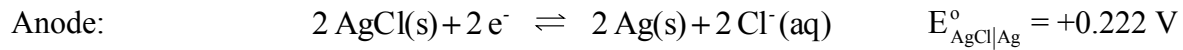


Bubble formation can adversely affect many electrochemical systems. In electrolytic cells, the bubbles formed on the surface of electrodes reduce their effective surface area, causing a fluctuation in current density and the rate of reaction. To ensure a proper performance of the designed systems, preventing bubble formation becomes indispensable.

In the systems with aqueous solution, either hydrogen or oxygen liberations are the major cause of bubble formation. Their occurrence is driven by redox reactions in the electrochemical systems. Thermodynamically, these reactions are not spontaneous, and supplying the energy is required to initiate the reactions. In this study, the conditions that trigger the gas evolution will be investigated using two electrolytic cells – one with a pair of Ag/AgCl electrodes and the other with a pair of Au electrodes.

The first electrolytic cell, shown in Figure 1, is composed of a pair of Ag/AgCl electrodes in KCl aqueous solution of neutral pH, and assumed to be maintained at 25 °C and atmospheric pressure. The cell is connected to a variable power supply, volt meter, and amp meter as indicated in Figure 1. Denote that the electrodes connected to the positive and negative terminals of the power supply are referred to as anode and cathode, respectively.

Hydrogen evolution is the major cause of bubble formation in this cell. As indicated in Figure 1, water is reduced at the cathode resulting in a hydrogen gas, while silver is oxidized plating silver chloride on the surface of anode. These redox reactions can be expressed, in forms of a reduction, as follow



where $E_{\text{AgCl|Ag}}^\circ$ and $E_{\text{H}_2\text{O|H}_2}^\circ$ are the standard reduction potentials. Assume that the power supply and amp meter were disconnected from the cell. The volt meter was reconnected with its polarities interchanged such that its negative and positive terminals were connected to the anode and cathode, respectively. Based on this configuration, the potential required for the reactions to occur is being calculated.

To compute the potential at each electrode, Nernst equation [1],

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{\prod_i [\text{product}]_i}{\prod_j [\text{reactant}]_j} \right) \quad (1)$$

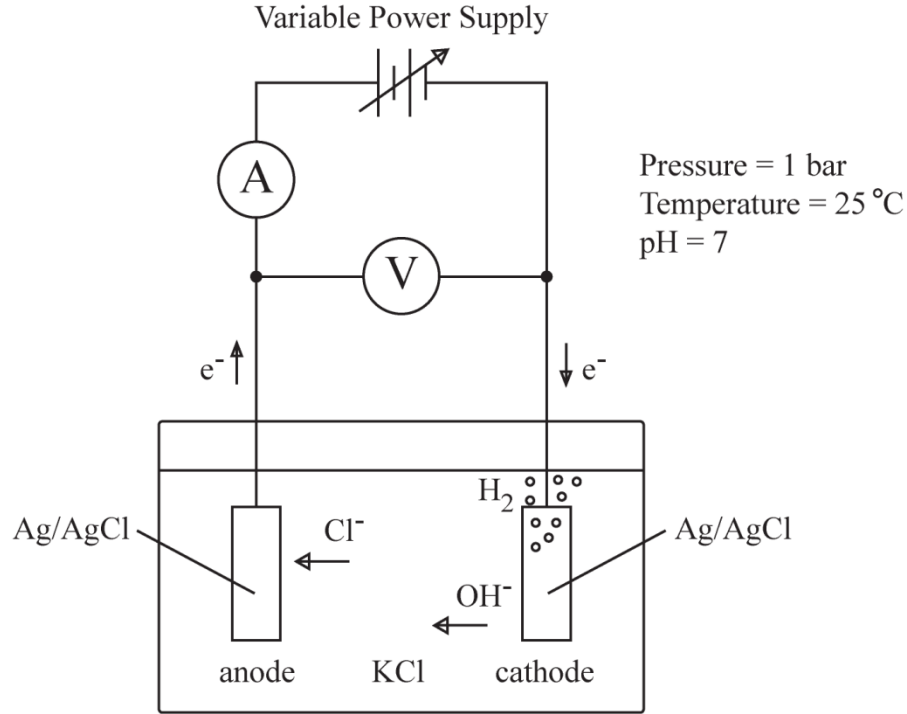


Figure 1 Diagram illustrating a hydrogen evolution in an electrolytic cell composed of a pair of Ag/AgCl electrodes in KCl solution at 25 °C, 1 bar of pressure, and pH neutral

is used where R is a gas constant ($8.314 \text{ J}/(\text{K} \cdot \text{mol})$), T is a temperature in Kelvin, n is the number of mole of electrons, F is a Faraday constant ($9.649 \times 10^4 \text{ C/mol}$), and $[\text{product}]_i$ and $[\text{reactant}]_j$ represent the concentration of i^{th} product and j^{th} reactant in forms of aqueous solution or gas. It is worth noting that the concentration of gas is expressed in terms of its pressure in a unit of bars. Using Nernst equation (1), the potentials at the anode and cathode is given as

$$E_{\text{anode}} = E_{\text{AgCl|Ag}}^{\circ} - \frac{RT}{2F} \ln([\text{Cl}^-]^2) \quad (2)$$

$$= 0.222 - 0.05916 \log([\text{Cl}^-])$$

$$E_{\text{cathode}} = E_{\text{H}_2\text{O|H}_2}^{\circ} - \frac{RT}{2F} \ln(P_{\text{H}_2} [\text{OH}^-]^2) \quad (3)$$

$$= -0.414 \text{ V}$$

As indicated by equation (2), the potential at the anode is a function of the concentration of Cl^- in the solution.

