Experiment 28
DIRECT METHANOL FUEL CELL

Objective
The purpose of this experiment is to learn the principle of direct methanol fuel cell (DMFC) and set up a simple apparatus to examine its performance.\(^1\)

Technique
You will learn the techniques of electrolysis, electroplating, setting up a direct methanol fuel cell, and the operation of DC power supply and a multimeter.

Introduction
I. Electrochemical cell
The energy released in a spontaneous redox reaction can be used to perform electric work through an electrochemical cell. Figure 28-1 shows a Cu-Zn cell as an example of this concept. The zinc metal is the anode which undergoes oxidation reaction to form zinc ions and electrons (equation 28-1). The electrons will then pass through the external circuit to the copper metal, which acts as the cathode. The copper ions in the solution accept the incoming electrons and undergo reduction reaction (equation 28-2) on the copper electrode. The overall reaction is shown in equation 28-3. The cathodic and anodic half-cells are connected with a salt bridge that contains an electrolyte solution to complete the circuit. The standard cell potential \(E^\circ_{\text{cell}}\) of a Cu-Zn cell under standard condition, i.e. \([\text{Zn}^{2+}]\) and \([\text{Cu}^{2+}]\) are both 1 M, and 25 °C is 1.10 V.

\[
\begin{align*}
\text{Anode, oxidation:} & \quad \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq, 1\, \text{M}) + 2e^- \\
\text{Cathode, reduction:} & \quad \text{Cu}^{2+}(aq, 1\, \text{M}) + 2e^- \rightarrow \text{Cu}(s)
\end{align*}
\]

Figure 28-1   A Cu-Zn electrochemical cell
Anodic half-reaction: \( Zn \rightarrow Zn^{2+} + 2e^- \)  \( (28-1) \)

Cathodic half-reaction: \( Cu^{2+} + 2e^- \rightarrow Cu \)  \( (28-2) \)

Overall cell reaction: \( Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \)  \( E^\circ_{\text{cell}} = +1.10 \text{ V} \)  \( (28-3) \)

II. Fuel cell

The thermal energy released by the combustion of fuels can be converted to electric energy. The heat may convert water to steam, which drives a turbine that in turns drives a generator. A maximum of only 40\% of energy from combustion is converted to electricity; the remainder is lost as heat.\(^{(2)}\) The direct production of electricity from fuels by an electrochemical cell could yield a higher rate of conversion of the chemical energy of the reaction. The electrochemical cells that perform this conversion using conventional fuels are called fuel cells.

The hydrogen/oxygen fuel cell system uses the reaction of \( H_2(g) \) and \( O_2(g) \) to form \( H_2O(l) \) as the only product (equation 28-4). The cell can generate electricity twice as efficiently as the best internal combustion engine. The schematic drawing of \( H_2-O_2 \) fuel cell shown in figure 28-2 is known as the proton-exchange membrane (PEM) fuel cell. The electrodes are typically made from graphite, and the reaction is catalyzed by a thin layer of platinum on each electrode. The anode and cathode are separated by a thin polymer membrane that is only permeable to protons.

\[ \begin{align*}
    \text{Anodic half-equation} & : \quad H_2 \rightarrow 2H^+ + 2e^- \\
    \text{Cathodic half-equation} & : \quad 1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \\
    \text{Overall cell reaction} & : \quad H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \quad E^\circ_{\text{cell}} = +1.23 \text{ V} 
\end{align*} \]
II. Direct methanol fuel cell

Because the storage and safe handling of hydrogen gas is troublesome, methanol, \( \text{CH}_3\text{OH} \), is used instead of hydrogen gas as a reactant. The reactions are shown in equations 28-7–28-9.

\[
\text{Anode: } \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad (28-7)
\]

\[
\text{Cathode: } 3/2\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \quad (28-8)
\]

\[
\text{Overall: } \text{CH}_3\text{OH}(l) + 3/2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \quad E^0_{\text{cell}} = 1.21 \text{ V} \quad (28-9)
\]

The standard electromotive force (emf) of an ideal DMFC is 1.21 V. However, because methanol may be incompletely oxidized which lead to the formation of methanal or methanoic acid, the emf produced is lower than the theoretical one. In this experiment, you will set up a DMFC that uses platinum (Pt) as catalyst and dilute sulfuric acid as the electrolyte. Methanol is the fuel at anode compartment and the oxygen gas dissolved in the solution will undergo reduction reaction at the cathode. You will also need to examine factors that affect the performance on DMFC.

