

Battery Systems TSFS19
Exercises

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List of Symbols

| | |
|--------------|--|
| a | Specific interfacial area (m^{-1}) |
| a_i | Activity of species i (unitless) |
| R | Universal gas constant ($8.3144621 \text{ J mol}^{-1} \text{ K}^{-1}$) |
| N_A | Avogadro's number ($6.022141 \times 10^{23} \text{ mol}^{-1}$) |
| k | Boltzmann's constant ($1.380649 \times 10^{-23} \text{ J K}^{-1}$) |
| q | Fundamental unit of charge ($1.602177 \times 10^{-19} \text{ C}$) |
| F | Faraday's constant ($96,485.34 \text{ C/equiv.}$ or 26.801 Ah/mol) |
| ϵ_0 | Permittivity of vacuum ($8.854188 \times 10^{-12} \text{ F m}^{-1}$) |
| c | Speed of light ($2.99792 \times 10^8 \text{ m s}^{-1}$) |
| h | Planck's constant ($6.626070 \times 10^{-34} \text{ J s}$) |
| T | Temperature (K) ($0^\circ\text{C} = 273.15 \text{ K}$) |
| P | Pressure (Pa) |
| g | Acceleration due to gravity (9.82 m s^{-2}) |

Formulas

This chapter contains formulas that are used in the exercises.

Anode reaction:



Cathode reaction:



Cell reaction:



Equation for Mass:

$$m = M \cdot n$$

- m is the mass (in grams),
- M is the molar mass (in grams per mole),
- n is the number of moles.

Faraday Law of Electrolysis:

$$m_i = \frac{M_i Q}{nF} \quad (4)$$

- m_i is the mass of species i [g]
- M_i is the molar mass of species i [g/mol]
- Q the passed amount of charge [C]
- n the number of electrons per species i
- F the Faraday constant [C/mol]

Gibbs free energy:

$$\Delta G = -nFU \quad (5)$$

- ΔG Gibbs energy per mol [J/mol].
- n the number of electrons per species i
- F the Faraday constant [C/mol]
- U the full cell potential [V = J/C]

Electrical work:

$$W_e \leq -\Delta G \quad (6)$$

$$W_e = nFU \quad (7)$$

- Theoretical charge density (specific charge) for a cell:

$$\left| \frac{\text{Ah}}{\text{g}} \right|_{\text{cell}} = \left(\left| \frac{\text{g}}{\text{Ah}} \right|_{\text{katod}} + \left| \frac{\text{g}}{\text{Ah}} \right|_{\text{anod}} \right)^{-1}$$

- Theoretical energy density:

$$\frac{\text{Wh}}{\text{g}} = U^0 \frac{\text{Ah}}{\text{g}}$$

Open circuit voltage:

$$V = U_0 - IR_i \quad (8)$$

Simplified activity correction:

$$U = U^0 - \frac{RT}{nF} \ln \left(\prod_{\text{ions}} \left(\frac{c_i}{c_i^0} \right)^{s_i} \prod_{\text{gas}} \left(\frac{p_i}{p_i^0} \right)^{s_i} \right) \quad (9)$$

- U^0 standard potential of cell [V]
- R universal gas constant 8.314 [J/(mol K)]
- T teperature [K]
- F the Faraday constant [C/mol]
- n the number of electrons per species i
- c_i is the activation of ionic species i (concentration given in molar mass M [g/mol])
- c_i^0 is the standard activation of ionic species i (1)
- p_i is the activation of gaseous species i
- p_i^0 is the standard activation of gaseous species i (1)
- s_i is the stoichiometric coefficient of species i (positive for products and negative for reactants)

Shepherd equation:

$$V_{cell} = U - IR_{int} - K \left(\frac{\mathcal{Q}}{\mathcal{Q} - It} \right) I + A \cdot \exp\{B\mathcal{Q}^{-1}It\} \quad (10)$$

- U represent the open circuit voltage of a battery at full capacity [V]
- I is the current [A]
- R_{int} is the internal resistance of the battery [Ω]
- K is the polarization resistance coefficient [Ω]
- \mathcal{Q} is the battery capacity [Ah]
- A is an emperical constant [V]
- B is an emperical constant [1/Ah]

Capacity consumed:

$$\mathcal{Q} = \int_0^{t_{co}} i(t) dt \quad (11)$$

where i is the current dependent of time and t_{co} is the time when the voltage reaches the cutt of voltage.

Depth of Discharge:

$$\text{DOD} = 1 - \text{SOC}, \quad (12)$$

where SOC is the State of Charge given in percentage %. Can also calculate the DOD based on the capacity consumed:

$$\text{DOD} = \frac{It_{disc}}{Q_{tot}}, \quad (13)$$

where I is the current, t_{disc} is the discharge time, and Q_{tot} is the total capacity of the cell.

State of Charge:

It is defined as $\text{SOC} = \frac{\text{remaining charge}}{\text{total capacity}}$, and can be expressed as

$$\text{SOC} = \frac{Q_{tot} - \text{DOD}}{Q_{tot}}, \quad (14)$$

using the depth of discharge (DOD) and total capacity Q_{tot} , given in [Ah].

SOC based on Coulomb counting:

$$z(t) = z(0) + \int_0^t \frac{\eta}{Q_{tot}} i(\tau) d\tau \quad (15)$$

or in discrete time:

$$z[k] = z[k-1] + \frac{\eta}{C_n} i[k] \Delta t \quad (16)$$

where Q_{tot} is the is total cell capacity, or known as nominal capacity, η is the Coulombic efficiency, i is the current, and Δt is the time step.

Resistance of a battery:

$$R_{batt} = V_{co}^{batt} \frac{V_{nom}^{batt} - V_{co}^{batt}}{P_{max}} = m_s^2 \cdot V_{co}^{cell} \frac{V_{nom}^{cell} - V_{co}^{cell}}{P_{max}} \quad (17)$$

where V_{co}^{batt} is the cut-off voltage of the battery, V_{nom}^{batt} is the nominal voltage of the battery, P_{max} is the maximum power of the battery, m_s is the number of cells in series.

Coulombic efficiency:

$$\eta_{coul} = \frac{\text{Number of coulombs on discharge}}{\text{Number of coulombs on charge}} \cdot 100\% \quad (18)$$

Voltage efficiency:

$$\eta_V = \frac{\text{Average discharge voltage}}{\text{Average charge voltage}} \cdot 100\% \quad (19)$$

Energy efficiency:

$$\eta_{energy} = \eta_{coul} \cdot \eta_V = \frac{\text{Energy out}}{\text{Energy in}} \cdot 100\% \quad (20)$$

Battery efficiency:

$$\eta_{batt} = \frac{P_{out}}{P_{out} + P_{loss}} \quad (21)$$

Cell efficiency:

$$\eta_{cell} = \frac{V_{out}}{V_{in}} \quad (22)$$

Battery packs formulas:

Consider a pack/module/battery of m cells in series and n cells in parallel ($mS - nP$).

- Number of cells: $N_c = mn$
- Voltage: $V_{batt} = mV_{cell}$
- Current: $I_{batt} = nI_{cell}$
- Capacity: $Q_{batt} = nQ_{cell}$
- Energy: $E_{batt} = N_c E_{cell} = N_c Q_{cell} V_{cell}$

The resistance for the whole battery is calculated by

$$R_{tot} = \underbrace{\frac{mR_i + (m+1)R_w}{n}}_{\text{string resistance}} = \underbrace{\frac{m}{n}R_i}_{R_{int}} + \underbrace{\frac{m+1}{n}R_w}_{R_{ext}} \quad (23)$$

where R_w is the connection resistance.

Proportional properties of the battery:

- $Q \sim m$
- $m \sim \mathbb{V}$

- $\mathbb{V} \sim \delta A_s$
- $A_s \sim \frac{1}{R_i}$

Where A_s is the electrode/seperator area, δ is the sheet thickness, $\mathbb{V} = A_s \delta$ is the volume and $m = \rho \mathbb{V}$ is the mass.

Cell balancing:

$$Q_{\text{batt}} = (1 - (z_{\text{max}} - z_{\text{min}})) Q_{\text{cell}} \quad (24)$$

$$E_{\text{batt}} \approx (1 - \Delta z) E_{\text{batt}}^{\text{nom}} \quad (25)$$

The temperature in a cylindrical cell depending on the radius can be described as:

$$T(r) = T_0 + \frac{\dot{q}_{\text{gen}}}{2k} \left(r_i^2 \ln \frac{r}{r_0} + \frac{1}{2} (r_0^2 - r^2) \right) \quad (26)$$

where k is the thermal conductivity ($\text{W}/(\text{m} \cdot \text{K})$), \mathbf{q} is the heat flux vector (W/m^2), and \dot{q}_{gen} (W/m^3) is the homogenous heat generation given by

$$\dot{q}_{\text{gen}} = \frac{R_i I^2}{\mathbb{V}} = \frac{R_i}{\mathbb{V} \cdot Q^2} (\text{C-rate})^2. \quad (27)$$

Mechanical formulas:

Kenetic energy:

$$E_k = \frac{1}{2} m v^2 \quad (28)$$

Aidrag force:

$$F_d = \frac{1}{2} \rho v^2 C_d A \quad (29)$$

where ρ is the air density, v is the velocity, C_d is the drag coefficient, and A is the cross-sectional area.

Rolling resistance:

$$F_r = f_r m g \quad (30)$$

where f_r is the rolling resistance coefficient, m is the mass of the vehicle, and g is the acceleration due to gravity.

And $P = Fv$.

pq-formula:

$$0 = x^2 + px + q \quad (31)$$

$$x = \frac{-p}{2} \pm \sqrt{\left(\frac{p}{2}\right)^2 - q} \quad (32)$$

Part I

Exercises

Introduction to Battery Systems

Exercise 1.1.

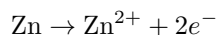
An electrochemical cell converts chemical energy into electrical energy through a reduction-oxidation reaction and consists of several main parts. Describe the parts listed below.

- a) Cathode
- b) Anode
- c) Electrolyte
- d) Separator
- e) External circuit

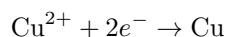
Exercise 1.2.

The half cell reactions for a primary zinc-copper cell are given as:

Anode:



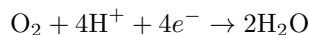
Cathode:



- a) Write full cell reaction.
- b) What is n for the full cell reaction? Here, n represents the number of moles of electrons transferred in the full cell reaction.

The anode is kept but the cathode is changed to an oxygen reaction:

Cathode:

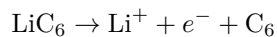


- c) What is the full reaction with the new cathode?
- d) What is n now?

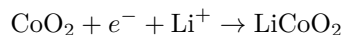
Exercise 1.3.

A common lithium-ion cell is the so-called Lithium Cobalt Oxide (LCO) cell, which, as the name suggests, uses lithium cobalt oxide (LiCoO_2) as the cathode material and graphite (LiC_6) as the anode material.

Anode:



Cathode:



- a) Write the full cell equation.
- b) The reactions are written for when the cell is discharging. What is the full cell reaction during charging?

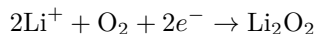
Exercise 1.4.

The lithium-air (Li-air) cell has gained attention for its potential to offer much higher energy densities than conventional lithium-ion batteries. One proposed cathode reaction is the formation of lithium peroxide (Li_2O_2)

Anode:



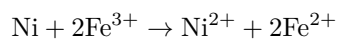
Cathode:



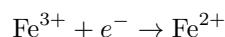
Write the full cell reaction.

Exercise 1.5.

The full cell reaction



has the following half cell reaction of the cathode

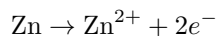


What is the anode half cell reaction if $n = 2$ for the full cell reaction?

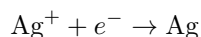
Exercise 1.6.

The silver-zinc battery is known for high energy density and has a history of being used in space applications. Given ambient standard states and the half-reactions:

Anode:



Cathode:



What is the standard cell potential?

