# Battery System

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## Exercise 1 - Determination of LIB theoretical capacity

**Considering the following overall reaction: $Li_{0.4}CoO_2 + Li_{0.6}C_6 \Leftrightarrow LiCoO_2 + C_6$**

a) **Write the corresponding anodic and cathodic reactions during discharge**
b) **Which one is the oxidizing and reducing reaction?**
c) **what is the Gibbs free energy of the overall cell reaction?**
d) **What is the theoretical gravimetric energy density?**
e) **How big is the theoretical gravimetric energy density with respect to the available energy density reported for the same material (table on slide)?**

### Lithium-Ion Batteries

*Charge example:*

*Positive electrode*: $Li_{1-x}MO_2 + xe^- + xLi^+ \rightarrow LiMO_2$

*Negative electrode*: $Li_xC_n \rightarrow C_n + xLi^+ + xe^-$

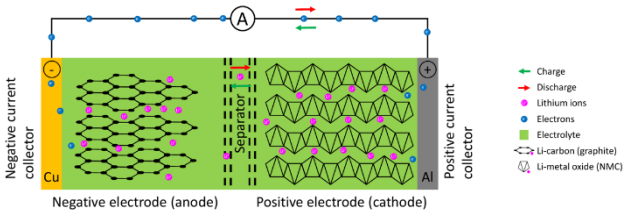
*Overall Reaction*: $Li_{1-x}MO_2 + Li_xC_n \longleftrightarrow LiMO_2 + C_n$

| Material (Kathode) | Mittlere Spannung (V) | Energiedichte (Wh/kg) |
|---|---|---|
| $LiCoO_2$ | 3,7 | 110–190 |
| $LiMnO_2$ | 4,0 | 110–120 |
| $LiFePO_4$ | 3,3 | 95–140 |
| $Li2FePO_4F$ | 3,6 | 70–105 |
| $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ | 3,7 | 95–130 |
| $Li_4Ti_5O_{12}$ | 2,3 | 70–80 |

- **Positive electrode active materials (cathode):** Co, Ni, Mn, LiFe-PO4.
- **Negative electrode (anode)**: intercalation of lithium ions between graphite planes, nanocrystalline or amorphous silicon or lithium titanate oxide (Li4Ti5O12)
- **Electrolytes:**

Solutions of high purity, anhydrous, organic solvents in which conducting salts (LiClO4, LiAsF6, LiBF4, LiPF6, LiCF3SO3) are dissolved in porous separator.

System of polymer (polyethylene oxide (PEO), ...) and a salt and a solvent.

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## Solution:

a) **Semi reactions**
b) **Oxidation/reducing reactions**

Cathode $Li_{0.4}CoO_2 + 0.6\,e^- + 0.6Li^+ \Leftrightarrow LiCoO_2$ → reducing – gaining of electrons
Anode $Li_{0.6}C_6 \Leftrightarrow C_6 + 0.6\,e^- + 0.6Li^+$ → oxidizing – loss of electrons
Overall reaction: $Li_{0.4}CoO_2 + Li_{0.6}C_6 \Leftrightarrow LiCoO_2 + C_6$

c) **Gibbs free energy of the overall reaction:**

Number of electrons transferred in the semi reactions between anode and cathode is 0.6
3.7V is the nominal voltage of a lithium battery cells made by graphite anode (C6) and $LiCoO_2$ Cathode

DG=n x F x U0 = 0.6 x 96485 As/mol x 3.7 J/As = 214196.7 J = 59.5 Wh/mol

d) **What is the theoretical gravimetric energy density?**

Weight of a mole $Li_{0.4}CoO_2$ (positive AM): 0.4*7 g + 58.9 g + 2x16 g = 93.7 g
Weight of a mole $Li_{0.6}C_6$ (negative AM): 0.6*7 g + 6x12 g = 76.2 g
MW: 93.7 g/mol + 76.2 g/mol = 169.9 g/mol
DG/MW = 59.5/0.1699= 350.2 Wh/kg

e) **How big is the theoretical gravimetric energy density with respect to the available energy density reported for the same material (table on slide 46 week 1 lecture slides)?**

Practical energy density 110-190Wh/kg → average 150Wh/kg
Theoretical energy density is almost 3 times higher than the available energy in the materials. Practical energy densities are significantly lower because of carrier materials, electrolytes, separators, current collectors and housing.