**Equipment**

DC power supply and connecting wire (2 pcs), multimeter, graphite rod, nickel-chromium wire (20 ~ 25 cm, 2 pcs), syringe (10 mL, 2 pcs), silicon tubing (2 mm i.d., 5 cm), beaker (30 mL, 2 pcs), plastic dropper (2 pcs), light-emitting diode (LED), clamp (2 pcs), timer, chopstick, label.

**Chemicals**

1 M sulfuric acid, \( \text{H}_2\text{SO}_4 \)
Methanol, \( \text{CH}_3\text{OH} \)
Hydrogen hexachloroplatinate(IV) hexahydrate, \( \text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O} \)
Hydrogen hexachloroplatinate(IV) solution: by dissolving 1 g of \( \text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O} \) in 250 mL of 1 M HCl

**Procedure**

I. Preparation of platinized Ni-Cr electrodes
1. **Prepare 2 pieces of spiral Ni-Cr electrode**
   Take 2 pieces of Ni-Cr wire of about 20 cm long. Wind the wire around a chopstick or a pencil into a spiral shape with a 4-mm-diameter core, leaving a 6 ~ 10 cm straight end for attaching electrodes.

2. **Electro-clean the spiral Ni-Cr wires**
   Transfer 25 mL of a 1 M sulfuric acid to a 30 mL beaker as the electrolyte. Check and ensure that all the adjustment buttons on the DC power supply are set to zero. Then, connect two Ni-Cr wires to the positive pole (red) of the power supply and the graphite rod to the negative one (black); immerse them both into the 1 M sulfuric acid. (Note: The two electrodes should NOT be in contact with each other.) Turn on the power and electro-clean the Ni-Cr wires at 0.2 A for 10 s, and then wash the wires with distilled water.

3. **Electroplating of platinum catalyst**
   Transfer about 20 mL of a hydrogen hexachloroplatinate(IV) electrolytic solution to a 30 mL beaker. Hang the two washed Ni-Cr wires on one end of the beaker and connect them to the negative pole of the DC power supply. The positive pole is connected to a graphite electrode. Electroplate the platinum catalyst on the Ni-Cr wires for 30 min at a current of approximately 20 mA (0.02 A) to deposit a suitable amount of platinum catalyst over the metal electrodes. After electroplating, immerse the platinized Ni-Cr electrodes in a 1 M sulfuric acid for about 30 s for cleaning, and store the electrodes in distilled water. Note that damage to the delicate platinum layer should be avoided.

II. **Setting up a fuel cell**

4. **Set up the cell**
   With reference to Figure 28-3, connect the luer tips of two 10-mL plastic syringes with 5-cm segments of silicone tubing; clamp the syringes on a stand. To one of the syringe, add 12 ~ 15 mL 1 M sulfuric acid slowly (Note: Formation of gas bubbles should be avoided). Then, position 2 platinized electrodes into the fuel cell compartments.

5. **Testing the fuel cell**
Connect the electrodes to the multimeter and measure the current without adding methanol. (The finished fuel cell will possess a few-millivolt potential difference which leads to an extremely small current passing through.) Then, add about 10 drops of methanol to the syringe connected to the negative pole (black) of the multimeter and observe the current output (a current output of about 0.5 mA will be produced immediately). The output value will drop continuously until a stable value is reached. At this time, a current can be produced again by injecting air into the syringe connected to the positive pole (red) of the multimeter with a plastic dropper.

6. Application of DMFC
   Connect several sets of fuel cells in series to supply a LED or alarm clock.
   Note: The long and short legs of the LED should be connected to the positive and negative pole of the electricity source, respectively.

III. Recycling after the experiment
7. After finishing the experiment, the platinized electrodes and graphite electrode should be recycled.
8. Uncontaminated hydrogen hexachloroplatinate(IV) electrolytic solution should be recycled to the assigned recycling flask for use next time. Those contaminated should be discarded to the heavy metal waste container.
9. Switch off the multimeter and DC power supply; ensure that they are both set to zero. Tidy up the connecting wire.

References
Figure 28-3 Set-up of DMFC
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I. Experimental Data and Results

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II. Questions and Discussion

1. Why should platinum be plated on the Ni-Cr wire? Can pure platinum electrode be used? Can it be replaced by a graphite electrode?

2. In procedure 5, the current output of the DMFC drops gradually until reaching a stable value. If air is injected to the syringe connected to the positive pole of the multimeter, current can be regenerated. Explain this observation and propose some improvements for it.