\text{brug}}$ ,  $\kappa^{\text{eff}} = \kappa \varepsilon^{\text{brug}}$  and  $D^{\text{eff}} = D \varepsilon^{\text{brug}}$  are used.

## Boundary Conditions

- Charge balance in the solid phase:

$$-\sigma \nabla \Phi_s = i \text{ für } x = 0, x = L$$

- Charge balance in the fluid phase:

$$-(\kappa(c_e) \nabla \Phi_e) + \left( \frac{2\kappa(c_e)RT}{F} \nabla \ln c_e \right) = 0 \text{ für } x = 0, x = L$$

- Concentration in the solid phase:

$$-D_s \frac{\partial c_s}{\partial r} \Big|_{r=0} = 0, \quad -D_s \frac{\partial c_s}{\partial r} \Big|_{r=R_s} = \frac{j}{aF}$$

- Concentration in the fluid phase:

$$\nabla c_e = 0 \text{ für } x = 0, x = L$$

Additionally a reference potential has to be defined! (e.g.  $\Phi_s(0) = 0$ )

## Initial Conditions

- Concentration in the solid phase:

$$c_s(r, 0) = c_{s,0}$$

- Concentration in the fluid phase:

$$c_e(x, 0) = c_{e,0}$$

## Modifications of the Equation System I

- Modification of the fluid potential after [1]:

$$\Phi_e = \Phi_e - \frac{2\kappa(c_e)RT}{F} \ln c_e$$

therby the charge balance in the fluid results as follows

$$-\nabla(\kappa(c_e)\nabla\Phi_e) = j \quad (7)$$

as well as

$$j = i_0 \left( e^{\frac{\alpha F}{RT}(\Phi_s - (\Phi_e + \frac{2\kappa(c_e)RT}{F} \ln c_e) - U_{OCV})} - e^{-\frac{(1-\alpha)F}{RT}(\Phi_s - (\Phi_e + \frac{2\kappa(c_e)RT}{F} \ln c_e) - U_{OCV})} \right) \quad (8)$$

for the Butler–Volmer equation.

## Modifications of the Equation System II

- Modification of the concentration in the solid phase by a variable substitution after [2]:

$$v = rc_s \quad (9)$$

Thus the equation for the concentration in the solid phase can now be written in the new coordinates as follows

$$\frac{\partial v}{\partial t} = \frac{\partial}{\partial r} \left( D_s \frac{\partial v}{\partial r} \right) \quad (10)$$

Not to forget the transformation of the boundary condition, because the equation is no longer associated to a sphere!

Due to these modification the equations can no be written as a system of linear differential equations coupled by an algebraic one.

## The Control Volume Method I

- CVM on the example of the charge transfer in the solid phase [3]:

$$-\nabla(\sigma \nabla \Phi_s) = -j \quad (11)$$

The integration of the equation for the 1D case yields

$$-\left(\sigma \frac{d\Phi_s}{dx}\right)_e - \left(-\sigma \frac{d\Phi_s}{dx}\right)_w = -\int_w^e j \, dx . \quad (12)$$

This equation can be discretized as follows

$$-\left(\frac{\sigma_e(\Phi_{s,E} - \Phi_{s,P})}{(\delta x)_e}\right) + \left(\frac{\sigma_w(\Phi_{s,P} - \Phi_{s,W})}{(\delta x)_w}\right) = -\bar{j} \Delta x . \quad (13)$$

## The Control Volume Method II

This brings us to a linear equation for each discretization point

$$a_P \Phi_{s,P} = a_E \Phi_{s,E} + a_W \Phi_{s,W} + b \quad (14)$$

with the coefficients

$$a_E = \frac{\sigma_e}{(\delta x)_w}, \quad a_W = \frac{\sigma_w}{(\delta x)_w}, \quad a_P = a_E + a_W \quad \text{and} \quad b = \bar{j} \Delta x .$$

The resulting set of equations is symmetric showing a tridiagonal structure. Systems of that kind can be solved by simple algorithms.

