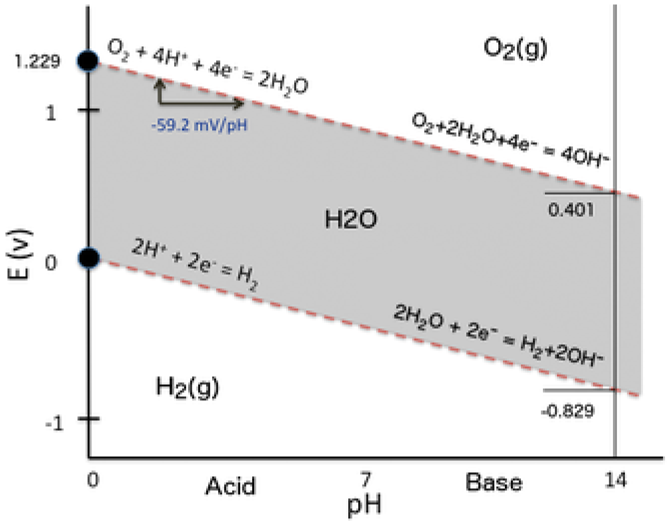
2022 Electrolysers solution

A lab scale 1 kW alkaline water electrolyser operates at 70% HHV efficiency. The stack is operated at 60°C and is electrically connected in series, with each cell having a surface of 100 cm^2. The supporting electrolyte used is 1 M potassium hydroxide (pH=14), in conjunction with Zirfon Perl UTP 500μm thick diaphragm separator. The nominal current density of operation is 0.5 A cm^{-2}. The Pourbaix diagram for water electrolysis is given in the figure below.



Calculate:

i) Reversible cell potential for hydrogen evolution ($E_{rev,H2}$) and oxygen evolution ($E_{rev,O2}$) reactions. (Considering pH=14)

The electrochemical reactions that occur at the anode, cathode and the full cell for alkaline electrolysers is given by equations *(1)*, *(2)* and *(3)*.

$$Cathode: 2H_2O(l) + 2e^- \longrightarrow 2OH^- + H_2(g) \quad : E_{Rev,H_2} \qquad (1)$$

$$Anode: 2OH^- \longrightarrow \frac{1}{2}O_2(g) + H_2O(l) \ + 2e^- : \ E_{Rev,O_2} \qquad (2)$$

$$Overall: H\_2O \ (l) \longrightarrow \mathrm{H\_2 \ (g)} + \frac{1}{2}O_2(g) : E_{Rev,H_2O} \qquad (3)$$

From the Pourbaix diagram, the hydrogen and oxygen evolution reversible potentials are defined by equations *(4)* and *(5)*.

$$E_{Rev,H_2} = \ -0.059 \ \times \mathrm{pH} \qquad (4)$$

$$E_{Rev,O_2} = 1.23 \ -0.059 \ \times \mathrm{pH} \qquad (5)$$

As 1 M KOH corresponds to pH=14, the direct substitution results in the values of $E_{Rev,H_2} = -0.826 \ V$ and $E_{Rev,O_2} = \ 0.404 \ V$. The overall voltage needed for water splitting reaction at STP (25°C and 1 atm pressure) does not change as $E_{Rev,H_2O} \ = E_{Rev,H_2} - \ E_{Rev,O_2} \ = -0.826 \ - \ 0.404 \ = -1.230 \ V$. The negative sign indicates the necessity to supply a minimum of 1.23 V to initiate water splitting reactions.

ii) The thermoneutral voltage (E_{tn}) at 25°C and at 60°C. (E_{tn} corresponds to -ΔH/nF)

From equations *(1)(2)*, it is evident that number of electrons transferred during the water splitting reaction is 2. Considering equation $E_{tn} = \frac{-\Delta H}{nF}$, the thermoneutral voltage at 25℃ and 60℃ is

$$\mathrm{E}_{\mathrm{tn},\,25℃} = \frac{285.83}{2 \times 96485} = 1.481\ V$$

$$E_{tn,\,60℃} = \frac{284.72}{2 \times 96485} = 1.475\ V$$

iii) The number of cells in the stack and the corresponding operating voltage of each cell.