(Use the table in [Appendix A: Standard Electrode Potentials](#))

Exercise 1.7.

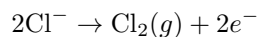
We would like to charge a lithium-ion battery using a current of 5 A for 3 hours.

- How many moles of lithium-ions are deposited on the anode?
- How much lithium (in grams) is deposited on the anode?

The half-reaction for lithium deposition is:

**Exercise 1.8.**

A current of 15 A passes through an aqueous NaCl (table salt) solution for 20 minutes. The electrode reaction for chlorine gas production is:



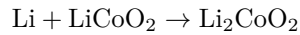
- How many grams of chlorine gas are produced?
- What volume of chlorine gas does this represent at 100 kPa and 25°C?
(You can use the ideal gas law here.)

Exercise 1.9.

Consider the half-cell and full-cell reactions for lithium and lithium cobalt oxide (LiCoO_2) in a lithium-ion battery:

Half-Cell Reactions:

- **Anode (Li):** $\text{Li} \rightarrow \text{Li}^+ + e^-$
- **Cathode (LiCoO_2):** $\text{LiCoO}_2 + \text{Li}^+ + e^- \rightarrow \text{Li}_2\text{CoO}_2$

Full-Cell Reaction:

Given data:

- Faraday's constant (F): 96485 C/mol
- Molar mass of lithium (Li): 6.94 g/mol
- Molar mass of lithium cobalt oxide (LiCoO_2): 97.87 g/mol

Questions:

- a) Using the formula for charge density

$$\frac{Q}{m_A} = \frac{F \cdot n}{M_A}$$

calculate the theoretical charge density (in Ah/g) for the anode reaction involving lithium.

- b) Using the same formula, calculate the theoretical charge density (in Ah/g) for the cathode reaction involving lithium cobalt oxide.
- c) Compute the total charge density (in Ah/g) for the full cell using both electrodes with the following equation:

$$\frac{\text{Ah}}{\text{g}_{\text{cell}}} = \left(\frac{\text{g}}{\text{Ah}_{\text{anode}}} + \frac{\text{g}}{\text{Ah}_{\text{cathode}}} \right)^{-1}$$

- d) Compute the energy density (in Wh/kg) for the full cell. Assume the voltage of the full cell reaction to be $V = 3.85$ V.

Exercise 1.10.

The overall cell reaction for discharge of a lead-acid battery is



What is the theoretical energy density if we have two moles of electrons and the average open circuit-voltage is 2 V?

Exercise 1.11.

Given the table of Standard Electrode Potentials in [Appendix A: Standard Electrode Potentials](#). It is possible to see that the electrochemical reaction $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ gives a standard potential $U^0 = 0.337$ [V]. A similar reaction $\text{Cu}^+ + e^- \rightarrow \text{Cu}$ gives a standard potential $U^0 = 0.5219$ [V].

- a) What is the Gibbs free energy for $\Delta G_{\text{Cu}^{2+}/\text{Cu}}^0$?
- b) Compute the standard potential $U_{\text{Cu}^{2+}/\text{Cu}^+}^0$ of $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$.

Exercise 1.12.

Compare the open circuit voltage (thermodynamic potential) for a lead-acid battery with sulfuric acid and a lithium-air battery with both with a concentration of 5 M at +25 and -25 °C.

Note: Full cell potential for Li-air is 2.96 V

- a) What battery is least sensitive to temperature?
- b) What happens if the concentration is changed to 1 M?
- c) Discuss findings in b)

Chapter 2

Battery Properties

Exercise 2.1.

- a) Sketch a container design of a battery cell and point out the following parts:
- Cathode
 - Anode
 - Electrolyte
 - Seperator
 - Conductor
 - Negative terminal
 - Positive terminal
- b) Name a characteristic property for the different battery designs listed below:
- Container
 - Cylindrical cell
 - Prismatic cell

Exercise 2.2.

Draw plots to fill the empty figures in Figure 2.1. The information for each cell or state is presented above the columns. The plots in the first column should represent a nominal cell at full capacity. The second column should represent the same cell from the first column but in a degraded state. The third column should show a nominal cell with the same chemistry and half the capacity as the cell in the first column.

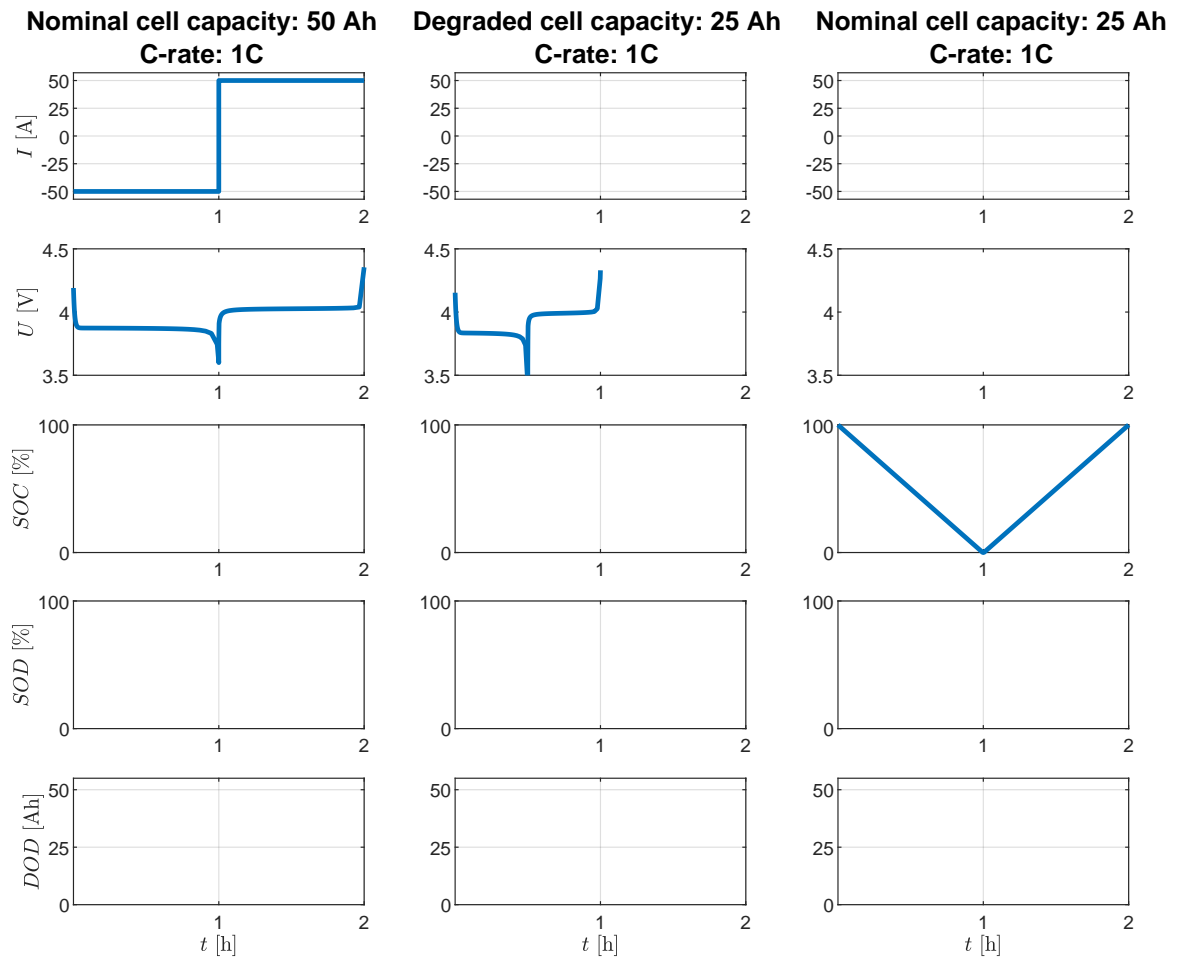


Figure 2.1: Fill in for Exercise 2.2

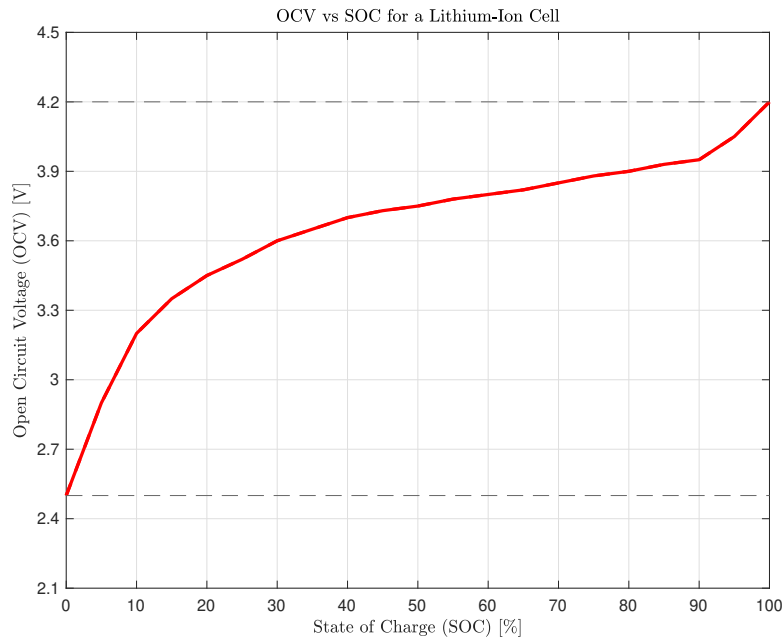


Figure 2.2: OCV for a lithium-ion cell.

Exercise 2.3.

Figure 2.2 shows how the OCV depends on the SOC for a lithium-ion cell with marked cut-off voltages. The cell has a capacity of 40 Ah, an internal resistance of 7.5 mΩ, and is charged and discharged using a 1C constant current (CC) rate.

- Approximately how much will the cell potential deviate from the OCV?
- Draw the general appearance of the cell potential if it is charged or discharged between 0% and 100% SOC. Consider charging and discharging as two different events, i.e., they are independent of each other.
- Draw the general appearance of the cell potential if the marked cut-off voltages are respected for charge and discharge. Consider charging and discharging as two different events, i.e., they are independent of each other.
- Comment on the difference between the two cases of charging and discharging.

Exercise 2.4.

Lets consider a NMC based Lithium-ion cell. The potential of the positive electrode is given by

$$\begin{aligned}
 U_+(x) = & -0.8090x + 4.4875 - 0.0428 \\
 & - 0.0428 \tanh(18.5138(x - 0.5542)) \\
 & - 17.7326 \tanh(15.7890(x - 0.3117)) \\
 & + 17.5842 \tanh(15.9308(x - 0.3120)),
 \end{aligned} \tag{2.1}$$

and the potential of the negative electrode is given by

$$\begin{aligned}
 U_-(x) = & 1.9793e^{(-39.3631x)} + 0.2482 \\
 & - 0.0909 \tanh(29.8538(x - 0.1234)) \\
 & - 0.04478 \tanh(14.9159(x - 0.2769)) \\
 & - 0.0205 \tanh(30.4444(x - 0.6103)),
 \end{aligned} \tag{2.2}$$

as a function of the stoichiometry x using parametrization¹. The functions can be loaded from `Exercise_2_4.mat`. The stoichiometry is defined as

$$x = \frac{c_s}{c_s^{\max}} \tag{2.3}$$

where c_s is the concentration of lithium and c_s^{\max} is the maximum concentration of lithium in the electrode. Assume the lithium stoichiometry ranges are [0.9084, 0.2661] for the positive electrode and [0.0279, 0.9014] for the negative electrode, respectively. Plotting the function against their stoichiometry range gives the Figure in 2.3 and 2.4.

