

## CHEM-E4255 Electrochemical energy conversion

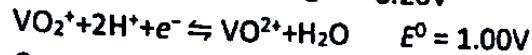
Exam 12.12.2016

Answer to all questions 1-4 and in addition select either 5A or 5B

### Answer to all questions 1-4:

1. Explain the following terms
  - a) faradic current
  - b) solid electrolyte interface (SEI layer)
  - c) electrochemical double layer
  - d) state of the charge (SoC)
  - e) light harvesting efficiency
  - f) current efficiency
2. Select one electrochemical energy conversion/storage device and describe its operation principle. What are the most common active materials used for the selected device (electrodes, electrolyte)? What are the biggest issues related to materials and/or operation of the device? What are typical applications of the device and its pros and cons for that application (in comparison to alternative technologies)?
3. A galvanic cell composed of copper metal in 1.0 M  $\text{Cu}(\text{NO}_3)_2$  solution and silver metal in 1.0 M  $\text{AgNO}_3$  solution. The two half-cells are connected by  $\text{KNO}_3$  salt bridge.
  - a) Which is the anode and cathode half-cell, respectively? Which metal (Ag or Cu) serves as the anode and which metal serves as the cathode? Write the anode half-cell reaction and the cathode half-cell reaction.
  - b) Write the cell diagram notation for the galvanic cell.
  - c) Show the directions in which  $\text{K}^+$  and  $\text{NO}_3^-$  ions flow in the salt bridge.
  - d) Calculate the cell potential ( $E^\circ_{\text{cell}}$ ) for this electrochemical cell and the cell potential ( $E_{\text{cell}}$ ) when  $[\text{Cu}^{2+}] = 1.0 \text{ M}$  and  $[\text{Ag}^+] = 0.0010 \text{ M}$ .
  - e) What is the value of  $\Delta G^\circ$  for the overall reaction at 25°C?
  - f) Calculate the maximum free energy available for work if 5.0 g of Cu is reacted at an average cell potential of 0.45 V.

4. The all-vanadium redox flow battery employs the V(II)/V(III) redox couple at one electrode and the V(IV)/V(V) redox couple at the other electrode, generally identified to exist in the form of  $\text{VO}^{2+}$  and  $\text{VO}_2^+$ . Standard reduction potentials of the half-cell reactions are



Concentration of all the vanadium species is  $10^{-2}$  M and supporting electrolyte is 1 M  $\text{H}_2\text{SO}_4$ . On graphite electrode  $\alpha = 0.42$  and  $k^0 = 3.0 \times 10^{-7} \text{cm/s}$  for the  $\text{VO}_2^+/\text{VO}^{2+}$  redox couple. Give the virtual total reaction of the vanadium battery. What is the potential at the OCP? What current is the current when  $\eta = 0.5E^{\text{OCP}}$ .

In addition select one of the following questions (5A or 5B):

5. A)

In the table below, reversible cell voltages are given for a hydrogen fuel cell open to atmosphere at different temperatures.

$T(^{\circ}\text{C})$	25	60	80	100
$E(\text{V})$	1.230	1.200	1.184	1.167

- Write down the reaction equations for the anode and the cathode in acidic conditions.
- Determine  $E(T = 50^{\circ}\text{C})$ .
- Determine  $\Delta G(T = 50^{\circ}\text{C})$ .
- Determine  $\Delta H(T = 50^{\circ}\text{C})$ .
- Calculate the ideal efficiency of the cell at  $T = 50^{\circ}\text{C}$ .
- In real applications, the efficiency is much lower. What kind of losses explain this?

Possibly useful thermodynamic relations:

$$G = H - TS, H = U + pV, U = q + w, S = -(\partial G / \partial T)_p, dS = dQ/T, \eta = W_{\text{out}}/Q_{\text{in}}$$

# Current voltage equation

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## Equilibrium and Nernst equation



In equilibrium an electrochemical reaction proceed with the same rate in both the directions i.e.  $i_c = i_a$  and  $i = 0$ .

