WS 2018/2019

Elektrochemie
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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.

$$Zn_{(s)} + 2\ MnO_{2(s)} \Leftrightarrow ZnO_{(s)} + Mn_2O_{3(s)}$$

(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 $Zn_{(s)}$ were converted to $ZnO_{(s)}$?

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 1 M sulphuric acid. The reversible potential of $PbO_2/PbSO_4$ 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.

(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 $Li_{1-x}CoO_2$.

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

(c) 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.

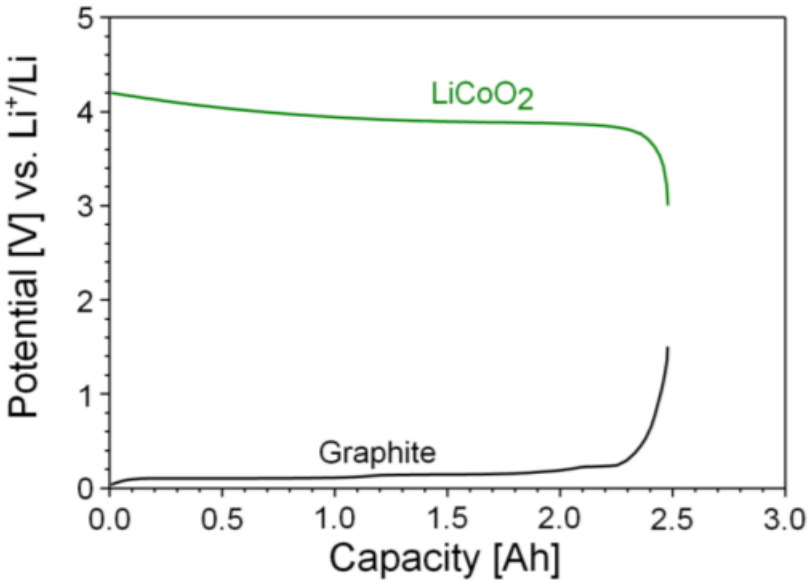

Figure 1. Potential vs. capacity profiles of both positive ($LiCoO_2$) and negative (graphite) electrodes during discharge in a 2.5 Ah cell.

(d) 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?

(e) 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.

(f) Imagine the case where the positive electrode of the lithium-ion cell would be replaced by its analogous compound, $Na_{1-x}CoO_2$, which contains sodium. What is the inherent disadvantage of this kind of battery?

Constants:
F = 96485 C/mol
Gibb's free energy of Pb-Acid overall reaction: $\Delta G° = -393.6$ kJ/mol
Gibb's free energy of Li-ion battery overall reaction: $\Delta G° = -405.2$ kJ/mol