- a) When the positive electrode is fully lithiated with a stoichiometry of 0.9084, what is the corresponding lithium stoichiometry of the negative electrode?
- b) How is state of charge (SOC) related to stoichiometry?
- c) Set up a function that provides the corresponding stoichiometry for a given SOC. SOC varies between 0% (fully lithiated positive electrode) and 100% (fully delithiated positive electrode). Optionally, plot the function.
- d) Calculate the full cell potential at 50% SOC.
- e) Briefly explain why imbalance occurs and its consequences.
- f) Consider an imbalance scenario where the upper limit of the stoichiometry range for the positive electrode is reduced by 20%, while the negative electrode remains unchanged. Calculate the full cell potential at 50% SOC in this case.

¹Chang-Hui Chen, Ferran Brosa Planella, Kieran O'Regan, Dominika Gastol, W. Dhammika Widanage, and Emma Kendrick. "Development of Experimental Techniques for Parameterization of Multi-scale Lithium-ion Battery Models." *Journal of the Electrochemical Society* 167 (2020): 080534.

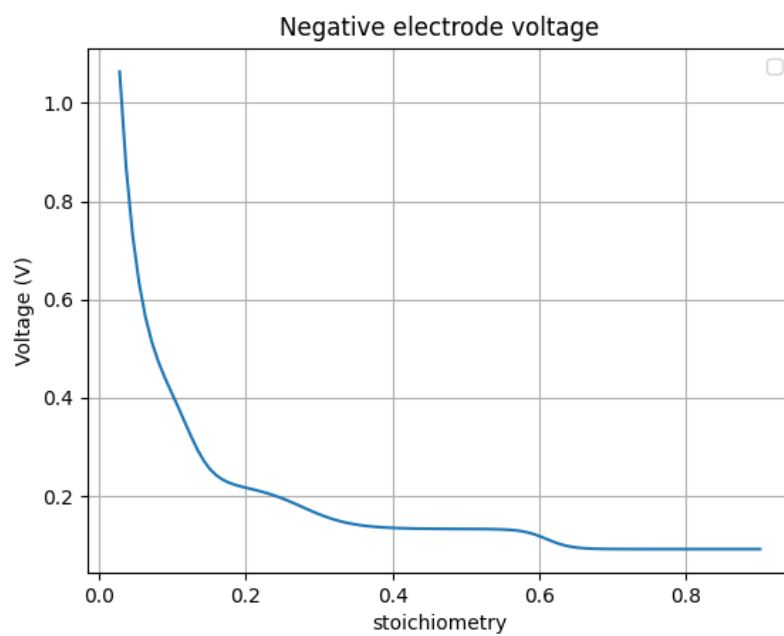


Figure 2.3: Potential of negative electrode

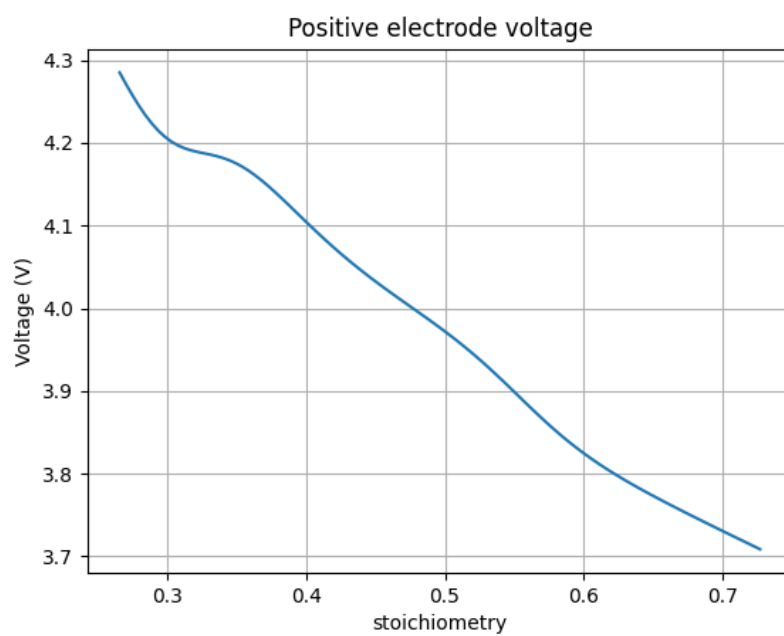


Figure 2.4: Potential of positive electrode

Exercise 2.5.

A 3 Ah lithium-ion battery is charged at 25 °C using the CCCV (Constant Current, Constant Voltage) method. The internal resistance of the battery is $R_i = 0.05 \Omega$, and the open circuit voltage (OCV) depends on the state of charge (SOC). During charging:

- In the constant current (CC) phase, the terminal voltage V_t is given by:

$$V_t = \text{OCV}(\text{SOC}) + I \cdot R_i,$$

where $I = 1C = 3 \text{ A}$.

- The constant voltage (CV) phase starts at $\text{SOC} = 95\%$, where $V_t = V_{\max} = 4.2 \text{ V}$. During the CV phase, the current I is given by:

$$I = \frac{V_{\max} - \text{OCV}(\text{SOC})}{R_i}.$$

Answer the following questions:

- During the CC phase, calculate the terminal voltage V_t at $\text{SOC} = 50\%$, given that $\text{OCV}(\text{SOC} = 50\%) = 3.6 \text{ V}$.
- During the CV phase, calculate the charging current I at $\text{SOC} = 97\%$, given that $\text{OCV}(\text{SOC} = 97\%) = 4.15 \text{ V}$.
- Explain how the CCCV charging method ensures safe and efficient battery charging, referring to both the CC and CV phases.

Exercise 2.6.

Cold Cranking Amps (CCA) measure a battery's ability to start an engine in cold climates. CCA tells you how many amps a 12-volt battery may support for 30 seconds at -17.8 degrees Celsius before the voltage drops to at least 7.2 volts per cell.

Use the following battery data for an internal combustion engine lead-acid starter battery given in Table 2.1.

Table 2.1: Battery data for a starter battery to a SAAB 9-5 BioPower.

| Unit | Value |
|--------------------------------|-------|
| Voltage [V DC] | 12 |
| Capacity [Ah] | 74 |
| Cold cranking amps (-18°C) [A] | 660 |
| Charge voltage [V DC] (max) | 16 |
| Charge current [A] (max) | 18 |

Use this data to calculate

- the C-rate at the rated cold cranking amps
- the crank power

Note: Cold-cranking amps (CCA) is a rating of how much current can be pulled from the battery in cold conditions. The rating is done at -18°C.

Exercise 2.7.

The rate capability of a lithium-ion cell is described by the modified Shepherd equation. Calculate the theoretical energy ($U \cdot Q$) and compare it with the energy available at discharge rates of

- a) 0.2C
- b) 1.5C
- c) 4C
- d) Compare the energy delivered at the different rates.

Assume the battery has a capacity of 5 Ah and is discharged to a cutoff potential of 2.5 V. The cell voltage (V_{cell}) is modeled as follows:

$$V_{\text{cell}} = 4.2 - 0.004I - 0.013 \left(\frac{Q}{Q - It} \right) I - 0.0015 \cdot \exp \left(\frac{0.09}{Q} \cdot It \right)$$

Where:

- I is the current in amperes.
- Q is the battery capacity (5 Ah).
- t is the discharge time in hours.
- The cutoff potential is 2.5 V.

Exercise 2.8.

The rate capability of a lithium-ion cell is described using the Shepherd equation. Calculate the theoretical energy $U \cdot Q$ and compare it with the energy available at discharge rates of 0.1C, 1.0C, and 3C.

Assume that the battery has a capacity of 6 Ah and is discharged to a cutoff potential of 2 V. The Shepherd equation for the voltage of the cell is given as:

$$V_{\text{cell}} = 4.131 - 0.00388I - 0.0151138 \left(\frac{Q}{Q - It} \right) I - 0.02 \exp \left(\frac{0.1}{Q} It \right)$$

Where:

- V_{cell} is the voltage of the cell,
- I is the discharge current (A),
- t is the time,
- $Q = 6$ Ah is the battery capacity,
- The cutoff voltage is $V_{\text{cutoff}} = 2$ V.

Exercise 2.9.

The following efficiencies are defined for a complete charge-discharge cycle:

- $\eta_{\text{coulomb}} = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}}$
 $Q_{\text{discharge}}$: Number of coulombs on discharge
 Q_{charge} : Number of coulombs on charge
- $\eta_{\text{voltage}} = \frac{V_{\text{discharge_avg}}}{V_{\text{charge_avg}}}$
 $V_{\text{discharge_avg}}$: Average discharge voltage
 $V_{\text{charge_avg}}$: Average charge voltage
- $\eta_{\text{energy}} = \frac{E_{\text{discharge}}}{E_{\text{charge}}}$
 $E_{\text{discharge}}$: Energy discharge
 E_{charge} : Energy charge

Given constant current I for both charging and discharging. Show that:
 $\eta_{\text{energy}} = \eta_{\text{coulomb}} \cdot \eta_{\text{voltage}}$

Exercise 2.10.

Use your computer to solve this question. Given the parameters in illustration 7.3 in the course book *Electrochemical Engineering* found in Table 2.2. Assume constant discharge currents I and use the Shepherds equation for the cell voltage $V(t)$. Assume $V_{co} = 2$ [V].

- a) Compute the specific energy as a function of power in a Rangone plot.
- b) Plot the average discharge efficiency of the battery as function of the discharge current and estimat the efficiency for 0.5C, 1C, 2C and 3C.
- c) Plot the momentary efficiency of a battery discharged at 1C as a function of DoD.

What is the highest efficiency and for what DoD is that obtained.

| Table 2.2: <i>Shepherd</i> model parameters | | | | |
|---|--------------|--------------|-------|------|
| U | R_{int} | K | A | B |
| [V] | [Ω] | [Ω] | [V] | [Ah] |
| 4.131 | 0.003881 | 0.015138 | -0.02 | 0.1 |

Chapter 3

Equivalent Circuit Models

Exercise 3.1.

The data from the **A123** cell can be found in the file named *A123_low_current_data.mat* use this to:

- (a) Estimate the battery capacity, Q . Use equation (11) in Formulas.
- (b) Estimate the OCV curve for the cell and create an OCV function.

Exercise 3.2.

Write down an equivalent circuit model (ECM) in time-continuous state-space form for the 2-RC circuit model shown in Figure 3.1.

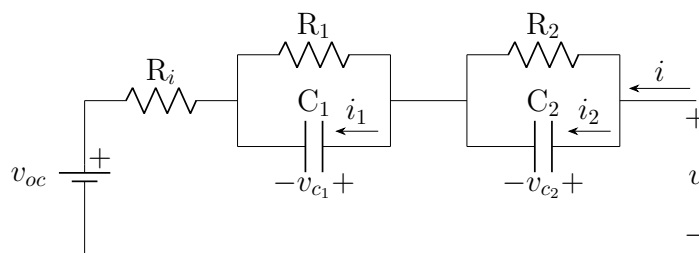


Figure 3.1: Circuit model for Exercise 3.2

Exercise 3.3.

Write Exercise 3.2 in discrete form.

Hint: Use the forward Euler method to discretize the equations.

$$\frac{dv_c}{dt}(t) \approx \frac{v_c(t + \Delta t) - v_c(t)}{\Delta t} = \frac{v_{c,k+1} - v_{c,k}}{\Delta t} \quad (3.1)$$

Exercise 3.4.

Using Figure 3.2, identify:

- (a) Internal resistance R_i .
- (b) Resistance R .
- (c) Capacitance C .

using the step responses in voltage. The cell is discharged with -1 A and the current is turned off at 100 s.