Using the potentials found in (2) and (3), a potential difference across the cell, defined as an open-circuit voltage, E_{open} , [2] can be derived as

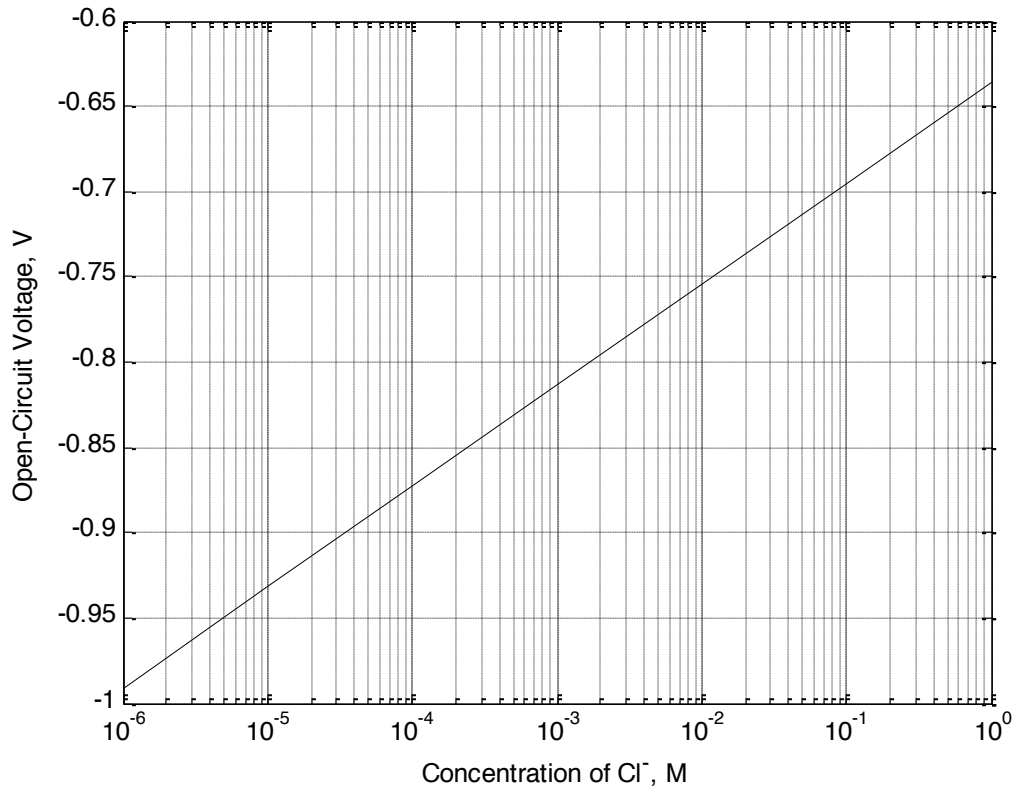


Figure 2 Open-circuit voltages for Ag/AgCl electrolytic cell plotted as a function of aqueous Cl⁻ ion concentrations at 25 °C and 1 bar of pressure

$$\begin{aligned}
 E_{\text{open}} &= E_{\text{cathode}} - E_{\text{anode}} \\
 &= -0.636 + 0.05916 \log([Cl^-])
 \end{aligned}
 \tag{4}$$

The open-circuit voltages of the cell at various concentrations of Cl⁻ ions are shown in Figure 2. It is worth mentioned that the negative open-circuit voltage indicates that the reaction is not spontaneous [2] and in fact the electrons tend to flow in the opposite direction to the one illustrated in Figure 1. Therefore, a power supply is needed to force the electrons to flow in the given direction and initiate the reactions. The applied voltages required for starting the hydrogen evolution have the same magnitude as the open-circuit voltages and are tabulated in Table 1 for a certain concentrations of KCl solution normally used in experiments.

Table 1 The applied voltages at the advent of hydrogen evolution at a certain concentrations of aqueous Cl^- ions in the Ag/AgCl electrolytic cell at 25 °C and 1 bar of pressure

Concentration of Cl^- , M	Applied Voltage, V
1.0	0.636
1.0×10^{-1}	0.695
1.0×10^{-2}	0.754
1.0×10^{-3}	0.814
1.0×10^{-4}	0.873
1.0×10^{-5}	0.932
1.0×10^{-6}	0.991

In conclusion, to avoid bubble formation in the experiments using this electrolytic system, the applied voltage must be below the value shown in Table 1 for the corresponding concentration of the KCl solution.

