

Elektrochemie
Prof. Petr Novák

Exercise 10 - Batteries

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Exercise 1:

- (a) What are “batteries” (Provide a definition)?

Batteries are electrochemical devices which store electrical energy in the form of chemical energy. The electrochemical cells may be connected in series or in parallel, or a combination thereof, to constitute a battery module or battery pack.

- (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.

Primary cells: Batteries that can only be discharged once and cannot be recharged (irreversible).

Examples: Alkaline batteries, primary zinc-air batteries, some lithium batteries

Advantages(+): Long calendar life/low self-discharge, very robust (large domain of applications)

Disadvantages(-): can only be used once (problem for recycling (trash), expensive)

Secondary cells: Batteries that can be charged and discharged multiple times (reversible).

Examples: nickel-cadmium battery, lead-acid battery, lithium-ion batteries,...

Advantages(+): reusable, low operating costs

Disadvantages(-): often high self-discharge, domain of application/storage under optimal conditions required, destruction due to depth of discharge, rapid charge or overcharge, high investment costs, often bad cycling stability,...

Examples of application domains:

Primary cells: constant and small energy extraction over long time periods – watches, data storage units, measurement devices,...

Secondary cells: high and permanent (mobile) energy demand (mobile phone, lap-tops, batteries for cars and electro-mobility), where there might be a need to recharge multiples times.

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 solution (KOH,aq) is typically used as the electrolyte.



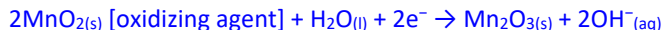
- (a) Which are the reducing and oxidizing agents? Write the corresponding anodic and cathodic reactions during discharge.

Upon battery discharge:

Negative electrode:



Positive electrode:



- (b) If the reversible cell voltage U° is 1.43 V, what is the Gibbs free energy of the overall cell reaction?

To calculate Gibbs free energy of the reaction, the following equation can be used:

$$\Delta G^\circ = -z F \Delta E^\circ$$

Where $z=2$; $F=96485 \text{ C/mol}$ and $\Delta E^\circ = 1.43 \text{ V}$.

The resulting Gibbs free energy is **-276 kJ/mol**

- (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 $\text{ZnO}_{(s)}$?

The mole of Zn converted in ZnO is equal to:

$$n_{\text{Zn}} = \frac{m_{\text{Zn}}}{M_{\text{Zn}}} = \frac{6.3 \text{ g}}{65.4 \text{ g/mol}} = 0.096 \text{ mol}$$

Then, remember that $Q = n \cdot z \cdot F$, it follows that

$$Q = 0.096 \text{ mol} \cdot 2 \cdot 96485 \text{ A} \cdot \frac{\text{s}}{\text{mol}} = 18525 \text{ A} \cdot \text{s}$$

By dividing the amount of charge by the given current, we obtain the discharge time of the cell:

$$t = \frac{Q}{i} = \frac{18525 \text{ A} \cdot \text{s}}{1.5 \text{ A}} = 12392 \text{ s} = \mathbf{3 \text{ h } 26}$$

Exercise 3: Lead-acid batteries are the oldest type of rechargeable battery. Owing to their extensive use as starter lighting ignition (SLI) 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.

Upon battery discharge:

Negative electrode:



Positive electrode:



Overall reaction:



- (b) What is special about the lead-acid battery compared with other battery systems in terms of the products of discharge?

The lead-acid battery is special as upon discharge the reduction of the positive electrode and the oxidation of the negative electrode lead to the same product (PbSO_4), which precludes the possibility of internal cross-contamination.

- (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 module with 24 V is needed? Should they be connected in series or in parallel?

To calculate the reversible cell potential, the following equation can be used:

$$\Delta G^\circ = -z F \Delta E^\circ$$

Where $z=2$; $F=96485 \text{ C/mol}$ and $\Delta G^\circ = -393.6 \text{ kJ/mol}$.

The resulting cell potential $\Delta E^\circ = 2.04 \text{ V}$

If you want to build a 24 V battery, then a **series of 12 Pb-acid cells** is needed ($\Delta E^\circ = 24.5 \text{ V}$).

- (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?