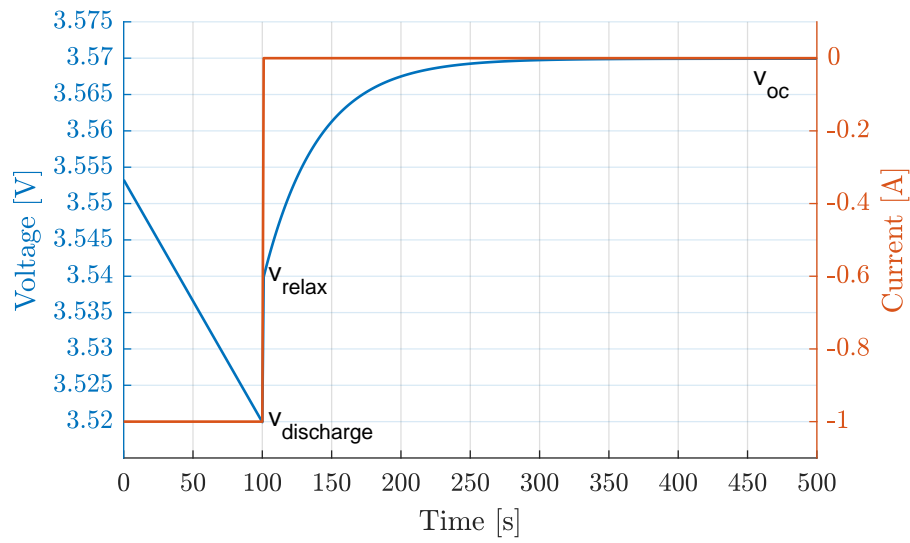


Figure 3.2: Step in current with voltage response over time.

Exercise 3.5.

In the previous exercises the model parameters are only estimated at a specific SOC, the one where the step is taken. Another way to estimate the parameters in the ECM is to use linear regression. By doing this, the parameters are estimated for a wider range of SOC. To use linear regression the dependent variable Y and the so called regressor X need to have a linear relationship. The regressor coefficient, Θ , describe how much the Y is expected to change as X increases, and it's Θ we want to find.

- a) Use the ECM in time discrete form from Exercise 3.3 to set up the system as

$$Y = X\Theta$$

Which means that for each step k , row k is expressed as

$$y_k = x_{k1}\theta_1 + x_{k2}\theta_2 + x_{k3}\theta_3$$

- b) Find the values of R_i , R , C using linear regression.

Hint: Θ can be computed in Matlab using $\Theta = X \backslash Y$

- c) Using the values estimated in b), simulate the ECM for the same time intervall. Compare the results with the measurements.
- d) Use Y and $X\Theta$, plot them in the same figure and compare the results.

Note that since the open circuit voltage is non-linear, since it changes with SOC, it needs to be removed to be able to use the linear regression. Do this by for example introducing a new variable $\tilde{V}_k = V_k - V_{OC,k}$.

Exercise 3.6.

Please examine the optimization codes provided in `Exercise_3_6.m`, which uses `fminunc` to identifying impedance parameters (R_i, C, R) from the dynamic operation of a lithium-ion battery. The tasks will be to evaluate different ways to initialize the optimization:

- Start the optimization with R_i , R , C from the linear regression in Exercise 3.5 and optimize these parameters.
- Start the optimization with R_i , R , C from the linear regression in Exercise 3.5, optimize these parameters and normalize the parameter values.
- Start the optimization with R_i , R , C from the linear regression in Exercise 3.5, initialize the SOC with v_1 and optimize these parameters.
- Start the optimization with R_i , R , C from the linear regression in Exercise 3.5, initialize the SOC with v_1 and normalize and optimixe the parameter values.
- Start the optimization with R_i , R , C from the linear regression in Exercise 3.5, initialize the SOC with v_1 and initialize the capacity, Q . Then normalize and optimixe the parameter values.

Given the result achieved in the subtasks, discuss whether the normalization is necessary or not.

Exercise 3.7.

In the lecture, we saw how to convert the potential of a parallel circuit, v_c , into a time-discrete form using the Euler forward method. We will now apply the same approach to the State of Charge (SOC) using Coulomb counting, denoted as $z(t)$.

Part II

Answers

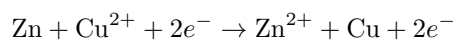
Introduction to Battery Systems

Exercise 1.1.

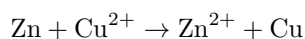
- a) Cathode: (positive electrode). Electrons are absorbed from the external circuit when the electrode is reduced.
- b) Anode: (negative electrode). Electrons are emitted to the external circuit when the electrode is oxidized.
- c) Electrolyte: (ion conductor). Medium for transport of charged ions between anode and cathode.
- d) Separator: physically separates the anode and cathode, preventing them from directly contacting each other, which would cause a short circuit. It allows ions to pass through but blocks the direct flow of electrons.
- e) External circuit: provides the route for electron flow, allowing the battery to deliver electrical energy to a device.

Exercise 1.2.

- a) To obtain the full cell reaction with electrons included, we combine the anode and cathode reactions:



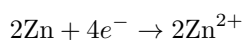
Removing the electrons gives the simplified full cell reaction:



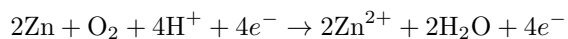
- b) Here, n represents the number of moles of electrons transferred in the full cell reaction. Since 2 moles of electrons are transferred from zinc to copper, we have:

$$n = 2$$

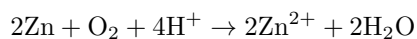
- c) To obtain the full reaction, we need to balance the electron transfer. The anode transfers 2 electrons, and the new cathode requires 4 electrons. Thus, we multiply the anode reaction by 2:



The balanced full cell reaction, including electrons, is:



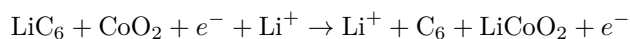
Removing the electrons gives the simplified full cell reaction:



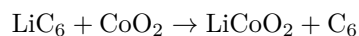
- d) Number of electrons involved in the full cell reaction: $n = 4$

Exercise 1.3.

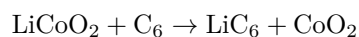
- a) Combining the anode and cathode reactions, we write the full cell reaction including electrons:



Removing the electrons gives us the simplified full cell reaction:



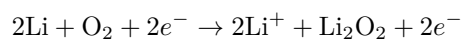
- b) During charging, the reactions are reversed. The full cell reaction for charging will be as for discharging but with the arrow in the other direction:



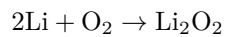
Exercise 1.4. To balance the electrons, we notice that the anode produces 1 electron while the cathode consumes 2 electrons. Therefore, we multiply the anode reaction by 2:



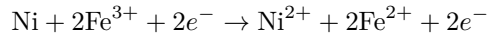
Now, combining these reactions gives us the full cell reaction including electrons:



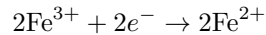
Removing the electrons yields the simplified full cell reaction:



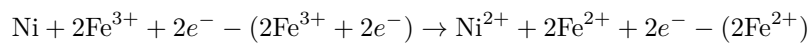
Exercise 1.5. Since $n=2$ it means that 2 moles of electrons are involved in the reaction. We can write the full cell reaction with the electrons included:



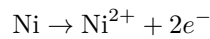
To subtract the cathode half cell reaction we need to balance it first:



Now subtracting it from the full cell reaction, we get the anode half cell reaction:



This simplifies to:



Exercise 1.6. 1.56 V

Exercise 1.7.

- a) The number of moles of lithium deposited on the anode is **0.5597 moles**.
- b) The mass of lithium deposited on the anode is **3.8849 g**.

Exercise 1.8.

- a) The mass of chlorine gas produced is **6.616 g**.
- b) The volume of chlorine gas produced is **0.2313 m³ = 231.6 liters**.

Exercise 1.9.

- a) Anode charge density: $3.86 \frac{\text{Ah}}{\text{g}}$
- b) Cathode charge density: $0.273 \frac{\text{Ah}}{\text{g}}$
- c) Full-cell charge density: $0.254 \frac{\text{Ah}}{\text{g}}$
- d) Energy density: $0.977 \frac{\text{Wh}}{\text{g}}$

Exercise 1.10. Using the molar mass Pb(207 g/mol), PbO₂(239 g/mol), and 2H₂SO₄(196 g/mol), the charge density is

$$\frac{Q}{m_A} = \frac{F \cdot n}{M_A} = \frac{96485 \cdot 2}{207 + 239 + 2 \cdot 196} = 83.5 \text{ Ah/kg}$$

Multiplying this with the average voltage of 2 V gives the theoretical energy density:

$$V \cdot \frac{Q}{m_A} = 2 \cdot 83.5 = 167 \text{ Wh/kg}$$

Exercise 1.11.

- a) Use $\Delta G_{Cu^{2+}/Cu}^0 = -2FU_{Cu^{2+}/Cu}^0 = -65.03$ [kJ/mol]
- b) Use $\Delta G_{Cu^{2+}/Cu}^0 = -2FU_{Cu^{2+}/Cu}^0$, $\Delta G_{Cu^+/Cu}^0 = -FU_{Cu^+/Cu}^0$
 and $\Delta G_{Cu^{2+}/Cu^+}^0 = -FU_{Cu^{2+}/Cu^+}^0$.
- This gives: $\Delta G_{Cu^{2+}/Cu^+}^0 = \Delta G_{Cu^{2+}/Cu}^0 - \Delta G_{Cu^+/Cu}^0$
- $\Leftrightarrow -FU_{Cu^{2+}/Cu^+}^0 = -2FU_{Cu^{2+}/Cu}^0 - (-FU_{Cu^+/Cu}^0)$
- $\Leftrightarrow U_{Cu^{2+}/Cu^+}^0 = 2U_{Cu^{2+}/Cu}^0 - U_{Cu^+/Cu}^0 = 0.1521$ [V]

Exercise 1.12.

- a) From Lecture 1 and Exercise 1.4

$$U = U^0 - \frac{RT}{nF} \ln \left(\prod_{\text{ions}} \left(\frac{c_i}{c_i^0} \right)^{s_i} \prod_{\text{gas}} \left(\frac{p_i}{p_i^0} \right)^{s_i} \right)$$

For lead-acid @ 25C: $2.041 - \frac{8.314 \cdot (273.15 + 25)}{2.96485} \ln \left(\frac{5}{1}^{-2} \cdot \frac{2.5}{1}^{-4} \right) = 2.20$ V

For lead-acid @ -25C: $2.041 - \frac{8.314 \cdot (273.15 - 25)}{2.96485} \ln \left(\frac{5}{1}^{-2} \cdot \frac{2.5}{1}^{-4} \right) = 2.17$ V

For Li-air @ 25C: $2.96 - \frac{8.314 \cdot (273.15 + 25)}{2.96485} \ln \left(\frac{5}{1}^{-1} \cdot \frac{5}{1}^{-1} \right) = 3.00$ V

For Li-air @ -25C: $2.96 - \frac{8.314 \cdot (273.15 - 25)}{2.96485} \ln \left(\frac{5}{1}^{-1} \cdot \frac{5}{1}^{-1} \right) = 2.99$ V

This shows Li-air is least sensitive to temperature changes

- b) For lead-acid @ 25C: $2.041 - \frac{8.314 \cdot (273.15 + 25)}{2.96485} \ln \left(\frac{1}{1}^{-2} \cdot \frac{2.1}{1}^{-4} \right) = 2.08$ V

For lead-acid @ -25C: $2.041 - \frac{8.314 \cdot (273.15 - 25)}{2.96485} \ln \left(\frac{1}{1}^{-2} \cdot \frac{2.1}{1}^{-4} \right) = 2.07$ V

For Li-air @ 25C: $2.96 - \frac{8.314 \cdot (273.15 + 25)}{2.96485} \ln \left(\frac{1}{1}^{-1} \cdot \frac{1}{1}^{-1} \right) = 2.96$ V

For Li-air @ -25C: $2.96 - \frac{8.314 \cdot (273.15 - 25)}{2.96485} \ln \left(\frac{1}{1}^{-1} \cdot \frac{1}{1}^{-1} \right) = 2.96$ V

In this case, Li-air has no dependence on temperature.

- c) If M=1, the natural logarithm sums to 1 and ln(1) is 0. No matter the temperature range, there will be no change in the potential for the lithium battery. This further proves that the model is simplified.

Chapter 2

Battery Properties

Exercise 2.1. See lecture slides

Exercise 2.2. See Figure 2.1.

