PAUL SCHERRER INSTITUT

Electrochemistry

Exercise 1: Faraday's Law

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Some electrochemical reactions involve the deposition or dissolution of products, resulting in a change of mass of the electrode involved. Faradays law of electrolysis establishes a quantitative relation between changes of electrode mass and the amount of charge transferred during an electrochemical reaction (Wikipedia, 10.1021/ed038p98):

$$\Delta m = \frac{QM}{zF} \qquad \text{Eqn. 1}$$

where *Δm* [g] is the change of mass, *Q* [C] is the amount of charge transferred in the course of the reaction, *M* [g/mol] is the molar mass of the product being deposited/dissolved, *z* is the number of electrons transfer per mol of product and *F* = 96 485 C/mol is the Faraday constant representing the amount of charge contained in one mol of electrons.

1. Metal dissolution

The manufacturing of metallic sodium involves the electrochemical deposition of elemental sodium into an iron or nickel electrode, using a NaOH electrolyte solution. Considering the reaction:

$$Na^{+} + e^{-} \rightarrow Na \qquad \text{Rx. 1}$$

If a 5.0 A current is used in the deposition process, calculate:

a) The amount of charge [C] transferred during 10 s.
b) The mass increase of the electrode [g] after 10 s.
c) The overall metallic sodium production [kg] after a continuous one year operation.

2. Corrosion

An active corrosion process involves the continuous dissolution of a metal due to its interaction with an aggressive environment. Faradays law allows relating the dissolution current –the corrosion rate- with mass and thickness changes of the metal, which are of more interest for engineering and industry. Consider the iron corrosion reaction:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad \text{Rx. 2}$$

It has been determined experimentally that in an acidic environment a piece of iron with 1 cm^2 surface area corrodes at a rate of 100 mA. Calculate:

a) The amount of charge [C] transferred after one day of immersion in the acid.
b) The dissolution rate [g/day], expressed as the mass loss of the metal per day.
c) The corroded thickness after a day, assuming that the face exposed to the solution (Fig. 1) corrodes uniformly (density of iron: 7.87 g/cm^3).

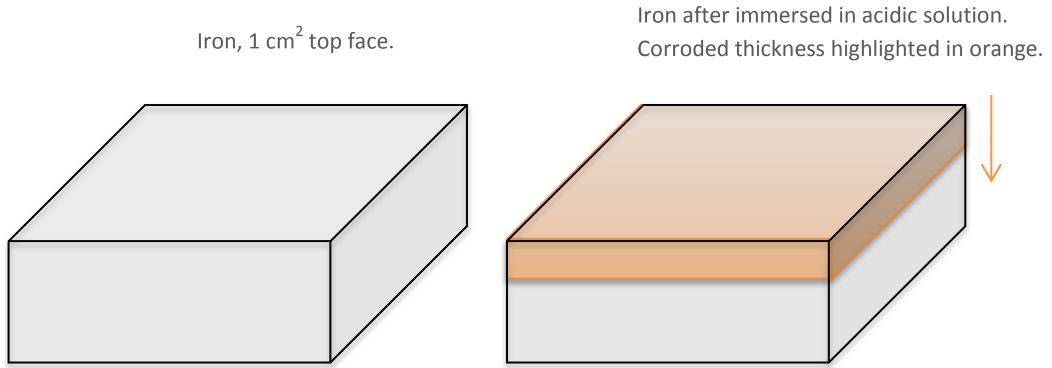

Figure 1. Schematic representation of uniform corrosion in iron.

d) Alloying iron with a small chromium percentage increases significantly its corrosion resistance. A Fe25Cr alloy is found to corrode at 0.1 mA in the same environment. Calculate the dissolution rate [g/day] assuming that only Rx. 2 happens. Compare with the dissolution rate of pure iron.
e) Compare the dissolution rate of the following metals assuming they all corrode at 1 mA:
   - Copper (to Cu^{2+}).
   - Lithium (to Li^{+}).
   - Zinc (to Zn^{2+}).
   - Aluminum (to Al^{3+}).

3. Lithium-ion battery

A lithium-ion battery is made of a stack of cells, each composed by a negative electrode (low potential), a positive electrode (high potential) and an electrolyte. Most common Li-ion cells have a negative electrode using graphite, a positive electrode using $LiCoO_2$ and an electrolyte consisting on a lithium salt dissolved in organic solvents. During discharge –when the battery powers your device- lithium ions and electrons are going out of the negative electrode by an oxidation reaction of the graphite (Rx. 3). Lithium ions are injected in the electrolyte and electron in the external electrical circuit (creating a current). At the positive electrode, Li-ions from the electrolyte and electrons from the electrical circuit are inserting in $Li_{0.5}CoO_2$ during the reduction reaction of the later material (Rx. 4). The electrons traveling in the external circuit provide the electrical energy used by a device (Fig. 2). During charge, the process is forced to reverse by applying an external potential.

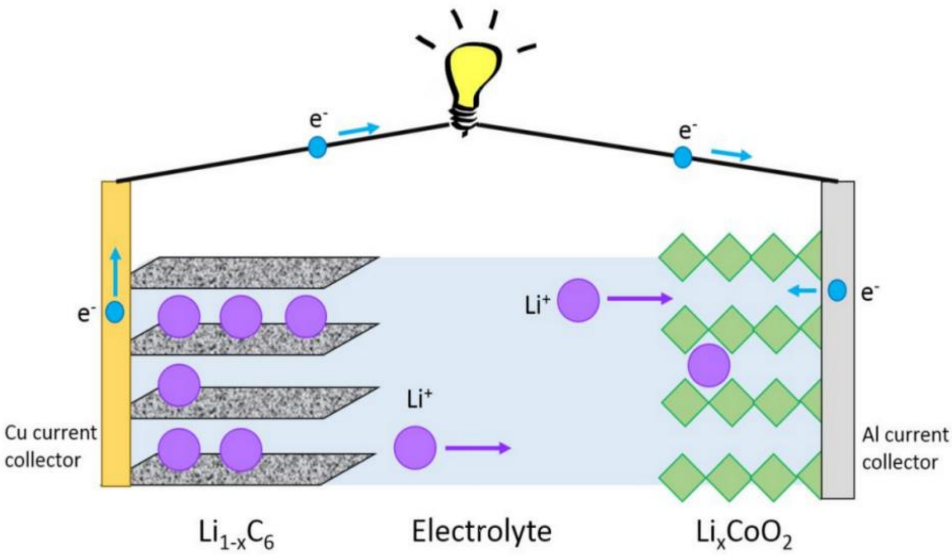

Figure 2. Representation of a Li-ion cell during discharge.

Rx. 3. Anode:

$LiC_6 \rightarrow Li^+ + C_6 + e^-$

Rx. 4. Cathode:

$Li_{0.5}CoO_2 + 0.5\ Li^+ + 0.5\ e^- \rightarrow LiCoO_2$

The amount of charge a battery can store is measured in miliamperes-hour. As an example, the battery of a Samsung Galaxy J7® mobile phone stores 3 000 mAh. Using Faraday's law (Eqn. 1), calculate:

a) The mass of graphite contained in a Samsung Galaxy J7® battery, considering Rx. 3, i.e. 6 carbon atoms per electron transferred.

b) The mass of cobalt oxide contained in the same battery, considering Rx. 4, i.e. two $Li_{0.5}CoO_2$ units present per electron transferred.

c) The battery not only contains the active materials, but also separators and metallic parts to form electrical contacts, guarantee mechanical stability and safe performance. If the battery weights in total 82 g, Calculate how much (in percentage) each active material contribute to the total battery weight.