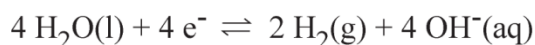
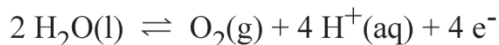
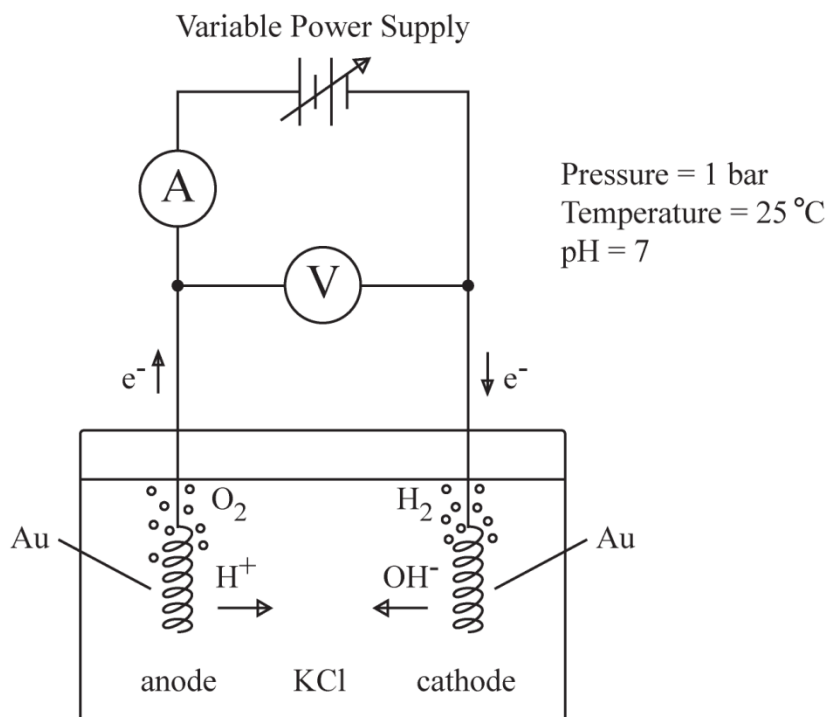
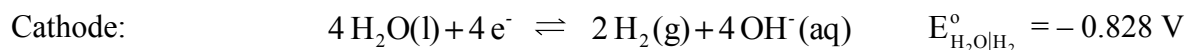
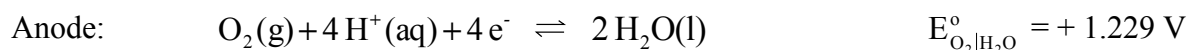


Figure 3 Diagram illustrating bubble formations caused by the electrolysis of water in an electrolytic cell composed of a pair of Au electrodes in KCl solution at 25 °C, 1 bar of pressure, and pH neutral

Figure 3 shows the second electrolytic cell to be investigated, which is consisted of a pair of gold electrodes in KCl aqueous solution of neutral pH, and assumed to be maintained at 25 °C and atmospheric pressure. The cell configuration and denotation are the same as the first one. Unlike the first cell, the source of bubble formations comes from the electrolysis of water from which not only the hydrogen gas, but also the oxygen gas is liberated. The redox reactions for the separation of hydrogen and oxygen gases from water are described in Figure 3. The half-reaction at each electrode, expressed in forms of a reduction, is described as follows.



where $E_{\text{O}_2|\text{H}_2\text{O}}^\circ$ and $E_{\text{H}_2\text{O}|\text{H}_2}^\circ$ are the standard reduction potentials. Using Nernst equation (1), the potentials at the anode and cathode can be computed as

$$E_{\text{anode}} = E_{\text{O}_2|\text{H}_2\text{O}}^\circ - \frac{RT}{4F} \ln \left(\frac{1}{(P_{\text{O}_2})[\text{H}^+]^4} \right) \quad (5)$$

$$= 0.815 \text{ V}$$

$$E_{\text{cathode}} = E_{\text{H}_2\text{O}|\text{H}_2}^\circ - \frac{RT}{4F} \ln \left((P_{\text{H}_2})^2 [\text{OH}^-]^4 \right) \quad (6)$$

$$= -0.414 \text{ V}$$

The open-circuit voltage can then be found as

$$E_{\text{open}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= -1.229 \text{ V}$$

Note that since the solubility constant $K_{\text{sp}} = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, the open-circuit voltage is independent of the pH of the solution.

The bubble formation in this cell is also not spontaneous as indicated by the negative open-circuit voltage. It is required to apply a voltage of 1.229 V to initiate the electrolysis of water at gold electrodes.

In conclusion, to avoid bubble formation in the experiments using this electrolytic system, the applied voltage must be below 1.229 V.

References

- [1] D. C. Harris, *Quantitative Chemical Analysis*. New York, NY: W. H Freeman and Company, 2007, pp. 279.
- [2] D. C. Harris, *Quantitative Chemical Analysis*. New York, NY: W. H Freeman and Company, 2007, pp. 350-352.