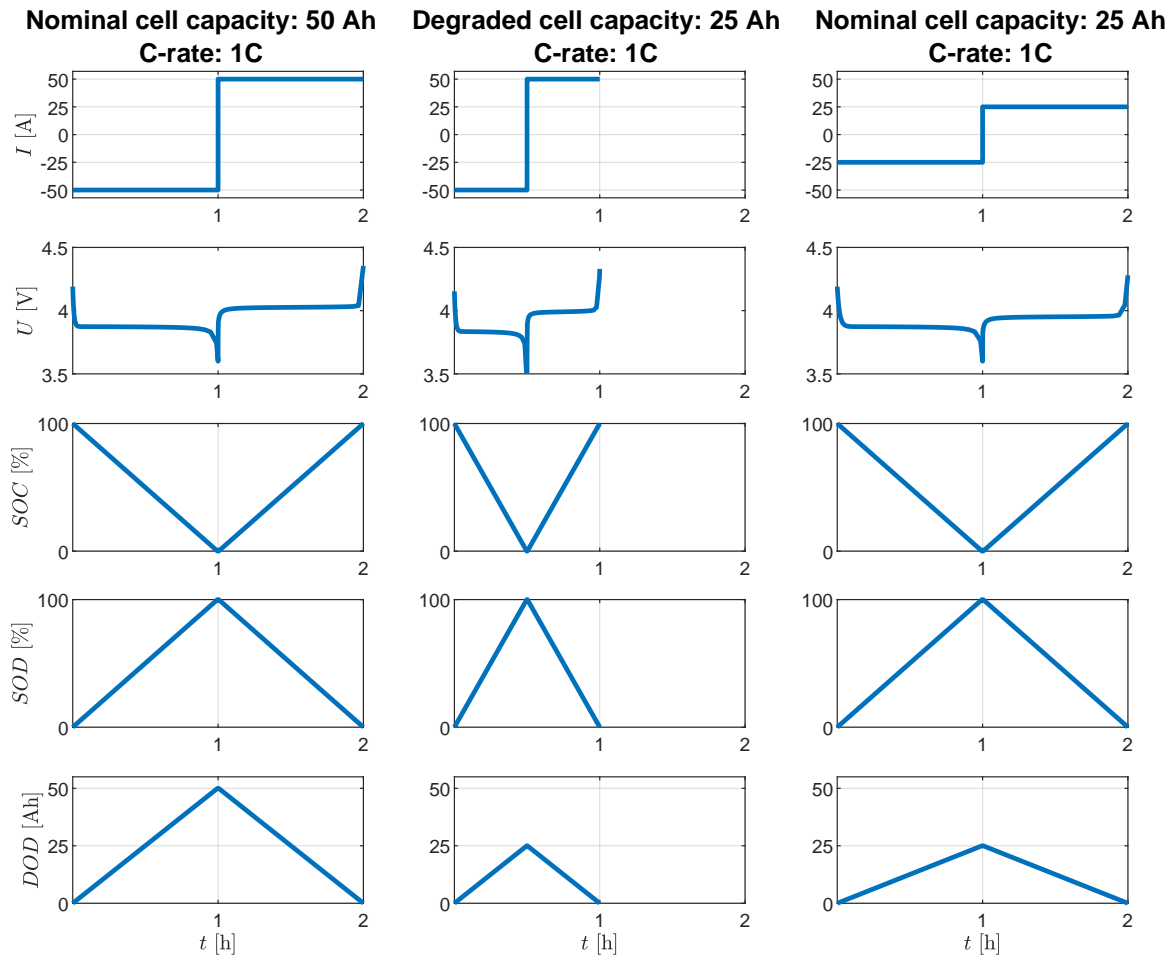


Figure 2.1: Answer to Exercise 2.2

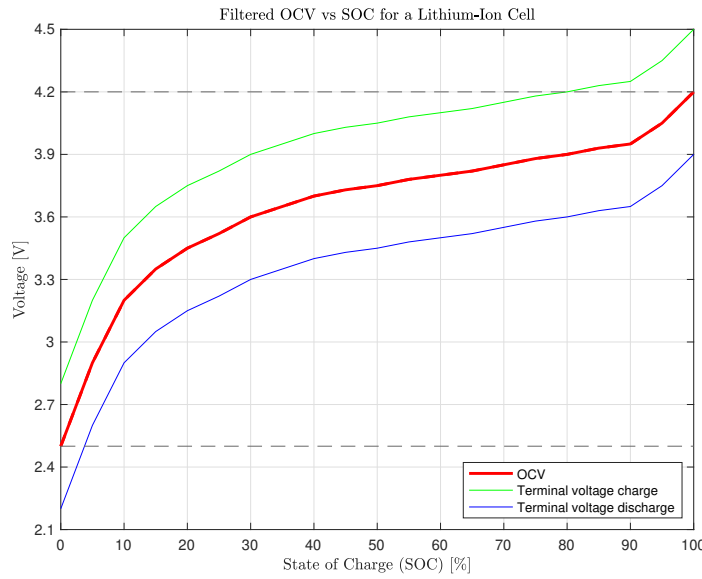


Figure 2.2: Cell potential for charge and discharge.

Exercise 2.3.

- a) Depending on if the cell is charging or discharging, the cell potential for this simplified case, will deviate $\pm IR = 0.3$ V. During charge:

$$V_{charge} = OCV(SOC) + IR$$

and during discharge:

$$V_{discharge} = OCV(SOC) - IR$$

- b) See Figure 2.2
- c) See Figure 2.3
- d) In the first case, when only considering the SOC, the cell potential goes beyond the cut-off voltages, and the cell can become overcharged or over-discharged. In the second case, the cell potential stays within the voltage limits, but the full SOC range is not utilized since we are charging and discharging at 1C. The terminal voltage will be reached quicker. Therefore, it is beneficial to start with constant voltage (CV) charging when reaching the cut-off voltage to safely reach the desired SOC range.

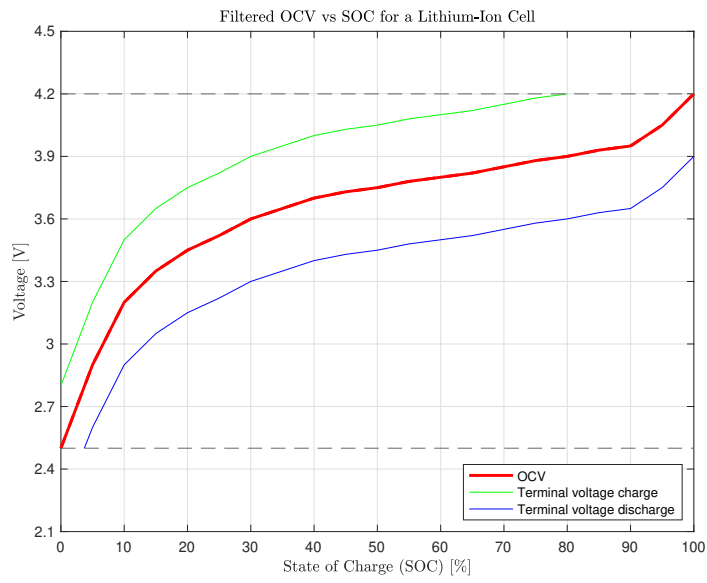


Figure 2.3: Cell potential for charge and discharge with cut-off voltages respected.

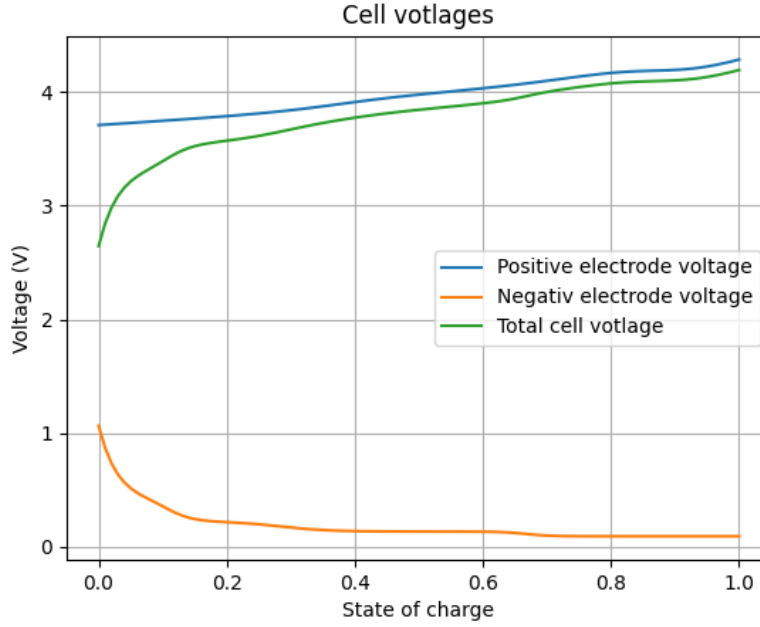


Figure 2.4: Potentials against SOC

Exercise 2.4.

- When the positive electrode is fully lithiated (stoichiometry = 0.9084), the corresponding stoichiometry for the negative electrode is 0.0279.
- SOC is linearly related to the stoichiometry because since it is proportional to the lithium content (stoichiometry) in the electrode material.
- Starting with positive electrode, when the electrode is fully lithiated (SOC = 0%), we get point (0, 0.9084). At 100% SOC, we get point (1, 0.2661). Therefore, the linear function relating SOC and stoichiometry is

$$x_+ = \frac{0.2661 - 0.9084}{1} \text{SOC} + 0.9084. \quad (2.1)$$

Similarly, for the negative electrode, the linear relationship is

$$x_- = \frac{0.9014 - 0.0279}{1} \text{SOC} + 0.0279. \quad (2.2)$$

This gives the plot in Figure 2.4, where total cell voltage is the difference between the half-cell potentials.

- Using the linear relations from part c), we calculate x_+ and x_- at 50% SOC. The full cell potential is determined by subtracting the half-cell potential of the anode from the cathode, yielding $U_+(x_+) - U_-(x_-) = 3.708$ V.
- Imbalance occurs due to cell aging and degradation, which can cause the capacity of one electrode to degrade faster than the other. This results in

a misalignment of the SOC between the electrodes, leading to a distorted open-circuit voltage (OCV) curve. In such cases, the model becomes inaccurate even before current is applied, as the electrodes reach their stoichiometric limits at different SOC levels.

- f) In the case of an imbalance where the upper stoichiometry limit of the positive electrode is reduced by 20%, the new upper limit becomes 0.7267. Calculating the full cell potential at 50% SOC in this scenario gives 3.843 V.

Exercise 2.5.

- a) The terminal voltage at $\text{SOC} = 50\%$ is 3.75 V.
- b) The charging current at $\text{SOC} = 97\%$ is 1.0 A.
- c) The CCCV algorithm combines fast charging in the CC phase with safe, gradual charging in the CV phase to protect the battery and extend its lifespan.

Exercise 2.6.

- a) The C-rate is calculated using the capacity of the battery and the CCA.

$$C = \frac{CCA}{Capacity} = \frac{660}{74} = 8.92.$$

During the 30 seconds at -18°C, the C-rate is 8.92.

- b) The crank power is calculated using the nominal power and the rated CCA

$$P = U \cdot I = 12 \cdot 660 = 7920 \text{ W} = 7.92 \text{ kW}$$

The maximum crank power is 7.92 kW.

Exercise 2.7. The Matlab code to this exercise is attached in the `Solution_2_7.m`.