As the stack is in electrical series, the current through all the cells is the same. A reasonable simplification at steady state operation is to assume each cell as a resistor, connected in series. Therefore, each cell experiences a potential drop across the terminals. The overall cell voltage then obeys Kirchhoff's law on conservation of energy.

The current flowing through each cell, $\mathrm{I} = \mathrm{J} \times A = \frac{0.5\ A}{cm2} \times 100\ cm^2 = 50\ \mathrm{A}$

Electric power consumed by the stack, $P = E_{Stack} \times I$

$$\Rightarrow \text{Stack Voltage, } E_{Stack} = \frac{P}{I} = \frac{1000}{50} = 20\ V$$

HHV Efficiency is defined as, $\eta_{HHV} = \frac{E_{tn,60℃}}{E_{Cell}}$

$$\Rightarrow Cell\ Voltage, E_{cell} = \frac{1.475}{0.70} = 2.108\ V$$

Therefore, number of cells,

$$N_{cells} = \frac{E_{Stack}}{E_{Cell}} = 9.5 \approx 10\ cells$$

iv) The water flowrate in L min^{-1} necessary at the cathode to reach a conversion rate of 80%, assuming a Faradaic efficiency (=current efficiency) of 100%.

The water flowrate is fundamental in determining the overall efficiency of an electrolyser system, as pumps constitute part of the parasitic power consumption.

The molar flowrate of hydrogen production is defined by

$$\dot{n}_{H_2} = \eta_f \left(\frac{N_{cells} I}{nF}\right) = 1 \times \frac{10 \times 50}{2 \times 96485} = 0.00259\ mol\ s^{-1}$$

The molar ratio of water to hydrogen at the cathode is based on equation *(1)*.

Therefore $\dot{n}_{H_2O} = 2 \times \dot{n}_{H_2}$

Therefore, the minimum flowrate of water required for 100% conversion,

$$V_{H_2O,100\%} = \frac{\dot{n}_{H_2O} m_{H_2O}}{\rho_{H_2O}} = \frac{2 \times 0.00259 \times 18.015}{997.047} = 9.364 \times 10^{-5} Ls^{-1} = 5.620\ mL\ min^{-1}$$

With 80% conversion, the water flowrate required is

$$V_{H_2O,80\%} = \frac{V_{H_2O,100\%}}{0.80} = 7.023\ mL\ min^{-1}$$

Reflecting on equations *(1)*, *(2)* and *(3)*, the water molecule is effectively transported to the anode (O_2 side), while being consumed at the cathode (H_2 side). Effectively, the cathode KOH increases in concentration while anode KOH is further diluted, thereby altering the pH of the solutions. The usual practice is to eventually mix the two electrolyte (anode and cathode) compartments to equalize the pH, while refilling the consumed water quantity. However, the mixed solution should be monitored for hydrogen and oxygen content, as aqueous KOH can dissolve both gases, leading to safety concerns. The lower explosion limit (LEL) for hydrogen in oxygen is 4 vol%. For safety reasons, the electrolytes are replaced - treated when the concentration of H_2 in O_2 reaches 2 vol% (or 50% of LEL).

Further thinking:

a) Is Faradaic efficiency of 100% a relevant assumption?
Ideally, the water splitting reaction is aided by the addition of the supporting electrolyte – potassium hydroxide (KOH). However, KOH exposure to air results in dissolution of atmospheric CO_2, forming potassium carbonates and bicarbonates. These products can undergo electrolysis to liberate syngas (CO + H_2) at the cathode and carbon dioxide at the anode (CO_2). As these are side reactions, a faradaic efficiency of > 95% is a realistic scenario.

b) How does the thermoneutral voltage change with the phase change of water to steam?

The primary difference in calculation of the thermoneutral voltage is the heat of formation of water $\Delta H_f \approx 44$ kJ mol^{-1}. If water is present in a 'vapor' state at 25℃, the thermoneutral voltage would then change to $E_{tn-H_2O(g),25℃} = \frac{242000}{2\times96485} = 1.253\ V$, which is ≈18% lower than 1.481 V. Having a lower thermoneutral voltage boosts efficiency, as total energy demand by the electrolyser is effectively reduced. This is the primary reason for improved intrinsic efficiencies with solid oxide electrolyser cells (SOE). However, the scalability and lifetime of SOE stacks are currently the limiting factors for large scale deployment.