

Elektrochemie
Prof. Petr Novák

Exercise 10 - Batteries

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Exercise 1:

- (a) What are “batteries” (Provide a definition)?
- (b) Batteries are divided in groups such as primary and secondary cells. Characterize both groups (definition) and give 2 examples for both types of cells. What are the advantages and disadvantages of both groups? Provide some applications for both types of cells.

Exercise 2: An alkaline battery is an example of a primary battery and the reaction shown below is the cell reaction during discharge. Potassium hydroxide (KOH) is typically used as the electrolyte.



- (a) Which are the reducing and oxidizing agents? Write the corresponding anodic and cathodic reactions during discharge.
- (b) If the cell voltage U° is 1.43 V, what is the Gibbs free energy of the overall cell reaction?
- (c) How many hours will it take to completely discharge the alkaline battery at a current of 1.5 A, when 6.3 g of $\text{Zn}_{(s)}$ were converted to $\text{ZnO}_{(s)}$?

Exercise 3: Lead-acid batteries are the oldest type of rechargeable battery. Owing to their extensive use as starter lighting ignition batteries in the automotive industry, they represent a significant share of the global battery market (despite their relatively low energy densities):

- (a) Identify the positive and negative electrode and write down the half-cell reactions together with the overall reaction during the discharge of the battery.
- (b) What is special about the lead-acid battery compared with other battery systems in terms of the products of discharge?
- (c) Using the equations derived from (a), calculate the reversible cell voltage U° [V]. How many of these single units are required if a battery block with 24 V is needed? Should they be connected in series or in parallel?
- (d) Consider a Pb-acid battery containing 4 M sulphuric acid. The reversible potential of $\text{PbO}_2/\text{PbSO}_4$ is higher than the reversible potential for the oxygen evolution reaction (OER). In addition, the reversible potential of PbSO_4/Pb is lower than the potential of the hydrogen evolution reaction (HER). Can you explain why the Pb-acid battery can operate outside the thermodynamic stability window of the water-based electrolyte?
- (e) Calculate the specific charge density Q [Ah/kg] and the specific energy density [Wh/kg] of the electrode materials when charged.

Exercise 4: Rechargeable lithium-ion batteries are among today's most advantageous battery systems. Consider a typical lithium-ion battery with LiCoO_2 as the positive electrode and graphite as the negative electrode, which can be found in phones and laptops.

- Which one is the cathode and which one is the anode during charging according to IUPAC definition? Write down the overall reaction during charging using the following species: C_6 , Li_xC_6 , LiCoO_2 and $\text{Li}_{1-x}\text{CoO}_2$.
- Calculate the reversible cell voltage U° [V].
- In Figure 1 typical potential profiles of both positive and negative electrodes during discharge in a 2.5Ah LiCoO_2 /graphite cell are shown. Draw in the figure the energy that can be provided by this cell.

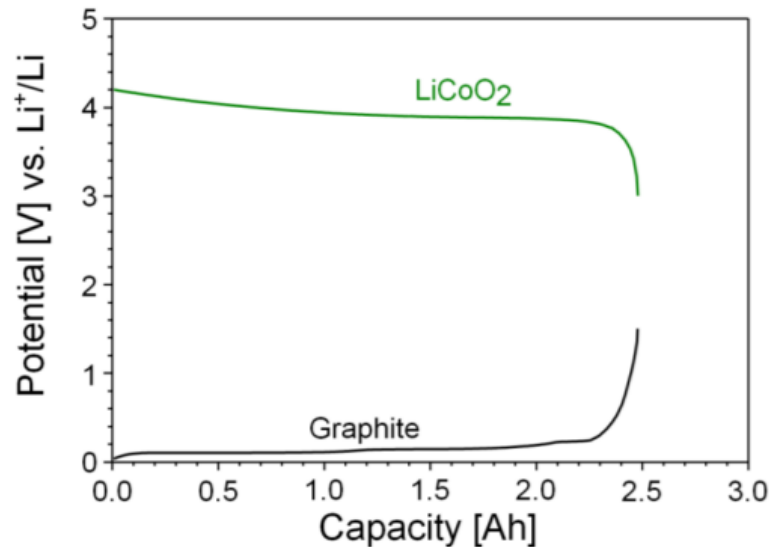


Figure 1. Potential vs. capacity profiles of both positive (LiCoO_2) and negative (graphite) electrodes during discharge in a 2.5 Ah cell.

- Compare the specific charge density Q [Ah/kg] and the specific energy density [Wh/kg] to the values of the lead-acid battery in Exercise 2. What are the two main reasons for this noticeable improvement?
- You want to power a small sound system (20 W) using the LiCoO_2 /graphite battery considering the average voltage (not the thermodynamic value calculated in (b)) and a capacity of 2.5 Ah. Considering that the battery is fully charged, how long will it last?
Note: refer to Figure 2 to calculate the average potential of the battery.

Exercise 5 (Bonus-not mandatory): Silicon is a negative electrode which undergoes a so called alloying mechanism and can be lithiated to the phase $\text{Li}_{22}\text{Si}_5$. Graphite is another negative electrode which undergoes a so called lithium intercalation mechanism to form the most lithiated phase LiC_6 . Calculate

the theoretical specific charge for both electrode materials and their theoretical volume change. Which of the two materials is more prone to mechanical cracks?

Constants:

$$F = 96485 \text{ C/mol}$$

Gibb's free energy of Pb-Acid overall reaction:

$$\Delta G^\circ = - 393.6 \text{ kJ/mol}$$

Gibb's free energy of Li-ion battery overall reaction:

$$\Delta G^\circ = - 405.2 \text{ kJ/mol}$$

$$*\rho(\text{C}_6) = 2.25 \text{ g/cm}^3$$

$$*\rho(\text{LiC}_6) = 2.24 \text{ g/cm}^3$$

$$*\rho(\text{Si}) = 2.329 \text{ g/cm}^3$$

$$*\rho(\text{Li}_{22}\text{Si}_5) = 1.181 \text{ g/cm}^3$$

*Data collected from Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden Württemberg,
<https://www.zsw-bw.de/>