According to thermodynamics, neither PbO_2 nor Pb is stable in aqueous solution at low pH. However, the hydrogen evolution overpotential on the Pb negative electrode (see Figure 1) and the oxygen evolution overpotential on the PbO_2 positive electrode are high. That means, the reaction rates of H_2 and O_2 evolution are low (kinetic limitation). Making use of such high overpotential enables the Pb-acid battery to be cycled outside the thermodynamic stability window of the water-based electrolyte (See Figure 1).

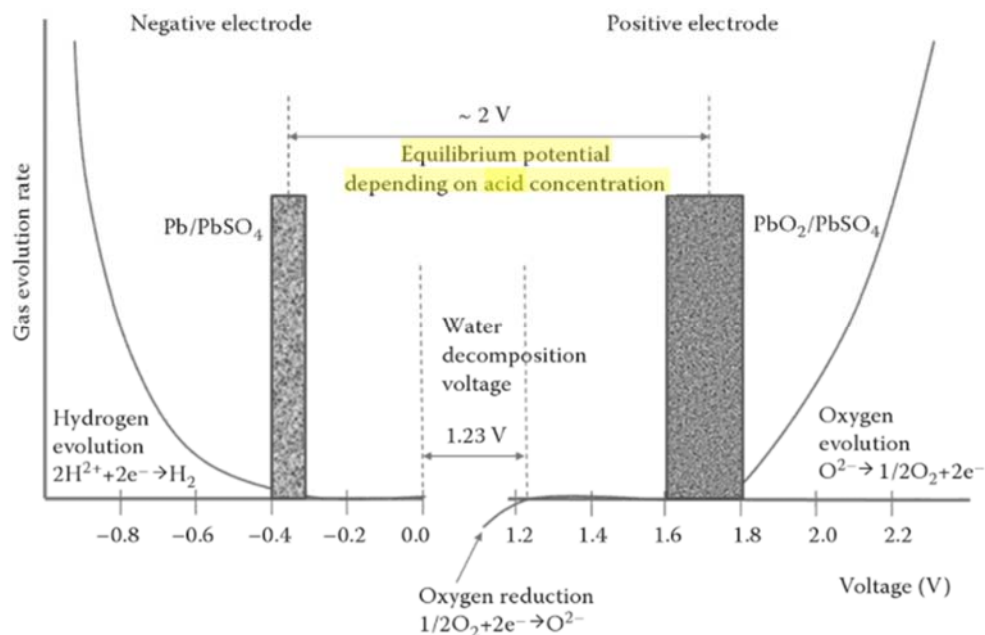


Figure 1. Hydrogen (H_2) and oxygen (O_2) gas evolution rates as a function of the potential compared to the working potential of a lead-acid battery. The high overpotential of for the H_2 and O_2 evolution

reactions makes possible the existence of such a battery. (From Pavlov, Lecture Course on VRLA, Beijing, China, 2000).

- (e) Calculate the specific charge Q [Ah/kg] and the specific energy W [Wh/kg] of the electrode materials when charged.

For the specific charge Q in Ah/Kg, we can use Faraday's law:

$$Q = \frac{z \cdot F}{\sum_i M_i} \quad \sum_i M_i = 1 \cdot M(\text{Pb}) + 1 \cdot M(\text{PbO}_2) + 2 \cdot M(\text{H}_2\text{SO}_4) = \mathbf{642.4 \text{ g/mol}}$$

$$\text{Considering } z=2; F = 26.8 \text{ Ah} \quad F = \frac{96485 \text{ C/mol}}{1 \frac{\text{C}}{\text{A} \cdot \text{s}} \cdot 3600 \text{ s/h}} = 26.8 \text{ Ah/mol}$$

$$Q = \frac{2 \cdot 26.8 \frac{\text{Ah}}{\text{mol}}}{642.6 \frac{\text{g}}{\text{mol}}} = 0.0834 \frac{\text{Ah}}{\text{g}} = \mathbf{83.4 \text{ Ah/kg}}$$

The energy density can be obtained from the specific charge Q by multiplying by the reversible cell voltage calculated in (c):

$$\begin{aligned} \text{Since: } & \text{voltage } U \text{ (V)} \cdot \text{current } I \text{ (A)} = \text{power } P \text{ (W)} \\ & \text{Power } P \text{ (W)} \cdot \text{time } t \text{ (sec or hrs)} = \text{energy (Wh or Ws)} \end{aligned}$$

$$W = Q \cdot U^\circ = 83.4 \text{ Ah/kg} \cdot 2.04 \text{ V} = \mathbf{170.1 \text{ Wh/kg}}$$

Please note that the voltage of 2.04 V calculated in (c) represents a thermodynamic value. During normal operation of a lead-acid battery, the voltage can drop by 200-250 mV during discharge, due to overpotential.