The theoretical energy of the battery can be calculated by assuming it discharges at a constant nominal voltage. The energy is the product of capacity and nominal voltage:

$$\text{Energy } (U \cdot Q) = V_{\text{nominal}} \cdot Q$$

The nominal voltage is given as 4.2 V and the capacity is 5 Ah. Therefore:

$$\text{Energy}_{\text{theoretical}} = 4.2 \cdot 5 = 21 \text{ Wh}$$

- a) The discharge current for 0.2C is:

$$I = 0.2 \cdot 5 = 1 \text{ A}$$

We can now use the Shepherd equation to estimate the energy delivered at this rate. The voltage equation for 0.2C is:

$$V_{\text{cell}}(0.2C) = 4.2 - 0.004(1) - 0.013 \left(\frac{5}{5 - 1 \cdot t} \right) 1 - 0.0015 \cdot \exp \left(\frac{0.09}{5} \cdot 1 \cdot t \right)$$

The energy delivered can be calculated by integrating the product of voltage and current over the discharge time until the voltage drops to the cutoff voltage of 2.5 V with $t_{\text{cut-off}} = 4.96$.

The energy delivered is calculated by integrating the power over the discharge time:

$$E = \int_0^{t_{\text{cut-off}}} I V_{\text{cell}}(t) dt = I \cdot \int_0^{t_{\text{cut-off}}} V_{\text{cell}}(t) dt \quad (2.3)$$

then for 0.2C:

$$E = I \cdot \int_0^{4.96} V_{\text{cell}}(t) dt = 20.4905$$

- b) The discharge current for 1.5C is:

$$I = 1.5 \cdot 5 = 7.5 \text{ A}$$

Using the Shepherd equation for 1.5C:

$$V_{\text{cell}}(1.5C) = 4.2 - 0.004(7.5) - 0.013 \left(\frac{5}{5 - 7.5t} \right) 7.5 - 0.0015 \cdot \exp \left(\frac{0.09}{5} \cdot 7.5 \cdot t \right)$$

The energy delivered can be calculated by integrating the product of voltage and current over the discharge time until the voltage drops to the cutoff voltage of 2.5 V with $t_{\text{cut-off}} = 0.6256$.

By using Equation (2.3) in 1.5C:

$$E = I \cdot \int_0^{0.6256} V_{\text{cell}}(t) dt = 18.1996$$

c) The discharge current for 4C is:

$$I = 4 \cdot 5 = 20 \text{ A}$$

Similarly, we calculate the voltage at each time step using the Shepherd equation for 4C:

$$V_{\text{cell}}(4C) = 4.2 - 0.004(20) - 0.013 \left(\frac{5}{5 - 20t} \right) 20 - 0.0015 \cdot \exp \left(\frac{0.09}{5} \cdot 20 \cdot t \right)$$

The energy delivered can be calculated by integrating the product of voltage and current over the discharge time until the voltage drops to the cutoff voltage of 2.5 V with $t_{\text{cut-off}} = 0.209$.

By using Equation (2.3) in 4C:

$$E = I \times \int_0^{0.209} V_{\text{cell}}(t) dt = 14.8648$$

d) After performing these calculations, we compare the energy delivered at different C-rates (0.2C, 1.5C, and 4C) with the theoretical energy. The available energy at each discharge rate can be seen in Table 2.1. The cell voltage as a function of discharged energy is shown in Figure 2.5.

Table 2.1: Available Energy at Different Discharge Rates

| Discharge Rate | Available Energy (Wh) |
|----------------|-----------------------|
| 0.2C (1 A) | 20.4905 |
| 1.5C (7.5 A) | 18.1996 |
| 4C (20 A) | 14.8648 |

Exercise 2.8.

The Matlab code to this exercise is attached in the `Solution_2_8.m`.

The theoretical energy of the battery is calculated as:

$$E_{\text{theoretical}} = V_{\text{OC}} \cdot Q$$

where:

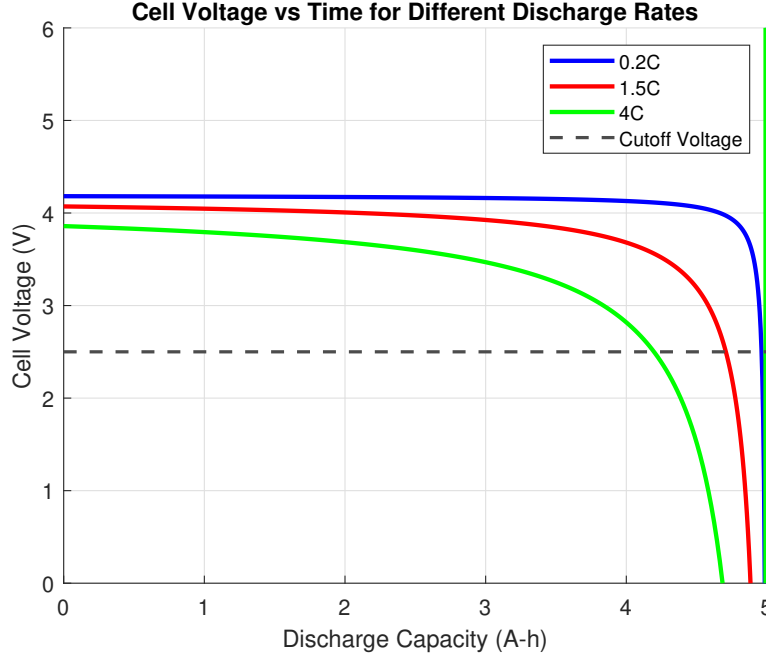


Figure 2.5: Cell voltage as function of discharged energy.

- $V_{OC} = 4.131 \text{ V}$ is the open circuit voltage,
- $Q = 6 \text{ Ah}$ is the battery capacity.

Thus:

$$E_{\text{theoretical}} = 4.131 \text{ V} \cdot 6 \text{ Ah} = 24.786 \text{ Wh}$$

The available energy is calculated by integrating the power over the discharge time. Power is the product of current and voltage, and the energy is:

$$E = I \cdot \int_0^{t_{\text{cut-off}}} V_{\text{cell}}(t) dt$$

For each discharge rate, we will first calculate the discharge current:

- At $0.1C$: $I = 0.1 \cdot Q = 0.1 \cdot 6 = 0.6 \text{ A}$
- At $1.0C$: $I = 1.0 \cdot Q = 1.0 \cdot 6 = 6 \text{ A}$
- At $3C$: $I = 3 \cdot Q = 3 \cdot 6 = 18 \text{ A}$

To find the energy available for each C-rate, use

$$E = \int_0^{t_{\text{cut-off}}} IV_{\text{cell}}(t) dt = I \cdot \int_0^{t_{\text{cut-off}}} V_{\text{cell}}(t) dt \quad (2.4)$$

The cut-off time for each case:

$$t_{\text{cut-off } 0.1\text{C}} = 9.956$$

$$t_{\text{cut-off } 1.0\text{C}} = 0.9568$$

$$t_{\text{cut-off } 3\text{C}} = 0.289$$

Then the Energy calculated by Equation (2.4) is

$$E_{0.1\text{C}} = 24.2422 \text{ Wh}$$

$$E_{1.0\text{C}} = 21.7516 \text{ Wh}$$

$$E_{3\text{C}} = 17.7245 \text{ Wh}$$

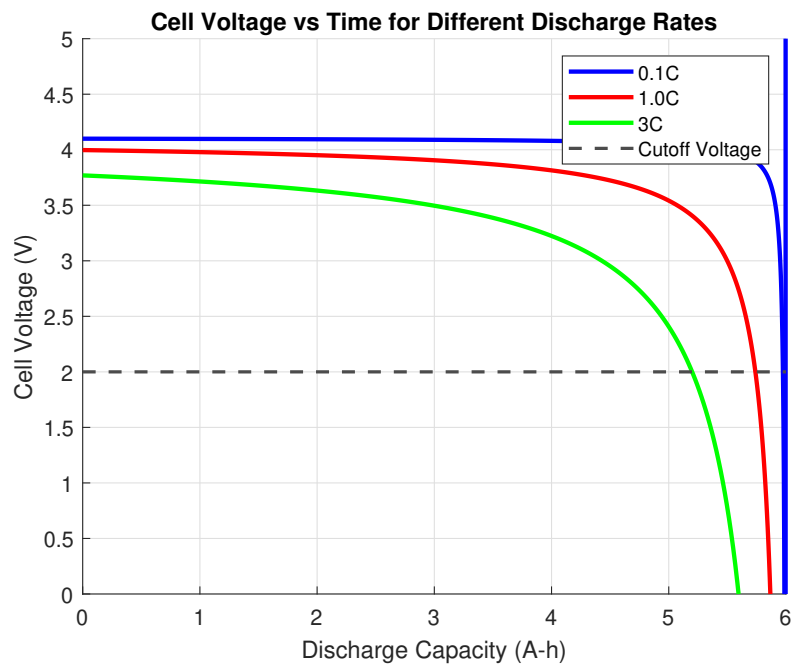
The theoretical energy of the battery is:

$$E_{\text{theoretical}} = 24.786 \text{ Wh}$$

The energy available at different discharge rates is:

Table 2.2: Available Energy at Different Discharge Rates

| Discharge Rate | Available Energy (Wh) |
|-----------------------|------------------------------|
| 0.1C (0.6 A) | 24.2422 |
| 1.0C (6 A) | 21.7516 |
| 3C (18 A) | 17.7245 |



Exercise 2.9.**Discharge:**

$$Q_{discharge} = I \cdot t_{discharge}$$

$$E_{discharge} = I \cdot \int_0^{t_{discharge}} V_{discharge}(t) dt = I \cdot V_{discharge_avg} \cdot t_{discharge} = V_{discharge_avg} \cdot Q_{discharge}$$

Charge:

$$Q_{charge} = I \cdot t_{charge}$$

$$E_{charge} = I \cdot \int_0^{t_{charge}} V_{charge}(t) dt = I \cdot V_{charge_avg} \cdot t_{charge} = V_{charge_avg} \cdot Q_{charge}$$

Energy efficiency:

$$\eta_{energy} = \frac{E_{discharge}}{E_{charge}} = \frac{V_{discharge_avg} \cdot Q_{discharge}}{V_{charge_avg} \cdot Q_{charge}} = \eta_{voltage} \cdot \eta_{coulomb}$$

Exercise 2.10. The code for the tasks can be found in `Solution_2_10.m`

- a) Start by calculating the current based on the battery capacity Q and the C-value. Then implement the Shepherd equation (Equation (10)) with the parameters found in Table 2.2. Estimate the cell potential for each timestamp and plot the results for a few values of C . Read out the charge discharged, the intersection between the curve and the cut off voltage, can be read out on the x-axis. Calculate the energy by

$$\text{Energy} = \int_0^{t_{co}} IV(t) dt = I \int_0^{t_{co}} V(t) dt. \quad (2.5)$$

```
% a) For Battery energy, Power and Efficiency

% Set the parameter values

% Calculate the current based on C and Q value

% Shepherds equation
V_cell = @(t) U - I.*R_int - ...;

% Create a time vector that is long enough [s]
t_vec = ...;

% Calculate the cell potential for each time step

% Pick the first element smaller then V_co.
CoV_ind = find(cell_potential < CoV, 1, 'first');

charge = ...;
energy = ...;
```

b) The efficiency of the different levels of discharge currents are:

$$\eta_{0.5C} = 0.9536$$

$$\eta_{1C} = 0.9215$$

$$\eta_{2C} = 0.8705$$

$$\eta_{3C} = 0.8285$$

A plot of the voltage drop over time depending on the discharge current can be seen in Figure 2.6

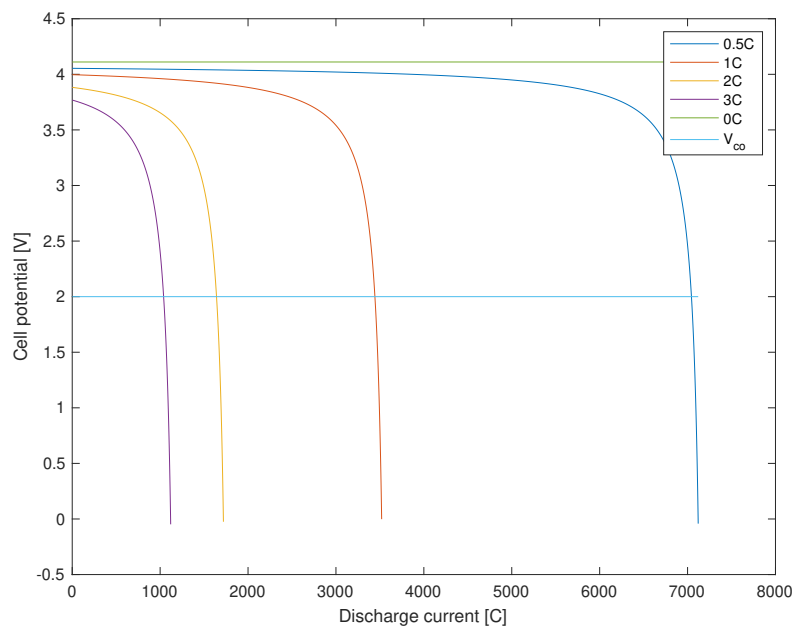


Figure 2.6: Voltage drop as function of the discharge current.