Thermodynamic equilibrium state is characterized by the Nernst equation

$$E = E^\circ + \frac{RT}{nF} \ln \left[ \frac{C_{\text{Ox}}}{C_{\text{Red}}} \right] \quad (4)$$

$C_{\text{Ox}}$  and  $C_{\text{Red}}$  refer to the bulk concentration. In equilibrium  $C_{\text{Ox}}^0 = C_{\text{Ox}}^s$  and  $C_{\text{Red}}^0 = C_{\text{Red}}^s$  where  $s$  refers to the electrode surface.

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29

## Rate of an electrochemical reaction



Rate of the electrochemical reaction  $v$  is proportional to the surface concentrations of the reaction species  $C_0$

$$v_o = \frac{1}{A} \frac{dn_o}{dt} = k_o C_{\text{O}}(0, t) \quad (1)$$

According to the Fraday law

$$n_o = \frac{It}{n_o F} \quad (2)$$

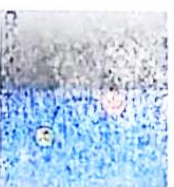
Combining (1) and (2) we obtain

$$v = v_o = v_r = k_o C_{\text{O}}(0, t) = k_r C_{\text{R}}(0, t) = \frac{i_c - i_a}{n_o F} = \frac{i}{n_o F} \quad (3)$$

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30

## Current voltage equation (1/5)



By definition (for one e<sup>-</sup> transfer)

$$\Delta G = -F\Delta E = -F(E - E^\circ) \quad (5)$$

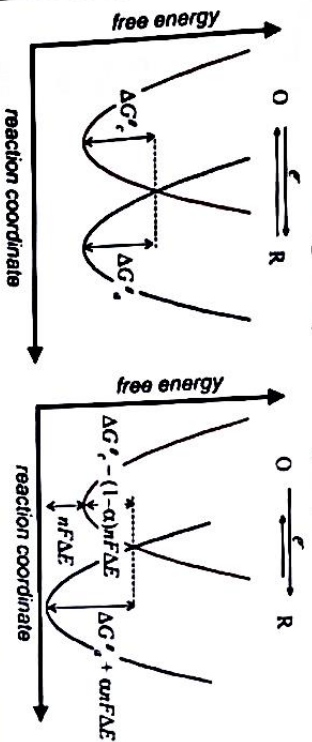
Change of the electrode potential affects the energy of the "reacting" electron. Setting the potential of the electrode to a more negative value increases the energy of the electron. Consequently, the barrier for reduction becomes lower and that for oxidation rises leading to an increase of  $i_c$  and decrease of  $i_a$ .

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30



## Current voltage equation (2/5)



Change in the Gibbs free energy is proportional to that in the electrode potential  
 $\Delta G^\ddagger = \Delta G^\ddagger_0 - (1-\alpha)F(E - E^\circ)$  and  $\Delta G^\ddagger' = \Delta G^\ddagger_0 - (1-\alpha)F(E - E^\circ)$  (6)

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 11

## Current voltage equation (4/5)

Applying the Nernst eq (4) gives us

$$i_r = F B_r \exp\left(\frac{-\Delta G^\ddagger_r}{RT}\right) C_O^{(1-\alpha)} C_R^\alpha \quad \text{and} \quad i_o = F B_o \exp\left(\frac{-\Delta G^\ddagger_o}{RT}\right) C_O^{(1-\alpha)} C_R^\alpha \quad (10)$$

In equilibrium ( $i_o = i_r$ ) holds

$$i^0 = B_r \exp\left(\frac{-\Delta G^\ddagger_r}{RT}\right) = B_o \exp\left(\frac{-\Delta G^\ddagger_o}{RT}\right) \quad (11)$$

where  $k^0$  is standard rate constant. It is independent of the reference potential and stands for the reaction rate. Current in the equilibrium, exchange current,  $i_0$  is given

$$i_0 = F i^0 C_O^{(1-\alpha)} C_R^\alpha \quad (12)$$

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 12

## Current voltage equation (3/5)

Let us assume that the rate constants obey the Arrhenius form

$$i_r = B_r \exp\left(\frac{-\Delta G^\ddagger_r}{RT}\right) \quad \text{and} \quad i_o = B_o \exp\left(\frac{-\Delta G^\ddagger_o}{RT}\right) \quad (7)$$