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

- (a) 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 $\text{Li}_{1-x}\text{CoO}_2$.

According to IUPAC definition, the cathode is the electrode where reduction takes place and the anode is the electrode where oxidation takes place. During charging, the LiCoO_2 is being oxidized (anode), while the graphite is being reduced (cathode). The situation is reversed during battery discharge. However, LiCoO_2 is always the positive electrode and the graphite is the negative electrode. This is why the terms "negative and positive electrodes" are preferable to "cathode" and "anode" in rechargeable battery nomenclature.

Overall reaction:



- (b) Calculate the reversible cell voltage U° [V].

To calculate the reversible cell potential, as shown in the previous question, we can use the following equation:

$$\Delta E^\circ = - \frac{\Delta G^\circ}{z \cdot F}$$

Where ΔG° for the full cell is -405.2 kJ/mol , $z=1$ and $F = 96485 \text{ C/mol}$.

It follows that $\Delta E^\circ = 4.2 \text{ V}$

As discussed for the lead-acid batteries, the calculated potential refers only to a thermodynamic value.

- (c) In Figure 2 typical potential profiles of both positive and negative electrodes during discharge in a 2.5Ah LiCoO₂/graphite cell are shown. Draw in the figure the energy that can be provided by this cell.

The energy delivered by the cell can be expressed as:

$$E(J) = \int U \left(\frac{J}{C} \right) \cdot dQ (C) \quad \text{or}$$

$$E(Wh) = \int U (V) \cdot dQ (Ah)$$

It follows that the energy is equal to the area between the potential profiles of the positive and negative electrode.

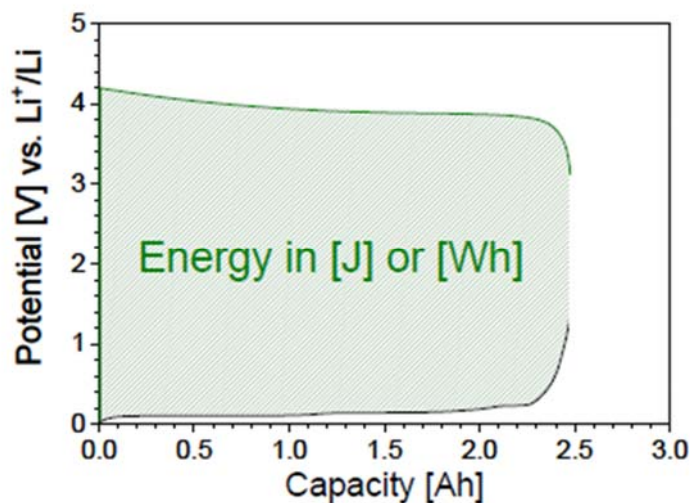


Figure 2. Potential vs. capacity profiles of both positive (LiCoO₂) and negative (graphite) electrodes during discharge in a 2.5 Ah cell. The area highlighted in green between the potential curves of the positive and negative electrode represents the electrical energy delivered by the cell.

- (d) Compare the specific charge Q [Ah/kg] and the specific energy [Wh/kg] to the values of the lead-acid battery in Exercise 2. What are the two main reasons for this noticeable improvement?

To calculate the specific charge Q , we use Faraday's law, with the Faraday constant expressed in Ah unit, for convenience:

$$Q = \frac{z \cdot F}{\sum_i M_i}; \quad \sum_i M_i = 1 \cdot M(\text{LiC}_6) + 1 \cdot M(\text{CoO}_2) = 169.8 \frac{\text{g}}{\text{mol}}$$

$$Q_{\text{Li-ion}} = \frac{1 \cdot 26.8 \text{ Ah/mol}}{169.8 \text{ g/mol}} = 0.158 \frac{\text{Ah}}{\text{g}} = \mathbf{158 \text{ Ah/kg}}$$

$$\rightarrow E_{\text{Li-ion}} = 158 \text{ Ah/kg} \cdot 4.2 \text{ V} = \mathbf{663.6 \text{ Wh/kg}}$$

$$Q_{\text{Pb-acid}} = 83.4 \text{ Ah/kg} \quad \rightarrow \quad E_{\text{Pb-acid}} = 170.1 \text{ Wh/kg}$$