## The Control Volume Method III

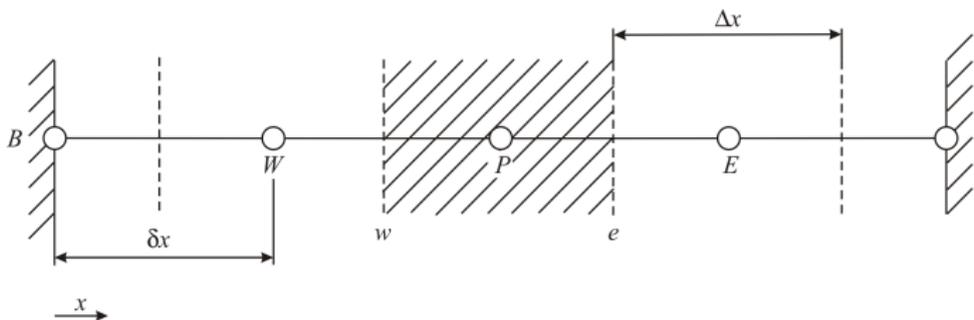


Abbildung 4: Discretization of the charge balance in the solid phase after [3].

Basically this method solves balance equations, therefore the conservation equations are always fulfilled.

You have to consider that the boundary elements represent only half control volumina!

## The Control Volume Method IV

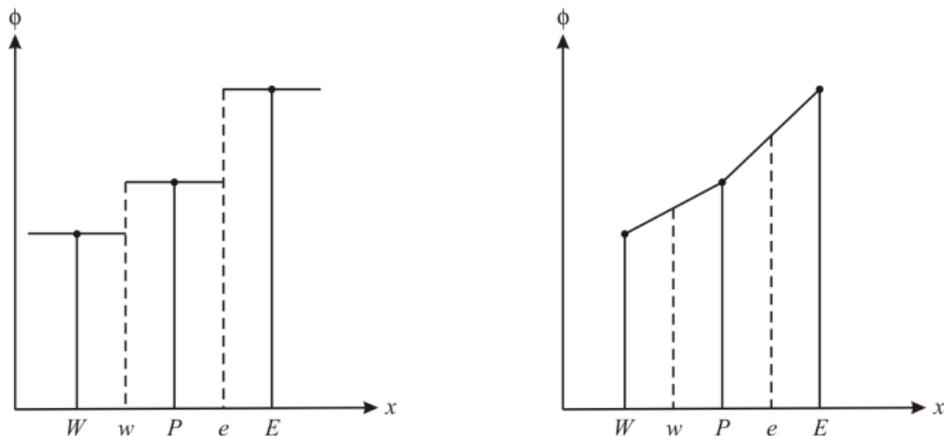


Abbildung 5: Possibilities for the discretization of the profiles; left: step profile, right: piecewise linear profil after [3].

For all calculations the step profile was used. This holds for the source term linearization as well.

## The Control Volume Method V

- Time discretization on the example of the modified concentration equation in the solid phase (fully implicit scheme):

$$\frac{\partial v}{\partial t} = \frac{\partial}{\partial r} \left( D_s \frac{\partial v}{\partial r} \right) \quad (15)$$

$$\frac{(v_P^1 - v_P^0)}{\Delta t} \Delta r = \left( \frac{D_{s,e}(v_E^1 - v_P^1)}{(\delta r)_e} \right) - \left( \frac{D_{s,w}(v_P^1 - v_W^1)}{(\delta r)_w} \right) \quad (16)$$

with the new coefficients for the equation system

$$a_E = \frac{D_{s,e}}{(\delta r)_w}, \quad a_W = \frac{D_{s,w}}{(\delta r)_e}, \quad a_P^0 = \frac{\Delta r}{\Delta t}, \quad a_P = a_E + a_W + a_P^0$$

and  $b = a_P^0 v_P^0$ .

This discretization has the advantage that its always stable!

## The Finite Difference Method

- Discretization on the example of the concentration in the solid phase after [4]:

$$\frac{\partial c_s}{\partial t} = D_s \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial c_s}{\partial r} \right] \quad (17)$$

$$\frac{\partial c_{s,P}}{\partial t} = \frac{D_{s,e}}{\Delta r (\delta r)_e} \frac{r_e^2}{r_p^2} (c_{s,E} - c_{s,P}) - \frac{D_{s,w}}{\Delta r (\delta r)_w} \frac{r_w^2}{r_p^2} (c_{s,P} - c_{s,W}) \quad (18)$$

This discretization leads to an asymmetric system matrix!