Inserting activation energies (6) gives

$$i_r = B_r \exp\left(\frac{-\Delta G^\ddagger_r}{RT}\right) \exp[(1-\alpha)F(E - E^\circ)] \quad \text{and} \quad i_o = B_o \exp\left(\frac{-\Delta G^\ddagger_o}{RT}\right) \exp[-\alpha F(E - E^\circ)] \quad (8)$$

Combining (8) with equation (1) - (3) gives

$$i_r = F i^0 \exp\left(\frac{-\Delta G^\ddagger_r}{RT}\right) \exp[(1-\alpha)F(E - E^\circ)] \quad \text{and} \quad i_o = F C_O B_o \exp\left(\frac{-\Delta G^\ddagger_o}{RT}\right) \exp[-\alpha F(E - E^\circ)] \quad (9)$$

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 13

## Current voltage equation (5/5)

Combining (3), (9), (10) and (11)

$$i = F i^0 \left[ \frac{i_r}{i_o} \right] \exp\left[-\alpha F(E - E^\circ)\right] - C_O(0,t) \exp[(1-\alpha)F(E - E^\circ)] \quad (13)$$

Equation (13), describing kinetics of heterogeneous reactions, is called the Butler-Volmer equation.

Reactions involving several electron transfer steps can be formulated using several reaction steps. One of these is usually slower than the other, so called rate determining step (RDS). This determines the rate of the overall reaction whereas the other reactions are in equilibrium. Eq (14) is written for the RDS.

$$i = n F i_{RDS}^0 \left[ \frac{i_r}{i_o} \right] \exp\left[-\alpha F(E - E^\circ_{RDS})\right] - C_O(x,t) \exp[(1-\alpha)F(E - E^\circ_{RDS})] \quad (14)$$

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 14

# Overpotentials – Yipotentialaait

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## Activation overpotential, $\eta_{act}$ (1/3)

- Electrochemical reaction step is rate controlling
- The lower  $i_0$  the higher  $\eta_{act}$

Let us calculate ratio  $i/i_0$  using eqs (12) and (13)

$$\frac{i}{i_0} = \left( \frac{C_i}{C_o} \right)^a \exp[-aF(E - E^*)] - \left( \frac{C_o}{C_i} \right)^{1-a} \exp[(1-a)F(E - E^*)] \quad (17)$$

Close to the  $E_{eq}$  concentration ratio of can be expressed by the Nernst eq (4) resulting in

$$\frac{i}{i_0} = \exp[-aF(E - E_{eq})] - \exp[(1-a)F(E - E_{eq})] \quad (18)$$

This equation gives us current density at certain  $\eta_{act}$

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## Overpotential, $\eta$

Definition: overpotential  $\eta$  is the deviation from the equilibrium potential

$$\eta = E - E_{eq} \quad (15)$$

$$\Rightarrow E - E^* = E - E_{eq} + E_{eq} - E^* = \eta + E_{eq} - E^* \quad (16)$$

- $E_{eq}$  is often not well defined because of complex reaction kinetics
- Measured open circuit voltage (OCV) often deviates from thermodynamic equilibrium
- Overpotential results from slow rate of at least one of the partial electrode processes of the overall electrode process
- Various overpotentials are named after the rate-controlling step
- Overpotentials are observed as voltage losses in galvanic and electrolysis cells

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## Activation overpotential, $\eta_{act}$ (2/3)

Special case: large activation overpotential (slow reaction rate)

These eqs are derived for high cathodic overpotential  $|\eta| \gg \frac{RT}{F}$  and  $i_c \gg i_0$ . This situation holds for e.g. oxygen reduction reaction met in  $H_2/O_2$  fuel cells.

The last term on the right hand side of eq (18) can be omitted. Combining this with definition of the overpotential eq (15) gives us

$$\eta_{act} = -\frac{RT}{aF} \ln \frac{i}{i_0} \quad (19)$$

This can be formulated as

$$\eta_{act} = \frac{RT}{aF} \ln i_0 - \frac{RT}{aF} \ln i = a \times b \log i \quad (20)$$

The right hand side eq is known as the Tafel equation

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### Activation overpotential, $\eta_{act}$ (3/3)

Special case: small activation overpotential (high reaction rate)

These eqs are derived for low anodic overpotential  $|\eta_{an}| \leq \frac{RT}{F}$ . This situation holds for e.g. hydrogen oxidation reaction met in  $H_2/O_2$  fuel cells.