A plot of the efficiency as function of the discharge current can be seen in Figure 2.7.

```
%% b)
% The efficiency is estimated usin eta(DoD) = V(t)
%   /OCV(t).
% OCV comes from V_cell = U + A when I = 0.
% The code for this task can be optimized

clc
clear all
close all

U = 4.131;
```

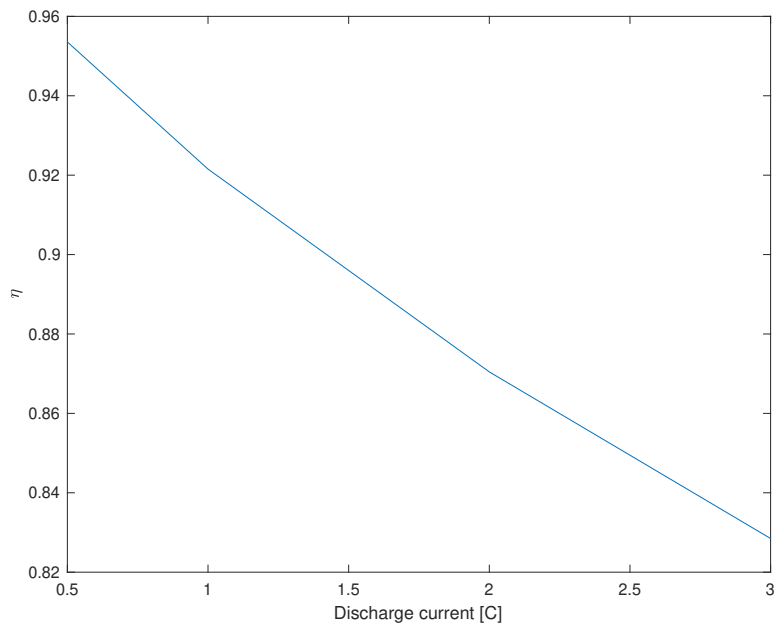


Figure 2.7: Voltage drop as function of the discharge current.

```

R_int = 0.003881;
K = 0.015138;
A = -0.02;
B = 0.1;
Q = 6; % Ah
CoV = 2; % [V] Cut off voltage

V_oc = U + A;
t_vec = 1:(2*3600); % [s]

c_vec = [0.5,1,2,3]; % Vector including all the
    discharge currents

% Shepherds equation
V_cell_b2 = @(t,amp) U - amp.*R_int - K*(Q/(Q-amp
    .*t)).*amp + A.*exp(B./Q.*amp.*t);

% Create a vector with the cut off voltage and the
    open circuit voltage
V_co_vec = ones(1,length(t_vec))*CoV;
V_oc_vec = ones(1,length(t_vec))*V_oc;

for c_ind = 1:4
    C = c_vec(c_ind);

```

```

I = C*Q;
for i_1 = t_vec
    ii_1 = i_1/3600; % Convert to hours
    cell_potential_vec(c_ind,i_1) = V_cell_b2(
        ii_1,I);
end

% Find the index of the element smaller than
% cut off voltage and 0
CoV_ind_vec(c_ind) = find(cell_potential_vec(
    c_ind,:) < CoV,1,'first');
zero_V_ind_vec(c_ind) = find(
    cell_potential_vec(c_ind,:) < 0,1,'first');

% Plot the result
figure(10)
plot(t_vec(1:zero_V_ind_vec(c_ind)),
    cell_potential_vec(c_ind,1:zero_V_ind_vec(
        c_ind)))
hold on

% Estimate the efficiency of the energy
% discharged from the battery
spec_energy_vec(c_ind) = sum(
    cell_potential_vec(c_ind,1:CoV_ind_vec(
        c_ind)));
oc_energy_vec(c_ind) = sum(V_oc_vec(1:
    CoV_ind_vec(c_ind)));
eta_vec(c_ind) = spec_energy_vec(c_ind)/
    oc_energy_vec(c_ind);
end
figure(10)
plot(t_vec(1:zero_V_ind_vec(1)),V_co_vec(1:
    zero_V_ind_vec(1)))
plot(t_vec(1:zero_V_ind_vec(1)),V_oc_vec(1:
    zero_V_ind_vec(1)))
xlabel('Discharge current [C]')
ylabel('Cell potential [V]')
legend('0.5C','1C','2C','3C','0C','V_{co}')

figure(20)
plot(c_vec,eta_vec)
xlabel('Discharge current [C]')
ylabel('\eta')

```

- c) The highest efficiency is found when the battery still has SoC 100% and is $\eta = 0.9722$. This can be seen in Figure 2.8. The result is achieved by making small changes to the code in task a).

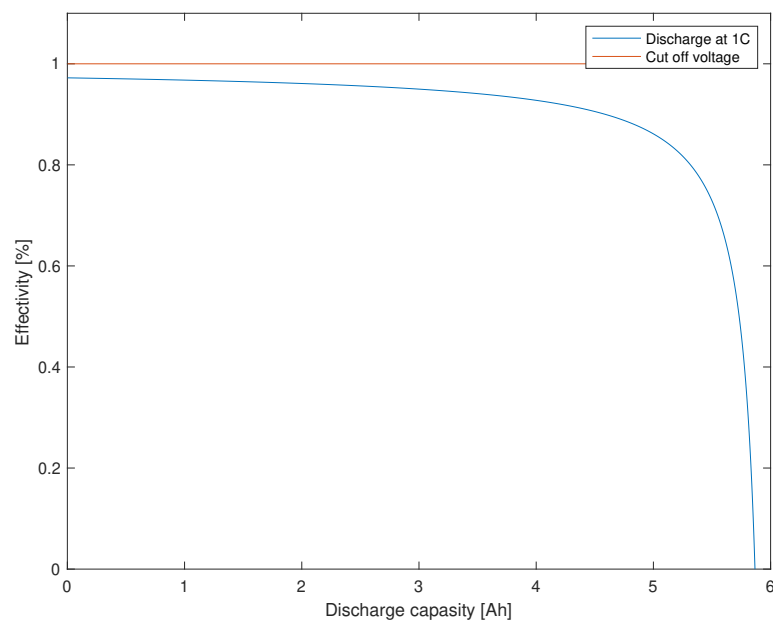


Figure 2.8: The momentary efficiency for a discharge current of 1C.

Chapter 3

Equivalent Circuit Models

Exercise 3.1.

- (a) The capacity is $Q \approx \pm 1.0865$ [Ah]. The capacity is calculated by the integral of the current vs time area.

$$Q_{charge} = \int_{empty}^{full} i(t) dt$$

$$Q_{discharge} = \int_{full}^{empty} i(t) dt$$

In Matlab the charge capacity can be calculated by

`Q_charge = trapz(Time,Current)`. The file data should be divided into two different sets, one for charging and one for discharging. The capacity is the integral of the current vs time area. The code can be found in `Solution_3_1.m`.

- (b) The OCV curve can be seen in Figure 3.1 and the OCV function can be found in the code.

Exercise 3.2.

Start with the KVL of the circuit:

$$v = v_{oc} + R_i i + v_{c_1} + v_{c_2} \quad (3.1)$$

The capacitance of the circuit:

$$i_{c_1} = C_1 \cdot \frac{dv_{c_1}}{dt} \quad (3.2)$$

$$i_{c_2} = C_2 \cdot \frac{dv_{c_2}}{dt} \quad (3.3)$$

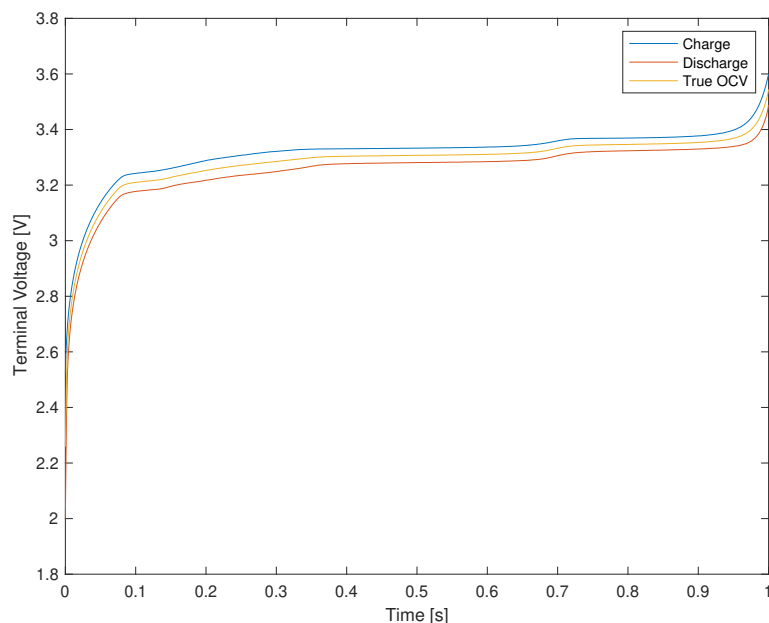


Figure 3.1: The OCV curve for the A123 cell.

Again the KVL for the individual RC-circuits gives:

$$v_{c_1} = R_1 (i - i_{c_1}) \quad (3.4)$$

$$v_{c_2} = R_2 (i - i_{c_2}) \quad (3.5)$$

which, inserted to Equation (3.2) gives

$$\frac{dv_c}{dt} = \frac{i_c}{C} = \frac{1}{C} \left(i - \frac{v_c}{R} \right) \quad (3.6)$$

Combining the equations above gives the answer to the question

$$\begin{cases} \frac{dv_{c_1}}{dt} = \frac{i}{C_1} - \frac{v_{c_1}}{R_1 C_1} \\ \frac{dv_{c_2}}{dt} = \frac{i}{C_2} - \frac{v_{c_2}}{R_2 C_2} \\ v = v_{c_1} - v_{c_2} + v_{oc} + R_i i \end{cases} \quad (3.7)$$

Exercise 3.3. The expression for the time continuous state-space form from Exercise 3.2 is:

$$\begin{cases} \frac{dv_{c_1}}{dt} = \frac{i}{C_1} - \frac{v_{c_1}}{R_1 C_1} \\ \frac{dv_{c_2}}{dt} = \frac{i}{C_2} - \frac{v_{c_2}}{R_2 C_2} \\ v = v_{c_1} - v_{c_2} + v_{oc} + R_i i \end{cases} \quad (3.8)$$

Using equation (3.1) together with equation (3.8) gives the discrete form of the

ECM:

$$\begin{cases} \frac{v_{c_1,k+1} - v_{c_1,k}}{\Delta t} = \frac{i_k}{C_1} - \frac{v_{c_1,k}}{R_1 C_1} \\ \frac{v_{c_2,k+1} - v_{c_2,k}}{\Delta t} = \frac{i_k}{C_2} - \frac{v_{c_2,k}}{R_2 C_2} \\ v_k = v_{c_1,k} - v_{c_2,k} + v_{oc,k} + R_i i_k \end{cases} \Leftrightarrow \begin{cases} v_{c_1,k+1} = v_{c_1,k} \left(1 - \frac{\Delta t}{R_1 C_1} \right) + \frac{i_k}{C_1} \Delta t \\ v_{c_2,k+1} = v_{c_2,k} \left(1 - \frac{\Delta t}{R_2 C_2} \right) + \frac{i_k}{C_2} \Delta t \\ v_k = v_{c_1,k} - v_{c_2,k} + v_{oc,k} + R_i i_k \end{cases}$$

Exercise 3.4.