# Implementation in MATLAB<sup>®</sup> I

- Description of the whole system as a pseudo-2D model:

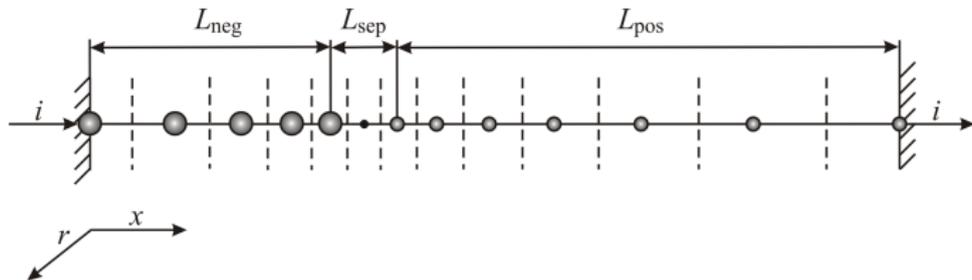


Abbildung 6: Discretization of the equations in pseudo-2D coordinates.

Discretization in  $x$ :  $N_n = 5$ ,  $N_{sep} = 3$ ,  $N_p = 7$ , scale = 1.3

Discretization in  $r$ :  $N_{p-n} = 50$ ,  $N_{p-p} = 5$ , scale = 1

## Implementation in MATLAB® II

### ■ Time discretization with variable time steps:

For the reduction of computing time the following algorithm after [5] with an error measurement  $\delta$  and a reference  $\delta_g$  was used.

```

if       $\delta < \frac{1}{2}\delta_g$ 
    accept solution +  $\Delta t = \Delta t \cdot 1,5$ 
elseif  $\frac{1}{2}\delta_g \leq \delta < \delta_g$ 
    accept solution +  $\Delta t = \Delta t$ 
elseif  $\delta_g \leq \delta \leq 2\delta_g$ 
    accept solution +  $\Delta t = \Delta t \cdot 0,5$ 
elseif  $\delta > 2\delta_g$ 
    decline solution +  $\Delta t = \Delta t \cdot 0,5$ 
end
    
```

## Implementation in MATLAB<sup>®</sup> III

The error measurement is determined as follows

$$\delta = \frac{\|v_f - v_c\|_2}{\|v_f\|_2}, \quad (19)$$

with  $v_f$  being calculated using  $\frac{\Delta t}{2}$  and  $v_c$  using  $\Delta t$  for the step size.

For the diffusion equations in the solid phased

$$\delta_g = 1e^{-2} \text{ was used.}$$

For the concentration in the liquid phase

$$\delta_g = 1e^{-3} \text{ was used.}$$

The step size can vary in the interval

$$1 \text{ ms} < \Delta t < 60 \text{ s} .$$

# Implementation in MATLAB® IV

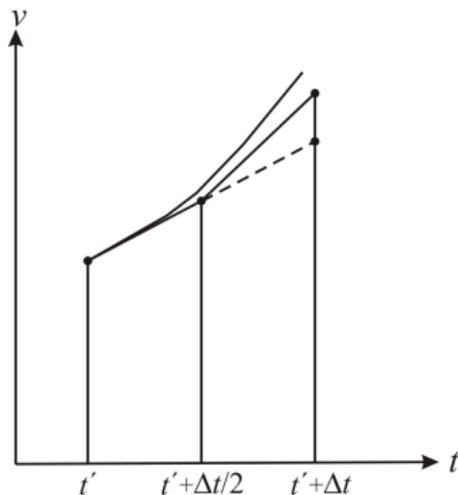


Abbildung 7: Error due to nonlinearity in  $t$  after [6].

Strong nonlinearities can lead to errors using a coarse step size!

## Implementation in MATLAB<sup>®</sup> V

- Calculation of the potentials using an extended Newton–method regarding to [7]:

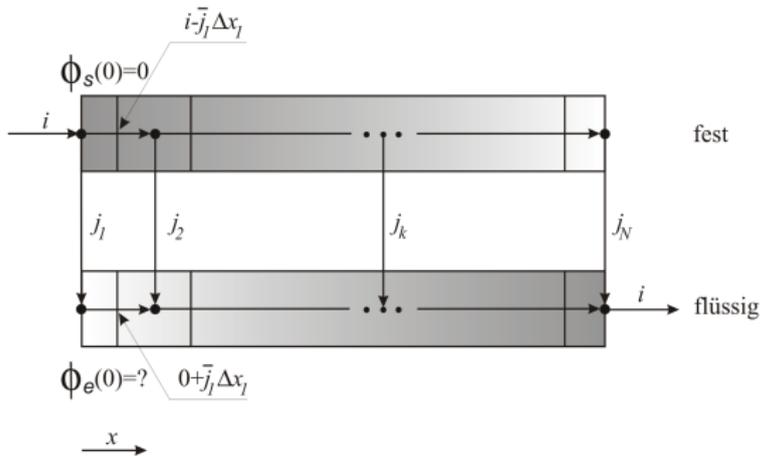


Abbildung 8: Current distribution between the solid and the liquid phase for the calculation of both potentials in the negative electrode.