The reasons of the difference between Pb-acid and Li-ion cells are:

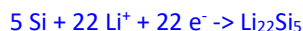
1. the increase of the cell voltage (double for the $\text{LiCoO}_2/\text{graphite}$ cell)
2. Less weight of the active material (almost four times less for the $\text{LiCoO}_2/\text{graphite}$ cell)

- (e) You want to power a small sound system (20 W) using the $\text{LiCoO}_2/\text{graphite}$ 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.

$$E = 2.5 \text{ Ah} \cdot 3.7 \text{ V} = 9.25 \text{ Wh}$$

$$t = 9.25 \text{ Wh} / 20 \text{ W} = 0.463 \text{ h} = \mathbf{27.8 \text{ min}}$$

Exercise 5 (Bonus-not mandatory): Silicon is a negative electrode material 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 material which undergoes a so called lithium intercalation mechanism to form the highest 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? Cite a paper where the mechanical issues in Li-ion batteries are reported on one of the two electrode materials and a technique to identify mechanical issues in battery materials.



Theoretical specific charge of silicon:

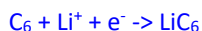
$$Q = \frac{z \cdot F}{\sum_i M_i} = \frac{22 \cdot 96485 \text{ A}\cdot\text{s/mol}}{5 \cdot 28.0855 \text{ g/mol}} = \frac{22 \cdot 26.8 \text{ Ah/mol}}{5 \cdot 28.0855 \text{ g/mol}} = 4.198 \text{ Ah/g} = \mathbf{4198 \text{ mAh/g}}$$

Molar volume V_m :

$$5\text{Si}: V_m(\text{Si}) = \frac{MW(5\text{Si})}{\rho(\text{Si})} = \frac{140.4275 \text{ g/mol}}{2.329 \text{ g/cm}^3} = \mathbf{60.3 \text{ cm}^3/\text{mol}}$$

$$\text{Li}_{22}\text{Si}_5: V_m(\text{lithiated Si}) = \frac{MW(\text{Li}_{22}\text{Si}_5)}{\rho(\text{Li}_{22}\text{Si}_5)} = \frac{293.132 \text{ g/mol}}{1.181 \text{ g/cm}^3} = 248.21 \text{ cm}^3/\text{mol}$$

$$\text{Volume change of Si upon lithiation : vol\%} = \frac{V_m(\text{lithiated Si}) - V_m(\text{Si})}{V_m(\text{Si})} = \frac{248.21 - 60.3 \text{ cm}^3/\text{mol}}{60.3 \text{ cm}^3/\text{mol}} = 311.6\%$$



Theoretical specific charge of graphite:

$$Q = \frac{z \cdot F}{\sum_i M_i} = \frac{1 \cdot 96485 \text{ A} \cdot \text{s/mol}}{6 \cdot 12.01 \text{ g/mol}} = \frac{1 \cdot 26.8 \text{ Ah/mol}}{6 \cdot 12.01 \text{ g/mol}} = 0.3719 \text{ Ah/g} = 371.9 \text{ mAh/g}$$

Molar volume V_m :

$$\text{C}_6: V_m(\text{graphite}) = \frac{MW(\text{C}_6)}{\rho(\text{C}_6)} = \frac{72.06 \frac{\text{g}}{\text{mol}}}{2.25 \frac{\text{g}}{\text{cm}^3}} = 32.026 \text{ cm}^3/\text{mol}$$

$$\text{LiC}_6: V_m(\text{lithiated graphite}) = \frac{MW(\text{LiC}_6)}{\rho(\text{LiC}_6)} = \frac{79.001 \frac{\text{g}}{\text{mol}}}{2.24 \frac{\text{g}}{\text{cm}^3}} = 35.27 \text{ cm}^3/\text{mol}$$

$$\text{Volume change of graphite upon lithiation : vol\%} = \frac{V_m(\text{LiC}_6) - V_m(\text{C}_6)}{V_m(\text{C}_6)} = \frac{35.27 - 32.026 \text{ cm}^3/\text{mol}}{32.026 \text{ cm}^3/\text{mol}} = 10.12\%$$

Constants:

F = 96485 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:

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

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

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

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

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