1. $R_i = 20 \text{ m}\Omega$.
2. $R = 30 \text{ m}\Omega$.
3. $C \approx 1.3 \text{ kF}$.

Exercise 3.5.

a) The time discrete form of the ECM:

$$\frac{v_{c,k+1} - v_{c,k}}{\Delta t} = -\frac{v_{c,k}}{RC} + \frac{i_k}{C} \quad (3.9)$$

$$v_k = v_{c,k} + v_{OC,k} + R_i i_k \quad (3.10)$$

And we want to write it in the form:

$$Y = X\Theta$$

First we remove the non-linearity by introducing a new variable

$$\tilde{V}_k = V_k - V_{OC,k}$$

equation (3.10) becomes:

$$\tilde{V}_k = v_{c,k} + R_i i_k$$

from which we want to extract $v_{c,k}$ (since its unknown) and substitute it into equation (3.9):

$$\frac{(\tilde{v}_{k+1} - R_i i_{k+1}) - (\tilde{v}_k - R_i i_k)}{\Delta t} = -\frac{1}{RC}(\tilde{v}_k - R_i i_k) + \frac{i_k}{C} \quad (3.11)$$

b) The parameters that we want to estimate are R_i , R , C and we can identify them as a product or sum of each other in equation (3.11). By rearranging the equation we get:

$$\frac{\tilde{v}_{k+1} - \tilde{v}_k}{\Delta t} = R_i \left(\frac{i_{k+1} - i_k}{\Delta t} \right) + \frac{1}{RC} (-\tilde{v}_k) + \left(\frac{R_i}{RC} + \frac{1}{C} \right) i_k$$

Now, row k in the Y vector can be identified as $y_k = \frac{\tilde{v}_{k+1} - \tilde{v}_k}{\Delta t}$. Row k in the Θ vector can be identified: $\theta_1 = R_i$, $\theta_2 = \frac{1}{RC}$, $\theta_3 = \frac{R_i}{RC} + \frac{1}{C}$ and in the X matrix as $x_{k1} = \frac{i_{k+1} - i_k}{\Delta t}$, $x_{k2} = -\tilde{v}_k$, $x_{k3} = i_k$ so that each row k is:

$$y_k = x_{k1}\theta_1 + x_{k2}\theta_2 + x_{k3}\theta_3$$

Now we have everything to construct the whole Y and X vector just by completing all the rows, and then determine the Θ vector as

$$\Theta = X^{-1}Y$$

(in Matlab: $\Theta = X \backslash Y$).

Once $\Theta = [\theta_1, \theta_2, \theta_3]^T$ is obtained, the parameters can be calculated as the following:

$$R_i = \theta_1 \quad (3.12)$$

$$C = \frac{1}{\theta_3 - \theta_1 \theta_2} \quad (3.13)$$

$$R = \frac{\theta_3}{\theta_2} - \theta_1 \quad (3.14)$$

The parameters obtained using the code in `Solution_3_5.m` are:

$$R_i = 0.2 \, \Omega$$

$$R = 0.08 \, \Omega$$

$$C = 10.2 \, \text{kF}$$

Now that the parameters are estimated they can be used in the ECM to simulate a cell during operation.

- c) To simulate the cell during operation, use the estimated parameters and simulate a 1-RC model. The model can be simulated by

```
n = numel(i);
vc = zeros(n,1);
z = SOCf(v(1));
vhat = zeros(n,1);
for k = 1:n-1
    z(k+1) = z(k) + i(k)*dt/Q;
    v(k) = vc(k) + OCVf(z(k)) + Ri*i(k);
    vc(k+1) = vc(k)*(1 - dt/(R*C)) + i(k)*dt/C;
end
v(n) = vc(n) + OCVf(z(n)) + Ri*i(n);
```

The result of the simulated model compared to the measured data is shown in Figure 3.2.

- d) The code to plot the results can be seen in `Exercise_3_5.m`. As seen in Figure 3.3.

Exercise 3.6. The result from each of the subtasks can be seen in Table 3.1.

Table 3.1: Estimated impedance parameters using different initialization methods.

| Task | R_i [Ω] | C [F] | R [Ω] | SOC [%] | Q [Ah] | ΔV [mV] |
|-----------|--------------------|---------|------------------|---------|----------|-----------------|
| a) | 0.1996 | 1016.9 | 0.0577 | 99.64 | 1.0865 | 0.0853 |
| b) | 0.2020 | 1710.2 | 0.0580 | 99.64 | 1.0865 | 0.0626 |
| c) | 0.1994 | 1016.9 | 0.0572 | 99.50 | 1.0865 | 0.0797 |
| d) | 0.2019 | 1763.5 | 0.0576 | 99.48 | 1.0865 | 0.0555 |
| e) | 0.2012 | 1656.0 | 0.0477 | 99.53 | 0.9603 | 0.0340 |

As seen in Table 3.1 the tasks with bold text is the ones normalized in the optimization. These are also the tasks where C and R_i clearly decreases and

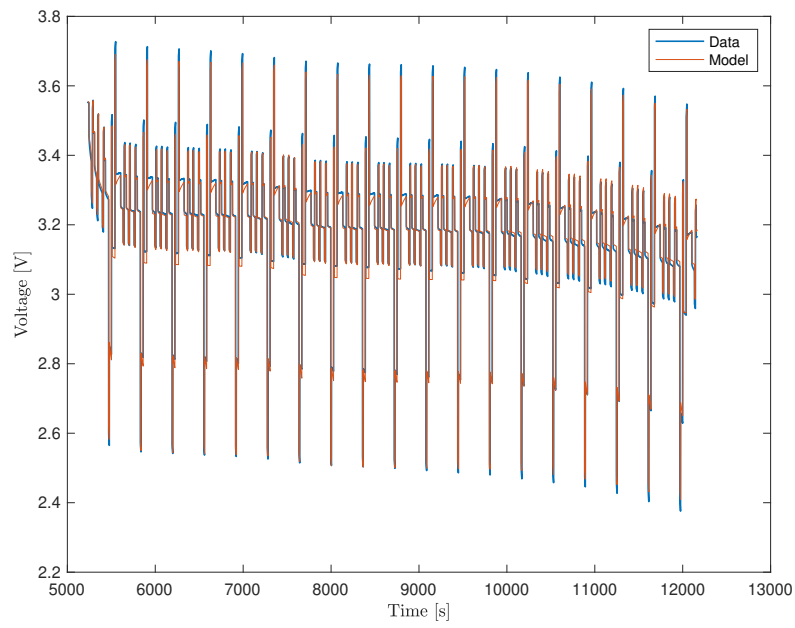


Figure 3.2: The model compared to the measured data.

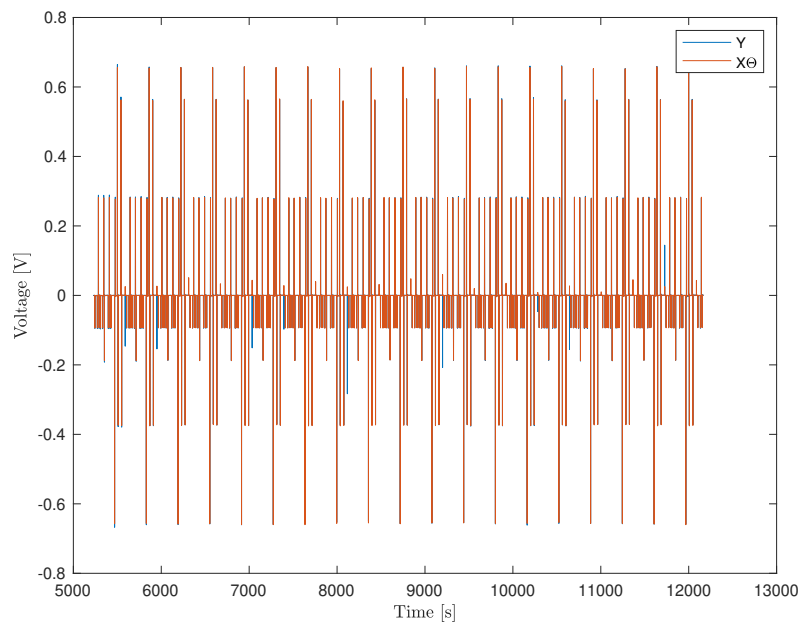


Figure 3.3: Y and $X\Theta$ plotted against each other.

increases. Implying that normalizing the parameters makes them find another minimum compared to the once without normalization. There might be multiple local minimum. The tasks with bold text also have a lower error in the voltage prediction, which is a good sign. This means that the optimization is more sensitive to the parameters when they are normalized.

Exercise 3.7. The State of Charge is given by $z(t) = z(0) + \int_0^t \frac{\eta}{Q_{tot}} i(\tau) d\tau$ using Coulomb counting. Differentiating with respect to time, we get

$$\dot{z}(t) = \frac{\eta}{Q_{tot}} i(t). \quad (3.15)$$

Applying the Euler forward method, we approximate

$$\frac{dz}{dt} \approx \frac{z(t + \Delta t) - z(t)}{\Delta t} = \frac{z_{k+1} - z_k}{\Delta t}. \quad (3.16)$$

This yields the SOC in discrete form as

$$z[k] = z[k - 1] + \frac{\eta}{Q_{tot}} i[k] \Delta t. \quad (3.17)$$

Part III

Appendix

Appendix A: Standard Electrode Potentials

| | Electrochemical Reaction | Standard Potential, U^θ (V) |
|-----|--|------------------------------------|
| 1. | $\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$ | 2.87 |
| 2. | $\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$ | 1.685 |
| 3. | $\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$ | 1.3595 |
| 4. | $\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$ | 1.229 |
| 5. | $\text{Br}_2(\text{aq}) + 2e^- \rightarrow 2\text{Br}^-$ | 1.078 |
| 6. | $\text{Ag}^+ + e^- \rightarrow \text{Ag}$ | 0.7991 |
| 7. | $\text{Hg}_2^{2+} + 2e^- \rightarrow 2\text{Hg}$ | 0.7898 |
| 8. | $\text{Cu}^+ + e^- \rightarrow \text{Cu}$ | 0.5219 |
| 9. | $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$ | 0.401 |
| 10. | $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ | 0.337 |
| 11. | $\text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$ | 0.2676 |
| 12. | $\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$ | 0.222 |
| 13. | $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$ | 0.153 |
| 14. | $\text{HgO} + \text{H}_2\text{O} + 2e^- \rightarrow \text{Hg} + 2\text{OH}^-$ | 0.098 |
| 15. | $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ | 0 |
| 16. | $\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$ | -0.126 |
| 17. | $\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$ | -0.356 |
| 18. | $\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$ | -0.44 |
| 19. | $\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$ | -0.74 |
| 20. | $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$ | -0.763 |
| 21. | $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$ | -0.828 |
| 22. | $\text{Cr}^{2+} + 2e^- \rightarrow \text{Cr}$ | -0.912 |
| 23. | $\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$ | -1.18 |
| 24. | $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$ | -1.66 |
| 25. | $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$ | -2.357 |
| 26. | $\text{Na}^+ + e^- \rightarrow \text{Na}$ | -2.714 |
| 27. | $\text{K}^+ + e^- \rightarrow \text{K}$ | -2.936 |
| 28. | $\text{Li}^+ + e^- \rightarrow \text{Li}$ | -3.045 |

Standard states:

- (a) Gases: pure ideal gas at 25°C, 100 kPa
- (b) Liquids and solids: pure substances
- (c) Aqueous solutions: hypothetical 1 molal solution.