Sample: Physical Chemistry - Electrochemical Reactions

1. Suppose that urea, which has a chemical formula $(NH_2)_2CO$ or N_2H_4CO and is a component of urine, is oxidized in the reaction. Suppose the overall reaction for the fuel cell can be written as :

$$N_2H_4CO + 3/2\ O_2 \rightarrow N_2 + CO_2 + 2H_2O$$

a) What are the balanced anodic and cathodic reactions in the microbial urine fuel cell? The pH of urine is slightly acidic, so use the acidic version of the O_2 reduction reaction.

Solution

a) **Acidic version of the O_2 reduction reaction is (cathode reaction):**

$$\boldsymbol{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$$

Anode Reaction:

$$\boldsymbol{N_2H_4CO + \ 1/2\ O_2 \rightarrow N_2 + CO_2 + 4H^+ + 4e^-}$$

So Overall Cell Reaction is:

$$\boldsymbol{N_2H_4CO + \ 3/2\ O_2 \rightarrow N_2 + CO_2 + 2H_2O}$$

b) What is the theoretical cell voltage for the urine fuel cell? The Gibbs free energy of formation for urea is ΔG_f^0 = -196.8 kJ/mol.

Solution

b) Standard potential E0 for the cell reaction, i.e. the potential at standard temperature and pressure (STP) when no current is drawn, is obtained by dividing the Gibbs' energy change of the reaction at STP, ΔG^0 by the Faraday constant F ($96\,485.3 \frac{C}{mol}$) and the number of electrons transferred in one reaction z,

$$E^0 = -\frac{\Delta G^0}{z * F}$$

For urine fuel cell:

$$\Delta G^0 = \Delta G_f^0(CO_2) + \Delta G_f^0(H_2O) - \Delta G_f^0(urine) = -394.39 - 2 * 237.14 + 196.8$$
$$= -671.87\ kJ/mol$$
$$z = 4$$

Thus:

$$E^0 = \frac{671.87 * 10^3}{4 * 96485.3} \approx \mathbf{1.74\ V}$$

c) Non-microbial fuel cells that run off of urea or urine have also been developed. These fuel cells use an alkaline electrolyte, so the alkaline version of the O_2 reduction reaction is used.

i.e. $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ E^0 = +0.4 V

Assuming the overall reaction is the same as in the microbial urine fuel cell, what are the balanced anodic and cathodic reactions for the alkaline direct urea fuel cell?

c) **As it is given (cathode reaction):**

$$\boldsymbol{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-}$$

Thus, anode Reaction:

$$\boldsymbol{N_2H_4CO + \frac{1}{2}O_2 + 4OH^- \rightarrow N_2 + CO_2 + 4H_20 + 4e^-}$$

So Overall Cell Reaction is:

$$\boldsymbol{N_2H_4CO + 3/2\, O_2 \rightarrow N_2 + CO_2 + 2H_2O}$$

d) What are the standard reduction potentials for the anodic half reactions for the acidic and alkaline urea fuel cells? Assume that the theoretical cell voltage is the same for both types of fuel cells.

Solution

d) Standard potential for the cell reaction calculated in part b is"

$$E^0 = 1.74\ V$$

$$E^0(alkine) = 1.74 - 0.4 = \mathbf{1.34\ V}$$

$$E^0(acidic\ ) = 1.74 - 1.23 = \mathbf{0.51\ V}$$

2. *Hydrogen fuel cell* [10 points]. Commercial fuel cells often operate using the fuel at a higher pressure than 1 atm. What happens to the cell voltage for a hydrogen fuel cell if the pressure of the H_2 fuel is increased by a factor of 10? Assume the operating temperature is 25 °C, the product is pure water, and the O_2 pressure remains at 1 atm.

Solution

The central equation describing the thermodynamics of fuel cells is the Nernst equation

$$U_0 = U_0^0(T^0, p^0) - \frac{RT}{zF} ln\left(\frac{p_{H_2O}}{p_{H_2} * \sqrt{p_{O_2}}}\right)$$

As all reactions in a fuel cell take place in the gas phase, these activities are equal to the partial pressures in bar. In our case the Nernst equation can be simplified a bit by assuming the activity of water is 1. This is possible because the cell is kept so humid that the activity of water does not change dramatically for different temperatures or gas pressures. The simplified equation is

$$U_0 = U_0^0(T^0, p^0) + \frac{RT}{zF} ln(p_{H_2} * \sqrt{p_{O_2}})$$

We are given

$$p'_{H_2} = 10 * p_{H_2}.$$

Thus:

$$U'_0 = U_0^0(T^0, p^0) + \frac{RT}{zF} ln\left(p'_{H_2} * \sqrt{p_{O_2}}\right) = U_0^0(T^0, p^0) + \frac{RT}{zF} ln(10 * p_{H_2} * \sqrt{p_{O_2}})$$
$$= U_0^0(T^0, p^0) + \frac{RT}{zF} ln(p_{H_2} * \sqrt{p_{O_2}}) + \frac{RT}{zF} \ln 10 = \boldsymbol{U_0} + \boldsymbol{\frac{RT}{zF}} \mathbf{ln\ 10}$$

$$\frac{RT}{zF} \ln 10 = \frac{8.31 * (273 + 25)}{2 * 96485.3} * \ln 10 \approx \mathbf{0.0295\ V}$$

$Answer$: Cell voltage increases by 0.0295V.