## Implementation in MATLAB® VI

For the negative electrode the potential  $\phi_e(0)$  is varied until the current is transferred from the solid to the liquid phase or vice versa.

$$i = \int j dx = \sum_k \bar{j}_k \Delta x_k \quad (20)$$

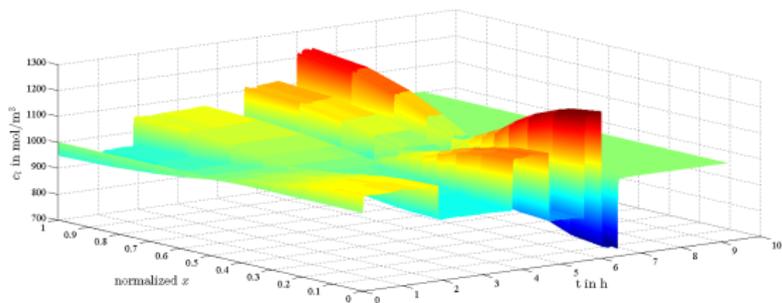
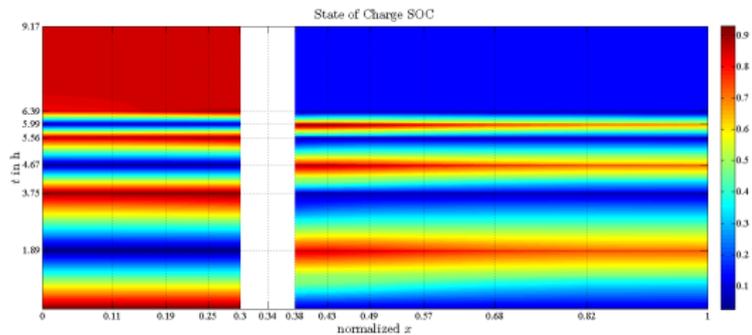
For the positive electrode the reaction runs into the opposite direction. The only difference is now that  $\phi_e(L_n + L_{sep})$  is known and  $\phi_s(L_n + L_{sep})$  has to be determined.

stopping criteria:

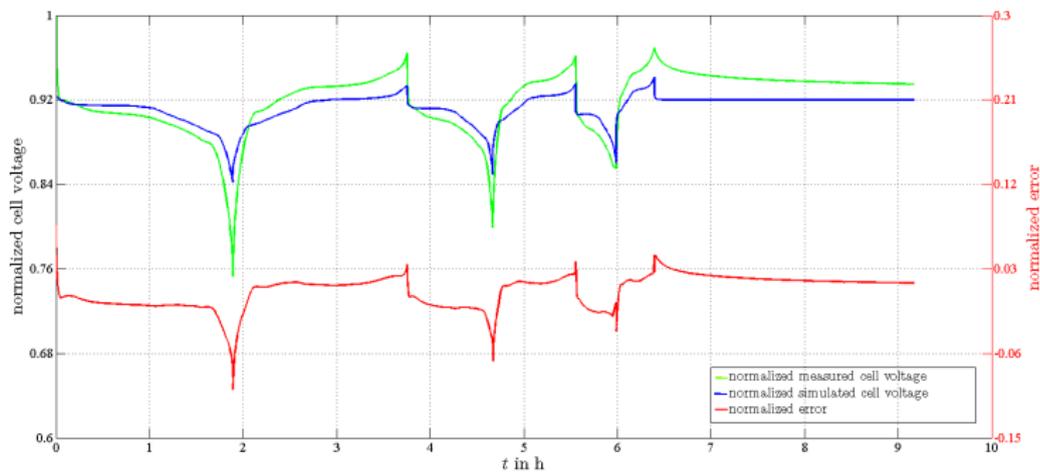
$$(i - \sum_k j_k \Delta x_k) \leq 1e^{-6}, \quad \text{maxiter} = 500, \quad s_{\min} = 1 \text{ pV}, \quad s_{\max\_p} = 50 \text{ mV},$$

$$s_{\max\_n} = 100 \text{ mV}.$$

# Simulation Results I



# Simulation Results II



# Problems

- Dealing with source term in potential equations (iterative methods)
- Discretization dependencies (not known)
- Low  $i_0$  causes problems
- Number of parameters
- Errors
  - Physics
  - Mathematical Formulation
  - Realization

Thank You For Your Attention!

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