The first term on the right hand side of eq (18) is omitted. Let us use series expansion  $e^x = 1 + x + \frac{x^2}{2} + \dots$  for all values of  $e$ . Let us take into account only the first two terms.

$$\frac{i}{i_0} = 1 + \alpha f \eta - 1 + (1 - \alpha) f \eta \quad (21)$$

Consequently

$$\eta_{an} = \frac{i}{a_i F} \quad (22)$$

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### Concentration overpotential, $\eta_{diff}$ (1/3)

- Mass transfer controls the reaction rate
- O and R react at the electrode surface so fast that mass transfer from the bulk solution to the electrode surface is not able to level out of the concentrations of the reactants → concentration gradients are formed

$\eta_{diff}$  can be expressed by combining definition of the overpotential eq (15) and the Nernst eq (4)

$$\eta_{an} = E_{an} - E = \left( E^0 + \frac{RT}{a_i F} \ln \frac{C_i}{C_i^0} \right) - \left( E^0 + \frac{RT}{a_i F} \ln \frac{C_i^0}{C_i^0} \right) = \frac{RT}{a_i F} \ln \frac{C_i}{C_i^0} \quad (23)$$

Let us use Fick 1st law and the Faraday law (24), (25) to give relation between (i) mass flux and concentration and (ii) mass flux and current, respectively.

$$-\frac{1}{A} \frac{dn_i}{dt} = -D_i \left( \frac{dn_i}{dx} \right)_{x=0} = \frac{i}{a_i F} \quad (24)$$

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### iR overpotential, $\eta_{ohm}$

- Irreversible ohmic losses
- Reactants form finite conductivity of electrodes, electrolytes, contact resistances, connections etc.
- Most often the major source is limited conductivity of the electrolyte

iR overpotential is described by the Ohm law

$$\eta_{ohm} = iR \quad (25)$$

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### Concentration overpotential, $\eta_{diff}$ (2/3)

Let us assume that the concentration profiles are linear

$$\left( \frac{dn_i}{dx} \right)_{x=0} = \frac{C_i^0 - C_i}{\delta_i} \quad \text{and} \quad \left( \frac{dn_i}{dx} \right)_{x=\delta_i} = \frac{C_i - C_i^0}{\delta_i} \quad (26)$$

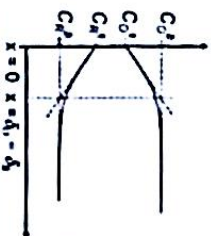
Combining eqs (24) – (26)

$$i_a = \frac{a_i F D_i (C_i^0 - C_i)}{\delta_i} \quad \text{and} \quad i_c = \frac{a_i F D_i (C_i - C_i^0)}{\delta_i} \quad (27)$$

Mass transfer limited current reaches the limiting value  $i_l$  when  $C_i = 0$

$$i_{l,a} = \frac{a_i F D_i C_i^0}{\delta_i} \quad \text{and} \quad i_{l,c} = \frac{a_i F D_i C_i^0}{\delta_i} \quad (28)$$

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### Concentration overpotential, $\eta_{dif}$ (3/3)

Unknown variables are eliminated by calculating  $i/i_0$  from eqs (27) and (28)

$$\frac{i_0}{i_a} = \frac{C_u - C_a^*}{C_u} \quad \text{and} \quad \frac{i_0}{i_c} = \frac{C_a - C_a^*}{C_a} \quad (29)$$

After inserting above eq (29) in the  $\eta_{dif}$  eq (23)

$$\eta_{dif} = \frac{RT}{n_a F} \left[ \ln \frac{C_a^*}{C_a} - \ln \frac{C_a^*}{C_a} \right] = \frac{RT}{n_a F} \left[ \ln \left( 1 - \frac{i_0}{i_a} \right) - \ln \left( 1 - \frac{i_0}{i_c} \right) \right] \quad (30)$$

(23)